Quantum Mechanics

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Preface to the English Edition

This book is specifically a "textbook" for learning the physical content of quantum mechanics. There is a pleasing progression from the gross quantum effects (blackbody radiation, photoelectric effect, specific heats) to typical quantum mechanical behavior (spreading of wave packets, barrier penetration, stationary states, spin and angular momentum multiplets) to the more refined quantum phenomenology (fine structure, effect of the nucleus on atomic structure, quantum fluctuations of the electromagnetic field, coupling of angular momentums in multielectron atoms and molecules). At each stage of remoteness from everyday experience some of the conceptually and computationally abstruse parts of the theory are dealt with in explicit detail that emphasizes the real observability of the phenomenon. The mathematical form of the theory is thereby dictated by the necessity of having a notational apparatus that is sufficiently rich and flexible to embrace the scope of actual observable effects.

While it is an exposition of the principles of quantum mechanics, the selection of material is unusual because the book includes much that is ordinarily regarded as atomic structure and omits any long excursion into the formal mathematical structure of the theory. The formalism is a part of the practice of quantum mechanics, however, so to be complete we ought to recognize these tools and provide some guide to their practical utilization. To accomplish this we added two appendices in which are collected many definitions and formal statements and a few examples to show how the notational apparatus is used. The material is presented in a way that is very abstract and condensed. It is not intended as an expository treatment of the subject but rather as an outline of useful reference material on the formal aspects of the theory. The justification for this mode of presentation is that textbook expositions are widely available and that once the material is grasped a concise summary of definitions and results is often all that is needed for reference.

The active participation of the student in solving problems is an indispensable part of the discipline of quantum mechanics. We have therefore included a relatively large number of problems to supplement the text. The problems are coordinated with the organization of material in the text so that they serve to illustrate in context the applications and principal ramifications of the theory.

GRAHAM FRYE

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PROBLEMS
Preface

This textbook is based on my lectures to students at the Moscow Regional Pedagogical Institute (1945 to 1948) and Moscow University from 1945 on. In writing this book we set ourselves the difficult task of treating in a single volume the fundamentals of atomic theory, that is, Schrödinger’s nonrelativistic theory, Dirac’s relativistic theory, the theory of multielectron atoms, and the basic applications of quantum mechanics to solid state physics. Our aim was to combine the exposition of general theoretical principles with examples of the application of quantum mechanics to specific problems connected with atomic structure. To avoid overloading this book, we have abridged the treatment of certain specialized topics, but in such cases we have endeavored to supply references to standard works on the subject.

In most textbooks the solution of specific problems with the help of Schrödinger’s equation is handled in fairly elegant form. The basic mathematical tools required for this purpose are a knowledge of second-order differential equations and various special functions (including the Hermite, Legendre and Laguerre polynomials). However, applications of Dirac’s theory to specific problems (such as the hydrogen atom) are on the whole handled less satisfactorily. In some cases the calculations are so long and cumbersome that it is difficult to perceive the physical meaning of the solutions. In others there is no actual derivation of the results or only a rough proof is given. In an attempt to avoid these pitfalls, we have used an approximate form of Dirac’s equation for our treatment of the hydrogen atom (Chapter 19). This approximation still enables us to obtain the formula for the fine structure of the energy levels and the selection rules (Chapter 18 and 20). Our analysis of the Lamb shift due to the electron-positron vacuum is also somewhat simplified (Chapter 22).

Several good problem books in quantum mechanics are available, and therefore we shall consider only a few problems chosen with the aim of elucidating and supplementing the general discussion.

The first part of this book was written jointly by me and Yu. M. Loskutov, and the second part jointly by me and I. M. Ternov. Great assistance was rendered by M. M. Kolesnikova in condensing notes based on my lectures on quantum mechanics and in preparing the manuscript for the press. Chapter 25 was carefully
read by N. N. Kolesnikov, who made a number of valuable comments. I would like to mention the great pains taken by S. I. Larin in editing the whole manuscript.

A. A. Sokolov
Quantum mechanics dates only from the 1920's. This important branch of theoretical physics deals with the fundamental problem of the behavior of microparticles (for instance, the behavior of electrons in an atom). As a theory, quantum mechanics represents an extension of classical mechanics, electrodynamics (including the theory of the electron and the theory of relativity), the kinetic theory of matter, and other branches of theoretical physics.

Historically, the development of every branch of theoretical physics involves two main stages. First comes the accumulation of experimental facts, the discovery of semiempirical laws, and the development of preliminary hypotheses and theories. This is followed by the discovery of general laws, which provide a basis for interpreting a large number of phenomena. For example, the first or pre-Newtonian stage of mechanics consisted of the discovery of a number of seemingly unrelated laws: the law of inertia, the law of free fall under the action of a gravitational field and Kepler's laws of planetary motion. Most of these laws were discovered only after years of painstaking work by many scientists. Thus, many astronomical observations preceded the discovery of Kepler's laws. We may recall the great efforts of Copernicus, Bruno, Galileo, and others to establish that the Sun is the center of our planetary system and that the Earth is only a planet like Mars, Venus, or Jupiter. It was only after working for fifteen years on Tycho Brahe's extremely valuable observational data that Kepler found the semiempirical laws describing planetary motion. After these preliminary, seemingly independent laws had been established, Newton was able to show that they all rested on the same theoretical foundation. Newton's three laws of motion and the law of universal gravitation opened a new stage in the development of theoretical mechanics. One of the great triumphs of Newtonian mechanics was Leverrier's prediction of the existence of a new planet, Neptune, from perturbations in the motion of Jupiter.

In a similar fashion, Maxwell's formulation of the laws of electrodynamics was preceded by the discovery of empirical laws describing various electric and magnetic phenomena. Coulomb's law of interaction between electric charges and magnetic poles¹ and the Biot-Savart law of interaction between an electric current and a magnetic pole were found by analogy with Newton's law of

¹As magnetic monopoles do not exist in nature, Coulomb's law in magnetostatics is verified by means of magnetic dipoles.
gravitation. All of these phenomena were explained on the basis of the principle of "action at a distance," according to which one charge acts directly on another through the intervening space.

After Newton, and independently of investigations of electric and magnetic phenomena, considerable attention was devoted to optics. At a relatively early stage, it was established that light consists of transverse waves, propagating with a finite velocity of $c \approx 3 \times 10^{10}$ cm/sec. The nature of these waves, however, remained unknown.

All of these preliminary studies belonged to the first stage of development of electrodynamics: they prepared the ground for Maxwell's theory, which had approximately the same unifying role in electrodynamics as Newton's laws in mechanics. Maxwell's equations provided a powerful tool for the investigation of electric, magnetic and optical phenomena. Maxwell's theory predicted the existence of electromagnetic fields, which carry the interaction continuously from point to point, and of electromagnetic waves, which were later discovered by Hertz. The theory of propagation of electromagnetic waves underlies all of modern radio engineering.

Another important result of Maxwell's theory was a proof of the wave nature of light.

The view that matter and electricity have an atomic structure was of considerable importance in connection with the appearance of quantum mechanics. This view had very ancient roots, but remained without scientific foundation until the discovery of the fundamental law of chemistry—the law of exact proportions. The kinetic theory of matter and, in particular, the kinetic theory of gases—based on the classical Maxwell-Boltzmann statistics—were important steps in the development of atomic theory. It is worth noting that the classical Maxwell-Boltzmann statistics, which rests on probability theory, cannot be completely explained in terms of Newtonian mechanics and contains certain features that are characteristic only of large collections of particles (for example, the irreversibility of certain processes). Statistical methods made it possible to explain a number of macroscopic properties of matter, such as temperature and specific heat; this provided indirect evidence of the atomic structure of matter.

One of the decisive proofs of the atomic theory of matter was the discovery of fluctuations, that is, statistical fluctuations in the behavior of individual molecules. Brownian motion was particularly important in this connection, as it provided the evidence of molecular movement in a liquid. Even more suggestive proofs of the atomic structure of matter were provided by Laue's observation of the diffraction of x-rays in crystals and Aston's mass-spectrographic measurements of the atomic weights of individual isotopes of various elements.

From an analysis of Faraday's laws of electrolysis, Helmholtz showed that there must be a fundamental quantity of electricity,
equal to $4.8 \times 10^{-10}$ esu, such that any charge, positive or negative, is an integral multiple of this charge. Studies of anode rays indicated that positive charges always appear as ions; that is, a positive charge is always associated with the basic mass of an atom. The lightest positive ion is that of a hydrogen atom. It is known as a proton and its mass is nearly the same as the mass of a neutral hydrogen atom. The carrier of a negative charge can take the form of a negative ion or of a much lighter particle known as an electron. From measurements of the deflection of cathode rays (a beam of electrons) in electric and magnetic fields, it was found that the mass of the electron was about $1/1836$ of the mass of the proton.\(^2\)

These discoveries led to Lorentz's electron theory, which represents an interesting synthesis of Maxwell's electrodynamics for a vacuum and the atomic view that matter consists of positive and negative charges. In Lorentz's theory the magnetic permeability, dielectric constant, and conductivity of a medium were obtained by averaging Maxwell's equations for a vacuum over charges and currents of particles of the medium. A conductor was treated as a medium filled with free electrons or, in other words, an "electron gas." It followed from Lorentz's theory that the dielectric constant depends on the frequency of electromagnetic waves, whereas in Maxwell's theory it had been assumed that this quantity is a constant. Lorentz's theory provided an explanation of the dispersion of light. The appearance of this theory was accompanied by the extension of electrodynamics to frames of reference traveling with constant relative velocities; this culminated in the special theory of relativity. It is well known that all laws of motion—whether they be Newton's laws or Maxwell's equations for the motion of an electromagnetic field—must be associated with a frame of reference. Newton believed that his laws were related to an absolute frame of reference. Even in his writings, however, this notion remained purely metaphysical, and Newton himself discovered the principle of relativity in mechanics according to which it is impossible to detect a uniform rectilinear motion of a body (or a frame of reference) relative to this absolute system, because all frames of reference moving linearly with constant relative velocities with respect to each other are completely equivalent.

Consider the Galilean–Newtonian transformation from one inertial system to another, moving along the $x$ axis with relative velocity $v$

\[ x' = x - vt, \quad y' = y, \quad z' = z, \quad t' = t, \]

\(^2\)In 1932, a particle with a positive charge and mass equal to that of an electron, known as the positron, was discovered. Positrons are formed in small quantities when cosmic rays pass through matter. Under ordinary conditions a positron cannot exist for any significant length of time because it combines with an electron and the two particles are converted into gamma-ray photons (see Chapters 3 and 22).
where the primed coordinates refer to the moving system, and the unprimed coordinates to the stationary system. We find that accelerations and forces are identical in the two frames of reference, and therefore the equations of mechanics (in which the velocity does not appear) are invariant under this transformation. If the Galilean-Newtonian transformation is applied to the Maxwell-Lorentz equations, they assume different forms in different inertial systems, because the equations contain the velocity of propagation of electromagnetic waves which, added vectorially, has different values in different inertial systems. The original Michelson-Morley and other numerous experiments showed, however, that the speed of light is the same in any direction in all inertial coordinate systems. As a result, Einstein generalized the Newtonian principle of relativity in a way that led directly to the so-called Lorentz transformations

\[ x' = \frac{x - vt}{\sqrt{1 - \beta^2}}, \quad y' = y, \quad z' = z, \]

\[ t' = \frac{t - \beta \frac{x}{c}}{\sqrt{1 - \beta^2}}, \quad \beta = \frac{v}{c}. \]

The classical laws of electrodynamics are invariant under this transformation. Since the equations of Newtonian mechanics, however, are not invariant under the Lorentz transformations, they had to be replaced by relativistic equations in which the mass \( m \) of a moving particle was related to its velocity \( v \) and its rest mass \( m_0 \) by the relationship

\[ m = \frac{m_0}{\sqrt{1 - \beta^2}}. \]

At low velocities, where \( \beta^2 \approx 0 \), the relativistic equations reduce to the Newtonian formulations.

The Maxwell-Lorentz equations for an electromagnetic field and the relativistic equations of motion of an electron constituted the culminating stage of the classical electron theory. According to this theory, light consists of electromagnetic waves and an electron is a particle whose motion is described by relativistic mechanics. The success of the Maxwell-Lorentz theory in accounting for certain microscopic phenomena (the propagation and dispersion of light, the motion of an electron in electric and magnetic fields, and so forth) was accompanied by the discovery of experimental facts that could not be explained with classical concepts. These experiments will be described in Chapters 1—3, and therefore we shall mention them here only very briefly.

In the first place, it was found that black-body radiation, the photoelectric effect, and the Compton effect could be explained only
on the basis of corpuscular properties of light. This was the implicit assumption of the Planck-Einstein photon theory, in which the discrete structure of light was described in terms of Planck's constant \( h = 6.62 \cdot 10^{-27} \text{ erg} \cdot \text{sec} \). The photon theory was also successfully used by Bohr in constructing the first quantum theory of the atom, based on the planetary model suggested by Rutherford. In the second place, a number of experimental facts, including the electron diffraction, indicated that in addition to its corpuscular properties, an electron has wave properties. De Broglie's definition of the wavelength of an electron also included Planck's constant \( h \). This led eventually to the development of a new science—electron optics—which provides a theoretical basis for electron microscopy.

The Schrödinger wave equation (1926) was the first general theoretical treatment that explained both of these classes of phenomena and unified the preliminary theories of Planck, Einstein, Bohr, and de Broglie. This equation made it possible to discover the laws of behavior of electrons and other elementary particles and to construct a relatively systematic theory of radiation that took into account the quantum nature of light. For atomic physicists, the Schrödinger equation was one of the most powerful tools. Many phenomena associated with the behavior of an electron in an atom and with the absorption and emission of light by an atom were provided with a theoretical explanation (see Chapters 4-14). The later development of quantum theory showed that the Schrödinger equation did not describe all the properties of atoms. In particular, it could not explain correctly the interaction of an atom with a magnetic field (for instance, the anomalous Zeeman effect) and it could not be used to construct a theory of multielectron atoms. One of the main reasons for this was that the Schrödinger theory did not take into account the electron spin.

Dirac's relativistic theory (see Chapters 15-17) was an extension of the Schrödinger theory that considered relativistic and spin effects of moving electrons (see Chapters 18-20). It turned out that the quantitative corrections due to relativistic effects were relatively small, but that spin effects were of fundamental importance in connection with the fine structure of multielectron atoms (see Chapters 23 and 24). These effects explained the filling of electron shells in an atom and gave a theoretical basis to Mendeleyev's periodic table of elements (see Chapters 25 and 26).

Although the fundamental problems related to the structure of the atom were basically solved with the appearance of Dirac's equation, we are constantly adding further details to our knowledge. At present a great deal of attention is being devoted to the influence of the electron-positron vacuum and magnetic moments on the energy levels of atoms (see Chapters 21 and 22). Quantum mechanics has also been applied to simple molecules (Chapter 27), solid state physics (Chapter 6), and the atomic nucleus.
Part I

Nonrelativistic Quantum Mechanics
The Quantum Theory of Light

Before the supremacy of classical physics was challenged by the advent of quantum mechanics in the beginning of this century, particle motion was sharply distinguished from wave motion. According to the classical picture, the world consisted of particles (for example, electrons and ions) and fields (for example, light). This picture was completed by Maxwell's theory (1873), which appeared to have definitely established that fields had wave-like properties.

Towards the end of the nineteenth century and in the first years of this century, this state of affairs was disturbed by the discovery of experimental facts that did not fit into the classical conceptual framework. On the one hand, there were certain phenomena, such as the radiation spectrum of an ideal black body, the photoelectric effect, and the Compton effect, which could be understood only in terms of particle-like properties of light. On the other hand, electrons were observed to have wave-like properties, such as diffraction, which later served as a basis for the development of electron optics.

A. PRINCIPLES OF THE ELECTRON THEORY

The behavior of the electromagnetic field produced by a given distribution of charge and current is described by the well-known Maxwell-Lorentz equations

\[
\begin{align*}
\nabla \times \mathbf{H} - \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} &= \frac{4\pi \rho}{c}, \\
\nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{H}}{\partial t} &= 0, \\
\n\nabla \cdot \mathbf{E} &= 4\pi \rho, \\
\n\nabla \cdot \mathbf{H} &= 0,
\end{align*}
\]

where \( \mathbf{E} \) and \( \mathbf{H} \) are the electric and magnetic field intensities, respectively, \( \rho \) is the charge density (for example, of the electron), and \( \mathbf{v} \) is its velocity.
To start with, an electromagnetic field transmits interactions between the charges. The interaction between stationary charges \( e \) is transmitted by an electrostatic field which satisfies Coulomb's law \( V = \frac{e_1 e_2}{r} \), whereas the interaction between moving charges is transmitted by a system of electric and magnetic fields, since a moving charge can be regarded as an electric current and it is well known that a current interacts with a magnetic field. Electromagnetic fields are always associated with sources of the appropriate type (for example, charges).

Secondly, electromagnetic fields may be regarded as electromagnetic waves, which propagate with the velocity of light \( c \) (radio or light waves). As a particular example of a source of light waves, we can take an accelerated charge. The latter emits radiant energy; per unit time, this energy is

\[
W = \frac{2}{3} \frac{e^2 w^2}{c^3},
\]

where \( e \) is the charge, and \( w \) its acceleration. Once electromagnetic waves have been produced, they can exist independently of their sources.

The equation describing the propagation of a light wave is obtained from Eqs. (1.1) by setting the charge density \( \rho \) equal to zero. We can then eliminate the vector \( \mathbf{H} \) from the second Maxwell equation by taking the curl of this equation and substituting into it the first equation. Since \( \nabla \cdot \mathbf{E} = 0 \), we can use the vector relation

\[
\nabla \times \nabla \times \mathbf{E} = \nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = -\nabla^2 \mathbf{E},
\]

to obtain the following wave equation, which holds for the components of both vectors \( \mathbf{E} \) and \( \mathbf{H} \):

\[
\nabla^2 f - \frac{1}{c^2} \frac{\partial^2 f}{\partial t^2} = 0,
\]

where \( f \) is any component of the vectors \( \mathbf{E} \) or \( \mathbf{H} \).

A more detailed analysis of the Maxwell-Lorentz equations shows that electromagnetic waves are transverse. This means that the electric field intensity \( (\mathbf{E}) \) and magnetic field intensity \( (\mathbf{H}) \) are mutually orthogonal, and also orthogonal to the wave vector \( \mathbf{k} \), which points in the direction of propagation of the electromagnetic wave. The vectors form a triad such that when a right-handed screw is turned from \( \mathbf{E} \) to \( \mathbf{H} \), it moves along the direction of \( \mathbf{k} \):

\[
\mathbf{H} = \mathbf{k} \times \mathbf{E},
\]

where \( k = k |k| \) is a unit vector.
A charge (say, an electron) moving in externally applied electric and magnetic fields experiences a force

\[ F = e \left( E + \frac{1}{c} \mathbf{v} \times \mathbf{H} \right), \]  

which is called the Lorentz force.

Taking into account the relativistic variation of mass, the equation of motion of an electron in an external field has the form

\[ \frac{d}{dt} \frac{m_0 v}{\sqrt{1 - \beta^2}} = e \left( E + \frac{1}{c} \mathbf{v} \times \mathbf{H} \right), \]  

where

\[ \beta = \frac{v}{c}. \]

We can select a Lagrangian function \( \mathcal{L} \) in such a manner that the variational principle

\[ \delta \int \mathcal{L}(\dot{x}_i, x_i, t) \, dt = 0, \]  

or, in more explicit form,

\[ \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{x}_i} - \frac{\partial \mathcal{L}}{\partial x_i} = 0 \quad (i = 1, 2, 3), \]

will yield the equation of motion of an electron (1.6). Here \( x_1 = x, \) \( x_2 = y, \) \( x_3 = z \) are the spatial coordinates, and the \( \dot{x}_i \) denote the corresponding velocities. To obtain (1.6), we must set

\[ \mathcal{L} = -m_0 c^2 \sqrt{1 - \beta^2} - e \Phi + \frac{e}{c} \mathbf{v} \cdot \mathbf{A}, \]

where \( \mathbf{A} \) and \( \Phi \) are the vector and scalar potentials of the electromagnetic field. These potentials are related by the Lorentz condition

\[ \nabla \cdot \mathbf{A} + \frac{1}{c} \frac{\partial \Phi}{\partial t} = 0. \]

The electric and magnetic field intensities can be expressed in terms of \( \mathbf{A} \) and \( \Phi \) by means of the relations

\[ E = -\nabla \Phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}, \]
\[ H = \nabla \times \mathbf{A}. \]

We find the following expression for the electron momentum:

\[ p_i = \frac{\partial \mathcal{L}}{\partial \dot{x}_i} = \frac{m_0 \dot{x}_i}{\sqrt{1 - \beta^2}} + \frac{e}{c} A_i. \]
Similarly, for the generalized force acting on the electron, we obtain

\[ Q_i = \frac{\partial \mathcal{L}}{\partial x_i} = -e \frac{\partial \phi}{\partial x_i} + \frac{e}{c} \left( \mathbf{v} \frac{\partial A}{\partial x_i} \right). \tag{1.13} \]

Substituting (1.12) and (1.13) into (1.8) and taking into account (1.10) and (1.11), we obtain Eq. (1.6) for the motion of an electron. Thus, our choice of the Lagrangian is justified.

Since we know \( \mathcal{L} \), we may also determine the Hamiltonian \( H \):

\[ H = \sum_i p_i \dot{x}_i - \mathcal{L} = \frac{m_0 v^2}{\sqrt{1 - \beta^2}} + m_0 c^2 \sqrt{1 - \beta^2} + e\Phi = \frac{m_0 c^2}{\sqrt{1 - \beta^2}} + e\Phi. \]

It is well known that the Hamiltonian should not be expressed in terms of the velocity \( c \), but in terms of the generalized momentum \( P = p - \frac{e}{c} A \), which, according to (1.12), is related to \( c \) by the equation

\[ c^2 p^2 + m_0 c^4 = \frac{c^2 m_0^2 v^2}{1 - \beta^2} + m_0^2 c^4 = \frac{m_0^2 c^4}{1 - \beta^2}. \]

Therefore, the relativistic form of the Hamiltonian is

\[ H = \sqrt{c^2 P^2 + m_0^2 c^4} + e\Phi. \tag{1.14} \]

We note that if the potentials are time-independent, the Hamiltonian is equal to the total energy \( E = H \).

In the nonrelativistic approximation \( P \ll m_0 c \), Eq. (1.14) can be written in the form

\[ H = H' + m_0 c^2, \]

where \( H' \) is approximately equal to the nonrelativistic part of the Hamiltonian

\[ H' \approx H_{\text{nonrel.}} = \frac{p^2}{2m_0} + e\Phi = \left( \frac{p - \frac{e}{c} A}{2m_0} \right)^2 + e\Phi. \tag{1.15} \]

From this it can be seen that the relativistic equation for the Hamiltonian (1.14) also includes the rest-mass energy \( m_0 c^2 \) of the electron. It is very important to take this rest-mass energy into account in studying transformations of elementary particles.
B. THE CLASSICAL THEORY OF BLACK-BODY RADIATION

Among all the phenomena associated with electromagnetic fields, special importance can be attached to the properties of cavity radiation. This can be described as the radiation inside a cavity completely surrounded by opaque walls, which are heated to a certain constant temperature $T$, or, alternatively, as radiation in equilibrium with an isothermal enclosure. A small hole made in the wall of such an enclosure behaves like an ideal black body, because practically no external rays incident on the opening are reflected. In other words, essentially all rays entering the cavity through the hole are absorbed, or, more precisely, the probability that they reemerge from the hole is negligibly small. Consequently, the cavity radiation escaping from the hole may be regarded as the radiation which would be obtained from an ideal black body, and it is generally referred to as black-body radiation.

The analysis of black-body radiation played a particularly important role in the foundation of quantum theory. Although a more or less reasonable classical explanation could be found for many other phenomena, every single theory of black-body radiation constructed on the basis of classical concepts failed to agree with the experimental facts. A systematic theory of black-body radiation was developed only in the beginning of this century, when Planck introduced the concept of a quantum of energy. This concept was later to play an important role in the development of the first quantum theory of the atom, and afterwards in the development of quantum mechanics.

We shall now consider the theory of black-body radiation, confining ourselves for the time being to classical concepts. Let the radiation be characterized by its spectral density $\rho_\omega$, which is related to the ordinary electromagnetic energy density

$$ u = \frac{1}{8\pi} (E^2 + H^2) $$

(1.16)

by the relation

$$ \rho_\omega = \frac{du}{d\omega}, $$

(1.17)

---

1In the literature, the function $\rho_\nu$ is sometimes used for the spectral density. The function $\rho_\omega$ is related to $\rho_\nu$ by the equation

$$ \rho_\omega = \frac{1}{2\pi} \rho_\nu, $$

since $\omega = 2\pi \nu$. 

where $d\omega$ is the energy density of the radiation in the frequency range from $\omega$ to $\omega + d\omega$. Obviously,

$$u = \int_{\omega}^{\infty} \rho_{\omega} d\omega. \quad (1.18)$$

On the basis of the second law of thermodynamics, Kirchhoff showed that the density $\rho_{\omega}$ is determined only by the temperature of the walls of the closed cavity and is entirely independent of the material of which the walls are made; that is, $\rho_{\omega} = f(\omega, T)$.

Consequently, the walls of the cavity may be considered as a set of oscillators. The average energy of these oscillators is completely determined by the spectral density of the black-body radiation. We shall show this starting with the equation of motion for an oscillator and taking into account Planck's radiation damping

$$x + \omega^2 x - \frac{2}{3} \frac{e^2}{m_0 c^2} x = \frac{e}{m_0} E_x. \quad (1.19)$$

Here $e$ and $m_0$ are the charge and rest mass of the oscillator, $\omega$ is its natural frequency of oscillations, and $E_x$ is the $x$ component of the electric field intensity of the black-body radiation.

Representing $E_x$ in the form of a Fourier series

$$E_x = \sum_{n=-\infty}^{\infty} E_{xn} e^{in\omega_0}, \quad (1.20)$$

where $E_{xn}$ is the amplitude of an individual oscillation of the field with frequency

$$\omega_n = n\omega_0, \quad (1.21)$$

we obtain the following equation for $x(t)$ from Eq. (1.19):

$$x = \sum_{n=-\infty}^{\infty} \frac{e}{m_0} \frac{E_{xn} e^{in\omega_0 t}}{\omega^2 - (n\omega_0)^2 + i \frac{2}{3} \frac{e^2}{m_0 c^2} (n\omega_0)^3}. \quad (1.22)$$

The average energy of the oscillator, which, according to the virial theorem, is twice the average kinetic energy, is given by

$$\bar{E} = \frac{m_0 \bar{x}^2}{m_0} = m_0 \left\{ \sum_{n=-\infty}^{\infty} \frac{(in\omega_0) e}{m_0} \frac{E_{xn} e^{in\omega_0 t}}{\omega^2 - (n\omega_0)^2 + i \frac{2}{3} \frac{e^2}{m_0 c^2} (n\omega_0)^3} \right\}^2, \quad (1.23)$$

where the bar denotes averaging over time. Since

$$\left\{ \sum_{n=-\infty}^{\infty} f_n e^{in\omega_0 t} \right\}^2 = \sum_{n, n'} f_n f_{-n} e^{in\omega_0 t} (n-n'),$$
where \( f_{-n} = f_{n}^* \), and since, moreover,

\[
e^{i\omega t (n-n')} = \frac{1}{\tau} \int_{-\tau/2}^{\tau/2} e^{i\omega t (n-n')} dt = \begin{cases} 1 & \text{for } n' = n, \\ 0 & \text{for } n' \neq n, \end{cases}
\]

where \( \tau = 2\pi/\omega_0 \), Eq. (1.23) can be reduced to the form

\[
\frac{\hbar \omega}{m_0} \Delta^2 = 2m_0 \sum_{n' = 0}^{\infty} \frac{(\hbar \omega_0)^3}{[(\hbar \omega_0)^2 - \omega^2 + \frac{2}{3} \frac{\hbar \omega_0^3}{m_0 c^3}]} |E_{xn_0}|^2.
\]

This equation has a very sharp maximum in the neighborhood of frequency \( \omega \), and hence the total energy of the oscillator will actually depend only on those terms of the series for which \( n \omega_0 \approx \omega \). Consequently, in the above equation, the square modulus of the amplitude \( |E_{xn_0}|^2 \) can be replaced by \( |E_{xn_0}| \), where \( n_0 = \frac{\omega}{\omega_0} \), and at the same time the sum can be changed to an integral. According to (1.21,2)

\[
d\omega_n = \omega d\omega n = \omega_n = \frac{\omega}{n_0},
\]

since \( dn = 1 \). Therefore, we obtain

\[
\bar{E} = 2 \frac{n_0 \hbar^2}{m_0} \frac{|E_{xn_0}|^2}{\omega} \int_0^{\infty} \frac{\omega_n^2 d\omega_n}{\left\{ \omega_n^2 - \omega_0^2 \right\}^2 + \left( \frac{2}{3} \frac{\hbar \omega_0^3}{m_0 c^3} \right)^2}.
\]

Replacing the frequency \( \omega_n \) by \( \omega \) everywhere except in the difference \( \omega_n - \omega \), introducing the variable of integration \( \xi = \omega_n - \omega \), and extending the limits of integration to \( \pm \infty \), we find

\[
\bar{E} = 2 \frac{n_0 \hbar^2}{m_0} \frac{|E_{xn_0}|^2}{\omega} \int_{-\infty}^{\infty} \frac{d\xi}{4\xi^2 + \left( \frac{2}{3} \frac{\hbar \omega_0^3}{m_0 c^3} \right)^2} = \frac{3\pi n_0 \hbar^2}{2 \omega^3} \cdot |E_{xn_0}|^2.
\]

On the other hand, the energy density \( u \), which is related to the electromagnetic field of the radiation by Eq. (1.16), can also be expressed in terms of \( |E_{xn_0}|^2 \). Since the radiation is isotropic we have, on the basis of Eq. (1.16),

\[
u = \frac{1}{8\pi} (E^2 + H^2) = \frac{1}{4\pi} \left( E_x^2 + E_y^2 + E_z^2 \right),
\]
Using the expansion (1.20) and the rule (1.24) for averaging over $t$, we obtain

$$u = \frac{3}{4\pi} \frac{E_x}{x} = \frac{3}{4\pi} \sum_{n=-\infty}^{\infty} |E_{x,n}|^2 = \frac{3}{2\pi} \int_{0}^{\infty} |E_{x,n}|^2 \, dn.$$  
(1.29)

Hence, taking into account Eq. (1.18) together with the relationship

$$dn = \frac{d\omega_n}{n_0} = n_0 \frac{d\omega_n}{\omega},$$
(1.30)

for $\omega_n = \omega (n = n_0)$, we obtain

$$\rho_\omega = \frac{3n_0 |E_{x,n_0}|^2}{2\pi \omega}.$$  
(1.31)

Comparing Eqs. (1.31) and (1.27), we find the relationship between the average energy $\bar{E} = m_0 \bar{\omega}^3$ of the oscillator and the spectral density of the radiation $\rho_\omega$

$$\rho_\omega = \frac{\omega^2}{\pi^2 c^3} \bar{E},$$
(1.32)

which forms the basis of the theory of black-body radiation.

In classical statistical physics, the energy distribution of particles is given by the function

$$N(E) = Ae^{-zE},$$
(1.33)

where $z = 1/kT$; $k = 1.38 \cdot 10^{-16}$ erg-deg$^{-1}$ is Boltzmann's constant, and $T$ is the temperature of the medium. The average energy of the particles is

$$E = \frac{\frac{A}{\delta} \int_{0}^{\infty} E e^{-zE} \, dE}{\frac{A}{\delta} \int_{0}^{\infty} e^{-zE} \, dE} = -\frac{\partial}{\partial z} \ln \int_{0}^{\infty} e^{-zE} \, dE =$$
(1.34)

$$= \frac{\partial}{\partial z} \ln z = kT.$$

Substituting this value of $\bar{E}$ into Eq. (1.32), we obtain the Rayleigh-Jeans formula

$$\rho_\omega = \frac{\omega^2}{\pi^2 c^3} kT.$$  
(1.35)
This equation satisfies the *Wien's thermodynamic law*

\[
p_\omega = \omega^3 f\left(\frac{\omega}{T}\right),
\]

(1.36)

which was based on various results in thermodynamics and the electromagnetic theory of light. In the region of long wavelengths (low frequencies), the Rayleigh-Jeans formula is in good agreement with experimental data. At short wavelengths, however, it completely fails to agree with experiment (see Fig. 1.1).

![Fig. 1.1. Radiation spectrum of an ideal black body. The heavy dotted line indicates the Rayleigh-Jeans curve \( p_\omega = \rho_0 \omega^2 \), and the solid line the Planck curve \( p_\omega = \rho_0 \omega^3 / (e^{\omega/kT} - 1) \), which is the same as the experimental curve. Here \( \rho_0 = (kT/\pi^2 c^3) \), \( \omega = \omega_0 x \), and \( \omega_0 = kT/\hbar \).

In exactly the same way, the use of the Rayleigh-Jeans formula for calculation of the radiation energy density [see Eq. (1.18)] results in a divergent integral, that is, we obtain the obviously absurd relationship

\[
u = \int_0^\infty p_\omega d\omega = \frac{kT}{\pi^2 c^3} \int_0^\infty \omega^3 d\omega = \infty.
\]

(1.37)

This was called the "ultraviolet catastrophe" by Ehrenfest. Thus, the classical theory was completely unable to give a satisfactory description of black-body radiation.

**C. PLANCK'S EQUATION**

In 1900, Planck put forward an important hypothesis which removed the ultraviolet catastrophe and radically changed a number of fundamental principles of classical physics. According to this
hypothesis, the energy of microscopic systems (atoms, molecules, and so forth) does not vary continuously and assumes only certain specific discrete values. In particular, the energy of a harmonic oscillator must be a multiple of a certain minimum value $\varepsilon$:

$$E = n\varepsilon,$$

(1.38)

where $n = 0, 1, 2, \ldots$.

In order to determine the average value of the energy, we must replace the integral (1.34) by the sum

$$E = -\frac{\partial}{\partial x} \ln \sum_{n=0}^{\infty} \varepsilon e^{-n\varepsilon x} = -\frac{\partial}{\partial x} \ln \frac{\varepsilon}{1 - e^{-\varepsilon x}} = \frac{\varepsilon}{e^{\varepsilon x} - 1}.$$

Substituting this value of $E$ into Eq. (1.32), we obtain the spectral density of the radiation

$$\rho_\omega = \frac{\omega^3}{\pi^2 c^3} \frac{\varepsilon}{e^{\omega/kT} - 1}.$$

(1.40)

We can bring this equation into agreement with Wien's thermodynamic law by letting $\varepsilon$ be proportional to $\omega$:

$$\varepsilon = \hbar \omega.$$

(1.41)

We then obtain Planck's equation

$$\rho_\omega = \frac{\hbar \omega^3}{\pi^2 c^3 (e^{\hbar \omega/kT} - 1)},$$

(1.42)

which was a brilliant achievement of quantum theory.

The quantity $\hbar = 1.05 \cdot 10^{-34}$ erg sec, which has the dimensions of action, is called Planck's constant.\(^3\)

At low frequencies ($\hbar \omega/kT \ll 1$), the exponential $e^{\hbar \omega/kT}$ may be expanded in the form of a power series in $\hbar \omega/kT$. Restricting ourselves to the linear terms of the expansion, we have

$$e^{\hbar \omega/kT} \approx 1 + \frac{\hbar \omega}{kT}.$$

\(^3\)In the literature, Planck's constant is more often taken as the quantity $\hbar = 2\pi \hbar = 6.6249 \cdot 10^{-27}$ erg sec, which relates the energy $\varepsilon$ to the frequency $\nu$:

$$\varepsilon = \hbar \nu.$$
Thus, Planck's equation (1.42) reduces to the Rayleigh-Jeans formula (1.35).

In the case of high frequencies $\left(\frac{\hbar \omega}{kT} \gg 1\right)$, we may neglect the 1 in the denominator of Eq. (1.42) and write $\rho_\omega$ in the form

$$\rho_\omega = \frac{\hbar \omega^3}{\pi^2 c^3} e^{-\hbar \omega / kT}. \quad (1.43)$$

Planck's equation (1.42), which describes the dependence of the spectral density $\rho_\omega$ of thermal radiation on the frequency $\omega$, is in excellent agreement with experiment (see Fig. 1.1).

From Eqs. (1.42) and (1.18), we can find the total radiation density

$$u = \int_0^\infty \rho_\omega \, d\omega = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3 \, d\omega}{e^{\hbar \omega / kT} - 1}. \quad (1.44)$$

Introducing the variable $\xi = \hbar \omega / kT$ and considering that

$$\int_0^\infty \frac{\xi^2 \, d\xi}{e^{\xi} - 1} = \frac{\pi^4}{15},$$

we obtain the well-known Stefan-Boltzmann law

$$u = \frac{\pi^4 k^4}{15 c^3 h^3} a T^4, \quad (1.45)$$

where

$$a = \frac{\pi^2 k^4}{15 c^3 h^3} = 7.56 \cdot 10^{-18} \text{ erg} \cdot \text{cm}^{-3} \cdot \text{deg}^{-4}. \quad (1.46)$$

From Eq. (1.42), it can be seen that the spectral density of black-body radiation has a maximum at some value of $\omega$ and that the position of this maximum changes with temperature. The equation governing the position of this maximum is called Wien's displacement law. More often, Wien's displacement law is expressed

---

4 Usually it is not the density $u$ which is measured, but the energy $\sigma T^4$ which is radiated per second per square centimeter of the black body's surface within a solid angle of $2n$ ($\Omega = 2n$). In this case, the Stefan-Boltzmann constant is $\sigma = 2\pi \frac{c}{8 \pi} a = \frac{c}{4} a = 5.67 \cdot 10^{-8}$ erg · cm$^{-2}$ · deg$^{-4}$ · sec$^{-1}$. 
in terms of the spectral distribution with respect to the wavelengths \( \lambda \). To determine \( \rho_\lambda \), we can use the expression for \( u \)

\[
    u = \int_0^\infty \rho_\lambda \, d\lambda.
\]

Since \( \lambda = \frac{2\pi c}{\omega} \), transforming to the spectral distribution over the frequencies, we have

\[
    u = \int_0^\infty \frac{\lambda^2}{2\pi c} \rho_\omega \, d\omega = \int_0^\infty \rho_\omega \, d\omega, \quad (1.47)
\]

from which we find

\[
    \rho_\lambda = \frac{2\pi c}{\lambda^2} \rho_\omega = \frac{16\pi^2 c \hbar}{2\pi c \hbar \lambda^4 (e^{\frac{kT\lambda}{\hbar}} - 1)}. \quad (1.48)
\]

To determine the wavelength \( \lambda_{\text{max}} \) at which \( \rho_\lambda \) has its maximum, we set \( \frac{\partial \rho_\lambda}{\partial \lambda} = 0 \):

\[
    \left\{ -5 + \frac{\frac{2\pi c \hbar}{kT\lambda_{\text{max}}} \cdot e^{\frac{2\pi c \hbar}{kT\lambda_{\text{max}}}}}{e^{\frac{2\pi c \hbar}{kT\lambda_{\text{max}}}} - 1} \right\} = 0.
\]

Setting \( \frac{2\pi c \hbar}{kT\lambda_{\text{max}}} = y \), we obtain the equation

\[
    y = 5(1 - e^{-y}),
\]

whose solution can be given with good accuracy in the form

\[
    y55(386,798),(478,850)(1 - e^{-y}) = 4.965.
\]

Thus \( \lambda_{\text{max}} \) is related to the temperature \( T \) by the equation

\[
    \lambda_{\text{max}} T = \frac{2\pi c \hbar}{4.965k} = b = 0.29 \text{ cm} \cdot \text{deg}, \quad (1.49)
\]

which expresses Wien's displacement law, and where \( b \) is the Wien's constant. According to this law, as the temperature of an ideal black body increases, the maximum of the radiation intensity is shifted towards shorter wavelengths (see Fig. 1.2).
Equations (1.46) and (1.49) relate Planck's constant $\hbar$ and Boltzmann's constant $k$ to the constants $a$ and $b$.

Knowing the numerical values of $a$ and $b$, we can determine $\hbar$ and $k$. This is the way in which a numerical value was first obtained for $\hbar$ and a better value found for $k$.

![Fig. 1.2. Wien's displacement law.](image)

Curves of the spectral energy distribution as a function of temperature for an ideal black body: $\lambda_{\text{max}} T \geq 0.29 \text{ cm}\cdot\text{deg}$.

Recapitulating, it follows from Planck's hypothesis that processes such as emission and absorption involve discrete quanta. In other words, the energy change of particles involved in these processes is discontinuous and not smooth as would follow from the laws of classical physics.

D. EINSTEIN'S PHOTON THEORY

In deriving his equation, Planck assumed that the energy of the oscillators is quantized. The original version of the theory, however, does not provide any physical justification for this property. Indeed, Planck himself chose to attribute the "special properties" to the heated body rather than to the electromagnetic radiation.

The second important step towards the development of quantum theory consisted of Einstein's hypothesis that oscillators absorb and emit radiation in discrete amounts because electromagnetic radiation itself consists of discrete particles, called photons, which carry an amount of energy $\hbar \omega$. In effect, Einstein interpreted Planck's equation as a description of the corpuscular properties of light.

We shall now attempt to develop an elementary theory of photons.
According to classical theory, the energy of a light wave is

\[ \varepsilon = \frac{1}{8\pi} \int (E^2 + H^2) \, d^3x = \frac{1}{4\pi} \int E^2 \, d^3x, \quad (1.50) \]

where \( d^3x \) is an element of volume, and the integration extends over all space. The electromagnetic momentum \( \pi \) of the light wave in classical theory is

\[ \pi = \frac{1}{4\pi c} \int E \times H \, d^3x, \quad (1.51) \]

According to Eq. (1.4), this can also be written in the form

\[ \pi = \frac{\hbar^2}{4\pi c} \int E^2 \, d^3x. \quad (1.51a) \]

Comparing (1.51a) and (1.50), we find the relation between the momentum \( \pi \) and the energy \( \varepsilon \):

\[ \pi = k^0 \frac{\varepsilon}{c}. \quad (1.52) \]

In the theory of relativity, a similar relation between energy and momentum holds for particles with zero rest mass and it can easily be obtained from Eq. (1.14) by substituting \( m_0 = 0, \Phi = 0 \) and \( A = 0 \).

From these considerations, Einstein concluded that an electromagnetic field can be considered as a set of particles called photons, with zero rest mass and the energy

\[ \varepsilon = \hbar \omega. \quad (1.53) \]

For the photon momentum the following equation is obtained:

\[ \pi = k^0 \frac{\hbar \omega}{c} = k^0 \frac{\hbar}{\lambda} = \hbar k, \quad (1.54) \]

where \( h = 2\pi\hbar \), and \( k = \frac{2\pi k^0}{\lambda} \) is the wave vector (\( k = \frac{2\pi}{\lambda} \) is the wave number).

On the basis of these concepts, in 1905, Einstein constructed a quantitative theory of the photoelectric effect, which had been discovered by Hertz in 1887. What is observed in the photoelectric effect is the following: the potential difference required for a spark to jump between two small charged spheres is reduced if the
cathode is illuminated. To explain this phenomenon, Einstein postulated the simple equation

$$\frac{m_0 v^2}{2} = \hbar \omega - W.$$  

(1.55)

This is essentially the law of conservation of energy and indicates that the kinetic energy \(\frac{m_0 v^2}{2}\) of the ejected electron is equal to the difference between the energy of the absorbed photon \(\hbar \omega\) and the work function \(W\) of an electron in the metal. It is obvious that if \(\hbar \omega < W\), electrons cannot be ejected from the metal. Only if the energy of the incident photons exceeds \(W\) can electrons leave the metal.

The experimental verification of Einstein's theory of the photoelectric effect provided striking confirmation of his basic conclusion that the energy of the ejected electrons depends only on the frequency of the incident light and not on its intensity, and that the emission of photoelectrons begins only when the frequency of light \(\omega\) exceeds a certain limit (so-called threshold frequency)

$$\omega > \frac{W}{\hbar}.$$  

The implications of the photon theory were brought out and verified in 1923 by experiments on the scattering of x-rays by free electrons (the Compton effect). The Compton effect was particularly interesting because it confirmed not only the law of conservation of energy (which was already verified by the photoelectric effect) but also the law of conservation of momentum.

It is well known that, in classical theory, the frequency of light does not change when it is scattered by a free electron \((\omega' = \omega)\). By contrast, in quantum theory, part of the photon's energy \(\varepsilon = \hbar \omega\) is transferred to the electron (see Fig. 1.3). Consequently, the energy and frequency of a scattered photon should generally be somewhat smaller \((\varepsilon' < \varepsilon, \omega' < \omega)\). To find the dependence of frequency on the scattering angle, let us write the laws of conservation of energy and momentum, treating the photons as particles:

$$\hbar \omega - \hbar \omega' = c^2 (m - m_0),$$
$$\hbar k - \hbar k' = mv.$$  

(1.56)

Here \(m_0\) and \(m = m_0/\sqrt{1 - \beta^2}\) represent the mass of the electron before and after collision; \(v\) is its velocity; \(\beta = v/c\); \(\hbar k = \hbar \omega/c\) and

![](https://via.placeholder.com/150)
\( \hbar k' = \hbar \omega'/c \) represent the momentum of the photon before and after scattering. We rewrite Eq. (1.56) in the form

\[
\begin{align*}
\omega - \omega' &= \frac{c^2}{\hbar} (m - m_0), \\
\hbar k - \hbar k' &= \frac{m_0 c}{\hbar}.
\end{align*}
\]

(1.56a)

Taking the square of these equations and subtracting the first equation from the second, we obtain

\[
\omega \omega' (1 - \cos \theta) = \frac{m_0 c}{\hbar} (c \omega - c \omega').
\]

(1.57)

Substituting \( \lambda = 2 \pi c/\omega \), \( \lambda' = 2 \pi c/\omega' \), and dividing (1.57) by \( \omega \omega' \), we find an expression for the increase in wavelength of the scattered light

\[
\Delta \lambda = \lambda' - \lambda = 2 \lambda_0 \sin \frac{\theta}{2},
\]

(1.58)

where \( \lambda_0 \) is the Compton wavelength of the electron

\[
\lambda_0 = \frac{2 \pi \hbar}{m_0 c} = \frac{\hbar}{m_0 c} = 2.4 \times 10^{-12} \text{ cm}.
\]

We therefore see that, according to quantum concepts, the wavelength of the scattered light \( \lambda' \) must be greater than the initial wavelength \( \lambda (\lambda' > \lambda) \) since \( \omega' < \omega \). This difference increases with the scattering angle \( \theta \). Since the Compton wavelength \( \lambda_0 \) is relatively small, Compton scattering is observed at relatively short wavelengths (x-rays and gamma rays). Indeed, for visible light (\( \lambda \sim 10^{-5} \text{ cm} \))

\[
\frac{\Delta \lambda}{\lambda} \sim \frac{\lambda_0}{\lambda} \sim 10^{-5} \sim 10^3 \text{ } \%
\]

whereas for x-rays (\( \lambda \sim 10^{-8} - 10^{-9} \text{ cm} \))

\[
\frac{\lambda_0}{\lambda} \sim 10^{-1} = 10\%.
\]

Therefore, the Compton shift can be observed experimentally only in the second case.

In his experiments, Compton studied the scattering of radiation from an x-ray tube by graphite and other substances (lithium, beryllium, sodium, potassium, iron, nickel, copper, and so on) at different angles \( \theta \). The spectral distribution of the intensity of the scattered radiation at different scattering angles was measured by means of an ionization chamber.
Figure 1.4 shows the spectral distribution of incident and scattered waves. If the incident wave (upper curve) has one maximum, the scattered wave (lower curve) will have, in addition to this maximum, a second maximum at a longer wavelength. The distance between the wavelengths of the two maxima must correspond to the Compton shift; this is because the distance increases with the scattering angle, and, in addition, it does not depend on the type of scattering material [both these facts are in accord with Eq. (1.58)\(^5\)]. The unshifted maximum corresponds to scattering by electrons which are strongly bound to the nucleus (or more precisely, electrons whose binding energy is greater than the energy of the x-ray quanta). The shifted maximum corresponds to scattering by electrons which are so weakly bound to the nucleus that, in practice, they can be regarded as free.

Thus the results of Compton's experiments completely confirm the quantum nature of light (that is, the photon theory).

\(^5\)Only the intensity of the maxima depends on the type of scattering substance. As the atomic weight of the scattering substance increases, the intensity of the unshifted maximum increases, and that of the shifted maximum decreases.
Chapter 2

The Bohr Quantum Theory

A. BASIC INFORMATION ON PROPERTIES OF ATOMS

A theory of the atom was developed only after reliable experimental data had been obtained from studies of the effects described below.

1) Emission of light by atoms. From careful studies of the radiation of atoms, it was established that they have bright-line spectra and that the lines are arranged in certain definite series. For example, all the lines of hydrogen are described by Balmer's formula

\[ \omega = R \left( \frac{1}{n'^2} - \frac{1}{n^2} \right), \quad (2.1) \]

where \( R \) is the Rydberg constant, and \( n' \) and \( n \) are integers. Setting \( n' = 1 \) and \( n = 2, 3, 4, \ldots \), we obtain the Lyman series, which lies in the ultraviolet part of the spectrum. For \( n' = 2 \) and \( n = 3, 4, 5, \ldots \), we have the Balmer series, which is located in the visible part of the spectrum and is, therefore, easiest to study.

Formula (2.1) can also be written in the form of a difference between two quantities

\[ \omega_{nn'} = T_{n'} - T_n, \quad (2.1a) \]

In spectroscopy, it is customary to write Balmer's formula in the form

\[ \frac{1}{\lambda} = R_{sp} \left( \frac{1}{n'^2} - \frac{1}{n^2} \right), \]

where the Rydberg constant for hydrogen is \( R_{sp} = 109,677.6 \text{ cm}^{-1} \). The value of the Rydberg constant in Eq. (2.1) is related to \( R_{sp} \) by the equation

\[ R = 2\pi c R_{sp} = 2\pi \cdot 3.29 \cdot 10^{15} \text{ sec}^{-1} = 20.66 \cdot 10^{15} \text{ sec}^{-1}. \]

Equation (2.1) is not too convenient for spectroscopic use, since it is usually the wavelengths which are experimentally determined. In developing a theory, we do not need to take this reservation into account, since we can always transform from the frequency \( \omega \) to the wavelength \( \lambda \)

\[ \frac{1}{\lambda} \omega = \frac{2\pi c}{R}. \]
which are called *spectral terms*. For the hydrogen atom, these terms are given by

\[ T_n = \frac{R}{n^2}. \]

This possibility of representing the radiation frequencies \( \omega \) as a difference between two terms is a consequence of the Ritz combination principle, which has important spectroscopic applications in regard to the hydrogen atom, as well as more complex atoms. For example, hydrogen was initially found to have two series, corresponding to \( n' = 1 \) (the Lyman series) and to \( n' = 2 \) (the Balmer series). On the basis of the Ritz combination principle,\(^2\) a third series was predicted with \( n' = 3 \) and \( n = 4, 5, 6, \ldots \). This series was later discovered by Paschen in the infrared region of the spectrum.

2) The behavior of an atom in external electric and magnetic fields and, in particular, the interaction of the atoms of a substance with fast particles passing through it. The most important experiments in this area were conducted by Rutherford, who succeeded in finding the distribution of positive charges inside the atom from the analysis of fast-\( \alpha \)-particle scattering.

3) Finally, investigation of various properties of molecules provided important data pertaining to the properties of atoms. For example, the formation of simple homopolar molecules and the valence theory found their explanation only on the basis of the modern quantum theory of the atom.

**B. THE CLASSICAL MODEL OF THE ATOM**

Once it had been established that an atom consists of a positively charged part associated with most of the mass, and of light, negatively charged electrons, attempts were made to construct a static model. The reason this approach to the problem was adopted is that, in classical electrodynamics, an accelerated electron emits radiation, the amount of energy emitted per unit time being

\[ W = -\frac{\partial E}{\partial t} = \frac{2}{3} \frac{e^2 w^2}{c^3}, \tag{2.2} \]

\(^2\)The Ritz combination principle was first formulated as follows: if there are two different frequencies belonging to the same series, the difference between these frequencies is also a frequency which can also be emitted by the atom, but belongs to another series. The concept of "terms", permits a relatively simple explanation of this. Indeed

\[ \omega_{nn'} = T_{n'} - T_n, \quad \omega_{n'n'} = T_{n'} - T_{n''}. \]

Hence

\[ \omega_{nn'} - \omega_{n'n'} = T_n - T_n \quad \omega_{nn''}, \]

and thus the Ritz combination principle leads directly to Eq. (2.1a).
where \( e = -e_0 \) is the electron charge (\( e_0 = 4.80 \times 10^{-10} \) esu is the elementary charge), \( \omega \) is the acceleration of the electron, and \( c \) is the velocity of light in vacuum. The minus sign in front of \( \partial E/\partial t \) shows that the energy of the electron decreases as a result of the emission of radiant energy. Since an atom does not radiate in the ground state, it follows from the classical theory that the charges in the atom should be at rest.

The most interesting classical model was that of Thomson, according to which the positive charge uniformly filled the entire atomic volume, and the electronic, that is, negative point charges were located inside the atom.

For example, in the hydrogen atom, the positive charge was supposed to fill uniformly a sphere of radius \( R_0 \) (see Fig. 2.1). The charge density inside the sphere was (for \( Z = 1 \))

\[
\rho = \frac{3e_0}{4\pi R_0^3}.
\]

In the ground state, the electron was supposed to be located at the center of the sphere, where the electric field is zero. At a distance \( r = x < R_0 \) from the center, the electric field \( E \) is directed along the radius and its intensity can be found from Gauss' law:

\[
E_r r^2 = \rho \frac{4\pi}{3} r^3 = \frac{e_0 r^3}{R_0^3}.
\]

Hence

\[
E = \frac{e_0}{R_0^3} r.
\]

Therefore, if an electron with charge \( e = -e_0 \) and mass \( m_0 \) is placed at a distance \( x \) from the center of the atom, it experiences a quasi-elastic attractive force towards the center

\[
F = -e_0 E = -\frac{e_0^2}{R_0^3} x = -m_0 \omega_0^2 x.
\]

With this force, the differential equation describing the motion of the electron is

\[
x + \omega_0^2 x = 0,
\]

The solution of this equation is

\[
x = A \cos (\omega_0 t + \varphi_0),
\]
where

$$\omega_0 = \sqrt{\frac{e^2}{m_0 R_0^2}}.$$  

Substituting for $\omega_0$ the fundamental frequency observed in the Balmer series, we obtain a very reasonable value for the radius of the atom, namely, $R_0 \sim 10^{-8}$ cm. This value is many times greater than the classical radius of the electron

$$r_0 = \frac{e^2}{m_0 c^2} \approx 2.8 \cdot 10^{-13} \text{ cm}.$$  

The Thomson model agreed completely with the classical Lorentz theory, according to which atoms can be represented as harmonic oscillators. Unfortunately, the Thomson model could not explain the regularities of the line spectra of atoms and, in particular, the spectral series of hydrogen that are described by Eq. (2.1). Indeed, from the standpoint of classical theory, the Thomson model could emit radiant energy only at the fundamental frequency $\omega_0$ or, at best, at its harmonics

$$\omega_n = n\omega_0,$$  

where $n = 1, 2, 3, \ldots$

The decisive blow to the Thomson model was dealt by the experiments of Rutherford, who showed that the positive charge is not distributed throughout the entire volume of the atom, but is concentrated virtually at one point. Nevertheless, the Thomson potential inside a nucleus of finite dimensions, with a charge $Ze_0$ uniformly distributed through the volume, is

$$\Phi = Z e_0 \left( \frac{3}{R_0} - \frac{1}{2} \frac{r^2}{R_0^2} \right),$$  

(2.6)

---

3If the charge of the nucleus is $Ze_0$, the electric field intensity inside the nucleus is

$$E = \frac{Ze_0}{R_0^3} \frac{1}{r} \frac{\partial \Phi}{\partial r} \frac{r}{r},$$

from which, using the boundary condition that at $r = R_0$ the potential is the same as for a point charge

$$\Phi_{r=R_0} = \frac{Ze_0}{R_0},$$

we obtain Eq. (2.6).
does play an important role, especially when corrections for the volume of the nucleus must be made. Moreover, when mesic atoms with large $Z$ are formed (in a mesic atom, an electron is replaced by a negative $\mu$ meson, whose mass is 207 times larger than the mass of the electron), there may be states in which the negative $\mu$ meson is always inside the nucleus. In this case, the motion of the $\mu$ meson will be determined mainly by the potential (2.6). The appropriate equations of motion will, however, be quantum-mechanical, rather than classical (see Chapter 21).

C. RUTHERFORD'S EXPERIMENTS AND CONCEPTS OF ATOMIC STRUCTURE

Our present model of the atom is based on the famous experiments conducted by Rutherford in 1911 on the passage of alpha particles through matter. It is well known that alpha particles, which are products of nuclear disintegration, possess a sufficient energy to penetrate into an atom. At the time when Rutherford conducted his experiments, there was no other source which could produce sufficiently heavy particles (that is, particles with a mass comparable to the nucleus) with an energy great enough to penetrate the atom.

By passing alpha particles through thin sheets of metal (foil), Rutherford showed\(^4\) that most of the alpha particles which pass through the foil are scattered through relatively small angles (2-3°) from their initial direction of motion. Within the framework of the Thomson model, these small deflections could be explained in terms of the statistical theory of random processes, because of the relatively weak interaction between the atoms and the alpha particles. Rutherford and his co-workers, however, also detected individual deflections of alpha particles through very large angles of up to 180°. Although the number of these deflections was very small (for example, when a beam of 8000 primary alpha particles from RaC is passed through platinum foil, at most one particle is deflected through an angle greater than 90°), it was, nevertheless, much larger than the number which could be predicted on the basis of superposition of a large number of small random deflections.

Large scattering angles were also observed when alpha particles were passed through a gas. These could be easily seen in photographs taken in a Wilson cloud chamber.

From a general analysis of his experiments, Rutherford established, first, that atoms are fairly transparent to alpha particles.

\(^4\)In earlier experiments, Rutherford and his co-workers had established that alpha particles have the same mass as the helium atom, and a positive charge which is twice the magnitude of the electron charge. It is now known that alpha particles are the nuclei of helium atoms.
(that is, their structure is relatively "open"); and, second, that large deflections can take place only if a very strong electric field exists inside the atom. This electric field must be produced by a positive charge which is associated with a large mass and concentrated in a very small volume. We note in this connection that, according to Eq. (2.6), the largest field produced by a nucleus of radius $R_0$ is

$$\Phi_{\text{max}} = \frac{Ze_0}{R_0}.$$  

To explain these results, Rutherford proposed a planetary model of the atom in which the structure of the atom resembles a planetary system. A positively charged nucleus constituting almost the entire mass of the atom is concentrated at the center in a very small volume of radius $R_0 \sim 10^{-13} - 10^{-14}$, and charged electrons move about this nucleus in closed orbits like planets around the Sun. We note that the potential energy of the Newtonian attraction between a planet of mass $m$ and the Sun (of mass $M$)

$$V_{\text{Newt}} = -\frac{\chi m M}{r},$$

where $\chi$ is the gravitational constant and has the same form as the potential energy of the Coulomb attraction between an electron and a nucleus

$$V_{\text{Coul}} = -\frac{Ze_0^2}{r}.$$  

From this model, Rutherford developed a quantitative theory of scattering. His calculations were based on the assumption of a Coulomb interaction between the alpha particles and the nucleus. The influence of the atomic electrons was neglected in the first approximation, since their energy is considerably lower than the energy of the bombarding particles.

Let us find, following Rutherford, the trajectory of an alpha particle moving in the field of an infinitely heavy\(^5\) point nucleus having a charge $Ze_0$. Our calculations will be carried out in a

---

\(^5\)If the finiteness of the nuclear mass $M_{\text{nuc}}$ is taken into account, the nucleus has a certain recoil (like that of the alpha particle) as a result of the interaction. In this case, all the calculations must be performed in the center-of-mass system and, in the results obtained for the case $M_{\text{nuc}} \sim \infty$, it is necessary to replace the mass of the alpha particle $M_0$ by the reduced mass

$$M_{\text{red}} = \frac{M_0 M_{\text{nuc}}}{M_0 + M_{\text{nuc}}}$$

(see Chapter 12, Section C for a discussion of the reduced mass).
coordinate system whose origin coincides with the nucleus (see Fig. 2.2). Since the field produced by the nucleus is centrally symmetric, in determining the trajectory of the alpha particles we can use both the law of conservation of energy

\[ E = \text{const}, \quad (2.7) \]

and the law of conservation of angular momentum

\[ L = M_0 (r \times v) = \text{const}, \quad (2.8) \]

where \( M_0 \) is the mass of the alpha particle, \( r \) is its coordinate, and \( v \) is its velocity.

Let us introduce the polar coordinates \( r \) and \( \varphi \). The velocity of the particle is given by

\[ \mathbf{v} = v^r \hat{r} + v^\varphi \hat{\varphi}, \quad (2.9) \]

where \( v^r = \dot{r} \) and \( v^\varphi = \dot{\varphi} \) are the components of velocity parallel and perpendicular to the radius vector \( r \), respectively, and \( \dot{r} = \frac{dr}{dt} \) and \( \dot{\varphi} = \frac{d\varphi}{dt} \). We then obtain, instead of Eqs. (2.7) and (2.8),

\[ E = \frac{M_0 v^r}{2} + V = \frac{M_0}{2} (\dot{r}^2 + r^2 \dot{\varphi}^2) + \frac{2Ze_0}{r} = \text{const}, \quad (2.10) \]

\[ L_z = M_0 (r \times v)_z = M_0 r^2 \dot{\varphi} = \text{const}. \quad (2.11) \]

In the absence of interaction, the alpha particle would pass the nucleus at a distance \( b \) (this distance \( b \) is called the impact parameter). Setting the initial velocity equal to \( v_0 \) (that is, the velocity
\( r \to -\infty \) and \( \varphi \to \pi \), as follows from Fig. 2.2), then (2.10) and (2.11) can be reduced to the form

\[
\frac{M_0}{2} \left( \dot{r}^2 + r^2 \dot{\varphi}^2 \right) + \frac{2Ze_0^3}{r} = E_0, \tag{2.12}
\]

\[
|Mr^2 \dot{\varphi}| = M_0 bv_0, \tag{2.13}
\]

where the initial energy \( E_0 \) is related to the initial velocity \( v_0 \) by the equation

\[
\frac{M_0 v_0^2}{2} = E_0. \tag{2.14}
\]

Introducing the new variable

\[
u = \frac{1}{r} \tag{2.15}
\]

and noting that then, according to (2.13),

\[
|\dot{\varphi}| = \frac{v_0 b}{r^2} = v_0 bu', \tag{2.16}
\]

and

\[
|\dot{r}| = \left| \frac{dr}{d\varphi} \dot{\varphi} \right| = |v_0 bu'|, \tag{2.17}
\]

where \( u' = \frac{du}{d\varphi} \), we transform Eq. (2.12) to

\[
u'' + u^2 + \frac{4Ze_0^3}{M_0 v_0^2 b^2} u - \frac{1}{b^2} = 0. \tag{2.18}
\]

Differentiating this equation with respect to \( \varphi \), we obtain

\[
u'' + u' + \frac{2Ze_0^3}{M_0 v_0^2 b^2} = 0. \tag{2.19}
\]

Hence

\[
u = A \cos \varphi + B \sin \varphi - \frac{2Ze_0^3}{M_0 v_0^2 b^2}. \tag{2.20}
\]

The unknown constant coefficients \( A \) and \( B \) can be determined from the initial conditions

\[
\lim_{\varphi \to \pi} r = \lim_{\varphi \to \pi} \frac{1}{u} = \infty, \tag{2.21}
\]

and

\[
\lim_{\varphi \to \pi} r \sin \varphi = \lim_{\varphi \to \pi} \frac{\sin \varphi}{u} = b. \tag{2.22}
\]
Setting \( \varphi = \pi \) and \( u = 0 \) in Eq. (2.20), we obtain

\[
A = -\frac{2Ze^2}{M_0v_0^2b},
\]

and, consequently, applying the condition (2.22) to Eq. (2.20), we have

\[
B = \frac{1}{b}.
\]

Thus, we finally obtain

\[
u = \frac{1}{b} \sin \varphi - \frac{2Ze^2}{M_0v_0^2b^2} (1 - \cos \varphi).
\]

This equation gives the relationship between the absolute value of the radius vector \( r \) and the polar angle \( \varphi \), and thus describes the trajectory of the alpha particle in the Coulomb field of the nucleus. It is an equation for a hyperbolic trajectory in polar coordinates.

By definition, the scattering angle \( \Theta \) is equal to the angle \( \varphi \) \((\varphi \neq \varphi_0 = \pi)\) at which the length of the radius vector \( r \) becomes infinite (that is, from Fig. 2.2, \( u = \frac{1}{r} = 0 \)). Therefore, from (2.25), we find

\[
\cot \frac{\Theta}{2} = \frac{M_0b_0^2}{2Ze^2} = \frac{bE_0}{Ze^2}.
\]

It follows that the scattering angle increases as \( b \) decreases, attaining 180° for \( b = 0 \) (see Fig. 2.3).

Equation (2.26) can be checked experimentally by photographing the tracks of alpha particles in a Wilson cloud chamber. From the maximum scattering angle, it is possible to compute the minimum
value of $b$, which turns out to be of the order of the nuclear radius. The actual form of interaction between an alpha particle and a nucleus can, however, be determined more accurately from an investigation of the cross section for the scattering of alpha particles by nuclei. For this purpose, Rutherford calculated the relative number of particles scattered at an angle $\theta$ or, to be precise, the number of scattered particles which we would expect to find within the solid angle

$$d\Omega = 2\pi \sin \theta \, d\theta.$$  \hfill (2.27)

Suppose $N$ particles impinge per unit time on a unit surface placed perpendicularly to the original velocity of the particles. From Eq. (2.26), it follows that the scattering angle depends only on the impact parameter $b$. For a particle to be scattered through an angle $\theta$, it must strike a ring formed by two circles with radii $b$ and $b - db$. The area of this ring is $2\pi b \, db$. Therefore, the number of particles which hit this area and then, as a result of scattering, are found within the solid angle $d\Omega$ is

$$dN = N \cdot 2\pi \left| b \, db \right|.$$  \hfill (2.28)

From Eq. (2.26), we obtain for the relative number of particles scattered through an angle $\theta$

$$\frac{dN}{N} = \pi \left| db^3 \right| = \pi \left( \frac{Ze^4}{E^*} \right)^3 \left| d \cot^2 \frac{\theta}{2} \right|.$$  \hfill (2.29)

The ratio $dN/N$ has the dimensions of area and is called the differential cross section. It is usually denoted by $d\sigma$. Taking the derivative of $\cot^2 \frac{\theta}{2}$ in Eq. (2.29), we obtain the Rutherford formula for elastic scattering of alpha particles by a Coulomb center:

$$d\sigma = \left( \frac{Ze^4}{2E^*} \right)^3 \frac{d\Omega}{\sin^4 \frac{\theta}{2}}.$$  \hfill (2.30)

This formula no longer depends on parameter $b$.

If all the quantities in this equation are kept constant, with the exception of $\theta$, we would expect the following equation to hold:

$$d\sigma \sin^4 \frac{\theta}{2} = \left( \frac{Ze^4}{2E^*} \right)^3 \, d\Omega \approx \text{const.}$$  \hfill (2.31)

For $\theta = \pi$, it is found, however, that the quantity $\sin^4 \frac{\theta}{2} \, d\sigma$ ceases to be constant and begins to decrease somewhat. This fact was explained by Blackett, one of Rutherford's students, who studied
the limits of applicability of the Coulomb law. Blackett took a large number of photographs of tracks of particles in a Wilson cloud chamber and calculated the frequencies with which the various scattering angles occur. From analysis of the experimental data, he established that the number of particles observed at large scattering angles [according to (2.26), large angles correspond to small values of the parameter $b$] is markedly smaller than the number yielded by the formula (2.30). On this basis, Blackett concluded that, in air, for example, Coulomb's law is valid down to distances of the order of $3 \times 10^{-12}$ cm. At smaller distances, there is a deviation from Coulomb's law. Indeed, at $b \sim 10^{-13}$ cm, the interaction between the alpha particle and the nucleus appears to take the form of a strong mutual attraction. Further experimental investigations have confirmed the existence of a characteristic attractive force at distances less than $10^{-12}$ cm. This attraction drops off rapidly with increasing distance from the nucleus.

The Rutherford formula (2.30) can be used to find the number $Z$ from an experimental determination of $dN$ and $N$. This was undertaken by Chadwick, another of Rutherford's students. Chadwick showed that the value of $Z$ is very close to the atomic number, which gives the element's position in Mendeleyev's periodic table. The existence of this phenomenon was rigorously proved at a later date.

Thus the experiments of Rutherford and his colleagues definitely established the planetary model of the atom. These experiments proved that the positive charge of the electron is concentrated in a nucleus with dimensions of $10^{-13} - 10^{-12}$ cm, and that, inside the atom, Coulomb forces keep the electrons moving in orbits with a radius of the order of $10^{-8}$ cm.

**D. THE BOHR THEORY**

First of all, let us attempt to develop Rutherford's planetary model of the atom on the basis of classical theory. We shall restrict ourselves to the case of a hydrogen-like atom, namely, an atom with a nucleus of charge $Ze_0$, with a single electron (of charge $e = -e_0$) moving around it. Particular examples of hydrogen-like atoms include hydrogen ($Z = 1$), ionized helium ($Z = 2$), and so forth.

Introducing the polar coordinates $r$ and $\varphi$ ($x = r \cos \varphi$, $y = r \sin \varphi$), we obtain the following equations for the kinetic energy and the Coulomb potential energy:

$$T = \frac{m_0}{2} (\dot{r}^2 + \frac{1}{r^2} \dot{\varphi}^2),$$

$$V = -\frac{Ze_0^2}{r}.$$
Then the Lagrangian is
\[ \mathcal{L} = \frac{m_0}{2} (\dot{r}^2 + r^2 \dot{\varphi}^2) + \frac{Ze_0}{r}, \]  
(2.32)
where \( m_0 \) is the mass of the electron.\(^6\)

From this Lagrangian, we obtain the following equations for the motion of the electron:
\[ \frac{d}{dt} p_\varphi - \frac{\partial \mathcal{L}}{\partial \dot{\varphi}} = 0, \]
\[ \frac{d}{dt} p_r - \frac{\partial \mathcal{L}}{\partial \dot{r}} = 0. \]
(2.33)

Here
\[ p_\varphi = \frac{\partial \mathcal{L}}{\partial \dot{\varphi}} = m_0 r^2 \dot{\varphi} \]
and
\[ p_r = \frac{\partial \mathcal{L}}{\partial \dot{r}} = m_0 \dot{r} \]
(2.34)
represent the generalized momenta associated with the \( \varphi \) and \( r \) coordinates, respectively. Since \( \varphi \) does not occur explicitly in \( \mathcal{L} \) (in other words, it is a cyclic coordinate), it follows that \( \frac{\partial \mathcal{L}}{\partial \dot{\varphi}} = 0 \). Therefore, the corresponding generalized momentum is a constant of the motion
\[ p_\varphi = m_0 r^2 \dot{\varphi} = \text{const.} \]
(2.35)
This is the law of conservation of angular momentum, which is well known from classical mechanics. The second conservation law, namely, the law of conservation of energy
\[ E = T + V = \text{const} \]
(2.36)
is obtained from the condition that the time \( t \) does not occur explicitly in the Lagrangian.

We shall consider only the simplest case, that of circular orbits, for which \( \dot{r} = 0 \). Accordingly, \( p_r = m_0 \dot{r} \) vanishes, and from (2.33) we have
\[ \frac{\partial \mathcal{L}}{\partial r} = m_0 r^2 \dot{\varphi}^2 - \frac{Ze_0^2}{r^2} = 0, \]
(2.37)

\(^6\)In the following chapters, the mass of the electron in nonrelativistic theory shall be denoted by \( m_0 \), since \( m \) will be used for the magnetic quantum number.
Hence
\[ \psi^2 = \frac{Ze^2}{m_0 r^2}. \] (2.38)

Therefore, we obtain for the energy of the electron
\[ E = \frac{m_0}{2} r^2 \psi^2 = -r \frac{Ze^2}{r} = -\frac{1}{2} \frac{Ze^2}{r} = \frac{1}{2} V. \] (2.39)

Let us now express the basic parameters of the atom in terms of the adiabatic invariants, which were introduced by Ehrenfest. According to Ehrenfest's definition, in the case of periodic motion, the quantities
\[ \int p_i \, dx_i = I_i \] (2.40)

\((p_i\) is a generalized momentum, and \(x_i\) a generalized coordinate) remain constant during slow (adiabatic) changes of the parameters of the system (for instance, the charge).

In our case, there is only one degree of freedom \((\kappa_i = \phi)\). The conditions (2.35) and (2.40) yield the equation
\[ p_\phi = m_0 r^2 \phi = \frac{l}{2\pi}, \] (2.41)
or
\[ \psi = \frac{l}{2\pi m_0 r^2}. \] (2.42)

From Eqs. (2.38) and (2.42), we can obtain expressions for \(r\) and \(\psi\) in terms of the adiabatic invariant:
\[ r = \frac{l^2}{4\pi^2 m_0 Z^2 e^2}, \] (2.43)
\[ \psi = \omega_0 = \frac{8\pi^3 m_0 Z^2 e^2}{l^2}. \] (2.44)

According to Eq. (2.39), the energy of the electron is then
\[ E = -2\pi^3 \frac{m_0 Z^2 e^2}{l^2}. \] (2.45)

It follows that the frequency of mechanical oscillation \(\gamma_0\) is given by the derivative of the energy with respect to the adiabatic invariant:
\[ \gamma_0 = \frac{\partial E}{\partial l} = \frac{4\pi^3 m_0 Z e^2}{l^2}. \] (2.46)
This relation holds not only for the case under consideration, but also for any periodic or quasi-periodic motion. Moreover, a system performing any periodic motion can generally emit radiation not only at the first harmonic $k=1$, but also at the harmonics $k=2, 3, 4, \ldots$. The following expression is, therefore, obtained for the classical frequency of radiation:

$$\nu = k \nu_0 = k \frac{\partial E}{\partial t}. \tag{2.46a}$$

The classical theory of the planetary model of the atom led to a number of difficulties when it was used to explain the radiation of atoms. Since this model is dynamic, it follows from classical electrodynamics that the centripetal acceleration of the electron ($a = \frac{v^2}{a}$, where $v$ is its velocity, and $a$ is the radius of its orbit) will cause the electron to lose energy at the rate

$$-\frac{\partial E}{\partial t} = \frac{2}{3} \frac{e^2 v^2}{c^2}$$

until it falls into the nucleus. This is not, however, what actually takes place, and atoms can exist in a non-radiating state for an arbitrarily long time. Moreover, according to the classical theory, the frequency of the radiation should be the same as the frequency of mechanical oscillation (the fundamental frequency $\omega = \omega_0 = 2\pi \nu_0$) or, alternatively, an integral multiple of this frequency (one of the harmonics $\omega_n = n\omega_0$, where $n = 2, 3, 4, \ldots$). Once again, this prediction does not explain Balmer's experimentally established formula (2.1) for the lines in the spectrum of radiation.

---

7 We define periodic motion as a motion in which a point returns to its initial position after a certain period of time. As examples of this, we can take harmonic motion

$$x = a \cos \omega t$$

or motion about an ellipse

$$x = a \cos \omega t \quad \text{and} \quad y = b \sin \omega t,$$

a special case of which is motion about a circle ($a = b$). Quasi-periodic motion is motion in which a point does not return, as a rule, to its initial position, but each individual coordinate reassumes its initial value after a certain period of time (which is different for each of the coordinates). As an example of quasi-periodic motion, we can take

$$x = a \cos \omega_1 t,$$

$$y = b \cos \omega_2 t,$$

where the frequency $\omega_1$ is incommensurable with $\omega_2$. 
The solution to these difficulties was found in 1913 by Niels Bohr, who added two postulates to the classical laws of motion.

First, Bohr assumed that each atom has a series of discrete stationary states in which the electron does not emit radiation, even though its motion is accelerated (the postulate of stationary states). According to Bohr's theory, these stationary states can be determined by quantizing the adiabatic invariants:

$$\oint p_i \, dq_i = nh,$$  \hspace{1cm} (2.47)

where the quantum number $n$ can assume only integral values, that is, $n = 1, 2, 3, \ldots$ (in classical mechanics, the adiabatic invariant $I$ could assume any constant value).

Second, Bohr hypothesized that, when an electron passes from a stationary state with energy $E_n$ (the initial state) to a state with an energy $E_n' < E_n$ (the final state), the atom radiates a quantum of energy $h\nu = h\omega$ (the frequency postulate), whose angular frequency $\omega$ is

$$\omega = \frac{E_n - E_n'}{n}.$$  \hspace{1cm} (2.48)

This equation can be written in a form similar to the classical expression (2.46a) for the frequency of radiation:

$$\nu = (n - n') \frac{\Delta E}{\Delta I} = k \frac{\Delta E}{\Delta I}.$$  \hspace{1cm} (2.48a)

Here the quantum number $k = n - n'$ can be interpreted as the corresponding harmonic, and, moreover, the derivative of $E$ with respect to $I$, which occurs in the classical expression, is replaced by the ratio of the finite increments.

Bohr's postulate that the stable energy states of atoms form a discrete spectrum was confirmed in experiments conducted in 1919 by Franck and Hertz. Passing an electron beam (a current) through mercury vapor, they showed that, for electron energies less than 4.9 ev, the collisions of electrons with Hg atoms do not effect the magnitude of the current. When the electron energy attains 4.9 ev (see Fig. 2.4), the current suddenly drops. With further increase of the electron energy, periodic sharp dips of the current are observed (approximately every 4.9 ev). This phenomenon can be very simply interpreted from the point of view of the Bohr theory. Let us suppose that the energy of an unexcited Hg atom (that is, the atom before collision) is $E_0$ and, in conformity with the first Bohr postulate, let us take the next possible energy value to be $E_i = E_0 + 4.9$ ev. It then follows that a beam of electrons of energy $E < 4.9$ ev is not sufficient to raise the atoms to an excited state;
therefore, the collisions are elastic and the current does not change. If however, \( E \geq 4.9 \text{ ev} \), the electrons in the beam may give up a part of their energy (namely, 4.9 ev) to the atoms, and therefore, the current will change. If the electrons' energy lies in the range \( 14.7 \text{ ev} > E > 9.8 \text{ ev} \), the transfer of energy to the atoms can occur twice; 4.9 ev is given up in the first collision and 4.9 ev in the second.

![Graph](image)

Fig. 2.4. The dependence of current on electron energy in the Franck-Hertz experiment (1 ev = \( e_0 / 300 = 1.6 \times 10^{-12} \) erg).

We shall now use the first and second Bohr postulates [Eqs. (2.47) and (2.48)] to construct a theory of the hydrogen-like atom. In the equation for the radius of the orbit (2.43) and the equation for the energy (2.45), let us substitute for \( l \) its quantized value, which from Eq. (2.47) is

\[
l = 2\pi nh,
\]

We thus have

\[
r_n = \frac{n^2\hbar^2}{m_0Ze_n^2}, \tag{2.49}
\]

\[
E_n = -\frac{m_0Z^2e_0^2}{2n^2\hbar^2}. \tag{2.50}
\]

For \( n=1 \), we obtain the energy of the lowest (ground) state of the atom

\[
E_1 = -\frac{m_0Z^2e_0^2}{2\hbar^2}, \tag{2.51}
\]

and the corresponding radius

\[
r_1 = \frac{\hbar^2}{m_0Ze_0^2} = \frac{1}{Z} a_0. \tag{2.52}
\]
where

\[ a_0 = \frac{\hbar^2}{m_e e_0^2} \approx 0.529 \times 10^{-8} \text{ cm} \]  

(2.53)

is the radius of the first Bohr orbit.

The second Bohr postulate (2.48), combined with Eq. (2.50) for the frequency of radiation \( \omega_{nn'} \), gives

\[ \omega_{nn'} = \frac{E_n - E_{n'}}{\hbar} = \frac{m_0 Z^2 e_b}{2 \hbar^3} \left( \frac{1}{n'^2} - \frac{1}{n^2} \right). \]  

(2.54)

Accordingly, for \( Z = 1 \), we obtain Balmer’s formula (2.1). The Bohr theory also relates the Rydberg constant, established prior to this on a purely empirical basis, with the Planck constant \( \hbar \):

\[ R = \frac{m_0 e_1}{2 \hbar^3}. \]  

(2.55)

This derivation of Balmer’s formula, with a value for the Rydberg constant that agreed with experiment, was one of the greatest achievements of the Bohr theory. In spite of this success, however, the Bohr theory has a number of inherent defects, which became increasingly important in its further development.

In the first place, the Bohr theory was obviously semiclassical in nature. In addition, the Bohr theory could be used to compute only the frequency of the spectral lines, and not their intensity. To find the intensity, it was necessary to resort to classical electrodynamics, on the basis of the so-called correspondence principle. Finally, the Bohr postulates could not be used to construct a satisfactory theory of multielectron atoms, including that of helium, which possesses only two electrons.

---

8According to the correspondence principle, in the limit, all the results of a previous theory (here, classical electrodynamics) should follow from a new theory (here, the Bohr theory).

For instance, for \( \hbar \to 0 \) (or at the limit of large quantum numbers), the results of quantum mechanics should approach the classical results. In exactly the same way, when \( \hbar^2 \to 0 \), the results of the relativistic theory should approach the nonrelativistic results, and so on. Thus, the correspondence principle enables us to check the extension of a theory by requiring it to reduce to the classical picture at the limit.

In the initial stages of a new theory, when it cannot yet be used to investigate certain phenomena, the correspondence principle may be used for reasonable extensions of the predictions of the old theory to the new theory. Thus, for example, the Bohr theory could be used to calculate the frequency of the radiation, but not its intensity. Bohr was able to determine the intensity from the correspondence principle, according to which the only changes of the quantum number \( n \) that were allowed (the selection rules \( \Delta n : n - n' \)) were those that coincided with the classically allowed harmonics of the radiation. The quantum theory of radiation of light was completed only with the development of quantum electrodynamics.
Accordingly, we shall not discuss in greater detail the subsequent history of the Bohr theory. This theory represented only an intermediate stage in the development of quantum mechanics, a theory which can be used to determine both the frequency and intensity of the radiation of atoms. However, we thought that at least a brief discussion of the basic principles of the Bohr theory was advisable, for this theory still retains considerable heuristic significance. In particular, the Bohr theory often serves as the starting point in the analysis of many results related to quantization.

The conclusions that follow from Eq. (2.54) will be discussed in Chapter 13, where the problem of the hydrogen-like atom will be solved quantum-mechanically.

Problem 2.1. Using the Bohr theory, quantize a hydrogen-like atom for the case of elliptic orbits (that is, find the spectrum of the energy levels). Show that, in the non-relativistic approximation, the coordinates \( r \) and \( \varphi \) have the same frequency of variation; that is, the motion is periodic. Show that the formula for the frequency of the radiation of an atom remains the same as in the case of circular orbits.

What new feature is introduced in the theory by considering elliptic orbits?

Solution. Using condition (2.40) and noting that, in this problem, the generalized momenta corresponding to the \( \varphi \) and \( r \) coordinates are

\[
p_\varphi = m_0 r^2 \dot{\varphi} = \text{const and } p_r = m_0 \frac{r^2}{r^2} = \sqrt{2m_0 E + \frac{2m_0 Z e_0^2}{r} - \frac{p_\varphi^2}{r^2}}.
\]

we find

\[
l_\varphi = \int_0^{2\pi} p_\varphi d\varphi = 2\pi p_\varphi, \quad l_r = 2 \int_{r_{\text{min}}}^{r_{\text{max}}} p_r dr = 2\pi \left( -p_\varphi + Ze_0^2 \sqrt{\frac{m_0}{-2E}} \right).
\]

There the second integral was calculated from the formula

\[
2 \int_{r_{\text{min}}}^{r_{\text{max}}} \sqrt{-\frac{2B}{r} - \frac{C}{r^2}} dr = 2\pi \left( \frac{B}{\sqrt{A}} - \sqrt{BC} \right).
\]

Hence the energy \( E \) is

\[
E = -\frac{4\pi^2 m_0 Z^2 e_0^4}{2(l_r + l_\varphi)^2} < 0.
\]

By direct differentiation of this equation with respect to the variables \( l_r \) and \( l_\varphi \), it is easily shown that the frequencies with which the \( r \) and \( \varphi \) coordinates change

\[
\omega_r = \frac{\partial E}{\partial l_r} \quad \text{and} \quad \omega_\varphi = \frac{\partial E}{\partial l_\varphi}
\]

coincide with one another. Using the Bohr quantization rule (2.47), we replace the adiabatic invariants \( l_r \) and \( l_\varphi \) by \( n_r \hbar \) and \( n_\varphi \hbar \), respectively, obtaining

\[
E_n = -\frac{m_0 Z^2 e_0^4}{2\hbar^2 n^2},
\]
where \( n = n_r + n_\varphi \), \( n_r = 0, 1, 2, 3, \ldots \) and \( n_\varphi = 1, 2, 3, \ldots \). This expression is completely identical with Eq. (2.50), which was derived for the case of circular orbits; therefore, the radiation frequencies remain the same as before.

States with a given \( n_r \) and different \( n_\varphi \) have the same energy, but differ in eccentricity \( \varepsilon \):

\[
\varepsilon = \sqrt{1 - \frac{n_\varphi^2}{n_r^2}}.
\]

In particular, when \( n_\varphi = n \), we have a circular trajectory. As \( n_\varphi \) decreases, the elliptic trajectory becomes more elongated.

The new feature to appear in the case of elliptic orbits is the selection rules \( \Delta n_\varphi = \pm 1, \Delta n = \pm 1, \pm 2, \pm 3, \ldots \). These account for the appearance of series that can also be found from the correspondence principle. In the case of circular orbits, \( \Delta n = \Delta n_\varphi = \pm 1 \) (see also Chapter 13).

Problem 2.2. Find the classical equation of motion and the trajectory of an electron about the nucleus according to relativistic theory. Show that, in this case, the \( r \) and \( \varphi \) coordinates change with different frequencies; that is, the motion is quasi-periodic. Determine the angle through which the perihelion of the electron is shifted during "one" revolution. Obtain a formula for the energy levels and find their splitting. Compare the results with the corresponding nonrelativistic problem 2.1.

Solution. Using the relativistic Lagrangian function

\[
\mathcal{L} = -m_0 c^2 \sqrt{1 - \beta^2} + \frac{Ze_0^2}{r}, \tag{2.57}
\]

where

\[
\beta^2 = \frac{\beta^2}{c^2} = \frac{1}{c^2} (r^2 - r_0^2 y^2),
\]

we obtain the equation of motion

\[
\frac{d}{dt} \frac{m_0 \beta}{\sqrt{1 - \beta^2}} = -\frac{Ze_0^2}{r^3} r.
\]

From Eq. (2.57) we determine the generalized momenta \( \beta_\varphi = \frac{\partial \mathcal{L}}{\partial \dot{\varphi}} \) and \( p_r = \frac{\partial \mathcal{L}}{\partial \dot{r}} \). Since \( p_r = \frac{p_r'}{r'} \), where \( r' = \frac{dr}{d\varphi} \), it follows, in accordance with the law of conservation of energy, that

\[
E = \frac{1}{c} \sqrt{m_0^2 c^4 + p_\varphi^2 + \frac{p_r^2}{r^2} r^2 \varepsilon^2} \text{ const},
\]

which implies that

\[
\frac{dr}{d\varphi} = \frac{p_r'}{c \beta_\varphi} \sqrt{\left( E + \frac{Ze_0^2}{r^2} \right) - m_0^2 c^2 - \frac{c^2 p_\varphi^2}{r^2 \varepsilon^2}}.
\]

Hence we obtain the equation of the trajectory

\[
r = \frac{q}{1 + \varepsilon \cos \varphi}, \tag{2.58}
\]
where

\[ \gamma = \sqrt{1 - \frac{Z^2 e^2}{\epsilon^2 p^2}}, \]
\[ q = \frac{\gamma^2 e^2 p^2}{Z e^2 E}, \]
\[ \epsilon = \sqrt{1 + \frac{\gamma^2 (1 - \frac{m_e c^4}{2 E^2})}{1 - \frac{\gamma^2}{4}}}. \]

It is apparent from Eq. (2.58) that the motion is quasi-periodic. For the shift \( \Delta \varphi \) of the perihelion, we have from (2.58)

\[ \Delta \varphi = \frac{2 \pi (1 - \gamma)}{\gamma} \approx \frac{\pi Z^2 e^4}{c^2 p^2}. \]

With the help of (2.40) and (2.56) we get

\[ I_\varphi = 2 \pi p_{\varphi}, \]
\[ I_r = 2 \pi \left( \frac{B}{\sqrt{A}} - \sqrt{C} \right), \]

where

\[ A = m_e^2 c^2 \left( 1 - \frac{E^2}{m_e^2 c^4} \right), \]
\[ B = \frac{Ze^2 E}{\epsilon^2}, \quad C = p_{\varphi}^2 - \frac{Z^2 e^4}{c^2}. \]

Then, for the energy \( E \), we obtain the expression

\[ E = m_0 c^2 \left( 1 + \frac{Z^2 e^2}{c^2 \left[ \frac{I_r}{2 \pi} + \sqrt{\frac{I_r^2}{4 \pi^2} - \frac{Z^2 e^4}{c^2}} \right]} \right)^{-1/2}. \] (2.59)

From this it is evident that the frequencies \( \omega = \frac{\partial E}{\partial I_\varphi} \) and \( \omega_r = \frac{\partial E}{\partial I_r} \) will be different.

Using the Bohr quantization rule (2.47), we transform Eq. (2.59) to

\[ E_{n_r, n_\varphi} = E - m_0 c^2 \left( 1 + \frac{Z^2 a^2}{\left[ n_r + \sqrt{n_r^2 - Z^2 a^2} \right]} \right)^{-1/2} - m_0 c^2, \] (2.60)

where \( a = \frac{e^2}{\epsilon h} \approx \frac{1}{137} \) is the fine-structure constant.

Expanding the formula (2.60) into a series in \( a^2 \) and restricting ourselves to quantities of the order of \( a^4 \), we have

\[ E_{n_r, n_\varphi} = -\frac{R \hbar Z^2}{n^3} \left[ 1 + \frac{a^2 Z^2}{n^3} \left( \frac{n}{n_\varphi} - \frac{3}{4} \right) \right]. \] (2.51)

Since \( n_\varphi \) varies from 1 to \( n_r \), it follows from Eq. (2.61) that the energy levels, which are determined by the principal quantum number \( n = n_r + n_\varphi \), are split into \( n \) closely spaced sublevels (this close spacing is a consequence of the smallness of \( a^2 \)).
The fine-structure splitting is
\[ \Delta E_{n,\ell} = E_{n,\ell} - E_{n-1,\ell-1} = \frac{a^2 Z^4 R \hbar}{n^2 n_{\ell} (n_{\ell} - 1)}. \]

The splitting, or fine structure, of the levels, is a characteristic result of relativistic effects and essentially distinguishes the predictions of relativistic theory from those of nonrelativistic theory (see Problem 2.1).

Problem 2.3. An electron is located in a central field
\[ V = -\frac{A}{r^2}, \quad A > 0. \]
Determine the values of \( s \) at which stable states of the system are possible.

Answer, \( s < 2 \).

Hint. Use the expression for the effective potential energy
\[ V_{\text{eff}} = \frac{p^2}{2m_{\text{eff}}} - \frac{A}{r^2} \]
and make use of the fact that stable motion is possible if \( V_{\text{eff}} \) has a minimum.

Problem 2.4. Find the scattering cross section for nonrelativistic electrons by nuclei (Coulomb point charges). Compare the result with the scattering cross section for alpha particles.

Answer.
\[ d\sigma = \left( \frac{Ze_0^2}{4E_0} \right)^2 \frac{d\Omega}{\sin^4 \frac{\theta}{2}}. \]

Problem 2.5. Show that in the relativistic scattering, unlike the nonrelativistic case, electrons can be captured by nuclei. Obtain the total capture cross section.

Solution. According to nonrelativistic theory, the trajectory of electrons in the Coulomb field of a nucleus is given by the equation
\[ r = \frac{q}{1 + \epsilon \cos \varphi}, \]
where
\[ q = \frac{p_{\varphi}^2}{m_0 Z e_0^2}, \quad \epsilon = \sqrt{1 + \frac{2Ep_{\varphi}^2}{m_0 Z^2 e_0^4}}. \]

At \( E > 0 \), this equation describes hyperbolic motion, and therefore the capture of electrons is impossible.

In relativistic mechanics, the equation of the trajectory has the form of Eq. (2.58).

If \( \frac{Z^2 e_0^4}{\epsilon} \gg 1 \) in this equation, \( \gamma \) becomes imaginary. Therefore, \( r \rightarrow 0 \) for \( \varphi \rightarrow \infty \); that is, the particle falls to the center, which means it is captured.

Since the angular momentum \( p_{\varphi} \) of the electron is related to the initial momentum \( p \) and the impact parameter \( b \) by the expression \( p_{\varphi} = pb \), the condition for capture can be written in the form \( b^2 \ll \frac{Z^2 e_0^4}{\epsilon p^2} \). Hence the total capture cross section is
\[ \sigma_{\text{cap}} = \pi b_{\text{max}}^2 = \frac{\pi Z^2 e_0^4}{\epsilon p^2}. \]
Chapter 3

Wave Properties of Particles

A. DE BROGLIE WAVES

As we mentioned in Chapter 1, the development of modern quantum theory began with the discovery that light has particle properties in addition to wave properties (characterized by the wavelength $\lambda$ and the frequency $\omega$). The energy $\varepsilon$ and momentum $\pi$ of a quantum of light (photon) were established by Einstein as

$$\varepsilon = h\omega = h\nu, \quad \pi = \hbar k = \frac{h}{\lambda} k_0. \quad (3.1)$$

Analyzing these equations, the French physicist de Broglie suggested that they could be generalized to apply to ordinary particles and, in particular, electrons. Generally speaking, de Broglie assumed that the wave-particle duality is not an exclusive property of light, but is also a characteristic of electrons and all other particles. Accordingly, a beam of free electrons, whose relative energy $E$ and momentum $p$ are related to the velocity $v$ by the equation

$$E = \gamma m_0 c^2 \frac{m_0 c^2}{\gamma^2 - \beta^2}, \quad p = \gamma m_0 v \frac{m_0 v}{\gamma^2 - \beta^2}, \quad (3.2)$$

should also exhibit wave-like properties. The corresponding frequency and wave number were defined by equations similar to Einstein's:

$$E = h\omega \quad \text{and} \quad p = \hbar k. \quad (3.3)$$

---

1. This hypothesis was made by de Broglie with a twofold purpose: first, to provide a physical basis for the Bohr quantization; second, to explain the first experiments on electron diffraction (see below).

2. From now on, we shall leave it to the reader to distinguish between the relativistic energy (which includes the rest mass energy) and the nonrelativistic energy. Only in cases in which the two energies appear in the same equation will they be distinguished by some kind of index, for example,

$$E = E' + m_0 c^2.$$
Consequently, the de Broglie wavelength of the moving particles is

\[ \lambda = \frac{2\pi}{k} = \frac{h}{p}. \]  

(3.4)

The de Broglie relations (3.3) thus generalized Einstein equations (3.1), derived from the photon theory. These now became equally applicable to the analysis of light in terms of its particles and of moving electrons in terms of their wave properties. It is worth noting that the dual character of particles and light disappears if Planck's constant \( \hbar \) is allowed to go to zero (the correspondence principle).

Taking de Broglie's equations (3.3) as the basis of discussion, we may describe the motion of free particles (along, say, the \( x \) axis) by the so-called wave function, which for this particular case is analogous to that of light and represents a plane wave:

\[ \psi(x, t) = Ae^{-2\pi i \left( \frac{vt - x}{\lambda} \right)} = Ae^{-i (\omega t - kx)} = Ae^{-\frac{i}{\hbar} (Et - px)}. \]  

(3.5)

From the standpoint of Eq. (3.5), we can attempt to explain Bohr's postulate of stationary states [see Eq. (2.47)]. The physical interpretation which we can offer is as follows: the only allowed circular orbits are those which are divisible by an integral number of de Broglie wavelengths, that is,

\[ \frac{2\pi r}{\lambda} = n. \]  

(3.6)

Indeed, the wave function is single-valued only when this condition is satisfied. Furthermore, since in the nonrelativistic case

\[ \lambda = \frac{h}{m_0 v}, \]

Eq. (3.6) yields the Bohr condition for stationary states:

\[ p \xi = m_0 e v = \hbar n. \]  

(3.7)

B. EXPERIMENTAL OBSERVATION OF THE WAVE PROPERTIES OF PARTICLES

To investigate the wave properties of electrons and to prove that electrons have a specific wavelength \( \lambda \), it is first of all necessary to obtain a monochromatic electron beam (a beam of electrons moving with the same velocity). One possible way of producing such a beam is by means of an "electron gun" (see Fig. 3.1),
which emits electrons with a certain definite velocity $v$. In the nonrelativistic case ($v \ll c$), this velocity is given by the equation

$$\frac{m_0 v^2}{2} = e_0 \Phi \frac{\Delta}{300},$$  \hspace{1cm} (3.8)

where $\Phi$ is the accelerating potential (in volts) of grid $A$ relative to the cathode $C$. Thus, after passage through grid $A$ (at which point no further acceleration is imparted), the electrons will have a de Broglie wavelength of

$$\lambda = \frac{h}{m_0 v} = \frac{h}{\sqrt{m_0 e_0 \Phi}} = \frac{1.2 \cdot 10^{-7}}{\sqrt{\Phi}} \text{ cm.}$$  \hspace{1cm} (3.9)

To exhibit the wave properties in the most pronounced form, one must impart to them the longest possible wavelength $\lambda$. This can be done by decreasing $\Phi$. Since, however, a certain amount of energy, known as the work function, is expended in the ejection of electrons from metal (this energy is of the order of several ev and gives rise to a certain spread in the electron velocities), the smallest potential $\Phi$ at which the beam will be relatively monochromatic is 15-20 volts. At these conditions, the de Broglie wavelength of the electrons is approximately the same ($\lambda \sim 10^{-8}$ cm) as the wavelength of soft x-rays.

Before we consider the physical nature of the wave-like character of an electron beam, let us discuss several experiments that have led to the direct detection of de Broglie waves. To begin with, we shall take the electron diffraction experiments of Davisson and Germer, who were the first to make experimental observations of electron waves. Since the de Broglie wavelength of an electron is of the order of $10^{-8}$ cm, they proceeded in the same way as for soft x-rays, using a crystal with a lattice constant of the order of $10^{-8}$ cm for the diffraction grating. The set-up of the Davisson-Germer experiments is depicted in Fig. 3.2. After coming out of the electron gun, the beam impinges perpendicularly on the surface of the crystal, where the electrons are scattered at various angles by the surface lattice. Since the penetration of the electrons into the crystal can be neglected, the diffraction grating can be regarded as two-dimensional. Accordingly, the position of the diffraction maxima can be determined from the condition that the path difference $s \approx d \sin \theta$ ($d$ is the
two-dimensional lattice constant and $\theta$ is the scattering angle) is equal to an integral number of wavelengths (see Fig. 3.3):

$$d \sin \theta_n = n \lambda = n \frac{1.2 \cdot 10^{-7}}{V \Phi},$$

where the integer $n$ is the order of the given diffraction maximum. The diffraction maxima were detected with a galvanometer, which registered the intensity of the beam of scattered electrons at different angles (see Fig. 3.2).

A second prediction of the de Broglie theory was also verified: namely, the prediction that as the potential $\Phi$ increases, the angle $\theta_n$ corresponding to the $n$th diffraction maximum, will decrease in accordance with Eq. (3.10). Thus the correctness of de Broglie's equations was completely confirmed by these investigations.

It is well known that x-ray diffraction patterns are produced not only by single crystals, but also by polycrystalline formations. This was shown, for example, by Debye and Scherrer. Tartakovski and Thomson obtained diffraction patterns similar to these x-ray diffraction patterns by extending this technique to electron waves and passing an electron beam through a foil.\(^3\) The following theoretical explanation can be given for the diffraction pattern of electrons. The electron beam, with an energy of several thousands or even tens of thousands of electron volts, impinges upon a polycrystalline foil, where it

\(^3\)To reduce the absorption of electrons, a relatively thin foil (thickness of the order of $10^{-5}$ cm) was used.
encounters single crystals and is reflected from them. The path difference $s$ of two rays (see Fig. 3.4) is related to the lattice constant $d$ of the three-dimensional crystal by the relation

$$s = 2d \sin \varphi,$$

(3.11)

where $\varphi$ is the angle between the ray and the lattice plane. Since the single crystals of the foil are oriented at random, a ray can leave the foil at any angle with respect to the original direction (see Fig. 3.5). Among the crystals, there will be some that are oriented at just the right angle to satisfy Bragg's law

$$2d \sin \varphi = n \lambda = n \frac{1.2 \cdot 10^{-7}}{V \Phi},$$

(3.12)

where $n$ is an integer. Whenever this is the case, a diffraction maximum occurs and a bright spot $Q$ is found on the screen. Since the experimental apparatus is cylindrically symmetric, the bright spots form diffraction rings, whose radii $R_n$ can be found from the relation (see Fig. 3.5)

$$\tan 2\varphi = \frac{R}{L},$$

(3.13)

where $L$ is the distance from the screen to the polycrystalline foil. Since the angle $\varphi$ is very small in these experiments ($\varphi \approx \sin \varphi \approx \tan \varphi$), Eqs. (3.12) and (3.13) yield

$$R_n = n \frac{L}{d} \frac{1.2 \cdot 10^{-7}}{V \Phi},$$

(3.14)

that is, at constant $L, d$ and $n$,

$$R \cdot V \Phi = \text{const.}$$

(3.15)

These relations were completely confirmed by Thomson's experiments. Electron diffraction patterns and Debye-Scherrer x-ray diffraction patterns are now widely used in studies of crystal structure.

It is worth noting that de Broglie's formula does not only apply to electrons and other elementary particles such as protons and neutrons, but also to complex nuclei, multielectron atoms, and even to molecules. True, their de Broglie wavelength is very small because of their relatively large mass. Nevertheless, Stern and Esterman have succeeded in observing the diffraction of beams of
helium atoms and hydrogen molecules in reflections from LiF crystals.

![Diagram](image)

**Fig. 3.5. Diffraction of electron waves in a polycrystalline substance (the Tartakovskiy-Thomson experiments).**

A method involving neutron diffraction has been found extremely useful in analyzing the structure of substances. Neutrons have no electric charge and, therefore, pass freely through matter even at low energies (thermal neutrons), when their de Broglie wavelength is relatively large. All these facts provide convincing evidence that wave properties are displayed in some degree or other by all particles and that the de Broglie formula for $\lambda$ is of universal validity.

The analogy between light waves and electron waves has led to the development of a new branch of physics, electron optics, which is devoted to the study of wavelike processes in electron beams. With the help of this new science, it has been possible to design and construct electron microscopes, which have found wide application in modern techniques. In ordinary optical microscopes, the upper limit of the resolving power (and, consequently, the magnification) is of the order of the wavelength of the light which is utilized. To achieve the highest possible magnification, it is necessary to reduce the wavelength of the light. The wavelength, however, cannot be made arbitrarily small: it is impossible, for instance, to construct an x-ray microscope, since no appropriate lens exists for x-rays. On the other hand, satisfactory electric and magnetic lenses can be produced for electron waves. Thus, the electric lens consists of a capacitor which has an aperture in the middle of the plate, while the magnetic lens consists of ordinary magnetic coils.\(^4\)

\(^4\)Modern optical microscopes give a magnification of approximately one or two thousand. An electron microscope can give a magnification of more than 100,000. Besides the electron microscope, the proton microscope is also widely used at present. Its resolving power can be made even greater than that of the electron microscope.
C. WAVE PACKETS. GROUP AND PHASE VELOCITIES

From de Broglie's hypothesis it follows that the motion of a free material particle having an energy $E = mc^2$ and a momentum $p = mv$, can be described by means of the plane wave (3.5). The velocity $u$ of the de Broglie wave can be found as the time rate of displacement of a constant phase

$$E t - px = \text{const};$$

that is, the phase velocity is

$$u = \frac{dx}{dt} = \frac{E}{p} = \frac{c^2}{v}.$$  

(3.17)

According to the theory of relativity, the velocity of the particle $v$ cannot exceed that of light in vacuum ($c$). However, the calculated phase velocity of the wave appears larger than $c$. This would indicate that it is theoretically impossible for a monochromatic wave to transport a particle or carry energy, since all particles and energy must travel with a velocity smaller than that of light, in accordance with the principle of relativity.

---

5This equation can be obtained from the following simple considerations. The wave function depends only on the phase $\phi = (Et - px) \frac{1}{\hbar}$; therefore, at the time $t_1 = t + \Delta t$, this phase moves to the point $x_1 = x + \Delta x$, which can be found from the equation

$$Et_1 - px_1 = Et - px = \text{constant}.$$

Thus

$$E\Delta t - p\Delta x = 0.$$  

Hence the rate of propagation of the constant phase (which is also the velocity of the wave as a whole, as can be seen from Fig. 3.6) is

$$u = \frac{\Delta x}{\Delta t} = \frac{E}{p}.$$  

---

Fig. 3.6. The propagation of a monochromatic wave. During the time $\Delta t$, the wave as a whole moves a distance $\Delta x$. The phase velocity of the wave is $\frac{\Delta x}{\Delta t}$. 
An escape from this dilemma was found in the early stages of the development of quantum mechanics. This solution retained the wave properties of particles, which had received such striking experimental confirmation. Thus, each particle was associated with a group of waves of nearly equal frequencies, rather than with a single monochromatic wave. This was further suggested by the fact that the diffraction lines of electron waves were always observed to have a certain definite width. Thus, it seemed that several waves with very nearly equal frequencies were diffracted, rather than an individual wave. Yet another basis for this solution was provided by spectroscopic studies, which showed that all spectral lines are also characterized by a certain definite width.

One advantage which results from using a set of waves with nearly equal frequencies rather than an individual monochromatic wave is that it is always possible to construct a wave packet whose resultant amplitude is appreciably different from zero only in a certain small region of space. This small region of space can be associated with the position of the particle.

On the basis of these considerations, let us attempt to describe the motion of a particle by constructing a wave packet out of a continuous set of waves, assuming that the momentum \( p' \), which is connected with the wave number \( k' \) by the de Broglie relationship

\[
k' = \frac{p'}{\hbar},
\]

ranges from \( p - \frac{\Delta p}{2} \) to \( p + \frac{\Delta p}{2} \) \((\Delta p \ll p)\). We shall take the amplitudes \( A(p') \) of the individual waves to be

\[
A(p') = \begin{cases} 
0, & p' < p - \frac{\Delta p}{2}, \\
\frac{\Delta p}{\Delta p}, & p - \frac{\Delta p}{2} \leq p' \leq p + \frac{\Delta p}{2}, \\
0, & p' > p + \frac{\Delta p}{2}.
\end{cases}
\]

The resultant wave function \( \psi \) is

\[
\psi = \int_{p - \frac{\Delta p}{2}}^{p + \frac{\Delta p}{2}} \frac{\Delta p}{\Delta p} e^{-\frac{i}{\hbar} (E' - p' \chi)} dp'.
\]

In this equation, let us change from the variable \( p' \) to the variable \( p^* = p' - p - \frac{\Delta p}{2} \leq p^* \leq \frac{\Delta p}{2} \), \( dp' = dp^* \) and expand \( E' \) in a series about the central point \( p' = p \):

\[
E' = \mathcal{E} + \frac{p^* \partial \mathcal{E}}{\partial p^*} + \frac{1}{2} p'^4 \frac{\partial^2 \mathcal{E}}{\partial p^*} + \ldots.
\]
Restricting ourselves for present purposes to the first-order terms (terms proportional to $p' \sim \Delta p$) and integrating Eq. (3.19) with respect to $dp$, we obtain

$$\psi = Be^{-\frac{i}{\hbar} (Et - px)}.$$  \hspace{1cm} (3.21)

where the amplitude of the wave packet is

$$B = A \frac{\sin \xi}{\xi},$$

$$\xi = \frac{\Delta p}{2\hbar} \left( x - \frac{\partial E}{\partial p} \cdot t \right).$$  \hspace{1cm} (3.22)

From this equation, it follows that $B$ does not remain constant either in space or in time.

To determine the velocity of the wave packet as a whole, that is, the group velocity $\bar{u}$ corresponding to the motion of some specific amplitude, we shall use the same procedure as for the phase velocity. Let us take a certain constant value of the amplitude such that

$$\xi = \frac{\Delta p}{2\hbar} \left( x - \frac{\partial E}{\partial p} \cdot t \right) = \text{const.}$$ \hspace{1cm} (3.23)

We then obtain the following equation for $\bar{u}$:

$$\bar{u} = \frac{dx}{dt} = \frac{\partial E}{\partial p}.$$  \hspace{1cm} (3.24)

Since $E = c \sqrt{p^2 + m_0^2 c^2}$ for a free particle, and

$$\frac{\partial E}{\partial p} = \frac{c^2 p}{E},$$ \hspace{1cm} (3.24a)

we find

$$\bar{u} = \frac{c^2}{u} = v,$$ \hspace{1cm} (3.24b)

which shows that the group velocity $\bar{u}$ of the wave packet as a whole is exactly equal to the velocity $v$ of the particle itself.

From the expression for the amplitude $B(t) = A \frac{\sin \xi}{\xi}$ of the wave packet at time $t = 0$ (when the amplitude corresponds to $\xi = \frac{\Delta p}{2\hbar} x$; see Fig. 3.7), it is readily seen that the maximum value of this amplitude $B(0) = A$ lies at the point $x = 0$. At all other points corresponding to the relative maxima the amplitude is smaller. In particular, considering different values of the argument $\xi$, we have

$$B \left( \frac{3}{2} \pi \right) = -\frac{2}{3\pi} A,$$

$$B \left( \frac{5}{2} \pi \right) = \frac{2}{5\pi} A.$$
At the point \( \xi = \pi \), the amplitude vanishes \( (B(\pi) = 0) \). Consequently, at \( t = 0 \) the wave packet may be regarded as localized in the region of the first maximum, that is, in the region \( \Delta \xi = \frac{\Delta p}{2\hbar} \Delta x \sim \pi \). Hence, we obtain the relation

\[
\Delta p \Delta x \sim \hbar, \tag{3.25}
\]

which is known as the **uncertainty principle**.

![Diagram of wave packet](image)

Fig. 3.7. Form of the wave packet at \( t = 0 \).

Since the center of mass of the wave packet (that is, its principal maximum) travels with the velocity of the particle \( (\bar{v} = v) \), the wave packet describes the localization of the particle. In particular, it follows from other hypotheses that have been made that the position of the particle is characterized by the square modulus of the amplitude of the \( x \) wave, namely,

\[
|B|^2 = \psi^* \psi.
\]

Consequently, the quantities \( \Delta x \) and \( \Delta p \) may be regarded as a measure of the accuracy with which it is possible to compute the momentum and position of a particle in space by means of the wave theory.

It was also necessary to determine whether \( \phi \) waves could be identified with the structure of particles, or whether these waves characterize only their motion. The first interpretation of the relationship between a particle and its associated wave was proposed by Schrödinger. In terms of his hypothesis, a particle is a wave-like formation and the density of its "smearing out" over space is given by \( \phi^* \phi \).
In theory, a group of waves can always be used to form a wave packet whose size is of the order of the radius of any given particle (for example, an electron). This representation of the particle is, however, unstable. Indeed, as follows from Eq. (3.17), the phase velocity of each of the monochromatic waves contained in the wave packet depends on the corresponding wave number, or momentum $p$. Accordingly, each of these monochromatic waves propagates with its own phase\footnote{It can be seen from this that a stable wave packet can be formed only for a particle which has zero rest mass ($m_0 = 0$) and which is moving in a vacuum (as an example of such a particle, we may take the photon). It is only in this case that the phase velocities of all the components of the wave package are the same regardless of the wave number.}

$$u = \frac{E}{p} = c \frac{\sqrt{p^2 + m_0^2c^4}}{p}.$$ 

As a result, the wave packet gradually spreads out with time. The "spreading" time is determined by the time interval in which the initially disregarded part of the phase of $\psi$ in (3.21) becomes commensurate with $\pi$. According to (3.20), the neglected part of the phase is proportional to $p^2 \sim (\Delta p)^2$. Thus, from (3.20) we can obtain a measure of the time $\Delta t$ which elapses between the initial formation of the wave packet and its distortion:

$$\Delta t \cdot \frac{(\Delta p)^2}{\hbar} \cdot \frac{\partial^2 E}{\partial p^2} \sim \pi.$$ 

Or, the time interval starting with the formation of the wave packet and ending when the distortion of the latter can no longer be neglected is

$$\Delta t \sim \frac{2\pi \hbar}{(\Delta p)^2 \frac{\partial^2 E}{\partial p^2}}.$$ 

Let us replace $\Delta p$ by its value from (3.25). Then, in the non-relativistic case ($p \ll m_0c$), Eq. (3.24a) yields

$$\frac{\partial E}{\partial p} = \frac{p}{m_0},$$

$$\frac{\partial^2 E}{\partial p^2} = \frac{1}{m_0}.$$ 

Thus we obtain for the "spreading" time of the wave packet

$$\Delta t \sim \frac{m_0}{\hbar} (\Delta x)^2.$$ 

(3.27)
For a particle with $m_0 \sim 1 \text{ g}$ and $\Delta x \sim 0.1 \text{ cm}$, the "spreading" time is $\Delta t \sim 10^{-28} \text{ sec}$, and thus the wave packet does not actually spread. In the case of electrons, however, $m_0 \sim 10^{-27} \text{ g}$ and $\Delta x \sim 10^{-13} \text{ cm}$. Therefore, the wave packet of an electron begins to spread out after $\Delta t \sim 10^{-28} \text{ sec}$, that is, almost instantaneously. Thus, the electron is not a stable formation in the Schrödinger theory of the "smeared" electron. This is an obvious contradiction with the experimental facts. Moreover, it becomes impossible to explain the phenomenon of diffraction if a monochromatic wave, which provides an appropriate description of the motion of several electrons, is replaced by a set of several wave packets.

At present, another approach has been adopted, namely, Max Born's statistical interpretation of the wave function (the quantity $|\psi|^2 = \psi^*\psi$) as the probability density, or probability of finding the electron at various points in space. The statistical interpretation is not concerned with the structure of the electron, and the electron can remain a point charge (or, to be more precise, a charge whose radius $r_0$ does not exceed $10^{-13} \text{ cm}$). Only the probability of finding the electron at different points in space changes as the wave function changes with time, but the structure of the electron remains completely unaffected.

From the standpoint of Born's statistical interpretation, the quantum-mechanical treatment of problems involving many electrons in identical states presents certain methodological similarities with the treatment of various problems in the kinetic theory of gases on the basis of Maxwell's distribution function (it should be noted, however, that the quantum-mechanical distribution function $f = \psi^*\psi$ is devoid of the temperature term). For example, in Born's interpretation, the diffraction pattern of an electron beam may be explained in the following manner. The bright spots correspond to the maxima of the function $f = |\psi|^2$, and thus the greatest numbers of electrons travel towards bright spots. On the contrary, the probability is smallest for electron motion in the direction of dark regions.

One attempt to explain a certain "freedom of behavior" of an individual electron is based upon the complementarity principle, a solution adopted by Bohr, Heisenberg, and others (see also Chapter 7). The complementarity principle asserts the theoretical impossibility of extending our knowledge of the microscopic world beyond a certain finite, even though small, limit of accuracy, since our measuring apparatus necessarily must exert certain indeterminable effects on the experimental object (an electron, for example). In particular, for canonically conjugate quantities, such as the position and momentum, the degree of accuracy with which they can be measured is given by the uncertainty principle.

Heisenberg attempted to provide a more rigorous foundation for the complementarity principle by means of the following hypothetical
experiment. Suppose we wish to determine the position of an electron with the aid of an "ultramicroscope," that is, an instrument that is designed for precisely this task and that utilizes a light beam of appropriate wavelength $\lambda$ (it is not actually possible to construct such a microscope). We shall assume that the electron is located at the vertex of a cone of revolution with angle $2\varphi$, (the objective being the base), where $\varphi$ — the angle between the incident (wavelength $\lambda$) and scattered light beams. Any light that enters the objective after being scattered by the electron must have traveled within this cone of directions. From the laws of optics, it follows that the uncertainty in the determination of any of the electron coordinates in the plane parallel to the plane of the objective is

$$\Delta x \sim \frac{\lambda}{\sin \varphi}.$$  

(3.28)

Moreover, since the light has a momentum $p = \frac{h}{\lambda}$, part of this momentum is imparted to the electron (the Compton effect). Accordingly, the momentum of the electron in the given direction can only be determined with an uncertainty of

$$\Delta p_x \sim \frac{h}{\lambda} \sin \varphi.$$  

(3.29)

The product of these two uncertainties yields the uncertainty relation.

From (3.28), it is seen that to determine the position of the electron with the maximum degree of accuracy, it is necessary to use light of the smallest possible wavelength $\lambda$. Equation (3.29) shows, however, that the smaller the wavelength, the greater is the momentum imparted to the electron (the position and momentum are canonically conjugate quantities). Thus, according to the complementarity principle, there would have to be two classes of experimental apparatus. One of these would be designed to measure the spatial coordinates with any desired degree of accuracy (in the case of "ultramicroscopes," instruments with $\lambda \to 0$), the other, to measure the corresponding momenta (instruments with $\lambda \to \infty$). Then the observer using an instrument of the first class imparts all of the indeterminable effects to the momentum, whereas the instrument of the second class imparts all of the indeterminable effects to the position. Accordingly, in the opinion of the adherents of the Copenhagen school, we cannot at any given time ascertain both the position and the momentum of the object, although each of these variables can be measured separately with any desired degree of accuracy.
Problem 3.1. Show that there is an integral number of de Broglie wavelengths in an elliptic electron orbit.

Solution. According to Bohr, the set of stationary elliptic orbits may be found from the two conditions

$$\oint p_r \, dr = n_r h \quad \text{and} \quad \oint \rho_\varphi \, d\varphi = n_\varphi h,$$

where

$$p_r = \frac{\partial \mathcal{L}}{\partial \dot{r}} \quad \text{and} \quad \rho_\varphi = \frac{\partial \mathcal{L}}{\partial \dot{\varphi}}.$$  

Since \(2T = \sum_k \dot{q}_k \dot{p}_k\), that is,

$$2 \oint T \, dt = \sum_k \oint \dot{p}_k \dot{q}_k \, dt = \sum_k \oint \rho_\varphi \, dq_k = nh,$$

where

$$n = n_\varphi + n_r \quad \text{and} \quad 2T \, dt = m_0 v \, ds = \frac{h}{\lambda} \, ds,$$

we obtain the required result

$$\oint \frac{ds}{\lambda} = n.$$

Problem 3.2. Show that the wave

$$\varphi(x) = \begin{cases} e^{i k_0 x} & |x| < \frac{l}{2}, \\ 0 & |x| > \frac{l}{2}, \end{cases}$$

is not monochromatic for finite values of \(l\). Find the range of wave numbers \(\Delta k = k - k_0\) over which the amplitudes of the individual harmonics may be regarded as nonzero.

Solution. Let us represent \(\varphi(x)\) in the form of a Fourier integral

$$\varphi(x) = \sum_{-\infty}^{+\infty} A(k) e^{ikx} \, dk,$$

where the amplitudes \(A(k)\) are given by the formula

$$A(k) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \varphi(x) e^{-ikx} \, dx.$$

Substituting the expression for \(\varphi(x)\), we find

$$A(k) = \frac{\sin \frac{1}{2} (k - k_0) l}{\pi (k - k_0) l}.$$  

Hence it follows that the largest amplitude corresponding to \(k = k_0\) is \(A(k_0) = l/2\pi\). Although all the other amplitudes are not equal to zero, in practice only those amplitudes which are of the same order as \(A(k_0)\) need be regarded as nonzero. These amplitudes lie within the range \(\Delta k = |k - k_0| \sim \frac{2\pi}{l}\). The quantity \(\Delta k \approx 2\pi/l\) may be regarded as the
"spread" of the wave vector due to the finite width of the wave packet. Setting $\Delta k = \frac{\Delta \rho}{\hbar}$, and $l \sim \Delta x$, we again obtain the uncertainty relation:

$$\Delta \rho \Delta x \sim \hbar.$$

Problem 3.3. Find the mean velocity and the "spreading" time of the wave packet

$$\psi(x, t) = \int_{-\infty}^{\infty} A(k) e^{-i(\omega t - kx)} \, dk$$

If the amplitude $A(k)$ is in the form of a Gaussian curve:

$$A(k) = e^{-\frac{(k-k_0)^2}{2q^2}}.$$

Solution. Substituting the expression for $A(k)$ into Eq. (3.30) and integrating, we find for $t = 0$

$$\psi(x, 0) = V \pi q e^{-\frac{q^2 x^2}{4} e^{ih_0 x}}.$$

It follows that the particle is initially localized in the region $\Delta x \sim \frac{2}{q}$. This in effect is equivalent to the uncertainty relation (3.25).

To obtain the shape of the wave packet at any other instant of time, we take into account the equation

$$\hbar^2 \omega^2 = m_0 c^4 + e^2 k^2 \hbar^2.$$

In the nonrelativistic approximation ($k \ll m_0 c/\hbar$), we then have

$$\omega = \frac{m_0 c^2}{\hbar} + \frac{\hbar k^2}{2m_0}.$$

Substituting this expression into Eq. (3.30), we obtain, after integration

$$\psi(x, t) = q \pi \frac{\sqrt{\pi}}{1 + (\frac{ihq^2 t}{2m_0})^{1/2}} e^{-\frac{q^2 (x - \frac{h \rho t}{m_0})^2}{4 (1 + (\frac{ihq^2 t}{2m_0})^{1/2})}} + i (h k_0 x - \omega_0 t),$$

where

$$\omega_0 = \frac{m_0 c^2}{\hbar} + \frac{\hbar k_0^2}{2m_0}.$$

Hence we have for the probability density

$$|\psi(x, t)|^2 = \frac{nq^2}{\sqrt{1 + \left(\frac{hqa t}{2m_0}\right)^2}} e^{-\frac{q^2 (x - \nu_0 t)^2}{2 \left[1 + \left(\frac{hqa t}{2m_0}\right)^2\right]}},$$

where $\nu_0 = \frac{h k_0}{m_0}$ is the velocity of the center of mass of the wave packet. From this formula it is seen that the maximum of the wave packet, that is, the point $x = \nu_0 t$, moves with the velocity $\nu_0$ of the particle.
The effective width of the wave packet at time $t$ is found to be

$$\Delta x_t \approx \frac{2}{\hbar} \sqrt{1 + \left(\frac{\hbar q t}{2m_0}\right)^2}.$$ 

If we substitute $q \sim \frac{1}{\Delta x}$ into this formula, the "spreading" time of the wave packet is expressed by a relationship which coincides with Eq. (3.27).

Problem 3.4. Show that a damped oscillatory motion

$$x(t) = e^{-\gamma t} \cos \omega_0 t$$

results in broadening of the spectral line.

Solution. The damped oscillation can be represented in the form of a Fourier integral

$$x(t) = \int_0^\infty a(\omega) \cos \omega t \, d\omega,$$

where

$$a(\omega) = \frac{2}{\pi} \int_0^\infty x(t) \cos \omega t \, dt = \frac{1}{\pi} \frac{\gamma}{\gamma^2 + (\omega - \omega_0)^2}.$$ 

For the largest amplitude, we obtain

$$a(\omega_0) = \frac{1}{\pi \gamma}.$$ 

The amplitudes with the same order of magnitude correspond to frequencies lying in the range

$$\Delta \omega = |\omega - \omega_0| \approx \gamma.$$ 

It is this equation which represents the line broadening since, in effect, only the amplitudes corresponding to these frequencies differ from zero.

Since the damping coefficient $\gamma$ is connected with the mean life of the damped oscillations by the relation $\Delta t \sim 1/\gamma$, the above equation yields the familiar optical relationship connecting the broadening of the spectral lines and the mean life of the atom:

$$\Delta t \Delta \omega \sim 1.$$ 

Hence, since $\Delta \omega = \Delta E/h$, we obtain what is known as the fourth uncertainty relation

$$\Delta E \Delta t \sim h.$$
Planck's quantum theory, Bohr's postulates, and de Broglie's hypothesis represented very important steps in the development of the theoretical foundations of atomic physics. However, they were overshadowed by the discovery of a fundamental differential equation describing the electron and accounting for its wave properties, and the construction of a theory accounting for the quantum nature of radiation. The crucial move in this connection was made by Schrödinger in 1926, when he proposed a partial differential equation that turned out to be generally applicable to the motion of charged particles in the nonrelativistic case ($v \ll c$). This equation represented a generalization of the classical Hamilton-Jacobi equation to cases in which the de Broglie wavelength differs from zero. The Schrödinger equation stands in approximately the same relation to the Hamilton-Jacobi equation as does wave optics to geometrical optics.

A. DERIVATION OF THE TIME-INDEPENDENT SCHRODINGER EQUATION

We shall show how the Schrödinger equation can be obtained most simply. We must insist that there can be no question of a rigorous or general derivation of this equation, since it is not, in general, possible to set up a new theory entirely on the basis of old postulates. We shall adopt a mode of presentation which consists essentially of a reasonable generalization of the wave equation from classical electrodynamics or optics

$$\nabla^2 \varphi (r, t) - \frac{1}{u^2} \frac{\partial^2 \varphi (r, t)}{\partial t^2} = 0 \tag{4.1}$$

to the case of de Broglie waves. Here $\varphi$ is a function describing a wave disturbance propagating with velocity $u$. If the wave is monochromatic, a solution to Eq. (4.1) may be sought in the form

$$\varphi (r, t) = e^{-i\omega t} \varphi (r), \tag{4.2}$$
where \( \omega = 2\pi v \) is the angular frequency, and the spatial part \( \psi(r) \) of the wave function satisfies the equation

\[
\nabla^2 \psi(r) + \frac{\omega^2}{\mu^2} \psi(r) = 0. \quad (4.3)
\]

In this equation, we can use a single parameter in place of the two parameters \( \omega \) and \( \mu \), namely, the wavelength

\[
\lambda = \frac{2\pi \mu}{\omega}. \quad (4.4)
\]

We then have

\[
\nabla^2 \psi(r) + \frac{4\pi^2}{\lambda^2} \psi(r) = 0. \quad (4.5)
\]

From this general equation, we can obtain a wave equation describing the wave motion of electrons by substituting the de Broglie wavelength

\[
\lambda = \frac{\hbar}{m_0 v} = \frac{2\pi \hbar}{p}. \quad (4.6)
\]

Using the law of conservation of energy

\[
\frac{p^2}{2m_0} + V(r) = E = \text{const},
\]

we have

\[
\frac{4\pi^2}{\lambda^2} = \frac{2m_0}{\hbar^2} [E - V(r)]. \quad (4.7)
\]

Substituting this expression into (4.5), we obtain the \emph{time-independent} (or stationary) \emph{Schrödinger equation}

\[
\nabla^2 \psi(r) + \frac{2m_0}{\hbar^2} [E - V(r)] \psi(r) = 0. \quad (4.8)
\]

Once we have found the space-dependent part \( \psi(r) \) of the wave function from (4.8), we can use Eq. (4.2), which is valid for all monochromatic waves, to obtain the complete wave function, which depends on both (spatial and time) coordinates. Substituting \( \omega = \frac{E}{\hbar} \), we have \(^1\)

\[
\psi(t) = e^{-i \frac{E}{\hbar} t} \phi. \quad (4.9)
\]

\(^1\)From now on, we shall write the wave functions which depend on both position and time in the form \( \psi(t) \), while the wave functions whose only argument is the position will be denoted as \( \psi \).
For the complex conjugate function, whose space-dependent part also satisfies Eq. (4.8), we have

$$\psi^*(t) = e^{\frac{iE}{\hbar} t} \psi^*. \tag{4.9a}$$

**B. RESTRICTIONS ON THE WAVE FUNCTIONS. EIGENVALUES AND EIGENFUNCTIONS**

The functions $\psi(t)$ which describe the behavior of a particle may be statistically interpreted by means of the Schrödinger theory. In particular, the quantity $\psi^*(t) \psi(t) = \psi^* \psi$, which plays the role of a distribution function, represents the *probability density*, or probability of finding the particle at any particular region in space. If the probability density differs from zero only in some arbitrarily large, but finite, region of space $\Omega$, it is accurate enough to say that the particle is located somewhere in this region. In other words, the probability of detecting the particle in the region $\Omega$ is unity. Mathematically, this can be expressed in the form

$$\int_{\Omega} \psi^* \psi d^3x = 1. \tag{4.10}$$

In quantum mechanics, relationship (4.10) is called the *normalization condition*.

It is important to note that the region of nonzero probability density is not always finite. There are cases where $\psi^* \psi$ does not go to zero over all of space (the simplest of these cases is that of the motion of a free particle, which we shall consider below). When this happens, $\int \psi^* \psi d^3x$ diverges, and a somewhat different formulation of the normalization condition must be given.

We shall now give a general analysis of the Schrödinger wave equation. The Schrödinger equation (4.8) is a second-order partial differential equation. Its solution resembles the solution of certain classical problems of mathematical physics, such as the problem of a vibrating string. We note, first, that certain conditions must be imposed on the wave function $\psi$, since it is a solution satisfying a second-order Sturm–Liouville equation. It must be *continuous* and have a *continuous derivative*. Moreover, it must be *single valued* and *finite over all of space*. Finally, it must satisfy certain *boundary conditions*. In general, solutions which satisfy these requirements do not exist for all values of the parameters, but only for certain specific values, which are known as *eigenvalues*. In the case of the Schrödinger wave equation, the energy $E$ is a parameter of this sort, its eigenvalues being

$$E_1, E_2, E_3, \ldots. \tag{4.11}$$
The solutions of the wave equation corresponding to these eigenvalues

\[ \psi_1, \psi_2, \psi_3, \ldots \]  

are said to be eigenfunctions. The possible values of the energy form the energy spectrum. We shall see below that, if the motion of a particle is not bounded, its energy spectrum is continuous. If, however, the position of the particle in space is bounded, the energy spectrum is discrete.

Let us show that the eigenfunction \( \psi_n \) satisfy the orthonormality condition

\[ \int \psi_n^* \psi_{n'} d^3x = \delta_{nn'} \]  

where \( \delta_{nn'} \) is the Kronecker-Weierstrass symbol, which is equal to unity for \( n' = n \) (the normalization condition), and to zero for \( n' \neq n \) (the orthogonality condition). To prove Eq. (4.13), we write the Schrödinger equations for \( \psi_n \) and \( \psi_n^* \):

\[ \nabla^2 \psi_n + \frac{2m}{\hbar^2} (E_n - V) \psi_n = 0, \]  

\[ \nabla^2 \psi_n^* + \frac{2m}{\hbar^2} (E_n' - V) \psi_n^* = 0. \]

If we multiply the first of these equations by \( \psi_n^* \), and the second by \( (-\psi^*_n) \), and then add the two resulting equations, we obtain

\[ \psi_n^* \nabla^2 \psi_n - \psi_n \nabla^2 \psi_n^* + \frac{2m}{\hbar^2} (E_n - E_n') \psi_n^* \psi_n = 0. \]

Since

\[ \psi_n^* \nabla^2 \psi_n - \psi_n \nabla^2 \psi_n^* = \nabla \cdot B, \]

where

\[ B = \psi_n^* \nabla \psi_n - \psi_n \nabla \psi_n^*, \]

integration of Eq. (4.14) over all of space yields

\[ \int \nabla \cdot B d^3x + \frac{2m}{\hbar^2} (E_n - E_n') \int \psi_n^* \psi_n d^3x = 0. \]

Since the \( \psi \) function tends to zero at infinity, we obtain\(^2\)

\[ \int \nabla \cdot B d^3x = \int B_n dS = 0, \]

---

\(^2\)The surface \( S \) tends to infinity at \( r \to \infty \). Therefore, the integral goes to zero at \( r \to \infty \) if the wave function \( \psi \) tends to zero more rapidly than \( r^{-1} \). This condition is always satisfied for a discrete spectrum since the wave function, as a rule, approaches exponentially zero at infinity. The case of the continuous spectrum will be considered separately.
Therefore, instead of Eq. (4.15), we have

\[(E_n - E_{n'}) \int \phi_n^* \phi_n d^3x = 0. \tag{4.16}\]

We shall now assume that \(E_n \neq E_{n'}\) (that is, \(n' \neq n\)). According to Eq. (4.16), the following equation then holds (orthogonality condition):

\[\int \phi_n^* \phi_n d^3x = 0. \tag{4.17}\]

If, however, \(n' = n\) (or \(E_n = E_{n'}\)), this integral does not go to zero and we may impose the requirement that it be equal to unity (the normalization condition):

\[\int \phi_n^* \phi_n d^3x = 1. \tag{4.18}\]

Thus the eigenfunctions \(\phi_1, \phi_2, \text{ and } \phi_3\), which correspond to the eigenvalues \(E_1, E_2, \text{ and } E_3\), do indeed possess the property of orthonormality (4.13). This is one of the most important characteristics of eigenfunctions.

C. A PARTICLE IN A POTENTIAL WELL

As an example of the calculation of eigenvalues and eigenfunctions, we shall consider the motion of a particle in a potential well. Since the chief interest of this problem is simply that it provides an illustration of methods used in the solution of this example, we may assume a very simple dependence of the potential energy on distance (see Fig. 4.1):

\[V(x) = \begin{cases} V_0 & \text{for } -\infty < x < 0 \text{ (region I)} \\ 0 & \text{for } 0 < x < l \text{ (region II)} \\ V_0 & \text{for } l < x < \infty \text{ (region III)} \end{cases} \tag{4.19}\]

In the potential well (region II), where \(V > 0\), the Schrödinger equation takes the form

\[\phi''_{II} + k^2 \phi_{II} = 0, \tag{4.20}\]

where

\[\phi'' = \frac{d^2 \phi}{dx^2}, \]

and

\[k^2 = \frac{2m}{\hbar^2} E = \frac{p^2}{\hbar^2} > 0. \tag{4.20a}\]
We note that the case $E < 0$ has no physical meaning in this problem. Since the general solution of Eq. (4.20) is oscillatory, we have

$$\psi_{\parallel} = B_{\parallel} \cos kx + A_{\parallel} \sin kx. \quad (4.21)$$

In regions I and III, the Schrödinger equation has the form

$$\psi'' + \frac{2m_0}{\hbar^2} (E - V_0) \psi = 0. \quad (4.22)$$

Here two cases must be distinguished. In the first case ($E > V_0$), the solution for these regions is also oscillatory in character (an equation of the elliptic type). It is given by Eq. (4.21), the value of $k$ being

$$k = \frac{1}{\hbar} \sqrt{2m_0 (E - V_0)}.$$

No restrictions need to be imposed on the wave functions at infinity. Therefore, the energy $E$ can assume any value in a continuous spectrum of energies. It is better, however, not to investigate the case of a continuous spectrum on the basis of this example, but rather on the basis of the motion of a free particle (see below). The potential well only adds to the mathematical difficulties of the problem, without changing the general character of the solution.

In the second case, namely, the case of a potential barrier ($E < V_0$), the solution of Eq. (4.22) is exponential in character (an equation of the hyperbolic type). The general solution can be written in the form

$$\psi_{\parallel, \text{III}} = A_{\parallel, \text{III}} e^{x^*} + B_{\parallel, \text{III}} e^{-x^*}, \quad (4.23)$$

where

$$x^* = \frac{1}{\hbar^2} \frac{1}{2m_0} (V_0 - E) = \frac{|p|^2}{\hbar^2} > 0. \quad (4.24)$$
If the energy can assume any value without restriction, the wave function inside the potential barrier \(0 < E < V_0\) will contain both an exponentially increasing part and an exponentially decreasing part (see Fig. 4.2). Therefore, we must choose only those values of \(E\) for which exponentially increasing solutions do not exist inside the potential barrier. Accordingly, we require that the coefficient \(B_1 = 0\) in region I \((x < 0)\), and the coefficient \(A_{III} = 0\) in region III \((x > l)\).\(^3\) We then have

\[
\begin{align*}
\psi_1 &= A_1 e^{x} = Ae^{x|x|}, \\
\psi_{III} &= B_{III} e^{-x} = Be^{-x(x-l)},
\end{align*}
\] (4.25)

where, for the sake of simplicity, we have made

\[B_{III} = Be^{x}.
\]

By joining the solutions\(^4\) at the boundary of regions I and II \((x = 0)\), and also at the boundary of regions II and III \((x = l)\), and making use of the requirement that the exponentially increasing solution vanish, we obtain the equation for the eigenvalues of the energy \(E\).

We shall now further simplify our problem by requiring that \(V_0\), together with \(x\), go to infinity (see Fig. 4.3). It is apparent from Eq. (4.25) that \(\psi_1 = \psi_{III} = 0\), and therefore the boundary conditions for the solution (4.21) inside the potential well (region II) take the form

\[\psi_II = 0 \text{ for } x = 0\] (4.26)

and

\[\psi_{II} = 0 \text{ for } x = l\] (4.27)

\(^3\)When \(E < V_0\), the number of unknown coefficients in the wave function is smaller than the number of imposed conditions. Accordingly, solutions are possible only for certain values of \(E\) and a discrete spectrum is obtained.

\(^4\)In joining the solutions, we must match the actual wave functions (and also their first derivatives) at the appropriate point.
Applying Eq. (4.26) and (4.27) to the general solution (4.21) in region II, we find that $B_{11} = 0$, and the eigenvalue are described by the equation

$$\sin kl = 0,$$

from which

$$kl = \pi n,$$  \hspace{1cm} (4.29)

where $n = 1, 2, 3, 4, \ldots$. We exclude the value $n = 0$ from further considerations, since the wave function in this case is identically equal to zero. It is not necessary to consider separately the negative values of $n$, since the wave functions for negative $n$ are equal to the wave functions for positive $n$, taken with the opposite sign. Since $k^2 = \frac{2m_0}{\hbar^2} E$, we obtain the following equation for the energy spectrum (the eigenvalues): 

$$E_n = \frac{\pi^2 \hbar^2 n^2}{2m_0 l^2}.$$  \hspace{1cm} (4.30)

The wave functions corresponding to these values of energy (eigenfunctions) are

$$\psi_n = A_n \sin \frac{\pi n x}{l}.$$  \hspace{1cm} (4.31)

The coefficient $A_n$ can be found from the normalization condition

$$\int_0^l \psi_n^2 dx = A_n^2 \int_0^l \sin^2 \frac{\pi n x}{l} dx = \frac{l}{2} A_n^2 = 1,$$
which gives

\[ A_n = \sqrt{\frac{2}{l}}. \]

Substituting the expression for \( A_n \) into Eq. (4.31), we finally obtain

\[ \psi_n = \sqrt{\frac{2}{l}} \sin \frac{\pi n}{l} x. \tag{4.32} \]

According to the general theorem of eigenfunctions [see Eq. (4.17)] the eigenfunctions (4.32) of the Schrödinger equation satisfy the orthogonality condition

\[ \int_0^l \psi_n^* \psi_{n'} dx = 0 \quad \text{for} \quad n' \neq n, \tag{4.33} \]

as can be readily seen by performing the direct integration after substituting Eq. (4.32) for \( \psi_n \).

We shall now write down a few specific eigenvalues \( E_n \) and eigenfunctions \( \psi_n \), shown in Fig. 4.3:

\[ E_1 = \frac{\pi^2 \hbar^2}{2m_l^2}, \quad \psi_1 = \sqrt{\frac{2}{l}} \sin \frac{\pi x}{l}, \tag{4.34} \]

\[ E_2 = 4E_1, \quad \psi_2 = \sqrt{\frac{2}{l}} \sin 2\pi \frac{x}{l}, \tag{4.35} \]

\[ E_3 = 9E_1, \quad \psi_3 = \sqrt{\frac{2}{l}} \sin 3\pi \frac{x}{l}. \tag{4.36} \]

These solutions are very similar to the familiar standing-wave solutions for a vibrating string with fixed ends. The case \( n = 1 \) [see (4.34)] corresponds to the fundamental mode, the case \( n = 2 \) [see (4.35)], to the first harmonic, etc.

D. THE MOTION OF FREE PARTICLES.
NORMALIZATION OF WAVE FUNCTIONS IN THE CASE OF A CONTINUOUS SPECTRUM

We shall consider the motion of a free particle (taking the one-dimensional case first), when the Schrödinger equation (4.8) has the same form in all of space \((- \infty < x < \infty)\):

\[ \frac{d^2 \psi}{dx^2} + k^2 \psi = 0, \tag{4.37} \]
where
\[ k^2 = \frac{2 m_e E}{\hbar^2} = \frac{p^2}{\hbar^2}. \]  
(4.38)

The solution of this equation is
\[ \psi = Ae^{ikx} + Be^{-ikx}. \]  
(4.39)

To determine the physical meaning of each term in Eq. (4.39), we write the complete, time-dependent function
\[ \psi(t) = e^{-i\omega t} \psi = Ae^{-i(\omega t-kx)} + Be^{-i(\omega t+kx)}. \]  
(4.40)

It is seen that the first term \( Ae^{-i(\omega t-kx)} \) describes the motion of the particle in the positive direction of the \( x \) axis, and the second term \( Be^{-i(\omega t+kx)} \), the motion in the negative direction. If we restrict ourselves to the traveling wave which is propagated in the direction of positive \( x \), we have
\[ \psi = Ae^{ikx}. \]  
(4.41)

It is readily seen that the integral \( \int_{-\infty}^{+\infty} \psi^* \psi dx \) diverges. Consequently, we must revise the method of normalization [see Eq. (4.10)]. There are two basic methods of normalizing \( \psi \) functions of this sort. We shall devote most of our attention to one of them, which was proposed by Born. Thus, rather than imposing a boundary condition, we shall subject the wave function to a periodicity condition
\[ \psi(x) = \psi(x+L), \]  
(4.42)

where the length \( L \) is said to be the period. It can be made arbitrarily large. As a rule, \( L \) does not appear in the final result. Rewriting (4.42) in the form
\[ Ae^{ikx} = Ae^{ikx+ikL}, \]
we obtain \( e^{ikL} = 1 \), which implies
\[ k = \frac{2\pi n}{L}, \]  
(4.43)

where \( n = 0, \pm 1, \pm 2, \pm 3, \ldots \). From Eqs. (4.38) and (4.43), the energy levels are
\[ E_n = \frac{\hbar^2 k^2}{2m_e} = \frac{2\pi^2 \hbar^2 n^2}{m_e L^2}. \]  
(4.44)
Since the $\psi$ function is periodic in the interval $L$, the normalization condition becomes

\[ \int_{-L/2}^{L/2} \psi^* \psi \, dx = 1. \]  

(4.45)

Substituting the expression (4.41) for $\psi$, we have

\[ A = \frac{1}{\sqrt{L}}. \]  

(4.46)

Therefore, the normalized solutions are

\[ \psi_n = \Delta \frac{1}{2} e^{ikx} = L \frac{1}{2} e^{\frac{2\pi n}{L} x}. \]  

(4.47)

The direct integration shows that the functions (4.47) are orthonormal. As can be readily shown by direct integration:

\[ \int_{-L/2}^{L/2} \psi_n^* \psi_{n'} \, dx = \frac{1}{L} \int_{-L/2}^{L/2} e^{-\frac{2\pi in'x}{L}} \sin \frac{\pi (n-n')}{L} \, dx = \begin{cases} 0 & \text{for } n' \neq n, \\ 1 & \text{for } n' = n. \end{cases} \]  

(4.48)

Therefore, introducing the artificially defined period, we can transform the continuous energy spectrum into a discrete one. If, however, the length $L$ is allowed to go to infinity, the discrete spectrum again becomes continuous. Since $k = \frac{p}{\hbar} = \frac{m_0 v}{\hbar}$ and $\Delta n = 1$, the energy difference between two neighboring levels is

\[ \Delta E = \frac{\hbar^2 k}{2m_0 L} = \frac{2\pi \hbar}{L}. \]  

(4.49)

It immediately follows that $\Delta E \to 0$ if $L \to \infty$; that is, the energy spectrum becomes continuous.

We shall now generalize the free particle problem to the three-dimensional case. The Schrödinger equation can be written in the form

\[ \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + k^2 \right) \psi = 0. \]  

(4.50)

Just as in the one-dimensional case, the quantity $k^2$ is given by Eq. (4.20a). We shall solve Eq. (4.50) by the method of separation of variables; that is, we assume a solution of the form:

\[ \psi = \psi(x) \psi(y) \psi(z). \]  

(4.51)
Substituting this expression into \((4.50)\) and multiplying by \(\frac{1}{\psi} = \frac{1}{\psi(x)\psi(y)\psi(z)}\), we find

\[
\frac{\psi''(x)}{\psi(x)} + \frac{\psi''(y)}{\psi(y)} + \frac{\psi''(z)}{\psi(z)} + k^2 = 0,
\]

where the primes denote the derivatives of the corresponding \(\phi\) function with respect to its argument. We note that an equation of this type is satisfied only if each term (fraction) is independent of the coordinates and is equal to a certain constant. We thus obtain the following equations for the functions \(\psi(x), \psi(y)\) and \(\psi(z)\):

\[
\psi''(x) + k_1^2 \psi(x) = 0, \quad \psi''(y) + k_2^2 \psi(y) = 0, \quad \psi''(z) + k_3^2 \psi(z) = 0,
\]

where

\[
k_1^2 + k_2^2 + k_3^2 = k^2.
\]

Taking a traveling wave propagating in some specific direction as a solution for each of Eqs. \((4.53)\), we get

\[
\psi(x) = Ae^{ik_1x}, \quad \psi(y) = Be^{ik_2y}, \quad \psi(z) = Ce^{ik_3z}.
\]

The unknown coefficients \(A, B\) and \(C\) are determined from the normalization condition, assuming that the functions \(\psi(x), \psi(y)\) and \(\psi(z)\) are periodic in the interval \(L\). We thus obtain

\[
\psi(x) = L^{-\frac{1}{2}} e^{ik_1x}, \quad \psi(y) = L^{-\frac{1}{2}} e^{ik_2y},
\]

\[
\psi(z) = L^{-\frac{1}{2}} e^{ik_3z},
\]

where

\[
k_1 = n_1 \frac{2\pi}{L}, \quad k_2 = n_2 \frac{2\pi}{L}, \quad k_3 = n_3 \frac{2\pi}{L},
\]

and

\[
n_1, n_2, n_3 = 0, \pm 1, \pm 2, \pm 3, \ldots
\]

In this case, the particle has energies of

\[
E_n = \frac{2\pi^2 \hbar^2}{m_0 L^2} \left( n_1^2 + n_2^2 + n_3^2 \right) = \frac{2\pi^2 \hbar^2 n^2}{m_0 L^2},
\]

where

\[
n^2 = n_1^2 + n_2^2 + n_3^2.
\]
Substituting the functions (4.56) into Eq. (4.51), we have

$$\psi_k = L^{-\frac{3}{2}} e^{i k \cdot r}. \quad (4.60)$$

These wave functions will satisfy the orthonormality condition

$$\int \psi_{n_1 n_2 n_3}^{*} \psi_{n_1 n_2 n_3} d^3 x = \delta_{n_1 n_1'} \delta_{n_2 n_2'} \delta_{n_3 n_3'}. \quad (4.61)$$

The complete, or time-dependent, wave function can now be written in the form

$$\psi(t) = L^{-\frac{3}{2}} e^{-i \frac{\hbar}{\hbar} (E - p \cdot r)}. \quad (4.62)$$

where

$$p = \hbar k, \ E = \frac{p^2}{2m}. \quad (4.63)$$

We note that the energy spectrum is again continuous, just as in the case of one-dimensional motion. This can readily be shown in the same way as before by finding the energy difference between two adjacent levels and then letting $L$ go to infinity.

E. FUNDAMENTAL PROPERTIES OF $\delta$ FUNCTIONS.

$\delta$-FUNCTION NORMALIZATION OF THE WAVE FUNCTION IN THE CASE OF A CONTINUOUS SPECTRUM

As we have already mentioned, one of the fundamental properties of eigenfunctions is their orthonormality [see Eq. (4.13)]. An arbitrary function $F(x)$ with no "special" properties can thus be expanded in a series of orthonormal functions belonging to a complete set:

$$F(x) = \sum_n C_n \psi_n(x). \quad (4.64)$$

Multiplying this equation by $\psi_{n'}^*(x) dx$ and integrating over the entire range of $x$, we obtain

$$\int \psi_{n'}^*(x) F(x) dx = \sum_n C_n \int \psi_{n'}^*(x) \psi_n(x) dx.$$

Because of the orthonormality condition, we have

$$C_n = \int \psi_{n'}^*(x) F(x) dx. \quad (4.65)$$

In order to bring $\psi_n(x)$ under the integral sign, we change here the variable of integration $x$ to $x'$ and substitute the expression for $C_n$ into the expression (4.64):

$$F(x) = \sum_n \int d x' F(x') \psi_{n'}^*(x') \psi_n(x). \quad (4.66)$$
This expansion is a generalized Fourier series. We can obtain the ordinary Fourier series from it by substituting the harmonic functions (4.47) for \( \psi_n(x) \).

We note that the sum over \( n \) in Eq. (4.66) is a \( \delta \) function:

\[
\sum_n \psi_n^*(x') \psi_n(x) = \delta(x-x'),
\]

since it transforms the function \( F(x') \) into \( F(x) \).

In this respect, this \( \delta \) function resembles the Kronecker-Weierstrass \( \delta \) symbol, which possesses a similar property with respect to the subscripts \( n \) and \( n' \):

\[
\sum_n f_n \delta_{nn'} = f_n.
\]

It follows that the \( \delta \) function differs from zero only in a very narrow region \( x' \sim x \), just as the \( \delta \) symbol differs from zero only for \( n' = n \). By setting \( F(x') = 1 \) in (4.66), we obtain one of the fundamental properties of the \( \delta \) function:

\[
\delta(x-x') dx' = 1.
\]

It is interesting to note that the relations (4.66) and (4.68) are completely independent of the particular set of orthonormal functions used to construct the \( \delta \) function. In the simplest case, the \( \delta \) function can be constructed from the orthonormal functions (4.47), which are used in expansion into a Fourier series:

\[
\delta(x-x') = \frac{2}{L} \sum_n e^{i2\pi n x/L}.
\]

Introducing a new variable \( k = \frac{2\pi n}{L} \) and making use of the relation \( \Delta k = \frac{2\pi}{L} \Delta n = \frac{2\pi}{L} \) (since \( \Delta n = 1 \), we can transform (4.69) to

\[
\delta(x-x') = \frac{1}{2\pi} \sum \Delta k e^{i\Delta k (x-x')}. \tag{4.69}
\]

If we now let \( L \) go to infinity (\( \Delta k \to 0 \)), the last sum is changed into an integral:

\[
\delta(x-x') = \frac{1}{2\pi} \int dk e^{i\Delta k (x-x')}. \tag{4.70}
\]

The range of integration over \( k \) should be taken from \(-\infty\) to \(+\infty\). We note that the \( \delta \) function belongs to the class of functions that are known as "improper functions." This is manifested in the impossibility of direct evaluation of the integral (4.70), since it diverges at \( x = x' \). Therefore, if we wish to obtain a representation of the \( \delta \) function, we have to "smear out" somewhat the integrand of (4.70). For instance, the \( \delta \) function may be "smear out" as follows:

\[
\delta(x-x', a) = \frac{1}{2\pi} \int dk e^{-a |k|} e^{i\Delta k (x-x')} = \frac{1}{\pi} \int_0^{\infty} e^{-ak} \cos k (x-x') dk = \frac{1}{\pi} \frac{\alpha}{\alpha^2 + (x-x')^2}. \tag{4.71}
\]

A graph of the smeared \( \delta \) function is given in Fig. 4.4. At the limit \( a \to 0 \), the function must have the following properties:
\[ \delta(x - x') = \infty \text{ for } x = x', \]
\[ \delta(x - x') = 0 \text{ for } x \neq x', \quad (4.72) \]

As we approach the limit \( a \to 0 \), the area between the \( \delta \) function and the \( x \) axis remains unchanged:
\[ \int \delta(x - x') \, dx' = \lim_{a \to 0} \frac{1}{\pi} \int \frac{dx'}{a^2 + (x' - x)^2} = 1. \quad (4.73) \]

The three-dimensional \( \delta \) function can be similarly defined as
\[ \delta(r) = \delta(x) \delta(y) \delta(z) = \frac{1}{8\pi^3} \int d^3 k e^{ikr}. \quad (4.74) \]

It satisfies the following conditions:
\[ \delta(r) = 0 \quad \text{if} \quad r \neq 0, \]
\[ \int \delta(r) \, d^3 x = 1. \quad (4.75) \]

The integrals (4.74) and (4.75) are three-dimensional. The former extends over the entire wave-number space \((k)\), and the latter, over the entire coordinate space \((r)\).

It is very convenient to express the density of a point charge with the help of a three-dimensional \( \delta \) function:
\[ \rho(r) = e \delta(r). \quad (4.76) \]

Substituting this expression into Poisson's equation
\[ \nabla^2 \Phi = -4\pi \rho(r) = -\frac{e}{2\pi^2} \int d^3 k e^{ikr}, \]
we can determine the potential of a point charge\(^1\)
\[ \Phi = \frac{e}{2\pi^2} \int d^3 k \frac{e^{ikr}}{k^2} = \frac{2e}{\pi r} \int_0^\infty dk \frac{\sin kr}{k} = \frac{e}{r}. \quad (4.77) \]

Thus, the three-dimensional \( \delta \) function enables us to describe the singularity at the point \( r \to 0 \) of the Laplacian operator applied to \( 1/r \):
\[ \nabla^2 \frac{1}{r} = -4\pi \delta(r). \quad (4.78) \]

\(^1\)In determining the potential \( \Phi \), we made use of the rule for dividing an exponential function by the Laplacian operator:
\[ (\nabla^2)^{-1} e^{ikr} = \frac{e^{ikr}}{-k^2}. \]

The validity of this rule is immediately obvious, since
\[ \nabla^2 (\nabla^2)^{-1} e^{ikr} = \nabla^2 \frac{e^{ikr}}{-k^2} = \frac{e^{ikr}}{-k^2}. \]
We shall not discuss the properties of the \( \delta \) function any further and shall proceed to use it to normalize the continuous spectrum for one-dimensional free motion. From (4.41), the wave functions for this case are of the form

\[
\psi(p) = A e^{\frac{ip}{\hbar} x}, \quad \psi^*(p') = A e^{-\frac{i p'}{\hbar} x}.
\]

(4.79)

The normalization of these functions is related to the \( \delta \) function in the following way:

\[
\int_{-\infty}^{+\infty} \psi^*(p') \psi(p) dx = A^2 \int_{-\infty}^{+\infty} dx e^{ix(\frac{p}{\hbar} - \frac{p'}{\hbar})} = A^2 \sqrt{2\pi \hbar} \delta(p - p').
\]

(4.80)

From this, we obtain

\[
A = \frac{1}{\sqrt{2\pi \hbar}}.
\]

Therefore,

\[
\psi(p) = \frac{1}{\sqrt{2\pi \hbar}} e^{\frac{i p}{\hbar} x}.
\]

(4.81)

Let us compare the ordinary normalization of wave functions with the \( \delta \) function normalization. We can write the orthonormality condition for functions normalized by the ordinary method as follows:

\[
\sum_{n=1}^{n_2} \int_{n_1}^{n_2} \phi_n^* \phi_m dx = \begin{cases} 1, & \text{if } n \text{ lies inside the range } n_1 < n < n_2, \\ 0, & \text{if } n \text{ lies outside the range } n_1 < n_2. \end{cases}
\]

(4.82)

Similarly, replacing the sum in Eq. (4.82) by an integral, we can obtain the following generalized form for wave functions which are normalized with the help of a \( \delta \) function:

\[
\int_{p_1}^{p_2} dp' \int_{p_1}^{p_2} \phi^*(p') \phi(p) dx = \begin{cases} 1, & \text{if } p \text{ lies inside the range } p_1 < p < p_2, \\ 0, & \text{if } p \text{ lies outside the range } p_1 < p_2. \end{cases}
\]

(4.83)

Analyzing the solutions that we have obtained for a particle in a potential well and for a free particle, we arrive to the following conclusions. If the condition \( V > E \) is satisfied at all points of space at infinity, the energy spectrum is discrete. If, on the other hand, there are regions at infinity in which \( V < E \), the energy spectrum is continuous. While this conclusion was obtained on the basis of solutions for a rectangular potential well, it is quite general as long as the potential energy is a continuous function of \( x, y, \) and \( z \).
Chapter 5

The Time-Dependent Schrödinger Wave Equation

It has been shown that the solution of the time-independent or stationary Schrödinger wave equation (4.8) amounts to a determination of eigenvalues $E_n$ (the spectrum of energy levels) and eigenfunctions. The time-dependent wave function $\psi_n(t)$ of a given state was found by multiplying $\psi_n$ by $e^{-i\omega_n t}$. The function $\psi_n(t)$ obtained in this way describes only strictly monochromatic processes (that is, with only one value of energy). There is, however, a more general form of the Schrödinger equation, which depends explicitly on time and may be used in a much larger class of problems. This equation is known as the time-dependent Schrödinger wave equation.

A. TRANSITION TO THE TIME-DEPENDENT SCHRODINGER WAVE EQUATION

To obtain the time-dependent Schrödinger wave equation, it is necessary to eliminate the energy $E$ from the time-independent equation, where it appears as a constant parameter. The time-independent Schrödinger wave equation (4.8) can be written in the form

$$E\psi(t) + \left(\frac{\hbar^2}{2m} \nabla^2 - V\right)\psi(t) = 0.$$  \hspace{1cm} (5.1)

The relation that is used to eliminate $E$ from this equation is

$$-\frac{\hbar}{i} \frac{\partial \psi(t)}{\partial t} = E\psi(t).$$  \hspace{1cm} (5.2)

Accordingly, the time-dependent Schrödinger wave equation is

$$\left(-\frac{\hbar}{i} \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} \nabla^2 - V\right)\psi(t) = 0.$$  \hspace{1cm} (5.3)

This equation is more general than the previous one. In particular, it can be used for the description of processes in which the potential energy $V$ is a function of both position and time.
If the potential energy $V$ does not depend on time, it is necessary to solve only the time-independent Schrödinger equation by finding all the possible energy eigenvalues $E_n$ and the corresponding eigenfunctions $\psi_n$. The wave function which satisfies Eq. (5.3) is related to these partial solutions by the linear equation

$$\psi(t) = \sum_n C_n e^{-\frac{it}{\hbar} E_n t} \psi_n.$$  \hspace{1cm} (5.4)

To prove this, we substitute (5.4) into (5.3), remembering that $C_n$ are constant coefficients and that $\psi_n$ satisfies the equation

$$\nabla^2 \psi_n + \frac{2m_0^2}{\hbar^2} (E_n - V) \psi_n = 0,$$  \hspace{1cm} (5.5)

It is then readily seen that $\psi(t)$ is a general solution of (5.3), since

$$\left( -\frac{\hbar}{i} \frac{\partial}{\partial t} + \frac{\hbar^2}{2m_0} \nabla^2 - V \right) \psi(t) =$$

$$= \sum_n C_n e^{-\frac{it}{\hbar} E_n t} \left( E_n + \frac{\hbar^2}{2m_0} \nabla^2 - V \right) \psi_n = 0.$$  \hspace{1cm} (5.6)

The case of a monochromatic wave is a special case of the general solution (5.4). The appropriate wave function can be obtained from (5.4) by setting $C_{n_0} = 1$ and $C_n = 0$ (if $n \neq n_0$).

As we have presented it, transition from the time-independent equation (5.1) to the time-dependent equation (5.3) is essentially equivalent to a simple replacement of the energy $E$ by the expression $\hbar \frac{\partial}{\partial t}$. In quantum mechanics, this expression is known as the energy operator$^1$

$$E = \hbar \frac{\partial}{\partial t}.$$  \hspace{1cm} (5.7)

The effect of this operator on any function amounts to an ordinary differentiation of the function with respect to time. Thus, $E$ is a linear differential operator. In the case of a monochromatic wave, for which

$$\psi(t) = e^{-\frac{it}{\hbar} E_n t} \psi_n,$$

we have

$$E \psi(t) = E_n \psi(t).$$
Hence, it is seen that the energy $E_n$ is an eigenvalue of the energy operator $E$.

There are other operators besides the energy operator in quantum mechanics. The most important of these is the momentum operator

$$p = \frac{\hbar}{i} \nabla = \frac{\hbar}{i} \frac{\partial}{\partial r}, \quad (5.8)$$

which takes its name from the fact that in the case of a free particle, its eigenvalue is identical to classical momentum. Indeed, operating with $p$ on the wave function of a free particle [see Eq. (4.62)], we have

$$p \psi(t) = \frac{\hbar}{i} \nabla \{ \mathcal{L} \psi - \frac{i}{\hbar} (E \psi - p \phi) \} = p \psi(t).$$

Thus, in this particular case, the eigenvalue of the operator $p$ is the classical momentum $p$.

With this operator notation, which helps to bring out more clearly the relationship between the quantum-mechanical and classical laws of motion, the Schrödinger equation (5.3) has the form

$$\left(E - \frac{p^2}{2m_0} - V\right) \psi(t) = 0. \quad (5.9)$$

Thus, to carry out the formal transition from the classical theory to quantum mechanics, it is necessary to replace the energy $E$ and momentum $p$ in the classical equation for the law of conservation of energy\(^2\)

$$E - \frac{p^2}{2m_0} - V = 0$$

by the corresponding operators and to operate with them on the wave function. The operator $\frac{p^2}{2m_0}$ is known as the kinetic-energy operator $T$, and $T + V$, as the Hamiltonian operator $H$. For the sake of brevity, we shall call the latter the Hamiltonian.

\(^2\)If the electron is in both an electric field and a magnetic field, which is characterized by the vector potential $A$, then, using the classical expression (1.15) for the Hamiltonian, the time-independent Schrödinger equation can be written in the form

$$\left\{ E - \frac{(p - eA)^2}{2m_0} - e\Phi \right\} \psi = 0. \quad (5.9a)$$
Using this operator notation, Eq. (5.9) can be rewritten in the form

\[(E - H) \psi(t) = 0.\]  \hspace{1cm} (5.10)

For the time-independent potential \(V\), the following relation is obtained:

\[E \psi_n(t) = E_n \psi_n(t)\] \hspace{1cm} (5.11)

and, therefore, the time-independent Schrödinger equation reduces to the form

\[(E_n - H) \psi_n = 0.\] \hspace{1cm} (5.12)

It is apparent from this that, in stationary problems, the eigenvalues of the Hamiltonian are equal to the eigenvalues of the energy, just as, in the classical case, a Hamiltonian function which does not depend explicitly on time is equal to the energy of the system.

**B. CHARGE DENSITY AND CURRENT DENSITY. QUANTUM ENSEMBLES**

In classical electrodynamics, an important role is played by the equation of continuity

\[\frac{\partial \rho}{\partial t} + \nabla \cdot j = 0,\] \hspace{1cm} (5.13)

which involves the charge density \(\rho\) and the current density \(j\). This equation basically represents a general form of the law of conservation of charge. To show this, we multiply (5.13) by \(d^3x\) and integrate over all space

\[\int \frac{\partial \rho}{\partial t} d^3x + \int \nabla \cdot j d^3x = 0.\] \hspace{1cm} (5.14)

Reversing the order of differentiation and integration in the first integral (this is allowed since time here is only a parameter), and changing the second from a volume to a surface integral, we obtain

\[\int_0^d \rho d^3x + \int j_n dS = 0.\] \hspace{1cm} (5.15)

If there are no charges or currents at infinity, the surface integral vanishes, and we obtain the law of conservation of charge

\[\rho = \int \rho d^3x = \text{const.}\] \hspace{1cm} (5.16)
We shall now use the wave theory to find an expression for the charge and current densities. For this purpose, we take the Schrödinger equation (5.3), writing it in the form:

$$\frac{\partial \psi(t)}{\partial t} = -\frac{i\hbar}{2m_o} \nabla^2 \psi(t) + \frac{iV}{\hbar} \psi(t) = 0.$$ \hspace{1cm} (5.17)

Similarly, for the complex conjugate equation, we have

$$\frac{\partial \psi^*(t)}{\partial t} = -\frac{i\hbar}{2m_o} \nabla^2 \psi^*(t) - \frac{iV}{\hbar} \psi^*(t) = 0.$$ \hspace{1cm} (5.18)

Multiplying Eq. (5.17) by $\psi^*(t)$, and Eq. (5.18) by $\psi(t)$, and adding the two equations, we obtain

$$\frac{\partial \psi^*(t)}{\partial t} \psi(t) + \frac{i\hbar}{2m_o} \nabla \{ \psi(t) \nabla \psi^*(t) - \psi^*(t) \nabla \psi(t) \} = 0.$$ \hspace{1cm} (5.19)

Comparing (5.19) with the equation of continuity (5.13), and considering that the charge density is equal to the charge $e$ of one particle multiplied by the number of particles per unit volume (that is, in this case the probability density), we have

$$\rho = e\psi^*(t) \psi(t).$$ \hspace{1cm} (5.20)

From (5.19) and (5.20), we find the current density

$$j = \frac{i\hbar}{2m_o} \{ \psi(t) \nabla \psi^*(t) - \psi^*(t) \nabla \psi(t) \}. \hspace{1cm} (5.21)$$

It should be noted that for a monochromatic wave

$$\psi(t) = e^{-\frac{i}{\hbar} kt} \psi,$$

both the charge density

$$\rho = e\psi^* \psi$$ \hspace{1cm} (5.22)

and the current density

$$j = \frac{i\hbar}{2m_o} (\psi \nabla \psi^* - \psi^* \nabla \psi)$$ \hspace{1cm} (5.23)

are independent of time.

In the case of real wave functions ($\psi^* = \psi$), the current density is always identically equal to zero. For instance, the current density of an electron in an infinitely deep, one-dimensional potential
well (see Fig. 4.3) is zero ($j=0$). This is quite natural, since oscillations described by real wave functions are actually standing waves, and standing waves cannot give rise to a particle flux.

The case of motion of a free particle is somewhat different. According to (4.60), the wave function for this case describes a traveling wave:

$$\psi = L^{1/2} e^{iP r / \hbar}.$$  

Substituting this expression for $\psi$ into (5.22) and (5.23), we obtain the following expressions for the charge density and the current density, respectively:

$$\rho = e \psi^* \psi = L^{-3} e,$$
$$j = \frac{e}{m_0 L^2} p = \rho v.$$

Hence, when the charge is distributed with uniform probability over the entire volume, its density is equal to the charge divided by the volume, as was to be expected. Moreover, the relationship between the current density and the charge density remains the same as in classical electrodynamics.

Let us now explain the physical meaning of the coefficients $C_n$ which appear in the solution $\psi(t)$ of the time-dependent wave equation [see (5.4)]. For this purpose, we substitute the expression for $\psi(t)$ into Eq. (5.16), which serves to define the conservation of total charge. Then, using (5.20), we obtain

$$\sum_n \sum_n C_n^* C_n e^{-i (E_n - E_0) t} \int \psi_n^* \psi_n d^3 x = 1.$$ 

Since the wave functions must satisfy the orthonormality condition

$$\int \psi_n^* \psi_n d^3 x = \delta_{nn},$$

we have

$$\sum_n C_n^* C_n = \sum_n |C_n|^2 = 1.$$  

(5.25)

We can now give a physical interpretation to the coefficients $C_n$ as quantities characterizing the probability that a particle exists in the quantum state $n$. Indeed, if we know with certainty that the particle is in the state $n_0 (E = E_{n_0})$, all of the coefficients $C_n$, except $C_{n_0}$, will have to be equal to zero; that is, we must set $C_n = \delta_{nn_0}$. If the particle has a nonzero probability of occurring in two or more states, then, accordingly, two or more coefficients will differ from
zero. The actual probability that a particular state is occupied is given by $|C_n|^2$, while the probability density of the distribution of the state over entire space is given by $|\phi_n|^2$.

When there is a large number $N$ of particles in a region of space, we have, instead of (5.25),

$$\sum_n |C_n|^2 = N.$$ 

Here the coefficients $C_n$ characterize the distribution of the total number of particles among the different quantum states.

In this connection, we shall introduce the concept of quantum ensembles: namely, a collection of identical quantum states that are described by the same wave function $\phi$. A quantum ensemble can be used to describe an electron beam, photon flux, and so on.\(^3\)

Two different cases are possible.

1) All of the particles are in the same quantum state $n_0$: $|C_{n_0}|^2 = N$ and $|C_n|^2 = 0$ for $n \neq n_0$.

2) The particles have a definite distribution among the various quantum states:

$$|C_{n_1}|^2 = N_{n_1}, \quad |C_{n_2}|^2 = N_{n_2}, \quad |C_{n_3}|^2 = N_{n_3}, \ldots,$$

where

$$\sum_i N_{n_i} = N.$$ 

In the second case, the motions of particles, say, in the states $n = n_1$ and $n = n_2$, cannot be considered independently of one another, because whenever two states $\phi_{n_1}$ and $\phi_{n_2}$ are both possible, the total wave function is a superposition of the individual states, namely,

$$\psi(t) = C_{n_1} \phi_{n_1}(t) + C_{n_2} \phi_{n_2}(t) + \ldots.$$ 

This is important in determining the total probability of a state, which is proportional to the product $\psi^*(t) \psi(t)$. In addition to terms such as $\psi_{n_1}(t) \phi_{n_1}(t)$, this product will contain mixed terms of the form $\psi_{n_1}(t) \phi_{n_2}(t)$. In other words, each particle will possess a definite probability of being in both quantum states. The mixed terms differ from zero for coherent $\phi$ waves (a pure ensemble), and this leads to interference of the de Broglie waves, which does not happen with incoherent waves (a mixed ensemble). Thus, in a pure ensemble, waves are added, whereas in a mixed ensemble, intensities are added. Quantum ensembles are useful with regard

to the statistical interpretation of the results of wave theory. For a large number of particles or a large number of states occupied by single particles, it follows from the law of large numbers that the probability of some particular process, when calculated on the quantum-mechanical basis, should agree with the distribution that can be observed in experiment (see Chapter 7). Similarly, in classical statistical physics, the probability distribution agrees with experiment independently of the nature of the "hidden" parameters.

C. CONNECTION BETWEEN THE SCHRÖDINGER THEORY AND THE CLASSICAL HAMILTON-JACOBI EQUATION

The Hamilton-Jacobi equation, which is used in classical mechanics to describe the motion of a material particle in a field of force, is a first-order nonlinear differential equation. We shall briefly recapitulate its derivation, starting from the classical law of conservation of energy

\[ E = \frac{p^2}{2m} + V = T + V. \]  

(5.27)

Let us introduce the action function

\[ S(t) = \int_0^t \mathcal{L} \, dt = \int_0^t (2T - E) \, dt = S - Et, \]  

(5.28)

where

\[ S = \int_0^t 2T \, dt. \]  

(5.29)

As we shall show, the dependence of \( S \) and \( t \) in (5.29) is only implicit, namely, \( S = S(x(t), y(t), z(t)) \), and therefore we have written it without including \( t \) as an argument. Thus, we can distinguish between the stationary action function \( S \) and the time-dependent action function \( S(t) \) in the same way as we distinguish between the stationary wave function and the time-dependent wave function.

To show that \( S \) is not an explicit function of \( t \) in (5.29), we take the total differential of \( S \):

\[ dS = 2T \, dt. \]

From the equations

\[ dS = \frac{\partial S}{\partial t} \, dt + \frac{\partial S}{\partial x} \, dx + \frac{\partial S}{\partial y} \, dy + \frac{\partial S}{\partial z} \, dz, \]  

(5.30)

\[ 2T \, dt = m_0 (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \, dt = p_x \, dx + p_y \, dy + p_z \, dz, \]
we find that
\[ \frac{\partial S}{\partial t} = 0 \]
and thus \( S \) does not depend explicitly on \( t \). Moreover,
\[ p = \nabla S. \]  

From Eqs. (5.31) and (5.27), we obtain the stationary Hamilton-Jacobi equation
\[ \frac{1}{2m} (\nabla S)^2 + V - E = 0. \]  
We can introduce the time-dependent action function
\[ S(t) = S - Et \]
into this equation by making use of the relation \( p = \nabla S = \nabla S(t) \), and eliminate the parameter \( E \) with the help of the relation \( E = -\frac{\partial S(t)}{\partial t} \). We then obtain the time-dependent Hamilton-Jacobi equation, which can be used in nonstationary problems:
\[ \frac{1}{2m} \left[ \nabla S(t) \right]^2 + V + \frac{\partial S(t)}{\partial t} = 0. \]  

The stationary and time-dependent Hamilton-Jacobi equations correspond to the stationary and time-dependent Schrödinger equations, respectively.

It can be readily shown that in the case of motion of a free particle \( (V = 0, \ p = \text{const}, \ i = \text{const}) \), the action function is
\[ S(t) = -Et + pr. \]  

To see this, it is sufficient to substitute the expression (5.34) for \( S(t) \) into (5.33). Let us take special note of the fact that the function \( \psi(t) \) for the motion of a free particle is [see (4.60)]
\[ \psi(t) = A e^{i\left( -Et + pr \right)} = A e^{\frac{i}{\hbar} S(t)}. \]  

The relationship between the wave function and the action function will hold in general form whenever we make the transition from the Schrödinger equation to the Hamilton-Jacobi equation. We shall consider further only the stationary case, for which
\[ \psi = A e^{\frac{i}{\hbar} S}. \]
We start with the Schrödinger equation in operator form

\[
\left( \frac{\hat{p}^2}{2m_0} + \hat{V} - \hat{E} \right) \psi = 0. \tag{5.37}
\]

Making use of the momentum operator \( \hat{p} = -i\hbar \nabla \), we obtain from (5.36)

\[
\hat{p} \psi = (\nabla S) \psi, \tag{5.38}
\]

\[
\frac{\hat{p}^2}{2m_0} \psi = \frac{1}{2m_0} (\nabla S)^2 - i\hbar \nabla S \psi. \tag{5.39}
\]

We note from Eq. (5.38) that Eq. (5.36) leads to the same relation between the momentum operator \( \hat{p} \) and the action function \( S \) as in the classical theory if we replace the momentum operator by the classical momentum \( p \). Substituting (5.39) into (5.37), we obtain

\[
\frac{1}{2m_0} (\nabla S)^2 + V - E - \frac{i\hbar}{2m_0} \nabla S = 0, \tag{5.40}
\]

which is simply the transformed Schrödinger equation.

To obtain the Hamilton-Jacobi equation, we must neglect the last term in (5.40), that is, set \( \hbar = 0 \). It is a well known fact that the quantum-mechanical equations transform exactly into the classical equations when \( \hbar = 0 \). If, on the other hand, \( \hbar \neq 0 \), but the condition

\[
(\nabla S)^2 \gg \hbar |\nabla S|
\]

is satisfied, the quantum-mechanical terms provide only small corrections to the classical equations. The approximation corresponding to this case is known as the quasi-classical approximation.

Since \( p = \nabla S \), the above condition can be rewritten as

\[
\frac{\hbar}{p^2} |\nabla \cdot p| \ll 1.
\]

In particular, for the one-dimensional case, we have

\[
\frac{\hbar}{p^2} \left| \frac{dp}{dx} \right| = \left| \frac{d(h \rho p)}{dx} \right| = \left| \frac{d\rho}{2m_0 dx} \right| \ll 1. \tag{5.41}
\]

Thus, the quasi-classical approximation turns out to be sufficiently accurate in cases where the de Broglie wavelength is constant or changes very little over distances of the order of the wavelength. Since

\[
p = \sqrt{2m_0(E - V)},
\]
we can rewrite the condition (5.41) in the form

\[ \frac{\hbar}{\rho^2} \left| \frac{dp}{dx} \right| \leq \left| \frac{m_F \hbar}{\rho^2} \right| \leq 1, \]

(5.42)

where \( F = -\frac{dV}{dx} \) is the classical force acting on the particle. From this, it follows that the quasi-classical approximation becomes inapplicable at small values of the momentum and, in particular, at the points where a particle would come to a stop in the classical theory \( (E = V, p = 0) \). Such a state of affairs is obtained, for example, in a potential well at the points where the direction of a particle is reversed as a result of reflection from the potential barrier (the turning points). A simple explanation can be given for this conclusion: namely, the de Broglie wavelength tends to infinity as \( p \to 0 \) and, when this happens, the wave-like properties of a particle become too important for the particle to be treated quasi-classically.

D. THE WENTZEL-KRAMERS-BRILLOUIN APPROXIMATION METHOD (WKB METHOD)

As mentioned above, Eq. (5.40) is completely equivalent to the Schrödinger equation. Therefore, it would be possible to take Eq. (5.40) as the basis of the wave theory by treating the term which is proportional to \( \hbar \) and which does not appear in the classical equation as a new quantum-mechanical potential energy

\[ \nu^{\text{quan}} = -\frac{i\hbar}{2m_0} \nabla S, \]

(5.43)

which has to be added to the Hamilton-Jacobi equation. The general solution of the nonlinear Schrödinger equation (5.40) is, however, much more complicated than the solution of the linear Schrödinger equation, and therefore the many attempts to develop the quantum theory by means of further analysis of Eq. (5.40) met with failure. Fortunately, Wentzel, Kramers and Brillouin succeeded in finding an approximate solution of the Schrödinger equation (5.40) by taking only the terms of the order of \( \hbar \). This solution was found to be applicable to a number of problems in quantum mechanics. It is referred to as the WKB approximation.

For the sake of simplicity, we shall consider only the one-dimensional case, assuming that the potential energy is a relatively smooth function of \( x \) (see Fig. 5.1). For particles with energy \( E \), the range of variation of \( x \) can be divided into two regions. In the first region \( (x < x_0) \), the energy \( E \) is greater than the potential energy \( (E > V) \), and in the second region \( (x > x_0) \), \( E < V \). It is obvious
that \( E = V(x_0) \) at the boundary \( (x = x_0) \) of the two regions. For the one-dimensional case, the original equation (5.40) becomes

\[
S'' - i\hbar S'' = 2\hbar_0 (E - V) = \rho^2.
\] (5.44)

First, we shall find the solution of this equation for region I \( (E > V) \), where the quantity \( \rho^2 > 0 \) can be interpreted as the square of the classical momentum. The solution will be sought in the form of a series

\[
S = S_0 + S_1 + S_2 + \ldots,
\] (5.45)

where the quantity \( S_0 \) is independent of \( \hbar \), \( S_1 \) is proportional to \( \hbar \), \( S_2 \) is proportional to \( \hbar^2 \), etc. Substituting the series (5.45) into (5.44) and neglecting quantities proportional to \( \hbar^2 \) and to the higher powers of \( \hbar \), we obtain

\[
S_0'' + 2S_0'S_1' - i\hbar S_0'' = \rho^2.
\] (5.46)

Taking both sides of the equation, we equate terms that are independent of \( \hbar \) and, similarly, terms that are directly proportional to \( \hbar \) (here it is necessary to bear in mind that the quantity \( S_1 \) is proportional to \( \hbar \)). We thus obtain

\[
S_0'' = \rho^2, \quad 2S_0'S_1' = i\hbar S_0''.
\] (5.47)

Hence, it follows that

\[
S_0 = -\frac{1}{\hbar} \int_{x}^{x_0} p dx, \quad S_1 = i\hbar \ln V_{\rho}.
\] (5.48)

---

This approximate method of solution is basically the same as the perturbation method, which is also successfully used in the solution of the Schrödinger equation (see Chapter 14 below).
Therefore, retaining only terms of the order of $\hbar$, we have

$$S = S_0 + S_1 = \pm \int_x^{x_0} p \, dx + i\hbar \ln V^{-}.$$  

(5.49)

Substituting (5.49) into (5.36), we obtain the following expression for the wave function in the first region ($x < x_0$):

$$\psi_{x < x_0} = \frac{1}{\sqrt{p}} \left( A \cos \frac{1}{\hbar} \int_x^{x_0} p \, dx + B \sin \frac{1}{\hbar} \int_x^{x_0} p \, dx \right).$$  

(5.50)

In exactly the same way, for the second region ($x > x_0$), in which $p^2 < 0$, we obtain

$$\psi_{x > x_0} = \frac{1}{\sqrt{|p|}} (D e^{- \frac{1}{\hbar} \int_{x_0}^{x} |p| \, dx} - C e^{- \frac{1}{\hbar} \int_{x_0}^{x} |p| \, dx}),$$  

(5.51)

where

$$|p| = \sqrt{2m_e (V - E)}.$$

The wave functions (5.50) and (5.51) are the desired approximate solutions. From these equations it is seen that, when $E > V$, the wave function is cosinusoidal or sinusoidal, as in the case of a potential well [see Eq. (4.21)] or a free particle [see Eq. (4.47)], whereas, when $V > E$, it changes exponentially, as in the case of transmission through a potential barrier [see Eq. (4.23)].

Comparing the solutions for $V = \text{const}$ with the solutions for the case where the potential energy is a function of $x$, we see that the transition from one case to the other is simply equivalent to replacing the area of the rectangular barrier contained between the $x$ axis and an axis indicating the constant quantity $x = \frac{\sqrt{2m_e (V - E)}}{\hbar} = \frac{|p|}{\hbar}$ by the area enclosed between the $x$ axis and the curve for $V = V(x)$.

Schematically this transition can be represented in the following manner:

$$\frac{|p|}{\hbar} x \rightarrow \frac{1}{\hbar} \int_0^x |p| \, dx.$$  

(5.52)

A similar transition is made in the case of a potential well.

Thus the specific form of the dependence of the potential energy on $x$ does not alter the character of the solution. Indeed the solution is determined only by the sign of the difference between $E$ and $V$, as we indicated at the end of the preceding chapter.

The solutions (5.50) and (5.51) give a good approximation only for regions that are relatively far from the special point $x_0$ (the
classical turning point) where the quantity $|p|$ is relatively large. Near the special point ($x \to x_0$) the quantity $p^* \to 0$; therefore, the denominator in Eqs. (5.50) and (5.51) vanishes and the actual solution diverges. If we could express the coefficients $C$ and $D$ in terms of $A$ and $B$, the foregoing approximation would be entirely adequate for many problems, since the region $|x - x_0| \to 0$ is comparatively narrow. However, the relation between these coefficients can be found only if we can connect the functions across the boundary ($x = x_0$) of the regions (by connection of the solutions we mean matching the wave functions and also their first derivatives at the boundary $x \to x_0$). The approximate expression for $\psi$ must, therefore, be represented in such a form that at large $p^2$ Eq. (5.50) holds, while for $x = x_0$, when

$$p^2 = -(x - x_0) 2m_0 V'(x_0) = -a h^2 (x - x_0),$$

the approximate solution satisfies the equation

$$\psi'' - a (x - x_0) \psi = 0. \quad (5.53)$$

At large $z$, the cosine function can be expressed asymptotically in terms of an $n$th order Bessel function:

$$\cos \left( z - \frac{n \pi}{2} - \frac{\pi}{4} \right) \approx \sqrt{\frac{n \pi}{2}} J_n(z). \quad (5.54)$$

Therefore, if we set

$$z = \frac{1}{h} \int_x^z p \, dx, \quad (5.55)$$

then

$$\psi_{x < x_0} = \frac{A'}{\sqrt{p}} \sqrt{\frac{n \pi}{2}} J_n(z). \quad (5.56)$$

For large $z$ (and any $n$), because of the asymptotic formula (5.54), the solution (5.56) transforms into the solution (5.50) found by the WKB method. Let us attempt to choose the order $n$ of the Bessel function in such a way that the solution (5.56) satisfies the Schrödinger equation not only for large $z$, when $x < x_0$, but also near the turning point $x = x_0$, that is, when

$$p \to h \sqrt{a (x_0 - x)} \to 0 \text{ and } z = \frac{2}{3} \frac{\sqrt{a}}{h} (x_0 - x)^{3/2} \to 0. \quad (5.57)$$

In this case ($x \to x_0 - 0$), the asymptotic expression for $\psi$ becomes

$$\psi_{x \to x_0 - 0} = A' \sqrt{\frac{\pi}{3h}} \frac{\sqrt{a}}{3} J_n \left( \frac{2}{3} \frac{\sqrt{a}}{h} (x_0 - x)^{3/2} \right). \quad (5.58)$$
Substituting (5.58) into (5.53), we find that \( J_n \) must satisfy the equation
\[
\frac{d^2J_n}{dx^2} - \frac{1}{x_0 - x} \frac{dJ_n}{dx} + \left( \frac{x}{x_0 - x} - \frac{1}{4(x_0 - x)^2} \right) J_n = 0.
\]

Introducing the new variable \( z = \frac{2\sqrt{n}}{3} (x_0 - x)^{3/2} \) (the argument of the Bessel function) into this equation, and denoting by primes the derivatives with respect to this argument,
\[
J_n' + \frac{1}{z} J_n' + \left( 1 - \frac{1}{9z^2} \right) J_n = 0. \tag{5.59}
\]

If the Bessel function is to satisfy Eq. (5.59) and if, at the same time, the wave function is to obey the asymptotic equation (5.53), we must put \( n = \pm \frac{1}{3} \). Thus, instead of the approximate solution (5.50), we have
\[
\psi_{x \leq x_0} = \sqrt{\frac{\pi}{2x_0 p}} \int_{x_0}^{x} dx \left\{ A J_{1/3} \left( \frac{1}{h} \int_{x_0}^{x} p \, dx \right) + B J_{-1/3} \left( \frac{1}{h} \int_{x_0}^{x} p \, dx \right) \right\}. \tag{5.60}
\]

Similarly, in place of (5.51), we obtain for the second region \( (E < V) \)
\[
\psi_{x > x_0} = \sqrt{\frac{\pi}{2x_0 p}} \int_{x_0}^{x} dx \left\{ C I_{1/3} \left( \frac{1}{h} \int_{x_0}^{x} \frac{|p|}{d\lambda} \, dx \right) + D I_{-1/3} \left( \frac{1}{h} \int_{x_0}^{x} \frac{|p|}{d\lambda} \, dx \right) \right\}, \tag{5.61}
\]

where \( I_{1/3} \) and \( I_{-1/3} \) are the Bessel functions of an imaginary argument.

In order to connect the two solutions, we must find the asymptotic forms of Eqs. (5.60) and (5.61) for the region \( x \rightarrow x_0 \). The appropriate values of \( z \) and \( \rho \) are determined from (5.57). For the Bessel function, it is enough to take only the first term of its expansion:
\[
J_n(z) = I_n(z) = \frac{1}{\Gamma(n + 1)} \left( \frac{z}{2} \right)^n. \tag{5.62}
\]

The solutions (5.60) and (5.61) become, respectively,
\[
\psi_{x = x_0-0} = \frac{A \sqrt{\pi}}{h^{1/3} \Gamma(1/3)} (x_0 - x) + \frac{B \sqrt{\pi}}{h^{1/3} \Gamma(1/3)} \Gamma(2/3),
\]
\[
\psi_{x = x_0+0} = \frac{C \sqrt{\pi}}{h^{1/3} \Gamma(1/3)} (x - x_0) + \frac{D \sqrt{\pi}}{h^{1/3} \Gamma(1/3)} \Gamma(2/3). \tag{5.63}
\]
Connecting the solutions at the point \( x = x_0 \), we find

\[ D = B, \quad C = -A. \]

Considering the asymptotic forms of the ordinary Bessel function [see (5.54)] and of the Bessel function of imaginary argument\(^5\)

\[ I_n(z) \approx \frac{1}{\sqrt{2\pi z}} \left( e^z + e^{-z} \cos \pi \left( n + \frac{1}{2} \right) \right), \quad (5.64) \]

\(^5\)The Bessel function of imaginary argument is related to the Bessel function of the first kind by the equation

\[ I_n(z) = i^{-n} J_n(iz) = e^{-\frac{n\pi}{2}} J_n(x), \]

where

\[ x = ze^{-\frac{\pi}{2}}. \]

The asymptotic form of the Bessel function with \( x = |x|e^{i\phi} \) can be calculated either for \( \phi = \frac{\pi}{2} + 0 \)

\[ J_n(x) \approx e^{i\pi(n+\frac{1}{2})} \sqrt{\frac{2}{\pi x}} \cos \left( x + \frac{1}{2} \pi(n + \frac{1}{2}) \right) \text{ for } \frac{\pi}{2} < \phi < \frac{3}{2} \pi, \quad (5.64a) \]

or for \( \phi = \frac{\pi}{2} - 0 \)

\[ J_n(x) \approx \sqrt{\frac{2}{\pi x}} \cos \left( x - \frac{1}{2} \pi(n + \frac{1}{2}) \right) \text{ for } -\frac{\pi}{2} < \phi < \frac{\pi}{2}, \quad (5.64b) \]

(see, for example, P. Morse, and H. Feshbach, Methods of Theoretical Physics, New York: McGraw-Hill, 1953, Vol. I, p. 622). Therefore, the asymptotic form of \( I_n \) for real \( z \) has a discontinuity (Stokes phenomenon). Indeed, using (5.64a) and (5.64b), we find for the two cases

\[ I_n(z) = \frac{1}{\sqrt{2\pi z}} \left( e^z + e^{-z} e^{\pi i \left( n + \frac{1}{2} \right)} \right) \text{ for } \phi = \frac{\pi}{2} + 0, \quad (5.64c) \]

\[ I_n(z) = \frac{1}{\sqrt{2\pi z}} \left( e^z + e^{-z} e^{-\pi i \left( n + \frac{1}{2} \right)} \right) \text{ for } \phi = \frac{\pi}{2} - 0. \quad (5.64d) \]

Unfortunately, many authors, including Morse and Feshbach (see Methods of Theoretical Physics, Vol. II, p. 1097), use (5.64c) in analyzing the passage of particles through a potential barrier and thus obtain a complex asymptotic expression for the real function \( I_n(z) \).

The correct procedure at \( \phi = \frac{\pi}{2} \) (where the function has a discontinuity) is to take the half-sum of (5.64c) and (5.64d) in order to obtain the asymptotic expression (5.64), which, as expected, is real.
and also taking account of the relation between the coefficients, we find that for large \( z \), the formulas (5.60) and (5.61) take the form

\[
\psi_{x<x_0} = \frac{1}{\sqrt{p}} \left\{ A \cos \left( \frac{1}{\hbar} \int_x^{x_0} p \, dx - \frac{5\pi}{12} \right) + B \cos \left( \frac{1}{\hbar} \int_x^{x_0} p \, dx - \frac{\pi}{12} \right) \right\},
\]

(5.65)

\[
\psi_{x>x_0} = \frac{1}{\sqrt{|p|}} \left\{ (B - A) e^{-x_0} \right\}.
\]

Setting \( B = A = \frac{a}{\sqrt{3}} \) in the last equality, we find the first pair of connected solutions

\[
\psi_{x<x_0} = \frac{a}{\sqrt{p}} \sin \left( \frac{1}{\hbar} \int_x^{x_0} p \, dx + \frac{\pi}{4} \right),
\]

(5.66)

\[
\psi_{x>x_0} = \frac{a}{2 \sqrt{|p|}} e^{-x_0},
\]

(5.67)

for which the exponentially decreasing solution (5.67) in the region \( x>x_0 \) is the analytic extension of the sinusoidal solution (5.66) for the region \( x<x_0 \).

To determine the analytic extension of the exponentially increasing solution \( (x>x_0) \), we must set \( B = -A = b \). We then obtain the second pair of connected solutions

\[
\psi_{x<x_0} = \frac{b}{\sqrt{p}} \cos \left( \frac{1}{\hbar} \int_x^{x_0} p \, dx + \frac{\pi}{4} \right),
\]

(5.68)

\[
\psi_{x>x_0} = \frac{b}{\sqrt{|p|}} e^{x_0}.
\]

(5.69)

According to Eqs. (5.66) and (5.68), the expression for \( \psi \) in region I \( (x<x_0) \) is of the form of standing waves. It can also be written in the form of traveling waves. Indeed, setting

\[
b = (g + h), \quad a = i(g - h),
\]
we have

\[ \psi_{x < x_0} = \frac{1}{\sqrt{p}} \left[ ge^{i \left( \int_{-\infty}^{x_0} p\,dx + \frac{\pi}{4} \right)} + he^{-i \left( \int_{-\infty}^{x_0} p\,dx + \frac{\pi}{4} \right)} \right]. \quad (5.70) \]

The appearance of the factor \( \sqrt{p} \) in the denominator of (5.70) means that the probability of finding a particle in a unit volume (that is, a quantity proportional to \( |\psi|^2 \)) is smaller, the greater the velocity. Inside the barrier the exponential solution that is connected to (5.70) takes the form

\[ \psi_{x > x_0} = \frac{1}{\sqrt{|p|}} \left[ (g + h) e^{\frac{i}{\hbar} \int_{x_0}^{x} |p|\,dx} + i \frac{(g - h)}{2} e^{-\frac{i}{\hbar} \int_{x_0}^{x} |p|\,dx} \right]. \quad (5.71) \]

In cases where the potential barrier is located to the left of the turning point, we must interchange the limits of integration, so that the lower limit will always be less than the upper limit.

On the basis of these results, we are able to quantize the problem of the potential well (that is, find the energy levels of the particles) in the WKB approximation. Let us assume that we have a potential well of arbitrary shape, as illustrated in Fig. 5.2. Obviously,

![Fig. 5.2. Quantization in a potential well according to the WKB method.](image)

the process of quantization in the WKB method will consist in finding the conditions under which the exponentially increasing solutions on both sides of the potential barrier \((x < x_1\) and \(x > x_0)\) vanish.

According to (5.66), the wave function for this case has the following form in that region of the potential well which is adjacent to the boundary of the barrier at \(x = x_1\) (there being only an exponentially decreasing solution inside the barrier):

\[ \psi_{x < x_0} = -\frac{a}{\sqrt{p}} \sin \left( \frac{i}{\hbar} \int_{x_0}^{x_2} p\,dx + \frac{\pi}{4} \right). \quad (5.72) \]
Because of the requirement of an exponentially decreasing solution inside the potential barrier in the region $x \ll x_1$, the following solution is obtained for the potential well in the region $x \gg x_1$:

$$\psi_{x>x_1} = \frac{a}{\sqrt{p}} \sin\left(\frac{1}{\hbar} \int_{x_1}^{x} p \, dx + \frac{\pi}{4}\right).$$  \hspace{1cm} (5.73)

Two solutions must be identical at any arbitrary point $x$ in the potential well ($x_1 < x < x_2$), as long as we do not take points too close to the boundary of the potential barrier. Joining the solutions (5.72) and (5.73) at some point $x$ (that is, matching the two wave functions and also their derivatives), we have

$$a' \sin\left(\frac{1}{\hbar} \int_{x_1}^{x_2} p \, dx + \frac{\pi}{4}\right) - a \sin\left(\frac{1}{\hbar} \int_{x_1}^{x} p \, dx + \frac{\pi}{4}\right) = 0,$$

$$a' \cos\left(\frac{1}{\hbar} \int_{x_1}^{x_2} p \, dx + \frac{\pi}{4}\right) + a \cos\left(\frac{1}{\hbar} \int_{x_1}^{x} p \, dx + \frac{\pi}{4}\right) = 0.$$

If this system of homogeneous equations is to have a nontrivial solution for $a$ and $a'$, the determinant of the system must vanish. We then obtain the relation

$$\sin\left(\frac{1}{\hbar} \int_{x_1}^{x_2} p \, dx + \frac{\pi}{4}\right) = 0.$$

The integral $\int_{x_1}^{x_2} p \, dx$ cannot be negative, since $p = \sqrt{2m_0 (E-V)} \equiv 0$. Hence

$$\frac{1}{\hbar} \int_{x_1}^{x_2} p \, dx + \frac{\pi}{4} = (n + 1) \pi, \quad n = 0, 1, 2, \ldots$$  \hspace{1cm} (5.74)

Thus the quantization rules obtained from the WKB approximation (that is, with an accuracy up to the terms of the order of $\hbar$) have the form

$$\int p \, dx = 2\pi \hbar \left(n + \frac{1}{2}\right).$$  \hspace{1cm} (5.75)

These quantization rules differ from the Bohr quantization rules by the presence of a nonzero term $\frac{1}{2} 2\pi \hbar$, which corresponds to the lowest state ($n = 0$). A more exact solution of a similar problem in wave theory (for example, the harmonic oscillator problem) shows that a zero-point energy necessarily exists, although it does not affect the radiation spectrum.

Let us now find the normalization coefficient of the wave function for the case of a potential well. In normalizing the function, we can restrict ourselves to integration over the interval $x_1 \leq x \leq x_2$ (potential well), since $\psi$ decreases exponentially everywhere outside this region. The normalization coefficient can be then found from the equation

$$a^2 \int_{x_1}^{x_2} \frac{dx}{p} \sin^2\left[\frac{1}{\hbar} \int_{x_1}^{x} p \, dx + \frac{\pi}{4}\right] = 1.$$  \hspace{1cm} (5.76)

Since the sinusoidal function oscillates rapidly, its square can be replaced by its average value, $1/2$, without significantly affecting the accuracy. We then have

$$\frac{1}{2} a^2 \int_{x_1}^{x_2} \frac{dx}{p} = 1.$$  \hspace{1cm} (5.77)
The oscillation period \( T \) (\( \omega \) is the angular frequency) is
\[
T = \frac{2\pi}{\omega} = \frac{2}{\sqrt{m_0}} \int_{x_1}^{x_2} \frac{dx}{\sqrt{\frac{1}{m_0} x}}.
\]
where \( v = \frac{p}{m_0} \) is the velocity of the particle. Hence, for the normalization coefficient, we obtain the expression
\[
a = \sqrt{\frac{2\omega m_0}{\pi}}.
\]
Consequently, the eigenfunction (5.73) in the WKB approximation assumes the form
\[
\psi \approx \sqrt{\frac{2\omega}{\pi V}} \sin \left( \frac{1}{\hbar} \int_{x_1}^{x} p \, dx + \frac{\pi}{4} \right),
\]
(5.78)

**Problem 5.1.** Determine the eigenfunctions and eigenvalues of the energy of a particle in a three-dimensional potential well bounded by an infinitely high potential barrier:
\[
V(x, y, z) = \begin{cases} 0 & \text{for } 0 < x < l_1, \ 0 < y < l_2, \ 0 < z < l_3, \\ \infty & \text{outside the potential well}. \end{cases}
\]
Find the conditions under which different wave functions correspond to the same energy value \( E \), that is, the conditions under which the energy levels are degenerate.

**Answer.**
\[
E_{n_1 n_2 n_3} = \frac{\pi^2 \hbar^2}{2m_0} \left( \frac{n_1^2}{l_1^2} + \frac{n_2^2}{l_2^2} + \frac{n_3^2}{l_3^2} \right),
\]
\[
\psi_{n_1 n_2 n_3} = \sqrt{\frac{8}{l_1 l_2 l_3}} \sin \frac{n_1 x}{l_1} \sin \frac{n_2 y}{l_2} \sin \frac{n_3 z}{l_3} \quad (n_1, n_2, n_3 = 1, 2, 3, ...).
\]
In particular, when \( l_3 = l_1 \), we have degeneracy for the case of the two different wave functions \( \psi_{n_1 n_2 n_3} \) and \( \psi_{n_1 n_2 n_3} \):
\[
E_{n_1 n_2 n_3} = E_{n_1 n_2 n_3}.
\]

**Problem 5.2.** Find two classes of solutions (symmetric and antisymmetric) for a particle in a one-dimensional symmetric potential well:
\[
V(x) = \begin{cases} V_0 & \text{for } x < -l \quad \text{(region I)} \\ 0 & \text{for } -l < x < l \quad \text{(region II)} \\ V_0 & \text{for } x > l \quad \text{(region III)} \end{cases}
\]

Show that, when \( V_0 \) can have any arbitrary value, only the symmetric solution must always have at least one energy level. Find the condition under which an antisymmetric solution is possible. Show that the antisymmetric solutions corresponding to \( x > 0 \) also represent a complete solution of the system in the case where \( V(x) \) is described by the function
\[
V(x) = \begin{cases} \infty & \text{for } x < 0, \\ 0 & \text{for } 0 < x < l, \\ V_0 & \text{for } x > l. \end{cases}
\]
(5.80)

*These problems are based on the material contained in both Chapters 4 and 5.*
Plot a graph of the potential energy and of the symmetric and antisymmetric wave functions.

Solution. The wave functions in regions I, II and III have the form

\[ \psi_1 = D_1 e^{i(x+l)}, \quad (x < -l), \]
\[ \psi_{II} = A_2 \sin kx + B_2 \cos kx, \quad (-l < x < l), \]
\[ \psi_{III} = C_2 e^{-i(x-l)}, \quad (x > l), \]

where

\[ k = \sqrt{\frac{2m_0 E}{\hbar^2}}, \quad x = \sqrt{\frac{2m_0}{\hbar^2}} (V_0 - E). \]

The exponentially increasing solutions have been discarded because they diverge (indeed, this is the factor that is ultimately responsible for the discrete values of the energy).

From the boundary conditions at \( x = \mp l \), it follows that \( \psi_{I, III}(x) = \psi_{II}(x) \) and \( \frac{d\psi_{I, III}(x)}{dx} = \frac{d\psi_{II}(x)}{dx} \). From this, we find that it is possible to have either a symmetric solution, for which \( \psi(x) = \psi(-x) \), or an antisymmetric solution, for which \( \psi(x) = -\psi(-x) \).

For the symmetric solution \( A_1 = 0 \), \( C_2 = D_1 \), and the energy levels are found from the equation

\[ \tan a = \sqrt{\frac{\beta^2 - \alpha^2}{\alpha^2}}, \quad (5.81) \]

where

\[ \alpha = l \sqrt{\frac{2m_0 E}{\hbar^2}}, \quad \beta = l \sqrt{\frac{2m_0 V_0}{\hbar^2}}. \]

Since \( \sqrt{\beta^2 - \alpha^2} \alpha > 0 \), the minimum value of the angle \( \alpha \) must lie in the first quadrant and can be found from the condition

\[ \cos \alpha = \frac{1}{\sqrt{1 + \tan^2 \alpha}} = \frac{\alpha}{\beta}. \]

This equation will always have one root for any value of \( \beta \) in the region \( 0 < \alpha < \frac{\pi}{2} \), as is easily shown graphically from the fact that \( \beta = \text{const} > 0 \).

For the antisymmetric solution \([\psi(x) = -\psi(-x)]\), we have \( B_1 = 0 \) and \( C_2 = -D_1 \). The energy levels are determined from the equation

\[ \tan a = \frac{\alpha}{\sqrt{\beta^2 - \alpha^2}}, \quad (5.82) \]

Since the right-hand side of (5.82) has a negative sign, the minimum value of the angle \( \alpha \) must now lie in the second quadrant and can be found from the condition

\[ \sin \alpha = -\frac{\tan \alpha}{\sqrt{1 + \tan^2 \alpha}} = \frac{\alpha}{\beta}. \]

Introducing the notation

\[ \alpha = \frac{\pi}{2} + \gamma, \]

where the angle \( \gamma \) lies in the first quadrant, we find

\[ \cos \gamma = \frac{\pi}{2} + \frac{\gamma}{\beta}. \]
It is evident that this equation has at least one root only when

$$\beta > \frac{\pi}{2}, \text{ i.e., for } V_0 > \frac{\pi^2\hbar^2}{8ml^2}.$$  

Since the wave function of the antisymmetric solution vanishes at \(x=0\), the antisymmetric solution for \(x > 0\) is also the solution for a particle in a potential field described by (5.80).

Problem 5.3. Find the transmission coefficient \(D\) of a particle through a potential barrier of rectangular shape (see Fig. 5.3), if the particle energy \(E\) is less than the height of the potential barrier \(V_0\).

![Fig. 5.3. Transmission of a particle through a potential barrier.](image)

The solution of the Schrödinger equation for the various regions has the form:

- For \(x < 0\) (region I):
  $$\psi_1 = A_1 e^{ikx} + B_1 e^{-ikx}$$

- For \(0 < x < a\) (region II):
  $$\psi_2 = A_2 e^{-ikx} + B_2 e^{ikx}$$

- For \(x > a\) (region III):
  $$\psi_3 = A_3 e^{ik(x-a)} + B_3 e^{-ik(x-a)}$$

Here \(k^2 = \frac{2mE}{\hbar^2}, x^2 = \frac{2m}{\hbar^2} (V_0 - E), A_1 e^{ikx}\) and \(B_1 e^{-ikx}\) characterize the incident and reflected waves, respectively; \(A_3 e^{ik(x-a)}\) characterizes the transmitted wave; and \(B_3 e^{-ik(x-a)}\) characterizes the reflected wave coming from infinity. Since we have no reflected wave from infinity in our case, we must set \(B_3 = 0\).

To determine the transmission coefficient we shall use the boundary conditions at \(x = a\) and \(x = 0\). We first express \(A_2\) and \(B_2\) in terms of \(A_3\), making use of the fact that \(x^2 \geq 1\):

- \(A_2 = \frac{1 - \ln n}{2} A_3 e^{\pi a}\)
- \(B_2 = \frac{1 + \ln n}{2} A_3 e^{-\pi a} \approx 0\),

and then express \(A_1\) in terms of \(A_3\):

$$A_1 = \frac{(1 - \ln n)(1 + \frac{1}{n})}{4} e^{\pi a} A_3.$$  

The transmission (diffusion) coefficient \(D\) is then found to be

$$D = \frac{\abs{A_1}^2}{\abs{A_2}^2} \approx \frac{16n^2}{(1 + n^2)^2} I n (e^{-2\pi a} + \ln \frac{16n^2}{(1 + n^2)^2}),$$
where

\[ n = \frac{k}{\varepsilon} = \sqrt{\frac{I}{V_0 - E}}. \]

Neglecting the second term in the exponential for \( D \) (this is possible because the quantity \( \frac{16n^2}{(1 + n^2)^2} \) is only slightly different from unity), we finally obtain

\[ D \approx e^{-\frac{2a}{\hbar} \sqrt{2m_0(V_0 - E)}}. \]

When \( \hbar = 0 \), we get the classical result \( D = 0 \).

Problem 5.4. A particle is in a potential field of the form

\[
\begin{aligned}
0, & \quad x < 0, \\
V_0, & \quad 0 < x < l, \\
0, & \quad l < x < l_1 \\
0, & \quad l_1 < x
\end{aligned}
\]

(a) Show that the spectrum is continuous.

(b) Show that for \( \xi \gg 1 \) and \( \xi (l_1 - l) = \gamma \gg 1 \) \( (0 < E < V_0) \) there must exist quasi-levels, that is, states such that there is only a transmitted wave in region III (see Problem 5.3).

(c) Construct a graph of the wave function corresponding to a quasi-level.

(d) Find the squared modulus of the wave function inside the potential well and explain why it decays exponentially with time.

Solution. In the various regions, the wave function has the following form (see the notation of Problem 5.3):

\[
\psi_1 = A_1 \sin kx, \\
\psi_{\text{II}} = C_2 e^{-\xi x} + D_2 e^{\xi x}, \\
\psi_{\text{III}} = C_3 e^{i k (x - l_1)} + D_3 e^{-i k (x - l_1)}. \\
\]

From the boundary conditions, we find

\[
\begin{align*}
C_2 &= \frac{1}{2} C_3 e^{-\gamma a} \left( 1 \pm \frac{i \xi}{k} \right) + \frac{1}{2} D_2 e^{\gamma a} \left( 1 \mp \frac{i \xi}{k} \right), \\
C_3 &= \frac{1}{2} A_1 \left( \sin k l \mp \frac{k}{x} \cos kl \right).
\end{align*}
\]

These relations hold for any value of \( E \), and therefore the spectrum is continuous.

We obtain quasi-levels by requiring that there should be only a transmitted wave in the external region (region III), that is, only a wave moving in the positive \( x \) direction. Setting \( D_3 = 0 \), we obtain the following equation for the energy of the quasi-levels:

\[
\tan \alpha + \frac{a}{\sqrt{\beta^2 - a^2}} = e^{\frac{-2a}{\hbar} \sqrt{2m_0(V_0 - E)}} \times \\
\frac{\sqrt{\beta^2 - a^2} + ia}{\sqrt{\beta^2 - a^2} - ia} \left( \tan \alpha - \frac{a}{\sqrt{\beta^2 - a^2}} \right). \\
\]

(5.84)

It should be noted that the amplitude \( C_3 \) in this case is much smaller than the amplitude \( A_1 \):

\[
|C_3| \sim A_1 e^{-\frac{a}{\hbar} \sqrt{2m_0(V_0 - E)}}.
\]
For \( a = \infty \), Eq. (5.84) becomes exactly the same as Eq. (5.82) which gives the energy levels of the potential well (5.80).

We let \( E_0 \) denote the value of the energy of a particle in the potential well which we obtain from (5.82) and, for present purposes, we disregard all real corrections to \( E_0 \), as they make no essential difference to the problem. We then obtain the following expression for the energy:

\[
E \approx E_0 - \frac{1}{2} \hbar \lambda,
\]

where

\[
\lambda = \frac{\nu}{2l} e^{-2a} \sqrt{\frac{2m_0}{\hbar^2} (V_0 - E_0)}, \quad E_0 = \frac{m_0 v^2}{2},
\]

and where

\[
\gamma \approx \frac{16n^2}{(1 + n^2)^2}, \quad n = \sqrt{\frac{E}{V_0 - E}},
\]

under the condition \( \gamma \gg 1 \).

The presence of an imaginary part in the expression (5.85) for the energy indicates that the wave function decays exponentially with time. The transmission coefficient through the potential barrier for this case can also be found from (5.85). Indeed, the squared modulus of the wave function inside the well is:

\[
|\psi|^2 = \text{const.} e^{-\lambda t},
\]

and thus \( \lambda \), which is called the decay constant, characterizes the decrease of the probability of finding the particle inside the potential well. The quantity \( \lambda \) is related to \( D \), the transmission coefficient for a single collision of the particle with the potential barrier, by the equation

\[
\lambda \approx \frac{\nu}{2l} D,
\]

where \( \frac{\nu}{2l} \) is the number of collisions with the barrier per unit time. Hence we obtain an expression for \( D \):

\[
D \approx e^{-2a} \sqrt{\frac{2m_0}{\hbar^2} (V_0 - E)}.
\]

The same expression for \( D \) was obtained in another way in Problem 5.3. In Chapter 6 we shall obtain it for the general case in which the potential energy is an arbitrary function of the coordinates.

The constant \( \lambda \) also determines the duration of radiation \( T_{\text{rad}} = \frac{1}{\lambda} \) (see also Problem 3.4). Therefore, the quantity \( \Delta \xi \sim \hbar \lambda \) should characterize the width of an energy level.
Chapter 6

Basic Principles of the Quantum Theory of Conductivity

A. TRANSMISSION OF A PARTICLE THROUGH A POTENTIAL BARRIER (TUNNEL EFFECT)

According to the classical theory a particle can be located only at those points in space where the potential energy \( V \) is less than its total energy \( E \). This follows because the kinetic energy of a particle

\[
\frac{p^2}{2m} = E - V
\]  

must always remain positive. In a region where \( V > E \) (a potential barrier), the momentum has an imaginary value and, classically, the particle cannot exist in such a region. Therefore, if two regions of space in which \( E > V \) are separated from one another by a potential barrier inside which \( V > E \), the classical theory does not allow a particle to penetrate from one region into the other. In the wave theory, however, an imaginary value of the momentum (see the WKB approximation method, Chapter 5) simply corresponds to an exponential dependence of the wave function on the coordinates. Since the wave function does not vanish inside the potential barrier, it is quite possible for a particle to leak through it. This phenomenon is observed in the case of microparticles. The penetration through a potential barrier is called the tunnel effect. It is a specifically quantum-mechanical effect and has no analog in classical mechanics.

With the WKB method, it is a relatively simple matter to determine the probability of penetration of a particle through a potential barrier of an arbitrary but sufficiently smooth shape (see Fig. 6.1).

Let us assume that a particle is moving in the direction of positive \( x \) in the region I \(( -\infty < x < x_1 )\), where \( E > V(x) \). It encounters a potential barrier \(( x_1 < x < x_2 )\), where \( E < V(x) \), at the point \( x = x_1 \), and then falls into the region III \(( x > x_2 )\), where again \( E > V(x) \). The beginning and end points of the potential barrier can be found from the condition

\[
V(x) = E. \tag{6.2}
\]  


The de Broglie waves corresponding to the motion of this particle will be partially reflected from the potential barrier and partially transmitted through it. The transmitted waves will then propagate in the region III \((x > x_2)\). To determine the probability of penetration of a particle through the potential barrier, let us begin by analyzing the wave in region III, where the solution has the simplest form, since in this region there can be no wave moving in the direction of negative \(x\). According to Eq. (5.70), the solution in region III has the form

\[
\psi_{III} = \frac{1}{i\rho} \left[ g_{III}e^{i\left(\frac{1}{\hbar} \int_{x_2}^{x} \rho dx + \frac{\pi}{4}\right)} + h_{III}e^{-i\left(\frac{1}{\hbar} \int_{x_2}^{x} \rho dx + \frac{\pi}{4}\right)} \right],
\]

where

\[
\rho = \sqrt{2m_0(E - V(x))}.
\]

We define the transmission coefficient as the absolute value of the ratio of the flux density of the particles transmitted through the barrier to the flux density of the incident particles:

\[
D = \left| \frac{J_{tr}}{J_{inc}} \right|.
\]

To determine the particle flux, we shall make use of Eq. (5.23). Setting the constants \(e\) and \(m_0\) equal to unity (which we are allowed to do because we are interested only in the ratio of the particle fluxes), we obtain
Substituting (6.3) into (6.5), we find
\[
j_{\text{III}} = |g_{\text{III}}|^2 \quad \text{for} \quad h_{\text{III}} = 0,
\]
\[
j'_{\text{III}} = -|h_{\text{III}}|^2 \quad \text{for} \quad g_{\text{III}} = 0.
\]

It is seen from the above that the amplitude \( g_{\text{III}} \) characterizes the wave propagating in the direction of positive \( x \), and the amplitude \( h_{\text{III}} \) the wave propagating in the direction of negative \( x \). Since, as has been already mentioned, there is no wave propagating in the negative \( x \) direction in region III, we must set \( h_{\text{III}} = 0 \). Then
\[
j_{\text{IR}} = |g_{\text{III}}|^2,
\]
and the corresponding joined solution inside the potential barrier (region II) can be found from Eq. (5.71). Setting \( h = 0 \) and \( g = g_{\text{III}} \) in Eq. (5.71), we find
\[
\phi_{\text{II}} = \frac{1}{\sqrt{|\rho|}} \left[ g_{\text{III}} e^{-\frac{i}{\hbar} \int_{x}^{x_3} |\rho| dx} - \frac{i}{2} g_{\text{III}} e^{-\frac{i}{\hbar} \int_{x}^{x_3} |\rho| dx} \right].
\]
where
\[
|\rho| = \sqrt{2m_0 (V - E)}.
\]

Using the equation
\[
\frac{1}{\hbar} \int_{x_1}^{x_2} |\rho| dx = \gamma - \frac{1}{\hbar} \int_{x_1}^{x_1} |\rho| dx,
\]
where
\[
\gamma = \frac{1}{\hbar} \int_{x_1}^{x_3} |\rho| dx = \frac{1}{\hbar} \int_{x_1}^{x_3} \sqrt{2m_0 (V - E)} dx,
\]
the solution (6.9) can be put into a form such that it can be connected to the solution in region I by means of Eq. (5.70). Thus we have
\[
\phi_{\text{II}} = \frac{1}{\sqrt{|\rho|}} \left[ g_{\text{III}} e^{-\frac{i}{\hbar} \int_{x_1}^{x} |\rho| dx} - \frac{i}{2} g_{\text{III}} e^{-\gamma} \right].
\]
According to Eq. (5.70), the solution in region I \((x < x_i)\) has the form

\[
\psi_1 = \frac{1}{\sqrt{p}} \left[ g_{i1} e^{i \left( \frac{1}{\hbar} \int_{x}^{x_i} p \, ds + \frac{\pi}{4} \right)} - i h_{i1} e^{i \left( \frac{1}{\hbar} \int_{x}^{x_i} p \, ds + \frac{\pi}{4} \right)} \right].
\] (6.14)

Substituting this solution into (6.5), the following expressions for the incident and reflected waves are obtained:

\[
\begin{align*}
\frac{1}{\text{inc}} &= |h_i|^2; \\
\frac{1}{\text{ref}} &= -|g_i|^2.
\end{align*}
\] (6.15, 6.16)

Equations (5.70) and (5.71) can be used to relate the coefficients \(g_i\) and \(h_i\) with \(g_{11} e^{i}\) and \(\frac{1}{2} \imath g_{11} e^{-i}:\)

\[
\begin{align*}
g_i + h_i &= \frac{t}{\hbar} \imath g_{11} e^{-i}, \\
g_i - h_i &= -2 \imath g_{11} e^{i}.
\end{align*}
\] (6.17, 6.18)

From this, we find

\[
\begin{align*}
h_i &= \imath g_{11} \left( e^{i} + \frac{1}{4} e^{-i} \right), \\
g_i &= -\imath g_{11} \left( e^{i} - \frac{1}{4} e^{-i} \right).
\end{align*}
\] (6.19, 6.20)

In accordance with the definition of the transmission coefficient (6.4a), we have

\[
D = \frac{|j_{\text{tr}}|}{|j_{\text{inc}}|} = \frac{|g_{11}|^2}{|h_i|^2} = \frac{1}{\left( e^{i} + \frac{1}{4} e^{-i} \right)^2}.
\] (6.21)

In exactly the same way, we find the reflection coefficient

\[
R = \frac{|j_{\text{ref}}|}{|j_{\text{inc}}|} = \left( \frac{e^{i} - \frac{1}{4} e^{-i}}{e^{i} + \frac{1}{4} e^{-i}} \right)^2.
\] (6.22)

From these formulas, it follows that the sum of the transmission and reflection coefficients is equal to unity:

\[
R + D = 1.
\] (6.23)
For cases where the quantity $\gamma$ is much larger than unity (these are the only ones of practical interest), the transmission coefficient (6.21) is given by the expression:

$$D \approx e^{-\gamma} = e^{-\frac{2}{\mathcal{R}} \int_{x_1}^{x_2} \sqrt{2m_0 (V - E)} \, dx}.$$  \hspace{1cm} (6.24)

In the classical limit ($\hbar \to 0$), it is evident that the transmission coefficient becomes zero, as we would expect, and thus the penetration of particles through the potential barrier is impossible.

B. THE TUNNEL EFFECT AS A MANIFESTATION OF WAVE PROPERTIES

The penetration of particles through a potential barrier is a typical manifestation of their wave properties. Therefore, an analog of this effect must occur in every type of wave theory.

In optics, this analog is the well-known phenomenon of total internal reflection, which occurs when light is reflected from an optically less dense medium. Let us assume that a ray of light propagating in glass strikes a glass-air interface (air being the optically less dense medium). (See Fig. 6.2.) Then the wave field, which can be characterized by the electric or magnetic field strength, is described in glass (where the index of refraction $n > 1$) and in air ($n = 1$), by the following equations, respectively:

$$\varphi_\| = A_\| e^{-i\omega t + \frac{i\omega \eta}{c} (x \sin \theta_1 + y \cos \theta_1)},$$

$$\varphi_{\perp} = A_{\perp} e^{-i\omega t + \frac{i\omega \eta_{\perp}}{c} (x \sin \theta_{\perp} + y \cos \theta_{\perp})}. \hspace{1cm} (6.25)$$

In solving the similar problem of penetration of a particle through a rectangular potential barrier (see Problem 5.3), we obtained the same exponent as in (6.24), but in front of the exponential there was a factor $\frac{16\pi^2}{(1 + n^2)^2}$, which was of the order of unity. In the case of a smooth barrier (that is, a barrier exerting a force which is continuous at all points), this factor becomes exactly unity.
Equating these functions\(^2\) at the interface (at the plane \(y=0\)), we obtain the familiar laws of refraction:

\[
\omega_{\text{II}} = \omega_i; \quad \sin \theta_{\text{II}} = n \sin \theta_i; \quad \cos \theta_{\text{II}} = \sqrt{1 - n^2 \sin^2 \theta_i}.
\]

Substituting these values into (6.25a) we find for the refracted wave

\[
\varphi_{\text{II}} = A_{\text{II}} e^{i \omega t} e^{i \frac{\omega_i}{c} (x n \sin \theta_i + y \sqrt{1 - n^2 \sin^2 \theta_i})}.
\]

From this it is seen that, if \(n \sin \theta_i < 1\), an ordinary wave will be propagated in region II. In the case where \(n \sin \theta_i > 1\), we have total internal reflection, the physical analysis of which cannot be given on the basis of the laws of geometrical optics. From the standpoint of physical optics, which accounts for the wave properties of light, the electric and magnetic fields are exponentially decaying:

\[
\varphi_{\text{II}} = e^{- \frac{n}{c} \sqrt{n^2 \sin^2 \theta_i - 1} y - i \omega t + \frac{i \omega_i}{c} x n \sin \theta_i}.
\]

If in the case of total internal reflection the refracted wave encounters a second glass surface (region III) (that is, we have two pieces of glass separated by an air layer), then in region III the wave is again propagated according to Eq. (6.25). Its amplitude, however, will be an exponentially decreasing function of the width of the air layer \(l\).

\[
A_{\text{III}} = A_{\text{II}} e^{- \frac{n}{c} \sqrt{n^2 \sin^2 \theta_i - 1} l}.
\]

A diagram of the tunnel effect in optics is shown in Fig. 6.3.

Before concluding the physical analysis of the penetration of particles through a potential barrier, we should also consider the so-called “tunnel effect paradox.” This paradox lies in the fact that, at first glance, it seems as though the real classical particles inside the potential barrier are in a peculiar state characterized by an imaginary momentum. However, it is important to remember that in this purely quantum-mechanical phenomenon, it is only the probability of a particle being somewhere inside the barrier which decreases exponentially as we recede from the boundary into the potential barrier. Inside the barrier, the momentum and position of a particle are real, and are both given within the framework of the ordinary

\(^2\)We shall not write here the expression for the reflected wave.
uncertainty relation. In order to show this, let us consider a potential barrier with constant $V$. In the first approximation, the wave function inside the barrier changes according to the equation

$$\varphi_{II} = Ae^{-x},$$  \hspace{1cm} (6.27)

where

$$x = \frac{1}{\hbar} \sqrt{2m_0(V - E)} = \text{const.} \hspace{1cm} (6.28)$$

The right-hand side of (6.27) can be represented in the form of a Fourier integral

$$e^{-x} = \int_{\delta}^{\infty} f(k) \cos kx \, dk,$$  \hspace{1cm} (6.29)

where

$$f(k) = \frac{2x}{\pi(x^2 + k^2)}, \hspace{1cm} (6.29a)$$

which means that it can be represented as a set of wave functions having real momenta. Obviously, the amplitudes $f(k)$ will effectively differ from zero only when $k$ varies in the range from 0 to $x$.

Thus the uncertainty in momentum is

$$\Delta p \sim \hbar x.$$ 

According to wave mechanics, the position of a particle inside the potential barrier can be determined only to an accuracy within the order of the width of the barrier:

$$l = x_2 - x_1, \hspace{1cm} \Delta x \sim l.$$  

Multiplying $\Delta p$ and $\Delta x$ we obtain

$$\Delta p \Delta x \sim \hbar l.$$ 

Since our equations are valid only for the case $\lambda \gg 1$, the accuracy in determining the momentum of the particle and its position inside the potential barrier will not contradict the uncertainty relation.

C. MOTION OF ELECTRONS IN A METAL

The theory of the tunnel effect has a number of very important applications both in the theory of metals and in nuclear physics. On the basis of this theory it is now possible to explain a number of phenomena which could not be accounted for in classical physics,  

---

such as cold emission (the emission of electrons from a metal under the action of an electric field), contact potentials, etc. Before discussing these phenomena, we shall say a few words about the theory of an electron gas, which underlies the electron theory of the conductivity of metals.

The high conductivity of metals indicates that electrons are able to move relatively freely inside the entire crystal lattice of a metal. Their escape from the metal into vacuum is, however, hindered because this requires the expenditure of a certain energy, the so-called "work function." This suggests that as a first approximation, we may simply consider the metal as a potential well, inside which the potential energy of an electron can be taken as equal to zero \( V = 0 \), while outside the metal (that is, in a vacuum) \( V = V_0 > 0 \).

This simplified model enables us to explain several phenomena occurring in metals. Some of its fundamental results, obtained for the case of free electrons, can be extended (with the help of quantum mechanics) to include the periodic field of a crystal (see below the simplest one-dimensional Kronig-Penney model, which correctly describes at least the qualitative aspects of many phenomena).

The electron gas model of a metal was first considered in classical theory (the theories of Drude, Lorentz and others). In this version of the model, the classical Maxwell-Boltzmann statistics, which had successfully explained many phenomena in the kinetic theory of gases, was now applied to electrons. However, the electron gas model encountered great difficulties in developing a theory of specific heat. In accordance with the theorem of equipartition of energy, well-known from classical statistical mechanics, each degree of freedom must have, on the average, an energy

\[
\frac{1}{3}E_{av} = \frac{1}{2}kT,
\]

where \( k \) is Boltzmann's constant. From this, it is evident that the contribution of each free electron to the total specific heat will be the same as that of a free atom:

\[
c_{s}^{el} = \frac{\partial E_{av}}{\partial T} = \frac{3}{2}k.
\]

This contradicts the experimental facts which indicate that the specific heat of a monatomic metal is the same as that of the lattice atoms; that is, in the first approximation, free electrons make no contribution to the specific heat of a metal.

\[1\] The specific heats of monatomic substances will be considered in greater detail in Chapter 12 (see formula (12.66)).
This contradiction was resolved by Sommerfeld, who showed that electrons in a metal do not obey the classical distribution

\[ f = A e^{-\frac{E}{kT}}. \]

Instead, the distribution is characterized by the Fermi-Dirac distribution function

\[ f_{\text{F-D}} = \frac{1}{e^{E/kT} + 1}. \]

The Fermi-Dirac quantum statistics is based on the Pauli exclusion principle, according to which each energy level can be occupied by at most two electrons (two quantum states which differ only by the direction of spin).

If we are given a three-dimensional potential well of a cubic shape, with side length equal to \( L \), then, according to Eq. (4.57), the components of momentum \( p = \hbar k \) will be related to the integers \( n_1, n_2 \) and \( n_3 \) characterizing the energy level by the expressions

\[ p_x = \frac{2\pi \hbar n_1}{L}, \quad p_y = \frac{2\pi \hbar n_2}{L}, \quad p_z = \frac{2\pi \hbar n_3}{L}. \]

We note that a unit interval of quantum numbers

\[ (\Lambda n_1 = \Lambda n_2 = \Lambda n_3 = 1) \]

\[ \Delta n_1 \Delta n_2 \Delta n_3 = \frac{L^3}{8\pi^2\hbar^2} d^3p \]  

(6.30a)

is associated with only one level, occupied by two electrons. Therefore, if there are \( \rho_0 \) electrons per unit volume, the maximum momentum of an electron at absolute zero \( (T = 0) \) can be determined from the relation

\[ \rho_0 = \frac{2}{L^3} \sum \Delta n_1 \Delta n_2 \Delta n_3 = \frac{2}{8\pi^2\hbar^2} \int_0^{\rho_{\text{max}}} p^2 dp = \frac{\rho_{\text{max}}}{3\pi^2\hbar^3} \]  

(6.31)

or

\[ p_{\text{max}} = \hbar (3\pi^2\rho_0)^{1/3}. \]  

(6.32)

The corresponding maximum kinetic energy is

\[ E_{\text{max}} = \frac{p_{\text{max}}^2}{2m_0} = \frac{\hbar^2}{2m_0} (3\pi^2\rho_0)^{2/3}. \]  

(6.33)

This energy is called the Fermi energy.
As an example, let us compute the value of this energy for silver. The density of silver is 10.5, and its atom weight is 107.9. Assuming that the number of free electrons is equal to the number of atoms per unit volume, we have

\[ \rho_0 = \frac{10.5}{107.9} \times 6.02 \times 10^{23} = 5.8 \times 10^{22} \]

where we have used the Avogadro number (the number of atoms in one gram-atom, equal to \( 6.02 \times 10^{23} \)). Hence, Eq. (6.33) gives

\[ E_{\text{max}}^0 = 8.5 \times 10^{-12} \text{ erg} = 5.3 \text{ ev.} \]

Since the work function for silver is \( \Phi = 3.7 \text{ ev} \), the depth of the potential well in silver is found to be equal to 9 ev. A schematic diagram of the filling of energy levels in a metal is given in Fig. 6.4.

The average energy of an electron in a metal is given by the equation

\[ E_{\text{av}} = \frac{2}{\rho_0} \int_0^{E_{\text{max}}} \frac{\rho^2}{2m_0} d\rho = \frac{3}{5} E_{\text{max}}^0. \]  

In agreement with experiment, it follows that at relatively low temperatures the electron gas makes no contribution to the specific heat, since

\[ c_{\text{el}} = \frac{\partial E_{\text{av}}}{\partial T} = 0. \]

If the temperature differs from zero, some of the electrons will jump into higher energy levels. The distribution of electrons in the higher levels will not be characterized by a Maxwellian distribution, but by the Fermi distribution function

\[ f = \frac{1}{\lambda} e^{E/kT} + 1. \]  

At \( T = 0 \) (the case considered above), this function equals unity if \( E < E_{\text{max}} \) and zero if \( E > E_{\text{max}}^0 \). For \( T \neq 0 \) the average energy can be obtained from the expression

\[ E_{\text{av}}^T = \frac{3}{5} E_{\text{max}}^0 + \frac{\pi^2 k^2 T^2}{2 E_{\text{max}}^0} + O(T^4). \]
Hence, the contribution of each electron to the specific heat is

$$ c_v^{el} = -\frac{\partial U_v^{av}}{\partial T} = \frac{\pi^2 k^2 T}{2 E_{max}^0} \ll \frac{3}{2} kT, \quad (6.35) $$

which vanishes as \( T \to 0 \). At high temperatures, when the quantity \( \frac{1}{A} e^{E_{av}/kT} \) becomes much greater than unity, the Fermi-Dirac distribution function (6.34) approaches the classical Maxwell-Boltzmann distribution

$$ f = A e^{-E/kT}, \quad (6.36) $$

which, as we know, implies the following expression for the average energy of a free electron:

$$ E_{av}^{el} = \frac{3}{2} kT. \quad (6.37) $$

By comparing this expression with the average energy at low temperatures [see Eq. (6.33a)] and using the condition

$$ E_{av}^{el} > E_{av}^0 \quad (6.38) $$

it is possible to define the degeneracy temperature

$$ T_{deg} \sim \frac{h^2}{k m_0} (3\pi^2 p_0)^{2/3}. \quad (6.39) $$

At temperatures higher than \( T_{deg} (T > T_{deg}) \), we can use classical statistics to describe the behavior of electrons in the metal. If we substitute the value of \( p_0 \), say, for silver, we obtain \( T_{deg} \sim 10 - 20 \) thousand degrees. Thus, at all temperatures at which a metal exists in the solid state, the electron gas has a certain degree of degeneracy. This means that in discussing the properties of electrons, we must use only Fermi-Dirac statistics, and, moreover, the principal term in the expression for the kinetic energy of free electrons is independent of temperature.

This large value of the degeneracy temperature is associated with the small mass of the electron \( m_0 \). Ions and molecules have a mass thousands of times greater than the mass of an electron, and therefore classical statistics applies to them at ordinary temperatures.

D. REMOVAL OF ELECTRONS FROM A METAL.
COLD EMISSION

From the potential-well model of electrons in a metal (see Fig. 6.4) we can see that to remove an electron from a metal
it is necessary to impart to it an amount of energy no smaller than the work function

$$W = V_0 - E_{\text{max}}.$$  \hspace{1cm} (6.40)

As we know, in the external photoelectric effect an electron receives an energy $\hbar \omega$ from the absorbed photon. Thus, an electron can leave the metal with a kinetic energy

$$\frac{1}{2} m_0 v^2 = \hbar \omega - W$$  \hspace{1cm} (6.41)

(Einstein's equation). It follows that the work function represents the minimum amount of energy that must be added to the electron in order to make its energy greater than the height of the potential barrier.

In a metal at $T = 0$ some of the electrons occupy energy levels lying above the Fermi level. If we increase the kinetic energy of the electron gas by heating the metal, a certain fraction of electrons may acquire an energy exceeding the height of the potential barrier, and thus a current will flow from the metal. This phenomenon, which is known as thermionic emission, is used to obtain an electron beam in electron tubes. Under the action of an external electrostatic field, this current may also arise even at lower temperatures. Let us consider the influence of an external electric field $\mathcal{E}$ applied to the surface of a conductor in the negative $x$ direction. The potential energy for this case is

$$V(x) = V_0 - e_0 \mathcal{E} x,$$  \hspace{1cm} (6.42)

where $e = e_0$ is the electron charge and $\mathcal{E}$ is the electric field intensity (see Fig. 6.5).
In addition to the external electric field, the electron experiences an electric force called the image force. This force arises because an electron with charge \(-e_0\) induces an "image" charge \(e_0\) at the surface of the metal (see Fig. 6.6).

Thus the total force acting on the electron is

\[
F = e_0 \delta - \frac{e_0^2}{4x^2}.
\]

The effective potential energy, taking into account the image force, is of the form

\[
V_{\text{eff}} = V_0 - e_0 \delta x - \frac{e_0^2}{4x^2}.
\]

The quantity \(V_{\text{eff}}\) has a maximum at the point \(x_0\):

\[
\frac{dV_{\text{eff}}}{dx} = -e_0 \delta + \frac{e_0^2}{4x_0^2} = 0; x_0 = \frac{1}{2} \sqrt{\frac{e_0}{\delta}}.
\]

The maximum value of \(V_{\text{eff}}\) is less than \(V_0\) because

\[
V_{\text{max}} = V_0 - \sqrt{e_0 \delta}.
\]

Thus, taking into account the electric image force shows that when an external field is applied, the work function decreases and becomes equal to

\[
W' = W - \sqrt{e_0 \delta}.
\]

The electric image forces, however, do not explain cold emission. In fact, an estimate of the maximum current (with \(W' = 0\)) for tungsten, for instance, gives the value

\[
\delta = \frac{W^2}{e_0^2} \approx 2 \cdot 10^8 \text{ v/cm},
\]

whereas experimentally rather strong current is obtained with a field as low as \(\delta \approx 4 \cdot 10^5\) v/cm (Millikan).
Thus, within the framework of the classical theory it is impossible to explain quantitatively the cold emission of electrons.

In the quantum theory of this phenomenon (essentially the transmission of electrons through a potential barrier), we limit ourselves to Eq. (6.42) for the potential energy and neglect the electric image force since it does not significantly affect the final result. It can be seen from the graph of potential energy (see Fig. 6.5) that the external electric field produces a potential barrier of finite width. Because of the tunnel effect an electron can penetrate this barrier, the transmission coefficient being given by

\[ D = e^{-\frac{2}{\hbar} V_0^2 m_0 \int_0^{x_1} \sqrt{V(x) - E} \, dx} \]  

(6.49)

The integral in the exponent must be taken over the entire width of the barrier from \( x = 0 \) to the point \( x = x_1 \) given by the condition

\[ V_0 - e_0 \Phi x_1 = E, \text{ that is, } x_1 = \frac{V_0 - E}{e_0 \Phi}. \]  

(6.50)

Then

\[ \int_0^{x_1} \sqrt{V(x) - E} \, dx = \int_0^{x_1} \sqrt{V_0 - e_0 \Phi x} - E \, dx = \]

\[ = \sqrt{e_0 \Phi} \int_0^{x_1} \sqrt{x_1 - x} \, dx = \frac{2}{3} \sqrt{e_0 \Phi} x_1^{3/2}. \]  

(6.51)

Finally, we obtain the following expression for the transmission coefficient \( D \):

\[ D = e^{-\frac{1}{\hbar} V_0^2 m_0 \left( \frac{V_0 - E^{3/2}}{e_0 \Phi} \right)} = e^{-\frac{e_0 \Phi}{\Phi}}, \]  

(6.52)

where the quantity \( \Phi_0 \) depends on the nature of the metal and the energy of the free electrons inside the metal. The cold emission current is proportional to the transmission coefficient

\[ J = J_0 D = J_0 e^{-\frac{e_0 \Phi}{\Phi}}. \]  

(6.53)

It follows from the last equation that cold emission should be observed for an electron field of \( \Phi \sim 10^4 \) V/cm. This result is in good agreement with experimental data.
E. CONTACT POTENTIALS

Contact potentials, which were discovered by Volta, can also be explained on the basis of the tunnel effect. Let us consider two different metals with different work functions and different Fermi energies (see Fig. 6.7). If these two metals are brought into contact, they will still be separated by a potential barrier of finite width.

![Fig. 6.7. Two metals before they are placed in contact with each other.](image)

$W_1$ and $W_2$ are work functions; $E_{01}$ and $E_{02}$ are the upper limits of the filled levels (the Fermi energies).

Since a certain number of filled energy levels in metal I lie above the highest filled level of metal II, electrons can move from metal I into the empty levels of metal II by the tunnel effect. From Fig. 6.7, it is seen that no flow in the opposite direction is possible, since electrons of metal II would then have energies corresponding to filled levels of metal I. It is obvious that the electric current from metal I to II ceases only when the uppermost filled levels of both metals are of the same energy.

![Fig. 6.8. Two metals after they have been brought into contact. Formation of the contact potential.](image)

As a result of the tunnel effect, metal II acquires an excess of electrons and is charged negatively, whereas metal I is charged positively. Thus, the energy levels of metal II are shifted upwards relative to those of metal I (see Fig. 6.8). After the Fermi levels
in both metals are equalized, the electric current ceases, but then there arises a potential difference proportional to the difference between the work functions of the metals:

\[ \Delta \Phi = \Phi_1 - \Phi_2 = \frac{W_2 - W_1}{\varepsilon_0}. \]  

(6.54)

This quantity is called the contact potential.

F. THE MOTION OF ELECTRONS IN A PERIODIC ELECTRIC FIELD (THE ONE-DIMENSIONAL KRONIG-PENNEY MODEL)

As has been previously mentioned, the representation of the motion of an electron in a metal in terms of the potential well model is an approximation in which we average out the periodic potential of the lattice. A number of characteristic features of the motion of electrons in a crystal appear only when the periodic variation of the potential is taken into account. In the general case, the solution of the problem is very complicated. In order to determine some of the qualitative features of this motion, we may consider, however, a simplified model of a crystal.

In the one-dimensional Kronig-Penney model, the periodic electric field produced by the positive ions of the crystal is approximated by a periodic square-well potential of the form shown in Fig. 6.9. The width of each well is denoted by \( a \), and the width of the barrier between two successive wells by \( b \). Thus, the period of the potential (the equivalent of the lattice constant) is \( c = a + b \). The barrier height is set equal to \( V_0 \).

The solution of Schrödinger's equation for the \( n \)th section of the periodic potential has the following form:

for the potential well:

\[ \psi_n = A_n \sin kx_n + B_n \cos kx_n, \]  

(6.55)

for the potential barrier:

\[ \psi_b = A'_n \sinh z(x_n - c) + B'_n \cosh z(x_n - c). \]  

(6.56)
Here \( k = \sqrt{\frac{2mE}{\hbar^2}} \), \( x = \sqrt{\frac{2m(V_a - E)}{\hbar^2}} \), \( x_n = x - cn \); the coordinate \( x_n \) is measured from the origin of the \( n \)th section (that is, the \( n \)th well). Similarly, for the \( (n+1) \)st section, we can write

\[
\psi_{n+1} = A_{n+1} \sin kx_{n+1} + B_{n+1} \cos kx_{n+1}.
\]  

(6.57)

We first join solutions (6.55) and (6.56) at the point \( x = cn + a \) (that is, at \( x_n = a \)), obtaining

\[
A_n \sin ka + B_n \cos ka = - A' \sinh xb + B' \cosh xb,
\]

(6.57a)

\[
A_n \cosh ka - B_n \sinh ka = \frac{x}{k} (A'_n \cosh xb - B'_n \sinh xb).
\]

Next, joining the solutions (6.56) and (6.57) at the point \( x = c(n+1) \) and noting that \( x_n = c \) and \( x_{n+1} = 0 \), we obtain

\[
B'_n = B_{n+1},
\]

\[
A'_n = \frac{k}{x} A_{n+1}.
\]

(6.58)

Let us substitute (6.58) into (6.57a) and simplify the problems by considering the limiting Kronig-Penney case in which the width of the barrier between two wells tends to zero \( (b \to 0) \), the height \( V_a \) tends to infinity, and the width of the well remains constant:

\[
\frac{x^2 a b}{2} = P = \text{const}.
\]

Then, since \( \cosh xb \to 1 \) and \( \sinh xb \to xb \), we have

\[
A_n \sin ka + B_n \cos ka = B_{n+1},
\]

\[
A_n \cos ka - B_n \sin ka = A_{n+1} - \frac{2P}{ka} B_{n+1}.
\]

(6.59)

Equations (6.59) are linear difference equations; their solutions should be sought in the form

\[
A_n = C_1 r^n, \quad B_n = C_2 r^n.
\]

(6.60)

Substituting (6.60) into (6.59) and dividing both equations by \( r^n \), we obtain an equation from which we can determine the quantity \( r \) and the relationship between the coefficients \( C_1 \) and \( C_2 \):

\[
C_1 \sin ka = C_2 (r - \cos ka),
\]

\[
C_2 \left( \frac{2P}{ka} r - \sin ka \right) = C_1 (r - \cos ka).
\]

(6.61)
Multiplying these equations together and dividing both sides of the resulting equation by $C_1C_2$, we obtain an equation for $r$:

$$r^2 - 2r \cos k'a + 1 = 0,$$  
(6.62)

where $\cos k'a$ is given by the equation

$$\cos k'a = \frac{P}{ka} \sin ka + \cos ka.$$  
(6.63)

As we shall see below, (6.63) is the fundamental equation for the energy levels in the periodic field of a crystal.

The solution of (6.62) has the form

$$r = \cos k'a \pm i \sin k'a = e^{\pm ik'a}.$$  
(6.64)

We note that if the right-hand side of (6.63) is greater than unity, $k'$ will be imaginary, and in this case we get an exponential solution

$$r = e^{\pm ik'a} = e^{\pm x'a}.$$  
(6.65)

Let us examine in greater detail the solution for the case of real values of $k'$

$$r = e^{ik'a}.$$

From Eqs. (6.61) and (6.60), we have

$$C_1 = C_0 \frac{r - \cos ka}{\sin ka}, \quad A_n = C_0 \frac{(e^{ik'a} - \cos ka) e^{ik'an}}{\sin ka},$$

$$C_2 = C_0, \quad B_n = C_0 e^{ik'an}.$$

Substituting the values of $A_n$ and $B_n$ into (6.65) and using the fact that $x_n = x - an$ when $b \to 0$, we find an expression for the wave function in the crystal:

$$\psi = C_n e^{ik'x} U_n,$$  
(6.66)

where $U_n$ is a function with the same periodicity as the crystal lattice

$$U_n = \frac{1}{\sin ka} \left[ e^{-ik'(x_n - a)} \sin kx_n - e^{-ik'x_n} \sin k(x_n - a) \right].$$  
(6.67)

In particular, if $P = 0$ (that is, there is no barrier), we find from (6.63) that $k' = k$; in this case the function $U_n$ becomes unity.

It follows from (6.66) that an electron can move freely in the crystal if $k'$ is a real quantity, that is, if the right-hand side of (6.63) is less than unity.
G. BASIC PRINCIPLES OF THE ELECTRON THEORY OF CONDUCTIVITY OF CRYSTALS

The quantum theory of electron motion in a crystal lattice provides a key to distinguishing between conductors, dielectrics or insulators, and semiconductors (which in a sense form an intermediate class of solids). We do not intend to treat this subject quantitatively and shall confine ourselves to a few qualitative remarks based on the one-dimensional Kronig-Penney model.

As the starting point of our analysis, we shall use Eq. (6.63) to determine the possible values of the electron energy in a crystal lattice. This equation is

\[
\cos k'a = \frac{P}{ka} \sin ka + \cos ka,
\]

where \(a\) is the lattice constant, and the quantity \(k = \frac{\sqrt{2mE}}{h}\) gives the electron energy. The eigenvalues of the electron energy can be found from the condition that \(k'\) must be real. This condition means that the right-hand side of Eq. (6.63) must be less than unity.

Setting \(P = \infty\), we obtain the energy spectrum of isolated atoms (in this case the atoms are separated from one another by an impenetrable barrier). The energy spectrum will then consist of a separate set of levels for each well:

\[
k' = k = \pi n a,
\]

where \(n = 1, 2, 3 \ldots\). We shall not consider the negative values of \(n\), since they give exactly the same values of energy, but correspond to the motion of electrons in the negative \(x\) direction. The first two levels \((n = 1, 2)\)

\[
E_1 = \frac{\pi^2 \hbar^2}{2m a^2}, \quad E_2 = 4E_1
\]

of isolated atoms are shown in Fig. 6.10.

![Energy levels of isolated atoms and crystal lattice](image)

Fig. 6.10. The formation of energy bands in a crystal lattice.

If \(P\) is finite [see Eq. (6.63)], it is easiest to determine the energy levels graphically (see Fig. 6.11). The allowed values of \(k\) (and therefore of the energy) correspond to the values of the right-hand side of Eq. (6.63) lying between \(-1\) and \(+1\). In Fig. 6.11, these allowed values are denoted by a heavy line. Thus, in a crystal lattice containing \(N\) atoms each energy level of an isolated atom is split into \(N\) levels. Each of these groups of levels is called a band (see Fig. 6.10).
The electrons in the crystal tend to occupy the lowest energy levels and, according to the Pauli exclusion principle, each level is occupied by at most two electrons with opposite spins.

For example, the crystal lattice of an alkali metal contains \( N \) valence electrons if there are \( N \) atoms. The electrons occupy only half of the lower band (since there can be at most two electrons in each level). In the ground state, half of the electrons move in one direction, and the other half in the opposite direction; consequently, the average current is equal to zero. When an electric field is applied, more than half of the electrons move in some preferred direction, thus producing an electric current and moving up into higher energy levels. Therefore, in a metal, either the first band must contain a sufficient number of unfilled levels, or it must come into contact with a second empty band, called the conduction band.

On the contrary, in a perfect insulator all levels in the first or valence band are occupied and the levels of the second (conduction) band are all empty. The energy spacing between these bands is usually several electron volts. It is easy to show that, when a field is applied, the electrons cannot acquire a preferred direction of motion. The direction of motion of an electron can be reversed only if the electron goes into a different energy state. But since all the energy levels are occupied, this can only happen if the electron occupying that other energy state makes the opposite transition to the state originally occupied by the first electron. Therefore, on the average, there can be no preferred direction of motion of the electrons even when a field is applied. A diagram of the energy levels of a conductor and a dielectric is given in Fig. 6.12.

![Energy levels in a crystal lattice](image1)

![Energy levels in a crystal lattice](image2)

Nevertheless, every dielectric possesses some (very small) conductivity. The conductivity is much greater in semiconductors, where the forbidden band is considerably smaller than in dielectrics; it is of the order of 1 ev, and sometimes even less (for example, in germanium, the width of the allowed band is 0.66 ev at \( T = 300^\circ K \)). At absolute zero, semiconductors behave like dielectrics; however, their conductivity increases with rising temperature, particularly in the presence of impurities. At room temperature, the resistivity of semiconductors is found to be of the order of \( 10^{-2} - 10^2 \) ohm·cm. At the same time, the resistivity of dielectrics lies within the range of \( 10^3 - 10^{19} \) ohm·cm, and that of metals in the range of \( 10^{-6} - 10^{-9} \) ohm·cm.

The conductivity of dielectrics and semiconductors can be of two types. Let us assume that under the influence of thermal excitation or the internal photoelectric effect (absorption of light by electrons), some of the electrons jump from the valence into the conduction band, leaving vacant states ("holes") in the valence band. The electrons that have jumped...
The quantum theory of conductivity explains how into the conduction band become carriers of electric charge, thus producing a current. On the other hand, as soon as several states become empty in the valence band, an electric current can also be produced due to the motion of electrons in the valence band itself. It can be shown that the motion of a system of electrons in an almost completely filled valence band can be treated in terms of the motion of a set of vacant states or "holes." Obviously, the holes move in a direction opposite to the direction of electron motion, so that they behave like positively charged particles. Thus, there are two ways in which charge can be transported and, therefore, two types of electric current in solids: $n$ type (due to the motion of electrons) and $p$ type (due to the motion of holes).

With the help of the band theory, we can easily give a qualitative explanation of a number of interesting phenomena.

For example, the conductivity of a metal increases with decreasing temperature because its resistance is due to the interaction between free electrons and the vibrations of the lattice. Since the vibrations of the lattice diminish as the temperature decreases, the resistance will also decrease. On the contrary, the conductivity of semiconductors decreases as the temperature is lowered, because the number of electrons in the conduction band becomes increasingly smaller. The existence of $p$ type conductivity in semiconductors has been demonstrated in investigations of the Hall effect and thermoelectric emf. The sign of the potentials appearing in these phenomena is determined by the sign of the current carriers. Experiment shows that in some semiconductors the sign of the potentials corresponds to electron carriers, whereas in other semiconductors the sign of the potentials is reversed; that is, the current carriers act as if they were positively charged particles. A natural explanation for this is provided by the concept of "holes."

The above conclusions in regard to the conductivity due to transitions of electrons from the valence band into the conduction band (the long arrow on the left-hand side of Fig. 6.13) and due to the motion of holes in the valence band are based on the assumption of a perfect crystal. This type of conductivity is known as intrinsic conductivity.

Another type of conductivity, known as impurity conductivity, also plays a significant role in semiconductors. It is caused by the presence of foreign impurities or other structural defects in the lattice. Such disruptions of the perfect periodicity of the lattice lead to local deviations of the field from a perfectly periodic one. As a result, discrete levels may appear in the forbidden band of the energy spectrum of the electrons (see Fig. 6.13). In practice, the wave functions associated with these levels differ from zero only in a certain region near the given defect. Thus, discrete levels are sometimes called impurity levels. They do not themselves contribute to the current (the electrons occupying them are not free). However, they may affect the number of electrons contained in both the conduction and the valence bands.

Impurity levels (denoted by short arrows on the right-hand side of Fig. 6.13) can be divided into two types: donor levels and acceptor levels. A donor is capable of supplying electrons to the conduction band, so that free electrons will appear in the conduction band. In contrast to a donor, an acceptor absorbs electrons; as a result a "hole" is formed in the filled band so that electrons in this band are able to jump into higher energy states ($p$ type conductivity).

If the impurity levels are located sufficiently close to the edge of the corresponding bands, ionization (or other effects) can arise fairly easily due to the energy of thermal motion of the lattice. Therefore, an appreciable number of free electrons (or holes) can exist in bands even under conditions when direct excitation of electrons from the valence band into the conduction band is highly improbable.

In the case of impurity conduction, the magnitude and type of the conductivity are determined mainly by the nature and concentration of the impurities. By varying the impurities, it is possible to control within a wide range the magnitude of the conductivity as well as its type ($n$ type or $p$ type). This fact is widely utilized in semiconductor...
electronics. It constitutes the basis of operation of modern high-quality crystal diodes and transistor devices which are capable of rectifying AC currents, as well as of amplifying and generating electrical oscillations.

In conclusion, we would like to draw attention to two important approximations which we have implicitly assumed in the electron theory of solids. First, in developing the theory of metals and semiconductors, we were actually concerned only with the problem of single electrons. Accordingly, this theory is called the single-electron theory. The collective properties of electrons in solids were taken into account only in connection with the filling of energy levels by free electrons, when we calculated certain statistical quantities (the Fermi energy, specific heat, etc.). Even in those cases we completely neglected interactions between electrons, although they do in fact experience mutual Coulomb repulsions. It is easy to show that, for the electron densities which we observed in metals, the average energy of this repulsion is not necessarily small in comparison with the Fermi energy. There naturally arises the question of the extent to which this crude single-electron model represents the properties of a real metal. The answer to this question is given in the many-electron theory of solids, which we cannot consider here since this recently developed theory is a highly specialized subject. We may note that the fundamental notion of the electron gas as a free carrier obeying Fermi-Dirac statistics is retained in the multielectron theory. Accordingly, the laws of purely statistical character obtained in the single-electron theory still hold true, such as, for example, the linear dependence of the electronic specific heat on temperature. At most, certain numerical coefficients will have to be slightly changed because of the specific form of the wave functions for a system of electrons. These refinements, however, involve exceptionally large computational difficulties.

On the other hand, in dynamical problems, where it is essential to take into account the interactions between electrons, the simplified approach used above (the single-electron theory) is inadequate. One case of this type is the problem of the strength of a metal. The second approximation which is implicit in the single-electron theory concerns the crystal lattice, which is regarded simply as the source of a certain statistical field. The situation is actually more complicated because the lattice ions execute a vibrational motion, which, as we know, persists even at absolute zero (zero-point vibrations). In order to take this fact into account, it is necessary to consider the crystal lattice as a quantum-mechanical system rather than simply as the source of a field (see Chapter 12, D). The essential point in this connection is that the lattice is not isolated from the system of electrons, but coupled to it since the electrons interact with the lattice ions. The energy of this interaction can be uniquely represented by the sum of two terms. One of them represents the potential energy of interaction between the electrons and the stationary lattice. The motion of electrons in a field of this type was considered above in the simple case of the Kronig-Penney model. The second term is connected with the deviations of the ions from their equilibrium positions and represents the interaction energy between the electrons and the lattice vibrations. The average value of this interaction energy is extremely small in comparison with the energy of the electrons at the Fermi level, because the amplitudes of the vibrations of the lattice ions are small (except at temperatures near the melting point).

The vibrations of the lattice, however, may play an important role at low temperatures, when the interaction of each electron with the vibrations of the lattice gives rise to an additional interaction in a pair of electrons. If these two electrons have opposite spins, the interaction results in an attraction (in contrast to electrostatic repulsion). As a result, the pair of electrons begins to move with a certain degree of correlation. Such a system is found to have the property of superconductivity. The smallness of the interaction which causes the correlation explains why superconductivity is observed only at extremely low temperatures.

A theory of superconductivity based on these concepts was developed independently by the American physicists Bardeen, Cooper, and Schrieffer, and by the Russian physicist Bogolyubov. [See N. Bogolyubov, V. Tolmachev, D. Shirkov, A New Method in the Theory of Superconductivity (trans.), New York: Consultants Bureau, 1959.]

Chapter 7

Statistical Interpretation of Quantum Mechanics

A. ELEMENTS OF THE THEORY OF LINEAR OPERATORS

In our general investigation of the Schrödinger wave equation (Chapter 5), we saw that in quantum mechanics the momentum operator \( p = -i\hbar \frac{\partial}{\partial x} \) is associated with the classical momentum \( p \) of the particle, the energy operator \( E = i\hbar \frac{\partial}{\partial t} \) with the energy \( E \), the Hamiltonian operator or simply Hamiltonian \( H \) with Hamilton's function \( H \), etc. Before analyzing the physical meaning of the quantities represented by operators in quantum theory, let us consider certain general aspects of the theory of operators.

In the same way as a function relates a number \( x \) with another number \( y = f(x) \), an operator \( M \) associates one function \( f(x) \) with another function

\[
\psi(x) = Mf(x),
\]

according to some given rule.

In order to satisfy the principle of superposition, only linear operators with the two following fundamental properties are used in quantum mechanics:

\[
\begin{align*}
M(f_1 + f_2) &= Mf_1 + Mf_2, \\
CMf &= CMf,
\end{align*}
\]

(7.2)

where \( C \) is an arbitrary constant.

The linear operators most commonly encountered are the differentiation sign (for example, the momentum operator \( M = \frac{\hbar}{i} \frac{\partial}{\partial x} \) and the Laplacian \( M = \nabla^2 \)) and the integration sign.

In Poisson's equation

\[
\nabla^2 f(r) = \rho(r)
\]

(7.3)
the operator is the Laplacian which converts the function \( f(r) \) into another function \( \rho(r) \). Conversely, we can solve Poisson's equation and find

\[
f(r) = \nabla^2 \rho(r) = - \int \rho(r') K(r, r') \, d^3x'. \tag{7.3a}
\]

Here the operator \( \nabla^2 \) has the form of a definite integral, the kernel of the operator being

\[
K(r, r') = -\frac{1}{4\pi |r - r'|} = -\frac{1}{4\pi \sqrt{(x - x')^2 + (y - y')^2 + (z - z')^2}}.
\]

The operators \( \nabla^2 \) and \( \nabla^{-2} \), which have the same effect as multiplication by unity when they are applied in succession, are called inverse operators.

The Hamiltonian operator

\[
H = T + V,
\]

consists of the sum of the kinetic energy operator \( T = -\frac{\hbar^2}{2m_0} \nabla^2 \), which is directly proportional to the Laplacian, and the potential energy \( V \), which is simply a function of the coordinates.

We can regard the action of the potential energy \( V(x) \) on the wave function as the action of a linear operator, because conditions (7.2) are satisfied. Therefore, besides differential and integral operators, the linear operators that may be used in quantum mechanics include any function of coordinates whose action on the wave function is simply to multiply it. For example, the coordinate \( r \) is just as entitled to be considered an operator (the position operator)\(^1\) as the momentum operator \( p = -i\hbar \nabla \), which is a differential operator. It is worth noting in this connection that in quantum mechanics \( r \) does not represent the position of a particle, but is an argument of the wave function and determines its value in the coordinate space. The quantity which is equivalent to the position can be found from the operator \( r \) and the function \( \psi(r) \) in the same way as the momentum of a particle is found from the momentum operator, that is, by averaging (see the following).

---

\(^1\) This will become particularly clear when we write the Schrödinger equation in momentum space (see below), where the wave function depends on \( p \). In this case, the momentum operator \( p \) will correspond to multiplication by an ordinary function, and the position operator \( x \) to differentiation with respect to \( p \).
B. ELEMENTS OF REPRESENTATION THEORY

The position operators \( x, y \) and \( z \) obviously commute with each other, since operating with them is equivalent to multiplying by ordinary numbers. Accordingly, \( xy = yx, xz = zx \), and so on. The operators \( p_x = -i\hbar \frac{\partial}{\partial x}, p_y = -i\hbar \frac{\partial}{\partial y} \) and \( p_z = -i\hbar \frac{\partial}{\partial z} \) also commute with each other, since the result of differentiation is independent of the order in which it is performed

\[
\frac{\partial^2}{\partial x \partial y} = \frac{\partial^2}{\partial y \partial x}, \quad \frac{\partial^2}{\partial y \partial z} = \frac{\partial^2}{\partial z \partial y}, \text{ and so on.}
\]

Similarly, it can readily be seen that the pairs of operators \( p_x \) and \( y \), \( p_y \) and \( x \), and so on, also commute with each other:

\[
p_x y \psi = -i\hbar \frac{\partial}{\partial x} y \psi = -i\hbar y \frac{\partial \psi}{\partial x} = y p_x \psi,
\]

that is,

\[
p_x y = y p_x.
\]

An example of a pair of noncommuting operators is provided by \( x \) and \( p_x \). Indeed,

\[
x p_x \psi = -i\hbar x \frac{\partial \psi}{\partial x}, \quad (7.4)
\]

whereas

\[
p_x x \psi = -i\hbar \frac{\partial x \psi}{\partial x} = -i\hbar \left(1 + x \frac{\partial}{\partial x}\right) \psi. \quad (7.5)
\]

Consequently,

\[
(p_x x - x p_x) \psi = -i\hbar \psi, \quad (7.6)
\]

that is,

\[
p_x x - x p_x = -i\hbar. \quad (7.7)
\]

In a similar fashion, it is readily shown that

\[
p_y y = y p_y = p_z z - z p_z = -i\hbar. \quad (7.8)
\]

The noncommutativity of these operators, as expressed by Eqs. (7.7) and (7.8), is a significant feature of quantum mechanics.

The specific choice of the form of position and momentum operators \( x \) and \( p_x = -i\hbar \frac{\partial}{\partial x} \) satisfying Eqs. (7.7) and (7.8) corresponds to the so-called coordinate representation, in which the wave function depends only on the spatial coordinate \( r \mid \psi = \psi(r) \).
The Schrödinger equation can also be written in the momentum representation. For the sake of simplicity, let us take the one-dimensional case. Using the \( \delta \) functions [see (4.70)], we expand \( \psi(x) \) into a Fourier integral

\[
\psi(x) = \int \psi(x') \delta(x - x') \, dx' = \frac{1}{2\pi} \int dk \, \phi(k) e^{ik(x-x')}.
\]

Since \( k = \frac{p}{\hbar} \), where \( p = p_x \), we can rewrite this equation in the form

\[
\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int \varphi(p) e^{i\frac{p}{\hbar}x} \, dp, \tag{7.9}
\]

\[
\varphi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int \psi(x') e^{-i\frac{p}{\hbar}x'} \, dx'. \tag{7.10}
\]

The Fourier transform of the function \( \psi(x) \), namely, the function \( \varphi(p) \) which depends on momentum, is called the wave function in the momentum representation. Equations (7.9) and (7.10) relate the wave functions in the coordinate and the momentum representations.

Let us find what operator in the momentum representation corresponds to the position coordinate \( x \). We note that in this representation we need not write \( p \) as an operator (that is, in roman type). If we substitute \( \psi(x) \) for \( x\psi(x) \) in Eq. (7.10), then

\[
x\varphi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int x\psi(x) e^{-i\frac{p}{\hbar}x} \, dx = \hbar \frac{\partial \varphi(p)}{\partial p}, \tag{7.11}
\]

and thus in the momentum representation the operator \( x \) has the form

\[
\hat{x} = \hbar \frac{\partial}{\partial p}.
\]

It is easily verified that Eq. (7.7) continues to hold true in the momentum representation, since

\[
(xp - px) \varphi(p) = \hbar \left( \frac{\partial \varphi(p)}{\partial p} - p \frac{\partial \varphi(p)}{\partial p} \right) = i\hbar \varphi(p).
\]

In exactly the same way, the fundamental relation (7.7) will be satisfied if \( x \) and \( p \) are replaced by certain appropriate matrices. This form of representation is called matrix representation; it was introduced by Heisenberg somewhat before the discovery of Schrödinger's equation.

The remainder of our discussion of operators will be conducted in the coordinate representation.
C. AVERAGE VALUES OF OPERATORS

In classical mechanics the motion of an individual point is exactly specified by a function relating its position to time. This dependence can be uniquely determined from the fundamental differential equation of motion

\[ m \ddot{r} = - \nabla V(r). \]

Once we have determined \( r \) as a function of time, we can also determine the momentum and energy of the particle.

The situation is somewhat different if there are many particles involved, as, for example, in the kinetic theory of gases. In this case statistical laws characteristic of a large collection of particles must be used. It turns out that the particles of such a collection obey certain distribution laws, which, generally speaking, apply to both coordinate space and momentum space (that is, a distribution describing both the velocities and the energies). The function \( f \) that characterizes this distribution is called the distribution function. Thus, when we deal with a large collection of particles, we can only consider a probability that a particle possesses particular coordinate and momentum values. From the distribution function we can find that average values of the position and momentum.

\[ \bar{x} = \int x f d^3x d^3p, \quad \bar{p}_x = \int p_x f d^3x d^3p, \]

and the mean square of these quantities

\[ \bar{x}^2 = \int x^2 f d^3x d^3p, \text{ and so on}, \]

which in accordance with the law of large numbers should agree with the corresponding experimental values.

We must mention one characteristic feature of these statistical laws. In classical physics they are a result of averaging over the so-called "hidden" parameters, which determine the motion of each particle in accordance with Newton's equations. These hidden parameters do not appear in the final results. In principle, however, classical theory enables us to explain why, at any instant of time, the coordinates and momenta of individual particles differ from the average values, even though this explanation may be very complicated mathematically.

In quantum mechanics the behavior of particles is described by the wave function \( \psi(r, t) \), which is a probability function even when the system it describes consists only of a single particle. Thus, quantum mechanics allows us to determine only the average values
of dynamic variables regardless of whether there is a large number of microparticles or only one. It must be emphasized that in quantum theory it is in principle impossible to explain the deviations of observed variables from the average values.\(^2\) The method of calculating averages in quantum mechanics is similar to that used in statistical mechanics. The basic formula used for this purpose is

\[
\bar{M} = \int \psi^*(t) M \psi(t) \, d^3x, \tag{7.12}
\]

where \(M\) is an arbitrary operator (as a special case, it may be a number), and the quantity \(\psi^*(t) \psi(t)\) plays the role of the distribution function \(f\) provided that the wave functions \(\psi(t)\) are normalized:

\[
\int \psi^*(t) \psi(t) \, d^3x = 1.
\]

The average values of the position and momentum, as has already been mentioned, are in fact computed in basically the same way:

\[
\bar{x} = \int \psi^*(t) x \psi(t) \, d^3x,
\]

\[
\bar{\rho}_x = \int \psi^*(t) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(t) \, d^3x. \tag{7.13}
\]

Here \(\bar{x}\) is the coordinate of the center of mass of the wave packet associated with the function \(\psi(t)\), and \(\rho_x\) is the momentum of this center of mass.

Since the outcome of a physical measurement is a real quantity, the average values must be represented by real numbers. Therefore, the following equation must hold:

\[
(\bar{M})^* = \bar{M}. \tag{7.14}
\]

When this requirement is satisfied, the corresponding operators are said to be self-conjugate (or Hermitian).

In particular, we shall show that the operator \(p_x\) satisfies the condition (7.14), even though it appears to be purely imaginary. As a preliminary, we must first prove an important theorem for "transferring" a derivative. This theorem is as follows. Suppose we have an integral

\[
G = \int_{-\infty}^{\infty} \psi^{(n)}(x) dx, \tag{7.15}
\]

\(^2\)Von Neumann has demonstrated that hidden parameters cannot be the basis for the statistical laws of quantum mechanics. Von Neumann's proof, however, is valid only within the limits of the actual framework of quantum mechanics itself, and if quantum mechanics is not taken as an ultimate theory, Von Neumann's theorem cannot be regarded as generally valid.
where \( v^{(n)} = \frac{d^n v}{dx^n} \). Then, if all terms of the type

\[
[u v^{(n-1)}]_{-\infty}^{\infty}, \quad [u^{(1)} v^{(n-2)}]_{-\infty}^{\infty}, \ldots, \quad [u^{(n-1)} v]_{-\infty}^{\infty}
\]

vanish, the result of integration of \( G \) is not altered if we transfer the \( n \)th derivative of the function \( v \) to the function \( u \) in (7.15) and place the factor \((-1)^n\) in front of the integral:

\[
\int_{-\infty}^{\infty} u v^{(n)} dx = (-1)^n \int_{-\infty}^{\infty} u^{(n)} v dx.
\]  \(7.17\)

Indeed, if we carry out an \( n \)-fold integration by parts in (7.15) and assume that all terms in (7.16) vanish, we obtain the relationship (7.17). In the case of a discrete spectrum, the conditions (7.16) are always satisfied because the wave function decreases exponentially at infinity. In the case of free motion (that is, a continuous spectrum), these expressions vanish as a consequence of the periodicity condition. Physically, the fulfillment of condition (7.16) means that no particles or currents exist at infinity.

Returning to the proof of the self-conjugateness of the operator \( p_x \), we substitute

\[
u = \psi^* (t), \quad v = -i\hbar \psi (t) \text{ and } n = 1
\]

into Eq. (7.17). From this it immediately follows that

\[
P_x = -\int \psi^* (t) i\hbar \frac{\partial}{\partial x} \psi (t) dx = \int \psi (t) i\hbar \frac{\partial}{\partial x} \psi^* (t) dx = (\bar{p}_x)^*,
\]

and thus the self-conjugateness condition (7.14) is satisfied for \( p_x \).

We note that unlike the operator \( p_x = -i\hbar \frac{\partial}{\partial x} \), the real operator \( \frac{\partial}{\partial x} \) is not self-conjugate and its average value has no physical meaning.

If an operator \( M \) has only one eigenvalue \( \lambda \) (and one eigenfunction \( \psi \)), it is readily seen that this eigenvalue is identical with the average value of the operator. Indeed, using the general rule (7.12) for determining the average value of an operator and substituting the equation

\[
M \psi (t) = \lambda \psi (t),
\]  \(7.18\)

we obtain for \( \bar{M} \)

\[
\bar{M} = \int \psi^* (t) M \psi (t) d^3x = \lambda \int \psi^* (t) \psi (t) d^3x = \lambda.
\]  \(7.19\)
On the other hand, suppose that the operator $M$ [Eq. (7.18)] has several eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_n, \ldots$, corresponding to the functions $\phi_1(t), \phi_2(t), \ldots, \phi_n(t), \ldots$ (for example, this may be the case for the energy operator $E = \hbar \frac{\partial}{\partial t}$, for which $\lambda_i = E_n$). Then since the general solution $\psi(t)$ can be written in the form

$$\psi(t) = \sum_n C_n \phi_n(t), \quad (7.20)$$

we find that the average value of the energy operator $E = \hbar \frac{\partial}{\partial t}$ is

$$\bar{E} = \sum_n |C_n|^2 E_n. \quad (7.21)$$

Here each $|C_n|^2$ is the probability that the particle is in the corresponding quantum state. If all $C_n$ except one, $C_n_0$, are equal to zero, then $E = E_{n_0}$, and thus the average energy corresponds to the eigenvalue $E_{n_0}$. Consequently, the eigenvalue $E_{n_0}$ corresponds to the experimentally observed energy. In the case where several coefficients $C_n$ differ from zero: $C_{n_1}, C_{n_2}, \ldots, C_{n_i}, \ldots$, we can obtain any of these values of energy in experimental measurements. If the experiment is repeated many times, the number of measurements which yield an energy $E_{n_i}$ should be proportional to the corresponding theoretical probability $|C_{n_i}|^2$. 

Chapter 8

Average Values of Operators. Change of Dynamic Variables with Time

A. DERIVATION OF THE UNCERTAINTY PRINCIPLE

As indicated in the preceding chapter, the observable dynamic quantities associated with the operators must be regarded as average values, given by Eq. (7.12). This is true regardless of whether these operators commute with the Hamiltonian, that is, regardless of whether the corresponding physical quantities are constants of the motion.

We shall now show that if two dynamic quantities correspond to noncommuting operators, they do not have simultaneous definite values in quantum mechanics. Of greatest importance in this respect is the calculation of the deviations from the average values of two canonically conjugate quantities—the position \(x\) and momentum \(p_x\). Our discussion will be carried out in the coordinate representation and we shall restrict ourselves to the case in which the wave function is independent of time (the stationary case). Then the average values of the position and momentum can be found from the relations

\[
\bar{x} = \int \psi^* x \psi \, dx, \quad (8.1)
\]

\[
\bar{p}_x = - \int \psi^* i\hbar \frac{\partial \psi}{\partial x} \, dx. \quad (8.2)
\]

First of all, we note that even though the average error or average deviation from the mean, which is given by

\[
(\Delta x) = \int \psi^* (x - \bar{x}) \psi \, dx = \bar{x} - \bar{x} = 0, \quad (8.3)
\]

is equal to zero, it in no way follows that the particle cannot occupy positions other than \(\bar{x}\). The reason for this is that the deviations have different signs relative to the mean \(\bar{x}\), and consequently they cancel out on the average. Accordingly, the deviation from the average value of the operator should be characterized by the variance (mean-square deviation), which is positive for all deviations
from \( \delta \). The variance of the position can be calculated from the formula

\[
(\overline{\Delta x})^2 = \int \psi^* (x - \bar{x})^2 \psi \, d^3x = \bar{x}^2 - 2 \langle \bar{x} \rangle^2 + \langle \bar{x} \rangle^2 = \bar{x}^2 - (\bar{x})^2. \tag{8.4}
\]

We note, incidentally, that if the variance is \( (\Delta x)^2 = 0 \), it follows that the probability of the electron occupying a position in space differs from zero only at \( x = \bar{x} \). In this case the average value of the position is equal to the exact value; that is, the corresponding probability of the particle's position can be described by a function similar to the \( \delta \) function.

Similarly, the variance of the momentum is given by

\[
(\overline{\Delta p_x})^2 = \int \psi^* (p_x - \bar{p}_x)^2 \psi \, d^3x = \bar{p}_x^2 - (\bar{p}_x)^2. \tag{8.5}
\]

In order to establish the relationship between \( (\overline{\Delta x})^2 \) and \( (\overline{\Delta p_x})^2 \), let us take a coordinate system whose origin lies at the center of mass of the wave packet \( (x = 0) \), and which moves with the same velocity as the center of mass \( (\bar{p}_x = 0) \). (The use of this coordinate system does not involve any restriction on the generality of the discussion.)

In this case

\[
(\overline{\Delta x})^2 = \bar{x}^2 = \int \psi^* x^2 \psi \, d^3x, \tag{8.6}
\]

\[
(\overline{\Delta p_x})^2 = \bar{p}_x^2 = \int \psi^* \left( -i \hbar \frac{\partial}{\partial x} \right)^2 \psi \, d^3x.
\]

Let us consider the integral

\[
I (\tau) = \int (x \psi^* + \frac{\partial \psi^*}{\partial x})(x \psi + \frac{\partial \psi}{\partial x}) \, d^3x, \tag{8.7}
\]

where \( \tau \) is some arbitrary real quantity independent of \( x \). Equation (8.7) can be written in the form

\[
I (\tau) = Ax^2 + Bx + C, \tag{8.7a}
\]

where

\[
A = \int \psi^* x^2 \psi \, d^3x = \bar{x}^2 > 0,
\]

\[
B = -\int \left( \frac{\partial \psi^*}{\partial x} x \psi + x \psi^* \frac{\partial \psi}{\partial x} \right) \, d^3x = -\int x \frac{\partial \psi^*}{\partial x} \, d^3x = \int \psi^* \psi \, d^3x = 1,
\]

\[
C = \int \frac{\partial \psi^*}{\partial x} \frac{\partial \psi}{\partial x} \, d^3x = \frac{1}{\hbar^2} \int \psi^* \left( -i \hbar \frac{\partial}{\partial x} \right)^2 \psi \, d^3x = \frac{\bar{p}_x^2}{\hbar^2} > 0.
\]
Since the integrand in (8.7) is essentially a positive quantity

\[ I(a) \geq 0, \quad (8.9) \]

condition (8.9) imposes a certain definite restriction on the coefficients \( A, B \) and \( C \). Indeed, if this relation is satisfied for \( a = a_0 \), corresponding to the minimum of the function \( I(a) \), it will also be satisfied for any arbitrary \( a \). The value of \( a_0 \) can be found from the condition

\[ I'(a_0) = 2Aa_0 - B = 0, \text{ that is, } a_0 = \frac{B}{2A}, \]

and

\[ I''(a) = 2A > 0. \]

Hence the minimum value of \( I(a) \) will be equal to

\[ I_{\text{min}} = I(a_0) = -\frac{B^2}{4A} + C \geq 0. \]

From this it follows that inequality (8.9) will hold for all real values of \( a \), provided the following condition is satisfied:

\[ B^2 \leq 4AC. \quad (8.10) \]

Substituting the values for \( A, B \) and \( C \) from (8.8) and using (8.6), we obtain the relationship between \( (\Delta p_x)^3 \) and \( (\Delta x)^3 \)

\[ (\Delta x)^3 \cdot (\Delta p_x)^3 \geq \frac{\hbar^2}{4}. \quad (8.11) \]

This inequality represents a rigorous formulation of the uncertainty principle.

By using the relation \( p_x x - xp_x = -i\hbar \) [see Eq. (7.7)], we can rewrite (8.11) in the form

\[ (\Delta x)^3 \cdot (\Delta p_x)^3 \geq \frac{1}{4} |p_x x - xp_x|^3. \quad (8.12) \]

Generalizing (8.12), we can say that whenever two operators \( M_1 \) and \( M_2 \) do not commute with each other, they satisfy the uncertainty relation

\[ (\Delta M_1)^3 \cdot (\Delta M_2)^3 \geq \frac{1}{4} |M_1 M_2 - M_2 M_1|^3, \quad (8.13) \]

where

\[ (\Delta M_i)^3 = \int \psi^* (M_i - \hat{M}_i)^3 \psi \, dx, \quad (i = 1, 2). \quad (8.14) \]
As we have already mentioned, the uncertainty principle is a consequence of the wave-particle duality that underlies quantum mechanics and is in no way connected with the experimental limitations. Experiments may only prove the results which follow from the uncertainty principle. The basic meaning of the uncertainty principle consists in the following fact: the probability distributions of variables whose operators do not commute cannot simultaneously take the form of a \( \delta \) function (see Fig. 8.1). Moreover, if the probability distribution of one variable approaches a \( \delta \) function, the probability distribution of the other variable will spread out. In the limit, when, for instance, the probability function for \( x \) (that is, \( \varphi(x) \)) takes the form of a \( \delta \) function \( (\Delta x)^2 = 0 \), the probability function for the momentum \( p_x \) (that is, \( |\varphi(p_x)|^2 \)) becomes such that it is constant for all values of \( p_x \). \( (\Delta p_x)^2 = \infty \).

![Fig. 8.1. The probability distribution function in (a) coordinate space and (b) momentum space: \( (\Delta x)^2 (\Delta p)^2 \)^{1/2} = \hbar/2. If the distribution in coordinate space (a) contracts, the distribution in momentum space (b) spreads.](image)

The necessary condition for simultaneous measurement of two dynamic quantities is the condition of commutativity of their corresponding operators.

**B. POISSON BRACKETS IN CLASSICAL AND QUANTUM THEORY**

The state of a system in classical mechanics is defined by its dynamic variables. The quantities appearing in the canonical, or Hamilton's, equations of motion in classical mechanics depend on the coordinates \( x_i \), momenta \( p_i \), and time \( t \), that is,

\[
f = f(p_i, x_i, t). \tag{8.15}
\]
For example, in a one-dimensional time-independent problem, the Hamiltonian depends only on \(x\) and \(p_x\):

\[
H = \frac{p_x^2}{2m_x} + V(x).
\] (8.16)

With the help of the canonical (Hamilton's) equations of motion we obtain

\[
\dot{x} = \frac{\partial H}{\partial p_x} = \frac{p_x}{m_x} \quad \text{and} \quad \dot{p}_x = -\frac{\partial H}{\partial x} = -\frac{\partial V}{\partial x},
\] (8.17)

or

\[
m_0 \ddot{x} = -\frac{\partial V(x)}{\partial x}.
\]

If there are \(n\) degrees of freedom \((i = 1, 2, \ldots, n)\), Eqs. (8.17) take the form

\[
\dot{x}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial x_i}.
\] (8.17a)

Hence the time rate of change of the quantity \(f\) [see (8.15)] is given by the equation

\[
\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum_i \left( \frac{\partial f}{\partial x_i} \dot{x}_i + \frac{\partial f}{\partial p_i} \dot{p}_i \right).
\]

Using the canonical equations (8.17a), we obtain

\[
\frac{df}{dt} = \frac{\partial f}{\partial t} + [H, f],
\] (8.18)

where the expression

\[
[H, f] = \sum_i \left( \frac{\partial H}{\partial p_i} \frac{\partial f}{\partial x_i} - \frac{\partial H}{\partial x_i} \frac{\partial f}{\partial p_i} \right)
\] (8.19)

is called the classical Poisson bracket.

If \(f\) does not depend explicitly on \(t\), then \(\frac{\partial f}{\partial t} = 0\), and consequently the variation of \(f\) is completely determined by the Poisson bracket:

\[
\frac{df}{dt} = [H, f].
\] (8.20)

If the Poisson bracket vanishes \(([H, f] = 0)\), the quantity \(f\) does not depend on time, or it is conserved.

\(f = \text{const.}\)
For example, if the energy does not depend explicitly on time, then $\frac{\partial H}{\partial t} = 0$. Since obviously $[H, H] = 0$, it follows that Hamilton's function (the energy in this case) is a constant ($H = \text{const}$). Furthermore, substituting the coordinate $x_i$, and then the momentum $p_i$ for $\dot{x}$ into (8.20), we obtain the relations (8.17a), that is, Hamilton's equations of motion.

We shall now generalize the classical Poisson brackets, which can be used to find the time variation of any dynamic variable, to the quantum case.

First of all, we recall that in quantum mechanics physical meaning can be attached only to the average values of operators (position, momentum, and so on). It is the time rate of change of these average values that we must determine. The average value of any operator $\hat{f}$ is given in quantum mechanics by Eq. (7.12), in which the time $t$ occurs as a parameter. From this equation, we can find the total derivative of $\hat{f}$ with respect to time:

$$
\frac{df}{dt} = \frac{d}{dt} \int \psi^* (t) \hat{f} \psi (t) \, d^3x =
\int \psi^* (t) \frac{\partial \hat{f}}{\partial t} \psi (t) \, d^3x + \int \frac{\partial \psi^*(t)}{\partial t} \, \bar{\psi} (t) \, d^3x + \int \psi^* (t) \hat{f} \frac{\partial \psi (t)}{\partial t} \, d^3x.
$$

Substituting for $\frac{\partial \psi^*(t)}{\partial t}$ and $\frac{\partial \psi (t)}{\partial t}$ the expressions $\left( \frac{i}{\hbar} \hat{H} \psi^* \right)$ and $\left( - \frac{i}{\hbar} \hat{H} \psi \right)$, respectively, we can reduce (8.21) to the form

$$
\frac{df}{dt} = \int \psi^* (t) \frac{\partial \hat{f}}{\partial t} \psi (t) \, d^3x +
\frac{i}{\hbar} \int [ \{ \hat{H}, \psi^* (t) \} (\hat{f} \hat{\psi} (t)) - \hat{\psi}^* (t) \hat{f} (\hat{H} \hat{\psi} (t))] \, d^3x,
$$

where

$$
\hat{H} = \frac{\hat{p}^2}{2m_o} + V.
$$

Using the theorem for transferring a derivative [Eq. (7.17)] and keeping in mind that the potential energy is an ordinary function of coordinates, we readily obtain

$$
\int (\hat{H} \hat{\psi}^* (t)) (\hat{\psi} (t)) \, d^3x = \int \psi^* (t) \hat{H} \hat{\psi} (t) \, d^3x.
$$

Consequently, the change of $\hat{f}$ with time will be given by the equation

$$
\frac{df}{dt} = \frac{\partial \hat{f}}{\partial t} + \frac{i}{\hbar} \int \psi^* (t) \{ \hat{H}, \hat{f} \} \, d^3x = \frac{\partial \hat{f}}{\partial t} + \{ \hat{H}, \hat{f} \}.
$$
The expression
\[ \{H, f\} = -\frac{i}{\hbar} (Hf - fH) \quad (8.24) \]
is the generalization of the Poisson bracket (8.19) to the quantum-mechanical case and is called the quantum Poisson bracket.

Obviously, in the case where \( \frac{\delta f}{\delta t} = 0 \) (as a rule an operator \( f \) does not contain the time explicitly), Eq. (8.23) becomes
\[ \frac{d\hat{f}}{dt} = \{\hat{H}, \hat{f}\} = \hat{f}. \quad (8.25) \]
It follows that in this case the time change of \( \hat{f} \) is completely determined by the quantum Poisson bracket. Furthermore, if the operator \( \hat{f} \) commutes with the Hamiltonian operator \( \hat{H} \), the physical quantity \( \hat{f} \) corresponding to this operator is conserved, as can be seen from (8.25).

With the help of (8.25) it is easy to prove that the energy of a particle moving in a time-independent potential field \( V(r) \) is conserved. The expression \( \{\hat{H}, \hat{H}\} = -\frac{i}{\hbar} (\hat{H}\hat{H} - \hat{H}\hat{H}) \) vanishes in this case and therefore from (8.25) we have
\[ \hat{H} = \text{const}. \quad (8.26) \]
On the other hand, \( \hat{H}\hat{\psi}_n = E_n\hat{\psi}_n \) according to the time-independent Schrödinger equation, and therefore, when \( \hat{\psi} = \hat{\psi}(t) \), we have [see Eq. (7.20)]
\[ \hat{H} = \int \hat{\psi}^* \hat{H} \hat{\psi} d^3x = \sum_n |C_n|^2 E_n = E; \]
that is, Eq. (8.26) is nothing but the law of conservation of energy \( (E = \text{const}) \) for a particle moving in a time-independent field of force.

C. EHRENFEST'S THEOREM

We shall now find the quantum analog of the classical equations of motion (8.17). For this purpose we shall use the quantum Poisson brackets. Noting that \( \hat{x} \) and \( \hat{p}_x \) do not contain the time explicitly, let us use Eq. (8.25) to determine \( \dot{x} \) and \( \dot{\hat{p}}_x \), substituting into it either \( f = x \) or \( f = \hat{p}_x \), as the case may be. In the case of \( f = x \), we find
\[ \dot{x} = \{\hat{H}, x\} = \frac{i}{\hbar} (\hat{Hx} - x\hat{H}), \quad (8.27) \]
where
\[ H = \frac{p_x^2}{2m_0} + V(x). \] (8.28)

Since \( x \) and \( V(x) \) commute, Eq. (8.27) can be reduced to the form
\[ \dot{x} = \frac{i}{2m_0 \hbar} (p_x x - x p_x). \] (8.29)

Adding the quantity \((p_x^2 p_x - p_x x p_x)\) to the right-hand side of this equation, we have
\[ \dot{x} = \frac{i}{2m_0 \hbar} (p_x (p_x x - x p_x) + (p_x^2 x - x p_x) p_x). \] (8.30)

Then, using Eq. (7.7), we obtain
\[ \dot{x} = \frac{\vec{p}_x}{m_0}. \] (8.31)

In order to determine the time rate of change of the momentum we must substitute the momentum operator \( p_x \) for the operator \( i \) in (8.25). Then, since \( p_x^2 p_x - p_x^2 p_x = 0 \), we find for \( \dot{p}_x \)
\[ \dot{p}_x = \{H, p_x\} = \frac{i}{\hbar} (Vp_x - p_x V) = -\frac{\partial V}{\partial x}. \] (8.32)

Hence, using (8.31), we obtain
\[ m_0 \ddot{x} = -\left(\frac{\partial V}{\partial x}\right) = F(x). \] (8.33)

Equations (8.31)-(8.33) constitute Ehrenfest's theorem, according to which the fundamental equations of classical mechanics can be generalized to quantum mechanics by replacing the classical variables by the average values of the corresponding operators.

D. TRANSITION FROM QUANTUM TO CLASSICAL EQUATIONS OF MOTION

Let us compare the classical equation of motion
\[ m_0 \ddot{x} = F(x) \] (8.34)

with the corresponding quantum-mechanical form (8.33). As was previously stated, \( x \) is the quantity which corresponds to the classical position coordinate in quantum theory. Accordingly, we
could assume the quantum-mechanical equation to be identical with the classical equation if we had
\[ m_0 \ddot{x} = F(\bar{x}), \quad (8.35) \]

instead of (8.33). This would be equivalent to replacing \( x \) by its average value \( \bar{x} \) in the classical equation relating the force and the position. Ehrenfest's theorem asserts, however, that the equation of motion for the quantum case contains the average value of the actual force, that is, \( \bar{F}(\bar{x}) \). Therefore, in order to make a transition from quantum equations of motion to classical equations, we must first establish the relationship between \( \bar{F}(\bar{x}) \) and \( F(\bar{x}) \).

Let us represent the force operator \( F(x) \) in the form
\[ F(x) = F(\bar{x} + \Delta x), \quad (8.36) \]

where \( \Delta x = x - \bar{x} \), and expand \( F(x) \) in a Taylor series about the point \( x = \bar{x} \). Then we obtain
\[ F(x) = F(\bar{x}) + (\Delta x) F'(\bar{x}) + \frac{(\Delta x)^2}{2} F''(\bar{x}) + \ldots. \quad (8.37) \]

Taking the average of this expression in accordance with Eq. (7.12) and considering that \( (\Delta x) = (x - \bar{x}) = 0 \), we obtain
\[ \bar{F}(\bar{x}) = F(\bar{x}) + \frac{(\Delta x)^2}{2} \bar{F}''(\bar{x}) + \ldots. \quad (8.38) \]

The quantum-mechanical equation of motion (8.33), therefore, takes the form
\[ m_0 \ddot{x} = F(\bar{x}) + \frac{(\Delta x)^2}{2} \bar{F}''(\bar{x}). \quad (8.39) \]

Here the expression \( \frac{(\Delta x)^2}{2} \bar{F}''(\bar{x}) \) is the quantum-mechanical correction to Newton's classical equation. Clearly, the criterion which must be satisfied in transition from quantum equations of motion to classical equations is the inequality
\[ (\Delta x)^2 \ll 2 \left| \frac{F(\bar{x})}{\bar{F}''(\bar{x})} \right|. \quad (8.40) \]

It should be noted, however, that mere satisfaction of this inequality is still not sufficient to allow us to apply all classical concepts to the description of the motion of a particle. Indeed, in quantum mechanics the average value of the kinetic energy \( \overline{T} \) is defined as
\[ \overline{T}(\overline{p}_x) = \frac{(\overline{p}_x)^2}{2m_0}, \quad (8.41) \]
whereas the classical analog of the quantum-mechanical kinetic energy should actually be taken as

\[ T(\hat{p}_x) = \frac{\hat{p}_x^2}{2m_0}. \]  

(8.42)

Let us now express the quantum-mechanical definition of the kinetic energy \( T(p_x) \) in terms of its classical analog \( T(\hat{p}_x) \). For this purpose, we shall use the equation

\[ T(p_x) = T(\hat{p}_x + \Delta p_x) = \frac{(p_x + \Delta p_x)^2}{2m_0}, \]

(8.43)

where \( \Delta p_x = p_x - \hat{p}_x \). Removing the parentheses in (8.43) and considering that after averaging

\[ \Delta p_x = (p_x - \hat{p}_x) = 0, \]

we have

\[ \overline{T(p_x)} = T(\hat{p}_x) + \frac{1}{2m_0} (\Delta p_x)^2. \]  

(8.44)

From this we obtain the condition under which we can make a transition from the quantum-mechanical expression for the kinetic energy \( 8.41 \) to the classical expression

\[ (\Delta p_x)^2 \ll \hat{p}_x^2 = 2m_0 T(\hat{p}_x). \]  

(8.45)

Multiplying (8.45) by (8.40), we obtain the general condition for the validity of the classical approximation in the microscopic world:

\[ (\Delta x)^2 \cdot (\Delta p_x)^2 \ll 4m_0 T(\hat{p}_x) \left| \frac{F(\hat{\phi})}{F''(\hat{\phi})} \right|. \]

(8.46)

If we take into account the uncertainty relation

\[ (\Delta x)^2 \cdot (\Delta p_x)^2 \gg \frac{\hbar^2}{4}, \]

condition (8.46) becomes

\[ m_0 T(\hat{p}_x) \left| \frac{F(\hat{\phi})}{F''(\hat{\phi})} \right| \gg \frac{\hbar^2}{16}. \]

(8.47)

Let us apply this condition to the hydrogen atom, when

\[ V = -\frac{\epsilon^2}{r}, \quad T = -\frac{1}{2} V = \frac{\epsilon^2}{2r}, \]

\[ F = -\frac{\epsilon^2}{r^2}, \quad F'' = -\frac{6\epsilon^2}{r^4}. \]
AVERAGE VALUES OF OPERATORS

Substituting these values into (8.47), we obtain the inequality

\[ r \gg \frac{3}{4} \frac{\hbar^2}{m_e e_0^2}. \]  

(8.48)

Since \( \frac{\hbar^2}{m_e e_0^2} = a_0 \), where \( a_0 \) is the radius of the first Bohr orbit, and \( r = n^2 a_0 \), we obtain instead of (8.48)

\[ n \gg \sqrt{\frac{3}{4}}. \]

(8.49)

and therefore, in the limit of large quantum numbers, the results of quantum theory approach the classical results.

Problem 8.1. Determine the wave function of a freely moving electron in the \( \rho \) representation. Write the normalization condition in the \( \rho \) representation.

Find the average values of the operators for the momentum and energy of a particle. Solve the problem in the one-dimensional case, and then generalize it to the three-dimensional case.

Solution. Let us choose the \( x \) axis along the direction of motion of the electron. The wave function of a free electron in the \( x \) representation, normalized in terms of \( \delta (p' - p_0) \), will have the form [see (4.81)]

\[ \psi (p_0, x) = \frac{1}{\sqrt{2\pi \hbar}} e^{i \frac{p_0}{\hbar} x}. \]

To transform to the \( \rho \) representation, we use Eq. (7.10) in the form

\[ \varphi (p_0, \rho) = \frac{1}{\sqrt{2\pi \hbar}} \int \psi (p_0, x^\prime) e^{-i \frac{\rho}{\hbar} x^\prime} dx^\prime, \]

obtaining

\[ \varphi (p_0, \rho) = \delta (\rho - p_0). \]

The normalization condition has the same form in both \( x \) and \( \rho \) representations:

\[ \int \varphi^* (p_0, x) \psi (p_0, x) dx = \int \varphi^* (p_0, \rho) \varphi (p_0, \rho) d\rho = \delta (p_0 - p_0). \]

The average value of the operators should be calculated from the equations

\[ \bar{M} = \int_{p_0 - \Delta p}^{p_0 + \Delta p} dp \int dp_0 \int dp_0' \varphi^* (p_0, x) M \varphi (p_0, x) dx = \int_{p_0 - \Delta p}^{p_0 + \Delta p} dp_0 \int dp_0' \varphi^* (p_0', p) M \varphi (p_0, p) dp. \]

which gives us

\[ \bar{p} = p_0, \quad \bar{E} = \frac{p_0^2}{2m_0}. \]

1The problems in this chapter refer to Chapters 6 and 7 as well.
In the three-dimensional case, we have
\[ \varphi(p_0, \mathbf{p}) = \delta(p - p_0). \]

**Problem 8.2.** Determine the probability of the various values of the momentum of a particle in the ground state, the particle being in a one-dimensional square well with infinitely high walls. Verify the normalization in the \( p \) representation.

Solution. Taking the value of the wave function from Chapter 4
\[ \psi(x) = \sqrt{\frac{2}{l}} \sin \frac{\pi}{l} x \]

and using Eq. (8.50), we have
\[ \varphi(p) = \frac{1}{\sqrt{\pi \hbar}} \int_0^l \sin \frac{\pi}{l} x e^{-i \frac{p}{\hbar} x} \, dx. \]

Evaluating the integral and squaring its modulus, we obtain the required probability distribution
\[ |\varphi(p)|^2 = \frac{4\pi \hbar^4}{(2\pi \hbar)^2 - p^2} \cos^2 \frac{p}{2\hbar}, \]
which satisfies the normalization condition
\[ \int_{-\infty}^{+\infty} |\varphi(p)|^2 \, dp = 1. \]

In evaluating the last integral we may use the relation
\[ \int_{-\infty}^{+\infty} \cos ap \, dp = \frac{\sin \pi a}{b}, \]
which should then be differentiated with respect to the parameter \( b \).

**Problem 8.3.** Investigate the motion of a charged particle in a constant and uniform electric field \( \mathbf{E} \).

Solution. This problem is solved most simply in the momentum representation. Since, according to Eq. (7.11), the potential energy in momentum space can be represented in the form
\[ V = -e\mathbf{E} \cdot \mathbf{x} = -F \mathbf{p} = -F \hbar \frac{\partial}{\partial p}, \]
the corresponding Schrödinger equation in momentum space becomes
\[ \left( E - \frac{p^2}{2m_0} + iF \hbar \frac{\partial}{\partial p} \right) \varphi(E, p) = 0. \]

The solution of this equation is
\[ \varphi(E, p) = \frac{1}{\sqrt{2\pi \hbar F}} e^{\frac{i}{\hbar F} (Ep - \frac{p^3}{6m_0})}, \]
where, because of the continuity of the spectrum, the normalization coefficient was found from the condition for \( \lambda \)-function normalization:
\[ \int_{-\infty}^{+\infty} \varphi^*(E', p) \varphi(E, p) \, dp = \delta(E' - E). \]
The wave function in the position space can be determined with the help of Eq. (7.9)
\[ \psi(x) = \frac{1}{\sqrt{\pi}} \left( \frac{4m_0^2}{\hbar^2} \right)^{1/4} \Phi(-\xi), \]
where
\[ \Phi(-\xi) = \frac{1}{\sqrt{\pi}} \int_0^\infty \cos \left( \frac{u^3}{3} - u\xi \right) du \]
is the Airy function, which is proportional to the Bessel function of order 1/3 (see Chapter 5), and \( \xi = \frac{1}{2} \left( x + \frac{E}{F} \right) \left( \frac{2m_0F}{\hbar^2} \right)^{1/4}. \) Examining the asymptotic behavior of the Airy function
\[ \Phi(-\xi) \approx \begin{cases} 
\frac{1}{2^{1/4}} \xi^{3/2} e^{-\zeta \xi^{1/3}} & \text{for } \xi < 0, \\
\frac{1}{(\xi)^{1/4}} \sin \left( \frac{2}{3} \xi^{3/2} + \frac{\pi}{4} \right) & \text{for } \xi > 0,
\end{cases} \]
it is readily shown that the region of large negative values of \( x, \) where \( -Fx > E, \) represents a potential barrier, whereas the region where \( E > -Fx \) is quasi-classical, because
\[ \frac{1}{\hbar} S = \frac{1}{\hbar} \int pdx = \frac{1}{\hbar} \int \sqrt{2m_0(E + Fx)} dx + \text{const} = \]
\[ = \frac{2}{3} \xi^{3/2} + \text{const}. \]

Problem 8.4. An electron moves in a constant and uniform magnetic field. Find the time derivative of the average value of the position and momentum of the electron (in other words, generalize the Ehrenfest theorem for the case of motion in a magnetic field).

Solution. According to Eq. (5.9a), the Hamiltonian of an electron in a magnetic field is
\[ H = \frac{1}{2m_0} \left( \frac{p - e}{c} A \right)^2. \]
Choosing the direction of the uniform magnetic field to be along the \( z \) axis \((H_z = 0, H_x = H_y = 0),\) the field can be specified by the vector potential
\[ A_x = A_z = 0, \ A_y = xH_z. \]

In order to determine the time rate of change of the electron's position, let us use the quantum-mechanical equation of motion
\[ \hat{v} = i \hbar [H, \hat{r}]. \]
Substituting \( H, \) we readily find
\[ v = \frac{i}{\hbar} \left( \frac{p - e}{c} A \right) = \frac{P}{m_0}. \] \( \text{Eq. (8.51)} \)
For the time derivative of the \( x \) component of the momentum operator, we obtain
\[ \frac{dP_x}{dt} = \frac{i}{\hbar} \left[ HP_x - P_x H \right] = \frac{e}{m_0c} \left( p_y - \frac{e}{c} A_y \right) H_z = \frac{e}{c} v_y H_z. \]
Similarly, it can be shown that
\[ \frac{d\mathcal{L}}{dt} = -\frac{e}{c} v_x H_z, \quad \frac{d\mathcal{P}_z}{dt} = 0. \]
Combining these equations, we have
\[ \frac{d\mathcal{P}}{dt} = \frac{e}{c} [vH]. \quad (8.52) \]
Equations (8.51) and (8.52) constitute the required result.

Problem 8.5. As we know, the behavior of an electron in a metal \((x < 0)\) can be described with a sufficient degree of accuracy by the following potential energy function (see Chapter 6):
\[ V(x) = \begin{cases} 0, & x < 0, \\ V_0, & x > 0. \end{cases} \]
Determine the coefficient of reflection from the surface of the metal for electrons located inside the metal \((x < 0)\) in the following cases: (a) \(E < V_0\) and (b) \(E > V_0\). Show that, even though in case (a) the electrons do penetrate into the region \((x > 0)\), ultimately they return back into the metal. Construct a graph of the change of the potential energy and of the wave function of the moving electrons.

**Answer.**

a) For \(E < V_0\), \(R = 1\), even though \(\psi(x > 0) \neq 0\).

b) For \(E > V_0\), \(R = \frac{V_0^2}{(\sqrt{E} - V_0 + \sqrt{E})^2} \).

**Hint.** In choosing the solution for \(x > 0\) (outside the metal), only the exponentially decreasing solution should be retained in case (a), and only the solution corresponding to a wave traveling along the \(x\) axis in case (b).
Chapter 9

Elementary Theory of Radiation

A. SPONTANEOUS AND INDUCED TRANSITIONS

According to classical electrodynamics, an accelerated charge is a source of electromagnetic radiation. The amount of energy radiated per unit time is given by the well-known equation

$$W_{\text{cl}} = \frac{2}{3} \frac{e^2}{c^2} (\ddot{r})_{\text{av}}^2,$$

(9.1)

where $\ddot{r} = \ddot{w}$ is the acceleration of the particle.

If the source of radiation is a one-dimensional harmonic oscillator

$$x = a \cos \omega t,$$

(9.2)

the frequency of the emitted radiation is the same as the mechanical frequency of vibration of the oscillator, and its intensity is proportional to $a^2$.

In the case where the motion of a charge is governed by a more complicated periodic function $x = f(t)$ with a period $\tau = \frac{2\pi}{\omega}$, we can expand the function $f(t)$ in a Fourier series:

$$x = \sum_{k} a_k \cos k\omega t,$$

(9.2a)

and treat the radiation as if it were generated by a set of oscillators with frequencies $\omega_k = k\omega$, where $k = 1, 2, 3, \ldots$. Radiation will be emitted both at the fundamental frequency ($k = 1$) and at harmonics $k\omega$ of the fundamental frequency. The intensity corresponding to the $k$th harmonic will be proportional to $a_k^2$.

Thus, according to classical theory, the radiation of a system is completely determined by its mechanical properties. Indeed, the

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1In this chapter the quantum-mechanical averages will be distinguished from time averages by writing the latter with the subscript "av." In accordance with the previous notation, quantum-mechanical averages will be indicated by a bar.
The frequency of the radiation is either equal to or is a multiple of the mechanical frequency of oscillation of the system, and the intensity of the corresponding harmonic is proportional to the square of the amplitude.

In quantum mechanics, the problem of radiation must be approached in a somewhat different manner. According to quantum theory, radiation is emitted only when a particle (or a system) makes a transition from one energy state to a lower energy state (so-called "downward" transition).

The first quantum treatment of the problem of radiation was proposed in 1917 by Einstein. He introduced the coefficients $A$ and $B$ (now called the Einstein coefficients) to characterize the spontaneous transitions and the induced transitions (that is, transitions due to some external effects) of a system from one energy level to another; Einstein also obtained an equation relating these two coefficients.

The basic elements of the quantum theory of radiation are the following. Suppose one of the electrons of an arbitrary atomic system is in the excited state $n$ with an energy $E_n$. Then there is a definite probability $A_{nn'}$ per unit time of a spontaneous transition of this electron into a lower energy state $n'$ with an energy $E_{n'}$. The transition is accompanied by the emission of a photon with an energy $\hbar \omega = E_n - E_{n'}$. If the number of excited atoms is equal to $N_n$, the energy radiated per unit time during spontaneous transitions only can be written as

$$W_{\text{em}}^{\text{spon}} = N_n A_{nn'} \hbar \omega. \tag{9.3}$$

When the atoms are subjected to the influence of external electromagnetic radiation, the latter will cause both upward and downward induced transitions. The upward transitions will, of course, be associated with the absorption of photons.

Adopting the notation introduced by Einstein, we designate the probabilities of an induced transition from level $n$ to $n'$ by $B_{nn'}$ and from level $n'$ to $n$ by $B_{n'n}$. Since the number of induced transitions should be proportional to the spectral energy density $\rho_\omega$ of the external radiation, we obtain the following equations for the energy radiated and absorbed per unit time in induced transitions:

$$W_{\text{em}}^{\text{ind}} = N_n B_{nn'} \rho_\omega \hbar \omega, \tag{9.4}$$
$$W_{\text{abs}}^{\text{ind}} = N_n B_{n'n} \rho_\omega \hbar \omega, \tag{9.5}$$

where $N_n$ is the number of atoms in state $n'$. 
Let us consider the case in which the number of upward and downward transitions is the same (see Fig. 9.1):

\[ N_n A_{nn'} = N_n \rho_{\omega} B_{nn'} = N_{n'} \rho_{\omega} B_{n'n} , \]

that is, when a state of thermodynamic equilibrium exist between the heated atoms and the light radiated by them (black-body radiation), which in turn interacts with the atoms. In this state, the atoms and the radiated light form a closed system.

Since, in this case, the energy distribution of the electrons is given by the Maxwell distribution

\[ N_n = Ce^{-E_n/kT} , \quad N_{n'} = Ce^{-E_{n'}/kT} , \]

we obtain

\[ A_{nn'} e^{-E_{n'}/kT} + \rho_{\omega} B_{nn'} e^{-E_n/kT} = \rho_{\omega} B_{n'n} e^{-E_{n'}/kT} . \]

Dividing by the factor \( e^{-E_{n'}/kT} \) and noting that \( E_n - E_{n'} = h\omega \), we obtain

\[ \rho_{\omega} = \frac{A_{nn'}}{B_{nn'} e^{h\omega/kT} - 1} . \]

Since the spectral energy distribution of black-body radiation is completely independent of the specific structure of the atoms or molecules involved, Eq. (9.8) is essentially the same as Planck's formula [see (1.42)]

\[ \rho_{\omega} = \frac{h\omega^3}{\pi^2 c^3} \frac{1}{e^{h\omega/kT} - 1} . \]

Comparing (9.8) with (9.9) we find

\[ B_{nn'} = B_{n'n} = \frac{\pi^2 c^3}{h\omega^3} A_{nn'} . \]

It is seen from Eq. (9.10) that the probability coefficients of upward and downward induced transitions are equal to each other and proportional to the coefficient of spontaneous transition \( A_{nn'} \). Therefore, to describe the radiation of atoms or molecules, it is sufficient to determine only one of these coefficients.

**B. CALCULATION OF PROBABILITIES OF SPONTANEOUS AND INDUCED TRANSITIONS**

In quantum mechanics induced transitions are explained in terms of an interaction between the electrons of an atom and external electromagnetic radiation. The problem of determining the causes of spontaneous transitions was left unexplained by the Schrödinger theory.
The answer was obtained only after the development of a theory of radiation in which quantization of the electromagnetic field (second quantization) was used. The general features of the theory are outlined below.

Electrons interact not only with real photons, but also with virtual photons (photons which are in an unobservable state) or, as they are called, vacuum fluctuations of the electromagnetic field (for further details on vacuum fluctuations, see Chapter 22). This interaction causes spontaneous transitions. The classical analog of the interaction between the electrons and the field of virtual photons is the effect of Planck’s radiation damping on a moving electron

\[ F_{\text{rad}} = \frac{2}{3} \frac{e^2}{c^3} \mathbf{\mathbf{x}}, \]

which represents the self-interaction of the electron with its own electromagnetic field. Under certain conditions this electromagnetic field may detach itself from the electron in the form of electromagnetic radiation. In the language of quantum electrodynamics this amounts to a transition of photons from a virtual state into a real state.

The exact expression for the coefficients \( A \) and \( B \) can be found on the basis of quantum electrodynamics and, therefore, problems of radiation can be completely solved.\(^2\)

In the present discussion we shall obtain coefficient \( A \) by means of an appropriate generalization of the results of classical radiation theory to the quantum case. It should be emphasized that this generalization leads to the same results as the rigorous method of second quantization.

In our derivation we shall use the correspondence principle to generalize the classical expression for the radiated energy [Eq. (9.1)] to the quantum case. First, we replace the classical variable \( r \) by the quantum-mechanical quantity

\[ \tilde{r} = \int \psi^* (l) r \psi (l) \, d^3x. \] (9.11)

In addition, we use an expression for the radiated energy which is consistent with the quantum theory:

\[ W_{\text{quant}} = g_n g_n' \hbar \omega A_{nn'}, \] (9.12)

where the coefficients \( g_n \) and \( g_n' \) characterize the occupancy of states \( n \) and \( n' \) by electrons, since according to the Pauli exclusion

\(^2\text{See also Chapter 29, where the coefficient } A \text{ is obtained by the methods of quantum electrodynamics.}\)
principle it is impossible for two electrons to be in the same quantum state (for more on the Pauli exclusion principle, see Chapter 24).

Combining Eqs. (9.12) and (9.1) and substituting (9.11) we obtain

\[ g_n g_n' \hbar \omega A_{nn'} = \frac{2}{3} \alpha^2 \left( \frac{\omega^3}{c^3} \right)^\frac{3}{2} (r)_{av} \]  

(9.13)

Let us note that Eq. (9.13) contains two averages. One is the quantum-mechanical average, denoted by a bar, and the other is the time average, denoted by the subscript "av."

We shall now assume that the electron has only two possible states with energies \( E_n \) and \( E_{n'} \). Then the wave function can be written as

\[ \psi(t) = C_n e^{-i \frac{E_n}{\hbar} t} \psi_n + C_{n'} e^{-i \frac{E_{n'}}{\hbar} t} \psi_{n'} . \]  

(9.14)

The average (over the quantum-mechanical states) value of the radius vector is

\[ \bar{r} = |C_n|^2 r_{nn} + |C_{n'}|^2 r_{n'n'} + C_n C_{n'} e^{i\omega t} r_{nn'} + C_n C_{n'} e^{-i\omega t} r_{n'n} , \]  

(9.15)

where

\[ \omega = \omega_{nn'} = \frac{E_n - E_{n'}}{\hbar} . \]  

(9.15a)

The matrix elements

\[ r_{n'n} = \int \psi^*_n r \psi_n d^3x \]  

(9.16)

form a certain infinite matrix

\[ (r) = \left( \begin{array}{cccc} r_{00} & r_{01} & r_{02} & \ldots \\ r_{10} & r_{11} & r_{12} & \ldots \\ r_{20} & r_{21} & r_{22} & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{array} \right) . \]  

(9.17)

From (9.16), it follows that this matrix changes into its complex conjugate when the rows are replaced by columns, and columns by rows

\[ r_{nn'}^* = r_{n'n} . \]

Matrices satisfying this condition are called Hermitian or self-adjoint matrices. Let us also emphasize that the matrix elements (9.16) are independent of time, and therefore substitution of (9.15) into (9.13) yields

\[ g_n g_n' \hbar \omega A_{nn'} = \frac{4 \alpha^2}{3c^2} \omega^4 |C_n|^2 |C_{n'}|^2 |r_{n'n}|^2 . \]  

(9.18)
Here we have used the fact that the time average of a periodic function is zero, since

\[(e^{\pm 2i\omega t})_{av} = \frac{1}{T} \int_0^T e^{\pm 2i\omega t} dt = 0.\]

For further analysis of Eq. (9.18), we must introduce an additional assumption, which can be rigorously justified only on the basis of quantum electrodynamics. As we already know, quantum mechanics deals with stationary processes and, therefore, there is no ambiguity in interpreting the quantity \(|C_n|^2 = \text{const}\) as the probability of finding an electron in the state \(n\). When the emission of radiation is present, the coefficients \(C_n\) change discontinuously and their physical meaning cannot be simply explained within the usual formalism of quantum mechanics. We shall, therefore, base our conclusions on simple physical considerations, which are rigorously proved only in quantum mechanics.

Let us substitute the initial values for the coefficients \(C_n\) into Eq. (9.18), bearing in mind that the Pauli exclusion principle allows transition only in the case when the quantum state \(n\) is initially occupied, while the quantum state \(n'\) is empty. Then setting

\[g_{nn'} = |C_n|^2|C_{n'}|^2 = |C_n|^2(1 - |C_{n'}|^2),\]  

we find that for \(C_n = 1\) and \(C_{n'} = 0\) the product \(g_{nn'} = 1\). Hence

\[A_{nn'} = \frac{4}{3} \frac{e^2 \omega^2}{\hbar c^3} |r_{n'n'}|^3,\]  

\[B_{nn'} = B_{n'n} = \frac{4\pi e^2}{3\hbar^2} |r_{n'n'}|^3,\]  

\[W_{nn'} = \hbar \omega A_{nn'} = \frac{4}{3} \frac{e^2 \omega^2}{c^3} |r_{n'n'}|^3.\]

In these equations

\[|r_{n'n'}|^2 = |x_{n'n'}|^2 + |y_{n'n'}|^2 + |z_{n'n'}|^2,\]  

where

\[x_{n'n'} = \int \varphi_{n'}^* x \varphi_n d^3x,\]

and so forth.

Thus, the energy eigenvalues can be used to find the frequency of the radiation and the eigenfunctions to find its intensity. Thus, all basic classical radiation properties can be completely generalized to the quantum case by means of the Schrödinger equation.

From the last equation above it is evident that the intensity of radiation will be different from zero only for those transitions for
which at least one of the matrix elements \( x_{nn'}, y_{nn'}, \) and \( z_{nn'} \) is non-zero. These transitions are called in quantum mechanics the \textit{allowed transitions}.

It should be noted that in very many quantum-mechanical problems it is sufficient to calculate the matrix elements alone and thus to set up \textit{selection rules}, that is, to find the changes in quantum numbers that correspond to allowed transitions. From a knowledge of the selection rules, one can answer the question of possible frequencies of radiation. In the language of classical electrodynamics, the selection rules correspond to a specification of the harmonics at which radiation can be emitted by a given system. If the matrix elements for a given change (difference) in quantum numbers are equal to zero, there will be no radiation at the corresponding frequencies, and these transitions are said to be \textit{forbidden}.

Here, in speaking of \textit{forbidden transitions}, we are restricting the use of this term to electric dipole transitions. By electric dipole transitions we simply mean transitions whose probability depends on matrix elements

\[
\mathbf{r}_{nn'} = \int \psi^*_n \psi_{n'} d^3x.
\]

In addition to the dipole transitions, there are also cases of quadrupole transitions, multipole transitions of higher orders, and magnetic dipole transitions. The intensity of these transitions turns out to be much smaller than that of the allowed dipole transitions. As an example, if the intensity of an electric dipole transition is of the order

\[
W_{\text{dipole}} = \frac{2}{3} \frac{\hat{p}^2}{c^2} \sim \frac{\omega^4}{c^2} (ea)^3,
\]

where \( a \) is the linear dimension of the atom, then the intensity of electric quadrupole radiation is of the order

\[
W_{\text{quad}} \sim W_{\text{dipole}} \cdot \left(\frac{a}{\lambda}\right)^8.
\]

For an atom \( a \sim 10^{-8} \text{ cm} \) and \( \lambda \sim 10^{-8} \text{ cm} \) and, therefore, the intensity of dipole radiation is 10 times greater than that of quadrupole radiation. Nevertheless, quadrupole radiation plays a very important part in a number of phenomena. Indeed, if the electric dipole transition is forbidden, it is still possible that a weak quadrupole radiation will be emitted, which can be detected with a very sensitive spectroscope. We note that no dipole radiation occurs in a system consisting of particles having the same charge to mass ratio. The

\footnote{This subject is treated more fully for the case of a harmonic oscillator in Chapter 10 [see Problem (10.4)].}
The electric dipole moment of such a system is proportional to the coordinate of the center of mass \( r_{\text{c.m.}} \), \( \mathbf{p} = e(r_1 + r_2) = 2er_{\text{c.m.}} \), and therefore the derivative of the dipole moment with respect to time vanishes. This is the situation that should hold for gravitational radiation, since the gravitational charge, or rather the gravitational mass, is proportional to the inert mass \( m_0 \). Therefore, if gravitational radiation does exist at all, it can only be of quadrupole character. Quadrupole radiation is also of importance in nuclear physics since the charged particles of the nucleus (protons) have the same charge and mass.\(^4\)

Problem 9.1. Find the probability of quadrupole radiation in the quantum case as a generalization of the classical formula by applying the corresponding principle.

Solution. In the classical case the intensity of quadrupole radiation is given by the equation

\[
W = \frac{1}{180c^6} (D_{ab})^2,
\]

(9.25)

where the quadrupole moment is

\[
D_{ab} = e (3x_ax_b - r^2_{ab}) \quad (a,b = 1,2,3).
\]

To generalize (9.25) to the quantum case, it is necessary to consider that, in quantum theory, radiation occurs as a result of a transition of the system from one quantum state \( n \) to another, \( n' \). Following the procedure similar to the derivation of Eqs. (9.13)-(9.18), we first replace the classical expression for the quadrupole moment \( D_{ab} \) by the matrix element

\[
(D_{n'n})_{ab} = \int \psi^*_{n'} D_{ab} \psi_{n'} d^3x.
\]

Next, using Eq. (9.3), which relates the intensity of radiation \( W_{n'n} \) to the emission probability \( \Lambda_{n'n} \), we obtain

\[
\Lambda_{n'n} = \frac{\omega_{n'n}}{90c^6\hbar^2} (D_{n'n})^2_{ab} (D_{n'n})_{ab},
\]

(9.26)

where the frequency of radiation \( \omega \) is given by Eq. (9.15a).

Problem 9.2. Find the selection rules for dipole and quadrupole radiation for a particle in an infinitely deep potential well.

Answer. For dipole radiation \( \Delta n \) must be an odd number, and for quadrupole radiation \( \Delta n \) is an even number.

Hint. Using the wave function (4.32), it can be shown that the average value of the \( x \) coordinate is

\[
\bar{x} = \int \psi^*_{n} x \psi_{n} dx = \frac{f}{2}.
\]

Therefore, the matrix elements corresponding to dipole \( (j = 1) \) and quadrupole \( (j = 2) \) radiation should be calculated from the equation

\[
\Lambda_{n'n} = \int \psi^*_{n'} (x - \bar{x})^2 \psi_{n} dx.
\]

The solution of this equation has the form

\[ x = a \cos \omega t, \]  

(10.3)

where \( \omega = \frac{2\pi}{\tau} = \sqrt{\frac{k}{m_0}} \) is the angular frequency and \( a \) is the amplitude of oscillation. From Eq. (10.3), it follows, in particular, that the acceleration

\[ \omega = \ddot{x} = -a \omega^2 \cos \omega t \]  

(10.4)

differs from zero and, consequently, that the oscillation of a charged particle will be accompanied by radiation, the intensity of which (that is, the radiant energy) is given by the following equation in accordance with Eqs. (10.4) and (2.2):

\[ W_{\text{cl}} = \frac{2e^2}{3c^3} (\mathcal{V})_{\text{av}} = \frac{e^2 a^2 \omega^4}{3c^3}. \]  

(10.5)

In deriving (10.5), we calculated the average value of \( \cos^2 \omega t \) from the equation

\[ \frac{1}{\tau} \int_{0}^{\tau} \cos^2 \omega t \, dt = \frac{1}{2}. \]  

(10.6)

We shall now express the intensity of radiation \( W_{\text{cl}} \) in terms of the total energy \( E = T + V \) of the harmonic oscillator. From the well-known equations for the potential energy

\[ V(x) = -\int_{0}^{x} F(x) \, dx = \frac{m_0 \omega^2 x^2}{2} = \frac{m_0 \omega^2 a^2}{2} \cos^2 \omega t \]  

(10.7)

and kinetic energy

\[ T = \frac{m_0 x^2}{2} = \frac{m_0 \omega^2 a^2}{2} \sin^2 \omega t \]  

(10.8)

of a harmonic oscillator, we find

\[ E = V(x) + T = \frac{m_0 \omega^2 a^2}{2} = \text{const}. \]  

(10.9)

With this equation, we can eliminate the quantity \( a^2 \) from (10.5), obtaining

\[ W_{\text{cl}} = \frac{2e^2 \omega^4 E}{3m_0 c^4}. \]  

(10.10)

Thus, on the basis of classical theory one can determine both the intensity and frequency of the radiation; it is also found that this
frequency is the same as the frequency of mechanical vibrations of the harmonic oscillator. The energy of the harmonic oscillator, according to the classical theory, can have any value in a continuous range from zero to infinity.

Several new features were introduced in the problem of the harmonic oscillator by the Bohr quantum theory. For example, according to Bohr’s theory, the energy levels had to be discrete and could be found from the quantization rule

\[ p_x dx = 2\pi \hbar n, \quad (10.11) \]

where

\[ p_x = \frac{\partial T}{\partial x} = m \ddot{x}. \quad (10.12) \]

Let us substitute \( p_x dx = m \ddot{x} \frac{dx}{dt} dt = m \omega^2 a^2 \sin^2 \omega t dt \) into Eq. (10.11). Then, taking into account Eq. (10.9) and integrating over a complete period, we find

\[ E_n = n \hbar \omega, \quad (10.13) \]

where the quantum number \( n = 0, 1, 2, 3, \ldots \).

We showed above that, according to Bohr’s theory, the energy of a harmonic oscillator can take only discrete values, and radiation will be emitted only when the oscillator makes a transition from one energy level to another.

The discovery of a discrete spectrum of energy levels of a harmonic oscillator played an important part in the theory of black-body radiation. Planck’s law was first obtained under the assumption that the harmonic oscillator could radiate and absorb light only in the form of discrete quanta of energy \( \hbar \omega \).

**B. EIGENFUNCTIONS AND EIGENVALUES OF THE ENERGY**

In order to determine the behavior of the wave function in the harmonic oscillator problem, let us first give a graphical representation (Fig. 10.1) of the dependence of the potential energy \( V \) on \( x \)

\[ V = \frac{m \omega^2 x^2}{2}. \]

From the graph, it is seen that inside the potential well, where the total energy \( E \) of the harmonic oscillator is greater than \( V (E > V) \), the solutions for \( \psi \) will take the form of harmonic functions. Inside the potential barrier \( (E < V) \), the solutions will contain two parts,
one exponentially decreasing and the other exponentially increasing (see Fig. 10.1). It is clear that the solution of the problem reduces to finding the conditions under which there is no exponentially increasing solution. Just as in the case of a rectangular potential well with infinitely high walls (Chapter 4), such levels exist only at certain discrete values of the energy, which we must determine.

Fig. 10.1. Wave function of the harmonic oscillator for an arbitrary value of the energy.

Since the potential energy $V$ of a harmonic oscillator depends only on the $x$ coordinate, the Schrödinger equation can be written as

$$\frac{d^2\psi}{dx^2} + \frac{2m_0}{\hbar^2} \left( E - \frac{m_0 \omega^2 x^2}{2} \right) \psi = 0.$$  (10.14)

Setting

$$x = \frac{2m_0 E}{\hbar^2}, \quad \beta = \frac{1}{x_o^2} = m_0 \omega^2 \hbar, \quad \frac{a}{\beta} = \lambda = \frac{2E}{\hbar \omega},$$

and introducing a new variable

$$\xi = x \sqrt{\beta} = \frac{x}{x_o}$$  (10.15)

we obtain

$$\varphi'' + (\lambda - \xi^2) \varphi = 0,$$  (10.16)

where

$$\varphi'' = \frac{d^2 \varphi}{d\xi^2}.$$  (10.17)

First, let us find the asymptotic behavior of the wave function at $\xi = \infty$, that is, when the constant $\lambda$ is negligible in comparison with $\xi$. Then

$$\varphi'' \xi \varphi'_{\infty} = 0.$$  (10.18)
We shall seek a solution of this equation in the form

\[ \psi_\infty = e^{it^2}. \]  \hfill (10.19)

Since

\[ \psi_\infty'' = (4\varepsilon \xi^2 + 2\varepsilon) e^{it^2} \approx 4\varepsilon \xi^2 e^{it^2}, \]

we find

\[ \varepsilon = \pm \frac{1}{2} \] \hfill (10.20)

and, consequently,

\[ \psi_\infty = C_1 e^{-\varepsilon \xi^2} + C_2 e^{\varepsilon \xi^2}. \] \hfill (10.21)

Since the wave function must remain finite at \( \xi = \pm \infty \), coefficient \( C_1 \) must be set equal to zero. Coefficient \( C_2 \) can be taken to be equal to unity, since the wave function has not yet been normalized. Thus, the asymptotic behavior of the wave function \( \psi \) is described by the function

\[ \psi_\infty = e^{-\xi^2}. \] \hfill (10.21a)

We shall seek a solution of the wave function in the general form

\[ \psi = \psi_\infty \mu = e^{-\varepsilon \xi^2} \mu, \] \hfill (10.22)

which already takes in account the behavior at infinity. Substituting (10.22) into (10.16) and considering that

\[ (e^{-\varepsilon \xi^2} \mu)'' = [\mu'' - 2i\mu' + (\varepsilon^2 - 1) \mu] e^{-\varepsilon \xi^2}, \]

we obtain the following equations for \( \mu \):

\[ \mu'' - 2i\mu' + (\lambda - 1) \mu = 0. \] \hfill (10.23)

Let us look for a solution of this equation in the form of a series

\[ \mu = \sum_{k=0} \beta_k \xi^k. \] \hfill (10.24)

Substituting this expression for \( \mu \) into Eq. (10.23) and collecting terms with the same power of \( \xi \), we find

\[ \sum_{k=0} \xi^k [(k+2)(k+1)\beta_{k+2} - \beta_k (2k+1-\lambda)] = 0. \]

Equating the coefficients of \( \xi^k \) to zero, we obtain a recursion formula for the coefficients \( \beta_k \)

\[ \beta_{k+2} = \beta_k \frac{(2k+1-\lambda)}{(k+2)(k+1)}. \] \hfill (10.25)

This formula relates the coefficients \( \beta_k \) to \( \beta_{k+2} \), and, therefore, the series (10.24) will consist of even powers (if the minimum subscript \( k \) is even) or odd powers (if the minimum subscript \( k \) is odd).
If the series (10.24) does not terminate at a certain maximum power, then beginning with \( k > \frac{n}{2} \), every term is positive and, consequently, the series diverges for large values of \( \xi \). This leads to the second asymptotic solution \( \psi_{\text{asym}} \sim e^{i/\xi^2} \) at \( \xi \rightarrow -\infty \), which we disregarded earlier because it diverges.\(^2\) Therefore, in order for the boundary conditions to be satisfied (\( \psi = 0 \) at \( \xi \rightarrow -\infty \)), we must terminate the series (10.24) at a certain \( k_{\text{max}} = n \). We thus require

\[
\begin{align*}
0 &< b_n, b_{n+1} = 0. & (10.26)
\end{align*}
\]

From (10.26) and (10.25), we find

\[
\lambda = 2n + 1, \\
E_n = \hbar \omega (n + \frac{1}{2})
\]

and, consequently,

\[
E_n = \hbar \omega (n + \frac{1}{2})
\]

where \( n \) can assume any positive integral value, including zero. These are the only energy values for which the wave function vanishes at infinity.

Comparing this expression with the one obtained from the Bohr theory [see (10.13)], we note the appearance of a term called the zero-point energy

\[
E_0 = \frac{1}{2} \hbar \omega.
\]

Later, we shall show that the existence of the zero-point energy is related to the uncertainty principle and thus to the wave properties of particles. The zero-point energy does not affect the frequency of the radiation, however, since it cancels out in the expression for the frequency \( \omega_{nm'} = \frac{E_n - E_{n'}}{\hbar} \).

Let us now find the wave function of the harmonic oscillator. The recursion formula (10.25) for the coefficients \( b_k \) when \( \lambda = 2n + 1 \) takes the form

\[
\begin{align*}
0 \neq b_k, b_{k+1} = 0. \\
0 \neq b_k, b_{k+1} = 0. \\
E_n = \hbar \omega (n + \frac{1}{2})
\end{align*}
\]

\[
E_n = \hbar \omega (n + \frac{1}{2})
\]

This follows from the fact that at large \( k \) the ratio of the coefficients \( b_k/b_{k+2} \rightarrow k \geq 2 \) is the same as for the series expansion of the function \( e^{\xi^2} \)

\[
\sum_{k=0, 2, 4} \frac{1}{k} \xi^k.
\]

Therefore,

\[
\psi_{\text{asym}} \sim e^{\xi^2} \psi_0 + e^{\xi^2} \psi_1 + \cdots.
\]
where \( k \leq n \). Setting the coefficient of the highest power \( k_{\text{max}} := n \) equal to

\[
b_n = 2^n,
\]

we obtain

\[
b_{n-k} = -2^{n-k} \frac{n(n-1)}{k!},
\]

\[
b_{n-4} = 2^{n-4} \frac{n(n-1)(n-2)(n-3)}{2!}
\]

and so forth. \( \text{(10.31)} \)

The power series with a finite number of terms obtained for the function \( u \) is called the Hermite polynomial

\[
u = H_n(z) = (2z)^n - \frac{n(n-1)}{1!} (2z)^{n-2} + \ldots + \begin{cases} b_k^2 & \text{for odd } n \\ b_k & \text{for even } n \end{cases}
\]

\( \text{(10.32)} \)

In particular,

\[
H_0(z) = 1, \quad H_1(z) = 2z, \quad H_2(z) = 4z^2 - 2, \\
H_3(z) = 8z^3 - 12z.
\]

\( \text{(10.33)} \)

The Hermite polynomials \( H_n(z) \) can be written in closed form

\[
H_n(z) = (-1)^n e^{z^2} \frac{d^n e^{-z^2}}{dz^n}.
\]

\( \text{(10.34)} \)

---

3. This coefficient can always be chosen arbitrarily, since the normalization factor of the wave function \( \psi \) is still undetermined.

4. To show this, we introduce the function \( v = e^{-x^2} \), which satisfies the equation

\[v' + 2xv = 0.
\]

Differentiating this equation \( n + 1 \) times, and using the Leibnitz formula

\[(yz)^{(n)} = y^{(n)}z + ny^{(n-1)}z' + \frac{n(n-1)}{2!} y^{(n-2)}z^2 + \ldots ,\]

we obtain

\[v^{(n+2)} + 2xv^{(n+1)} + 2(n+1)v^{(n)} = 0.\]

Making the substitution

\[v^{(n)} = e^{-x^2} w,
\]

we find that the function \( w \) satisfies Eq. (10.35), and thus it is proportional to the Hermite polynomial

\[w = e^{x^2} \frac{d^n e^{-x^2}}{dx^n} = A_n H_n.
\]

The proportionality factor \( A_n \) can be found by equating the coefficients of \( x^{2n} \). As a result, it is found that \( A_n = (-1)^n \), from which we obtain Eq. (10.34).
From (10.32) it is clear that \( H_n(\xi) \) satisfies Eq. (10.23) provided
\[
\lambda = 2n - 1
\]
\[
H_n' - 2\xi H_n' + 2n H_n = 0.
\]
(10.35)

According to (10.22) and (10.32), the solution of the Schrödinger equation for a harmonic oscillator is
\[
\psi_n = C_n e^{-\frac{1}{2}\xi^2} H_n(\xi),
\]
(10.36)
where \( \xi \) is related to the coordinate \( x \) by Eq. (10.15). The coefficient \( C_n \) can be determined from the normalization condition
\[
\int_{-\infty}^{\infty} \psi_n^* \psi_n d\xi = x_0 C_n^2 \int_{-\infty}^{\infty} e^{-\xi^2} H_n(\xi) H_n(\xi) d\xi = 1.
\]
(10.37)

Substituting the closed form (10.34) for one of the polynomials \( H_n(\xi) \), we obtain
\[
(-1)^n x_0 C_n \int_{-\infty}^{\infty} H_n(\xi) \frac{d^n e^{-\xi^2}}{d\xi^n} d\xi = 1.
\]
(10.38)

Using the rule for transferring the derivative of one function to another [see (7.17)] (that is, we integrate by parts \( n \) times), we obtain
\[
x_0 C_n \int_{-\infty}^{\infty} e^{-\xi^2} \frac{d^n H_n(\xi)}{d\xi^n} d\xi = 1.
\]
(10.39)

Noting that from (10.32)
\[
\frac{d^n}{d\xi^n} H_n(\xi) = 2^n n!
\]
(10.40)
and
\[
\int_{-\infty}^{\infty} e^{-\xi^2} d\xi = \sqrt{\pi},
\]
(10.41)
we find
\[
C_n = \frac{1}{\sqrt{2^n n!}} \frac{1}{\sqrt{\pi} x_0},
\]
that is,
\[
\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \frac{1}{\sqrt{\pi} x_0} e^{-\frac{1}{2} \left( \frac{x}{x_0} \right)^2} H_n \left( \frac{x}{x_0} \right).
\]
(10.42)
In a similar manner, we can easily prove the orthogonality condition for the wave functions. To do this, it is enough to represent one of the Hermite polynomials, specifically, the one with larger \( n \), in closed form (10.34). The orthogonality condition also follows from the general investigation of the Schrödinger equation; it can be proved that the eigenfunctions corresponding to the different eigenvalues are orthogonal.

![Fig. 10.2. The energy eigenvalues and the behavior of the corresponding eigenfunctions of the harmonic oscillator for small quantum numbers \( n = 0, 1, 2 \). For comparison, the classical probability distribution functions \( \rho_n \) are indicated by the dotted lines.](image)

In the case of a harmonic oscillator, the orthonormality condition is

\[
\int_{-\infty}^{+\infty} \psi_n^* \psi_n \, dx = \delta_{nn'}.
\] (10.43)

For small quantum numbers \( n = 0, 1, 2, \ldots \), when

\[
E_0 = \frac{1}{2} \hbar \omega, \quad \psi_0 = C e^{-\frac{1}{2} x^2},
\]
\[
E_1 = \frac{3}{2} \hbar \omega, \quad \psi_1 = C_1 2^{\frac{1}{2}} e^{-\frac{1}{2} x^2},
\] (10.44)
\[
E_2 = \frac{5}{2} \hbar \omega, \quad \psi_2 = C_2 (4 \frac{1}{2}^2 - 2) e^{-\frac{1}{2} x^2},
\]
the probability distribution functions $|\psi_n|^2$ (see Fig. 10.2) differ considerably from the corresponding classical probability functions. In the classical case the probability of a particle being at a certain point is proportional to the amount of time the particle spends there, and, consequently, is inversely proportional to the particle velocity; therefore, the classical probability is proportional to $\frac{1}{(a^2 - x^2)^{1/2}}$, where $a$ is the maximum displacement of a classical oscillator from the equilibrium position. As we would expect, it is only for large quantum numbers that there is a relatively close agreement, on the average, between the quantum and classical probabilities (see Fig. 10.3).

C. ZERO-POINT ENERGY OF THE HARMONIC OSCILLATOR AND THE UNCERTAINTY PRINCIPLE

We have seen that in quantum mechanics the minimum energy of the harmonic oscillator is given by Eq. (10.29) and cannot go to zero, whereas in the classical theory or the Bohr theory, the minimum energy is equal to zero.

We shall now show that the existence of the zero-point energy (10.29) in the Schrödinger theory is, as mentioned above, very closely related to the uncertainty principle (8.11). For the case of a harmonic oscillator the uncertainty principle becomes

$$\langle x^2 \rangle \langle \rho^2 \rangle \geqslant \frac{\hbar^2}{4}. \quad (10.45)$$

This can be easily shown on the basis of the following simple qualitative considerations. The probability of finding a particle at a particular point can be roughly characterized by the absolute value of the reciprocal of its velocity, since the time a particle spends in a region will be greater in regions where the velocity is smaller than in regions where it is greater. Consequently, the probability of finding a particle in a region with larger velocities will be smaller than that for a region with smaller velocities. In the case of a harmonic oscillator, we have from Eq. (10.3) $x/a = \cos \omega t$ and $x/\omega a = -\sin \omega t$. Taking the square of both equations and adding them, we get

$$|x| \sim \left( a^2 - x^2 \right)^{1/2},$$

and therefore,

$$\rho \sim \frac{1}{|x|} \sim \left( a^2 - x^2 \right)^{-1/2}.$$
Here we have replaced \((\Delta x)^2\) by \(\bar{x}^2\) and \((\Delta p)^2\) by \(\bar{p}^2\). This is justified by the fact that the wave functions are real and are either even or odd. Indeed, since the expression \(\phi^* x \phi = x \phi^2\) is odd, we have

\[
\bar{x} = \int \phi^* x \phi \, dx = 0.
\]

Hence

\[
(\Delta x)^2 = \bar{x}^2 - x^2 = \bar{x}^2.
\]

Similarly, using the boundary conditions at infinity, we find

\[
\bar{p} = \frac{\hbar}{i} \int \phi \frac{d\phi}{dx} \, dx = \frac{\hbar}{2i} \phi^2 \bigg|_{-\infty}^{+\infty} = 0,
\]

that is,

\[
(\Delta p)^2 = \bar{p}^2 - (\bar{p})^2 = \bar{p}^2.
\]

Substituting the value of \(\bar{p}^2\) from (10.45) into the equation for the total energy

\[
E = \bar{H} = \frac{\bar{p}^2}{2m_0} + \frac{m_0 \omega^2 \bar{x}^2}{2},
\]

we obtain

\[
E \geq \frac{\hbar^2}{8m_0 (\bar{x}^2)} + \frac{m_0 \omega^2 (\bar{x}^2)}{2}.
\]  

(10.47)

From this it is seen that the energy \(E\) cannot vanish at any value of \((\bar{x}^2)\). Indeed, although the second term vanishes for \((\bar{x}^2) = 0\), the first term becomes infinite. Conversely, when \((\bar{x}^2) = \infty\), the first term vanishes and the second becomes infinite.

Thus, the fact that \(E_{\text{min}}\) differs from zero is directly connected with the uncertainty relation (10.45) or, in other words, with the fact that it is impossible to calculate exactly the position and momentum simultaneously.

Let us find that value of \((\bar{x}^2)\) at which Eq. (10.47) has a minimum. Setting the derivative of this function with respect to \((\bar{x}^2)\) equal to zero, we obtain

\[
\frac{m_0 \omega^2}{2} - \frac{\hbar^2}{8m_0 (\bar{x}^2)} = 0,
\]

or

\[
(\bar{x}^2) = \frac{\hbar}{2m_0 \omega} = \frac{1}{2} \chi_0^2.
\]
Substituting this into (10.47), we have

\[ E \geq \frac{\hbar \omega}{4} + \frac{\hbar \omega}{4} = \frac{\hbar \omega}{2}. \]  

(10.48)

Hence, \( E_{\text{min}} = \frac{\hbar \omega}{2} \), which is exactly the same as the value for \( E_0 \) found from the wave theory [see (10.29)].

The existence of a finite zero-point energy of the harmonic oscillator is one of the most characteristic manifestations of the wave properties of particles. Thus, the experimental verification of the zero-point vibrations was of great significance for quantum mechanics. The zero-point energy \( E_0 \) was first observed experimentally in the scattering of x-rays by crystals at low temperatures. If there were no lattice vibrations at low temperatures (\( E_0 = 0 \)), as predicted, for example, by the Bohr theory, there would be no interaction between the x-rays and the crystal lattice, and consequently no scattering would occur. If, on the other hand, the minimum energy were different from zero \( (E_0 \neq 0) \) for \( T \to 0 \), the scattering cross section at low temperatures should approach a finite limit. Experiments have confirmed that the second situation corresponds to the true state of affairs and, therefore, the conclusions of the Schrödinger wave theory are justified.

D. SELECTION RULES. INTENSITY OF RADIATION

Let us consider the problem of radiation from the harmonic oscillator on the basis of wave mechanics. For this purpose, as was indicated in Chapter 9 [see (9.22)], we must calculate the matrix elements

\[ x_{n',n} = \int \psi_{n'}^* \psi_n dx, \]  

(10.49)

where \( \psi_n \) is given by Eq. (10.36).

As a preliminary step, we shall derive a recurrence relation for the Hermite polynomials, which will be necessary in our further discussion. From the definition (10.32) of the Hermite polynomials \( H_n(\zeta) \), we find

\[ H_n'(\zeta) = 2n \left\{ (2\zeta)^{n-1} - \frac{(n-1)(n-2)}{1!} (2\zeta)^{n-3} + \ldots \right\} = 2nH_{n-1}(\zeta), \]

From which it follows that

\[ H_n''(\zeta) = 2nH_{n-1}(\zeta) = 2n \cdot 2(n-1)H_{n-2}(\zeta). \]  

(10.50)
Next, substituting these equations for the derivatives into Eq. (10.35) and replacing \( n \to n' + 1 \), we obtain a recurrence relation for the Hermite polynomials

\[ tH_{n'}(\xi) = n'H_{n'-1}(\xi) + \frac{1}{2} H_{n'+1}(\xi). \] (10.51)

By means of this formula, the matrix element (10.49) can be reduced to the form

\[ x_{n'n} = x^2_n C_n C_n' \left\{ \frac{1}{2} \int_{-\infty}^{+\infty} e^{-\xi^2} H_{n'+1}(\xi) H_n(\xi) d\xi + n' \int_{-\infty}^{+\infty} e^{-\xi^2} H_{n'-1}(\xi) H_n(\xi) d\xi \right\}. \]

In terms of the wave functions \( \psi \), we obtain

\[ x_{n'n} = x_0 \left\{ \frac{1}{2} \int_{-\infty}^{+\infty} \psi_{n'+1} \psi_n dx + n' \int_{-\infty}^{+\infty} \psi_{n'-1} \psi_n dx \right\}. \] (10.52)

Since the functions \( \psi_n \) are orthonormal, we have

\[ x_{n'n} = x_0 \left\{ \frac{1}{2} \frac{C_{n+1}}{C_n} \delta_{n'+1,n} + (n + 1) \frac{C_{n+1}}{C_n} \delta_{n'-1,n} \right\}. \] (10.53)

From this expression it follows that the only nonvanishing matrix elements are those for which \( n' = n - 1 \) or \( n' = n + 1 \); therefore, the selection rules for the quantum number \( n \) are expressed by the equation

\[ \Delta n = n - n' = \pm 1, \] (10.54)

which indicates that only transitions between neighboring levels are possible.

For the wave function as given by Eq. (10.42), we obtain from Eq. (10.53)

\[ x_{n-1,n} = x_0 \sqrt{\frac{n}{2}}, \]
\[ x_{n+1,n} = x_0 \sqrt{\frac{n+1}{2}}, \] (10.55)

where \( x_0 \) is determined from Eq. (10.15). For the frequency of the radiation, we obtain exactly the same expression as in the classical theory:

\[ \omega_{n,n-1} = \frac{E_n - E_{n-1}}{\hbar} = \omega. \] (10.56)
The energy levels and allowed transitions are shown in Fig. 10.4.

Since spontaneous emission is possible only when transitions occur from higher to lower energy levels \( E_n > E_{n-1} \), it follows from (9.22) that the intensity of radiation of the harmonic oscillator \( W = W_{n,n-1} \) is

\[
W_{n,n-1} = \frac{2 e^{2} \omega^{2}}{3 m_{0} c^{3} n \hbar \omega} = \frac{2 e^{2} \omega^{2}}{3 m_{0} c^{3}} (E_n - E_0). \tag{10.57}
\]

Comparing this equation with Eq. (10.10), which was obtained from the classical theory, we see that for large quantum numbers \( n \gg 1 \), when \( E_n \gg E_0 \), both equations yield practically the same result. Transitions to higher energy levels \( n \rightarrow n + 1 \) are possible in the case of induced transitions. The occurrence of spontaneous upward transitions is also possible under the condition that the energy loss in the harmonic oscillator is compensated by the simultaneous liberation of a large amount of energy, as for example, in transitions of atomic electrons (see Chapter 12, spectra of diatomic molecules).

Problem 10.1. Find the eigenvalues of the harmonic oscillator using the WKB method.

Solution. According to (10.14), the wave function for the harmonic oscillator is

\[
\psi'' + (a - \beta^2 x^2) \psi = 0,
\]

where

\[
a = \frac{2m_{0}E}{h^2}, \quad \beta^2 = \frac{m_{0}^2 \omega^2}{h^2}.
\]

According to Eq. (5.75), the eigenvalues are determined from the equation

\[
\int_{-\infty}^{\infty} \frac{V_{c}^n}{V} a - \beta^2 x^2 dx = \pi \left( n + \frac{1}{2} \right).
\]

Evaluating this integral, we find that the energy eigenvalues are the same as in (10.28); that is, the zero-point energy is also present.

Problem 10.2. Construct the theory of the harmonic oscillator in the \( p \) representation (for the one-dimensional case). Find the equation of motion, the eigenvalues and the eigenfunctions.

Solution. Since \( x = -h^2 d^2 \rho \), in the \( p \) representation, we can write the Schrödinger equation as

\[
\left( i; - \frac{p^2}{2m_{0}} + \frac{m_{0} \omega^2 h^2}{2} \frac{d^2}{dp^2} \right) \psi (p) = 0;
\]
that is, transforming the wave equation for the harmonic oscillator from the \( x \) representation to the \( p \) representation and introducing the new parameters
\[
\lambda = \frac{2E}{\hbar \omega}, \quad \gamma = \frac{p}{\rho_0},
\]
where
\[
\rho_0 = \sqrt{m_0 \hbar \omega},
\]
we find that the wave equation changes identically into itself
\[
\varphi'' + (\lambda - \gamma^2) \varphi = 0
\]
(the prime indicates the derivative with respect to \( \gamma \)). Using the solutions (10.28) and (10.42), we can write in the \( p \) representation
\[
E_n = \hbar \omega \left( n + \frac{1}{2} \right)
\]
and
\[
\varphi_n(p) = \frac{1}{\sqrt{2^n n! \sqrt{\pi} \rho_0}} \exp\left(-\frac{p^2}{2 \rho_0^2}\right) H_n\left(\frac{p}{\rho_0}\right).
\]
It is easily verified that this wave function satisfies the normalization condition
\[
\int |\varphi_n(p)|^2 dp = 1.
\]

Problem 10.3. Find the eigenfunctions and energy spectrum of an electron \((e = -e_0 < 0)\) moving in a constant, uniform magnetic field. Show that, according to the quantum theory, the "electron gas" must be diamagnetic.

Solution. Let the magnetic field be directed along the \( z \) axis \((H_y = H_z = 0, H_x = \mathcal{B}z)\). We can then write for the components of the vector potential \( A_y = x_0 \mathcal{B}, A_x = A_z = 0 \). The motion of an electron is described by the Schrödinger equation (see also Problem 8.4)
\[
\frac{\hbar^2}{2m_0} \varphi'' + \frac{e_0 \mathcal{B}^2 \varepsilon^2}{m_0 c^2} x \frac{\varphi'}{y} + \left( E - \frac{e_0 \mathcal{B} \varepsilon^2}{2m_0 c^2} x^2 \right) \varphi = 0.
\]

Since the coordinates \( y \) and \( z \) do not appear explicitly in this equation, we shall look for a solution in the form
\[
\psi = \frac{1}{L} e^{i(k_2 z + k_3 x)} f(x).
\]
For the function \( f(x) \), we obtain the equation
\[
\frac{d^2 f}{dx^2} + \frac{2m_0}{\hbar^2} \left( E' - \frac{e_0 \mathcal{B} \varepsilon^2}{2m_0 c^2} (x + b)^2 \right) f = 0,
\]
where
\[
E' = E - \frac{\hbar^2 k_3^2}{2m_0}, \quad b = \frac{e_0 \mathcal{B}}{e_0 \mathcal{B} \varepsilon}.
\]
It is easily seen that this equation has the same form as Eq. (10.14) for the harmonic oscillator.

Consequently, we can use solutions (10.27) and (10.36) to determine the eigenfunctions and eigenvalues. We thus find
\[
\psi_{nk_2k_3} = \frac{C_n}{L} e^{i(k_2 y + k_3 z)} e^{-\frac{1}{2} \frac{\varepsilon^2}{\hbar}} H_n(\varepsilon), \quad (10.58)
\]
where \( H_n(z) \) is the Hermite polynomial, \( C_n = \left( \frac{2m_0}{\pi \hbar^2 n!} \right)^{1/4} \) is the normalization coefficient, \( \omega = \frac{e_b H^2}{2m_0} \) is the frequency of Larmor precession, and

\[
\xi = \sqrt{\frac{2m_0}{\hbar}} \left( x + \frac{k_x e_b H}{e_b H} \right).
\]

For the eigenvalues, we have

\[
E_n = \frac{e_b H^2}{2m_0} (2n + 1) - \frac{\hbar^2 k_z^2}{2m_0}.
\]

The last term in this equation is simply the kinetic energy of a free electron moving along the \( z \) axis, and is of no special interest.

The first term

\[
E_n = \mu_0 H (2n + 1),
\]

where \( \mu_0 \) is the Bohr magneton, corresponds to the additional energy acquired by an electron in the magnetic field. This additional term represents the energy of electron motion in the \( xy \) plane, which is perpendicular to the magnetic field.

This conclusion is in agreement with classical theory, according to which an electron placed in a magnetic field precesses with the Larmor frequency \( \omega \) in a plane perpendicular to the magnetic field.

In the classical theory, however, the energy of an electron in a magnetic field is determined entirely by its unquantized kinetic energy. Therefore, according to the classical theory, an electron gas generally exhibits no diamagnetic properties.

In the quantum theory the energy (10.59) can be interpreted in terms of the appearance of an additional magnetic moment \( \mu \) of an electron, with the following contribution to the energy:

\[
E_{\text{magn}} = -\mu_0 H.
\]

Comparing (10.60) with (10.59), we find

\[
\mu_z = -\mu_0 (2n + 1).
\]

Since the number \( 2n + 1 \) assumes only positive values (\( n = 0, 1, 2, 3, \ldots \)), the additional moment of an electron will be directed along the negative \( z \) axis. This naturally leads to the diamagnetism of free electrons in a metal.

It should be noted that in quantum mechanics, solution (10.58) corresponds to harmonic vibrations along the \( z \) axis only, whereas in classical theory the circular trajectory means that there are harmonic vibrations along both \( x \) and \( y \) axes, with a phase difference of \( \frac{\pi}{2} \). The reason for this is that the energy is independent of the momentum \( \hbar k_z \). Consequently, degeneracy occurs and the solution for a given energy has the form

\[
\psi_{n, k_z = 0} = \sum_{k} C_{k} \psi_{n k_2, k_z = 0},
\]

where the coefficients \( C_{k} \) are arbitrary amplitudes satisfying the normalization condition

\[
\sum_{k} |C_{k}|^2 = 1.
\]

In classical theory there is also an indeterminacy, since the center of the circular trajectory is not uniquely specified.

The general solution (10.61) corresponds to a set of circular trajectories having different centers located along the \( y \) axis.
Concluding the above discussion, let us note that the solution (10.61) includes the
harmonic oscillations along both \(x\) and \(y\) axes. This can be seen by examining the expression for the energy [Eq. (10.59)] which represents a sum of the energies of two harmonic
oscillators (note that \(\nu_0 \phi_{2\omega} = \phi\))

\[
E_n = 2\hbar \left( n + \frac{1}{2} \right).
\]

Problem 10.4. Show that the matrix element of the product of two operators \(M(x)\) and \(N(x)\), which are independent of quantum numbers, is equal to the sum of the products of the matrix elements of these operators, that is,

\[
\langle MN \rangle_{n'\ell n} = \sum_k M_{n'\ell} N_{\ell n'}
\]

(10.62)

Solution. Writing

\[
\langle MN \rangle_{n'\ell n} = \int \int \delta(x-x') M(x) \delta(x-x') N(x') \psi_n(x') dx dx'
\]

and using the relation (see Chapter 4)

\[
\delta(x-x') = \sum_k \psi_k^*(x') \psi_k(x),
\]

together with the fact that the operators \(M(x)\) and \(N(x')\) are independent of quantum
numbers, we readily prove Eq. (10.62).

Problem 10.5. Find the selection rules for quadrupole radiation emitted by the
harmonic oscillator. Find the intensity of spontaneous quadrupole radiation and compare
it with the intensity of dipole radiation. Obtain Eq. (9.24), which relates the intensity
of quadrupole radiation to that of dipole radiation.

Solution. In Problem 9.1 we found that the quadrupole radiation is proportional
to the matrix element, which according to the preceding problem can be written as

\[
(x^2)_{n'n} = \sum_{k=0}^{\infty} x_{n'k} x_{k'n}.
\]

Substituting the values of \(x_{n'k}\) from Eq. (10.55), we find the following nonvanishing matrix
elements of the quadrupole radiation:

\[
(x^2)_{n-n-2} = \frac{x_2^2}{2} V(n-1); \\
(x^2)_{n+n+2} = \frac{x_2^2}{2} V(n+2)(n+1), \\
(x^2)_{n,n} = x_2^2 \left( n + \frac{1}{2} \right).
\]

(10.63)

That is, the selection rules for the quadrupole radiation of the oscillator are

\[
\Delta n = 0, \pm 2.
\]

The probability of spontaneous emission \((n' = n-2, \Delta n = 2)\) is calculated from Eq.
(9.26). For large quantum numbers when \(E \geq n \hbar \omega\), we have

\[
\wp_{\text{quad}} = \frac{16}{15} \frac{e^2 \omega^2 E^2}{m_e c^5}.
\]

According to (10.57), the intensity of dipole radiation is

\[
\wp_{\text{dipole}} = \frac{2}{3} \frac{e^2 \omega^2 E}{m_e c^3} \sim (ea)^2 \omega \frac{1}{c^3}.
\]
Using the last two equations, we obtain
\[ \psi_{\text{quad}} = \frac{4}{5} \left( \frac{\omega}{c} \right)^2 a^2 \sim \left( \frac{a}{\hbar} \right)^a, \]
where \(a^2 = \frac{2E}{m_0 \omega^2}\) is the square of the classical amplitude of oscillations. This relation is in agreement with Eq. (9.24).

**Problem 10.6.** Show that the center of a wave packet composed of the solutions for the harmonic oscillator moves according to the laws of classical mechanics.

Show that this wave packet does not spread with time. Obtain the transition to the quasi-classical case (\(n \gg \nu \gg 1\), where \(2\nu + 1\) is the number of waves in the wave packet).

**Solution.** Let us assume, for simplicity, that the wave packet is composed of \(2\nu + 1\) eigenfunctions of equal amplitudes
\[ \psi(x, t) = \frac{1}{\sqrt{2\nu + 1}} \sum_{j=-\nu}^{\nu} \psi_{n+j} e^{-i\omega(n+j+\frac{1}{2})t}, \]
where \(\psi_{n+j}\) are the eigenfunctions of the harmonic oscillator, and \(\omega\) is the mechanical frequency of vibration.

The coordinate \(x\) of the center of the wave packet is given by
\[ \bar{x} = \frac{1}{2\nu + 1} \sum_{j=-\nu}^{\nu} x \psi_{n+j} e^{-i\omega(n+j+\frac{1}{2})t} = A \cdot \cos \omega t, \]
with
\[ A = \frac{a}{2\nu + 1} \sum_{j=-\nu}^{\nu} \sqrt{\frac{2(n+j+1)}{2n+1}}, \]
where \(a = \sqrt{\frac{\hbar}{m_0 \omega}}\) is the classical amplitude of oscillations.

It follows from the last two equations that \(\bar{x}\) obeys the classical equation of motion for the harmonic oscillator
\[ \ddot{x} + \omega^2 \bar{x} = 0. \]

Evaluating \(\bar{x}^2\) in a similar manner, we obtain \((\Delta x)^2 = \bar{x}^2 - \bar{x}^2\) for the mean-square deviation
\[ (\Delta x)^2 = \left( C^2 - \frac{A^2}{2} \right) + \left( B^2 - \frac{A^2}{2} \right) \cos 2\omega t, \]
where
\[ C^2 = \frac{a^2}{2}, \quad B^2 = \frac{a^2}{2} \frac{1}{2\nu + 1} \sum_{j=-\nu}^{\nu-2} \frac{(n+j+1)(n+j+2)}{n+\frac{1}{2}}. \]

Consequently, \((\Delta x)^2\) oscillates about a certain mean value and, therefore, does not spread with time.
In the quasi-classical case, we have

\[ A \approx a \left( 1 - \frac{1}{2v+1} \right), \quad B^2 \approx \frac{a^2}{2} \left( 1 - \frac{2}{2v+1} \right), \]

and thus

\[ \bar{x} \approx a \cos \omega t, \quad (\Delta x)^2 \approx \frac{a^2}{2v+1} = \text{const.} \]

From this it follows that the larger the number of waves, the smaller will be the width of the packet, and finally, for \((2v+1) \gg 1\), the width tends to zero.
General Theory of Motion of a Particle in a Centrally Symmetric Field

The problem of the motion of a particle in a central field of force (a field in which the potential depends on the distance alone, and not on the angles) is one of the standard problems of quantum mechanics. This problem provides a basis for the quantum theory of the rotator, which is of considerable importance in connection with the spectra of diatomic molecules, the theory of the hydrogen atom, the nonrelativistic theory of the deuteron, and so on. It is worth noting that in a central field of force the dependence of the wave function on the angles \( \theta \) and \( \varphi \) is completely unrelated to the specific form of the potential energy. Accordingly, the spherical harmonics are of general validity; they are applicable to any centrally symmetric field. The classical analog of the quantum-mechanical investigation of the angular parts of the wave function is the derivation of the law of conservation of angular momentum in a central field of force. This law is also independent of the specific form of the potential energy.

A. SCHRODINGER'S EQUATION IN SPHERICAL COORDINATES

The problem of the motion of a particle in a central field of force

\[
F = F(r) \frac{r}{r},
\]

(11.1)

is usually solved in the spherical coordinates \( r, \theta \) and \( \varphi \), which are related to the Cartesian coordinates (see Fig. 11.1) by the equations

\[
x = r \cos \varphi, \quad y = r \sin \varphi, \quad z = r \cos \theta, \quad p = r \sin \theta.
\]

(11.2)

We shall now write the Schrödinger equation in spherical coordinates.

First, using the general definition of the potential energy \( V \) as a quantity whose negative gradient is equal to the force \( F \), we have

\[
dV = -(F \cdot dr).
\]

(11.3)
For the case of central forces (11.1), we obtain

$$dV = -\frac{F}{r}(xdx + ydy + zdz) = -Fdr,$$  

(11.3a)

and hence

$$V (r) = -\int_{\infty}^{r} F (r) \, dr,$$  

(11.4)

where the lower limit of integration is chosen in accordance with the convention that $V (r)$ vanishes at infinity.

In particular, if the central forces are due to Coulomb interaction

$$F = -\frac{Ze_{0}^{2}}{r^{2}} \cdot r,$$

where $Ze_{0}$ is the nuclear charge ($e = -e_{0}$ is the charge of an electron moving around the nucleus), we obtain for the potential energy

$$V (r) = \int_{\infty}^{r} \frac{Ze_{0}^{2}}{r^{2}} \, dr = -\frac{Ze_{0}^{2}}{r}.$$  

(11.5a)

Now let us find the expression for the Laplacian $\nabla^{2}$ in spherical coordinates. Using the identity

$$\nabla^{2} \psi = \nabla \cdot \nabla \psi,$$  

(11.6)

we shall first find the components of a vector

$$B = \nabla \psi$$  

(11.7)

in spherical coordinates.

Bearing in mind that a gradient expresses the spatial rate of a change of scalar field in a certain direction ($\mathbf{B} = \nabla \psi = \frac{\partial \psi}{\partial r}$), we obtain, in accordance with Fig. 11.1,

$$B_r = \frac{\partial \psi}{\partial r}, \quad B_\theta = \frac{\partial \psi}{r \partial \theta},$$  

$$B_\phi = \frac{\partial \psi}{r \sin \theta \partial \phi},$$  

(11.8)

Let us use the definition of divergence

$$\nabla \cdot \mathbf{B} = \lim_{S \to 0} \frac{\int_{S} (\mathbf{B} \cdot dS)}{S} = \frac{1}{d^{3}x} \sum_{i} \frac{\partial}{\partial x_{i}} (B_{i} dS_{i}) \, dx_{i},$$  

(11.9)
where $d^4x$ is the volume element in spherical coordinates

$$d^4x = r^2 \sin \theta \, dr \, d\theta \, d\phi$$

($x_i$ stands for the coordinates $r$, $\theta$ and $\phi$), and $dS_i$ stands for elementary areas perpendicular to the directions $dr$, $r d\theta$, and $r d\phi$ respectively:

$$dS_r = r \sin \theta \, dr \, d\phi,$$
$$dS_{\theta} = r \sin \theta \, dr \, d\phi,$$
$$dS_{\phi} = r \, dr \, d\phi.$$  

With the help of Eq. (11.8), we obtain

$$V_B = \frac{1}{r^2 \sin \theta \, dr \, d\theta} \left\{ \frac{\partial}{\partial r} \left( \frac{\partial \psi}{\partial r} \right) \left( r^2 \sin \theta \, dr \, d\phi \right) dr + \frac{\partial}{\partial \theta} \left( \frac{\partial \psi}{\partial \theta} \right) \left( r \sin \theta \, dr \, d\phi \right) d\theta + \frac{\partial}{\partial \phi} \left( \frac{\partial \psi}{\partial \phi} \right) \left( r \sin \theta \, dr \, d\phi \right) d\phi \right\},$$

from which we readily find the expression for the Laplace operator in spherical coordinates:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}.$$  

(11.13)

Setting in Eq. (11.13)

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) = \nabla^2 r,$$

and

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} = \nabla^2 \theta, \phi,$$

we have

$$\nabla^2 = \nabla^2 r + \frac{1}{r^2} \nabla^2 \theta, \phi,$$

so that the Schrödinger equation (4.8) takes the form

$$\left( \nabla^2 r + \frac{1}{r^2} \nabla^2 \theta, \phi \right) \psi + k^2(r) \psi = 0,$$

where

$$k^2(r) = \frac{2m_e}{\hbar^2} [E - V(r)].$$

is, according to Eq. (11.4), a function of the radius $r$ only.

**B. SEPARATION OF VARIABLES. EIGENFUNCTIONS**

We shall solve Eq. (11.17) by the method of separation of variables. Let us represent the desired function as a product of the radial and angular parts

$$\psi = \Phi(r) \cdot \theta(\theta, \phi).$$  

(11.19)
Multiplying the original equation by \( \left( \frac{r^2}{\mathcal{R}} \right) \), we obtain

\[
\frac{r^2 \nabla^2 R}{\mathcal{R}} + r^2 \mathcal{K} = -\frac{\nabla^2 \phi Y}{\mathcal{R}^2}. \tag{11.20}
\]

Since the left-hand side depends only on \( r \) and the right-hand side only on the angles \( \theta \) and \( \phi \), this equation can be satisfied only if both the left- and right-hand sides are separately equal to a constant \( \lambda \), called the separation constant.

We, therefore, obtain the following equations for the radial and angular parts, respectively:

\[
\nabla^2 R + \left( \frac{k^2 - \frac{\lambda}{r^2}}{\mathcal{R}} \right) R = 0, \tag{11.21}
\]

\[
\nabla_\theta \phi Y + \lambda Y = 0. \tag{11.22}
\]

The important point to note is that the angular part of the wave function does not contain the variable \( r \) and is independent of the specific form of the potential energy \( V \). Consequently, as we mentioned at the beginning of this chapter, the angular solution will be valid for any central force.

Using the method of separation of variables for the angular part alone, we set

\[
\phi = \theta (\theta) \Phi (\phi), \tag{11.23}
\]

and thus obtain the following equations for the functions \( \theta \) and \( \Phi \):

\[
\nabla^2 \theta + \left( \lambda - \frac{m^2}{\sin^2 \theta} \right) \theta = 0, \tag{11.24}
\]

\[
\nabla^2 \Phi + m^2 \Phi = 0. \tag{11.25}
\]

Here \( m^2 \) is the separation constant and we have used the following notation:

\[
\nabla_\theta = \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d}{d\theta} \right), \tag{11.26}
\]

\[
\nabla_\phi = \frac{d^2}{d\phi^2}, \tag{11.27}
\]

where partial derivatives are replaced by total derivatives, since each of the functions \( \theta \) and \( \Phi \) depends only on a single variable.

Thus, we have obtained three equations—(11.21), (11.24) and (11.25)—for the energy eigenvalues \( E_i \) and the corresponding eigenfunctions \( \psi_i \). The last equation contains only a single parameter \( m^2 \), whereas the first and second contain two parameters each.

Since the solution of one equation yields the eigenvalues for only one parameter, we must begin the solution of the entire problem by
solving (11.25); then, knowing \( m^2 \), we proceed to solve (11.24) and finally (11.21).

To find the normalization constant, we use the relation

\[
\int \varphi^* \varphi \, d^3x = \int_0^\infty R^* R^2 dr \int_0^\pi \Theta^* \Theta \sin \theta d\theta \int_0^{2\pi} \Phi^* \Phi d\varphi,
\]

which shows that each of the functions can be normalized separately:

\[
\int_0^\infty R^* R^2 dr = 1, \quad (11.28)
\]

\[
\int_0^\pi \Theta^* \Theta \sin \theta d\theta = 1, \quad (11.29)
\]

\[
\int_0^{2\pi} \Phi^* \Phi d\varphi = 1. \quad (11.30)
\]

The particular solution for the azimuthal function [see Eq. (11.25)] can be written in two ways:

\[
\Phi = C e^{im\varphi} \quad (11.31)
\]

or

\[
\Phi = A \cos (m\varphi + \varphi_0). \quad (11.32)
\]

Each of these solutions has a different physical interpretation. The solution (11.31) represents a wave traveling around the circumference of a circle and corresponds, for example, to uniform circular motion of an electron. On the other hand, the solution (11.32) is associated with standing waves and corresponds, for example, to oscillations of an electron along an arc. In order for the function \( \Phi \) to describe the motion of an electron around the nucleus, it must have the form of traveling waves (11.31). Moreover, since a solution proportional to \( e^{im\varphi} \) can be obtained from the first solution by replacing \( m \) by \( -m \), we can take, without any loss of generality,

\[
\Phi = C e^{im\varphi}, \quad (11.33)
\]

where the quantity \( m \) assumes both positive and negative values.

Since the wave function must be unique (see Chapter 4, Section B), the function \( \Phi(\varphi) \) must be periodic with a period

\[
\Phi(\varphi) = \Phi(\varphi + 2\pi). \quad (11.34)
\]

It follows that

\[
e^{2\pi im} = 1,
\]
and therefore the quantity \( m \), which is called the magnetic quantum number, assumes only integral values

\[
m = 0, \pm 1, \pm 2, \pm 3, \ldots.
\]  

From the normalization condition (11.30), we find \( C = \frac{1}{\sqrt{2\pi}} \). It is readily shown by direct calculation that the functions

\[
\Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\varphi}
\]  

satisfy the condition of orthonormality

\[
\int_0^{2\pi} \Phi_m^{*} \Phi_n d\varphi = \delta_{mn}.
\]

Since we now know the eigenvalues \( m \) and the wave function associated with the azimuthal angle \( \varphi \), we can proceed to solve Eq. (11.24). Introducing the new variable

\[
x = \cos \vartheta
\]  
and denoting derivatives with respect to \( x \) by primes, Eq. (11.24) becomes

\[
[(1 - x^2) \Theta']' + \left( \lambda - \frac{m^2}{1 - x^2} \right) \Theta = 0.
\]  

It can be seen that (11.38) has singular points at \( x = \pm 1 \), that is, points at which one of the coefficients of \( \Theta \) becomes infinite. To eliminate this divergence, we shall look for a solution \( \Theta \) in the form

\[
\Theta = (1 - x^2)^{\pm m} u.
\]  

Substituting (11.39) into (11.38) and dividing all the terms by \( (1 - x^2)^{3/2} \), we obtain

\[
(1 - x^2) u'' - 2x(s + 1) u' + \left[ \lambda - s^2 - s + \frac{s^2 - m^2}{1 - x^2} \right] u = 0.
\]  

We eliminate the singularity in the last term by setting

\[
s = \pm m.
\]

Since the fundamental equation for \( H \) depends only on \( m^2 \), the solutions corresponding to these two values of \( s \) both satisfy the
same equation, and, consequently, there must be a simple linear relationship between them:

\[ \Theta(m) = A \Theta(-m). \]  

(11.41)

It is, therefore, sufficient to solve Eq. (11.40) for

\[ s = m \geq 0. \]  

(11.42)

With the help of Eq. (11.41), the solution can be automatically extended to the negative values of \( m \). Under the condition (11.42), Eq. (11.40) becomes

\[ (1 - x^2) u'' - 2x(m + 1) u' + (\lambda - m(m + 1)) u = 0. \]  

(11.43)

Since this equation has no singularities, its solution may be represented as a polynomial

\[ u = \sum_{k=0} a_k x^k. \]  

(11.44)

Substitution of this polynomial into Eq. (11.43) gives

\[ \sum_{k=0} \{ k(k-1)a_k x^{k-2} + a_k [\lambda - (k+m)(k+m+1)] x^k \} = 0. \]

Collecting the terms with the same powers of \( x \), we obtain

\[ \sum_{k=0} \{ (k+2)(k+1)a_{k+2} + [\lambda - (k+m)(k+m+1)] a_k \} x^k = 0. \]

This yields a recurrence relation

\[ (k+2)(k+1)a_{k+2} = -[\lambda - (k+m)(k+m+1)] a_k, \]  

(11.45)

which gives the relationship between the coefficients of the series (11.44). Since the coefficients \( a_{k+2} \) are expressed in terms of \( a_k \) and thus only alternate terms are related, the function \( u \) will be either even or odd depending on whether the main term is even or odd.

We require that the series (11.44) terminate at some maximum power \( k \leq q \), so that

\[ a_{q+2} = 0, \quad a_q \neq 0. \]

Then from (11.45) we obtain

\[ \lambda = (q+m)(q+m+1), \]  

(11.46)

where

\[ q = 0, 1, 2, 3, \ldots \]  

(11.47)
MOTION OF A PARTICLE IN A CENTRALLY SYMMETRIC FIELD

(that is, \( q \) is equal to the power at which the series is terminated).

Introducing the orbital angular momentum quantum number \( l \)

\[
l = q + m, \quad (11.48)
\]

we find that, just like the numbers \( q \) and \( m \), this number can assume only positive integral values (including zero), that is,

\[
l = 0, 1, 2, 3, \ldots, \quad (11.49)
\]

and from (11.48) it follows that

\[
l \geq m. \quad (11.50)
\]

According to (11.48) and (11.46), we have

\[
\lambda = l(l+1), \quad (11.51)
\]

and, therefore, Eq. (11.40) can be reduced to the form

\[
(1-x^2)u'' - 2x(m+1)u' + [l(l+1) - m(m+1)]u = 0, \quad (11.52)
\]

where

\[
u = a_{l-m}x^{l} - m + a_{l-m-2}x^{l-m-2} + \ldots + \frac{a_0}{a_1x^l}. \quad (11.53)
\]

Instead of determining the relationship between the coefficients \( a_q \) and \( a_{q+1} \) by means of the recurrence relation (11.45), let us represent the solution (11.53) in a closed form. For this, we introduce the function

\[
v = (x^2 - 1)^l, \quad (11.54)
\]

satisfying the equation

\[
(1-x^2)v' + 2xlv = 0, \quad (11.55)
\]

which is easily obtained by taking the first derivative of \( v \) with respect to \( x \). Differentiating Eq. (11.55) with the help of Leibnitz's rule [see (10.34a)] and setting

\[
v^{(l+m)} = \frac{d^{l+m}}{dx^{l+m}} (x^2 - 1)^l = u_1, \quad (11.56)
\]

we obtain the following equation for the function \( u_1 \):

\[
(1-x^2)u''_1 - 2x(m+1)u'_1 + (l+m+1)(l-m)u_1 = 0. \quad (11.57)
\]
We note that this equation is exactly the same as the differential equation (11.52) for the function $u$. Consequently, functions $u$ and $u_i$ must be proportional to each other

$$u = \text{const} \cdot u_i.$$  

(11.58)

Since the normalization coefficient of the function $\Theta$ has not yet been determined, we can set this proportionality constant equal to $\frac{1}{2^{l_l}}$ in order to make the solution (11.58) for $m = 0$ identical with the Legendre polynomial

$$P_l (x) = \frac{1}{2^{l_l}!} \frac{d^l (x^2 - 1)^l}{dx^l}.$$  

(11.59)

We thus obtain

$$u = \frac{1}{2^{l_l}!} \frac{d^{l+m} (x^2 - 1)^l}{dx^{l+m}}$$

from which, with the help of Eq. (11.39), we find the following expression for the function $\Theta$:

$$\Theta_l^m = C_l^m P_l^m (x).$$  

(11.60)

Here $P_l^m$ is an associated Legendre polynomial defined by the equation

$$P_l^m (x) = (1 - x^2)^{m/2} \frac{d^{l+m}}{dx^{l+m}} \left[ \frac{(x^2 - 1)^l}{2^{l_l}!} \right],$$  

(11.61)

and $C_l^m$ is the normalization coefficient.

Although (11.61) was obtained for positive values of $m$, it can also be extended to include the negative values of $m$ by using the well-known relation

$$P_l^m (x) = (-1)^m \frac{(l + m)!}{(l - m)!} P_l^{-m} (x),$$  

(11.62)

To prove Eq. (11.62), we put it in the following form with the help of (11.61):

$$\langle l - | m \rangle \langle x^2 - 1 \rangle^{| m |} \frac{d^{l+| m |}}{dx^{l+| m |}} (x^2 - 1)^l = \langle l + | m \rangle \left[ \frac{d^{l-| m |}}{dx^{l-| m |}} (x^2 - 1)^l \right].$$  

(11.63)

Since $P_l^m$ and $P_l^{-m}$ must be linearly related to each other (see (11.41)), it is sufficient for us to show that the coefficients of the leading power of $x$ on both sides of Eq. (11.63) are equal to each other, that is,

$$\langle l - | m \rangle \langle x^2 - 1 \rangle^{| m |} \frac{d^{l+| m |}}{dx^{l+| m |}} x^{2l} = \langle l + | m \rangle \frac{d^{l-| m |}}{dx^{l-| m |}} x^{2l}. $$

This is easily shown since

$$\frac{d^k x^n}{dx^k} = \begin{cases} \frac{n!}{(n-k)!} x^{n-k} & \text{for } k \leq n, \\ 0 & \text{for } k > n. \end{cases}$$  

(11.64)
From (11.61) and (11.62), it follows that the range of variation of the quantum number \( m \) is

\[ m = 0, \pm 1, \pm 2, \ldots, \pm l; \]

since for \(|m| > l\) the solution \( P_l^m \) vanishes.\(^2\)

The coefficient \( C_l^m \) in (11.60) can be found from the normalization condition

\[ \int_0^\pi \Theta_l^n \Theta_l^m \sin \theta \, d\theta = \int_{-1}^{1} (x) \Theta_l^n (x) \, dx = 1. \]

Substituting the solution (11.60) and using (11.62), we obtain

\[ \frac{(-1)^m (l+m)!}{(2l)!} |C_l^m|^2 \int_{-1}^{1} \left( \frac{d^{l-m}}{dx^{l-m}} (x^2 - 1)^l \right) \left( \frac{d^{l+m}}{dx^{l+m}} (x^2 - 1)^l \right) \, dx = 1. \]

Transferring the derivative from the second factor in the integrand to the first factor \( l + m \) times (that is, expanding the integral by parts \( l + m \) times), we obtain

\[ \frac{1}{(2l)!} \frac{(l+m)!}{(l-m)!} |C_l^m|^2 \int_{-1}^{1} (1 - x^2)^l \frac{d^{2l}}{dx^{2l}} (x^2 - 1)^l \, dx = 1. \]

Using the equation [see also (11.64)]

\[ \frac{d^{2l}}{dx^{2l}} x^n = \begin{cases} 2l! & (n = 2l), \\ 0 & (n < 2l), \end{cases} \]

and

\[ \int_{-1}^{1} (1 - x^2)^l \, dx = \frac{(l)!^2 2^{2l+1}}{(2l+1)!}, \]

we find

\[ C_l^m = \sqrt{\frac{(2l+1)!}{2} \frac{(l-m)!}{(l+m)!}}. \quad (11.65) \]

Because of the linear relationship between \( P_l^m \) and \( P_l^{-m} \), many authors present the solution for the function \( \Theta \) in the form

\[ \Theta = CP_l^{|m|} (x). \]

We shall not use this form, since in this case the recurrence relation between the associated Legendre polynomials is more complicated than for the solution (11.60) (the recurrence relation is important in connection with the selection rules and the solution of the Dirac equation).
Then
\[ \theta_i^m = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} P_l^m(x). \] (11.66)

For the spherical harmonic \( Y_i^m(\theta, \varphi) \), which satisfies Eq. (1.22), the relations (11.23), (11.36) and (11.66) yield
\[ Y_i^m(\theta, \varphi) = \theta_i^m \delta_m = \sqrt{\frac{2l+1}{4\pi(l+m)!}} P_l^m(\cos \theta)e^{im\varphi}. \] (11.67)

The orthonormality condition for the spherical harmonics takes the form
\[ \delta(Y_i^m)^* Y_i^m d\Omega = \delta_{l'l} \delta_{mm'}. \] (11.68)

After having obtained the eigenvalues of the parameters \( m \) and \( \lambda \), we may proceed to the solution of Eq. (11.21) for the radial part in which there remains only one unknown parameter. The radial solution, however, can be obtained only if the form of the potential energy \( V(r) \) is specified, and therefore, we shall leave this question aside until we come to consider various specific forms of \( V(r) \) in the following chapters.

C. PHYSICAL MEANING OF THE QUANTUM NUMBERS \( l \) AND \( m \). ANGULAR MOMENTUM

We have found that the quantum number \( l \) characterizes the eigenvalue \( \lambda = l(l+1) \) of the operator \(-\hat{\mathbf{r}} \cdot \hat{\mathbf{s}}_\varphi \) [see (11.22) and (11.51)], which is a part of the Hamiltonian
\[ H = -\frac{\hbar^2 \mathbf{\nabla}^2}{2m_o} + V(r) = -\frac{\hbar^2 \mathbf{\nabla}^2}{2m_o} - \frac{\hbar^2 \mathbf{\hat{r}} \cdot \mathbf{\nabla}}{2m_o r^2} + V(r). \] (11.69)

Comparing this Hamiltonian with the classical Hamiltonian function
\[ H = \frac{m_o \mathbf{\hat{r}}^2}{2} + V(r) = \frac{p_r^2}{2m_o} + \frac{l^2}{2m_o r^2} + V(r), \] (11.70)

\[ \frac{1}{2\pi} \int_0^{2\pi} e^{i(l-m')\varphi} d\varphi = \delta_{mm'}. \]

Integrating the Legendre polynomials over the angle \( \delta \), we can set \( m' = m \). Then without loss of generality, we can take \( l' \leq l \). The case \( l' - l \) was considered above in connection with the determination of the normalization coefficient. In similar fashion, it can be readily shown that for \( l' \leq l \) the integral (11.68) vanishes as a result of transferring the derivative from the function with subscript \( l \) to the function with subscript \( l' \).
where \( p_r = m \dot{r} \) and \( L = m r^2 \dot{\phi} \), we see that the operator \( -(\hbar^2 \nabla \nabla_x) \) corresponds to the square of the angular momentum \( L^2 \) in the classical case, and the operator \( -(\hbar^2 \nabla \nabla_x^2) \) to the square of the radial momentum \( p_r^2 \).

Let us investigate these analogs in more detail. As we know from classical mechanics, the angular momentum \( L \) is defined as

\[
L = r \times p. \tag{11.71}
\]

If external forces \( F \) exert a torque \( M = r \times F \), the time rate of change of \( L \) is given by

\[
\frac{dL}{dt} = M. \tag{11.72}
\]

In the case of central forces \( (F \parallel r) \), no torque \( M \) is exerted and, consequently,

\[
L = \text{const.}
\]

In classical mechanics this result is known as the law of conservation of angular momentum; it appears in Kepler's theory of planetary motion as the law of conservation of areal velocities (that is, the law of areas).

To generalize the classical expression for the angular momentum to the quantum case, we replace the classical momentum \( p \) in (11.71) by the momentum operator \( p = -i\hbar \nabla \). We then obtain

\[
L = r \times p = \frac{\hbar}{i} r \times \nabla. \tag{11.73}
\]

or

\[
L_x = y p_z - z p_y, \\
L_y = z p_x - x p_z, \\
L_z = x p_y - y p_x. \tag{11.74}
\]

We note that the angular momentum operators \( L_x, L_y \) and \( L_z \) do not commute with each other. For example, by direct calculation of the commutation relation between \( L_x \) and \( L_y \), we find

\[
L_x L_y - L_y L_x = (y p_z - z p_y)(z p_x - x p_z) - (x p_z - z p_x)(y p_z - z p_y). \tag{11.75}
\]

Using the commutation relation between the momenta and the corresponding coordinates [see (7.7) and (7.8)], we find

\[
L_x L_y - L_y L_x = -i\hbar (y p_x - x p_y) = i\hbar L_z. \tag{11.75}
\]

Similarly, it can be shown that

\[
L_y L_z - L_z L_y = i\hbar L_x, \\
L_z L_x - L_x L_z = i\hbar L_y. \tag{11.76}
\]
To express the square of the angular momentum operator

$$L^2 = L_x^2 + L_y^2 + L_z^2$$  \hspace{1cm} (11.77)

in spherical coordinates, we must first determine the components $L_x$, $L_y$, and $L_z$ in these coordinates. Using the relations (11.2) between Cartesian and spherical coordinates, we have

$$
\frac{\partial \psi}{\partial \theta} = \frac{\partial \psi}{\partial \phi} \frac{\partial \phi}{\partial \theta} + \frac{\partial \psi}{\partial \phi} \frac{\partial \phi}{\partial \theta} + \frac{\partial \psi}{\partial \phi} \frac{\partial \phi}{\partial \theta} = \begin{align*}
&= r \cos \phi \cos \theta \frac{\partial \psi}{\partial x} + r \cos \theta \sin \phi \frac{\partial \psi}{\partial y} - r \sin \theta \frac{\partial \psi}{\partial z} = \\
&= \frac{xz}{r} \frac{\partial \psi}{\partial x} + \frac{yz}{r} \frac{\partial \psi}{\partial y} - \frac{r}{r} \frac{\partial \psi}{\partial z},
\end{align*}
$$

$$
\frac{\partial \psi}{\partial \theta} = \frac{\partial \psi}{\partial \phi} \frac{\partial \phi}{\partial \theta} + \frac{\partial \psi}{\partial \phi} \frac{\partial \phi}{\partial \theta} + \frac{\partial \psi}{\partial \phi} \frac{\partial \phi}{\partial \theta} = \\
= -r \sin \theta \sin \phi \frac{\partial \psi}{\partial x} + r \sin \theta \cos \phi \frac{\partial \psi}{\partial y} = -y \frac{\partial \psi}{\partial x} + x \frac{\partial \psi}{\partial y}. \hspace{1cm} (11.78)
$$

Multiplying Eq. (11.78) by $\frac{x}{r}$ and Eq. (11.79) by $\left(-\frac{y}{r} \right)$, adding these products, and remembering that $r^2 = x^2 + y^2$, we obtain the relation

$$
z \frac{\partial \psi}{\partial x} - x \frac{\partial \psi}{\partial z} = \cos \phi \frac{\partial \psi}{\partial \theta} - \sin \phi \cot \theta \frac{\partial \psi}{\partial \phi}. \hspace{1cm} (11.80)
$$

Now let us multiply Eq. (11.78) by $\left(- \frac{y}{r} \right)$ and Eq. (11.79) by $\left(- \frac{z}{r} \right)$. Then, proceeding in the same way as before, we obtain

$$
y \frac{\partial \psi}{\partial z} - z \frac{\partial \psi}{\partial y} = -\left( \sin \phi \frac{\partial \psi}{\partial \theta} + \cos \phi \cot \theta \frac{\partial \psi}{\partial \phi} \right). \hspace{1cm} (11.81)
$$

Using Eqs. (11.79) and Eqs. (11.74), we find

$$
L_x = -\frac{\hbar}{i} \left\{ \sin \phi \frac{\partial}{\partial \phi} + \cos \phi \cot \theta \frac{\partial}{\partial \theta} \right\}, \hspace{1cm} (11.82)
$$

$$
L_y = \frac{\hbar}{i} \left\{ \cos \phi \frac{\partial}{\partial \phi} - \sin \phi \cot \theta \frac{\partial}{\partial \theta} \right\}, \hspace{1cm} (11.83)
$$

$$
L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}. \hspace{1cm} (11.84)
$$

Introducing the variable $x = \cos \theta$ (which should not be confused with the Cartesian coordinate $x$), Eqs. (11.82) and (11.83) can be written in the form

$$
L_x \pm iL_y = \hbar e^{\pm i\phi} \left( i \frac{x}{\sqrt{1-x^2}} \frac{\partial}{\partial \phi} \mp \sqrt{1-x^2} \frac{\partial}{\partial x} \right). \hspace{1cm} (11.85)
$$
To determine the effect of these operators on the spherical harmonics, let us take advantage of the fact that a particular spherical harmonic can be represented either as (11.67) or as

$$Y_l^m = (-1)^m \sqrt{\frac{2l+1}{4\pi}} \frac{(l+m)!}{(l-m)!} P_l^m(\cos \theta) e^{im\phi}. \quad (11.86)$$

Operating directly with $L_z$ on the spherical harmonic, we find

$$L_z Y_l^m = \hbar m Y_l^m. \quad (11.87)$$

From this it follows that the quantum number $m$ characterizes the $z$ component of the angular momentum.

To determine the effect of the operator $L_x + iL_y$ on the spherical harmonic $Y_l^m$, we use the expression (11.67), and for the effect of the operator $L_x - iL_y$ we use the equivalent expression (11.86). Then from the equation

$$e^{\pm i\phi} \left( \frac{i}{\sqrt{1-x^2}} \frac{\partial}{\partial \theta} + \sqrt{1-x^2} \frac{\partial}{\partial \phi} \right) e^{im\phi} (1-x^2)^{\pm m/2} f(x) =$$

$$= \mp e^{i\phi} (m \pm b) (1-x^2)^{\pm m/2} \frac{\partial f(x)}{\partial x}$$

It follows that

$$(L_x \pm iL_y) Y_l^m = -\hbar \sqrt{(l+1 \pm m)(l \mp m)} Y_l^{m \pm 1}. \quad (11.88)$$

Equations (11.87) and (11.88) yield

$$L^2 Y_l^m = \left[ \frac{1}{2} (L_x + iL_y)(L_x - iL_y) + \frac{1}{2} (L_x - iL_y) \times \times (L_x + iL_y) + L_z^2 \right] Y_l^m = -\hbar^2 \nabla^2 Y_l^m =$$

$$= \hbar^2 (l+1) Y_l^m. \quad (11.88a)$$

The last equation shows that $Y_l^m$ is an eigenfunction of the operators $L_z$ and $L_z^2$. This follows from the fact that the operators $L_z$ and $L_z^2$ commute not only with each other, but also with the Hamiltonian $H$. Since the operators $L_x$ and $L_y$ do not commute with $L_z$, it is impossible to find a wave function that would be a simultaneous eigenfunction of the operator $L_z$ and the operators $L_x$ or $L_y$. This does not mean, however, that the direction of the $z$ axis is a preferred direction, since it can be chosen arbitrarily.

The spherical harmonic can be written in such a manner that it will be an eigenfunction of the operators $L_x$ and $L_z^2$. In this case, it will no longer be an eigenfunction of the operator $L_z$ (see Problem 12.2).
Quantum-mechanical results are generally analyzed either by finding their classical analogs or by comparison with the results of Bohr's semi-classical theory, which has a simple physical interpretation. To apply Bohr's theory to the motion of a central field, we start from the classical law of conservation of angular momentum; we then conclude that the motion takes place in a single plane and that the angular momentum vector (which is perpendicular to this plane) has the magnitude

\[ L = p_\phi = \frac{\partial T}{\partial \phi} = m_r \dot{\phi} = \text{const.} \quad (11.89) \]

Applying the quantization rules, we find the discrete values that the angular momentum can assume

\[ \oint p_\phi \, d\phi = 2\pi L_B = 2\pi \hbar n_\phi. \]

Hence

\[ L_\phi = n_\phi \hbar, \quad (11.90) \]

where

\[ n_\phi = 1, 2, 3, \ldots \quad (11.91) \]

If the \( z \) axis is not perpendicular to the plane of the orbit, then the Bohr theory allows us to quantize the projection of the angular momentum vector on the \( z \) axis. This is known as space quantization. Then

\[ (L_B)_z = \hbar n_\phi, \quad (11.92) \]

where

\[ n_\phi = -n_r, -n_r + 1, \ldots, 0, \ldots, n_r - 1, n_r. \quad (11.93) \]

It follows from this that the angle \( \alpha \) between the direction of the angular momentum \( L \) and the \( z \) axis is given by the equation

\[ \cos \alpha = \frac{n_\phi}{n_\phi}; \quad (11.94) \]

that is, it can assume only certain discrete values.

Space quantization is illustrated in Fig. 11.2, which shows that \( n_r = -n_\phi \) corresponds to the case when \( L \) is parallel to the \( z \) axis (Fig. 11.2a), where \( n_\phi = -n_r \) corresponds to the case of anti-parallel \( L \). (Fig. 11.2b). Finally, for \( n_\phi = 0 \), the vectors are mutually
perpendicular (Fig. 11.2c). It is obvious that space quantization has a meaning only when there is some preferred direction in space, for example, the direction of the magnetic field intensity vector.\(^4\) If there is no preferred direction, the orientation of the \(z\) axis may be taken as perpendicular to the plane of the orbit.

![Fig. 11.2. Space quantization according to the Bohr theory (for \(L = 1\); in units of \(\hbar\)).](image)

Now let us compare the quantum-mechanical results with those of the Bohr theory for the square and the \(z\) components of the angular momenta:

\[
L_{\text{qm}}^z = \hbar^2 (l - 1), \quad L_B^z = \hbar^2 n_\varphi.
\]

\(l = 0, 1, 2, 3, \ldots\) \(\quad n_\varphi = 1, 2, 3, 4, \ldots\)

\[
L_z = \hbar m, \quad (L_B)_z = \hbar n_\varphi,
\]

\(-l \leq m \leq l, \quad -n_\varphi \leq n_\varphi \leq n_\varphi.
\]

It is seen that \(L_{\text{qm}}^z\) is zero when \(l = 0\), whereas \(L_B^z\) can never be zero. This means that the state with \(l = 0\) has no classical analog. It follows that the angular momentum of an atom in the lowest state is equal to zero, contrary to the results of the Bohr theory. The experimental data from atomic spectroscopy fully confirm this quantum-mechanical result.

\(^4\)It is, of course, understood that in the presence of a magnetic field the central symmetry is disturbed.
In the Bohr theory the direction of the z axis can be taken to coincide with that of the orbital angular momentum. In this case \( n_z = n' \) and, therefore,

\[
L_z^B = (L_B)^{z\text{max}}. \tag{11.95}
\]

In the wave theory this case corresponds to \( m = l \), when

\[
L_z^{\text{max}} = \hbar l, \tag{11.96}
\]

whereas

\[
L_{\text{qm}}^z = \hbar^2 l^2 + \hbar^2 l = L_z^{\text{max}} + \hbar^2 l. \tag{11.97}
\]

The appearance of the additional orbital angular momentum \( \hbar^2 l \) is related to the noncommutativity of the angular momentum operators \( L_x, L_y, \) and \( L_z \), as a result of which the angular momentum components cannot have simultaneous definite values. Therefore, when \( L_z = L_z^{\text{max}} = \hbar l \), the components \( L_x \) and \( L_y \) do not vanish but have certain minimum values satisfying the relation

\[
L_{\text{qm}}^z = L_z^{\text{max}} + (\Delta L_x)^z_{\text{min}} + (\Delta L_y)^z_{\text{min}}. \tag{11.98}
\]

The minimum value of \( (\Delta L_x)^z \) and \( (\Delta L_y)^z \) may be obtained with the help of the uncertainty principle [see (8.13)]:

\[
(\Delta L_x)^z_{\text{min}}(\Delta L_y)^z_{\text{min}} = \frac{1}{4} |L_x L_y - L_y L_x|^2 = \frac{1}{4} \hbar^2 L_z^{\text{max}} = \frac{1}{4} \hbar^4 l^2. \tag{11.99}
\]

Since the problem is symmetric with respect to the x and y axes, we may set \( (\Delta L_x)^z_{\text{min}} = (\Delta L_y)^z_{\text{min}} \). Hence, we obtain

\[
(\Delta L_x)^z_{\text{min}} = (\Delta L_y)^z_{\text{min}} = \hbar^2 \frac{l}{2}, \tag{11.100}
\]

and the sum of \( (\Delta L_x)^z_{\text{min}} \) and \( (\Delta L_y)^z_{\text{min}} \) is exactly equal to the additional angular momentum \( \hbar^2 l \). As a result we arrive at Eq. (11.97). Thus the nature of this additional term is the same as that of the zero-point energy of the harmonic oscillator. Both are related to the uncertainty principle. For large values of the orbital angular momentum quantum number \( l \), we can neglect the term \( \hbar^2 l \) in (11.96) in comparison with \( \hbar^4 l^2 \), so that in fact we have the Bohr semiclassical solution.
Chapter 12

The Rotator

Spherical harmonics, which are the eigenfunctions of the square of the angular momentum, have their main application in the quantum theory of the rotator, that is, in the quantum-mechanical description of the free motion of a point over a sphere. The results of the theory of the rotator can be used directly in connection with the spectra of diatomic molecules. Since, however, the angular part of the wave function in a central field is also described by spherical harmonics, many predictions from the theory of the rotator (for instance, the angular dependence of the wave function \( \psi \) and the selection rules for the quantum numbers \( l \) and \( m \)) remain unchanged in the theory of a particle in a central field (for example, a particle in a Coulomb field in the problem of the hydrogen atom).

A. EIGENFUNCTIONS OF THE ROTATOR

We shall first write the basic results of the quantization of the rotator according to Bohr's theory. These will be used as a starting point in our further discussion.

Suppose a point is moving over a sphere of radius \( r = a = \text{const} \). Let the origin of the coordinate system be at the center of the sphere. The potential energy \( V(r) \) is then

\[
V(r) = V(a) = \text{const}.
\]

Since the reference level of the potential energy can be specified in any desired manner by defining its value at some point as zero, we set

\[
V(a) = 0. \tag{12.1a}
\]

The total energy of the rotator is then equal to its kinetic energy

\[
E = T = \frac{m_o a^2 \dot{\phi}^2}{2}. \tag{12.2}
\]

The generalized momentum \( p_\phi \), which here has the meaning of the angular momentum, is found to be

\[
p_\phi = \frac{\partial T}{\partial \dot{\phi}} = m_o a^2 \dot{\phi}. \tag{12.3}
\]
Using Bohr’s quantization rule, we obtain
\[ p_y = n_y \hbar, \]  
and, consequently,
\[ E_{n_y} = \frac{n_y^2 \hbar^2}{2J}, \]  
where \( J = m_0 a^2 \) is the moment of inertia.

The quantum-mechanical theory of the rotator is a special case of the problem of motion of a point in a central field of force. Consequently, we shall use Eq. (1.21) to determine the radial function \( R(r) \):
\[ \nabla^2 R(r) + \left[ \frac{2m_0E}{\hbar^2} - \frac{l(l+1)}{r^2} \right] R(r) = 0. \]  

We have here set the potential energy equal to zero and substituted \( J = l(l+1) \) in accordance with Eq. (11.51). Since \( r = a = \text{const} \) for the rotator, function \( R(r) = R(a) = \text{const} \), that is, \( \nabla^2 R(a) = 0 \). The energy \( E \) is now easily found from Eq. (11.51)
\[ E_i = \frac{\hbar^2 l(l+1)}{2m_0a^2} = \frac{\hbar^2 l(l+1)}{2J}. \]  

Comparing this equation with Eq. (12.5), we see that in the Bohr theory \( E \sim n_y^2 \), whereas in quantum mechanics \( E \sim l(l+1) \). As has already been mentioned in Chapter 11 (Section D), this difference is due to the noncommutativity of the components of \( L_x, L_y \) and \( L_z \) of the angular momentum operator; it is one of the characteristic features of quantum mechanics. Both equations become identical only for large quantum numbers, that is, when \( l \gg 1 \).

According to Eq. (12.7), the energy of the rotator depends only on the orbital angular momentum quantum number \( l \). The magnetic quantum number \( m \), which characterizes the projection of the angular momentum \( L \) on the \( z \) axis (and, consequently, the orientation of the angular momentum in space), does not appear in the expression for \( E_i \). The eigenfunctions \( Y_l^m \) corresponding to the eigenvalue \( E_i \) [see (11.67)] do, however, depend on \( m \). Since \( m \) can vary from \( -l \) to \( +l \) [see (11.50)], each energy eigenvalue \( E_i \) will have \( 2l + 1 \) corresponding mutually orthogonal eigenfunctions; they describe the state of the rotator and differ only in the orientation of their angular momentum \( L \) relative to the \( z \) axis. In this case the energy level \( E_i \) is said to be \((2l + 1)\)-fold degenerate.

In general, a state of a system (or a given level) is said to be \( N \)-fold degenerate if \( N \) linearly independent eigenfunctions correspond to the given energy eigenvalue.
The physical explanation for the degeneracy of the energy levels of the rotator is that the rotator forms a centrally symmetric system, and consequently all directions passing through the origin of coordinates are equivalent. From these considerations it follows that degeneracy will occur in any centrally symmetric system.

If there exists a preferred direction, for example, one determined by the direction of a magnetic field, the central symmetry is disturbed and the possible directions of the angular momentum \( L \) are no longer equivalent. As a result, the degree of degeneracy is either reduced, or the degeneracy can be completely removed.

In spectroscopic notation the energy levels are called terms; for example, the level corresponding to \( l = 0 \) is called the \( s \) term and the level corresponding to \( l = 1 \), the \( p \) term. For the \( d \) term, \( l = 2 \); for the \( f \) term, \( l = 3 \); for the \( g \) term, \( l = 4 \); and so on. Correspondingly, the rotator is said to be in the \( s \) state when \( l = 0 \), in the \( p \) state when \( l = 1 \), and so on.

Let us consider in more detail the \( s \) and \( p \) states of the rotator. Since \( l = m = 0 \), in the \( s \) state, it follows from Eq. (11.67) that the eigenfunction \( Y_0 \) corresponding to the energy eigenvalue \( E_0 = 0 \) is

\[
Y_0 = \frac{1}{\sqrt{4\pi}} \tag{12.8}
\]

and the probability density \( |Y_0|^2 \) is given by

\[
|Y_0|^2 = \frac{1}{4\pi}. \tag{12.9}
\]

In the \( p \) state \( l = 1 \), and the quantum number \( m \) can have any of the three values \(-1, 0, -1\). Consequently, the energy eigenvalue \( E_1 = \frac{\hbar^2}{J} \) is associated with the three eigenfunctions:

\[
Y_{l=1}^m = -\sqrt{\frac{3}{8\pi}} e^{im\theta} \sin \theta, \tag{12.10}
\]

\[
Y_l^1 = \sqrt{\frac{3}{4\pi}} \cos \theta, \tag{12.11}
\]

\[
Y_l^{-1} = \sqrt{\frac{3}{8\pi}} e^{-i\theta} \sin \theta. \tag{12.12}
\]

The corresponding probability densities are

\[
|Y_{l=1}^m|^2 = |Y_l^1|^2 = \frac{3}{8\pi} \sin^2 \theta, \tag{12.13}
\]

\[
|Y_l^{-1}|^2 = \frac{3}{4\pi} \cos^2 \theta. \tag{12.14}
\]
The probability distribution functions (12.9), (12.13) and (12.14) are plotted in Fig. 12.1; they are shown only in the $zy$ plane because $|Y_l^m|$ does not depend on the angle $\theta$. To obtain a complete picture, it is necessary to rotate the graph about the $z$ axis.

![Graph showing probability density distribution functions for the rotator.](image)

It can be seen from Eq. (12.9) and Fig. 12.1a that, for a rotator in the $s$ state, the angle $\varphi$, which gives the direction of the angular momentum $L$ relative to the $z$ axis, is arbitrary. This was to be expected since the angular momentum $L^2 = \hbar^2 (l + 1)$ is equal to zero in this case. A material particle at rest has an equal probability of being at any point on the spherical surface of radius $a$. In other words, all positions of the rotator are possible. There is no classical analog of this state.

From Eq. (12.13) and Fig. 12.1b it follows that in the $p$ state, when $l = 1$ and $m = \pm 1$, the most probable of all the possible orbits of the rotator is the one located in the $xy$ plane. The states with $m = 1$ and $m = -1$ will have different directions of rotation: for $m = 1$ the rotator will rotate clockwise (the angular momentum $L$ is parallel to the $z$ axis); for $m = -1$ it will rotate counterclockwise (the angular momentum $L$ is antiparallel to the $z$ axis). When $l = 1$ and $m = 0$, the most probable orbit of the rotator lies in a plane passing through the $z$ axis [see Eq. (12.14) and Fig. 12.1c]. In this case, the orientation of the angular momentum is perpendicular to the $z$ axis.

It is worth mentioning that a similar analysis of the angular part of the wave function applies to all systems characterized by central symmetry.
B. SELECTION RULES

As has already been shown, the selection rules indicating the changes of the quantum numbers that correspond to allowed transitions can be expressed in terms of the matrix elements

\[ (r)_{lm}^{m'} = \int (Y_i^{m'})^* r Y_l^{m} d\Omega. \]  

(12.15)

If the matrix element vanishes for some particular change of the quantum numbers, the corresponding transition is forbidden (there will be no radiation). Once we know the selection rules, we can immediately find both the frequency and the intensity of the radiation [see Eq. (9.22)].

Let us replace the coordinates \( x, y \) and \( z \) (that is, replace \( r \)) in Eq. (12.15) by the following new variables:

\[ z = a \cos \theta, \]  

(12.16)

\[ \xi = x + iy = a \sin \theta e^{i\varphi}, \]  

(12.17)

\[ \eta = x - iy = a \sin \theta e^{-i\varphi}. \]  

(12.18)

From the physical point of view, this is equivalent to resolving the motion of the rotator into three parts—an oscillation along the \( z \) axis described by the \( z \) component; a clockwise rotation in the \( xy \) plane (the \( \xi \) component); and a counterclockwise rotation in the \( xy \) plane (the \( \eta \) component). In combination, these three components completely describe the motion of a point over the surface of a sphere.

In terms of the new variables the determination of the selection rules reduces to a calculation of the matrix elements:

\[ (z)_{lm}^{m'} = \int (Y_i^{m'})^* \cos \theta Y_l^{m} d\Omega, \]  

(12.19)

\[ (\xi)_{lm}^{m'} = \int (Y_i^{m'})^* \sin \theta e^{i\varphi} Y_l^{m} d\Omega, \]  

(12.20)

\[ (\eta)_{lm}^{m'} = \int (Y_i^{m'})^* \sin \theta e^{-i\varphi} Y_l^{m} d\Omega, \]  

(12.21)

where, for the sake of simplicity, we have set \( a = 1 \).
Using the recurrence relations for spherical harmonics\(^1\)

\[
\cos \theta Y^m_l = A Y^m_{l+1} + B Y^m_{l-1},
\]

\[
\sin \theta e^{i\varphi} Y^m_l = A\pm Y^m_{l+1} + B\pm Y^m_{l-1},
\]

(12.22)

(12.23)

together with the orthonormality condition (11.68), we find

\[
(z)_{lm}' = \text{const}\delta_{m',m}\delta_{l',l},
\]

(12.24)

\[
(\bar{z})_{lm}' = \text{const}\delta_{m',m+1}\delta_{l',l},
\]

(12.25)

\[
(\bar{\eta})_{lm}' = \text{const}\delta_{m',m-1}\delta_{l',l}.
\]

(12.26)

Therefore, we obtain the following selection rules:

(a) for vibration along the \(z\) axis

\[
\Delta m = m - m' = 0, \quad \Delta l = l - l' = \pm 1;
\]

(12.27)

(b) for clockwise rotation

\[
\Delta m = -1, \quad \Delta l = \pm 1;
\]

(12.28)

(c) for counterclockwise rotation

\[
\Delta m = 1, \quad \Delta l = \pm 1.
\]

(12.29)

We have just shown that the only allowed transitions are those for which the changes of the magnetic quantum number \(m\) and the orbital quantum number \(l\) are

\[
\Delta m = 0, \pm 1,
\]

\[
\Delta l = \pm 1.
\]

(12.30)

(12.31)

\(^1\)The coefficients \(A\) and \(B\) can be found in a fairly simple way. We substitute the expansion (11.67) into Eq. (12.22), setting

\[
(l^m_l) = \frac{(2l)!}{2^l l! (l-m)!} \left\{ \frac{m}{2^{l-m} (l-m)(l-m-1)} x^{l-m-2} + \ldots \right\}.
\]

Then, dividing all the terms by \(x^{l-m+1/2}\) and equating the coefficients of \(x^{l-m+1/2}\) and the coefficients of \(x^{l-m-1/2}\) on the left- and right-hand sides (nothing further is obtained by equating the coefficients of the remaining powers of \(x\), we find

\[
A(l, m) = \sqrt{\frac{(l+1-m)(l+1+m)}{(2l+1)(2l+3)}},
\]

\[
B(l, m) = \sqrt{\frac{(l+m)(l-m)}{(2l+1)(2l-1)}}.
\]

(12.22a)

Similarly, we find

\[
A_{\pm}(l, m) = \sqrt{\frac{(l+1+2m)(l+1+m)}{(2l+1)(2l+3)}},
\]

\[
B_{\pm}(l, m) = \sqrt{\frac{(l+m)(l-1+m)}{(2l+1)(2l-1)}}.
\]

(12.23a)
We note that these selection rules for the quantum numbers $m$ and $l$ will hold for any centrally symmetric system including, in particular, the hydrogen atom.

From the selection rules, we can find the possible emission (or absorption) frequencies of the rotator:

$$\omega_{ll'} = 2\pi \gamma_{ll'} \frac{E_l - E_{l'}}{h}. \quad (12.32)$$

Substituting the expression for the energy $E_l$ [see Eq. (12.7)] and considering that the moment of inertia of the rotator does not change in this case, we can reduce Eq. (12.32) to the form

$$\omega_{ll'} = \frac{\hbar}{2J} [l(l + 1) - l'(l' + 1)]. \quad (12.33)$$

From Eqs. (12.31) and (12.33), we obtain

$$\omega_{l, l-1} = \frac{\hbar}{J} l, \quad (12.34)$$

$$\omega_{l, l+1} = -\frac{\hbar}{J} (l + 1), \quad (12.35)$$

where the frequency $\omega_{l, l-1}$ corresponds to a transition from a higher energy level to a lower one (a downward transition) and $\omega_{l, l+1}$ to an upward transition.

C. SPECTRA OF DIATOMIC MOLECULES

There are three main types of spectra—the continuous spectrum of radiation emitted by a heated body (for example, black-body radiation, with a spectral distribution described by Planck's formula); line spectra (or atomic spectra), caused by transitions of atomic electrons between energy levels (for example, the Balmer series for the hydrogen atom); and finally, band spectra characterizing molecular radiation. A band spectrum consists of bright bands with a sharp edge on the low-frequency side and a diffuse boundary on the high-frequency side. Only a high-resolution spectrograph can show that the band actually consists of a series of individual lines.

As we shall see below, band spectra are directly related to the rotational motion of molecules.

Let us consider a molecule consisting of two atoms with masses $m_1$ and $m_2$ separated by a constant distance $r$ (see Fig. 12.2). An
example of such a molecule is provided, in a first approximation, by the diatomic HCl molecule. It is well known that in the case of two or more particles, the center of mass moves as a single particle whose mass is equal to the sum of the masses of all the particles:

\[ m_{\text{sum}} = \sum m_i. \]  

(12.36)

The relative motion of the particles is characterized by the reduced mass \( m_{\text{red}} \), the reciprocal of which is equal to the sum of the reciprocals of the masses of all the particles:

\[ \frac{1}{m_{\text{red}}} = \sum \frac{1}{m_i}. \]  

(12.37)

To prove this, let us write the Lagrangian \( \mathcal{L} \) of a system consisting, for example, of two mutually interacting particles with masses \( m_1 \) and \( m_2 \):

\[ \mathcal{L} = \frac{m_1 x_1^2}{2} + \frac{m_2 x_2^2}{2} - V(x_2 - x_1), \]  

(12.38)

where \( x_1 \) and \( x_2 \) are the coordinates of the first and second particles, respectively, and \( x_2 - x_1 \) is the distance between them. Introducing the relative coordinate \( x = x_2 - x_1 \) and the coordinate of the center of mass

\[ x_{\text{c.m.}} = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}, \]  

(12.39)

we obtain

\[ \mathcal{L} = \frac{m_{\text{sum}} x_{\text{c.m.}}^2}{2} + \frac{m_{\text{red}} x^2}{2} - V(x) \]

from which, using the Lagrange equation

\[ \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{x}_i} - \frac{\partial \mathcal{L}}{\partial x_i} = 0, \]

we find that the motion of the center of mass is characterized by the total mass

\[ m_{\text{sum}} \dot{x}_{\text{c.m.}} = \text{const}, \]  

(12.40)

and the relative motion of a particle by the reduced mass

\[ m_{\text{red}} \ddot{x} = - \frac{\partial V}{\partial x}. \]  

(12.41)
If the center of mass is at rest \((c.m.=0)\), the coordinates \(x_1\) and \(x_2\) are related to the relative coordinate \(x\) by the equations

\[
x_1 = -\frac{m_2 x}{m_1 + m_2}, \quad x_2 = \frac{m_1 x}{m_1 + m_2}.
\]

Accordingly, the moment of inertia of a diatomic molecule is

\[
I = m_1 x_1^2 + m_2 x_2^2 = m_{\text{red}} x^2 \quad (12.42)
\]

which is similar to the expression for the moment of inertia of a single material particle whose mass is equal to the reduced mass and whose coordinate is equal to the relative coordinate. Therefore, in all the results obtained for the rotator, we must substitute Eq. (12.42) for the moment of inertia, setting \(x = u\).

If the radiation is caused only by rotational transitions, it follows from Eq. (12.34) that its frequency is

\[
\omega_{l, l-1} = 2Bl, \quad (12.43)
\]

where

\[
B = \frac{\hbar}{2j} = \frac{\hbar}{2m_{\text{red}} a^2}. \quad (12.44)
\]

From this it is seen that rotational spectra (molecular spectra that result from transitions between rotational levels) consist of sets of equally spaced lines (see Fig. 12.3). The rotational spectrum, however, lies in the far infrared region (radiation wavelengths of the order of 100–300 \(\mu\)) and its investigation is rather difficult. Absorption lines of this type have been discovered, for example, in the spectra of HCl molecules. A measurement of the spacing between the lines enables us to determine the moment of inertia of the molecule.

In addition to pure rotational spectra, there are vibrational-rotational spectra, which result from the internal vibrations of a molecule in conjunction with its rotation. These spectra are not situated as far in the infrared as the rotational spectra and are more easily studied.

Let us consider in general form the theory of a diatomic molecule with varying interatomic distance. This diatomic molecule represents an oscillating rotator. Without considering in detail the atomic interactions in the molecule, and using only simple
qualitative arguments, let us find the general form of the potential energy curve $V(r)$.

First, we must set $V(r \to 0) \to \infty$, since the atoms cannot be arbitrarily close to one another. Second, the interaction between the atoms must become negligibly small as $r \to \infty$, and hence $V(r \to \infty) \to 0$. Moreover, since a molecule is a stable system, the potential energy $V$ must be negative at a certain finite interatomic distance $r = a$, where it has a minimum. Otherwise, if $V \geq 0$ the molecule would rapidly dissociate (see Chapter 27 for a more detailed account of the bonding energy of atoms in molecules). The general form of the dependence of the potential energy of atoms in a molecule on the interatomic distance is illustrated in Fig. 12.4.

![Fig. 12.4. Potential energy diagram for a diatomic molecule.](image)

If the departures $x = r - a$ of the molecule from the equilibrium position ($r = a$) are relatively small ($x \ll a$), the potential energy $V(r)$ can be expanded in a series in the neighborhood of the equilibrium point $r = a$

$$V(r) = V(a + x) = V(a) + xV'(a) + \frac{x^2}{2} V''(a) + \ldots \quad (12.45)$$

Keeping only the first three terms of this expansion and noting that the function $V$ has a minimum at the point $r = a$ [$V'(a) = 0$ and $V''(a) > 0$], Eq. (12.45) can be reduced to the form

$$V(r) = -D + \frac{m \omega^2 a^2 x^2}{2}. \quad (12.46)$$
Here \( V''(a) = m_{\text{red}} \omega^2 \) and \( V(a) = -D \) are the elastic constant and the dissociation energy of the molecule, respectively.\(^\text{2}\)

To find the energy levels of the molecule (and thus its energy spectrum), we take the Schrödinger equation (11.21) for the radial part of the wave function, since in our approximation the potential energy (12.46) possesses a spherical symmetry.

Since we are interested only in the relative motion of the atoms, we replace the mass \( m \) by \( m_{\text{red}} \) in Eq. (11.21). The resulting equation is

\[
\nabla^2 R + \left[ \frac{2m_{\text{red}}}{\hbar^2} (E - V(r)) - \frac{l(l + 1)}{r^2} \right] R = 0.
\]  

(12.47)

Noting that

\[
\nabla^2 R = \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} = \frac{1}{r} \frac{d^2 (rR)}{dr^2},
\]  

(12.48)

and introducing the function

\( rR = u \),

(12.49)

we obtain after substituting (12.46) into (12.47)

\[
\frac{d^2 u}{dr^2} + \frac{2m_{\text{red}}}{\hbar^2} \left( E + D - m_{\text{red}} \frac{\omega^2 x^2}{2} - \frac{\hbar^2 l(l + 1)}{2m_{\text{red}} r^2} \right) u = 0.
\]  

(12.49a)

Since \( x \ll a \), we may assume in this equation that \( \frac{1}{r^2} \approx \frac{1}{(a+x)^2} \approx \frac{1}{a^2} \).

Then setting

\[
E + D - B\hbar l(l + 1) = E',
\]  

(12.50)

where \( B = \frac{\hbar}{2J} \) and \( J = m_{\text{red}}a^2 \), we reduce Eq. (12.49a) to the form

\[
u'' + \frac{2m_{\text{red}}}{\hbar^2} \left( E' - m_{\text{red}} \frac{\omega^2 x^3}{2} \right) u = 0
\]  

(12.51)

This equation is exactly the same as Eq. (10.14) for the harmonic oscillator, and, therefore,

\[
E' = \hbar \omega \left[ k + \frac{1}{2} \right],
\]  

(12.52)

where \( k = 0, 1, 2, 3, \ldots \)

\(^2\)The dissociation energy \((-D)\) is defined as the work required to split the molecule into atoms (neglecting the vibrational energy). This energy is usually of the order of several electron volts.
Thus, when we consider both the vibrational and the rotational motion, the energy of the molecule is

$$E = -D + Bh\ell (\ell + 1) + \hbar \omega (k + \frac{1}{2}). \quad (12.53)$$

The first term here represents the dissociation energy, while the second and third terms describe the rotation and vibration of the molecule, respectively.

We note that the molecule has only a finite number of discrete energy levels, since it is dissociated when

$$Bh\ell (\ell + 1) + \hbar \omega \left(k + \frac{1}{2}\right) \geq D.$$ 

Qualitatively, the dissociation of a molecule at large quantum numbers can be explained as follows. When $k \gg 1$, the amplitude of vibration may become so large that the atoms will in effect stop interacting over this distance and the molecule will cease to exist as a bound system. Moreover, if the orbital angular momentum numbers $l$ which characterize the rotational energy are too large, centrifugal forces can also split the molecule.

We shall now proceed to investigate the vibrational-rotational spectrum. We shall assume that the spectrum is determined primarily by the vibrational energy of the oscillations because its order of magnitude is larger than the rotational energy ($\lambda_{\text{vib}} \sim 10\mu$ and $\lambda_{\text{rot}} \sim 100\mu$). We must bear in mind that spontaneous transitions can occur only from higher to lower energy levels, that is, with a change from $k$ to $k - 1$ [in accordance with the selection rules, the quantum number $l$ may change to either lower ($l \rightarrow l - 1$) or higher ($l \rightarrow l + 1$) values]. Then for the frequency of the radiation

$$\omega' = \frac{E(k, l) - E(k - 1, \ell + 1)}{\hbar}$$

we obtain from (12.53)

$$\omega' = \omega_{\text{vib}}' = \omega_{\text{vib}}.$$ 

Here, in accordance with (12.34) and (12.35), we have $\omega_{l, l-1} = 2Bl$, $\omega_{l, l-1} = 2B(l + 1)$, and

$$\omega = \frac{E_k - E_{k-1}}{\hbar}.$$ 

Thus, two branches are obtained (see Fig. 12.5):

$$\omega' = \omega_{\text{vib}} = 2Bl \quad \text{and} \quad \omega = 2B(l + 1) \quad (12.55)$$
Such vibrational-rotational spectra are observed, for instance, in HCl and CO molecules, and the investigation of vibrational-rotational spectra is of great importance for the study of molecular structure. From these spectra it is possible to determine various properties of molecules, such as their moments of inertia and the isotopic composition (since the moments of inertia of two molecules consisting of different isotopes of the same element will be somewhat different).

![Vibrational-rotational spectrum of a diatomic molecule.](image)

To conclude this section, let us consider the spectrum of a molecule when one of the atoms is in an excited state. In this case the vibrational-rotational radiation is accompanied by the transition of one of the atomic electrons from an energy level \( n \) to a lower level \( n' \).

The energy of such a molecule can be written in the form

\[
E_M = E_n + E_k + E_i, \tag{12.56}
\]

where \( E_n \) is the energy of the excited atom. For hydrogen, \( E_n \) is given by the Balmer formula (see Chapter 2)

\[
E_n = -\frac{R \hbar}{n^2}. \tag{12.57}
\]

The energies of the vibrational and rotational motions are, respectively,

\[
E_k = -D + \hbar \omega \left( k + \frac{1}{2} \right) \tag{12.58}
\]

and

\[
E_i = B \hbar l (l + 1). \tag{12.59}
\]

As a result of the transition, the energy \( E_{M'} \) of the molecule changes and becomes equal to

\[
E_{M'} = E_{n'} + E_{k'} + E_{i'}. \tag{12.56a}
\]
Since the main part of the radiant energy is now due to the electronic transition $n \rightarrow n'$ in the atom, the quantum numbers $k$ and $l$ may either increase or decrease

$$k' = k \pm 1, \quad l' = l \pm 1. \quad (12.60)$$

Regardless of the changes in $k$ and $l$, the overall change in energy is a decrease because of the emission of radiation due to the electronic transition.

This case is characterized by a further important feature, namely, the strong dependence of the energy bonding the atoms in a molecule on the number of the particular shell in which the electron is located. Therefore, a transition causes a change in the bonding energy, which in turn leads to a change in the interatomic distance $a$. In transitions from an excited to the ground state the distance generally increases, together with the moment of inertia $J = m_r a^2$, whereas the quantity $B = \frac{n^2}{2J}$ decreases. Owing to the change $B \rightarrow B'$, there is an additional slight change in the rotational part of the energy, which now becomes

$$E' = B' hl' (l' + 1), \quad (12.59a)$$

where $B' < B$ in the present case.

Taking into account all possible vibrational and rotational transitions, we find that the frequency of radiation $\omega_{M} = \frac{E_M - E_{M'}}{h}$ is

$$\omega_{M} = \frac{E_n - E_{n'}}{h} + \omega + \omega_{l, l'}, \quad (12.61)$$

where

$$\omega_{l, l'} = Bl (l + 1) - B'l' (l' + 1). \quad (12.62)$$

With the notation $\omega_0 = \frac{E_n - E_{n'}}{h} - \omega$, we can write Eq. (12.61) as

$$\omega_{M} = \omega_0 + \omega_{l, l'}. \quad (12.61a)$$

Finally, we obtain three frequency branches for the molecular band spectra

$$\omega^+ = \omega_0 + \omega_{l, l'}, \quad (12.63)$$
$$\omega^- = \omega_0 + \omega_{l, l' - 1}, \quad (12.64)$$
$$\omega^0 = \omega_0 + \omega_{l, l}. \quad (12.65)$$

In these formulas the first or positive branch (the $R$ branch) corresponds to downward transitions between the rotational levels.
and the second or negative branch (the \( P \) branch) to upward transitions. The third branch (called the zero branch or \( Q \) branch) appears when there are no transitions between rotational levels; it is due entirely to changes in the moment of inertia caused by transitions within the atom.

Using Eq. (12.62) we can represent \( \omega^+ \), \( \omega^- \) and \( \omega^0 \) in the form

\[
\omega^+ = \omega_0 + (B - B') l^3 + (B + B') l, \tag{12.63a}
\]
\[
\omega^- = \omega_0 + (B - B') (l + 1)^3 - (B + B') (l + 1), \tag{12.64a}
\]
\[
\omega^0 = \omega_0 + (B - B') (l^2 + l). \tag{12.65a}
\]

These branches are depicted in Fig. 12.6, where the frequency is plotted along the abscissa and the orbital angular momentum quantum number \( l \) along the ordinate. It can be seen from this diagram that the superposition of the rotational lines \( \omega_{l, l'} \) on the electronic-vibrational line \( \omega_0 \) gives rise to a whole band of lines with a sharp edge on the left and a diffuse edge on the right. This is in complete agreement with the experimental facts.
Problem 12.1. Find the explicit form of the spherical harmonics for the cases when the orbital angular-momentum quantum number is \( l = 2 \) and \( l = 3 \). Verify their orthonormality by direct calculation. Plot a graph of \( |Y^m_3|^2 \) for \( m = 0, \pm 1, \pm 2 \).

Answer,

\[
Y^2_2 = \sqrt{\frac{5}{4\pi} \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)},
\]
\[
Y^2_0 = \pm \sqrt{\frac{15}{8\pi}} \sin \theta \cos \phi e^{\pm i\phi},
\]
\[
Y^2_2 = \pm \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{\pm 2i\phi},
\]
\[
Y^3_3 = \sqrt{\frac{7}{4\pi}} \left( \frac{5}{2} \cos^3 \theta - \frac{3}{2} \cos \theta \right),
\]
\[
Y^3_1 = \pm \frac{1}{4} \sqrt{\frac{21}{4\pi}} \sin \theta \cos \theta e^{\pm 2i\phi},
\]
\[
Y^3_3 = \pm \frac{1}{4} \sqrt{\frac{35}{4\pi}} \sin^3 \theta e^{\pm 2i\phi}.
\]

Problem 12.2. Find the eigenfunction of the operator \( L_x \), given that its eigenvalue is zero and the orbital angular momentum quantum number is \( l = 1 \).

Solution. Let us look for a solution of the equation for \( l = 1 \) and

\[ L_x \psi = 0 \]

in the form

\[ \psi = C_1 Y_1^1 + C_{-1} Y_1^{-1} + C_0 Y_0. \]

Using (11.88), with \( l = 1 \) and \( m = \pm 1, -1, 0 \), and applying the normalization condition

\[ \int \psi^* \psi \sin \theta d\theta d\phi = 1, \]

we find

\[ \psi = \frac{1}{\sqrt{2}} (Y_1^1 - Y_1^{-1}) = \sqrt{\frac{3}{4\pi}} \sin \theta \cos \phi. \]

Problem 12.3. Investigate the general form of the motion of a free particle in spherical coordinates. Determine the normalized functions for \( l = 0 \)(s states).

Solution. The Schrödinger equation for a free particle in spherical coordinates is written as

\[ \frac{1}{r} \frac{d}{dr} \left( \frac{dR}{dr} \right) + \left( \hbar^2 - \frac{l(l+1)}{r^2} \right) R = 0, \tag{12.66} \]

where

\[ \hbar^2 = \frac{2m \omega}{h^3}. \]

3 The problems in this chapter apply also to Chapter 11.
Introducing the new function \( \chi := \sqrt{r} R \), we transform Eq. (12.79) to

\[
\chi'' + \frac{1}{r} \chi' + \left( k^2 - \frac{(l + \frac{1}{2})^2}{r^2} \right) \chi = 0.
\]

The solution of this equation is a Bessel function of half-integral order. Since the wave function must remain finite as \( r \to 0 \), we retain only the Bessel function of the first kind. Then

\[
R = \text{const} \frac{J_{l + \frac{1}{2}}(kr)}{\sqrt{kr}},
\]

and for a free particle with a given energy the general solution of the wave equation in spherical coordinates can be written as

\[
\psi(k, r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} C_l^m Y_l^m(\theta, \varphi) \frac{1}{\sqrt{kr}} J_{l + \frac{1}{2}}(kr).
\]

In particular, for \( l = 0 \) (s state), we have

\[
R(k, r) = \frac{C}{r} \sin kr.
\]

Since the spectrum is continuous, this expression must be normalized by a \( \delta \) function

\[
\int_0^\infty R^*(k', r) R(k, r) r^4 dr = \delta(k - k').
\]

Hence, we find: \( C = \sqrt{\frac{2}{\pi}} \).

Problem 12.4. Find the selection rules for quadrupole radiation from a rotator.

Solution. It is necessary to find the transitions for which the matrix element of the quadrupole moment

\[
Q_{ss'} = \epsilon \int \psi_{l m}^* (3 x_s x_{s'} - a^2 \delta_{ss'}) \psi_{l m} d\Omega =
\]

\[
= \epsilon (3 \int x_s x_{s'} \psi_{l m}^* \psi_{l m} d\Omega - a^2 \delta_{ss'} \int \psi_{l m} \psi_{l m} d\Omega)
\]

does not vanish. Here

\[
x_s = \begin{cases} 1, 2, 3; x_s = z = \alpha \cos \theta, \\
x_{1,3} = \pm i \pm y = \alpha \sin \theta e^{\pm i \theta} = \frac{\pm \eta}{\eta}.
\end{cases}
\]

Since the matrix element of a bilinear combination can be expressed as the sum of the products of linear matrix elements (see Problem 10.4),

\[
(x_s x_{s'})_{l m m'} = \sum_{m'', l''} (x_s x_{s''})_{l'' m''} (x_{s'} x_{s''})_{l m m'},
\]

and, moreover, it follows from Eqs. (12.24), (12.25) and (12.26) that the only nonvanishing linear matrix elements are of the form

\[
\delta_{l', m', l, m}, \delta_{l, m + 1}, \delta_{l, m - 1}, \delta_{l', m', l, m},
\]

we obtain the following selection rules for the quadrupole radiation from a rotator:

\[
\Delta m = 0, \pm 1, \pm 2, \Delta l = 0, \pm 2.
\]
As we shall see later, the parity of a spherical harmonic is determined only by the value of \( I \) and is independent of \( m \) (see Chapter 17). Consequently, for dipole radiation, the only allowed transitions are from an odd state to an even state or vice versa (\( \Delta I = \pm 1 \)), whereas for quadrupole radiation, the transitions can occur only between even states or between odd states.

Problem 12.5. Expand the plane wave

\[ \psi = e^{ikz} = e^{i \theta \cos \theta} \]  

(12.69)
in terms of spherical waves.

Solution. Introducing the notation \( kr = y \) and \( \cos \theta = x \), let us look for a solution in the form of an expansion in Legendre polynomials

\[ e^{i \theta y} = \sum_{l=0}^{\infty} B_l(y) P_l(x). \]

Using the orthonormality condition for Legendre polynomials [see (11.68)], we find

\[ B_l = \left(l + \frac{1}{2}\right) \int_{-1}^{1} e^{i \theta y} P_l(x) \, dx. \]

Substituting the expression for the Legendre polynomials as given by Eq. (11.59) and transferring the derivative from the function \( (x^2 - 1)^l \) to the function \( e^{i \theta y} \), \( l \) times (that is, integrating by parts \( l \) times), we obtain

\[ B_l = \frac{1}{2l} \left(l + \frac{1}{2}\right) \int_{-1}^{1} (1 - x^2) e^{i \theta y} \, dx. \]

Using the well-known relation from the theory of Bessel functions\(^4\)

\[ \int_{-1}^{1} (1 - x^2) e^{i \theta y} \, dx = \sqrt{\pi} \frac{\Gamma\left(\frac{1}{2} + l\right)}{y^{1/2}} J_{l + 1/2}(y), \]

we determine the coefficients \( B_l \). The desired expansion of a plane wave in terms of the spherical waves is now written as

\[ e^{i \theta y} = \sqrt{\frac{\pi}{2}} \sum_{l=0}^{\infty} i^l (2l + 1) \frac{1}{\sqrt{kr}} J_{l + 1/2}(kr) P_l(\cos \theta). \]  

(12.70)

Let us emphasize that the plane wave \( e^{i \theta y} \) satisfies the Schrödinger equation for a free particle

\[ \nabla^2 \psi + \kappa^2 \psi = 0 \]

and, therefore, the right-hand side of Eq. (12.83) also represents a linear combination of particular solutions of the above equation written in spherical coordinates. This explains the expected proportionality between the coefficients \( B_l \) and the Bessel functions \( J_{l + 1/2}(kr) \).

\(^4\)See, for example, P. M. Morse and H. Feshbach, Methods of Theoretical Physics, part I, p. 572, McGraw-Hill Book Co.
Chapter 13

The Theory of the Hydrogen-like Atom
(Kepler's Problem)

The Bohr theory of the hydrogen-like atom (see Chapter 3) is
semiclassical in nature and can only provide a very incomplete
explanation of some of the basic properties of the atom. It does not
enable us to calculate the intensity of radiation emitted by an atom
or to construct a theory of an atom with more than one electron.
The wave-mechanical theory of the atom is able to deal with these
problems without any fundamental difficulties. The problem of the
hydrogen-like atom presents in addition a certain methodological
interest since it can be solved exactly, like the harmonic oscillator
and rotator problems. Mathematically this problem can be regarded
as a generalization of the classical problem of the motion of a
planet around the sun (Kepler's problem).

A. ENERGY EIGENFUNCTIONS AND EIGENVALUES

The energy of interaction between an electron and a nucleus

\[ V = -\frac{Ze_0^2}{r} \]  

depends only on the distance \( r \) between them. The problem of the
hydrogen-like atom—a single electron moving about a nucleus—is,
therefore, a typical example of motion in a central field of force.
If the origin of the coordinate system is at the center of the nucleus,
we may regard the angular part \( Y_l^m \) of the wave function as known
[see Eq. (11.67)] and find the energy levels and the radial part
\( R(r) \) from Eq. (11.21), which for the present case is written as

\[ \nabla^2 R + \frac{2m_e}{\hbar^2} \left( E + \frac{Ze_0^2}{r} - \frac{\hbar^2 l(l+1)}{2m_e r^2} \right) R = 0. \]  (13.2)
Let us introduce the effective potential energy of the electron

\[ V_{\text{eff}} = -\frac{Ze_0^2}{r} + \frac{\hbar^2 l(l + 1)}{2m_0r^2}, \]

where the first term represents the Coulomb interaction and the second the centrifugal forces.

![Graph of effective potential energy](image)

**Fig. 13.1.** The effective potential energy (solid line) as a function of distance.

\[ V_{\text{eff}} = -\frac{Ze_0^2}{r} + \frac{\hbar^2 l(l + 1)}{2m_0r^2}. \]

The dashed line shows the behavior of the wave function.

A graph of \( V_{\text{eff}} \) is given in Fig. 13.1. This graph shows that if the total energy of an electron is negative \( (E < 0) \), it moves within...

---

\(^1\)We shall attempt to interpret Eq. (13.3) from the standpoint of the classical theory, using the classical relationship

\[ \frac{p_r^2}{2m_0} = E - \left( -\frac{Ze_0^2}{r} + \frac{p_\theta^2}{2m_0r^2} \right). \]

Since \( p_\theta \) constant for central forces, we may write

\[ V_{\text{eff}} = -\frac{Ze_0^2}{r} + \frac{\hbar^2 l(l + 1)}{2m_0r^2}. \]

To generalize this expression for the quantum case, we must replace \( p_r^2 \) by its quantum-mechanical value \( \hbar^2 l(l + 1) \). In the same way we can regard the expression \( \frac{1}{2m_0} \left( \frac{\hbar^2}{i} \frac{\nabla}{r} \right)^2 \) in Eq. (13.2) as corresponding to the term \( \frac{p_r^2}{2m_0} \) in the classical theory.
a region bounded on both sides by potential barriers (the case of elliptic orbits in the classical analog), so that the energy spectrum will be discrete.

For $E > 0$, there is no barrier on the right ($r \to \infty$) and the position of an electron can range to infinitely large $R$ (the case of hyperbolic orbits in the classical analog). Since the electron's position in the atom must be bounded by a certain $r_{\text{max}}$ (elliptic orbits), it is necessary to assume that $E < 0$ in order to develop a theory of the atom. Accordingly, Eq. (13.2) becomes

$$\frac{d^2R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left\{ - A + \frac{2B}{r} - \frac{l(l+1)}{r^2} \right\} R = 0,$$

where

$$\frac{m_eZ^2}{\hbar^2} = B > 0 \quad \text{and} \quad -\frac{2m_eE}{\hbar^2} = A > 0.$$  \hspace{1cm} (13.5)

Introducing the new variable

$$\rho = 2 \sqrt{A} r,$$  \hspace{1cm} (13.6)

we obtain the equation

$$R'' + \frac{2}{\rho} R' + \left\{ - \frac{1}{4} + \frac{B}{\sqrt{A}\rho} - \frac{l(l+1)}{\rho^2} \right\} R = 0,$$  \hspace{1cm} (13.7)

where $R' = (dR/d\rho)$.

From the graph of $V_{\text{eff}}$, we can see the general nature of the solution. Clearly, inside the well ($r_{\text{min}} < r < r_{\text{max}}$) the solution will be oscillatory, whereas outside the well ($r \to 0$ and $r \to \infty$) there are two solutions (on each side): one that tends to zero and a second that tends to infinity. To make the solution an acceptable wave function, we must impose on it restrictions that will eliminate the solution that tends to infinity. Just as in the problem of the harmonic oscillator, it turns out that this requirement can be satisfied only for certain discrete values of the energy of the electron.

Since the potential well is not symmetric, we shall look for asymptotic solutions for $\rho \to 0$ and for $\rho \to \infty$ separately. The asymptotic solution for $\rho \to \infty$ may be found, according to Eq. (13.7), from

$$R_\infty^* - \frac{1}{4} R_\infty = 0,$$  \hspace{1cm} (13.8)

which gives

$$R_\infty = C_1 e^{-1/\rho} + C_2 e^{1/\rho}.$$  \hspace{1cm} (13.9)
To eliminate the exponentially increasing solution, we must set \( C_j = 0 \). Coefficient \( C_i \) can be included in the normalization coefficient of the wave equation and can, therefore, be set equal to unity. We then have

\[ R_\infty = e^{-t\sigma}. \quad (13.10) \]

The asymptotic solution for \( \rho \to 0 \) can be obtained from Eq. (13.7), which in this case reduces to the form

\[ R_0 + \frac{2}{\rho} R_0 - \frac{l(l+1)}{\rho^2} R_0 = 0, \quad (13.11) \]

Setting \( R_0 = \rho^q \), we find \( q(q+1) - l(l+1) = 0 \), and thus \( q_1 = l \), \( q_2 = -(l+1) \). Consequently,

\[ R_0 = C_1 \rho^l + C_2 \rho^{l+1}. \quad (13.12) \]

Setting \( C_2 = 0 \) (to exclude the solution increasing to infinity at \( \rho = 0 \)) and \( C_1 = 1 \), we obtain

\[ R_0 = \rho^l. \quad (13.13) \]

Equation (13.7) can be rewritten as

\[ \frac{d^2 p R}{dp^2} + \left\{ -\frac{1}{4} + \frac{B}{\rho \sqrt{A}} - \frac{l(l+1)}{\rho^2} \right\} p R = 0, \quad (13.7a) \]

and we assume its general solution to be of the form

\[ R = R_\infty R_{\psi u}. \quad (13.14) \]

In this case

\[ p R = p^{l+1} e^{-t\sigma} u = vu, \quad (13.15) \]

and for an unknown function \( u \) we obtain the equation

\[ u'' + 2u' \frac{v'}{v} + \left\{ \frac{v''}{v} - \frac{1}{4} + \frac{B}{\rho \sqrt{A}} - \frac{l(l+1)}{\rho^2} \right\} u = 0. \quad (13.16) \]

According to (13.15),

\[ \ln v = -t\sigma + (l+1) \ln \rho, \]

and, therefore,

\[ \frac{v'}{v} = (\ln v)' = -\frac{1}{2} + \frac{l+1}{\rho}, \text{ that is, } v' = \left( -\frac{1}{2} + \frac{l+1}{\rho} \right) v. \]
Furthermore, we have
\[ v'' = -\frac{l+1}{p^2} v + \left( -\frac{1}{2} + \frac{l+1}{p} \right) v, \text{ and } \frac{v''}{v} = \frac{1}{4} - \frac{l+1}{p} + \frac{l(l+1)}{p^2}. \]

Using these formulas, we transform (13.16) to
\[ \rho u'' + \left[ 2(l+1) - \rho \right] u' + \left[ \frac{B}{V} - l - 1 \right] u = 0, \quad (13.17) \]

If the behavior of the solution for \( R \) is to be determined at the origin and at infinity, by the asymptotic formulas (13.10) and (13.13), we must find the conditions under which the function \( u \) will be a finite polynomial of degree \( k \) without negative powers:
\[ u = \sum_{v=0}^{k} a_{v} r^{v}. \quad (13.18) \]

Substituting (13.18) into (13.17) and collecting powers of \( p \), we have
\[ \sum_{v=0}^{k} p^{v} \left[ a_{v} \left( \frac{B}{V} - l - 1 - v \right) + a_{v+1} [v(v+1) + 2(v+1)(l+1)] \right] = 0. \quad (13.19) \]

Since \( a_{k+1} = 0 \) and \( a_{k} \neq 0 \), we obtain
\[ \frac{B}{V} = k + l + 1 = n. \quad (13.20) \]

Here the quantum number \( n \), which is equal to the sum of the orbital angular momentum quantum number
\[ l = 0, 1, 2, 3, ... \]
and the radial quantum number
\[ k = 0, 1, 2, 3, ... \quad (13.21) \]
plus unity, is called the principal quantum number \( n \). It may assume the values
\[ n = 1, 2, 3, ..., \quad (13.22) \]

To determine the unknown coefficients \( a_{v} \) of the series (13.18), we derive a recurrence relation with the aid of Eqs. (13.19) and (13.20):
\[ a_{v}(k - v) = -a_{v+1}(v + 1)(v + 2l + 2). \quad (13.23) \]
Setting the coefficient of the highest power in (13.18) \( a_k = (-1)^k \) and calculating all the remaining coefficients with the help of (13.23), we obtain the following expression for the function \( u \):

\[
u = (-1)^k \left\{ r^k - \frac{k(k+s)}{1!} r^{k-1} + \frac{k(k-1)(k+s)(k+s-1)}{2!} r^{k-2} - \ldots \right\} = \sum_{j=0}^{k} (-1)^{k+j} r^{k-j} \frac{k!}{j!(k-j)!} \frac{(k+s)!}{(k+s-j)!}, \tag{13.24}
\]

where \( s = 2l + 1 \). The series (13.24) is an associated Laguerre polynomial \( Q^i_k(p) \) of order \( k \) and may also be represented in closed form:

\[
u = Q^i_k(p) = e^{s} \rho^{-s} \frac{d^k}{dp^k} (e^{-\rho \rho^{k+s}}). \tag{13.25}
\]

Thus, for the radial function \( R_{nl}(r) \) we finally obtain

\[
R_{nl}(\rho) = C_{nl} e^{-(l+\rho^k)} Q_{n-1}^{l+1}(\rho), \tag{13.26}
\]

where \( \rho = 2 \sqrt{A} r \). Recalling that \( \frac{B}{\sqrt{A}} = n \), and substituting the value of \( B \) from Eq. (13.5), we find

\[
\rho = \frac{2Z}{na_0} r, \tag{13.27}
\]

where \( a_0 = \frac{\hbar^2}{m a^2} \) is the radius of the first Bohr orbit. Calculating the coefficient \( C_{nl} \) from the normalization condition (see below), we obtain

\[
C_{nl} = \left( \frac{Z}{na_0} \right)^{l+s} \sqrt{\frac{4}{n(n-1)n(n+1)}}, \tag{13.28}
\]

---

2We shall show here that the function \( u \), written in the closed form (13.25), satisfies Eq. (13.17). The function \( v = e^{-\rho \rho^{k+s}} \) satisfies the equation \( \rho v' + (\rho - k - s)v = 0 \), as can be easily verified by taking the first derivative of \( v \) with respect to \( \rho \). Differentiating this equation \( k + 1 \) times according to Leibnitz's rule, we reduce it to the form

\[
\rho v^{(k+2)} + (\rho - s + 1)v^{(k+1)} + (k + 1)v^{(k)} = 0.
\]

Introducing the new function \( \omega = v^{(k)} \rho^{-s} \), we obtain the differential equation

\[
\omega'' + (s + 1 - \rho) \omega' + kw = 0,
\]

which is identical with Eq. (13.17) for the function \( u \) [since \( (B/\sqrt{A}) - l - 1 - k \)]. Since it can be readily shown that the coefficient of the leading term \( (\rho^k) \) of the function

\[
u = e^{s} \rho^{-s} \frac{d^k}{dp^k} (e^{-\rho \rho^{k+s}})
\]

is identical with the corresponding coefficient of (13.24), we have demonstrated that the relation (13.25) is correct.
Therefore, the radial wave function is

\[ R_{nl} = \left( \frac{Z}{na_0} \right)^{1/2} \sqrt{\frac{4}{n(n-l-1)! (n+l)!}} \left( \frac{2Zr}{na_0} \right)^l e^{-\frac{Zr}{na_0}} Q_{n-l-1}^{2l+1} \left( \frac{2Zr}{na_0} \right). \]  

(13.28a)

As we know, the normalization condition for the radial part of the wave function is

\[ \int_0^\infty r^2 R_{nl}^2 \, dr = 1. \]

Substituting the expression for \( R_{nl} \) from (13.26) and replacing \( r \) by \( \frac{na_0}{2Z} \rho \), in accordance with (13.27), we obtain

\[ C_{nl} \left( \frac{na_0}{2Z} \right)^3 \int_0^\infty e^{\frac{3l+3}{2} - \rho} Q_k^{2l+1} \, d\rho = 1. \]

Now let us represent one of the polynomials \( Q_k^{2l+1} \) as a series (13.24), leaving the other polynomial in the closed form (13.25). The normalization condition then becomes

\[ C_{nl} \left( \frac{na_0}{2Z} \right)^3 \int_0^\infty \rho (-1)^k \{ \rho^k - k (2l + 1) \rho^{k-1} - \ldots \} \, d\rho = 1. \]

Applying the theorem for the transfer of a derivative (see Chapter 7, Section C) to this equation, we find

\[ C_{nl} \left( \frac{na_0}{2Z} \right)^3 \int_0^\infty e^{-\frac{3l+3}{2} - \rho} \rho^{2l+k} \, d\rho = 1. \]

It is obvious that the remaining terms in the series representing the function \( Q_k^f \) vanish, since the order of the successive derivatives is higher than the corresponding powers of \( \rho \). Using the well-known integral

\[ \int_0^\infty e^{-\rho} \, d\rho = 1, \]

(13.29)

we obtain the expression (13.28) for \( C_{nl} \). In a similar fashion, we can determine the average value of \( (r^{-\nu}) \) \((\nu = 1, 2, 3, 4)\), which will be useful in the later development:

\[ \overline{(r^{-\nu})} = \int r^{-\nu} \psi_{nlm}^* r^{-\nu} \psi_{nlm} \, dx = \int_0^\infty R_{nl}^2 r^{-\nu+3} \, dr. \]

On the basis of the above equations we can rewrite this as

\[ \overline{(r^{-\nu})} = C_{nl} \left( \frac{na_0}{2Z} \right)^{3\nu} \int_0^\infty \rho^{-\nu+1} (-1)^k \{ \rho^k - k (2l + 1) \rho^{k-1} + \ldots \} \, d\rho = 1. \]
Setting \( v = 1, 2, 3 \) and 4 in the last expression, and using once again the theorem for the transfer of a derivative, we obtain after a few simple operations

\[
\begin{align*}
\langle r^{-2} \rangle &= \left( \frac{Z}{a_o} \right) \frac{1}{n^3}, \\
\langle r^{-3} \rangle &= \left( \frac{Z}{a_o} \right)^2 \frac{1}{n^3(l + 1/2)}, \\
\langle r^{-4} \rangle &= \left( \frac{Z}{a_o} \right)^3 \frac{1}{n^2l(l + 1/2)(l + 1)}, \\
\langle r^{-5} \rangle &= \frac{1}{2n^3} \left( \frac{Z}{a_o} \right)^4 \frac{3n^2 - 1}{l(l + 1)(l + 1/2)}.
\end{align*}
\]  

(13.29a)

In calculating \( r^{-1} \), we retain only the leading term \( r^k \) in the polynomial \( Q^k \). On the contrary, in calculating \( r^{-3} \), we retain only the last term \( r^0 \). For \( r^{-2} \), we retain the last two terms, and so on. The expressions for \( r^{-3} \) and \( r^{-4} \) are obtained under the assumption that \( l \neq 0 \). For the \( s \) states (\( l = 0 \)), interactions which are usually proportional to either \( r^{-2} \) or \( r^{-3} \) are generally replaced by a contact interaction (see below, Chapters 19 and 20).

To supplement this general treatment, we shall calculate the normalization coefficient of the wave function \( \psi_{nlm} = R_{nl}Y_l^m \) for the ground (or lowest) energy state, which is characterized by the quantum numbers

\[ n = 1, \ l = m = k = 0. \]

According to Eq. (12.9), the spherical harmonic \( Y_l^m \), is a constant for \( l = m = 0 \), as is the polynomial \( Q^{k+1}_l \) for \( k = 0 \). Consequently, from (13.26) we have for \( \psi_{100} \)

\[
\psi_{100} = Ce^{-\frac{Zr}{a_o}}, \quad (13.30)
\]

and, therefore, the normalization condition takes the form

\[
\int \psi_{100}^* \psi_{100} d^3x = \int \psi_{100}^* \psi_{100} r^2 dr d\Omega = 1. \quad (13.31)
\]

Substituting the explicit form of the wave function \( \psi_{100} \) and bearing in mind its independence of the angles \( \theta \) and \( \varphi \), we obtain

\[
C^2 4\pi \int_0^\infty e^{-\frac{2Zr}{na_o}} r^3 dr = 1. \quad (13.31a)
\]

Introducing the variable \( x = \frac{2Zr}{na_o} \) and using (13.29), we find

\[
C = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_o} \right)^{1/4}.
\]

The same value for \( C \) can also be obtained from the general equation (13.28) by setting \( n = 1 \) and \( l = 0 \). Therefore, the wave function for the ground state is
The energy spectrum of the hydrogen-like atom is found from Eqs. (13.20) and (13.5):

\[
E_n = -\frac{Z^2e^2}{2a_0n^2} = -\frac{R_0Z^2}{n^2},
\]

(13.33)

where \( R \) is the Rydberg constant

\[
R = \frac{e_0^4m_e}{2\hbar^3}.
\]

This expression for the energy, which we note is in complete agreement with the corresponding expression of the Bohr theory [see Eq. (2.50)], depends only on the principal quantum number \( n = l + k + 1 \) (that is, only on the sum of the orbital and radial quantum numbers \( l \) and \( k \)) and is independent of the magnetic quantum number \( m \). At the same time, the wave function \( \psi_{nlm} = R_{nl}Y_{l}^{m} \) depends on all three quantum numbers \( n, l \) and \( m \) individually. Consequently, it follows from the Schrödinger wave theory that the energy levels are degenerate. Since each value of \( l \) can vary from 0 to \( n - 1 \) and \( m \) can vary from \(-l\) to \(+l\) [see (13.20)], the degree of degeneracy is

\[
\sum_{l=0}^{n-1} \sum_{m=-l}^{l} 1 = \sum_{l=0}^{n-1} (2l + 1) = n^2.
\]

It was shown in Chapter 12 that the degeneracy with respect to \( m \) is characteristic of all central fields of force and is related to the fact that there is no preferred direction passing through the origin. The degeneracy with respect to the orbital angular momentum quantum number \( l \) appears, however, only in the case of pure Coulomb interaction. In most other centrally symmetric systems there is no \( l \) degeneracy; that is, the energy level for a given value of \( n \) is split into \( n \) sublevels corresponding to different \( l \).\(^3\) If the system is placed in an external field (for example, a magnetic field) which removes the central symmetry, the degeneracy with respect to \( m \) also disappears. In this case, the \( n \)th energy level is split into \( n^3 \) distinct sublevels.

\(^3\)In particular, as we shall see later, the degeneracy with respect to \( l \) vanishes even in the case of the hydrogen atom if we take into account the relativistic effects, the nuclear volume, and the so-called vacuum corrections. Similarly, in the spectrum of alkali metals, which have one valence electron in the outer shell, the influence of the electrons in the inner shell removes the degeneracy with respect to \( l \).
B. SEMICLASSICAL INTERPRETATION OF THE PRINCIPAL RESULTS OF THE QUANTUM-MECHANICAL THEORY OF THE HYDROGEN-LIKE ATOM

In classical theory the quantity
\[ \frac{1}{2m_0} p^2 = E + \frac{Ze^2}{r} - \frac{p^2_\phi}{2m_0r^2} \]  \hspace{1cm} (13.34)
[see (13.3a)] must be greater than zero. For elliptic orbits \((E = - E; < 0)\) it is seen that this is possible only when the radius \(r\) lies within certain limits \((r_{\text{min}} \leq r \leq r_{\text{max}})\) which can be found by setting the right-hand side of (13.34) equal to zero. Using the quantum-mechanical expression for the energy (13.33), we find

\[ r_{\text{max}} = \frac{n^2a_0}{Z} \left(1 \pm \sqrt{1 - \frac{p^2_\phi}{n^2\hbar^2}}\right). \]  \hspace{1cm} (13.35)

The equation of an ellipse in polar coordinates is
\[ r = \frac{p}{1 + \varepsilon \cos \varphi}, \]  \hspace{1cm} (13.36)

where the parameter \(p = \frac{b^2}{a}\) is defined as the ratio of the square of the semiminor axis \(b\) to the semimajor axis \(a\), and the eccentricity \(\varepsilon = \sqrt{\frac{a^2 - b^2}{a^2}}\) characterizes the elongation of the ellipse (for \(\varepsilon = 0\), the ellipse becomes a circle). From (13.36) we readily obtain equations for \(r_{\text{max}}\) and \(r_{\text{min}}\):

\[ r_{\text{max}} = a(1 + \varepsilon), \]
\[ r_{\text{min}} = a(1 - \varepsilon). \]  \hspace{1cm} (13.37)

Comparing Eqs. (13.37) with (13.35), we find

\[ \frac{n^2a_0}{Z} = a, \]  \hspace{1cm} (13.38)
\[ \sqrt{1 - \frac{p^2_\phi}{n^2\hbar^2}} = \varepsilon. \]  \hspace{1cm} (13.39)

We see that the classical analog of the quantity \(\frac{n^2a_0}{Z}\) turns out to be the semimajor axis of an ellipse whose eccentricity is given by Eq. (13.39).
Substituting into (13.39) the Bohr value of \( p_{\phi}^2 = \hbar^2 n_i^2 = \hbar^2 (l + 1)^2 \) and then the quantum-mechanical value of \( p_{\phi}^2 = \hbar^2 (l + 1) \), we obtain

\[
\varepsilon_B = \sqrt{1 - \frac{(l + 1)^2}{n^2}}, \tag{13.40}
\]

\[
\varepsilon_{\text{quan}} = \sqrt{1 - \frac{l(l + 1)}{n^2}}. \tag{13.41}
\]

From this it is clear that the eccentricity becomes exactly zero only in the Bohr theory \((l = n - 1)\). In wave mechanics, for \( l = n - 1 \) the eccentricity has a minimum nonzero value given by

\[
\varepsilon_{\text{quan}}^{\text{min}} = \sqrt{\frac{1}{n}}. \tag{13.42}
\]

This shows that in quantum mechanics, we can speak of the classical analog of states with circular orbits only when the quantum number \( l \) has the value \( n - 1 \). Furthermore, it should be noted that in the classical approximation, an \( s \) state \((l = 0)\) gives \( \varepsilon_{\text{quan}}^{\text{max}} = 1 \), which corresponds to a parabolic orbit. This case, however, cannot be associated with a parabolic orbit from the quantum-mechanical point of view. As we can see from Eq. (13.33), in quantum mechanics the energy is negative for all values of \( n \) (we recall that in the classical case the total energy is zero for parabolic orbits); consequently, the radius for \( l = 0 \) is limited only by its maximum value

\[
r_{\text{max}} = \frac{Ze_n^2}{|E|}. \]

This lack of agreement between the quantum-mechanical and classical solutions for the \( s \) state simply means that the case \( l = 0 \) has no classical analog.

In general, we are, of course, entitled to speak only of the probability of particular events in the context of wave mechanics. Therefore, all the results obtained from the Schrödinger theory must be interpreted in terms of probability considerations. Let us show, for instance, that the Bohr radius \( a = \frac{n^2 a_0}{Z} \) [see Eq. (13.38)] for the case of circular orbits \((l = n - 1)\) corresponds in wave mechanics to the most probable value of the position coordinate of the electron, \( r = a_0 \).

According to the normalization condition

\[
\int_0^{\infty} r^4 R_{nl}(r) dr = 1,
\]

the distribution of radial probability density \( D(r) \) is

\[
D(r) = r^4 R_{nl}^2. \tag{13.43}
\]
In the case of circular orbits, when \( l = n - 1 \) and \( k = 0 \), Eq. (13.43) gives

\[
D(r) = r^2 R_{n,n-1}^2. \tag{13.43a}
\]

According to Eqs. (13.25) and (13.26),

\[
R_{n,n-1} = \text{const} e^{-\frac{1}{2} \frac{1}{r} \rho^{n-1}},
\]

and, therefore, we find the following expression for \( D(r) \) (see Fig. 13.2):

\[
D(r) = \text{const} \ r^n e^{-\frac{2Zr}{na_0}}. \tag{13.44}
\]

Determining the value of \( r \) at which this function has a maximum:

\[
\left( \frac{\partial D(r)}{\partial r} \right)_{r=r_n} = 0,
\]

we obtain

\[
r_n = a = \frac{n^2}{Z} a_0. \tag{13.45}
\]

It is interesting to note that if we set \( Z = 1 \), the most probable radius \( r \) is the radius \( a_0 \) of the first Bohr orbit.

\[\text{Fig. 13.2. Radial probability density distribution function in the case of circular orbits.}\]

If the radial quantum number \( k \neq 0 \), the orbits can be said to be elliptical and the probability distribution \( D(r) \) assumes the form

\[
D(r) = \text{const} r^{2l+2} e^{-\frac{Zr}{na_0}} (Q_k^{2l+1})^2. \tag{13.46}
\]

The equation for the extremals of this function is

\[
\frac{\partial}{\partial r} (r^{2l+2} e^{-\frac{Zr}{na_0}} (Q_k^{2l+1})^2) = 0.
\]

\[
2l+2 \cdot r^{2l+1} e^{-\frac{Zr}{na_0}} (Q_k^{2l+1})^2 - \frac{Zr}{na_0} r^{2l+2} e^{-\frac{Zr}{na_0}} (Q_k^{2l+1})^2 = 0. \tag{13.47}
\]
Since $xQ^{d+1}_k$ is a polynomial of the $k$th degree, Eq. (13.47) has $k$ roots (not counting points $r = 0$ and $r = \infty$) and $k + 1$ maxima. This case is very similar to the probability distribution for the motion of a free particle inside a potential well (sinusoidal variation of the wave function, see Chapter 4) or for the motion of an oscillator (see Chapter 10, Fig. 10.2).

C. SELECTION RULES, EMISSION SPECTRA OF HYDROGEN-LIKE ATOMS

To determine the selection rules for hydrogen-like atoms (Kepler's problem), it is necessary to calculate the matrix elements

$$(r)_{n'l'm'}^{n'm'} = \int \psi_{n'l'm'}^* r \psi_{n'l'm'} d^3r.$$ \hspace{1cm} (13.48)

Substituting here $\psi_{n'l'm'} = Y_l^m R_{nl}$, we obtain

$$(r)_{n'l'm'}^{n'm'} = \int d\Omega (Y_l^m)^* r Y_l^m \int_0^\infty R_{nl'} r^3 R_{nl} dr.$$ \hspace{1cm} (13.48a)

As we know from Eqs. (12.24), (12.25) and (12.26), integration over the angles $\theta$ and $\phi$ gives the selection rules for the orbital angular momentum quantum numbers ($\Delta l = l - l' = \pm 1$) and the magnetic quantum numbers ($\Delta m = m - m' = 0, \pm 1$). Using these results we can write Eq. (13.48a) as

$$(r)_{n'l'm'}^{n'm'} = \text{const} \left[ \delta_{m',m} \delta_{l',l \pm 1} \right] \int_0^\infty R_{nl'} r^3 R_{nl} dr.$$ \hspace{1cm} (13.48b)

Evaluating the integral$^4$

$$\int_0^\infty r^3 R_{nl'} R_{nl} dr \sim \int_0^\infty r^{3+2l'+1} e^{-\frac{2Zr}{a_0}} \left( \frac{1}{n} + \frac{1}{n'} \right) Q_k^l \left( \frac{2Zr}{n' a_0} \right) \times$$

$$\times Q_{k'}^{l+1} \left( \frac{2Zr}{n a_0} \right) dr.$$ \hspace{1cm} (13.48c)

$^4$This integral can be evaluated by introducing the new variable $\rho = \frac{Zr}{a_0} \left( \frac{1}{n} + \frac{1}{n'} \right)$. Then, expressing $Q_k^l$ and $Q_{k'}^{l+1}$ in the form of polynomials, we can perform the integration term by term. It is found that only the integral

$$\int_0^\infty r^2 R_{nl'} R_{nl} dr = 0 \quad (n' \neq n)$$

vanishes because of the orthogonality condition.
it is easily shown that it does not vanish for any value of \( n' \); that is, for all allowed transitions the principal quantum number can change arbitrarily.

![Fig. 13.3. Spectral series of the hydrogen atom.](image)

The wavelengths corresponding to the indicated transitions are expressed in Angstrom units.

Having obtained the selection rules for the hydrogen-like atom, let us investigate its emission spectrum. We shall first introduce certain conventional symbols designating the energy levels of an atom. The spectral terms \((-E_n \hbar)\) which depend, in the general case, on both \( n \) and \( l \), are denoted by the symbol \((nl)\), that is,

\[
\left(-\frac{E_{nl}}{\hbar}\right) = (nl), \tag{13.49}
\]

where \( n = 1, 2, 3, \ldots \), and \( l \) is replaced by one of the letter symbols \( s, p, d, f, g, h, \ldots \) corresponding to \( l = 0, 1, 2, 3, 4, 5, \ldots \), as indicated in Chapter 12. Since the quantum number \( l \leq n - 1 \), the only possible terms are \( 1s, 2s, 2p, 3s, 3p, 3d; 4s, 4p, 4d, 4f; 5s, 5p, 5d, 5f, 5g; \) and so on.

\( n \) here cannot, for instance, be a \( 1p \) term, since in this case we would have \( n = 1 \) and \( l = 1 \), nor can there be a \( 3f \) term, since this would give us \( n = l = 3 \). The radiation frequencies expressed in term symbols \((nl)\) have the form
where it is necessary to bear in mind the selection rules for the orbital angular momentum quantum number \( l \), namely, \( l' = l \pm 1 \). Using Eq. (13.33), the term \((nl)\) can also be represented in the form

\[
(nl) = \frac{m_e e^4}{2\hbar^2} \frac{Z^2}{n^2} = \frac{R Z^2}{n^2},
\]

where \( R \) is the Rydberg constant \( R = \frac{m_e e^4}{2\hbar^2} \). We thus obtain the following equation for the radiation frequency \( \omega_{nn'}\):}

\[
\omega_{nn'} = R Z^2 \left( \frac{1}{n'^2} - \frac{1}{n^2} \right).
\]

In the case of the hydrogen atom \((Z = 1)\), the Lyman series (see Fig. 13.3), which corresponds to a transition to the lowest energy level \( n' = 1 \) (the \( 1s \) level), is given by

\[
\omega_{\text{Lyman}} = (1s) - (np) = R \left( \frac{1}{1^2} - \frac{1}{n^2} \right),
\]

where \( n = 2, 3, 4, \ldots \). For the Balmer series (see Fig. 13.4), which corresponds to a transition to the level \( n' = 2 \) from the levels \( n > 2 \), there are three types of allowed frequencies:

\[
\begin{align*}
\omega_{\text{Balmer}} &= (2s) - (np); \\
\omega_{\text{Balmer}}' &= (2p) - (ns); \\
\omega_{\text{Balmer}}'' &= (2p) - (nd).
\end{align*}
\]

Since the energy states of the hydrogen atom are degenerate with respect to the orbital quantum number, these three lines merge into one (see Fig. 13.3), and, consequently,

\[
\omega_{\text{Balmer}} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right).
\]

A similar result is obtained for the Paschen series, whose frequencies (see Fig. 13.3) are given by

\[
\omega_{\text{Paschen}} = R \left( \frac{1}{3^2} - \frac{1}{n^2} \right),
\]

where \( n = 4, 5, 6 \ldots \).
D. MOTION OF A PARTICLE IN A COULOMB FIELD
IN THE CASE OF A CONTINUOUS SPECTRUM

Although the wave function for a continuous spectrum can be expressed in terms of a confluent hypergeometric function, the usual procedure adopted in the investigation of the hyperbolic solution is to consider the asymptotic behavior of the hypergeometric function for large values of $r$. These asymptotic solutions can be obtained directly with the help of the quasi-classical WKB method. To investigate the hyperbolic orbits ($E > 0$), let us first use this approximation to obtain certain general results applicable to the case of central forces. According to Eqs. (11.21) and (11.51), the equation for the radial part of the wave function in the case of central forces is

$$u'' + \left(\frac{2m_0E}{\hbar^2} - \frac{2m_0}{\hbar^2} V(r) - \frac{l(l+1)}{r^2}\right)u = 0,$$

(13.57)

where

$$u = Rr.$$

(13.58)

In the WKB method, the potential energy $V(r)$ is required to decrease more slowly than $r^{-1}$ as $r \to 0$. Furthermore, we are entitled to choose the potential energy in such a way that

$$V(r = \infty) = 0.$$

Equation (13.57) has a singularity at the point $r \to 0$ associated with the term $l(l+1)r^{-1}$. The effective potential energy here forms a potential barrier of infinite height. Consequently, the asymptotic forms of the wave function which we obtained earlier for connecting the WKB solutions across a slowly varying potential barrier do not provide a good approximation in the present case. Therefore, in order to use the WKB method in the case of central forces, we must obtain either a different asymptotic expression in place of the Bessel functions of order $\nu$, or we must remove the singularity from the point $r = 0$ to the point $x = -\infty$ by introducing the new variable $x = \ln r$.

We shall use the second of these methods and introduce a new wave function $\chi(x)$:

$$u = e^{x/2} \chi(x).$$

(13.59)

Equation (13.57) then takes the form

$$\frac{d^2\chi}{dx^2} + e^{x/2}\left(\frac{2m_0E}{\hbar^2} - \frac{2m_0}{\hbar^2} V(e^x) - \left(l + \frac{1}{2}\right)e^{-2x}\right)\chi = 0,$$

(13.60)

to which the WKB method is applicable. For the argument $x$ which determines the asymptotic behavior of $\chi$ [see Eq. (5.55)], we obtain
THE THEORY OF THE HYDROGEN-LIKE ATOM

\[ z = \frac{1}{\hbar} \int e^x \sqrt{2m_0E - 2m_0V(e^x) - \hbar^2 \left(l + \frac{1}{2}\right)^2} e^{-2x} \, dx = \frac{1}{\hbar} \int |p| \, dx. \quad (13.61) \]

It should be noted that here \(|p|\) no longer represents the momentum.

Transforming back to the original independent variable \(r\), we obtain

\[ z = \frac{1}{\hbar} \int \sqrt{2m_0E - 2m_0V(r) - \hbar^2 \left(l + \frac{1}{2}\right)^2} \, dr. \quad (13.62) \]

From this it follows, in particular, that in using the quasi-classical expression for the one-dimensional radial equation, we must make the following change in the orbital angular momentum:

\[ l(l + 1) \rightarrow \left(l + \frac{1}{2}\right)^2. \quad (13.63) \]

Let us now apply Eq. (13.61) to the motion of a particle in a Coulomb field

\[ V(r) = -\frac{Ze^2}{r} \]

for the case of hyperbolic orbits \((E > 0)\). In the quasi-classical treatment of the problem, it is necessary to use the connected asymptotic solutions (5.66)–(5.69). This means that in our case [see (13.62)] we must evaluate the integral

\[ \int_{r_0}^{r} \frac{\sqrt{f(r)}}{r} \, dr = V f - V c \ln \frac{2c + br + 2 V_{\text{cf}}}{2c + br - 2 V_{\text{cf}}} + \]

\[ + \frac{b}{4 V a} \ln \frac{2ar + b + 2 V_{\text{af}}}{2ar + b - 2 V_{\text{af}}}, \quad (13.64) \]

where

\[ f = ar^2 + br + c, \quad (13.65) \]

and the value of \(r_0\) is found from the condition \(f(r_0) = 0\).

First let us determine the asymptotic solution of the wave function for \(r_0 \gg r \rightarrow 0\). Substituting

\[ c = \left(l + \frac{1}{2}\right)^2, \quad b = -\frac{2m_0Ze^2}{\hbar^2}, \quad a = -\frac{2m_0E}{\hbar^2} \]

into Eq. (13.64) and introducing the notation

\[ k = \frac{\sqrt{2m_0E}}{\hbar}, \quad \gamma = \frac{m_0 Ze^2}{\hbar^2 k} = \frac{Ze^2}{\hbar \omega}, \quad (13.66) \]
we obtain

\[ z = \frac{1}{\hbar} \int_{r}^{r_0} |p| \, d\ln r \approx -\left( t + \frac{1}{2} \right) \left( 1 - \ln \frac{2(t + \frac{1}{2})^2}{kr \sqrt{(t + \frac{1}{2})^2 + \gamma^2}} \right) + \]

\[ + \frac{\gamma + t(t + \frac{1}{2})}{2(t + \frac{1}{2})} \ln \frac{-\gamma + t(t + \frac{1}{2})}{-\gamma - t(t + \frac{1}{2})} = -\left( t + \frac{1}{2} \right) \ln kr + \text{const}. \]

On the basis of Eq. (5.51), the asymptotic solution for this case has the form

\[ \chi = \frac{1}{\sqrt{|p|}}(C_1 e^{-r} + D_1 e^r), \]

where

\[ |p| = \hbar \left( t + \frac{1}{2} \right) \]

in accordance with (13.61). Since, according to (13.58) and (13.59), the radial wave function \( R \) is related to \( \chi \) by the equation

\[ R = \frac{1}{\sqrt{r}} \chi, \quad (13.67) \]

we find

\[ R = C r^l + D r^{-(l+1)}. \]

In order for the solution to remain finite at the origin, we must set \( D = 0 \); that is, we choose the solution in the form

\[ R = C r^l, \quad (13.68) \]

which is in complete agreement with the asymptotic solution obtained by another method [see (13.13)].

For the other limiting case \( r \to \infty \), we have the following asymptotic solution [see (5.67) and (5.66)]:

\[ \chi_{r \to r_0} = \frac{\text{const}}{\sqrt{p}} \sin \left( z + \frac{\pi}{4} \right), \quad (13.69) \]

where, according to (13.61), \( p \) is equal to

\[ p = r\hbar k. \quad (13.70) \]

Equation (13.69) is an analytic extension of the asymptotic solution for \( r \to 0 \). To determine the quantity \( z \) from (13.62), we use the integral (13.64) with the following substitutions:
\begin{equation}
\begin{align*}
a = \frac{2m_eE}{\hbar^2}, \quad b = \frac{2m_eZe_a}{\hbar^2}, \\
c = -\left(1 + \frac{1}{2}\right)^3.
\end{align*}
\end{equation}

Then, since \(V \approx kr + \gamma\), we obtain at \(r \to \infty\)

\begin{equation}
z \approx kr + \gamma - \frac{i\left(l + \frac{1}{2}\right)}{2} \ln \frac{\gamma + i\left(l + \frac{1}{2}\right)}{\gamma - i\left(l + \frac{1}{2}\right)} + \gamma \ln \frac{2kr}{\sqrt{(l + \frac{1}{2})^3 + \gamma^2}}.
\end{equation}

We shall also make use of the relations

\begin{equation}
\ln\left(\gamma + i\left(l + \frac{1}{2}\right)\right) = \\
= \ln \sqrt{\gamma^2 + \left(l + \frac{1}{2}\right)^2} + i\left(\frac{\pi}{2} - \arctan \frac{\gamma}{l + \frac{1}{2}}\right),
\end{equation}

\begin{equation}
\ln\left(\gamma - i\left(l + \frac{1}{2}\right)\right) = \\
= \ln \sqrt{\gamma^2 + \left(l + \frac{1}{2}\right)^2} + i\left(\frac{3\pi}{2} + \arctan \frac{\gamma}{l + \frac{1}{2}}\right).
\end{equation}

Here, in writing the imaginary part, we took account of the fact that \(\gamma > 0\) and \((l + \frac{1}{2}) > 0\), and therefore the angle determining the imaginary part of the logarithm in Eq. (13.73) lies in the first quadrant, and the angle of the logarithm in Eq. (13.73a) in the fourth quadrant.

The expression for the argument \(z\) may now be transformed to

\begin{equation}
z = kr + \gamma \ln 2kr - \frac{\pi}{2} l - \frac{\pi}{4} + \delta_l,
\end{equation}

where the phase \(\delta_l\) is\(^5\)

\begin{equation}
\delta_l = -\left(l + \frac{1}{2}\right) \arctan \frac{\gamma}{l + \frac{1}{2}} - \gamma \ln \sqrt{(l + \frac{1}{2})^2 + \gamma^2} + \gamma.
\end{equation}

\(^5\)From a more accurate calculation (a calculation of the asymptotic expression for the argument \(z\) from an expansion of the confluent hypergeometric function), the following value is obtained for the phase \(\delta_l\) (see P. M. Morse and H. Feshbach, Methods of Theoretical Physics, Part II, New York: McGraw-Hill, 1953):

\begin{equation}
\delta_l = -\arg \Gamma(l + 1 + i\gamma).
\end{equation}

If \(|l + i\gamma| \gg 1\), then using Stirling's formula

\begin{equation}
\Gamma(1 + l + i\gamma) = |\Gamma(1 + l + i\gamma)| e^{-i\delta_l} = \sqrt{2\pi} \left(\frac{l + i\gamma + \frac{1}{2}}{e}\right)^{l + i\gamma + \frac{1}{2}},
\end{equation}

we obtain for the approximation (13.74a) \(\delta_l\).
In particular, when \( l = 0 \) and \( \gamma \gg 1 \), we may write as an approximation

\[
\delta_0 = \gamma (1 - \ln \gamma) - \frac{\pi}{4}.
\]

Hence, taking into account Eqs. (13.69), (13.67) and (13.70), we find

\[
R_l(k) = \frac{C \sin \left( kr - \frac{\pi}{2} l + \delta_l \right)}{r}.
\]  \hspace{1cm} (13.75)

Here \( C \) is the normalization coefficient, and the total phase is

\[
\delta_l = \delta_l^* + \gamma \ln 2kr.
\]  \hspace{1cm} (13.76)

Setting \( \gamma = 0 \) in (13.76), we obtain the asymptotic form of the radial function for the case of free motion:

\[
R_l^{(r=0)}(k) = \frac{C \sin \left( kr - \frac{\pi}{2} l \right)}{r}.
\]  \hspace{1cm} (13.77)

Thus the potential energy in a central field of force is taken into account by means of the phase shift

\[
\delta_l = - \int_{r_0}^{r} \sqrt{k^2 - \left(l + \frac{1}{2}\right)^2 r^{-2}} \, dr + \int_{r_0}^{r} \sqrt{k^2 - \frac{2m_e}{\hbar^2} V(r) - \left(l + \frac{1}{2}\right)^2 r^{-2}} \, dr,
\]  \hspace{1cm} (13.78)

where \( r_0 \) is the root of the first integrand.

In the special case of a Coulomb field, this phase is given by Eq. (13.76). The presence of the logarithmic term depending on \( r \) in the phase shift is the result of the long-range character of electrostatic forces, which can influence the particle even at very large \( r \).

The phase shifts \( \delta_l \) are functions not only of \( l \), but also of \( \hbar^2 \) (that is, of the energy \( E = \frac{\hbar^2 k^2}{2m_e} \)). They are an essential characteristic of the eigenfunctions of the continuous spectrum. The value of the phase shift cannot be found in a general form. The quantity \( \delta_l \) has to be determined separately for each specific problem, usually by approximation methods. The phase shifts are of particular importance in scattering problems, where they are used to express the effective cross sections (see Chapter 29).

The wave functions of a continuous spectrum are normalized in terms of a \( \theta \) function. The expression (13.75) for the wave function is valid practically in all space; there is only a small region near the center where this expression takes a somewhat different form.
In evaluating the coefficient $C$ we may, therefore, assume that Eq. (13.75) gives a correct expression for the wave function; that is, valid in all space. In this case, the wave function is normalized by the relation

$$ I = \int_0^\infty R_i(k) R_i(k') r^6 dr = \delta (k-k'). $$

We substitute the expression (13.75) for $R_i(k)$ and neglect the logarithmic term in the expression for the phase shift $\delta_i$ because it increases slowly compared with $r$. Consequently, we find

$$ I = \frac{C^2}{2} \int_0^\infty \cos r (k-k') dr - \frac{C^4}{2} \int_0^\infty \cos [r (k+k') - \pi l + 2\delta_i] dr \approx \frac{C^2}{2} \pi \delta (k-k'), $$

and the value of the normalization coefficient in the asymptotic solution for the central field of force is

$$ C = \sqrt{\frac{2}{\pi}}. \quad (13.79) $$

An energy level diagram for the hydrogen atom, showing both discrete levels and the continuous spectrum, is given in Fig. 13.3. This diagram clearly shows the degeneracy with respect to $l$, which results in a merging of all levels with the same $n$ into a single level.

Besides the ordinary transitions between discrete levels, two other processes can take place—ionization and capture. Basically, each of these processes is the reverse of the other. In ionization, an electron jumps from a discrete level ($E < 0$), such as, for example, the ground state, to the region of positive energies ($E > 0$) which forms a continuous spectrum (hyperbolic orbits). This process involves the absorption of energy. Conversely, in the process of electron capture, a free electron jumps into one of the possible discrete levels, at the same time liberating a corresponding amount of energy.

A certain amount of energy is required to transfer an electron from the ground state ($n=1$) to the region $E > 0$. This energy is given by (see Fig. 13.3)

$$ E^{\text{ion}} = T - E_i = R\hbar + T, $$

where $T = \frac{m_e v^2}{2}$ is the kinetic energy of an electron which is no longer bound to the nucleus. The energy $E^{\text{ion}}$ represents the ionization energy of the atom. It is at its minimum when $T = 0$; this corresponds to the minimum energy ($E = 0$) transition of an electron.
from the level \( n = 1 \) to the continuous spectrum. As a result of this transition, the electron can leave the atom. For the hydrogen atom

\[
E_{\text{min}}^{\text{ion}} = R \hbar = \frac{e^2}{2a_0} = 13.59 \text{ ev.}
\]

**E. CALCULATION OF THE EFFECTS OF THE MOTION OF THE NUCLEUS**

In developing the theory of hydrogen-like atom; we have until now ignored the motion of the nucleus. Accordingly, our theory is rigorous only for the case of infinitely large nuclear mass. In general, this is a relatively rough approximation, particularly in the case of light elements such as hydrogen and helium. By taking into account the motion of the nucleus, it is possible to explain a number of important experimental facts.

We shall allow for the effects of the nuclear mass \( M \) in the same way as we did in our discussion of the spectra of diatomic molecules (Chapter 12), replacing everywhere the electron mass \( m_e \) by the reduced mass

\[
m_{\text{red}} = \frac{m_e}{1 + \frac{M}{m_e}} \approx m_e \left( 1 - \frac{m_e}{M} \right). \tag{13.80}
\]

The Rydberg constant then becomes

\[
R_M = \frac{m_{\text{red}} e^2}{2 \hbar^2} = R_\infty \left( 1 - \frac{m_e}{M} \right). \tag{13.81}
\]

As a consequence of this change, the term values are slightly shifted:

\[
(nl) = \frac{Z^2 R_\infty}{n^2} \left( 1 - \frac{m_e}{M} \right). \tag{13.82}
\]

The radiation frequency is therefore given by the relationship

\[
\omega_{nn'} = Z^2 R_\infty \left( 1 - \frac{m_e}{M} \right) \left( \frac{1}{n'^2} - \frac{1}{n^2} \right), \tag{13.83}
\]

which differs from the previous one [see Eq. (13.52)] by the factor

\[
\left( 1 - \frac{m_e}{M} \right).
\]

Since the frequency of the radiation depends on the nuclear mass \( M \), atomic weights can also be determined by spectroscopic methods, as well as by conventional chemical methods. One successful outcome of the application of the spectroscopic method was the
proof of the existence of heavy hydrogen and ionized helium. Previously, the average atomic weight of hydrogen (relative to oxygen) was found by chemical means. The mass spectrograph made it possible to measure the atomic weight of each atom. These measurements gave somewhat different values for the atomic mass:

\[
\frac{M_{\text{chem}} - M_{\text{spec}}}{M_{\text{chem}}} \times 100\% \approx 0.0145\%.
\] (13.84)

This led Birge and Menzel to predict the existence of a hydrogen isotope, called deuterium or heavy hydrogen, with an atomic weight twice that of hydrogen (D=\(\text{H}_2\)). The presence of deuterium in natural hydrogen explains the greater atomic weight obtained in chemical measurements. The mass spectrograph measures the atomic weight of \(\text{H}_1\) along, while the spectral lines of \(\text{H}_2\) atoms fall at a different place on the scale.

Deuterium, like hydrogen, can enter into reactions forming, for example, heavy water \(\text{D}_2\text{O}\), discovered by Urey and Osborn in 1932. Deuterium is usually obtained via the electrolytic decomposition of water. The rate of evolution of ordinary hydrogen, at the cathode, greatly exceeds the rate of evolution of deuterium; thus, the concentration of deuterium in the residual electrolyte increases. (It is almost impossible to detect deuterium in natural water because of its low concentration.) The presence of deuterium was confirmed by spectroscopic studies which showed that not only does the Balmer series \((n' = 2)\) consist of the lines

\[
\omega_{\text{Balmer}}^{\text{H}} = R_{\infty} \left(1 - \frac{1}{1840}\right) \left(\frac{1}{n^2} - \frac{1}{n'^2}\right),
\] (13.85)

but that each of these lines is associated with a second line situated somewhat to the right. This second series of lines (see Fig. 13.5) is described by the equation\(^6\)

\[
\omega_{\text{Balmer}}^{\text{D}} = R_{\infty} \left(1 - \frac{1}{3630}\right) \left(\frac{1}{n^2} - \frac{1}{n'^2}\right),
\] (13.86)

\(^6\) According to the latest experimental data,

\[
R_{\infty} = 2\pi c \cdot 109737, \quad R_{\text{H}} = 2\pi c \cdot 109678, \quad R_{\text{D}} = 2\pi c \cdot 109707,
\]
where the numbers represent the values of \(R_{sp}\) (see footnote, page 20).
which can be readily obtained from (13.83) by setting the mass $M$

equal to twice the mass of the hydrogen nucleus and substituting $Z = 1$. It is worth noting that the large relative difference between the masses of the deuterium and hydrogen atoms causes far greater differences in their physical and chemical properties than is usual with isotopes of other elements. Thus, although heavy water outwardly resembles ordinary water, its melting and boiling points are $3.81 \degree C$ and $101.4 \degree C$, respectively, its viscosity is greater and it is a poorer solvent for salts. With the development of nuclear physics, heavy water has become particularly important because it is a good moderator for fast neutrons, and can also be used as a source of deuterium.

At present, we know of a third hydrogen isotope, namely tritium ($T = ^1H^3$), whose nucleus consists of two neutrons and one proton. It forms a compound with oxygen similar to water. The ratio of tritium atoms to $^1H^1$ atoms in natural water is approximately $10^{-18}$, whereas the ratio of $^1D^2$ atoms to $^1H^1$ atoms is $1/6800$. In a mixture with deuterium, tritium is a very important substance for the production of thermonuclear reactions: the reaction between $^1D^2$ and $^1T^3$ nuclei leads to the formation of $^4He$ and one neutron. Each such reaction releases more than 17 Mev of energy. Tritium is also a beta emitter (with a half-life of 12 years) and consequently is widely used as a radioactive indicator in chemical and biological investigations. The positions of spectral lines of tritium are slightly displaced relative to the hydrogen and deuterium lines (see Fig. 13.5) and are given by the equation

$$\omega_{Balmer} = R_{\infty} \left(1 - \frac{1}{5520}\right) \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$  \hspace{1cm} (13.87)

Another very important consequence of accounting for the motion of the nucleus was the discovery of ionized helium, first detected in spectroscopic studies of the sun. The solar spectrum was found to contain a series of lines, with positions described by the equation

$$\omega_{2n_1} = R \left(\frac{1}{n_1^2} - \frac{1}{n_1^4}\right),$$  \hspace{1cm} (13.88)

\footnote{Energy is released in the fusion of deuterium and tritium into helium, just as in the fission of $^{235}U$ or $^{239}Pu$ under neutron excitation. Fusion, however, is possible only if the potential barrier of the Coulomb repulsion between the D and T nuclei is overcome. High temperatures ($\sim 10^8$ degrees) are therefore required if this reaction is to be self-sustaining, whereas in the case of fission even low-energy neutrons can easily penetrate the nucleus, and that even at low temperatures. To obtain a thermonuclear reaction, a mixture of deuterium and tritium must first be heated to a temperature of tens of millions of degrees. Such temperatures may be created in an atomic explosion.}
where \( n_1 \) takes the values

\[
n_1 = \frac{5}{2}, \ 3, \ \frac{7}{2}, \ 4, \ \frac{9}{2}, \ldots. \tag{13.89}
\]

This series is, in effect, the Balmer hydrogen series \((n_1 = 3, 4, 5, \ldots)\) with a number of intermediate lines, which form the so-called Pickering series, characterized by the half-integral quantum numbers \( n_1 = 5/2, 7/2, 9/2, \ldots \). At first, the Pickering series was explained by assuming that hydrogen was in a special state in the Sun, so that the quantum number \( n \) could assume half-integral values. The spectral lines, however, were later found to be located further to the right than is indicated by Eq. (13.89), and consequently this assumption had to be abandoned. The second hypothesis assumed that the observed spectrum arises from singly ionized helium \((^1\text{He}^+)\), whose nuclear mass is \( M = 7360m_0 \) and whose charge is \( Z = 2 \). According to (13.83), its radiation frequencies then are

\[
\omega_{\text{He}} = 2^2R_{\text{He}} \left( \frac{1}{n_1^2} - \frac{1}{n^2} \right). \tag{13.90}
\]

Setting \( n' = 4 \), we reduce (13.90) to the form

\[
\omega_{\text{He}} = R_{\text{He}} \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \tag{13.91}
\]

where \( n = 5, 6, 7, 8, \ldots \).

To answer the question of whether the Pickering series was due to the radiation of hydrogen atoms (under the assumption that the quantum numbers may assume half-integral values) or to the radiation of ionized helium atoms (with the usual integral values of the quantum numbers), it was necessary to find an experimental value of the Rydberg constant. In the case of hydrogen,

\[
R_{\text{H}} = R_\infty \left( 1 - \frac{1}{1840} \right), \tag{13.92}
\]

whereas for helium

\[
R_{\text{He}} = R_\infty \left( 1 - \frac{1}{7360} \right). \tag{13.93}
\]

Careful spectroscopic studies confirmed that the Rydberg constant has the value (13.93), and thus it was shown that the Pickering series represents the spectrum of ionized helium.
Problem 13.1. Starting with Eqs. (13.26) and (13.28), show that the radial wave functions $R_{nl}$ for the principal quantum numbers $n = 1, 2$ and 3 are as follows:

$$R_{1s} = 2Ne^{-\eta^2/2},$$

$$R_{2s} = \frac{1}{2 \sqrt{2}} Ne^{-\eta^2/2} (2 - \eta),$$

$$R_{1p} = \frac{1}{2 \sqrt{6}} Ne^{-\eta^2/2} \eta,$$

$$R_{3s} = \frac{1}{9 \sqrt{3}} Ne^{-\eta^2/2} (6 - 6\eta + \eta^2),$$

$$R_{1d} = \frac{1}{9 \sqrt{6}} Ne^{-\eta^2/2} (4 - \eta),$$

$$R_{3p} = \frac{1}{9 \sqrt{30}} Ne^{-\eta^2/2} \eta^2,$$

where

$$N = \left( \frac{Z}{\alpha_0} \right)^{1/2} \text{ and } \eta = \frac{2Zr}{n\alpha_0}. $$

On the basis of these specific examples, show that the functions $R_{nl}$ are orthonormal, that is,

$$\int_0^\infty r^2 R_{nl} R_{n'l} dr = \delta_{nn'}.$$

Hint. In proving orthonormality, make use of the fact that at different $n$ and $n'$, the corresponding values for $\eta$ also differ from one another.

Problem 13.2. Show that the average electrostatic potential produced by a hydrogen-like atom in the ground state is

$$\Phi = e_0 \left( \frac{Z - 1}{r} \right) + e_0 \left( \frac{Z}{\alpha_0} + \frac{1}{r} \right) e^{-2Zr/\alpha_0} \left( \alpha_0 = \frac{\hbar^2}{m_e e_0^2} \right).$$

Hint. Find the average electrostatic potential produced by the electron $\Phi_1 (r) = -e_0 \int \frac{1}{r - \prime} \psi (r') \psi (r') d^3r'$ and add it to the potential of the nucleus. Integrating over the solid angle $\Omega'$, use the identity

$$\int \frac{dQ'}{|r - r'|} = 4\pi \begin{cases} \frac{1}{r} & r < r', \\ \frac{1}{r'} & r > r. \end{cases}$$

Problem 13.3. Show that at $Z = 1$, the maximum of the probability density distribution $D = r^2 R^2$ in the states $1s$, $2p$ and $3d$ occurs at distances of $a_0$, $4a_0$ and $9a_0$ from the nucleus (circular orbits). Why do the $2s$, $3s$ and $3p$ states have several maxima (see Fig. 13.6)?
Problem 13.4. Using the functions given in Problem 13.1, verify the following equations for \( n = 1, 2 \) and 3:

\[
\bar{r}^2 = \left( \frac{n^2 a_0}{Z} \right)^2 \left[ 1 + \frac{1}{2n^2} + \frac{3}{2} \left( 1 - \frac{l(l+1)}{n^2} \right) \right],
\]

and

\[
\bar{r} = \frac{n^2 a_0}{Z} \left[ 1 + \frac{1}{2} \left( 1 - \frac{l(l+1)}{n^2} \right) \right].
\]

Find the spread \((\Delta r)^2 = \bar{r}^2 - \bar{r}^2\) of the radial deviations for these states.

On the basis of Fig. 13.6 and the uncertainty principle, explain why \((\Delta r)^2\) does not vanish for circular orbits in the quantum theory.

Problem 13.5. By means of the quasi-classical WKB method, find the discrete energy spectrum of the hydrogen-like atom.

Solution. According to (5.75) and (13.62), the eigenvalues of the discrete spectrum \((E < 0)\) may be found from the equation

\[
l = \int_{r_1}^{r_2} \sqrt{\frac{2B}{r^2} - \left( \frac{l + \frac{1}{2}}{r^2} \right)^2} \, dr = \pi \left( k + \frac{1}{2} \right),
\]

where \(r_1\) and \(r_2\) are roots of the integrand and

\[
A = -\frac{2m_0 E}{\hbar^2}, \quad B = \frac{m_0 Z e^2}{\hbar^2}.
\]

Since the value of this integral is\(^8\)

\[
l = \pi \left( \frac{B}{\sqrt{A}} - l - \frac{1}{2} \right),
\]

we obtain exactly the same expression for the energy of the hydrogen-like atom as via the Schrödinger theory.

\(^8\)This integral can be easily evaluated from (13.64) by setting \(a = -A, \ b = 2B\) and \(c = -(l + 1/2)^2\), and regarding \(r_1\) and \(r_2 > r_1\) as roots of the equation \(f(r) = 0\). The logarithm of the complex quantity \([\text{assuming that } a \text{ tends to zero from the direction of positive numbers } (a = +0)]\) may be taken as:

\[
\ln (\beta + i\alpha) = \ln |\beta| + \begin{cases} i0 & \beta > 0, \\ i\pi & \beta < 0. \end{cases}
\]

\[
\ln (\beta - i\alpha) = \ln |\beta| + \begin{cases} i2\pi & \beta > 0, \\ i\pi & \beta < 0. \end{cases}
\]
Problem 13.6. Determine that magnetic field intensity at the center of the hydrogen atom which is due to the orbital motion of an electron. Find its numerical value for the $2p$ state.

Answer. $H_x = H_y = 0,$

$$H_z = -m e_0 h \left( \frac{m_0 e_0^2}{\hbar^2} \right)^3 \frac{1}{n^2 (l + \frac{1}{2})(l + 1)}.$$ 

For the $2p$ state ($m = 1$)

$$H_z \sim 10^4 \text{ gauss.}$$

Hint. Take the classical expression $H = -\frac{e_0}{m_0 c r^3} \mathbf{r} \times \mathbf{p}$ for the intensity of the magnetic field produced by a moving charge. Transform to a quantum treatment of the problem by replacing $\mathbf{r} \times \mathbf{p}$ by the angular momentum operator $\mathbf{L}$. Then, using Eq. (13.29a), calculate the average value of $\mathbf{H}$. 

A. BASIC PRINCIPLES OF THE PERTURBATION TREATMENT OF PROBLEMS

A relatively large number of problems in quantum mechanics cannot be solved exactly with present-day mathematical methods. Thus, various approximate calculations have to be used. One of the most widely used approximations is the perturbation theory method, which was first developed to handle problems in celestial mechanics. It is well known that in Newtonian mechanics it is possible to solve exactly only the two-body problem (for example, the Earth-Sun or the Moon-Earth problems). We cannot, however, neglect interplanetary forces and consider only the attraction of the planets by the Sun since many delicate phenomena are associated with these additional interactions (it is worth recalling in this connection that Leverrier predicted the existence of Neptune on the basis of the orbital deviations of Jupiter, after which the planet was discovered by astronomers). It thus became necessary to consider the many-body problem, which has no exact solution in classical mechanics. In celestial mechanics it was found that the perturbation problems could be handled by means of an approximation based on the fact that the forces between the planets are much smaller than the force of attraction to the Sun. In this method, one starts by solving the two-body problem (the zero-order approximation), then takes the "perturbation" into account and finds the correction to the solution (the first-order approximation). In other words, the "perturbation method" involves taking the principal forces acting on a body, finding the rigorous solution for these forces, and then taking the "perturbing" forces into account.

Similarly, in the quantum-mechanical treatment of the motion of several electrons in an atom, it is necessary to consider first the principal forces, such as, for example, the force between the nucleus and an electron. In this case, the perturbing forces may be taken to be the Coulomb forces of mutual repulsion between the electrons. In the problem of an atom subjected to an external electric or magnetic field whose strength is small relative to the electric field of the nucleus, the perturbation may be taken to be the energy of the electron in the external field.
We shall now develop the perturbation theory in a form suitable for stationary problems, that is, problems in which the Hamiltonian of the system does not depend on time. Suppose the Hamiltonian has the form

$$ H = T + V = T + V^0 + V', \quad (14.1) $$

where the perturbation energy $V' \ll V^0$, and the main part of the potential energy $V^0$ is chosen in such a manner that the Schrödinger equation of the system

$$ (E - H) \psi = 0 \quad (14.2) $$

has an exact solution, characterized by $E_0$ and $\psi_0$, when the perturbation $V'$ is neglected. Setting $T + V^0 = H^0$ (the zero-order approximation) and using Eq. (14.1), we can write (14.2) as

$$ (E - H^0 - V') \psi = 0. \quad (14.2a) $$

The basic problem in perturbation theory is to calculate from this equation the energy values $E_n$ and the corresponding eigenfunctions $\psi_n$. The solutions are sought in the form of the series

$$ \psi = \psi_0 + \psi' + \psi'' + \ldots, \quad (14.3) $$

$$ E = E_0 + E' + E'' + \ldots, \quad (14.4) $$

where $\psi'$ and $E'$ are terms of the first order of smallness relative to $\psi_0$; $E_0$, $\psi''$ and $E''$ are terms of the second order of smallness; and so on.

As a rule, the perturbation energy $V'$ can be represented in the form of a potential energy of the same order as $V_0$, multiplied by some small parameter $\lambda (\lambda \ll 1)$. The solutions (14.3) and (14.4) should then appear as expansions in terms of $\lambda$. Thus, $E_0$ and $\psi_0$ will be independent of this parameter, $E'$ and $\psi'$ will be proportional to $\lambda$, $E''$ and $\psi''$ to $\lambda^2$, and so on. In the expressions for $\psi$ and $E$, let us restrict ourselves to terms of the first order of smallness (that is, we shall retain only terms which are independent of $\lambda$ or directly proportional to $\lambda$). Substituting (14.3) and (14.4) into (14.2a), we obtain the following equation for $\psi'$ and $E'$:

$$ (E^0 + E' - H^0 - V') (\psi_0 + \psi') = 0. \quad (14.2b) $$

Collecting terms of the same order, we have

$$ (E^0 - H^0) \psi_0 + [(E' - V') \psi_0 + (E^0 - H^0) \psi'] + (E' - V') \psi' = 0. \quad (14.2c) $$
Equation (14.2c) may be regarded as an exact equation, since we have not neglected any terms in it, and since \( \psi \) and \( E' \) may be taken to represent the sums of all terms of different orders of smallness (that is, \( \psi \to \psi + \psi'' + \ldots \), \( E' \to E' + E'' + \ldots \)). To obtain the first-order approximation of perturbation theory, we neglect the second-order term \( (E' - V') \psi \) in (14.2c) and use the equation for the zero-order approximation

\[
(E^0 - H^0) \psi^0 = 0. \tag{14.5}
\]

This equation yields the zero-order eigenvalues

\[
E^0_1, E^0_2, E^0_3, \ldots, E^0_n, \ldots,
\]

and eigenfunctions

\[
\psi^0_1, \psi^0_2, \psi^0_3, \ldots, \psi^0_n, \ldots,
\]

which are connected by the relationship

\[
(E^0_n - H^0) \psi^0_n = 0. \tag{14.6}
\]

Keeping all this in mind, we shall now investigate the equation for the first-order approximation of perturbation theory

\[
(E^0 - H^0) \psi' = -(E' - V') \psi^0. \tag{14.7}
\]

We assume that at the beginning, the system is in the quantum state \( n' = n \). Since \( E^0 = E_n \) and \( \psi' = \psi_n^0 \) in the zero-order approximation, and \( E' = E_n' \) and \( \psi' = \psi_n' \) in the first-order approximation, Eq. (14.7) becomes

\[
(E^0_n - H^0) \psi_n' = -(E_n' - V') \psi_n^0. \tag{14.7a}
\]

We recall that an arbitrary function can be expanded in a series of orthonormal functions forming a complete set and satisfying the same boundary conditions as the original function; therefore, we may assume the solution for \( \psi_n' \) to be of the form

\[
\psi_n' = \sum_{n'} C_{n'n} \psi_n^0. \tag{14.8}
\]

Our problem, therefore, reduces to determination of the unknown coefficients \( C_{n'n} \) of a generalized Fourier series. Substituting (14.8) into (14.7a), we have

\[
\sum_{n'} C_{n'n} (E^0_n - H^0) \psi_n^0 = -(E_n' - V') \psi_n^0, \tag{14.9}
\]
or, taking into account (14.6), we find

$$\sum_{n'} C_{n'} (E_n^0 - E_{n'}^0) \psi_n^0 = -(E_n^0 - V') \psi_n^0. \quad (14.9a)$$

C. NONDEGENERATE CASE

Let us suppose that the system is nondegenerate. Therefore, each energy eigenvalue \(E_n^0\) corresponds to one and only one eigenfunction \(\psi_n^0\). Then, multiplying Eq. (14.9a) on the left by \(\psi_n^0*\) and integrating over all space, we have

$$\sum_{n'} C_{n'} (E_n^0 - E_{n'}^0) \delta_{nn'} = -E_n^0 + \int \psi_n^0* V' \psi_n^0 d^3x. \quad (14.10)$$

In obtaining this equation, we have made use of the orthonormality of the eigenfunctions \(\psi_n^0\):

$$\int \psi_n^0* \psi_{n'} d^3x = \delta_{nn'}.$$

Since the left-hand side of Eq. (14.10) is equal to zero (\(E_n^0 - E_{n'}^0 = 0\) for \(n' = n\), and \(\delta_{nn'} = 0\) for \(n' \neq n\)), the energy correction \(E_n^0\) is

$$E_n^0 = \delta_{nn}, \quad (14.11)$$

where

$$V'_{nn} = \int \psi_n^0* V' \psi_n^0 d^3x. \quad (14.11a)$$

Thus, the energy correction \(E_n^0\) of the system quite naturally turns out to be equal to the average value of the perturbation energy \(V'\).

It is worth noting that the expression (14.11) for the energy correction \(E_n^0\) was obtained by setting the left-hand side of Eq. (14.7a) equal to zero after it had been multiplied by \(\psi_n^0*\) and integrated over all space. Since \(\psi_n^0*\) is a solution of the homogeneous equation (14.6), it follows that the right-hand side of the inhomogeneous equation

$$M \psi = f \quad (14.12)$$

is orthogonal to the solution of the corresponding homogeneous equation \(M \psi' = 0\), that is,

$$\int \psi^0* f d^3x = 0. \quad (14.13)$$
Let us now proceed to determine the wave functions (that is, the coefficients $C_n$) of the Schrödinger equation (14.7a) in first-order perturbation theory. We write Eq. (14.9a) as

$$\sum_{n''} C_{n''}(E_n - E_{n''}) \phi^o_{n''} = -(E_n - V) \phi^o_n.$$  

Multiplying on the left by $\phi^o_{n'} (n' \neq n)$, using the orthonormality condition, and integrating over all space, we obtain

$$C_{n'} = \frac{V_{n'n}}{E_n - E_{n'}}. \quad (14.14)$$

where

$$V_{n'n} = \int \phi^o_{n'} V \phi^o_n d^3x. \quad (14.15)$$

Thus, for $\psi_n'$ we have

$$\psi_n' = C_n \phi^o_n + \sum_{n'} C_n' \phi^o_{n'}, \quad (14.16)$$

where the prime on the summation symbol indicates that the sum is taken over all $n'$ except $n' = n$. Finally, the as yet undetermined coefficient $C_n$ of the zero-order wave function can be found from the normalization condition

$$\int \phi^* \phi_n d^3x = 1 \quad (14.17)$$

for the total wave function

$$\psi_n = \phi^o_n + \phi_n' = C_n \phi^o_n + \sum_{n'} C_n' \phi^o_{n'}, \quad (14.18)$$

where

$$C_n = 1 + C_n. \quad (14.19)$$

Substituting (14.18) into (14.17) and keeping only terms up to the first order, we have

$$|C_n|^2 \int \phi^* \phi_n d^3x +$$

$$+ \sum_{n'} \{ C_n^* C_{n'} \int \phi^* \phi_{n'} d^3x + C_n C_n' \int \phi^* \phi_{n'} d^3x \} = 1. \quad (14.20)$$
Making use of the orthonormality condition and ignoring the phase factor, which is of no interest to us, we obtain

\[ C_n^2 = 1, \quad (14.21) \]

and therefore \( C_n = 0 \).

Consequently, for the wave function \( \psi_n \) in the first-order perturbation theory, we finally obtain

\[ \psi_n = \psi_n^0 + \sum_{n'} \frac{V_{n'n}}{E_n^0 - E_{n'}^0} \psi_{n'}^0. \quad (14.22) \]

From Eqs. (14.22) and (14.11), it can be seen that both \( \psi_n' \) and \( E_n' \) are proportional to the first power of the perturbation energy (that is, to the parameter \( \lambda \)). If we were to compute the corrections to the energy and the wave function in second-order perturbation theory, both \( E_n'' \) and \( \psi_n'' \) would turn out to be proportional to the second power of \( V' \) (that is, to \( \lambda^2 \)).

**D. DEGENERATE CASE**

We shall now develop the perturbation theory in a form applicable to degenerate systems, in which, in the absence of any perturbation, a given energy eigenvalue \( E_n^0 \) has associated with it \( j \) eigenfunctions

\[ \psi_n^0, \psi_n^1, \ldots, \psi_n^j. \]

It is obvious that any linear combination of these functions

\[ \psi_n^0 = \sum_{l=1}^{j} C_l \psi_{n_l}^l \]

(14.23)

is itself a solution of the wave equation in the zero-order approximation

\[ (E_n^0 - \lambda^0) \psi_n^0 = 0, \]

in which the eigenvalue of the energy is \( E_n^0 \).

If there is a perturbation \( V' \), this arbitrariness is removed and the coefficients \( C_l \) may become connected with one another by certain definite relationships. Let us show this, proving first that, just as in the case of nondegenerate states, any particular solution of the homogeneous equation (14.6) is orthogonal to the right-hand side of the inhomogeneous equation (14.7a) of first-order
perturbation theory. For this purpose, we multiply (14.7a) on the left by $\phi_{n_i}^* \psi$ and integrate over all space. We then obtain

$$
\int \phi_{n_i}^* (E_n - H') \psi \, d^3x = -\int \phi_{n_i}^* (E_n' - V') \psi \, d^3x. \tag{14.24}
$$

Using the theorem for the transfer of a derivative [see Eq. (7.17)], we have

$$
\int \phi_{n_i}^* (E_n - H') \phi_{n_i} \, d^3x = -\int \phi_{n_i}^* (E_n' - V') \phi_{n_i} \, d^3x. \tag{14.25}
$$

Since $\phi_{n_i}^*$ is a solution of the Schrödinger equation $(E_n - H_0) \phi_{n_i} = 0$, we arrive at the equation

$$
\int \phi_{n_i}^* (E_n - V') \sum_{i'=1}^j C_{i'i} \phi_{n_i} \, d^3x = 0. \tag{14.26}
$$

Without any restriction on the generality, we may assume that all the eigenfunctions $\phi_{n_i}$ are orthonormal. Then, since

$$
\int \phi_{n_i} \phi_{n_i'} \, d^3x = \delta_{n_in_i'},
$$

we obtain instead of (14.26)

$$
C_{i'i} (E_n - V') = \sum_{i'=1}^j C_{i'i} V_{ii'}, \tag{14.27}
$$

where

$$
V_{ii} = \int \phi_{n_i}^* V \phi_{n_i} \, d^3x, \tag{14.28}
$$

$$
V_{ii'} = \int \phi_{n_i}^* V' \phi_{n_i'} \, d^3x. \tag{14.29}
$$

and the prime on the summation sign indicates that the sum extends over all $i'$'s, except $i' = i$. Since the subscript $i$ in (14.27) can take any value from 1 to $j$, we have a system of $j$ homogeneous equations from which we can determine the energy $E_n'$ and the coefficients $C_{i'i}$:

$$
C_{i'i} (E_n - V'_{ii}) - C_{i'i} V_{12} - \ldots - C_{i'i} V_{ij} = 0, \tag{14.30}
$$

$$
\begin{align*}
-C_{i'i} V_{21} + C_{i'i} (E_n' - V'_{22}) - \ldots - C_{i'i} V_{i2} &= 0, \\
&\quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \\
&\quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \\
&\quad -C_{i'i} V_{n'} + C_{i'i} V_{i'n} - \ldots + C_{i'i} (E_n - V'_{ij}) = 0.
\end{align*}
$$

1If the functions $\psi_{n_i}$ are not orthonormal, it is always possible to construct from them by means of linear transformations, new functions which possess this property.
Recalling that the wave function $\psi_n^a$ must satisfy the normalization condition

$$\int \psi_n^a \psi_n^a \, d^3x = 1,$$  \hspace{1cm} (14.17a)

we see that the correction $E_n'$ to the energy of the unperturbed state $E_n$ of the system is uniquely determined, as are the coefficients $C_i$ (and hence also $\psi_n^a$). Since, in particular, the system of equations (14.30) can have a nontrivial solution only if its determinant is equal to zero, we have the following equation for $E_n'$:

$$\begin{vmatrix}
(E_n - V_{11}), -V_{12}, \ldots, -V_{1j} \\
-V_{21}, (E_n - V_{22}), \ldots, -V_{2j} \\
\vdots & \vdots & \ddots & \vdots \\
-V_{nj}, -V_{j2}, \ldots, (E_n - V_{jj})
\end{vmatrix} = 0. \quad (14.31)
$$

This equation is called the secular equation, a term taken from celestial mechanics.

If the secular equation has several roots (not necessarily $j$ different roots), each one of them will correspond to a completely determined set of coefficients $C_i$, which can be found from (14.17a) and (14.30) by substituting the given root $E_n$ for $E_n'$. Consequently, the different corrections $E_n'$ to the energy lead to different zero-order wave functions. Thus, if a system is $j$-fold degenerate in the absence of any perturbation, a possible effect of a perturbation is to reduce or completely remove the degeneracy [this will occur in the case when Eq. (14.31) has $j$ different roots].

E. THE STARK EFFECT

If an atom is placed in an electric field, its spectral lines are generally split into components. This phenomenon was discovered by Stark in 1913. Experiments have shown that the effect of an electric field on a hydrogen atom is different than that on other atoms. In a weak field, the splitting of the energy levels of hydrogen (for example, the Balmer series) is proportional to the first power of the field intensity (the linear Stark effect), whereas for all other atoms the splitting is proportional to the second power of the field intensity (the quadratic Stark effect). In a stronger field (of the order of $10^5$ volts/cm), there is an additional splitting effect, proportional to higher powers of the field intensity (second power in the case of hydrogen). In very strong electric fields, the spectral lines disappear completely.

The Stark effect could not be explained before the development of quantum mechanics. In terms of classical concepts, the motion of
an electron in an atom can always be resolved into three mutually orthogonal oscillations. Let us consider the oscillation along the \( z \) axis, which can be taken to coincide with the direction of the constant electric field \( E(E_x = E_y = 0, E_z = 0) \). The equation describing the motion of the electron along the \( z \) axis is (for \( e = -e_0 \))

\[
m_0 \ddot{z} + m_0 \omega_0^2 z = -e_0 \phi, \tag{14.32}
\]

where \( m_0 \) is the electronic mass and \( \omega_0 \) is the angular frequency of oscillations. It is readily seen that the solution of Eq. (14.32) is

\[
z = -\frac{e_0 \phi}{m_0 \omega_0^2} + A \cos (\omega_0 t + \varphi). \tag{14.33}
\]

It is clear that in classical theory the only effect of the constant force \( (-e_0 \phi) \) is to change the position of the point of equilibrium of the system. The frequency of oscillations remains completely unaffected. Consequently, classical concepts imply that the frequency of the radiation emitted by an atom remains the same whether or not the atom is placed in an electric field, since the frequency of the radiation is the same as the mechanical frequency of oscillations of the atomic electrons. Accordingly, an electric field cannot produce any shift of the spectral lines in classical theory.

We shall now consider the Stark effect in terms of quantum concepts. As we have just mentioned, there are two basic forms of the Stark effect: namely, linear and nonlinear. The linear effect is characteristic only of hydrogen-like atoms because they are degenerate not only with respect to the magnetic quantum number \( m \), but also with respect to the orbital angular momentum quantum number \( l \) (see Chapter 13), with which the linear Stark effect is associated. In all other atoms, there is no degeneracy with respect to \( l \), and therefore the linear Stark effect is not observed.

Let us discuss in greater detail the theory of the linear Stark effect for the hydrogen atom. We shall confine our treatment to the second quantum level \( (n = 2) \).\(^3\) The external electric field (which is of the order of \( 10^4 - 10^5 \) volts/cm in experiments) is much weaker than the intraatomic field produced by the nucleus, which is

\[
\phi_{\text{nucl.}} = \frac{e_0}{a_0^2} \approx 5 \cdot 10^9 \text{ volts/cm},
\]

where \( a_0 \) is the radius of the first Bohr orbit. Therefore, we may use the results of perturbation theory (in the form developed for

\(^2\)The electric field intensity will have no effect on the oscillations along the \( x \) and \( y \) axes, which are perpendicular to \( E \).

\(^3\)The first quantum level \( (n = 1) \) is nondegenerate and, therefore, is not split.
degenerate problems). For the perturbation $V'$, we must take the potential energy of the electron in the external electric field

$$V' = e_0 \delta z. \quad (14.34)$$

In the unperturbed state, the energy of the electron is [see Eq. (13.33)]

$$E^0 = -\frac{\hbar^2}{4},$$

which has four wave functions associated with it:

\[
\psi_1 = \psi_{2,0,0} = R_{20}(r)Y_0 = \frac{1}{\sqrt{4\pi}} R_{20}(r),
\]

\[
\psi_2 = \psi_{2,1,0} = R_{21}(r)Y_1 = \sqrt{\frac{3}{4\pi}} R_{21}(r) \cos \theta,
\]

\[
\psi_3 = \psi_{2,1,1} = R_{21}(r)Y' = \sqrt{\frac{3}{4\pi}} R_{21}(r) \frac{\sin \theta}{\sqrt{2}} e^{iy},
\]

\[
\psi_4 = \psi_{2,1,-1} = R_{21}(r)Y_1' = -\sqrt{\frac{3}{4\pi}} R_{21}(r) \frac{\sin \theta}{\sqrt{2}} e^{-iy}.
\]

When $\theta$ and $\varphi$ are replaced by Cartesian coordinates, these wave functions take the form:

\[
\psi_1 = f_1(r), \quad (14.35a)
\]

\[
\psi_2 = f_2(r) z, \quad (14.36a)
\]

\[
\psi_3 = f_2(r) \frac{x + iy}{\sqrt{2}}, \quad (14.37a)
\]

\[
\psi_4 = -f_2(r) \frac{x - iy}{\sqrt{2}}, \quad (14.38a)
\]

where

\[
f_1(r) = \frac{1}{\sqrt{4\pi}} R_{20}(r), \quad (14.39a)
\]

\[
f_2(r) = \sqrt{\frac{3}{4\pi}} \frac{R_{21}(r)}{r}.
\]
The general wave function of an electron will have the form

$$\psi^0 = \sum_{i=1}^{4} C_i \phi_i. \quad (14.40)$$

Since the degree of degeneracy is four ($j = 4$), we have the following system of four equations for determining the unknown coefficients $E'_i$ and the corrections $C_i$ to the energy $E'_i$ of the unperturbed state:

$$C_i (E'_i - V_{1i}) - C_i V_{13} - C_i V_{14} = 0,$$
$$- C_i V_{2i} + C_i (E'_i - V_{2i}) - C_i V_{23} - C_i V_{24} = 0,$$
$$- C_i V_{3i} - C_i V_{32} + C_i (E'_i - V_{3i}) - C_i V_{34} = 0,$$
$$- C_i V_{4i} - C_i V_{42} - C_i V_{43} + C_i (E'_i - V_{4i}) = 0,$$

where

$$V_{ij} = \int \phi_i^* \phi_j d^3 x =$$
$$= e_0 \int \phi_i^* \phi_j d^3 x. \quad (14.42)$$

When we integrate over the volume, the matrix elements $V_{11}, V_{22}, V_{33}, V_{44}, V_{13}, V_{14}, V_{23}, V_{24}, V_{31}, V_{32}, V_{34}, V_{41}, V_{42}$ and $V_{43}$ vanish, since for each of them the integrand must be an odd function with respect to at least one of the coordinates $x, y$ and $z$. Only the matrix elements

$$V_{13} \quad \text{and} \quad V_{31} = V_{13},$$

which are even functions of all three coordinates, differ from zero

$$V_{13} = V_{31} = e_0 \int f_1 (r) f_2 (r) z^2 d^3 x. \quad (14.43)$$

Let us substitute the values of Eq. (14.39) for $f_1 (r)$ and $f_2 (r)$ and note that, according to Eq. (13.28a),

$$R_{20} = \frac{1}{2} \frac{1}{\sqrt{2} a_0^{3/4} \left(2 - \frac{r}{a_0}\right)} e^{-\frac{r}{2a_0}},$$

and

$$R_{21} = \frac{1}{2} \frac{1}{\sqrt{6} a_0^{5/4} \left(2 - \frac{r}{a_0}\right)} e^{-\frac{r}{2a_0}}.$$
Then, integrating (14.43) over the angles $\theta$ and $\varphi$ (remembering that $z = r \cos \theta$), we obtain

$$V'_{i2} = V'_{i1} = \frac{e_0}{24a_0^4} \int_0^\infty \! \int_0^{\pi} \! \int_0^{2\pi} \! r^4 \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{a_0}} dr \, d\varphi \, d\theta.$$  \hspace{1cm} (14.43a)

Next, taking into account the equality

$$\int_0^\infty e^{-r^2} \, dr = \frac{\pi}{2},$$

we obtain

$$V'_{i2} = V'_{i1} = -3e_0 \delta a_0.$$  \hspace{1cm} (14.44)

Using the obtained values of the matrix elements $V'_{ii}$, we find, in accordance with (14.31), that the secular equation for the corrections $E'_i$ is

$$
\begin{vmatrix}
E'_i & 3a e_0 \delta & 0 & 0 \\
3a e_0 \delta & E'_i & 0 & 0 \\
0 & 0 & E'_i & 0 \\
0 & 0 & 0 & E'_i \\
\end{vmatrix} = 0,
$$

which can be rewritten in the form

$$E'_i (E'_i^2 - 9a^2 e^2_0 \delta^2) = 0.$$  \hspace{1cm} (14.45a)

This equation has four roots:

$$E'_i^{(1)} = -3a e_0 \delta,$$

$$E'_i^{(2)} = 3a e_0 \delta,$$

$$E'_i^{(3)} = E'_i^{(4)} = 0,$$  \hspace{1cm} (14.46)

each one of which, according to Eq. (14.41), is associated with a quite specific set of coefficients:

$$C'_i^{(1)} = C'_i^{(2)} = 0; \quad C'_i^{(3)} = -C'_i^{(4)} = 0; \quad C'_i^{(4)} = C'_i^{(5)} = 0; \quad C'_i^{(5)} = C'_i^{(6)} = 0.$$  \hspace{1cm} (14.47)

Here the superscript $j$ of the coefficients $C'_i^j = C'_i$ indicates the solution (or root) of Eq. (14.45a) with which it is associated. Thus, it follows from (14.40) and (14.47) that the energy level

$$E_i^{(1)} = E_i + E_i^{(1)} = -\frac{R \hbar}{4} - 3\epsilon_0 a_0 \delta$$  \hspace{1cm} (14.48)
is associated in the zero-order approximation with the wave function

$$\psi^0(1) = C_i^1(\psi_{2,0,0} + \psi_{2,1,0}).$$

Because of the normalization condition

$$\int \psi^0(1) \psi^0(1)^* d^2x = 1,$$

this wave function becomes

$$\psi^0(1) = \frac{1}{\sqrt{2}} (\psi_{2,0,0} + \psi_{2,1,0}). \quad (14.49)$$

In a similar fashion, it can be shown that the state with energy

$$E_2^{(2)} = E_2^0 + E_2^{(3)} = -\frac{R}{4} + 3a_0e_0\beta$$

is described by the zero-order wave function

$$\psi^0(2) = \frac{1}{\sqrt{2}} (\psi_{2,0,0} - \psi_{2,1,0}). \quad (14.51)$$

To describe the states with energy

$$E_2^{(3)} = E_2^{(4)} = E_2^0,$$

which remain unperturbed by the electric field in the first-order approximation, we may equally well take the function

$$\psi^0(3) = \psi_{2,1,1} \quad (m = 1),$$

or

$$\psi^0(4) = \psi_{2,1,-1} \quad (m = -1)$$

or, alternatively, we may take a linear combination of these functions, since the system remains degenerate for $m = \pm 1$ even in the presence of an electric field. Thus, when the $z$ component of the angular momentum is not equal to zero ($m = \pm 1$ in units of $\hbar$), that is, the electron is moving largely in the $xy$ plane (see Chapter 12, Section A), there will be no splitting of the energy levels (and, therefore, of spectral lines) in an electric field. If, on the other hand, the orientation of the angular momentum is such that its $z$ component is equal to zero $m = 0$ and, consequently, the electron
is moving in a plane which includes the z axis (again, see Chapter 12, Section A), then an electric field does lead to splitting of the spectral lines (see Fig. 14.1).

\[
\begin{align*}
\frac{\hbar}{4} + 3e_o a_o \xi & \quad \frac{\hbar}{4} - 3e_o a_o \xi \\
\frac{\hbar}{4} & \quad \frac{\hbar}{4} - 3e_o a_o \xi \\
a & \quad b
\end{align*}
\]

Fig. 14.1. Splitting of the second spectral term of hydrogen in an electric field (the linear Stark effect): 

a) energy level in the absence of a field (\(\xi = 0\));
b) energy level in the presence of a field (\(\xi \neq 0\)).

Qualitatively, the Stark effect for \(n = 2\) may be interpreted as follows. Since the wave function describing the motion of the electron for \(n = 2\) (see Fig. 12.1) is not centrally symmetric, the atom has a certain electric moment \(p\). Consequently, when the atom is placed in an electric field

\[(E_x = E_y = 0, E_z = \xi),\]

it acquires an additional energy

\[V' = -(pE) = -p \xi \cos \gamma, \quad (14.52)\]

where \(\gamma\) is the angle between the direction of the electric dipole moment of the atom and the z axis. Comparing this expression with (14.46), we see that the electric dipole moment of the atom is \(p = 3a_e e_o\). The solution \(\psi^{(1)}\) corresponds to the case \(\gamma = 0\) and the solution \(\psi^{(2)}\) to the case \(\gamma = \pi\). For the third and fourth solutions, it is necessary to set \(\gamma = \pm \frac{\pi}{2}\). We note that, in the last case, the electric dipole moment is oriented perpendicularly to the electric field and, consequently, no additional energy appears. To conclude this discussion, the linear Stark effect arises because of the intrinsic electric dipole moment of the hydrogen atom at \(n = 2\).

Predictions obtained on the basis of quantum mechanics are in good agreement with experimental data only in the case of weak fields (10^4 volts/cm). At higher field intensities (~10^3 volts/cm), there is an additional splitting (the quadratic Stark effect) due to the removal of the degeneracy with respect to the magnetic quantum number \(m\). Finally, at field intensities greater than 10^3 volts/cm, the Stark effect completely disappears. This is the result of autoionization of the atoms, that is, removal of electrons from the excited levels.
F. PRINCIPLES OF THE CLASSICAL THEORY OF DISPERSION

Perturbation theory has many important applications in studies of the interaction between light and matter. The predictions obtained in this way differ from classical results and receive excellent confirmation from experiment. This section is concerned with the classical theory of dispersion (that is, the scattering of light) in a dielectric medium. According to classical notions, a dielectric is characterized by the index of refraction

\[ n = \sqrt{\varepsilon}, \]

where \( \varepsilon \) is the dielectric permittivity (the magnetic permeability \( \mu \) is taken to be equal to unity). If the index of refraction \( n \) becomes larger as the frequency of light increases (that is, \( \frac{dn}{d\omega} > 0 \)), the dispersion is said to be normal. A typical example of normal dispersion is the spectral resolution of white light by a glass or quartz prism (the deflection of violet rays from their initial direction is larger than that of red rays). If, however, \( \frac{dn}{d\omega} < 0 \) in a certain range of frequencies, the dispersion in this region is said to be anomalous. As a rule, anomalous dispersion occurs at frequencies at which light is absorbed by the medium.

To determine the index of refraction (one of the most important problems in the theory of dispersion), we use the equation relating the electric field intensity \( E \), the displacement vector \( D \), and the polarization vector \( P \)

\[ D = \varepsilon E = E + 4\pi P. \]  

(14.53)

Since \( \varepsilon = n^2 \), we have

\[ P = \frac{n^2 - 1}{4\pi} E. \]  

(14.53a)

Thus, to determine \( n \) we are required to find the relationship between \( P \) and \( E \) on the basis of the microscopic picture of the structure of matter. We shall be better able to appreciate the contribution of quantum theory in this connection after we have completed our review of the basic principles of the classical theory of dispersion.

According to the Lorentz classical theory, atoms may be regarded as harmonic oscillators in which, in the simplest case, all the electrons oscillate with the same angular frequency \( \omega \). If

---

\(^4\)The polarization \( P \) is defined as the total dipole moment of the atoms per unit volume.
we take the $z$ axis to be parallel to the direction of propagation of the electromagnetic wave, then, since the wave is transverse, we may direct vector $E$ along the $x$ axis ($E_x = \varnothing$, $E_y = E_z = 0$), and vector $H$ along the $y$ axis. If we neglect the force exerted on the atomic electrons by the magnetic field (since the magnitude of this force is only a fraction $\left(\frac{\varnothing}{c}\right)$ of the force exerted by the electric field), the oscillation of the electrons can be described by the equation

$$m_0 \ddot{x} + m_0 \omega_0^2 x = - e_0 \varnothing.$$  \hfill (14.54)

We shall assume that the frequency of the incident light wave is $\omega$. Then

$$\varnothing = \varnothing_0 \cos \left(\omega t - \frac{2\pi x}{\lambda}\right).$$  \hfill (14.55)

If the energy transported by the wave is much smaller than the bonding energy of the electrons in the atom, it follows that the ratio $\frac{\lambda}{x}$ may be neglected because it is small compared to the atomic dimensions ($x \sim a \sim 10^{-8}$ cm, while the wavelength $\lambda$ is of the order of $10^{-6}$ cm). Thus, under the assumptions we have made, the electric field of the wave may be considered to be quasi-stationary inside the atom. As a result of this simplification, Eq. (14.54) becomes

$$\ddot{x} + \omega_0^2 x = \frac{e_0}{m_0} \varnothing = \frac{e_0}{m_0} \varnothing_0 \cos \omega t.$$  \hfill (14.54a)

Multiplying (14.54a) by $(-e_0 N)$, where $N$ is the number of atoms per unit volume, and substituting

$$-e_0 x = p_x, \text{ and } P_x = Np_x = \mathcal{P}, \quad P_y = P_z = 0,$$

we reduce this equation to the form

$$\dot{\mathcal{P}} + \omega_0 \mathcal{P} = \frac{Ne_0^2}{m_0} \varnothing_0 \cos \omega t,$$  \hfill (14.54b)

from which we obtain

$$\mathcal{P} = \frac{Ne_0^2}{m_0} \frac{1}{\omega_0^2 - \omega^2} \varnothing_0 \cos \omega t.$$  \hfill (14.56)

Comparing Eqs. (14.56) and (14.53a), we obtain an equation for the index of refraction which should be familiar from optics:

$$\frac{n^2 - \frac{1}{4\pi}}{\frac{1}{4\pi}} = N \frac{e_0^2}{m_0} \frac{1}{\omega_0^2 - \omega^2}.$$  \hfill (14.57)
We note that if the atom is assumed to contain electrons with different eigenfrequencies

\[ \omega_0, \omega_1, \omega_2, \ldots, \omega_k, \ldots, \]

a more general equation is obtained instead of (14.57):

\[
\frac{n^2 - 1}{4\pi} = \frac{e^2}{m_0} \sum_k \frac{N_k}{\omega_k^2 - \omega^2},
\]

(14.57a)

where \(N_k\) is the number of electrons per unit volume oscillating with the frequency \(\omega_k\).

It follows from (14.57) that at radio frequencies \((\omega \ll \omega_0)\) the index of refraction may be assumed to be constant, without significantly affecting the accuracy. Its value is given by the relation

\[
\frac{n^2 - 1}{4\pi} \approx \frac{Ne_0^2}{m_0 \omega_0^2}.
\]

(14.58)

On the other hand, for frequencies \(\omega \gg \omega_0\), the value of the index of refraction is given by the relation

\[
\frac{n^2 - 1}{4\pi} \approx -\frac{Ne_0^2}{m_0 \omega^2}.
\]

(14.59)

The index of refraction is, therefore, a constant greater than unity for \(\omega \ll \omega_0\), whereas for \(\omega \gg \omega_0\) it is less than unity, approaching it as \(\omega \to \infty\).

At frequencies close to \(\omega_0\), the magnitude of the index of refraction increases without limit, and at \(\omega = \omega_0\) it has a discontinuity (see Fig. 14.2). The reason for this behavior of the function is that Eq. (14.54) does not include the radiation damping of the electron \(F_{\text{damp}} = \frac{2}{3} \frac{e^2}{c^3} \vec{x}\), which arises from the interaction between the moving electron and its own field. When \(F_{\text{damp}}\) is included, the dispersion curve has the form indicated by the dotted line in Fig. 14.2. Consequently, the dispersion is anomalous near the resonance frequency \(\omega_0\). Since the region of anomalous dispersion coincides with the region of the eigenfrequencies of oscillation of electrons in the atom, it follows that anomalous dispersion is accompanied by strong absorption.

![Fig. 14.2. Classical dispersion curve \(a = \frac{Ne_0^2}{m_0 \omega_0^2}\).](image)
Let us now develop a quantum theory of dispersion. By analogy with the classical case, we shall assume that all the electrons in the atoms are in the same quantum state $k_s$. We shall use the perturbation method to solve our problem, since the energy of the interaction with the external field is generally small compared with the bonding energy of the electrons. In the nonrelativistic case (when we may neglect the "magnetic" force), the external force which acts on an electron can be obtained from Eq. (14.55)\(^6\):

$$F_x = -e_0 \delta_0 \cos \omega t, \quad F_y = F_z = 0.$$  

The perturbation energy is given by

$$V' = e_0 \delta_0 \cos \omega t.$$  

Consequently, the Schrödinger equation for the electron is

$$\left(-\frac{\hbar}{i} \frac{d}{dt} - H^0 - V'\right) \psi_k(t) = 0. \tag{14.61}$$

Let us suppose that Eq. (14.61) has an exact solution for $V' = 0$:

$$\psi_k(t) = \psi_k e^{-i/\hbar H_k} = \psi_k e^{-i\omega_k t}, \tag{14.62}$$

where $\psi_k$ and $E_k$ satisfy the equation

$$(E_k - H^0) \psi_k = 0. \tag{14.63}$$

In accordance with perturbation theory, we shall look for a solution in the form

$$\psi(t) = \psi_k(t) + \psi_k(t). \tag{14.64}$$

Since (14.62) and (14.63) yield

$$\left(-\frac{\hbar}{i} \frac{d}{dt} - 11^0\right) \psi_k(t) = 0,$$  

\(^1\)This assumption is analogous to the assumption made in the classical treatment, according to which all the electrons have the same eigenfrequencies of oscillation.

\(^6\)Just as in the classical case, we have assumed here that the electric field is quasi-stationary over distances of the order of the dimensions of the atom.
the equation for \( \psi'(t) \) and the first-order correction to the energy \( E_k \) is

\[
\left(-\frac{\hbar}{i}\frac{\partial}{\partial t} - H_0\right)\psi'_k(t) = V'\psi'_k(t). \tag{14.65}
\]

Substituting \( V' \) from (14.60), we have

\[
\left(-\frac{\hbar}{i}\frac{\partial}{\partial t} - H_0\right)\psi'_k(t) = \frac{1}{2} e_0 x_0 y_0 \psi_k \left\{ e^{-i(\omega_k - \omega) t} + e^{-i(\omega + \omega_k) t} \right\}. \tag{14.65a}
\]

To eliminate the time \( t \) from this equation, let us look for a solution \( \psi'_k(t) \) in the form

\[
\psi'_k(t) = u e^{-i(\omega_k - \omega) t} + v e^{-i(\omega + \omega_k) t}. \tag{14.66}
\]

We then have the following equations for the functions \( u \) and \( v \):

\[
\{\hbar (\omega_k - \omega) - H_0\} u = \frac{1}{2} e_0 x_0 y_0 \psi_k, \tag{14.67}
\]

\[
\{\hbar (\omega_k + \omega) - H_0\} v = \frac{1}{2} e_0 x_0 y_0 \psi_k. \tag{14.68}
\]

We note that these two equations have exactly the same form. Consequently, it is only necessary to solve Eq. (14.67) for \( u \), since the solution for \( v \) of Eq. (14.68) can be obtained from \( u \) by substituting \( -\omega \) for \( \omega \). Since the time does not appear explicitly in Eq. (14.67), we can find \( u \) by the perturbation method in the form applicable to stationary problems. Thus we shall look for a solution in the form of an expansion in eigenfunctions of the unperturbed problem [see (14.8)]:

\[
u = \sum_{k'} C_{k''} \psi''_{k''}, \tag{14.69}
\]

where the \( \psi''_{k''} \) satisfy the equation

\[
(E_{k''} - H_0) \psi''_{k''} = 0. \tag{14.70}
\]

Accordingly, we may reduce (14.57) to the form

\[
\hbar \sum_{k''} C_{k''} (\omega_{kk''} - \omega) \psi''_{k''} = \frac{e_0 x_0 y_0}{2} \psi_k, \tag{14.67a}
\]

where the frequency of radiation is

\[
\omega_{kk''} = \frac{E_k - E_{k''}}{\hbar}. \tag{14.71}
\]
Let us multiply (14.67a) on the left by $\phi_k^{\ast}$ and integrate over all space, taking into account the orthonormality of the eigenfunctions $\left(\int \phi_k^{\ast} \phi_{k'} d^3x = \delta_{k'k}\right)$. We then obtain the following equations for the coefficients $C_k$ and the function $u$:

$$C_k = -\frac{e\phi_0}{2\hbar} \frac{x_{k'k}}{\omega_{k'k} + \omega}, \quad (14.72)$$

$$u = \sum_k \left(-\frac{e\phi_0}{2\hbar}\right) \frac{x_{k'k}}{\omega_{k'k} + \omega} \phi_{k'}, \quad (14.73)$$

where the matrix element $x_{k'k}$ is equal to

$$x_{k'k} = \int \phi_k^{\ast} \phi_{k'}^2 d^3x. \quad (14.74)$$

Substituting $-\omega$ for $\omega$ in (14.73), we obtain an expression for the function $v$:

$$v = \sum_k \left(-\frac{e\phi_0}{2\hbar}\right) \frac{x_{k'k}}{\omega_{k'k} - \omega} \phi_{k'}. \quad (14.75)$$

From (14.64), (14.66), (14.73) and (14.75), it follows that the total wave function $\psi_k(t)$ is

$$\psi_k(t) = e^{-i\omega t} \left\{ \phi_k - \frac{e\phi_0}{\hbar} \sum_k \frac{x_{k'k} \phi_{k'}}{\omega_{k'k} - \omega} \left[ \omega_{k'k} \cos(\omega t - i\omega \sin \omega t) \right] \right\}. \quad (14.76)$$

From the wave function $\psi_k(t)$ of the electron in the external field, we can readily obtain the polarization vector of the medium $\mathcal{P}$. In the classical theory we had

$$\mathcal{P} = Np = -Ne_0 e. \quad (14.77)$$

To generalize this expression to the quantum case, we must replace $p$ by its average value. Then

$$\mathcal{P} = N\bar{p} = -Ne_0 \int \psi_k^{\ast}(t) x \psi_k(t) d^3x. \quad (14.77)$$

Substituting $\psi_k(t)$ from (14.76) and retaining only first-order terms in $\omega_0$, we have

$$\mathcal{P} = \frac{2Ne_0^2}{\hbar} \sum_k \frac{\omega_{k'k} |x_{k'k}|^2}{\omega_{k'k}^2 - \omega^2} \phi_0 \cos(\omega t). \quad (14.78)$$
In deriving this expression, we used the relation

\[ \int \phi_k^* x^0 \phi_k^0 dx = \int |\phi_k^0|^2 x d^3x = 0, \]

which follows from the fact that the integrand is an odd function of \( x \). Comparing Eqs. (14.78) and (14.53a), we obtain the dispersion formula

\[ \frac{n^2 - 1}{4\pi} = \frac{2n_e^2}{\hbar} \sum_{k'} \frac{\omega_{k'k} |x_{k'k}|^2}{\omega_{k'k}^2 - \omega^2}. \] (14.79)

By introducing the new variable

\[ f_{k'k} = \frac{2m_0}{\hbar} \omega_{k'k} |x_{k'k}|^2, \] (14.80)

which is called the oscillator force, we transform Eq. (14.79) to

\[ \frac{n^2 - 1}{4\pi} = \frac{Ne^2}{m_0} \sum_{k'} \frac{f_{k'k}}{\omega_{k'k}^2 - \omega^2}. \] (14.81)

Here let us make an observation similar to the one made in regard to the classical treatment: namely, if we had included the radiation damping in the quantum-mechanical treatment, we should have obtained a finite value of \( n^2 \) for frequencies \( \omega \) in the neighborhood of \( \omega_{k'k} \) (see Fig. 14.3a, the dotted line).

Equation (14.81) has a structure similar to the classical equation (14.57). In actual fact, however, the quantum results are fundamentally different from the classical results. From quantum theory it follows that anomalous dispersion occurs in the neighborhood of frequencies corresponding to allowed transitions, and not,
as in classical theory, in the neighborhood of the eigenfrequencies of oscillation of the electrons. This particular conclusion can be seen to be directly related to the role of the oscillator force $f_{k'}^k$ in (14.81), which is specified by the matrix element $x_{k'k}$ [see (14.80)] which characterizes the selection rules (and thus the allowed transitions). This prediction of quantum theory was experimentally verified by D. S. Rozhdestvenskii.

A second, very important difference from the classical results is that quantum theory leads to negative dispersion (see Fig. 14.3b)—a phenomenon which has no classical analog. This can be understood by simply noting that when light is scattered by excited atoms, it is necessary to take into account the states with $E_k > E_{k'}$ for which

$$f_{k'k} \sim \omega_{k'k} = \frac{E_{k'} - E_k}{\hbar} < 0.$$  

For these states the dispersion formula (14.81) becomes

$$\frac{n^2 - 1}{4\pi} = -\frac{N\hbar}{m_0} \sum_{k'} |f_{k'k}| \omega_{k'k}^2 \omega^2,$$  

(14.81a)

and the dispersion curve is represented by the dotted line in Fig. 14.3b. The experimental discovery of negative dispersion was made by Ladenburg; thus, this prediction of quantum theory was also confirmed.

Let us now find the value of the oscillator force $f_{k'k}$ and the dispersion formula for a harmonic oscillator. The only nonvanishing matrix elements in this case are [see (10.55)]

$$x_{k,1,k} = \sqrt{\frac{\hbar (k + 1)}{2m_0\omega_0}} \quad \text{and} \quad x_{1,k,k} = \sqrt{\frac{\hbar k}{2m_0\omega_0}}.$$  

"By chance," it turns out that the quantum-mechanical frequencies of radiation are identical with the eigenfrequencies of oscillation

$$\omega_{k,1,k} = \omega_0 \quad \text{and} \quad \omega_{k,1,k} = -\omega_0.$$  

We thus obtain

$$f_{k,1,k} = (k + 1), \quad f_{k-1,k} = -k.$$  

(14.82)

Consequently (since $\sum_{k'} f_{k'k} = 1$), the dispersion formula (14.81) can be written as
\[
\frac{n^2 - 1}{n} = \frac{Ne_0^2}{m_0} \frac{k \cdot l}{\omega_0^2 - \omega^2} - \frac{Ne_0^2}{m_0} \frac{k}{\omega_0^2 - \omega^2} = \frac{Ne_0^2}{m_0} \left( \frac{1}{\omega_0^2 - \omega^2} \right).
\]

(14.83)

We can see that in this particular problem the quantum and classical theories yield the same value for the index of refraction \( n \). The phenomenon of negative dispersion is not observed. The reason for this is that the regions of positive and negative dispersion coincide since \(|\omega_{k,1,k}|^2 = |\omega_{k,1,k}|^2\), so that the stronger effect of positive dispersion masks the negative dispersion.

G. RAMAN EFFECT

Let us consider the phenomenon of dispersion from the standpoint of energy diagrams. Suppose that a photon with energy

\[
\varepsilon = \hbar \omega \tag{14.84}
\]

impinges on an atom with only three energy levels \( E_{k''} < E_k < E_{k'} \) (see Fig. 14.4). In general, the scattering of this photon (that is, dispersion) will be a second-order effect. The first form which this process can take is absorption of the photon. This is accompanied by excitation of an electron from level \( k \) to some intermediate state (which may even be a forbidden state\(^7\); see Fig. 14.4, I) and, subsequently, by emission of a photon. If, as a result, the electron returns to its initial state, it follows from the law of conservation of energy that the frequency \( \omega \) of the scattered photon is the same as the frequency \( \omega \) of the incident photon.

Alternatively, the order of the process may be reversed: the atom first emits a photon (see Fig. 14.4, II) and then absorbs the incident photon. As in the preceding case, the frequency \( \omega' \) of the scattered photon will be equal to the frequency \( \omega \) of the incident photon if the atom returns to its initial state.

\(^7\) More precisely, the law of conservation of energy may be violated in intermediate states. It is required to hold only in the final result.
Finally, resonance occurs when $\omega \approx \omega_{k'k}$. In this case, both processes—scattering and absorption of the photons—take place (see Fig. 14.4, III); as a result of the last process the electrons in the atom undergo induced transitions. The probability of these transitions is given by the Einstein coefficient $B_{kk'}$ [see (9.21)]. An external field increases the number of downward transitions (see Fig. 14.4, IV), which results in some additional radiation proportional to the coefficient $B_{kk'}$.

So far, we have been concerned with cases in which atoms return to their initial state after scattering. It may happen, however, that after the atom has absorbed the incident photon, the electron does not return from the intermediate state to the level $k$, but instead makes a transition to the level $k'$ or $k''$ (see Fig. 14.5). In this case, the frequency of the scattered light ($\omega'$ or $\omega''$) is not equal to the frequency of the incident light. This type of scattering is called the Raman effect, after the Indian physicist who first discovered this phenomenon in liquids. In solids the Raman effect was discovered by the Soviet physicists L. I. Mandel'shtam and G. S. Landsberg (1928).

From Fig. 14.5, it can be seen that the frequency of the scattered photon may be either lower or higher than the frequency of the incident photon. In the former case, the lines

$$\omega' = \omega - \omega_{k'k} < \omega$$

correspond to excitation of the atom, since the atom ends up in a higher energy state. These lines are known as "Stokes" lines (the levels are shifted towards the red part of the spectrum). The second case corresponds to "anti-Stokes" lines (shifting towards the violet part of the spectrum):

$$\omega'' = \omega + \omega_{kk''} > \omega;$$

these lines appear only when the light is scattered by excited atoms. It is obvious that at low temperatures only Stokes lines can be observed. As the temperature increases and the atoms of the substance begin to undergo transitions to excited states, anti-Stokes lines appear.

The Raman effect provides much important information in studies of molecular structure. In Chapter 12, Section C, we saw
that the rotational and vibrational levels (and also the vibrational-rotational levels), which provide data on molecular structure, are all located in the far infrared region of the spectrum and are very difficult to observe. In studies of the Raman effect, it is possible to use visible light in determining molecular spectra, since these spectra are superposed on the lines in the spectrum of the incident light. The experimental values of $\omega'$ and $\omega''$ (see Fig. 14.6) yield the molecular frequencies

$$\omega'_{kk'} = \omega - \omega'$$
$$\omega''_{kk'} = \omega'' - \omega,$$

from which the selection rules can be derived.

Problem 14.1. Find the energy correction for a system in second-order perturbation theory.

Solution. Including the terms up to and including the second order in the expansions of the wave function $\psi$ (14.3) and the energy $E$ (14.4), and substituting these expansions into the Schrödinger equation (14.2a), we obtain the equation

$$\left( H - E_n \right)|\psi_n\rangle = - \left( H_n - V_n \right)|\psi_n\rangle = E_n^0|\psi_n\rangle.$$

Since the solution $\psi_n$ of the homogeneous equation $\left( H - E_n \right)|\psi_n\rangle = 0$ is orthogonal to the right-hand side and since we can substitute the expression (14.22) for $\psi_n$, we have

$$E_n'' = \sum_{n'} \left| V_{n'n} \right|^2 \frac{E_{n''}}{E_{n'''}},$$

(14.85)

The value of $V_{n'n}$ is given by (14.15), and we have used the relationship

$$V_{n'n'} = V_{n'n},$$

which holds for Hermitian operators.

We note that the second-order correction (14.85) to the energy of the ground state is always negative, since all the other levels $E_n'$ are higher than the level $E_n$, that is, $E_n' > E_n$.

Problem 14.2. Using the results of the perturbation theory, find the energy of the anharmonic oscillator including the terms up to the order of $\hbar^2$; take the Hamiltonian of the system to be equal to

$$H = \frac{p^2}{2m_0} + \frac{m_0 \omega^2 x^2}{2} + V',$$

where $V' = \alpha x^3 + \beta x^4$ (the constants $\alpha$ and $\beta$ are classical quantities).

Solution. The energy of a harmonic oscillator ($V' = 0$) is

$$E_n = \hbar \omega \left( n + \frac{1}{2} \right).$$

Taking $V'$ as the perturbation energy, the first-order approximation gives

$$E_n = V_{nn} = \alpha (x^3)_{nn} + \beta (x^4)_{nn}. $$
It can easily be shown that

\[ (x^3)_{nn} = \int_{-\infty}^{+\infty} |\psi_n|^2 x^3 dx = 0, \]

since the integrand is an odd function.

To calculate the matrix elements \( \hat{\beta} (x^3)_{nn} \), we use the multiplication rule for matrix elements (see Problem 10.4), obtaining

\[ (x^3)_{nn} = \sum_k (x^2)_{nk} (x^2)_{kn} = ((x^2)_{n,n-2})^2 + ((x^2)_{n,n})^2 + ((x^3)_{n,n+2})^2. \]

Substituting the value of \( (x^2)_{nb} \) from Problem 10.5, we obtain the following expression for the first approximation of the perturbation energy \( E_n \):

\[ E_n = \frac{3}{2} \hbar^2 \frac{a^2}{m_0 \omega^2} \left( n^2 + n + \frac{1}{2} \right). \]  

(14.86)

Our problem, however, is not yet fully solved, since in the second-order approximation there is a contribution proportional to \( \frac{x^6}{\hbar^2} \sim \hbar^2 \) which arises from the first term of the perturbation energy \( \alpha x^2 \), and we must take this contribution into account. The second-order contribution from the term \( \alpha x^4 \) is proportional to \( \frac{x^8}{\hbar^4} \sim \hbar^4 \) and accordingly it may be neglected in our approximation. The second-order correction arising from the first term of the perturbation energy can be calculated from Eq. (14.85):

\[ E_n' = \frac{a^2}{\hbar \omega} \sum_{n'} (x^3)_{nn} (x^3)_{n'n}. \]

The only nonvanishing matrix elements are [see Eq. (10.55) and Problem 10.5]

\[ (x^3)_{n,n-1} = (x^3)_{n,n} (x)_{n,n-1} = (x^3)_{n,n-2} (x)_{n,n-2,n-1} = 3x_0^3 \sqrt{\left( \frac{n}{2} \right)^3} , \]

\[ (x^3)_{n,n-2} = (x^3)_{n,n} (x)_{n,n-2,n-2} = x_0^3 \sqrt{\frac{n(n-1)(n-2)}{8}}, \]

\[ (x^3)_{n,n+1} = (x^3)_{n,n+1,n}, \]

\[ (x^3)_{n,n+2} = (x^3)_{n,n+2,n} , \]

where \( x_0 = \sqrt{\frac{\hbar}{m_0 \omega_0}}. \)

Hence

\[ E_n'' = - \frac{15}{4} \hbar^2 \frac{a^2}{m_0 \omega^2} \left( n^2 + n + \frac{11}{30} \right). \]  

(14.87)
Part II

Relativistic Quantum Mechanics
A. RELATIVISTIC MECHANICS AND THE KLEIN-GORDON EQUATION: RELATIVISTIC INVARiance

The Schrödinger wave equation is nonrelativistic: it is suitable only for particles whose velocity $v$ is much smaller than the velocity of light $c$. It is not invariant with respect to the Lorentz transformations of the special theory of relativity since there is an asymmetry between the time and space coordinates (the equation contains a first derivative with respect to time, and second derivatives with respect to the space coordinates). According to the special theory of relativity, it is necessary for the time and space coordinates to be treated on the same basis.

It is interesting to note that the de Broglie relations

$$\rho = h\kappa, \quad E = \hbar \omega$$

are relatively invariant. In the Lorentz transformation, they behave like a four-vector $\rho_\mu$ with components

$$\rho_1, \rho_2, \rho_3 = p, \quad \rho_4 = \frac{ie}{c}. \quad (15.2)$$

This indicates that it is possible to generalize quantum mechanics to the case of particles traveling with a velocity of the order of the velocity of light.

A method of extending the nonrelativistic wave equation in a way consistent with the special theory of relativity was proposed by Klein and Gordon in 1926. (This method was also put forward by Schrödinger and by Fok.) The simplest way of obtaining the Klein-Gordon equation consists in taking the relativistic relationship between the energy $E$, momentum $p$, and rest mass $m_0$ of a free particle

$$E^2 - c^2p^2 - m_0^2c^4 = 0, \quad (15.3)$$
substituting the energy and momentum operators

\[ E = \hbar \frac{\partial}{\partial t}, \quad p = -i\hbar \nabla, \]

which act on the wave function \( \psi(r, t) \). Replacing \( m_0 \) by \( \hbar k_0/c \) and dividing by \( \hbar^2 c^2 \), we obtain

\[ \left( \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - k_0^4 \right) \psi = \left( \frac{\partial}{\partial x_\mu} \frac{\partial}{\partial x_\mu} - k_0^2 \right) \psi = 0. \]  

(15.5)

Here

\[ x_1 = x, \quad x_2 = y, \quad x_3 = z, \quad x_4 = i c t \]  

(15.6)

(a double occurrence of the subscript \( \mu \) in a term indicates that it should be summed from 1 to 4). Since our initial equation was the relativistic relationship (15.3), Eq. (15.6) is relativistically invariant and, therefore, it is symmetric with respect to the space and time coordinates. We shall not attempt to prove the invariance of the Klein-Gordon equation more rigorously, and shall now proceed to examine its properties.

**B. THE CHARGE AND CURRENT DENSITY**

As in the nonrelativistic theory, equations for the charge and current density can be obtained on the basis of the equation of continuity

\[ \nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} = 0. \]  

(15.7)

We multiply (15.5) on the left by \( \psi^* \), and the complex conjugate of this equation [that is, Eq. (15.5) with \( \psi^* \) substituted for \( \psi \)] by \( \psi \). Then we subtract the second of the resulting equations from the first

\[ \psi^* \psi - \psi \psi^* - \frac{1}{c^2} \left( \psi^* \frac{\partial^2}{\partial t^2} \psi - \psi \frac{\partial^2}{\partial t^2} \psi^* \right) = 0. \]  

(15.8)

After some simple transformations, Eq. (15.8) becomes

\[ \nabla \cdot \left( \psi^* \frac{\partial^2}{\partial t^2} \psi - \psi \frac{\partial^2}{\partial t^2} \psi^* \right) + \frac{1}{c^2} \frac{\partial}{\partial t} \left( \psi^* \frac{\partial}{\partial t} \psi - \psi \frac{\partial}{\partial t} \psi^* \right) = 0. \]  

(15.9)
Defining the charge density and the current density as

\[ \rho = \frac{i\hbar}{2m_\phi c^2} \left[ \phi^* \frac{\partial \phi}{\partial t} - \left( \frac{\partial \phi^*}{\partial t} \right) \phi \right], \tag{15.10} \]

and

\[ j = \frac{e\hbar}{2im_\phi} \left[ \phi^* \nabla \phi - (\nabla \phi^*) \phi \right], \tag{15.11} \]

we note that these expressions satisfy the equation of continuity (15.7). Moreover, they define a four-dimensional vector

\[ j_\mu = \frac{e\hbar}{2m_\phi} \left[ \phi^* \frac{\partial \phi}{\partial x_\mu} - \left( \frac{\partial \phi^*}{\partial x_\mu} \right) \phi \right], \tag{15.12} \]

where

\[ x_1 = icl, \quad j_\parallel = ic \phi. \tag{15.13} \]

The current density (15.11) is identical with the nonrelativistic expression (5.21), and the charge density (15.10) reduces to the nonrelativistic expression (5.20) when \( v \ll c \). Substituting \( i\hbar \frac{\partial}{\partial t} \rightarrow E \) [see (15.4)] into (15.10), we obtain

\[ \rho = \frac{eE}{mc^2} \phi^* \phi, \tag{15.14} \]

which becomes the usual expression \( \rho = e\phi^* \phi \) in the nonrelativistic approximation \( E \sim m_\phi c^2 \). Thus we have selected a normalization in which the relativistic values of \( \rho \) and \( j \) reduce to the corresponding nonrelativistic expressions when \( \left( \frac{v}{c} \right)^2 \ll 1 \).

It is worth noting that the definition of the particle density (as distinguished from the charge density)

\[ \rho_0 = \frac{\rho}{\epsilon} = \frac{i\hbar}{2m_\phi c^2} \left[ \phi^* \frac{\partial \phi}{\partial t} - \left( \frac{\partial \phi^*}{\partial t} \right) \phi \right] \tag{15.15} \]

gives rise to some difficulties in the relativistic theory. The Klein-Gordon wave equation is a second-order differential equation and, therefore, both \( \phi \) and \( \frac{\partial \phi}{\partial t} \) can be arbitrarily defined at some given time \( t \). Consequently, the density \( \rho_0 \) (15.15) is not positively defined, unlike the nonrelativistic probability density

\[ \rho_0 = \phi^* \phi. \tag{15.16} \]
Accordingly, the expression (15.15) cannot be interpreted as the particle density (that is, the "number of particles per unit volume"). The underlying reason for this is that the same relativistic equation describes particles with either positive or negative charge (and, indeed, π mesons, to which the Klein-Gordon equation is applicable, may be either positive or negative in charge). The quantity $\rho_0$, therefore, can have both signs.

C. RELATIVISTIC THEORY OF THE HYDROGEN ATOM
(NEGLECTING THE ELECTRON SPIN)

To treat the interaction of a particle with an electromagnetic field (defined as usual by a vector potential $A$ and a scalar potential $\Phi$), we introduce the same operators as in the nonrelativistic case

\[ F = i\hbar \frac{\partial}{\partial t} - e\Phi, \quad P = -i\hbar \nabla - \frac{e}{c} A. \]  (15.17)

From (15.3), we can obtain the Klein–Gordon equation

\[ \left\{ \left( i\hbar \frac{\partial}{\partial t} - e\Phi \right)^2 - c^2 \left( i\hbar \nabla + \frac{e}{c} A \right)^2 - m_0^2 c^4 \right\} \psi = 0. \]  (15.19)

We shall use this equation to study the spectrum of the hydrogen-like atom. Setting $A = 0$ and $V = e\Phi = -\frac{Ze^2}{r}$ in (15.19), we have

\[ \nabla^2 \psi + \frac{1}{c^2 \hbar^2} \left\{ (E - V)^2 - m_0^2 c^4 \right\} \psi = 0. \]  (15.20)

Since the potential energy does not depend on time in this equation, we can transform to the time-independent case by means of the substitution

\[ \psi(r, t) = \psi(r) e^{-\frac{i}{\hbar} (E + m_0 c^2) t}. \]

In this equation, we have not included the rest mass energy $m_0 c^2$ of the particle in the energy $E$. As a result, Eq. (15.20) becomes

\[ \nabla^2 \psi + \frac{1}{c^2 \hbar^2} \left\{ \left( E + m_0 c^2 + \frac{Ze^2}{r} \right)^2 - m_0^2 c^4 \right\} \psi = 0. \]  (15.21)

---

2 This equation can also be obtained from the relativistic Hamiltonian for a particle in an electromagnetic field

\[ H = \sqrt{c^2 \left( \frac{\hbar}{c} A \right)^2 + m_0^2 c^4} \pm e\Phi. \]  (15.18)

It is only necessary to transfer $e\Phi$ to the left-hand side, square both sides, and replace $p$ and $A$ by their quantum-mechanical operators.
Just as in the Schrödinger theory, we shall look for a solution to this equation in the form
\[ \psi = R(r) Y^m_l(\theta, \varphi). \]  

(15.22)

The equation for the radial part is
\[ \left( \nabla^2 - A + \frac{2B}{r} - \frac{l(l+1)}{r^2} - \frac{a^2 Z^2}{r^2} \right) R = 0. \]  

(15.23)

Here \( \alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137} \) is a dimensionless quantity, called the fine structure constant, and
\[ A = \frac{m_e c^2}{\hbar^2} \left[ 1 - \left( 1 + \frac{E}{m_e c^2} \right)^2 \right], \]
\[ B = \frac{m_e Z e^2}{\hbar^2} \left[ 1 + \frac{E}{m_e c^2} \right]. \]  

(15.24)

When \( c^2 \to \infty \), the expressions (15.24) reduce exactly to their non-relativistic counterparts (see Chapter 13).

The somewhat improved values that we have obtained for \( A \) and \( B \) by taking into account the relativistic effect do not change in any way the general character of the solution that was obtained in nonrelativistic theory. Formally, the additional term \( \frac{Z^2 a^2}{r^2} \) in Eq. (15.23) can be treated as a relativistic, attractive potential energy, which obeys an inverse square law and which affects the solution under certain conditions. A detailed analysis of the role of this term will be given below.

First of all, let us consider the asymptotic solution \( R_0 \) as \( r \to 0 \). In this case, Eq. (15.23) reduces to
\[ \frac{1}{r} \frac{d^2 (r R_0)}{dr^2} - \frac{l(l+1)}{r^2} Z^2 a^2 R_0 = 0. \]  

(15.25)

We shall look for a solution of this equation in the form
\[ R_0 = Cr^s. \]

We then obtain an equation for \( s \)
\[ s(s+1) - l(l+1) + Z^2 a^2 = 0, \]  

(15.26)

the solution of which is
\[ s_{1,2} = -\frac{1}{2} \pm \sqrt{\left( l + \frac{1}{2} \right)^2 - Z^2 a^2}. \]  

(15.27)

Consequently,
\[ R_0 = C_1 r^{s_1} + C_2 r^{s_2}. \]  

(15.28)
If

\[ Z \alpha < \frac{1}{2}, \]

both roots \( s_1 \) and \( s_2 \) will be real for all values of \( l \) \((l = 0, 1, 2, \ldots)\). We retain only the solution for \( rR_0 \) that does not diverge at \( r = 0 \); that is, we set \( C_1 = 0 \). Similarly, only the exponentially decreasing solution for the wave function as \( r \to \infty \) should be kept when \( E < 0 \) \((A > 0)\). The asymptotically decreasing solutions for the two limiting values of \( r \) yield the same equation for the energy spectrum as in the Schrödinger theory, as can be seen from Eq. (13.20) by substituting \( s_1 \) for \( l \). Thus, for the eigenvalues we have the equation

\[ \frac{B}{\sqrt{A}} = k + \frac{1}{2} + \sqrt{(l + \frac{1}{2})^2 - Z^2\alpha^2}. \]

Substituting the relativistic values (15.24) of the constants \( A \) and \( B \), we have (for \( n = k + l + 1 \))

\[ F_{nl} = m_0c^2 \left[ 1 + \frac{Z^2\alpha^2}{\left( k + \frac{1}{2} + \sqrt{(l + \frac{1}{2})^2 - Z^2\alpha^2} \right)^2} \right]^{-\frac{1}{2}} - m_0c^2. \]

Expanding this expression into a series of powers of \( Z^2\alpha^2 \) and retaining only the first two nonvanishing terms, we obtain an energy spectrum which includes relativistic effects:

\[ E_{nl} = -\frac{R_n^2Z^2}{n^2} \left[ 1 + \alpha^2Z^2 \left( \frac{n}{n^2} \left( l + \frac{1}{2} \right) - \frac{3}{4} \right) \right]. \]

The first term is identical to the nonrelativistic expression. The second term, which is proportional to the square of the fine structure constant \( \alpha \approx 1/137 \), gives the relativistic correction.

The relativistic correction for the hydrogen atom \((Z = 1)\) is interesting because it removes the degeneracy with regard to \( l \). The level for a given \( n \) is split into \( n \) closely spaced sublevels (the close spacing is a consequence of the smallness of \( \alpha^2 \)) because the orbital quantum number \( l \) can assume \( n \) different values \((l = 0, 1, 2, \ldots, n - 1)\). In order to compare these results with experiment, let us compute the distance between the doublet states of the Balmer series \((n = 2)\). We find

\[ \Delta \omega = \frac{E_{21} - E_{20}}{\hbar} = \frac{8}{3} \frac{R \alpha^2}{16}. \]

Experimental data show that the actual distance between doublet states in the Balmer series is only one third of the distance
given by Eq. (15.32). This discrepancy arises because the fine structure of the hydrogen levels cannot be explained entirely in terms of the relativistic relationship between mass and velocity. As we shall see in Chapter 19, it is also necessary to consider the electron spin (that is, the intrinsic angular momentum of the electron, which gives rise to a magnetic moment). At first it was thought that the Klein-Gordon equation could be used to describe a relativistic electron. As a result of the discrepancies between its predictions and experiment, however, it was established that it describes particles with spin of 0, whereas the electron has a spin of 1/2. Consequently, the Klein-Gordon equation can be used for \( \pi \) mesons, which have a spin of 0.

Finally, let us consider the case in which

\[ Z \alpha > \frac{1}{2} \]  

(15.33)

in Eq. (15.27). In this case, the solution does not consist of a correction added to the nonrelativistic solution, but is fundamentally new. Indeed, for \( l = 0 \) both roots \( s_1 \) and \( s_2 \) are complex. Therefore, the asymptotic solution (15.28) is

\[ R_0 = \frac{1}{\sqrt{\gamma}} (C_1 e^{i\theta} + C_2 e^{-i\theta}), \]  

(15.34)

where \( \gamma = \sqrt{Z^{2} \alpha^{2} - \frac{1}{4}} \). We cannot impose the condition \( C_2 = 0 \) (or \( C_1 = 0 \)) on our problem because both solutions have the same singularity as \( r \to 0 \). Since the solution remains unrestricted by a potential barrier at small \( r \), even when \( E < 0 \), the energy spectrum for \( l = 0 \) is continuous. Consequently, the particle will "fall" to the center.

The question of the stability of the motion of the particle is very important in studies of the central forces. The above results can be used to analyze the solution of the Schrödinger equation in the general case of an attractive potential

\[ V = \frac{-\hbar^{2} \beta^{2}}{2m_{0} r^{2}}. \]  

(15.35)

On obtaining the asymptotic solution for \( r \to 0 \) [15.25], we see that the solution will vanish at the origin only for a maximum value of \( q \) equal to 2 and that the particle will not fall to the center if

\[ \beta < \frac{1}{2}. \]

It is interesting to note in this connection that the \( r^{-3} \) dependence of potential energy occurs fairly frequently in the theory of
elementary particles since the potential energy of this form characterizes the interaction of two elementary magnetic dipoles. Actually, two cases have to be distinguished. In the first case, \( V \sim r^{-3} \) only at relatively large distances, while at small distances \( V \) varies as \( r^{-2} \). This behavior of \( V \) is observed for the spin-orbit interaction in the Dirac theory and it does not give rise to any difficulties. Moreover, it is found that stable motion corresponds to a value of \( Z \) greater than any in the present periodic system of elements \( (Z < 137) \) because the spin effects reduce the influence of the relativistic effects (whereas in the Klein-Gordon theory \( Z \) is confined to relatively small values \( Z < \frac{2}{3} \cdot 137 \)).

In the second case, \( V \) continues to vary as \( r^{-3} \) even at small distances \((r \to 0)\), and particles cannot be combined into atomlike systems. This case can be observed in the meson theory of nuclear forces, where quasi-magnetic interactions are of considerable importance. The formation of an atomlike system becomes possible only if the potential is cut off at small distances from the origin.

Problem 15.1. Find an expression for \( p \) and \( j \) if the scalar relativistic equation contains a term arising from the presence of an electromagnetic field.

Solution. Let us substitute \( p = p - \frac{e}{c} A, E = E - e \Phi \) in the Klein-Gordon equation, which now describes the motion of a particle in an electromagnetic field,

\[
\left\{ \left( \nabla - \frac{ie}{\hbar c} A \right)^2 - \frac{1}{c^2} \left( \frac{\partial}{\partial t} + \frac{ie\Phi}{\hbar} \right)^2 - k^2 \right\} \psi = 0.
\]

Repeating the calculations that lead to Eq. (15.15), we obtain the generalization

\[
f_\mu = \frac{e \hbar}{2m_0} \left\{ \psi^* \frac{\partial \psi}{\partial x_\mu} - \frac{\partial \psi^*}{\partial x_\mu} \psi - \frac{2ie}{\hbar c} \psi^* \psi A_\mu \right\},
\]

where the four-dimensional potential \( A_\mu \) has the components

\[ A_\mu = \{ A, i \Phi \}. \]

Problem 15.2. Show that in the case of time-independent potentials \( A \) and \( \Phi \), the space and time coordinates in the Klein-Gordon equation can be separated and the wave function can be written as

\[
\varphi (r, t) = \psi (r) e^{-i \frac{E}{\hbar} t}.
\]

Problem 15.3. Find the wave function of a free particle described by the Klein-Gordon equation using for normalization the expression for the density \( p \). Show that in the relativistic case, \( p \) is the charge density rather than the particle density.

Solution. Suppose the momentum of the particle is directed along the \( z \) axis and that the particle travels in a segment of length \( L \) (the one-dimensional case). The solution of the Klein-Gordon equation can be written in the form

\[
\psi = \frac{1}{V} \{ A e^{-i\beta t - ikz} + B e^{i\beta t - ikz} \},
\]
where \( E = \pm c^2 K \) is the energy of the particle. Since the charge density is given by the expression

\[
\rho = \frac{ie\hbar}{2m_0c^2} \left\{ \psi^* \frac{\partial \psi}{\partial t} - \frac{\partial \psi^*}{\partial t} \psi \right\},
\]

the total charge is [see (15.14)]

\[
\int_{-L/2}^{L/2} \rho \, dz = \frac{e|E|}{m_0c^2} (A^*A - B^*B).
\]

It follows that \( \rho \) is the charge density rather than the particle density, since this relation can be interpreted only if it is assumed that particles described by an amplitude \( B \) (negative energies) have a charge of opposite sign from particles described by an amplitude \( A \) (\( E > 0 \)).
Chapter 16

Motion of an Electron in a Magnetic Field.

Electron Spin

In 1896, Zeeman found that when atoms are placed in a strong magnetic field, their spectral lines are split into several components. This phenomenon is known as the Zeeman effect. The Zeeman effect played an important role in the investigation of the structure and magnetic properties of the atom. It led in particular to the discovery of the spin (intrinsic mechanical moment) and magnetic moment of the electron. Accordingly, it is worth elaborating the theory of this effect in some detail.

A. THE CLASSICAL THEORY OF THE ZEEMAN EFFECT

The simplest model of the radiating atom in Lorentz’ selection theory is based on the assumption that the electron moves under the influence of an elastic force

\[ F = -kr. \quad (16.1) \]

The elastic constant \( k \) is related to the electron mass and the angular frequency of oscillation \( \omega_0 \) by the expression

\[ k = m_0 \omega_0^2. \quad (16.2) \]

The equation for the oscillations of an electron in a homogeneous, constant magnetic field \( H \), therefore, becomes

\[ m_0 \dddot{r} + m_0 \omega_0^2 r = -\frac{e_0}{c} \dddot{r} \times H, \quad (16.3) \]

where \( e = -e_0 \) is the electron charge. Taking the components of (16.3) along the coordinate axes (the \( z \) axis is chosen in the direction of the field \( H \), so that \( H_x = H_y = 0, \ H_z = \mathcal{H} \)), we find

\[ \dddot{x} + \omega_0^2 x - \frac{e_0}{m_0 c} \dddot{x} \mathcal{H} = 0, \quad \dddot{y} + \omega_0^2 y - \frac{e_0}{m_0 c} \dddot{y} \mathcal{H} = 0, \quad \dddot{z} + \omega_0^2 z = 0. \quad (16.4) \]
Multiplying the second equation by $i (i = \sqrt{-1})$ and adding it to the first, we obtain

$$\dot{\xi} + \omega_0^2 \xi - 2i\eta \xi = 0 \quad (16.5)$$

where $\omega = \frac{e\mathbf{B}}{2m_e c}$ is the Larmor frequency of precession and $\xi = x + iy$.

For $\omega < \omega_0$ the solution of (16.5) is of the form

$$\xi = e^{i\omega t} \left\{ A e^{i \omega_0 t} + B e^{-i \omega_0 t} \right\} \quad (16.6)$$

and it follows from (16.4) that the $z$ component is

$$z = Ce^{i \omega_0 t}. \quad (16.7)$$

From the above expressions it can be seen that the frequency of oscillation of the electron (a three-dimensional oscillator) changes under the influence of a magnetic field. An atom placed in a magnetic field should emit radiation at three frequencies:

$$\omega_0 - \omega, \omega_0, \omega_0 + \omega. \quad (16.8)$$

According to the classical theory, an oscillator does not emit energy in the direction of oscillation. Therefore, when we observe the light emitted by an atom in the $z$ direction (the direction of the magnetic lines of force), we are able to detect only two lines (there will be no component $\omega_0$ due to oscillations along the $z$ axis). In other directions, we are able to observe all three components (the normal Zeeman effect). Equations (16.6) and (16.7) indicate that the oscillations are resolved in a longitudinal component in the direction of the magnetic field (the $z$ axis) and two transverse components corresponding to two directions of rotation (a right-handed rotation and a left-handed rotation). Thus, the magnetic field has no effect on the longitudinal oscillations and acts only on the circular rotations in the plane perpendicular to the magnetic field.

In quantum theory a change in the frequency of oscillation is always associated with a change of energy. At first glance, it may seem strange that the magnetic field changes the energy of the electron, since the Lorentz force $F = \frac{e}{c} \mathbf{v} \times \mathbf{H}$ is perpendicular to the velocity, and therefore the work done by this force, just as the work done by any centripetal force, must be equal to zero. On the

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$^1$Even in the case of very strong fields ($\mathbf{B} \sim 10^6$ gauss) the quantity $\omega$ is of the order of $10^{15} \text{ sec}^{-1}$, whereas the frequency of oscillation of an electron in an atom (the optical spectrum) is $\omega_0 \sim 10^{16} \text{ sec}^{-1}$. Therefore, the inequality $\omega \ll \omega_0$ is practically always satisfied.
other hand, it is well known that an electron rotating in a circle
(that is, a current loop) forms a dipole. The energy of this dipole
in a magnetic field is equal to

\[ v_{\text{mag}} = -\vec{p} \cdot \vec{H}. \]  

These two conflicting conclusions may be explained in the following
manner. As the magnetic field changes from zero to a certain
constant value \( H_z = \mathcal{H} \), the electron experiences a force directed
along one of the components of the electric field \( E \). This force
imparts an additional energy to the electron. The magnitude of
this component of the electric field can be found from Faraday’s
law of induction (second Maxwell equation):

\[ \oint E \, dl = -\frac{1}{c} \frac{d}{dt} \int \mathcal{H} \, dS. \]

Assuming that \( \mathcal{H} \) and \( E \) depend only on time and that the switching
on of the magnetic field does not alter the radius of the stationary
orbit, we find

\[ E = -\frac{r}{2c} \frac{dH_z}{dt}. \]

The additional velocity imparted to the electron \( (e = -e_0) \) by this
electric field can be found from the equation

\[ \frac{d}{dt} v_{\text{mag}} = -\frac{e_0 E}{m_0} = -\frac{e_0}{2m_0c} \frac{d\mathcal{H}}{dt}, \]

which gives

\[ v_{\text{mag}} = \frac{e_0}{2m_0c} \mathcal{H}. \]

As we can see, \( v_{\text{mag}} \) is independent of the rate of change of the
magnetic field when it is switched on. Since the magnetic field is
directed along the \( z \) axis and the induced electric field (and there­
fore also \( v_{\text{mag}} \)) is perpendicular to it and to the radius of the orbit,
we may write in vector form

\[ v_{\text{mag}} = \frac{e_0}{2m_0c} \mathcal{H} \times r. \]

From this it is clear that the magnetic field produces an additional
rotation of the electron (Larmor precession) with an angular
velocity \( \omega = \frac{e_0}{2m_0c} \mathcal{H} \).

We may now determine the unknown additional energy acquired
by a rotating electron when the magnetic field is switched on. Since
the energy of an electron placed in a magnetic field is determined
tirely by its kinetic energy, we have
MOTION OF AN ELECTRON IN A MAGNETIC FIELD

\[ V^{\text{mag}} = \frac{m_e}{2} (v + v^{\text{mag}})^2 - \frac{m_e v^2}{2}, \]

where \( v \) is the velocity of the electron before the magnetic field is switched on. Retaining only terms that are linear with respect to \( v^{\text{mag}} \), we obtain

\[ V^{\text{mag}} = \frac{e}{2c} \mathbf{v} \cdot (\mathbf{H} \times \mathbf{r}) = \frac{e}{2c} \mathbf{H} \cdot (\mathbf{r} \times \mathbf{v}). \] (16.10)

Comparing (16.10) with (16.9), we see that the magnetic moment of an electron moving in a circle is given by the expression

\[ \mathbf{\mu} = -\frac{e}{c} \mathbf{r} \times \mathbf{v}. \] (16.11)

Recalling that its angular momentum is equal to

\[ \mathbf{L} = m_e \mathbf{r} \times \mathbf{v}, \]

we find a simple relation between these two quantities

\[ \mathbf{\mu} = -\frac{e}{2m_e c} \mathbf{L}. \] (16.12)

It is worth noting that the magnitude of the magnetic moment can also be found from other considerations. As we know, the magnetic moment of a current loop is

\[ \mathbf{\mu} = \frac{JS}{c} \mathbf{n} \]

where \( \mathbf{n} \) is a unit vector normal to the plane of the current loop. In the above relationship the current strength is equal to

\[ J = -\frac{e}{T} = -\frac{e v}{2\pi r}, \]

where \( T = \frac{2\pi r}{v} \) is the period of rotation, while the area enclosed by the current is

\[ S = \pi r^2. \]

Combining these last relations we again obtain the expression (16.11) for the quantity \( \mathbf{\mu} \).

B. THE ZEEMAN EFFECT IN THE NONRELATIVISTIC SCHröDINGER THEORY

In order to obtain the Schrödinger equation for an electron moving in a magnetic field, we shall use the general rule for transformation of the classical Hamiltonian to the quantum case (see, for
example, Chapter 5). To do this, we substitute the momentum operator $p$ into the classical expression for the energy of an electron in the presence of electrostatic and magnetic fields. The Schrödinger equation for the central forces in the presence of a magnetic field characterized by the vector potential $A$ then takes the form

$$(E - H^S) \psi = 0 \quad (16.13)$$

where the Hamiltonian of the Schrödinger equation is

$$H^S = e\Phi(r) + \frac{p^2}{2m_0} \quad (16.14)$$

and the operator $P = p - \frac{e}{c} A$ is called the generalized momentum operator. For the case of a constant, homogeneous magnetic field directed along the $z$ axis ($H_x = H_y = 0, H_z = \mathcal{H}$), we may write

$$A_x = -\frac{1}{2} y \mathcal{H}, \quad A_y = \frac{1}{2} x \mathcal{H}.$$  

Using the fact that

$$(p \cdot A) \psi = -i\hbar (\nabla \cdot A) \psi + (A \cdot p) \psi,$$

where

$$\nabla \cdot A = 0,$$

and neglecting the terms proportional to the square of the magnetic field strength $\mathcal{H}$, we find

$$\left\{ E - e\Phi(r) - \frac{p^2}{2m_0} + \frac{e}{m_0 c} A \cdot p \right\} \psi = 0. \quad (16.15)$$

Remembering that

$$\frac{e}{m_0 c} A \cdot p = \frac{e\mathcal{H}}{2m_0 c} L_z, \quad (16.16)$$

where

$$L_z = -i\hbar \frac{\partial}{\partial \phi},$$

we reduce the Schrödinger equation to the form

$$\left\{ \nabla^2 + \frac{2m_0}{\hbar^2} \left[ E + \frac{e\mathcal{H}}{2m_0 c} L_z - e\Phi(r) \right] \right\} \psi = 0. \quad (16.17)$$
It is easy to show that this equation is satisfied by the usual wave function for a centrally symmetric field:

\[ \psi = R(r) Y^m_i(0, \varphi). \quad (16.18) \]

Substituting this solution into (16.17) and recalling that

\[ L_y Y^m_i = \hbar m Y^m_i, \]

we obtain the equation

\[ \left\{ \nabla^2 + \frac{2m_0}{\hbar^2} \left( E + \frac{e\mathcal{A} \hbar}{2m_0c} m - e\Phi(r) \right) \right\} \psi = 0, \]

which also includes the effect of the magnetic field on the atom. This equation may be written as

\[ (E - H^S) \psi = 0, \]

\[ H^S = \frac{p^2}{2m_0} - e\Phi(r) + \frac{e_0 \mathcal{A} \hbar}{2m_0c} m, \quad (16.19) \]

where we take the charge of the electron as

\[ e = -e_0. \]

The last term in the Hamiltonian may be attributed to the presence of the orbital magnetic moment of the atom, which gives rise to an additional energy

\[ V^{mag} = - \mu \cdot H = - \mu_0 \mathcal{A} \mathcal{H} = \frac{e_0 \hbar}{2m_0c} m \mathcal{H}. \quad (16.20) \]

Therefore, the orbital magnetic moment obtained on the basis of the Schrödinger theory is

\[ \mu_z = - \frac{e_0 \hbar}{2m_0c} m. \quad (16.21) \]

Recalling the expression for the \( z \) component of the angular momentum

\[ L_z = \hbar m, \]

we obtain the same relation between the magnetic moment and the angular momentum as in the classical theory [see (16.12)]:

\[ \frac{\mu_z}{L_z} = - \frac{e_0}{2m_0c}. \quad (16.22) \]

It follows, therefore, that the components of the orbital magnetic moment are multiples of a certain unit magnetic moment.
which is called the Bohr magneton.

The orbital magnetic moment of an electron is one of the most important magnetic properties of an atom. It can be seen from Eq. (16.20) that the additional energy of an orbital electron placed in a magnetic field is given by the expression

\[ E_{\text{mag}} = V_{\text{mag}} = \frac{e_0 h}{2 m_0 c} m = \omega \hbar m, \]  

(16.24)

since \( V_{\text{mag}} \) is a constant, where \( \omega \) is the Larmor frequency. Because of the selection rules for the magnetic quantum number (\( \Delta m = 0, \pm 1 \)), the additional radiation frequencies due to the Zeeman splitting are the same as in the classical theory [see (16.8)], namely,

\[ \Delta \omega = \frac{\Delta E_{\text{mag}}}{n} = \omega \Delta m = 0, \pm \omega. \]  

(16.25)

The normal Zeeman splitting\(^2\) of the spectral lines (triplets and doublets) is encountered only in the case of a strong field (the Paschen-Back effect) or in the case when the total spin of the electrons in the atom is equal to zero (for example, in parahelium, whose outer shell consists of two electrons with oppositely directed spins). In cases in which the spectral lines are split into more than three components, the Zeeman effect is said to be anomalous. The anomalous Zeeman effect is connected with the spin properties of electrons, and an explanation of this effect can be constructed only on the basis of Dirac's theory, which takes into account the spin effects (see Chapter 20).

C. THE EXPERIMENTAL DISCOVERY OF ELECTRON SPIN

It was shown in the last section that the Schrödinger theory is able to explain only the orbital angular momentum and magnetic moment of an electron. The basic equations characterizing these properties are Eq. (16.22) for the ratio of the orbital magnetic moment and

\(^{2}\)Let us note that the reasons for the use of the terms "normal Zeeman effect" and "anomalous Zeeman effect" are purely historical. Before the discovery of electron spin, only the classical theory of triplet splitting (normal Zeeman effect) was known. When a more complicated splitting was discovered it was called the anomalous Zeeman effect because no theoretical explanation could be given for it until the development of the theory of electron spin.
the orbital angular momentum and Eq. (16.24), which indicates that the number of possible orientations of the magnetic moment relative to the z axis is necessarily odd, since the number of states with different quantum numbers \( m \) is equal to \( 2l + 1 \). The Schrödinger theory, however, does not adequately account for all the experimental data, the analysis of which led to the discovery of the spin properties of electron. Let us briefly discuss these experimental results.

1. First of all let us consider the Einstein-de Haas experiment (1915), which was carried out in order to verify Eq. (16.22):

\[
\frac{\mu_z}{L_z} = -g \frac{e}{2m_e c},
\]

where \( g \), the Landé factor, should be equal to unity for orbital moments. In this experiment, a ferromagnetic rod is suspended on a quartz fiber and magnetized by passing a current through a coil (see Fig. 16.1). As a result, the rod acquires a magnetic moment and an angular momentum whose magnitude can be determined from the angular rotation of the quartz fiber. If an alternating current is passed through the coil, an alternating torque will arise, causing torsional vibrations in the ferromagnetic sample. In addition, resonance can be used to enhance the rotational effect. Experimental measurements of the gyromagnetic ratio (16.22) show that the sign of this ratio is negative, so that it can be definitely concluded that the magnetization of the ferromagnetic sample is due to the motion of electrons. The value of the Landé \( g \) factor, however, turned out to be equal to two \( (g = 2) \), rather than to the unity that was required by the classical or Schrödinger theories. This \( g \) value was not explained until the development of the theory of electron spin (see below).
2. Stern and Gerlach (1921) studied the behavior of a beam of atoms in an inhomogeneous magnetic field in order to check the theoretical result (16.23)

\[ \mu_z = -\mu_0 m, \]

which describes the spatial quantization. In their classical experiments a beam of monovalent atoms (hydrogen, lithium, silver), traveling along the \( x \) axis, crossed a magnetic field directed along the \( z \) axis \((H_x = H_y = 0, H_z = H)\). This magnetic field was very inhomogeneous, so that it had large gradients. Then a magnetic dipole of moment

\[ \mu = e_{\text{mag}} l, \quad (16.26) \]

where \( e_{\text{mag}} \) is the "magnetic charge" and \( l \) is the length of the dipole, will experience a force directed along the \( z \) axis

\[ F_z = e_{\text{mag}} \left\{ \mathcal{H}(z) - \mathcal{H}(z - l \cos \alpha) \right\} =
\]

\[ = e_{\text{mag}} l \cos \alpha \frac{\partial \mathcal{H}}{\partial z} = \mu_z \frac{\partial \mathcal{H}}{\partial z} = -\mu_0 \frac{\partial \mathcal{H} \cdot }{\partial z} m. \quad (16.27) \]

Let us calculate in a simplified fashion the displacement experienced by a particle under the action of the force \( F_z \) during the time \( t \). If the particle moves with a velocity \( v \) perpendicular to the magnetic field (that is, to the \( z \) axis) and travels a distance \( L = vt \), the displacement along the direction of the \( z \) axis will equal

\[ \delta z = \frac{1}{2} \omega t^2 = \frac{1}{2} \frac{L^2}{v^2} \mu_z \frac{\partial \mathcal{H} \cdot }{\partial z}. \quad (16.28) \]

In this case the acceleration is \( \omega = \frac{F_z}{M} \), where the force \( F_z \) is given by (16.27), and \( M \) is the mass of the atom. Consequently, a beam of particles possessing a magnetic moment \( \mu \) will be split into components as it passes through an inhomogeneous magnetic field. The number of components is determined by the possible number of projections of the magnetic moment \( \mu \) on the direction of the field.

In their experiments, Stern and Gerlach studied the splitting of a beam of atoms in the \( s \) state. In this state, the angular momentum and consequently the magnetic moment of an atom are equal to zero \((l = m = 0)\), and therefore there should be no splitting. If the electron is in the \( p \) state \((l = 1)\), then triple splitting should

---

\(^3\text{We note that in order to determine the motion of the center of mass of the magnetic dipole, it is quite immaterial whether we regard it as a rigid dipole or a current loop.}\)}
be observed because of the three possible values of the magnetic quantum number

$$\delta z = 0 \ (m = 0), \quad \delta z = \frac{1}{2} \frac{I^2}{v^2} \frac{\mu_0}{M} \frac{\partial \mathcal{H}}{\partial z} \ (m = \pm 1).$$

Experiments on hydrogen, lithium, silver, and other atoms show, however, that the beam is split into only two components. This proved the existence of a magnetic moment for atoms in the s state. The projection of this magnetic moment on the z axis can assume only two values. The measurements of the quantity \(\mu\) showed that it is equal to one Bohr magneton

$$\mu_0 = \frac{e\hbar}{2mc}. \quad (16.29)$$

In order to reconcile the results of these two classical experiments, Uhlenbeck and Goudsmit introduced the hypothesis that an electron possesses an intrinsic angular momentum in addition to its orbital angular momentum. At first it was believed that this intrinsic angular momentum could be treated by analogy with a top spinning about an axis, and therefore it was called the electron spin. It must, however, be emphasized that no rigorous classical theory of spin exists. According to the hypothesis of Uhlenbeck and Goudsmit, the intrinsic angular momentum of an electron is equal to

$$s_z = \pm \frac{1}{2} \hbar; \quad (16.30)$$

that is, the quantum number characterizing its projection on the z axis takes on half-integral values \(m_s = \pm \frac{1}{2}\). The important distinction between the integral (orbital magnetic quantum number \(m\)) and the half-integral (spin quantum number \(m_s\)) values of quantum numbers lies in the number of possible states. Integral quantum numbers always give us an odd number of states (for \(l=0\) we have one state \(m=0\); for \(l=1\) there are three states \(m=0, 1, -1\); and so on). On the other hand, half-integral quantum numbers give us an even number of states (for example, for \(s=\frac{1}{2}\) there are two states \(m_s = \frac{1}{2}, -\frac{1}{2}\); for \(s=\frac{3}{2}\) there are four states; and so on).

The assumption of the half-integral quantum numbers was introduced even before Uhlenbeck and Goudsmit in order to explain the double splitting of terms for the monovalent atoms. The Stern-Gerlach experiment showed that there are two possible electron states in a monovalent atom; that is, the electron spin must be
described by the half-integral quantum numbers corresponding to two opposite orientations. Recalling that the Einstein-de Haas experiment showed that the Landé $g$ factor in Eq. (16.29) is equal to two ($g = 2$) and the intrinsic angular momentum is given by Eq. (16.30), we find the following expression for the $z$ component of an intrinsic magnetic moment:

$$\mu_{sz} = -\frac{e_0}{m_0 c} s_z = \mp \mu_e,$$

(16.31)

which is simply one Bohr magneton. The introduction of the electron spin also made it possible to explain the multiple splitting of the spectral lines of atoms, as well as their magnetic properties.

**D. PAULI EQUATION**

A nonrelativistic wave equation that includes the intrinsic magnetic moment of the electron was first proposed by Pauli. For this purpose he took the ordinary Hamiltonian of the Schrödinger equation and added to it a term representing the interaction between the magnetic moment of the electron $\mu$ and the external magnetic field $H$:

$$V^P = -\mu \cdot H.$$ 

(16.32)

Then the time-independent Schrödinger equation takes the form

$$\{ E - HS + \mu \cdot H \} \psi = 0,$$

(16.33)

where the Hamiltonian $H_S$ is

$$\hat{H}_S = \frac{\hbar}{2 m_0} \left[ p - \frac{e}{c} A \right]^2 + e\Phi.$$

(16.34)

Next, it was necessary to find suitable quantities to describe the intrinsic magnetic moment of the electron. It is well known that introduction of the spin is related to introduction of a fourth quantum number, characterizing the internal properties of an electron. On the other hand, the wave function $\psi$ of a particle depends only on three quantum numbers, corresponding to quantization of the three spatial coordinates. In order to describe spin, Pauli introduced two wave functions $\psi_1$ and $\psi_2$ in place of the single wave function $\psi$. One of the wave functions describes a state with one spin orientation and the other wave function describes a state with the opposite spin orientation. The actual wave equation represents a system of two equations. It is possible to represent a system of two or more equations, such as
by a single equation in matrix notation

\[(a) (\Psi) = \left( \begin{array}{c|c} a_{11} & a_{12} \\ \hline a_{21} & a_{22} \end{array} \right) \left( \begin{array}{c} \Psi_1 \\ \Psi_2 \end{array} \right) = 0, \]

where the multiplication is carried out according to the rule for the multiplication of matrices \((c) = (a)(b)\); namely, an element of a matrix product is obtained by multiplying each element in the appropriate row of the first matrix by the corresponding elements of the appropriate column of the second matrix and taking the sum of these products, that is,

\[c_{ik} = \sum_n a_{in} b_{nk}. \]

Pauli suggested selecting the wave function \(\Psi\) in the form of a one-column matrix \(\Psi = \left( \begin{array}{c} \Psi_1 \\ \Psi_2 \end{array} \right)\) and setting the intrinsic magnetic moment of an electron equal to

\[\mu = -\mu_0 \sigma'. \]

where \(\mu_0\) is the Bohr magneton and \(\sigma'\) stands for the three \(2 \times 2\) Pauli matrices

\[\sigma_i = \left( \begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array} \right), \quad \sigma_i' = \left( \begin{array}{cc} 0 & -i \\ i & 0 \end{array} \right), \quad \sigma_i'' = \left( \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right). \]

These matrices are denoted by the letter \(\sigma\) with a prime (the same letter without a prime will be used to denote the \(4 \times 4\) Dirac matrices). These matrices characterize the components of the spin vector along the coordinate axes.

Using the rule (16.36) for matrix multiplication, it can be readily shown that the square of each Pauli matrix is equal to unity

\[\sigma_i'^2 = \sigma_i'^* = \sigma_i'' = 1, \]

where \(I'\) denotes a \(2 \times 2\) unit matrix \(\left( \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right)\). It can also be shown that different matrices anticommute with one another:

\[\sigma_i' \sigma_i' = -\sigma_i' \sigma_i' = i\sigma_i', \]

\[\sigma_i' \sigma_i' = -\sigma_i' \sigma_i' = i\sigma_i', \]

\[\sigma_i' \sigma_i' = -\sigma_i' \sigma_i' = i\sigma_i'. \]
In terms of the above matrix expressions, the nonrelativistic Pauli equation has the form

\[
\left\{ (E - HS) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \mu_0 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} H_x + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} H_y + \right. \\
\left. + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} H_z \right\} \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix} = 0.
\] (16.41)

This matrix equation is equivalent to a system of two ordinary equations, each of which corresponds to one of the rows of the matrix

\[
\begin{align*}
(E - HS - \mu_0 H_z) \Psi_1 - \mu_0 (H_x - iH_y) \Psi_2 &= 0, \\
(E - HS + \mu_0 H_z) \Psi_2 - \mu_0 (H_x + iH_y) \Psi_1 &= 0.
\end{align*}
\] (16.42)

Let us consider the case of an electron moving in a magnetic field directed along the \(z\) axis \((H_x = H_y = 0, H_z = \mathcal{H})\). Using the Hamiltonian (16.19), which includes the effect of a magnetic field, we obtain two equations of motion for the electron

\[
\begin{align*}
\{ E + e_0\Phi - \mu_0\mathcal{H} m - \mu_0\mathcal{H} - \frac{p^2}{2m_0}\} \Psi_1 &= 0, \\
\{ E + e_0\Phi - \mu_0\mathcal{H} m + \mu_0\mathcal{H} - \frac{p^2}{2m_0}\} \Psi_2 &= 0,
\end{align*}
\] (16.43)

where \(\mu_0\mathcal{H} m\) is the energy of interaction between the magnetic field \(\mathcal{H}\) and the orbital magnetic moment, and \(\pm \mu_0\mathcal{H}\) is the energy of interaction between the magnetic field and the spin magnetic moment. In the \(s\) state the magnetic quantum number \(m\) is equal to zero, so that the Pauli equation takes the form

\[
\begin{align*}
\{ E + e_0\Phi - \mu_0\mathcal{H} - \frac{p^2}{2m_0}\} \Psi_1 &= 0, \\
\{ E + e_0\Phi + \mu_0\mathcal{H} - \frac{p^2}{2m_0}\} \Psi_2 &= 0;
\end{align*}
\] (16.44)

that is, the wave function \(\Psi_1\) describes a state in which the intrinsic magnetic moment of the electron is parallel to the \(z\) axis, and the wave function \(\Psi_2\), a state in which the magnetic moment is antiparallel to the \(z\) axis. These are the orientations of the intrinsic magnetic moment which were observed in the Stern-Gerlach experiment.

As the function \(\Psi^+\) Pauli suggested taking the Hermitian adjoint of \(\Psi\), that is, the matrix \(\Psi^+ = (\Psi^*\Psi^*)\), whose elements are obtained by taking the complex conjugates of the elements of \(\Psi\) and transposing them (interchanging rows and columns). Thus, if
Ψ is a column matrix, \( \Psi^r \) will be a row matrix. The probability density will be given by

\[
\Psi^\dagger \Psi = (\Psi^r \Psi^s) (\Psi_i^s) = \Psi_i^r \Psi_i^s - \Psi_i^s \Psi_i^r,
\]

(16.45)

which includes the possibility of two spin orientations.

The other matrix elements are formed in a similar manner. For example,

\[
\Psi \sigma_z \Psi = (\Psi^r \Psi^s) (\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}) (\Psi_i^s) = (\Psi^r \Psi^s) (\begin{pmatrix} \Psi_i^s \\ -\Psi_i^s \end{pmatrix}) = \Psi_i^r \Psi_i^s - \Psi_i^s \Psi_i^r;
\]

(16.46)

that is, \( \Psi^r \Psi_i^s \) and \( \Psi_i^s \Psi_i^s \) represent the probability densities of states in which the electron has a spin orientation parallel and antiparallel to the z axis, respectively. Using the expression for the intrinsic magnetic moment in the Pauli theory

\[
\mu = -\frac{e \hbar}{2m_e c} \sigma',
\]

and the Einstein-de Haas relation between the intrinsic magnetic moment and the angular momentum

\[
\mu = -\frac{e}{m_e c} S,
\]

we find that

\[
S = \frac{1}{2} \hbar \sigma'.
\]

(16.47)

Thus, in agreement with the other experimental facts, the \( z \) component of the spin angular momentum is equal to \( \pm \frac{1}{2} \).

Since the spin operator is expressed in terms of the matrices \( \sigma' \), the spin components do not commute. In this they resemble the components of the orbital angular momentum, which are operators depending on derivatives [see (11.75) and (11.76)]. The commutation relations satisfied by the spin operators can be easily established from (16.40) and (16.47):

\[
\begin{align*}
S_x S_y - S_y S_x &= i\hbar S_z, \\
S_y S_z - S_z S_y &= i\hbar S_x, \\
S_z S_x - S_x S_z &= i\hbar S_y.
\end{align*}
\]

(16.48)
Concluding our discussion, we note that the Klein-Gordon theory, which includes the relativistic effects but neglects the spin effects, and the Pauli theory, which, on the contrary, neglects the relativistic effects but includes the spin effects, were predecessors of the more rigorous theory of the electron developed by Dirac, which predicts all the elementary properties of the electron. It should be noted in this connection that the absolute value of the intrinsic magnetic moment was introduced in the Pauli theory from purely empirical considerations.

Problem 16.1. Show that in nonrelativistic quantum mechanics, just as in the classical theory, the Zeeman effect is due to the precessional motion of the orbit in a magnetic field, the motion having the Larmor frequency.

Solution. From the Hamiltonian of the Schrödinger equation for the case of an electron moving in a magnetic field directed along the z axis

\[ H = \frac{p^2}{2m} + \alpha L_z, \]

we can find the time derivatives of the angular momentum

\[ \frac{dL_x}{dt} = \frac{i}{\hbar} (L_x - L_z H) = -\alpha L_y, \quad \frac{dL_y}{dt} = \alpha L_x, \quad \frac{dL_z}{dt} = 0, \]

where \( \alpha \) is the Larmor frequency. It follows that the component of the angular momentum in the field direction (z axis) is a constant of the motion. The components along the x and y axes, however, precess around the z axis with the frequency \( \alpha \).

Problem 16.2. Show that the spin operator \( S \) is vectorial; that is, if we construct the linear combination

\[ S'_x = \alpha_1 S_x + \beta_1 S_y + \gamma_1 S_z, \quad S'_y = \alpha_2 S_x + \beta_2 S_y + \gamma_2 S_z, \]

and so on.

Problem 16.3. Show that in a homogeneous magnetic field which is a function of time only, the wave function of the Pauli equation can be resolved into a product of coordinates and spin functions. What form does this solution take if the field is time independent?

Solution. Let us look for a solution of the Pauli equation in the form

\[ \left( \begin{array}{c} \psi_1 (r, t) \\ \psi_2 (r, t) \end{array} \right) = \phi (r, t) \left( \begin{array}{c} C_1 (t) \\ C_2 (t) \end{array} \right), \]

It is readily shown that the coordinate part of the wave function \( \psi (r, t) \) satisfies the ordinary Schrödinger equation without the spin

\[ i\hbar \frac{\partial \phi}{\partial t} (r, t) = \hat{H} \phi (r, t), \]

while the spin part of the wave function may be obtained from the equation

\[ i\hbar \frac{\partial}{\partial t} \left( \begin{array}{c} C_1 (t) \\ C_2 (t) \end{array} \right) = \mu_0 (\sigma \cdot H) \left( \begin{array}{c} C_1 (t) \\ C_2 (t) \end{array} \right). \]
The spin part of the wave function is normalized as follows

\[ (C_t^* C_0) \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = C_1^* C_1 + C_2^* C_2 = 1. \]

In the case of a stationary magnetic field it is easy to determine the time-dependent part in the above equations. We simply set

\[ \begin{pmatrix} C_1(t) \\ C_2(t) \end{pmatrix} = e^{-\frac{i}{\hbar} (E - E_s) t} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}, \]

\[ \psi(r, t) = e^{-\frac{i}{\hbar} (E - E_s) t} \psi(r). \]

Then the time-independent parts of the wave function are determined from

\[ (E - E_s) \psi = H \psi, \]

\[ E_s \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \mu_s (\mathbf{s} \cdot \mathbf{H}) \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}. \]

Problem 16.4. Find the eigenvalues of the operator of a spin component along the direction specified by the spherical angles \( \theta \) and \( \varphi \). Investigate the particular cases in which this direction is the \( x \), \( y \) or \( z \) axis.

Solution. Consider first the case in which the spin is directed along the \( z \) axis. Then the initial equation takes the form

\[ S_z \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \hbar \lambda \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}, \]

where

\[ S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \]

This matrix equation is equivalent to two homogeneous algebraic equations

\[ \frac{1}{2} C_1 - \lambda C_1 = 0, \]

\[ \frac{1}{2} C_2 + \lambda C_2 = 0. \]

The normalized solutions of these equations have the form

\[ \lambda = \frac{1}{2}, \quad C_{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \lambda = -\frac{1}{2}, \quad C_{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \]

The first evidently corresponds to the case in which the spin is directed along the \( z \) axis; the second to the case in which the spin is directed along the \( -z \) axis.

The operator for the component of spin along the direction defined by the spherical angles \( \theta \) and \( \varphi \) with respect to the coordinate axes is equal to

\[ S = \sin \theta \cos \varphi S_x + \sin \theta \sin \varphi S_y + \cos \theta \cos \varphi S_z, \]

where

\[ S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \]
Hence from the equation
\[
S \left( \frac{C_1}{C_2} \right) = \hbar \left( \frac{C_1}{C_2} \right)
\]
we find two solutions:

(a) the solution corresponding to the case in which the spin is parallel to this direction

\[
\lambda = \frac{1}{2}, \quad C_{1/2} = \begin{pmatrix}
\cos \frac{\theta}{2} \\
\sin \frac{\theta}{2} e^{i\varphi}
\end{pmatrix};
\]

(b) the solution corresponding to the case in which the spin is antiparallel to this direction

\[
\lambda = -\frac{1}{2}, \quad C_{-1/2} = \begin{pmatrix}
-\sin \frac{\theta}{2} \\
\cos \frac{\theta}{2} e^{i\varphi}
\end{pmatrix}.
\]

Setting \( \theta = 0, \varphi = 0 \) we obtain the same solution as above. The cases in which the spin is directed along the x or y axes may be obtained by setting, respectively,

\[
\theta = \frac{\pi}{2}, \varphi = 0 \quad \text{or} \quad \theta = \frac{\pi}{2}, \varphi = \frac{\pi}{2}.
\]

Problem 16.5. The electron spin is parallel to the z axis. Find the probability that the component of the spin (a) in a direction parallel to the x axis, and (b) in a direction making an angle \( \theta \) with the z axis, will have the values \( \frac{1}{2} \hbar \) and \( -\frac{1}{2} \hbar \).

Hint. Take the wave function describing the state in which the spin is parallel to the z axis and then expand it in terms of the functions corresponding to the cases in which the spin is parallel and antiparallel to the direction forming an angle \( \theta \) with the z axis. Both these functions are given in Problem 16.4. Without loss of generality we may set the angle \( \varphi = 0 \).

Then the squared modulus of the expansion coefficients gives the probabilities

\[
w_{1/2} = \cos^2 \frac{\theta}{2}, \quad w_{-1/2} = \sin^2 \frac{\theta}{2}
\]
of the components of the spin along the corresponding directions; these are equal to

\[\pm \frac{1}{2} \hbar.\]

In order to find the x component of the spin, we must set \( \theta = \frac{\pi}{2} \) in the last equations.
Chapter 17

The Dirac Wave Equation\(^1\)

A. LINEARIZATION OF THE ENERGY OPERATOR.
DIRAC MATRICES AND THEIR RELATION TO PAULI MATRICES

As indicated in Section 15, relativistic quantum mechanics is based on the well-known relativistic relation between the energy \(E\), momentum \(p\), and rest mass \(m_0\):

\[
E = c\sqrt{p^2 + m_0^2c^2}.
\]

(17.1)

To obtain the wave equation describing a free particle, we substitute the appropriate operators into this equation

\[
E = ih\frac{\partial}{\partial t}, \quad p = -ih\nabla,
\]

(17.2)

and act with these operators on the wave function. It is impossible, however, to make a direct transition to operators in (17.1) because we cannot determine the action of the differential operator under the radical sign. It is therefore necessary to get rid of the square root in (17.1). One way of doing this is to take the square of Eq. (17.1). This gives the relativistic Klein-Gordon wave equation with a one-component wave function.\(^2\) As already noted, this equation describes the motion of spinless particles and is not applicable to electrons, whose spin is equal to 1/2 (in units of \(\hbar\)).

A different method of obtaining a linear relativistic wave equation was adopted by Dirac (1928). This method gave a first-order wave equation and consisted in linearizing the relation (17.1). It led to the discovery of the relativistic wave equation for the electron. This equation plays a fundamental role in relativistic quantum mechanics and quantum field theory since it provides a

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\(^2\)More exactly, we in fact have a function with two components \(\psi_1 = \psi\) and \(\psi_2 = \frac{\partial \psi}{\partial t}\), since a second derivative with respect to time appears in the fundamental equation. One degree of freedom corresponds to particles with positive energy, the other to particles with negative energy. It was shown by Pauli and Weisskopf that the negative energy states can be eliminated by carrying out a second quantization of the scalar equation and introducing spinless particles with charges of opposite signs.
suitable description of the motion of particles of spin 1/2. The discovery of this equation was the most important advance in the theory of the electron since the Maxwell-Lorentz equations of classical electrodynamics. Bohr's semiclassical theory and non-relativistic quantum mechanics served only as transitional theories.

The relativistic relation between energy and momentum is linearized by "extracting" the square root of the four-term polynomial with the aid of matrices. For this purpose we represent (17.1) in the form

\[ E = c \sqrt{p^2 + m_0^2 c^2} = c \sum_{\mu = 0}^{3} a_\mu p_\mu, \]  

where

\[ p_0 = m_0 c, \quad p_1 = p_x, \quad p_2 = p_y, \quad p_3 = p_z. \]  

We note that

\[ E^2 = c^2 \sum_{\mu = 0}^{3} p_\mu p_\mu = c^2 (p^2 + m_0^2 c^2). \]  

To determine what conditions the quantities \( a_\mu \) must satisfy, we square both sides of (17.3). Then, if the operators \( p_\mu \) and \( p_\mu' \) commute, we have\(^3\)

\[ E^2 = c^2 \sum_{\mu} \sum_{\mu'} p_\mu p_\mu' a_\mu a_{\mu'} = \frac{e^2}{2} \sum_{\mu} \sum_{\mu'} p_\mu p_\mu' (a_\mu a_{\mu'} + a_{\mu'} a_\mu). \]  

Equation (17.6) coincides with (17.5) only if

\[ a_\mu a_{\mu'} + a_{\mu'} a_\mu = 2 \delta_{\mu\mu'}, \]  

that is, all four quantities \( a_\mu \) anticommute with one another

\[ a_\mu a_{\mu'} + a_{\mu'} a_\mu = 0 \quad \mu \neq \mu' \]  

and the square of each of them is equal to unity

\[ a_\mu^2 = 1. \]  

We recall that the 2x2 Pauli matrices also possess analogous properties

\[ \sigma_i = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_j = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_k = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \]  

\(^3\)These operators commute with each other if there is no electromagnetic field. Therefore, Dirac proposed that one should first extract the square root of the operator for a free particle, and then generalize the resulting equation to the case when fields are present.
since they anticommute [see (16.40) and the square of each is equal to unity [see (16.39)]. To extract the square root of the four-term polynomial, however, it is necessary to have four relations (17.7) \((\mu = 0, 1, 2, 3)\), instead of three [Eqs. (16.39) and (16.40)] that are satisfied by the Pauli matrices.

Accordingly, Dirac proposed that we take a system of 4 \times 4 matrices \(a_n\) and \(p_n\) that are related to the 2 \times 2 matrices by the expressions

\[
\begin{align*}
\sigma_n &= \begin{pmatrix} \sigma'_{\mu} & 0' \\ 0' & \sigma'_{n} \end{pmatrix} \quad (\mu = 1, 2, 3), \\
p_1 &= \begin{pmatrix} 0' & 1' \\ 1' & 0' \end{pmatrix}, \quad p_2 = \begin{pmatrix} 0' & -i1' \\ i1' & 0' \end{pmatrix}, \quad p_3 = \begin{pmatrix} 1' & 0' \\ 0' & -1' \end{pmatrix},
\end{align*}
\]

(17.11) (17.12)

where \(\sigma'_{n}\) are the Pauli matrices

\[
\begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.
\]

Hence we find, for example,

\[
\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}
\]

and so on.

The properties of these matrices are similar to those of the Pauli matrices, as may be easily checked by direct multiplication. In particular, it turns out that their squares are equal to unity

\[
\sigma_n^2 = p_n^2 = I (17.13)
\]

or, more exactly, are equal to the 4 \times 4 unit matrix

\[
\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \end{pmatrix}.
\]

(17.14)

As in the case of Pauli matrices, we have

\[
\begin{align*}
\sigma_1\sigma_2 &= -\sigma_2\sigma_1 = i\sigma_3, \quad p_1p_2 &= -p_2p_1 = ip_3 \quad \text{and so on.} \\
\sigma_n\sigma_{n'} &= \rho_{n'}\sigma_n \quad (n, n' = 1, 2, 3).
\end{align*}
\]

(17.15)

From this it follows that the different matrices \(\sigma\) anticommute with one another (a similar conclusion is also true for the system of \(p\) matrices):

\[
\sigma_n\sigma_{n'} + \sigma_{n'}\sigma_n = \rho_{n}\rho_{n'} + \rho_{n'}\rho_{n} = 2\delta_{nn'}.
\]

(17.16)

The matrices \(\sigma_n\) and \(\rho_{n'}\), however, commute with each other.
Dirac proposed that the matrices $\sigma_n$ [see Eq. (17.3)] be chosen as follows:

$$a_n = \rho_1 \sigma_n = \begin{pmatrix} 0 & \sigma_n' \\ \sigma_n & 0 \end{pmatrix} \quad (n = 1, 2, 3), \quad (17.17)$$

$$a_0 = \rho_3 = \begin{pmatrix} 0' & 0 \\ 0 & -1' \end{pmatrix}. \quad (17.18)$$

In conventional notation these $4 \times 4$ matrices have the form

$$a_1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad a_2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ -i & 0 & 0 & 0 \end{pmatrix},$$

$$a_3 = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad a_0 = \rho_3 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \quad (17.19)$$

Multiplying the above matrices by one another, it is easy to show that they satisfy the relations (17.7).

**B. THE DIRAC EQUATION. CHARGE DENSITY AND CURRENT DENSITY**

Let us substitute the corresponding operators into the linearized relativistic relation (17.3) between the energy and momentum. We obtain the Dirac equation for a free particle$^4$

$$(E - H) \psi = 0, \quad (17.20)$$

where the operators $E$ and $p$ are, as usual, equal to

$$E = i\hbar \frac{\partial}{\partial t}, \quad p = -i\hbar \nabla,$$

$^4$Because of the four components of the wave function $\psi$, each state can have either positive or negative energies (see below) and two directions of the spin (see Chapter 18).

In the classical case the relation (17.1) between the energy and momentum can be represented in a form similar to (17.20)

$$E = -v \cdot p - \sqrt{1 - \beta^2} m_0 c^2 = 0.$$

This equation is easily verified if it is remembered that for a free particle

$$E = \frac{m_0 c^2}{\sqrt{1 - \beta^2}} \quad \text{and} \quad p = \frac{m_0 \beta v}{\sqrt{1 - \beta^2}}.$$
and the Hamiltonian $H$ is given by

$$H = c(\alpha \cdot p) + \rho_\alpha m_0 c^2.$$  \hfill (17.21)

Since $\alpha$ and $\rho_\alpha$ are $4 \times 4$ matrices, the wave function $\psi$ must have four components, which we combine to form a single-column matrix

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}.$$  \hfill (17.22)

The complex conjugate of this function is understood to be the Hermitian adjoint, that is, the row matrix

$$\psi^+ = (\psi_1^* \psi_2^* \psi_3^* \psi_4^*).$$  \hfill (17.23)

The Dirac wave equation (17.20) is therefore equivalent to a system of four equations

\begin{align*}
(E - m_0 c^2) \psi_1 - c(p_x - ip_y) \psi_4 - cp_x \psi_3 &= 0, \\
(E - m_0 c^2) \psi_2 - c(p_x + ip_y) \psi_3 + cp_x \psi_4 &= 0, \\
(E + m_0 c^2) \psi_3 - c(p_x - ip_y) \psi_2 - cp_x \psi_1 &= 0, \\
(E + m_0 c^2) \psi_4 - c(p_x + ip_y) \psi_1 + cp_x \psi_2 &= 0.
\end{align*}  \hfill (17.24)

In the case of motion of an electron in the electromagnetic field specified by the given vector and scalar potentials $A$ and $\Phi$, we can still use Eqs. (17.20) and (17.24), but the energy and momentum operators have to be generalized in accordance with the general laws of quantum mechanics:

\begin{align*}
F &= i \hbar \frac{\partial}{\partial \alpha} - e \Phi, \\
P &= -i \hbar \nabla - \frac{e}{c} A.
\end{align*}  \hfill (17.25)

The complex conjugate of the wave equation may also be represented in the form of a single matrix equation

$$\psi^+ (F - c(\alpha \cdot P) - \rho_\alpha m_0 c^2) \psi = 0,$$  \hfill (17.26)

where the action of the operators $i \hbar \frac{\partial}{\partial \alpha}$ and $-i \hbar \nabla$ on the wave function which is on their left should be taken to be the same as in Eq. (17.20) but with opposite sign, that is,

$$-\psi^+ i \hbar \nabla = i \hbar \nabla \psi^+; \quad \psi^+ i \hbar \frac{\partial}{\partial \alpha} = -i \hbar \frac{\partial}{\partial \alpha} \psi^+.$$  \hfill (17.27)

For a free particle, Eqs. (17.20) and (17.26) now become

\begin{align*}
i \hbar \frac{\partial}{\partial t} \psi + i c(\alpha \cdot \nabla) \psi - \rho_\alpha m_0 c^2 \psi &= 0, \\
i \hbar \frac{\partial}{\partial t} \psi^+ + i c(\nabla \psi^+ \cdot \alpha) + m_0 c^2 \psi^+ \rho_\alpha &= 0.
\end{align*}  \hfill (17.28, 17.29)
Multiplying (17.28) on the left by $\psi^*$ and (17.29) on the right by $\psi$ and adding them, we obtain

$$\frac{1}{c} \frac{\partial}{\partial t} \psi^* \psi + \nabla \cdot \psi^* \alpha \psi = 0,$$

(17.30)

which may be interpreted as the equation of continuity for the probability density $\rho$ and the current density $j$:

$$\frac{\partial}{\partial t} \rho + \nabla \cdot j = 0,$$

(17.31)

where $^5$

$$\rho = e\psi^* \psi, \quad j = ec\psi^* \alpha \psi.$$  

(17.32)

If we write the last equation in terms of components of the wave functions, rather than in terms of matrices, we obtain

$$\rho_0 = \frac{e}{c} = \psi^* \psi = (\psi_1^* \psi_2^* \psi_3^* \psi_4^*) \left( \begin{array}{c} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{array} \right) = \psi_1^* \psi_1 + \psi_2^* \psi_2 + \psi_3^* \psi_3 + \psi_4^* \psi_4;$$

(17.33)

that is, $\rho_0$ is a matrix consisting of a single element (it is just a number). In exactly the same way it is readily shown that

$$J_x/e = \frac{\psi^* \sigma_1 \psi}{c} = (\psi_1^* \psi_2^* \psi_3^* \psi_4^*) \left( \begin{array}{cccc} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{array} \right) \left( \begin{array}{c} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{array} \right) = (\psi_1^* \psi_2^* \psi_3^* \psi_4^*) \left( \begin{array}{c} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{array} \right)$$

$$= \psi_1^* \psi_1 + \psi_2^* \psi_2 + \psi_3^* \psi_3 + \psi_4^* \psi_4.$$  

(17.33a)

We note that, contrary to the Klein-Gordon theory, the density $\rho_0$ is a positively defined quantity. This does not mean, however, that in the Dirac theory $\rho_0$ can be considered the particle density. Just as in the Klein-Gordon theory, there will be particles with a sign opposite to that of the electrons (positrons). From Eq. (17.32) it can again be concluded that $\alpha$ should be regarded as the velocity operator.

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$^5$Similar relations will also hold in the case when a field is present.

$^6$In second quantization, the definition of $\rho_0$ as a positive quantity means only that Fermi statistics should be applied to the particles (for example, in the case of the Dirac equation), if $\rho_0$ may take either positive or negative values (for example, in the case of the Klein-Gordon equation), then Bose statistics should be applied to the particles.
C. TRANSFORMATION PROPERTIES OF THE WAVE FUNCTION UNDER LORENTZ TRANSFORMATIONS AND SPATIAL ROTATIONS

According to the general principles of the special theory of relativity, physical laws must be independent of the choice of the Lorentz frame of reference. Therefore, the Maxwell equations, the Klein-Gordon equation, and the Dirac equation must all be invariant under the Lorentz transformations. Let us investigate the transformation properties of the Dirac wave function. The Lorentz transformations can be written as

\[ c't = ct \cosh \gamma - x' \sinh \gamma, \quad x' = x \cosh \gamma - ct \sinh \gamma, \quad y' = y, \quad z' = z, \]  

(17.34)

where

\[ \cosh \gamma = \frac{1}{\sqrt{1 - \beta^2}}, \quad \sinh \gamma = \frac{\beta}{\sqrt{1 - \beta^2}}, \quad \beta = \frac{v}{c}. \]

This transformation must be satisfied by all four-dimensional vectors, including, in particular, the charge and current densities

\[ c\rho' = c\rho \cosh \gamma - j_x \sinh \gamma, \quad j'_x = j_x \cosh \gamma - c\rho \sinh \gamma, \quad j'_y, z = j_y, z. \]  

(17.35)

The definition of these quantities, according to the Dirac theory, gives

\[ \psi'^{\dagger} = \psi^{\dagger} (\cosh \gamma - a_1 \sinh \gamma) \psi = \psi^{\dagger} e^{-\gamma a_1} \psi, \]

\[ \psi^{\dagger} a_1 \psi' = \psi^{\dagger} (a_1 \cosh \gamma - \sinh \gamma) \psi = \psi^{\dagger} a_1 e^{-\gamma a_1} \psi, \]

\[ \psi'^{\dagger} a_{2,3} = \psi^{\dagger} a_{2,3}. \]

(17.36)

Here we have used the fact that \( e^{-\gamma a_1} = \cosh \gamma - \sinh \gamma \), \( a_1 = a_1 \sinh \gamma \), since \( x_1^{2n} = 1, \ x_1^{2n+1} = x_1 \), where \( n \) is an integer. In order to satisfy the above relations, we must set

\[ \psi' = \left( \cosh \frac{\gamma}{2} - x_1 \sinh \frac{\gamma}{2} \right) \psi = e^{-\frac{\gamma}{2} x_1} \psi, \]

\[ \psi'^{\dagger} = \left( \cosh \frac{\gamma}{2} - x_1 \sinh \frac{\gamma}{2} \right) \psi^{\dagger} e^{-\frac{\gamma}{2} x_1}. \]  

(17.37)

Then, since

\[ x_1 e^{-\frac{\gamma}{2} x_1} = e^{-\frac{\gamma}{2} x_1} x_1, \quad x_1 e^{-\frac{\gamma}{2} x_1} = e^{\frac{\gamma}{2} x_1} x_1, \]

(17.38)

it is easy to show that the relations (17.36) are correct. From (17.37) it can be seen that the wave functions do not transform as
vectors (whole angle $\gamma$) or as tensors (double angles $\gamma$), but as spinors, the transformation of which is characterized by the angles $\gamma/2$. Spinors are also called tensors of rank $1/2$.

In a similar manner, it may be shown that the transformation law of a spinor under an ordinary spatial rotation (for example, around the $z$ axis by the angle $\varphi$) is as follows:

$$\psi' = e^{i\sigma_3 \frac{\varphi}{2}} \psi, \quad \psi'^+ = \psi^+ e^{-i\sigma_3 \frac{\varphi}{2}}. \quad (17.39)$$

The above relations follow from the transformations for the current vector:

$$j'_x = j_x \cos \varphi + j_y \sin \varphi,$$
$$j'_y = j_y \cos \varphi - j_x \sin \varphi,$$
$$j'_z = j_z; \quad (17.40)$$

these transformations are represented in the Dirac theory as

$$\psi'^+ a_1 \psi' = \psi^+ (a_1 \cos \varphi + a_2 \sin \varphi) \psi,$$
$$\psi'^+ a_3 \psi' = \psi^+ a_3 \psi \quad \text{and so on.} \quad (17.41)$$

By substituting the values for $\psi'$ from (17.39), and using the fact that

$$a_1 e^{i\sigma_3 \frac{\varphi}{2}} = a_1 \left( \cos \frac{\varphi}{2} + i\sigma_3 \sin \frac{\varphi}{2} \right) = \left( \cos \frac{\varphi}{2} - i\sigma_3 \sin \frac{\varphi}{2} \right) a_1 =$$
$$= e^{-i\sigma_3 \frac{\varphi}{2}} a_1, \quad a_3 e^{i\sigma_3 \frac{\varphi}{2}} = e^{i\sigma_3 \frac{\varphi}{2}} a_3,$$

we can obtain the relations (17.40).
Chapter 18

The Dirac Theory of the Motion of an Electron in a Central Field of Force

A. ORBITAL, SPIN AND TOTAL ANGULAR MOMENTA. CONSERVATION LAWS

We shall determine the angular momentum of an electron from the conservation laws characterizing the motion of an electron in a central field of force:

\[ V = e\Phi(r) \]  

(for example, an electron moving in the Coulomb field of a nucleus \( V = -\frac{Ze^2}{r} \)). It was shown in the nonrelativistic Schrödinger theory that the orbital angular momentum is conserved in a central field

\[ L = r \times p. \]

In the Dirac theory, however, which takes into account the electron spin, the component of the orbital angular momentum does not commute with the Hamiltonian

\[ H = c(\alpha \cdot p) + \frac{\hbar}{2m} c^0 + V(r) \]

and therefore it is not a constant of the motion. Indeed

\[ H L_z - L_z H = \frac{\hbar}{i} (x_1 p_y - x_3 p_x) \neq 0. \]

In order to generalize the law of conservation of angular momentum to particles having spin, we shall use the relation

\[ H \sigma_3 - \sigma_3 H = \frac{2\hbar}{i} (x_3 p_x - x_1 p_y). \]

It follows from this that the operator

\[ J = L + \frac{1}{2} \hbar \sigma = L + S \]
commutes with the Hamiltonian operator $H$ and thus is a constant of the motion.\footnote{Since only the total quantity \eqref{eq:18.6} is conserved, the separation of the angular momentum into spin and orbital parts is not rigorous in the general case. This separation is found to be possible only in certain special cases (see Chapter 20).}

This result may be interpreted in the following manner. The electron has an intrinsic angular momentum (spin). We have just found that only the total angular momentum is conserved (the orbital angular momentum plus the spin). The orbital angular momentum in the $s$ state is equal to zero, and therefore we have here the law of conservation of spin angular momentum. For the square of the spin we obtain

$$S^2 = \frac{1}{4} \hbar^2 (s^2 + s^2 + s^2) = s(s + 1) \hbar^2 = \frac{3}{4} \hbar^2; \quad (18.7)$$

that is, the electron spin takes half-integral values $s = 1/2$ (in units of $\hbar$).

**B. PROPERTIES OF THE TOTAL ANGULAR MOMENTUM OPERATORS. QUANTIZATION OF THE TOTAL ANGULAR MOMENTUM. VECTOR MODELS**

We shall now show that the operators for the components of the total angular momentum in the Dirac theory satisfy the same commutation relations as the operators for the components of the orbital angular momentum in the nonrelativistic quantum theory (see Chapter 11). It can be seen that the operators $L$ and $S$ commute with each other, because they act on different variables. Therefore,

$$J_x J_y - J_y J_x = (L_x + S_x)(L_y + S_y) - (L_y + S_y)(L_x + S_x) = L_x L_y - L_y L_x + S_x S_y - S_y S_x = i\hbar (L_x + S_x) = \quad (18.8)$$

and

$$J_x J_y - J_y J_x = i\hbar J_z,$$

$$J_y J_z - J_z J_y = i\hbar J_x,$$

$$J_z J_x - J_x J_z = i\hbar J_y.$$

The last two relations are obtained from the first by cyclic permutation of the coordinates

$$x \rightarrow y, \quad y \rightarrow z, \quad z \rightarrow x.$$
The operator of the square of the total angular momentum is seen to be

$$J^2 = (L + S)^2 = L^2 + S^2 + 2(L_x S_x + L_y S_y + L_z S_z),$$  \hspace{1cm} (18.10)

which commutes not only with the Hamiltonian but also with any of its components, for example, with the z component:

$$J_z J - J_z J^2 = 0.$$ \hspace{1cm} (18.11)

By analogy to the orbital and spin angular moments, we conclude that the square of the total angular momentum and one of its components (for example, $J_z$) may have simultaneous eigenvalues.

The quantization rules of the total angular momentum may be found from the quantization rules of its orbital component (for a spinless particle):

$$L^2 = \hbar^2 l (l + 1), \quad (l = 0, 1, \ldots), \quad L_z = \hbar m, \quad (m = -l, \ldots, +l)$$ \hspace{1cm} (18.12)

and its spin component (for example, for $l = 0$)

$$S^2 = \hbar^2 s (s + 1), \quad (s = \frac{1}{2}), \quad S_z = \hbar m_s, \quad (m_s = \pm \frac{1}{2})$$ \hspace{1cm} (18.13)

This problem can be solved exactly in general form in the Dirac theory. For the sake of simplicity we shall, however, solve it in the Pauli approximation, that is, taking into account the spin of the particle and assuming that the particle itself is nonrelativistic.

If the particle moves in a central field of force, the components of the wave function

$$\Psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix},$$ \hspace{1cm} (18.14)

which obeys the Pauli equation (see Chapter 16), can be related by means of the law of conservation of angular momentum

$$J_z \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} \mathbf{L} + \frac{1}{2} \hbar \sigma \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \hbar^2 j (j + 1) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix},$$

$$J_z \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} \mathbf{L} \sigma \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \hbar m_s \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix},$$ \hspace{1cm} (18.15)

where $L = \mathbf{r} \times \mathbf{p}$ is the orbital angular momentum operator and $\sigma$ are the two-component Pauli matrices. We shall look for a solution of the system of equations (18.15) in the form\(^2\)

$$\Psi_1 = C_1 Y_l^{m-1}, \quad \Psi_2 = C_2 Y_l^m,$$ \hspace{1cm} (18.16)

---

\(^2\)In this particular choice of a solution, only the square of the orbital angular momentum is conserved, not its projection on the z axis.
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where \( Y_l^m \) are the spherical harmonics (see Chapter 11). Then, since

\[
L^q (\Psi_i) = \hbar^q (l + 1) (\Psi_i),
\]

(Eq. 18.17)

Eqs. (18.15), (18.12) and (18.13) give

\[
\frac{1}{\hbar} (\mathbf{s} \cdot \mathbf{L}) (\Psi_i) = \left[ j (j + 1) - l (l + 1) - \frac{3}{4} \right] (\Psi_i)
\]

or

\[
\frac{1}{\hbar} [(L_x - iL_y) \Psi_1 + L_z \Psi_1] = q \Psi_1,
\]

\[
\frac{1}{\hbar} [(L_x + iL_y) \Psi_1 - L_z \Psi_1] = q \Psi_2,
\]

where

\[
q = j (j + 1) - l (l + 1) - \frac{3}{4}.
\]

Using the relations (11.87) and (11.88), we have

\[
L_z Y_l^m = - \hbar \frac{\partial}{\partial \gamma} Y_l^m = m \hbar Y_l^m,
\]

\[
(L_x \pm iL_y) Y_l^m = - \hbar \sqrt{(l + 1 \pm m)(l \mp m)} Y_l^{m \pm 1}.
\]

Then, taking into account (18.16), we may write Eq. (18.18) as

\[
(q - m + 1) C_1 + \sqrt{(l + 1 - m)(l + m)} C_2 = 0,
\]

\[
\sqrt{(l + 1 - m)(l + m)} C_1 + (q + m) C_2 = 0.
\]

From the requirement that the determinant of the system be equal to zero, we find two values of \( q \) corresponding to the two possible types of solution

\[
q = l, \quad j = l + \frac{1}{2}, \quad C_2 = - \sqrt{\frac{l - m + 1}{l + m}} C_1,
\]

\[
q = -(l + 1), \quad j = l - \frac{1}{2}, \quad C_2 = \sqrt{\frac{l + m}{l - m + 1}} C_1.
\]

The coefficients \( C_1 \) and \( C_2 \), which determine the relationship between the spherical harmonics in the sum of the orbital and spin angular momenta, are called the Clebsch-Gordan coefficients.

\[3\] We note that this relationship between the spherical harmonics is obtained only in the case of spin-orbit interaction, which we have taken into account with the aid of the relations (18.15). If there is no interaction, the two solutions will be completely independent.
Using also the normalization condition \( C_i^* C_j = 1 \), we may write the first type of solution when \( j = l + \frac{1}{2}, \ l = 0, 1, \ldots \), in the following form:

\[
\Psi(j = l + \frac{1}{2}) = \left\{ \begin{array}{c}
\sqrt{\frac{l + m}{2l + 1}} Y_l^{m-1} \\
-\sqrt{\frac{l + 1 - m}{2l + 1}} Y_l^m
\end{array} \right\} = Y_l^j(l = l + \frac{1}{2}), \tag{18.24}
\]

For \( j = l - \frac{1}{2}, \ l = 1, 2, \ldots \) (the second type of solution), the wave function has the form

\[
\Psi(j = l - \frac{1}{2}) = \left\{ \begin{array}{c}
\sqrt{\frac{l - m + 1}{2l + 1}} Y_l^{m-1} \\
\sqrt{\frac{l + m}{2l + 1}} Y_l^m
\end{array} \right\} = Y_l^j(l = l - \frac{1}{2}), \tag{18.25}
\]

where \( Y_l^j \) are the so-called spherical spinors. The orthonormality condition for the spherical spinors can be written as

\[
\int d\Omega Y_i^j Y_j^i = \delta_{jj'} \delta_{ll'} \delta_{mm'}, \tag{18.26}
\]

where \( j = l + \frac{1}{2} \) corresponds to the case in which the spin and orbital angular momenta are parallel, and \( j = l - \frac{1}{2} \) to the case when they are antiparallel. This condition follows immediately from the fact that the spherical spinor \( Y_l^j \) is a single-row matrix and from the orthonormality condition for spherical harmonics. The spherical spinors (18.24) and (18.25) are spinor generalizations of the ordinary spherical harmonics (see Chapter 11) and represent the angular part of the solution for all problems involving the motion of a particle of half-integral spin in a central field of force.

Substituting these solutions for the function \( \Psi \) into (18.15), we find that the component \( J_z \) of the total angular momentum takes the value \( J_z = \hbar m_j \), where the quantum number \( m_j \) is equal to \( m_j = m - \frac{1}{2} \).

For the first type of solution (\( j = l + \frac{1}{2} \)), it can be seen from (18.24) that it ranges from \( -l \ (m_j = -l - \frac{1}{2} = -j) \) to \( l + 1 \ (m_j = l + \frac{1}{2} = j) \), since the coefficient at the function \( Y_l^{m-1} \), which does exist for the last value of \( m \), vanishes. In exactly the same way the number \( m \) in the second type of solution (\( j = l - \frac{1}{2} \)) ranges from \( -l + 1 \ (m_j = -j) \) to \( l \ (m_j = j) \).

Thus our results can be summarized as follows. The square of the total angular momentum has the eigenvalues

\[
J^2 = \hbar^2 j(j + 1), \quad j = \begin{cases}
\frac{l \pm \frac{1}{2}}{2}, & l \neq 0, \\
\frac{1}{2}, & l = 0,
\end{cases} \tag{18.26a}
\]
that is, it is quantized similarly to the orbital angular momentum, except that the quantum number \( j \), which is called the total angular momentum quantum number, takes half-integral values. The eigenvalues of the component of the angular momentum along any axis are also characterized by half-integral quantum numbers

\[
J_z = \hbar m_j, \quad m_j = -j, \ldots, +j.
\] (18.27)

From the relations (18.6) and (18.7) and the quantization rules (18.26) and (18.27), it is easy to obtain quantization rules for the scalar products \( L \cdot S \) and \( J \cdot S \), which are important in spectroscopy

\[
L \cdot S = \frac{1}{2} (J^2 - L^2 - S^2) = \frac{\hbar^2}{2} [j(j + 1) - (l + 1)(l + 1) - s(s + 1)], \quad (18.28)
\]

and by analogy

\[
J \cdot S = \frac{1}{2} (J^2 - L^2 + S^2) = \frac{\hbar^2}{2} [j(j + 1) - (l + 1)(l + 1) + s(s + 1)]. \quad (18.29)
\]

We shall consider here the vector model of the addition of angular moments. In spite of the lack of mathematical rigor of this model, it enables us to resolve a number of complicated questions and often gives accurate results. As we know, the orbital angular momentum does not have a specific direction in space in quantum mechanics. The absolute value (square) of the angular momentum and one of its components, for example, along the \( z \) axis, have, however, simultaneous definite values. These facts can be represented geometrically by an angular momentum vector that describes a cone about the \( z \) axis. The projection of the angular momentum on the \( z \) axis will then have a well-defined value, whereas the projections on the \( x \) and \( y \) axes remain indeterminate. These arguments apply with equal validity to the spin angular momentum since it has the same commutation properties as the orbital angular momentum. The spin and orbital angular momentum vectors are oriented in space in such a way that their sum forms a vector \( J \) that is constant in magnitude. Thus, the vectors \( L \) and \( S \) do not have arbitrary directions; they precess about \( J \) like two coupled gyroscopes.

The dimensionless quantities \( j^* \), \( l^* \), and \( s^* \) are drawn in Fig. 18.1. Each of the vectors \( l^* \) and \( s^* \) is defined on the surface of a cone. They "precess" around \( j^* \) like a coupled system. We note that, according to Eq. (18.26), the addition of the vector \( l^* \) \((l = 0, 1, 2, \ldots)\) and the vector \( s^* \) \((s = \pm \frac{1}{2})\) leads to the total angular-momentum vector \( j^* \) with half-integral values of the total angular momentum quantum number \( j = l \pm \frac{1}{2} \).

---

1The number \( j \) is also called the internal quantum number. This number was introduced by spectroscopists before the discovery of spin on a purely empirical basis. It expressed certain internal properties of particles that were still unclear at that stage.

2The lack of mathematical rigor lies, for example, in the fact that the square of the vector \( j \) is equal to \( j(j + 1) \) rather than to \( j^2 \).

3From the standpoint of the classical theory, this coupling can be interpreted as a coupling of the orbital motion by the magnetic field.
From the vector model we can quickly find a number of quantities. For example, we can find the quantization rule of the angle between the vectors $I^s$ and $S^s$. From the oblique triangle we obtain

$$\cos \left( I^s S^s \right) = \frac{1}{2 I^s S^s} \left[ j^s - l^s - s^s \right],$$

that is,

$$\cos \left( I^s S^s \right) = \frac{j(j + 1) - l(l + 1) - s(s + 1)}{2 \sqrt{l(l + 1)s(s + 1)}}$$

(18.30)

(18.31)

C. MOTION IN A CENTRAL FIELD OF FORCE INCLUDING SPIN EFFECTS. THEORY OF THE ROTATOR

If we wish to investigate the motion of a particle in a central field in the nonrelativistic approximation with the inclusion of spin effects, we must use spherical spinors $Y_{l m}^{l_j}$ characterizing the states in which the total angular momentum (orbital plus spin) is conserved, instead of the spherical harmonics $Y_l^m$ describing the states where only the orbital angular momentum is conserved. Since the spherical spinors (in the nonrelativistic approximation) are composed of spherical harmonics having the same quantum number $l$, we obtain the same radial equation as for a nonrelativistic spinless particle, that is,

$$\nabla^2 R - \left( \frac{2m_0 E}{h^2} - \frac{l(l + 1)}{r^2} \right) R = 0.$$  

(18.32)

For the wave functions of an electron in a central field we obtain

$$\Psi_{l m}^{l_j} = R Y_{l m}^{l_j},$$

(18.33)

where the spherical spinor $Y_{l m}^{l_j}$ is defined by the expressions (18.24) and (18.25).

In particular, for the rotator we may set $r = a = \text{const}$ and the radial part of the wave function $R = 1$. It is seen that the spin effects in the nonrelativistic approximation do not give any additional terms for the rotator energy, which will be given by the same expression (12.7) as for a spinless particle, that is,

$$E_l = \frac{\hbar^2 l(l + 1)}{2m_0 a^2}.$$

The wave function will be given by the spherical spinor $Y_{l m}^{l_j}$, therefore we must find the selection rules for the quantum numbers $l$, $m_l$ and $j$. These selection rules hold not only for the rotator, but also for any problem of motion of a particle in a central field of force (for example, the electron in the hydrogen atom).
In place of Eq. (12.19), from which the selection rules for spinless particles were established, we now have

\[ (q)_{l m_j}^{l' m_j'} = \int \left( Y_{l''}^{m''} \right)^* q Y_{l'}^{m'} d\Omega, \quad (18.35) \]

where \( q \) may have three values

\[ q = z = \cos \theta, \quad q = x \pm iy = \sin \theta e^{\pm i\phi} \quad (18.36) \]

(for simplicity let us take the radius of the rotator equal to unity: \( a = 1 \)). If in place of the spherical spinors we substitute their values from (18.24) and (18.25), the matrix element (18.35) becomes

\[ (q)_{l m_j}^{l' m_j'} = D^{(1)} \int \left( Y_{l''}^{m''-1} \right)^* q Y_{l'}^{m'-1} d\Omega + C^{(1)} \int \left( Y_{l''}^{m''} \right)^* q Y_{l'}^{m} d\Omega. \quad (18.37) \]

From this it is seen that the two integrals in (18.37) agree exactly with the integrals in Eqs. (12.19)-(12.22). The selection rules for the quantum numbers \( l \) and \( m \) will therefore be the same as for a spinless rotator, that is,

\[ \Delta l = l - l' = \pm 1, \quad \Delta m = 0 \quad (q = z), \quad \Delta m = \pm 1 \quad (q = x \pm iy). \]

We shall now find the selection rules for the quantum numbers \( m_j \) and \( j \). Since \( m_j \) is related to \( m \) by the relation \( m_j = m - \frac{1}{2} \) for both types of solutions, the selection rules for \( m_j \) will be the same as for \( m \), that is,

\[ \Delta m_j = 0, \quad \pm 1. \]

To determine the selection rules for \( j \) let us consider first the case in which the transitions occur between states characterized by the same type of solutions \( (j' = l' + \frac{1}{2} \rightarrow j = l + \frac{1}{2} \) or \( j' = l' - \frac{1}{2} \rightarrow j = l - \frac{1}{2} ) \). It follows from (18.24) and (18.25) that the coefficients \( D^{(1)} \) and \( C^{(1)} \) are always positive and therefore such transitions are always allowed. In this case the possible change of \( j \) must be the same as the change of the orbital quantum number \( l \), that is, \( \Delta j = \Delta l = \pm 1 \).

If the transitions occur between states characterized by different types of solution \( (j' = l' + \frac{1}{2} \rightarrow j = l - \frac{1}{2} \) or \( j' = l' - \frac{1}{2} \rightarrow j = l + \frac{1}{2} ) \), then by taking into account \( \Delta l = \pm 1 \), we obtain three possible values for \( \Delta j = 0, \pm 2, \pm 2 \). Here, however, we must consider the fact that the coefficients \( D^{(1)} \) and \( C^{(1)} \) have different signs. For \( \Delta j = \pm 2 \) the two terms cancel each other, so that this transition
is forbidden. For $\Delta j=0$ the difference between the two terms is not zero, but owing to the fact that the two terms occur with different signs, the intensity of the radiation will be weaker than in the case of transitions between states characterized by the same type of solutions, when $\Delta j=\pm 1$. This can be shown with the help of a specific example. Let us suppose that the initial state is $j=l-1/2$ and the final state is $j'=l'+1/2$. We shall consider the case $\Delta m=m'-m=0$. Then, using (12.22), we reduce the appropriate matrix element (18.37) to the form

$$\langle \zeta | m' \rangle_j''^{r, l} = \delta_{r, r+1} [D^{(r', l)} A(l, m-1) + C^{(r', l)} A(l, m)] + \delta_{r', r-1} [D^{(r', l)} B(l, m-1) + C^{(r', l)} B(l, m)],$$

where $j'=l'+1/2$ and $j=l-1/2$. Substituting the expressions

$$D^{(r', l)} = \frac{1}{\sqrt{(2l'+1)(2l+1)}} \sqrt{l'+m' \sqrt{l'+1-m}}$$

and

$$C^{(r', l)} = -\frac{1}{\sqrt{(2l'+1)(2l+1)}} \sqrt{l'+1-m' \sqrt{l'+m}}$$

from (18.24) and (18.25), and the expressions for $A$ and $B$ from (12.22a), we find that the coefficient of $\delta_{r, r+1}$ vanishes; that is, the transition $\Delta j=-2$ is forbidden. At the same time, the coefficient of $\delta_{r', r-1}$ does not vanish, that is, the transition $\Delta j=0$ is allowed, but the intensity of the lines is weak in comparison with $\Delta j=\pm 1$. In a similar manner it is easy to show that the transition $\Delta j=2$ is forbidden not only for $q=z$, but also for $q=x \pm iy$ ($\Delta m=\pm 1$).

In accordance with the above discussion, the selection rules for the quantum numbers which characterize the state of a particle in a central field of force, when the spin is taken into account, have the form

$$\Delta l = \pm 1, \quad \Delta m = 0, \pm 1, \quad \Delta j = \begin{cases} \pm 1 & \text{(normal intensity)}, \\ 0 & \text{(weaker intensity)}. \end{cases}$$

**D. PARITY OF A STATE**

In connection with the formulation of the law of conservation of angular momentum for Dirac particles, we shall now define more clearly the meaning of the quantum numbers $l$ and $j$ in the Dirac theory of a particle in a central field. In nonrelativistic quantum
theory, the orbital quantum number $l$ is associated with the square of the angular momentum $L^2 = \hbar^2 (l + 1)$, which is a constant of the motion; therefore in both Schrödinger's and Pauli's theory the quantum number $l$ represents a quantity that is constant in time.

In the Dirac theory the orbital angular momentum does not commute with the Hamiltonian, and therefore it is not a constant of the motion. Consequently the quantum number $l$ has only an approximate meaning when used in connection with the law of conservation of angular momentum.

It turns out, however, that $l$ characterizes an additional property of a particle in quantum theory, namely, the parity of a state. By the parity of a state we mean the behavior of the wave function with respect to space inversion:

$$x = -x', \quad y = -y', \quad z = -z'.$$

(18.40)

The parity operator is defined as follows:

$$I \psi(r) = \psi(-r);$$

(18.41)

that is, it reverses the signs of the space coordinates. The eigenvalues $\lambda$ of this operator may be found by applying this operator twice:

$$I^2 \psi = \lambda^2 \psi.$$

(18.42)

This double application of the parity operator leaves the coordinates unaltered. From (18.41) and (18.42) it follows that

$$\lambda = \pm 1;$$

(18.43)

that is, either the wave functions remain unchanged with respect to space inversion (even functions, $\lambda = 1$), or they reverse their sign (odd functions, $\lambda = -1$).

We shall now find the quantities which determine the parity of a wave function in a central field. In the spherical coordinate system $r, \theta, \phi$, space inversion affects only the angular part

$$r' = r, \quad \theta' = \pi - \theta, \quad \phi' = \phi + \pi,$$

(18.44)

as can easily be seen from the fact that the sign of the coordinates

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta$$

(18.45)

---

7 This operator converts a right-handed system of coordinates into a left-handed system, and vice versa. In the Dirac theory $I \psi(r) = \psi(-r)$. 
changes. The radial part of the wave function remains unchanged with respect to space inversion, whereas the angular part changes in accordance with the relationship

\[ lY_i^m(\theta, \phi) = Y_i^m(\pi - \theta, \pi + \phi) = \text{const} \ P_i^m(-\cos\theta) e^{im(\phi + \pi)} = (-1)^l Y_i^m, \]  

(18.46)

because

\[ P_i^m(-x) = (-1)^l + m P_i^m(x). \]

Thus the parity of a state in a spherically symmetric field is determined by the parity of the number \( l \).

Furthermore, it can be seen that the Hamiltonian in a central field remains unchanged under space inversion; therefore, the inversion operator \( I \) and the Hamiltonian operator \( H \) commute with each other. It follows that the parity of a state is a constant of the motion, since

\[ \frac{d}{dt} I = \frac{i}{\hbar} (HI - IH) = 0. \]  

(18.47)

The law of conservation of parity has no classical analog, unlike the other conservation laws (energy, momentum, angular momentum). Consequently, in nonrelativistic wave mechanics the number \( l \) characterizes two constants of the motion: the square of the angular momentum and the parity of a state. In the Dirac theory, the number \( l \) does not have the significance of the square of the angular momentum, but the relationship between this number and the parity of a state is preserved.

We shall see later that parity plays a particularly important role in the physics of elementary particles. All wave functions—whether for one or more particles—can be classified as functions of odd or even parity. Dipole transitions can occur between states with different parities. In the case of two or more particles, the parity depends on the total spin of the system and also on the type of statistics obeyed by the particles. These concepts will be analyzed in some more detail in the treatment of specific examples.

E. SOLUTION OF THE DIRAC EQUATION FOR A FREE PARTICLE

Let us consider the motion of a free particle of spin 1/2 and constant momentum such as, for example, an electron. Without loss of generality we may take the \( z \) axis to lie along the direction of momentum; that is, in Eq. (17.20) we set

\[ p_x = p_y = 0, \quad p_z \neq 0. \]  

(18.48)
The Dirac equation then takes the form

\[
\left( i\hbar \frac{\partial}{\partial t} + c x_i \hbar \frac{\partial}{\partial x_i} - p_0 m_0 c^2 \right) \psi = 0. \tag{18.49}
\]

We shall look for a solution of this equation in the form

\[
\psi = \frac{1}{L^3} b e^{-i\epsilon K t + i k z}, \tag{18.50}
\]

where \( L^3 \) is the normalization volume, and the wave number \( k \) has the same value as in the nonrelativistic Schrödinger theory, namely,

\[
k = \frac{2\pi n}{L} (n = 0, 1, 2, \ldots),
\]

\[
K = \sqrt{k^2 + k_0^2}, \quad k_0 = \frac{m_0 c}{\hbar},
\]

and the \( 4 \times 4 \) matrix

\[
b = \begin{pmatrix}
b_1 \\
b_2 \\
b_3 \\
b_4
\end{pmatrix}
\]

satisfies the normalization condition

\[
b^* b = b_1^* b_1 + b_2^* b_2 + b_3^* b_3 + b_4^* b_4 = 1. \tag{18.51}
\]

To determine the quantity \( \epsilon \) and the coefficients \( b_\mu \), we use the system of equations (17.24), setting

\[
p_x = p_y = 0, \quad E \psi = \hbar \epsilon K \psi, \quad p_z \psi = \hbar k \psi.
\]

We then obtain

\[
(\epsilon K - k_0) b_1 - k b_3 = 0, \quad (\epsilon K - k_0) b_2 + k b_4 = 0,
\]

\[
(\epsilon K + k_0) b_3 - k b_1 = 0, \quad (\epsilon K - k_0) b_4 + k b_2 = 0. \tag{18.52}
\]

Hence we find two values for the quantity \( \epsilon \): \( \epsilon = 1 \) (the energy of the electron is positive) and \( \epsilon = -1 \) (the energy of the electron is negative); while we obtain four values for the matrix \( b \), the components of which satisfy the normalization condition (18.51). Two of the values of the matrix \( b \) refer to states with \( \epsilon = 1 \):

\[
b^{(1)} = \frac{1}{\sqrt{2}} \begin{pmatrix} \sqrt{1 + \frac{k_0}{K}} & 0 \\ 0 & \sqrt{1 - \frac{k_0}{K}} \end{pmatrix}, \quad b^{(2)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & \sqrt{1 + \frac{k_0}{K}} \\ \sqrt{1 - \frac{k_0}{K}} & 0 \end{pmatrix}. \tag{18.53}
\]
and two of them refer to states with $\varepsilon = -1$:

$$b^{(a)} = \frac{1}{\sqrt{2}} \begin{pmatrix} \sqrt{1 - \frac{k_0}{K}} \\ 0 \\ -\sqrt{1 + \frac{k_0}{K}} \\ 0 \end{pmatrix}, \quad b^{(b)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ \sqrt{1 - \frac{k_0}{K}} \\ 0 \\ \sqrt{1 + \frac{k_0}{K}} \end{pmatrix}; \quad (18.54)$$

that is, the states (18.53) differ from the states (18.54) in the sign of the energy.

To determine the physical significance of the states $b^{(i)}$ with different $i = 1, 2, 3, 4$, let us find the projection of the spin on the direction of motion, that is, on the $z$ axis. First of all, we note that, since $L_z = xp_y - yp_x = 0$ when a particle is moving along the $z$ axis, the projection of spin on the $z$ axis must be conserved. This follows directly from the fact that the matrix $s_3$ commutes with the Hamiltonian in (18.49).

We can find the eigenvalues of this operator $s_3$ by applying it to the spin functions $b^{(i)}$. We have then

$$\frac{1}{2} s_3 b^{(i)} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ \sqrt{2} \\ -\sqrt{2} \end{pmatrix} \begin{pmatrix} \sqrt{1 - \frac{k_0}{K}} \\ 0 \\ -\sqrt{1 + \frac{k_0}{K}} \\ 0 \end{pmatrix} = \frac{1}{2} b^{(i)}; \quad (18.55)$$

that is, for this solution the eigenvalue of the operator $\frac{1}{2} s_3$ equals $\frac{1}{2}$. In exactly the same way it is easy to show that

$$\frac{1}{2} s_3 b^{(a)} = -\frac{1}{2} b^{(a)}, \quad \frac{1}{2} s_3 b^{(b)} = \frac{1}{2} b^{(b)} \quad \text{and} \quad \frac{1}{2} s_3 b^{(c)} = -\frac{1}{2} b^{(c)}.$$

Thus, the four possible states correspond to the four possible combinations of the sign of the energy and the spin direction. The solution $b^{(1)}$ corresponds to positive energy ($\varepsilon = 1$) and the projection of this spin along the positive $z$ direction ($s = 1$). In a similar way we have $\varepsilon = 1$, $s = -1$ for the solution $b^{(2)}$ and we have $\varepsilon = -1$, $s = 1$ and $\varepsilon = -1$, $s = -1$ for the solutions $b^{(3)}$ and $b^{(4)}$, respectively, where $s$ is double the projection of the spin in the direction of the momentum.

In the nonrelativistic limit ($v \ll c$), the wave functions $\psi_3$ and $\psi_4$ will be of the order of $\frac{h}{K} \sim \frac{v}{c}$ times the wave functions $\psi_1$ and $\psi_2$ ($\psi_3 \sim \frac{v}{c} \psi_1$) for positive energy states ($\varepsilon = 1$). For states with negative energies [see (18.54)], on the contrary, $\psi_1 \sim \frac{v}{c} \psi_3$. 
We have considered the special case of motion of a particle along the $z$ axis. This does not restrict, however, the generality of the investigation of the general motion of a particle. Whenever the direction of momentum is characterized by spherical angles $\theta$ and $\phi$, it is always possible to choose a primed coordinate system in such a manner that the $z'$ axis is directed along the momentum. Then, by carrying out two rotations, one rotation through an angle $\theta$ around the $y'$ axis directed perpendicularly to the $zz'$ plane, the other, second rotation through an angle $\phi$ around the $z$ axis, we may transform from the solution in the primed coordinate system (momentum along the $z'$ axis) to the general case (direction of momentum characterized by the spherical angles $\theta$, $\phi$).

Using the fact that under a rotation of the coordinate system the wave function changes in accordance with (17.39), we may write the solution for this general case as:

$$\psi = \frac{1}{L^{3/2}} e^{-\frac{i}{2} \left( \frac{p_z + \theta_z}{2} \right)} \left( \sqrt{1 + \frac{\hbar^2}{K}} \right) \left( \sqrt{1 - \frac{\hbar^2}{K}} \right) e^{-i\hbar K x + i\hbar r}, \quad (18.56)$$

which is a generalization of Eqs. (18.50), (18.53) and (18.54).

Problem 18.1. Show that the energy and momentum operators $E = i\hbar \frac{\partial}{\partial t}$ and $p = -i\hbar \nabla$, respectively, transform like a four-vector under the Lorentz transformations:

$$E' = \frac{E'}{c} = \frac{p'_x + \frac{E'}{c} \beta}{\sqrt{1 - \beta^2}}; \quad p_x = \frac{p'_x + \frac{E'}{c} \beta}{\sqrt{1 - \beta^2}}, \quad p_y = p'_y, \quad p_z = p'_z,$$

where

$$\beta = \frac{v}{c}, \quad E' = i\hbar \frac{\partial}{\partial t}, \quad \text{and so on.}$$

**Hint.** Use the Lorentz coordinate transformation [Eq. (17.34)] and change to new variables in the process of differentiation.

Problem 18.2. Prove the relativistic invariance of the scalar equation for a free particle.

**Hint.** First, let us prove the invariance of the operator relation

$$E'^2 - c^2 p'^2 = E^2 - c^2 p^2$$

by using the results of the preceding problem.

Problem 18.3. Show that in the case of spatial rotation of the coordinate system around the $y$ axis by the angle $\theta$, the wave function transforms according to the relation

$$\psi' = \left( \cos \frac{\theta}{2} + i \sin \frac{\theta}{2} \right) \psi = e^{i \frac{\theta}{2} \sigma_y} \psi.$$

**Hint.** Use the method which leads to the relation (17.39).

Problem 18.4. With the aid of the vector model of addition of angular moments, find the angles between $j^*$ and $s^*$ and between $j^*$ and $l^*$ taking into account the geometric vector addition in quantum mechanics; that is, find

$$\cos (j^* s^*); \quad \cos (j^* l^*).$$

---

8 These problems also refer to the material in Chapter 17.
Hint. Use a method similar to the one that led to Eqs. (18.30) and (18.31).

Problem 18.5. Show that the wave function \( \bar{\psi} = C \psi^* \), where \( C = i \alpha_0 \beta_0 \), and \( \psi^* \) is the complex conjugate (but not the Hermitian adjoint, that is, not \( \psi^\dagger \)) of the Dirac wave function for an electron with negative energy satisfies the Dirac equation with positive energy and opposite (positive) sign of the charge, that is, describes the motion of a positron (a charge conjugate transformation).

Solution. The Dirac equation is

\[
\begin{align*}
\left\{ \frac{-\hbar}{i} \frac{\partial}{\partial t} - e\Phi - c \left[ a_1 \left( \frac{\hbar}{i} \frac{\partial}{\partial x} - \frac{e}{c} A_x \right) + a_2 \left( \frac{\hbar}{i} \frac{\partial}{\partial y} - \frac{e}{c} A_y \right) + \\
+ a_3 \left( \frac{\hbar}{i} \frac{\partial}{\partial z} - \frac{e}{c} A_z \right) \right] - \rho s m_0 c^2 \right\} \psi = 0;
\end{align*}
\]

for the complex conjugate of this equation, we may write (taking into account the fact that \( a_1^* = a_1 \), \( a_2^* = -a_2 \), \( a_3^* = a_3 \), \( \beta_0^* = \beta_0 \)):

\[
\begin{align*}
\left\{ \frac{-\hbar}{i} \frac{\partial}{\partial t} + e\Phi + c \left[ a_1 \left( \frac{\hbar}{i} \frac{\partial}{\partial x} + \frac{e}{c} A_x \right) - a_2 \left( \frac{\hbar}{i} \frac{\partial}{\partial y} + \frac{e}{c} A_y \right) + \\
+ a_3 \left( \frac{\hbar}{i} \frac{\partial}{\partial z} + \frac{e}{c} A_z \right) \right] - \rho s m_0 c^2 \right\} \psi^* = 0.
\end{align*}
\]

We note that the complex conjugate \( \psi^* \) differs from \( \psi^\dagger \) (the Hermitian conjugate): namely,

\[
\psi^* = \left( \psi_1^* \psi_2^* \psi_3^* \psi_4^* \right),
\]

whereas

\[
\psi^\dagger = (\psi_1^\dagger \psi_2^\dagger \psi_3^\dagger \psi_4^\dagger).
\]

Let us substitute \( \bar{\psi} = i \alpha_0 \beta_0 \psi^* \) into the complex conjugate of the Dirac equation, We then find that \( \bar{\psi} \) satisfies the Dirac equation if the charge \( e \) is replaced by \( -e \).

Since the state \( \psi (r, t) = e^{-i E t / \hbar} \psi (r) \) is treated as a state with positive energy \( (E = |E|) \),

and the state \( \psi^* (r, t) = e^{-i E t / \hbar} \psi^* (r) \) is treated as a state with negative energy \( (E = -|E|) \), we must interpret the sign of the energy in \( \bar{\psi} \) differently than in \( \psi^* \).
The Dirac Equation in Approximate Form

In many problems which are solved by the Dirac theory, we retain only the relativistic corrections of the order of \( \left( \frac{v}{c} \right)^3 \) in the final results. Therefore we may immediately write the Dirac equation in an approximate form, retaining quantities of the order of \( \left( \frac{v}{c} \right)^3 \).

It will be shown below that the role of both the relativistic and spin terms is clearly displayed in this approximation.

Let us consider the motion of an electron with positive energy \( E > 0 \) in an electromagnetic field which does not depend on time. In this case we may replace the energy operator by its eigenvalue, separating out the rest mass energy \( m_0c^2 \):

\[
E - m_0c^2 \mp E.
\]  

The wave equation (17.20) then becomes

\[
(E - e\Phi) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = c (\sigma \cdot P) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}, \quad (2m_0c^2 + E - e\Phi) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = c (\sigma \cdot P) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix},
\]  

where \( \sigma \) stands for the Pauli matrices [see (16.18)], and \( P \equiv p - \frac{e}{c} A \). Equations (19.2) are simply a different form of the exact Dirac equation. For the components of \( \psi \), we obtain from (19.2)

\[
(E - e\Phi) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} - c (P_x - iP_y) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} - cP_z \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = 0
\]

and so on. This equation can also be obtained from the first of Eqs. (17.24), if we substitute into it both (19.1) and (17.25).

As was mentioned in the preceding section, in the nonrelativistic limit the components \( \psi_3 \) and \( \psi_4 \) are "small" for positive energy states, since they are of the order of \( \frac{v}{c} \) times the "large functions" \( \psi_1 \) and \( \psi_2 \). The transition to the approximate Dirac equation consists in eliminating the "small" components \( \psi_3 \) and \( \psi_4 \) from Eqs. (19.2) and retaining terms of the order of \( \left( \frac{v}{c} \right)^2 \) in the remaining equations for the "large" components \( \psi_1 \) and \( \psi_2 \). Thus from (19.2) we obtain

\[
\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{1}{2m_0c} \begin{pmatrix} 1 - 

(1 - E - e\Phi) (\sigma \cdot P) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}.
\]  

}\] (19.3)
First of all we change from the four-component wave functions
\[ \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} \]
to the two-component functions \( \begin{pmatrix} W_1 \\ W_2 \end{pmatrix} \) by setting
\[ \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = N \begin{pmatrix} W_1 \\ W_2 \end{pmatrix}, \tag{19.4} \]
where \( N \) is the normalization coefficient. This coefficient may be determined from the "renormalization" relationship
\[ (\psi_1 \psi_2 \psi_3 \psi_4) \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = (W_1 W_2) \begin{pmatrix} W_1 \\ W_2 \end{pmatrix}. \tag{19.5} \]
Since the "small" wave functions \( \psi_3 \) and \( \psi_4 \) occur as squares in (19.5), we may set
\[ \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{\sigma^\prime \cdot p}{2m_0 c} N \begin{pmatrix} W_1 \\ W_2 \end{pmatrix}; \tag{19.6} \]
that is, in (19.3) we neglect second-order terms and replace \( P \) by \( p \). This change of operators is permissible in calculating the normalization coefficient since they differ from one another by a first-order term (inversely proportional to the velocity of light). When applied to second-order terms (squares of the "small" wave functions), this term of \( P \) gives only third-order terms, which we discard. Then, substituting Eqs. (19.4) and (19.6) into the left-hand side of (19.15) and using the equation
\[ (\sigma^\prime \cdot a)(\sigma^\prime \cdot b) = (a \cdot b) + \left[ i\sigma^\prime \cdot (a \times b) \right], \tag{19.7} \]
which holds both for the Pauli and Dirac matrices, we find
\[ (\psi_1 \psi_2) \left( N^2 + N \frac{p^2}{4m_0^2 c^2} N \right) \begin{pmatrix} W_1 \\ W_2 \end{pmatrix} = (W_1 W_2) \begin{pmatrix} W_1 \\ W_2 \end{pmatrix}. \tag{19.8} \]
From this we obtain
\[ N = 1 - \frac{p^2}{8m_0^2 c^2}. \]
This approximation gives us, in accordance with (19.3) and (19.4),
\[
\left( \frac{\psi_i}{\psi}\right) = \frac{1}{2m_e c} \left[ (\sigma \cdot p) - \frac{E - e\Phi}{2m_e c^2} (\sigma \cdot p) - \frac{e^2 p^2}{8m_e^2 c^2} \right] \left( \psi_i^1 \right).  \tag{19.9}
\]
Substituting (19.9) into the first of Eqs. (19.2) and neglecting terms of the order of \((v/c)^3\), we find
\[
\left\{ E - e\Phi - \frac{1}{8m_e^2 c^2} (E - e\Phi)p^2 \right\} \left( \psi_i^1 \right) = \nonumber
\]
\[
\left\{ \frac{1}{2m_e} (\sigma \cdot p)(\sigma \cdot p) - (\sigma \cdot p) \frac{E - e\Phi}{4m_e^2 c^2} (\sigma \cdot p) - \frac{p^2}{16m_e^2 c^2} \right\} \left( \psi_i^1 \right) \tag{19.10}
\]
Using the relation (19.7), we have
\[
(\sigma \cdot p)(\sigma \cdot p) = P^2 + i [\sigma \cdot (P \times P)] = P^2 - (\sigma \cdot (P \times A) + (A \times p)) \nonumber
\]
\[
= P^2 - \frac{e \hbar}{c} [\sigma \cdot (\nabla \times A)] = P^2 - \frac{e \hbar}{c} \sigma \cdot H, \tag{19.11}
\]
where \( H \) is the magnetic field since the operator \( \nabla \) acts only on the vector potential \( A \), and not on \( \psi \).

In exactly the same way, with the aid of the relations
\[
(\sigma \cdot p)(E - e\Phi)(\sigma \cdot p) = (E - e\Phi) p^2 - i \hbar e (\sigma \cdot E)(\sigma \cdot p) =
\]
\[
= (E - e\Phi) p^2 - i \hbar e (E \cdot p) + e \hbar [\sigma \cdot (E \times p)] \quad \tag{19.12}
\]
and
\[
\frac{p^2}{2m_e} = (E - e\Phi) = (E - e\Phi) p^2 + \frac{2\hbar e}{\imath} E \cdot p + \hbar^2 \nabla^2 \Phi, \quad \tag{19.13}
\]
where \( E = -\nabla \Phi \) is the electric field intensity, we may reduce the Dirac equation (19.10) to the following approximate form:
\[
\left( E - e\Phi - \frac{p^2}{2m_e} \right) \left( \psi \right) = \left[ - \frac{p^2}{8m_e^2 c^2} - \frac{e \hbar}{2m_e c} (\sigma \cdot H) - \frac{\hbar^2}{8m_e^2 c^2} \nabla^2 \Phi \right] \left( \psi \right). \tag{19.14}
\]
The left-hand side of Eq. (19.14) describes the motion of a particle with a nonrelativistic velocity in a stationary electromagnetic field. The right-hand side of (19.14) contains an additional interaction energy that describes the relativistic and spin corrections.
The first term on the right-hand side of (19.14)

\[ v^{\text{rel}} = - \frac{p^i}{8m_0^2c^4} \]  

takes into account the correction due to the relativistic velocity of the particle. A similar additional energy must also appear in the relativistic Klein-Gordon equation. The classical analog of this term will be obtained if the relativistic expression for the Hamiltonian is expanded in a series, retaining terms of the order of \((v/c)^2\)

\[ H = \sqrt{m_0^2c^4 + \frac{p^2c^2}{2m_0}} - \frac{p^i}{8m_0^2c^4}. \]

The second term on the right-hand side of (19.14) may be written as

\[ v^{\text{mag}} = - \mu \cdot H. \]  

From this it is clear that the quantity \(\mu = \frac{e\hbar}{2m_0c}\) \(\sigma'\) may be treated as the Dirac magnetic moment of an electron, which appears explicitly in the nonrelativistic approximation only through this transition. This interaction energy turns out to be of the order of \(v/c\). From the intrinsic angular momentum [Eq. (18.6)] of the electron

\[ S = \frac{\hbar}{2} \sigma', \]

we find the relationship between \(S\) and \(\mu\) that is required by experiment and follows automatically from the Dirac theory

\[ \mu = \frac{e}{m_0c} S. \]

The next term of the expansion characterizes the so-called spin-orbit interaction

\[ v^{\text{so}} = - \frac{e\hbar}{4m_0^2c^4} [\sigma' \cdot (E \times p)], \]

which describes the interaction of a moving magnetic dipole with an electric field.

This interaction may also be interpreted from the classical point of view in the following way: a magnetic dipole moving with a velocity \(v\) (the spatial component of a tensor
quantity) acquires an additional electric moment (space-time component of the same tensor quantity)

\[ \mu_{el} = \frac{1}{c} \mathbf{v} \times \mathbf{\mu} = \frac{1}{mc^2} \mathbf{P} \times \mathbf{\mu}, \]  

(19.20)

which interacts with the electric field of the nucleus. This additional energy of interaction is

\[ V^{cl} = -E\mu_{el} = -\frac{e\hbar}{2m^2e^2} [\phi(E\phi)] \]  

(19.21)

This classical expression for the interaction energy is twice as large as the corresponding quantum expression [see (19.19)]. Even before the advent of the Dirac theory, an attempt was made to explain the fine structure by the semiclassical introduction of spin-orbit interaction. To obtain an agreement with experiment, Thomas and Frenkel suggested that we substitute the coefficient $1/2$ into the classical expression for the interaction energy (19.21). This interaction, which follows automatically from the Dirac theory, is called the Thomas-Frenkel correction.

In particular, for the Coulomb field of a nucleus

\[ \Phi = \frac{Ze}{r}, \quad E = \frac{Ze^2}{r^3}, \quad e = -e_0. \]  

(19.22)

The interaction between the moving magnetic dipole and the nucleus according to (19.19) becomes

\[ V_{s.o.} = -\frac{Ze^2}{2m^2e^2r^3} \mathbf{S} \cdot \mathbf{L}, \]  

(19.23)

where $S = \hbar \sigma'/2$ is the spin, and $L = r \times p$ is the orbital angular momentum.

We note that there is no spin-orbit interaction for an atom in the $s$ state since the orbital angular momentum in this state vanishes. Finally, the last term of the interaction, which in the case of the Coulomb field is equal to

\[ V^{cont} = \frac{\hbar^2e}{8m^2e^2} \nabla^2 \Phi = \frac{\pi h^2r_s^2}{2m^2e^2} \delta(r), \]  

(19.24)

is called the contact interaction. The additional energy corresponding to it

\[ \Delta E^{cont} = \int \psi^* V^{cont} \psi \, d^3x \]  

(19.25)

---


3 In the derivation of (19.24), we have used the fact that, according to (4.78),

\[ \nabla^2 \frac{1}{r} = -4\pi \delta(r) - 4\pi \delta(x) \delta(y) \delta(z). \]  

(19.24a)
is proportional to $|\Psi(0)|^2$, and it will differ from zero only for the $s$ state since, according to (13.28a), only in this case $|\Psi(0)|^2 \neq 0$. For all other states ($l \neq 0$) this square of the wave function vanishes when $r = 0$. In this sense the contact term may be regarded as the spin-orbit interaction for the $s$ state. We can see now that the last two terms in the interaction energy (19.14) characterize the spin properties of an electron.

Problem 19.1. Show that the matrix $\gamma \alpha$ is the velocity operator, and that in the case of a free particle $\alpha$ is not a constant of the motion, unlike the momentum operator ($p = -i\hbar \nabla$). Explain this difference. Determine in what case the average velocity

$$v = \int \psi^* \gamma \alpha \psi d^3x$$

will be related to the average momentum by the classical relation

$$v = \frac{c^2 \bar{p}}{E}. \quad (19.26)$$

Hint. From the Hamiltonian (17.21) it is possible to obtain the velocity operator

$$\dot{r} = \frac{i}{\hbar} (\hat{H} r - r \hat{H}) = \gamma \alpha,$$

It can also be shown that the velocity is not a constant of the motion, since $\alpha \neq 0$. Consequently, if for a given $k$ we take a linear combination of positive and negative energy states [see Eqs. (18.53), (18.54)] there will exist interference terms that will fluctuate with time ($\sim e^{-2i\xi t}$). As a result, Ehrenfest's theorems will hold only on the average in the Dirac theory. The interference terms will disappear in the calculation of the average value of the momentum operator.

Equation (19.26) holds only if the states with positive energies are retained ($\varepsilon = 1$).
The Fine Structure of the Spectra of Hydrogen-like Atoms

A. STATEMENT OF THE PROBLEM.

The problem of the motion of an electron in a hydrogen-like atom (Kepler's problem) is rightfully considered as the touchstone of all forms of quantum theory. There are two main reasons for this. First, it has great physical significance, since the problem of motion in a Coulomb field can be solved exactly. Second, the results may be compared with experiment to a high degree of accuracy; for example, the emission spectra of atoms can be observed by optical and microwave spectroscopy.

The solution of the problem of motion of an electron in a Coulomb field of a nucleus (hydrogen atom) on the basis of the Schrödinger equation, obtained in Chapter 13, gives an expression for the energy

$$E_n = -\frac{R\mu Z^2}{n^2},$$

(20.1)

which is in good agreement with experimental data. This expression for the energy may be taken as the zero-order approximation. A more detailed study of atomic spectra shows, however, that the spectral lines have a fine structure which, of course, must be associated with the detailed structure of the energy levels. The Schrödinger theory does not give an adequate description of the regularities frequently occurring in spectra, since it neglects at least two important facts: the relativistic dependence of mass upon velocity and the spin properties of the electron. Both these facts, as we already know, are accounted for by the Dirac theory, and therefore application of the Dirac equation to the Kepler problem gives results that accurately describe the multiplet structure of energy levels.

As was pointed out, the Kepler problem can be solved exactly in the Dirac theory. The solution, however, requires many tedious calculations (much more complicated than in the Schrödinger theory, because in this case we have not one but four equations). Moreover, in the course of these calculations one does not always
perceive the physical meaning of the results, the analysis of which is of primary importance to us. We shall therefore use a more elementary method, based on the approximate equations of the preceding section. This method not only enables us to obtain formulas characterizing the fine structure up to terms of the order of \( \left( \frac{v}{c} \right)^2 \), but also to interpret the individual terms as manifestations of relativistic or spin properties of the electron.

**B. RELATIVISTIC AND SPIN EFFECTS**

As follows from Chapter 18 [see (18.24) and (18.25)], the wave function of a particle obeying the Dirac equation, taking into account the spin properties, is

\[
\Psi = R_{nl} Y_{lm}^{(j)}.
\]

(20.2)

Here \( R_{nl} \) is the radial part of the wave function and \( Y_{lm}^{(j)} \) is a spherical spinor: for \( j = l + \frac{1}{2} \) the spin is parallel to the orbital angular momentum and for \( j = l - \frac{1}{2} \) it is antiparallel.

Although terms of the order of \( (v/c)^2 \) are not formally accounted for in Eq. (20.2), the relationship between the spherical harmonics in the spherical spinor that determines the zero-order approximation of the wave function is established by the spin-orbit interaction, which is of the order of \( (v/c)^1 \).

The spherical spinor can therefore be used only when the atom is not subject to external perturbing forces of magnitude greater than those involved in the spin-orbit interaction. If that is not the case, the spin-orbit coupling will be disrupted and a new set of premises must be set forth in order to establish a relationship between the spherical functions.

Spherical spinors, just as spherical harmonics, satisfy the equation

\[
\nabla^2_{\theta, \phi} Y_{lm}^{(j)} = - l(l + 1) Y_{lm}^{(j)};
\]

(20.3)

therefore, taking into account (11.17), the radial function in (20.2) satisfies the same equation that was derived in the nonrelativistic Schrödinger theory:

\[
\nabla^2_{r} R_{nl} + \left( \frac{2m_e E_n}{\hbar^2} + \frac{2m_e Z e^3}{\hbar^2} \frac{l(l + 1)}{r^2} \right) R_{nl} = 0.
\]

\(^1\)There are several cases in quantum mechanics in which a small interaction energy enables us to find a relation between the coefficients of the functions in the zero-order approximation. We have already encountered a similar situation in the treatment of the Stark effect (see Chapter 14).
The wave function (20.2) completely determines the selection rules for all quantum numbers. The selection rules for the quantum numbers \( l, j, \) and \( m_f \) are given by formula (18.39), while the selection rules for the principal quantum number \( n \) will evidently be the same as in Schrödinger's theory [see (13.48c)], since the radial function remains unchanged. Considering all this, we obtain the following selection rules for a theory of the hydrogen-like atom which takes into account spin effects:

\[
\Delta l = \pm 1, \ \Delta j = 0, \ \Delta m_f = 0, \ \pm 1 \quad (\Delta n \text{ is an integer}). \tag{20.4}
\]

As for the expression for the energy, we cannot restrict ourselves in this problem to its nonrelativistic value (20.1), since the latter does not determine the fine structure of the energy levels.

Knowing the zero-order approximation of the wave function (20.2), and also the additional perturbation energy describing the relativistic [see (19.15)] and spin [see (19.23) and (19.24)] effects, we may find the energy levels characterizing the multiplet structure of the spectrum.

According to formula (19.15), the relativistic correction to the energy levels is

\[
\Delta E^{\text{rel}} = - \int \left( \frac{p^2}{2m_0} \Psi (r) \right) \Psi (r) \, d^3 x. \tag{20.5}
\]

Since in the present case

\[
\frac{p^2}{2m_0} \Psi (r) = \left( E_n + \frac{Ze_n^2}{r} \right) \Psi (r),
\]

\[
\Psi (r)^+ \frac{p^2}{2m_0} = \Psi (r)^+ \left( E_n + \frac{Ze_n^2}{r} \right), \tag{20.6}
\]

we see that this additional energy will be independent of the solid angles \( \theta, \varphi \); that is, integrating over the solid angle we get

\[
\int_0^\pi \sin \theta \ d\Omega \ Y_l(m)^+ Y_l(m) = 1. \tag{20.7}
\]

Then the additional energy characterizing the relativistic effects is

\[
\Delta E^{\text{rel}} = - \frac{1}{2m_0 c^2} \left[ \left( E_n^+ \right)^2 + 2E_n^+ Ze_n^+ \left( \frac{r}{r} \right) + Z^2 c_0^2 \left( \frac{r}{r} \right) \right] = \frac{R \hbar Z \alpha}{n^2} \left( \frac{n}{l + \frac{1}{2}} - \frac{3}{4} \right), \tag{20.8}
\]

where \( \alpha = \frac{e^2}{\hbar c} \sim \frac{1}{137} \) is the fine structure constant.
In the derivation of (20.8) we have used (13.29a)

\[
\begin{align*}
\frac{1}{r} &= \frac{Z}{a_0} \frac{1}{w^2} = \frac{2\hbar Z}{e^2 w^2}, \\
\frac{1}{r^2} &= \left(\frac{Z}{a_0}\right)^2 \frac{1}{n^2 (l + \frac{1}{2})} = \frac{2\hbar^2 m_e}{\hbar^2 (l + \frac{1}{2})}.
\end{align*}
\]

Equation (20.8) agrees exactly with the formula for the relativistic energy, which was calculated in identical approximation by means of the relativistic Klein-Gordon equation [see (15.31)].

In a similar manner, with the aid of (19.23), we find the additional energy due to the spin-orbit interaction

\[
\Delta E_{s.o.} = \frac{Z e^2}{2m_e c^2} (S \cdot L) \left(\frac{1}{r^3}\right).
\]

Using expression (13.29a) for \(\frac{1}{r^3}\)

\[
\left[\frac{1}{r^3}\right] = \left(\frac{Z}{a_0}\right)^3 \frac{1}{n^2 (l + \frac{1}{2}) (l + 1)},
\]

and expression (18.28) for \(S \cdot L\)

\[
S \cdot L = \begin{cases} 
\frac{\hbar^2}{2} q & \text{for } l \neq 0, \\
0 & \text{for } l = 0,
\end{cases}
\]

we obtain the following value\(^2\) for the energy (20.9):

\[
\Delta E_{s.o.} = R\hbar \frac{Z e^2 \hbar}{2m_e c^2} \frac{q (1 - b_{10})}{l (l + 1)}.
\]

In these equations

\[
q = j (j + 1) - l (l + 1) - s (s + 1) = \begin{cases} 
-1 & \text{for } j = l + \frac{1}{2}, \\
(l + 1) & \text{for } j = l - \frac{1}{2},
\end{cases}
\]

\(^2\)At first glance it may seem that the spin-orbit interaction, which is inversely proportional to the third power of the distance, cannot give a stable state. This, however, is not so. At small distances the spin-orbit interaction behaves just like the relativistic interaction; that is, it is inversely proportional to the square of the distance. Indirect proof of this is the fact that \(\Delta E_{s.o.}\) differs from \(\Delta E_{rel}\) only by a numerical factor of the order of unity.
and the quantity
\[ \delta_{l0} = \begin{cases} 0 & \text{for } l \neq 0, \\ 1 & \text{for } l = 0. \end{cases} \]  
(20.12)

Finally, the energy corresponding to the contact interaction, according to (19.24), is given by
\[ \Delta E_{\text{cont}} = \frac{\hbar^2 Z e_0^2}{2m^2 c^3} |\Psi(0)|^9, \]
where
\[ |\Psi(0)|^9 = R_{nl}^3(0) Y_{lm}^{j*} Y_{lm}^j. \]  
(20.13)

Furthermore, considering the expression for
\[ |R_{nl}(0)|^9 = \frac{4}{n^3} \delta_{l0} \bigg( \frac{Z}{\alpha_0} \bigg)^3 \]
[see (13.28a)], and using the fact that \( |Y_{lm}^{j*}|^2 = \frac{1}{4\pi} \) when \( l = 0 \) and \( j = \frac{1}{2} \), we find
\[ |\Psi(0)|^9 = \frac{\delta_{l0}}{4\pi n^3} \bigg( \frac{Z}{\alpha_0} \bigg)^3, \]  
(20.14)
that is,
\[ \Delta E_{\text{cont}} = R\hbar \frac{Z^2 e_0^2}{n^3} \delta_{l0}. \]  
(20.15)

From this we obtain the following expression for the additional energy which accounts for the relativistic effects, the spin-orbit and contact interactions:
\[ \Delta E = \Delta E_{\text{rel}} + \Delta E_{\text{so}} + \Delta E_{\text{cont}} = -R\hbar \frac{Z^2 e_0^2}{n^3} \left[ \frac{n + i}{2l + 1/2} - \frac{3}{4} \frac{qn l (l + 1/2)}{2l (l + 1/2) (l + 1) n^2} \right]. \]

\[ \delta_{l0} \]

[Incidentally, Eq. (20.10) for the contact interaction may be obtained when the expression for the spin-orbit interaction (Eq. 20.10) is allowed to go to the limit as \( l \to 0 \), if we discard the factor \( \delta_{l0} \) in 20.10. Therefore, many authors use this procedure and neglect the contact interaction in deriving the fine-structure formula. However, the agreement between the two formulas is accidental since for the states the numerator of Eq. (20.10) is always zero, while the denominator vanishes only in the nonrelativistic approximation. In a number of other problems, for example, an atom containing several electrons, the energy associated with contact interaction is no longer a limit of the expression for the spin-orbit interaction.]
Substituting here the value of $q$ from (20.11), we have

$$\Delta E_{nj} = -R\hbar \frac{Za^2}{n^4} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right). \tag{20.16}$$

Therefore, summing both results [(20.1) and (20.16)], we obtain the fine structure formula for the spectrum of a hydrogen-like atom

$$E_{nj} = E_n^0 + \Delta E_{nj} = -\frac{R\hbar Z^2}{n^2} \left[ 1 + \frac{Z^2a^2}{n^2} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right]. \tag{20.17}$$

From this it is seen that the splitting of the levels is proportional to the square of the fine structure constant.

C. THE FINE STRUCTURE IN THE DIRAC THEORY

When we take the fine structure into account the position of the energy levels in the hydrogen atom is found to depend also on the total angular momentum quantum number $j$. Therefore the terms will be denoted in the following manner:

$$(nl_j) = -\frac{E_{nj}}{\hbar} = \frac{RZ^2}{n^2} \left[ 1 + \frac{Z^2a^2}{n^2} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right]. \tag{20.18}$$

From this formula it is seen that the fine structure, according to the Dirac theory, depends only on the principal quantum number $n$ and the total angular momentum quantum number $j$. In contrast to the Klein-Gordon theory, it is independent of the orbital angular momentum quantum number $l$ (up to terms of the order of $a^3$).

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4 This problem can be solved exactly in the Dirac theory. We then obtain a closed formula for the energy levels; in this formula, the first expansion term (which is independent of $a^2$) gives the nonrelativistic formula (20.1). The second term, which is proportional to $a^2$, gives the additional energy (20.16). The third expansion term, which is proportional to $a^4$ in this approximation, can be neglected, since it is smaller than the so-called vacuum corrections, which are proportional to $a^3$ (see Chapter 22).

5 An exact solution of the Dirac equation gives the following generalization of Eq. (15.30), which takes into account the relativistic effects in the case where spin is also present:

$$E_{nj} = m_0c^2 \left[ 1 + \frac{Z^2a^2}{(n-j-\frac{1}{2} + \sqrt{(j+\frac{1}{2})^2 - Z^2a^2})^2} \right]^{-\frac{1}{2}} - m_0c^2. \tag{20.17a}$$

Equation (20.17) may be obtained from (20.17a), if the latter is expanded in a series and we restrict ourselves to the first two terms.

Since the minimum value of $j$ is equal to $1/2$, we find that stable motion in the Coulomb field of a point nucleus, according to the Dirac theory, will extend to $Z_{cr} = 137$, whereas in the Klein-Gordon theory it was limited by $Z_{cr} = \frac{1}{2} \cdot 137$ [see (15.33)]. Such an increase of $Z_{cr}$ is, as we have already mentioned, due to the slight compensation of the relativistic effects by the spin effects.
The diagram given in Fig. 20.1 shows that all terms are doubly split, since to each value of \( l \) there correspond two values of \( j \); for example, instead of a single term \( 2p \ (l = 1) \) we now have two terms \( 2p_{\downarrow} \) and \( 2p_{\uparrow} \). The exceptions are the \( s \) terms \((l = 0)\), for which \( j \) can have only one value \((j = \frac{1}{2})\). Thus the relativistic and spin effects somewhat reduce but do not split the \( s \) terms (see Fig. 20.1).

The degree of degeneracy also changes owing to splitting of the energy levels. We know that the principal quantum number may take the following values: \( n = 1, 2, 3, 4, \ldots \). The orbital angular momentum quantum number \( l \) varies from \( l = 0 \) \((s \) state\) to \( l = n - 1 \). The total angular momentum quantum number \( j \) takes the values \( j = l + \frac{1}{2} \) \((l \neq 0)\) and \( j = \frac{1}{2} \) \((l = 0)\) and, finally, the magnetic quantum number \( m_j = -j, \ldots, +j \), that is, for a given \( j \) there are \( 2j + 1 \) half-integral values of \( m_j \). The degree of degeneracy, which is characteristic for any central field of force and is related to the equivalence of the various directions in space, is therefore equal to \( 2j + 1 \) for particles with a spin of \( 1/2 \) (we remember that for spinless particles it was equal to \( 2l + 1 \)). In contrast to the relativistic spinless theory, the degeneracy with respect to \( l \) is still present when we take into account terms of the order of \( \alpha^2 \) and even the following expansion terms proportional to \( \alpha^4 \). When the finite size of the nucleus is taken into account, the degeneracy with respect to \( l \) is removed. We note incidentally that even greater splitting with respect to \( l \) is due to vacuum fluctuations (see Chapter 22). The magnitude of the splitting of spectral lines can be determined from the selection rules (20.4). For the Lyman series we then have two lines (instead of a single one):

\[
\omega^{(1)} = (1s_{\uparrow/2}) - (np_{\downarrow/2}),
\]

(weak line, since \( \delta j = 0 \) )

\[
\omega^{(2)} = (1s_{\uparrow/2}) - (np_{\uparrow/2}).
\]

The Balmer series lines are split as follows:

\[
\omega^{(1)} = (2s_{\uparrow/2}) - (np_{\downarrow/2}),
\omega^{(2)} = (2s_{\uparrow/2}) - (np_{\uparrow/2}),
\omega^{(3)} = (2p_{\downarrow/2}) - (ns_{\downarrow/2}),
\omega^{(4)} = (2p_{\uparrow/2}) - (ns_{\uparrow/2}),
\omega^{(5)} = (2p_{\downarrow/2}) - (nd_{\downarrow}),
\omega^{(6)} = (2p_{\uparrow/2}) - (nd_{\uparrow}).
\]
and, finally, the transition $2p_{1/2} \rightarrow nd_{1/2}$ is forbidden, because in this case $\Delta j = 2$. If the degeneracy with respect to $l$ is not removed, the lines $\omega^{(l)}$ and $\omega^{(l)}$ coincide, since the initial and final levels have the same values of the principal quantum number $n$ and the total angular momentum quantum number $j$. In a similar manner we may determine the splitting of all other lines. The lowest split energy level corresponds to $n = 2$. Let us consider in greater detail the splitting of this level in the case of the hydrogen atom ($Z = 1$), which is the one most carefully investigated experimentally. In general, the $n = 2$ level would be split into three sublevels, and, according to our theory, two of these sublevels would combine:

$$(2s\lambda/3) = (2p\lambda/3) = R \left[ 1 + \frac{a^2}{4} \left(2 - \frac{3}{4}\right)\right],$$

$$(2p\lambda/4) = R \left[ 1 + \frac{a^2}{4} \left(1 - \frac{3}{4}\right)\right].$$

The transition frequency between these levels is, according to the Dirac theory,

$$\Delta \omega^D = (2s\lambda/3) - (2p\lambda/4) = R \frac{a^2}{16},$$

which is about $1.095 \times 10^4$ Mc. If only the relativistic effects are taken into account (Klein-Gordon equation) the corresponding splitting is [see (15.32)]

$$\Delta \omega^{K-G} = (2s) - (2p) = \frac{8}{3} \frac{R a^2}{16};$$

that is, the frequency is almost three times greater than the one found from the Dirac theory. Consequently, the spin properties of particles somewhat reduce the influence of the relativistic effects.

The conclusions of Dirac's theory have been accurately confirmed by experiment.

It is interesting to note that the fine structure of the spectrum of the hydrogen atom was first theoretically calculated by Sommerfeld who applied a relativistic Hamiltonian to the steady states of the Bohr classical theory. Sommerfeld obtained [see (2.61)]

$${}^6$$

Mc = $10^6$ sec$^{-1}$; that is, the angular frequency $\omega$, expressed in sec$^{-1}$, is connected with the frequency $\nu$, expressed in Mc, by the relation

$$\omega = 2\pi \cdot 10^6 \nu.$$
the following expression for the relativistic theory (20.22) without taking into account the spin effects:

$$\Delta \omega_{\text{Somm}} = (2s) - (2p) = \frac{R_a^9}{16}.$$  \hspace{1cm} (20.24)

Agreement of the Sommerfeld result with the conclusion of Dirac's theory was, however, only accidental. Sommerfeld's theory did not take into account the spin effects, and therefore it was unable to predict the splitting of the $n=2$ level into three sublevels, the presence of which was later confirmed experimentally.

D. EXPERIMENTAL VERIFICATION OF THE FINE STRUCTURE THEORY

The major accomplishment of Dirac's theory was its treatment of the fine structure. The theory was in good agreement with the experimental facts and was able to explain this structure as a manifestation of the relativistic and spin effects caused by the motion of the electrons within the atom. However, further and more detailed studies showed divergencies between the theory and fact. Thus, special attention was given to the $2s_{1/2}$ and $2p_{1/2}$ levels which, according to the Dirac theory [see (20.21)], should coincide in a hydrogen atom. Among spectroscopists, doubts about the validity of this conclusion were expressed as early as 1934. However, the techniques of the time did not allow greater experimental accuracy, and the discrepancy between the theory and optical observations (that is, the splitting of the levels) being small, no great attention was paid to it. Better experimental data on this splitting were obtained considerably later, when microwave spectroscopic techniques were used.

The microwave spectroscopic method was invented and rapidly developed in the postwar years as a result of technical progress in microwave engineering. Microwave spectroscopy, which has now developed into a special branch of physics, gives valuable results when used in the investigation of nuclei, atoms and molecules. Microwave spectroscopic methods are also applied to the physics of solids and liquids. In 1947 Lamb and Rutherford employed this method to studies of the $2s_{1/2}$ and $2p_{1/2}$ levels, making use of a special property characteristic of the $2s_{1/2}$ state. This state is

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7By microwave ultrahigh-frequency radio emission we mean the region of the electromagnetic spectrum located in the wavelength range from millimeters to tens of centimeters ($10^6 - 10^3$ Mc). Successful application of microwave spectroscopy to the investigation of atomic spectra is due to the fact that the distances between the components of the levels split by the relativistic, spin and vacuum effects are of the same order of magnitude as the wavelengths in the microwave region.
metastable, since a dipole transition from the $2s_{1/2}$ state to the lower $1s_{1/2}$ state is forbidden by the selection rules $\Delta l = 0$ [see Eq. (20.4)].

Transition from the metastable state may be associated either with the emission of two photons (the probability of such a transition is $10^8$ lower than that for the allowed transition), or with a preliminary transition to the $2p$ level. Lamb and Rutherford investigated the latter type.

Let us describe the general features of their experiment (see Fig. 20.2). A beam of hydrogen atoms in the unexcited $1s_{1/2}$ state is obtained as a result of dissociation of molecular hydrogen at high temperatures (tungsten furnace). A bombarding beam of electrons then excites some fraction of the atoms in the hot beam (approximately one out of $10^4$) to the metastable state $2s_{1/2}$. The metastable atoms, unlike the unexcited atoms, readily give up their energy of excitation upon striking a metallic target. In so doing they remove electrons from the metal. The resulting current is measured by a sensitive galvanometer.

![Fig. 20.2. Diagram of the Lamb-Rutherford experiments on the detection of the splitting of the $2s_{1/2}$ and $2p_{1/2}$ levels: 1) tungsten furnace emitting a beam of hydrogen atoms; 2) beam of electrons exciting the hydrogen atoms; 3) radio frequency field; 4) target; 5) galvanometer.](image)

If the beam of metastable atoms is subjected in transit to a perturbation capable of causing a $2s \rightarrow 2p$ transition, then the atoms will almost instantaneously pass to the $1s_{1/2}$ state (prior to reaching the target). As a result, the current reading on the galvanometer is lower.

In the Lamb–Rutherford experiment such transitions were induced by microwave radiation (the probability of the corresponding spontaneous transition, proportional to $\omega^4$, is vanishingly small as a consequence of the smallness of $\omega$); a strong damping

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8This is correct for a dipole transition, but calculation shows that the quadrupole transition between these states is also forbidden.
action, resulting in a decrease of target current, was observed at some frequency \( \omega \). This \( \omega \) was assumed to be the resonance frequency which causes transitions \( 2s_{1/2} \rightarrow 2p_{1/2} \) or \( 2s_{1/2} \rightarrow 2p_{3/2} \) with a subsequent practically instantaneous transition to the \( 1s_{1/2} \) level; the energy difference between these corresponds to \( \hbar \omega \). Thus, one can very precisely measure the relative positions of the levels

\[ 2s_{1/2}, 2p_{1/2} \text{ and } 2p_{3/2}. \]

These measurements showed that the level \( 2s_{1/2} \) is shifted upwards relative to the level \( 2p_{1/2} \) by approximately one tenth of the distance between the doublet levels \( 2p_{3/2} - 2p_{1/2} \), which is equal to \( \frac{3}{16} R \). The arrangement of the levels of a hydrogen-like atom \((n = 2)\) derived from the Lamb-Rutherford experiment is given in Fig. 20.3. The disposition of these levels according to the Dirac theory is given for comparison. According to the latest data, the shift of the \( 2s_{1/2} \) level is approximately 1057.77 Mc or, in wavelengths, \( \sim 28 \) cm.

![Fig. 20.3. Splitting of energy levels in the hydrogen atom. a) experimental data; b) according to the Dirac theory (neglecting vacuum effects). The frequencies of the corresponding transitions and the distances are given in Mc.](image)

This apparently negligible discrepancy between theory and experiment led to remarkable progress in theoretical physics and, in particular, in quantum electrodynamics. This subject will be considered in greater detail in Chapter 22.

In the experiments of Lamb and Rutherford, the frequency of the microwave radiation was fixed and the resonance condition, corresponding to the difference in the Zeeman components between the states \( 2s_{1/2} \) and \( 2p_{1/2} \) or \( 2p_{3/2} \), was obtained by adjusting the magnetic field \( -\mathcal{H} \). Then, extrapolating the results to the case \( -\mathcal{H} = 0 \), the authors found the level shift.
E. ANOMALOUS ZEEMAN EFFECT

The complete theory of the Zeeman effect (both normal and anomalous) must be based on the Dirac theory, because the latter takes into account both the relativistic and the spin corrections. Since the anomalous Zeeman effect is due to the spin effects in the atom, neither classical theory nor Schrödinger's wave mechanics was able to give a satisfactory explanation of the Zeeman effect, and for obvious reasons.

As a starting point of the theory let us take the approximate Dirac equation (19.14), in which these effects are taken into account up to the terms \( \left( \frac{v}{c} \right)^2 \). Let the magnetic field be directed along the z axis, that is, \( H_x = H_y = 0, H_z = \mathcal{H} \). Then, using the fact that, according to (16.16),

\[
\frac{p_z^2}{2m_0} = \frac{p_z^2}{2m_0} + \frac{e_0}{m_0 c} \mathbf{A} \cdot \mathbf{p} = \frac{p_z^2}{2m_0} - \mu_n i \mathcal{H} \frac{\partial}{\partial \mathcal{H}}, \tag{20.25}
\]

we reduce Eq. (19.14), describing the motion of an electron in the Coulomb field of a nucleus, to the form

\[
\left( E + \frac{Z r^2}{r} - \frac{p_z^2}{2m_0} \right) \psi_i = (V_{\text{rel}} + V_{s.o.} + V_{\text{cont}} + V_{\text{mag}}) \psi_i, \tag{20.26}
\]

where \( V_{\text{rel}}, V_{s.o.} \) and \( V_{\text{cont}} \) are given by Eqs. (19.15), (19.23) and (19.24), respectively. Upon averaging of these terms

\[
\Delta E_{n_f} = \int (\psi_i^* \psi_f) \left( V_{\text{rel}} + V_{s.o.} + V_{\text{cont}} \right) \psi_i \psi_f d^3 \chi \tag{20.27}
\]

we obtain the fine structure formula (20.16), that is,

\[
\Delta E_{n_f} = - \frac{\mathcal{H} Z^2 a^2}{\hbar} \left( \frac{n}{j} + \frac{j}{2} - \frac{3}{4} \right). \tag{20.28}
\]

When a magnetic field is present, we obtain on the right-hand side of Eq. (20.26) the interaction

\[
V_{\text{mag}} = \mu_n \mathcal{H} \left( - i \frac{\partial}{\partial \mathcal{H}} + \sigma_j \right), \tag{20.29}
\]

Generally speaking, the spin-orbit interaction \( V_{s.o.} \) is of fundamental importance in this case. Since, however, the relativistic terms are of the same order as the spin-orbit interaction, we may set

\[
\Delta E_{s.o.} \sim \Delta E_{n_f}. \]

---

\(^{10}\) Generally speaking, the spin-orbit interaction \( V_{s.o.} \) is of fundamental importance in this case. Since, however, the relativistic terms are of the same order as the spin-orbit interaction, we may set

\[
\Delta E_{s.o.} \sim \Delta E_{n_f}. \]
which gives the following value for the additional energy of the atom:

\[ \Delta E_{\text{mag}} = \mu_0 \mathcal{H} \int (\Psi_1^* \Psi_2^*) \left( -i \frac{\partial}{\partial \varphi} + \sigma^2 \right) (\Psi_1^* \Psi_2) d^3x. \]  

(20.30)

The appearance of either anomalous (case of a weak magnetic field) or normal (case of a strong magnetic field) Zeeman effects depends on the relative proportion between the additional energies on the right-hand side of (20.26).

Let us assume that we have a comparatively weak magnetic field, whose interaction with the atomic electrons is smaller than the relativistic or spin-orbit interaction.

Then the zero-order approximation will be expressed by the wave functions (20.2) that are obtained when the spin-orbit coupling is retained.

Substituting these functions into (20.30), the additional energy becomes

\[ \Delta E_{\text{mag}} = \mu_0 \mathcal{H} \int_0^\infty |R_{nl}|^2 r^2 dr \int d\Omega (Y_{lm})^* \left( -i \frac{\partial}{\partial \varphi} + \sigma^2 \right) Y_{lm}. \]  

(20.31)

In (20.31) we should note that the integral over \( r \) is equal to unity

\[ \int_0^\infty |R_{nl}|^2 r^2 dr = 1. \]  

(20.32)

Substituting in place of the spherical spinors their values from (18.24) and (18.25), and using the orthogonality condition for the spherical harmonics

\[ \int (Y_t^m)^* (Y_t^m) d\Omega = 1, \]

we find the following expression for the additional energy when \( j = l + \frac{1}{2} \):

\[ \Delta E_{\text{mag}} = \frac{\mu_0 \mathcal{H}}{2l + 1} [(l + m) m + (l + 1 - m) (m - 1)] = \mu_0 \mathcal{H} \frac{2(l + 1)}{2l + 1}. \]

In exactly the same way when \( j = l - \frac{1}{2} \) we obtain

\[ \Delta E_{\text{mag}} = \frac{\mu_0 \mathcal{H}}{2l + 1} [(l - m + 1) m + (l + m) (m - 1)] = \mu_0 \mathcal{H} \frac{2l}{2l + 1}. \]
Recalling that \( m_j = m - \frac{1}{3} \), the last two expressions may be written as a single formula

\[
\Delta E_{\text{mag}} = \mu_0 \mathcal{H} g m_j = \nu h g n_j.
\]  

(20.33)

where \( \nu = \frac{e \mathcal{H}}{2 m_0 c} \) is the Larmor frequency, and the Landé \( g \) factor is

\[
g = \frac{j + \frac{1}{3}}{j + \frac{1}{5}}.
\]  

(20.34)

Thus, in the case of the anomalous Zeeman effect, the expression for the additional energy contains the Landé \( g \) factor, which in the case of the normal Zeeman effect [see (16.23)] is equal to unity.

The additional energy (20.33) does not lead to the usual triplet splitting (normal Zeeman effect), but to a more complex splitting pattern (anomalous Zeeman effect).

In view of the fact that \( m_j \) can assume \( 2j + 1 \) different values, each level in the case of the anomalous Zeeman effect is split into \( 2j + 1 \) separate sublevels; that is, the external magnetic field completely removes the degeneracy, which is present even in the relativistic theory of the hydrogen atom.

To obtain the splitting pattern, it is necessary to take into account the value of the Landé \( g \) factor (\( g = 2 \) for the \( s_{1/2} \) states, \( g = \frac{5}{3} \) for the \( p_{1/2} \) states, \( g = \frac{7}{3} \) for the \( p_{3/2} \) states, and so on) and also the selection rules for the magnetic quantum number \( m_j \). In particular, when \( \Delta m_j = 0 \), the emitted components are polarized parallel to the \( z \) axis (that is, parallel to the magnetic field), and when \( \Delta m_j = \pm 1 \) the components are polarized perpendicular to the magnetic field.
Equation (20.33) gives us the following value for the frequency of the radiation:
\[ \omega = \omega_0 + \alpha (g^2 m_{j}' - g m_j), \tag{20.35} \]
where \( \omega_0 \) is the frequency of the radiation in the absence of a magnetic field (\( B'' = 0 \)); \( g^0 \) and \( g \) are the Landé g factors of the initial and final states; the magnetic quantum number \( m_j \) of the final state may take three values: \( m_j = m_j', \ m_j' \pm 1 \).

Figure 20.4b shows the splitting of the spectral levels \( 1^3s_{1/2} \) and \( 2^3p_{1/2} \) in a weak magnetic field, the Larmor frequency being taken as the unit of the splitting. From Fig. 20.4b it is seen that in this case there are four, and not three (as in the normal Zeeman effect) shifted lines. The magnitude of the displacement is given by (20.35).

In the case of a weak field [according to (20.34)] we find
\[ g^0 = \frac{1}{3}, \quad g = 2. \]
Hence
\[ \Delta \omega_1 = \omega_1 - \omega_0 = \frac{2}{3} \alpha, \quad \Delta \omega_2 = -\frac{4}{3} \alpha, \]
\[ \Delta \omega_3 = \frac{4}{3} \alpha, \quad \Delta \omega_4 = -\frac{2}{3} \alpha. \tag{20.36} \]

Equation (20.34) for the Landé g factor is applicable to the hydrogen atom and to atoms having a single valence electron. In the general case, the Landé g factor becomes
\[ g = 1 + \frac{J(J + 1) - L(L + 1) + S(S + 1)}{2J(J + 1)}, \tag{20.37} \]
where \( L, S, \) and \( J \) are the orbital, spin and total angular momenta of the atoms and
\[ J = |L \pm S|. \]
In particular, for elements of the first group \( (J = j, \ L = l, \ s = \frac{1}{2}) \), Eqs. (20.37) and (20.34) are identically the same. The Landé g factor attains its maximum value for \( s \) states \( (l = 0, \ j = s = \frac{1}{2}) \):
\[ g_s = 2. \tag{20.38} \]

For atoms with two electrons in the outer shell (for example, helium atoms), single lines \( (S = 0, \ J = l) \) are possible along with the triplet state \( S = 1 \). For the single lines we have \( g = 1 \), and, therefore, in this case spin effects should be of no importance; only the normal Zeeman effect (that is, triplet splitting) should be observed in either a weak or strong field.
F. STRONG MAGNETIC FIELDS. PASCHEN-BACK EFFECT

It has been indicated that the anomalous Zeeman effect appears in the case of weak fields, when the external magnetic field cannot disrupt the spin-orbit coupling.

Mathematically this means that $\Delta E^\text{mag}$ [see (20.33)] is much smaller than the natural splitting of the lines $\Delta E^{s.o.}$ given by Eq. (20.28)

$$\Delta E^{s.o.} \gg \Delta E^\text{mag}.$$  \hspace{1cm} (20.39)

In the latter case we first solved the problem by taking into account the spin-orbit interaction; this establishes a relation between the spherical harmonics that form the spherical spinor (18.24) or (18.25); then we found an additional energy that leads to the anomalous Zeeman effect, since the Lande $g$ factor does not equal unity.

In the case of strong fields, when the splitting due to the external magnetic field is greater than that due to the spin-orbit interaction

$$\Delta E^\text{mag} \gg \Delta E^{s.o.},$$  \hspace{1cm} (20.39a)

the magnetic field "breaks" the spin-orbit coupling and the zero-order approximation solutions, expressed in terms of spherical spinors [see (18.24 and 18.25)], are no longer true.

In this case we may neglect the interactions $V^{\text{rel}}, V^{s.o.}$ and $V^{\text{cont}}$ in (20.26), which, when (20.29) is taken into account, becomes

$$\left( E + \frac{Ze_5^2}{r} - \frac{\hbar^2}{2m_0} \right) \Psi_i = \mu_0 g \mathcal{H} \left( -i \frac{\partial}{\partial \gamma} + \mathbf{\sigma} \cdot \mathbf{\gamma} \right)\Psi_i.$$  \hspace{1cm} (20.40)

Using the fact that the functions $\Psi_1$ and $\Psi_2$ must be proportional to the spherical harmonics $Y^m_l$, with $-i \frac{\partial}{\partial \gamma} Y^m_l = m Y^m_l$, we find two independent equations for these wave functions:

$$\begin{align*}
\left( E + \frac{Ze_5^2}{r} - \frac{\hbar^2}{2m_0} - \mu_0 g \mathcal{H} (m + 1) \right) \Psi_1 &= 0, \\
\left( E + \frac{Ze_5^2}{r} - \frac{\hbar^2}{2m_0} - \mu_0 g \mathcal{H} (m - 1) \right) \Psi_2 &= 0,
\end{align*}$$  \hspace{1cm} (20.41)

from which it is evident that the additional energy equals

$$\Delta E^\text{mag}_{m_2} = \mu_0 g \mathcal{H} (m + 2m_2),$$  \hspace{1cm} (20.42)

and

$$\Delta (\Delta E^\text{mag})_{m_2} = \mu_0 g \mathcal{H} (\Delta m + 2\Delta m_2);$$
that is, the wave function $\Psi_1$ corresponds to the case in which the electron spin is directed along the magnetic field ($m_s = \frac{1}{2}$), and the wave function $\Psi_2$ corresponds to the case in which the spin direction is opposite to that of the magnetic field.

If we choose $m$ such that the same energy value is obtained for both functions, then we must set $m_1 = m - 1$ for the function $\Psi_1$, and $m_2 = m + 1$ for the function $\Psi_2$.

In this case the wave functions

$$\Psi_1 = R_n Y_i^{m-1}, \quad \Psi_2 = R_n Y_i^{m+1}$$

(20.43)

will be mutually orthogonal, so that

$$\int \Psi_1^* \Psi_2 \, d^3x = \int_0^\infty |R_n|^2 r^2 \, dr \int_0^{\pi} (Y_i^{m-1})^* Y_i^{m+1} = 0.$$  \hspace{1cm} (20.44)

Since the interaction between the atom and the external magnetic field (20.29) contains only the matrix $a_3$, which does not couple the wave functions $\Psi_1$ and $\Psi_2$, transitions from the state with $m_i = \frac{1}{2}$ to the state with $m_i = -\frac{1}{2}$, induced by this interaction, will be forbidden in this case and hence $A_{m_s} = 0$.

Taking into account this circumstance, and also the selection rules for the quantum number $m$ ($\Delta m = 0, \pm 1$), we find from (20.42) an expression for the Zeeman splitting of the spectral lines

$$\Delta \omega = a_1 \Delta m = 0, \pm \omega,$$

(20.45)

which agrees with the result of Schrödinger’s theory, which explains the normal Zeeman effect (triplet splitting of the spectral lines).

Thus, in strong fields ($\Delta E_{mag} \gg \Delta E_{s,0}$), the anomalous effect becomes the normal effect, which is in agreement with experimental data (Paschen-Back effect). It is interesting to note that the passage from the anomalous Zeeman effect to the normal effect can be illustrated by Fig. 20.4, if the Landé $g$ factor is set equal to unity (see case c). Then the splitting will be

$$\Delta \omega_1 = \Delta \omega_2 = 0, \quad \Delta \omega_3 = \omega, \text{ and } \Delta \omega_4 = -\omega;$$

that is, we obtain three components of the split line instead of four.

In special cases, when $\Delta E_{s,0} < \Delta E_{mag}$ for one energy level and conversely $\Delta E_{s,0} > \Delta E_{mag}$ for the other level, or when the energies of both levels are of the same order of magnitude, the Zeeman splitting becomes complex. Since these are all special cases, we shall not elaborate them here.
Problem 20.1. Investigate the diamagnetism and paramagnetism of atoms by placing them in a constant homogeneous magnetic field \( H_x = H_y = H_z = H \); contrary to the investigation of the Zeeman effect, keep all terms containing \( \mathcal{H} \) as well as terms proportional to \( \mathcal{H}^2 \) in the Hamiltonian [see (20.25)].

Indicate the atoms in which diamagnetism may be observed.

Solution. When terms proportional to \( \mathcal{H} \) are taken into account, we have, instead of (20.25)

\[
\frac{p^2}{2m_0} = \frac{p^2}{2m_0} - \mu_0 \mathcal{H} \frac{\partial}{\partial q} + \frac{e_s^2}{8m_0c^2} (x^2 + y^2) \mathcal{H}^2.
\]

Consequently, on the right-hand side of (20.26) we have another term

\[
\nu_{\text{diam}} = \frac{e_s^2}{8m_0c^2} (x^2 + y^2) \mathcal{H}^2,
\]

which in conjunction with (20.33) gives the following expression for the additional energy of an electron in a magnetic field:

\[
\Delta E_{\text{mag}} = \mu_0 \mathcal{H} g m_j + \frac{e_s^2 \mathcal{H}^2}{12m_0c^2} r^2.
\]

Here when calculating the perturbation energy proportional to \( x^2 + y^2 \), we have used the spherical symmetry, which must occur in the zero-order approximation \( \mathcal{H} = 0 \), and have set

\[
\int \Psi^* (x^2 + y^2) \Psi \, d^3x = \frac{2}{3} \int \Psi^* r^2 \Psi \, d^3x = - \frac{2}{3} \frac{r^2}{r^2}.
\]

Hence the magnetic moment of an atom in a magnetic field is

\[
\mu_{\text{atom}} = - \frac{\partial \Delta E_{\text{mag}}}{\partial \mathcal{H}} = - \mu_0 g m_j - \frac{e_s^2 \mathcal{H}^2}{6m_0c^2} = \mu_{\text{param}} + \mu_{\text{diam}}.
\]

The latter relationship is a generalization of a familiar equation relating \( \Delta E_{\text{mag}} \) to \( \mathcal{H} \) in the case where \( \Delta E_{\text{mag}} \) is a nonlinear function of \( \mathcal{H} \).

The diamagnetism of atoms is characterized by the second term of Eq. (20.47), which is proportional to \( \mathcal{H}^2 \).

The magnetic susceptibility per gram-atom is

\[
\chi_{\text{diam}} = \frac{\partial \mu_{\text{diam}}}{\partial \mathcal{H}} = - \frac{e_s^2 N}{6m_0c^2} r^2,
\]

where \( N \) is Avogadro's number.

The quantity \( \chi_{\text{diam}} \) is never zero and must always be negative \((r^2 > 0)\). Therefore, the diamagnetic effect must occur in all atoms.

As for the first term on the right-hand side of Eq. (20.47), which is proportional to \( m_j \), it may take either positive or negative values, since \( m_j = \pm \frac{1}{2}, \pm \frac{3}{2}, \ldots, \pm j \).

In a state of thermodynamic equilibrium, however, the negative values for \( m_j \), which give a smaller value for the energy, will be preferred. On the average we therefore obtain a positive value for the paramagnetic susceptibility \(^\text{11}\)

\[
\chi_{\text{param}} = \frac{\mu_0 g^2}{kT} \frac{f(j + 1)}{3}.
\]

Expression (20.47) is obtained for a weak magnetic field, when the anomalous Zeeman effect occurs. It can, however, be easily extended to the case of a strong magnetic field. To do this we must set \( g = 1 \), \( m_j = m \) in (20.47) [see (20.42)].

\(^{11}\)See R. Becker, Electron Theory.
Since the paramagnetic susceptibility is considerably larger than the diamagnetic susceptibility ($\chi_{\text{param}} \gg \chi_{\text{diam}}$), the atoms exhibit paramagnetic properties when $j \neq 0$. For hydrogen-like atoms $j$ differs from zero (the minimum value of $j$ equals $1/2$) and, therefore, they are always paramagnetic. Only for atoms with an even number of electrons can the quantum number $j$ vanish (for example, parahelium in the ground state, see Chapter 24). Such an atom will be diamagnetic.

Problem 20.2. Adding geometrically the orbital and spin angular momenta, show that the anomalous Zeeman effect is associated with the fact that the total magnetic moment $\mu$ is not parallel to the total angular momentum $J$. With the aid of the geometric model, also explain the Paschen-Back effect.

Solution. First let us find geometrically the angular and the magnetic moment vectors

$$J = L + S; \quad \mu = -\frac{e_0}{2m_0c} (L + 2S).$$

In the geometric representation (see Fig. 20.5), we may choose the scale so that $\mu = -\frac{e_0}{2m_0c}$ (it is immaterial at the moment whether the vectors are parallel or antiparallel).

Then $\mu_L = L$, and $\mu_S = 2S$.

Fig. 20.5. Geometric interpretation of the anomalous Zeeman effect.

that is, the total magnetic moment $\mu$ will undergo two rotations in a magnetic field: one with an angular velocity $\omega$ around the direction of the total angular momentum (this angular velocity corresponds to the frequency associated with the transition between components of the spin-orbit splitting of the spectral lines $\omega \sim R\alpha^2$), and the other corresponding to the Larmor frequency of precession around the direction of the magnetic field $\mathbf{H} (H_x = H_y = 0, H_z = e_0c/2m_0c)$.

When $\omega \gg \omega$, the additional energy should be calculated from the relation

$$\Delta E_{\text{mag}} = -\frac{(\mathbf{\mu} \cdot \mathbf{J}) (\mathbf{J} \cdot \mathbf{H})}{J^2}.$$

Since the magnetic moment is directed on the average along $J$, we have

$$\Delta E_{\text{mag}} = g_0 h \mu J,$$

where $\alpha = \frac{e_0 c}{2m_0 c}$, and the Landé $g$ factor is equal to

$$g = \frac{L}{J} \cos (L \cdot J) + 2 \frac{S}{J} \cos (S \cdot J).$$

Substituting the values of the cosines of the angles

$$\cos (S \cdot J) = \frac{J^2 - L^2 + S^2}{2JS}, \quad \cos (L \cdot J) = \frac{J^2 - S^2 + L^2}{2JL},$$

and remembering that $J^2 = \hbar^2 (J + 1)$, and so on, we obtain the expression (20.37) for the Landé $g$ factor. Let us pay attention to the fact that if the vectors $\mu$ and $J$ were parallel, the Landé $g$ factor would be unity.
In strong fields $a \gg \omega$ we must consider independently the rotation of the orbital and the spin moments $\mu$ around the $z$ axis. Then the additional energy becomes

$$\Delta E_{\text{mag}} = -\mu \cdot H = \frac{e_0 \hbar c}{2m_e} (L_z + 2S_z) = \hbar (m + 1),$$

which leads directly to the normal Zeeman splitting (Paschen-Back effect).

Problem 20.3. By means of the relativistic scalar wave equation and the Dirac equation, find the frequency of the allowed transitions between the $n = 2$ and $n = 3$ states. Show that, according to the Dirac theory, there are seven lines, five of which are distinct, and that, according to the scalar theory, there are only three distinct lines.
The Effect of Nuclear Structure on Atomic Spectra

A. INTRODUCTORY REMARKS

As has been mentioned in Chapter 13, the position of the spectral lines is shifted when the finiteness of the nuclear mass is taken into account. The Rydberg constant $R$ in the expression for the energy of a hydrogen-like atom

$$E_n = -\frac{R \hbar Z^2}{n^3}$$  \hspace{1cm} (21.1)

is somewhat reduced and becomes equal to

$$R = R_\infty \left(1 - \frac{m_0}{M}\right)$$ \hspace{1cm} (21.2)

where

$$R_\infty = \frac{m_0 \epsilon_0^2}{2 \hbar^2}$$

is the Rydberg constant corresponding to infinite nuclear mass. Consequently, the Rydberg constant will have somewhat different values for hydrogen, deuterium, and tritium. With the great accuracy attainable in modern spectroscopic techniques, this effect can be used to detect the presence of different isotopes (see Chapter 13).

In a similar fashion, the finite size and the magnetic moment of the atomic nucleus have certain effects on atomic spectra.

B. EFFECT OF THE FINITE SIZE OF THE NUCLEUS

When the motion of an electron in the field of a nucleus is treated as a problem in classical theory, it is quite immaterial whether the nucleus is regarded as a point or as a particle with finite dimensions. All that matters is that the electron should at all times be outside the nucleus and that the nuclear charge should be spherically symmetric, since the potential outside a spherically symmetric charge distribution is the same as the potential of a point charge.

In quantum mechanics the situation is somewhat different. The wave function must differ from zero inside the nucleus; therefore, there is a certain probability (however small) that the electron will be located inside the nucleus. Consequently, the charge distribution inside the nucleus must in some manner influence the energy levels of the electrons in the atom.

To estimate the effect of the finite nuclear size on the energy spectrum of a hydrogen-like atom, we shall assume that the nucleus can be represented by a sphere of radius $R_N$ with charge distributed uniformly throughout the volume. The potential energy will be given by (see Fig. 21.1)

$$V = -\frac{Z e^2}{R_N} \left(\frac{3}{2} - \frac{1}{2} \frac{r^2}{R_N^2}\right) \quad \text{for} \quad r < R_N,$$  \hspace{1cm} (21.3)
The shift of energy levels due to the finite size of the nucleus can be calculated with the help of perturbation theory. We shall assume that the perturbation energy consists of the difference between the potential energy of a point nucleus and the potential energy of a nucleus with charge uniformly distributed over the nuclear volume

\[ V^{\text{vol}} = Z e^2 \left( \frac{1}{r} - \frac{1}{R_N^*} \left( \frac{3}{2} - \frac{1}{2} \frac{r^*}{R_N^*} \right) \right) \epsilon (r), \]  

with

\[ \epsilon (r) = \begin{cases} 1 & \text{for } r < R_N^* \\ 0 & \text{for } r \geq R_N^* \end{cases} \]

The perturbing force therefore differs from zero only inside the nucleus.

In first-order perturbation theory the shift of the levels is given by

\[ \Delta E^{\text{vol}} = \int \psi^{\text{vol}} \psi d^3x \cdot \]  

Since \(|\psi|^2\) does not change appreciably in the region \(r \leq R_*\) this integral can be readily evaluated by substituting for \(|\psi|^2\) its value at the origin.

\[ \Delta E^{\text{vol}} = 4\pi Z e^2 |\psi (0)|^2 \int_0^{R_N^*} r^* \left( \frac{1}{r} - \frac{1}{R_N^*} \left( \frac{3}{2} - \frac{1}{2} \frac{r^*}{R_N^*} \right) \right) dr = \]

\[ = \frac{2\pi}{5} Z e^2 R_N^* |\psi (0)|^2. \]
Substituting the expression (20.14) for $|\psi(0)|^2$, we obtain

$$\Delta E_{\text{vol}} = \frac{2}{5} \frac{Z^4 R^8 \hbar^2}{a^5 n^8} \left( \frac{R}{a} \right)^2,$$

that is, in nonrelativistic theory, the shift of the energy levels is different from zero only for $s$ states ($l = 0$).

It can be shown that for $p$ levels this shift will contain a factor of the order $\left( \frac{R}{a} \right)^2$ (where $a_n = a_0 \frac{n^2}{Z}$), and for $d$ states a factor of the order of $\left( \frac{R}{a} \right)^4$, and so on. Consequentely, the shift in the energy levels for $p$ and $d$ states can be neglected in the first approximation.

For hydrogen, the first-order shift in the energy levels is about 1 Me; this is much too small to account for the Lamb shift, which is equal to approximately 1,057 Me (see Chapter 20).

The volume of the nucleus is important in connection with the isotope shift, that is, the shift in the energy levels of atoms with the same atomic number $Z$ and different mass numbers $A$. The chief factors that give rise to the isotope shift are the different masses (the mass effect) and different volumes (the volume effect) of the isotopes. The mass effect is manifested in a shift of the spectrum lines towards the ultraviolet as the mass number $A$ increases. For example, for $Z = 1$ the highest frequencies are found in tritium with $A = 3$, then deuterium with $A = 2$, and, finally, ordinary hydrogen with $A = 1$ [see (21.2) and also Chapter 13]. On the other hand, the volume effect is manifested in a shift of the spectrum lines towards the infrared as $A$ increases. For instance, it can be seen from Eqs. (21.1), (21.9) and (21.13) [see below], that the energy levels of a hydrogen-like atom will be given by the following expression when the shift due to the volume effect is taken into account:

$$E_n = -\frac{Z^2 e^2}{n^2} \left( 1 - \frac{4}{5} \frac{Z^2 R^8}{a^5 n^8} A^{3/8} \right).$$

Experiment shows that an isotope shift towards ultraviolet is observed in elements whose atomic number $Z$ is less than 40-50. For elements with a larger value of $Z$ an isotope shift in the opposite direction is observed, that is, towards the infrared. This indicates that, for relatively light elements, the isotope shift is caused mainly by the mass effect, whereas for heavier elements it is caused by the volume effect. This, however, is a rather simplified picture of the isotope effect, and other features associated with the structures of the atom (for example, nuclear spin and polarization of nuclei by electrons) also have to be taken into account.

C. MESIC ATOMS

The finite size of the nucleus has a particularly important effect on the position of energy levels in a mesic atom—an atomic system consisting of a $\mu$ meson revolving about a nucleus. The $\mu$ meson is a particle that has the same spin as the electron (that is, spin

---

1To calculate the shift of the $p$ levels we must substitute the second term in the expansion of $|\psi(r)|^2$ into (21.7), namely,

$$|\psi(r)|^2 \cdot r^2 \left( \frac{\partial |\psi(r)|^2}{\partial r} \right) \mid_{r \rightarrow 0},$$

since the main term $|\psi(0)|^2$ vanishes for $p$ states.
1/2 in units of \( \hbar \) and a mass 207 times greater (\( m_\mu = 207m_0 \)), so that the \( \mu \) meson is basically a "heavy" electron. Mesic atoms can be produced by passing negative \( \mu \) mesons through matter. After losing its energy and slowing down, a \( \mu \) meson may be captured in an orbit about a nucleus, forming in this way a \( \mu \)-mesic atom. Mesic atoms have been obtained for almost all elements of the periodic system, from hydrogen up to the heavy elements (uranium, neptunium, and so on).2

The motion of a \( \mu \) meson about the nucleus is determined mainly by the Coulomb attraction, just like the motion of an electron. A \( \mu \) meson, however, also has non-electromagnetic interactions with the electron–neutrino and nuclear fields; these interactions may result in spontaneous decay of the \( \mu \) meson into an electron, neutrino, and antineutrino (the lifetime of a \( \mu \) meson at rest is \( \tau = 2.2 \times 10^{-6} \) sec). The \( \mu \) meson has, in addition, a definite probability of being captured by a nucleus. Thus the lifetime of a \( \mu \)-mesic atom is determined by two competing processes: natural decay of a \( \mu \) meson into an electron, neutrino, and antineutrino and nuclear capture of the \( \mu \) meson. In light mesic atoms \((Z < 10)\) the probability of the first process is greater than the probability of the second; that is, the lifetime of a mesic atom is determined by the lifetime of a \( \mu \) meson at rest \((\tau \approx 10^{-6} \) sec). For \( Z > 10 \), nuclear capture begins to predominate and the lifetime slowly decreases to \( \approx 7 \times 10^{-8} \) sec \((\text{for } Z = 82)\).3

In the theory of \( \mu \)-mesic atoms, ordinary electrostatic interaction plays a fundamental role. In the first approximation, we can regard the nucleus as a point charge and calculate the energy of the mesic atom and the radius of the orbit using the equations derived for an ordinary hydrogen-like atom, replacing the electronic mass by the mass of a \( \mu \) meson. Then the energy and radius of the orbit will be given by [see (13,33), (13,45)]

\[
E_n = -\frac{m_\mu Z^2 e^4}{2\hbar^2 n^2}, \quad r_n = \frac{\hbar^2}{m_\mu e^3 Z},
\]

where \( m_\mu = 207m_0 \). It can be seen that the energy of the \( \mu \) meson in a mesic atom is 207 times greater than the corresponding energy of an electron in the atom, and that the radius of the orbit on the contrary is reduced by the same factor. If electrons remain in the atom along with the \( \mu \) mesons, they will move about the nucleus in considerably larger orbits than the \( \mu \) meson and therefore cannot exert a significant influence on the \( \mu \) meson rotating around the nucleus. A mesic atom, therefore, may be regarded as a hydrogen-like atom that can have both large and small values of \( Z \).

Since the radius of the "Bohr" orbit of the meson is 207 times smaller than that of the electron orbit, the probability that the meson will be located in the nucleus is considerably greater than for an electron in a hydrogen-like atom. The main correction to the energy levels of a mesic atom will therefore come from the volume effect. The equation for the energy of \( s \) states can be obtained from (21,9) and (21,10) by replacing the Bohr radius \( a_0 \) by the corresponding radius in a mesic atom

\[
a_\mu = \frac{\hbar^2}{m_\mu e^3 Z}, \quad \text{(21.11)}
\]

obtaining, therefore,

\[
E_n, l=0 = -\frac{m_\mu Z^2 e^4}{2\hbar^2 n^2} \left( \frac{4}{5} \frac{Z^2 R_N^6}{n a_\mu^2} \right), \quad \text{(21.12)}
\]

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2 These subjects are treated in more detail in a paper by D. D. Ivanenko and G. E. Pustovalova, Uspekhi fizicheskikh nauk, 61, 27 (1957).

3 For \( \pi \) mesons, which strongly interact with nuclei and are responsible for nuclear forces, the lifetime with respect to decay into a \( \mu \) meson and neutrino is equal to \( 2.6 \times 10^{-8} \) sec, whereas the lifetime with respect to capture by a nucleus is many times smaller. In particular, for \( \pi \)-mesic hydrogen the capture time of a negative pion from the orbit is of the order of \( 10^{-15} \) sec.
Using the fact that the nuclear radius is related to the mass number \( A \sim 2Z \) by the expression
\[
R_N = R_0 A^{1/8} \approx R_0 (2Z)^{1/8},
\] (21.13)
where \( R_0 = \text{const} \), we obtain in the first approximation
\[
E_n, l = 0 = -\frac{m_e Z^2 e^4}{2\hbar^2} \left[ 1 - \frac{4 \cdot 2^{8/9}}{5n} \frac{Z^8}{(a_\mu)^3} \right].
\] (21.14)

It follows that, for the \( s \) levels, the energy correction due to the nuclear volume will be proportional to \( 2^{8/9} \), and therefore attains very large values for heavy elements.

In heavy elements, the orbit of a \( \mu \) meson may even be inside the nucleus, at large \( Z \) and small \( n \). The Bohr radius of the mesic atom becomes equal to the nuclear radius for \( Z = Z_{cr} \approx 45 \).

For orbits inside the nucleus \( (Z > Z_{cr}) \), the main part of the potential will no longer be determined by the Coulomb law (21.4) but instead by formula (21.3) which corresponds to the potential of a three-dimensional harmonic oscillator (on the assumption of a simplified model of the nucleus in which the charge is uniformly distributed over the volume). Thus the energy has to be determined from the following equation instead of (13.4):
\[
\frac{d^2 R}{dp^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2m_\mu}{\hbar^2} \times \\
\times \left( E + \frac{3Z^2 e^4}{2R_N} - \frac{1}{2} \frac{Z^2 e^4 \hbar^2}{R_N^2} - \frac{(l + 1) \hbar^2}{2m_\mu a_\mu^3} \right) R = 0.
\] (21.15)

In Eq. (21.15) let us change the variable by setting \( R = \sqrt{r} R', r = \sqrt{r}. \) Since
\[
\sqrt{r} R = 4p^{5/4} \left( \frac{d^2 R'}{dp^2} + \frac{2}{p} \frac{dR'}{dp} + \frac{3}{16p^2} R' \right)
\]

it follows that the equation for the energy of a three-dimensional harmonic oscillator is formally identical with the equation for the hydrogen-like atom
\[
\frac{d^2 R'}{dp^5} + \frac{2}{p} \frac{dR'}{dp} + \left( -A + \frac{2B}{p} - \frac{C}{p^2} \right) R' = 0,
\] (21.16)

but has different values of the constants, namely,
\[
A = \frac{Z^2 e^4 m_\mu}{4\hbar^2 R_N^3}, \quad B = \frac{m_\mu}{4\hbar^2} \left( E + \frac{3Z^2 e^4}{2R_N^3} \right),
\]
\[
C = \frac{1}{4} \left( l^2 + l - \frac{3}{4} \right) = l'(l' + 1),
\] (21.17)
\[
l' = \frac{1}{2} \left( l - \frac{1}{2} \right).
\]

To determine the eigenvalues of the energy we may use Eq. (13.20), according to which
\[
\frac{B}{\sqrt{A}} = l' + k + 1.
\]

Substituting for \( B, A \) and \( l' \) their values from (21.17) and using the fact that \( k = n \quad l = l' \), we can find the energy of the meson in an orbit inside the nucleus:
\[
E_{kl} = -V_0 + \hbar\omega (2k + l + l' + 2),
\] (21.18)
where the frequency of mechanical vibrations of the three-dimensional oscillator is

\[ \omega = \sqrt{\frac{Ze^2}{m_R R^2_N}}. \]

The quantity \( \frac{Ze^2}{m_R R^2_N} \) represents the zero-point energy of the three-dimensional oscillator; it is three times greater than the corresponding zero-point energy of a one-dimensional oscillator. The quantity \( V_0 = \frac{3}{2} \frac{Ze^2}{R_N} \) is the greatest depth of the oscillator potential well.

Equation (21.18) is correct on the assumption that the potential energy varies in accordance with (21.3) from zero to infinity. If the finite size of the nucleus is taken into account, an additional energy is obtained that represents the difference between the potential energy of the particle in the oscillator well and its potential energy in the Coulomb field (this difference being averaged over the space outside the nucleus). The equation for the additional energy is

\[ \Delta E_{\text{vol}} = Ze^2 \int_{\frac{3}{2} R_N}^{\infty} \left| \psi \right|^2 \left( \frac{3}{2} - \frac{r^2}{2R_N^2} \right) - \frac{1}{r} \, r^2 dr. \]  

Since the wave function of a spherical oscillator is similar to the wave function for a Coulomb field (it is determined from the same wave equation with \( r \) replaced by \( r^2 \)), it decreases exponentially as \( r \) increases. The correction (21.19) is therefore significant only when the radius \( R_N \) of the mesic atom is close to \( R_N \).

As an example, let us consider the \( 2p - 1s \) transition in lead \( (Z = 82) \). If the mesic atom of lead is assumed to have a point nucleus, the energy released in this transition can be found from (21.10)

\[ E_2 - E_1 = \frac{3m_e Z^2 e^4}{8\hbar^2} = 14 \text{ Mev}. \]

The relativistic and spin effects in the \( 2p_{3/2} - 1s_{1/2} \) transition increase this energy by the amount

\[ \Delta (\Delta E) \approx 2 \text{ Mev}. \]

Incidentally, such a significant role of the relativistic and spin effects is due to the fact that the energy is expanded in terms of \((Za)^2\). This quantity is comparatively large for lead \( (Z = 82, a = 1/137) \). Comparison with experiment shows, however, that in this transition an energy of 6 Mev is liberated instead of the predicted 16 Mev. This discrepancy between theory and experiment arises because the \( 1s \) state for lead lies inside the nucleus. In the \( 2p \) state the orbit lies outside the nucleus and the volume effect of the nucleus is small. If we take the energy of the \( 1s \) level from (21.18), and the energy of the \( 2p \) level from (21.10) for a point nucleus, the energy of the \( 2p - 1s \) transition will be 3.6 Mev. If we add to this the correction (21.19) for the energy of the \( 1s \) level, the energy of the transition will come to about 5 Mev, which is relatively close to the experimental value.

A study of the multiplet structure of the \( 2p \) level in mesic atoms enables us to determine the spin of a \( \mu \) meson. For a particle with integral spin, the level splits into an odd number of components (for spin 0 no splitting occurs, for spin 1 three lines are observed, etc.). Since the \( 2p \) level splits into two components \( (2p_{3/2} \text{ and } 2p_{1/2}) \), it was established that the spin of a \( \mu \) meson is 1/2. On the assumption of a point nucleus, the theoretical splitting calculated from Eq. (20.17) should amount to about 0.55 Mev, with the \( 2p_{3/2} \) and \( 2s_{1/2} \) levels coinciding. When the finite size of the nucleus is taken into account in a mesic lead atom, the splitting of the \( 2p_{3/2} - 2p_{1/2} \) levels is reduced to 0.2 Mev and the \( 2s_{1/2} \) level is raised above the \( 2p_{3/2} \) level. This is illustrated in
Fig. 21.2. From the above data it follows that heavy mesic atoms will emit gamma quanta having energies of several Mev. Lighter mesic atoms emit x-rays. Because of the significant influence of the size of the nucleus on the spectra of heavy mesic atoms, the charge distribution inside the nucleus can be determined from an analysis of the spectra. It has been found that the value that should be substituted for $R_0$ in the formula for the electromagnetic radius of a nucleus with mass number $A$:

$$R_N = R_0 A^{1/4}$$

is $1.2 \times 10^{-13} \text{ cm}$ rather than $1.4 \times 10^{-13} \text{ cm}$ (the value assumed for nuclear interactions).

Similarly, the multiplet structure of the spectral lines of mesic atoms can be used to determine the magnetic moment of the $\mu$ meson; its value is close to the muon magneton

$$\mu_\mu = \frac{e e_0 \hbar}{2m_\mu c}$$

where the Landé $g$ factor is $g = 2$.

The theory of $\mu$-mesic atoms is based mainly on electromagnetic interactions. By contrast, in the theory of $\pi$-mesic atoms, a great part is played by the nuclear interactions, the theory of which is far from complete. Further experimental study of $\pi$-mesic atoms and an explanation of the semiempirical laws that describe their behavior will have important bearings on future work in the theory of nuclear forces. These topics, however, lie beyond the scope of this textbook.

**D. APPLICATION OF THE DIRAC EQUATION TO THE NEUTRON AND THE PROTON**

The Dirac equation describes the motion of particles with spin $1/2$. It applies to electrons as well as to protons and neutrons. In the presence of an electromagnetic field it is necessary to take into account the charge of the proton, as well as the so-called anomalous magnetic moments of the proton and the neutron. We recall that the energy of interaction between a charged Dirac particle and an electromagnetic field is

$$V_e = e \psi \overleftrightarrow{A} \psi$$

In the nonrelativistic approximation this expression contains a magnetic moment due to the intrinsic (spin) angular momentum $(\hbar/2\alpha)$

$$\mu_e = \frac{e \hbar}{2m_0 c} \sigma.$$  \hspace{1cm} (21.25)

This quantity is known as the kinematic or Dirac magnetic moment. In passing to the relativistic equation, we must replace the mass $m_0$ in Eq. (21.25) by its relativistic value $m_0 \sqrt{1 - \gamma^2}$, and, therefore, the Dirac magnetic moment vanishes as the velocity approaches the velocity of light $(v \sim c)$.

In addition to the Dirac magnetic moment, which appears only in the nonrelativistic approximation and which depends on the charge, a particle may have an anomalous magnetic moment that does not vanish even in the relativistic case and is independent of the particle's charge.

We shall now find the energy of interaction due to the anomalous magnetic moment. The energy of interaction (21.24) of an electron with an electromagnetic field is a scalar quantity, since in four-dimensional space $i\phi = A_0, A_x = A_1, A_y = A_2, A_z = A_3$, in the same way the unit matrix $I$ is the fourth component of the velocity matrix $a_\mu$ (that is, $a_4 = 1$). The interaction energy (21.24) may, therefore, be represented as a scalar quantity in four-dimensional notation

$$V_e = -e \sum_{\mu=1}^{4} a_\mu A_\mu$$

(21.26)

\[ ^4 \text{More precisely, the quantity } j_\mu = e\sigma_{\mu}^\nu \phi \overleftrightarrow{A_\nu} \psi \text{ (see (17.32)), where } a_1, a_2, a_3, a_4 = i. \]
The electromagnetic field forms an antisymmetric tensor of second rank
\[ H_{\mu \nu} = \frac{\partial A_\nu}{\partial x^\mu} - \frac{\partial A_\mu}{\partial x^\nu}, \]  
(21.27)

where
\[ x_4 = ict. \]

It follows that
\[ H_x = H_{28}, \quad H_y = H_{31}, \quad H_z = H_{13}, \]
\[ iE_x = H_{41}, \quad iE_y = H_{43}, \quad iE_z = H_{11}. \]

The interaction energy of the anomalous magnetic moment with the electromagnetic field is, therefore, given by
\[ V_m = \mu \sum_{\mu, \nu = 1}^4 a_{\mu \nu} H_{(\nu \lambda)}, \]
(21.29)

where \( a_{\mu \nu} \) is a second rank tensor composed of the Dirac matrices.\(^5\)

Using the rules for transformation of a wave function under the Lorentz (see (17.38)) and spatial rotations (see (17.39)), we can show that the quantities
\[ a_{28} = \rho_1 \sigma_1, \quad a_{31} = \rho_2 \sigma_2, \quad a_{12} = \rho_3 \sigma_3, \quad a_{41} = -i \sigma_z, \]
\[ a_{12} = -i \rho_3 \sigma_z, \quad a_{43} = -i \rho_2 \sigma_z \]
(21.30)

are the matrix elements forming a second rank tensor. The energy of interaction between the anomalous magnetic moment and the electromagnetic field takes the form
\[ V_m = \mu \left[ p_2 \sigma \cdot H + p_3 \sigma \cdot E \right]. \]
(21.31)

An electron has a charge, a spin, and also a Dirac magnetic moment. Its anomalous magnetic moment is relatively small (see below). A neutron has no charge, but it does have an anomalous magnetic moment; this magnetic moment determines the interaction between the neutron and the electromagnetic field. As for the proton, it has both a charge and a spin, and hence a Dirac magnetic moment; in addition, it has an anomalous magnetic moment. It should be noted that nuclear interactions are of great importance in the theory of nucleons.

**E. EXPERIMENTAL DETERMINATION OF THE MAGNETIC MOMENT OF THE NEUTRON AND THE PROTON**

The procedure for determining the magnetic moment of the neutron, proton, and complex nuclei is basically the same as for the magnetic moment of the electron (the Stern-Gerlach experiment). The basic principle consists in applying a magnetic field perpendicular to the direction of motion of the particle. The particle will react differently depending on whether its magnetic moment is oriented parallel or antiparallel to the field.

Let us first consider the possibility of determining the Dirac magnetic moment and the anomalous magnetic moment of a free particle. Suppose a free particle moves perpendicularly to the \( z \) axis. The Hamiltonian describing its motion has the form
\[ H = c \sigma_1 \tau_y p_x + c \sigma_2 \tau_y p_y + \frac{p_m \sigma_1 c^2}{2}, \]
(21.32)

The component of the intrinsic angular momentum perpendicular to the direction of this motion
\[ S_z = \frac{1}{2} \hbar \sigma_3, \]
(21.33)

\(^5\)More precisely, the quantity \( \psi^+ a_{\mu \nu} \psi \nu \) is a second rank tensor.
does not commute with this Hamiltonian. The component of the total angular momentum along the z axis does commute with the Hamiltonian

\[ J_z = y p_x - x p_y + \frac{1}{2} \hbar z, \]  

(21.34)

and can therefore be determined exactly together with the energy.

Let us evaluate the error in the determination of the orbital angular momentum by means of the uncertainty relation. If the origin of the coordinate system is taken to be at the center of the wave packet, the error in the orbital angular momentum will be

\[ \Delta L_z \approx \Delta y \Delta p_x - \Delta x \Delta p_y. \]

In accordance with the uncertainty relation, we have \( \Delta p_x \sim \frac{\hbar}{\Delta x}, \Delta p_y \sim \frac{\hbar}{\Delta y}. \) Since the errors may be either positive or negative, we find

\[ |\Delta L_z| \sim \hbar \left( \frac{\Delta y}{\Delta x} \right) + \left( \frac{\Delta x}{\Delta y} \right). \]  

(21.35)

The error \( \Delta L_z \) will be minimum when \( |\Delta x| = |\Delta y| \). Thus the error \( \Delta L_z \) due to the translational motion of the particle is of the order of the spin, and therefore the perpendicular components of the intrinsic angular momentum and the Dirac magnetic moment cannot be determined simultaneously.

![Fig. 21.3. Experiments for determining the magnetic moment of the neutron.](image)

We recall that the Stern-Gerlach experiment allowed for the determination of a magnetic moment of a bound electron; since, however, the orbital angular momentum in the s state is zero, it was the spin (or Dirac) magnetic moment that was actually measured.

In accordance with (21.31), the interaction energy associated with the perpendicular component of the anomalous magnetic moment is

\[ V_m = \mu q_2 \beta. \]  

(21.36)

This component commutes with the Hamiltonian (21.32) and can therefore be measured exactly. Consequently, it is possible to measure the magnetic moment of a free neutron when the magnetic field is perpendicular to its motion, as was done by Bloch and Alvarez (1940).\(^6\) In their experiments when a beam of neutrons was passed through a piece of magnetized iron,\(^7\) the most pronounced scattering was observed for those neutrons whose magnetic moment was parallel to the magnetic induction vector inside the iron. The emerging beam consisted, therefore, mostly of neutrons whose magnetic moment was antiparallel to the magnetic induction vector. If the neutron beam passes now through two magnetized iron plates in succession, the experiment is completely analogous to the transmission of light through two Nicol prisms; that is, the first iron plate acts as

---

\(^6\) Similarly, it may be shown that only the longitudinal component of spin commutes with the Hamiltonian. In principle, therefore, it also can be measured experimentally.

\(^7\) Neutrons have no electric charge and they pass quite freely through matter. Actually, their only interactions occur on collisions with the nuclei.
a polarizer and the second as an analyzer. This phenomenon was used to determine the magnetic moment of the neutron.

A schematic diagram of the Bloch–Alvarez experiments is given in Fig. 21.3.

Unpolarized neutrons moving along the direction of the $x$ axis pass through the polarizer (first iron plate, with a magnetic induction vector directed upwards). The emerging beam consists mostly of neutrons whose magnetic moment is directed downwards. These polarized neutrons will pass freely through the analyzer if its magnetic induction vector is directed upwards, like that of the polarizer. On the contrary, they will be transmitted much more weakly if the iron plates are oppositely magnetized.

Between the polarizer and analyzer there is a device that reorients the neutron spin. This device is similar in principle to the one used by Rabi in his nuclear magnetic resonance experiments to determine the magnetic moment of the proton and of heavier nuclei. The basic principle of the instrument is as follows. In the space between the polarizer and the analyzer, a relatively strong, constant magnetic field is applied parallel to their magnetization vectors (see Fig. 21.3). A neutron whose magnetic moment is antiparallel to this magnetic field acquires the additional energy

$$\Delta E_{\text{anti}} = \mu_n B.$$  \hspace{1cm} (21.37)

If, however, the magnetic moment is parallel to the field, the neutron loses an energy

$$\Delta E_{\text{par}} = -\mu_n B.$$  \hspace{1cm} (21.38)

In addition, there is a relatively weak oscillatory magnetic field applied perpendicularly to the field $B$.

$$H_y = A \cos \omega_0 t.$$  \hspace{1cm} (21.39)

This oscillatory field will reorient the spin of the neutron particularly strongly when the frequency $\omega_0$ is close to the resonance frequency

$$\omega_0 = \frac{\Delta E_{\text{anti}} - \Delta E_{\text{par}}}{\hbar} = \frac{2\mu_n B}{\hbar}. \hspace{1cm} (21.39)$$

At this resonance frequency, the number of neutrons undergoing a reorientation of the magnetic moment reaches its maximum value. To find when this happens, it is necessary to determine when the number of neutrons passing through the analyzer is minimum in the case of parallel magnetic induction vectors, or maximum in the case of antiparallel magnetic vectors.

Once the frequency $\omega_0$ has been determined (it is, in effect, twice as great as the Larmor frequency of precession), the magnetic moment of the neutron can be found. According to recent data it is equal to

$$\mu_n = -1.9131 \hbar \varepsilon_{\text{nuc}}$$

where the unit for measuring magnetic moments is the nuclear magneton

$$\mu_{\text{nuc}} = \frac{e_0 \hbar}{2m_p c} = \frac{m_0}{m_p} \mu_0 = \frac{1}{1836.1} \mu_0 = 0.505 \cdot 10^{-23} \text{ erg} \cdot \text{ gauss}^{-1},$$

where $m_p$ is the mass of a proton and $\mu_0$ is the Bohr magneton.

From the resonance frequency of the oscillatory field, we can determine the magnitude of the magnetic moment but not its sign. If, however, we replace the oscillatory magnetic field by a rotating magnetic field, we can also determine the sign of the moment, since for resonance it is necessary that the vector equation $\omega_0 = -2o$ should hold, where $o = \frac{1}{\hbar} \frac{H}{B}$ is the Larmor frequency of precession of the neutron spin. The minus sign shows that the magnetic moment of the neutron, just as for the electron, is directed opposite to the spin.

\footnote{Subsequent improvements on the Bloch and Alvarez experiments are described in E. Segre, Experimental Nuclear Physics, Vol. I, 1953.}
we obtain
\[ V \hbar s = \frac{8\pi}{3} \mu_\text{p} \sigma_p \cdot \sigma'_p \, \ell (r). \] (21.42)

Consequently, in the first approximation, the interaction of magnetic moments—just like the contact interaction—influences only the s state. The expression \((\sigma'_p \cdot \sigma_p)\) in (21.42) can be found from the following simple considerations.

The spin matrices of the proton \(\sigma_p\) and the electron \(\sigma'_p\) must satisfy the relation
\[ \frac{1}{4} \hbar^2 (\sigma'_p + \sigma_p \sigma_p \sigma'_p)^2 = \hbar^2 S (S + 1), \] (21.43)

where \(S\) is the absolute value of the total spin, which is equal to either zero (antiparallel spins) or to unity (parallel spins). Then
\[ \frac{1}{4} [\sigma'_p \sigma'_p + 2 (\sigma'_p \cdot \sigma_p)] = S (S + 1). \]

Using the fact that \(\sigma'_p \cdot \sigma'_p = 6\), we obtain
\[ (\sigma'_p \cdot \sigma_p) = 2S (S + 1) - 3. \] (21.44)

Since integration when the \(\delta\) function is present gives
\[ \int d^3x \psi^\dagger \psi \delta (r) = |\psi (0)|^2, \]
we obtain the following expression for the shift of s levels (hyperfine structure) of hydrogen:
\[ \Delta E_s = \frac{8}{3} \mu_\text{p} \frac{1}{\hbar^2 a_o^3} [2S (S + 1) - 3], \] (21.45)

where \(a_o = \frac{\hbar^2}{m_e e_o}\) is the radius of the first Bohr orbit, and the value of \( |\psi (0)|^2 \) is taken from Eq. (20.14).

Two cases should be distinguished:
(1) Spins of the proton and the electron are antiparallel \((S = 0)\); then
\[ \Delta E_{s=0} = -8 \mu_\text{p} \frac{1}{n^2 a_o^3}. \] (21.46)

(2) Spins of the proton and the electron are parallel \((S = 1)\); then
\[ \Delta E_{s=1} = \frac{8}{3} \mu_\text{p} \frac{1}{n^2 a_o^3}. \] (21.47)

The difference between these levels represents splitting of the s term due to the interaction between the electron and the magnetic moment of the nucleus
\[ \Delta \omega = \frac{\Delta E_{s=1} - \Delta E_{s=0}}{\hbar} = \frac{32 \mu_\text{p} \frac{1}{n^2 a_o^3}}{\hbar}. \] (21.48)

If we use (21.48) to calculate the s-term splitting for the case \(n = 1\), then substituting the value of \(\mu_p\) obtained in Rabi's experiments and setting \(\mu_o\) equal to the Bohr magneton, we find
\[ \Delta \omega_{\text{theor}} = 1417 \text{ Me}. \]

On the other hand, a careful experimental verification of the splitting of this level by microwave spectroscopic methods has given the value
\[ \Delta \omega_{\text{exp}} = 1420 \text{ Me}. \]
The relativistic corrections and the corrections for the finiteness of the nuclear mass do not raise the frequency $\Delta \omega_{\text{theor}}$ to the required value $\Delta \omega_{\text{exp}}$. The proton's magnetic moment has also been measured very accurately. To explain this anomaly, therefore, it remained to assume that the magnetic moment of the electron is not exactly equal to the Bohr magneton, but is instead somewhat larger. Kusch and Foley showed that to obtain agreement with experiment the magnetic moment of the electron must be taken to be

$$\mu_{\text{el}} = -\mu_0 (1 + b),$$

(21.49)

where, according to recent data,

$$b = 0.00116.$$

These considerations show that an electron will have a very small anomalous magnetic moment $\mu_{\text{el}}^{\text{anom}} = \mu_0 b$ in addition to the Dirac or kinematic magnetic moment ($-\mu_0$). We shall discuss the nature of the anomalous magnetic moments in the next chapter.

Concluding this section, it is necessary to point out that the hyperfine structure cannot explain the Lamb shift of the $2s_{1/2}$ level (1.058 Me relative to the $2p_{1/2}$ level). First of all, it follows from (21.48) that the splitting of the $2s_{1/2}$ term is of the order of 200 Mc, and, in addition, the center of mass of the $s$ terms is not shifted. Suppose, the level with $S = 1$ (parallel spins of the electron and the proton) is raised by a certain amount [see (21.47)]; then the level with $S = 0$ (antiparallel spins of the electron and the proton) is lowered by an amount three times as large [see (21.46)]. Since a state with $S = 1$ is three times more probable than a state with $S = 0$ (when $S = 1$ the spin may be directed along the $z$ axis, opposite to the $z$ axis and perpendicular to the $z$ axis), the center of mass of the $s$ states remains unaltered, so that it occurs in the same position as when the magnetic moment of the nucleus is neglected. The hyperfine structure cannot therefore account for the Lamb shift. The theory of this effect will be considered in the next chapter.

Problem 21.1. Find the shift of the $1s$ levels in the light $p$-mesic atoms as a result of the influence of the nuclear structure, taking into account the nuclear motion and also the variation of the wave function within a distance comparable to the size of the nucleus.

Hint. The shift of energy levels should be calculated by the perturbation method. We use Eqs. (21.5) and (21.7) where the wave functions are those of hydrogen-like atoms with the meson mass substituted for the electron mass. Because of the finiteness of the nuclear mass, the motion of the nucleus has much greater influence on the position of the energy levels of a mesic atom than on the levels of an ordinary atom. It is therefore necessary to use the reduced meson mass in more accurate calculations. The wave functions of a meson change appreciably inside the nucleus; therefore, the quantity $|\psi|^2$ can be replaced by its value at the origin only in a comparatively crude qualitative estimate, as in the derivation of (21.14).

Answer. In the general case

$$3E_{10} = -2E_{10} \left\{ 1 - \frac{3}{2b} + \frac{3}{2b^3} - \left[ \frac{3}{2b^3} + \frac{3}{b^3} + \frac{3}{2b} \right] e^{-2b} \right\},$$

where

$$b = \frac{R_N Z}{a_\mu}, \quad E_{10} = -\frac{m_\mu e^4 Z^2}{2\hbar^2 \left( 1 + \frac{m_\mu}{M} \right)}.$$

For small $b$ and $M \to \infty$, this expression may be obtained from Eq. (21.12).
Chapter 22

The Electron-Positron Vacuum and the Electromagnetic Vacuum

A. Dirac Theory of "Holes." Discovery of the Positron

The Dirac theory, which includes spin effects and relativistic effects, was able to account for the fine structure of the spectral lines of hydrogen-like atoms and the anomalous and normal Zeeman effects. The Dirac theory, however, also gave rise to a number of major difficulties in connection with the interpretation of negative energy states. These difficulties were not overcome for some time, but they eventually led to fundamental new discoveries in relativistic quantum mechanics.

In our treatment of the motion of a free particle (Chapter 17), we mentioned that the Dirac equation allowed solutions corresponding to both positive and negative values of energy. It is worth noting in this connection that solutions with negative energy are not characteristic of the Dirac theory alone, but appear in any relativistic theory. In relativistic mechanics, the energy of a free particle is connected with the momentum and rest mass by the well-known expression

\[
E = \pm \sqrt{c^2p^2 + m_0^2c^4},
\]

which has two roots

\[
E = \pm \sqrt{c^2p^2 + m_0^2c^4}.
\]

The regions of positive and negative energies are separated by an interval equal to \(2m_0c^2\) (see Fig. 22.1). At first glance, states with negative energy do not appear to have a real physical meaning, since the region of negative energies extends to infinity \((E = -\infty)\) and, therefore, there is no lowest state. This would imply that no ordinary state is stable, since a spontaneous transition to a lower energy state would always be possible. Furthermore, a particle with negative mass (negative energy) would have a number of strange properties; for example, it would repel a particle with positive mass.

In classical physics, states with negative energy do not cause any difficulties, because the energy of a moving particle can only change continuously; therefore, transitions from the states with positive energy to the states with negative energy cannot take place, since the energy would have to change discontinuously by the amount \(\Delta E \geq 2m_0c^2\). Defining the energy to be positive from the start, we may, therefore, neglect the negative energy states.

The situation is quite different in quantum theory, where transitions can take place between the states in a discrete spectrum, as well as in a continuous spectrum. States with negative energy cannot be excluded simply by defining the energy to be positive.

Fig. 22.1. Allowed energy levels of a free Dirac particle.
at the initial time, because the probability of the transition between the states with energy $+m_0c^2$ and $-m_0c^2$ is not equal to zero.

In order to avoid transitions of electrons to negative states, Dirac suggested (1931) that we regard all negative energy levels as occupied by electrons (see Fig. 22.2), so that an electron with a positive energy cannot jump into a negative energy level under ordinary conditions. The state in which all negative energy levels and no positive energy levels are occupied is called the "electron vacuum."

Let us now assume that a $\gamma$-ray photon with energy $\epsilon > 2m_0c^2$ excites an electron from the electron vacuum into a positive energy state. In this case, the absorbed $\gamma$-ray photon will be replaced by an electron with positive energy, and a "hole" will appear in one of the negative energy states (see Fig. 22.3).

The decisive factor that led to the success of Dirac's hypothesis was that he interpreted the "hole" as a particle (the "positron") with positive mass equal to the mass of the electron, but with the opposite charge. Let us suppose that there are no particles at the initial time. Then the "zero-point energy" $E_{\text{vac}}$ (the energy of the electron vacuum) is equal to the sum of the energies of the electrons in the negative energy states $n_-$.

$$E_{\text{vac}} = \sum_{n_-} E_{n_-}.$$  \hspace{1cm} (22.1)

The "zero-point charge" is equal to

$$e_{\text{vac}} = -\sum_{n_-} e_0.$$  \hspace{1cm}

Thus, from the standpoint of the hole theory, the absence of any real particles means that all positive energy states are empty, and all negative energy states are occupied. This case corresponds to the electron vacuum (see Fig. 22.2).

When an electron jumps from a negative energy state $n_-$ to a positive energy state $n_+$, the total energy change of the system is

$$\Delta E = E_{n_+} + \sum_{n_-} E_{n_-}' - \sum_{n_-} E_{n_-} = E_{n_+} - E_{n_-} = E_{n_+} + |E_{n_-}|.$$  \hspace{1cm} (22.2)

This change represents the sum of the positive energies of two nascent particles. Similar arguments with regard to charge show that the charge of the nascent particle corresponding to the "hole" is opposite to the electron charge

$$\epsilon = -e_{n_+} - \sum_{n_-} e_0 + \sum_{n_-} e_0 = -e_{n_+} + e_{n_-} = -e_0 + e_0.$$  \hspace{1cm} (22.3)

1. In accordance with the Pauli exclusion principle (see Chapter 6), only one electron can occupy each state.

2. A similar conclusion was reached in the treatment of the hole theory of semiconductors (see the discussion of the band theory of conduction in Chapter 6).

3. The prime attached to the summation sign ($\sum'$) means that the summation extends over all states $n_- \neq n_-$ except the state $n_- = n_-$. A similar conclusion was reached in the treatment of the hole theory of semiconductors (see the discussion of the band theory of conduction in Chapter 6).
Thus, the transition of an electron from a negative energy state to a positive energy state (as a result of the absorption of a $\gamma$-ray quantum with energy greater than $2mc^2$) leads to the creation of a pair of particles. The unoccupied negative energy state ("hole") may be regarded as a state occupied by a particle with positive charge $+e_0$ and positive energy. This particle, which was predicted by Dirac, was called a "positron" and was discovered by Anderson in cosmic radiation (1932).

Once it is interpreted in this way, the Dirac theory describes in a natural manner both the electron and the positron. The positron is an antiparticle; its wave function satisfies the Dirac equation with positive energy and positive charge (see Problem 18.5).

In the Dirac theory, pair annihilation—a process which is the reverse of pair creation—is also allowed. This process takes place when an electron with positive energy jumps into a hole. In this case the electron and positron are converted into $\gamma$-rays.

In these transformations, the laws of conservation of energy and momentum are rigorously obeyed. As already mentioned, pair creation due to the absorption of a $\gamma$-ray photon can occur only in the presence of a third particle (for example, a nucleus), that takes up the excess momentum of the photon

$$\gamma + Z\gamma_0 \rightarrow Z\gamma_0 + e_+ + e_-.$$  \hspace{1cm} (22.4)

Similarly, the conversion of an electron-positron pair into $\gamma$-rays takes place in accordance with the laws of conservation of energy and momentum; as a result of pair annihilation, at least two $\gamma$-ray photons are created

$$e_+ + e_- \rightarrow 2\gamma.$$  \hspace{1cm} (22.5)

In order to show this, we may choose, without the loss of generality, a coordinate system in which the electron and positron move with opposite momenta, so that $k_+ = -k_-$ (the center-of-mass system). Then, according to the law of conservation of momentum, the total momentum of the two photons which are formed as a result of annihilation must also equal zero

$$h (k_1 + k_2) = 0.$$  \hspace{1cm} (22.5a)

Using the law of conservation of energy

$$c\hbar (k_1 + k_2) = 2 \sqrt{m^2c^4 + c^2\hbar^2k^2},$$  \hspace{1cm} (22.5b)

we find that $k_1 = -k_2$, and the energy of each of the photons is equal to

$$\epsilon = c\hbar k_1 = c\hbar k_2 = \sqrt{m^2c^4 + c^2\hbar^2k^2}.$$  \hspace{1cm}

The lowest value of the photon energy is obtained when $k = 0$ (that is, when the electron and positron are at rest). Then $\epsilon_{\text{min}} = mc^2$. These two $\gamma$-ray photons move apart with the same energy and oppositely directed momenta. It is easy to see that the electron-positron pair cannot be converted into a single $\gamma$-ray photon ($k_2 = 0$), since the laws of conservation of energy and momentum cannot be satisfied simultaneously with only one $\gamma$-ray photon.

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$^4$With the help of quantum field theory, we can construct a theory of the electron-positron vacuum that is symmetric with respect to charge. However, even with the theory described above, which is asymmetric with respect to electrons and positrons (an electron is a particle, whereas a positron is a "hole") we can give a clear explanation of many phenomena involving the transformation of particles.
The law of conservation of total angular momentum (orbital plus spin) is also very important in the annihilation processes. If an electron moves with a nonrelativistic velocity, this law (as shown in Chapter 18) can be resolved into a law of conservation of orbital angular momentum and a law of conservation of spin.

The law of conservation of spin can be observed particularly clearly in the annihilation of positronium (a hydrogen atom in which the proton is replaced by a positron, or more exactly, a system in which an electron and a positron rotate about their common center of mass). In this atom, the nucleus (that is, the positron) and the electron have the same mass, and therefore the reduced mass is \( \frac{m_0}{2} \). The energy of levels in the positronium atom will, therefore, be one half as large as in the hydrogen atom

\[
E_n = -\frac{R\hbar}{2n^2},
\]

while the radius of the orbit will be twice as large. The velocities of the electron and positron may be regarded as nonrelativistic, just as in the hydrogen atom, if the spins of the electron and positron are antiparallel (parapositronium), positronium can decay into two \( \gamma \)-ray photons (the corresponding mean life is \( 1.25 \cdot 10^{-10} \) sec).

The total spin of parapositronium is equal to zero, and therefore the two photons move apart with opposite directions of spin (that is, their total spin is zero).

If, however, the spins of the electron and positron are parallel (orthopositronium) the system must decay into three \( \gamma \)-ray photons (the corresponding mean life is \( 1.4 \cdot 10^{-7} \) sec). The spin of orthopositronium is equal to unity. Orthopositronium cannot decay into one \( \gamma \)-ray photon with spin \( \frac{1}{2} \), because in this case the law of conservation of momentum would be violated. It cannot decay into two \( \gamma \)-ray photons because then the law of conservation of spin would be violated (the total spin of two \( \gamma \)-ray photons is either two or zero). Only if orthopositronium decays into three \( \gamma \)-ray photons will the law of conservation of momentum and the law of conservation of spin be satisfied.

The discovery of the positron opened a new stage in the study of elementary particles. This discovery showed that particles had a new fundamental property—interconvertibility—and confirmed the existence of antiparticles. We can regard the creation of a positron as the conversion of a \( \gamma \)-ray photon into an electron-positron pair, and the annihilation of an electron-positron pair as the conversion of an electron-positron pair into \( \gamma \)-ray photons.

B. THE LAMB SHIFT OF ENERGY LEVELS OF ATOMIC ELECTRONS

When an electron moves in an atom, it interacts with the electromagnetic vacuum, as well as with the atomic nucleus and the electron-positron vacuum. The interaction between the electron and the electromagnetic vacuum exerts a particularly strong influence on the motion of the electron in the atom, and it explains the shift of the \( 2s_{1/2} \) level upwards relative to the \( 2p_{1/2} \) level (in the hydrogen atom).

A complete theory of this phenomenon can be constructed only by means of quantum electrodynamics, which is based on the theory of second quantization. But even without referring to this theory we can still obtain the appropriate equations with accuracy up to coefficients of the order of unity, while using comparatively simple physical arguments.

One of the basic ideas of the quantum field theory is that each wave or field can be associated with a particle. Thus, for example, the Dirac \( \psi \) waves correspond to electrons and positrons, and light waves correspond to photons. It is very well known, however, that Maxwell's equations describe not only light waves, but also electrostatic and magnetic fields, which depend on charges and their velocities (an accelerating charge produces electromagnetic or light waves). The electrostatic and magnetic fields can be associated with "pseudo-photons," which have observable effects only in the presence of charges. An electrostatic field can be expanded in a Fourier series, that is, schematically represented as a set of oscillators with different frequencies. An analogous expansion holds for the vacuum field of "pseudo-photons"

\[
E_{\text{p.p.}} = \sum_{\omega} E(\omega) \cos \omega t.
\]
Since the rest mass of a "pseudo-photon" is zero, we may write the relation between its frequency $\omega$ and the wave number $k$ as follows:

$$\omega = \frac{4}{\hbar} = \frac{e^p}{\hbar} = \epsilon \sqrt{k_x^2 + k_y^2 + k_z^2}. \quad (22.7)$$

The components $k_x, k_y, k_z$ are related to the integers $n_1, n_2, n_3$ and the period $L$ (see Chapter 6) by the expressions

$$k_x = \frac{2\pi n_1}{L}, \quad \text{and so forth},$$

where $n_1 = \pm 1, \pm 2, \pm 3, \ldots$. Hence

$$\Delta k_x = \frac{2\pi \Delta n_1}{L} = \frac{2\pi}{L} = \Delta k_y = \Delta k_z,$$

so that

$$\Delta k_x \Delta k_y \Delta k_z = k^2 d k d \Omega,$$

or

$$\frac{\omega^2 d\omega}{c^3} d\Omega = \frac{8\pi^3}{L^3}.$$

If the system is spherically symmetric, this relation may be written as

$$\frac{1}{L^3} = \frac{\omega^2 d\omega}{c^3} \frac{1}{2\pi^2} \quad (22.8)$$

With the aid of Eq. (22.6), we find that the energy of the electrostatic field inside a region of volume $L^3$ is

$$\epsilon_{p.p.} = \frac{1}{4\pi} \int (E)^2 d^3 x = \frac{L^3}{8\pi} \sum_\omega (E(\omega))^2. \quad (22.9)$$

In deriving this expression, we have used the relation

$$(\cos \omega t \cos \omega' t)_{avg} = \frac{1}{2} \delta_{\omega \omega'}.$$

Just as in the theory of the harmonic oscillator, the energy of the field in the lowest energy state is not equal to zero, but instead is equal to the sum of the zero-point energies of the harmonic oscillator (see Chapter 10)

$$\epsilon_0 = 2 \sum_\omega \frac{1}{2} \hbar \omega. \quad (22.10)$$

The coefficient 2 in front of the summation sign takes into account the fact that each harmonic corresponds to two different states of polarization of the "pseudo-photons."

In the state where there are no real photons the total energy of an electromagnetic field (the vacuum), must be equal to this zero-point energy ($\epsilon_{p.p.} = \epsilon_0$). Hence, taking (22.8) into account, we find

$$(E(\omega))^2 = \frac{8\pi}{L^3} \hbar \omega = \frac{4\hbar}{\pi} \frac{\omega^3 d\omega}{c^3}. \quad (22.10a)$$

In the absence of real particles and external fields, the vacuum (including the electromagnetic one containing photons and pseudo-photons) does not, as a rule, have any observable effects because it is isotropic. On the other hand, when real particles
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and external fields are present, the isotropy is disrupted and virtual particles ("pseudo-photons" or electron-positron pairs) are created and subsequently annihilated (vacuum fluctuations).

A simple physical picture of a few basic notions involved in the theory of the vacuum was obtained somewhat unrigorously by Welton by means of a semiclassical, nonrelativistic treatment of the motion of an electron, taking into account its interaction with the vacuum fluctuations. As an illustration of Welton's calculations, let us attempt to give a more concrete meaning to the zero-point fluctuations (22.10). In a rough approximation we can use the ordinary classical equation

\[ m_0 f = eE_{p,p}, \quad (22.11) \]

to find how an electron will be affected by the vacuum field of "pseudo-photons." Expanding \( E_{p,p} \) in a Fourier series

\[ E_{p,p} = \sum_{\omega} E(\omega) \cos \omega t \quad (22.12) \]

and integrating Eq. (22.11), we find the displacement of the electron positron due to the vacuum field:

\[ r = -\frac{e}{m_0} \sum_{\omega} E(\omega) \frac{\cos \omega t}{\omega^2}. \quad (22.13) \]

The mean-square deviation of the position is given by

\[ (\Delta r)^2 = (\langle r \rangle)^2 - \langle \hat{r} \rangle^2 = \frac{e^2}{2m^3_0} \sum_{\omega} \frac{(E(\omega))^2}{\omega^4}, \quad (22.14) \]

since

\[ \cos \omega t = 0, \quad \cos \omega t \cos \omega' t = \frac{1}{2} \delta_{\omega \omega'}. \]

and therefore \( \hat{r} = 0 \). Substituting (22.10a), we obtain a divergent integral

\[ (\Delta r)^2 = \frac{2}{\pi} \frac{e^2}{\hbar c} \left( \frac{\hbar}{m_0 c} \right)^2 \int \frac{d\omega}{\omega}, \quad (22.15) \]

from which a finite (observable) part can be separated out if the range of variation of the frequency is cut off from above at a frequency corresponding to the rest energy of the electron

\[ \omega_{\text{max}} \approx \frac{m_0 e^2}{\hbar}, \quad (22.16) \]

and from below at a frequency corresponding to the minimum energy of the electron in an atom\(^5\)

\[ \omega_{\text{min}} = \frac{|E|}{\hbar} = \frac{m_0 e^4}{2\hbar^2 n_i}. \quad (22.17) \]

Substitution of (22.17) and (22.16) into (22.15) gives

\[ (\Delta r)^2 = \frac{2}{\pi} \frac{e^2}{\hbar c} \left( \frac{\hbar}{m_0 c} \right)^2 \ln \frac{2\hbar^2 n_i}{\omega^2}. \quad (22.18) \]

---

\(^5\)The limits of the range of variation of \( \omega \) are specified more accurately in renormalization theory.
Thus it can be seen that the vacuum field of "pseudo-photons" will cause the electron to perform a motion somewhat resembling Brownian motion with a definite value of the mean square displacement. It is well known that the Brownian motion of a particle is due to its collisions with randomly moving molecules of the surrounding medium. In similar fashion, an electron undergoes "collisions" (of a special kind) with the assembly of virtual particles forming the vacuum.

As was shown by N. Bogolyubov and S. Tyablikov, the vacuum fluctuations cause a certain "smearing out" of a point electron. As a result, the electronic radius turns out to be the geometric mean of the classical radius and the Compton wavelength

\[ r \approx \sqrt{\frac{e^2}{m_e c^2}} \frac{\hbar}{m_e c} = V \frac{\hbar}{m_e c}. \]  

(22.19)

The existence of this effective radius should have several consequences. In particular, the interaction between the electron and the nuclear charge should be changed, and this, in turn, should lead to an additional coupling energy and thus to a shift of the energy levels. The usual expression for the potential energy of an electron in the field of a nucleus

\[ V = -e_0 \Phi(r) \]  

(22.20)

is replaced by

\[ V' = -e_0 \Phi(r + \Delta r) = -e_0 \left[ 1 + \left( \frac{\Delta r}{r} \right) + \frac{1}{2} \left( \frac{\Delta r}{r} \right)^2 + \ldots \right] \Phi(r). \]  

(22.21)

Changing to the average values and using the relations

\[ \Delta r = 0, \quad \left( \Delta r \Phi \right)^2 = \frac{1}{3} \left( \Delta r \right)^2 \Phi^2, \]  

(22.22)

we obtain

\[ V' = -e_0 \left\{ 1 + \frac{1}{6} \left( \Delta r \right)^2 \Phi^2 + \ldots \right\} \Phi(r). \]  

(22.23)

The additional energy of interaction between the electron and the nucleus is given by

\[ \Delta V_{p_s} = V' - V = -e_0 \frac{1}{6} \left( \Delta r \right)^2 \Phi^2 = \frac{4}{3} e_0^2 \left( \frac{\hbar}{m_e c} \right)^2 \ln \left( \frac{2n^2}{a_s^2} \right) \Phi(r), \]  

(22.24)

since the Coulomb potential of the hydrogen nucleus satisfies the Poisson equation

\[ \nabla^2 \Phi = -4\pi e_0 \delta(r). \]  

(22.25)

To obtain an expression for the shift of energy levels in the hydrogen atom, it is necessary to average the additional interaction energy over the corresponding state

\[ \Delta E_{p_s} = \int \left( V' - V \right) |\psi(r)|^2 \, d^3r = \frac{4}{3} e_0^2 \left( \frac{\hbar}{m_e c} \right)^2 |\psi(0)|^2 \ln \left( \frac{2n^2}{a_s^2} \right). \]  

(22.26)

This shift occurs only for s states, since the quantity  |\psi(0)|^2 in the approximation under consideration vanishes for other states (l = 1, 2, 3, ...), whereas for the s state

\[ |\psi(0)|^2 = \frac{1}{\pi n^2 a_0^2}, \]  

(22.27)

where \( a_0 = \hbar^2/m_e e_0^2 \) is the radius of the first Bohr orbit of the hydrogen atom, and \( n \) is the principal quantum number. If we now substitute this value into (22.26), we obtain a formula for the s-level shift

\[ \Delta E_{p_s} = \frac{8}{3\pi} \frac{R \hbar}{n^3} \ln \frac{2n^2}{a_s^2}. \]  

(22.28)

This formula was first derived by Bethe.
A substitution of numerical values for the 2s state \( (n = 2) \) gives
\[
\Delta E_{p,p} = 17.8 R = 1040 \text{ Me} \quad (22.29)
\]
This is in fairly good agreement with recent experimental data \( (\Delta E = 1057.77 \text{ Me}) \) for the Lamb shift (see Chapter 20).

A complete study of the shift of energy levels of atomic electrons with the help of relativistic quantum field theory gives considerably better agreement between theoretical and experimental results than the semiclassical formula (22.28). The discrepancy is reduced to less than 1 Me.

For the sake of brevity, we shall not discuss the modern theory of the vacuum in greater detail, and we shall confine ourselves to a mere enumeration of the main results that this theory has yielded.

C. ELECTRON-POSITRON VACUUM

Equation (22.28) for the Lamb shift was obtained from a calculation of the interaction between electrons and the electromagnetic vacuum. In addition to the electromagnetic vacuum, there exists an electron-positron vacuum and also vacuum states of other particles. The method of second quantization (which is in some measure applicable to all fields) can be used to calculate the influence of the electron-positron vacuum.

In modern quantum field theory, the study of the properties of the vacuum states of different particles plays a particularly important role. The vacuum gives rise to interactions between particles. In particular, the electromagnetic interaction of two electrons (Coulomb's law) may be regarded as an interaction which takes place through the electromagnetic vacuum, with one electron emitting a virtual photon and the other electron absorbing it.

On the other hand, the vacuum represents a sort of "reservoir," from which real particles are "drawn" when they are created, and to which they "return" when they are annihilated. We have already come across the electron-positron vacuum as a "collection" of electrons in negative energy states. Unfortunately, it has no classical analog and therefore we cannot use a semiclassical analysis, as was possible in the case of the electromagnetic vacuum. The Coulomb field of a nucleus can polarize the electron-positron vacuum (so that an electron will behave as if it were in a dielectric), giving rise to an additional interaction
\[
V_{e^-p^+} = -\frac{4}{15} e^2 \alpha \left( \frac{\hbar}{m_e c} \right)^2 \delta (r) \quad (22.30)
\]
Comparing (22.30) with (22.24), we see that the level shift due to interaction with the electron-positron vacuum is about 1/40 times as large as the level shift due to the fluctuations of the electromagnetic field, and is opposite in sign.

The electron-positron vacuum exerts a particularly strong influence on the magnetic properties of the electron. It was shown by Schwinger that the magnetic moment of the electron becomes somewhat larger than the Bohr magnetron
\[
\mu_{e^-p^+} = \mu_0 \left( 1 + \frac{a}{2\pi} \right) \quad (22.31)
\]
The change in the magnetic moment of the electron, with the second-order term taken into account,
\[
\Delta \mu_{e^-p^+} = \left( \frac{\alpha}{2\pi} \right) \mu_0 - 0.0011596 \mu_0 \quad (22.32)
\]
is in good agreement with experimental data obtained with the aid of microwave spectroscopic methods (see Chapter 21). Qualitatively, the appearance of the additional magnetic moment of the electron and the sign of the moment can be explained as follows. The initial electron \( A \) (see Fig. 22.4), whose spin is directed upwards (we specify in this manner a preferred direction), creates a virtual pair—electron \( A' \) and positron \( B' \)—which generally
have opposite spin directions. Since we have a preferred direction (determined by the spin of electron A) the spins of electron A' and positron B' can be directed in two ways: either the spin of A will be antiparallel to the spin of A' and parallel to the spin of B' (case 1 in Fig. 22.4), or the spin of A will be parallel to the spin of A' and antiparallel to the spin of B' (case 2 in Fig. 22.4).

In determining the additional magnetic moment, it is necessary to consider the following possibilities of pair creation and annihilation:

(a) Pair A'B' is created and then annihilated. This is possible in case 1 and case 2. No correction to the magnetic moment should arise, because the probability of the creation process is the same in both cases, and the magnetic moments have opposite signs in the two cases.

(b) Since A and B' have opposite spins in case 2, positron B' may be annihilated together with A', as well as with the initial electron A. In case 1, however, this process is less probable, since the spins of pair A and B' are parallel to one another. This process gives a preferred state in which the additional magnetic moment of electron A, since, as can be easily seen, the magnetic moment of all three particles (A, A' and B') is directed downwards. Consequently, there arises an additional magnetic moment of the electron, equal to

\[ \Delta m_{el-p} = -2\mu_\gamma, \]

where \( \gamma \) is a numerical factor which determines the probability that the initial electron A will be annihilated together with positron B'.

These simple considerations give the correct sign of this anomalous magnetic moment. More rigorous calculations led to Eq. (22.32).

In addition to the Dirac magnetic moment, \( \mu_D = -\mu_\sigma \), an electron will have an anomalous magnetic moment \( \mu_{\text{an}} = -\frac{\alpha}{2\pi} \mu_\rho \rho \), which arises owing to the interaction between the electron and the electron-positron vacuum.

The anomalous magnetic moment of nucleons (neutrons and protons) can be explained in meson theory. The accuracy of the results, however, is much less striking than in calculations of the anomalous magnetic moment of the electron. This is due to the fact that meson theory is still in a much less satisfactory state than quantum electrodynamics.

According to the meson theory, protons and neutrons interact with the \( \tau \)-meson field. Since the proton can dissociate into a neutron and a positively charged \( \tau \)-meson, and the neutron into a proton and a negatively charged \( \tau \)-meson, the anomalous magnetic moments of protons and neutrons due to the \( \tau \)-meson field must be approximately equal in magnitude and opposite in sign.

The appearance of the additional magnetic moment of a neutron is explained as follows. The neutron has a definite probability of dissociating into a proton and a \( \tau \)-meson. Since the spin of a \( \tau \)-meson equals 0, it does not possess an intrinsic magnetic moment. Therefore, there will be a contribution to the magnetic moment of the neutron from a pion which is, for example, in a \( \rho \) state (we recall that the orbital angular momentum in the \( s \) state is also equal to 0). The magnetic moment of a \( \tau \)-meson is \( \frac{m_\rho}{m_\tau} \approx 7 \) times greater than the nuclear magneton, and therefore the \( \tau \)-meson produces the main contribution to the anomalous magnetic moment of the neutron. For the virtual process to fulfill the law of conservation of angular momentum, it is necessary that the direction of the orbital angular momentum (equal to 1) of the virtual \( \tau \)-meson should coincide with the direction of spin of the neutron, while the spin of the virtual proton (equal to \( \frac{1}{2} \), just like the spin of the neutron) should be directed opposite to the spin of the neutron so that \( s_n = s_p = \frac{1}{2}, s_p = -s_n \). Since the \( \tau \)-meson has a negative charge and its angular momentum is parallel to the spin of the neutron, it gives rise to the negative magnetic moment of the neutron,
In order to explain the magnitude of the anomalous magnetic moment of the neutron, one must assume that the neutron spends \( \frac{1}{8} \) of its time in its dissociated state. This estimate is perfectly reasonable and gives the correct sign and order of magnitude of the magnetic moment of the neutron \( \mu_n \sim -2 \mu_{\text{nuc}} \). Similarly, it can be shown that the dissociation of the proton into a neutron and a \( \pi^- \) meson gives rise to a positive anomalous magnetic moment of the proton \( \mu_p \sim +2 \mu_{\text{nuc}} \). Moreover, the proton has a Dirac magnetic moment \( \mu_p = \mu_{\text{nuc}} \). More accurate data on the magnitude of the magnetic moment of the proton and neutron are given in the preceding chapter.

Thus we have a basis for regarding the anomalous magnetic moment of Dirac particles as a secondary effect which can be explained on the basis of the field theory. This moment does not appear in the initial equations, but arises as a result of the interaction either between the electric charge and the electron-positron field (in the case of electrons), or between the nuclear charge and the \( \pi^- \)-meson field (in the case of protons and neutrons).

### D. Renormalization

One of the most important sections of modern quantum field theory is concerned with the question of renormalization. This subject is not yet in a mathematically satisfactory state, but a number of important results have been obtained.

The basic idea involved in renormalization is the separation of finite, observable terms from the divergent terms describing the interaction between an electron and the electromagnetic or electron-positron vacuum.

In effect, the question of renormalization first arose in classical electrodynamics—for example, in the theory of the electromagnetic mass of the electron. If we assume that the electron charge is distributed inside a sphere of radius \( r_0 \), its classical electromagnetic mass will be equal to

\[
m_{\text{field}} = \gamma \frac{e^2}{r_0 c^2}, \tag{22.33}
\]

where \( \gamma \) is a factor of the order of unity which depends on the charge distribution inside the sphere. The attempts to construct a classical electrodynamics in which a finite radius \( r_0 \sim 10^{-13} \text{ cm} \) would give a reasonable value for \( m_{\text{field}} \) (the Lorentz theory, the nonlinear Born-Infeld theory, the Hoppe-Podolsky theory with higher derivatives) did not give any satisfactory results. Moreover, all these theories gave rise to fundamental difficulties in connection with quantization.

On the other hand, the theory of a point electron leads to an infinite value of the mass as \( r_0 \to 0 \) both in the classical and quantum forms of the theory. It was therefore a major achievement of renormalization in modern quantum field theory that it was able to separate, from the infinite interaction energy, finite terms associated with the Lamb shift of the atomic levels and the additional magnetic moment of the electron.

Modern renormalization theory extends to the problem of the self-mass and charge of the electron. It has been found that when the electron-positron vacuum and the electromagnetic vacuum are taken into account, the electromagnetic mass \( (22.33) \) drops out completely. Therefore, the main mass of the electron (the so-called "bare" mass) will not be associated with the electromagnetic field. The interaction with the vacuum (in this case the main contribution is obtained when the electromagnetic vacuum and the electron-positron vacuum are taken into account simultaneously) yields an additional mass which diverges only logarithmically

\[
\Delta m_{\text{field}} = a \ln \frac{m_{\text{max}}}{m_{\text{bare}} c^2}. \tag{22.34}
\]

Renormalization is faced with the important question of finding the value \( \varepsilon_{\text{max}} \) at which the logarithmically divergent expression should be cut off. This problem is a theoretically important one, although in practice the logarithmically divergent terms may be regarded to be of the order of unity, and therefore the quantity \( \Delta m \) will remain of the order \( m_{\text{bare}} / 137 \) over a comparatively wide range of values \( \epsilon_{\text{max}} \).
In exactly the same way, the interaction of the electron with the electron-positron vacuum (rather than with the electromagnetic vacuum) leads to a decrease of its "bare charge" by the amount

\[ \Delta e = -\alpha e_c \ln \frac{e_{\text{max}}}{m_0 c^2}. \]  

The field corrections to the mass and charge of the electron have not yet been experimentally separated, and this important subject requires further investigation.6

Problem 22.1. When can the emission of photons take place for the free motion of an electron in a medium with index of refraction \( n > 1 \) (the Cherenkov effect)?

Why does this emission become impossible in a vacuum \( (n = 1) \)?

Solution. In order for the emission to be possible, it is necessary that the laws of conservation of energy and momentum

\[ p = p' + \hbar k \]

be satisfied, where \( p \) and \( p' \) are the initial and final moments of the electron and \( \hbar k \) is the photon momentum.

Squaring these relations and then subtracting one from the other, we obtain the following expression for the cosine of the angle of photon emission:

\[ \cos \theta = \frac{\omega}{c k} \left( \frac{\omega^2}{c^2 k^2} - 1 \right). \]

Using the relation for the index of refraction \( n \) of the medium

\[ \epsilon = \hbar \omega = c' \hbar k = \frac{\hbar c}{n} \]

\((c' = \frac{c}{n} \text{ is the phase velocity of light in the medium}), we obtain

\[ \cos \theta = \frac{1}{\beta n} + \frac{\hbar k}{2p} \left( 1 - \frac{1}{n^2} \right). \]

Radiation can take place when \( \beta n > 1 \) (that is, when the electron velocity \( v \) remains less than the phase velocity of light in vacuum, but becomes greater than the velocity of light in the medium \( c > v' > c' \)). In the classical case \( (\hbar = 0) \), the angle at which the photon is emitted satisfies the relation

\[ \cos \theta = \frac{1}{\beta n}. \]

The emission of radiation in vacuum is impossible because for \( n = 1 \) we have \( \cos \theta = \frac{c}{v} \), and the velocity \( v \) cannot become greater than the velocity of light \( c \).

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Chapter 23

Theory of the Helium Atom Neglecting Spin States

A. BASIC PRINCIPLES OF THE THEORY OF MULTIELECTRON ATOMS

The helium atom is the simplest multielectron atom; it consists of two electrons moving about a nucleus of charge \( Z = 2 \). In spite of its simplicity, this system exhibits several important features characteristic of the many-body problem in quantum mechanics.

In classical theory two electrons can always be identified by subscripts 1 and 2, and the motion of each electron can be followed separately. According to quantum theory two electrons can, in practice, be distinguished from each other only when the distance between them is large. If electrons 1 and 2 are so close to each other that there are points in space where their wave functions are both simultaneously different from zero, then, since electrons are identical particles, we shall be unable to distinguish whether an electron occurring at the point is electron 1 or 2.

This indistinguishability or identity of particles is a special feature of quantum theory. It gives rise to the so-called exchange forces, which have no classical analog.

In multielectron atoms, spin properties are very important; these properties are neglected in the classical and Bohr theories and are taken into account only in quantum mechanics. In fact, only in the case of a one-electron atom can the spin corrections be neglected in the first approximation. This explains why the predictions of the Bohr theory are applicable only to hydrogen-like atoms. The Bohr theory could not be extended to atoms with two or more electrons, since it could not account for either the exchange forces or the spin states.

In order to investigate the basic features of the quantum theory of the many-body problem, we shall consider in some detail the problem of helium-like atoms (for example, neutral helium, singly ionized Li\(^+\), doubly ionized Be\(^{++}\), and so on).
B. SOLUTION OF THE PROBLEM OF THE HELIUM ATOM VIA METHODS OF PERTURBATION THEORY

To start with, let us determine the physical nature of the exchange forces which are related to the indistinguishability of electrons. We shall neglect the spin properties of the particles.\(^1\)

We shall assume that the position of the first and second electrons is given by the position vectors \(r_1\) and \(r_2\), respectively (their origin coincides with the stationary nucleus; see Fig. 23.1). For the sake of brevity, states with quantum numbers \((n_1, l_1, m_1)\) and \((n_2, l_2, m_2)\) will be denoted by, respectively, \(\psi_1\) and \(\psi_2\) (in this notation, therefore, \(n\) stands for the whole set of quantum numbers). If there were no interaction between the electrons, we could determine the motion of each electron separately from the Schrödinger equation

\[
(E_{n_j} - H_j) \psi_{n_j}(r_j) = 0,
\]

where

\[
H_j = T_j + V_j, \quad T_j = \frac{\hbar^2}{2m_0} \left( \frac{\partial}{\partial r_j} \right)^2, \quad V_j = -\frac{Ze_0}{r_j},
\]

and the subscript \(j\) takes two values: \(j = 1\) in the case of the first electron, and \(j = 2\) in the case of the second electron. From these equations we can obtain the energy values \(E_{n_j}\) (see Chapter 13)

\[
E_{n_j} = -\frac{R\hbar^2 Z^2}{n_j^2}.
\]

The eigenfunctions \(\psi_{n_j}\) will be the same as the wave functions of a hydrogen-like atom; they will satisfy the orthonormality condition

\[
\int \psi_{n_j}^*(r) \psi_{n_j'}(r) d^3x = \delta_{n_j n_j'}.
\]

If we now take into account the interaction of the two electrons

\[
V' = \frac{e_0^2}{|r_1 - r_2|} = \frac{e_0^2}{r_{12}}.
\]

\(^1\)We are allowed to do this because in this approximation the problem has a solution in the form of a product of two functions, depending on the spatial and spin coordinates, respectively (see Chapter 24).
their motion can no longer be regarded as independent. The Hamiltonian of the complete system will be

$$H = H_1 + H_2 + V' \equiv H^0 + V',$$

and to describe this system we must take the Schrödinger equation in the form

$$(E - H^0 - V')\psi(r_1, r_2) = 0,$$  \hspace{1cm} (23.7)

where $E$ is the total energy, and $\psi(r_1, r_2)$ is the total wave function, which depends on the coordinates of both electrons. The quantity $\psi^*(r_1, r_2)\psi(r_1, r_2)$ characterizes the probability of finding the first electron at position $r_1$ and the second electron at position $r_2$. Therefore, the normalization condition for $\psi(r_1, r_2)$ takes the form

$$\int \psi^*(r_1, r_2)\psi(r_1, r_2) d^3x_1 d^3x_2 = 1,$$  \hspace{1cm} (23.8)

where the integration extends over the coordinates of both particles.

Since the exact solution of Eq. (23.7) entails insurmountable difficulties, we shall use the perturbation theory developed in Chapter 14, assuming that the mutual interaction of the electrons causes only a small change in their individual motions in the Coulomb field of the nucleus (the justification for this approximation will be examined in greater detail later).

We shall first consider the zeroth approximation, in which the perturbation energy $V'$ can be neglected. The Schrödinger equation (23.7) becomes

$$(E^0 - H^0)\psi^0(r_1, r_2) = 0.$$  \hspace{1cm} (23.9)

Since the zero-order Hamiltonian $H^0$ can be resolved into a sum of two Hamiltonians $H_1 + H_2$, each of which depends only on a single variable (either $r_1$ or $r_2$), it is obvious that in the zeroth approximation the wave function may be written in the form ($\psi^0 = u$)

$$u = \psi_{n_1}(r_1)\psi_{n_2}(r_2).$$  \hspace{1cm} (23.10)

Substituting (23.10) into (23.9) and using (23.1), we get

$$(E^0 - H^0) u = \{E^0 - (H_1 + H_2)\} \psi_{n_1}(r_1)\psi_{n_2}(r_2) =$$

$$= E^0 u - \{\psi_{n_2}(r_2) H_1 \psi_{n_1}(r_1) + \psi_{n_1}(r_1) H_2 \psi_{n_2}(r_2)\} =$$

$$= E^0 u - \{\psi_{n_2}(r_2) E_{n_1} \psi_{n_1}(r_1) + \psi_{n_1}(r_1) E_{n_2} \psi_{n_2}(r_2)\} =$$

$$\equiv \{E^0 - (E_{n_1} + E_{n_2})\} u = 0.$$

---

2The problem of the helium-like atom is a three-body problem and cannot be solved exactly, even in the classical approximation.
Hence, the energy in the zeroth approximation

$$E^0 = E_{n_1} + E_{n_2},$$

(23.11)

where $E_{n_1}$ and $E_{n_2}$ are the energies of the two electrons on the assumption of no mutual interaction. This result can be explained as follows. In the absence of the perturbation $V'$, the motion of the electrons is determined by their interaction with the nucleus $Z$; that is, their motion is completely described by the Schrödinger equation (23.1) which has the eigenvalues $E_{n_j}$ [see (23.3)] and eigenfunctions $\psi_{n_j}$. Since one of the electrons is in a state $n_1$ and the second in a state $n_2$, the total energy of the system is $E_{n_1} + E_{n_2}$ when $V' = 0$.

Since the two electrons move independently of one another, the total wave function will be the product of the corresponding two independent one-electron wave functions obtained in the one-electron problem. By direct substitution into Eq. (23.9) it is, however, easy to show that, in addition to the first solution (23.10), there will be a second solution ($\psi^0 = \psi$) corresponding to the same energy eigenvalue (23.11):

$$\psi = \psi_{n_1}(r_1)\psi_{n_2}(r_2).$$

(23.12)

This solution differs from $u$ by a permutation of the electrons. The first electron is now in state $n_2$ and the second electron is in state $n_1$.

This state of the system has, therefore, an additional degeneracy which is due entirely to the indistinguishability of the electrons; this is known as exchange degeneracy.

If both electrons are in identical states ($n_1 = n_2$), the wave functions $u$ and $v$ are identical and there will be no exchange degeneracy since

$$u = v = \psi_{n_1}(r_1)\psi_{n_2}(r_2).$$

(23.12a)

In the case $n_1 \neq n_2$, however, functions $u$ and $v$ are different, and therefore the following linear combination should be taken as the general solution $\psi^0$ of the Schrödinger equation (23.9):

$$\psi^0 = C_1u + C_2v,$$

(23.13)

where $C_1$ and $C_2$ are arbitrary constant coefficients, which are related only by the normalization condition

$$\int \psi^0 \psi^0 d^3x_1 d^3x_2 = 1.$$
account), according to the perturbation theory, we shall look for the solutions of \( E \) and \( \psi \) in the form:

\[
E = E^0 + E' ; \\
\psi = \psi^0 + \psi'.
\]  

(23.14)

We use a first approximation of the Schrödinger equation (23.7), and write it in the form

\[
(E^0 - H^0) \psi^0 = -(E' - V') (C_1 u + C_2 v).
\]  

(23.15)

From Chapter 14, we recall that the solution of the homogeneous equation for the unperturbed problem must be orthogonal to the right-hand side of the inhomogeneous equation for the first-order approximation of the wave function [see (14.13)]. Since the functions \( u \) and \( v \) are solutions of the unperturbed problem, we have

\[
\int u^* (E' - V') (C_1 u + C_2 v) d^3x_1 d^3x_2 = 0,
\]  

(23.16)

\[
\int v^* (E' - V') (C_1 u + C_2 v) d^3x_1 d^3x_2 = 0.
\]  

(23.17)

In (23.17), let us substitute \( r_2 \) for \( r_1 \) and \( r_1 \) for \( r_2 \). The function \( v \) [see (23.12)] then becomes \( u \) [see (23.10)], and the function \( u \) becomes \( u \), while the perturbation energy \( V' \) remains unchanged since \( |r_1 - r_2| = |r_2 - r_1| \). Thus Eq. (23.17) takes the form

\[
\int u^* (E' - V') (C_2 u + C_1 v) d^3x_1 d^3x_2 = 0.
\]  

(23.17a)

It is, therefore, sufficient to consider only Eq. (23.16) since the results can be extended to Eq. (23.17a) by substituting \( C_1 \rightarrow C_2 \) and \( C_2 \rightarrow C_1 \).

Let us substitute into Eq. (23.16) the explicit expressions (23.10) and (23.12) for \( u \) and \( v \), and introduce the notation

\[
\psi_{n_1} (r_1) \psi_{n_1} (r_1) = \rho_{11} (r_1),
\]  

(23.18)

\[
\psi_{n_2} (r_2) \psi_{n_2} (r_2) = \rho_{22} (r_2),
\]  

(23.19)

\[
\psi_{n_1} (r_1) \psi_{n_2} (r_1) = \rho_{12} (r_1),
\]  

(23.20)

\[
\psi_{n_2} (r_2) \psi_{n_1} (r_2) = \rho_{21} (r_2).
\]  

(23.21)

Here \( \rho_{11} (r_1) \) and \( \rho_{21} (r_2) \) characterize the probability density distribution of electrons in the states \( n_1 \) and \( n_2 \), respectively, whereas
\( \rho_{1n}(r_1) \) and \( \rho_{2n}(r_2) \) characterize the so-called density of mixed (or exchange) states,\(^3\) when each electron is partially in state \( n_1 \) and partially in state \( n_2 \).

The orthonormality condition gives

\[
\int u^* u \, d^3x_1 \, d^3x_2 = \int \rho_{11}(r_1) \, d^3x_1 \int \rho_{22}(r_2) \, d^3x_2 = 1,
\]

and

\[
\int u^* v \, d^3x_1 \, d^3x_2 = \int \rho_{12}(r_1) \, d^3x_1 \int \rho_{21}(r_2) \, d^3x_2 = 0,
\]

and therefore we can reduce (23.16) to the form

\[
E' c_1 - \left\{ c_1 e_0 \int \frac{\rho_{11}(r_1) \rho_{22}(r_2)}{|r_1 - r_2|} \, d^3x_1 \, d^3x_2 + c_2 e_0 \int \frac{\rho_{12}(r_1) \rho_{21}(r_2)}{|r_1 - r_2|} \, d^3x_1 \, d^3x_2 \right\} = 0. \tag{23.22}
\]

The first integral in Eq. (23.22) is simply the Coulomb interaction of two "smeared-out" electrons

\[
K = e_0^2 \int \frac{\rho_{11}(r_1) \rho_{22}(r_2)}{|r_1 - r_2|} \, d^3x_1 \, d^3x_2. \tag{23.23}
\]

The second integral gives the so-called exchange energy

\[
A = e_0^2 \int \frac{\rho_{12}(r_1) \rho_{21}(r_2)}{|r_1 - r_2|} \, d^3x_1 \, d^3x_2. \tag{23.24}
\]

corresponding to the interaction of two electrons when each is in a mixed state \( n_1 \) and \( n_2 \). Unlike the Coulomb energy \( K \), the exchange energy \( A \) has no classical analog; it is essentially a quantum-mechanical concept.

Using Eqs. (23.23) and (23.24), we obtain instead of Eq. (23.22) the following expression:

\[
C_1 (E' - K) - C_2 A = 0. \tag{23.25}
\]

From Eq. (23.25), we obtain the equation corresponding to (23.17a) by substituting \( C_2 \rightarrow C_1 \) and \( C_1 \rightarrow C_2 \):

\[
C_2 (E' - K) - C_1 A = 0. \tag{23.26}
\]

\(^3\)These densities have no classical analog.
Equations (23.25) and (23.26) give

1) \( E' = K + A, \ C_1 = C_2 \) \hspace{1cm} (23.27)

and

2) \( E' = K - A, \ C_1 = -C_2 \) \hspace{1cm} (23.28)

Accordingly, we have two solutions for the wave function [see (23.13)] and for the total energy

1) symmetric

\[
\psi^s = C_1(u + v),
\]

\[
E^s = E^0 + K + A
\]

and

2) antisymmetric

\[
\psi^a = C_1(u - v),
\]

\[
E^a = E^0 + K - A
\]

We can determine the coefficient \( C_1 \) from the normalization condition of the wave functions \( \psi^s \) and \( \psi^a \):

\[
\int \psi^s \psi^s d^3x_1 d^3x_2 = \int \psi^a \psi^a d^3x_1 d^3x_2 = 1.
\]

Hence, \( 2C_1^2 = 1 \) or \( C_1 = \frac{1}{\sqrt{2}} \). Thus for \( \psi^s \) and \( \psi^a \) we finally have

\[
\psi^s = \frac{1}{\sqrt{2}} (u + v),
\]

\[
\psi^a = \frac{1}{\sqrt{2}} (u - v).
\]  

(23.29a)  

(23.31a)

When both electrons are in the same quantum state \((n_1 = n_2)\), the functions \( u \) and \( v \) are identical. In this case Eqs. (23.16) and (23.17) reduce to the same equation

\[
\int u^* (E' - V') u d^3x_1 d^3x_2 = 0.
\]

(23.33)

From this it is readily seen that

\[
E' = K,
\]

(23.34)

---

4 We recall that under a permutation of coordinates (that is, when \( r_1 \) and \( r_2 \) are interchanged) the function \( u \) and \( v \) transform into one another. The wave function \( \psi^s \) does not change sign as a result of this operation (symmetric function), whereas the function \( \psi^a \) reverses its sign (antisymmetric function).
and thus the exchange energy disappears in this case. For the wave function we obtain a unique symmetric solution

$$\psi^s = \psi_{n_1}(r_1) \psi_{n_1}(r_2),$$

(23.35)

with the corresponding energy of the system

$$E^s = E^0 + K.$$  

(23.36)

Summarizing the results of this section, we can make the following statement: Application of the perturbation method to the problem of the helium atom\(^\text{5}\) leads to two types of solutions—a symmetric or antisymmetric solution. This is in complete agreement with the general theory of systems of identical particles (see below).

C. COULOMB INTERACTION BETWEEN ELECTRONS

Let us find an expression for the Coulomb energy of two electrons in the lowest energy state \((n_1 = n_2 = 1)\). In this case the energy and the wave function of each electron are given by

$$E_1 = -\frac{Z^2 e^4}{2a_0^2}; \quad \psi_1(r) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{1/2} e^{-\frac{Zr}{a_0}},$$

(23.37)

where \(a_0 = \frac{n^2}{m_0 e^2}\) is the radius of the first Bohr orbit.

The Coulomb energy of interaction between the two electrons is

$$K = \int \psi_1^*(r_1) \psi_1^*(r_2) \frac{e^4}{|r_1 - r_2|} d^3x_1 d^3x_2.$$  

(23.38)

Here \(|r_1 - r_2| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \vartheta}\), and \(\vartheta\) is the angle between the vectors \(r_1\) and \(r_2\). To integrate (23.38), let us choose the direction of the \(z\) axis along the direction of the vector \(r_1\). Substituting the expression (23.37) for the wave functions into Eq. (23.38) and integrating over the angles, we find\(^6\)

---

\(^5\) This is due to the fact that the perturbation removes the degeneracy, and therefore the coefficients that were indeterminate in the zeroth approximation can now take specific values. (See also Chapter 14, the Stark effect.)

\(^6\) In integrating over the angle \(\vartheta (x = \cos \vartheta)\), we used the relation

$$l = \int_{-1}^{1} \frac{dx}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 x}} = \begin{cases} \frac{2}{r_1} & \text{for } r_1 < r_2, \\ \frac{2}{r_2} & \text{for } r_1 > r_2. \end{cases}$$

(continued)
Next, integrating over \( r_1 \) and \( r_2 \), we finally obtain

\[
K = \frac{5}{8} \frac{Ze^2}{a_o}. \tag{23.39}
\]

Since the zero-order energy is

\[
E^0 = 2E_1 = -\frac{Ze^2}{a_o}, \tag{23.40}
\]

the total energy of two electrons in the ground state is equal to

\[
E = E^0 + K = -\frac{Ze^2}{a_o} + \frac{5}{8} \frac{Ze^2}{a_o}. \tag{23.41}
\]

Let us now find the ionization energy of the helium atom, that is, the energy that must be expended in order to remove one electron from the first orbit. For a singly ionized helium atom (a hydrogen-like atom) the bonding energy between the electron and the nucleus is simply \( E_1 \) [see (23.37)]. The ionization energy of a helium-like atom is therefore

\[
E_{\text{ion}} = E_1 - E = \frac{e^2}{2a_o} \left( Z^2 - \frac{5}{4} Z \right), \tag{23.42}
\]

so that for helium \((Z = 2)\) we have

\[
E_{\text{ion}} = 0.75 \frac{e^2}{a_o}. \tag{23.43}
\]

According to experimental data, the ionization energy of helium is

\[
E_{\text{ion}}^{\text{exp}} = 0.9 \frac{e^2}{a_o} = 24.48 \text{ ev.} \tag{23.43a}
\]

The discrepancy between the theoretical value and the experimental data is a result of the fact that the perturbation energy \( K = \frac{Ze^2}{4 a_o} \) is not very small as compared with the zero-order energy \(|E^0| = \frac{4e^2}{a_o}\) (their ratio is \( \sim 1/3 \)). Perturbation theory, therefore, gives us

\[
K = \frac{32 Ze^2}{a_o} \int_0^\infty r_1^2 dr_1 e^{-\frac{2Zr_1}{a_o}} \int_0^\infty r_2 e^{-\frac{2Zr_2}{a_o}} dr_2. \tag{23.38a}
\]

Considering that the integrand \( \psi_1^2(r_1) \psi_2^2(r_2) \) is symmetric with respect to the variables \( r_1 \) and \( r_2 \), we replace (for \( r_1 \gg r_2 \)) the radius \( r_1 \) by \( r_2 \) and vice versa, obtaining

\[
l = \begin{cases} 
4 & \text{for } r_1 < r_2, \\
r_2 & \text{for } r_1 > r_2.
\end{cases}
\]

This expression was used in evaluating the integral (23.38).
only qualitative aspects of the problem. The accuracy of the method is not very great because $K$ and $E^0$ have the same order of magnitude.

D. THE VARIATIONAL METHOD

The variational method developed by Ritz, Hylleraas and others was first successfully used to find the ground-state energy of atomic systems, and in recent years it has been applied in collision theory.

As we know, the average energy of an atomic system is given by

$$\bar{E} = \int \phi^* H \phi \, d^3x.$$  \hfill (23.44)

If the wave function is represented as

$$\phi = \sum C_n \phi_n,$$  \hfill (23.44a)

where the coefficients $C_n$ give the probability of an electron being in state $n$, the average value of the energy will be given by the relation [see (7.21)]

$$\bar{E} = \sum_n |C_n|^2 E_n.$$  \hfill (23.45)

Replacing each eigenvalue $E_n$ in the summation by the lowest eigenvalue $E_{\text{min}}$ and using the fact that for normalized functions

$$\sum_n |C_n|^2 = 1,$$

we find that

$$E_{\text{min}} \leq \int \phi^* H \phi \, d^3x;$$  \hfill (23.46)

that is, the lowest value of the integral $\int \phi^* H \phi \, d^3x$ can be used to determine the upper limit of the ground-state energy of the system.

It was found that the variational method gives very good results when the perturbation energy $E'$ is of the same order as the energy $E_0$ of the zero-order approximation. The variational method can therefore be used in cases where perturbation theory gives poor results (for example, in calculation of the ground-state energy of the helium atom). When a problem is solved by the variational method, both the additional interaction $V'$ and the main interaction are treated equally in the Hamiltonian $H$ of Eq. (23.7). A test function $\phi$ then depends on several parameters and is selected in such a way that the integral can be calculated exactly. The energy $E$ will then be a function of these parameters and it is obvious that the minimum value of this function will be close to the true value if the test function resembles the true function.
The most difficult part of the method lies in the choice of the best test function. All the available information on the properties of the system must be used in making this choice. It is impossible in the general case to indicate the form of the test function, and therefore it is frequently necessary to rely on physical and mathematical intuition. Very often, a test function is similar in form to the solution of the unperturbed equation.

We shall now use the variational method to calculate the ground-state energy of the helium atom. Our procedure will be based on that of Hylleraas (1927). At the end of the discussion we shall compare both perturbation and variational methods.

For the test function, Hylleraas chose the ground-state function (23.27) of the hydrogen atom, replacing the charge \( Z \) by a certain effective charge \( Z' \). The quantity \( Z \) is the unknown parameter which has to be determined from the variational principle. The test function

\[
\psi_1(r) = \frac{1}{\sqrt{\pi}} \left( \frac{Z'}{a_0} \right)^{1/2} e^{-\frac{Z'r}{a_0}}
\]

will obviously be normalized to unity, just like (23.37), since its normalization is independent of the value of \( Z' \).

The Hamiltonian \( \hat{H} \) in (23.46) must include both the zero-order approximation Hamiltonian \( \hat{H}^0 \) and the perturbation potential energy \( V' \). We thus obtain

\[
\hat{H} = T + V_1 + T_2 + V_2 + V',
\]

where \( T_j \) and \( V_j (j=1,2) \) are given by (23.2) and the perturbation potential energy \( V' \) is given by (23.5).

Since the wave functions are normalized and since \( T_1 + V_1 \) does not depend on \( r_2 \) and \( T_2 + V_2 \) is independent of the coordinate \( r_1 \), the average value of the Hamiltonian is

\[
\bar{H} = 2\overline{T_1} + 2\overline{V_1} + \overline{V'},
\]

where

\[
\begin{align*}
\overline{T_1} &= \frac{1}{2m_0} \int \psi_1(r_1) \left( \frac{\hbar}{i} \nabla \right) \overline{\psi_1(r_1)} \, d^3x_1, \\
\overline{V_1} &= -\int \psi_1^*(r_1) \frac{Zr_0^3}{r_1^4} \, d^3x_1, \\
\overline{V'} &= \int \psi_1^*(r_1) \psi_1^*(r_2) \frac{e_0^3}{|r_1 - r_2|} \, d^3x_1 d^3x_2.
\end{align*}
\]
The integral (23.50b) agrees exactly with integral (23.38); therefore, setting \( Z = Z' \), we obtain in accordance with (23.39)

\[
\bar{V}' = \frac{5}{8} \frac{Z'e_0^2}{a_0}. \tag{23.51}
\]

The quantity \( \bar{T}_1 \) in Eq. (23.49) represents the average value of the kinetic energy of a hydrogen-like atom with atomic number \( Z' \) when the electron is in the lowest state. This value is related to the total energy of the hydrogen-like atom by the well-known expression

\[
\bar{T}_1 = -E_1 = \frac{Z^2 e_0^2}{2a_0}. \tag{23.52}
\]

In exactly the same way, replacing \( Z' \) in (23.50a) by \( Z \), we can obtain the average value of the potential energy of a hydrogen-like atom, since it is well known that the potential energy is twice the total energy \( (\bar{V} = 2E_1) \). Consequently,

\[
\bar{V}_1 = \frac{Z}{Z'} 2E_1 = -\frac{Z^2 e_0^2}{a_0}. \tag{23.53}
\]

It follows from (23.49) that the average value of the energy is given by the expression

\[
E(Z') = \frac{e_0^2}{a_0} (Z^2 - 2ZZ' + \frac{5}{8} Z'), \tag{23.54}
\]

which is a function of the parameter \( Z' \).

Let us now find the value of the parameter \( Z' \) corresponding to the minimum energy of the system. Differentiating \( E(Z') \) with respect to \( Z' \) and setting the derivative equal to zero, we find

\[
Z' = Z - \frac{5}{16}.
\]

The minimum energy of electrons in the helium atom is therefore

\[
E_{\text{min}} = - \left( Z - \frac{5}{16}\right) \frac{e_0^2}{a_0}. \tag{23.55}
\]

For the ionization energy we have

\[
E_{\text{ion}} = E_1 - E_{\text{min}} = \frac{e_0^2}{2a_0} (Z^2 - \frac{5}{4} Z + \frac{25}{128}).
\]

In particular, for helium \( (Z = 2) \) we obtain

\[
E_{\text{ion}} \approx 0.85 \frac{e_0^2}{a_0}. \tag{23.56}
\]
This result is considerably closer to the experimental value [see (23.43a)] than (23.43) obtained from the perturbation theory. Hylleraas later improved the agreement with the experiment by using several variational parameters. The result (23.55) for $E_{\text{min}}$ has a simple physical interpretation, namely: the interaction between the electrons results in a screening of the positive nuclear charge.

The variational method can also be used to find the upper energy limit of one or several excited states. In this case the test function has to be chosen in such a way that it is orthogonal to the wave functions of all the lower states. When the energy levels are arranged in order of increasing magnitudes ($E_0, E_1, E_2, \ldots$), it can easily be shown that since $\psi$ is orthogonal to functions $\psi_0, \psi_1, \psi_2, \ldots$, the corresponding expansion coefficients $C_0, C_1, C_2, \ldots$ are all equal to zero. Therefore, in accordance with (23.45), the energy is

$$
\bar{E} = \sum_{n=n_0}^{\infty} E_n |C_n|^2,
$$

where $n_0$ is the quantum number of the given excited state. Using the relation $\sum_n |C_n|^2 = 1$, we find that the minimum value of this energy corresponds to the unknown energy $E_{n_0}$ of the excited state. The application of this method to the calculation of the energies of the highest excited states is rather difficult, because of the necessity of introducing a large number of additional conditions to ensure that the wave function of a given state will be orthogonal to the wave functions of the lower states.

E. DERIVATION OF THE SCHRODINGER EQUATION
BY THE VARIATIONAL METHOD

We shall consider one of the most general forms of the variational problem, when the choice of the test wave function $\psi$ that is used to find the average value of the Hamiltonian

$$
\bar{E} = \int \psi^* H \psi \, d^4x
$$

(23.58)

describing the motion of a single particle is restricted only by the normalization condition

$$
\int \psi^* \psi \, d^4x = 1.
$$

(23.59)

Upon varying $\bar{E}$ with respect to $\psi$ and using the hermiticity of the operator $H$, we obtain

$$
\delta \bar{E} = \int (\delta \psi^* H \psi + H \delta \psi^* \psi) \, d^4x = 0.
$$

(23.60)
Here the variations \( \delta \psi \) and \( \delta \psi^* \) cannot be regarded as independent since they are connected by the normalization condition (23.59). These variations can be made independent by varying the condition (23.59)

\[
\int \delta \psi^* \psi \, d^3x + \int \delta \psi \psi^* \, d^3x = 0.
\]

Multiplying this equation by a constant Lagrangian multiplier \( \lambda \), which is chosen in such a way that the variations are now independent, we add the resulting equation to (23.60). Since the variations \( \delta \psi \) and \( \delta \psi^* \) are now arbitrary, the variational principle gives automatically the Schrödinger equation for \( \psi \) and \( \psi^* \):

\[
(H - E) \psi = 0, \quad (H^* - E) \psi^* = 0,
\]

and the physical meaning of the parameter \( \lambda \) becomes clear: it is the negative of the energy \( E \) (i.e., \( \lambda = -E \)).

Consequently, the variational principle and the normalization condition together lead to the Schrödinger equation. It is apparent from the above results that the eigenvalues of the Schrödinger equation (23.61) give the extremals of the variational integral. A more detailed analysis shows that these extremals are minima and that the energy of the ground state corresponds to the absolute minimum—the smallest possible energy value. In order to calculate excited states, it is necessary to impose orthogonality conditions on the wave functions of the lower energy state (as mentioned above), whereas orthogonality follows automatically in the Schrödinger theory.

### F. HARTREE-FOCK METHOD OF SELF-CONSISTENT FIELDS

We have considered two extreme cases of the variational method. In one case (the Ritz-Hylleraas method) the variation of the wave function amounted to a determination of the "best values" of parameters in a specially chosen wave function. In the other case, the choice of the wave functions was restricted only by the normalization condition. This case led to the Schrödinger equation. There is also an intermediate case in which the wave function is not specified, but is assumed to be a product of one-electron functions depending on the coordinates only. The specific form of these functions is found by using the method of successive approximations to solve an equation derived on the basis of the variational principle.

One such method was proposed by Hartree (1928). This method, whose interpretation from the point of view of the variational principle was given later by Fock, may be described as follows. Let us start with the variational principle for two particles in general form

\[
E = \int \psi^* (r_1, r_2) H \psi (r_1, r_2) \, d^3x_1 \, d^3x_2.
\]

As an additional condition, we require that the total wave function should be a product of one-electron functions

\[
\psi (r_1, r_2) = \psi_1 (r_1) \psi_2 (r_2).
\]

\(^7\)This integral can be generalized in a similar fashion to the case of three or more particles.
It is also necessary to allow for the normalization condition

$$\int \psi_1^* \psi_2 \psi_1 \psi_2 d^3 x_1 d^3 x_2 = 1, \quad (23.64)$$

which can be written for each particle separately

$$\int \psi_i^* \psi_i d^3 x_i = \int \psi_j^* \psi_j d^3 x_j = 1.$$

Substituting the test function (23.63) into (23.62) and varying \( \psi_i \) and \( \psi_j \), we obtain

$$\int \left[ (\delta \psi_i^* \phi_2^* + \psi_i^* \delta \phi_2^*) (H_1 + H_2 + \frac{e_i^2}{r_{12}}) \phi_1 \psi_2 + \right]$$

$$+ \phi_1^* \phi_2^* \left( H_1 + H_2 + \frac{e_2^2}{r_{12}} \right) (\delta \psi_2 \phi_2 + \phi_2 \delta \phi_1) d^3 x_1 d^3 x_2 = 0, \quad (23.65)$$

where \( H_j = p_j^2 \frac{1}{2m_0} + V_j (r_j) \) is the Hamiltonian describing the motion of a single electron \((j = 1, 2)\), and \( \frac{e_j^2}{r_{12}} \) represents the interaction energy between the electrons.

From the normalization condition (23.64) we obtain a relation between the variations

$$\int \left( \delta \psi_1^* \psi_2 + \psi_1^* \delta \phi_2 \psi_2 + \psi_2^* \delta \phi_1 \psi_2 + \phi_2^* \phi_1 \delta \phi_1 \right) d^3 x_1 d^3 x_2 = 0.$$

Multiplying this equation by the Lagrange multiplier \( \lambda = -E \) and adding it to (23.65), we can select \( \lambda \) so that all the variations \( \delta \phi_1^*, \delta \phi_2^* \), and so on, will be independent. Therefore, we obtain the Hartree equations

$$\left( H_1 + \int \phi_2^* H_2 \phi_2 d^3 x_2 + \int \phi_2^* \frac{e_2^2}{r_{12}} \phi_2 d^3 x_2 - E \right) \phi_1 = 0,$$

$$\left( H_2 + \int \phi_1^* H_1 \phi_1 d^3 x_1 + \int \phi_1^* \frac{e_1^2}{r_{12}} \phi_1 d^3 x_1 - E \right) \phi_2 = 0. \quad (23.66)$$

Analogous equations can also be obtained for the complex conjugate functions. We multiply the first equation by \( \phi_1^* \) and integrate it over the whole coordinate space of the second particle; in a similar fashion, we multiply the second Hartree equation by \( \phi_2^* \) and integrate it over the coordinate space of the first particle. Adding the two resulting equations and dividing the total sum by 2 we obtain the expression for the energy

$$E = \sum_j \int \phi_j^* H_j \phi_j d^3 x_j + \frac{1}{2} \sum_j \sum_{j'} \int \phi_j^* \phi_j^* \frac{e_j^2}{r_{jj'}} \phi_j \phi_{j'} d^3 x_j d^3 x_{j'}. \quad (23.66a)$$
where in the case of two particles \( j, j' = 1, 2 \). This equation can also be used successfully for a larger number of particles.

If we neglect the interaction energy (that is, if we set the terms containing \( \frac{e^2}{r_{ij}} \) equal to zero) and use the relations

\[
E = E_1 + E_2
\]

and

\[
E_j = \int \psi_j^* H \psi_j \, d^3 x_j,
\]

Hartree's equation can be resolved into a system of two independent equations

\[
(H_j - E_j) \psi_j = 0
\]

describing the motion of each particle individually.

In problems treated by the Hartree method, the field in which each electron moves is composed of an external field (for example, the nuclear field) and the field produced by all the other electrons. This method is, therefore, known as the self-consistent field method.

Fock (1930) generalized the Hartree method by taking into account the exchange effects. For this purpose it is necessary that the test function in the initial equation (23.62) be consistent with the Pauli exclusion principle. The choice of test functions is, therefore, further restricted by the requirement of antisymmetry (antisymmetric functions satisfying the exclusion principle will be considered in greater detail in the next chapter).

Hartree's system of equations (for example, for an electron shell in an atom) is solved by the method of successive approximations. First of all, the wave functions in the zeroth approximation (that is, neglecting mutual interaction between the electrons) are determined. These wave functions together with the interaction potential between the electrons are then used to obtain the first approximation equations. The first approximation wave function is substituted back into the Hartree-Fock equations to obtain the next approximation and so on. This process is continued until the solutions obtained in successive approximations are identical (within the desired accuracy), that is, until the solutions are self-consistent. Hartree's system of equations can be solved only by means of numerical methods of integration. With the help of modern computers it is now possible to use Hartree's method to determine the energies and the wave functions for both light and heavy atoms.

Another approximation which can be used in treating heavy atoms is the Thomas-Fermi statistical method. Although this method is not as accurate as the self-consistent field method,
it is comparatively simple and predicts many properties of multi-electron atoms. This method will be used in our subsequent investigations, and we shall consider it in Chapters 25 and 26 in connection with the theory of the periodic system of elements.

G. INVESTIGATION OF THE EXCHANGE ENERGY

Let us consider in somewhat greater detail the physical meaning of the exchange energy (23.24), which represents the average value of the Coulomb interaction between two electrons that are both partly in state $n_1$ and partly in state $n_2$. In accordance with Eqs. (23.30) and (23.32), the total energy of the system is related to the Coulomb energy $K$ and the exchange energy $A$ by the expression

$$ E = E^0 + K \pm A, \quad (23.67) $$

where the plus sign corresponds to $\psi^s$, and the minus sign to $\psi^a$. In order to analyze the exchange energy in greater detail, we shall examine the behavior of the system in time, taking into account the exchange energy. The wave functions of the symmetric and antisymmetric states may be written as

$$ \psi^s(t) = \psi^s e^{-i \frac{K^s t}{\hbar}} \quad \text{and} \quad \psi^a(t) = \psi^a e^{-i \frac{K^a t}{\hbar}}. \quad (23.68) $$

Introducing the notation

$$ \frac{E^s + K^s}{\hbar} = \omega, \quad \frac{A}{\hbar} = \delta, \quad (23.69) $$

Eq. (23.68) may be represented as

$$ \psi^s(t) = \frac{1}{\sqrt{2}} (u + v) e^{-i\omega t - i\delta t}, $$

$$ \psi^a(t) = \frac{1}{\sqrt{2}} (u - v) e^{-i\omega t + i\delta t}. \quad (23.70) $$

Let us consider a state of the system described by a superposition of the solutions $\psi^s(t)$ and $\psi^a(t)$

$$ \Psi(r_1, r_2, t) \equiv \Psi(t) = C^s \psi^s(t) + C^a \psi^a(t). \quad (23.71) $$

It is easy to show that the function $\Psi(t)$ represents the general solution of the Schrödinger equation (23.7) in the first-order perturbation theory.

We shall now assume that at the initial instant of time ($t=0$) one of the electrons is in state $n_1$, and the other is in state $n_2$. Then the function

$$ \Psi(0) = \frac{1}{\sqrt{2}} \{(C^s + C^a) u + (C^s - C^a) v\} \quad (23.72) $$
is simply equal to the function \( u \). It follows that
\[
\frac{1}{\sqrt{2}} (C^s + C^n) = 1, \text{ and } C^s - C^n = 0,
\]
that is,
\[
C^s = C^n = \frac{1}{\sqrt{2}}.
\]

According to Eqs. (23.70), (23.71) and (23.73), at a certain later time \( t \), the function \( \Psi(t) \) becomes
\[
\Psi(t) = e^{-i\omega t} [u \cos \delta t - iv \sin \delta t] = e^{-i\omega t} \{C_u u + C_v v\},
\]
where
\[
C_u = \cos \delta t, \quad C_v = -i \sin \delta t.
\]

It is obvious that the amplitudes \( C_u \) and \( C_v \), which satisfy the normalization condition
\[
|C_u|^2 + |C_v|^2 = 1,
\]
characterize the probability of a system being in states described by \( u \) and \( v \), respectively.

Since at \( t = 0 \) we have \( C_v = 0 \) and \( C_u = 1 \), the system is initially in a state represented by the function \( u \). However, after a time
\[
\tau = \frac{\pi}{2b}
\]
(so that \( \delta t = \frac{\pi}{2} \)), it can be seen from (23.75) that the coefficients \( C_u \) and \( C_v \), will have the values
\[
C_u = 0 \text{ and } C_v = -1.
\]

At the time \( t = \tau \), the state of the system will therefore no longer be described by the function \( u \), but instead by the function \( v \). This indicates that whereas at time \( t = 0 \) one of the electrons of the system is in state \( n_1 \) and the other in state \( n_2 \), after a time \( \Delta t = \tau \), the first electron will be in state \( n_2 \) and the second electron in state \( n_1 \). The time \( \tau \) (23.77) during which the "exchange" of electronic states occurs is called the "exchange time." It is connected with the exchange energy \( \lambda \) by the simple relationship
\[
\tau = \frac{\pi}{2b} = \frac{\pi \hbar}{2A}.
\]
It is readily seen that if there is no exchange energy \((A = 0)\) then \(\tau = \infty\).

To conclude this section, let us evaluate the exchange energy when the first electron is in the state \(n_1 = 1s\), and the second electron is in the state \(n_2 = 2s\). The wave function \(\psi_{n_1} = \psi_1\) is given by (23.37) and the wave function \(\psi_{n_2} = \psi_2\) can be found from (13.26) and (13.28)\(^8\)

\[
\psi_2(r) = \frac{1}{\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{2a_0}} \left(1 - \frac{Zr}{2a_0}\right).
\]

(23.79)

For the exchange energy, instead of (23.38), we obtain

\[
A = \int \psi_1(r_1) \psi_2(r_2) \frac{e^2}{|r_1 - r_2|} \psi_1(r_1) \psi_2(r_1) d^3x_1 d^3x_2.
\]

(23.80)

Carrying out the integration in the same way as was done for the evaluation of energy, we obtain, instead of (23.38a),

\[
A = \frac{4Ze_0^2}{a_0^3} \int_0^\infty \int_0^{r_1} \int_0^{r_2} \left(1 - \frac{Zr_1}{2a_0}\right) e^{-\frac{Zr_1}{2a_0}} dr_1 \int_0^\infty \left(1 - \frac{Zr_2}{2a_0}\right) e^{-\frac{Zr_2}{2a_0}} dr_2.
\]

Evaluating these integrals (which is a relatively simple process) we find that

\[
A \approx \frac{2^4Ze_0^2}{3^2a_0}.
\]

(23.81)

In accordance with (23.78), the exchange time of electrons in the \(1s\) and \(2s\) states in the helium atom \((Z = 2)\) has the value

\[
\tau = \frac{3^3\pi\hbar a_0}{2^8e_0^5} \approx 0.8 \cdot 10^{-15} \text{ sec}.
\]

The exchange time in the case where one of the electrons is in the \(1s\) state and the other in the \(10s\) state is of the order of several years, and there is practically no exchange. Consequently, it can be seen that the exchange energy plays a significant part only when the probability densities \(|\psi_{n_1}|^2\) of different states mutually overlap to a considerable extent. When the overlapping of the wave functions is insignificant, the exchange energy \(A\) is very small. This situation somewhat resembles the transfer of energy from one coupled pendulum to another. It is well known that an oscillating pendulum transfers its energy to another pendulum,

\(^8\) See also Problem 13.1.
initially at rest, and its amplitude of oscillations after a certain time interval becomes equal to zero. The exchange time of the oscillatory energy depends to a great extent on the relationship between the natural frequencies of oscillation of the two pendulums; the time of exchange attains a maximum when the two frequencies coincide (the case of resonance). It must be emphasized that this analogy is purely formal and is possible only because of the wave properties manifested in both phenomena.
Chapter 24

Elementary Theory of Multielectron Atoms Including Spin States

A. SYMMETRIC AND ANTISYMMETRIC STATES

As we pointed out at the beginning of Chapter 23, the quantum-mechanical theory of assemblies of identical particles contains several features that have no classical analog. The most important of these features arise from the fact that the state of a system is unaffected by interchange of identical particles. This is known as the principle of indistinguishability.

We shall consider here the general properties of a wave function that describes a system composed of two identical particles. The state of the system is characterized by the position vector $r$, three spatial quantum numbers $n$, $l$ and $m$, and the spin quantum number $s$. For the sake of brevity, we let $n$ denote all three of the quantum numbers $n$, $l$ and $m$. The wave function of the system has the form

$$\Psi(n_1s_1r_1; n_2s_2r_2), \quad (24.1)$$

where subscripts 1 and 2 refer to the first and second particles, respectively.

Let us introduce an operator $P$ which permutes the position coordinates $r_1$ and $r_2$ or the quantum numbers $n_1$, $s_1$ and $n_2$, $s_2$

$$P\Psi(n_1s_1r_1; n_2s_2r_2) = \Psi(n_1s_1r_2; n_2s_2r_1); \quad (24.2)$$

It is easy to find the eigenvalues of this operator

$$P\Psi(n_1s_1r_1; n_2s_2r_2) = \lambda \Psi(n_1s_1r_1; n_2s_2r_2). \quad (24.3)$$

It follows from (24.2) that two successive applications of $P$ lead to the initial wave function

$$P^2\Psi(n_1s_1r_1; n_2s_2r_2) = P\Psi(n_1s_1r_2; n_2s_2r_1) = \Psi(n_1s_1r_1; n_2s_2r_2). \quad (24.4)$$
On the other hand, it follows from (24.3) that
\[ \rho_1^2 \psi(n_1s_1r_1; n_2s_2r_2) = \lambda^2 \psi(n_1s_1r_1; n_2s_2r_2). \] (24.5)
The eigenvalues of the permutation operator are therefore
\[ \lambda = \pm 1. \] (24.6)
This result means that interchanging the particles leaves the wave function unchanged (\textit{symmetric wave functions}, with \( \lambda = 1 \))
\[ \psi^s(n_1s_1r_1; n_2s_2r_2) = \psi^s(n_1s_1r_2; n_2s_2r_1), \] (24.7)
or causes the wave function to reverse its sign (\textit{antisymmetric wave functions} with \( \lambda = -1 \))
\[ \psi^a(n_1s_1r_1; n_2s_2r_2) = -\psi^a(n_1s_1r_2; n_2s_2r_1). \] (24.8)

According to a principle of quantum mechanics, a set of identical particles can only exist in states with a definite type of symmetry. A state is either symmetric (described by a symmetric wave function) or antisymmetric (described by an antisymmetric wave function). Quantum transitions between symmetric and antisymmetric states are impossible; states with different types of symmetry do not mix. This suggests that there are two kinds of particles: one kind described by symmetric wave functions, and the other by antisymmetric wave functions.

**B. FERMI-DIRAC AND EINSTEIN-BOSE STATISTICS.**

**THE PAULI EXCLUSION PRINCIPLE**

Experimental and theoretical investigations of the properties of systems of identical particles have shown that there are two kinds of particles with fundamentally different statistical properties, and that this difference is essentially related to the spin. Particles with half-integral spin \( s = \frac{1}{2}, \frac{3}{2}, \ldots \) in units of the Planck constant \( \hbar \) obey Fermi-Dirac statistics. These particles are known as fermions and include electrons, protons, neutrons, \( \mu \) mesons and hyperons (all with spin \( \frac{1}{2} \)). On the other hand, particles with integral spin \( s = 0, 1, \ldots \) obey Einstein-Bose statistics. These particles are known as bosons and include \( \pi \) mesons, K mesons (both with spin 0), and photons (spin 1).

We may note here, without going into a detailed analysis of the statistical properties of aggregates of particles, that in Einstein-Bose statistics an unlimited number of particles can occupy each state. On the contrary, in Fermi-Dirac statistics only a single particle can occupy each state defined by four quantum numbers.
This characteristic feature of fermions was established empirically by Pauli (1923) before the discovery of quantum mechanics and quantum statistics; it is known as the Pauli exclusion principle.

In order to establish the relationship between the type of symmetry of a state and the kind of statistics that is appropriate for this state, let us consider a system of two particles which have a negligible mutual interaction. The wave function for the system can be written in the form of the product

$$\Psi(n_1s_1r_1; n_2s_2r_2) = \psi_{n_1s_1}(r_1) \psi_{n_2s_2}(r_2),$$

(24.9)

where $\psi_{n_1s_1}$ and $\psi_{n_2s_2}$ are the wave functions of the individual particles. The solution (24.9) corresponds to a state in which the particles with positions $r_1$ and $r_2$ are in states characterized by the quantum numbers $n_1s_1$ and $n_2s_2$, respectively. Because of the identity of the particles, the state of the system is not changed when the particles are interchanged. The following solution is therefore just as valid as (24.9):

$$\Psi(n_2s_2r_1; n_1s_1r_2) = \psi_{n_2s_2}(r_1) \psi_{n_1s_1}(r_2)$$

(24.10)

(that is, particles with coordinates $r_1$ and $r_2$ are in the states $n_2s_2$ and $n_1s_1$, respectively).

Both wave functions (24.9) and (24.10) describe the same physical state of the system. We note that any linear combination of these functions will also describe the same physical state. One of the possible linear combinations is the sum of the solutions (24.9) and (24.10), namely,

$$\Psi^s = \frac{1}{\sqrt{2}} \{ \psi_{n_1s_1}(r_1) \psi_{n_2s_2}(r_2) + \psi_{n_2s_2}(r_1) \psi_{n_1s_1}(r_2) \}$$

(24.11)

(we have assumed that the functions $\psi_{n_1s_1}$ and $\psi_{n_2s_2}$ are mutually orthogonal and normalized to unity, and therefore we have introduced the normalization factor $\frac{1}{\sqrt{2}}$). This solution is symmetric with respect to interchange of the spatial and spin coordinates

$$\Psi^s(n_1s_1r_1; n_2s_2r_2) = \Psi^s(n_2s_2r_1; n_1s_1r_2).$$

(24.12)

Another possible linear combination is the difference between (24.9) and (24.10)

$$\Psi^a = \frac{1}{\sqrt{2}} \{ \psi_{n_1s_1}(r_1) \psi_{n_2s_2}(r_2) - \psi_{n_2s_2}(r_1) \psi_{n_1s_1}(r_2) \},$$

(24.13)

which gives an antisymmetric solution since

$$\Psi^a(n_1s_1r_1; n_2s_2r_2) = -\Psi^a(n_2s_2r_1; n_1s_1r_2).$$

(24.14)
From the form of $\Psi^s$ and $\Psi^a$ it follows directly that particles obeying Fermi-Dirac statistics can be described only by antisymmetric solutions. The Pauli exclusion principle (Fermi statistics) is satisfied only by a solution of the form (24.13) since when both particles are in the same state (that is, $n_1 = n_2 = n$ and $s_1 = s_2 = s$), we have

$$\Psi^a (nsr_1; nsr_2) = 0, \text{ but } \Psi^s (nsr_1; nsr_2) \neq 0. \quad (24.15)$$

On the other hand, $\Psi^a$ does not satisfy the requirement of Einstein-Bose statistics, in which an arbitrary number of particles can occupy the same state.

It is easy to generalize the antisymmetric and symmetric wave functions to the case of a system composed of $N$ noninteracting particles. The antisymmetric solution may be represented by the determinant

$$\Psi^a = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{n_1s_1}(r_1) \psi_{n_2s_2}(r_2) & \ldots & \psi_{n_1s_1}(r_N) \\ \psi_{n_2s_2}(r_1) \psi_{n_2s_2}(r_2) & \ldots & \psi_{n_2s_2}(r_N) \\ \vdots & \ldots & \vdots \\ \psi_{nNsN}(r_1) \psi_{nNsN}(r_2) & \ldots & \psi_{nNsN}(r_N) \end{vmatrix} \quad (24.16)$$

The antisymmetric nature of this solution is obvious since interchanging any two columns changes the sign of the determinant. Moreover, it is obvious that the function (24.16) satisfies the Pauli principle because if any of the sets of quantum numbers are equal (for example, $n_1 = n_2$, $s_1 = s_2$) the determinant vanishes.

The symmetric wave function can be written in the form of a sum of products

$$\Psi^s = \frac{1}{\sqrt{N!}} \{ \psi_{n_1s_1}(r_1) \psi_{n_2s_2}(r_2) \ldots \psi_{nNsN}(r_N) +$$

$$+ \psi_{n_2s_2}(r_1) \psi_{n_1s_1}(r_2) \ldots \psi_{nNsN}(r_N) + \ldots \} \quad (24.17)$$

C. ADDITION OF ANGULAR MOMENTA. RUSSELL-SAUNDERS COUPLING. CLEBSCH-GORDAN COEFFICIENTS

Let us consider more fully the antisymmetric wave function for a system composed of two particles

$$\Psi^a = \frac{1}{\sqrt{2}} \{ \psi_{n_1s_1}(r_1) \psi_{n_2s_2}(r_2) - \psi_{n_1s_1}(r_2) \psi_{n_2s_2}(r_1) \}. \quad (24.18)$$

In the many-body problem, we are faced with the question of how to add the angular momenta. In the two-particle case, each
particle is characterized by orbital angular momentum quantum numbers $l_1$ and $l_2$, respectively, for which
\[ L^2 = \hbar^2 (l_1 + 1) \] (24.19)
and spins $s_1$ and $s_2$, for which
\[ S^2 = \hbar^2 (s_1 + 1). \] (24.20)

There are two different ways in which these four quantities can be added. One of these involves adding the orbital and spin angular momenta separately and then finding their total sum
\[ L = L_1 + L_2, \quad S = S_1 + S_2, \quad J = L + S. \] (24.21)

This type of coupling of the particles in an atom is called \textit{LS} coupling or Russell-Saunders coupling. It corresponds to the case in which the total orbital angular momentum and the total spin angular momentum are conserved separately. This situation is encountered most often in light elements.

The second way of combining the angular momenta involves the addition of the orbital and spin angular momenta of each electron individually and then finding the total angular momentum of all the particles
\[ J_1 = L_1 + S_1, \quad J_2 = L_2 + S_2; \quad J = J_1 + J_2. \] (24.22)

This type of coupling is called \textit{jj} coupling and is encountered mainly in heavy elements. It corresponds to the case in which only the total angular momentum is conserved, and therefore it is important when there is a strong spin-orbit interaction.

We shall now compare the order of magnitude of the Coulomb and spin-orbit interactions in the helium atom. The Coulomb energy [see (23.23)] has the form
\[ K = e_0^2 \int \frac{\rho_{11}(r_1) \rho_{22}(r_2) d^3x_1 d^3x_2}{|r_1 - r_2|} \sim \gamma R \hbar \] (24.23)
($\gamma$ lies approximately between 0.1 and 1). The existence of \textit{LS} coupling depends on the Coulomb energy since the orbital and spin angular momenta are conserved separately in this interaction. The spin-orbit interaction for the helium atom
\[ E_{s.o.} = \frac{Ze^2}{2m_0^2 \hbar^2} L \cdot S \cdot \frac{1}{r^3} \sim R \hbar Z^2 \] (24.24)
($z = 1/\alpha^2$) is considerably smaller than the Coulomb interaction, and therefore the coupling is of the \textit{LS} or Russell-Saunders type. It can
be seen from (24.24) that the order of magnitude of the spin-orbit interaction depends strongly on the nuclear charge \(Z\) (\(\sim Z^2\)), so that for large \(Z\) (heavy elements) the value of \(E^{s.o.}\) may be quite large. In this case the coupling will be of the \(jj\) type.

Let us consider the problem of the addition of the orbital angular momenta of two particles and find the function \(Y_{LM}(1,2)\) which is an eigenfunction of the operator for the \(z\) component of the total angular momentum \(L = L_1 + L_2\)

\[
L_z Y_{LM}(1,2) = (L_{z1} + L_{z2}) Y_{LM}(1,2) = \hbar MY_{LM}(1,2),
\]

(24.25)

and of the operator for the square of the total angular momentum

\[
L^2 Y_{LM}(1,2) = \{L_1^2 + L_2^2 - (L_{1y}^2)(L_{2y}^2) + (L_{1x} + iL_{1y})(L_{2x} - iL_{2y}) + 2L_{1z}L_{2z}\} Y_{LM}(1,2) = \hbar^2 \lambda Y_{LM}(1,2); \quad \lambda = L(L+1).
\]

(24.26)

As we shall show, the eigenfunction \(Y_{LM}(1,2)\) can be written as a linear combination of products

\[
Y_{LM}(1,2) = \sum_{m_1 m_2} b_{m_1 m_2} Y_{m_1}^{l_1}(1) Y_{m_2}^{l_2}(2),
\]

(24.27)

where the wave functions \(Y_{m_1}^{l_1}(1)\) and \(Y_{m_2}^{l_2}(2)\) refer to the first and second particles, respectively, and

\[
L_{1z} Y_{m_1}^{l_1}(1) = \hbar m_1 Y_{m_1}^{l_1}(1); \quad L_{2z} Y_{m_2}^{l_2}(2) = \hbar m_2 Y_{m_2}^{l_2}(2);
\]

\[
L_{1y}^2 Y_{m_1}^{l_1}(1) = \hbar^2 l_1 (l_1 + 1) Y_{m_1}^{l_1}(1); \quad L_{2y}^2 Y_{m_2}^{l_2}(2) = \hbar^2 l_2 (l_2 + 1) Y_{m_2}^{l_2}(2).
\]

(24.28)

The numerical coefficients \(b_{m_1 m_2}\) in the linear superposition (24.27) are called the vector summation coefficients of Clebsch-Gordan coefficients.

For simplicity, we shall restrict ourselves to the case \(l_1 = l_2 = 1\). Substituting (24.27) into Eq. (24.25)

\[
L_z Y_{LM}(1,2) = \sum_{m_1 m_2} b_{m_1 m_2} \hbar (m_1 + m_2) Y_{m_1}^{l_1}(1) Y_{m_2}^{l_2}(2) = \hbar MY_{LM}(1,2),
\]

(24.29)

we find that \(M = m_1 + m_2\) and \(b_{m_1 m_2} = b_{m_2 m_1}\).

Without loss of generality we may set \(M = 0\); that is, we make the \(z\) axis perpendicular to the total angular momentum. Then it follows from (24.27) that

\[
Y_{L0}(1,2) = b_1 Y_1^0(1) Y_1^0(2) + b_1 Y_{1}^{-1}(1) Y_{1}^{-1}(2) + b_1 Y_{1}^{1}(1) Y_{1}^{1}(2).\]

(24.30)

Taking into account the equation for spherical harmonics [see (11,88)]

\[
(l_{1x} \pm i l_{1y}) Y_1^{m_1}(1) = -\hbar \sqrt{(l_1 + 1 \pm m_1)(l_1 + m_1)} Y_{1}^{m_1 \pm 1}(1),
\]

(24.31)

and using Eq. (24.26), we obtain

\[
L^2 Y_{L0}(1,2) = \hbar^2 \{b_1 [2Y_1^0 Y_1^0 + 2Y_1^1 Y_1^1] + b_1 [2Y_{1}^{-1} Y_{1}^{-1} + 2Y_{1}^{1} Y_{1}^{1}] + b_0 [4Y_1^0 Y_1^0 + 2Y_1^1 Y_1^1 + 2Y_{1}^{-1} Y_{1}^{-1} + 2Y_{1}^{1} Y_{1}^{1}]\} = \lambda (b_1 Y_1^0 Y_1^0 + b_1 Y_{1}^{-1} Y_{1}^{-1} + b_1 Y_{1}^{1} Y_{1}^{1}).
\]

(24.32)

This equation is equivalent to a system of three homogeneous equations for the unknown Clebsch-Gordan coefficients

\[
2b_0 + (2 - \lambda) b_1 = 0 \quad 2b_0 + (2 - \lambda) b_{-1} = 0 \quad (4 - \lambda) b_0 + 2b_1 + 2b_{-1} = 0.
\]

(24.33)
This system has a nonvanishing solution if its determinant is equal to zero

\[
\begin{vmatrix}
2 & 2-\lambda & 0 \\
2 & 0 & 2-\lambda \\
4-\lambda & 2 & 2
\end{vmatrix} = 0.
\] (24.34)

Calculating this determinant and subjecting the wave function \( Y_{LM} \) to the normalization condition

\[
\int |Y_{LM}|^2 d\Omega_1 d\Omega_2 = 1,
\]

that is,

\[
\beta_0^2 + \beta_1^2 + \beta_{-1}^2 = 1,
\]

we obtain three possible solutions:

1) \( \lambda = 0, \quad \beta_1 = \beta_{-1} = -\beta_0 = \frac{1}{\sqrt{3}} \).

From the conditions \( \lambda = L (L + 1) \) we find that \( L = 0 \); that is, this solution corresponds to the case in which the vectors \( l_i \) and \( l_2 \) are antiparallel

\[
l_1 \uparrow \quad \downarrow \quad l_2.
\]

2) \( \lambda = 2, \quad \beta_0 = 0, \quad -\beta_1 = \beta_{-1} = \frac{1}{\sqrt{2}}, \quad L = 1 \).

This case corresponds to the addition of the angular momentum vectors at an angle of 60°

\[
\begin{array}{c}
l_1 \\
L
\end{array}
\]

\[
\begin{array}{c}
l_2
\end{array}
\]

3) \( \lambda = 6, \quad L = 2, \quad \beta_0 = \frac{2}{\sqrt{6}}, \quad \beta_1 = \beta_{-1} = \frac{1}{\sqrt{6}} \).

This solution corresponds to parallel \( l_1 \) and \( l_2 \)

\[
l_1 \uparrow \quad \uparrow \quad l_2.
\]

We conclude, therefore, that two vectors \( l_1 \) and \( l_2 \), whose absolute values are integral quantum numbers, can be oriented at angles such that the vector representing their sum \( L \) is also characterized by integers. For \( l_1 \geq l_2 \) these values are

\[
L = l_1 + l_2, \quad l_1 + l_2 - 1, \quad \ldots, \quad l_1 - l_2 + 1, \quad l_1 - l_2
\] (24.35)

(a total of \( 2l_2 + 1 \) values).

This method of adding the angular momenta is based on a vector model of the atom. We can obtain our previous results by setting \( l_1 = l_2 = 1 \) and \( M = 0 \). It is interesting to note that the same values of the Clebsch-Gordan coefficients would also be obtained in adding the orbital angular momentum to a spin angular momentum equal to unity (for example, for photons). In this case, however, one would have to use the normalized spin
function instead of the spherical harmonics $Y^{m_2}_{l_2}$. It is easy to show that the Clebsch-Gordan coefficients will satisfy the following conditions:

$$
\sum_{m_3} b_{m_3}^{L M} b_{m_3}^{L' M'} = b_{L L'}^{L' L'}
$$

$$
\sum_{L} b_{L_3}^{L M} b_{L_3}^{L M'} = b_{L_3}^{L M} b_{L_3}^{L M'}
$$

In general the Clebsch-Gordan coefficients $b_{m_3}$ will depend not only on the quantum number $m_3 = M - m_1$, but also on $L$ and $M$. If the orbital angular momentum of the second particle is $l_2 = 1$, then adding both orbital angular momenta, we obtain

$$
Y^{m_2}_{L M} = \sum_{m_3=-1}^{1} b_{m_3}^{L M} Y^{m_3}_{l_1 - m_2} (1) Y^{m_2}_{l_2 = 1 (2)}
$$

for which the Clebsch-Gordan coefficients are given in Table 24.1.

D. WAVE FUNCTION OF THE HELIUM ATOM INCLUDING SPIN

We shall now consider more fully the wave function of the helium atom, for which, as we know, the interaction between the spins and the orbital angular momenta of the electrons is of the Russell-Saunders type. Since, therefore, the orbital and spin angular momenta are added independently of one another, the wave function can be written as a product of two parts, one of which depends on the spins of the particles and the other on their coordinates. The wave function must be an antisymmetric function with four quantum numbers

$$
\Psi^a = C(s_1, s_2) \phi_{n_1 n_2} (r_1, r_2) = -C(s_2, s_1) \phi_{n_2 n_1} (r_1, r_2) = -C(s_1, s_2) \phi_{n_1 n_2} (r_2, r_1).
$$

There are two possible cases: either the function is symmetric with respect to the spins and antisymmetric with respect to the coordinates, or the reverse case is true. We have therefore the following two types of solution:

$$
\Psi^a = C^s (s_1, s_2) \phi^s_{n_1 n_2} (r_1, r_2),
$$

$$
\Psi^a = C^a (s_1, s_2) \phi^a_{n_1 n_2} (r_1, r_2).
$$

We recall that the spatial part of the wave function has already been obtained (see Chapter 23). For $n_1 \neq n_2$,

$$
\phi^s_{n_1 n_2} (r_1, r_2) = \frac{1}{\sqrt{2}} (u + v),
$$

$$
\phi^a_{n_1 n_2} (r_1, r_2) = \frac{1}{\sqrt{2}} (u - v).
$$
Table 24.1

<table>
<thead>
<tr>
<th>( l_1 )</th>
<th>( l_1 - 1 )</th>
<th>( l_1 + 1 )</th>
<th>( l_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m_2 )</td>
<td>( -1 )</td>
<td>( 0 )</td>
<td>( 1 )</td>
</tr>
</tbody>
</table>

\[
\frac{b_{LM}}{b_{m_2}} = \begin{cases} 
\sqrt{\frac{(l_1 + M)(l_1 - M + 1)}{2(l_1 + 1)(2l_1 + 1)}}, & \text{for } l_1 = 1 \\
\sqrt{(l_1 + M)(l_1 - M + 1)}, & \text{for } l_1 = 0 \\
\sqrt{\frac{(l_1 + M)(l_1 - M + 1)}{2(l_1 + 1)(2l_1 + 1)}}, & \text{for } l_1 = -1 
\end{cases}
\]
where

\[ u = \psi_{n_1} (r_1) \psi_{n_2} (r_2), \]
\[ v = \psi_{n_1} (r_3) \psi_{n_2} (r_1). \]  

(24.41)

Let us now investigate the spin part of the wave function. It has already been mentioned that in Russell-Saunders coupling the spin angular momenta are added independently of the orbital angular momenta. The law of conservation of spin, therefore, provides a basis for the construction of the spin wave function for the two-electron system. We shall take the spin function of each electron to be an eigenfunction of the operator for the \( z \) component of the spin

\[ S_z = \frac{\hbar}{2} \sigma_z, \]  

(24.42)

and also of the operator for the square of the spin

\[ S^2 = \frac{\hbar^2}{4} (\sigma_1^2 + \sigma_2^2 + \sigma_3^2). \]  

(24.43)

Here we write \( 2 \times 2 \) Pauli matrices \( \sigma \) (see Chapter 16) without primes

\[ \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \]

Thus the spin function \( \mathbf{C} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \) of a single particle satisfies two equations

\[ S_z \mathbf{C} = \frac{\hbar}{2} \sigma_z \mathbf{C} = \frac{\hbar}{2} \sigma_z \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \hbar \lambda \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}, \]  

(24.44)

\[ S^2 \mathbf{C} = \frac{\hbar^2}{4} (\sigma_1^2 + \sigma_2^2 + \sigma_3^2) \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \hbar^2 \lambda \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}. \]  

(24.45)

Since \( \sigma_1^2 = 1 \), and so on, we obtain from Eq. (24.45) \( \lambda \equiv \frac{3}{4} \). The matrix equation (24.44) for \( \lambda \) is equivalent to a system of two homogeneous algebraic equations

\[ c_1 \left( \frac{1}{2} - \lambda \right) = 0, \]
\[ c_2 \left( \frac{1}{2} + \lambda \right) = 0, \]  

(24.46)

from which it follows that there are two solutions corresponding to the two possible orientations of the spin with respect to the \( z \) axis

1) \( \lambda = \frac{1}{2}, \ c_1 = 1, \ c_2 = 0. \)  

(24.47)
Here the spin is parallel to the $z$ axis. The wave function corresponding to the eigenvalues $\frac{1}{2}$ is

$$C\left(\frac{1}{2}\right) = \left| \begin{array}{c} 1 \\ 0 \end{array} \right|,$$

(24.48)

$$\lambda_1 = -\frac{1}{2}, \ c_1 = 0, \ c_2 = 1.$$  

(24.49)

In this case the spin is antiparallel to the $z$ axis. The corresponding wave function is

$$C\left(-\frac{1}{2}\right) = \left| \begin{array}{c} 0 \\ 1 \end{array} \right|.$$  

(24.50)

In Eqs. (24.48) and (24.50) the value of the $z$ component of the spin is indicated in the parentheses following the amplitude $C$. It is easily shown that both spin parts of the wave function satisfy the orthonormality condition. If, in accordance with the definition, we take the Hermitian conjugate spin function to be a single-row matrix

$$C^\dagger = (c_1^* c_2^*),$$

then from (24.48) and (24.50) we see that

$$C^\dagger \left(\frac{1}{2}\right) C \left(\frac{1}{2}\right) = C^\dagger \left(-\frac{1}{2}\right) C \left(-\frac{1}{2}\right) = 1,$$

and

$$C^\dagger \left(\frac{1}{2}\right) C \left(-\frac{1}{2}\right) = 0.$$

The effect of Pauli matrices on the spin function, according to Eqs. (24.50), (24.48) and (24.44), is

$$\sigma_1 C \left(\pm\frac{1}{2}\right) = C \left(\mp\frac{1}{2}\right); \quad \sigma_2 C \left(\pm\frac{1}{2}\right) = \pm i C \left(\mp\frac{1}{2}\right);$$

$$\sigma_3 C \left(\pm\frac{1}{2}\right) = \pm C \left(\pm\frac{1}{2}\right).$$

(24.51)

We shall look for the spin function $C$ of the two electrons of the helium atom in the form of a superposition

$$C = a_1 C_1 \left(\frac{1}{2}\right) C_2 \left(\frac{1}{2}\right) + a_2 C_1 \left(\frac{1}{2}\right) C_2 \left(-\frac{1}{2}\right) +$$

$$+ a_3 C_1 \left(-\frac{1}{2}\right) C_2 \left(\frac{1}{2}\right) + a_4 C_1 \left(-\frac{1}{2}\right) C_2 \left(-\frac{1}{2}\right),$$

(24.52)
where \(C_1\left(\pm \frac{1}{2}\right)\) and \(C_2\left(\pm \frac{1}{2}\right)\) are the spin functions of the first and second electrons, respectively, while \(a_1\), \(a_2\), \(a_3\) and \(\sigma_1\) are the Clebsch-Gordan coefficients that have to be determined. Let us now attempt to select the coefficients \(a_\alpha\) of the function (24.52) in such a way that the latter will be an eigenfunction of the operator for the \(z\) component of the total spin

\[
S_z = S'_z + S''_z = \hbar \left(\sigma'_z + \sigma''_z\right),
\]

and also of the operator for the square of the total spin

\[
S^2 = (S' + S'')^2 = \frac{\hbar^2}{4} \{\sigma'^t + \sigma''^t + 2 \sigma' \cdot \sigma''\} = \\
= \hbar^2 \left(\frac{3}{2} + \frac{1}{2} \sigma' \cdot \sigma''\right).
\]

Here the primes and the double primes on the Pauli matrices indicate that these matrices act on the spin functions of the first and second electrons, respectively. We thus have two matrix equations

\[
\frac{\hbar}{2} (\sigma'_z + \sigma''_z) C = \hbar \lambda_1 C, \tag{24.55}
\]

\[
\hbar^2 \left(\frac{3}{2} + \frac{1}{2} \sigma' \cdot \sigma''\right) C = \hbar^2 \lambda_3 C. \tag{24.56}
\]

Substituting the total spin function (24.52) and taking into account the effect of the Pauli matrices on the spin functions of the individual electrons [see (24.51)], we find from (24.55)

\[
a_1 C_1 \left(\frac{1}{2}\right) C_2 \left(\frac{1}{2}\right) - a_1 C_1 \left(- \frac{1}{2}\right) C_2 \left(\frac{1}{2}\right) = \\
= \lambda_1 \left[ a_1 C_1 \left(\frac{1}{2}\right) C_2 \left(\frac{1}{2}\right) + a_1 C_1 \left(\frac{1}{2}\right) C_2 \left(- \frac{1}{2}\right) + \\
+ a_1 C_1 \left(- \frac{1}{2}\right) C_2 \left(\frac{1}{2}\right) + a_1 C_1 \left(- \frac{1}{2}\right) C_2 \left(- \frac{1}{2}\right) \right].
\]

Equating the coefficients at the same spin functions on both sides of the equation, we obtain the equations for the parameter \(\lambda_1\) and the coefficients \(a_\alpha\)

\[
a_1 (1 - \lambda_1) = 0, \quad a_2 \lambda_1 = 0, \quad a_3 \lambda_1 = 0, \quad a_4 (1 + \lambda_1) = 0. \tag{24.57}
\]
Similarly, using the relation
\[(\sigma' \cdot \sigma) C = a_2 C_1 \left( \frac{1}{2} \right) C_2 \left( \frac{1}{2} \right) - a_2 \left[ C_1 \left( \frac{1}{2} \right) C_2 \left( - \frac{1}{2} \right) - 2C_1 \left( - \frac{1}{2} \right) C_2 \left( \frac{1}{2} \right) \right] + a_4 C_1 \left( - \frac{1}{2} \right) C_2 \left( - \frac{1}{2} \right), \tag{24.58} \]
which can be obtained with the aid of (24.51), we obtain from (24.56)
\[2a_1 = \lambda_2 a_1, \quad 2a_4 = \lambda_2 a_4, \tag{24.59} \]
As usual we set \(\lambda_2 = S(S + 1)\), where \(S\) is the eigenvalue of the total spin. We note that the systems of equations (24.57) and (24.59) must be satisfied simultaneously. From these equations we find that the possible nonvanishing solutions have eigenvalues
\[\lambda_2 = 2, \text{ with } \lambda_1 = +1, 0, -1 \quad \text{(triplet)}, \]
\[\lambda_2 = 0, \text{ with } \lambda_1 = 0 \quad \text{(singlet)}. \]
Consider now four cases. Case 1. Total spin is equal to unity and is directed along the \(z\) axis. The spins of both particles are parallel. The corresponding solution, given by (24.52), is symmetric:
\[C^s = C_1 \left( \frac{1}{2} \right) C_2 \left( \frac{1}{2} \right), \quad \left( s_1 \uparrow \uparrow s_2 \right), \tag{24.60} \]
\[\lambda_2 = 2, \quad a_1 = 1, \]
\[\lambda_1 = +1, \quad a_3 = a_2 = a_4 = 0. \]
Case 2. Total spin is equal to unity and is antiparallel to the \(z\) axis. The spins of both particles are parallel. The corresponding symmetric solution is
\[C^s = C_1 \left( - \frac{1}{2} \right) C_2 \left( - \frac{1}{2} \right), \quad \left( s_1 \downarrow \downarrow s_2 \right), \tag{24.61} \]
\[\lambda_2 = 2, \quad a_4 = 1, \]
\[\lambda_1 = -1, \quad a_1 = a_2 = a_3 = 0. \]
Case 3. Total spin is directed perpendicular to the \(z\) axis and is equal to unity. The spins of both particles are parallel. The corresponding symmetric solution is
\[C^s = \frac{1}{\sqrt{2}} \left[ C_1 \left( \frac{1}{2} \right) C_2 \left( - \frac{1}{2} \right) - C_1 \left( - \frac{1}{2} \right) C_2 \left( \frac{1}{2} \right) \right], \quad \left( \frac{s_1}{s_{\perp}} \right), \tag{24.62} \]
\[\lambda_2 = 0, \quad a_4 = -a_3 = \frac{1}{\sqrt{2}}, \]
\[\lambda_1 = 0, \quad a_1 = a_2 = 0. \]
Case 4. Total spin is equal to zero. The spins of the particles are antiparallel. The solution is antisymmetric:

\[
C^a = \frac{1}{\sqrt{2}} \left\{ C_1 \begin{pmatrix} 1 \\ \frac{1}{2} \end{pmatrix} C_2 \begin{pmatrix} -1 \\ -\frac{1}{2} \end{pmatrix} - C_1 \begin{pmatrix} -1 \\ -\frac{1}{2} \end{pmatrix} C_2 \begin{pmatrix} 1 \\ \frac{1}{2} \end{pmatrix} \right\}, \quad \left( \frac{s_1^2}{s_2^2} \right).
\]  
(24.63)

\[
\lambda_2 = 0, \quad a_4 = -a_4 = \frac{1}{\sqrt{2}},
\]

\[
\lambda_1 = 0, \quad a_1 = a_1 = 0.
\]

We note that the choice of the nonvanishing Clebsch-Gordan coefficients was such that all four solutions are normalized to unity.

Returning once again to the spatial part of the wave function for the helium atom and using the fact that the total solution must be antisymmetric we have, in accordance with (24.37) and (24.39),

\[
\Psi^a = C^a \left( s_1, s_2 \right) \psi^a \left( r_1, r_2 \right)
\]  
(24.64)

(three states) and

\[
\Psi^{a'} = C^a \left( s_1, s_2 \right) \psi^{a'} \left( r_1, r_2 \right)
\]  
(24.65)

(one state). The spin functions are given by Eqs. (24.60)-(24.63), and the spatial part of the wave function for \( n_1 \neq n_2 \) is

\[
\psi^a = \frac{1}{\sqrt{2}} (u \pm v).
\]  
(24.66)

In the case where both electrons are in the same state \( (n_1 = n_2) \), there is only one solution with a symmetrical spatial part:

\[
\Psi^{a'} = C^a \left( s_1, s_2 \right) \psi^{a'}; \quad \psi^s = u = \varphi_{n_1} \left( r_1 \right) \varphi_{n_1} \left( r_2 \right).
\]  
(24.67)

**E. PARAHELIUM AND ORTHOHELIUM**

We have obtained the wave functions that describe two states. One state (parahelium) is characterized by antiparallel spins of the electrons [the wave function (24.65), which is symmetric with respect to interchange of the coordinates]. The other state (orthohelium) corresponds to parallel spins [the wave function (24.64), which is antisymmetric with respect to interchange of the coordinates; see Fig. 24.1]. A very interesting property of these states is that both types of helium are stable; in other words, parahelium and orthohelium are not converted into one another. We can convince ourselves that both systems are closed by direct
calculation. The matrix element of the dipole moment corresponding to a dipole transition from orthohelium to parahelium

\[
\bar{r}_{s-a} = \int \psi_s^* (r_1, r_2)(r_1 + r_2) \psi_a (r_1, r_2) d^3x_1d^3x_2 =
\]

\[
= \int \psi_s^* (r_2, r_1)(r_1 + r_2) \psi_a (r_2, r_1) d^3x_1d^3x_1 =
\]

\[
= -\int \psi_s^* (r_1, r_2)(r_1 + r_2) \psi_a (r_1, r_2) d^3x_1d^3x_1 = (24.68)
\]

turns out to be equal to zero, since

\[
\bar{r}_{s-a} = -\bar{r}_{s-a} = 0 .
\] (24.69)

[In (24.68) we have changed the variables of integration and used the symmetry properties of the wave functions.] Dipole transitions from one state to another are therefore forbidden.

Mutual conversion of these states may, however, take place under the action of other particles. For example, the bombardment of orthohelium by electrons may lead to the replacement of an ejected electron by another electron with opposite spin, and thus orthohelium can be transformed into parahelium, and vice versa.

F. ENERGY SPECTRUM OF THE HELIUM ATOM

It has already been noted that the total orbital angular momentum \( L \), which is a result of the addition of the orbital angular momenta \( l_1 \) and \( l_2 \) of two electrons, assumes integral values (Russell-Saunders coupling). In the particular case where \( l_1 = l_2 = 1 \) (both electrons are in the \( p \) state), the total orbital angular momentum takes the values \( L = 2, 1, 0 \). In terms of the vector model, these values correspond to the following situations:

1. \( L = 2 \). The angular momenta are parallel;

\[ l_1 \uparrow \uparrow l_2 \quad L = l_1 + l_2 = 2. \]

2. \( L = 1 \). The angular momenta are at an angle of 60°;

\[ L = l_1 \pm l_2 - 1 = 1. \]
3. $L = 0$. The angular momenta are antiparallel;

$$l_1 \uparrow \downarrow l_2 \quad L = l_1 - l_2 = 0.$$ 

In the general case where $l_1 \geq l_2$, the number $L$ takes all possible integral values

$$L = l_1 + l_2, \quad l_1 + l_2 - 1, \quad l_1 + l_2 - 2, \ldots \quad l_1 - l_2. \quad (24.70)$$

In denoting the energy levels for multielectron atoms, we follow the same rules as for hydrogen-like atoms, except that the states with a definite value of the orbital angular momentum $L$ are denoted by capital letters

- $L = 0$: $S$ state
- $L = 1$: $P$ state
- $L = 2$: $D$ state
- $L = 3$: $F$ state, and so on.

Let us enumerate the energy levels of the helium atom. The lowest level corresponds to the total orbital angular momentum $L = 0$ with both electrons in the $s$ state. This singlet term of parahelium is denoted by

$$(1s1s)^1S_0$$

and corresponds to an antiparallel spin orientation. The superscript at the upper left-hand side of the letter characterizing a particular term indicates the number of states (the multiplicity of states).

The next term corresponds to the case when one of the electrons is in the $1s$ state and the other is in the $2s$ state. In this case, both parahelium

$$(1s2s)^1S_0$$

and orthohelium

$$(1s2s)^3S_1$$

are possible. Orthohelium, unlike parahelium, has a spin angular momentum and exhibits anomalous Zeeman splitting in a magnetic field.

We note that the $(1s2s)^3S_1$ level of orthohelium is metastable, because a transition to the lower energy state belonging to parahelium is forbidden by the selection rules. The levels of parahelium are singlets (spin 0), and those of orthohelium are triplets (spin 1).
The splitting can be easily explained in terms of the vector model of the orbital and spin angular momenta. According to the vector model, the sum of the two vectors $L$ and $S$ (that is, the total angular momentum vector) can take the values

\[ J = L + S, \quad L + S - 1, \quad \ldots, \quad |L - S|. \]  

(24.71)

For $L > S$, the total number of these values is

\[ 2S + 1, \]  

(24.72)

whereas for $L < S$ it is

\[ 2L + 1. \]  

(24.73)

It follows that for the $S$ term ($L = 0$), the total number of possible states for both ortho-helium and para-helium is equal to one. In exactly the same way, the $s$ term of the hydrogen atom (one valence electron) is a single, and the number of states is equal to two (that is, the levels are doublets) only for $p$, $d$ terms (for which $l > s$).

The total spin $S$ of helium assumes two values: $S = 0, 1$. For $S = 0$ the number of states ($2S + 1$) is equal to unity, and for $S = 1$ it is equal to three ($2S + 1 = 3$); that is, the state is a triplet. A general diagram of the energy levels of the helium atom is given in Fig. 24.2.

For elements of the third group ($S = \frac{3}{2}$ and $S = \frac{1}{2}$), the states are quartets or doublets. Thus the number of valence electrons (see Chapter 25) completely determines the splitting of the spectral lines.

The theory of multielectron atoms is treated in several books.¹

Problem 24.1.² A particle is in the Yukawa potential well

\[ V = - g^2 \frac{e^{-r/\lambda}}{r}. \]


²These problems refer to Chapters 23 and 24.
Choose a test function in the form \( \psi_i = A_i e^{-\beta_i r} \) and determine the upper limit of the values of \( x \) at which at least one discrete level will exist. Using the obtained solution, consider the special case of a Coulomb potential \( (r^2 = e_i^2, x = 0) \). Show that discrete levels always exist for the Coulomb potential. Determine the lowest energy level and the corresponding wave function.

Solution. The normalized wave function is of the form [see (23.47)]:

\[
\psi_i = \frac{1}{\sqrt{\pi}} \alpha_{1/2}^3 \ e^{-\beta_i r}.
\]

The average values of the kinetic and potential energies are [see (23.52), (23.53)]

\[
\overline{T} = \frac{\beta_i^2 \hbar^2}{2m_0}, \quad \overline{V} = -\frac{431r^2}{(z_0^2 + x)^2}.
\]

The appearance of the first discrete level is possible under the conditions

\[
E_1 = \overline{T} + \overline{V} = 0, \quad \frac{\partial E_1}{\partial \beta_i} = 0,
\]

from which we find

\[
\chi_{\text{max}} = \frac{m_0 \hbar^2}{\hbar^2}.
\]

Discrete levels exist for \( E < 0 \). This happens when \( x < \chi_{\text{max}} \). For a Coulomb field \( x = 0 \), and therefore this condition is always satisfied. The average energy in the Coulomb case is

\[
\overline{E_1} = \frac{\beta_i^2 \hbar^2}{2m_0} - \beta_i e_i^2.
\]

Using the condition that \( \overline{E_1} \) must be minimum, we find

\[
\beta_i = \frac{1}{a_0},
\]

where \( a_0 = \frac{\hbar^2}{m_0 e_i^2} \) is the radius of the first Bohr orbit. The expressions for the wave function and the average energy will be exactly the same as those yielded by the Schrödinger equation for the Is level of the hydrogen atom (see Chapter 13).

Problem 24.2. Calculate the diamagnetic susceptibility of the ground state of one gram-atom of parahelium, using the expression (23.47) obtained for the wave function by the variational method.

Solution. In the ground state of parahelium, the orbital and spin angular momenta are equal to zero \( (j = 0) \), and therefore parahelium must be diamagnetic (see Problem 20.1).

In accordance with (20.48), the diamagnetic susceptibility per gram-atom is given by the expression

\[
\chi = \frac{e^2 N}{6m_0 c^2} (r_1^2 + r_2^2), \quad (24.74)
\]

where \( N \) is Avogadro's number and

\[
r_1^2 + r_2^2 = \int (r_1^2 + r_2^2) |\psi(r_1, r_2)|^2 \, d^3x_1 \, d^3x_2. \quad (24.75)
\]

From (23.47) we obtain an approximate expression for \( \psi(r_1, r_2) \)

\[
\psi(r_1, r_2) = \frac{Z^2}{\pi a_0^3} \ e^{-Z^2(r_1 + r_2)/a},
\]
where for helium

\[ Z' = Z - \frac{5}{16} = \frac{27}{16}. \]

Evaluating the integral (24.75) with the above expression for \( \psi \), we obtain

\[ \frac{r_1^2 + r_2^2}{2z^2}. \]

The diamagnetic susceptibility is therefore

\[ \chi_{\text{theor}} = -1.67 \cdot 10^{-6}, \]

which is in fairly good agreement with the experimental value

\[ \chi_{\text{exp}} = -1.90 \cdot 10^{-6}. \]
Chapter 25

Optical Spectra of Alkali Metals

A. GENERAL DISCUSSION OF THE STRUCTURE OF COMPLEX ATOMS

It has already been pointed out that the position of an atom in the periodic table of elements is determined by the atomic number \( Z \). This number characterizes the nuclear charge in units of \( e_0 \); that is, it is an integer that is equal to the number of protons in the nucleus and also to the number of electrons in the neutral atom. Thus, for example, sodium has 11 electrons \( (Z=11) \) and uranium has 92 \( (Z=92) \).

The most important questions in the theory of a complex atom concern the electron density distribution and the energy spectrum. In studying these questions it is necessary to consider the mutual interaction between all the electrons, in addition to the attraction between the electrons and the nucleus. Owing to the interelectronic interaction, the energy values of the electrons will be smaller (in absolute value) than those given by the well-known expression

\[
E = -\frac{Z^2 \hbar^2}{n^2},
\]

Just as in the hydrogen atom, each electron in a complex atom is characterized by four quantum numbers. For Russell-Saunders coupling (the case where the spins and orbital angular momenta of the individual electrons in a given shell are added separately), these quantum numbers are as follows:

1. the principal quantum number \( n = 1, 2, 3, 4, \ldots \),
2. the orbital angular momentum quantum number \( l = 0, 1, 2, \ldots, (n-1) \),
3. the magnetic quantum number \( m = 0, \pm 1, \ldots, \pm l \), and
4. the spin quantum number \( m_s = \pm 1/2 \) (characterizing the projection of the spin on the \( z \) axis).

In the case of \( jj \) coupling, the four quantum numbers are as follows:

1. the principal quantum number \( n \),
2. the orbital angular momentum quantum number \( l \),
3. the total angular momentum quantum number \( j = |l \pm 1/2| \), and
(4) $m_l = -j, -j+1 \ldots j-1, j$ (characterizing the component of the total angular momentum along the $z$ axis).

As we have already said, Russell-Saunders coupling (or $LS$ coupling) is characteristic of light elements, while $jj$ coupling is characteristic of heavy elements. Both types of coupling give the same number of levels.

A group of closely spaced energy levels, which is separated from other energy levels by an appreciable gap, forms a shell made up of several subshells. Just as for the hydrogen atom, the classification of the shells is based, as a rule, on the principal quantum number $n$. The relationship between the principal quantum number $n$ and the letters which are used to denote the shells in x-ray spectroscopy is as follows:

<table>
<thead>
<tr>
<th>$n$</th>
<th>Shell symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$K$</td>
</tr>
<tr>
<td>2</td>
<td>$L$</td>
</tr>
<tr>
<td>3</td>
<td>$M$</td>
</tr>
<tr>
<td>4</td>
<td>$N$</td>
</tr>
<tr>
<td>5</td>
<td>$O$</td>
</tr>
<tr>
<td>6</td>
<td>$P$</td>
</tr>
<tr>
<td>7</td>
<td>$Q$</td>
</tr>
</tbody>
</table>

Within the shells, electrons with values of the orbital quantum number $l$ equal to 0, 1, 2, 3, ... form the $s$, $p$, $d$, $f$, ... subshells. To determine how the shells and subshells are filled, one should take into account the Pauli exclusion principle, according to which there can be only one electron in each quantum state characterized by four quantum numbers. In a state with fixed values of $n$, $l$, $m$, there can be at most two electrons, differing in spin direction. Since the quantum number $m$, which varies from $-l$ to $+l$, can take $2l + 1$ values, we obtain the following expression for the maximum number of electrons in a given subshell:

$$N_{nl} = N_l = 2(2l + 1).$$

The same value for $N_l$ is found for $jj$ coupling. For given values of the three quantum numbers $n$, $l$, $j$, the fourth quantum number $m_j$ may take the values $-j, \ldots, -\frac{l}{2}, \frac{l}{2}, \ldots, j$, corresponding to $2j + 1$ states. Hence we obtain the same value for $N_l$:

$$N_l = \sum_{i} (2j + 1) = 2(2l + 1),$$

where

$$j = \left| l + \frac{1}{2} \right|.$$
It follows that the maximum number of electrons in the subshells $s(l=0)$, $p(l=1)$, $d(l=2)$ and $f(l=3)$ is as follows:

$$N_s = 2, \quad N_p = 6, \quad N_d = 10, \quad N_f = 14.$$  

Subshells with a larger value of $l$ are not encountered in unexcited atoms, and therefore we shall not discuss them here.

We can now find the maximum number of electrons which can occupy a given shell

$$N_n = \sum_{l=0}^{n-1} N_l = 2(1 + 3 + \ldots + (2n - 1)) = 2n \frac{1 + 2n - 1}{2} = n^2. \quad (25.2)$$

Thus there can be at most two electrons in the $K$ shell, eight electrons in the $L$ shell, eighteen electrons in the $M$ shell, 32 electrons in the $N$ shell, and so on. It should be mentioned that these relations between the quantum number and the number of states in the various shells are true, generally speaking, only for hydrogen-like atoms.

To establish the order in which the shells and subshells are filled in complex atoms, it is necessary to consider the mutual interaction of the electrons. As we have emphasized several times, this problem cannot be solved exactly. The application of quantum mechanics to multielectron systems, however, has led to the discovery of various important properties of such systems, including, in particular, the exchange interaction. Moreover, the development of approximation methods has made it possible to obtain highly satisfactory quantitative results for complex atoms. As indicated in Chapter 23, the simplest approximation methods are the variational methods developed by Ritz, Hylleraas, and others; these give comparatively good results for the light atoms (up to potassium). A more complete analysis of the structure of an atom can be made by means of the self-consistent field method developed by Hartree and Fock. This method has been used to determine the energy and the electron distribution in heavy and light atoms (see Chapter 23). This method also gives the shell structure of complex atoms.  

Unfortunately, the use of the self-consistent field involves some very complicated computations, which can be carried out only by computers. As a result, the eigenfunctions characterizing the electron distribution are obtained in the form of numerical tables rather than analytical expressions.

---

B. THE THOMAS—FERMI STATISTICAL METHOD

Besides the approximation methods, there are statistical methods that have been introduced on the basis of principles developed by Thomas and Fermi. These methods apply mainly to heavy atoms.

In the statistical treatment, the electrons of an atom are regarded as a degenerate gas with \( T = 0 \), just as in the theory of metals (see Chapter 6). The Thomas—Fermi statistical method is, of course, less accurate than the Hartree—Fock self-consistent field method, because many features of the behavior of the individual electrons are neglected. In spite of this general shortcoming, the Thomas—Fermi method provides a fairly simple explanation of many important properties which are characteristic for the average behavior of electrons in an atom.

The Thomas—Fermi method does not enable us to find the shell structure of an atom, but it does explain several important features of the filling of the electron shells. This method can be used for calculating the total bonding energy of electrons in an atom and the radii of atoms and ions. It can also be used to determine the influence of screening electron shells on the scattering of fast electrons, bremsstrahlung, and the creation of electron—positron pairs due to absorption of x-ray photons in the nuclear field.

Presently statistical methods are being successfully used to construct a theory of heavy nuclei and a theory of matter at high pressures (for example, inside stars).

In heavy atoms the positively charged nucleus is surrounded by a cloud of negatively charged electrons, which partially screen the electric charge of the nucleus. The potential of an ionized atom at distances greater than its radius is given in the first approximation by the following expression:

\[
\phi_{\infty} = \frac{(Z - N) e_0}{r},
\]  

(25.3)

where \( Z \) is the atomic number, and \( N \) is the number of electrons. For a neutral atom \( N = Z \) and, therefore, \( \phi_{\infty} = 0 \); that is, the electrons completely screen the charge of the nucleus.

In constructing a statistical theory, three forms of energy should be taken into account.

1. The electrostatic energy of attraction between the electrons and the nucleus. This energy is related to the electron density \( \rho_0 \) (the number of electrons per unit volume) by the expression

\[
V_{n-c} = - e_0 \int \rho_0 |V_n| dV,
\]

(25.4)

where \( e = - e_0 \) is the charge of the electron, and \( V_n = \frac{Ze_0}{r} \) is the potential produced by the nucleus.
2. The electrostatic energy of repulsion between the electrons

\[ V_{\text{e-e}} = -\frac{e_0}{2} \int \rho_0 \Phi_c \, d^3x, \]  

(25.4a)

where

\[ \Phi_c (r) = -e_0 \int \frac{\rho_0 (r')}{|r - r'|} \, d^3x'. \]

3. The kinetic energy of the electrons in the atom. Just as in the theory of solids at absolute zero, the average kinetic energy of an individual electron is related to the electron density \( \rho_0 \) by the following expression. In accordance with Eqs. (6.33) and (6.33a):

\[ T_{\text{av}} = x \rho_0^{5/3}, \]  

(25.4b)

where

\[ x = \frac{3}{10} \frac{\hbar^2}{m_0} (3\pi^2)^{5/3} = \frac{3}{10} \frac{e_0^2 a_0}{\varepsilon_0} (3\pi^2)^{5/3}. \]  

(25.5)

Hence the kinetic energy of the electrons is

\[ T = x \int \rho_0^{5/3} \, d^3x. \]  

(25.6)

The total energy of an electron gas in the field of a nucleus is equal to the sum of the potential energy, which consists of two parts [see (25.4) and (25.4a)], and the kinetic energy [see (25.6)]. Thus the total energy is

\[ E = T + \sum_{\text{e-e}} + V_{\text{n-e}} = \]  

\[ = x \int \rho_0^{5/3} \, d^3x - e_0 \int \rho_0 \Phi_n \, d^3x + \frac{1}{2} e_0^2 \int \rho_0 (r) \rho_0 (r') \, d^3x \, d^3x'. \]  

(25.7)

The density of the electron gas must satisfy the condition

\[ \int \rho_0 \, d^3x = N, \]  

(25.8)

where \( N \) is the number of electrons in the atom.

With the auxiliary condition (25.8), the variational principle can be formulated as follows:

\[ \delta \{ E + e_0 \Phi_0 N \} = 0. \]  

(25.9)

Using this principle, we can find a relationship between the total potential \( \Phi = \Phi_n + \Phi_0 \) and the density of electrons \( \rho_0 \)

\[ \rho_0 = \frac{1}{3\pi^2 a_0^3} (2m_0 e_0 (\Phi - \Phi_0))^{5/3}, \]  

(25.10)

These formulas were obtained on the assumption that at most two electrons can occupy each quantum state characterized by three quantum numbers. Thus the Thomas-Fermi statistical theory automatically incorporates the Pauli exclusion principle, which is of fundamental importance in the theory of complex atoms.
where the Lagrangian multiplier $\Phi_0$, which plays the role of a constant potential, must be found from the boundary conditions. In the derivation of (25.10), we have used the relations

$$
\frac{1}{3} \int \rho \rho^\prime d^3x = \frac{5}{3} \int \rho \rho^\prime d^3x,
$$

$$
\frac{1}{5} \int \rho \rho^\prime d^3x = \int \Phi \rho d^3x,
$$

$$
\frac{1}{7} \int \rho \rho^\prime d^3x = \int \Phi \rho d^3x.
$$

Substituting Eq. (25.10) for the electron density into Poisson's equation for a spherically symmetric electron distribution

$$
\nabla^2 \Phi = \frac{1}{r} \frac{d^2}{dr^2} r \Phi = 4\pi \epsilon_0 \rho_0
$$

and recalling that $\Phi_0 = \text{const}$, we obtain the Thomas-Fermi equation which forms the basis of the statistical model of the atom

$$
\frac{1}{r} \frac{d^2}{dr^2} r (\Phi - \Phi_0) = \frac{4\epsilon_0}{3\pi \hbar^2} (2m_0 \epsilon_0)^{3/2} (\Phi - \Phi_0)^{1/2}.
$$

When a specific problem is investigated, the solution of Eq. (25.13) must satisfy certain definite boundary conditions. For an atom the boundary conditions can be given in the form

$$
\Phi = \Phi_0 = \frac{Z \epsilon_0}{r} \quad \text{for} \quad r \to 0
$$

and

$$
\Phi = \frac{(Z - N) \epsilon_0}{r_0} \quad \text{for} \quad r = r_0.
$$

Here $r_0$ is determined from the condition that the electron density should be equal to zero at $r = r_0$, that is, $\rho_0 (r_0) = 0$. Hence, in accordance with (25.10), we find

$$
\Phi_0 = \frac{(Z - N) \epsilon_0}{r_0}.
$$

With the help of Poisson's equation (25.12) and (25.13), the condition (25.8) may be written as

$$
\frac{r_0}{2} \int \rho_0 (r) \rho_0 (r') \frac{d^3x d^3x'}{|r - r'|} = -\epsilon_0 \int \Phi \rho_0 d^3x; \quad \int \rho_0 d^3x = N \epsilon_0.
$$

It follows from (25.16) that $\Phi_0 = 0$ and $r_0 = \infty$ for a neutral atom ($N = Z$). Instead of (25.17) we get, therefore,

$$
\int_0^\infty r \frac{d^3r \rho r}{d^3r} dr = Z \epsilon_0.
$$

This condition will hold if the second boundary condition is satisfied

$$
\lim_{r \to \infty} r \rho = 0.
$$
We note that the Thomas-Fermi equation (25.13) has one exact solution

\[ \Phi = \Phi_0 = \frac{81 \pi^4 h^4}{8m^2 e^6 r^4}, \]

(25.19)
as can be easily shown by substituting (25.19) into (25.13).

This solution for a neutral atom (\(\Phi_0 = 0\)) will satisfy one of the boundary conditions for \(r \to \infty\) [see (25.18)]. The second boundary condition for \(r \to 0\) [see (25.14)], however, will not be satisfied.

Unfortunately, solutions of the Thomas-Fermi equation which satisfy both boundary conditions cannot be expressed in analytic form.\(^4\)

Substituting (25.14) into (25.10), we find the behavior of the density \(\rho_0\) as \(r \to 0\),

\[ \rho_0 = \text{const} r^{-4/3}, \]

(25.20)
The solution (25.19) for a neutral atom gives too high a value for \(\Phi\) as \(r \to \infty\). The more exact Hartree-Fock method shows that the electron density will decrease exponentially as \(r \to \infty\).

Since we are interested only in the basic principles of the statistical method, we shall construct an approximate statistical theory of the atom with the help of the variational method. This will enable us to formulate a solution of the problem in analytic form with only small quantitative deviations which are of no importance to us.

**C. SOLUTION OF THE THOMAS-FERMI PROBLEM BY THE RITZ VARIATIONAL METHOD**

Solving a problem by the Ritz variational method, one can propose any number of test functions which depend on the different values of the variational parameter \(\lambda\).

We shall choose the test function on the basis of the following considerations. The function should agree roughly with the solution of the Thomas-Fermi equation for

\[ \Phi(r) = \frac{Ze_0}{r} f(x), \]

where

\[ x = \frac{r}{a}, \quad a = a_0 \left( \frac{9\pi^2}{128Z} \right)^{1/3}. \]

With the function \(f(x)\), Eq. (25.13) becomes

\[ \sqrt{x} \frac{d^2 f}{dx^2} = \frac{f}{x^{3/2}}, \]

(25.13a)

and the boundary conditions (25.14) and (25.18) become

\[ f(x) = 1 \quad \text{for} \quad x \to 0, \quad f(x) = 0 \quad \text{for} \quad x \to \infty. \]

(25.14a)

These equations are of a universal character, that is, they do not necessarily depend on the quantity \(Z\). Therefore, after numerically integrating the Thomas-Fermi equation, we can change the variable (which depends on \(Z\)) and use the equation to investigate any heavy atom. This cannot be done with the Hartree-Fock equation.

---

\(^4\)We may note that the numerical integration of this equation presents two advantages over the numerical integration of the Hartree-Fock equations. First, the Thomas-Fermi equation is much simpler than the Hartree-Fock equations. Second, this equation and the boundary conditions (for example, \(\Phi = 0\) for a neutral atom with \(Z = N\)) can be transformed into a universal form which is independent of \(Z\). To do this, we must replace \(\Phi(r)\) by a new function

\[ \Phi(r) = \frac{Ze_0}{r} f(x), \]

where

\[ x = \frac{r}{a}, \quad a = a_0 \left( \frac{9\pi^2}{128Z} \right)^{1/3}. \]

With the function \(f(x)\), Eq. (25.13) becomes

\[ \sqrt{x} \frac{d^2 f}{dx^2} = \frac{f}{x^{3/2}}, \]

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and the boundary conditions (25.14) and (25.18) become

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These equations are of a universal character, that is, they do not necessarily depend on the quantity \(Z\). Therefore, after numerically integrating the Thomas-Fermi equation, we can change the variable (which depends on \(Z\)) and use the equation to investigate any heavy atom. This cannot be done with the Hartree-Fock equation.
\( r \to 0 \) (this region is the most important with regard to the solution of the problem as a whole), and it should have a comparatively simple form, so that it can be exactly integrated in the calculation of the total energy. One test function which satisfied these requirements is

\[
\rho_0 = \frac{N\lambda^{3/2}}{16\pi^{3/2}} e^{-\sqrt{\lambda r}}.
\]

(25.21)

This function is already normalized to the total number of electrons

\[
\int \rho_0 \, d^3x = \frac{N\lambda^{3/2}}{4} \int_0^\infty Vr \, e^{-\sqrt{\lambda r}} \, dr = N,
\]

(25.21a)

and therefore the auxiliary condition (25.8) will be satisfied automatically.

For \( r \to 0 \), the test function (25.21) changes in the same way (\( \rho_0 \sim r^{-3/2} \)) as the solution of the Thomas-Fermi equation [see (25.20)]. As we shall see later, this explains the good quantitative agreement between results obtained by means of the test function (25.21) and those obtained by means of the potential satisfying the Thomas-Fermi equation.

The potential due to the electrons in the atom is

\[
\Phi_e = -\frac{Ne_0}{r} \left(1 - e^{-\sqrt{\lambda r}} - \sqrt{\lambda r} e^{-\sqrt{\lambda r}}\right).
\]

(25.22)

This can be easily shown by substituting Eqs. (25.21) and (25.22) for \( \rho_0 \) and \( \Phi_e \) into the equation

\[
\nabla^2 \Phi_e = 4\pi e_0 \rho_0.
\]

Using also the expression \( \Phi_n = \frac{Ze_0}{r} \), we can see that the total potential satisfies the boundary condition (25.15) for \( r = r_0 \to \infty \), when the charge density vanishes together with the exponential term \( e^{-\sqrt{\lambda r}} \).

We can also find an expression for the kinetic energy \( T \) in terms of the variational parameter \( \lambda \). From Eqs. (25.6) and (25.21) we have

\[
T = 4\pi \left(\frac{N}{16\pi}\right)^{3/2} \lambda^{3/2} \int_0^\infty \frac{e^{-5/2} V_{\sqrt{\lambda r}}}{\sqrt{r}} \, dr = \frac{9}{400} \left(\frac{3\pi}{2}\right)^{2/3} N^{5/3} \lambda^{2/3} e_0 a_0.
\]

(25.23)

We have the following expressions for the potential energy due to the interaction between the nucleus and the electrons [see (25.4)] and for the potential due to the mutual interaction of the electrons [see (25.4a)]:

\[
V_{n-e} = -\frac{ZNe_0^2}{8} \lambda^{3/2} \int_0^\infty \frac{e^{-\sqrt{\lambda r}}}{\sqrt{r}} \, dr = -\frac{ZNe_0^2 \lambda}{2},
\]

(25.24)

\[
V_{e-e} = \frac{N^2e_0^2}{8} \lambda^{3/2} \int_0^\infty \frac{dr}{\sqrt{r}} \left(1 - e^{-\sqrt{\lambda r}} - \sqrt{\lambda r} e^{-\sqrt{\lambda r}}\right) = \frac{N^2e_0^2 \lambda}{16}.
\]

(25.25)
Adding Eqs. (25.23)-(25.25), we find that the total energy (25.7) of the electron cloud is

\[ E = A\lambda^2 - B\lambda, \]  

(25.26)

where

\[ A = \frac{9}{400} \left(\frac{3\pi}{2}\right)^{2/3} \frac{N^{2/3}}{8} \rho^2 a_0, \quad B = \frac{1}{2} Ne_0^2 \left( Z - \frac{N}{8} \right). \]  

(25.27)

The variational parameter \( \lambda \), corresponding to the reciprocal of the effective radius of the atom, can be found from the condition for the minimum of the total energy \( E \) of the atom, that is, \( \frac{\partial E}{\partial \lambda} = 0 \). Hence we find

\[ R_{\text{eff}} = \frac{1}{\lambda} = \frac{9}{100} \left(\frac{3\pi}{2}\right)^{2/3} \frac{N^{2/3}}{8} a_0, \]  

(25.28)

\[ E = \frac{1}{2} V = -\frac{B^2}{4A} = -\frac{25}{9} \left( \frac{2}{3\pi} \right)^{2/3} \frac{e_0^2}{a_0} N^{2/3} \left( Z - \frac{N}{8} \right)^2. \]  

(25.29)

For a neutral atom \((N = Z)\), we have

\[ R_{\text{eff}} \approx 0.3 \cdot \frac{a_0}{Z^{2/3}}, \]  

(25.30)

\[ E = -\frac{2549}{64} \left( \frac{2}{3\pi} \right)^{2/3} \frac{e_0^2}{a_0} Z^{7/3} = -0.758 \ldots \frac{e_0^2}{a_0} Z^{7/3}. \]

It is worth noting that numerical integration of the Thomas-Fermi equation leads to a value for the energy of the atom which is very close to that given by (25.30)

\[ E_{\text{T-F}} = -0.769 \ldots \frac{e_0^2}{a_0} Z^{7/3} = -20.94 Z^{7/3} \text{ ev.} \]  

(25.30a)

The expression (25.30a) (with the sign reversed) represents the total bonding energy (or ionization energy) \( W \) of a neutral atom, that is, the energy required to remove all the electrons from the atom.

The theoretical values obtained for \( W \) from (25.30a) are quite reasonable even in the case of the hydrogen atom, but they are somewhat higher than the corresponding experimental values. The relative error decreases with increasing \( Z \) (see Table 25.1).

<table>
<thead>
<tr>
<th>Table 25.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical and experimental values of the total ionization energy ( W ) of atoms (in units of ( e_0^2/a_0 ))</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>( W^{\text{theor}} )</th>
<th>( W^{\text{exper}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.769</td>
<td>0.5</td>
</tr>
<tr>
<td>Li</td>
<td>9.982</td>
<td>7.5</td>
</tr>
<tr>
<td>Na</td>
<td>206.9</td>
<td>162</td>
</tr>
<tr>
<td>Hg</td>
<td>21207</td>
<td>18130</td>
</tr>
</tbody>
</table>
Concluding this section, let us compare the curves which are obtained for the charge distribution in neutral argon \((Z = 18)\) on the basis of the Thomas-Fermi statistical theory and on the basis of Hartree's method of the self-consistent field (see Fig. 25.1). It can be seen from the graph that the curve of \(\rho_0\) computed according to the Hartree method (Curve B) has characteristic maxima and minima corresponding to the electron shells, whereas the curve calculated according to the Thomas-Fermi statistical theory (Curve A) describes only the average behavior of the electron density, and therefore has no relative maxima. For large values of \(r\) there is also a marked lack of agreement between the two curves; the Hartree-Fock method gives functions which decrease exponentially with increasing \(r\), whereas in the statistical theory the decrease is proportional to \(r^{-4}\) [see (25.19)].

Fig. 25.1. Comparison of the electron density distributions in argon \((Z = 18)\) obtained on the basis of the Thomas-Fermi method (Curve A) and the Hartree-Fock method (Curve B). A pseudologarithmic scale is used for the ordinate axis (we have plotted the quantity \(\ln(1 + D\alpha_0)\), where \(D = 4\pi r^2\rho_0\)). Therefore, the graph will be linear for small \(D\alpha_0\), and logarithmic for large \(D\alpha_0\). The choice of this scale enables us to follow the variation of \(\rho_0\) at large values of \(r\), as well as for \(r < \alpha_0\).

D. ENERGY LEVELS OF ALKALI METAL ATOMS

In studying spectral lines in complex atoms, it is necessary to distinguish between outer and inner shells.

In the hydrogen atom there is only an outer shell (the \(K\) shell), which contains one electron. In helium \((Z = 2)\), the \(K\) shell is completely filled (a noble or inert gas). In lithium (an alkali metal in Group I of the periodic table, \(Z = 3\)), the inner shell (\(K\) shell) is completely filled, but the outer \(L\) shell has only one electron. The filling of the \(L\) shell is completed in Ne \((Z = 10)\). In sodium (an alkali metal, \(Z = 11)\), the inner \(K\) and \(L\) shells are completely

\[A\ \text{detailed exposition of the statistical theory of an atom is given in P. Gombas, Die statistische Theorie des Atoms und ihre Anwendungen, Vienna: Springer-Verlag, 1949.}\]
filled, but there is one electron in the outer $M$ shell. The filling of the shells in these atoms is illustrated in Fig. 25.2.

It should be noted that the bonding energy of an electron in an inner shell is much greater that that of an electron in an outer shell. An indication of this is provided by the ionization energy, which is more than 20 ev for inert gases, whereas for alkali metals it is only slightly more than 5 ev. The removal of the first valence electron in lithium requires the expenditure of 5.39 ev, but removal of the second and third electrons from the inner shells requires the expenditure of 76 and 122 ev, respectively.

![Fig. 25.2. Diagram of the filling of electron shells in different atoms. On the right, atoms with completely filled shells (inert gases). The dark spots represent electrons and the light spots (with a plus sign in the middle) represent nuclei.](image)

The atoms in Group I of the periodic table (Li, Na, K, Rb, Cs, etc.) are known as alkali metals; each has an outer shell containing one electron, just like the hydrogen atom. Their optical and chemical properties, therefore, should be essentially the same as those of the hydrogen atom (for example, all of these elements are monovalent and they all exhibit doublet splitting of the spectral terms).

The optical spectrum is caused by the transition of a valence electron (that is, an electron in the outer shell) from an excited state to a lower state. The excitation of electrons in the inner shells generally requires considerably more energy than does that of electrons in the outer shells; therefore, downward transitions from excited states to the ground states of the inner shell are accompanied
by the emission of x-rays (see Chapter 26). The atomic nucleus and the electrons in the inner shells together form what is known as the atomic core. Thus the charge of the atomic core is equal to \( Z_a = Z - N \), where \( N \) is the number of electrons in the inner shells. For alkali metals (Li, Na, etc.) \( N = Z - 1 \), and thus the charge of the atomic core is equal to unity \( (Z_a = 1) \). Therefore, the main part of the potential energy which retains the outer electron in the metal is the same as for hydrogen, namely,

\[
V_a = -\frac{e_0^2}{r} Z_a = -\frac{e_0^2}{r}.
\]

The analysis of the spectra of alkali metals can thus be based on the corresponding expression for the energy which was obtained in Chapter 13

\[
E_n = -\frac{R \hbar}{n^2}.
\]

Similarly, we can use the hydrogen wave functions as the zero-order approximation of the wave functions

\[
\psi^0 = \psi_{nlm}.
\]

In alkali metals, however, we cannot confine ourselves to the Coulomb energy in treating the interaction between the valence electron and the atomic core, and we must also take into account the polarization forces and the "smearing" of the atomic core over a finite volume. This yields various corrections and removes the degeneracy which occurs in hydrogen.

In Bohr's semiclassical theory, the orbits of valence electrons were rigorously divided into orbits which penetrate the atomic core, and those which do not. In the case of "nonpenetrating" orbits (orbits with nearly circular trajectories) we need to consider only the polarization forces, since the potential outside the atomic core (that is, outside the inner shells) is completely independent of the radial distribution of a spherically symmetric charge. The radial distribution is very important only for "penetrating" orbits (elongated ellipses) (see Fig. 25.3).

In quantum theory the concept of a trajectory is no longer meaningful. In order to classify orbits as "nonpenetrating" or "penetrating," we must introduce a new convention; namely, if the wave function describing the behavior of the valence electron can be set equal to zero inside the atomic core, the orbit is "nonpenetrating," and if on the contrary the wave function cannot be set equal to zero inside the atomic core, the orbit is "penetrating."
It should be noted in this connection that the s orbit of a complex atom is always penetrating, since its wave function differs from zero inside the atomic core and, indeed, even inside the nucleus.

\[ |\psi(0)|^2 = \frac{1}{\tau n^2 u_0^2}. \]  

(25.34)

We shall now calculate the polarization forces that arise between an outer electron and the atomic core. The outer electron will obviously repel electrons in the inner shells and attract the nucleus. As a consequence, the atomic core is polarized, and a polarization force arises between it and the outer electron.

\[ F_p = - (Z - 1) e^0 \left[ \frac{1}{r^2} - \frac{1}{(r + x)^2} \right] = - \frac{2e_0^2 (Z - 1)x}{r^3}. \]  

(25.35)

The quantity \( e_0 (Z - 1)x = \beta \) represents the polarization of the atomic core.

If we regard the atomic core as an elastic dipole, we can set

\[ p = \beta \mathcal{E}, \]  

(25.36)

where \( \beta \) is the polarizability of the atom, and

\[ \mathcal{E} = \frac{e_0}{r^2} \]  

(25.37)

is the electric field produced by the outer electron at the center of the atomic core. Thus we can obtain the following expression for the potential energy associated with the polarization:

\[ V_p = \int F_p \, dr = - \int \frac{2\beta e_0^2}{r^3} \, dr = - \frac{\beta e_0^2}{2r^2}. \]  

(25.38)

Since the polarization can be regarded as a perturbation in this problem, we have the following expression for the polarization energy:

\[ \Delta E_p = \int \psi_{nlm}^* V_p \psi_{nlm} \, d^3x = - \frac{\beta e_0^2}{2} \left( \frac{1}{r^2} \right). \]  

(25.39)

---

The coefficient of polarization \( \beta \) is usually determined from semiempirical formulas. Its numerical values for alkali metal ions (cores) are as follows (in units of \( 10^{-24} \text{ cm}^3 \)):

- 0.03 (Li⁺);
- 0.19 (Na⁺);
- 0.89 (K⁺);
- 1.50 (Rb⁺);
- 2.60 (Cs⁺).
Since, according to (13.29a),
\[
\left( \frac{1}{r^3} \right) = \frac{3}{2a_0^2} \frac{1 - \frac{l(l+1)}{3n^2}}{n^s (l-\frac{1}{2}) l (l+\frac{1}{2}) (l+1) \left( l + \frac{3}{2} \right)}
\]
relation (25.39) may be reduced to
\[
\Delta E_p = -\frac{e_0^s 2b}{2a_0 n^s}, \quad (25.40)
\]
where
\[
\delta = \delta_1 - \frac{\delta_2}{n^3},
\]
\[
\delta_1 = \frac{3n^s}{4a_0^2 (l - \frac{1}{2}) l (l + \frac{1}{2}) (l+1) \left( l + \frac{3}{2} \right)}, \quad \delta_2 = \frac{l(l+1)}{3n^s} \delta_1. \quad (25.41)
\]

We can, therefore, find the total energy, which in this case depends upon both \( l \) and \( n \) (for the time being, we are neglecting spin corrections)
\[
E_{nl} = -\frac{R\hbar}{n^s} + \Delta E_p.
\]
Substituting expression (25.40) for \( \Delta E_p \) and using the relation
\[
\frac{R\hbar}{n^s} = \frac{e_0^s}{2a_0 n^2},
\]
we obtain
\[
E_{nl} = -\frac{e_0^s}{2a_0 n^2} - \frac{e_0^s 2b}{2a_0 n^s} \approx -\frac{e_0^s}{2a_0 (n - \delta)^2}, \quad (25.42)
\]
since
\[
\frac{1}{(n - \delta)^2} = \frac{1}{n^2} \left( 1 - \frac{\delta}{n} \right)^{-2} \approx \frac{1}{n^2} + \frac{2b}{n^3}.
\]
Introducing the "effective principal quantum number" \( n_{\text{eff}} = n - \delta \), we get
\[
E_{nl} = -\frac{e_0^s}{2a_0 n_{\text{eff}}^2}. 
\]
It should be noted that Eq. (25.41) cannot be used for s states, since the coefficient \( \ell \) becomes infinite when \( \ell = 0 \). This happens because polarization forces can be introduced meaningfully only in the case where the outer electron is at a sufficiently great distance from the atomic core. For s terms the wave function does not vanish even when \( r = 0 \) [see (25.34)].

The influence of the inner electrons on the s orbits (penetrating) is due mainly to the "smearing" of the electronic cloud of the atomic core. In general, the additional energy due to the "smearing" of the electrons over the volume of the atomic core is given by

\[
\Delta E_{\text{vol}} = \int |\psi(r)|^2 V_{\text{vol}} d^3x,
\]

where \( V_{\text{vol}} \) is the difference between the potential energy produced by the electrons of the atomic core, taking into account their distribution over a finite volume, and the potential energy produced by an equivalent charge concentrated at the center.

To estimate the order of magnitude of the correction \( \delta \) for s terms, let us assume that the \( Z - 1 \) electrons of the inner shells fill uniformly a volume of radius \( R \). We then have

\[
V_{\text{vol}} = -\frac{(Z-1)e_0^2}{r} \left(1 - \frac{3}{2} \frac{r}{R} + \frac{1}{2} \frac{r^3}{R^3}\right). \tag{25.45}
\]

Replacing the wave function for the s states by its value at the origin [see (25.34)], we find the following approximate expression for the additional energy of the s terms:

\[
\Delta E_{\text{vol}} \approx -\frac{2}{5} \frac{Ze_0^2 R^2}{a_0^2 n^3} = \frac{e_0^2}{2a_0} \frac{2h}{n^2}, \tag{25.46}
\]

where

\[
\delta = \frac{2}{5} \frac{ZR^2}{a_0^2}. \tag{25.47}
\]

This expression no longer diverges.

\( ^7 \)As a rule, the correction \( \delta \) for penetrating orbits is taken into account in the following manner. It is assumed that the orbit consists of two parts: an outer part and an inner one. In the outer part of the orbit the electron is acted upon by a point charge \( e_0 Z_i \) (in alkali metals \( Z_i = 1 \)); in the inner orbit, the electron experiences the effect of point charge \( e_0 Z_i \) which should be greater than \( e_0 Z_i \) because the screening effect of the inner electrons is reduced. It is difficult to determine the charge \( Z_i \), theoretically, and it is usually regarded as an empirical parameter.

We thus obtain the following equation for \( \delta \):

\[
\delta_l = \frac{a}{a_0} Z_i \frac{1}{\sqrt{2 \frac{a}{a_0} Z_i - l(l+1)}} - \left(l + \frac{1}{2}\right), \tag{25.43}
\]

where \( a \) is the maximum distance from the nucleus to the electron in the inner ellipsoid (that is, the radius of the atomic core). It is easily shown that the quantity \( \delta_l \) decreases rapidly with increasing \( l \). A particularly good value of \( \delta_l \) is obtained for s terms.
We may note here that according to the Thomas–Fermi model, the radius of an atom [see (25.28)] is

\[ R = \frac{\gamma a}{Z^{1/4}}, \]  

(25.48)

where the coefficient \( \gamma \), which characterizes the distribution of the charge inside the atom, is of the order of unity.

Consequently, for the total energy of an electron in the case of "penetrating" s orbits, we again obtain an equation of the same form as (25.42)

\[ E_{n,l=0} = - \frac{Rh}{(n-\delta)^2} = -\frac{\epsilon_0^2}{2a_n n_{eff}^2}, \]  

(25.49)

where \( n_{eff} = n - \delta \), but now \( \delta \) is given by (25.47).

In order to analyze the difference between the corrections \( \delta \) for "penetrating" and "nonpenetrating" orbits, we shall take as an example the Li atom.

In this atom the p orbit \( (l = 1) \) is nonpenetrating. Equation (25.41) gives the value \( \delta_o \sim 0.04 \) for the lowest state \( (n = 2) \). According to (25.47), the corresponding expression for \( \delta_s \) for penetrating s orbits must be one order of magnitude greater.

It should be noted that for increasing \( n \) and \( l = \text{const} \), the eccentricity approaches unity; that is, the elliptical "orbits" become more and more elongated:

\[ \epsilon^2 = 1 - \frac{l(l+1)}{n^2}. \]  

(25.50)

In heavy nuclei, therefore, there will also be penetrating orbits with \( l = 0 \) as well as those with larger values of \( l \). This is reflected in the corrections \( \delta \) for the alkali metal spectra, whose values are given in Table 25.2.

Table 25.2

<table>
<thead>
<tr>
<th>( \nu )</th>
<th>Element</th>
<th>( \delta_s )</th>
<th>( \delta_p )</th>
<th>( \delta_d )</th>
<th>( \delta_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3</td>
<td>Li</td>
<td>0.412*</td>
<td>0.041</td>
<td>0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>11</td>
<td>Na</td>
<td>1.373*</td>
<td>0.883*</td>
<td>0.010</td>
<td>0.001</td>
</tr>
<tr>
<td>19</td>
<td>K</td>
<td>2.230*</td>
<td>1.776*</td>
<td>0.140*</td>
<td>0.007</td>
</tr>
<tr>
<td>37</td>
<td>Rb</td>
<td>3.195*</td>
<td>2.711*</td>
<td>1.233*</td>
<td>0.012</td>
</tr>
<tr>
<td>55</td>
<td>Cs</td>
<td>4.131*</td>
<td>3.649*</td>
<td>2.418*</td>
<td>0.022</td>
</tr>
</tbody>
</table>

---

*The values of \( \delta \) for penetrating orbits are indicated by an asterisk.*
It follows from Eq. (25.49) and also from the Table 25.2 that, for a given \( n \), the largest downward shift (that is, in the direction of decreasing energy) associated with the "smearing" of the inner electrons over a finite volume occurs in states with the lowest \( l \). In other words, the largest shift occurs for \( s \) terms.  

The hydrogen atom alone has no penetrating orbits. For the Li atom \((Z=3; \) that is, the next element after hydrogen in the first group of the periodic table), the only penetrating orbit is the outer \( s \) orbit. In the next alkali metal, namely, the Na atom \((Z=11)\), the \( s \) and \( p \) orbits are penetrating.

**E. FUNDAMENTAL SERIES**

The energy levels of the hydrogen atom without relativistic corrections are given by the well-known relation

\[
- \frac{E_{nl}}{\hbar} = \frac{R}{n^2}. \tag{25.51}
\]

From this we can find the values of the spectral terms

\[
(1s) = \frac{R}{1^2} = R,
\]

\[
(2s) = (2p) = \frac{R}{2^2} = \frac{R}{4}, \tag{25.52}
\]

\[
(3s) = (3p) = (3d) = \frac{R}{3^2} = \frac{R}{9}.
\]

It follows that the states of hydrogen are degenerate with respect to both \( l \) and \( m \). A schematic diagram of the energy levels in the hydrogen atom is given in Fig. 25.4.

In the Li atom, the energy levels of the \( K \) shell \((n=1)\) are filled (see Fig. 25.2), and therefore it is the \( L \) shell which is the outer one. Table 25.2 shows that the \( K \) shell exerts the strongest influence on \( s \) terms, and for the corresponding terms we have

\[
(ns) = \frac{R}{(n-0.412)^2} = \frac{R}{(n-1+0.588)^2}.
\]

This shift is so large that it was difficult to determine experimentally whether it belonged to \( n \) states or \( n-1 \) states. In order

---

9In Chapter 21, when the finite size of the nucleus was taken into account, it was also found that the largest shift occurs for \( s \) terms. In that case, however, it was the positive charge that was spread over a finite volume, and therefore the terms were shifted upwards and not downwards.
to make the term notation resemble that of hydrogen, spectroscopists have originally attributed the shift to the \( n - 1 \) state:

\[
(ns) = (n^*s) = \frac{R}{(n - \delta_s)^2} = \frac{R}{(n^* + s)^2},
\]

(25.52a)

where \( n^* = n - 1 \) and \( s = 1 - \delta_s = 0.588 \). We shall use an asterisk for the original notation \( (n^*s) \) in order to distinguish it from the correct one \( (ns) \).

![Energy-level diagram of monovalent atoms](image)

Fig. 25.4. Energy-level diagram of monovalent atoms. The potential is usually measured (in eV) from the lowest level upwards. Here, however, we wish to compare the energy levels of different atoms and, therefore, we have taken the potential at infinity as the zero level.

The shift of the other terms of lithium \((l=1, 2)\) relative to the corresponding terms of hydrogen is negligible

\[
(np) = (n^*p) = \frac{R}{(n + p)^2},
\]

\[
(nd) = (n^*d) = \frac{R}{(n + d)^2},
\]

---

10 If the principal quantum number \( n \) in lithium assumes the values \( n = 2, 3, 4 \) (the term \( n = 1 \) is occupied by two electrons and forms an inner shell), than the quantum number \( n^* \) takes the values \( n^* = 1, 2, 3 \ldots \).
where

\[ p = -\delta_p = -0.041, \]
\[ d = -\delta_d = -0.002. \]

The shell to which a shift belonged could be, therefore, uniquely determined and in the old notation the \( p, d \), and other terms were placed in shells which were later shown to be theoretically correct (that is, \( n^* = n \); see Fig. 25.4).

In the next alkali metal, Na \((Z = 11)\), the inner (filled) shells are the \( K \) and \( L \) shells (see Fig. 25.2). As can be seen from Table 25.2, the inner shells of Na have a pronounced influence on both the \( s \) terms and the \( p \) terms. The original notation which was used for the \( s \) terms was

\[
(n^*s) = (r^*_s) = \frac{R}{(n-1.375)^2} = \frac{R}{(n^* + 0.627)^2},
\]

(25.53)

where \( n^* = n - 2 \), and \( s = -\delta_s + 2 = 0.627 \). Thus, spectroscopists had originally assumed values of the principal quantum number for the \( s \) terms of sodium which were low by two units.\(^{11}\)

The original notation that was used for the \( p \) terms was

\[
(np) = (n^*p) = \frac{R}{(n-0.853)} = \frac{R}{(n^* + p)^2},
\]

(25.54)

where \( n^* = n - 1 \), \( p = 1 - \delta_p = 0.117 \). Thus, the principal quantum number for the \( p \) terms was reduced by one unit. The corrections for the states \( d, f, \ldots \) were negligible, and these terms had been assigned to the shells that were later obtained from the theory.

The energy-level diagram of Na is given in Fig. 25.4.

The spectral series of alkali metals are as follows.

1. The principal series. The variable term is the \( p \) (principal) term. The spectral frequencies in this series are given by

\[
\omega = (1s) - (n^*p),
\]

which means

\[
\text{for H:} (1s) - (np),
\]
\[
\text{for Li:} (2s) - (np),
\]
\[
\text{for Na:} (3s) - (np).
\]

\(^{11}\) At present, spectroscopists have also adopted a notation which follows from theoretical calculations. This is the notation used in Fig. 25.4.
2. The sharp series. The variable term is the \( s \) (sharp) term. The spectral frequencies are given by

\[
\omega = (2^*p) - (n^*s),
\]

which means

- for \( H: (2p) - (ns) \),
- for \( \text{Li}: (2p) - (ns) \),
- for \( \text{Na}: (3p) - (ns) \).

3. The diffuse series. The variable term is the \( d \) (diffuse) term. The spectral frequencies are given by

\[
\omega = (2^*p) - (n^*d),
\]

4. The fundamental series.

\[
\omega = (3^*d) - (n^*f).
\]

The variable term is the \( f \) (fundamental) term.

These series take into account the selection rule

\[ \Delta l = \pm 1. \]

The names of the series partly reflect the character of their multiplet structure.

F. MULTIPLET STRUCTURE OF THE SPECTRAL LINES

Just as in the hydrogen atom, the multiplet structure of the spectral lines of alkali metals is due to the spin and relativistic effects. To find the splitting of the terms, let us use a relation including both the relativistic and spin-orbit corrections for a hydrogen-like atom [see (20.18)]

\[
\frac{\Delta E_{nij}}{\hbar} = \frac{RZ^2a^2}{n^4} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right), \tag{25.59}
\]

where \( a = e^2/\hbar c = 1.137 \) is the fine-structure constant.

To account for the effect of electrons from the inner shells of alkali metals, we simply replace \( Z \) by a certain effective value \( Z_{\text{eff}} < Z \).
For "nonpenetrating" orbits, we may set $Z_{\text{eff}} = 1$, because all the $Z-1$ electrons will screen the positive charge of the nucleus. For "penetrating" orbits the best value of $Z_{\text{eff}}$ is chosen from a comparison with experiment.

For "nonpenetrating" orbits, we may set $Z_{\text{eff}} = 1$, because all the $Z-1$ electrons will screen the positive charge of the nucleus. For "penetrating" orbits the best value of $Z_{\text{eff}}$ is chosen from a comparison with experiment.

Since the total angular momentum quantum number $j$ assumes the values

$$j = \frac{1}{2} \quad \text{for } l = 0$$

and

$$j = l \pm \frac{1}{2} \quad \text{for } l \neq 0,$$

we may conclude that all spectral terms of alkali metals should be doublets, except for the $s$ term, where there is no splitting.

In order to find the magnitude of the splitting, let us calculate the value of the spectral terms for two cases: first, when the spin and the orbital angular momentum are parallel

$$- \frac{\Delta E_{j=1+1/2}}{\hbar} = \frac{R\alpha Z_{\text{eff}}}{n^4} \left( \frac{n}{l+1} - \frac{3}{4} \right); \quad (25.61)$$

and, second, when they are antiparallel

$$- \frac{\Delta E_{j=1-1/2}}{\hbar} = \frac{R\alpha Z_{\text{eff}}}{n^4} \left( \frac{n}{l} - \frac{3}{4} \right); \quad (25.62)$$
The splitting of the terms is equal to the difference between (25.62) and (25.61)\textsuperscript{12}

\[ \Delta \omega = \frac{R a^2 Z_{\text{eff}}}{n^4 (l + 1)}. \] (25.63)

We shall use this equation to explain the doublet splitting of the principal series, that is, transitions originating from the \( p \) levels. Setting \( l = 1 \) we find

\[ \Delta \omega_n = \frac{R a^2 Z_{\text{eff}}}{2n^3}. \] (25.64)

It is evident now that the decrease in splitting will be inversely proportional to the cube of the principal quantum number \( n \) (see Fig. 25.5); that is, the spectral of the main series are narrowing doublets.

In the sharp series, the initial level is a doublet and the final level (with variable \( s \)) is a singlet (see Fig. 25.5). The distance between the doublets in the sharp series is constant (equidistant doublets)

\[ \Delta \omega_2 = \Delta \omega_3 = \ldots = \Delta \omega_n = \frac{R a^2 Z_{\text{eff}}}{16}. \]

In particular, for the spectrum of Li we have \( Z_{\text{eff}} = 1 \), and \( n^* = 2 \) (the \( p \) orbit is "nonpenetrating"), so that this constant splitting is equal to

\[ \Delta \omega_2 = \frac{R a^2}{16}. \]

A diagram of the multiplet structure of the principal and sharp series of sodium (\( Z = 11 \)) is given in Fig. 25.6.

The diffuse series does not obey such an explicit law for the splitting of spectral lines. Each line will be split into three rather than four levels (see Fig. 25.7), since in this case in addition to the selection rules \( \Delta l = \pm 1 \), it is also necessary to take into

\textsuperscript{12}Several other formulas have also been proposed for the doublet splitting. For example, on the basis of the quasi-classical picture of penetrating orbits, Landé proposed a formula replacing in (25.63) \( n \) by \( n_{\text{eff}} = n - \delta \) and \( Z_{\text{eff}} \) by \( Z_a Z_{\text{i}} \), where \( Z_a \) is the total charge of the ion and \( Z_i \) is the effective charge of the nucleus in the inner region [see Eq. (25.43)] into which the orbit penetrates. For further details we refer the reader to E. Condon and G. Shortley, \textit{Theory of Atomic Spectra}, New York: Cambridge University Press, 1958.
account the selection rule for the total angular momentum quantum number

\[ \Delta j = 0, \pm 1. \]

The spectral lines of the fundamental series are also split into three components.

The multiplet splitting of the spectral lines of monovalent atoms may be explained only by taking into account the spin properties of electrons. We have already and repeatedly stated that only the half-integral quantum numbers (which characterize the spin) can lead to doublet splitting of the terms (as in the Stern-Gerlach experiments).

Fig. 25.7. Splitting of the diffuse series.
A. X-RAY SPECTRA OF ATOMS

X-ray spectra provide important information on the structure of the inner shells of atoms and are therefore useful in studying the sequence in which the shells are filled by electrons. We recall that x-rays are emitted when a beam of fast electrons strikes the plate of a cathode-ray tube (see Fig. 26.1). An analysis of the emerging x-rays shows that they consist of two different types of spectra—a continuous and a line spectrum. The continuous x-ray spectrum arises as a result of the deceleration of electrons when they strike the target. The continuous spectrum is therefore a type of bremsstrahlung. If the deceleration of electrons is equal to \( \omega (\omega < 0) \), then according to classical electrodynamics, the energy radiated by the electrons per unit time is given by the relation

\[
\frac{\partial E}{\partial t} = \frac{2}{3} \frac{e^2 \omega^2}{c^2}.
\]

A characteristic feature of the continuous spectrum is that it is cut off at short wavelengths. The wavelength \( \lambda_{\text{min}} \) at which this occurs decreases as the potential difference between the cathode and the anode increases; the cutoff wavelength \( \lambda_{\text{min}} \) can be determined from the law of conservation of energy

\[
V = h\omega + \frac{m_0 \nu^2}{2},
\]

where \( V = e_0 \Phi \) is the electron energy before colliding with the target, \( \Phi \) is the potential difference between the anode and the cathode, \( h\omega \) is the energy of the emitted bremsstrahlung photon, and \( \frac{m_0 \nu^2}{2} \) is the kinetic energy of the electron after colliding with the target.

Introducing the wavelength \( \lambda = \frac{2\pi c}{\omega} \) instead of the frequency \( \omega \), we find that

\[
\lambda = \frac{ch}{V - \frac{1}{2} m_0 \nu^2}.
\]
From the last equation it is evident that \( \lambda \) can vary from \( \lambda = \infty \) (as in the case when an electron does not lose any energy during the collision with the target, \( \frac{1}{2} m_0 v^2 = V \)) to a certain minimum value

\[
\lambda_{\text{min}} = \frac{eh}{v},
\]  

(26.1)

as in the case when an electron loses all its energy in the collision, \( \frac{m_0 v^2}{2} = 0 \).

![Schematic diagram of an x-ray tube.](image)

**Fig. 26.1.** Schematic diagram of an x-ray tube.
C — cathode; T — target.

The dependence of the radiation intensity on \( \lambda \) is plotted in Fig. 26.2 for two values of the energy of the primary electrons (25 and 50 kev). It is clearly seen that an increase in \( \Phi \) corresponds to a decrease of the cutoff wavelength \( \lambda_{\text{min}} \), in accordance with Eq. (26.1). This equation was successfully used in the determination of a more accurate value of Planck's constant \( h \) than was given by the Wien and the Stefan-Boltzmann laws (see Chapter 1).

When the energy of the electrons incident on the target exceeds a certain critical value, determined by the target material, a line spectrum, which is known as the characteristic spectrum, is superposed on the continuous spectrum. The line spectrum characterizes material of which the target is made (or rather, the structure of the inner shells of the target material) in the same way as the optical spectrum characterizes the structure of the outer shells of the atom. For example, in the case of a rhodium target, a line
spectrum begins to be superposed on the continuous spectrum at an energy of 31.8 kev.

The properties of the line spectrum are identical for all chemical compounds of a given element. The characteristic x-ray spectrum and the optical spectrum are different in this respect, since the latter depends on whether the substance occurs in atomic or molecular state (for example, the optical spectra of atomic oxygen, the \( \text{O}_2 \) molecule, and the \( \text{H}_2\text{O} \) molecule are completely different). This can be readily understood since only electrons of the outer orbits participate in chemical bonding.

The spectral lines of the characteristic x-ray spectrum form regular sequences or series, just like the optical lines of atoms. These series are designated by the capital letters \( K, L, M, N, \ldots \); the \( K \) series has the shortest wavelength, followed by the \( L \) series, and so on.

### B. CHARACTERISTIC SPECTRA OF ATOMS AND THE STRUCTURE OF THEIR INNER SHELLS

The mechanism which is responsible for the characteristic x-ray spectrum of an element was first explained by Kossel (1914). Let us suppose that an electron which is incident on a target removes an electron from, for example, the \( K \) shell of the target atom, and thus leaves a vacant site in the \( K \) shell (see Fig. 26.3). An electron may jump from the \( L, M, N, \ldots \) shells to this vacant site, giving rise to x-ray lines (denoted by \( K_\alpha, K_\beta, K_\gamma, \ldots \)). The characteristic x-ray spectrum is thus formed as a result of transitions of electrons from one inner shell to another. Since the bonding energy of electrons moving in the inner orbits is much greater than that of the outer electrons. Electrons of much greater energy (several tens of keV) are required for production of the characteristic x-ray spectrum than for the excitation of optical spectra (where several tens of ev are sufficient).

Two methods that can be used in constructing a theory of the complex atom, while taking into account the interaction of atomic electrons. In the first method the main potential is taken to be the potential of the nucleus when it is completely screened by the inner electrons. We used this method in constructing the theory of the optical spectra of alkali metals. The potential was determined...
by the nuclear charge \( (Z\varepsilon_0) \) and the charge of the electrons in the inner orbitals \(- (Z - 1)\varepsilon_0 \). The total potential was equal to

\[
\Phi = \frac{\varepsilon_0}{r} (Z - (Z - 1)) = \frac{\varepsilon_0}{r}.
\] (26.2)

As the perturbation potential we selected an additional potential which took into account the polarization and the space distribution of the electron cloud. This method is particularly suitable for outer electrons, as, for example, in atoms of alkali metals.

In studying the motion of electrons in the inner shells, it is convenient to use the potential of the nucleus

\[
\Phi = \frac{Z\varepsilon_0}{r}
\] (26.3)
as the main term in the expression for the potential, and to regard the additional potential produced by the electron shell as a correction. In this case, the presence of electron shells will result in a screening (an effective decrease) of the nuclear charge \( Z\varepsilon_0 \) by the amount \( S_n\varepsilon_0 \), and the total potential will be

\[
\Phi = \frac{(Z - S_n)\varepsilon_0}{r}.
\] (26.4)

For example, in the investigation of helium-like atoms, it was shown that the interaction of the electrons in the \( K \) shell reduces the effective nuclear charge [see (25.35)], which then becomes

\[
Z' = Z - \frac{5}{16}.
\]

Thus the quantity \( S_n \) is equal to \( \frac{5}{16} \) in this case.

The screening constant \( S_n \) must be a function of both \( n \) and \( l \). It becomes larger as \( n \) increases since there is a greater number of electrons screening the nucleus. It also becomes larger (but more slowly) as \( l \) increases, since the orbits become less and less penetrating and the effective charge decreases somewhat on the average. In the first approximation it may be assumed that the screening constant is independent of \( l \).

The potential (26.4) gives the same formula for the spectral terms as was obtained for a hydrogen-like atom, except that the quantity \( Z \) is replaced by \( Z - S_n \):

\[
E_n = -\frac{(Z - S_n)^2 R e h}{n^2}. \tag{26.5}
\]

From (26.5) we can obtain an expression for the frequency of the \( K_s \) line

\[
\omega_{K_s} = \frac{E_s - E_t}{h} = R \left[ \frac{(Z - S_1)^2}{1^2} - \frac{(Z - S_2)^2}{2^2} \right]. \tag{26.6}
\]
It follows that the frequency of the x-ray spectral lines increases monotonically as a function of the atomic number $Z$. This was first deduced by Mosley (1914), from an analysis of empirical data; he wrote this relationship in a somewhat different form

$$\omega_{K} = R(Z - S)^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right). \quad (26.7)$$

This formula can be obtained from (26.6) if it is assumed that the screening constant for $K$ and $L$ shells is the same, i.e., $S_1 = S_2 = S$. We know, however, that this is not quite correct, and, therefore, in studying x-ray spectra, just as for optical spectra, we should express the frequencies as differences of spectral terms. In accordance with (26.5), the spectral terms may be represented in the form

$$V \sqrt{\frac{T_n}{R}} = V \sqrt{\frac{E_n}{R\hbar}} = \frac{Z - S_n}{n}. \quad (26.8)$$

This relation is called Moseley's law; it is usually analyzed graphically. Ascribing different values to the principal quantum number $n$, we get (see Fig. 26.4):

- for $K$ terms ($n = 1$)
  $$V \sqrt{\frac{T_1}{R}} = \frac{Z - S_1}{1}; \quad (26.9a)$$

- for $L$ terms ($n = 2$)
  $$V \sqrt{\frac{T_2}{R}} = \frac{Z - S_2}{2}; \quad (26.9b)$$

- for $M$ terms ($n = 3$)
  $$V \sqrt{\frac{T_3}{R}} = \frac{Z - S_3}{3}. \quad (26.9c)$$

Investigations of the experimental curves $V \sqrt{\frac{T_n}{R}} \approx f(Z)$ have given the following average values for the screening constants: $S_1 = 1, S_2 = 3.5, S_3 = 10.5$. It has also been established the x-ray spectra change monotonically with increasing $Z$ and that no periodic regularities are observed. This represents a further difference between x-ray spectra and optical spectra, in which periodicity exists (see Section C).

---

1See A. Sommerfeld, Atombau und Spectrallinien I, Vieweg., Braunschweig, 1951, Chapters 4 and 5.
Thus, periodic properties appear only in valence electrons, and not in inner electrons. The study of x-ray spectra made it possible to prove definitely that the atomic number \( Z \), introduced by Mendeleyev, is determined by the charge of the nucleus, and not by its mass. It turned out that Mendeleyev had correctly arranged the elements Co—Ni, Ar—K, Te—I in a sequence which was not the same as the order in which their atomic weight increased.

There were also doubts concerning the correct sequence of the rare earths (elements from \( Z = 58 \) to \( 71 \)), whose chemical properties are very similar. Moseley's law made it possible to verify their arrangement in the periodic system. In addition, the study of x-ray spectra made it possible to determine the filling of the inner shells of the ferromagnetic metals and lanthanides, where the Moseley curve is discontinuous.

**C. MULTIPLET STRUCTURE OF X-RAY SPECTRA**

X-ray spectral terms are primarily determined by the quantum state characterized by quantum numbers \( n, l \), and \( j \), from which the electron has been removed, leaving a "hole."

As a rule, \( LS \) coupling occurs for outer electrons, whereas \( jj \) coupling occurs for inner electrons (in sufficiently heavy atoms). In the heaviest atoms \( jj \) coupling begins to play an important role for outer electrons as well.

Since the inner electrons are relatively close to the nucleus, they are mainly under the influence of the field of the nucleus, and therefore, their energy states are close to those of a hydrogen-like atom. We may, therefore, take the following formula as a starting point:

\[
E_{nj} = -\frac{Rhz^2}{n^2} - \frac{RhZ^4}{n^4} \frac{\alpha^2}{n^2} \left( \frac{n}{j + \frac{3}{4}} \right),
\]

where the fine structure constant is

\[
\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}.
\]

In order to account for the screening of neighboring electrons, we must make the substitution \( Z \rightarrow Z - S_{nl} \) in (26.10). We assume in this approximation that the screening constant depends not only on \( n \), but also on \( l \). Then for the x-ray spectra we obtain

\[
\frac{E_{nlj}}{R} = -\frac{E_{nlj}}{R} = \frac{(Z - S_{nl})^2}{n^2} + \frac{(Z - S_{nl})^4}{n^4} \left( \frac{n}{j + \frac{3}{4}} \right).
\]
Taking the approximate square root we find a generalization of Moseley's law to the case that includes relativistic and spin effects

\[ \sqrt{\frac{T_{nlj}}{R}} \approx \frac{Z - S_{nl}}{n^2} + \frac{1}{2} \frac{(Z - S_{nl})^3 a^2}{n^3} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right). \] (26.11)

This formula shows that in Moseley's curves there appears a term \( \sim Z^3 \) in addition to the term which is proportional to \( Z \). The influence of this additional term becomes marked only at large values of \( Z \). This conclusion is in agreement with experimental data.

In addition, Eq. (26.11) explains the multiplet structure of x-ray terms. We note, first of all, that there is no splitting of the \( K \) term, since only one state (\( 1s_{1/2} \)) is possible (\( n = 1, l = 0, j = 1/2 \)).

For \( L \) terms, we have three components: \( L_1 \sim 2s_{1/2} (n = 2, l = 0, j = 1/2), L_{11} \sim 2p_{1/2} (n = 2, l = 1, j = 1/2) \) and \( L_{111} \sim 2p_{3/2} (n = 2, l = 1, j = 3/2) \).

To make Eq. (26.11) agree with the experimental data for screening constants, we must set

\( S_{2s} = 3, \quad S_{2p} = 4. \)

We obtain the following equations for the corresponding terms:

\[ \sqrt{\frac{T_{2s_{1/2}}}{R}} = \frac{Z - 3}{2} + \frac{1}{16} (Z - 3)^3 \frac{5}{4} (L_1 \text{ terms}); \]

\[ \sqrt{\frac{T_{2p_{1/2}}}{R}} = \frac{Z - 4}{2} + \frac{1}{16} (Z - 4)^3 \frac{5}{4} (L_{11} \text{ terms}); \] (26.12)

\[ \sqrt{\frac{T_{2p_{3/2}}}{R}} = \frac{Z - 4}{2} + \frac{1}{16} (Z - 4)^3 \frac{1}{4} (L_{111} \text{ terms}). \]

These relations are represented graphically in Fig. 26.5.

In exactly the same way, it is easily shown that the \( M \) terms contain five components

\[ M_1 (3s_{1/2}), \quad M_{11} (3p_{1/2}), \]

\[ M_{111} (3p_{3/2}), \quad M_{11V} (3d_{3/2}), \quad M_{1V} (3d_{3/2}), \]

where the screening constants are \( S_{3s} = 8.5, \quad S_{3p} = 10, \quad S_{3d} = 13. \)

There are seven components for the \( N \) terms.

The parallel doublet \( L_1 \) and \( L_{11} \) [see (26.12)], which is due to the screening of the nucleus by the electrons is known as an irregular doublet, whereas the diverging doublet \( L_1 \) and \( L_{111} \) is known as a regular doublet. The reasons for the adoption of this terminology
go back to the first stage of the theory of multiplet splitting of x-ray spectra. It may be recalled that a theory of the fine structure was first constructed by Sommerfeld, starting with a relativistic generalization of the Bohr theory. Sommerfeld's formula gave a correct value for the splitting of the spectral terms (see Chapter 2), but neglected the spin properties. For x-ray spectra this formula is

\[ \sqrt{\frac{\mu}{R}} = \frac{(Z - S_{nn})}{n} + \frac{1}{2} \frac{(Z - S_{nn})^2}{n^3} \left( \frac{n}{n - \frac{3}{4}} \right), \]

where \( n_v = l + 1 \). Applying this equation to the analysis of the \( l \) terms, it can be shown that these terms split into only two components which correspond to the diverging doublet \( L_1 \) and \( L_{III} \) in our notation. Thus, only this doublet was explained in Sommerfeld's relativistic theory. Accordingly, it was called the regular doublet. The doublet \( L_1 \) and \( L_{II} \), for which no theoretical explanation was given for a long time, was called the irregular doublet. With the advent of the Dirac theory, the irregular doublet also found an explanation. Therefore, the reasons for the adoption of this terminology are entirely historical (just as for the "normal" and "anomalous" Zeeman effect). The correct theory of the multiplet structure of x-ray spectra (and of the anomalous Zeeman effect) was developed much later, when the spin properties of electrons were taken into account.

**D. THE DISCOVERY OF MENDELEYEV'S PERIODIC LAW**

Upon arranging the known elements in order of increasing atomic weight, Mendeleyev discovered that various chemical properties tend to recur quasi-periodically. For example, the chemical properties of sodium, potassium and other alkali metals are similar to those of lithium, and the chemical properties of chlorine, bromine, iodine and so on, are similar to those of fluorine.

Mendeleyev ascribed to each element a number \( Z \) (the atomic number) giving its position in the periodic system. Although the increase of \( Z \) is for the most part parallel to the increase of the mass number of the elements, there are several exceptions—for instance, (\( ^{37}\text{CO} - ^{36}\text{Ni} \)), (\( ^{19}\text{Ar} - ^{17}\text{K} \)), (\( ^{32}\text{Te} - ^{31}\text{I} \))—where the element with the smaller atomic number has a larger atomic weight.
Moreover, as we now know, there exists a large number of isotopes, that is, atoms having the same \( Z \), but different masses (for example, \( ^1\text{H} \), \( ^2\text{D} \), \( ^3\text{T} \)).

The periodic law has acquired particular significance in connection with recent discoveries concerning atomic and nuclear structure. In particular, the study of x-ray spectra and experiments on the scattering of \( \alpha \) particles by atoms have established that the atomic number \( Z \) characterizes the charge of the nucleus (and the number of electrons in the neutral atom).

Sixty-three elements were known when Mendeleyev discovered the periodic law (1869). He predicted the existence of ten more elements, and even described the basic chemical and physical properties of three elements which were subsequently discovered, namely, scandium (\( ^{47}\text{Sc} \)), gallium (\( ^{69}\text{Ga} \)) and germanium (\( ^{72}\text{Ge} \)). The inert (noble) gases were discovered at the end of the 19th century. In Mendeleyev's time, only three elements from the rare earth group (lanthanides) were known: cerium, didymium (a mixture of praseodymium and neodymium) and erbium. At the present time the properties of all fourteen rare-earth elements have been investigated.

By 1937, ninety-two elements were known, but four of these had not yet been observed. It was later found that these four elements were radioactive and virtually nonexistent in nature. They were produced in the laboratory as a result of nuclear reactions.

In 1937, E. Segre produced an element with \( Z = 43 \), called technetium, by neutron bombardment of molybdenum. The half-life of its most stable isotope, \( ^{43}\text{Tc}^{97} \), was found to equal \( 2.6 \times 10^6 \) years.

In 1938, it was first reported that an isotope of the last rare-earth element with \( Z = 61 \) had been produced as a result of deuteron bombardment of neodymium. The half-life of the most stable isotope of this element, \( ^{143}\text{Pm}^{143} \), is about 20 years.

In 1940, E. Segre discovered an element with \( Z = 85 \) by irradiating bismuth with \( \alpha \) particles. He called this element astatine. The half-life of its most stable isotope, \( ^{210}\text{At}^{210} \), is 8.3 hours.

A short-lived element with \( Z = 87 \), called francium, was discovered in 1939 by a Frenchwoman, Mlle. Perey. This element is produced in the \( \alpha \) decay of \( ^{236}\text{Ac}^{236} \). The half-life of its most stable isotope, \( ^{223}\text{Fr}^{223} \), is equal to 22 minutes.

And finally, we must mention that with the development of nuclear physics, it has become possible to produce transuranium elements. These range from neptunium (\( Z = 93 \)) to lawrencium (\( Z = 103 \)). Thus, the periodic system now consists of 103 elements without any intervening gaps.

---

\(^2\) The largest number of transuranium elements has been discovered by G. Seaborg and his students. The discovery of lawrencium (Lw) with \( Z = 103 \) was recently announced.
E. FILLING OF THE ELECTRON SHELLS

In quantum mechanics, the levels of the electron shells are filled in accordance with the following rules.

(a) There can be at most one electron in each quantum state (Pauli's exclusion principle), and therefore the maximum number of electrons with a given \( l \) is equal to \( 2(2l+1) \) (see Chapter 25). Thus the \( s, p, d \) and \( f \) subshells can contain no more than 2, 6, 10 and 14 electrons, respectively.

(b) Electrons tend to occupy the lowest energy levels. Therefore, the shells with \( n = 1 \) will be filled first, then those with \( n = 2, n = 3 \), and so on.

The shells would be filled in this way in an ideal scheme in which the wave function of an atomic electron could be calculated on the basis of the assumption that the charge of the nucleus and the charges of the \( Z - 1 \) electrons are all located at the center. In this case the energy levels of the remaining electron would be the same as in the hydrogen atom, and therefore they would be degenerate with respect to \( l \). As was shown in the investigation of alkali metals, however, the distribution of the electrons over a finite volume removes the \( l \) degeneracy, so that terms with a fixed value of the principal quantum number \( n \) (that is, the terms in a specific shell) are arranged in order of increasing \( l \). The \( s \) term is therefore filled first, then the \( p \) term, and finally, the \( d \) term.

Moreover, the \( 4s \) subshell is located below the \( 3d \) subshell (and \( 5s \) is below \( 4d \)), while the \( 6s \) subshell is below both the \( 5d \) subshell and the \( 4f \) subshell (similarly, \( 7s \) is below \( 5f \)). It turns out that the outer shell (in an unexcited atom) can consist only of \( s \) and \( p \) subshells. The \( d \) and \( f \) subshells can be filled when they lie in the first or second inner shell, respectively (the first inner shell is taken to be the shell directly adjacent to the outer shell)\(^3\). We shall make an attempt to substantiate this by an investigation of the ground-state configuration of the electrons in individual atoms (see Fig. 26.6).

---

\(^3\)The order in which the electron subshells are formed can be remembered most simply with the help of the following empirical rule: the levels are filled in the order in which the sum of the principal and orbital quantum numbers, \( n + l \), increases, and levels with the same value of this sum are filled in order of increasing \( n \). Since \( l \) takes the values 0, 1, 2, ..., \( n - 1 \), we can find the rule for filling the terms in any shell. For example, the fourth period (see below) will be filled in the order

\[ 4s (n + l = 4); \quad 3d (n + l = 5); \quad 4p (n + l = 5) \]

and the sixth period in the order

\[ 6s (n + l = 6); \quad 4f (n + l = 7); \quad 5d (n + l = 7); \quad 6p (n + l = 7). \]
Within the first and second periods of Mendeleyev's system, the order in which the levels are filled conforms to the sequence of levels in the hydrogen atom (the ideal scheme). If this ideal scheme were applicable to complex atoms, the 3d subshell would start to be filled beginning with potassium \((Z = 19)\). According to the table given in Chapter 25, however, \(\delta_3 = 0.146\), and \(\delta_4 = 2.23\), for potassium, and therefore the energy of the electrons in the 3d and 4s states will be

\[
E_{3d} = -\frac{R_h}{(3 - 0.146)^2} = -\frac{R_h}{2.854^2},
\]

\[
E_{4s} = -\frac{R_h}{(4 - 2.23)^2} = -\frac{R_h}{1.77^2}.
\]

It can be seen that \(E_{3d} > E_{4s}\), and hence the 4s level will be filled before the 3d level. Consequently, the third period will contain only seven elements \((11 \text{Na} - 18 \text{Ar})\), just like the second period.
After the 4s subshell is filled in Ca (Z = 20), one might expect that the filling of the subshell would begin with scandium (Z = 21). Spectroscopic data show, however, that in elements 2\text{Sc} — 2\text{Ni} the 3d subshell is filled first. This subshell becomes filled at the expense of electrons from 2\text{Cu} to 2\text{Zn} of the 4s subshell, which then must be refilled after all available states in the 3d subshell are occupied. Only after that can the refilling of the 4p subshell start. Thus the fourth period contains 18 elements and consists of the 4s, 3d and 4p subshells (see Fig. 26.6). The fifth period repeats the fourth period (the 5s, 4d, 5p subshells are filled), and thus it also contains 18 elements (2\text{Rb} — 2\text{Xe}).

The sixth period contains 32 elements (2\text{Cs} — 2\text{Rn}), because besides the outer shell, consisting of 6s and 6p states, the first inner subshell (ten electrons) and the second inner subshell 4f (the 14 electrons of the lanthanide or rare-earth elements) will be filled.

In exactly the same way the seventh period should repeat the sixth period; that is, it should contain 32 elements (the 7s, 5f, 6d, 7p subshells). So far, however, only 17 elements of this period have been discovered. The so-called actinides, in which the second inner subshell 5f is filled (2\text{TH}—element 103) should have properties similar to those of the lanthanides.

The first period therefore contains two elements, the second and third periods eight elements each, the fourth and fifth periods 18 elements each, and the sixth and seventh period 32 elements each (except that the seventh period is incomplete). The order in which the states are filled is illustrated in Fig. 26.6.

F. APPLICATION OF THE THOMAS-FERMI METHOD TO THE THEORY OF THE PERIODIC SYSTEM OF ELEMENTS

We shall now attempt to treat the ground-state configuration of the elements more rigorously.

In a paper devoted to the statistical theory of the atom (1928), Fermi proposed a method, now known as the Thomas-Fermi method (see Chapter 25), to explain the periodic system of elements. With this method, he obtained the minimum values of Z for which s, p, d and f states are filled in atoms. He obtained these values by starting from the following quasi-classical ideas.

In classical theory the angular momentum of a particle \( L \) is related to the momentum \( p \) by the expression

\[
\vec{L} = \vec{r} \times \vec{p}.
\]

Consequently,

\[
p^z_n = \frac{L^2}{r^2},
\]

where \( p_n \) is the component of momentum perpendicular to the position vector \( r \).

Obviously, the square \( p^z_n \) of this component of momentum cannot be greater than the square of the maximum momentum, which we shall denote by \( P \). Therefore for a given \( P \) and \( r \) the possible values of the angular momentum \( L \) must satisfy the inequality

\[
P^2 > \frac{L^2}{r^2}.
\] (26.14)
It was shown in Chapter 13 that, in the quasi-classical treatment of the atom, the square of the angular momentum must be [see (13.62)]

\[ L^2 = \hbar^2 \left( l + \frac{1}{2} \right)^2. \]  

(26.15)

This relation represents a compromise between the Bohr relation \( L_B^2 = \hbar^2 (l + 1)^2 \) and the quantum mechanical relation \( L^2 = \hbar^2 (l + 1) \).

The maximum momentum \( P \) is related to the density of the electron gas (electrons in the atom) \( p_0 \) by the expression (6.32)

\[ P^2 = \hbar^2 (3 \pi^2 p_0)^{2/3}. \]  

(26.16)

The electron density \( p_0 \) may be found from the Thomas-Fermi equation (see Chapter 25), which, as we have already indicated, can be solved only by approximate or numerical methods. A good approximation for \( p_0 \), as follows from a solution of the Thomas-Fermi equation, is provided by the expression [see (25.21)]

\[ p_0 = \frac{Z^{4/3}}{16 \pi r^{3/2}} e^{-V/\lambda r}, \]  

(26.17)

where the coefficient \( \lambda \) is found by the Ritz variational method.

Substituting these values for \( P^2 \) and \( L^2 \) into the inequality (26.14), we get

\[ \left( \frac{3 \pi Z^{4/3}}{16} \right) \frac{\lambda}{r} e^{- \frac{2}{3} V / \lambda r} \geq \frac{(l + \frac{1}{2})^3}{r^2}. \]  

(26.18)

Introducing the new variable \( \lambda r = x \), we find

\[ e^{- \frac{2}{3} V / x} > \frac{D}{x}, \]  

(26.19)

where

\[ D = \left( l + \frac{1}{2} \right)^2 \left( \frac{16}{3 \pi Z} \right)^{4/3}. \]  

(26.20)

From the inequality (26.19) it is evident that the right-hand side of (26.19) becomes greater than the left-hand side as \( x \to 0 \) \((r \to 0)\) and as \( x \to \infty \). The electrons in the atom therefore can have a given value of \( l \) if \( x \) lies in the range \( x_1 < x < x_2 \) for which the inequality (26.19) is satisfied. Here \( x_1 \) and \( x_2 \) are roots of the equation

\[ e^{- \frac{2}{3} V / x} = \frac{D}{x}. \]  

(26.21)

The condition for the appearance of states with a given value of \( l \) is the equality of both roots

\[ x_1 = x_2. \]

In this case we should equate not only the two functions themselves, but also their derivatives. Then, in addition to Eq. (26.21), we will have

\[ \frac{1}{3} \sqrt[3]{V_x} e^{- \frac{2}{3} V / x} = \frac{D}{x^2}. \]  

(26.22)
These two relations will be satisfied for

$$\sqrt{x} = 3,$$

that is, when

$$D = 9e^{-2}.$$

Substituting the value for $D$ from (26.20), we find the value of $Z$ at which electrons with a given $l$ will first appear

$$Z = \frac{2e^{2}}{81\pi} (2l + 1)^{2} = \gamma (2l + 1)^{2},$$

(26.23)

where $e = 2.718\ldots$ is the base of the natural logarithms and the coefficient $\gamma$ is equal to 0.158.

A numerical solution of the Thomas-Fermi equation gives a very similar value for $\gamma$

$$\gamma_{T-F} = 0.155.$$

This again is a convincing demonstration that the density (26.17) represents a good approximation to the density which is given by a numerical solution of the Thomas-Fermi equation.

Equation (26.23) enables us to calculate the $Z$ values at which the $s, p, d,$ and $f$ states begin to be filled. The results of this calculation are given in Table 26.1. The first row gives fractional values of $Z$ computed from formula (26.23) with $\gamma_{T-F} = 0.155$. The values of $Z$, calculated with $\gamma_{T-F} = 0.158$, for which $s, p, d,$ and $f$ states first appear are practically identical with those calculated with $\gamma_{T-F} = 0.155$. The second row gives the nearest greater integral value of $Z$. The last row of the table gives the empirical values of $Z$ at which the states first appear, and also the symbol of the corresponding elements.

**Table 26.1**

<table>
<thead>
<tr>
<th>$l$</th>
<th>$s$</th>
<th>$p$</th>
<th>$d$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical value (Thomas-Fermi)</td>
<td>$Z$</td>
<td>$0.15$</td>
<td>$4.2$</td>
<td>$19.4$</td>
</tr>
<tr>
<td>Empirical value</td>
<td>$Z$</td>
<td>$1$ (H)</td>
<td>$5$ (B)</td>
<td>$21$ (Sc)</td>
</tr>
</tbody>
</table>

From this table it can be seen that this approximate theory is in good agreement with the experimental data. We may note that complete agreement is obtained if the coefficient $\gamma$ is taken to be 0.169 instead of 0.155.

It is well known that in light elements ($Z = 1, 2, 3, 4$) only $s$ states are filled. The filling of the $p$ states begins with boron ($Z = 5$); this is in complete agreement with theoretical data. Table 26.1 shows (in spite of the crudeness of the statistical model) that the filling of the $3d$ subshell does not begin, as might be expected, in potassium ($Z = 19$), but in scandium ($Z = 21$); that is to say, it does not begin until the $4s$ subshell is completely filled. Similarly, the Thomas-Fermi model explains the "delay" in the filling of the $4f$ subshell, which might be expected to begin in Ag ($Z = 47$). According to the theory, however, the filling of the $4f$ subshell should be shifted, and should begin only in cerium ($Z = 58$). It follows from (26.3) that the filling of the $5g$ subshell ($l = 4$) would begin in the element with $Z = 124$.

The Thomas-Fermi model accounts for a very important feature of the ground-state configuration of atoms and explains the departure of the filling of the levels from the ideal scheme (the hydrogen scheme) in terms of the "smearing" of the electron cloud.
G. PERIODICITY IN THE PROPERTIES OF ELEMENTS

The periodicity in the properties of the elements can be explained quite naturally in quantum mechanics. It is connected with the periodic nature of the filling of the outer shell, which contains at most eight electrons (s and p states) and which determines the chemical and optical properties of atoms. All elements, therefore, can be divided into eight groups, depending on the number of electrons in the outer shell.

The elements in Group I (hydrogen and alkali metals) have an outer shell containing a single electron. As a result, the optical terms (except the s term) are doublets and the elements are monovalent, as will be shown below. The elements of Group II—the alkaline earth metals (beryllium, magnesium, calcium, etc.)—have two valence electrons; their spectral terms must therefore be singlets and triplets, and the valence is equal to two. The elements of Group III have an outer shell containing three electrons, and therefore the maximum splitting of their optical terms must be equal to four (quartets); their maximum valence is three.

On the contrary, the elements of Group VII—the halogens (fluorine, chlorine, etc.)—lack just one electron to fill the outer shell completely. Therefore, in addition to the maximum (positive) valence of seven, they may have a negative valence of \(-1\) (the number of electrons required to obtain a stable configuration). They exhibit this valence in the so-called ionic compounds (see Chapter 27).

Finally, in the inert gas group (neon, argon, krypton, etc.) the outer shell is completely filled. We may even say that there is no outer shell in these elements, because the energy bonding these electrons in the outer shell is larger than that bonding all other shells in the molecule and thus it would be more correct to ascribe it to the inner shell. Thus, these elements may be assigned to the “zeroth” group. The elements of the zeroth group do not as a rule enter into any chemical reactions, and thus these elements are said to be chemically inactive.

There are, however, a number of exceptions to the rule that there are eight elements in each period. The first exception is constituted by hydrogen \((Z = 1)\) and helium \((Z = 2)\), which form the first period. In this period there are only two elements, and not eight. This is due to the fact that the K shell does not include p states. Consequently, the properties of these elements are of a dual nature. Because there is only one electron in the outer shell, hydrogen should have the same chemical and optical properties as the alkali metals. Indeed, just like in these elements, the maximum splitting of the spectral terms of hydrogen is two, and its valence is one. Hydrogen, however, also resembles the halogen group in that it lacks just one electron for a complete outer shell, and it can
therefore acquire a second electron forming, in the same way as the halogens, a negatively charged ion.

Helium resembles the alkaline earth metals of the second group in that it also has two electrons in the outer shell. The spectral terms of both helium and the alkaline earth elements are either singlets (spin 0), or triplets (spin 1). However, in its chemical properties, helium is a typical representative of the inert gases, because its outer K shell is completely filled; hence it does not participate in normal chemical reactions.

The maximum valence of elements is determined, as a rule, by the number of electrons in the outer shell; that is, the valence of atoms varies from unity (for atoms of the first group) to seven (halogen group). There are, however, certain exceptions among the elements in which the inner shells are filled after the outer shells.

It can be seen from the periodic table that there will be two electrons in the outer shell of all elements from scandium (Z = 21) to nickel (Z = 28), with the exception of chromium, where there is only one. Owing to transitions of electrons from 3d states to 4p states, however, the maximum valence of scandium (Z = 21) is equal to three, and that of manganese (Z = 25) is equal to seven. Consequently, it was necessary to place these elements in groups corresponding to their maximum valences (this was correctly done by Mendeleyev). Mendeleyev placed iron (Z = 26), cobalt (Z = 27) and nickel (Z = 28) in a special group (Group VIII). The introduction of this group is justified from the point of view of modern quantum mechanics, since at most eight electrons can occupy the outer shell. In general, however, iron behaves either as a bivalent or trivalent element. All of these elements have similar properties. In particular, they have distinctive ferromagnetic properties caused by uncompensated spins of the 3d electrons in the inner shell. The presence of these states is due to the fact that from the energy standpoint, the 3d state is more favorable during formation of the crystal lattice than the other states in which the spins of the electrons can be compensated.

In the elements following the ferromagnetic, the 3d subshell is the first to be completely filled; the filling of the levels then continues in the 4s and then the 4p subshells. Krypton completes the structure of the M shell (n = 4); therefore its optical and chemical properties will be characteristic of the inert gases.

As we have already mentioned, the fifth period, which extends from the alkali metal rubidium (Z = 37) to the inert gas xenon (Z = 54), is a repetition of the fourth period and exhibits no new features.
Quantum theory also explains the characteristic properties of the elements in the lanthanide series (the rare-earth elements), which comes immediately after lanthanum and extends from cerium \((Z = 58)\) to lutetium \((Z = 71)\). The elements in this series are formed by consecutive addition of electrons to the deeper 4f subshell (the second inner \(N\) shell), even though the first inner shell \((\text{O})\) and the outer shell \((P)\) are still incompletely filled. Since the chemical properties are determined mainly by the electrons of the outer shells, all 14 rare-earth elements are much closer with regard to chemical properties than are the elements in which the first inner \(d\) subshell is filled.

For a long time hafnium \((Z = 72)\) was also included in the lanthanide series. A theoretical analysis performed by Bohr showed, however, that there can be at most fourteen elements in this group (the possible number of \(f\)-states) and that, therefore, hafnium must be a chemical analog of zirconium. Careful experiments have confirmed this theoretical conclusion.

The actinide series in the seventh and last period is analogous to the lanthanide group. Beginning with thorium \((Z = 90)\), the elements of this series are formed by the consecutive addition of electrons to the deep-lying 5f subshell of the \(O\) shell, while the 6s, 6p and 7s subshells remain completely filled and the 6d subshell is partially filled. The actinides include protactinium \((Z = 91)\), uranium \((Z = 92)\) and also the following artificially produced transuranium elements: neptunium \((Z = 93)\), plutonium \((Z = 94)\), americium \((Z = 95)\), curium \((Z = 97)\), californium \((Z = 98)\), einsteinium \((Z = 99)\), fermium \((Z = 100)\), mendelevium \((Z = 101)\), nobelium \((Z = 102)\) and the recently discovered element 103 (lawrencium).

The question of how many elements can be produced by artificial means and experimentally detected, and the question of where the periodic system ends, have not yet been finally answered. It is clear, however, that the periodic system ends because of the instability of nuclei (due mainly to their spontaneous fission).

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Chapter 27

The Theory of Simple Molecules

A. BASIC FORMS OF THE CHEMICAL BOND

The chemical properties and the optical spectrum of an element are determined mainly by the outer electrons of the atom. Therefore, the regularities in the structure of the outer shell, which account for the optical periodicities, also provide a basis for the construction of a theory of the periodically recurrent chemical properties of the elements. It should be noted that the chemical properties, unlike the optical properties, are not exhibited by isolated atoms, but appear only in the presence of other atoms, with which the atom forms chemical compounds.

The inner electrons have almost no influence on chemical processes, since they are much more strongly bound to the nucleus than the outer electrons. Chemical reactions therefore liberate much less bonding than the energy of the inner electrons.

In discussing the chemical properties of an atom, we must distinguish between two main types of chemical bonds: ionic (or heteropolar) and atomic (or homopolar). We shall consider both of these types in greater detail.

B. HETEROPOLAR MOLECULES

Inorganic salts consist of positive and negative ions held together by an electrostatic (Coulomb) attraction to form a molecule. Compounds of this type are called ionic, and their molecules are said to be heteropolar. The ions may be either positive or negative. The sign of the charge on the ion depends, on the one hand, upon the ionization potential, that is, the energy that must be expended in order to remove an electron from the outer shell; and, on the other hand, on the electron affinity, that is, the energy which the atom must acquire to hold an additional electron in the outer shell.

Let us assume that a neutral atom with atomic number $Z$ contains $N$ electrons in the inner orbitals and $Z_0 = Z - N$ electrons in the outer orbitals. The electrons in the inner orbitals
will completely screen a corresponding fraction of the nuclear charge, but will do so only in the region outside this inner shell (starting at the outer shell). Thus, the Coulomb potential energy holding the electrons in the outer shell is

\[ V = -\frac{Z_a e_0}{r}. \]

However, inside the atomic core the charge will be \( Z_i > Z_a \); that is, the screening of the nuclear charge will not be complete (see Chapter 25). In exactly the same way, the outer electrons will completely screen the remaining part of the nuclear charge \( (Z_a e_0) \) only in the region outside the outer shell (that is, only in the case of excited states). While in this case there appear polarization forces proportional to \( r^{-3} \), they are not able to hold an additional electron. In the outer shell itself the charge will be incompletely compensated; for this reason (but provided there are unfilled states in the outer shell), the incompletely screened part of the nuclear charge will hold additional electrons in this shell, thus forming a negative ion. The rule is that the less electrons there are in the outer shell of a neutral atom, the larger the total screening of the nuclear charge in this shell. Therefore, an alkali metal will lose the one electron in its outer shell more readily than it will acquire additional electrons.

A curve showing the dependence of the ionization potential on \( Z \) is plotted in Fig. 27.1. It shows a minimum for alkali metals and a maximum for inert gases. This curve reproduces rather faithfully the periodicity exhibited by the number of electrons in the outer shell.

In inert gases the ionization potential reaches its largest value; the removal of an electron from the outer shell and its transfer to another atom require a very large expenditure of energy. In addition, no further electrons can be held in the outer shell, which is completely filled. Therefore, inert gases do not participate in ordinary heteropolar compounds (we shall also see that they do not form homopolar bonds), and hence, as a rule, they exist as unassociated atoms.

Atoms of alkali and alkaline earth metals readily give up their valence electrons to another atom (the ionization potential is at

1For example, in sodium \((Z = 11)\), the ten electrons in the inner shell completely screen ten units of nuclear charge, which leaves only the eleventh unit of nuclear charge to be (partially) screened by the outer electron. In chlorine \((Z = 17)\) the ten inner electrons completely screen only ten units of nuclear charge, so that the seven electrons of the outer shell must screen the remaining charge, which they can accomplish only partially. Therefore, a chlorine atom is able to hold an additional electron more easily than sodium, and is thus converted into the negative ion \( \text{Cl}^- \). On the other hand, a sodium atom gives up its outer electron more readily, and in this way forms a positive ion \( \text{Na}^+ \).
its minimum here), and thus convert to positive ions (for example, a Na⁺ ion).

On the contrary, atoms in Group VI (including oxygen) and in Group VII (halogens), and also hydrogen (which resembles Group VII with regard to the number of missing electrons), have a higher electron affinity than the other elements (see Table 27.1). The electron affinity of sodium is practically equal to zero, like that of inert gases.

**Table 27.1**

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron affinity (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.71</td>
</tr>
<tr>
<td>F</td>
<td>4.13</td>
</tr>
<tr>
<td>Cl</td>
<td>3.72</td>
</tr>
<tr>
<td>O</td>
<td>3.07</td>
</tr>
</tbody>
</table>

The first successful attempt to construct a theory of the ionic bond was due to Kossel (1916), who made use of the Bohr theory of the atom.

Kossel's theory was based on the fact that the eight-electron shells of the inert gases are closed, so that these atoms have zero valence. Positive valence (or valence with respect to hydrogen) is determined by the number of electrons in the outer shell in atoms in which these electrons are readily lost (atoms of Groups I or II). Negative valence (valence with respect to fluorine or twice the valence with respect to oxygen) is determined by the number of electrons which the atom can acquire, that is, the number of vacant states in the outer shell (see Chapter 26).
Negative valence is particularly pronounced in elements of Group VI and VII, although both types of valence may be exhibited by a given element. For example, in the typical heteropolar compound HCl, chlorine has a valence of -1, although other compounds in which chlorine has a valence of -1. An example is Cl₂O₇. We do not intend here to develop a complete theory of the chemical bond, and shall restrict ourselves to the examination of one typical ionic molecule, namely, the heteropolar molecule NaCl.² The energy bonding an outer electron in the atomic sodium is 5.1 ev.³ When the valence electron of sodium is transferred to the outer shell of the chlorine (that is, upon formation of Na⁺ and Cl⁻ ions), it carries somewhat less bonding since its affinity for chlorine (F⁻Cl = 3.7 ev) is somewhat lower than the ionization energy of sodium (F⁺Na = 5.1 ev). However, in the formation of the molecule, this deficiency is compensated by the Coulomb energy of attraction between Na⁺ and Cl⁻ ions.

The total energy bonding these atoms in the NaCl molecule is given by the expression

$$\Delta U_{\text{NaCl}} = U^\text{Com} - U^\text{Coul} - U^\text{aff} - U^\text{ion}.$$

This energy has been very carefully determined from experiment and found to be equal to: ΔU\text{NaCl} = 4.2 ev. Hence for the Coulomb energy:


³The binding energy of an electron in an atom (or molecule) is equal to the energy that must be expended in order to remove an electron. It is, therefore, equal to the negative of the energy holding the electron in the compound (W = -V); that is, it will be a positive quantity.
bonding energy between the ions we find

\[ W_{\text{Coul}}^{\text{eff}} = W_{\text{Na}}^{\text{ion}} + W_{\text{NaCl}}^{\text{bond}} = 5.6 \text{ ev}; \]

Since \( W_{\text{Coul}}^{\text{eff}} = -\frac{e^2}{R} \), we obtain a perfectly reasonable value for the interatomic distance in the NaCl molecule: \( R = 2.5 \times 10^{-8} \text{ cm.} \)

![Diagram](image)

Fig. 27.3. The formation of an NaCl molecule from Na\(^+\) and Cl\(^-\) ions. The ionization potential of sodium (5.1 ev) and the affinity of the chlorine atom for an electron (3.7 ev) are indicated in parentheses. The Coulomb bonding energy between the ions in the molecule is 5.6 ev.

It should be noted that we have not considered here all the interactions that occur in a heteropolar molecule. In addition to the Coulomb forces of attraction, there will also be repulsive forces; these exceed the Coulomb forces at small distances and prevent the two atoms from approaching closer than the distance \( R \). In any case, this elementary discussion explains the principal physical processes involved in the formation of heteropolar molecules; it also explains, however qualitatively, the ionic structure of their crystal lattice and the dissociation of these molecules into individual ions, a process which occurs in solutions.

C. THE MOLECULAR HYDROGEN ION

Aside from ionic compounds, there exist molecules formed directly from the neutral atoms, rather than from ions. The simplest representatives of these molecules are H\(_2\), O\(_2\) and N\(_2\). These are called homopolar molecules.

The formation of homopolar molecules cannot be explained on the basis of classical theory or Bohr's semiclassical theory. These theories are useful only for compounds held together by electrostatic forces such as, for example, ionic compounds. Before discussing the formation of homopolar molecules, let us
consider a very simple case, namely, the molecular hydrogen ion \( \text{H}^+ \), which consists of two hydrogen nuclei and a single electron. This analysis is important for methodological reasons, because it enables us to express in comparatively simple mathematical form the features of the bond that arises between two hydrogen nuclei owing to the exchange of an electron (exchange forces). The same forces also appear in the homopolar hydrogen molecule \( \text{H}_2 \).

Let us denote the distance between the two hydrogen nuclei \( a \) and \( a' \) by \( R \) and assume that \( R \) changes adiabatically; that is, \( R \) changes so slowly that it can be regarded as a constant in solving the Schrödinger equation. In a more exact treatment, it is necessary to take into account the vibrations of the nuclei about the equilibrium position (the vibrational spectrum), and the rotation of the nuclei about the center of mass (the rotational spectrum). These questions have been treated in detail in Chapter 12.

Suppose \( r \) and \( r' \) represent the distances between the electron and the nuclei \( a \) and \( a' \), respectively. The Schrödinger equation for the ionized hydrogen molecule can then be written as

\[
(E - H) \psi = 0.
\]  

(27.1)

Here the Hamiltonian is

\[
H = T - \frac{e^2_a}{r} - \frac{e^2_a}{r'} + \frac{e^2_e}{R},
\]  

(27.2)

and the kinetic energy operator has the form

\[
T = \frac{1}{2m_e} \left( \frac{\hbar}{i} \nabla \right)^2 = \frac{1}{2m_e} \left( \frac{\hbar}{i} \nabla' \right)^2,
\]  

(27.3)

where \( \nabla \equiv \nabla \) (\( \nabla \equiv \frac{\partial}{\partial x} \)), \( \nabla' \equiv \frac{\partial}{\partial x'} \) since

\[
r' = r - R,
\]  

(27.4)

and \( R \) may be regarded as a constant in the problem under consideration.

We shall restrict ourselves to an investigation of the ground state, and carry out our calculations with the help of perturbation theory. The spin effects can be neglected in the case of a single electron.

In the zeroth approximation we assume that the electron is under the influence of either nucleus \( a \) or nucleus \( a' \) (see Fig. 27.4). The Schrödinger equations describing these two possible unperturbed states are

\[
(E_a - T + \frac{e^2_e}{r}) \psi_a = 0,
\]  

(27.5)

\[
(E_{a'} - T + \frac{e^2_e}{r'}) \psi_{a'} = 0.
\]
Both eigenvalues and eigenfunctions are identical and correspond to the 1s state of the hydrogen atom. Since one of the wave functions is associated with nucleus $a$, and the other with nucleus $a'$, we may write ($n=1$, $l=m=0$)

$$E_a = E_{a'} = E_1 = - Rh,$$
$$\psi_a = \psi_{100}(r), \quad \psi_{a'} = \psi_{100}(r').$$  

(27.6)

where $\psi_{nlm} = \psi_{100}$ is the wave function of the ground state of the hydrogen atom [see (13.32)], namely,

$$\psi_{100}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}. $$  

(27.7)

The total energy of the system and the zero-order eigenfunction are as follows:

$$E^0 = E_1 = - Rh,$$
$$\psi^0 = C_1 \psi_a + C_2 \psi_{a'}. $$

(27.8)

The uncertainty in $\psi^0$ is due to the fact that the presence of two nuclei leads to a degenerate state of the system. In solving (27.1) by perturbation theory, we must set

$$E = E^0 + E' + \ldots,$$
$$\psi = \psi^0 + \psi' + \ldots$$

(27.9)

Substituting (27.9) into (27.1) and restricting ourselves to the first-order quantities, we find

$$\left(E^0 - T + \frac{e_a^2}{r} + \frac{e_{a'}^2}{r'}\right) \psi' = - C_1 \left(E' + \frac{e_a^2}{r'} - \frac{e_{a'}^2}{R} \right) \psi_a - $$
$$- C_2 \left(E' + \frac{e_a^2}{r} - \frac{e_{a'}^2}{R} \right) \psi_{a'}. $$

(27.10)

For the solution $\psi_a$ (the electron near nucleus $a$), $-\frac{e_a^2}{r}$ represents the main interaction, and $-\frac{e_{a'}^2}{r'}$ the perturbation. On the contrary, for the solution $\psi_{a'}$ (the electron near $a'$), the main interaction is $-\frac{e_a^2}{r}$, and the perturbation is $-\frac{e_{a'}^2}{r'}$.

From Eq. (27.10) we can find the additional energy $E'$, and also a relationship between the coefficients $C_1$ and $C_2$ in the wave function $\psi^0$. This can be done because the perturbation energy removes the degeneracy (just as in the case of the helium atom).
To solve this problem, we can make use of the theorem which states that the solution of the homogeneous equation (that is, one of the solutions of Eqs. (27.5)) must be orthogonal to the right-hand side of the same equation, that is, Eq. (27.10). Assuming that the electron is near the nucleus \( a \), we can neglect the perturbation energy \( \frac{e^2}{r^2} \) on the left-hand side of the equation, since it gives us a second-order term when multiplied by \( \psi' \). Then the solution of the homogeneous equation will be the function \( \psi_a \) and according to the theorem we have just stated, it must be orthogonal to the right-hand side of Eq. (27.10)

\[
C_1 \int \psi_a \left( E' + \frac{e^2}{r^2} - \frac{e^2}{R} \right) \psi_a \, d^3x + C_2 \int \psi_a \left( E' + \frac{e^2}{r^2} - \frac{e^2}{R} \right) \psi_a \, d^3x = 0. \tag{27.11}
\]

Here we have used the fact that the wave function \( \psi_a \) of the ground state of the hydrogen atom is real.

In exactly the same way, assuming that the electron is near the nucleus \( a' \), we may neglect the perturbation energy on the left-hand side of Eq. (27.10) (in this case the perturbation energy is \( \frac{e^2}{r} \)). Since the solution of the homogeneous equation will now be the function \( \psi_a' \), we obtain a second equation for the unknown quantities

\[
C_1 \int \psi_a' \left( E' + \frac{e^2}{r^2} - \frac{e^2}{R} \right) \psi_a \, d^3x +
-C_2 \int \psi_a' \left( E' + \frac{e^2}{r^2} - \frac{e^2}{R} \right) \psi_a \, d^3x = 0. \tag{27.12}
\]

When \( r \) is replaced by \( r' \), \( \psi_a \) becomes \( \psi_a' \), whereas in the reverse substitution \( \psi_a' \) becomes \( \psi_a \). In both cases, the volume element \( d^3x \) remains unchanged \( (d^3x = d^3x') \). Therefore, we can reduce (27.12) to a form that is in agreement with (27.11), but with the coefficients \( C_1 \) and \( C_2 \) interchanged

\[
C_2 \int \psi_a \left( E' + \frac{e^2}{r^2} - \frac{e^2}{R} \right) \psi_a \, d^3x +
-C_1 \int \psi_a' \left( E' + \frac{e^2}{r^2} - \frac{e^2}{R} \right) \psi_a \, d^3x = 0. \tag{27.13}
\]

In further transforming Eq. (27.11), we must not forget that the function \( \psi_a \) is normalized to unity

\[
\int \psi_a^2 \, d^3x = 1, \tag{27.14}
\]

but is not orthogonal to the function \( \psi_a' \)

\[
\int \psi_a \psi_{a'} \, d^3x = S(R). \tag{27.15}
\]
This follows from the fact that, although the expression \( S(R) \) vanishes for \( R \to \infty \) (there will be no points where the two functions \( \psi_a \) and \( \psi_a' \), both differ from zero), it becomes equal to unity for \( R = 0 \) (\( \psi_a = \psi_a' \)).

Let us introduce the notation

\[
K = \int \psi_a \left( \frac{\psi_a}{R} - \frac{\psi_a'}{r} \right) d^3x
\]

and

\[
A = \int \psi_a \psi_a' \left( \frac{\psi_a}{R} - \frac{\psi_a'}{r} \right) d^3x,
\]

where \( K \) is the Coulomb energy of interaction between the hydrogen atom and the (atomic) hydrogen ion, and \( A \) is the exchange energy, which has no classical analog. This energy arises because the electron can be in both states \( \psi_a \) and \( \psi_a' \), simultaneously (that is, exchange occurs between states \( a \) and \( a' \)). Formally, the existence of the exchange energy is reflected in the fact that the expression for \( \psi \) contains \( \psi_a' \), as well as \( \psi_a \). As we shall see in what follows, it is this exchange energy which gives rise to an attractive force between the nuclei. At certain values of the internuclear separation, this force exceeds the force of repulsion, and as a result the \( \text{H}_2^+ \) molecular hydrogen ion is formed. It is worth noting that this mixed state cannot arise in the Bohr theory, and therefore the existence of an ionized hydrogen molecule can be explained only in terms of quantum mechanics.

With the help of (27.14)-(27.16), we can reduce Eqs. (27.11) and (27.13) to the form

\[
C_1 (E' - K) + C_2 (E'S - A) = 0,
\]
\[
C_1 (E'S - A) + C_2 (E' - K) = 0,
\]

obtaining two solutions: a symmetric one \((C_1 = C_2)\) and an antisymmetric one \((C_1 = -C_2)\). The symmetric solution is

\[
\psi_s = \frac{1}{V^2(1+S)} (\psi_a + \psi_a'),
\]
\[
E's = V^s (R) = K + \frac{A - SK}{1 + S},
\]

and the antisymmetric solution is

\[
\psi_a = \frac{1}{V^2(1-S)} (\psi_a - \psi_a'),
\]
\[
E'a = V^a (R) = K - \frac{A - SK}{1 - S}.
\]
The factor \( \frac{1}{\sqrt{2(1 \pm S)}} \) is the normalization coefficient. We may note here that the symmetric and antisymmetric solutions are already mutually orthogonal

\[
\int \psi^2 \psi^S \, d^3x = 0.
\]

The quantity \( E' \) may be regarded as an additional interaction \( V(R) \), which binds the \( H \) atom and the \( H^+ \) ion into a stable hydrogen molecule. In order to find the specific form of this interaction as a function of \( R \), we must calculate the values of \( S \), \( K \) and \( A \). For this purpose we use the well-known expansion of the function \( \frac{e^{- \kappa r}}{r} \) into a triple Fourier integral

\[
\frac{e^{- \kappa r}}{r} = \frac{1}{2\pi^2} \int \frac{e^{ikr} \, d^3k}{k^2 + k_0^2}.
\] (27.20)

After differentiating this expression with respect to the parameter \( k_0 \), we can easily write the wave function for the ground state of the hydrogen atom in the form of a Fourier integral

\[
\psi_{100}(r) = \frac{1}{\sqrt{\pi a_0^3}} \, e^{-\frac{r}{a_0}} \, \left( \frac{k_0}{\pi} \right)^{1/4} \int \frac{e^{ikr} \, d^3k}{(k^2 + k_0^2)^3}
\] (27.21)

where \( k_0 = \frac{1}{a_0} \).

In accordance with (27.15), the expression for \( S \) becomes

\[
S = \int \psi_{100}(r) \psi_{100}(r-R) \, d^3x.
\] (27.22)

We may replace \( \psi_{100}(r) \) and \( \psi_{100}(r-R) \) by their expressions in terms of the Fourier integral (27.21). Integrating with respect to volume, we obtain

\[
\int e^{i(k' - k) \cdot r} \, d^3x = 8\pi^3 \delta(k + k'),
\] (27.23)

and thus we find the following value for \( S \):

\[
S = \frac{8k_0^3}{\pi^2} \int \frac{e^{i \kappa R} \, d^3k}{(k^2 + k_0^2)^3} = \left( 1 + \frac{R}{a_0} \left( \frac{R}{a_0} \right)^2 \right) e^{- \frac{R}{a_0}}.
\] (27.24)
The integral in this equation can be calculated with the aid of Eq. (27.20), which should be differentiated three times with respect to the parameter \( k_0^4 \).

In order to calculate the additional Coulomb interaction, we shall use the relation

\[
\psi_{100}(r) = \frac{1}{\pi a_0^3} e^{-2r/a_0} = \frac{k_0^4}{8\pi^3} \int \frac{e^{i br}}{(k^2 + k_0^2)^{3/2}} d^3k,
\]

where we must set \( k_0 = \frac{2}{a_0} \). Then, putting \( k_0 = 0 \) in (27.20), we obtain

\[
\frac{1}{|R - r|} = \frac{1}{2\pi^3} \int \frac{e^{i \varphi (R - r)}}{k^2 + k_0^2} d^3k. \tag{27.25}
\]

In exactly the same way, we may represent the quantity \( 1/R \) in the form of the integral (27.25). Substituting these quantities into formula (27.16) and integrating over the volume \( d^3x \) with aid of (27.23), we find

\[
K = \frac{e^4}{2\pi^3} \int d^3k e^{i k x} \left( \frac{1}{k_0^2 + k^2} \right), \tag{27.26}
\]

Hence, using (27.20) and setting \( k_0 = \frac{2}{a_0} \), we obtain an expression for the additional Coulomb energy

\[
K = \frac{e^4}{R} e^{-R/a_0} \left( 1 + \frac{R}{a_0} \right). \tag{27.27}
\]

In calculating the exchange interaction

\[
A = \frac{e^4}{R} S - e^4 \int \frac{\psi_{100}(r)}{r} \psi_{100}(r - R) d^3x \tag{27.28}
\]

we may use (27.21) for \( \psi_{100}(r - R) \) and (27.20) for \( \frac{\psi_{100}(r)}{r} \)

\[
\frac{\psi_{100}(r)}{r} = \frac{k_0^{3/2}}{2\pi^{3/2}} \int \frac{e^{i br}}{k^2 + k_0^2} d^3k,
\]

where \( k_0 = \frac{1}{a_0} \). Hence

\[
A = \frac{e^4}{R} S - \frac{ke_0^4}{\pi^{3/2}} \int \frac{e^{i k R} d^3k}{(k^2 + k_0^2)^{3/2}} = \frac{e^4}{R} \left[ 1 - \frac{2}{3} \left( \frac{R}{a_0} \right)^2 \right] e^{-R/a_0}. \tag{27.29}
\]
Substituting the values found for $S$, $K$ and $A$ into the expression for the interaction energy [see (27.18) and (27.19)], we obtain the following expression ($R a_0 \equiv \xi$):

$$V^{a,s} = \frac{e_0^2}{R} \frac{(1 + \xi)e^{-\xi} \mp \left(1 - \frac{2}{3} \xi^2\right)}{1 \mp \left(1 + \xi + \frac{1}{3} \xi^2\right)e^{-\xi}}.$$  \hspace{1cm} (27.30)

Here the upper signs (-) refer to the antisymmetric solution $V^a$, while the lower signs (+) refer to the symmetric solution. For small values of $R (R \ll a_0)$, we have

$$V^a = V^s = \frac{e_0^2}{R} \text{when } R \ll a_0, \hspace{1cm} (27.31)$$

and thus the energy, as we would expect, is determined by the Coulomb energy of repulsion between the two nuclei. For large distances ($R \gg a_0$) we have

$$V^{a,s} = \mp \frac{2}{3} \frac{e_0^2}{a_0} R \frac{K}{a_0^2} e^{-\frac{R}{a_0}}, \hspace{1cm} (27.32)$$

that is, the antisymmetric solution (+) gives a repulsion, whereas the symmetric solution (-) gives an attraction.

The general nature of the variation of $V^a$ and $V^s$ as a function of $R$ is depicted in Fig. 27.5 which also shows the experimental data on the interaction energy. It can be seen from this figure that only the symmetric state is realized in practice.

Theoretical values obtained from the graph give the equilibrium distance as $R_e = 2.50 a_0 = 1.32 \text{ Å}$, and therefore the ionization energy is

$$D = -V(R_e) = -0.0646 \frac{e_0^2}{a_0} = 1.76 \text{ ev.} \hspace{1cm} (27.33)$$

The corresponding experimental values are

$$D^{\text{exp}} = 1.06 \text{ Å, } D^{\text{exp}} = 2.79 \text{ ev} \hspace{1cm} (27.34)$$

(the zero-point energy of oscillations is not included in the theoretical and experimental values given here).
The discrepancy between the theoretical and the experimental data is due to the fact that here, just as for the helium atom, the perturbation energy is commensurable with the energy of the zeroth approximation. Solving this problem by the variational method, using a test function of the form

$$\psi_n = \left( \frac{Z'^3}{\pi a_0^3} \right)^{1/2} e^{-Z'r/a_0},$$

(27.35)

where $Z'$, the effective charge of the nucleus, is taken as the variational parameter, we can obtain values for $R_0$ and $D$ which are in considerably better agreement with experiment

$$R_0^{\text{var}} = 1.06 \text{ Å}, \quad D^{\text{var}} = 2.25 \text{ ev}.$$ 

If several parameters are introduced, the variational method gives results that are in practically complete agreement with the experimental data.

It can be seen that the formation of the molecular hydrogen ion is essentially due to the quantum-mechanical exchange forces, which in the symmetric state give rise to a stable molecule. From the physical point of view, this can be explained as follows. The probability of the electron being in the symmetric state is

$$\rho^s_n = (\psi^s_n)^2 = \frac{1}{2(1+\delta)} (\psi^s_n + \psi^s_n + 2\psi_n^s \psi_n^s),$$

(27.36)

whereas the probability for the antisymmetric state is

$$\rho^a_n = (\psi^a_n)^2 = \frac{1}{2(1-\delta)} (\psi^a_n - \psi^a_n - 2\psi_n^a \psi_n^a).$$

(27.37)

If we plot the curves of constant probability density of the electron (see Fig. 27.6), we see that the electron tends to be located at the midpoint of the line joining the two nuclei in the case of the symmetric solution, whereas in the case of the antisymmetric solution the position probability vanishes at this point. Since the electron binds the two nuclei most strongly when it is halfway between them, it is natural to expect that the first solution, and not the second, will lead to the formation of a molecule. Moreover, in the case of the symmetric solution, the curves showing the electron distribution about the nuclei tend to merge when the nuclei approach one another; this provides a graphical characterization of the homopolar bond.\footnote{For more details see P. Gombas, \textit{Theorie und Lösungsmethoden des Mehrteilchenproblems der Wellenmechanik}, Basel: Birkhäuser-Verlag, 1950.}
Two hydrogen nuclei, or a hydrogen and a deuterium nucleus, can also be linked by other particles besides electrons. We may mention in this connection the $\mu$-mesic molecule (HD), in which the bonding between the hydrogen and deuterium nuclei is brought about by a negative $\mu$ meson. Alvarez produced a mesic molecule of this type by passing negative $\mu$ mesons through a bubble chamber. The radius of such a molecule, as calculated from the equation 

$$R = \frac{2.5}{\frac{h^2}{m_\mu c^2}},$$

will be 1/200 the radius of the molecular hydrogen ion, since the mass of the $\mu$ meson is approximately 1/200 as large as the electron mass. Thus, when the nucleus of the hydrogen atom approaches the nucleus of the deuterium atom, they form a common nucleus, namely that of the $^3$He molecule

$$^1\text{H}^1 + ^1\text{D}^2 \rightarrow ^3\text{He}^3.$$ 

As a result, an energy of 5.4 Mev is released and carried away by the $\mu$ meson. Thus the $\mu$ meson acts almost as a catalyst of the nuclear reaction.

**D. HOMOPOLAR ATOMIC MOLECULES**

The first successful attempt to give a theoretical explanation of the homopolar molecule was made by Heitler and London (1927) with the help of quantum mechanics. In a homopolar molecule, exchange forces play a fundamental role. In their treatment, Heitler and London used perturbation theory, which does not give completely accurate quantitative results. Although more accurate quantitative results can be obtained by means of the variational method, the Heitler-London theory enables us to bring out in a very simple way the physical features of the homopolar bond.

Let $r_1$ and $r_2$ denote the position vectors of the first and second electrons relative to nucleus $a$, and $r'_1$ and $r'_2$ the position vectors...
of the electrons relative to nucleus \( a' \) (see Fig. 27.2). Then \( r_i = r_1 - R, r_i' = r_1' - R \). In the zeroth approximation we obtain two wave functions which are products of the ground-state hydrogen wave functions

\[
\psi_{a,a'} = \psi_n(r_1) \psi_n(r_2) = \psi_{100}(r_1) \psi_{100}(r_2 - R),
\]

\[
\psi_{a,a'} = \psi_n(r_1) \psi_n(r_2) = \psi_{100}(r_1 - R) \psi_{100}(r_2).
\] (27.38)

The first solution \( \psi_{a,a'} \) corresponds to the case when the first electron is near the nucleus \( a \) (and the second electron near the nucleus \( a' \)), while the second solution \( \psi_{a,a} \) corresponds to the case when the first electron is near the nucleus \( a' \), and the second electron is near the nucleus \( a \). Both these possibilities are depicted in Fig. 27.7, where the solid arrows show the atomic bonds, and the dashed lines show the molecular bonds. When the distance between the nuclei tends to infinity \( (R \to \infty) \), all molecular bonds vanish.

![Fig. 27.7. Diagram of the interactions in the \( \text{H}_2 \) molecule. The solid lines join the particles whose interaction is taken into account in the zeroth approximation. The dashed lines denote interactions which are regarded as perturbations; \( a \) and \( a' \) are the nuclei of the hydrogen atoms; 1 and 2 are electrons.]

Just as in the problem of the molecular hydrogen ion, the main solutions (27.38) that give rise to an additional degeneracy of the system will not be orthogonal\(^5\)

\[
\mathcal{S} = \int \psi_{aa} \psi_{a'a'} d^3x_1 d^3x_2 \left\{ \int \psi_{100}^*(r) \psi_{100}^*(r - R) d^3x \right\}^2 = S^4,
\] (27.39)

\(^5\)A bar over a symbol denotes quantities referring to the neutral molecule.
where \( S \) for the \( \text{H}_2^+ \) ion is given by the expression (27.34). The Coulomb energy of interaction of the two atoms is given by

\[
\mathcal{K} = \int \phi_{aa'} \left\{ \frac{e_1^2}{R} + \frac{e_2^2}{r_{12}} - \frac{e_3^2}{r_1} - \frac{e_4^2}{r_2} \right\} d^4x_1 d^4x_2,
\]  

(27.40)

where the first and second parenthetic terms in the integrand correspond to the potential energy of repulsion between the two nuclei and the two electrons, and the third and fourth terms correspond to the potential energy of attraction between the first electron and the nucleus \( a' \) and between the second electron and the nucleus \( a \).

In exactly the same way, we obtain the exchange energy

\[
\mathcal{A} = \int \phi_{aa'} \phi_{a'a} \left\{ \frac{e_1^2}{R} + \frac{e_2^2}{r_{12}} - \frac{e_3^2}{r_1} - \frac{e_4^2}{r_2} \right\} d^4x_1 d^4x_2.
\]  

(27.41)

The expressions for \( \mathcal{K} \) and \( \mathcal{A} \) can be computed approximately by the same method as in the theory of the \( \text{H}_1^+ \) ion. For \( \mathcal{K} \) we obtain a comparatively simple result, and for \( \mathcal{A} \) a more complicated result, since \( \mathcal{A} \) is expressed in terms of an integral logarithm (as shown by Sigura). The general character of the solution, however, remains the same as in the theory of the \( \text{H}_1^+ \) ion. In particular, the main forces which hold the two neutral atoms in the molecule are the exchange forces. These forces have a minus sign at comparatively large interatomic distances and correspond to the mutual attraction of the atoms. Just as in the case of the molecular hydrogen ion, we have two solutions. The first solution is symmetric

\[
\psi^s = \frac{1}{\sqrt{2(1 + S)}} (\phi_{aa'} + \phi_{a'a}),
\]  

(27.42)

and the second is antisymmetric

\[
\psi^a = \frac{1}{\sqrt{2(1 - S)}} (\phi_{aa'} - \phi_{a'a}),
\]  

(27.43)

The general form of the curves of \( V^s \) for a neutral hydrogen molecule is approximately the same as for the \( \text{H}_1^+ \) molecular ion; therefore, only symmetric solutions will give stable molecules. For the radius corresponding to the equilibrium position [that is, the minimum of the potential energy \( V^s \) \((R) \) for the symmetric solution], we obtain \( R_0 = 1.51 \, \text{a}_0 = 0.80 \, \text{\AA} \). The corresponding value for the dissociation energy is

\[
D = - V^s(R_0) = 0.115 \frac{e^2}{a_0} = 3.2 \text{ ev}.
\]  

(27.44)
The experimental values of these quantities are

\[ R_{\text{exp}} = 0.74 \text{ Å}, \quad D_{\text{exp}} = 4.73 \text{ ev}. \]  

(27.44a)

We have omitted here the zero-point energy of oscillations, 0.27 ev (see Chapter 12), from both the theoretical and the experimental values.

E. SPIN AND THE SYMMETRY OF STATES

In the \( \text{H}^+ \) ion and the \( \text{H} \) atom, there is only one electron, and its spin leads only to insignificant spin-orbit interactions. On the other hand, there are two electrons in the \( \text{H}_2 \) configuration, and the spin plays an important role in the theory of this molecule, even though the spin-orbit and the spin-spin interactions give only small corrections. In the hydrogen molecule, just as in the helium atom, the mutual orientation of the spins of the two electrons determines the type of symmetry of the spatial part of the wave function; this is of primary significance in connection with the stability of a molecule. We shall therefore consider more fully the question of the relation of the spin to the symmetry properties of the molecule.

The total wave function \( \Psi \) must contain a spin part in addition to the spatial part. When the potential energy of the spin-orbit interaction can be neglected, then, just as in the case of Russell-Saunders coupling, the total wave function can be represented by a product of a spatial part and a spin part. For electrons (which obey Fermi statistics) the total wave function must change sign when coordinates and spins are interchanged (that is, the solution must be antisymmetric). We therefore have two possibilities

\[ \Psi_1 = C^a (s_1, s_2) \dot{\varphi}^s(r_1, r_2), \]  

(27.45)

\[ \Psi_2 = C^s (s_1, s_2) \dot{\varphi}^a(r_1, r_2). \]  

(27.46)

It has been shown in Chapter 24 that the antisymmetric spin function \( C^a \) describes two electrons with antiparallel spins, and therefore function \( \dot{\varphi}^s \), which is symmetric in the position coordinates, corresponds to a state with total spin 0. In exactly the same way the symmetric spin function \( C^s \), as well as the antisymmetric spatial function, describe a state with total spin 1 (the spins of both electrons are parallel). In the case of the hydrogen molecule, the only solutions which result in attraction is that corresponding to \( \dot{\varphi}^s \); thus, a stable molecule is obtained only in the case in which the electron spins are antiparallel.

We shall now proceed to a general analysis of the states of a molecule, using the symmetry properties. In this connection, we
note that in diatomic molecules the field of force possesses axial symmetry with respect to the line passing through the nuclei (the symmetry axis of the molecule). The absolute value of the component of the total orbital angular momentum along this axis of symmetry (which, incidentally, must be conserved) is denoted by $\Lambda$. States corresponding to different $\Lambda$ are denoted by the following letters: $\Sigma$ ($\Lambda = 0$); $\Pi$ ($\Lambda = 1$); $\Delta$ ($\Lambda = 2$); etc.

In addition, each electronic state must be characterized by the total spin $S$ of all the electrons in the molecule. For a given value of $S$, $\nu = 2S + 1$ states are possible. The quantity $\nu$, as in the case of an atom, determines the multiplicity of the energy level. In the case where the total spin is equal to zero ($S = 0$), we have $\nu = 1$. For states with $S = 1$, the multiplicity $\nu = 3$, etc. The total spin of electrons in a molecule can therefore be characterized by the multiplicity $\nu$, and the corresponding term can be denoted by $^\nu \Sigma$.

In this notation, the symmetric solution for the spatial part of the wave function (that is, the solution $\varphi^s$) corresponds to the term $^1\Sigma$ (that is, $\Lambda = 0, S = 0, \nu = 1$), while the antisymmetric solution ($\varphi^a$) corresponds to the term $^3\Sigma$ ($\Lambda = 0, S = 1, \nu = 3$). It is obvious that the $^3\Sigma$ term corresponds to three states: in two of the states the spin is directed along the symmetry axis of the molecule (in a parallel or antiparallel direction), while in the third state it is perpendicular to the symmetry axis.

It should be noted that symmetry plays a very important role in the theory of molecules (particularly in the case of complex molecules). If, for example, we reflect the wave function in a plane passing through the symmetry axis of the molecule (which we take as the $z$ axis), the energy of the molecule must remain unaltered. At the same time, if the component of the orbital angular momentum or of the spin along the symmetry axis differs from zero ($\Lambda \neq 0$ or $S \neq 0$), the rotations which are associated with these angular momenta will be reversed as a result of this reflection.

For simplicity, we restrict our treatment to the states in which the orbital angular momentum is zero, that is, $\Lambda = 0$ ($^\Sigma$ terms). In the case where the total spin of the electrons also vanishes, that is, $S = 0$, no change of states will occur in the mirror reflection.

---

5 In the case of reflection in the $zx$ plane, mirror reflection amounts to a replacement of $y$ by $-y$.

6 As is well known, the angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is an axial vector whose direction is a matter of convention (it has one direction in a right-handed system of coordinates, and the opposite direction in a left-handed system). The direction of the contour bounding the area and constructed from the vectors $\mathbf{r}$ and $\mathbf{p}$ remains, however, unaltered in both the right- and left-handed coordinate systems.
If, however, the spins of both electrons are parallel \((S = 1)\), the following cases are possible.

(a) The component of spin along the symmetry axis is equal to zero \((S_z = 0)\). In this case, the rotation characterizing the spin remains unaltered as a result of mirror reflection (see Fig. 27.8, where the initial and reflected spins are characterized by a rotation denoted by \(II\) and \(II'\)). The corresponding terms are designated by the symbol \(\Sigma^+\).

(b) The component of spin along the axis of symmetry \(z\) differs from zero \((S_z = \pm 1)\). In this case, the rotation which we associate with the spin is reversed as a result of mirror reflection (see Fig. 27.8, where the initial spin is characterized by the rotation \(I\) and the reflected spin by the rotation \(I'\)).

\[\text{Fig. 27.8. Change of the angular momentum on reflection in the } \Lambda \Lambda' \beta \beta' \text{ plane, which passes through the axis of symmetry } z. \text{ If the initial rotation characterizing the angular momentum occurs in a plane perpendicular to } \Lambda \Lambda' \beta \beta' \text{ (see } I), \text{ the direction of this rotation will be reversed after reflection (see } I'). \text{ If, however, the rotation takes place in the plane of reflection, it will be unaltered by reflection (} II = II').\]

The terms whose spin changes on reflection are designated by the symbol \(\Sigma^-\).

Therefore, the following terms of the ground state of the hydrogen molecule are possible:

\[1^1\Sigma^+ (\Lambda = 0, S = 0),\]
\[2^2\Sigma^+ (\Lambda = 0, S = 1, S_z = 0),\]
\[3^3\Sigma^- (\Lambda = 0, S = 1, S_z = -1),\]

where the last term is obviously twofold degenerate.

If the molecule consists of two identical atoms, there will be an additional symmetry property. A diatomic molecule with identical nuclei must have a center of symmetry, in addition to a plane of symmetry. This center of symmetry is the mid-point on the line joining the nuclei. In Fig. 27.8, it is located at the origin of the coordinate system, that is, at the point \(z = 0\). In this symmetry transformation we must change the sign of the coordinates of all
the electrons. In particular, under this symmetry transformation the positions of electron 1 and electron 2 will be interchanged in the hydrogen molecule (the coordinates of the nuclei are left unchanged). The symmetric wave function $\psi^s$ will remain unaltered; that is, it is even (this is denoted by the subscript $g$). The antisymmetric function $\psi^a$ changes its sign; that is, it is odd (this is denoted by the subscript $u$). The main possible states of the hydrogen molecule, taking into account both symmetry properties, can be therefore denoted as follows:

$$\Sigma^+_g, \Sigma^+_u, \Sigma^-_u$$

and so forth.

The importance of symmetry with regard to the formation of a molecule follows also from the fact that the ground state of most diatomic molecules is a state in which the wave function is invariant under all symmetry transformations. Thus, $\Sigma^+_g$ is the main term of the hydrogen molecule. The question of molecular symmetry, however, lies outside the scope of this book.

It should be noted that in stable states of the hydrogen molecule the spins of the two electrons are always oppositely directed. At the same time, there are two types of hydrogen molecules—parahydrogen and orthohydrogen. These names refer to the orientation of the nuclear spins, and not to the orientation of electron spins. In parahydrogen the spins of the nuclei are antiparallel, while in orthohydrogen they are parallel. Since the number of possible states for two particles with parallel spins is three times larger than in the case of particles with antiparallel spins, ordinary hydrogen at room temperature will consist of an equilibrium mixture of 25% parahydrogen and 75% orthohydrogen. As the temperature is lowered in the presence of a catalyst (for example, charcoal), the percentage of parahydrogen in the equilibrium mixture increases, and is practically 100% at 0°K. Parahydrogen produced at low temperatures is extremely stable and can be preserved in such an equilibrium system for a period of several weeks at room temperature. Orthohydrogen has not yet been obtained in pure form. The difference in the thermal conductivities at low temperatures (the thermal conductivity of parahydrogen is larger) is used for determining the composition of the mixture. Similarly, parahydrogen and orthohydrogen have somewhat different dissociation energies and optical properties.

F. THE VALENCE THEORY

We shall now explain the concept of chemical valence in terms of quantum mechanics. By chemical valence we mean the ability
of an atom to combine with a specific number of other atoms. As already mentioned, the first success of quantum theory in connection with the chemical properties of atoms was the explanation of heteropolar chemical compounds (Kossel's theory); these compounds are formed as a result of the redistribution of electrons in the outer shells of the participating atoms. According to this theory, the numerical value of the valence is determined by the number of electrons which an atom gives up to another atom (positive ionic valence) or acquires from another atom (negative ionic valence). In the formation of a molecule, the electrons in the outer shells of atoms are redistributed so that the valences of the atoms are saturated.

Further progress in the investigation of the formation of a molecule was made with the Heitler-London theory. This theory succeeded in explaining the formation of the simplest homopolar molecule $\text{H}_2$, which serves as the basis of our present concept of the covalent bond. According to the Heitler-London theory, the spins of the valence electrons are mutually compensated in the homopolar hydrogen molecule. Generalizing these results, it is possible to conclude that the formation of homopolar molecules occurs under the condition of mutual compensation of the spins of the valence electrons. Accordingly, this type of valence is also sometimes called the spin valence.

Since the saturation of valence bonds amounts to a compensation of the spins of the valence electrons, the chemical valence of atoms is given by the number of electrons with an uncompensated spin present in the outer shell.

To illustrate these general principles, let us consider some specific examples. Figure 27.9 gives the ground-state configurations of several elements of the periodic system. The electron states are shown as boxes, while the electrons are denoted by arrows whose directions correspond to their spin orientations. It is clear from this figure that the configuration of the outer shell of the hydrogen atom $(1s^1)$ corresponds to a single valence bond. The valence of hydrogen, which is equal to one, is smaller by a factor of one than the multiplicity of its terms, which is two (the multiplicity is designated by the superscript on the left-hand side of the term symbol $S$).

Similarly, the ground state of the helium atom has the configuration $(2s^2)$. It is evident that the multiplicity equals one ($^2S$), while the valence is equal to zero.

The boron atom ($Z = 5$) has the ground state $(1s^22s^22p^1)$, corresponding to the doublet ($^2P$), and consequently the valence equals one. The excited state $(1s^22s^22p^3)$, corresponding to the quartet ($^4P$) is also possible; in this state the valence of boron is equal to 3. Thus the presence of several different valences in the elements of various groups in the periodic system can be explained in comparatively simple form (see Table 27.2).
Although according to experiment the elements of oxygen and halogen groups can have several different valences, the O and F atoms themselves show only the principal valence. This is due to the fact that their multiplicity can be increased only if an electron is transferred to a shell with a larger value of the principal quantum number. This process is unfavorable from the energy standpoint (the \( d \) subshell is absent in O and F). On the contrary, for other elements of these groups there is a possibility of transition between states of the same shell, but having different values of \( l \).

Fig. 27.9. Diagram showing the filling of the electron shells of several atoms with the spin taken into account. Homopolar valence of atoms is denoted by a dot, and ionic valence is denoted by a + (positive) or – (negative) sign.

Table 27.2

Multiplicity and homopolar valence

<table>
<thead>
<tr>
<th>Group of the periodic system</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiplicity + Valence*</td>
<td>2</td>
<td>1, 3</td>
<td>1, 3</td>
<td>2</td>
<td>1, 3</td>
<td>1, 3</td>
<td>2, 4, 6</td>
</tr>
</tbody>
</table>

*The bold-face type indicates the principal valence.
According to the configuration given in Fig. 27.9, nitrogen in the ground state \((1s^22s^22p^3)\) is trivalent (the three electrons in the \(2p\) shell have parallel spins). However, it can also be univalent (antiparallel spins of the two electrons in the \(2p\) subshell) and even pentavalent \((1s^22s^12p^5)\) (the four spin valences, associated with the parallel spins of the electrons in the \(2s\) and \(2p\) subshells, are augmented by a fifth ionic valence associated with the removal of a second electron from the \(2s\) subshell). In this connection we note that the ionic valence of oxygen and fluorine is the same as the spin valence (covalence).

It should be emphasized that, in general, it is impossible to divide rigorously the chemical bonds into homopolar and heteropolar ones. The two types of bonds correspond to the limiting cases of the electron density distribution in the incomplete shells. The limiting case of asymmetry in the distribution of the electron density between the atoms corresponds to a heteropolar molecule. Such a molecule has a dipole moment and can be regarded as an ionic structure. The case of a homopolar bond corresponds to identical electron density distributions in the atoms of the molecule. A homopolar molecule has no dipole moment, and it can be considered as a structure formed from two neutral atoms.

Quantum theory provides a general method for the explanation of valence forces and deals with both types of bonds (homopolar and heteropolar) in a single scheme. One of the chief merits of the Heitler-London quantum-mechanical theory of the \(\text{H}_2\) molecule is that it explains the saturation of homopolar bonds in terms of the saturation of the spins of the electron shells when electrons combine into pairs with antiparallel spins. When a hydrogen atom approaches a \(\text{H}_2\) molecule no additional pairs with compensated spins are formed, and hence there is no gain in energy. The \(\text{H}_3\) molecule therefore cannot exist.

It must be emphasized, however, that the Heitler-London theory was developed only for molecules consisting of atoms in the \(s\) state, and therefore an extension of its conclusions to more complex atoms must be of a somewhat qualitative nature. Further development of the theory of homopolar bonds has shown that in the case of complex atoms quantum laws alone are not sufficient. In this case we must also include the influence of the specific properties characteristic of the chemical compounds.

G. MASERS AND LASERS

The electromagnetic waves radiated by conventional radio transmitters have a comparatively wide frequency band. Everyone who has used a radio receiver knows that transmitting stations which have nearly equal frequencies overlap one another. This is due to the fact that conventional transmitters have insufficient stability and often "drift" into another frequency band.
Thus, the stability of even the best existing quartz oscillators is inadequate in a number of cases (for example, high-stability oscillators are necessary for accurate determination of distances by means of radar). For this reason, one of the great achievements of recent times was the development of masers by Townes and coworkers, and independently by Basov and Prokhorov. In this device, quantum transitions between discrete energy levels in a molecule are used as microwave generators.

We note first of all that the process of spontaneous emission, which depends on the Einstein coefficient $A$, has no essential significance in the case of molecular emission, since its intensity is proportional to $\omega^4$ and is extremely small in the radiofrequency region (that is, in the range of frequencies that are low compared with light frequencies).

As far as induced transitions, which are proportional to the Einstein coefficient $B$, are concerned, the probability of upward transitions (resonance absorption) and the probability of downward transitions (induced emission) are identical (see Chapter 9); they are proportional to the energy of the field. Therefore, a system (molecule) with two levels will undergo a transition from one level to another under the influence of a sufficiently strong external field containing the resonant frequency, the transitions being accompanied by the emission and absorption of quanta.

![Fig. 27.10. Structure of the ammonia molecule showing two mirror-symmetric states $a$ and $b$ of the same energy.](image)

If external radiation is passed through a substance, it will interact with its molecules and cause resonant absorption as well as induced emission. In accordance with the Boltzmann distribution (the number of particles in an equilibrium system with energy $E$ is proportional to $e^{-E/kT}$), there must be fewer particles in the higher energy states than in the lower states; therefore, absorption dominates induced emission in the thermal equilibrium. The excess of absorbed energy is completely converted into the energy of thermal motion of the molecules, raising the temperature of the gas.

In order for the system to amplify and not absorb the radiation incident on it, it is necessary to disturb this thermal equilibrium in such a manner as to produce greater occupancy of the higher energy levels than of the lower ones. When this is done, such a system will generate electromagnetic waves with extremely small line width under the action of resonant radiation. The first masers were produced with ammonia ($\text{NH}_3$) molecules. The ammonia molecule consists of one nitrogen atom and three hydrogen atoms and forms a right pyramid. However, from the laws of symmetry, the stable state of the ammonia molecule corresponds not only to the case in which the nitrogen atom is located above the triangle composed of the hydrogen atoms (Fig. 27.10a), but also to the case in which the nitrogen atom is located at the same distance under the triangle (Fig. 27.10b). The stable states $a$ and $b$ have equal energies and correspond to the

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9 The term "maser" is an acronym formed from the first letters of microwave amplification by stimulated emission of radiation.

10 Such a state can also be described by the Boltzmann distribution function, if it is assumed that the temperature $T$, which in this case plays the role of a parameter, assumes negative values.
minima of the potential energy; they are thus separated by a potential barrier, so that classical theory does not allow transitions from one to the other. In quantum theory, however, the probability of penetration across the potential barrier is different from zero. Consequently, the nitrogen atom, which is above the triangle, may reposition itself below the triangle in the absence of any external action, and may then return to its original position. In molecular physics this phenomenon is called inversion. The process of inversion can be explained in terms of the existence of two perfectly identical potential wells, separated by a potential barrier of finite width. It is well known that this leads to a splitting of the spectral lines, in spite of the fact that the energy states in the two potential wells are completely identical to one another. For the ammonia molecule this splitting, expressed in wavelengths, is 1.27 cm for the most intense line; this corresponds to a radiofrequency wave.

Another remarkable property of the ammonia molecule is that, with the help of an electric field, it is fairly easy to separate the molecules in the upper and lower energy levels that have been formed as a result of inversion. It is found that when an ammonia molecule is placed in an electric field, the two levels are shifted in different directions, the upper inversion level being shifted upwards (the energy increases) and the lower inversion level downwards.

Since any system tends to a state in which its potential energy is minimum, we first pass a beam of ammonia molecules through a carefully evacuated vessel containing an electrostatic field which is produced by a quadrupole capacitor; this field decreases towards the symmetry axis (see Fig. 27.11).

In this separating system the molecules in the upper level will tend to move to a region where this field is minimum (since the field increases their energy); that is, they will be focused about the axis of the capacitor. The molecules that are in the lower level, however, tend to move to the region of maximum field (that is, to the periphery, where their energy will be minimum), and thus they will be ejected from the beam. After passing through the above separating system, the beam of molecules, which contains a predominance of excited molecules, enters a cavity resonator which, among its rather wide range of radio frequencies (produced by conventional radio frequency methods) also contains the resonant frequency of the molecular transitions.

This external radiation causes molecular transitions which are associated with a line of small width ($\sim 10 \text{ sec}^{-1}$) at a frequency of $2.4 \times 10^{10} \text{sec}^{-1}$ (that is, with a relative error no greater than $10^{-9}$), corresponding to the wavelength of 1.27 cm. This wavelength is determined mainly by the time of traverse of the molecules through the cavity resonator.

A molecular generator produced in such a way exhibits extremely stable frequency. The frequency stability is so high that molecular clocks constructed on this principle have an accuracy of approximately 1 sec per 300 years of continuous operation.\footnote{\textsuperscript{11}}

On the basis of this principle, several types of radio receivers working in the microwave region have been constructed. They all use paramagnetic crystals cooled to very low temperatures. These devices, known as quantum paramagnetic amplifiers, greatly increased the sensitivity of radio astronomical and radar equipment.

Recently, atoms and molecules have been used as generators and receivers in the visible spectrum. In this case, we speak of lasers (light amplification by stimulated emission of radiation).

What is the difference between an ordinary source of light and a laser? In an ordinary source of radiation, for example, the Sun, the spectrum consists of a broad frequency band and the individual incoherent quanta have arbitrary phases and directions. Optical lasers enable us to obtain a monochromatic beam of light of high intensity (when it is focused we obtain a radiation density a thousand times greater than that obtainable...}

\footnote{\textsuperscript{11} The stability of the frequency in masers made it possible to construct two standard independently operating, synchronized clocks. These clocks were used to measure the velocity of light in one direction under terrestrial conditions and therefore to check the fundamental conclusions of the special theory of relativity regarding first-order effects (proportional to the velocity $u = c \beta$).

We recall that all interference experiments similar to the Michelson experiment involve, in effect, only one standard clock and are used to measure the velocity of light over a closed path. Thus, only second-order effects (proportional to $\beta^2$) could be detected in these experiments.}
by focusing sunlight), great coherence and extreme sharpness (with telescopic apparatus a beam of light reaching the Moon would have a diameter of the order of 3 km). The first laser produced by Maiman was a three-level ruby laser. Chromium atoms, which are present in ruby (aluminum oxide) as a slight impurity, absorb light from a power klystron over a wide band in the green and yellow regions. Initially, these atoms give up (without emitting radiation) part of their energy to the crystal lattice and make a transition to a metastable state from which dipole transitions are forbidden, and hence they can be maintained in that state for a comparatively long time (of the order of several milliseconds).

![Fig. 27.11. Electrostatic field of the capacitor in the separating system.](image)

At a "negative" temperature (when the number of metastable atoms is greater than the number of unexcited atoms and under the action of stimulated emission, such a system is capable of generating almost instantaneously monochromatic waves with a wavelength of 6943 Å (red region). These transitions are induced by the first emitted quanta, which are retained in the ruby (the ruby has the shape of a circular rod, bounded by silvered parallel ends, one of which is semitransparent). Photons moving parallel to the axis induce the emission of photons having the same frequency and moving in the same direction. This chain process intensifies until a coherent ray finally passes through the semitransparent mirror (after multiple reflection from the ends).

The prospects for practical application of lasers are enormous. These devices can be used for the simultaneous transmission of various types of information, the establishment of cosmic communication, the control of chemical reactions induced by thermal excitation and so forth.
Part III

Some Applications to Nuclear Physics
Chapter 28

Elastic Scattering of Particles

A. TIME-DEPENDENT PERTURBATION THEORY

In the case when the Hamiltonian is an explicit function of time, it is not, as a rule, possible to obtain an exact solution of the Schrödinger equation. If the time-dependent part of the Hamiltonian $V'(t)$ is small in comparison with the time-independent part of the Hamiltonian $H^0$, time-dependent perturbation theory can be used to solve the problem.

It is obvious that time-dependent perturbation theory can also be applied when the perturbation energy is independent of time. In this case we obtain the same solutions as in the stationary perturbation theory of Chapter 14.

Including the perturbation $V'(t)$, we write the Schrödinger equation as

$$-\frac{\hbar}{i} \frac{\partial \psi(t)}{\partial t} = [H^0 + V'(t)] \psi(t). \tag{28.1}$$

The solution of this equation in the zeroth approximation ($V'(t) = 0$) is

$$\psi(t) = \sum_n C_n e^{-iE_n t/\hbar} \psi_n, \tag{28.2}$$

where the wave function $\psi_n$ is a solution of the unperturbed time-independent wave equation

$$E_n \psi_n = H^0 \psi_n, \tag{28.3}$$

and satisfies the orthonormality conditions

$$\int \psi_n^* \psi_n d^3x = \delta_{n'n}. \tag{28.4}$$

We shall look for a solution of Eq. (28.1) in the form of Eq. (28.2), assuming that the coefficients $C_n$ depend on time: $C_n \rightarrow C_n(t)$. This approximate method of solution was proposed by Dirac and is known as the method of variation of constants.
Substituting Eq. (28.2) into Eq. (28.1) and using Eq. (28.3), we obtain the following equation for the unknown coefficients $C_n$:

$$-\sum_{n''} \frac{\hbar}{i} \dot{C}_{n''} \psi_{n''} e^{-i \frac{t}{\hbar} E_{n''} t} = \sum_{n''} V'(t) C_{n''} \psi_{n''} e^{-i \frac{t}{\hbar} E_{n''} t}. \quad (28.5)$$

Multiplying Eq. (28.5) by $\psi_{n'} e^{i \frac{t}{\hbar} E_{n'} t}$, integrating the resulting expression over all space, and using the orthonormality condition (28.4), we obtain a system of equations for the unknown coefficients $C_{n'}$

$$-\frac{\hbar}{i} \dot{C}_{n'} = \sum_{n''} C_{n''} \psi_{n''} e^{-i \omega_{n'n''} t} V_{n'n''}'(t), \quad (28.6)$$

where

$$\omega_{n'n''} = \frac{E_{n'} - E_{n''}}{\hbar}, \quad (28.7)$$

and the matrix element

$$V_{n'n''}'(t) = \int \psi_{n'}^* V'(t) \psi_{n''} d^3x.$$

Dirac's system of equations (28.6), taken for all values of $n'$, is completely equivalent to the original wave equation.

The approximation used in perturbation theory consists in expanding the solution in the form

$$C_{n'} = C_{n'}^0 + C_{n'}^1 + C_{n'}^2 + \ldots, \quad (28.8)$$

where the zero-order coefficients $C_{n'}^0$ are independent of $V'$. The coefficients for the first and higher orders will be proportional to $V'$, $V''$, and so forth.

Substituting Eq. (28.8) into Eq. (28.6) and retaining only the first-order terms, we find the following system of equations for the coefficients $C_{n'}$:

$$\dot{C}_{n'}^0 = 0 \quad \text{(zeroth approximation),} \quad (28.9)$$

$$-\frac{\hbar}{i} \dot{C}_{n'}^1 = \sum_{n''} C_{n''}^0 \psi_{n''} e^{-i \omega_{n'n''} t} V_{n'n''}'(t) \quad \text{(first approximation) and so on.}$$

The first of the equations (28.9) shows that the unknown zero-order coefficients must be independent of time, that is,

$$C_{n'}^0 = \text{const.} \quad (28.10)$$
Their values are given by the initial conditions and characterize
the state of the electron before the perturbation is applied.

Let us assume that at \( t = t_0 \) the electron is in the state \( n \). Then
we may set

\[
C_n^{(0)} = \delta_{nn'}.
\]  

(28.11)

This expression specifies the initial conditions of the problem.
Substituting Eq. (28.11) into Eq. (28.9), we find

\[
C_{n'}(t) = -i \int_{t_0}^{t} dt e^{i\omega n' n} V_{n'n}(t).
\]  

(28.12)

In quantum mechanics one generally calculates the transition
probability \( \omega \) per unit time. Since the probability of finding a
particle in the state \( n' \) is given by \( |C_{n'}|^2 \), we obtain the following
expression for the transition probability:

\[
\omega = \frac{\partial}{\partial t} \sum_{n'} |C_{n'}|^2.
\]  

(28.13)

Equations (28.12) and (28.13) are the basis for the investigation
of many quantum-mechanical problems in the first-order time-
dependent perturbation theory.

**B. THE CROSS SECTION FOR ELASTIC SCATTERING**

We shall now apply the results obtained above to the study of
the elastic scattering of an electron.

We assume that at the initial time \( t_0 = 0 \) the particle is free;
that is, it moves uniformly with a momentum \( p = \hbar k \) and an energy
\[
E = \frac{p^2}{2m_0} = \frac{1}{2} \hbar K \left( K = \frac{k^2}{2k_0}, \ k_0 = \frac{m_0 c}{\hbar} \right).
\]

At the instant of time \( t_0 = 0 \), the particle comes within the
range of interactions; that is, it moves in a potential \( V(r) \).
The particle now has a finite probability of making a tran­
sition to the state with the momentum \( p' = \hbar k' \) and energy
\[
E' = \frac{1}{2} \hbar K' \left( K' = \frac{k'^2}{2k_0} \right);
\]  

that is, the particle is scattered as a result of interaction (Fig.
28.1).

![Fig. 28.1. Scattering of a particle by a cen­
ter of force: \( \hbar k \) is the momentum of the
incident particle; \( \hbar k' \) is the momentum of
the scattered particle; \( \vartheta \) is the angle of
scattering; \( O \) denotes the scattering center.](image)
The wave functions of the initial and final states, describing the free motion (in the zeroth approximation), are [see (4.62)]

\[
\psi(k) = L^{-1/2} e^{-ik't + ikr}, \\
\psi(k') = L^{-1/2} e^{-ik't + ik'r},
\] (28.14)

where \(L\) is the period, and the momentum components \(k_i\) and \(k'_i\) \((i = 1, 2, 3)\) are related to the integers \(n_i\) and \(n'_i\) by means of the expressions

\[
k_i = \frac{2\pi n_i}{L}, \quad k'_i = \frac{2\pi n'_i}{L}.
\] (28.15)

Substituting the wave functions (28.14) into Eq. (28.12), we find for the coefficient \(C_n'\)

\[
C_n'(t) = \frac{1}{L^3} V \frac{1 - e^{ic t (K' - K)}}{ch (K' - K)}.
\] (28.16)

where the matrix element of the perturbation energy is \([V' = V(r)]\)

\[
V_x = \int e^{ik'r} V(r) \, d^3x, \quad x = k - k'.
\]

Hence, the transition probability is

\[
\omega = \frac{\partial}{\partial t} \sum_{k'} |C_n'|^2 = \frac{1}{L^3} \sum_{k'} |V_x|^2 \frac{2 \sin ct (K' - K)}{ch^2 (K' - K)}.
\] (28.17)

We note that the function

\[
f = \frac{\sin ct (K' - K)}{\pi (K' - K)}
\] (28.18)

has a sharp maximum for sufficiently large values of \(t\) and \(K' - K \to 0\). This means that in practice we can restrict ourselves to only those changes of \(K'\) for which the following condition is satisfied:

\[
ct |K' - K| \sim 2\pi.
\]

Since the quantity \(t = t - t_0 = \Delta t\) is the time elapsed from the initial instant, and the quantity \(ch (K' - K) = \Delta E\) is the energy spread resulting from scattering, we find a relationship between these quantities

\[
\Delta t |\Delta E| \sim h.
\] (28.19)
This relation can be considered as a fourth uncertainty relation; it is usually obtained from the theory of transition processes.

The uncertainty in the energy is characteristic for any wave process; its optical analog is the familiar expression for the broadening of spectral lines, resulting from the finite duration of the emission.

For sufficiently large values of $t (t \rightarrow \infty)$ the uncertainty in energy tends to zero and Eq. (28.18) becomes a statement of the law of conservation of energy

$$K' = K.$$ 

This explains why this type of scattering is said to be "elastic." Mathematically, this follows from the fact that the function (28.18) is a $\delta$ function at $t = \infty$. Integration of the $\delta$ function leads to the replacement of $K'$ by $K$. To show this, let us consider the integral

$$I = \frac{1}{\pi} \int_0^\infty \frac{\sin ct (K' - K)}{K' - K} F(K') dK'. \quad (28.20)$$

Introducing a new variable

$$ct (K' - K) = \xi,$$

we get

$$I = \frac{1}{\pi} \int_{-ctK}^\infty \frac{\sin \xi}{\xi} F(\xi + \frac{\xi}{ct}) d\xi.$$

If the function $F$ has no singularities, we obtain as $t \rightarrow \infty$

$$I = F(K) \frac{1}{\pi} \int_{-\infty}^\infty \frac{\sin \xi}{\xi} d\xi = F(K).$$

On the other hand, from the definition of the $\delta$ function it follows that

$$\int_0^\infty \delta (K' - K) F(K') dK' = F(K). \quad (28.21)$$

---

1 An example of inelastic scattering is provided by bremsstrahlung—a scattering process in which an electron emits a photon, so that $K' < K$. 
Hence it is clear that expression (28.18) becomes a $\delta$ function as $t \to \infty$, and, consequently, Eq. (28.17) for the transition probability can be written as

$$w = \frac{2\pi}{L^2 \hbar^2} \sum_{k'} |V_x|^2 \delta (K' - K). \quad (28.22)$$

Replacing the summation (28.22) by integration we use, in accordance with Eq. (28.15), the following relation:

$$\left(\frac{2\pi}{L}\right)^4 = k'^2 dK'd\Omega = k_0 k'dK'd\Omega. \quad (28.23)$$

The scattering process is usually characterized by a cross section, which is equal to the ratio of the probability $w$ to the number of particles $N$ incident per unit time on a unit surface $S$ perpendicular to the incident beam. Obviously the particles that strike this surface per unit time are those located at a distance not exceeding the velocity of the particles $v$, that is, the particles contained in the volume $vS = v$. The number $N$ is equal to the number of particles per unit volume $\rho_0 = L^{-3}$ multiplied by a volume which is numerically equal to the velocity of the particle

$$N = \frac{v}{L^3} = \frac{c}{L^3} \frac{k}{k_0}. \quad (28.24)$$

With the aid of Eqs. (28.22) - (28.24), we find the following expression for the scattering cross section:

$$\sigma = \frac{w}{N} = \int \sigma (\theta, \varphi) d\Omega. \quad (28.25)$$

The integrand characterizing the number of scattered particles incident per solid angle $d\Omega$ ($d\Omega = \sin \theta d\theta d\varphi$, where $\theta$ and $\varphi$ are the spherical scattering angles), known as the differential cross section, is equal to

$$\sigma (\theta, \varphi) = \left(\frac{m_0}{2\pi \hbar^2}\right)^2 |V_x|^2. \quad (28.26)$$

In particular, when the scattering center is spherically symmetric, we have

$$V_x = \int_0^\infty V(r) r^3 dr \int e^{i\mathbf{kr} \cdot \mathbf{r}} d\Omega',$$

where $d\Omega'$ is the solid angle associated with the vector $r$, whereas in Eq. (28.25) $d\Omega$ is the solid angle associated with the vector $K'$. 
Integrating the last expression over the solid angle \( \Omega' \), we find
\[
V_x = 4\pi \int_0^\infty r \sin \varphi' V(r) \, dr.
\]

From this it is clear that the differential cross section of the elastic scattering is equal to
\[
\sigma(\Theta) = |f(\Theta)|^2,
\]
where
\[
x = |k - k'| = 2k \sin \frac{\theta}{2},
\]
and the quantity
\[
f(\Theta) = -\frac{2m_e}{\hbar^2} \int_0^\infty r \sin \varphi' V(r) \, dr
\]
is called the scattering amplitude.

Equation (28.27), describing the elastic scattering of the particles by a center of force \( V(r) \) in first-order perturbation theory, was originally developed by Born; it is therefore called the Born approximation.

We note that this problem can be also solved in the time-independent perturbation theory, since the potential energy of interaction is time-independent. To obtain the scattering cross section we have used, however, the time-dependent perturbation theory, the mathematical apparatus of which is comparatively simple but is much more general. In particular, it can be used to solve many problems in modern quantum electrodynamics, taking account of the interaction of electrons with the doubly quantized electromagnetic field (see Chapter 29).

The expression for \( \sigma(\Theta) \), obtained from the perturbation theory, is applicable only within some definite limits. In the case of short-range forces (nuclear forces, neutral atom, impenetrable spheres, and so forth), which can be neglected for \( r > R \), where \( R \) is a certain effective radius, the magnitude of the cross section must be either less or of the same order as their geometric cross section \( \pi R^2 \) (even if these forces create an absolutely impenetrable barrier). For short-range forces, therefore, the range of applicability of the perturbation method is given by
\[
\sigma < \pi R^2.
\]

Equation (28.27) is not applicable to long-range forces (Coulomb forces) if the scattering angle is small. This question requires a more detailed analysis (see below).
C. SCATTERING BY THE YUKAWA CENTER OF FORCE

The form of the potential energy for the Yukawa interaction is as follows:

\[ V = -A e^{-k_ar} \]  \hspace{1cm} (28.30)

where \( A \) is a constant related to the charge and \( R = 1/k_a \) is the effective range of these forces. The interaction (28.30) has some important applications in the theory of nuclear forces and, in particular, in meson theory.

For nuclear forces, the quantity \( A \) is equal to \( g^2 \), where \( g^2 \) determines the strength of the potential. The range of nuclear forces is equal to the Compton wavelength of a pion:

\[ R = \frac{\hbar}{m_e c} \sim 10^{-13} \text{ cm.} \] \hspace{1cm} (28.31)

In the case of fast-electron scattering (or \( \alpha \)-particle scattering) by neutral atoms, the interaction potential given by the Thomas-Fermi model can be approximated by the expression (28.30). In this case the quantity \( A = Z e^2 \), where \( Z \) is the atomic number, and the effective radius \( R \) of the atom in the Thomas-Fermi model is equal to:

\[ R = \frac{\gamma g_0}{Z^{1/3}}, \] \hspace{1cm} (28.32)

where \( \gamma \) is a numerical factor of the order of unity.

Finally, setting \( R \to \infty \), we obtain the Coulomb potential of the nuclear field which, consequently, can be considered as a limiting case of Eq. (28.30).

Substituting Eq. (28.30) into (28.27) and using the relation

\[ \int_0^\infty r \sin kr V(r) \, dr = -A \int_0^\infty \sin kr e^{-kr} \, dr = -A \frac{x}{x^2 + k^2}, \]

we obtain the following expression for the differential cross section of elastic scattering:

\[ \sigma(\theta) = \frac{4m_e^2 A^2 R^4}{k^4 (x^2 + k^2 + ij)^2}. \] \hspace{1cm} (28.33)

\[ ^2 \text{As has been mentioned in Chapters 25 and 27, a more accurate approximation of the Thomas-Fermi potential is given by the expression (25.22). The results of the two approximations, however, do not differ greatly from one another (which is a consequence of the short-range character of the forces). The approximation (28.30) is more convenient in calculations of scattering.} \]
Here, according to Eq. (28.27a),

\[ x^2 = 4k^2 \sin^2 \frac{\theta}{2} = 4 \frac{\rho^2}{\hbar^2} \sin^2 \frac{\theta}{2}, \]

where \( \rho \) is the momentum of the particle.

Two cases should be distinguished in the analysis of Eq. (28.33).

1. Scattering of relatively slow particles, when \( \pi R \ll 1 \) for all scattering angles. In this case Eq. (28.33) shows that \( \sigma(\theta) \) is independent of the angle \( \theta \) and becomes equal to

\[ \sigma(\theta) = \frac{4m^2 \lambda^2 R^4}{\hbar^4}. \]  

(28.34)

The independence of the scattering cross section of the angle \( \theta \) (isotropy) is a characteristic feature of scattering of relatively low-energy particles by a center of short-range forces.

2. In the case of relatively fast-particle scattering, the differential cross section becomes independent of \( R \) (the effective range of force) for all scattering angles satisfying the condition \( \pi R \gg 1 \). Equation (28.33) in this case reduces to

\[ \sigma(\theta) = \frac{4m^2 \lambda^2}{\hbar^4 k^4}. \]  

(28.35)

It is evident that for angles satisfying this condition the scattering by the Yukawa potential is the same as the scattering by a Coulomb center. Therefore, in the case of fast electrons or \( \pi \)-particle scattering by a neutral atom through comparatively large angles, the influence of atomic electrons is not important and the scattering is determined only by the potential of the nucleus.

Setting \( A = Ze^2 \) and \( x = \frac{2p}{\hbar} \sin \frac{\theta}{2} \) in Eq. (28.33), we obtain the familiar Rutherford equation

\[ \sigma(\theta) = \frac{Z^2 e^4 m^2}{4 \rho^4 \sin^4 \frac{\theta}{2}}, \]  

(28.36)

which was obtained by the classical method in Chapter 2. Equation (28.36) shows that for long-range forces there is a strong dependence of the scattering cross section on the scattering angle \( \theta \).

However, for any large values of the wave vectors \( k = \frac{p}{\hbar} \) we can always find small angles \( \theta \) such that the following inequality is true:

\[ \frac{2pR}{\hbar} \sin \frac{\theta}{2} \ll 1. \]  

(28.37)
In particular, as $\theta \to 0$, Rutherford's formula gives a divergent value for $\sigma(\theta)$; in this case we must take into account the short-range character of the forces resulting from the screening action of the electron shell. The condition (28.37) now determines the region of inapplicability of the Rutherford formula.

For $\theta = 0$, that is, for forward scattering ($\chi = 0$), we find from Eqs. (28.32) and (28.33) the following expression for the differential cross section:

$$
\sigma(\theta) = \frac{4\pi Z^2}{\theta} \sim Z^2/\theta.
$$

(28.38)

The total cross section can be obtained from Eq. (28.33)

$$
\sigma = \frac{8\pi m^2 \hbar^4}{\hbar^4} \int_0^\pi \sin \theta d\theta \left[ \frac{1}{1+2k^2\hbar^2(1-\cos \theta)} \right]^2 = \frac{16\pi m^2 \hbar^4}{\hbar^4} \frac{1}{4k^4 \hbar^2 + 1}.
$$

(28.39)

Finally, with the aid of Eq. (28.29), we can find the range of applicability of the perturbation method for our problem in the two limiting cases considered above

$$
A \ll \frac{\hbar^2}{m_0 R} \quad \text{for} \quad kR \ll 1,
$$

$$
A < \frac{\hbar^2}{m_0} \quad \text{for} \quad kR \gg 1.
$$

(28.40)

Problem 28.1. Represent the cross section for scattering of particles by a spherically symmetric potential as a sum of partial cross sections (the sum of the cross sections for waves with a well-defined value of the orbital quantum number $l$). Obtain the scattering cross section for the general case and for the Born approximation.

Solution. Suppose the incident particle has a momentum $p = \hbar k$ and velocity $v = \hbar k/m_0$, directed along the $z$ axis.

The wave function of the incident particle is of the form of a plane wave

$$
\psi_{\text{inc}} = e^{ikz}.
$$

A plane wave can be expanded in spherical harmonics (see Problem 21.5). Then, using the asymptotic expression for the Bessel function as $r \to \infty$

$$
J \left( kr \right) = \sqrt{\frac{2}{\pi kr}} \sin \left( kr - \frac{\pi l}{2} \right),
$$

the incident wave can be represented as

$$
e^{ikz} = \sum_{l=0}^{\infty} i^l (2l+1) \sin \left( kr - \frac{\pi l}{2} \right) P_l (\cos \theta).
$$

(28.41)
In the presence of the potential energy $V(r)$, the asymptotic expression for the wave function of the particle in a centrally symmetric field, in accordance with Eqs. (13.75) and (13.78), should be chosen in the form

$$
\psi_{as} = \sum_{l=0}^{\infty} C_l P_l(\cos \theta) \frac{\sin \left( kr - \frac{\pi l}{2} + \delta_l \right)}{kr},
$$

where the phase shift $\delta_l$ can be determined from the asymptotic solution of the Schrödinger equation for the radial function in the presence of the potential $V(r)$

$$
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ k^2 - \frac{l(l+1)}{r^2} - \frac{2m_e}{\hbar^2} V(r) \right] R = 0.
$$

Clearly the scattered wave is

$$
\psi_{\text{scat}} = \psi_{as} - \psi_{\text{inc}} = \frac{1}{r} \sum_{l=0}^{\infty} \frac{1}{2i k} P_l(\cos \theta) \left\{ e^{i \left( kr - \frac{\pi l}{2} \right)} \times \right.
$$

$$
\left. \times \left[ C_l e^{i \delta_l} - i l (2l+1) \right] - e^{-i \left( kr - \frac{\pi l}{2} \right)} \left[ C_l e^{-i \delta_l} - i l (2l+1) \right] \right\}.
$$

The unknown coefficients $C_l$ can be determined from the condition that the function $\psi_{\text{scat}}$ must be a diverging spherical wave. Thus the coefficient of the converging wave $e^{-i \left( kr - \frac{\pi l}{2} \right)}$ must be equal to zero. Then

$$
\frac{\psi_{\text{scat}}}{r} = \frac{f(\theta)}{e^{i kr}}.
$$

The function $f(\theta)$ is the scattering amplitude [see (28.28)], which, according to the exact theory, is equal to

$$
f(\theta) = \frac{1}{2i k} \sum_{l=0}^{\infty} (2l+1) (e^{i \delta_l} - i l) P_l(\cos \theta).
$$

The differential cross section characterizing the scattering of particles through an angle $\theta$ is equal to the ratio of the probability of scattered particles passing per unit time through an element of the spherical surface $dS = r^2 d\Omega$:

$$
dW_{\text{scat}} = \frac{\psi_{\text{scat}}^* \psi_{\text{scat}}}{\psi_{\text{inc}}^* \psi_{\text{inc}}} r^2 d\Omega = \nu |f(\theta)|^2 d\Omega
$$

to the number of particles incident per unit time on a unit surface perpendicular to their velocity, that is, perpendicular to the $z$ axis

$$
W_{\text{inc}} = \frac{\psi_{\text{inc}}^* \psi_{\text{inc}}}{\nu} = 1.
$$

From this we find the differential cross section

$$
d\sigma = \frac{dW_{\text{scat}}}{W_{\text{inc}}} = |f(\theta)|^2 \frac{2\pi \sin \theta}{2\pi \sin \theta d\theta}.
$$

Here, assuming the scattering field to be axially symmetric, we set the solid angle equal to

$$
d\Omega = 2\pi \sin \theta d\theta.
$$
Substituting the value obtained for the scattering amplitude and using the orthonormality property of Legendre polynomials, after integrating over the angles we get

\[ \int_0^\pi P_l(\cos \theta) P_{l'}(\cos \theta) \sin \theta d\theta = \frac{2}{2l+1} \delta_{ll'}, \]

which gives us the following expression for the total cross section:

\[ \sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \theta_l. \quad (28.45) \]

This expression for \( \sigma \) is the desired sum of partial cross sections.

Let us compare the expression for the scattering amplitude found in the Born approximation [see (28.28)] with the exact expression (28.43). The comparison shows that the exact expression gives the same result as the Born approximation for small values of the scattering phase angles \( \theta_l \). Indeed, when \( \theta_l \ll 1 \), expression (28.43) becomes

\[ f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) \delta_l P_l(\cos \theta). \quad (28.45a) \]

Solving Eq. (28.42) for a given \( I \) (for a partial wave) by perturbation methods, we can show that

\[ \delta_l = -\frac{n - m - m}{2k^2} \int_0^{\pi} V(r) r J_l \left( \frac{1}{2} \right) r dr. \quad (28.46) \]

Next, using the expansion

\[ \sin \frac{\pi r}{\lambda} = \frac{1}{2k} \sum_{l=0}^{\infty} (2l+1) J_l \left( \frac{1}{2} \right) P_l(\cos \theta), \]

where

\[ \lambda = 2k \sin \frac{\theta}{2}, \]

the scattering amplitude (28.45a) can be reduced to the form (28.28) found in the Born approximation.

Problem 28.2. Determine the cross section for scattering of particles by a spherically symmetric potential barrier of height \( V_0 \geq 0 \) and radius \( a \)

\[ V = \begin{cases} V_0 & \text{for } r < a, \\ 0 & \text{for } r > a, \end{cases} \]

when the radius \( a \) is much less than the de Broglie wavelength of the scattered particles, that is, when \( ka \ll 1 \).

Show that in this case the s wave (wave with \( l = 0 \)) is the main contributor to the scattering process.

Compare the exact solutions with those obtained by perturbation methods.

Solution. It may be seen from Eq. (28.46) that at \( ka \ll 1 \), the s wave \( (l = 0) \) is the main contributor.

Solving the problem by perturbation methods (Born approximation), that is, using Eq. (28.28), we find the scattering amplitude

\[ f(\theta) = -\frac{2m_v V_0}{\hbar^2} \int_0^a r^2 dr = -\frac{2m_v V_0 a^3}{3\hbar^2}. \]
Consequently, the cross section in the Born approximation is equal to

\[ \sigma_{l} = 2\pi \int_{0}^{\pi} \sin \theta |f(\theta)|^{2} d\theta = \frac{16\pi}{g} \cdot \frac{m_{0}^{2} V_{0}^{2} a^{8}}{h^{4}}. \tag{28.47} \]

Let us determine the scattering phase shift \( \delta \) in this simple problem. We restrict ourselves to a determination of the phase shift for \( l = 0 \) and low energies \( E \), when we can set \( ka \ll 1 \).

When \( l = 0 \), the wave equations have the form

\[ \begin{align*}
\gamma'_{0} + k^{2} \gamma_{0} & = 0 \quad \text{for} \quad r > a, \\
\gamma''_{0} - k^{2} \gamma_{0} & = 0 \quad \text{for} \quad r < a,
\end{align*} \tag{28.48} \]

where

\[ \gamma_{0} = R_{0} r, \quad k^{2} = \frac{2m_{0} E}{\hbar^{2}}, \quad \kappa^{2} = \frac{2m_{0}}{\hbar^{2}} (V_{0} - E) = \kappa^{2} - k^{2}. \]

Using the boundary conditions \( \gamma_{0}(0) = 0 \), the solution of Eq. \( (28.48) \) can be represented as

\[ \begin{align*}
\gamma_{0} & = \begin{cases} 
A \sinh x' r & \text{for} \quad r < a, \\
\sin (kr + \delta_{0}) & \text{for} \quad r > a.
\end{cases}
\end{align*} \tag{28.49} \]

Equating the wave functions and their derivatives at the boundary of the region \( r = a \), we find in our case of small \( E (E \ll V_{0}) \)

\[ \delta_{0} = \arctan \left[ \frac{k}{x'} \tanh x' a \right] - ka \approx ka \left( \frac{\tanh x a}{x a} - 1 \right), \tag{28.49a} \]

where

\[ x a = \sqrt{\frac{2m_{0} V_{0}}{\hbar^{2}}} a. \]

Hence, according to Eq. \( (28.45) \), we have

\[ \sigma = 4\pi a^{2} \left( \frac{\tanh x a}{x a} - 1 \right)^{2}. \tag{28.49a} \]

In the case \(^{3} \) \( xa \ll 1 \) \( \tag{28.50} \)

we can set

\[ \tanh x a \approx 1 - \frac{1}{3} (xa)^{2}. \]

Then Eq. \( (28.49) \) gives an expression for \( \sigma \) corresponding to the Born approximation [see \( (28.47) \)].

When \( xa \gg 1 \) (that is, when \( V_{0} \rightarrow \infty \)) the cross section reaches its maximum value

\[ \sigma = 4\pi a^{2}. \tag{28.51} \]

\(^{3}\)We note that the condition \( (28.50) \), which in this problem can also be written as

\[ \sigma_{B} \ll \pi a^{2}, \]

is equivalent to the condition \( (28.29) \) for the applicability of perturbation method.
The last expression is four times greater than the corresponding cross section for elastic scattering by an impenetrable sphere, calculated according to classical mechanics when $\sigma$ is determined simply by the geometric cross-section of the sphere $\pi a^2$. This discrepancy is due to the appearance of wave properties (diffraction) of the scattered particles.

Problem 28.3. Determine the cross section for scattering of slow particles ($ka \ll 1$) by a spherically symmetric potential well:

$$V = \begin{cases} -V_0 & \text{for } r \leq a, \\ 0 & \text{for } r > a. \end{cases} \quad (28.52)$$

Indicate what distinguishes the cross section for scattering of particles by a potential well from the cross section for scattering by a potential barrier.

Solution. In the exact solution of the problem, Eq. (28.48) should be replaced by

$$\gamma_0^\prime + k^2\gamma_0 = 0 \quad \text{for } r > a,$$

$$\gamma_0^\prime + k^2\gamma_0 = 0 \quad \text{for } r < a,$$

where

$$k^2 = \frac{2m_0}{\hbar^2} (E + V_0) = k^2 + x^2.$$ 

The phase shift $\delta_0$ is given by the following expression [instead of Eq. (28.49)]:

$$\delta_0 = \arctan \left( \frac{k}{k'} \tan k'a \right) - ka. \quad (28.54)$$

When $k'a \ll 1$ and $E < V_0$, we again obtain Eq. (28.47), which was derived in first-order perturbation theory. In this case the cross sections for scattering by a potential well and by a potential barrier are identical.

The difference appears when the quantity $\chi a \left( \chi = \frac{2m_0}{\hbar^2} V_0 \right)$ becomes comparable to or greater than unity. Thus, in the case of a potential barrier, the quantity $\frac{k^2a}{\chi a}$ monotonically approaches zero as $V_0$ increases, whereas in the case of a potential well the corresponding quantity $\frac{\tan k'a}{k'a}$ varies periodically over the range from 0 to $\infty$ as $V_0$ increases.

In particular, if the quantity $k'a$ approaches $\frac{\pi}{2}$, we find the following expression for the cross section in the region $\frac{k'a}{\tan k'a} \ll ka$:

$$\sigma_{res} = \frac{4\pi a^2}{k^2a^2}. \quad (28.55)$$

Because of the smallness of the quantity $k^2a^2 = \frac{2m_0E}{\hbar^2} a^2$, the expression for $\sigma$ is much greater than the maximum value for the cross section in the case of scattering by a potential barrier ($\sigma_{max} = 4\pi a^2$ when $V_0 \to \infty$ [see (28.51)]). Since the relation $k'a = \sqrt{\chi^2a^2 + k^2a^2} = \frac{\pi}{2}$ for $ka \ll 1$ is actually equivalent to the condition of appearance of the first level in the spherically symmetric potential well, $\chi a \approx \frac{\pi}{2}$, the cross section (28.55) corresponds to the case of "resonant" scattering. Subsequent resonance maxima of the cross section occur when $\chi a = \frac{3}{2} \pi, \frac{5}{2} \pi, \text{ and so forth}$.

Note. The scattering phase shift, together with the expression for the cross section, can be accurately determined for a very limited class of problems (scattering by a spherically symmetric potential barrier or potential well, scattering by a potential inversely proportional to the square of the distance, and so forth). However, in the general case we must use approximate methods. For intermediate values of the potential energy $V_0$ (for instance, in the case of scattering of charged particles by a Coulomb field the constant
characterizing the potential energy must satisfy the condition \( \frac{Z e^8}{\hbar^2} \ll 1 \). Perturbation theory (that is, the Born approximation) gives good results. In cases when the Born approximation is no longer applicable, the phase can be determined by other approximate methods, for example, the WKB method [see Eq. (13.78)], the variational method and so forth. In view of the special nature of these methods we shall not discuss them in this general treatment.\(^4\) It should be noted that many qualitative features, which are characteristic of the scattering of particles by various potentials, are very well illustrated in the scattering by a potential barrier or a potential well.

Chapter 29

Second Quantization

A. SECOND QUANTIZATION OF THE SCHRODINGER EQUATION

As an example of second quantization, we shall consider the nonrelativistic Schrödinger equation, and then generalize the results to the case of the Maxwell and Dirac relativistic equations.

In Chapter 5, it was shown that the solution of the time-dependent Schrödinger equation in the general case can be represented in the form

\[ \psi(t) = \sum_{n} C_n \phi_n e^{-i \frac{E_n}{\hbar} t} = \sum_{n} C_n(t) \phi_n, \] (29.1)

where the coefficient \( C_n(t) \), which characterizes the probability that a particle is in the state represented by \( \phi_n \), includes the time-dependent part of the wave function

\[ C_n(t) = C_n e^{-i \frac{E_n}{\hbar} t}. \] (29.2)

Here the quantities \( E_n \) are the energy eigenvalues, and the eigenfunctions \( \phi_n \) of the time-independent Schrödinger equation satisfy the orthonormality condition

\[ \int \phi_n^* \phi_{n'} d^3x = \delta_{nn'}. \] (29.3)

In transferring from classical quantities to quantum-mechanical ones, the position \( x \), the momentum \( p_x \), and the remaining quantities are replaced by their average values

\[ \bar{x} = \int \phi^* (t) x \phi (t) d^3x, \]

\[ \bar{p}_x = \int \phi^* (t) p_x \phi (t) d^3x. \] (29.4)
The time variation of these average values cannot be determined from the classical Poisson brackets, which in this case coincide with Hamilton's canonical equations

\[
\frac{dx_{\text{cl}}}{dt} = \frac{\partial H}{\partial p_{\text{cl}}},
\]

and must be calculated from the commutator relation

\[
\dot{x} = i \frac{\hbar}{\hbar} \overline{\{Hx - xH\}}.
\] (29.5)

Here the Hamiltonian is equal to

\[
H = \frac{p^2}{2m} + V(x).
\] (29.6)

The quantum equation of motion [Eq. (29.5)] can be considered as the fundamental equation describing the quantization of the classical equations of motion. This process is called first quantization. In order to connect \( \bar{p} \) and \( \bar{x} \) by the usual relation

\[
\dot{\bar{x}} = \frac{\bar{p}}{m},
\] (29.7)

we must assume that in Eq. (29.5) the operators \( p \) and \( x \) do not commute with each other and obey the commutation relation

\[
px - xp = \hbar \frac{i}{\hbar}.
\] (29.8)

Thus the commutation relation (29.8), which is basic to the Schrödinger theory, can be regarded as a consequence of the quantum equation of motion (29.5), and the transition from the classical equation of motion to the Schrödinger equation is equivalent to a transition from corpuscular concepts to the wave concepts.

In order to include in the theory the corpuscular properties of the de Broglie waves, it is necessary to introduce a number of additional hypotheses (for example, a hypothesis concerning the probabilistic nature of the \( \psi \) waves and the meaning of the coefficients \( |C_n|^2 \) as the probability of an electron being in state \( n \), and so forth).

The process of second quantization enables us to take into account both the corpuscular and wave properties of the particles. The name "second quantization" originated from the fact that in this case we quantize the equation which has already been quantized as a result of the first quantization. We note that as a
result of second quantization, the coefficients $C_n$ become operators ($q$ numbers), whereas in the Schrödinger theory they remained ordinary constants ($c$ numbers).

In order to carry out the second quantization, it is necessary to find the average value of the energy operator

$$\bar{H} = \int \psi^*(t) H \psi(t) d^3x. \quad \text{(29.9)}$$

Substituting (29.1) in place of $\psi(t)$ and recalling that $H \psi_n = E_n \psi_n$, we find

$$\bar{H} = \sum_{n, n'} E_n C_{n'}^*(t) C_n(t) \int \psi_{n'}^* \psi_n d^3x.$$

Taking into account the orthonormality condition Eq. (29.3), we obtain

$$\bar{H} = \sum_n E_n C_{n'}^*(t) C_n(t). \quad \text{(29.10)}$$

We note that the last expression is independent of $t$, since it is apparent from the equations

$$C_n(t) = C_n e^{-\frac{iE_n t}{\hbar}}, \quad C_{n'}^*(t) = C_{n'}^* e^{\frac{iE_{n'} t}{\hbar}} \quad \text{(29.11)}$$

that the time factor in the product $C_{n'}^*(t) \cdot C_n(t)$ is simply equal to unity

$$C_{n'}^*(t) C_n(t) = C_n C_n.$$

Expression (29.10) is not an operator in the Schrödinger theory, since the coefficients $C_n$ are ordinary numbers ($c$ numbers). In the theory of second quantization, however, these quantities and the Hamiltonian (29.10) should be regarded as operators, that is, as $q$ numbers.

To find the commutation relation for the coefficients $C_n$, we must substitute $C_n(t)$ and $C_{n'}^*(t)$ in place of $x$ and $p$ in the quantum equation of motion (29.5), and the operator $H$ must be replaced by its average value $\bar{H}$. We get

$$\frac{\partial C_n(t)}{\partial t} = \frac{i}{\hbar} (\bar{H} C_n(t) - C_n(t) \bar{H}). \quad \text{(29.12)}$$

According to Eq. (29.11),

$$C_{n'}^*(t) = -\frac{iE_{n'}}{\hbar} C_n e^{-\frac{iE_n t}{\hbar}}.$$
and therefore from (29.12) we find the following relation, which is a fundamental postulate of the second quantization:

\[-E_n C_{n'} = H C_{n'} - C_n H.\]  

(29.13)

Substituting $H$ from Eq. (29.10), we obtain

\[-E_n C_{n'} = \sum_n E_n (C_n C_{n'} - C_n C_n).\]  

(29.14)

The last equation has two solutions, corresponding to the Bose statistics and Fermi statistics, respectively. The first solution is

\[C_n C_{n'} - C_{n'} C_n = 0,\]

\[C_n C_n^* - C_n^* C_n = \delta_{nn'}.\]

(29.15)

This can be easily verified by substituting the expressions

\[C_n C_{n'} = C_{n'} C_n,\]

\[C_n C_n^* = C_n^* C_n + \delta_{nn'}\]

(29.16)

into the first and second terms, respectively, on the right-hand side of Eq. (29.14). We then obtain the identity

\[-E_n C_{n'} = - \sum_n E_n \delta_{nn'}.\]

From Eq. (29.15), it follows that the coefficients $C_n$ and $C_n^*$ are operators. Setting

\[C_n^* C_n = N,\]

(29.17)

where $N$ is the number of particles in the state $n$, we find from Eqs. (29.15)

\[C_n C_n^* = \mathbf{1} - N.\]

(29.18)

It follows, therefore, that these operators do not vanish even in the case where there are no particles present. Indeed, even though $C_n C_n = 0$ when $N = 0$, we still have in that case $C_n^* C_n = 1$. This nonzero value for the combination of coefficients $C$ gives rise to a relationship between the vacuum (the field of virtual particles) and the real particles.

---

1 It follows from Eq. (29.15) that the wave functions $\psi(r, t)$ and $\psi(r', t)$ commute, while $\psi$ and $\psi^*$ do not commute

\[\psi(r, t) \psi^*(r', t) - \psi^*(r', t) \psi(r, t) = \sum_n \psi_n^*(r') \psi_n(r) = \delta(r' - r).\]
It is clear from the above equations that the operator $C^*_n$ should be regarded as the "creation" operator for particles, and $C_n$ as the "destruction" operator. If at the initial time there are no particles present, the condition $C_nC^*_n = 1$ signifies that a particle can first appear (owing to the action of operator $C^*_n$), and then disappear (owing to the action of $C_n$). The condition $C^*_nC_n = 0$ implies that in the absence of particles the inverse process, in which a particle is first absorbed and then emitted, cannot occur.

In the solutions (29.17) and (29.18), the quantity $N$ must be a positive integer. It is not restricted to any maximum value. Therefore, these commutation relations correspond to the Bose statistics, which allows any number of particles to be present in one state.

The second solution of Eq. (29.14) can be represented as

\[ C^*_n C_n + C_n C^*_n = 0, \]
\[ C^*_n C_n + C_n C^*_n = \delta_{nn'}, \]

which is easily verified by the direct substitution of Eq. (29.19) into Eq. (29.14). Setting

\[ C^*_n C_n = N, \]

we find

\[ C_n C^*_n = 1 - N. \]

Noting that $C^*_n C_n$ and $C_n C^*_n$ cannot be negative, we find that the number of particles in the state $n$ can assume only two values: $N = 0$ and $N = 1$. Consequently, the Pauli exclusion principle is already included into this solution and the particles obey the Fermi statistics. In particular, if there are no particles present initially ($N = 0$), then just as in the case of the Bose statistics we have

\[ C^*_n C_n = 0, \quad C_n C^*_n = 1. \]

The equation obtained in second quantization describes, therefore, a state with a variable (integral) number of particles. Consequently, electrons will be similar to photons not only because their motion is described by a wave equation, but also because electrons, just like photons, can be created and destroyed.

Since the creation and annihilation of electrons requires an energy more than twice as great as the rest-mass energy of an electron (since an electron is always created together with a positron), the second quantization of the nonrelativistic Schrödinger equation is of purely methodological significance. In order to consider real wave processes associated with the creation or annihilation of particles, one should extend the method of second
quantization to relativistic equations—namely, the wave equation for photons (Maxwell’s equations) and the relativistic wave equation for electrons and positrons (Dirac’s equation).

B. QUANTIZATION OF MAXWELL’S EQUATIONS

It is well known that the photon field (electromagnetic field) can be described by a vector potential which satisfies the d’Alembert’s equation

$$\nabla^2 A - \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} = 0, \quad (29.23)$$

and is subjected to the following condition:

$$\nabla \cdot A = 0. \quad (29.24)$$

Since the vector potential $A$ is a real quantity, we can represent the solution of (29.23) as

$$A = \frac{1}{\sqrt{2} \pi} \sum_{\kappa} \sqrt{\frac{2 \pi \hbar}{\omega}} (a e^{-i \omega t - i \kappa \cdot r} + a^* e^{i \omega t - i \kappa \cdot r}), \quad (29.25)$$

where

$$\kappa = |\kappa|, \text{ and } \kappa_i = \frac{2 \pi}{L} n_i (n_i = 0, \pm 1, \pm 2, \pm 3 \ldots).$$

The condition (29.24) means that the vector $a$ is perpendicular to vector $\kappa$, that is,

$$\kappa \cdot a = 0. \quad (29.26)$$

The normalization coefficient $\frac{1}{\sqrt{\frac{2 \pi \hbar}{\omega}}}$ is determined from the condition that the energy of the electromagnetic field

$$\bar{H} = \frac{1}{8 \pi} \int [(E)^2 + (H)^2] d^3x = \frac{1}{8 \pi} \int \left\{ \left( \frac{1}{c} \frac{\partial A}{\partial t} \right)^2 + (\nabla \times A)^2 \right\} d^3x = \sum_{\kappa} \frac{\hbar \omega}{2} \left[ (a^* \cdot a) + (a \cdot a^*) \right] \quad (29.27)$$

must be equal to the sum of the products obtained by multiplying the energies $\hbar \omega$ of the individual particles by the corresponding squared amplitudes.

Since the Hamiltonian is proportional to the combinations of coefficients of the form $C^* C + CC^*$ (the amplitudes of $a$ in this case play the role of the coefficients $C$), the quantum equation of motion
(29.13) for the field of photons permits only a solution corresponding to the Bose statistics. Furthermore, taking into account the condition (29.24), we obtain the following commutation relations:

\[ a_i a^\dagger_i - a^\dagger_i a_i = A_{ii'} = \delta_{ii'} - \frac{x_{i'} x_i}{x^2}, \]

(29.28)

where \( i, i' = 1, 2, 3 \) and the amplitudes \( a_i \) and \( a^\dagger_i \) refer to the same vector \( \mathbf{x} \), which plays the role of the quantum number \( n \) [see Eqs. (29.15)]. The coefficient \( A_{ii'} \) expresses the transverse character of the photon field

\[ x_i A_{ii'} = x_{i'} A_{ii'} = 0. \]

(29.29)

In particular, if there are no photons present at the initial instant, only the following bilinear combination of amplitudes will be nonvanishing:

\[ a_i a^\dagger_i = \delta_{ii'} - \frac{x_{i'} x_i}{x^2}. \]

(29.30)

C. SPONTANEOUS EMISSION

In Chapter 9 we found the Einstein coefficients \( A \) for the spontaneous emission by using the correspondence principle. In such treatment, the reasons for transitions of electrons from higher to lower levels remained unexplained (see Chapter 9). Quantum electrodynamics (the name given to the theory that includes second quantization of the electromagnetic field) explains the transitions in terms of the interaction of an electron with the field of vacuum (virtual) photons.

As can be seen from Eq. (29.30), there are quadratic combinations of the quantized amplitudes of the electromagnetic field which differ from zero even in the absence of real photons.

The time-dependent Schrödinger equation, taking into account the doubly quantized field of photons, can be represented as

\[ \left[ -\frac{\hbar}{i} \frac{\partial}{\partial t} - V - \frac{1}{2m_0} \left( \mathbf{p} - \frac{e}{c} \mathbf{A} \right)^2 \right] \phi = 0. \]

(29.31)

Neglecting the second-order terms proportional to \( A^2 \), and taking into account the transverse character of the electromagnetic waves

\[ (\mathbf{p} \cdot \mathbf{A}) \phi = (A \cdot \mathbf{p}) \phi, \]

(29.32)

\(^2\text{If these amplitudes occur in the Hamiltonian in the combination } C^* C - CC^* \text{ (this happens, for example, for Dirac particles), then only the Fermi statistics would hold for the corresponding amplitudes. This is easily verified by substituting into the Hamiltonian the different solutions for the Bose statistics [see Eq. (29.16)] and for Fermi statistics [see Eq. (29.19)].} \)
since
\[ \mathbf{v} \cdot \mathbf{A} = 0. \]

Eq. (29.31) can be reduced to
\[
\left[ -\frac{\hbar}{i} \frac{\partial}{\partial t} - \mathcal{H}^0 - V'(t) \right] \psi = 0. \tag{29.33}
\]

Here the unperturbed Hamiltonian \( \mathcal{H}^0 = V + \frac{1}{2m_0} \mathbf{p}^2 \) is time-independent, and the operator of the perturbation energy is
\[ V'(t) = -\frac{\epsilon}{cm_0} \mathbf{A}'(t) \cdot \mathbf{p}. \]

Let us assume that the electron is initially in the state \( \mathbf{n} \). Then under the influence of virtual photons\(^3\)

\[ V'(t) = -\frac{\epsilon}{cm_0} \mathbf{A} \cdot \mathbf{p} = -\frac{\epsilon}{L^2 / \epsilon m_0} \sum_x \sqrt{\frac{2\pi \hbar}{\epsilon x}} \mathbf{e}^{i\omega x} \mathbf{e}^{-ixr} \mathbf{a}^* \cdot \mathbf{p} \tag{29.34} \]

the electron can jump into the state \( \mathbf{n}' \).

In accordance with Eq. (28.12), we obtain the following expression for the coefficient \( C_{n'}(t) \), characterizing this transition:

\[ C_{n'}(t) = \frac{i\epsilon}{L^2 / \epsilon m_0} \sum_x \sqrt{\frac{2\pi \hbar}{\epsilon x}} \left( 1 - \frac{\epsilon}{L(\omega_{nn'} - \omega)} \right) \mathbf{a}^* \cdot \mathbf{p}_{nn'}, \tag{29.35} \]

where the matrix element
\[ \mathbf{p}_{nn'} = \int \psi_n^* e^{-i\omega x} \mathbf{p} \psi_{n'} d^3x, \tag{29.36} \]

and \( \omega = \epsilon x \) is the frequency of the emitted photons.

The quantity \( \mathbf{x} \cdot \mathbf{r} \sim \frac{r}{\lambda} \) is small since the wavelength of the emitted light is \( \lambda \sim 10^{-3} \) cm, and the dimensions of the atom are of the order of \( r \sim 10^{-8} \) cm. Therefore, in a first approximation, the exponential factor in Eq. (29.36)

\[ e^{-i\omega x \cdot r} \approx 1 - i\mathbf{x} \cdot \mathbf{r} - \ldots \]

should be set equal to unity. Such transitions are called the dipole transitions.\(^4\)

---

\(^3\)Taking into account the commutation relations in (29.30) in the expression for the vector potential \( \mathbf{A} \) in the case when there are no photons, we should retain only amplitudes proportional to \( \mathbf{a}^* \), that is, operators for the creation of particles.

\(^4\)If we include the next term in the expansion we obtain quadrupole radiation. Quadrupole radiation is \( (r/\lambda)^4 \) times weaker than dipole radiation and is of importance only when dipole transitions are forbidden.
The probability of a spontaneous transition from the energy level \( n \) to the level \( n' \) is equal to

\[
A_{nn'} = \frac{\partial}{\partial t} C_{n'}^*(t) C_n(t) = \frac{e^2}{L^2m_0^2} \sum_k \frac{2\pi}{\hbar\omega} \sin t(\omega_{nn'} - \omega) \frac{1}{\omega_{nn'} - \omega} (a \cdot p^*_{n'}(a^* \cdot p_{n'}).
\]

Here instead of two sums over the wave numbers of amplitudes \( a \) we left only one, since the only combinations of amplitudes \( a \) and \( a^* \)

\[
a_i a_i^* = \delta_{ii'} \frac{\hbar^2 v_i'}{\chi^2},
\]

different from zero are those which refer to the same momentum \( \chi \).

Using the last commutation relations, we find

\[
(a \cdot p^*_{n'})(a^* \cdot p_{n'}) = \left| [\chi^2 p_{n'}] \right|^2.
\]

Let us replace the sum over \( \chi \) by an integral in Eq. (29.37) [see also Eq. (28.23)]

\[
\frac{1}{L^2} \sum_k \frac{1}{8\pi^3} \int d^3\chi = \frac{1}{8\pi^3c^2} \int \omega^2 d\omega d\Omega
\]

and include the fact that for sufficiently large values of time \( t \), we have, in accordance with (28.20),

\[
\frac{1}{\pi} \frac{\sin t(\omega - \omega_{nn'})}{\omega - \omega_{nn'}} = \delta(\omega - \omega_{nn'}).
\]

Then in the case of spontaneous transitions Eq. (29.39) reduces to the law of conservation of energy

\[
\omega = \omega_{nn'} = \frac{E_n - E_{n'}}{\hbar},
\]

since from Eq. (29.40) it follows that the energy of the emitted photon \( \hbar \omega \) is equal to the energy \((E_n - E_{n'})\) lost by the atom as a result of transition. For the probability of spontaneous emission, we obtain

\[
A_{nn'} = \frac{e^2 \omega_{nn'} |p_{n'n'}|^2}{2\pi \hbar c^2 m_0^2} \int \sin^2 \theta d\Omega.
\]

Evaluating this integral and remembering that \( p_{n'n'} = -i m_0 \omega_{nn'} r_{n'n'} \), we obtain the final expression for the probability of spontaneous emission

\[
A_{nn'} = \frac{4}{3} \frac{e^2 \omega_{nn'}^3}{\hbar c^2} |r_{n'n'}|^2,
\]
which was already derived in Chapter 9 with the aid of the semi classical correspondence principle [see Eq. (9.20)].

D. BETA DECAY

As another example of the application of second quantization let us consider the theory of $\beta$ decay. This phenomenon consists of the emission of an electron (positron) by a nucleus, leading to an increase (decrease) of the nuclear charge by unity.

The theory of $\beta$ decay, which resembles in some respects the emission of photons by atoms, was constructed on the basis of second quantization.

There are no photons in an atom. A photon is created from the vacuum when an atom makes a transition from one energy state to another. Similarly, a nucleus does not contain electrons; they are created only in the process of $\beta$ decay.

As a result of experimental investigation of $\beta$ decay it has been established that these electrons have a continuous spectrum bounded by a certain maximum energy equal to the difference in the energy of the nucleus before and after the decay. It was also established that in $\beta$ decay the angular momentum of the nucleus changes by a multiple of $\hbar$, whereas the angular momentum carried away by the electron equals $(1/2)\hbar$.

The apparent violation of the laws of conservation of energy and angular momentum in $\beta$ decay was resolved in the hypothesis of Pauli, who assumed that the emission of an electron is accompanied by the emission of another particle—a neutrino possessing half-integral spin and a rest mass close to zero.

According to the Fermi theory, constructed on the basis of this hypothesis, $\beta$ decay should be considered as the transformation of one of the nuclear neutrons ($n$) into a proton ($p$), an electron ($e^-$), and an antineutrino ($\bar{\nu}$)

$$n \rightarrow p + e^- + \bar{\nu}. $$

Similarly, the emission of positrons in $\beta$ decay should be considered as the transformation of a nuclear proton$^5$ into a neutron, a positron and a neutrino$^6$

$$p \rightarrow n + e^+ + \nu.$$

$^5$We note that since the rest mass of a neutron is greater than the total rest mass of the proton, electron, and antineutrino, it follows that the decay of a free neutron should also be observed. The decay of a free proton appears impossible from the energy standpoint and therefore, positron decay can be observed only in a bound proton, when the required energy can be taken up from the nucleus.

$^6$We shall explain the difference between the neutrino and antineutrino at the end of the present chapter in the discussion of the nonconservation of parity.
Furthermore, the capture of a bound electron is also possible; as a result of electron capture a proton is changed into a neutron and emits a neutrino \((p + e^- \rightarrow n + \nu)\). As a rule, an electron from the \(K\) shell is absorbed in this process, and therefore this phenomenon is called \(K\) capture. \(K\) capture is similar in nature to positron \(\beta\) decay, since in both cases the charge of the nucleus is reduced by unity.

We shall not consider here the details of \(\beta\) decay; our task will be to describe in general terms the creation of an electron and antineutrino following the Fermi theory.

The energy of interaction of a neutron with the electron-antineutrino field can be written as

\[
V_{ei} = f\psi_e^* \psi_{\nu}^*,
\]

where \(f\) is a coupling constant introduced by Fermi. The magnitude of \(f\) is very small \((f \approx 1.4 \times 10^{-49} \text{erg} \times \text{cm}^3)\) so that this interaction is called a weak interaction. The spontaneous decay of particles is caused mainly by weak interactions; therefore, the lifetime of elementary particles or nuclei is comparatively large and varies from a fraction of a second to billions of years. Nuclear processes, on the other hand, are caused by strong interactions, which sometimes are a thousand times larger than the electromagnetic interactions. The duration of the processes caused by such interactions is very short (of the order of \(10^{-23}\) sec).

Neglecting spin effects, the wave functions \(\psi_e^*\) and \(\psi_{\nu}^*\) can be represented as

\[
\begin{align*}
\psi_e^* &= L^{-1/2} a^* e^{i\xi L} e^{-iK \cdot r}, \\
\psi_{\nu}^* &= L^{-1/2} b^* e^{i\xi L} e^{-iK \cdot r}.
\end{align*}
\]

If there are no particles present at the initial instant, the following relations hold for the amplitudes \(a^*\) and \(b^*:\)

\[
a^*a = b^*b = 0, \quad aa^* = bb^* = 1.
\]

Then, according to Eq. (28.12), we have the following expression for the coefficient \(C(t)\):

\[
C(t) = -\frac{if}{\hbar L^3} V_{\rho n} a^* b^* \int_0^t dt e^{-i (\xi (K - r - K - r))}.
\]

Here \(E_n = c\hbar K_n\) is the neutron energy and \(E_p = c\hbar K_p\) is the proton energy. The matrix element of the interaction \(V_{\rho n}\) is

\[
V_{\rho n} = \int \gamma_n \gamma_\rho e^{-i(k + \xi) \cdot r} d^3 x.
\]
amplitudes of the wave functions of the electron and neutrino in Eq. (29.42). However, the influence of the specific choice of the Dirac matrices manifests itself only in the spin effects, which are neglected in the present treatment.

Just as in the investigation of dipole radiation, the quantity in the exponent in the matrix element (29.45) is much less than unity, that is, inside the nucleus

\[(k + \chi) \cdot r \sim |(k + \chi) \cdot R| \ll 1,
\]

where \( R \) is the nuclear radius. The exponential, therefore, may be expanded in a series

\[e^{-i(k + \chi) r} = 1 - i (k + \chi) \cdot r + \ldots\]

If the matrix element (29.45) does not vanish upon replacement of the exponential by unity, the corresponding transitions are said to be allowed \( \beta \) transitions.

We note that the allowed transitions, which correspond to the dipole transitions in the theory of photons, are associated with definite selection rules.\(^7\)

\(^7\)In the case of vector interaction, the matrix element

\[V_{pn} = \int \chi_P^+ \chi_N^0 d^3 x
\]

(the fourth component of the four-dimensional velocity; the first three components for the nucleon at rest vanish) will differ from zero (allowed transitions) if the spin of the nucleus (that is, the total angular momentum) remains unchanged in the \( \beta \) decay (\( \Delta J = 0 \), Fermi transitions). This Fermi selection rule is satisfied for the majority of nuclei.

There are, however, some cases of allowed \( \beta \) decay, for example, \( ^2\text{He}^6 \rightarrow ^3\text{Li}^6 + e^- + \bar{\nu} \) in which the spin of the nucleus changes by unity (\( \Delta J = 1 \)). The spin of the \(^2\text{He}^6\) nucleus is equal to zero (one alpha particle plus two neutrons with antiparallel spins), while the spin of the \(^3\text{Li}^6\) nucleus is equal to unity (one alpha particle plus one proton and one neutron with parallel spins, just as in deuterium).

In order to explain these selection rules, Gamow and Teller pointed out that when we form the interaction energy operator, which is a scalar \((V = V_{pn} V_{e\nu})\), one may take a product of two vectors, as well as other relativistically invariant combinations of the four wave functions. For example, we may take a product of two pseudovectors, which is also a relativistic invariant. The pseudovector interaction

\[V'_{pn} = \int \chi_P^+ \sigma \chi_N^0 d^3 x
\]

leads to the selection rules \( \Delta J = 0, \pm 1 \). It should be emphasized that for a nucleon at rest, the first three components will be different from zero.

In view of the fact that the pseudovector interaction forbids \( 0 \rightarrow 0 \) transitions, which were nevertheless observed experimentally, as well as for several other reasons, present-day theory uses a combination of vector and pseudovector interactions (as in the Feynman and Gell-Mann version of the theory of \( \beta \) decay). This version enables us to explain the basic experimental data obtained in the investigation of \( \beta \) decay.
In the subsequent discussion, we shall restrict ourselves to the treatment of allowed transitions; in this case it is sufficient to make the exponential term in the matrix element (29.35) equal to unity. We then obtain the following expression for the coefficient $C$:

$$C' = \frac{f}{\hbar L} V_{pn} a^* b^+ \frac{1 - e^{i\epsilon(k+z - K_{np})}}{\epsilon (K + z - K_{np})},$$  

(29.46)

where $E_0 = \hbar K_{np} = \hbar (K_n - K_p)$ is the energy carried away by the light particles (electron, neutrino or antineutrino) in $\beta$ decay.

Using Eq. (29.39) and changing the summation over the momenta of electron and neutrino to an integration [see (29.38)], we obtain an expression for the probability of $\beta$ decay

$$\omega = \frac{\partial}{\partial t} \sum_{k, \pm} C^* C = \frac{f^2 |V_{pn}|^2}{32\hbar^2 \pi^2} \int d^2 k d^3 k' (K + z - K_{np}).$$  

(29.47)

Integrating this expression over all possible angles at which the electron and antineutrino emerge from the nucleus and also over the energy of the antineutrino, we obtain an equation for the energy distribution ($E = \hbar K$) of the electrons (the $\beta$ spectrum)

$$\omega = \int_{m_0c^2}^{E_0} \omega (E) dE,$$  

(29.48)

where

$$\omega (E) = \frac{f^2 |V_{pn}|^2}{2\pi^2 e^2} \frac{E}{E^2 - m_0^2 c^4} (E_0 - E)^2.$$  

(29.49)
The energy-distribution curve of the $\beta$ electrons, obtained in the Fermi theory, is plotted in Fig. 29.1. From this curve it is clear that the energy of the emitted electrons lies between $E_{\text{min}} = m_0c^4$ and $E_{\text{max}} = E_0 = E_\alpha - E_\mu$.

According to the Pauli-Fermi theory, there is no violation of the law of conservation of energy, since the total energy of the emitted antineutrino and electron must always be equal to the total energy lost by the nucleus during $\beta$ decay.\(^8\)

**E. NONCONSERVATION OF PARITY IN THE DECAY OF PARTICLES**

One of the fundamental discoveries in the theory of weak interactions was the discovery of the nonconservation of parity by Lee and Yang (1956). This phenomenon gives rise to a spatial asymmetry in the spontaneous decay of elementary particles and, in particular, in nuclear $\beta$ decay.

The nonconservation of parity can be observed experimentally in the following two phenomena:

1. The asymmetry of the angular distribution of electrons in the $\beta$ decay of nuclei with an oriented spin (the number of $\beta$ electrons emerging along the direction of nuclear spin does not equal the number of electrons emerging in the opposite direction).
2. The existence of circular polarization (helicity) in the particles formed during decay (for example, electrons formed in $\beta$ decay or $\mu$ mesons formed in the decay of $\pi$ mesons), even in the case when the decaying system has zero spin.

The phenomenon of nonconservation of parity in $\beta$ decay or in the decay of a $\pi$ meson was explained with the help of the theory that assigned a definite circular polarization (helicity) to the neutrino. At one time it was thought that the neutrino (which is formed in positron $\beta$ decay) and the antineutrino (which is formed in electron $\beta$ decay) were identical particles (Majorana's hypothesis). It was suggested that this hypothesis could be tested in double $\beta$ decay.

If the neutrino and antineutrino were identical, one would expect comparatively large values for the probability of double $\beta$ decay without the emission of a neutrino (one neutron of the nucleus emits an electron and a neutrino, while another neutron emits an electron and absorbs this neutrino), that is, with the emission of only two electrons. If, however, double $\beta$ decay consisted simply of two successive identical $\beta$ decays with the emission of two electrons and two antineutrinos, the probability of decay should be much less. Experiment has confirmed the correctness of the second hypothesis and clearly demonstrated that the neutrino must be different from the antineutrino.

We note, incidentally, that both particles are neutral and have a spin $1/2$. Physicists, however, were able to establish a difference between the particles from phenomena associated with nonconservation of parity. It has been demonstrated experimentally that the asymmetry observed during positron $\beta$ decay of a nucleus with an oriented spin, when a neutrino is emitted together with a positron, is the reverse of the asymmetry that is observed during electron $\beta$ decay, in which an antineutrino is emitted together with an electron. It was assumed, therefore, that the neutrino differs from the antineutrino by the type of circular polarization. In order to explain the experimental data, it was necessary to postulate that a neutrino resembles a photon with left-hand circular polarization, while an antineutrino resembles a photon with right-hand polarization. The

\(^8\)It should be noted that the maximum of this curve is slightly shifted towards small energies. This asymmetry is due to the fact that the antineutrino mass is equal to zero, while the electron mass is different from zero. If the mass of the antineutrino were equal to the electron mass, this curve (neglecting the Coulomb attraction of the electron and the nucleus) would be symmetrical; that is, the maximum would occur at the point $E/2$.

only difference is that the spin of the photon is 1 (in units of $\hbar$), whereas the spin of the neutrino is 1/2.

![Fig. 29.2. Helicity of the neutrino and antineutrino. The neutrino has a left-hand circular polarization and the antineutrino has a right-hand circular polarization.]

The circular (longitudinal) polarization of the neutrino is generally called the helicity. The neutrino has left-hand circular polarization, or negative helicity. This means that if a left-handed screw rotates along the direction of polarization, it moves in the direction of the momentum. The antineutrino, however, has right-hand circular polarization, or positive helicity (see Fig. 29.2). In order to conserve helicity when changing from one Lorentz frame of reference to another, so that it can be adopted as a characteristic of the neutrino, it is necessary that the rest mass of the neutrino be exactly equal to zero. 10

Several authors describe polarization with the aid of an axial vector, which is perpendicular to the plane of rotation and has a different direction in the right-hand and left-hand coordinate systems (see Fig. 29.3). It should be noted, however, that, although the axial vector $s$ and the polar vector $p$ have different mutual orientations in the right-hand and left-hand coordinate systems, the helicity is nevertheless conserved; that is, the helicity of the neutrino is still negative, and only the method of description has changed. 11

Starting with the polarization properties of the neutrino, we shall make an attempt to give a qualitative explanation of the nonconservation of parity during the spontaneous decay of particles.

Let us consider, for example, the $\beta$ decay of nuclei with oriented spin. We note that the spin of the nucleus (its longitudinal polarization) is more naturally described by a rotation, since the direction of the axial spin vector is arbitrary. The spatial asymmetry which should be observed in the phenomena characterized by the nonconservation of parity is associated with the fact that in electron $\beta$ decay, right-handed antineutrinos are emitted upwards and downwards with spins oriented, respectively, parallel and antiparallel to the spin of the nucleus. The electrons will be formed predominantly with a helicity opposite to that of an antineutrino (that is, with a negative helicity). This produces a spatial asymmetry due to which the number of electrons emitted in the direction of nuclear spin does not equal the number of electrons emitted in the opposite direction (see Fig. 29.4). In general, we obtain the following equation for the number of emitted electrons as a function of the angle $\theta$ between the direction of electron momentum and the upward direction, which two directions form a right-handed system with the polarization of a nucleus:

$$w_e(\theta) = w_\nu(1 - a \cos \theta),$$  \hspace{1cm} (29.50)

where $a$ is positive and is equal to approximately 0.4.

10 If the rest mass of a particle differs from zero, the parallel spin and momentum vectors may be directed at an angle after transition from one Lorentz frame of reference to another.

11 Since the direction of the (axial) spin vector $s$ relative to the polar vector of the momentum $p$ is different in the right-hand and left-hand coordinate systems, Lee, Yang, Landau [Journal Experimental'noy i Teoreticheskoy Fiziki, 32, 405 (1957)], and others assume, on the contrary, that in this case the negative helicity of a neutrino changes to a positive helicity. In other words, they assume that the method of geometric description of the particle can change its internal properties (helicity).
Asymmetry was detected in the electron $\beta$ decay of Co 60 nuclei with oriented spins and also in the angular distribution of electrons in the $\beta$ decay of free, polarized neutrons (for which $\alpha \approx 0.1$).

Since a neutrino with a negative helicity emerges during positron decay, the asymmetry pattern will be opposite to the one described above. The number of emitted positrons is related to the angle $\theta$ by the equation

$$\psi_{\nu}^{\prime}(\theta) = \psi_{0,\nu} (1 - \alpha \cos \theta);$$  \hspace{1cm} (29.51)

that is, the positrons that are formed have mainly a positive helicity and are emitted primarily upwards. An asymmetry opposite to that of electron decay was observed experimentally in positron $\beta$ decay of Co 58 nuclei with oriented spins.

Longitudinal polarization was observed particularly clearly in the spontaneous decay of pions into muons and a neutrino. Let us choose a coordinate system in which the pion is at rest and consider the negative pion which decays into a negative muon and an antineutrino. Since the antineutrino has a positive helicity and the momenta of the muon and the antineutrino must be equal and opposite, we find that the muon also must have a positive helicity. Indeed, only in this case will the total spin of the muon-antineutrino system be equal to the initial spin, that is, zero. In the decay of positive pions into a neutrino and positive muons, the muons, however, will obviously have a negative helicity (see Fig. 29.5).
The total longitudinal polarization of the created muons has also been confirmed experimentally.

A more detailed discussion of the nonconservation of parity lies outside the scope of this book, and we must refer the reader to the special literature on this subject. ¹²

Appendix A

Hilbert Space and Transformation Theory

There is an elaborate formal structure of quantum mechanics that is important for several reasons: the wave mechanics and the matrix mechanics can be unified in one coherent scheme. The conceptual structure has a deep intuitive appeal that gives the theory a sense of completeness and solidity. The physical content can be embedded in an extensive and rigorous mathematical framework. And, most important for the validity of the physical theory, it is a powerful and flexible phenomenological tool that embraces a wide variety of empirical knowledge. The conceptual structure and statistical foundations of quantum mechanics are formulated most fully in the framework of "abstract Hilbert space." It is, however, not necessary to go into the mathematical technicalities to achieve an accurate physical grasp of the theory. For a complete treatment of the mathematical and statistical foundations one should consult the original literature.¹ In this appendix we shall outline some definitions and notational apparatus around three broad topics: vector spaces, operators and the inner product.

Vector Spaces

An abstract (complex) vector space is a set of abstract elements called vectors (or points in the space) which together with complex numbers obey the following axioms:

1. If \( \Psi_a \) and \( \Psi_b \) are vectors, \( \Psi_a + \Psi_b = \Psi_b + \Psi_a \) is also a vector.
2. \( \Psi_a + (\Psi_b + \Psi_c) = (\Psi_a + \Psi_b) + \Psi_c \).
3. If \( x \) and \( y \) are complex numbers and \( \Psi \) is a vector, then \( x\Psi \) is a vector and \( x(y\Psi) = (xy)\Psi \).
4. \( (x + y)\Psi = x\Psi + y\Psi \) and \( x(\Psi_a + \Psi_b) = x\Psi_a + x\Psi_b \).
5. There is a null vector \( \Psi_{\text{null}} = 0 \) such that \( \Psi + \Psi_{\text{null}} = \Psi \) and \( 0\Psi = \Psi_{\text{null}} \) for all \( \Psi \).

APPENDIX A

The structure of a vector space is appropriate for introducing the notion of linear independence: the set of vectors $\Psi_1, \Psi_2, \ldots, \Psi_k$ are linearly independent if the only set of complex numbers $z_1, z_2, \ldots, z_k$ satisfying the relation

$$z_1 \Psi_1 + z_2 \Psi_2 + \cdots + z_k \Psi_k = \Psi_{\text{null}}$$

is the trivial set $z_1 = z_2 = \cdots = z_k = 0$. If it is possible to specify $n$ linearly independent vectors but not $n + 1$, the space is said to be $n$-dimensional. If there is no limit to the number of linearly independent vectors that may be specified, then the space is "infinite dimensional." In an $n$-dimensional space a set of $n$ linearly independent vectors $\Psi_1, \Psi_2, \ldots, \Psi_n$ forms a basis that spans the space in the sense that any element $\Psi_a$ of the space can be written as a linear combination of the basis vectors $\Psi_i, i = 1, 2, \ldots, n$,

$$\Psi_a = \sum_{i=1}^n a_i \Psi_i$$

The coefficients $a_i, i = 1, 2, \ldots, n$ are complex numbers that characterize the vector $\Psi_a$ in the basis $\Psi_1, \Psi_2, \ldots, \Psi_n$. If $a_i$ and $b_i, i = 1, 2, \ldots, n$ are the components of the vectors $\Psi_a = \sum a_i \Psi_i$ and $\Psi_b = \sum b_i \Psi_i$, then $c_i = a_i + b_i$ are the components of the vector $\Psi_c = \sum c_i \Psi_i = \Psi_a + \Psi_b$ and $za_i$ are the components of the vector $z\Psi_a$, where $z$ is a complex number.

The geometric concept which is the $k$-dimensional generalization of the notion of "lines and planes passing through the origin," can be developed with the following definition:

A subset $\mathcal{M}$ of a vector space is called a linear manifold if it contains all the linear combinations $y_1 \Psi_1 + y_2 \Psi_2 + \cdots + y_k \Psi_k$ along with any $k (k = 1, 2, \ldots)$ of its elements $\Psi_1, \Psi_2, \ldots, \Psi_k$. Alternatively, if $\mathcal{M}$ is an arbitrary set of vectors containing the distinct vectors $\Psi_1, \Psi_2, \ldots, \Psi_k$, then the set of all linear combinations $x_1 \Psi_1 + x_2 \Psi_2 + \cdots + x_k \Psi_k$ (with arbitrary complex numbers $x_1, x_2, \ldots, x_k$) is a linear manifold $\mathcal{M}$. $\mathcal{M}$ is called the "linear manifold spanned by $\mathcal{M}$". If the vectors $\Psi_1, \Psi_2, \ldots, \Psi_k$ are linearly independent, the manifold is $k$-dimensional.

The utility of the concept of a linear manifold is that it is the domain of definition of a linear operator. In general an operator is a mapping or correspondence from a domain consisting of certain points in the vector space into a range consisting of certain other points, denoted symbolically by $\Psi \rightarrow R(\Psi)$. In quantum mechanics we are concerned with linear operators for which by definition

$$R(\Psi + \Phi) = R(\Psi) + R(\Phi) \quad \text{and} \quad R(a\Psi) = aR(\Psi).$$

That is, the domain of definition of the operator $R$ is a linear manifold. Note that a linear operator need not be defined for all vectors in the space. For example, if the space is the "function space" consisting of square integrable functions on the interval
\(-\infty < \chi < \infty\), then there are vectors (functions) \(\psi\) for which \(\chi \psi\) or \(\partial \psi / \partial \chi\) are not square integrable.

There is a "projection property" associated with a linear manifold: any vector \(\Psi\) may be resolved into the sum of two vectors \(\Psi = \Psi || + \Psi \perp\), where \(\Psi ||\) is in the manifold \(\mathcal{M}\) (i.e., there are complex numbers \(c_1, c_2, \ldots, c_k\) such that \(\Psi || = c_1 \Psi_1 + c_2 \Psi_2 + \cdots + c_k \Psi_k\), where \(\Psi_1, \Psi_2, \ldots, \Psi_k\) span the \(\mathcal{M}\) and \(\Psi \perp\) is entirely outside \(\mathcal{M}\). As a notational device we may define the linear operator \(P_{\mathcal{M}}\) as follows: \(\Psi || = P_{\mathcal{M}} \Psi\) for all \(\Psi\). The domain of definition of \(P_{\mathcal{M}}\) is the entire space, while the range consists of \(\mathcal{M}\) and the null vector. If \(\Psi_1\) lies outside \(\mathcal{M}\), \(P_{\mathcal{M}} \Psi_1 = \psi_{\text{null}}\). If \(\Psi_2\) lies wholly within \(\mathcal{M}\), \(P_{\mathcal{M}} \Psi_2 = \Psi_2\). If \(\Psi\) is an arbitrary vector, \(P_{\mathcal{M}}\) lies entirely within \(\mathcal{M}\) and \(P_{\mathcal{M}}^2 \Psi = P_{\mathcal{M}} (P_{\mathcal{M}} \Psi) = P_{\mathcal{M}} \Psi\). Since this relation holds for all \(\Psi\), we may assert the operator equation

\[
P_{\mathcal{M}}^2 = P_{\mathcal{M}}
\]

An (Hermitian) operator satisfying this relation is called idempotent or a projection operator. It has eigenvalues 0 and 1.

Operators

Let \(A\) stand for a physical observable which upon sharp measurement yields any one of a sequence of values \(A_1, A_2, \ldots\) which are characteristic of the observable. The set of values \(A_1, A_2, \ldots\) is called the spectrum of \(A\). An algebra of observables is set up as follows: let \(z\) be a complex number, then \(zA\) is an observable with characteristic values \(zA_1, zA_2, \ldots\) and if a measurement of \(A\) yields \(A_k\), the measurement of \(zA\) yields \(zA_k\). The observable \(A^2 = AA\) yields the measured value \((A_k)^2\) when \(A\) yields \(A_k\). If \(A\) and \(B\) are simultaneously measurable then the sum \(A + B\) is defined to be the observable that yields \(A_k + B_j\) when \(A\) yields \(A_k\) and \(B\) yields \(B_j\). Finally, the product \(AB\) may be defined by the artifice

\[
AB = \frac{1}{4} (A + B)^2 - \frac{1}{4} (A - B)^2
\]

if \(A\) and \(B\) are simultaneously measurable. These definitions provide a "physical" construction of polynomials of several simultaneously measurable observables \(A, B, \ldots\).

In quantum mechanics the mathematical idealization of an observable is a linear operator on a Hilbert space. Let us first outline the purely algebraic aspects of operators which can be defined without reference to the space on which they act. An abstract operator algebra is a collection of elements called operators which together with complex numbers are endowed with the structure of a vector space (in a technical sense, not to be confused with the Hilbert space) and in addition an operator product. Explicitly,
(1) If $M$ and $N$ are operators, then $M + N = N + M$ is also.
(2) $M + (N + 0) = (M + N) + 0$.
(3) Multiplication by a complex number is allowed; i.e., $xM$ is an operator and $x(yM) = (xy)M$.
(4) $(x \pm y)M = xM \pm yM$ and $x(M \pm N) = xM \pm xN$.
(5) There is a null operator $0$ such that $0 + M = M$ and $0M = 0$ for all $M$.

Furthermore, there is a composition law (the "operator product") which assigns to each ordered pair of operators $(M, N)$ another operator which is denoted by $MN$. The composition law obeys the following axioms (we now denote operators by $T_1, T_2, T_3$):

(a) $T_1T_2$ is a operator if $T_1$ and $T_2$ are; i.e., the operator algebra is closed with respect to the product.
(b) $T_1(T_2T_3) = (T_1T_2)T_3$ (associative rule).
(c) $T_1(aT_2 + bT_3) = aT_1T_2 + bT_1T_3$ and $(aT_2 + bT_3)T_1 = aT_2T_1 + bT_3T_1$.
(d) There is a unit operator $T_{\text{unit}} = 1$ such that $1T = T_1 = T$ for all operators $T$.

Once a concrete identification of the operators is made and a labeling scheme adapted a "multiplication table" can be set up. The multiplication table can be formulated with the help of the notion of linearly independent operators. Assuming there are only a finite number $n$ of linearly independent operators $T_1, T_2, \ldots, T_n$, we may express any operator as a linear combination of these. In particular, as the operator algebra is closed,

$$T_iT_j = \sum_{k=1}^{n} C_{ij}^k T_k,$$

where the complex coefficients $C_{ij}^k$ are the structure constants of the algebra.

The algebraic properties defined by operator axioms (1)-(5) and (a)-(d) can be realized concretely in terms of linear transformations on a vector space. The operator $T_1$ is identified with the transformation which maps $\Psi$ into $T_1\Psi$. The transformation is linear

$$T_1(a\Psi_1 + b\Psi_2) = aT_1\Psi_1 + bT_1\Psi_2.$$
The unique solution \( \Psi_1 \) may be expressed in terms of \( \Phi_1 \) by an operator \( S \) defined by the relation \( \Psi_1 = S\Phi_1 \). It then follows that \( \Psi_1 = ST\Psi_1 \). If this latter equation holds for all \( \Psi_1 \), we may assert the operator equation \( ST = 1 \); \( S \) is called the left inverse of \( T \). If \( TS = 1 \), then \( S \) is the right inverse of \( T \). If \( ST = 1 = TS \), then \( S \) is the inverse of \( T \) and is given the notation \( T^{-1} \) also. \( T = S^{-1} \). If \( A \) and \( B \) have inverses, then the inverse of \( AB \) is \( (AB)^{-1} = B^{-1}A^{-1} \) even if \( A \) and \( B \) do not commute. Finally, if the vectors \( \Psi_1, \Psi_2, \ldots, \Psi_k \) are linearly independent and span a manifold \( \mathcal{M} \), and if \( V \) is a nonsingular transformation, then \( V\Psi_1, V\Psi_2, \ldots, V\Psi_k \) are linearly independent and span the transformed manifold \( V\mathcal{M} \).

**Inner Product**

An Hermitian inner product is a mapping that assigns to each ordered pair of vectors \( \Psi, \Phi \) a complex number designated by \( (\Psi, \Phi) \). The number \( (\Psi, \Phi) \) is called the inner product of \( \Psi \) and \( \Phi \). An inner product has the following properties:

\[
(\Psi, \Phi) = (\Phi, \Psi)^* \quad \text{(Hermitian symmetry)}
\]

\[
(\Psi, a\Phi + b\Omega) = a(\Psi, \Phi) + b(\Psi, \Omega)
\]

\[
(\Psi, \Psi) \geq 0 \quad \text{and} \quad (\Psi, \Psi) = 0 \implies \Psi = \Psi_{\text{null}}.
\]

The *norm* or "length" of a vector \( \Psi \) is \( ||\Psi|| = \sqrt{(\Psi, \Psi)} \) and the distance between \( \Psi \) and \( \Phi \) is \( ||\Psi - \Phi|| \). If \( (\Psi, \Phi) = 0 \) the vectors are orthogonal. A set of vectors \( \Psi_1, \Psi_2, \ldots \) forms an orthonormal basis if \( (\Psi_i, \Psi_k) = \delta_{ik}; i, k = 1, 2, \ldots \). Some important theorems are the Schwartz inequality \( |(\Psi, \Phi)| \leq ||\Psi|| \cdot ||\Phi|| \) and the triangle inequality \( ||\Psi|| + ||\Phi|| \geq ||\Psi + \Phi|| \). For each linear manifold \( \mathcal{M} \) there is an orthonormal basis which spans \( \mathcal{M} \).

The projection operator \( P_{\mathcal{M}} \) of a manifold \( \mathcal{M} \) spanned by the vectors \( \Psi_1, \Psi_2, \ldots, \Psi_k \) can be written in terms of the inner product as

\[
P_{\mathcal{M}} \Psi = \sum_{i=1}^{k} \Psi_i (\Psi_i, \Psi)
\]

The projection operator onto the ray or one dimensional manifold defined by \( \Psi_i \) is \( P_i \Psi = \Psi_i (\Psi_i, \Psi) \). If \( \Psi_1, \Psi_2, \ldots \) is an orthonormal set the projection operators are related to the vectors by the equations \( P_i \Psi_k = \delta_{ik} \Psi_k \). The orthonormality property is \( P_i P_k = \delta_{ik} P_k \) and the completeness relation is \( \sum_i P_i = 1 \), the unit operator.

Let \( \Psi_1, \Psi_2, \ldots \) be the eigenfunctions of an operator \( M \) corresponding to the eigenvalues \( M_1, M_2, \ldots \). For simplicity, let us assume the eigenvalues are distinct, \( M_i \neq M_k \) for \( i \neq k \); then \( (\Psi_i, \Psi_k) = 0 \) and the vectors may be normalized so they form an orthonormal
basis. The relation of the projection operators $P_j$ of this orthonormal basis to the operator $M$ is the following: $MP_j = P_j M = M_j P_j$. The spectral resolution of $M$ is $M = \sum_{j=1}^{\infty} M_j P_j$. Let $F(\lambda)$ be an arbitrary function of a real or complex variable $\lambda$. The operator function $F(M)$ is defined by

$$F(M) = \sum_{j=1}^{\infty} F(M_j) P_j$$

In the mathematical realization of an observable $\mathcal{A}$ in terms of an operator $A$, the eigenvalues $A_1, A_2, \ldots$ of the operator $A$ are identified with the characteristic values $\mathcal{A}_1, \mathcal{A}_2$ of the observable. The construction of polynomials of observables is identified with the construction of functions of an operator given just above.

There is a particularly important notation, the Dirac notation, in which a ket $|\Psi\rangle$ is placed around the symbol $\Psi$ to denote a vector, $|\Psi\rangle$ is called a ket vector. The inner product between vectors $\Psi_a$ and $\Psi_b$ is denoted by $\langle \Psi_a | \Psi_b \rangle$. The expression $\langle \Psi_a |$ is regarded as a vector in its own right; it is called a bra vector or simply a bra. The primary distinction between bra and ket vectors is that if the abstract vector $\Psi$ transforms as $\Psi \rightarrow U\Psi$ under a unitary transformation $U$, the bra $|\Psi\rangle \rightarrow U|\Psi\rangle = |U\Psi\rangle$, while the ket $\langle\Psi|$ transforms (contragrediently) as $\langle\Psi| \rightarrow \langle U\Psi| = \langle\Psi|U^+ = \langle\Psi|U^{-1}$. Under these transformation properties the inner product $\langle\Psi|\Phi\rangle = \langle U\Psi|U\Phi\rangle$ remains invariant. Matrix elements of an operator $M$ are written as $\langle\Psi|M|\Phi\rangle = \langle\Psi,M\Phi\rangle$. In the Dirac notation, the defining equation for a projection operator reads

$$P_{\mathcal{A}} |\Psi\rangle = \sum_{i=1}^{n} |\Psi_i \rangle \langle \Psi_i | \Psi\rangle$$

for an arbitrary ket $|\Psi\rangle$. Since $|\Psi\rangle$ is arbitrary it is a permissible notational device to omit writing the $|\Psi\rangle$. Then the expression for a projection operator in the new notation is

$$P_{\mathcal{A}} = \sum_{i=1}^{n} |\Psi_i \rangle \langle \Psi_i |$$

where the sum runs over the vectors $\Psi_1, \Psi_2, \ldots, \Psi_n$ which span the manifold $\mathcal{A}$. An arbitrary operator $A$ may be expressed in terms of its matrix elements $A_{ik} = \langle \Phi_i, A \Phi_k \rangle$ in a complete orthonormal basis $\Phi_1, \Phi_2, \ldots$ by the notation

$$A = \sum_{i,k} A_{ik} |\Phi_i \rangle \langle \Phi_k |$$

There is a notational simplification possible when working with a particular basis $\Phi_1, \Phi_2, \ldots$ in that the ubiquitous $\Phi$ is a redundancy.
in the notation: the ket vector \(|\Phi_i>| can be abbreviated to read \(|i>|.

The Hilbert space for a specific physical problem is built on the canonical coordinates \(q_1, q_2, \ldots, q_k\) for a system of \(k\)-degrees of freedom. The abstract vectors have no numerical significance, rather the \(q\)'s serve to label what will be considered a complete orthonormal set, \(\Psi q_1, q_2, \ldots, q_k\). The ket will be denoted by \(|q_1, q_2, \ldots, q_k>|. In the (improper) \(\delta\)-function normalization scheme the orthonormality relation is

\[
<q_1', q_2', \ldots, q_k'|q_1, q_2, \ldots, q_k> = \delta(q_1 - q_1')\delta(q_2 - q_2')\cdots\delta(q_k - q_k')
\]

An arbitrary vector \(\Psi a\) may be expanded in the \(\Psi q\) basis:

\[
|\Psi a> = \int \cdots \int \psi_a(q_1, q_2, \ldots, q_k)|q_1, q_2, \ldots, q_k>dq_1 dq_2 \ldots dq_k
\]

where the expansion coefficient \(\psi_a(q_1, q_2, \ldots, q_k)\) is the probability amplitude for finding particle 1 at position \(q_1\), etc.; i.e., \(\psi_a(q_1, q_2, \ldots, q_k)\) is the Schrödinger wave function in the coordinate representation. Taking the inner product of \(|\Psi a>| with the bra \(<q_1, q_2, \ldots, q_K|\) and using the orthonormality relation, one may verify that

\[
\psi_a(q_1, q_2, \ldots, q_k) = <q_1, q_2, \ldots, q_k|\Psi a>.
\]

In quantum mechanics a particle may have a discrete internal degree of freedom, spin, for example, where the discrete variable \(\sigma\) takes on either of two values, \(\uparrow\) for spin up or \(\downarrow\) for spin down. For a particle with spin and one spatial degree of freedom \(x\), an arbitrary state \(\Psi a\) may be expanded as

\[
|\Psi a> = \sum_{\sigma} \int \Phi_\sigma(x)|\Psi x_\sigma> dx,
\]

where \(\Phi_\sigma(x)\) is the probability amplitude for finding the particle at \(x\) with spin \(\sigma\) (see Chapter 16).

Treating now a particle on the interval \(-\infty < x < \infty\) with no spin, we write the inner product of two vectors \(\Psi a\) and \(\Psi b\) by first expanding \(\Psi b\) in terms of the set \(\Psi x\)

\[
\Psi b = \int_{-\infty}^{\infty} \psi_b(x) \Psi x dx,
\]

then taking the inner product using the distributive rule under the integral. The result is

\[
(\Psi a, \Psi b) = \int_{-\infty}^{\infty} (\Psi a, \Psi x) \psi_b(x) dx = \int_{-\infty}^{\infty} \psi_a(x)^* \psi_b(x) dx,
\]
the ordinary function space inner product. The projection operator
$P_{ab}$ onto the interval $a < x < b$ is

$$P_{ab} \Psi = \int_{a}^{b} \Psi_x(x) \, dx,$$

or in the Dirac notation

$$P_{ab} = \int_{a}^{b} |\Psi_x > \, d\Psi_x .$$

An arbitrary operator $M$ is expressed in terms of its $x$-space
matrix elements $<x|M|y> = (\Psi_x, M \Psi_y)$ by the formula

$$M = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} <x|M|y> |\Psi_x > \, dx \, dy$$

the action of an operator $M$ on a (ket) state vector $|\Psi >$ is written as

$$M |\Psi > = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\Psi_x > <x|M|y> <y|\Psi > \, dx \, dy,$$

where it is now appropriate to call $<x|M|y>$ the kernel of the
integral operator $M$. The average value $\bar{M}$, or what is the same
thing, the expectation value of $M$ in the state $\Phi$, is

$$\bar{M} = <\Phi|M|\Phi> = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} <\Phi|x><x|M|y><y|\Phi> \, dx \, dy$$

An operator $V$ is called local if its matrix elements have the
special form $<x|M|y> = \delta(x - y)V(x)$, where $\delta(x - y)$ is the Dirac
$\delta$-function and $V(x)$ is an ordinary function. The expectation value
of a local operator is

$$\bar{V} = \int_{-\infty}^{\infty} <\Phi|x>V(x)<x|\Phi> \, dx .$$

The kinetic energy operator $T$ has the matrix element $<x|T|y> =
-\frac{\hbar^2}{2m} \nabla_x^2 \delta(x - y)$, which is also regarded as a local operator. With
the help of integration-by-parts the expectation value of $T$ can be
written

$$\bar{T} = \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \phi(x)^* \nabla_x^2 \phi(x) \, dx ,$$

where $\phi(x) = <x|\Phi >$. 
Appendix B

The Statistical Assertions of Quantum Mechanics

We consider a canonical system of $k$ degrees of freedom, employing the coordinates $q_1 \ldots q_k$ to specify its configuration and the canonically conjugate momenta to specify its condition of motion. In the wave mechanical mode of description, in the coordinate representation, everything that can be said about the “state of the system at one time” (its configuration, condition of motion and the values of all its physical quantities) must be derived from the wavefunction $\phi(q_1 \ldots q_k)$. The functions admitted as wave functions are those that are square integrable (normalizable, $||\phi||$ finite) and furthermore normalized to unity,

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} |\phi(q_1, \ldots, q_k)|^2 dq_1 \ldots dq_k = 1,$$

although in applications to continuous spectra this requirement may be relaxed. There are three primary statistical assertions:

1. the probability of finding the system within a volume $V$ of configuration space is

$$\int \cdots \int \int_{V} |\phi(q_1, \ldots, q_k)|^2 dq_1 \ldots dq_k,$$

2. if the energy of the system has the operator $H$ with eigenvalues $E_1, E_2, \ldots$ and eigenfunctions $\psi_1, \psi_2, \ldots$, then the probability that the system has the energy value $E_j$ in the state $\phi$ is

$$\left| \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \psi_j(q_1, \ldots, q_k)^* \phi(q_1, \ldots, q_k) dq_1 \ldots dq_k \right|^2,$$

and (3) the average value of a physical observable $\mathcal{A}$ to which the operator $A$ corresponds is

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \phi(q_1, \ldots, q_k)^* A \left( q_1, \ldots, q_k; \frac{\partial}{\partial q_1}, \ldots, \frac{\partial}{\partial q_k} \right) \phi(q_1, \ldots, q_k) dq_1 \ldots dq_k.$$
in the quantum state $\phi$. The interrelation of these three assertions will now be examined.

In order to present assertion (1) in a general form, we introduce the projection operators $P_j(l_j), j = 1, \ldots, k$, associated with the intervalue $I_j$ defined by $q_j^\prime < q_j \leq q_j^\ast$. The projection operator is defined by

$$P_j(l_j)\Phi(q_1, \ldots, q_k) = \begin{cases} \Phi(q_1, \ldots, q_k) \text{ for } q_j^\prime < q_j \leq q_j^\ast \\ 0 \text{ otherwise} \end{cases}$$

The projection operator associated with the (rectangular) volume $V$ is $P_1(l_1)P_2(l_2)\cdots P_k(l_k)$ and the integral specifying the probability of finding the particle described by $\phi$ in $V$ may be reduced to the expression

$$\| P_1(l_1)P_2(l_2)\cdots P_k(l_k)\Phi \|^2$$

For assertions (2), let $P_{E_n}$ denote the projection operator associated with the eigenvalue $E_n$ of $H$, that is,

$$P_{E_n}\psi_m = \psi_n \text{ for } m = n, \text{ and } = 0 \text{ for } m \neq n.$$ 

The probability of finding the value $E_n$ upon a sharp measurement of the energy of a system in the state $\Phi$ can then be put in the form

$$\| P_{E_n}\Phi \|^2.$$ 

The probability of finding the system within an energy interval $E^\prime < E \leq E^\ast$ is

$$\| P(l_E)\Phi \|^2,$$

where $P(l_E)$ is the projection operator associated with the interval

$$P(l_E) = \sum_{E^\prime < E_n \leq E^\ast} P_{E_n}.$$ 

Assertions (1) and (2) may now be unified in what is called "the most general probability assertion possible":

Statistical Postulate: The probability that in the state $\Phi$ the physical quantities with the operators $A_1, A_2, \ldots, A_m$ take on values from the respective intervals $l_1, l_2, \ldots, l_m$ is

$$\| P_1(l_1)P_2(l_2)\cdots P_m(l_m)\Phi \|^2,$$

where $P_1, P_2, \ldots, P_m$ are the projection operators belonging to the operators $A_1, \ldots, A_m$. 
Assertion (1) has \( m = k \), with \( A_1, q_1, A_2, q_2, \ldots, A_k, q_k \); while assertion (2) has \( m = 1 \), with \( A_1 = \mathbb{I} \). In order to insures that this postulate is a coherent statistical statement the following properties must be verified:

(a) Since the order of the operators is arbitrary in formulating the statistical question, the order of the projection operators in the statistical assertion must be immaterial. This implies that the projection operators must commute for arbitrary intervals \( I_1, I_2, \ldots, I_m \), and this in turn implies that the operators \( A_1, A_2, \ldots, A_m \) must commute among themselves.

(b) Vacuous propositions may be inserted at will, viz. if the interval \( I' \) is contained within the interval \( I \), \( P(I) P(I') = P(I') \), or the projection operator for obtaining any value whatever is the identity.

(c) If the interval \( I_j \) lies outside the spectrum of \( A_j \); for some \( j \), the corresponding projection operator is the null operator and the probability is zero.

(d) Probabilities are additive; i.e., if an interval \( I \) is resolved into two disjoint subintervals \( I = I' + I'' \), with operators \( P(I') \) and \( P(I'') \) corresponding to \( I' \) and \( I'' \), respectively, then

\[
\| P(I) \Phi \|^2 = \| P(I') \Phi \|^2 + \| P(I'') \Phi \|^2 .
\]

(e) The total probability \( W \) ranges over the values \( 0 \leq W \leq 1 \) for normalized \( \Phi \).

Assertion (3) at the beginning of this appendix, can be expressed in terms of the inner product. If we introduce the notation \( \text{Exp} | \mathbb{X}, \Phi \rangle \) to stand for the statement "the expectation value of the physical observable \( \mathbb{X} \) in the state \( \Phi \)," assertion (3) may be stated

\[
\text{Exp} | \mathbb{X}, \Phi \rangle = \bar{A} = (\Phi, A\Phi),
\]

where \( A \) is the operator corresponding to \( \mathbb{X} \). Let \( F(\lambda) \) be any function of the real parameter \( \lambda \). There is a theorem to the effect that if the observable \( \mathbb{X} \) has the operator \( A \), then the observable \( F(\mathbb{X}) \) has the operator \( F(A) \). Assertion (3) may then be generalized to read

\[
\text{Exp} | F(\mathbb{X}), \Phi \rangle = \bar{F}(A) = (\Phi, F(A)\Phi) \quad (3')
\]

Assertion (3') can be derived from the statistical postulate as follows: subdivide the interval \((-\infty, \infty)\) into a sequence of subintervals \( I_n = [\lambda_n, \lambda_{n+1}] \), where \(-\infty < \lambda_{-1} < \cdots < +\lambda_0 < \lambda_1 < \cdots > \lambda_n < +\infty \). Let \( \lambda_{\tau} \) be some number in the interval \( \lambda_j < \lambda_{\tau} < \lambda_{j+1} \). The average value \( \bar{F}(A) \) in this mesh is

\[
\bar{F}(A) = \sum_{j=-n}^{n} F(\lambda_j) (\Phi, P(I_j) \Phi)
\]
If we introduce the monotonic increasing projection operation $E(\lambda)$ defined by

$$E(\lambda) = \sum_{\lambda_j \leq \lambda} P(l_j)$$

(conversely, $P(l_j) = E(\lambda_{j+1}) - E(\lambda_j)$) and let the $n \to \infty$ and the mesh size vanish, the sum approaches the Stieltjes integral

$$\int_{-\infty}^{\infty} F(\lambda) \Phi dE(\lambda) \Phi,$$

which by definition of a function of an operator is $(\Phi, F(A) \Phi)$. So far we have indicated that assertions (3) and (3') follow from the Statistical Postulate. What is remarkable is that the converse is also true: the Statistical Postulate follows from assertion (3). The proof of this statement is obtained by a technical application of the following theorem: Let $A_1, A_2, \ldots, A_m$ be a set of mutually commuting operators; there exists an operator $R$ and functions $F_1(\lambda), F_2(\lambda), \ldots, F_m(\lambda)$ such that $A_1 = F_1(R), A_2 = F_2(R), \ldots, F_m = F_m(R)$.

In the preceding discussion we have assumed that the state is a pure state, that is, it is described by single vector $\Phi$. In general, in the physical preparation of a state some of the variables are left uncontrolled and the state is not completely specified. This situation can be formulated in terms of a classical probability distribution that is superimposed on top of the quantum mechanical uncertainty. Let us suppose that the system is in one of the states $\Psi_a, a = 1, 2, \ldots$, but we don't know precisely which one. Let $W_a$ be the classical probability that the system is in the state $\Psi_a$. The basic statistical postulate can now be reformulated as

$$W = \sum_a W_a \| P_1(l_1) P_2(l_2) \cdots P_m(l_m) \Psi_a\|^2$$

and assertion (3) can be generalized to read

$$\text{Exp} \{ \Psi; W_a, \Psi_a \} = \sum_a W_a \langle \Psi_a, A \Psi_a \rangle$$

The states $\Psi_a$ are an arbitrary set of states; they need not be mutually orthogonal. For the $W_a$'s it is required that $W_a \geq 0$ and $\sum W_a = 1$.

The statistical assertions can also be formulated in terms of the trace. The trace of an operator $A$ is

$$\text{tr} A = \sum_i \langle \Psi_i, A \Psi_i \rangle,$$

where the sum runs over a complete orthonormal basis $\Psi_1, \Psi_2, \ldots$. The trace is independent of which basis is used to define it. The
statistical assertions are

\[ W = \text{tr} \rho P_1(l_1)P_2(l_2) \cdots P_m(l_m) \]

and

\[ \text{Exp} \{ \mathcal{A} ; W_a, \Psi_a \} = \text{tr} \rho A \]

where \( \rho \) is the density matrix (operator)

\[ \rho = \sum_a W_a P_a = \sum_a |\Psi_a> W_a <\Psi_a| \]

The density matrix is useful for making a general statement about the time evolution of the system. Expectation values change with time according to the general rule

\[ \frac{d}{dt} \text{Exp} \{ \mathcal{A} ; W_a, \Psi_a \} = \text{tr} \{ \dot{\rho} A + \rho \dot{A} \} . \]

In the Schrödinger picture the burden of change is put on \( \rho \); namely, \( \dot{A} = 0 \) and \( +i\hbar \dot{\rho} = \hat{H}\rho - \rho \hat{H} \), where \( \hat{H} \) is the Hamiltonian. In the Heisenberg picture \( \dot{\rho} = 0 \) and \( -i\hbar \dot{A} = \hat{H}A - AH \), (see Problem 8.4). The Hamiltonian controls the evolution of an isolated system. When the system is subjected to a measurement of one of its observables \( R \) and the eigenvalue \( R' \) obtained the uncontrollable disturbance of the measuring process forces the system discontinuously into the state described by the eigenvector \( \Psi_{R'} \) corresponding to the eigenvalue \( R' \). If the measurement of \( R \) is repeated (before the evolution generated by the Hamiltonian moves the system into another state) the system is already in an eigenstate \( \Psi_{R'} \) of \( R \) and thus yields the value \( R' \) with certainty.
Problems

Chapter 1

1.1 Express the space and time dependence of \( E, H \) and \( A \) in terms of amplitudes and phase angles for a plane wave moving in the positive \( x \) direction. What are the conditions for plane or circularly polarized light? What is the initial data at \( t = 0 \) for solution of Maxwell’s equations or the wave equation for \( A \)? Express the solution in terms of a power series in time. Express the solution for \( t < 0 \) in terms of a solution for \( t > 0 \) with appropriate initial data.

1.2 Determine the magnitudes of \( E \) and \( H \) for unpolarized sunlight characterized by the solar constant (Poynting vector) \( S_x = 2 \text{ cal}^{-1}\text{cm}^{-2}\text{min}^{-1} \). What is the ratio of electric to magnetic force on an electron moving with the speed of an electron in the first Bohr orbit?

1.3 Compare the wave and photon descriptions of normal reflection of sunlight from a mirror. What is the energy density, pressure against the mirror and the density of photons? Take \( \lambda = 5500 \text{Å} \). What is the electric field intensity of a photon absorbed in a 1 cc detector?

1.4 Find an expression for the angular momentum density of an electromagnetic field. Show that a photon carries an angular momentum of magnitude \( \hbar \). Calculate the torque on a quarter wave plate by a normally incident left-circularly (right-screw) polarized light.

1.5 Determine the spectral density of radiation under the assumption that the oscillator representing the behavior of the walls for angular frequency \( \omega \) can assume the energy value \( E = 0 \) or any one of a continuum of values \( E \geq \hbar \omega \). Show that the gap in the energy spectrum is related to the behavior of \( \rho_\omega \) in the quantum region \( kT \ll \hbar \omega \).

Answer. The partition function \[ Z = \sum e^{-\alpha E_n} = 1 + e^{-\alpha \omega/a\omega}. \]

Chapter 2

2.1 Consider the scattering of 4 MeV alpha particles on gold atoms (\( Z = 79 \)). Show that the distance of closest approach is \[ r_{\text{min}} = \left( ZZ'c^2/2E_0 \right) \left( 1 + \csc \frac{1}{2} \theta \right) \] and evaluate it for scattering...
angles 5°, 20° and 80°. At what angles will the scattering deviate from the Rutherford formula?

2.2 Consider the scattering of alpha particles from gold foil. A radium source yields 4.8 MeV a-particles at a rate of 3.7 \times 10^{10} particles per second per gram of Ra. The target has 5.9 \times 10^{22} atoms-cm^{-3}, a thickness of 4 \times 10^{-5} cm, and a cross sectional area of 8 mm². The target is situated 1 cm from the source. Consider a detecting screen of 2 mm² area 5 cm from the target. What amount of radium is required for a counting rate of 30 per minute at scattering angles 10° and 120°?

2.3 Derive (2.46) for a general one-dimensional potential by evaluating \( dl/dE \) directly. Reduce the validity of the Bohr quantization rule for large \( n \) by equating the classical expression for the frequency of the expression in terms of the energy level spacing. (This application of the correspondence principle shows that (2.46) and (2.47) give a consistent classical limit if the same constant \( \hbar \) appears in both equations.)

2.4 Examine the classical and quantum descriptions of the emission of light from a harmonic oscillator. On the basis of the correspondence principle, argue that the \( \hbar \) appearing in the Bohr quantization rule is the same Planck's constant characterizing the corpuscular nature of light. Deduce the energy level spacing and infer the levels between which electric dipole transitions are possible (selection rules).

2.5 Use the correspondence principle to infer the energy levels of a rigid rotator consisting of a mass \( m \) held at distance \( b \) from a fixed axis of rotation. Note that the angular momentum is independent of the mechanical parameters.

2.6 Show that for circular motion in a general centrally symmetric field, the angular momentum is quantized in steps of \( \hbar \).

2.7 Find the energy levels of circular orbits in the Bohr planetary model of the hydrogen atom using the correspondence principle directly. Note that as usual \( n \) is left undetermined up to an additive constant of integration. Infer the selection rules for electric dipole transitions between circular orbits and find the accompanying angular momentum change.

2.8 Estimate the lifetime of a stationary Bohr orbit by computing the time required for the corresponding classical motion to radiate away an amount of energy equal to the quantum energy level spacing. Compute the cumulative time for several successive transitions between circular orbits and compare it with the time taken to radiate the same amount of energy classically.

2.9 Use the Bohr quantization conditions to determine the energy levels of an isotropic three-dimensional harmonic oscillator.
Let the potential energy be \( \frac{1}{2} m a r^2 \) and use polar coordinates in the plane of the classical motion.

2.10 Find the energy levels of the relativistic linear harmonic oscillator according to the Bohr-Sommerfeld quantization rule. Evaluate the lowest order correction to the non-relativistic energies. The potential may be introduced via the scalar potential \( \sqrt{\frac{\Phi}{\Phi}} = b \sqrt{\frac{1}{2}} \) or by replacing the mass invariant by \( M_0 c^2 + \frac{1}{2} k x^2 \).

Chapter 3

3.1 Calculate the deBroglie wave lengths of the following particles each with a kinetic energy 500 keV: photon, electron, proton, and alpha particles. Also of thermal oxygen atoms at 300°K.

3.2 What is the dispersion law \( \omega = \omega(h) \) if the group velocity is inversely proportional to the phase velocity? How is this case realized physically?

3.3 Compare the reflection of a particle and a wave from a moving surface. Show that \( \Delta E/\Delta \omega = \Delta p/\Delta k \), where \( \Delta E(\Delta p) \) is the change in the energy (momentum) of the particle and \( \Delta \omega(\Delta k) \) is the change in frequency (wave number) of the wave. Show this independently of the dispersion law of the wave and the energy-momentum relation of the particle. How can this result be generalized and what is its significance?

3.4 Calculate the deflection of a charged particle by a thin slab of magnetic field, expressing the change of momentum in terms of the vector potential. How is the deflection explained in terms of the wave picture? What is the relation between momentum and wave vector in the presence of a magnetic field?

Answer. \( \delta K = 0 \) across the slab and \( p + A e/c = \hbar k \).

3.5 Consider a particle bouncing back and forth in a rigid box of linear dimension \( L \). What is the minimum measurable kinetic energy of the particle? How much energy is required to constrain an electron to remain within a volume of nuclear size?

3.6 Determine the maximum time a free particle will remain within a volume of radius \( R \) by considering the limitations on the specification of the initial data in the classical description of motion.

3.7 Find an uncertainty relation connecting angular momentum and angular orientation. Consider a rigid rotator. What is the minimum uncertainty in \( L \)?

3.8 One billiard ball bounces on another with a center-to-center height of ten times the radius. What is the optimal horizontal
localization to maximize the number of bounces? What is the maximum number of bounces?

Answer. \( n \sim 50 \).

3.9 What is the optimal localization of an ideal pendulum to maximize the time it will remain balanced in an inverted position and what is the maximum time?

Answer. About six times the period for small oscillations.

Chapter 4

4.1 Under what circumstances can a narrow potential be approximated by a \( \delta \)-function? What is the effect of a \( \delta \)-function potential on the continuity property of a solution of Schrödinger's equation?

4.2 Show that the potential \( V(x) = -g \delta(x^2 - a^2) \) has a discrete antisymmetric eigenfunction for \( g > \hbar^2/m \) and not one for \( g \leq \hbar^2/m \).

4.3 Consider the potential \( V(x) = \infty \) for \( |x| > L \) and \( V(x) = -V_0 \delta(x) \) for \( |x| < L \). Show that for \( V_0 > 0 \) there is one eigenvalue \( E < 0 \) and that it remains discrete as \( L \) approaches infinity.

4.4 Find a complete set of orthonormal eigenfunctions for the potential \( V = -|V_0| \delta(x) \) on the interval \( -\infty < x < \infty \). Check the completeness relation (4.67).

4.5 (Sturm–Liouville theorem) Let \( \psi_1 \) and \( \psi_2 \) be solutions with energies \( E_1 \) and \( E_2 \) of two Schrödinger equations with potentials \( V_1 \) and \( V_2 \), respectively. Show that

\[
\int_a^b \left[ \psi_2^* \psi'_1 - \psi_1^* \psi'_2 \right] dx = (2m/\hbar^2) \int_a^b \psi_2^* \left[ (E_2 - V_2) - (E_1 - V_1) \right] \psi_1 \, dx
\]

for any interval \( a \leq x \leq b \). Show that if \( \psi_1 \) and \( \psi_2 \) are solutions for the same potential and if \( E_2 > E_1 \), then \( \psi_2 \) has at least one node between each pair of consecutive nodes of \( \psi_1 \). Over the entire interval, then, \( \psi_2 \) has at least one more node than \( \psi_1 \). (The eigenfunctions are ordered in energy according to the number of nodes. A set of eigenfunctions is complete if there is one for each integral number of nodes.)

4.6 (Comparison potential for discrete states) Consider the interval \( 0 < x < \infty \) with the boundary condition \( U(0) = 0 \). Find the potential for which \( U = x^n \) is a zero energy solution of the Schrödinger equation. Show that the potential obtained has no discrete eigenfunctions for \( n \) real. If \( n \) is complex, \( n = \frac{1}{2} + i \beta \), show that the potential has arbitrarily many bound (i.e., discrete) states. The solution may be taken to be real \( U = \sqrt{x} \cos \beta \ln x \).
4.7 Let $V_0$ be the comparison potential obtained in problem 4.6. Show the following:
(a) If $V > V_0$ for $x > x_0$, there is no discrete eigenfunctions of $V$ with a node located beyond $x_0$.
(b) If $V < V_0$ for $x > x_0$, there is a discrete eigenfunction with arbitrarily many nodes beyond $x_0$. There are infinitely many discrete states of $V$.
(c) If $V > V_0$ for $0 < x < x_0$, there is no solution for the potential $V$ with $E < 0$ that has a node in the interval $0 < x < x_0$.
(d) If $V < V_0$ for $x < x_0$ (i.e., if $V \to -\infty$ more rapidly than $V_0$), then there are eigenfunctions with arbitrarily many nodes in the interval.

4.8 Scale the function in problem 4.6 to find some eigenfunctions of the potential $V = \sim$ for $x < a$ and $x > b$, $V = -V_0(1/x^2 - 1/b^2)a^2b^2/(b^2 - a^2)$ for $0 < a < x < b$. Is there a restriction among the parameters $V_0$, $a$, and $b$ for this method to work? Can one find a complete set this way?

Chapter 5

5.1 Let a particle be prepared in the state $\psi(x,0) = \sqrt{2a} \theta(x_0 - x)$ 
\[ \exp[ip + a(x - x_0)] \text{ at } t = 0, \] where $a > 0$, $x_0 < 0$ and $\theta(x) = \frac{1}{2}(1 + \text{sign } x)$, Assume that no forces act on the particle for $t > 0$. Expand $\psi(x,0)$ in terms of energy-momentum eigenfunctions and show that for $t > 0$,
\[ \psi(x,t) = \frac{\sqrt{8a\beta}}{\pi} \exp[ipx + \beta x^2 + iy^2/4\beta] \int_0^\infty e^{-L^2 dL} \frac{1}{1 - izL^2}, \]
where $\beta = \hbar t/2m$, $y = x - x_0 - 2\beta p$, and $z = (1 + iy/2a\beta)^{-2}$. Interpret $\psi$ for $t \to \infty$.

5.2 Reconsider the initial wave function specified in problem 5.1. Assume the particle is in a potential field $V = -|V_0|\delta(x)$. Expand $\psi(x,0)$ in terms of the eigenfunctions of problem 4.4 and follow the motion in the dispersion-free approximation (3.20). Compute the probability of the particle being reflected by the potential. What is the probability of finding the particle in the ground state?

5.3 The initial value problem of the time-dependent Schrödinger equation can be solved in the form of an integral operator
\[ G_t(x,x') = \sum_n \psi_n(x) \psi_n^*(x') e^{-i\omega_n t}, \]
where $\psi_n$ is a complete set of orthonormal energy eigenfunctions.
(a) Find the differential equation and boundary conditions for $G_t$ in the case of a general one-dimensional potential.
(b) Show that the force-free motion of a non-relativistic particle in an $s$-dimensional Euclidian space is given by

$$G_t(r,r') = \frac{m}{2n_i} \frac{\exp(-m'(r-r'))}{2\pi\hbar t},$$

(cf. Problem 3.3 in the text. How can $G_t$ serve as an approximation to the $\delta$-function?)

5.4 Find the angular dependence and total current of charged particles flowing from a source at the origin. The wave function far from the source is $\cos \theta e^{ikr/r}$ in spherical coordinates.

5.5 A particle is in a uniform gravitational field in a region bounded from below by a perfectly reflecting surface. Adapt the WKB method to the case of an impenetrable wall and show that the energy levels go as $(n + 3/4)^{2/3}$ for large $n$. Show that $E_n - E_{n-1} \approx \hbar\omega$ for large $n$, where $\omega$ is the classical angular frequency.

Chapter 6

6.1 Find the probability for a particle of charge $+Ze_0$ and speed $v$ to penetrate through the Coulomb barrier to a nucleus of charge $Ze_0$. (Gamow factor)

6.2 Derive (6.35), using integration by parts to pick out terms of order $T^2$ in $E_n^T$.

6.3 Find the pressure exerted by the walls to contain a particle in a very deep potential well of volume $V$ at absolute zero temperatures.

6.4 Find a relation between the volume and pressure of an electron gas at $0^\circ$K.

6.5 Show that (6.66) holds for an arbitrary periodic potential (Block's theorem).

Chapter 7

7.1 Express $1/r$ as an integral operator in the momentum representation.

7.2 Find the kernels for the expression of $p^2$ and $\sqrt{p^2 + m^2c^2}$ as integral operators in the coordinate representation.

7.3 Evaluate the commutator $p_x V(r) - V(r)p_x$.

7.4 Let $R(r,p)$ be a polynomial in the components of $r$ and $p$. Show that

$$\frac{\partial R}{\partial p_x} = \frac{i}{\hbar} (Rx - xR)$$

and indicate explicitly the meaning of the partial derivative.

7.5 (a) Find an expression for the operator $(A - zB)^{-1}$ in powers of $z$, where $A$ and $B$ are non-commuting operators.
(b) Let $A$ and $B$ be $N \times N$ matrices and let $z_1$ be the root of the equation $\det(A - zB) = 0$ which is smallest in absolute value. Prove that the expansion of part (a) converges whenever $|z| < |z_1|$ and diverges whenever $|z| > |z_1|$.

7.6 Show that in general any quantum mechanical operator can be expressed as an integral operator.

7.7 Find an expression for the translation operator $T_a$, defined by $T_a \Psi(x) = \Psi(x + a)$.

7.8 The solution of the initial value problem of the time-dependent Schrödinger equation can be expressed in terms of an operator $U(t)$ that transforms the wave function at time $t = 0$ into the wave function at time $t$; that is, $\psi(t) = U(t) \psi(0)$.

(a) Upon what properties of the Schrödinger equation does this depend?

(b) Express $U(t)$ as an integral operator in terms of a complete set of energy eigenfunctions.

(c) Evaluate the kernel of the integral operator $U(t)$ for the motion of a free particle.

7.9 The concept of the quantum mechanical average value has its natural generalization in the notion of the "inner product" in the representation space (see Appendix). The average value $M = \langle \Psi, M \Psi \rangle$ is the inner product of $\Psi$ with the vector $M \Psi$. Demonstrate the following:

(a) Let $\Psi_i, i = 1 \ldots \infty$, be a complete set of basis vectors which is orthonormal with respect to the inner product, $(\Psi_i, \Psi_k) = \delta_{ik}$. Show that the action of an operator $M$ is completely determined by its matrix elements $M_{ik} = (\Psi_i, M \Psi_k)$.

(b) An operator $H$ is Hermitian if $(\Psi, H \Phi) = (H \Psi, \Phi)$ for all vectors $\Psi$ and $\Phi$. Show that the eigenvalues of $H$ are real, the eigenvectors corresponding to distinct eigenvalues are orthogonal, and there exists a basis in which $H$ is diagonal. Find the conditions on the matrix elements $H_{ik}$ such that $H$ is Hermitian.

(c) If $(\Psi, \hat{0} \Psi) = 0$ for all vectors $\Psi$ and if $\hat{0}$ is Hermitian, then $(\Phi, \hat{0} \Phi) = 0$ for all $\Psi$ and $\Phi$. One may then assert the operator equation $\hat{0} = 0$.

(d) If $(\Psi, A \Phi) = (B \Psi, \Phi)$ for all $\Psi$ and $\Phi$, then $B$ is said to be the Hermitian conjugate of $A$ and is given the special notation $B = A^+$. Find the relation between the matrix elements of $A$ and $A^+$. Show that $A$ is the Hermitian conjugate of $A^+$ and that a Hermitian matrix is self-conjugate, $H = H^*$. Express the Hermitian conjugate of the operator product $AC$ in terms $A^+$ and $C^+$.

(e) Show that if the inner product is positive definite, i.e., $(\Phi, \Phi) > 0$ for all $\Phi$ but the null vector, then the eigenvalues of $AA^+$ are non-negative.

(f) An operator $U$ is unitary if $(U \Psi, U \Phi) = (\Psi, \Phi)$ for all $\Psi$ and $\Phi$. 

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If $\Psi_i, i = 1...\infty$, is an orthonormal basis, then $\Psi'_i = U\Psi'_i$ is also. Find the conditions on the matrix elements $U_{ik}$ such that $U$ is non-singular. Show that $U$ is unitary.

(g) Show that the operators defined in problems 7.7 and 7.8 are unitary.

7.10 If $A$ and $B$ are $N \times N$ matrices and if $AB = I$, show that $BA = I$, $I$ being the $N \times N$ unit matrix. Construct a counter example to show this result is not true in general for "infinite matrices," i.e., $N \rightarrow \infty$.

Chapter 8

8.1 Show that the commutation relations between the operators for the velocity components of a charged particle in a magnetic field are $v_x v_y - v_y v_x = \frac{i e \hbar}{m^2 c} H_z$ and cyclic permutations.

8.2 Show that if $\Psi_i$ and $\Psi_k$ are energy eigenfunctions and if $M$ does not depend explicitly on time, then the time dependence of off-diagonal matrix elements is given by $\frac{d}{dt}(\Psi_i, M\Psi_k) = i \omega_{ik}(\Psi_i, M\Psi_k)$ where $\hbar \omega_{ik} = E_i - E_j$.

8.3 Let $U(t)$ be the operator that generates the solution $\Psi(t)$ of the time-dependent Schrödinger equation (with Hamiltonian $H$) from arbitrary initial data $\Psi(0)$ in the form $\Psi(t) = U(t) \Psi(0)$. See problem 7.8.

(a) Show that $U(t)$ satisfies the operator equation $i\hbar U'(t) = H U(t)$, with initial data $U(0) = 1$.

(b) Deduce from the differential equation that $U(t)$ is unitary.

(c) Specify under what conditions and in what sense $U(t)$ may be written as $U(t) = \exp(-iHt/\hbar)$.

8.4 In the Schrödinger picture observables are represented by operators that do not depend explicitly on time, the change of dynamic variables with time being described by the change of state vector $\Psi(t)$. In the Heisenberg picture the time dependence is transferred to the operators themselves by means of the unitary operator in problem 8.2. The procedure is $\tilde{M}(t) = (\Psi(t), M \Psi(t)) = (\Psi_0, \bar{M}(t) \Psi_0)$, where $\Psi_0 = \Psi(0)$ is the state vector at $t = 0$ and where $\bar{M}(t) = U(t)^{-1} M U(t)$.

(a) Show that $i\hbar \bar{M} = \bar{M} \dot{H} - \dot{\bar{M}}$ where $\dot{H} = U(t)^{-1} H U(t)$. If $H$ is independent of time $\dot{H} = 0$. This is the Heisenberg equation of motion.

(b) If $AB - BA = iC$, then $\bar{A} \bar{B} - \bar{B} \bar{A} = iC$.

(c) Derive an expression for the time derivative of the operator product $\bar{A}(t) \bar{B}(t)$.

(d) Find the position operator in the Heisenberg picture for the motion of a free particle. Express the result in the coordinate representation.
(e) Using the position operator in part (d), find the time dependence of the variance of the position of a freely moving particle.

8.5 Show that the mean value of the kinetic energy in a state belonging to the discrete spectrum is related to the mean value of the potential energy by the relation \( 2T = (r \cdot \nabla V) \). If \( V \) is a homogeneous function of degree \( a \), \( V(\lambda r) = \lambda^a V(r) \), then \( 2T = aV \) (virial theorem).

8.6 Verify the following "sum rules."

(a) \( \sum_{i} |r_{ik}|^2 = \left( \frac{\hbar^2}{2m_0} \right) \langle \Psi_k, r^2 \Psi_k \rangle \)

(b) \( \sum_{i} \omega_{ik} |r_{ik}|^2 = \frac{\hbar^2}{2m_0} \langle \Omega_k \rangle \) ("F-sum rule")

(c) \( \sum_{i} \omega_{ik}^2 |r_{ik}|^2 = \frac{2}{m_0} \mathcal{T}_k \)

(d) \( \sum_{i} \omega_{ik}^3 |r_{ik}|^2 = \frac{\hbar^2}{2m_0} \langle \nabla^2 V \rangle_k \)

(e) \( \sum_{i} \omega_{ik}^4 |r_{ik}|^2 = \) diverges

Here \( \hbar \omega_{ik} = E_i - E_k \). Note that \( \omega_{ik} \geq 0 \) if \( k \) designates the ground state. Sum rules are important because they provide a means of testing the physical content of the theory even though the mathematical problem cannot be solved completely.

Chapter 9

9.1 Formulate the set of coupled differential equations governing the population of a large number of quantum states. Show that the total number of levels occupied does not change with time. Identify the conditions under which the occupation numbers are positive definite. Derive the relations among the Einstein coefficients which specify the approach to thermodynamic equilibrium.

9.2 Compute the current density of the non-stationary state which describes the transition from the \( 2p \) to the \( 1s \) state of hydrogen and calculate the radiation field from this source. Identify the angular distribution and state of polarization for each value of the magnetic quantum number \( m \). See Chapter 13.

Chapter 10

10.1 At what quantum level can a wave packet in a harmonic oscillator be localized to 1% of the total excursion? Use the uncertainty principle.

10.2 Find the stationary states of a linear harmonic oscillator in a uniform electric field.
10.3 Suppose that at $t = 0$, a particle in the potential field $V = \frac{1}{2}m\omega^2x^2$ is described by the wave function $\Psi(x,0) = \text{const.}$, where $a^2 = m\omega/\hbar$. Calculate the probability amplitude for the particle being in each of the energy eigenstates. Find the wave function for $t > 0$. Discuss the spreading of the wave packet.

10.4 Show that $e^{-st^2} = \sum_{n=0}^{\infty} \frac{s^n}{n!} H_n(t)$ is the generating function for Tchebycheff-Hermite polynomials. Use it to establish the appropriate orthonormality relations.

10.5 Show that $\int_{-\infty}^{\infty} H_m(x)e^{-x^2}e^{ipx}dx = \sqrt{\pi} i^m p^m e^{-p^2/4}$.

10.6 Infer the matrix elements of the position operator of a harmonic oscillator from the spectrum, selection rules and the $F$-sum rule.

10.7 Solve the Heisenberg equations of motion to find the time-dependent Heisenberg operators for the position and momentum of a harmonic oscillator.

10.8 Find the time-dependent Green's function for the harmonic oscillator. Normalize by comparing it to the free particle Green's function at a time $\omega t \ll 1$.

10.9 Study the harmonic oscillator using the operator properties of the variables

$$a = \sqrt{(m\omega/2\hbar)}x + \sqrt{(\hbar/2m\omega)} \partial/\partial x,$$

$$a^+ = \sqrt{(m\omega/2\hbar)}x - \sqrt{(\hbar/2m\omega)} \partial/\partial x.$$ 

Prove the following statements:

(a) The Hamiltonian operator is $H = a^+a + \frac{1}{2}$ where the energy is measured in units of $\hbar\omega$.
(b) The commutation relations

$$aa^+ - a^+a = 1$$

$$Ha - aH = -a$$

$$Ha^+ - a^+H = a^+$$

hold as operator equations.
(c) The Hermitian conjugate (or adjoint) of $a$ is $a^\dagger$. $H$ is Hermitian (self-adjoint).
(d) If $U_\epsilon$ is an energy eigenfunction with eigenvalue $\epsilon$, then $aU_\epsilon$ is an eigenfunction with energy $\epsilon - 1$ and $(a^\dagger)^nU_\epsilon$ is an eigenfunction with eigenvalue $\epsilon + n$. This gives a series of equally spaced energy levels.
(e) There is a finite lowest eigenvalue.

(f) The series must terminate at the lower end by arriving at a "ground state" \( U_0 \) that satisfies the equation \( aU_0 = 0 \) (= the null vector). Solve this differential equation for \( U_0 \) and normalize.

(g) The "excited states" are \( U_n = (n!)^{-\frac{1}{2}}(a')^n U_0 \) with energies \( \left(n + \frac{1}{2}\right)\hbar\omega \). This gives a complete set of orthonormal eigenfunctions.

(h) Determine the matrix elements of \( a, a^\dagger, x \) and \( p \) by algebraic means. Show that there are no finite dimensional matrices which satisfy the specified multiplication properties.

Chapter 11

11.1 Prove the orthogonality and normalization condition of Legendre polynomials using the generating function \((1 - 2rx + r^2)^{-\frac{1}{2}} = \sum_{n=0}^{\infty} r^n P_n(x)\).

11.2 Derive the commutation relations between the components of angular momentum and the components of (a) the position operator, and (b) the momentum operator.

11.3 Let \( A_x, A_y \) and \( A_z \) satisfy the commutation relations \( L_x A_y - A_y L_x = i\hbar A_z, L_y A_z - A_z L_y = -i\hbar A_x, L_x A_x - A_x L_x = 0 \), and cyclic permutations, with respect to the angular momentum operators. Such operators are called "vector operators"; examples are \( r \) and \( p \). Prove the following relations:
   (a) \( L_x A_x^2 - A_x^2 L_x = 0 \)
   (b) \( L_x(A \cdot L) - (A \cdot L) L_x = 0 \)
   (c) \( L_x^2 A_x - A_x L_x^2 = i\hbar(A_y L_z + L_z A_y - A_z L_y - L_y A_z) \)
   (d) \( L_x^2(L_x^2 A_x - A_x L_x^2) - (L_x^2 A_x - A_x L_x^2) L_x^2 = 2(L_x^2 A_x + A_x L_x^2) - 4L_x(A \cdot L) \)
   (e) \( l(l + 1)(A)^{n^\prime l^\prime m^\prime} = (A \cdot A)^{n^\prime l^\prime} (L)^{l^\prime m^\prime} \).

11.4 Show that in a state \( \psi \) with a sharp value of \( L_\parallel \), \( L_\parallel \psi = m\psi \), the mean values of \( L_x \) and \( L_y \) are zero.

11.5 Suppose a system can be resolved into two weakly interacting subsystems 1 and 2 so that the total angular momentum \( L \) is \( L_1 + L_2 \). If the subsystems are in states characterized by definite values of the quantum numbers \( l_1 \), \( l_{1z} \) and \( l_2 \), \( l_{2z} \) respectively, what are the possible values of \( L_\parallel \) and what is the average value of \( L_\parallel^2 \)?

11.6 Express the spherical harmonics for \( l = 0, 1 \) and 2 as polynomials in \( x, y \) and \( z \).

11.7 Find the transformation rule of the spherical functions \( Y_{l_1}, Y_{l_0} \) and \( Y_{l-1} \) for a rotation of the coordinate system through Eulerian angles \( \alpha, \beta \) and \( \gamma \).
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11.8 Let \( L_\pm = L_x \pm iL_y \). Verify the following relations:

(a) \((L_\pm)^* = L_\mp\)
(b) \(L^2 = L_x^2 + \frac{1}{2} (L_+ L_+ + L_- L_-)\)
(c) \(L_+ L_- - L_- L_+ = \pm \hbar L_z\)
(d) \(L_+ L_- = L_- L_+ = 2\hbar L_z\)
(e) \(L^2 L_\pm - L_\pm L^2 = 0\)
(f) \(L^2 - L_z^2 = 0\)

11.9 Study the way in which the multiplication properties in problem 11.8 can be represented in terms of matrices, or what is the same thing, linear transformations on a finite dimensional vector space. Let \( \Psi_{\lambda \mu} \) be a finite set of degenerate eigenfunctions of \( L^2 \) with eigenvalue \( \lambda \). Here \( \mu \) labels the elements of the set. Show the following:

(a) \( L_\pm \Psi_{\lambda \mu} \) is an eigenfunction of \( L_z \).
(b) There is some linear combination of the \( \Psi \)'s which is an eigenfunction of \( L_z \). Denote the eigenvalue by \( m \hbar \) and the particular linear combination by \( \Psi_{\lambda \mu} \).
(c) \( L_\pm \Psi_{\lambda \mu} \) is an eigenfunction of \( L^2 \) with eigenvalue \( \lambda \).
(d) \( L_\pm \Psi_{\lambda \mu} \) is an eigenfunction of \( L_z \) with eigenvalue \( (m \pm 1)\hbar \).
(e) From the condition that the norm of \( L_\pm \Psi_{\lambda \mu} \) is nonnegative, it follows (respectively for \( \pm \)) that \( \lambda \geq m(m \pm 1)\hbar^2 \), the equality holding if the vector is null.
(f) The condition for the existence of finite multiplets is that the series generated by \( L_\pm^n \) terminates at both ends. This implies that \( \lambda \) has the form \( l(l + 1)\hbar^2 \), where \( l \) may have the values \( 0, 1/2, 1, 3/2, \ldots \), and that \( m \) runs over range \(-l, -l + 1, \ldots, l - 1, l \).
(g) Find the matrices of order \( 2l + 1 \) that represent the action of the operators \( L_z \) and \( L_\pm \) on the vector space spanned by \( \Psi_{lm} \), \(-l \leq m \leq l\), for a fixed value of \( l \). For example, \( \langle \Psi_{lm}, L_z \Psi_{lm'} \rangle = (L_z)_{mm'} = m \delta_{mm'} \). Select a phase convention compatible with (11.88).
(h) Write out the explicit matrices for \( l = 1/2 \) and verify the commutation relations by direct matrix multiplication.

Chapter 12

12.1 Find the energy levels and eigenfunctions of an isotropic three-dimensional harmonic oscillator. Find energy eigenfunctions that are also eigenfunctions of \( L_z \). What is the degeneracy of each level? What part of the degeneracy stems from isotropy of the potential?

12.2 Write out the explicit \( l = 1, m = 1, 0, -1 \), eigenfunctions of lowest energy of a three dimensional spherically symmetric harmonic oscillator. Express these eigenfunctions as linear combinations of the solution obtained by using separation of variables in Cartesian coordinates. If each triplet of wave
functions is orthonormal, show that the matrix of coefficients of the transformation is a unitary matrix.

12.3 For the isotropic potential \( V(r) = -\mu \delta(r - a) \), determine the range of \( g \) for which there is an \( l = 0 \) discrete state but no \( l = 1 \) discrete state.

12.4 In the case of a continuous spectrum, the wave function far from the scattering center is characterized by the "phase shift" \( \delta_l(k) \) defined as follows: \( rR_{l,m}(r) \sim c \sin(kr - \frac{l\pi}{2} + \delta_l(k)) \) for \( kr \gg 1 \) (for \( l = 0 \)), where \( \hbar k = \sqrt{2mE_k} \). For a "short range" potential, \( \delta_l \) is independent of \( r \) (see page 222 and Chapter 28B). Calculate the \( l = 0 \) phase shift for the potential in problem 12.3.

12.5 The combination \( \left( \frac{\pi}{2\rho} \right)^{\nu/2} J_{\nu/2}(\rho) = j_0(\rho) \) occurs frequently and is called the "spherical Bessel function." The second solution, irregular at the origin \( \rho = 0 \), is \( n_0(\rho) = (-i)^l \left( \frac{\pi}{2\rho} \right)^{\nu/2} J_{-\nu/2}(\rho) \), consistent with the definition of Neumann functions, \( N_0 = (J_0 \cos \nu \rho - J_{-\nu})/\sin \nu \rho \). Verify the following properties:

(a) differential equation,

\[
n''_l(\rho) + \frac{2}{\rho} n'_l(\rho) + \left( k^2 - \frac{l(l + 1)}{\rho^2} \right) n_l(\rho) = 0
\]

(b) explicit form,

\[
\begin{align*}
    j_0 &= \frac{\sin \rho}{\rho}, & n_0 &= -\frac{\cos \rho}{\rho}, \\
    j_0 &= \frac{\sin \rho}{\rho^2} - \frac{\cos \rho}{\rho}, & n_1 &= -\frac{\cos \rho}{\rho^2} - \frac{\sin \rho}{\rho}.
\end{align*}
\]

(c) recurrence relations,

\[
    j_{l+1} + j_{l-1} = \frac{2l + 1}{\rho} j_l, \quad j'_l = -\frac{l + 1}{\rho} j_l + j_{l+1}.
\]

(d) asymptotic form (\( \rho \gg l, \rho \gg 1 \)),

\[
\begin{align*}
    j_l(\rho) &\sim \frac{1}{\rho} \sin \left( \rho - \frac{l\pi}{2} \right) \\
    n_l(\rho) &\sim -\frac{1}{\rho} \cos \left( \rho - \frac{l\pi}{2} \right)
\end{align*}
\]

(e) behavior at \( \rho = 0 \),

\[
    j_l(\rho) = \frac{2^l l!}{(2l + 1)!} \rho^l
\]
\[ n_l(p) = -\frac{(2l)!}{2^l l!} p^{-l-1} \]

(f) integral representation (see page 202),
\[ i^l j_l(p) = \frac{1}{2} \int_{-1}^{+1} P_l(x) e^{i\rho x} dx \]

(g) orthonormality,
\[ \int_{-1}^{+1} j_l(kr) j_l(k'r) r^2 dr = \frac{1}{2\hbar^2} \delta(k,k') \]

12.6 Find the conditions under which the spherical potential well
\[ V = -|V_0| \text{ for } 0 < r < a, \text{ and } V = 0 \text{ for } r > a, \]
can support \( N \) s-wave bound states, but not \( N + 1 \).

12.7 In the limit of zero kinetic energy, an s-wave phase shift
behaves as, \( \delta_0(k) = -ka \), where \( a \) is the "scattering length."
Find an approximate relation between scattering length and
the energy of a loosely bound state, \( E_B = 0 \).

Chapter 13

13.1 Find the momentum distribution of an electron in the 1s, 2s
and 2p states of hydrogen.

13.2 Calculate the lifetime of a hydrogen atom in the 2p state.

13.3 Give an expression for the transition rates between consecu­tive circular orbits in a hydrogen-like atom.

13.4 Show that \( (1 - t)^{-1} \exp[xt/(1 - t)] = \sum_{k=0}^{\infty} \frac{(k!)^{-1}}{t^k} L_k(x) t^k \)
is the gener­ating function for Laguerre polynomials \( L_k(x) = Q_k^0(x) \).

13.5 At what quantum level is a muonic atom the same size as a
normal hydrogen atom in its ground state?

13.6 What is the probability of finding an electron with quantum
numbers \( n, l \) inside a nucleus of radius \( R_n \)?

13.7 Show that if the energy is regarded as a complex variable, the
Coulomb "scattering amplitude" for a definite value of \( l \),
\( \left(e^{2i\xi_l^0} - 1\right)/2ik \), has a simple pole singularity at the energy
value corresponding to each level of the discrete spectrum.

Chapter 14

14.1 Evaluate the shift in energy levels of a harmonic oscillator
produced by a perturbing \( \delta \)-function potential that is centrally
located. State the limit of validity of the approximation.

14.2 Calculate the lowest order effect on the spectrum of a linear
harmonic oscillator due to the relativistic increase in mass
of the particle. In what circumstance is the relativistic effect pronounced? When is the perturbation approximation valid? Cf. problem 2.10.

14.3 Treat the Stark effect of the \( n = 3 \) level of hydrogen. Determine the pattern of splitting and residual multiplicity by symmetry arguments. How does the secular equation factor in the representation in which \( L_z \) is diagonal? What linear combinations of unperturbed eigenfunctions are energy eigenfunctions in the presence of the field?

14.4 Evaluate the static \((\omega = 0)\) electronic polarizability of a hydrogen atom in its ground state.

14.5 For the continuous part of a spectrum, the states may be labeled by the eigenfunctions of the free particle Hamiltonian \( H_0 \) and an (exact) integral equation for the eigenfunctions \( \Psi_k(r) \) of the Hamiltonian \( H_0 + V \) set up along the pattern of perturbation theory. The integral form of the Schrödinger equation is

\[
\Psi_k(r) = \exp ik \cdot r + \int G_E(r,r') V(r') \Psi_k(r') d^3r',
\]

where \( G_E \) is the energy Green's function

\[
G_E(r,r') = -\frac{\exp ik|r-r'|}{4\pi|r-r'|},
\]

characteristic of the free particle Hamiltonian. The Green's function can be defined in terms of a complete set of energy eigenfunctions \( \phi_n(r) \) of the (any) Hamiltonian \( H_0 \) as follows:

\[
G_E(r,r') = \sum_n \frac{\phi_n(r)\phi_n(r')^*}{E - E_n}.
\]

(a) Formulate a differential equation and boundary conditions for the Green's function.

(b) Evaluate the explicit form of the free particle Green's function from its definition in terms of a complete set of energy eigenstates.

(c) Find the relation between the energy Green's function and the time Green's function \( G_t \). (See problem 5.3.)

(d) The effect of a "short range" potential on the wave function at large distances from the scattering center is described by the "scattering amplitude \( f(\theta) \)" defined by the asymptotic form (for \( r \to \infty \))

\[
\Psi_k(r) \sim e^{ik \cdot r} + f(\theta) \frac{e^{ikr}}{r}.
\]

(See Chapter 28, Section B) Derive an exact expression for \( f(\theta) \) in terms of the exact solution \( \Psi_k \) of the Schrödinger equation.
(e) Formulate a perturbation approximation for $\Psi_k$ and $f(\theta)$ on the basis of the above results.

14.6 For a definite value of the angular momentum the integral from of the Schrödinger equation for a spherically symmetric potential takes the form

$$u_{kl}(r) = \sin kr + \frac{2m_0}{\hbar^2} \int_0^\infty g_{E1}(r,r') V(r') u_{kl}(r') dr',$$

where

$$g_{E0}(r,r') = \frac{1}{2k} \left[ \sin k|r - r'| - \sin k|r + r'| \right].$$

for $l = 0$.

(a) Evaluate $g_{E1}(r,r')$ for $l > 0$.

(b) What is the relation between the wave functions and between the Green’s functions of the three-dimensional (problem 14.5) and the partial wave formulations. It is necessary to distinguish ingoing and outgoing wave boundary conditions $e^{\pm ikr/r}$. The addition formula for spherical harmonics is helpful,

$$P_l(\cos \Theta) = \frac{4\pi}{2l + 1} \sum_{m=-l}^l Y_{lm}(\theta, \phi)^* Y_{lm}(\theta', \phi').$$

where $\cos \Theta = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi')$.

(c) An exact expression for the s-wave phase shift is

$$h\tan \delta_0 = -\frac{2m_0}{\hbar^2} \int_0^\infty \sin kr V(r) u_k(r) dr.$$

Verify this relation and generalize it for $l > 0$. What normalization condition is implied for $u_k$? See problem 12.4.

Chapter 15

15.1 Identify the conditions under which the Klein-Gordon equation reduces to the Schrödinger. How does the initial data problem for the second order differential equation reduce to that of the first order equation?

15.2 Show that the function-space inner product

$$(\psi, \phi) = i \int \left[ \psi^* \frac{\partial \psi}{\partial t} - \frac{\partial \psi^*}{\partial t} \psi \right] d^3x$$

is independent of time if $\psi$ and $\phi$ are solutions of the Klein-Gordon equation. Find the form of the inner product in momentum space. Is the inner product positive definite?
15.3 A general solution of the Klein-Gordan equation is a superposition of a positive-frequency and a negative-frequency part, with time dependence \( e^{-i\omega t} \) and \( e^{+i\omega t} \), respectively. Show that under a Lorentz transformation that does not reverse the sense of time, a positive-frequency solution is transformed into a positive-frequency solution, i.e., that the decomposition is Lorentz invariant.

15.4 Find a complete set of positive-frequency solutions of the Klein-Gordan equation that are orthonormal with respect to the inner product in problem 15.2. Show that the completeness relation (for unequal times) is

\[
\sum_a f_a(x) f_a(x')^* = \frac{1}{(2\pi)^3} \int e^{-ik(x-x')} \frac{d^3k}{2\omega},
\]

where \( \omega = \omega(k) = c\sqrt{\hbar^2 + m^2 c^2/\hbar^2} \) and where the Minkowski space inner product is \( k(x-x') = \omega(t - t') - k \cdot (x - x') \).

Chapter 16

16.1 What is the value of the \( g \) factor of a particle described by the Hamiltonian \((1/2m_0) \left[ \sigma \cdot (p - (e/c) A) \right]^2 \)?

16.2 A particle of spin \( 1/2 \) and magnetic moment \( \mu \) moves in a precessing magnetic field

\[
H_x = \mu \sin \theta \cos \omega t, \quad H_y = \mu \sin \theta \sin \omega t, \quad H_z = \mu \cos \theta.
\]

At time \( t = 0 \), the spin is parallel to the \( z \) axis. What is the probability of the spin being antiparallel to the \( z \) axis at some later time?

16.3 Find the (time-dependent) position operators in the Heisenberg representation of a particle of spin \( 1/2 \) and magnetic moment \( \mu \) moving in a nonhomogeneous magnetic field

\[
H_x = 0, \quad H_y = -k \mu, \quad H_z = H_0 + k \mu.
\]

16.4 Determine the energy spectrum and wave functions of a charged particle moving in uniform electric and magnetic fields that are perpendicular to one another.

Chapter 17

17.1 Show that the four matrices \((I', \sigma')\) are Hermitian, linearly independent and form a complete basis for \(2 \times 2\) matrices.

17.2 How many matrices are required to form a complete set of Hermitian, linearly independent \(N \times N\) matrices? How many
mutually commuting, Hermitian, linearly independent $N \times N$ matrices are there?

17.3 In the Dirac theory, $a$ and $p$ are mutually commuting linear operators. Develop a notation for the linear vector space on which the operators act. Find an expression for the inner product in the composite (direct product) space. Show that the Dirac Hamiltonian is Hermitian.

17.4 Use the Heisenberg equation of motion to show

(a) \( \frac{d}{dt} (x + i \hbar \frac{p}{2mc} \alpha) = \frac{\hbar}{2} (p - (e/c) \gamma) / m \),

(b) \( \frac{d}{dt} (t + i \hbar \frac{p}{2mc^2}) = \frac{\hbar}{2} (H - e\Phi) / mc^2 \).

17.5 What transformation of the spinor wave function must be made to restore the form of the Dirac equation after a change of gauge in the electromagnetic potentials?

17.6 Show that the form of the Dirac equation remains unchanged by Lorentz transformation or spatial rotation.

Chapter 18

18.1 Suppose a system consists of two weakly interacting subsystems each of spin $1/2$. The total spin is $S = s_1 + s_2$. What are the possible eigenvalues of $S^2$ and $S_z$? Compute the value of $s_1 \cdot s_2$ in the triplet (spins parallel) and singlet (spins antiparallel) states of the composite system. Find eigenfunctions of $S^2$ and $S_z$ as linear combinations of products of eigenfunctions of the subsystems.

18.2 An electron moving in a central field of force is in a state specified by the quantum numbers $l m_l$. What are the possible values of the $z$ components of orbital and spin angular momentum and what is the average value of each?

18.3 Is the parity operator $\Pi$ a linear operator? Is it Hermitian? What are the commutation properties of $\Pi$ with the operators $r$, $p$, $I$, $S$ and $J$?

18.4 An axial vector transforms as a vector under proper rotations (i.e., rotations without space inversion) but does not change sign under inversion. Classify the following as being either vector or axial vector: $E$, $\Pi$, $A$, $S$, $I$, $p$ and $u \times v$ where $u$ and $v$ are vectors.

18.5 Show that if a system is in a state characterized by a sharp value $m_j$ for the $z$ component of the total angular momentum, the mean value of the total angular momentum about an axis $z'$ making an angle $\theta$ with the $z$ axis is $m_j \cos \theta$.

18.6 Evaluate the particle flux of positive energy and negative energy plane wave solutions of the Dirac equation. Also calculate the flux of the corresponding charge conjugate solutions.

18.7 Can the charge conjugation transformation be represented by a linear operator?
Chapter 19

19.1 Evaluate $\gamma$ and $j$ for a Dirac particle in an electromagnetic field. Verify that the Lorentz force is given correctly.

19.2 Calculate the spin-orbit and contact potentials for an electron outside a closed atomic core consisting of a hydrogen-like atom.

Chapter 20

20.1 Calculate the energy level splitting of a hydrogen atom in a weak electric field. Neglect the Lamb shift and assume the Stark effect is small in comparison with the fine structure. Account for the latter by using eigenfunctions of $J^2$, $J_z$ and $L^2$ for the unperturbed states.

20.2 Evaluate the Stark effect for the $n = 2, j = \frac{1}{2}$ level of hydrogen for the case where the Stark effect is comparable with the Lamb shift. Represent the Lamb shift by a phenomenological perturbation matrix element that touches only the $s$-state.

20.3 Study the hydrogen Stark effect for the level $n = 2$ in the transition region where the Stark effect and the fine structure are of the same order of magnitude. Plot the energy levels as a function of $E$.

20.4 Compute the lifetimes of the $2p_{1/2}$ and $2p_{3/2}$ states of hydrogen.

20.5 Find an expression for the lifetime of the metastable $2s_{1/2}$ state of hydrogen in a very weak electric field. At what field strength will the lifetime by $10^{-3}$ sec? Is the Stark level shift appreciable at this field strength? Hint: Evaluate the matrix element of $r$ using a perturbed $2s_{1/2}$ wave function that contains an admixture of the $2p_{1/2}$ state and take advantage of the smallness of the Lamb shift.

20.6 Find the mean value of the operator $\mu = L + g_s S$ in a state characterized by the quantum numbers $J$, $J_z$, $L$, $S$. (This gives a generalization of the Landé formula in the case where the $g$ factor of the electron is not exactly equal to two. See page 346.) Hint: Use problem 11.3(e).

Chapter 21

21.1 Determine the form of the contact interaction when the finite nuclear size is taken into account. Calculate the splitting of the $2s_{1/2} - 2p_{1/2}$ levels of hydrogen stemming from this effect. It is about $-0.1$ Me.
21.2 Calculate the hyperfine splitting of the 1s{\frac{1}{2}} state of hydrogen using a classical model in which the nucleus is represented by a uniformly magnetized sphere of radius \( R_N \). Give a classical explanation of the sign of the splitting.

21.3 Find the magnetic field at the nucleus of an s state electron.

21.4 Consider a hydrogen atom in the ground state in a uniform magnetic field. Find the appropriate linear combinations of electron-proton spin wave functions that are energy eigenfunctions in the case where the interaction with the external field is the same order of magnitude as the electron-proton dipole-dipole interaction.

21.5 Calculate the hyperfine splitting of a hydrogen-like atom in a state of non-zero orbital angular momentum. Hint: Use problem 11.3(e).

Chapter 22

22.1 Specify a complete set of commuting constants of the motion for positronium.

22.2 Calculate the fine structure of positronium. Obtain the Hamiltonian by semiclassical arguments. Account especially for "hyperfine" splitting, knowing that the magnetic moment of the positron is equal in magnitude and opposite in sign to that of the electron. Present the results in an energy level diagram for \( n = 1,2 \).

22.3 Evaluate the Lamb shift for positronium.

22.4 Construct a theory for positronium using a Dirac Hamiltonian for each particle and the Coulomb interaction between them. Separate the motion of the center of mass from the relative motion in the approximation of retaining only the lowest order relativistic corrections for the relative motion. Does the "hyperfine" interaction emerge automatically? Hint: The action of spin operators on a product wave function can be expressed as follows:

\[
(\sigma^{(1)} \pm \sigma^{(2)})(\phi \times \psi) = (\sigma^{(1)} \phi \times \psi) \pm (\phi \times \sigma^{(2)} \psi).
\]

Chapter 23

23.1 Construct a complete set of orthonormal two-particle eigenfunctions from a complete set of one-particle eigenfunctions.

23.2 Derive the Hartree-Fock equations for determining the best single-particle functions to give an antisymmetric (or symmetric) two-particle wave function of lowest energy.

23.3 Calculate the \( n = 1 \) and 2 levels of a hydrogen-like atom, including fine structure and the Lamb shift, using a variational method.
23.4 Show how the variational method with trial functions \( \psi = \sum \alpha_i e^{-a_i r} \) can be reduced to a matrix procedure if the \( \alpha \)'s are regarded as the variational parameters. The \( \alpha \)'s may be selected by intuition or by an iteration scheme. Note how this gives a finite set of orthonormal vectors.

23.5 Evaluate the ground state energy of helium using the following "self-consistent" variational method: assume the first electron is in a hydrogenic 1s state with \( Z = Z' \) and calculate the screened field seen by the second electron. Describe the second electron by a hydrogenic 1s function with \( Z = Z'' \). Vary \( Z' \) to find the lowest energy for a given \( Z'' \). Then impose the symmetry by setting \( Z' = Z'' \).

Chapter 24

24.1 Give the possible values of the total angular momentum for the following states (terms): \( 1\text{s}, 2\text{s}, 3\text{s}, 2\text{p}, 3\text{p}, 2\text{d} \) and \( 4\text{d} \).

24.2 Which terms are possible for the following two-electron configurations: (a) \( ns^n's \), (b) \( ns^n'p \), (c) \( ns^n'd \), and (d) \( np, n'p \)? Which terms are consistent with the exclusion principle if \( n = n' \)?

24.3 Couple three unit angular momenta \( l_1 = l_2 = l_3 = 1 \) to yield a resultant eigenstate \( L = 1, L_z = 0 \) of \( L^2 \), where \( L = l_1 + l_2 + l_3 \). How many independent states of this sort are there?

24.4 Estimate the low-lying excited state energies of helium in the approximation of neglecting exchange effects. Do this assuming that one electron is described by the 1s function found in the ground state calculation and carrying out the variational procedure for a hydrogenic 2s (and independently, 2p) wave function in the screened Coulomb field. The 2s state must be taken orthogonal to some appropriate 1s state. The root of the variational equation may be found by a rapidly converging iteration method.

24.5 Calculate the low-lying excited state energies of helium taking into account exchange and spin effects. Use appropriately symmetrized product eigenfunctions for the configurations \( (1\text{s}, 2\text{s}) \) and \( (1\text{s}, 2\text{p}) \), where the 1s function is that found in the ground state calculation. The required matrix elements are given in problem 24.6 for reference.

24.6 Consider the hydrogenic wave functions

\[
\Psi_{1s} = 2a^{3/2} e^{-a r} Y_{00} \\
\Psi_{2s} = b(1 - Br)e^{-\beta r} Y_{00} \\
\Psi_{2p} = c e^{-\gamma r} Y_{1m}
\]

where \( a = Z_{1s}/a_0 \), \( \beta = Z_{2s}/2a_0 \), and \( \gamma = Z_{2p}/2a_0 \) and where \( b, B \) and \( c \) are determined by the orthogonality and normalization
25.2 Using the virial theorem, show that in the Thomas-Fermi model of a neutral atom the energy of electrostatic repulsion between the electrons is $1/7$ the magnitude of the electrostatic attraction between the electrons and the nucleons.

25.3 Estimate the order of magnitude of the following quantities in a neutral atom according to the Thomas-Fermi model:
   (a) the size of the atom,
   (b) the average electrostatic repulsion between two electrons,
   (c) the average kinetic energy of one electron,
   (d) the average speed of an electron,
   (e) the average angular momentum of an electron,
   (f) the mean radial quantum number.

25.4 Show that the mean perturbation of all states of a given term is zero for the spin-orbit interaction.

25.5 Calculate the $L \cdot S$ splitting of the $^3P$ term of helium.

25.6 Evaluate the $L \cdot S$ splitting of a single $n$-electron in a spherically symmetric potential. Express the result in terms of an arbitrary radial matrix element. Estimate the radial matrix element for the doublet splitting of sodium.

25.7 Two electrons move in an $(np)^2$ configuration in a spherically symmetrical potential. Regarding the electrostatic repulsion between the electrons as a perturbation, evaluate the splitting of terms in first order approximation. Neglect the spin-orbit interaction. Use qualitative considerations to infer ordering of the terms. Hint: To facilitate diagonalization of the secular equation, use a representation in which $M_L$ and $M_S$ are diagonal and note that the sum of the roots of a secular equation is equal to the sum of the diagonal matrix elements.

Chapter 26

26.1 Find the possible atomic terms (a term is characterized by $L$ and $S$) in a configuration of two equivalent $d$-electrons. Give the total number of states and the number of states in each term. What values of $J$ are possible to each term?

26.2 In an atomic configuration the term that has the lowest energy can be determined by Hund's semi-empirical rules:
   (1) The ground state will have the largest value of $S$ consistent with the Pauli principle,
   (2) $L$ will have the largest value consistent with the value of $S$ determined in rule (1),
   (3) The total angular momentum of the ground state is $J = |L - S|$ if the unfilled subshell is half full or less than half full; it is $J = L + S$ if the subshell is more than half full.

Give a qualitative physical justification for each of these rules.
26.3 Using Hund's rules (see problem 26.2), find the ground state of the configuration \( np^x \) for \( x = 1, 2, \ldots, 6 \). For each value of \( x \), state an element for which this case is realized physically.

26.4 Do problem 26.3 for the configuration \( nd^x \) for \( x = 1, 2, \ldots, 10 \).

Chapter 27

27.1 Estimate the relative frequencies and separation of energy levels for the electronic, vibrational and rotational motions of a diatomic molecule.

27.2 Derive the Schrödinger equation describing the motion of the nuclei of a diatomic molecule in the approximation that the nuclei move much more slowly than the electrons and thus experience only an interaction with the electrons that is averaged over many electron revolutions. This procedure provides a separation of variables between the electronic and nuclear motions. The approximation is called the adiabatic or Born–Oppenheimer approximation.

27.3 What are the possible symmetry states of the diatomic molecules \( D_2, N_2, \text{LiH} \) formed from the bonding of the two atoms in their ground states?

27.4 What spin symmetries are possible for the rotational states of the deuterium molecule \( D_2 \) in the electronic ground state? The deuterium nucleus has spin 1.

27.5 Calculate the energy of a rigid electric dipole in a uniform electric field. Use second order perturbation theory.

27.6 Show that the force between two hydrogen atoms in their ground states varies as \( 1/R^7 \) if the atoms are separated by a large distance \( R \).

Chapter 28

28.1 The rate for making transitions from an initial state \( i \) to the final state \( f \) is

\[
w_{if} = \frac{2\pi}{\hbar} | \mathcal{M}^{' if} |^2 \rho_f(E),
\]

where \( \rho_f \) is the number of final states per unit energy interval ("Golden Rule No. 2").

(a) Find the expression for \( \mathcal{M}^{' if} \) in first order perturbation theory. What normalization convention is implied for the wave function?

(b) Derive an expression for \( \mathcal{M}^{if} \) in second order perturbation theory.
(c) Evaluate the density of states $\rho_f$ for a final state consisting of two free particles of definite total energy and momentum.

(d) Evaluate $\rho_f$ for a final state consisting of three equal mass (free) particles. Express the results in the center of mass system. How is the partition of energy among the three particles accounted for by a probability distribution?

(e) Calculate the dependence of $\rho_f$ on energy near the energy threshold for an $N$-particle final state.

28.2 Calculate the rate for induced transitions from state $m$ to state $n$ of an atomic system in an electric field with spectral density $\mathcal{E}(\omega)$ at transition frequency $\omega = \frac{1}{\hbar} (E_m - E_n)$. Identify the Einstein coefficient $B$ and thereby infer the rate for spontaneous emission.

28.3 Consider a particle of mass $m$ bound in a three-dimensional harmonic oscillator potential $\frac{1}{2} \hbar \omega^2$. The particle is irradiated with a mild pulse $\mathcal{E}(t) = \epsilon x^2 e^{-t^2/\tau^2}$ for the time interval $-\infty < t < \infty$. Determine which transitions are possible and calculate their probabilities. Identify the limiting cases of sudden and adiabatic perturbations. State the limits of validity of the perturbation calculation.

28.4 At $t = 0$, a hydrogen atom in its ground state is irradiated with a uniform periodic electric field. Determine the minimum frequency of the field necessary to ionize the atom and compute the ionization probability per unit time. As an approximation, the electron in the final state may be regarded as free. State the limits of validity of the approximation.

28.5 Show that the scattering of slow particles in a short range potential is characterized by $\delta_j(k) \sim k^{2l+1}$. Find the proportionality constant in Born approximation and state the conditions under which the approximation is valid.

28.7 Taking into account the symmetry of the wave function, give the differential cross section for elastic Coulomb scattering of an electron on an electron and of an alpha particle on an alpha particle. Distinguish spin states and also give the formula for the scattering of unpolarized electrons. Identify quantum effects and show how they disappear in the classical limit. For reference, the exact scattering amplitude for a fixed Coulomb potential is

$$f_c(\theta) = -\frac{\gamma^2}{2 \sin^2 \frac{\theta}{2}} \cdot \frac{\Gamma(1 + i\gamma)}{\Gamma(1 - i\gamma)} \cdot e^{-2 \gamma \ln \sin \theta/2}$$

where $\gamma = \frac{\epsilon \theta}{\hbar \nu}$. Cf. Chapter 13, Section D.

28.8 Compute in Born approximation the differential scattering cross section for the scattering of fast neutrons by a Coulomb field.
28.9 Set up coupled Schrödinger equations to describe the “two channel” reaction and scattering processes

\[(11) \quad a + b \rightarrow a + b,\]
\[(12) \quad a + b \rightarrow c + d,\]
\[(22) \quad c + d \rightarrow c + d,\]
\[(21) \quad c + d \rightarrow a + b.\]

Assume the particles are spinless and of unequal mass. Separate out the motion of the center of mass.

(a) How must the potentials \( V_{11}, V_{12}, V_{21}, V_{22} \) be related in order to describe a system that is invariant with respect to reversal of the sense of time? How are the cross sections for reactions (12) and (21) related? (detailed balance)

(b) Give expressions for the effective cross sections for these reactions in Born approximation.

(c) Formulate an expression for the reaction and scattering amplitudes in terms of partial wave amplitudes of definite angular momentum. What relation among \( f_{11}, f_{12}, f_{21}, f_{22} \) (for a definite value of \( l \)) is implied by conservation of probability?

Note: The results are presented most simply in terms of a matrix notation. The many-channel generalization of the quantity \( e^{2i\delta_l} \) is called the S-matrix.

Chapter 29

29.1 Verify the anticommutation relations

\[\psi_\alpha (r,t) \psi_\beta^+ (r',t) + \psi_\beta^+ (r',t) \psi_\alpha (r,t) = I_{\alpha\beta} \delta (r - r')\]
\[\psi_\alpha^+ (r,t) \psi_\beta (r',t) + \psi_\beta^* (r',t) \psi_\alpha^+ (r,t) = 0\]

satisfied by the second quantized Dirac wave function. The \( \alpha \) and \( \beta \) indicate components of the Dirac spinor and \( I_{\alpha\beta} \) is the unit 4 \( \times \) 4 matrix. The positive-frequency parts of \( \psi \) and \( \psi^+ \) describe the creation of positrons and electrons, respectively, while the negative-frequency parts describe the annihilation of electrons and positrons, respectively. Electrons and positrons are described by independent sets of mutually anticommuting creation and annihilation operators

\[C_n^{(p)} C_n^{(e)*} + C_n^{(e)} C_n^{(p)*} = 0,\]
\[C_n^{(p)} C_n^{(e)*} + C_n^{(e)*} C_n^{(p)} = 0.\]

29.2 Evaluate the commutation relations between components of the current and charge density of a quantized Dirac wave field, i.e., evaluate \( j_\mu (r,t) j_\nu (r,t) - j_\nu (r,t) j_\mu (r,t) \) at equal times.
29.3 Calculate the Born approximation matrix element for the production of an electron-positron pair in an external electric field

\[ \Phi(r,t) = \Phi_0 \cos kx \cos \omega t. \]

29.4 Express the energy and momentum operators of a quantized Dirac wave field in terms creation and destruction operators.

29.5 Let \( M(x) \) be a massive pseudoscalar meson field satisfying the Klein-Gordan equation. Calculate the force between two stationary Dirac "nucleons" in second order perturbation theory, assuming the interaction energy between the "nucleon" and meson fields is

\[ H' = g \int \psi^+(x) \rho_3 \rho_1 \psi(x) M(x) \, d^3 x. \]