

I. V. Savel'yev

FUNDAMENTALS
OF THEORETICAL
PHYSICS

Volume 2
Quantum
Mechanics

Mir Publishers Moscow

И. В. Савельев

**ОСНОВЫ ТЕОРЕТИЧЕСКОЙ
ФИЗИКИ**

Том 2

КВАНТОВАЯ МЕХАНИКА

ИЗДАТЕЛЬСТВО «НАУКА»

I.V.Savelyev

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by G. LEID**

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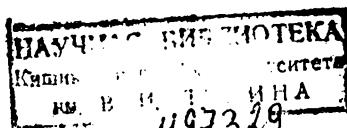
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PREFACE

The present book is the second volume of a guide to theoretical physics. As in the first volume, I have adhered to the rule of omitting what is explained in sufficient detail in modern general courses of physics. In particular, the experimental fundamentals of quantum physics are not discussed.

With a view to the fact that the mastering of the mathematical apparatus of quantum mechanics involves great difficulties, I have done everything in my power to make calculations as simple and as clear as possible. For this purpose, special care was taken in choosing the notation. Whenever this was possible and expedient, I used the symbolic writing of scalar products of functions in the form $\langle \varphi, \psi \rangle$ instead of the integral notation $\int \varphi^* \psi dV$. This has appreciably simplified a number of formulas and facilitated their analysis and memorizing.

The book is provided with mathematical appendices. Sometimes I refer to the mathematical appendices of Volume 1.

The book has been conceived first of all as a training aid for students of non-theoretical specialities of higher educational establishments. Acquaintance with it will facilitate a more detailed studying of the subject with the aid of fundamental guides.

Igor Savelyev

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Chapter 1

FOUNDATIONS OF QUANTUM MECHANICS

1. Introduction

The laws revealed in the microworld differ radically from those obeyed by macroscopic objects, i.e. from the laws of classical physics. Since only macroscopic bodies lend themselves to direct perception by our organs of sense, we have at our disposal only illustrative images of such bodies. The transfer of these images to microscopic objects (for instance, the representation of an electron as a microscopic sphere) is absolutely illegitimate and even harmful. Therefore, the best thing we can do in commencing to study the mechanics of the microworld (quantum mechanics) is to discard from the very beginning any tendency to construct illustrative images of the objects and processes being studied.

In its customary meaning, the word "to understand" means to form for oneself a clear image or a diagram of an object or process. No matter how paradoxically this sounds, quantum mechanics cannot be understood in this meaning. One of the founders of the quantum theory, P. Dirac, wrote in this respect: "...the main object of physical science is not the provision of pictures, but is the formulation of laws governing phenomena and the application of these laws to the discovery of new phenomena... In the case of atomic phenomena no picture can be expected to exist in the usual sense of the word 'picture', by which is meant a model functioning essentially on classical lines. One may, however, extend the meaning of the word 'picture' to include any way of looking at the fundamental laws which makes their self-consistency obvious. With this extension, one may gradually acquire a picture of atomic phenomena by becoming familiar with the laws of the quantum theory"¹.

Quantum mechanics can be outlined in different mathematical forms. Already at its birth, this science appeared simultaneously and independently in the form of E. Schrödinger's wave mechanics and W. Heisenberg's matrix mechanics. Dirac later developed the "vector" form of quantum mechanics. All the forms of quantum mechanics are equivalent—they lead to identical physical results and can be transformed into one another.

¹ P.A.M. Dirac. *The Principles of Quantum Mechanics*, 4th ed. Oxford, Clarendon Press (1958), p. 10.

The mathematical language of quantum mechanics is very peculiar and as a whole is not simple. The above circumstances, namely, the impossibility of visual representations and the intricate mathematical language make quantum mechanics a difficult science.

2. State

The concept of state is one of the fundamental and initial ones in quantum mechanics. It is therefore difficult to give a faultlessly strict definition of it. Dirac introduced the concept of state as follows: "...Let us take any atomic system, composed of particles or bodies with specified properties (mass, moment of inertia, etc.) interacting according to specified laws of force. There will be various possible motions of the particles or bodies consistent with the laws of force. Each such motion is called a *state* of the system".¹

Let us adopt Dirac's definition of a state as a preliminary one. The content of the term "state" will be disclosed completely in the process of setting out the essence of quantum mechanics.

Information on the state of a microsystem is obtained by performing measurements, i.e. by making the system interact with an instrument that is a macroscopic system. Consequently, the results of measurements performed on microsystems are necessarily expressed in terms developed for characterizing macroscopic bodies (coordinate, momentum, angular momentum, energy, and the like). These characteristics are called **dynamical variables**.

The properties of microparticles differ radically from those of macroscopic bodies. For this reason, the dynamical variables ascribed to macrobodies cannot be ascribed to microparticles. But when a microparticle interacts with an instrument (or a natural macrobody), it behaves as if it were characterized by at least a part of the dynamical variables named above. The peculiar nature of the properties of microparticles exhibits itself in that measurements do not yield definite values for all the variables. For example, states of an electron exist in which when interacting with macrobodies (i.e. in measurements) it behaves as if it had the momentum p_x , and no matter how many times we performed measurements with an electron in such a state, the same value is obtained every time for p_x . But if we attempt to determine the position of an electron in the same state, we shall obtain all values from $-\infty$ to $+\infty$ for the coordinate x with equal probability. Such a state of an electron is said to be one in which the electron has a definite value of the dynamical variable p_x .

States of an electron are also possible in which it behaves in measurements (i.e. in interactions with macrobodies) as if it had a quite

¹ P.A.M. Dirac. *Op. cit.*, p. 11.

definite value of the coordinate x . The momentum p_x in these states is absolutely indefinite. In this case, the electron is said to be in a state with a definite value of the coordinate x .

Finally, states of an electron exist in which neither x nor p_x have definite values. In this case, multifold measurements performed on the electron in one of such states yield values for x that are within a certain interval Δx , and for p_x that are within the interval Δp_x , the quantities Δx and Δp_x being related by the Heisenberg uncertainty relation:

$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2} \quad (2.1)$$

where \hbar is the Planck constant h divided by 2π , and is called the \hbar -bar or the Dirac \hbar .

The uncertainty relation shows to what extent we can use the concepts of classical mechanics for microparticles, particularly, with what degree of accuracy we can speak of the trajectories of microparticles. Motion in a trajectory is characterized by quite definite values of the coordinates and velocity at each instant. Rewriting relation (2.1) as

$$\Delta x \cdot \Delta v_x \geq \frac{\hbar}{2m}$$

we see that the greater the mass of a particle, the smaller is the uncertainty of its coordinates and velocity and, consequently, the greater is the accuracy with which we can apply the concept of a trajectory to the particle. Even if we take a microparticle only one micrometre in size, its mass will exceed that of an atom about 10^{12} times. For such a particle, the uncertainties in the values of x and v_x are beyond the limits of the accuracy in measuring these quantities, so that practically its motion will be indistinguishable from motion in a trajectory.

Hence, the greater the mass of a particle, the higher is the accuracy with which we can apply the concepts and laws of classical mechanics to its motion. This statement is a particular case of a more general one known as the **correspondence principle**. According to this principle, in the limiting process $\hbar \rightarrow 0$, the laws and relations of quantum mechanics transform into the relevant laws and relations of classical mechanics. In practice, this signifies that the smaller the role of effects proportional to the Planck constant \hbar , the closer is the behaviour of the system being considered to the classical one.

By bridging the gap between quantum and classical laws, the correspondence principle allows us to find the quantum mechanical analogues of classical quantities.

To characterize the state which a microsystem being considered is in, it is natural to take the values of the dynamical variables

having a definite value in the given state. The set of all the dynamical variables having definite values in a given state is called a **complete set**. The complete sets vary for different states. In a particular case, the complete set may consist of only a single dynamical variable. In such a state, all the variables except the one forming the complete set are indeterminate.

When speaking of dynamical variables in general (i.e. without specifying what variables— x , p_x , E , etc.—we have in view), we shall designate them by the letter Q , and sometimes by the letters R , A , B , etc.

The set of numerical values which a given dynamical variable can have is called its **spectrum**. If these values form a continuous sequence, the given quantity is said to have a **continuous spectrum** of values. If these values form a discrete sequence, the given quantity is said to have a **discrete spectrum** of values. In the general case, the spectrum of values of a dynamical variable may include both continuous and discrete parts.

We shall designate the different values of the variable Q by the symbol q . If the given value belongs to a discrete spectrum, we shall use a subscript on the symbol indicating the number of the value, i.e. write q_n . The absence of a subscript on q will signify that the given value belongs to a continuous spectrum.

We have already noted that the laws of the microworld differ radically from those observed for macroscopic bodies. This distinction manifests itself in that states and dynamical variables have to be characterized by mathematical quantities of a different nature than the ones used in classical physics. For each dynamical variable, there is a corresponding **linear operator**. The state of a system is characterized by a certain, generally speaking, complex function ψ that is called either a **wave function**, or a **psi-function**, or a **probability amplitude**. We shall use the term “psi-function”. Dirac introduced a complex vector of a special kind to characterize a state. He called it a **state vector**.

We must note that states are possible which no psi-functions can be made to correspond to. They are called **mixed states** as distinct from the pure states described by psi-functions. We shall consider only pure states. We shall therefore omit the word “pure” for brevity's sake and speak simply of the states of a system.

3. The Superposition Principle

A fundamental principle of quantum mechanics is the **principle of superposition of states**. The essence of this principle consists in the following statement. Assume that a system may be either in the state ψ_1 in which a quantity Q has the definite value q_1 or in the state ψ_2 in which the same quantity has the definite value q_2 . Hence,

there is the state $\psi = c_1\psi_1 + c_2\psi_2$ (where c_1 and c_2 are arbitrary complex numbers) in which measurement of the quantity Q yields either the result q_1 or the result q_2 .

It follows from the superposition principle that the superposition of the states ψ_1 and ψ_2 in which Q has definite values leads to a new state ψ in which Q is indefinite.

A similar result is obtained upon the superposition of more than two states. If the states $\psi_1, \psi_2, \dots, \psi_n$ exist in which the quantity Q has the definite values q_1, q_2, \dots, q_n , the state

$$\psi = \sum_{m=1}^n c_m \psi_m \quad (3.1)$$

(where c_m are arbitrary complex numbers) also exists, and measurement of the quantity Q in this state yields one of the values q_1, q_2, \dots, q_n .

The reverse statement also holds, consisting in that any state ψ of a quantum system can be represented as the result of the superposition of the states $\psi_1, \psi_2, \dots, \psi_n$ indicated above. This statement can also be a formulation of the superposition principle.

The behaviour of the quantities ψ_m corresponding to the states of a system described by Eq. (3.1) is similar to the behaviour of vectors. Indeed, multiplying the vectors $\mathbf{a}_1, \mathbf{a}_2, \dots, \mathbf{a}_n$ of an identical nature by the real numbers c_1, c_2, \dots, c_n and then finding their sum, we obtain a new vector of the same nature, i.e. $\mathbf{a} = \sum c_m \mathbf{a}_m$. This analogy is why Dirac treated the quantities corresponding to the states of a system as vectors in a special space.

By superposing a certain state ψ_m on itself, i.e. by assuming that $\psi_1 = \psi_2 = \psi_m$, we obtain, by (3.1), a state described by the function

$$\psi = c_1\psi_m + c_2\psi_m = (c_1 + c_2)\psi_m = c\psi_m$$

This state, like the initial state ψ_m , will be characterized by the fact that in measurements of the quantity Q we shall always obtain the result q_m . It is natural to assume that the state we have obtained does not differ from the initial one. An exception is the case when $c = c_1 + c_2 = 0$. In this case when multiplying ψ_m by c , we get no state ($\psi = 0$ signifies the absence of a state).

According to the above, the states described by the functions ψ and $c\psi$ (where c is an arbitrary non-zero complex number) are assumed to be identical. If we use the vector representation of states, the conclusion must be drawn from the last statement that a state is determined only by the direction of a vector, while the "length" of the vector is of no significance.

We must note that the superposition principle is also observed in classical mechanics, for example for the oscillations of a string. The arbitrary oscillation of a string can be represented as the super-

position of harmonic oscillations having frequencies that are multiples of the fundamental frequency. This analogy is why quantum mechanics was previously referred to as wave mechanics, and the quantity ψ corresponding to the state of a quantum-mechanical system was called the wave function. It must be borne in mind, however, that the above-mentioned analogy does not extend very far. There is a profound difference between the superposition in the quantum theory and any classical superposition. For example, the superposition of a state of an oscillating string with itself leads to a state with another oscillation amplitude so that the resultant oscillation differs from the initial one. In quantum mechanics, on the other hand, the superposition of a state with itself does not lead to the appearance of a new state. A quantum state has no characteristic similar to the amplitude of classical oscillations.

4. The Physical Meaning of the Psi-Function

In the coordinate representation, the psi-function is a function of the coordinates of the particles forming a system and of the time. Let us consider a system consisting of one particle. In this case, $\psi = \psi(x, y, z, t)$. The square of the magnitude of the psi-function, i.e. the quantity $|\psi|^2 = \psi^* \psi$ (here ψ^* is the complex conjugate of ψ) determines the density of the probability of detecting the particle at various points of space. If we multiply $|\psi(x, y, z, t)|^2$ by the volume element $dV = dx dy dz$ taken at the point x, y, z , we obtain the probability of the particle being detected within the limits of dV in measurement performed at the instant t :

$$dP = |\psi|^2 dV = \psi^* \psi dV \quad (4.1)$$

Similarly, for a system consisting of two particles, the quantity

$$dP = |\psi(x_1, y_1, z_1, x_2, y_2, z_2, t)|^2 dV_1 dV_2$$

(x_1, y_1, z_1 are the coordinates of the first particle, x_2, y_2, z_2 are the coordinates of the second particle, $dV_1 = dx_1 dy_1 dz_1$, and $dV_2 = dx_2 dy_2 dz_2$) gives the probability of the particle 1 being detected within the limits of the volume dV_1 , and the particle 2 within the limits of dV_2 in measurements performed at the instant t .

Since a particle with authenticity, i.e. with a probability of unity, must be somewhere, summation of the probabilities (4.1) over the entire space must yield unity. We thus arrive at the normalization condition for the psi-function:

$$\int |\psi|^2 dV = 1 \quad (4.2)$$

In Sec. 3, we established that the psi-function allows multiplication by any non-zero complex number. Consequently, if the integral is

finite, the condition (4.2) may be observed. A psi-function satisfying this condition is said to be **normalized**. It is obvious that a normalized psi-function is determined to within a **phase factor** of the form $e^{i\alpha}$ (where α is any real number).

Sometimes the integral (4.2) is a diverging one (i.e. becomes infinite), and it is impossible to normalize the psi-function in accordance with the condition (4.2). Therefore, $|\psi|^2$ cannot be interpreted as the probability density. In these cases too, however, the ratio of the values of $|\psi|^2$ for various points of space determines the relative probability of the relevant values of the coordinates.

Knowing the probabilities of different positions of a particle, we can calculate the mean values of its coordinates. For example, the mean value of the position vector of a particle $\langle \mathbf{r} \rangle^1$ is determined by the expression

$$\langle \mathbf{r} \rangle = \int \mathbf{r} dP = \int \mathbf{r} |\psi|^2 dV = \int \psi^* \mathbf{r} \psi dV$$

(to give the formula a symmetric form, we have placed \mathbf{r} inside the product $\psi^* \psi$). This vector equation is equivalent to three scalar ones:

$$\langle x \rangle = \int \psi^* x \psi dV, \quad \langle y \rangle = \int \psi^* y \psi dV, \quad \langle z \rangle = \int \psi^* z \psi dV \quad (4.3)$$

In a similar way, we can find the mean value of any function of coordinates, for example, the mean value of the potential energy of a particle:

$$\langle U \rangle = \int \psi^* U(x, y, z) \psi dV \quad (4.4)$$

Equation (4.4) has the following meaning. Assume that we are repeatedly determining the potential energy of a particle, and at the moment of each determination the particle is in the same state ψ . With an increase in the number of determinations, the mean value of the results obtained will tend to the value (4.4).

Hence, we have learned how to predict the probability with which different values of any position function will be obtained in measurements, and also the mean results of these measurements if we know the psi-function of a particle. But meanwhile the way of determining the probability of values of physical quantities that are not a particle's position functions (for instance, the momentum, angular momentum, and energy) remains unclear. How to find the psi-function of particles in different force fields also remains unclear. We shall now pass over to a treatment of these matters.

¹ The mean value is designated either by putting a bar over the symbol of the relevant quantity (for instance, $\bar{\mathbf{r}}$), or by putting the symbol in angle brackets ($\langle \mathbf{r} \rangle$). The latter notation is coming into greater and greater favour.

5. The Schrödinger Equation

The psi-function of a particle in a force field described by the potential¹ $U = U(x, y, z, t)$ can be found by solving the differential equation in partial derivatives presented by E. Schrödinger

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi = i\hbar \frac{\partial \psi}{\partial t}$$

or in a more compact form

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + U\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (5.1)$$

where $\nabla^2 = \Delta$ is the Laplacian operator, m is the mass of the particle, and \hbar is Planck's constant \hbar divided by 2π .

Without treating the ideas that led to the discovery of this equation², we shall only note that Eq. (5.1) should be considered as a fundamental initial assumption whose validity is confirmed by the coincidence of the conclusions following from it with the results of experiments.

Of special interest is the case when the potential U does not contain the time t explicitly. In this case, U has the meaning of potential energy. In this condition, the solution of Eq. (5.1) is simplified because the psi-function breaks up into two factors, of which one depends only on the coordinates of the particle, and the other only on the time³. To verify this statement, let us write the psi-function as

$$\psi(x, y, z, t) = \varphi(x, y, z) f(t)$$

and introduce this expression into Eq. (5.1). Taking into consideration that the operator ∇^2 acts only on the factor φ , and $\partial f/\partial t = df/dt$, we obtain

$$-\frac{\hbar^2}{2m} f \nabla^2 \varphi + U\varphi f = i\hbar \varphi \frac{df}{dt}$$

Dividing this equation by φf , we arrive at the relation

$$\frac{-\frac{\hbar^2}{2m} \nabla^2 \varphi + U\varphi}{\varphi} = \frac{i\hbar}{f} \frac{df}{dt} \quad (5.2)$$

The left-hand side of this relation contains only the coordinates of the particle, and the right-hand side only the time. Two functions

¹ See Vol. 1, Sec. 3.

² These ideas are treated in many textbooks of general physics. See, for example, I. V. Savelyev. *Physics. A General Course*. Translated by G. Leib, Vol. III, Sec. 4.4. Mir Publishers, Moscow (1981).

³ Here we are dealing with particular solutions. The general solution $\sum c_n \varphi_n(x, y, z) f_n(t)$ cannot be represented in the form of two factors of which one depends only on the coordinates and the other only on the time.

of different independent variables can equal each other at any values of these variables only if these functions equal the same constant quantity. Let E stand for this constant quantity. We thus arrive at two differential equations:

$$-\frac{\hbar^2}{2m} \nabla^2 \varphi + U\varphi = E\varphi \quad (5.3)$$

$$\frac{i\hbar}{f} \frac{df}{dt} = E \quad (5.4)$$

The second equation can be written as

$$\frac{df}{dt} + \frac{i}{\hbar} Ef = 0$$

We have arrived at a linear homogeneous equation with constant coefficients. Solving it with the aid of the substitution $f = e^{\lambda t}$, we find that

$$f = e^{-(i/\hbar)Et} \quad (5.5)$$

(we have omitted the arbitrary factor C in the general solution because the psi-function has been determined to within such a factor).

Let us turn to Eq. (5.3). We can use it to reveal the meaning of the constant quantity which we designated by E . The requirement that all the terms of Eq. (5.3) must have the same dimension shows that E has the same dimension as U , i.e. that of energy. In motion in a potential force field, the total energy of the system remains constant. For this reason, we shall identify E with the total energy of a particle.

Hence, when a particle moves in a potential force field, the psi-function has the form

$$\psi(x, y, z, t) = \varphi(x, y, z) \cdot e^{-(i/\hbar)Et} \quad (5.6)$$

where E is the total energy of the particle. It thus follows that the density of the probability of finding the particle at various points of space is $|\psi|^2 = |\varphi|^2$, i.e. is independent of the time. This is why states described by psi-functions of the form of (5.6) are called stationary.

The task of finding the psi-function for stationary states consists in essence in finding the function $\varphi(x, y, z)$, which is why this function is said to be the psi-function of a stationary state and is designated by the letter ψ . Substituting ψ for φ in Eq. (5.3), we arrive at the Schrödinger equation for stationary states:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + U\psi = E\psi \quad (5.7)$$

This equation is often written in the form

$$\nabla^2\psi - \frac{2m}{\hbar^2} (E - U) \psi = 0 \quad (5.8)$$

Assuming in (5.8) that $U = 0$, we obtain the Schrödinger equation for a free particle:

$$\nabla^2\psi + \frac{2mE}{\hbar^2} \psi = 0 \quad (5.9)$$

It is not difficult to verify that this equation is satisfied by the function

$$\psi = e^{\pm ikr} \quad (5.10)$$

where

$$k^2 = \frac{2mE}{\hbar^2} = \frac{\mathbf{p}^2}{\hbar^2} \quad (5.11)$$

(\mathbf{p} is the classical momentum of a particle).

Substituting \mathbf{p}/\hbar for \mathbf{k} in (5.10) and introducing the expression obtained into (5.6), we get the psi-function of a free particle:

$$\psi(\mathbf{r}, t) = \exp \left[-\frac{i}{\hbar} (Et \mp \mathbf{p}r) \right] \quad (5.12)$$

A similar function (more exactly, its real part) describes a plane wave with the frequency $\omega = E/\hbar$ and the wave vector $\mathbf{k} = \mathbf{p}/\hbar$. This coincidence reflects the dual, corpuscular-wave nature of micro-particles that manifests itself in experiments involving diffraction. For instance, when a beam of electrons that has passed through a crystal acts on a photographic plate, we obtain a pattern of diffraction rings similar to that obtained when the plate is acted upon by X-rays that have passed through the crystal.

We must note that the upper sign [plus in (5.10) and minus in (5.12)] corresponds to the wave running in the direction of \mathbf{k} , and the lower sign [minus in (5.10) and plus in (5.12)] to the wave running oppositely to the direction of \mathbf{k} . Consequently, when considering stationary states, we shall interpret a psi-function of the form $e^{i\mathbf{kx}}$ as a wave running along the x -axis to the right, and a psi-function of the form $e^{-i\mathbf{kx}}$, as a wave running to the left.

The superposition of two waves of the form of (5.10) is the general solution of the Schrödinger equation for a free particle with a definite value of the momentum, namely,

$$\psi = C_1 e^{i\mathbf{k}\mathbf{r}} + C_2 e^{-i\mathbf{k}\mathbf{r}} \quad (5.13)$$

When $C_1 = C_2$ or $C_1 = -C_2$, the function (5.13) can be written accordingly in the form

$$\psi = A \cos kr \quad \text{or} \quad \psi = B \sin kr \quad (5.14)$$

It is evident that both these functions describe a standing wave.

Let us consider the motion of a free particle whose position is localized within the interval Δx (for simplicity's sake we are considering a one-dimensional problem). According to the uncertainty principle, the momentum of the particle will have an indeterminacy of the order of $\hbar/\Delta x$.

In accordance with the superposition principle, the psi-function of a particle can be represented as the superposition of states of the form of (5.12) with values of the momentum confined within the interval from $p_0 - \Delta p$ to $p_0 + \Delta p$:

$$\psi(x, t) = \int_{p_0 - \Delta p}^{p_0 + \Delta p} b(p) \exp\left[-\frac{i}{\hbar}(Et - px)\right] dp$$

Substitution of the frequency $\omega = E/\hbar$ for E and of the wave number $k = p/\hbar$ for p yields

$$\psi(x, t) = \int_{k_0 - \Delta k}^{k_0 + \Delta k} c(k) e^{i(kx - \omega t)} dk \quad (5.15)$$

We have arrived at an expression describing a **wave packet**.

The frequency ω is a function of the wave number k , i.e. $\omega = \omega(k)$. Let us expand this function into a series in the vicinity of the point k_0 . Limiting ourselves to the two first terms of the expansion, we obtain

$$\omega(k) = \omega_0 + \left(\frac{d\omega}{dk}\right)_0 (k - k_0) \quad (5.16)$$

Assuming that the coefficient $c(k)$ in (5.15) is a slowly varying function, let us put it outside the integral (Δk is considered to be small). At the same time, we shall replace ω in the exponent with its value from (5.16) and introduce a new integration variable $\xi = k - k_0$. The result is:

$$\psi(x, t) = c(k_0) \exp[i(k_0 x - \omega_0 t)] \int_{-\Delta k}^{+\Delta k} \exp\left\{i\left[x - \left(\frac{d\omega}{dk}\right)_0 t\right]\xi\right\} d\xi$$

The integral is evaluated quite easily, and we arrive at the expression

$$\psi(x, t) = 2c(k_0) \frac{\sin\{(x - (d\omega/dk)_0 t)\Delta k\}}{[x - (d\omega/dk)_0 t]} e^{i(k_0 x - \omega_0 t)} = A(x, t) e^{i(k_0 x - \omega_0 t)} \quad (5.17)$$

Owing to the smallness of Δk , we may consider that the function (5.17) describes an almost monochromatic wave with an amplitude $A(x, t)$ slowly varying in time and space. The maximum of the amplitude is at the point for which the denominator of expression

(5.17) is zero. The centre of the wave packet (i.e. the point where the amplitude is maximum) has the coordinate

$$x_c = \left(\frac{d\omega}{dk} \right)_0 t \quad (5.18)$$

A glance at (5.18) shows that the centre of the wave packet moves with the velocity

$$v_{gr} = \left(\frac{d\omega}{dk} \right)_0 \quad (5.19)$$

where v_{gr} is the **group velocity**.

The non-relativistic expression for the energy of a free particle is $E = p^2/2m$. Replacing E with $\hbar\omega$ and p with $\hbar k$, we obtain a relation between ω and k :

$$\omega = \frac{k^2 \hbar}{2m} \quad (5.20)$$

Differentiating (5.20) with respect to k , we obtain for the velocity of the wave packet describing the motion of a free particle the value $k\hbar/m = p/m = v$, where v is the velocity of the particle. Hence, the wave packet moves with the same velocity as the particle itself.

By the width of a wave packet is meant the distance between two points at which the amplitude vanishes that are the closest to the centre of the packet. The value of x at which the argument of the sine in (5.17) is $\pm\pi$ (a zero value of the argument corresponds to the centre of the packet) corresponds to these points. Consequently, the coordinates of the boundaries of a packet satisfy the condition $|x - (d\omega/dk)_0 t| \Delta k = \pm\pi$, whence

$$x = \left(\frac{d\omega}{dk} \right)_0 t \pm \frac{\pi}{\Delta k} \quad (5.21)$$

From (5.21) we get the constant value $2\pi/\Delta k$ for the width of a wave packet. If we take into account the higher-order terms of the expansion in (5.20), we obtain a value for the width of a wave packet that increases with time—the wave packet diverges. This signifies that the localization of a particle in space in the course of its motion becomes less and less accurate.

6. Probability Flux Density

In addition to the concept of the density of the probability of finding a particle at various points of space, we can introduce the concept of the **density of the probability flux**. To arrive at this concept, let us consider the integral $\int |\psi|^2 dV$ evaluated not over the entire infinite volume, but over a finite volume V . This integral is

the probability of finding the particle in the given volume. Let us calculate the time derivative of this probability:

$$\frac{d}{dt} \int_V |\psi|^2 dV = \frac{d}{dt} \int_V \psi^* \psi dV = \int_V \left(\psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} \right) dV \quad (6.1)$$

By Eq. (5.1) we have

$$\frac{\partial \psi}{\partial t} = -\frac{\hbar}{2mi} \nabla^2 \psi + \frac{1}{i\hbar} U \psi, \quad \frac{\partial \psi^*}{\partial t} = \frac{\hbar}{2mi} \nabla^2 \psi^* - \frac{1}{i\hbar} U \psi^*$$

(the second equation is the complex conjugate of the first; it has been obtained from the first one by substituting ψ^* for ψ and $-i$ for i). With the aid of these relations, we can write the right-hand side of formula (6.1) as

$$-\int_V \frac{\hbar}{2mi} (\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*) dV + \frac{1}{i\hbar} \int_V (\psi^* U \psi - \psi U \psi^*) dV$$

The second of these integrals evidently vanishes. The first integral can be written as

$$-\int_V \frac{\hbar}{2mi} \nabla (\psi^* \nabla \psi - \psi \nabla \psi^*) dV \quad (6.2)$$

This ensues from the following elementary calculation:

$$\begin{aligned} \nabla (\psi^* \nabla \psi - \psi \nabla \psi^*) &= \nabla \psi^* \nabla \psi + \psi^* \nabla^2 \psi - \nabla \psi \nabla \psi^* \\ &\quad - \psi \nabla^2 \psi^* = \psi^* \nabla^2 \psi - \psi \nabla^2 \psi^* \end{aligned}$$

Hence, the right-hand side of formula (6.1) can be replaced with expression (6.2). The result is

$$\frac{d}{dt} \int_V |\psi|^2 dV = - \int_V \nabla \left\{ \frac{\hbar}{2mi} (\psi^* \nabla \psi - \psi \nabla \psi^*) \right\} dV \quad (6.3)$$

Using the Ostrogradsky-Gauss theorem, the right-hand side of this relation can be replaced with an integral over the surface S enclosing the volume V . This leads to the formula

$$-\frac{d}{dt} \int_V |\psi|^2 dV = \int_S \left\{ \frac{\hbar}{2mi} (\psi^* \nabla \psi - \psi \nabla \psi^*) \right\} dS \quad (6.4)$$

(we have transferred the minus sign to the left-hand side of the formula).

We can infer from relation (6.4) that the surface integral on the right determines the rate of diminishing of the probability that the particle will be found in the volume V and, consequently, is the flux

of the probability through the surface S . In this connection, we can interpret the quantity

$$\mathbf{j} = \frac{\hbar}{2mi} (\psi^* \nabla \psi - \psi \nabla \psi^*) \quad (6.5)$$

as the density of the probability flux.

Using the notation (6.5), we can write formula (6.3) as follows:

$$\frac{d}{dt} \int_V |\psi|^2 dV = \int_V \left\{ \frac{\partial}{\partial t} |\psi|^2 \right\} dV = - \int_V \nabla \cdot \mathbf{j} dV$$

Owing to the arbitrariness of choosing the volume V , the following condition must be observed at each point of space:

$$\frac{\partial}{\partial t} |\psi|^2 + \nabla \cdot \mathbf{j} = 0 \quad (6.6)$$

We have arrived at a typical continuity equation. A similar equation, for instance, in electrodynamics has the form $\partial\rho/\partial t + \nabla \cdot \mathbf{j} = 0$, where ρ is the charge density, and \mathbf{j} is the electric current density (see Vol. 1, formula (51.1)).

Substituting expression (6.5) for \mathbf{j} into (6.6), we obtain the condition which the psi-function must satisfy:

$$\frac{\partial}{\partial t} (\psi^* \psi) + \frac{\hbar}{2mi} \nabla \cdot (\psi^* \nabla \psi - \psi \nabla \psi^*) = 0 \quad (6.7)$$

Recall that $|\psi|^2$ determines the probability of finding a particle at different points of space. It thus follows that a psi-function must be (1) single-valued, (2) continuous, and (3) finite (except, perhaps, for singular points). In addition, it follows from the condition (6.7) that a psi-function must have a continuous and finite (except, perhaps, for singular points) first derivative.

The collection of requirements listed above which a psi-function must meet is called **standard conditions**.

Chapter II

MATHEMATICAL TOOLS OF QUANTUM MECHANICS

7. Fundamental Postulates

Quantum mechanics is based on several postulates. We may include among them the statement we already know that the psi-function corresponds to the state of a system, and also the Schrödinger equation. In this section, we treat three postulates¹.

The first of them states that every physical quantity can be represented as a linear operator.

By an operator is meant a rule with whose aid a function f is correlated with another function φ . This rule is written as

$$f = \hat{Q}\varphi \quad (7.1)$$

We shall designate operators by letters with circumflexes, for example \hat{Q} , \hat{A} , \hat{x} , and \hat{p} .

We call an operator linear if it satisfies the following conditions:

$$\hat{Q}(\varphi_1 + \varphi_2 + \dots + \varphi_n) = \hat{Q}\varphi_1 + \hat{Q}\varphi_2 + \dots + \hat{Q}\varphi_n,$$

$$\hat{Q}(c\varphi) = c\hat{Q}\varphi$$

where c is an arbitrary constant. These two conditions can be combined into the following compact form:

$$\hat{Q}\left(\sum_{m=1}^n c_m \varphi_m\right) = \sum_{m=1}^n c_m \hat{Q}\varphi_m \quad (7.2)$$

By comparing formulas (3.1) and (7.2), we can conclude that a linear operator conforms to the superposition principle.

We can exemplify linear operators by multiplication by x (here $\hat{Q} = x$) and differentiation with respect to x (here $\hat{Q} = \partial/\partial x$). Indeed,

$$x \sum \varphi_m = \sum x\varphi_m, \quad x(c\varphi) = cx\varphi$$

Similarly

$$\frac{\partial}{\partial x} \left(\sum \varphi_m \right) = \sum \frac{\partial \varphi_m}{\partial x}, \quad \frac{\partial}{\partial x} (c\varphi) = c \frac{\partial \varphi}{\partial x}$$

¹ The choice of the system of postulates of quantum mechanics is not completely unambiguous. There is meanwhile no generally adopted system of postulates.

In mathematics, the following equation corresponds to each operator:

$$\hat{Q}\psi = q\psi \quad (7.3)$$

where ψ is a function, and q is a parameter. Next the problem is posed of finding all the functions that transform Eq. (7.3) into an identity and at the same time satisfy certain additional conditions, for instance the standard conditions (see Sec. 6). For many operators, the solutions of Eq. (7.3) satisfying the set conditions are obtained not for any, but only for certain selected values of the parameter q . These special values of the parameter are called the **eigenvalues of the operator \hat{Q}** , and the functions ψ obtained from Eq. (7.3) when the eigenvalues are substituted for q in it are called the **eigenfunctions of the operator** belonging to the relevant eigenvalues. Several eigenfunctions may correspond to the same eigenvalue. Here, the given eigenvalue is said to be **degenerate**. The number of different functions belonging to an eigenvalue is called the **degree of degeneracy**.

The second postulate of quantum mechanics states that upon measuring a physical quantity Q represented by the operator \hat{Q} , we can obtain only one of the eigenvalues q_m of the operator \hat{Q} .

Hence, an equation of the form of (7.3) plays a highly important role in quantum mechanics. We must note that with a view to the **second postulate**, the parameter q in Eq. (7.3) must have the dimension of the quantity Q . The operator \hat{Q} must have the same dimension.

The set of eigenvalues of the operator \hat{Q} is known as the **spectrum of the operator** or the **spectrum of the quantity Q** . A spectrum may consist of the discrete values q_1, q_2, \dots ; it is correspondingly called **discrete**. In a **continuous spectrum**, the set of eigenvalues forms a continuous sequence. In the general case, a spectrum may include both discrete and continuous regions.

When dealing with a discrete spectrum, the eigenvalues and eigenfunctions of the operator \hat{Q} can be numbered:

$$\begin{aligned} q_1, q_2, \dots, q_m, \dots \\ \psi_1, \psi_2, \dots, \psi_m, \dots \end{aligned}$$

It is assumed in quantum mechanics that a set of eigenfunctions of any physical quantity forms a **complete set** (or system). This signifies that any continuous function ψ can be expanded in eigenfunctions, i.e. it can be written as

$$\psi = \sum c_m \psi_m \Rightarrow \psi \underset{\text{arrow}}{\sim} \sum c_m \psi_m \quad (7.4)$$

where c_m are constant coefficients, complex in a general case.

Let us write the psi-function of a certain state of a system in the form of (7.4). The third postulate of quantum mechanics states that in measurements performed on a system in the state ψ for determining the value of the quantity Q in whose functions Eq. (7.4) has been expanded, the probability of obtaining the value q_m equals (with the proper normalization of the functions) the square of the magnitude of the coefficient c_m .

In accordance with the meaning of the coefficients c_m , the condition

$$\sum |c_m|^2 = 1 \quad (7.5)$$

must be observed. We shall prove below that with proper normalization of the functions ψ_m , this condition is indeed observed.

If all the coefficients of the expansion except the one with the number m are zero, formula (7.4) becomes: $\psi = \psi_m$ (recall that the psi-function is determined with an accuracy to the phase factor $e^{i\alpha}$). In this case, we shall always obtain the result q_m in measurements. Consequently, the eigenfunction ψ_m is the psi-function of the state in which the quantity Q has a definite value equal to q_m .

When more than one coefficient in the expansion (7.4) is non-zero, the quantity Q does not have a definite value in the state ψ . In measurements, the values q_1, q_2, \dots will be obtained for it. It is quite natural to assume that the probability with which a certain value is obtained should be determined by the weight with which the relevant function ψ_m enters (7.4), i.e. by the "magnitude" of the coefficient c_m . The coefficient c_m itself, owing to its complex nature, cannot equal such a probability. Therefore, by analogy with the fact that the probability of detecting a particle inside the volume dV is determined not by the function ψ , but by the square of its magnitude, we must take the square of the magnitude of c_m as the probability. This reasoning cannot be considered as a proof of the third postulate. It is intended only to explain how we can arrive at this postulate. The postulate itself must be considered as an initial assumption that is one of the cornerstones of quantum mechanics.

We shall show in the following section that the eigenfunctions of any operator representing a physical quantity with a discrete spectrum form what is called an orthonormal system. This signifies that

$$\int \psi_m^* \psi_n dV = \delta_{mn} \quad (7.6)$$

The integral is evaluated over the entire region of change in the variables in which the functions ψ_k have been determined.

Mathematicians use the concept of the scalar product of the functions φ and ψ that is designated by the symbol $\langle \varphi | \psi \rangle$ and is determined as follows:

$$\langle \varphi | \psi \rangle = \int \varphi^* \psi dV \quad (7.7)$$

$(dV = dx dy dz)$. If a scalar product is zero, the functions are said to be **orthogonal**. Similarly, the scalar product of mutually perpendicular, i.e. orthogonal vectors is zero.

It follows from definition (7.7) that

$$\langle \varphi | \psi \rangle^* = \langle \psi | \varphi \rangle \quad (7.8)$$

The **scalar square of a function**, i.e. the scalar product of the function with itself

$$\langle \varphi | \varphi \rangle = \int \varphi^* \varphi dV = \int |\varphi|^2 dV$$

is evidently a real positive quantity.

Let us take a product of the form $\langle a\varphi | b\psi \rangle$, where a and b are complex numbers. With account of the definition (7.7), we can write that

$$\langle a\varphi | b\psi \rangle = a^* b \langle \varphi | \psi \rangle \quad (7.9)$$

Hence, when the constant coefficients are put outside the symbol of the scalar product, the coefficient of the first factor transforms into its complex conjugate, while the coefficient of the second factor remains unchanged.

Using the notation (7.7), we can write formula (7.6) expressing the condition of orthonormality of the eigenfunctions as

$$\langle \psi_m | \psi_n \rangle = \delta_{mn} \quad (7.10)$$

The unit vectors of rectangular coordinate axes satisfy a similar condition:

$$e_m e_n = \delta_{mn}$$

Condition (7.10) allows us to find an expression for the coefficients c_m in the expansion (7.4). For this purpose, we multiply scalarly relation (7.4) and ψ_n and take into account (7.10):

$$\langle \psi_n | \psi \rangle = \sum_m c_m \langle \psi_n | \psi_m \rangle = \sum_m c_m \delta_{nm} = c_n$$

We thus arrive at the formula

$$c_n = \langle \psi_n | \psi \rangle = \int \psi_n^* \psi dV \quad (7.11)$$

When we know the coefficients c_n , we can find the mean value of a physical quantity in the state in which this quantity has no definite value. The probability of obtaining the value q_m in measuring the quantity Q is $|c_m|^2$. Consequently, the mean value of this quantity is determined by the formula

$$\langle q \rangle = \sum_m |c_m|^2 q_m = \sum_m c_m^* c_m q_m \quad (7.12)$$

By (7.11), $c_m^* = \langle \psi | \psi_m \rangle$. Let us substitute this expression into formula (7.12):

$$\langle q \rangle = \sum_m \langle \psi | \psi_m \rangle c_m q_m = \sum_m \langle \psi | q_m \psi_m \rangle c_m$$

Now let us substitute $\hat{Q}\psi_m$ for $q_m\psi_m$ in accordance with (7.3), put c_m inside the symbol of the scalar product, and take advantage of the linearity of the operator:

$$\langle q \rangle = \sum_m \langle \psi | \hat{Q}\psi_m \rangle c_m = \sum_m \langle \psi | \hat{Q}c_m \psi_m \rangle = \langle \psi | \hat{Q} \sum_m c_m \psi_m \rangle$$

Finally, taking into account (7.4), we obtain

$$\langle q \rangle = \langle \psi | \hat{Q} \psi \rangle \quad (7.13)$$

or

$$\langle q \rangle = \int \psi^* \hat{Q} \psi \, dV \quad (7.14)$$

We have obtained one of the most important formulas of quantum mechanics. It allows us, when we know a psi-function of state, to find the mean value of the results of measuring any physical quantity. For this purpose, we must also know the form of the operator corresponding to the given quantity.

8. Linear Operators

Physical quantities are real. For this reason, they can be depicted only by operators whose eigenvalues are real. It is quite natural that such operators are the ones that are mainly considered in quantum mechanics. In performing calculations, however, auxiliary operators with complex eigenvalues are often helpful. In this connection, we have to acquaint ourselves with the properties of these operators too.

Let us begin with the basic definitions. Two operators \hat{Q}_1 and \hat{Q}_2 having the property

$$\langle \varphi | \hat{Q}_1 \psi \rangle = \langle \varphi^* | \hat{Q}_2 \psi^* \rangle \quad (8.1)$$

where φ and ψ are two arbitrary functions, are said to be transposes of each other. The operator that is the transpose of \hat{Q} is customarily designated by the symbol $\tilde{\hat{Q}}$. Therefore, if we designate \hat{Q}_1 in (8.1) simply by the symbol \hat{Q} , we must use the symbol $\tilde{\hat{Q}}$ for \hat{Q}_2 :

$$\langle \varphi | \hat{Q} \psi \rangle = \langle \psi^* | \tilde{\hat{Q}} \varphi^* \rangle \quad (8.2)$$

Hence, the operators \hat{Q} and $\tilde{\hat{Q}}$ satisfying the condition (8.2) are called the transposes of each other. With a view to the definition (7.7), we can write the condition (8.2) as

$$\int \varphi^* \hat{Q} \psi \, dV = \int \psi \tilde{\hat{Q}} \varphi^* \, dV \quad (8.3)$$

Let us correlate with the operator \hat{Q} the operator \hat{Q}^+ such that for any arbitrarily taken pair of functions φ and ψ , the equality

$$\langle \varphi | \hat{Q} \psi \rangle = \langle \hat{Q}^+ \varphi | \psi \rangle \quad (8.4)$$

is observed. The operator \hat{Q}^+ is called the **Hermitian conjugate** (or the adjoint) to the operator \hat{Q} . Whereas the operator \hat{Q} acts on the function at its right, the operator \hat{Q}^+ acts on the function at the left of \hat{Q} . Consequently, the addition of the adjoint sign “+” to the symbol of the operator \hat{Q} transfers the action of the operator from the function at its right to the function at its left. If we adopt a rule according to which the operator \hat{Q}^+ is written at the right of the function which it acts on, relation (8.4) determining the adjoint operator becomes

$$\langle \varphi | \hat{Q} \psi \rangle = \langle \varphi \hat{Q}^+ | \psi \rangle \quad (8.5)$$

Consequently, in expressions like (8.5), simultaneously with the addition of the adjoint sign to the symbol of an operator, we must transfer the “partition” from the left-hand position relative to the operator to the right-hand one.

We shall also define the operator \hat{Q}^* satisfying the condition

$$(\hat{Q}\varphi)^* = \hat{Q}^* \varphi^* \quad (8.6)$$

This operator is called the **complex conjugate** of the operator \hat{Q} .

Let us transform the right-hand side of Eq. (8.2) with a view to the property (7.8) of a scalar product:

$$\langle \psi^* | \tilde{\hat{Q}} \varphi^* \rangle = \langle \tilde{\hat{Q}} \varphi^* | \psi^* \rangle^* = \langle (\tilde{\hat{Q}} \varphi^*)^* | \psi \rangle = \langle \tilde{\hat{Q}}^* \varphi | \psi \rangle$$

We have taken advantage of the fact that in accordance with the definition (8.6), we have $(\tilde{\hat{Q}} \varphi^*)^* = \tilde{\hat{Q}}^* \varphi$. As a result, formula (8.2) becomes

$$\langle \varphi | \hat{Q} \psi \rangle = \langle \tilde{\hat{Q}}^* \varphi | \psi \rangle$$

A comparison with (8.4) shows that

$$\hat{Q}^+ = \tilde{\hat{Q}}^* \quad (8.7)$$

where \tilde{Q}^* stands for the complex conjugate operator of the transposed operator \tilde{Q} . Relation (8.7) shows that the Hermitian conjugate operator \hat{Q}^+ , generally speaking, does not coincide with the complex conjugate operator \hat{Q}^* .

Assume that an operator represents multiplication by a complex number: $\hat{C} = c$. Let us find the Hermitian conjugate operator. By (8.5), we have

$$\langle \varphi | \hat{C} \psi \rangle = \langle \varphi \hat{C}^+ | \psi \rangle$$

The operator \hat{C}^+ will evidently also be a number. Therefore, using the property (7.9), we can write that

$$\hat{C} \langle \varphi | \psi \rangle = (\hat{C}^+)^* \langle \varphi | \psi \rangle$$

whence it follows that $\hat{C} = (\hat{C}^+)^*$, i.e. $\hat{C}^* = \hat{C}^+$. Hence,

$$\text{if } \hat{C} = c, \text{ then } \hat{C}^+ = c^* \quad (8.8)$$

and, consequently, $\hat{C}^+ = \hat{C}^*$.

We have defined three kinds of operators that can be correlated with a given operator \hat{Q} : the transpose \tilde{Q} , the Hermitian conjugate (or adjoint) \hat{Q}^+ and the complex conjugate \hat{Q}^* . Now let us see what conditions an operator must satisfy for its eigenvalues to be real. Scalar multiplication of both sides of the equation $\hat{Q}\psi_n = q_n\psi_n$ by ψ_n yields

$$\langle \psi_n | \hat{Q} \psi_n \rangle = q_n \langle \psi_n | \psi_n \rangle$$

The square of ψ_n is clearly real (for normalized functions it equals unity). Therefore, for q_n to be real, the left-hand side of the equation must be real, i.e. the condition must be observed that

$$\langle \psi_n | \hat{Q} \psi_n \rangle = \langle \psi_n | \hat{Q} \psi_n \rangle^*$$

or with account taken of (7.8)

$$\langle \psi_n | \hat{Q} \psi_n \rangle = \langle \hat{Q} \psi_n | \psi_n \rangle$$

A comparison with (8.4) shows that this condition will be satisfied if the operator \hat{Q} and its adjoint operator \hat{Q}^+ coincide. An operator for which the equality

$$\hat{Q} = \hat{Q}^+ \quad (8.9)$$

holds is called a **self-adjoint** or **Hermitian operator**. With account taken of relation (8.7), the condition for an operator to be Hermitian can be written as

$$\hat{Q} = \tilde{\hat{Q}}^* \quad (8.10)$$

We have thus arrived at the conclusion that physical quantities must be depicted by self-adjoint (Hermitian) operators \hat{Q} for which the following relation holds:

$$\langle \varphi | \hat{Q} \psi \rangle = \langle \hat{Q} \varphi | \psi \rangle \quad (8.11)$$

[see (8.4) and (8.9)]. Considering \hat{Q} on the right-hand side as \hat{Q}^* , this relation can also be written as

$$\langle \varphi | \hat{Q} \psi \rangle = \langle \varphi \hat{Q}^* | \psi \rangle \quad (8.12)$$

(for self-adjoint operators, the “partition” may be placed at either side of the operator).

Examination of (8.11) shows that the following relation holds

$$\int \varphi^* \hat{Q} \psi \, dV = \int \psi \hat{Q}^* \varphi^* \, dV \quad (8.13)$$

which can also be considered as the definition of self-adjoint operators.

We shall show that the eigenfunctions of Hermitian operators are mutually orthogonal. Let us write Eq. (7.3) for the m -th and n -th eigenvalues of the quantity Q :

$$\hat{Q} \psi_m = q_m \psi_m, \quad \hat{Q} \psi_n = q_n \psi_n^1$$

We perform scalar multiplication of the first equation by ψ_n from the right, and of the second one by ψ_m from the left. The result is

$$\langle \hat{Q} \psi_m | \psi_n \rangle = q_m \langle \psi_m | \psi_n \rangle$$

$$\langle \psi_m | \hat{Q} \psi_n \rangle = q_n \langle \psi_m | \psi_n \rangle$$

↑ ψ_n is assumed

Owing to the Hermitian nature of the operator, the left-hand sides of these equations are equal [see (8.11)]. Therefore, subtracting the lower equation from the upper one, we find that

$$(q_m - q_n) \langle \psi_m | \psi_n \rangle = 0$$

whence it follows that when $q_m \neq q_n$ (in other words, when $m \neq n^1$) the scalar product of the eigenfunctions ψ_m and ψ_n is zero: $\langle \psi_m | \psi_n \rangle = 0$, and this is just what signifies that the above-mentioned functions are orthogonal.

¹ We assume that only one eigenfunction corresponds to each q_k , i.e. degeneracy is absent.

It was shown in Sec. 3 that a psi-function is determined to within any complex factor. For a discrete spectrum, this factor can always be chosen so that the square of each of the functions ψ_h will be unity. Consequently, the system of eigenfunctions will be orthonormal. We have thus proved formula (7.10). In the following, we shall assume that the eigenfunctions of a discrete spectrum are normalized to unity.

Finally, we shall use the property of eigenfunctions being orthonormal to prove relation (7.5). Let us substitute expression (7.4) into the condition for the normalization of a psi-function [see (4.2)], taking into account (7.10):

$$\begin{aligned} 1 &= \int \psi^* \psi dV = \int \left(\sum_m c_m^* \psi_m^* \right) \left(\sum_n c_n \psi_n \right) dV \\ &= \sum_{m,n} c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_{m,n} c_m^* c_n \delta_{mn} = \sum_m |c_m|^2 \end{aligned}$$

Q.E.D.

9. Matrix Representation of Operators¹

The equation

$$f = \hat{Q}\varphi \quad (9.1)$$

can be written in the matrix form. To do this, let us expand the functions f and φ in the eigenfunctions $\psi_k^{(r)}$ of an auxiliary operator \hat{R} and assume that the system of functions $\psi_k^{(r)}$ is orthonormal, i.e.

$$\langle \psi_m^{(r)} | \psi_n^{(r)} \rangle = \delta_{mn} \quad (9.2)$$

We thus assume that

$$\varphi = \sum_n a_n \psi_n^{(r)} \quad (9.3)$$

$$f = \sum_k b_k \psi_k^{(r)} \quad (9.4)$$

where

$$a_n = \langle \psi_n^{(r)} | \varphi \rangle, \quad b_k = \langle \psi_k^{(r)} | f \rangle \quad (9.5)$$

[see formula (7.11)].

With a fixed choice of the functions $\psi_m^{(r)}$, the function φ will be determined by the set of coefficients a_n , and the function f by the set

¹ Before beginning to read this section, our reader is invited to acquaint himself with Appendix VII of Vol. 1.

of coefficients b_k ¹. Therefore, say, the function φ can be represented as a column (i.e. as an $\infty \times 1$ matrix)

$$\varphi = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \\ \vdots \end{pmatrix} \quad (9.6)$$

or as a row (i.e. as a $1 \times \infty$ matrix)²

$$\varphi = (a_1 \ a_2 \dots \ a_n \dots) \quad (9.7)$$

The same also holds for the function f .

Let us substitute the expansions (9.3) and (9.4) into Eq. (9.1), having in view that a_n and b_k are numbers on which the operator \hat{Q} does not act. The result is

$$\sum_k b_k \psi_k^{(r)} = \sum_n a_n \hat{Q} \psi_n^{(r)}$$

Scalar multiplication of both sides of this equation by $\psi_m^{(r)}$ yields

$$\sum_k b_k \langle \psi_m^{(r)} | \psi_k^{(r)} \rangle = \sum_n a_n \langle \psi_m^{(r)} | \hat{Q} \psi_n^{(r)} \rangle$$

By formula (9.2), the coefficient of b_k is δ_{mk} . Therefore, the sum on the left-hand side equals simply b_m , and we arrive at the relation

$$b_m = \sum_n Q_{mn} a_n \quad (9.8)$$

where the symbol Q_{mn} stands for the following expression:

$$Q_{mn} = \langle \psi_m^{(r)} | \hat{Q} \psi_n^{(r)} \rangle = \int (\psi_m^{(r)})^* \hat{Q} \psi_n^{(r)} dV \quad (9.9)$$

Equation (9.1) establishes a rule by which the function φ is transformed into the function f . Equation (9.8) establishes a rule by which a set of the coefficients a_n (representing the function φ) is transformed into a set of the coefficients b_m (representing the function f). Consequently, Eq. (9.8) is another form of writing Eq. (9.1). The coefficients a_n represent in this equation the function φ , and the coefficients b_m represent the function f . The set of quantities Q_{mn}

¹ Similarly, with a given basis (i.e. system of unit vectors e_k), the vector a is determined by a set of the numbers a_k —its components.

² To simplify printing, we designate matrices not by double bars at their sides (as we did in Vol. 1), but by parentheses (in Vol. 1 we designated tensors in this way). This will not result in any confusion because no tensors will be encountered in the present volume.

represents the operator \hat{Q} . This set can be written as a square matrix with an infinite number of rows and columns:

$$\hat{Q} = \begin{pmatrix} Q_{11} & Q_{12} & \dots & Q_{1n} & \dots \\ Q_{21} & Q_{22} & \dots & Q_{2n} & \dots \\ \dots & \dots & \dots & \dots & \dots \\ Q_{m1} & Q_{m2} & \dots & Q_{mn} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} \quad (9.10)$$

The matrix relation between the functions f and φ can be given a form whose appearance is also similar to Eq. (9.1). For this purpose, we shall show that the expression

$$\begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_m \\ \vdots \end{pmatrix} = \begin{pmatrix} Q_{11} & Q_{12} & \dots & \dots & \dots \\ Q_{21} & Q_{22} & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & Q_{mn} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \\ \vdots \end{pmatrix} \quad (9.11)$$

where the right-hand side is the product of two matrices, is equivalent to formula (9.8).

According to the rule of matrix multiplication [see Vol. 1, formula (VII.28)], the elements β_{mk} of the matrix B are obtained from the elements γ_{mn} and α_{nk} of the matrices Γ and A being multiplied ($B = \Gamma A$) with the aid of the formula

$$\beta_{mk} = \sum_n \gamma_{mn} \alpha_{nk} \quad (9.12)$$

If the matrix A has only one column with the elements $\alpha_{n1} = \alpha_n$, formula (9.12) gives the values $\beta_{m1} = \sum_n \gamma_{mn} \alpha_n$ for the elements of the matrix B. Consequently, the product matrix is also a column with the elements $\beta_{m1} = \beta_m$, and

$$\beta_m = \sum_n \gamma_{mn} \alpha_n \quad (9.13)$$

Taking a_n , Q_{mn} , and b_m instead of α_n , γ_{mn} , and β_m , respectively, we arrive at Eq. (9.8). We have thus proved the legitimacy of the matrix representation (9.11).

Hence, the operator \hat{Q} can be written in the form of the matrix (9.10) whose elements are evaluated by formula (9.9). These elements depend on the choice of the "basis", i.e. the auxiliary operator \hat{R} whose eigenfunctions are used for expansion of the functions φ and f . The coefficients of the expansion of the functions φ and f also depend on the choice of \hat{R} . The set of coefficients a_n , the set of coefficients b_m , and the matrix Q_{mn} are said to be, respectively,

the ***r*-representation** of the function φ , the function f , and the operator \hat{Q} . If \hat{R} is a coordinate operator, we speak of the coordinate representation of the functions and operator. If \hat{R} is a momentum operator, we have a momentum representation, and so on. We must note that all the operators and functions in any relation always have to be taken in the same representation.

If we take the eigenfunctions $\psi_h^{(q)}$ of the operator \hat{Q} itself as the functions ψ_h in formula (9.9), we obtain an operator in its **own representation** (**eigenrepresentation**). Since here the functions that are used to calculate the matrix elements by formula (9.9) satisfy the equation $\hat{Q}\psi_n = q_n\psi_n$, the following simplification can be made:

$$Q_{mn} = \langle \psi_m^{(q)} | \hat{Q} \psi_n^{(q)} \rangle = \langle \psi_m^{(q)} | q_n \psi_n^{(q)} \rangle = q_n \delta_{mn} \quad (9.14)$$

The result obtained signifies that the matrix of an operator in its eigenrepresentation is diagonal, the diagonal elements coinciding with the eigenvalues of the operator:

$$(Q_{mn}) = \begin{pmatrix} q_1 & 0 & 0 & \dots \\ 0 & q_2 & 0 & \dots \\ 0 & 0 & q_3 & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \quad (9.15)$$

If the operator \hat{Q} is taken in its eigenrepresentation (the functions φ and f must also be taken in the *q*-representation), relation (9.8) is simplified as follows:

$$b_m = \sum_n Q_{mn} a_n = \sum_n q_n \delta_{mn} a_n = q_m a_m \quad (9.16)$$

This result signifies that the coefficient b_m is obtained from a_m by multiplication by the relevant diagonal element of the matrix determining the operator in its eigenrepresentation.

Let us take the eigenfunction $\psi_k^{(r)}$ of the operator \hat{R} as φ in Eq. (9.1):

$$f = \hat{Q} \psi_k^{(r)} \quad (9.17)$$

Therefore, by (9.2) and (9.5), we have $a_n = \delta_{nk}$. Substitution of this value into (9.8) yields

$$b_m = \sum_n Q_{mn} \delta_{nk} = Q_{mk}$$

Consequently, with a view to (9.4), the function (9.17) can be written as

$$\hat{Q} \psi_k^{(r)} = \sum_m Q_{mk}^{(r)} \psi_m^{(r)} \quad (9.18)$$

[we have used the superscript (r) on the matrix element to stress that it is calculated in the r -representation].

Relation (9.18) can have the interpretation that $|Q_{mk}|^2$ determines the probability of the system whose state is described by the function $\hat{Q}\psi_k^{(r)}$ being in the state $\psi_m^{(r)}$. In other words, $|Q_{mk}|^2$ gives the probability of the fact that the system as a result of the action described by the operator \hat{Q} will pass from the state $\psi_k^{(r)}$ to the state $\psi_m^{(r)}$. Accordingly, Q_{mk} is said to be the matrix element corresponding to a transition from the state k to the state m .

We shall set out a few definitions relating to matrices. The matrix \tilde{A} is said to be the transpose of the matrix A if the relation

$$(\tilde{A})_{mn} = A_{nm} \quad (9.19)$$

is observed.

Hence, the transpose of a matrix is obtained from the initial one by interchanging the rows with the columns.

The matrix A^* whose elements are the complex conjugates of the elements of the matrix A :

$$(A^*)_{mn} = (A_{mn})^* \quad (9.20)$$

is said to be the complex conjugate of the matrix A .

A matrix A^+ whose elements are determined with the aid of the rule

$$A_{mn}^+ = (\tilde{A}_{mn})^* = A_{nm}^* \quad (9.21)$$

is called the Hermitian conjugate (or adjoint) of the matrix A . Consequently, the matrix A^+ is obtained from the matrix A by the consecutive carrying out of the operations of transposition and complex conjugation. Relation (9.21) is similar to relation (8.7) defining a Hermitian conjugate operator.

Finally, the matrix A_{mn} satisfying the condition

$$A_{mn} = A_{nm}^* = A_{mn}^+ \quad (9.22)$$

is called self-adjoint or Hermitian [compare with (8.9) and (8.10)]. Hence, in a Hermitian matrix, the elements of the transpose matrix coincide with the complex conjugate elements of the initial matrix.

We shall show that the definition (9.21) of a Hermitian conjugate matrix agrees with the definition (8.7) of a Hermitian conjugate operator. In accordance with (9.9), (8.7), and (8.3), we have

$$A_{mn}^+ = \langle \psi_m | \psi_n \hat{A}^+ \rangle = \langle \psi_n \hat{A}^+ | \psi_m \rangle^* = \langle \psi_n | \hat{A} \psi_m \rangle^* = A_{nm}^*$$

Consequently, taking the definition (8.7) as the initial one, we have arrived at the definition (9.21).

Let us find the matrix expression equivalent to the scalar product of two functions $\langle \varphi | \psi \rangle$. We expand these functions in the eigenfunctions ψ_k of an operator \hat{R} :

$$\varphi = \sum_m a_m \psi_m, \quad \psi = \sum_n b_n \psi_n$$

Substitution of these expressions into formula (7.9) yields

$$\begin{aligned} \langle \varphi | \psi \rangle &= \left\langle \sum_m a_m \psi_m \mid \sum_n b_n \psi_n \right\rangle = \sum_{m,n} a_m^* b_n \langle \psi_m | \psi_n \rangle \\ &= \sum_{m,n} a_m^* b_n \delta_{mn} = \sum_n a_n^* b_n \end{aligned} \quad (9.23)$$

[see (7.10)].

In the r -representation, the functions φ and ψ are determined by the matrices

$$\varphi \sim A = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix}, \quad \psi \sim B = \begin{pmatrix} b_1 \\ b_2 \\ \vdots \end{pmatrix}$$

To obtain expression (9.23), we must multiply the matrices A^* and B . Indeed, according to the rule of matrix multiplication, we obtain

$$(a_1^* a_2^* \dots) \begin{pmatrix} b_1 \\ b_2 \\ \vdots \end{pmatrix} = \sum_n a_n^* b_n$$

We have thus arrived at the formula

$$\langle \varphi | \psi \rangle = A^* B \quad (9.24)$$

The Hermitian conjugate matrix in formula (9.24) corresponds to the complex conjugate function φ in the integrand in formula (7.7).

Let us find a matrix expression for the mean value of the quantity Q . For this purpose, we shall expand the psi-function of the state being considered in the eigenfunctions of an operator \hat{R} (i.e., we shall take the psi-function in the r -representation): $\psi = \sum c_k \psi_k^{(r)}$, and introduce this expansion into formula (7.14):

$$\langle q \rangle = \left\langle \sum_m c_m \psi_m \mid \hat{Q} \sum_n c_n \psi_n \right\rangle = \sum_{m,n} c_m^* c_n \langle \psi_m | \hat{Q} \psi_n \rangle$$

The expression $\langle \psi_m | \hat{Q} \psi_n \rangle$ is a matrix element of the operator \hat{Q} in the r -representation. Consequently,

$$\langle q \rangle = \sum_{m,n} c_m^* Q_{mn} c_n \quad (9.25)$$

The formula obtained is the matrix analogue of formula (7.14).

If we take the operator \hat{Q} in its eigenrepresentation (the psi-function too must be taken in the q -representation), the matrix elements will be $Q_{mn} = q_n \delta_{mn}$ [see (9.14)] so that formula (9.25) becomes

$$\langle q \rangle = \sum_{m,n} c_m^* q_n \delta_{mn} c_n = \sum_m c_m^* q_m c_m$$

This coincides with expression (7.42).

Finally, let us see how we can solve the equation $\hat{Q}\psi = q\psi$ in the matrix form, i.e. how, knowing the matrix Q_{mn} in the r -representation, we can find the eigenvalues q_n and the eigenfunctions (in the r -representation) of the quantity Q . We substitute for $\psi(x)$ in the equation its expansion in the eigenfunctions $\psi_n(x)$ of the operator \hat{R} :

$$\sum_n c_n \hat{Q} \psi_n(x) = q \sum_n c_n \psi_n(x)$$

Scalar multiplication of this relation by $\psi_m(x)$ yields

$$\sum_n c_n \langle \psi_m | \hat{Q} \psi_n \rangle = q \sum_n c_n \langle \psi_m | \psi_n \rangle$$

The multiplier of c_n on the left-hand side is Q_{mn} —a matrix element of the operator \hat{Q} in the r -representation, and the multiplier of c_n on the right-hand side is δ_{mn} . Consequently,

$$\sum_n c_n Q_{mn} = q \sum_n c_n \delta_{mn} = qc_m \quad (9.26)$$

Taking consecutively $m = 1, 2, \dots$ in (9.26), we obtain a system of an infinite number of linear homogeneous equations with an infinite number of unknowns c_1, c_2, \dots (the matrix Q_{mn} is assumed to be given):

$$\left. \begin{aligned} (Q_{11}-q)c_1 + Q_{12}c_2 &+ \dots + Q_{1m}c_m &+ \dots &= 0 \\ Q_{21}c_1 &+ (Q_{22}-q)c_2 + \dots + Q_{2m}c_m &+ \dots &= 0 \\ \dots &\dots &\dots &\dots \\ Q_{m1}c_1 &+ Q_{m2}c_2 &+ \dots + (Q_{mm}-q)c_m &+ \dots = 0 \end{aligned} \right\} \quad (9.27)$$

It was shown in Appendix VIII of Vol. 1 that a system of linear homogeneous equations has a non-zero solution only if the determinant of the system is zero:

$$\left| \begin{array}{cccc} Q_{11}-q & Q_{12} & \dots & Q_{1m} \\ Q_{21} & Q_{22}-q & \dots & Q_{2m} \\ \dots & \dots & \dots & \dots \\ Q_{m1} & Q_{m2} & \dots & Q_{mm}-q \end{array} \right| = 0 \quad (9.28)$$

Relation (9.28) is an equation of an infinitely great degree in the unknown q . It should be considered as the limit of an expression of the form of (9.28) written for the finite number N of rows and columns obtained when N tends to infinity. It is natural that Eq. (9.28) has a meaning only if such a limit exists.

Equation (9.28) has an infinitely large number of roots: $q_1, q_2, \dots, q_m, \dots$. They are the values of q at which non-zero values of the coefficients $c_1, c_2, \dots, c_n, \dots$ are obtained that determine $\psi(x)$ in the r -representation (in which the Q_{mn} 's are given). Consequently, the roots of Eq. (9.28) are the eigenvalues of the quantity Q .

Introducing $q = q_1$ into the system (9.27) and solving it for the unknowns c_n , let us find the set of coefficients c_n that determine the eigenfunction of the operator \hat{Q} corresponding to $q = q_1$. Introducing $q = q_2$ into (9.27), we find the set of coefficients determining the second eigenfunction, and so on. We shall thus solve the problem of finding the eigenvalues and eigenfunctions of the operator \hat{Q} set by the matrix Q_{mn} .

If the matrix Q_{mn} is determined in its eigenrepresentation, all the non-diagonal elements will vanish and Eq. (9.28) will become

$$\begin{vmatrix} Q_{11}-q & 0 & \dots & 0 & \dots \\ 0 & Q_{22}-q & \dots & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & Q_{mm}-q & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix} = 0$$

The roots of this equation are evidently $q_1 = Q_{11}, q_2 = Q_{22}, \dots, q_m = Q_{mm}, \dots$, so that we arrive at an already known result: the diagonal elements of a matrix written in its eigenrepresentation equal the eigenvalues of the given quantity.

Hence, to give a diagonal form to the matrix Q_{mn} , we must compile Eq. (9.28) and find its roots. The latter will be the elements of the matrix after it has been reduced to the diagonal form [see (9.15)].

⁷ Commuting operators have a common system of eigenfunctions (see the following section). Therefore, their matrices can be reduced simultaneously to a diagonal form.

10. The Algebra of Operators

Linear operators can be added and multiplied. In the following, to avoid repetition, we shall omit the word "linear", but shall always have in mind linear operators.

The sum of the operators \hat{A} and \hat{B} is defined to be the operator $\hat{C} = \hat{A} + \hat{B}$ determined by the condition

$$\hat{C}\varphi = (\hat{A} + \hat{B})\varphi = \hat{A}\varphi + \hat{B}\varphi \quad (10.1)$$

Substituting expression (10.1) into formula (9.9), we get the relation between the operators \hat{A} , \hat{B} and \hat{C} in the matrix form:

$$C_{mn} = A_{mn} + B_{mn} \quad (10.2)$$

This relation agrees with the rule of matrix addition [see Vol. 1, formula (VII.25)].

The product of the operators \hat{A} and \hat{B} is defined to be the operator $\hat{\Pi} = \hat{A}\hat{B}$ determined by the condition

$$\hat{\Pi}\varphi = (\hat{A}\hat{B})\varphi = \hat{A}(\hat{B}\varphi) \quad (10.3)$$

(to obtain the function $\hat{\Pi}\varphi$, we must find the function $\hat{B}\varphi$ and then act on it with the operator \hat{A}). By formula (9.8)

$$\Pi_{mn} = \langle \psi_m | \hat{A}\hat{B}\psi_n \rangle = \langle \psi_m | \hat{A}(\hat{B}\psi_n) \rangle \quad (10.4)$$

where ψ_k is the eigenfunction of the operator \hat{R} .

Like any other function, the function $\hat{B}\psi_n$ can be expanded into a series in the eigenfunctions ψ_k of the same operator \hat{R} , i.e. represented in the form $\hat{B}\psi_n = \sum c_k \psi_k$; for the coefficients c_k , formula (7.11) gives the value $c_k = \langle \psi_k | \hat{B}\psi_n \rangle$. The latter expression is the matrix element B_{kn} of the operator \hat{B} in the r -representation. Consequently,

$$\hat{B}\psi_n = \sum_k B_{kn} \psi_k \quad (10.5)$$

Substitution of expression (10.5) into (10.4) yields

$$\Pi_{mn} = \left\langle \psi_m \left| \hat{A} \left(\sum_k B_{kn} \psi_k \right) \right. \right\rangle = \sum_k B_{kn} \langle \psi_m | \hat{A} \psi_k \rangle = \sum_k B_{kn} A_{mk}$$

Finally, interchanging the places of the multipliers, we arrive at the formula

$$\Pi_{mn} = \sum_k A_{mk} B_{kn} \quad (10.6)$$

that agrees with the rule of matrix multiplication.

In accordance with the definition of a product of operators, by the square of an operator \hat{Q}^2 is meant the two-fold action of the operator \hat{Q} on a function:

$$\hat{Q}^2\varphi = \hat{Q}(\hat{Q}\varphi) \quad (10.7)$$

The higher powers of the operator are determined in a similar way.

Let us find the operator that is the transpose of the product of the operators $\hat{\Pi} = \hat{A}\hat{B}$. Using the definition (8.2) of a transpose

operator and the property (7.8) of the scalar product of two functions, we can write the following train of transformations:

$$\begin{aligned}\langle \varphi | \hat{A} \hat{B} \psi \rangle &= \langle (\hat{B} \psi)^* | \tilde{\hat{A}} \varphi^* \rangle = \langle \tilde{\hat{A}} \varphi^* | (\hat{B} \psi)^* \rangle^* \\ &= \langle (\tilde{\hat{A}} \varphi^*)^* | \hat{B} \psi \rangle = \langle \psi^* | \tilde{\hat{B}} (\tilde{\hat{A}} \varphi^*) \rangle = \langle \psi^* | \tilde{\hat{B}} \tilde{\hat{A}} \varphi^* \rangle\end{aligned}$$

At the same time by definition

$$\langle \varphi | \hat{\Pi} \psi \rangle = \langle \psi^* | \tilde{\hat{\Pi}} \varphi^* \rangle$$

A comparison of the relations obtained shows that

$$\tilde{\hat{A}} \tilde{\hat{B}} = \tilde{\hat{B}} \tilde{\hat{A}} \quad (10.8)$$

i.e. an operator that is the transpose of the product of two operators equals the product of the transposes of the multipliers written in the opposite order.

A similar relation holds for the transposed matrices. By (10.6), a matrix element of the product AB of the matrices A and B equals $(AB)_{mn} = \sum_k A_{mk} B_{kn}$. Taking advantage of relation (9.19), we can write

$$(\tilde{\hat{A}} \tilde{\hat{B}})_{mn} = (AB)_{nm} = \sum_k A_{nk} B_{km} = \sum_k \tilde{\hat{A}}_{kn} \tilde{\hat{B}}_{mk} = \sum_k \tilde{\hat{B}}_{mk} \tilde{\hat{A}}_{kn} = (\tilde{\hat{B}} \tilde{\hat{A}})_{mn}$$

whence

$$\tilde{\hat{A}} \tilde{\hat{B}} = \tilde{\hat{B}} \tilde{\hat{A}} \quad (10.9)$$

By formula (8.6), we have

$$(\hat{A} \hat{B} \varphi)^* = (\hat{A} \hat{B})^* \varphi^*$$

At the same time

$$(\hat{A} \hat{B} \varphi)^* = [\hat{A} (\hat{B} \varphi)]^* = \hat{A}^* (\hat{B} \varphi)^* = \hat{A}^* \hat{B}^* \varphi^*$$

A comparison of these expressions yields

$$(\hat{A} \hat{B})^* = \hat{A}^* \hat{B}^* \quad (10.10)$$

Finally, let us find the operator that is the Hermitian conjugate to the operator $\hat{A} \hat{B}$. Treating $\hat{A} \hat{B}$ as a single operator, we can write relation (8.5) as

$$\langle \varphi | \hat{A} \hat{B} \psi \rangle = \langle \varphi (\hat{A} \hat{B})^* | \psi \rangle$$

But if we have in view that $\hat{A}\hat{B}\psi = \hat{A}(\hat{B}\psi)$, we can write

$$\langle\varphi|\hat{A}\hat{B}\psi\rangle = \langle\varphi\hat{A}^+|\hat{B}\psi\rangle = \langle(\varphi\hat{A}^+)\hat{B}^+|\psi\rangle = \langle\varphi\hat{A}^+\hat{B}^+|\psi\rangle$$

A comparison of the two relations shows that

$$(\hat{A}\hat{B})^+ = \hat{A}^+\hat{B}^+ \quad (10.11)$$

The result obtained signifies that whereas before taking the conjugate the function is first acted upon by the operator \hat{B} and then the result obtained is acted upon by the operator \hat{A} , after the conjugate has been taken, the function is first acted upon by the operator \hat{A}^+ , and then the result obtained is acted upon by the operator \hat{B}^+ . Consequently, conjugation changes the order in which the operators \hat{A} and \hat{B} act. This also holds for more than two multipliers.

Let us take an operator of the form $\hat{C}\hat{Q}$, where the operator \hat{C} is simply multiplication by the number c . By (10.11), we have $(\hat{C}\hat{Q})^+ = \hat{C}^+\hat{Q}^+$. It was shown in Sec. 8 [see (8.8)] that if $\hat{C} = c$, we have $\hat{C}^+ = \hat{C}^*$. With a view to this circumstance, we can write the relation

$$(\hat{C}\hat{Q})^+ = \hat{C}^*\hat{Q}^+ \quad (10.12)$$

Particularly,

$$(i\hat{Q})^+ = -i\hat{Q}^+ \quad (10.13)$$

Let us find the matrix that is the Hermitian conjugate of the product of the matrices A and B . By (9.21), we have

$$(AB)_{mn}^+ = (AB)_{nm}^* = \left(\sum_k A_{nk} B_{km} \right)^* = \sum_k A_{nk}^* B_{km}^* = \sum_k B_{mk}^* A_{kn}^*$$

The result obtained signifies that

$$(AB)^+ = B^+A^+ \quad (10.14)$$

A matrix that is the Hermitian conjugate of the product of two matrices equals the product of the Hermitian conjugate matrices taken in the opposite order.

We are now in a position to explain why a Hermitian conjugate operator should be written at the right of the function which it acts on. For this end, let us turn to Eq. (9.8) describing the transformation of the function φ into the function f under the action of the operator \hat{Q} . We can write this equation as follows:

$$b_{m1} = \sum_n Q_{mn} a_{n1} \quad (10.15)$$

The subscript "1" indicates that the matrices a and b have only one column each.

Relation (10.15) can be written as

$$b = Qa \quad (10.16)$$

where b , Q , and a are the relevant matrices. Let us write a relation that is the Hermitian conjugate of (10.16), using formula (10.14):

$$b^+ = (Qa)^+ = a^+Q^+ \quad (10.17)$$

When taking the Hermitian conjugates of matrices, the columns are interchanged with the rows, and, in addition, the matrix elements are replaced with their complex conjugates [see (9.21)]. Consequently, the matrices b^+ and a^+ have only one row each. Writing the matrices appearing in (10.17) as arrays, we obtain

$$(b_1^* b_2^* \dots b_m^* \dots) = (a_1^* a_2^* \dots a_n^* \dots) \begin{pmatrix} Q_{11}^* & Q_{21}^* \dots \\ Q_{12}^* & Q_{22}^* \dots \\ \dots & \dots \\ \dots & \dots \end{pmatrix} \quad (10.18)$$

Here the matrix with the elements Q_{mn}^* represents the operator \hat{Q}^+ .

It is not difficult to see that the correct result can be obtained only if the matrix Q^+ in expressions (10.17) and (10.18) is at the right of the matrix a^+ (recall that in the multiplication of matrices, a row is multiplied by a column). Hence follows the rule according to which the operator \hat{Q}^+ must be written at the right of the function which it acts on.

The product of operators, generally speaking, is non-commuting:

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}$$

This can be verified, taking the example of the operators $\hat{A} = \partial/\partial x$ and $\hat{B} = x$. Indeed,

$$\left. \begin{aligned} (\hat{A}\hat{B})\varphi &= \frac{\partial}{\partial x}(x\varphi) = x\frac{\partial\varphi}{\partial x} + \varphi \\ (\hat{B}\hat{A})\varphi &= x\frac{\partial\varphi}{\partial x} \end{aligned} \right\} \quad (10.19)$$

* Operators \hat{A} and \hat{B} for which the condition

$$\hat{A}\hat{B} = \hat{B}\hat{A} \quad (10.20)$$

is observed are said to be **commutative**, or to **commute** with each other. If the condition (10.20) is not observed, the operators are said to be **non-commutative**.

Operators for which

$$\hat{A}\hat{B} = -\hat{B}\hat{A} \quad (10.21)$$

are called **anticommutative**.

The operator $\hat{A}\hat{B} - \hat{B}\hat{A}$ formed from the operators \hat{A} and \hat{B} is called the commutator of the given operators, and is designated by the symbol $[\hat{A}, \hat{B}]$. Hence,

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad (10.22)$$

By (10.19), we have

$$\left[\frac{\partial}{\partial x}, x \right] = \frac{\partial}{\partial x} x - x \frac{\partial}{\partial x} = 1$$

This signifies that by acting on a function φ with the operator $[\partial/\partial x, x]$, we have again obtained the same function φ . An operator that leaves a function unchanged is called a **unit operator**. Consequently, the commutator of the operators $\partial/\partial x$ and x equals a unit operator.

The commutator of commuting operators is zero.

In quantum mechanics, operators are used to depict physical quantities. Let us see how the rules for the addition and multiplication of operators agree with the concepts of the sum and product of physical quantities.

Assume that two physical quantities Q and R can simultaneously have definite values. The psi-function of the state in which the quantity Q has the value q_n , and the quantity R , the value r_n , must satisfy two equations simultaneously:

$$\hat{Q}\psi_n = q_n\psi_n \quad (10.23)$$

$$\hat{R}\psi_n = r_n\psi_n \quad (10.24)$$

i.e. must be the eigenfunction of both operators. Therefore, the operators of two simultaneously measurable quantities have common eigenfunctions. Summation of Eqs. (10.23) and (10.24) yields

$$(\hat{Q} + \hat{R})\psi_n = (q_n + r_n)\psi_n \quad (10.25)$$

Consequently, the eigenvalues of the operator $\hat{Q} + \hat{R}$ equal the sums of the eigenvalues of the operators \hat{Q} and \hat{R} . Correspondingly, we should understand the sum of the quantities Q and R to mean the quantity $Q + R$ whose eigenvalues equal the sums of the eigenvalues of the quantities being added.

By the product of the simultaneously measurable quantities Q and R is meant the quantity QR whose eigenvalues equal the products of the eigenvalues of the quantities being multiplied. Accordingly, designating the operator of the product of the quantities Q and R by the symbol $\hat{\Pi}$, we can write

$$\hat{\Pi}\psi_n = q_n r_n \psi_n \quad (10.26)$$

Let us act on Eq. (10.24) with the operator \hat{Q} , having in view Eq. (10.23):

$$\hat{Q}\hat{R}\psi_n = r_n\hat{Q}\psi_n = r_nq_n\psi_n = q_nr_n\psi_n \quad (10.27)$$

A comparison of the equation obtained with (10.26) yields the expression $\hat{H} = \hat{Q}\hat{R}$ agreeing with the rule (10.3) for the operator of the product of two quantities.

It follows from the above that the operator \hat{Q}^2 corresponds to the square of the quantity Q (here \hat{Q} is the operator of the quantity Q). Similarly, the operator \hat{Q}^* corresponds to the quantity Q^* .

Acting on Eq. (10.23) with the operator \hat{R} , we obtain, with account taken of (10.24),

$$\hat{R}\hat{Q}\psi_n = q_n\hat{R}\psi_n = q_nr_n\psi_n$$

A comparison with (10.27) allows us to conclude that $\hat{Q}\hat{R} = \hat{R}\hat{Q}$, i.e. that the operators \hat{Q} and \hat{R} commute.

The results obtained can be summarized as follows. If two quantities can simultaneously have definite values, then:

- (1) their operators have common eigenfunctions, and
- (2) their operators commute.

The statements (1) and (2) follow from each other. We have shown above how the statement (2) is obtained from the statement (1). Now we shall prove that the statement (1) follows from (2).

Assume that the operators \hat{A} and \hat{B} commute. Their eigenfunctions satisfy the equations

$$\hat{A}\psi_n^{(a)} = a_n\psi_n^{(a)} \quad (10.28)$$

$$\hat{B}\psi_n^{(b)} = b_n\psi_n^{(b)} \quad (10.29)$$

Let us act with the operator \hat{B} on Eq. (10.28) and take advantage of the fact that the places of \hat{A} and \hat{B} may be interchanged:

$$\hat{B}\hat{A}\psi_n^{(a)} = a_n\hat{B}\psi_n^{(a)} \Rightarrow \hat{A}[\hat{B}\psi_n^{(a)}] = a_n[\hat{B}\psi_n^{(a)}]$$

The result obtained signifies that the function $[\hat{B}\psi_n^{(a)}]$ to within the constant factor c coincides with the eigenfunction of the operator \hat{A} belonging to the eigenvalue a_n , i.e. that

$$\hat{B}\psi_n^{(a)} = c\psi_n^{(a)}$$

It follows from this equation, in turn, that $\psi_n^{(a)}$ is an eigenfunction of the operator \hat{B} , and $c = b_n$. Hence, any eigenfunction $\psi_n^{(a)}$ of the operator \hat{A} is also an eigenfunction of the operator \hat{B} . By acting with the operator \hat{A} on Eq. (10.29) and following the same reason-

ing, we arrive at the conclusion that any eigenfunction $\psi_n^{(b)}$ of the operator \hat{B} is also an eigenfunction of the operator \hat{A} . We have thus proved that commuting operators have a common system of eigenfunctions.

In concluding, we shall make a few remarks relating to the matrices depicting physical quantities. We have established above that the operator $\hat{Q}\hat{R}$ corresponds to the product of the simultaneously measurable quantities Q and R . Accordingly, the matrix of the product of these quantities is the matrix of the operator $\hat{Q}\hat{R}$, i.e. the matrix determined by relation (10.6):

$$(QR)_{mn} = \sum_k Q_{mk} R_{kn} \quad (10.30)$$

The result obtained signifies that the matrix of the product of two quantities equals the product of the matrices of the quantities being multiplied. Accordingly, the matrix of the square of the quantity Q is determined by the formula

$$(Q^2)_{mn} = \sum_k Q_{mk} Q_{kn} \quad (10.31)$$

11. The Uncertainty Relation

If the operators \hat{A} and \hat{B} do not commute, the quantities corresponding to these operators cannot have definite values simultaneously. Let us try to establish the ratio between the indeterminacies of the values of these quantities.

To characterize the spread of the results of measuring a quantity, we take the standard deviation of the results of individual measurements from the mean value of the given quantity. The deviation of an individual measurement from the mean value is

$$\Delta a = a - \langle a \rangle$$

Let us correlate the following operator with it:

$$\overline{\Delta A} = \hat{A} - \langle a \rangle \quad (11.1)$$

(the operator corresponding to $\langle a \rangle$ is simply a number).

The standard (root-mean-square) deviation by definition is $\sqrt{\langle (\Delta a)^2 \rangle}$. Hence, the task of finding the standard deviation consists in determining the quantity $\langle (\Delta a)^2 \rangle$. If the operator $\overline{\Delta A}$ is correlated with the quantity Δa , the operator $(\overline{\Delta A})^2$ must be correlated with

the quantity $(\Delta a)^2$ (see Sec. 10). By the general rule of evaluating mean values, we have

$$\langle (\Delta a)^2 \rangle = \int \psi^* (\widehat{\Delta A})^2 \psi dV \quad (11.2)$$

Similarly

$$\langle (\Delta b)^2 \rangle = \int \psi^* (\widehat{\Delta B})^2 \psi dV \quad (11.3)$$

Let us consider the auxiliary integral

$$\mathcal{I}(\eta) = \int [(\eta \widehat{\Delta A} - i \widehat{\Delta B}) \psi] \psi^* dV \geq 0 \quad (11.4)$$

depending on the arbitrary real parameter η . It is evident that this integral cannot have negative values. We shall write it as follows:

$$\begin{aligned} \mathcal{I}(\eta) &= \int [(\eta \widehat{\Delta A} - i \widehat{\Delta B}) \psi] [(\eta \widehat{\Delta A}^* + i \widehat{\Delta B}^*) \psi^*] dV \\ &= \int (\eta \widehat{\Delta A} \psi - i \widehat{\Delta B} \psi) (\eta \widehat{\Delta A}^* \psi^* + i \widehat{\Delta B}^* \psi^*) dV \end{aligned}$$

We open the parentheses in the integrand and write the integral as

$$\begin{aligned} \mathcal{I}(\eta) &= \eta^2 \int (\widehat{\Delta A} \psi) \widehat{\Delta A}^* \psi^* dV + i\eta \int (\widehat{\Delta A} \psi) \widehat{\Delta B}^* \psi^* dV \\ &\quad - i\eta \int (\widehat{\Delta B} \psi) \widehat{\Delta A}^* \psi^* dV + \int (\widehat{\Delta B} \psi) \widehat{\Delta B}^* \psi^* dV \end{aligned}$$

Taking advantage of the circumstance that the operators are self-conjugate, let us perform the transformation (8.13) in each of the integrals, considering the expression of the form $(\widehat{\Delta A} \psi)$ as one of the functions in (8.13). In addition, let us combine the second and third integrals. As a result, we arrive at the formula

$$\begin{aligned} \mathcal{I}(\eta) &= \eta^2 \int \psi^* (\widehat{\Delta A})^2 \psi dV - i\eta \int \psi^* (\widehat{\Delta A} \widehat{\Delta B} - \widehat{\Delta B} \widehat{\Delta A}) \psi dV \\ &\quad + \int \psi^* (\widehat{\Delta B})^2 \psi dV \geq 0 \quad (11.5) \end{aligned}$$

The first and third integrals equal $\langle (\Delta a)^2 \rangle$ and $\langle (\Delta b)^2 \rangle$, respectively [see (11.2) and (11.3)]. The commutator of the operators $\widehat{\Delta A}$ and $\widehat{\Delta B}$ is in the second integrand. To eliminate $i = \sqrt{-1}$ in (11.5), let us designate this commutator by the symbol $i\hat{K}$, i.e. introduce the notation

$$[\widehat{\Delta A}, \widehat{\Delta B}] = \widehat{\Delta A} \widehat{\Delta B} - \widehat{\Delta B} \widehat{\Delta A} = i\hat{K} \quad (11.6)$$

Let us substitute expression (11.1) for $\widehat{\Delta A}$ and a similar expression for $\widehat{\Delta B}$ into (11.6). We obtain

$$(\widehat{A} - \langle a \rangle)(\widehat{B} - \langle b \rangle) - (\widehat{B} - \langle b \rangle)(\widehat{A} - \langle a \rangle) = i\widehat{K}$$

Simple transformations convert the left-hand side into the commutator of the operators \widehat{A} and \widehat{B} . Consequently,

$$[\widehat{\Delta A}, \widehat{\Delta B}] = [\widehat{A}, \widehat{B}] = i\widehat{K} \quad (11.7)$$

so that we can consider $i\widehat{K}$ to be the commutator of the operators \widehat{A} and \widehat{B} . Using the notation (11.6), we can write the second term of formula (11.5) as

$$-i\eta \int \psi^* (i\widehat{K}) \psi dV = \eta \int \psi^* \widehat{K} \psi dV = \eta \langle k \rangle$$

where $\langle k \rangle$ is the mean value of the quantity depicted by the operator \widehat{K} .

With a view to everything said above, formula (11.5) can be written as follows:

$$\mathcal{I}(\eta) = \eta^2 \langle (\Delta a)^2 \rangle + \eta \langle k \rangle + \langle (\Delta b)^2 \rangle \geqslant 0 \quad (11.8)$$

Let us investigate the relation between the coefficients at which a trinomial of the form $\alpha x^2 + \beta x + \gamma$ (where $\alpha > 0$) cannot have negative values at any values of x . For this purpose, we perform the transformation

$$\alpha x^2 + \beta x + \gamma = \alpha \left(x + \frac{\beta}{2\alpha} \right)^2 + \gamma - \frac{\beta^2}{4\alpha}$$

The minimum value of this expression is $\gamma - \beta^2/4\alpha$ (it is achieved at the value of x at which the expression in parentheses vanishes). Consequently, for the trinomial to be non-negative, the following relation must hold:

$$\gamma - \frac{\beta^2}{4\alpha} \geqslant 0, \text{ or } \alpha\gamma \geqslant \frac{\beta^2}{4}$$

Applying the result obtained to the trinomial (11.8), we arrive at the condition

$$\langle (\Delta a)^2 \rangle \langle (\Delta b)^2 \rangle \geqslant \frac{\langle k \rangle^2}{4}$$

whence

$$\sqrt{\langle (\Delta a)^2 \rangle} \sqrt{\langle (\Delta b)^2 \rangle} \geqslant \frac{\langle k \rangle}{2} \quad (11.9)$$

Relation (11.9) is called the **uncertainty relation**. A result we already know follows from it, namely, if the operators \hat{A} and \hat{B} commute, i.e. if $\hat{K} = 0$, the quantities A and B can simultaneously have definite values.

12. The Continuous Spectrum

If the operator \hat{Q} has a continuous spectrum of eigenvalues q , the eigenfunctions cannot be numbered. To distinguish these functions from one another, we shall label the symbol of a function with a subscript formed by the eigenvalue q which the given function corresponds to:

$$\psi_{q'}, \psi_{q''}, \text{etc.}$$

Unlike formula (7.4), the expansion of any function ψ in the eigenfunctions of an operator with a continuous spectrum has the form of the integral

$$\psi(x) = \int c(q) \psi_q(x) dq \quad (12.1)$$

Integration is performed over the entire range of values which the quantity Q can have. The coefficient $c(q)$ is a function of q that determines the psi-function in the q -representation.

Substituting $\psi_{q'}$ for ψ_m , $\psi_{q''}$ for ψ_n and accordingly q' for q_m and q'' for q_n in the calculations following formula (8.13), we obtain the formula

$$\langle \psi_{q'} | \psi_{q''} \rangle = \int \psi_{q'}^* \psi_{q''} dV = 0 \quad (q' \neq q'') \quad (12.2)$$

from which it follows that the eigenfunctions of a continuous spectrum, like those of a discrete spectrum, are orthogonal.

Matters are more complicated with respect to the normalization of the eigenfunctions of an operator having a continuous spectrum. For such functions, the integral $\int \psi_q^* \psi_q dV$ always diverges (i.e. becomes infinite). We shall show this in Sec. 17 taking the eigenfunctions of the momentum operator as an example.

Functions belonging to a continuous spectrum are normalized with the aid of the Dirac delta function (see Appendix VIII).

When the functions ψ_n of a discrete spectrum are normalized to unity, the squares of the magnitudes of the coefficients c_n in the expansion (7.4) determine the probabilities of the values q_n for the quantity Q . We shall attempt to normalize the functions ψ_q so that the expression $|c(q)|^2 dq$ formed from the functions $c(q)$ would determine the probability of the quantity Q having a value within the limits from q to $q + dq$ in the state described by the function

(12.1). The mean value of the quantity Q will therefore be evaluated by the formula

$$\langle q \rangle = \int |c(q)|^2 q dq \quad (12.3)$$

that is an analogue of formula (7.12).

The sum of the probabilities of all possible values of a given quantity must be unity. Hence follows the condition imposed on the function $c(q)$:

$$\int |c(q)|^2 dq = 1 \quad (12.4)$$

This formula is an analogue of formula (7.5). It is also an analogue of formula (4.2).

For the requirement (12.4) to be observed, the functions ψ_q must satisfy definite conditions. To find these conditions, let us introduce the function (12.1) into the condition (4.2) for the normalization of the function ψ :

$$\left\{ \left\{ \int c^*(q') \psi_{q'}^* dq' \right\} \left\{ \int c(q'') \psi_{q''} dq'' \right\} dV = 1 \right.$$

Let us rewrite this expression as follows:

$$\int c^*(q') dq' \int c(q'') \left\{ \int \psi_{q'}^* \psi_{q''} dV \right\} dq'' = 1 \quad (12.5)$$

We shall show that the expression which we arrive at transforms into the condition (12.4) if the integral over dV in braces is replaced with the function $\delta(q' - q'')$, i.e. if we assume that

$$\langle \psi_{q'} | \psi_{q''} \rangle = \int \psi_{q'}^* \psi_{q''} dV = \delta(q' - q'') \quad (12.6)$$

This substitution reduces (12.5) to the form

$$\int c^*(q') dq' \int c(q'') \delta(q' - q'') dq'' = 1$$

According to the property (VIII.2), the integral over dq'' equals $c(q')$, so that we arrive at the relation

$$\int c^*(q') c(q') dq' = 1$$

that coincides with (12.4).

Hence, for the expression $|c(q)|^2 dq$ to represent the probability in the meaning indicated above, the functions ψ_q must satisfy the condition (12.6), i.e. must be normalized to the delta function.

We must note that formula (12.6) also includes the property (12.2). Consequently, the system of functions satisfying the condition

(12.6) can be called orthonormalized. Formula (12.6) is a generalization of formula (7.10) for a continuous spectrum.

We can now establish how to find the function $c(q)$. For this purpose, we perform scalar premultiplication of Eq. (12.1) by ψ_q :

$$\langle \psi_{q'} | \psi \rangle = \int c(q) \langle \psi_{q'} | \psi_q \rangle dq$$

Taking advantage of the condition (12.6), we obtain

$$\langle \psi_{q'} | \psi \rangle = \int c(q) \delta(q' - q) dq = c(q')$$

Finally, suppressing the prime on q , we arrive at the formula

$$c(q) = \langle \psi_q | \psi \rangle = \int \psi_q^* \psi dV \quad (12.7)$$

This formula is a generalization of formula (7.11) for a continuous spectrum.

Let us find the matrix form of the operator \hat{Q} when the auxiliary operator \hat{R} has a continuous spectrum (the nature of the spectrum of the operator \hat{Q} does not matter). Here the expansion of the functions φ and f in the operator equation

$$f = \hat{Q}\varphi \quad (12.8)$$

is as follows:

$$\varphi = \int a(r') \psi_{r'} dr', \quad f = \int b(r') \psi_{r'} dr'$$

[see (12.1); we have designated the integration variable by r' instead of r]. Substitution of these expressions into Eq. (12.8) yields

$$\int b(r') \psi_{r'} dr' = \int a(r') \hat{Q} \psi_{r'} dr'$$

We perform scalar multiplication of both sides of the equation by ψ_r :

$$\int b(r') \langle \psi_r | \psi_{r'} \rangle dr' = \int a(r') \langle \psi_r | \hat{Q} \psi_{r'} \rangle dr' \quad (12.9)$$

With a view to the normalization condition (12.6), we transform the left-hand side of the equation as follows:

$$\int b(r') \langle \psi_r | \psi_{r'} \rangle dr' = \int b(r') \delta(r - r') dr' = b(r)$$

Formula (12.9) can thus be written as

$$b(r) = \int Q_{r,r'} a(r') dr' \quad (12.10)$$

where

$$Q_{r,r'} = \langle \psi_r | \hat{Q} \psi_{r'} \rangle = \int \psi_r^* \hat{Q} \psi_{r'} dV \quad (12.11)$$

Formulas (12.10) and (12.11) are a generalization of formulas (9.8) and (9.9) for a continuous spectrum. They determine the transformation of the function $a(r)$ into the function $b(r)$ under the action of the operator \hat{Q} .

Expression (12.11) determines the operator \hat{Q} in the r -representation. The subscripts r and r' change continuously. Notwithstanding this circumstance, we can formally treat each of the expressions $Q_{r,r'}$ as a matrix element of the operator \hat{Q} , and the set of all the values of these elements as a matrix having innumerable rows and columns. With such an approach, the right-hand side of expression (12.10) can be interpreted as the product of matrices, the subscripts of whose elements change continuously, owing to which summation is replaced with integration.

13. Dirac Notation

We have already noted the similarity of the expressions

$$\psi = \sum_m c_m \psi_m \text{ and } \mathbf{v} = \sum_m v_m \mathbf{e}_m$$

The former is the expansion of a psi-function in the eigenfunctions of an operator, and the latter is the expression for a vector in multi-dimensional space in terms of the unit vectors of the coordinate basis and the components of the vectors along the axes. This similarity allows us to define the psi-function as a vector in what is called the **Hilbert infinite-dimensional space**. A system of orthonormalized eigenfunctions ψ_m can be considered in this case as the basis chosen in such a space, and the quantities c_m as the components of the vector ψ along the axes of this basis. We obtain a definite set of the components c_m depending on the form of the basis (i.e. on the choice of the system of eigenfunctions, on the choice of the representation).

This analogy gave Dirac the idea of correlating a state vector with each state of a system. He designated this vector by the symbol $| \rangle$ and by the term ket. For example, the state vector $|\alpha\rangle$ is correlated with the state described by the function $\psi_\alpha(x)$. The subscript α called a **state index** designates a set of values of physical quantities or the corresponding quantum numbers that determine a state.

To each ket vector (for example, to the vector $|\alpha\rangle$), there is made to correspond its conjugate bra vector designated by the symbol $\langle |$ (in our example it is $\langle \alpha |$)¹. To designate the conjugation of these vectors, Dirac used the same symbol “ \dagger ” that is employed to designate Hermitian conjugate operators. Hence, the bra and ket vectors are related by the expression

$$\langle \alpha | = |\alpha\rangle^\dagger \quad (13.1)$$

¹ The terms bra and ket originate from the word “bracket”. Having in view angular brackets $\langle \rangle$, the vector $\langle |$ corresponds to the first part of the word bracket, i.e. bra, and the vector $| \rangle$ to the last part, i.e. ket.

The state ψ_α can evidently be characterized by either the vector $|\alpha\rangle$ or the vector $\langle\alpha|$.

Dirac defined the scalar product of two state vectors to be the product of the bra vector of one state and the ket vector of the other state. This product is written as

$$\langle\alpha|\beta\rangle \quad (13.2)$$

It is a complex number.

The scalar product (13.2) corresponds to the scalar product of two psi-functions. It therefore has all the properties inherent in expression (7.7). Particularly,

$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^* \quad (13.3)$$

{see (7.8)!}.

For states whose psi-functions are orthogonal, the state vectors are also orthogonal:

$$\langle\alpha|\beta\rangle = 0 \quad (13.4)$$

If $\langle\alpha|\alpha\rangle = 1$, the state vector is normalized to unity.

State vectors can be acted upon by linear operators, the result being new state vectors. If a ket vector is acted upon by the operator \hat{Q} , the bra vector that is the conjugate of the ket vector must be acted upon by the conjugate operator \hat{Q}^+ . The action of \hat{Q} on the ket vector produces a new ket vector. The action of \hat{Q}^+ on the bra vector gives a new bra vector. In writing these operations, the operator \hat{Q} is placed at the left of the ket vector, and the operator \hat{Q}^+ at the right of the bra vector:

$$|\beta\rangle = \hat{Q}|\alpha\rangle, \quad \langle\beta| = \langle\alpha|\hat{Q}^+$$

When an operator is Hermitian, we have $\hat{Q} = \hat{Q}^+$, and the above relations now become

$$|\beta\rangle = \hat{Q}|\alpha\rangle, \quad \langle\beta| = \langle\alpha|\hat{Q} \quad (13.5)$$

Before continuing to set out the algebra of state vectors, we shall recall some concepts from the algebra of conventional vectors. The vector v in n -dimensional space is determined by its projections v_1, v_2, \dots, v_n onto the coordinate axes, i.e. onto the unit vectors e_1, e_2, \dots, e_n forming the basis of the coordinate system (these projections are also called the components of the vector). The projection v_m of the vector v onto the m -axis equals the scalar product of the vectors v and e_m :

$$v_m = e_m v \quad (13.6)$$

The vector \mathbf{v} is thus determined by a set of n numbers:

$$\mathbf{e}_1 \mathbf{v}, \mathbf{e}_2 \mathbf{v}, \dots, \mathbf{e}_n \mathbf{v} \quad (13.7)$$

Let us return to state vectors. We take as the basis in Hilbert space the set of state vectors $|q_m\rangle$ correlated with the complete set of orthonormalized eigenfunctions of the operator \hat{Q} . By analogy with (13.6), we can find the projection of the state vector $|\alpha\rangle$ onto the m -th unit vector of the basis by scalar multiplication of the state vectors $|q_m\rangle$ and $|\alpha\rangle$. The product is the complex number $\langle q_m | \alpha \rangle$. The set of such numbers

$$\langle q_1 | \alpha \rangle, \langle q_2 | \alpha \rangle, \dots, \langle q_m | \alpha \rangle, \dots \quad (13.8)$$

completely defines the vector $|\alpha\rangle$, and, consequently, the function ψ_α . Therefore, the set of numbers (13.8) is the function ψ_α in the q -representation. A comparison with the formula $\psi_\alpha(x) = \sum c(q_m) \times \psi_{q_m}(x)$ ¹ allows us to conclude that

$$c(q_m) = \langle q_m | \alpha \rangle \quad (13.9)$$

If the quantity q has a continuous spectrum, the set of discrete numbers (13.9) transforms into a continuous function

$$c(q) = \langle q | \alpha \rangle \quad (13.10)$$

that is the psi-function of the state α in the q -representation. It is very convenient to designate this function in the form of $\langle q | \alpha \rangle$, because it contains both the state index α and the representation index q . The latter indicates the variables which the psi-function depends on.

If we take the vectors $|x\rangle$ corresponding to the eigenfunctions of the coordinate x as the basis, the function (13.10) will be a psi-function in the coordinate representation, i.e. the function $\psi_\alpha(x)$. Consequently, in Dirac notation, the psi-function of the state α is written as

$$\psi_\alpha(x) = \langle x | \alpha \rangle \quad (13.11)$$

If the energy spectrum is discrete, by (13.9) $\psi_\alpha(x)$ in the energy representation will be determined by the set of coefficients

$$c(E_m) = \langle E_m | \alpha \rangle \quad (13.12)$$

Let us write the eigenfunctions ψ_{E_m} in Dirac notation in the coordinate representation. In accordance with (13.11)

$$\psi_{E_m}(x) = \langle x | E_m \rangle \quad (13.13)$$

¹ We have designated the coefficients of the expansion by the symbol $c(q_m)$ instead of $c_m^{(q)}$ for formula (13.10) to be obtained from (13.9) by simply discarding the subscript m .

In the given case, the state is characterized by the energy having the value E_m . Consequently, this value must be taken as the state index α .

Examination of (13.3) shows that $\psi_{E_n}^*(x) = \langle E_n | x \rangle$. Therefore, the property of orthonormalization of the functions ψ_{E_k} is written as

$$\int_{-\infty}^{+\infty} \langle E_n | x \rangle \langle x | E_m \rangle dx = \delta_{nm} \quad (13.14)$$

(we are considering a one-dimensional case for simplicity, which is why we have substituted dx for dV).

The psi-function of the state α in the p_x -representation has the form

$$c(p_x) = \langle p_x | \alpha \rangle$$

A comparison of the formulas obtained with (7.11) and (12.7) leads to the conclusion that the product of two state vectors coincides with the scalar product of the relevant psi-functions, for example

$$\langle E_m | \alpha \rangle = \langle \Psi_{E_m} | \psi_\alpha \rangle, \quad \langle p_x | \alpha \rangle = \langle \Psi_{p_x} | \psi_\alpha \rangle \quad (13.15)$$

Let us write a matrix element of the operator \hat{Q} in the r -representation. If the ket vector $|r_n\rangle$ is correlated with the function $\psi_n^{(r)}$, the state vector $\hat{Q}|r_n\rangle$ must be correlated with the function $\hat{Q}\psi_n^{(r)}$. Finally, the scalar product of the state vectors $|r_m\rangle$ and $\hat{Q}|r_n\rangle$ will correspond to the scalar product of the functions $\psi_m^{(r)}$ and $\hat{Q}\psi_n^{(r)}$. Therefore, the quantity (9.9) will be written in Dirac notation as follows:

$$Q_{mn} = \langle r_m | \hat{Q} | r_n \rangle \quad (13.16)$$

For a Hermitian operator, this expression can be interpreted either as the product of the bra vector $\langle r_m |$ and the ket vector $\hat{Q}|r_n\rangle$, or as the product of the bra vector $\langle r_m | \hat{Q}$ and the ket vector $|r_n\rangle$ [see (43.5)].

When there is no need to indicate the representation being used, expression (13.16) can be written in a simpler form:

$$Q_{mn} = \langle m | \hat{Q} | n \rangle. \quad (13.17)$$

Finally, let us find the Dirac form of writing relation (9.8). Recall that this relation expresses the operator equation $f = \hat{Q}\varphi$ [see (9.1)] in the matrix form. Let us correlate the vector $|\alpha\rangle$ with the function φ and the vector $|\beta\rangle$ with the function f . Now the coefficients determined by formulas (9.5) can be written as

$$a_n = \langle r_n | \alpha \rangle, \quad b_m = \langle r_m | \beta \rangle$$

Using these expressions, and also expression (13.16) in formula (9.8), we obtain

$$\langle r_m | \beta \rangle = \sum_n \langle r_m | \hat{Q} | r_n \rangle \langle r_n | \alpha \rangle \quad (13.18)$$

This is exactly formula (9.8) in Dirac notation. It can be written in a simpler form:

$$\langle m | \beta \rangle = \sum_n \langle m | \hat{Q} | n \rangle \langle n | \alpha \rangle \quad (13.19)$$

Formulas (13.18) and (13.19) determine the transformation of the vector $|\alpha\rangle$ into the vector $|\beta\rangle$ under the action of the operator \hat{Q} .

14. Transformation of Functions and Operators from One Representation to Another

Let us find the general rules for transforming psi-functions and operators from one representation to another. These transformations are performed with the aid of what is called the **unitary matrix** S or the **unitary operator** \hat{S} , and in this connection they are said to be **unitary transformations**.

Let us take the psi-function $\psi_\alpha(x)$ of a state (x stands for the set of coordinates x, y, z , and α is the state index). We shall consider two different representations of this function, which we shall call the a -representation and b -representation. We shall first consider for simplicity's sake that the operators \hat{A} and \hat{B} corresponding to these representations have discrete spectra of the eigenvalues a_n and b_n .

In the a -representation, the function $\psi_\alpha(x)$ is determined by the set of coefficients

$$c_m^{(a)} = \langle \psi_m^{(a)}(x) | \psi_\alpha(x) \rangle = \int [\psi_m^{(a)}(x)]^* \psi_\alpha(x) dV \quad (14.1)$$

[see (7.11)], where $\psi_m^{(a)}$ are the eigenfunctions of the operator \hat{A} . The numbers $c_m^{(a)}$ are the coefficients of the expansion of $\psi_\alpha(x)$ in the functions $\psi_m^{(a)}(x)$:

$$\psi_\alpha(x) = \sum_m c_m^{(a)} \psi_m^{(a)}(x) \quad (14.2)$$

Similarly, $\psi_\alpha(x)$ in the b -representation is determined by the set of coefficients

$$c_n^{(b)} = \langle \psi_n^{(b)}(x) | \psi_\alpha(x) \rangle \quad (14.3)$$

where $\psi_n^{(b)}(x)$ are the eigenfunctions of the operator \hat{B} . The numbers $c_n^{(b)}$ are the coefficients of the expansion

$$\psi_a(x) = \sum_n c_n^{(b)} \psi_n^{(b)}(x) \quad (14.4)$$

We must note that the functions $\psi_a(x)$, $\psi_m^{(a)}$ and $\psi_n^{(b)}$ in formulas (14.1)-(14.4) are psi-functions in a coordinate representation. If matters were different, these functions could not be integrated over V ($dV = dx dy dz$).

Our task is to establish the rule with whose aid the set of coefficients $c_m^{(a)}$ transforms into the set of coefficients $c_n^{(b)}$. The transformation of the components v_m of the vector v along the axes of the basis formed by the unit vectors e_m into the components v'_n of the same vector along the axes of the basis formed by the unit vectors e'_n is a similar problem. This transformation is known to have the form

$$v'_n = \sum_m \alpha_{nm} v_m \quad (14.5)$$

where $\alpha_{nm} = e'_n e_m$ [see Vol. 1, formulas (VI.36) and (VI.37)]. The vector v in the basis representations e_m and e'_n is determined by the expressions

$$v = \sum_m v_m e_m \quad \text{and} \quad v = \sum_n v'_n e'_n \quad (14.6)$$

A comparison of expressions (14.2) and (14.4) with (14.6) leads us to the conclusion that the systems of eigenfunctions $\psi_m^{(a)}$ and $\psi_n^{(b)}$ can be treated as different bases used for the representation of the function $\psi_a(x)$, and the sets of the coefficients $c_m^{(a)}$ and $c_n^{(b)}$ as the components of this function along the axes of the relevant basis.

To establish the rule for transition from the coefficients $c_m^{(a)}$ to the coefficients $c_n^{(b)}$, we expand each of the functions $\psi_m^{(a)}$ into a series in the functions $\psi_n^{(b)}$:

$$\psi_m^{(a)} = \sum_n S_{nm} \psi_n^{(b)} \quad (14.7)$$

In accordance with the general rule expressed by formula (7.11), the coefficients of the expansion designated by the symbol S_{nm} are determined as follows:

$$S_{nm} = \langle \psi_n^{(b)} | \psi_m^{(a)} \rangle \quad (14.8)$$

[now we can see the expediency of the sequence of the subscripts on S that we adopted in formula (14.7)].

Let us introduce expression (14.7) for $\psi_m^{(a)}(x)$ into formula (14.2):

$$\psi_a(x) = \sum_m c_m^{(a)} \sum_n S_{nm} \psi_n^{(b)}(x) = \sum_n \psi_n^{(b)}(x) \sum_m S_{nm} c_m^{(a)}$$

A comparison of the expression obtained with formula (14.4) allows us to conclude that

$$c_n^{(b)} = \sum_m S_{nm} c_m^{(a)} \quad (14.9)$$

In Dirac notation, this formula is written as follows:

$$\langle b_n | \alpha \rangle = \sum_m \langle b_n | a_m \rangle \langle a_m | \alpha \rangle \quad (14.10)$$

[see (13.15)].

Formula (14.9) gives the required rule for a transition from the a -representation to the b -representation. The coefficients of the transition determined by expression (14.8) form the matrix S with an infinitely great number of rows and columns:

$$S = \begin{pmatrix} \langle \psi_1^{(b)} | \psi_1^{(a)} \rangle & \langle \psi_1^{(b)} | \psi_2^{(a)} \rangle & \dots \\ \langle \psi_2^{(b)} | \psi_1^{(a)} \rangle & \langle \psi_2^{(b)} | \psi_2^{(a)} \rangle & \dots \\ \dots & \dots & \dots \end{pmatrix} \quad (14.11)$$

We must note that formula (14.9) is similar to formula (14.5), the matrix elements S_{nm} playing the role of the coefficients α_{nm} in the transformation. In this connection, a transformation carried out by the matrix S is said to correspond to "rotation" in Hilbert space.

The transformation (14.9) can be written symbolically as

$$c^{(b)} = Sc^{(a)} \quad (14.12)$$

where $c^{(b)}$ is a column matrix with the elements $c_n^{(b)}$, and $c^{(a)}$ is a similar matrix with the elements $c_m^{(a)}$.

It is obvious that the inverse transformation (i.e. the transformation from the b -representation to the a -representation) is determined by the formula

$$c^{(a)} = S'c^{(b)} \quad (14.13)$$

where S' is a matrix with the elements

$$S'_{nm} = \langle \psi_n^{(a)} | \psi_m^{(b)} \rangle \quad (14.14)$$

[compare with (14.8)]. Introducing (14.12) into (14.13), and then (14.13) into (14.12), we obtain two relations:

$$c^{(a)} = S'Sc^{(a)}, \quad c^{(b)} = SS'c^{(b)}$$

from which it follows that the product of the matrices S and S' , regardless of the order of the multipliers, must equal the unit (identi-

ty) matrix I [the elements of such a matrix equal δ_{mn} ; see Vol. 1, formula (VII.24)]:

$$S'S = I, \quad SS' = I$$

The matrices S and S' satisfying these relations are said to be the inverse of each other [see Vol. 1, formula (VII.38)]. The inverse matrix of S is customarily designated by the symbol S^{-1} . Hence, the matrix S' is the matrix S^{-1} . By (14.14), we have

$$S_{nm}^{-1} = \langle \psi_n^{(a)} | \psi_m^{(b)} \rangle = \langle \psi_m^{(b)} | \psi_n^{(a)} \rangle^*$$

A comparison with (14.8) shows that

$$S_{nm}^{-1} = S_{mn}^* = S_{nm}^+$$

We have thus established that the matrix S transforming a psi-function from one representation to another has the property

$$S^+ = S^{-1} \quad (14.15)$$

Since $S^+ \neq S$, the matrix S is not self-conjugate. Matrices satisfying the condition (14.15) are called **unitary**. This condition can be transformed by multiplying both sides of the equation by the matrix S . Hence, taking into account that $S^{-1}S = I$, we obtain

$$S^+S = I \quad (14.16)$$

The operator \hat{S} satisfying the condition

$$\hat{S}^+\hat{S} = 1 \quad (14.17)$$

is also called **unitary**.

With a view to everything said above, the formula for the expansion of the function $\psi_m^{(b)}(x)$ in the functions $\psi_n^{(a)}(x)$ can be written as

$$\psi_m^{(b)}(x) = \sum_n S_{nm}^{-1} \psi_n^{(a)}(x) = \sum_n S_{nm}^+ \psi_n^{(a)}(x) \quad (14.18)$$

[compare with (14.7)].

Now let us go over to establishing the rule for the transformation of operators from one representation to another. We take any operator \hat{Q} . In the a -representation, it is depicted by the matrix

$$Q_{mn}^{(a)} = \langle \psi_m^{(a)} | \hat{Q} \psi_n^{(a)} \rangle \quad (14.19)$$

and in the b -representation by the matrix

$$Q_{mn}^{(b)} = \langle \psi_m^{(b)} | \hat{Q} \psi_n^{(b)} \rangle \quad (14.20)$$

Let us write the expansion of the functions $\psi_m^{(b)}$ and $\psi_n^{(b)}$ in the functions $\psi_k^{(a)}$ and $\psi_l^{(a)}$. In accordance with (14.18)

$$\psi_m^{(b)} = \sum_k S_{km}^+ \psi_k^{(a)}, \quad \psi_n^{(b)} = \sum_l S_{ln}^+ \psi_l^{(a)}$$

Substitution of these expressions into formula (14.20) yields

$$\begin{aligned} Q_{mn}^{(b)} &= \left\langle \sum_k S_{km}^+ \psi_k^{(a)} \right| \hat{Q} \left| \sum_l S_{ln}^+ \psi_l^{(a)} \right\rangle \\ &= \sum_{k,l} (S_{km}^+)^* S_{ln}^+ \langle \psi_k^{(a)} | \hat{Q} \psi_l^{(a)} \rangle = \sum_{k,l} S_{mk} Q_{kl}^{(a)} S_{ln}^+ \end{aligned}$$

First we used the property (7.9), next the rule (9.21), and, finally, we took into account expression (14.19). We write the result obtained as

$$Q_{mn}^{(b)} = \sum_k S_{mk} \sum_l Q_{kl}^{(a)} S_{ln}^+ \quad (14.21)$$

The sum over l is the k, n -th matrix element of the product of the matrices $Q_{kl}^{(a)}$ and S_{ln}^+ . Let us designate it by the symbol $[Q^{(a)} S^+]_{kn}$. Hence

$$Q_{mn}^{(b)} = \sum_k S_{mk} [Q^{(a)} S^+]_{kn}$$

This expression is the m, n -th element of the product of the matrices S and $[Q^{(a)} S^+]$. Therefore, designating the matrix with the elements $Q_{mn}^{(b)}$ by the symbol $Q^{(b)}$, we can write that

$$Q^{(b)} = S Q^{(a)} S^+ \quad (14.22)$$

Formula (14.22) defines the required rule for the transition from the expression of the operator \hat{Q} in the a -representation to the expression of the same operator in the b -representation. The transition is performed with the aid of the matrix S [see (14.11)] and its conjugate matrix S^+ . The inverse transformation has the form

$$Q^{(a)} = S^+ Q^{(b)} S \quad (14.23)$$

This formula can be obtained by premultiplying relation (14.22) by S^+ , postmultiplying it by S , and taking into account that $S^+ S = S^{-1} S = I^1$. It is a simple matter to see with the aid of the rule (9.12) that for any matrix A the relations $IA = AI = A$ hold.

Hence, an operator is transformed from one representation to another with the aid of the **unitary transformation** (14.22). We know that when a matrix of an operator of a physical quantity is diagonal, the diagonal elements equal the eigenvalues of the given quantity. It thus follows that the task of determining the eigenvalues of any operator \hat{Q} consists in finding the unitary transformation S that gives the matrix Q a diagonal form. This is done in practice as was shown at the end of Sec. 9.

¹ The product of matrices is associative. This signifies that $ABC = A(BC) = (AB)C$.

For each matrix relation, there is a similar operator relation. Consequently, by introducing the unitary operator \hat{S} corresponding to the matrix S , we can write formula (14.9) in the form

$$\psi^{(b)} = \hat{S} \psi^{(a)} \quad (14.24)$$

where $\psi^{(a)}$ is a function in the a -representation, and $\psi^{(b)}$ is the same function in the b -representation.

Formula (14.22) can be written in the operator form as follows:

$$\hat{Q}^{(b)} = \hat{S} \hat{Q}^{(a)} \hat{S}^+ \quad (14.25)$$

where $\hat{Q}^{(a)}$ is the operator of the quantity Q in the a -representation, and $\hat{Q}^{(b)}$ is the operator of the same quantity in the b -representation. We stress that the operators $\hat{Q}^{(a)}$ and $\hat{Q}^{(b)}$ depict the same physical quantity Q . The same quantity will be depicted by an operator in any representation other than the a - and b -representations, a transition to which is achieved by means of a unitary transformation. Consequently, not one, but a multitude of operators between which there are relations of the form of (14.25) correspond to every physical quantity. It is clear that the properties of a physical quantity (its realness, spectrum of possible values, and so on) cannot depend on the choice of the representation, i.e. should not change in the unitary transformation (14.25).

Let us find the Hermitian conjugate operator of the operator (14.25). Having in mind that an operator which is the Hermitian conjugate of a product of operators equals the product of the Hermitian conjugate factors taken in the opposite sequence [see (10.11)]¹, we can write that

$$(\hat{Q}^{(b)})^+ = (\hat{S} \hat{Q}^{(a)} \hat{S}^+)^+ = \hat{S} (\hat{Q}^{(a)})^+ \hat{S}^+ = \hat{S} \hat{Q}^{(a)} \hat{S}^+ = \hat{Q}^{(b)}$$

Thus, if the operator $\hat{Q}^{(a)}$ is self-adjoint, i.e. $\hat{Q}^{(a)} = (\hat{Q}^{(a)})^+$, the operator $\hat{Q}^{(b)}$ will also be self-adjoint. Recall that the eigenvalues of self-adjoint operators are real.

We shall show that the spectrum of the eigenvalues of the operator does not change in unitary transformations. We act on both sides of the equation

$$\hat{Q}^{(a)} \psi_n^{(a)} = q_n \psi_n^{(a)} \quad (14.26)$$

¹ Since the product includes both \hat{Q}^+ and \hat{Q} , now we are not adhering to the rule according to which a conjugate operator is placed at the right of the function which it acts on.

with the operator \hat{S} . In addition, we substitute for the function $\psi_n^{(a)}$ on the left-hand side the function $\hat{S}^+ \hat{S} \psi_n^{(a)}$ equal to it [see (14.17)]. The resulting equation

$$\hat{S} \hat{Q}^{(a)} \hat{S}^+ \hat{S} \psi_n^{(a)} = q_n \hat{S} \psi_n^{(a)}$$

with account taken of (14.24) and (14.25), can be written as

$$\hat{Q}^{(b)} \psi_n^{(b)} = q_n \psi_n^{(b)} \quad (14.27)$$

Equations (14.26) and (14.27) contain the same factor q_n from which it follows that the operators $\hat{Q}^{(a)}$ and $\hat{Q}^{(b)}$ have identical eigenvalues.

Finally, we shall prove that a unitary transformation leaves the trace of the matrix Q , i.e. the sum of its diagonal elements, unchanged. Let us introduce the value of $Q_{mm}^{(b)}$ obtained by formula (14.21) into the expression for the trace of the matrix $Q^{(b)}$:

$$\text{Tr } Q^{(b)} = \sum_m Q_{mm}^{(b)} = \sum_m \sum_{k,l} S_{mk} Q_{kl}^{(a)} S_{lm}^+ = \sum_{k,l} Q_{kl}^{(a)} \sum_m S_{lm}^+ S_{mk}$$

The sum over m is the l, k -th element of the product of the matrices S^+ and S . Since $S^+ S = I$ [see (14.16)], this matrix element equals δ_{lk} . Consequently,

$$\text{Tr } Q^{(b)} = \sum_{k,l} Q_{kl}^{(a)} \delta_{lk} = \sum_l Q_{ll}^{(a)} = \text{Tr } Q^{(a)} \quad (14.28)$$

Q.E.D.

In concluding, let us see how the transition from one representation to another is performed if the spectra of the operators \hat{A} and \hat{B} are continuous. Now instead of formulas (14.2) and (14.1), we have

$$\psi_a(x) = \int c(a) \psi_a(x) da \quad (14.29)$$

$$c(a) = \langle \psi_a | \psi_a \rangle = \int \psi_a^*(x) \psi_a(x) dx \quad (14.30)$$

[see (12.1) and (12.7)]. The function $c(a)$ determines ψ_a in the a -representation. Formulas (14.4) and (14.3) become

$$\psi_a(x) = \int c(b) \psi_b(x) db \quad (14.31)$$

$$c(b) = \langle \psi_b | \psi_a \rangle = \int \psi_b^*(x) \psi_a(x) dx \quad (14.32)$$

Expanding the function $\psi_a(x)$ in the function $\psi_b(x)$, we get the expression

$$\psi_a(x) = \int S(b, a) \psi_b(x) db \quad (14.33)$$

where

$$S(b, a) = \langle \psi_b | \psi_a \rangle = \int \psi_b^*(x) \psi_a(x) dx \quad (14.34)$$

Let us introduce expression (14.33) into formula (14.29). As a result, we arrive at the relation

$$\psi_a(x) = \int c(a) da \int S(b, a) \psi_b(x) db = \int \psi_b(x) db \int S(b, a) c(a) da$$

Comparing it with expression (14.31), we arrive at the conclusion that

$$c(b) = \int S(b, a) c(a) da \quad (14.35)$$

[compare with (14.9)]. This formula gives the rule for the transition from the a -representation to the b -representation for a continuous spectrum. In Dirac notation, it has the form

$$\langle b | \alpha \rangle = \int \langle b | a \rangle \langle a | \alpha \rangle da$$

Assume that the operator \hat{A} has a discrete spectrum, and the operator \hat{B} , a continuous one. Now the following formula is used for the transition from the a -representation to the b -representation:

$$c(b) = \sum_m S(b, a_m) c_m^{(a)} \quad (14.36)$$

where

$$S(b, a_m) = \langle \psi_b | \psi_m^{(a)} \rangle = \int \psi_b^*(x) \psi_m^{(a)}(x) dx \quad (14.37)$$

Finally, assume that the operator \hat{A} has a continuous spectrum, and the operator \hat{B} , a discrete one. Now the formula for the transition from the a -representation to the b -representation is

$$c_n^{(b)} = \int S(b_n, a) c(a) da \quad (14.38)$$

where

$$S(b_n, a) = \langle \psi_n^{(b)} | \psi_a \rangle = \int [\psi_n^{(b)}(x)]^* \psi_a(x) dx \quad (14.39)$$

Chapter III

EIGENVALUES AND EIGENFUNCTIONS OF PHYSICAL QUANTITIES

15. Operators of Physical Quantities

Upon comparing formulas (4.3) and (4.4) with expression (7.14), we arrive at the conclusion that the operator of any of the coordinates is multiplication by the given coordinate:

$$\hat{x} = x, \quad \hat{y} = y, \quad \hat{z} = z \quad (15.1)$$

Similarly, an operator that is to be correlated with any function of the coordinates, for instance with the potential energy $U(x, y, z)$ also consists in multiplication by this function:

$$\hat{U}\psi = U\psi \quad \hat{U} = U \quad (15.2)$$

On the basis of Eq. (7.3), we can establish the form of the operator of another physical quantity. Indeed, designating the operator of the total energy by the symbol \hat{H}^1 , we can write the equation

$$\hat{H}\psi = E\psi \quad (15.3)$$

Comparing this equation with (5.7), we find that

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + U \quad (15.4)$$

This operator is called the **Hamiltonian**.

We have just established that U is the potential energy operator \hat{U} . The operator \hat{H} is the operator of the total energy. By analogy with the classical expression $H = T + U$, we can conclude that the operator of the kinetic energy must have the form

$$\hat{T} = -\frac{\hbar^2}{2m} \nabla^2 \quad (15.5)$$

Comparing this expression with the classical relation between the kinetic energy T and the momentum p of a particle

$$T = \frac{p^2}{2m}$$

¹ In quantum mechanics, the energy is always expressed in terms of the momentum, and not of the velocity. In analytical mechanics, the energy expressed in terms of the momenta is called the **Hamiltonian function** or the **Hamiltonian** and is designated by H (see Vol. 1, Sec. 30).

we can assume that the momentum operator \hat{p} must be proportional to $\hbar\nabla$ (∇ is the Hamiltonian operator). The minus sign in expression (15.5) for the kinetic energy operator can be obtained by introducing into \hat{p} the imaginary number $i = \sqrt{-1}$ taken with either a plus or a minus sign. Using a limiting process to go over to classical mechanics, we can show that the factor i must be taken with the minus sign. Consequently,

$$\hat{p} = -i\hbar\nabla \quad (15.6)$$

Accordingly, the operators of the momentum components will be

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \quad \hat{p}_y = -i\hbar \frac{\partial}{\partial y}, \quad \hat{p}_z = -i\hbar \frac{\partial}{\partial z} \quad (15.7)$$

We have always followed the rule adopted in quantum mechanics, namely, *the relations between operators must be similar to the relations between the relevant physical quantities observed in classical physics*. This rule is a corollary of the correspondence principle mentioned in Sec. 2.

Knowing the form of the operators \hat{p} and \hat{r} [by formulas (15.1), we have $\hat{r} = \mathbf{r}$], we can write an expression for the operator \hat{M} of the angular momentum. In classical mechanics, $M = [\mathbf{r}\mathbf{p}]$. Therefore,

$$\hat{M} = [\hat{r}\hat{p}] = [\mathbf{r}, -i\hbar\nabla] = -i\hbar [\mathbf{r}\nabla] \quad (15.8)$$

We write the vector product in the form of the determinant

$$\hat{M} = -i\hbar \begin{vmatrix} \mathbf{e}_x & \mathbf{e}_y & \mathbf{e}_z \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}$$

whence we can obtain expressions for the operators of the angular momentum components:

$$\begin{aligned} \hat{M}_x &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), & \hat{M}_y &= -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \\ \hat{M}_z &= -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \end{aligned} \quad (15.9)$$

The operator of the square of the angular momentum is determined in terms of the operators for the components:

$$\hat{M}^2 = \hat{M}_x^2 + \hat{M}_y^2 + \hat{M}_z^2 \quad (15.10)$$

It is generally more convenient to use expressions for the operators of the square and components of the angular momentum in spherical

coordinates. According to the formulas derived in Appendix I, we have

$$\hat{M}_z = -i\hbar \frac{\partial}{\partial\varphi} \quad (15.11)$$

$$\hat{M}^2 = -\hbar^2 \left[\frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta} \left(\sin\vartheta \frac{\partial}{\partial\vartheta} \right) + \frac{1}{\sin^2\vartheta} \frac{\partial^2}{\partial\varphi^2} \right] \quad (15.12)$$

The expression in brackets in formula (15.12) is the angular part of the Laplacian operator (or Laplacian) taken in spherical coordinates [see Vol. 1, formula (XI.88)]. Designating this expression by the symbol $\Delta_{\vartheta, \varphi}$, we can write

$$\hat{M}^2 = -\hbar^2 \Delta_{\vartheta, \varphi} \quad (15.13)$$

We must note that the coordinate r is not contained in any of the formulas (15.11)-(15.13).

The angular momentum operator is closely related to the operator of an infinitely small rotation through the angle $\delta\varphi$. Such a rotation can be interpreted in two ways. First, we can consider that the coordinate system remains stationary, while the system of particles being considered rotates about the origin of coordinates; second, we can consider that the system of particles remains stationary, while the system of coordinates rotates (the system K transforms into the system K'). In both cases, the coordinates of the particles change, i.e. the transformation $\mathbf{r} \rightarrow \mathbf{r}'$ is carried out: it is evident that to obtain an identical change of the coordinates, rotation in both cases must be performed in opposite directions.

A change in the coordinates in rotation of the coordinate axes must be considered as the result of action of the coordinate transformation operator \hat{g} :

$$\mathbf{r}' = \hat{g}\mathbf{r} \quad (15.14)$$

The inverse transformation has the form

$$\mathbf{r} = \hat{g}^{-1}\mathbf{r}' \quad (15.15)$$

The change in the coordinates upon rotation of the system of particles can be interpreted as the action of the operator \hat{G} :

$$\mathbf{r}' = \hat{G}\mathbf{r} \quad (15.16)$$

It is evident that

$$\hat{G} = \hat{g}^{-1} \quad (15.17)$$

(The consecutive use of the operators \hat{g} and \hat{G} leaves the coordinates of the particles unchanged: $\hat{G}\hat{g} = 1$.)

Let us consider the change in the psi-function due to the transformations of the coordinates (15.14) and (15.16).

In rotation of the system of particles (we shall consider for simplicity that the system consists of a single particle) through the infinitely small angle $\delta\varphi$, the position vector of the particle receives the increment $\delta\mathbf{r} = [\delta\varphi, \mathbf{r}]$ [see Vol. 1, formula (VI.46)], consequently,

$$\mathbf{r}' = \hat{G}\mathbf{r} = \mathbf{r} + \delta\mathbf{r} = \mathbf{r} + [\delta\varphi, \mathbf{r}] \quad (15.18)$$

The relevant change in the psi-function can be treated as the action of the rotation operator \hat{R}_G :

$$\psi(\mathbf{r}') = \hat{R}_G\psi(\mathbf{r}) \quad (15.19)$$

(the subscript G indicates that the change in the coordinates is due to rotation of the system of particles). With a view to (15.18), we can write

$$\psi(\mathbf{r}') = \psi(\mathbf{r} + \delta\mathbf{r}) = \psi(\mathbf{r}) + \nabla\psi(\mathbf{r}) \delta\mathbf{r} = \psi(\mathbf{r}) + \{[\delta\varphi, \mathbf{r}] \nabla\} \psi(\mathbf{r})$$

Performing a cyclic transposition in the scalar triple product of the vectors in braces, we obtain

$$\begin{aligned} \psi(\mathbf{r}') &= \psi(\mathbf{r}) + \delta\varphi [\mathbf{r} \nabla] \psi(\mathbf{r}) \\ &= (1 + \delta\varphi [\mathbf{r} \nabla]) \psi(\mathbf{r}) = \{1 + (i/\hbar) \delta\varphi \hat{\mathbf{M}}\} \psi(\mathbf{r}) \end{aligned}$$

[see (15.8)]. A comparison with (15.19) yields

$$\hat{R}_G = 1 + \frac{i}{\hbar} \delta\varphi \hat{\mathbf{M}} \quad (15.20)$$

Now let us find \hat{R}_g —the operator of the transformation of the psi-function in rotation of the coordinate system through the angle $\delta\varphi$. Since rotation of the coordinate system does not change the state of the system, the new function of the new coordinates must have the same value at a given point of space as the old function of the old coordinates, i.e.

$$\psi'(\mathbf{r}') = \psi(\mathbf{r}) \quad (15.21)$$

The rotation operator transforming the psi-function in rotation of the coordinate system is determined by the equation

$$\psi'(\mathbf{r}') = \hat{R}_g\psi(\mathbf{r}')$$

(the designation of the argument of the function is indifferent, we can substitute \mathbf{r} for \mathbf{r}' on both sides of the equation). Hence, taking account of (15.21), we obtain

$$\psi(\mathbf{r}) = \hat{R}_g\psi(\mathbf{r}') \quad (15.22)$$

With a view to (15.15), let us alter this relation as follows:

$$\psi(\mathbf{r}') = \hat{R}_g^{-1}\psi(\mathbf{r})$$

A comparison with (15.19) shows that $\hat{R}_{g^{-1}} = \hat{R}_G$, which agrees with (15.17).

We can use relation (15.20) to give a more general definition of the angular momentum operator than (15.8). This more general definition is not associated with the notion of "orbital" motion and can therefore be extended to more involved cases, for example to the spin angular momentum.

There are a few physical quantities for which operators cannot be obtained by using analogy with the classical formulas. These include quantities such as spin having no classical analogue. The operators of these quantities will be discussed on a later page.

16. Rules for Commutation of Operators of Physical Quantities

The operators of any two coordinates obviously commute ($xy - yx = 0$, etc.). Consequently, all three coordinates of a particle can simultaneously have definite values. The same also holds for the components of the momentum ($\partial/\partial x \cdot \partial/\partial y - \partial/\partial y \cdot \partial/\partial x = 0$).

Let us find the commutator of the operators $\hat{x} = x$ and $\hat{p}_x = -i\hbar\partial/\partial x$. For this end, let us consider the action of a commutator on a function ψ :

$$[\hat{x}, \hat{p}_x]\psi = x \left(-i\hbar \frac{\partial \psi}{\partial x} \right) - (-i\hbar) \frac{\partial}{\partial x} (x\psi) = i\hbar\psi$$

It follows from this relation that

$$[\hat{x}, \hat{p}_x] = i\hbar \quad (16.1)$$

By (11.7), the operator \hat{K} in this case equals \hbar , so that $\langle k \rangle = \hbar$, and relation (11.9) can be written as follows:

$$\sqrt{\langle (\Delta x)^2 \rangle} \sqrt{\langle (\Delta p_x)^2 \rangle} \geq \frac{\hbar}{2} \quad (16.2)$$

We have arrived at the Heisenberg uncertainty relation that is usually written in the form of (2.4). Now we know that Δx and Δp_x in relation (2.1) signify the standard deviations of the quantities from their mean values.

Since $x \cdot \partial\psi/\partial y = \partial(x\psi)/\partial y$, the operators \hat{x} and \hat{p}_y commute. Consequently, states of the particle in which x and p_y have definite values are possible. The same also holds for x and p_z , y and p_x , etc.

Using the notation

$$x = x_1, \quad y = x_2, \quad z = x_3, \quad p_x = p_1, \quad p_y = p_2, \quad p_z = p_3$$

the entire set of commuting relations between the operators of the coordinates and the momentum components can be written as a single expression:

$$[\hat{x}_k, \hat{p}_m] = i\hbar\delta_{km} \quad (16.3)$$

The coordinate x and the momentum component p_x are a particular case of the canonically conjugate quantities q and p (see Vol. 1, Sec. 30). The uncertainty relation

$$\Delta q \cdot \Delta p \geq \frac{\hbar}{2} \quad (16.4)$$

holds for any pair of canonically conjugate quantities q and p provided that the operators of these quantities have been determined on the same set of functions. For example, for the canonically conjugate variables φ and M_z (φ is the azimuth angle), the relation $\Delta\varphi \cdot \Delta M_z \geq \hbar/2$ holds only provided that $\langle(\Delta\varphi)^2\rangle \ll \pi^2$. This is due to the fact that the operator \hat{M}_z is self-adjoint only on the set of functions $\psi(\varphi)$ that are periodic with the period 2π . The variable φ , on the other hand, is not an operator on this set of functions because the function $\varphi\psi(\varphi)$ does not belong to this set.

The energy and time belong to canonically conjugate quantities. Consequently, the following relation holds:

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2} \quad (16.5)$$

This relation signifies that the determination of the energy within ΔE must take a time interval equal at least to $\Delta t \sim \hbar/\Delta E$. Since the process of measuring the energy of a state of a system can occur within the interval Δt not exceeding the lifetime τ of the state, the energy of the state has the indeterminacy $\Delta E \sim \hbar/\tau$. This quantity is known as the energy level breadth and is designated by the letter Γ . Hence,

$$\Gamma \sim \frac{\hbar}{\tau} \quad (16.6)$$

Let us find the commutation rules for the angular momentum operators with the operators of the coordinates and momenta. Taking formula (15.9) into account, we obtain

$$[\hat{M}_x, \hat{x}] \psi = -i\hbar \left\{ \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) (x\psi) - x \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \psi \right\} = 0$$

It thus follows that $[\hat{M}_x, \hat{x}] = 0$. A similar result is obtained for other operators of the angular momentum and coordinates. Hence,

$$[\hat{M}_x, \hat{x}] = 0, [\hat{M}_y, \hat{y}] = 0, [\hat{M}_z, \hat{z}] = 0 \quad (16.7)$$

Now let us act on ψ with the commutator $[\hat{M}_x, \hat{y}]$:

$$\begin{aligned} [\hat{M}_x, \hat{y}] \psi &= -i\hbar \left\{ \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) (y\psi) - y \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \psi \right\} \\ &= -i\hbar \left\{ y^2 \frac{\partial\psi}{\partial z} - zy \frac{\partial\psi}{\partial y} - z\psi - y^2 \frac{\partial\psi}{\partial z} + yz \frac{\partial\psi}{\partial y} \right\} = i\hbar z\psi. \end{aligned}$$

Consequently, $[\hat{M}_x, \hat{y}] = i\hbar z$. Performing a cyclic transposition we obtain

$$[\hat{M}_x, \hat{y}] = i\hbar z, \quad [\hat{M}_y, \hat{z}] = i\hbar x, \quad [\hat{M}_z, \hat{x}] = i\hbar y \quad (16.8)$$

We must note that formulas (16.7) and (16.8) can be written as the single relation

$$[\hat{M}_k, \hat{x}_l] = i\hbar \varepsilon_{klm} x_m \quad (16.9)$$

where $x_1 = x$, $x_2 = y$, $x_3 = z$, $M_1 = M_x$, etc., and ε_{klm} is the Kronecker skew-symmetric symbol [see Vol. 1, expression (VI.15)].

Inspection of the obtained formulas shows that a component of the angular momentum and the corresponding coordinate can have simultaneously definite values. The component M_x and the coordinate y (or z) cannot be determined simultaneously. The same holds for M_y and the coordinate z (or x), and also for M_z and the coordinate x (or y).

Let us act on ψ with the commutator $[\hat{M}_x, \hat{p}_x]$:

$$[\hat{M}_x, \hat{p}_x] \psi = (-i\hbar)^2 \left\{ \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \frac{\partial\psi}{\partial x} - \frac{\partial}{\partial x} \left(y \frac{\partial\psi}{\partial z} - z \frac{\partial\psi}{\partial y} \right) \right\} = 0$$

We have found that $[\hat{M}_x, \hat{p}_x] = 0$. The same result is also obtained for the other two similar commutators. Matters are different for commutators of the form $[\hat{M}_x, \hat{p}_y]$:

$$\begin{aligned} [\hat{M}_x, \hat{p}_y] \psi &= (-i\hbar)^2 \left\{ \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \frac{\partial\psi}{\partial y} - \frac{\partial}{\partial y} \left(y \frac{\partial\psi}{\partial z} - z \frac{\partial\psi}{\partial y} \right) \right\} \\ &= (-i\hbar)^2 \left\{ y \frac{\partial^2\psi}{\partial y \partial z} - z \frac{\partial^2\psi}{\partial y^2} - y \frac{\partial^2\psi}{\partial z \partial y} - \frac{\partial\psi}{\partial z} + z \frac{\partial^2\psi}{\partial y^2} \right\} \\ &= (-i\hbar)^2 \left(-\frac{\partial\psi}{\partial z} \right) = i\hbar \left(-i\hbar \frac{\partial\psi}{\partial z} \right) = i\hbar \hat{p}_z \psi \end{aligned}$$

The results obtained can be represented by the formula

$$[\hat{M}_k, \hat{p}_l] = i\hbar \varepsilon_{klm} \hat{p}_m \quad (16.10)$$

similar to formula (16.9).

It is a simple matter to obtain the commutators of the angular momentum components with the aid of formulas (16.9) and (16.10):

$$[\hat{M}_x, \hat{M}_y] = \hat{M}_x \hat{M}_y - \hat{M}_y \hat{M}_x = \hat{M}_x (\hat{z} \hat{p}_x - \hat{x} \hat{p}_z) - (\hat{z} \hat{p}_x - \hat{x} \hat{p}_z) \hat{M}_x \\ = \hat{M}_x \hat{z} \hat{p}_x - \hat{M}_x \hat{x} \hat{p}_z - \hat{z} \hat{p}_x \hat{M}_x + \hat{x} \hat{p}_z \hat{M}_x$$

Taking advantage of the fact that \hat{M}_x commutes both with \hat{x} and with \hat{p}_x , let us interchange the operators \hat{M}_x and \hat{x} in the second term, and also the operators \hat{p}_x and \hat{M}_x in the third term. The result is

$$[\hat{M}_x, \hat{M}_y] = \hat{M}_x \hat{z} \hat{p}_x - \hat{x} \hat{M}_x \hat{p}_z - \hat{z} \hat{M}_x \hat{p}_x + \hat{x} \hat{p}_z \hat{M}_x \\ = (\hat{M}_x \hat{z} - \hat{z} \hat{M}_x) \hat{p}_x - \hat{x} (\hat{M}_x \hat{p}_z - \hat{p}_z \hat{M}_x) \\ = i\hbar \epsilon_{xyz} \hat{y} \hat{p}_x - \hat{x} i\hbar \epsilon_{xyz} \hat{p}_y = i\hbar (\hat{x} \hat{p}_y - \hat{y} \hat{p}_x) = i\hbar \hat{M}_z$$

[we have used formulas (16.9) and (16.10); $\epsilon_{xyz} = \epsilon_{123} = -1$. Performing a cyclic transposition, we obtain

$$[\hat{M}_x, \hat{M}_y] = i\hbar \hat{M}_z, \quad [\hat{M}_y, \hat{M}_z] = i\hbar \hat{M}_x, \quad [\hat{M}_z, \hat{M}_x] = i\hbar \hat{M}_y \quad (16.11)$$

or

$$[\hat{M}_k, \hat{M}_l] = i\hbar \epsilon_{klm} \hat{M}_m \quad (16.12)$$

Finally, let us calculate the commutator of the operators $\hat{\mathbf{M}}^2$ and \hat{M}_x . With a view to (15.10), we have

$$[\hat{\mathbf{M}}^2, \hat{M}_x] = (\hat{M}_x^2 + \hat{M}_y^2 + \hat{M}_z^2) \hat{M}_x - \hat{M}_x (\hat{M}_x^2 + \hat{M}_y^2 + \hat{M}_z^2) \\ = \hat{M}_x^3 + \hat{M}_y^2 \hat{M}_x + \hat{M}_z^2 \hat{M}_x - \hat{M}_x^3 - \hat{M}_x \hat{M}_y^2 - \hat{M}_x \hat{M}_z^2 \quad (16.13)$$

Taking advantage of the fact that $\hat{M}_x \hat{M}_y - \hat{M}_y \hat{M}_x = i\hbar \hat{M}_z$ [see (16.11)], we transform the second and fifth terms as follows:

$$\hat{M}_y^2 \hat{M}_x - \hat{M}_x \hat{M}_y^2 = \hat{M}_y \hat{M}_y \hat{M}_x - \hat{M}_x \hat{M}_y \hat{M}_y \\ = \hat{M}_y (\hat{M}_x \hat{M}_y - i\hbar \hat{M}_z) - (\hat{M}_y \hat{M}_x + i\hbar \hat{M}_z) \hat{M}_y = -i\hbar (\hat{M}_y \hat{M}_z + \hat{M}_z \hat{M}_y)$$

Using the relation $\hat{M}_z \hat{M}_x - \hat{M}_x \hat{M}_z = i\hbar \hat{M}_y$, we perform a similar transformation of the third and sixth terms:

$$\hat{M}_z^2 \hat{M}_x - \hat{M}_x \hat{M}_z^2 = \hat{M}_z \hat{M}_z \hat{M}_x - \hat{M}_x \hat{M}_z \hat{M}_z \\ = \hat{M}_z (\hat{M}_x \hat{M}_z + i\hbar \hat{M}_y) - (\hat{M}_z \hat{M}_x - i\hbar \hat{M}_y) \hat{M}_z = i\hbar (\hat{M}_z \hat{M}_y + \hat{M}_y \hat{M}_z)$$

Substitution of the expressions we have transformed into formula (16.13) makes the right-hand side equal zero. The same result is obtained for the commutators of the operators \hat{M}^2 with \hat{M}_x and \hat{M}_z . Hence,

$$[\hat{M}^2, \hat{M}_x] = 0, \quad [\hat{M}^2, \hat{M}_y] = 0, \quad [\hat{M}^2, \hat{M}_z] = 0 \quad (16.14)$$

We conclude from formulas (16.11) and (16.14) that only the square of the vector M and one of its projections onto the coordinate axes can be determined simultaneously. The other two projections are indeterminate (except when all three components are zero). Consequently, all that we can know about the vector M is its "length" and the angle it makes with a certain axis. The direction of the vector M , however, does not lend itself to determination.

17. Eigenfunctions of the Coordinate and Momentum Operators

Let us find the eigenfunctions of a coordinate operator. Since $\hat{x} = x$, Eq. (7.3) has the form

$$x\psi_{x'} = x'\psi_x \quad (17.1)$$

where x' is a real number, and $\psi_{x'} = \psi_{x'}(x)$ is the eigenfunction corresponding to the eigenvalue of x equal to x' . Let us write relation (VIII.6) for the argument $x - x'$:

$$(x - x') \delta(x - x') = 0$$

Removing the parentheses, we obtain $x\delta(x - x') - x'\delta(x - x') = 0$, whence

$$x\delta(x - x') = x'\delta(x - x')$$

A comparison with Eq. (17.1) yields

$$\psi_{x'}(x) = \delta(x - x') \quad (17.2)$$

This is exactly the eigenfunction of the operator \hat{x} corresponding to $x = x'$. The spectrum of the operator \hat{x} is obviously continuous.

Let us evaluate the scalar product of the functions $\delta(x - x')$ and $\delta(x - x'')$. Since the function $\delta(x)$ is real, we have

$$\langle \delta(x - x') | \delta(x - x'') \rangle = \int_{-\infty}^{+\infty} \delta(x - x') \delta(x - x'') dx$$

This integral can be reduced to the form (VIII.2) if we assume that $\delta(x - x') = f(x)$ and $x'' = a$. According to (VIII.2), such an integral equals $f(a)$, i.e. $\delta(x'' - x')$. Hence,

$$\langle \delta(x - x') | \delta(x - x'') \rangle = \delta(x'' - x')$$

This signifies that the functions (17.2) are normalized to a delta function [see (12.6)].

Let us expand the function $\psi_\alpha(x)$ (here α is a state index) in the eigenfunctions (17.2) of the operator \hat{x} . By (12.1), we have

$$\psi_\alpha(x) = \int_{-\infty}^{+\infty} c(x') \psi_{x'}(x) dx' = \int_{-\infty}^{+\infty} c(x') \delta(x - x') dx' = c(x) \quad (17.3)$$

The result obtained signifies that the psi-function in the coordinate representation is $\psi_\alpha(x)$ itself. We can arrive at the same conclusion by calculating the function $c(x')$ by formula (12.7). The substitution of x' for q yields

$$c(x') = \langle \psi_x | \psi_\alpha \rangle = \int_{-\infty}^{+\infty} \psi_{x'}^*(x) \psi_\alpha(x) dx$$

The delta function is real, consequently $\psi_{x'}^* = \psi_{x'} = \delta(x - x')$. Hence,

$$c(x') = \int_{-\infty}^{+\infty} \delta(x - x') \psi_\alpha(x) dx = \psi_\alpha(x')$$

Dropping the prime on x , we arrive at the relation $c(x) = \psi_\alpha(x)$.

In a three-dimensional case, $\psi_\alpha = \psi_\alpha(x, y, z) = \psi_\alpha(\mathbf{r})$, and the eigenfunctions of the operator $\hat{\mathbf{r}}$ equal $\psi_{\mathbf{r}'}(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}')$ [this can be established by performing calculations similar to those that led us to formula (17.2)]. Expanding ψ_α into a series in the functions $\psi_{\mathbf{r}'}$, we get a result similar to (17.3):

$$\begin{aligned} \psi_\alpha(x, y, z) &= \psi_\alpha(\mathbf{r}) = \int c(\mathbf{r}') \psi_{\mathbf{r}'} dV \\ &= \int c(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') dV = c(\mathbf{r}) = c(x, y, z) \end{aligned} \quad (17.4)$$

Let us write Eq. (7.3) for the momentum operator $\hat{p}_x = -i\hbar\partial/\partial x$:

$$-i\hbar \frac{\partial \psi}{\partial x} = p_x \psi$$

The following function is a solution of this equation:

$$\psi = C e^{(i/\hbar) p_x x} \quad (17.5)$$

The spectrum of the operator \hat{p}_x is obviously continuous.

Let us attempt to normalize the function (17.5) to unity. For this end, we shall try to evaluate the integral

$$\int_{-\infty}^{+\infty} |Ce^{(i/\hbar)p_x x}|^2 dx = \int_{-\infty}^{+\infty} |C|^2 dx = |C|^2 \int_{-\infty}^{+\infty} dx$$

At any value of $C \neq 0$, the integral will be found to diverge (it becomes equal to infinity). It is therefore impossible to normalize the eigenfunctions of the operator \hat{p}_x to unity. It was already noted in Sec. 12 that the result we have arrived at is general for all eigenfunctions with a continuous spectrum. In this case, normalization to the delta function is performed.

Let us calculate the scalar product of two functions of the form of (17.5):

$$\begin{aligned} \langle \psi_{p'_x} | \psi_{p''_x} \rangle &= \int_{-\infty}^{+\infty} C^* \exp\left(-\frac{i}{\hbar} p'_x x\right) \cdot C \exp\left(\frac{i}{\hbar} p''_x x\right) dx \\ &= C^* C \int_{-\infty}^{+\infty} \exp\left(i \frac{p''_x - p'_x}{\hbar} x\right) dx \end{aligned}$$

Interchanging the roles of k and x in (VIII.12), we obtain the formula

$$\int_{-\infty}^{+\infty} e^{ikx} dx = 2\pi\delta(k) \quad (17.6)$$

According to this formula

$$\int_{-\infty}^{+\infty} \exp\left(i \frac{p''_x - p'_x}{\hbar} x\right) dx = 2\pi\delta\left(\frac{p''_x - p'_x}{\hbar}\right) = 2\pi\hbar\delta(p''_x - p'_x) \quad (17.7)$$

[we have taken advantage of the property (VIII.7)]. Hence,

$$\langle \psi_{p'_x} | \psi_{p''_x} \rangle = C^* C \cdot 2\pi\hbar\delta(p''_x - p'_x)$$

We thus conclude that for the function (17.5) to be normalized to the delta function, we must assume that $|C|$ equals $1/(2\pi\hbar)^{1/2}$. Since the psi-function is determined to within the phase factor e^{ia} , we must consider C to be real and equal to $1/(2\pi\hbar)^{1/2}$.

Therefore, the eigenfunctions of the momentum operator normalized to the delta function equal

$$\psi_{p_x}(x) = (2\pi\hbar)^{-1/2} e^{(i/\hbar)p_x x} \quad (17.8)$$

It is not difficult to see that the eigenfunctions of the operator \hat{p} normalized to the (three-dimensional) delta function have the form

$$\psi_p = (2\pi\hbar)^{-3/2} e^{(i/\hbar) \mathbf{p}\mathbf{r}} \quad (17.9)$$

18. Momentum and Energy Representations

Assume that we have the psi-function $\psi_\alpha(x)$ of a state α in a coordinate representation (in the x -representation). Let us find the expression for the same function in a momentum representation (in the p_x -representation). In this case, we must assume in formulas (14.35) and (14.34) that $a = x$ and $b = p_x$. The result is

$$c(p_x) = \int_{-\infty}^{+\infty} S(p_x, x) c(x) dx \quad (18.1)$$

$$S(p_x, x) = \int_{-\infty}^{+\infty} \psi_{p_x}^*(x') \psi_x(x') dx' \quad (18.2)$$

[we have designated the integration variable by the symbol x' to avoid confusing it with the variable x which $S(p_x, x)$ depends on]. By (17.8), $\psi_{p_x}^*(x') = (2\pi\hbar)^{-1/2} e^{-(i/\hbar)p_x x'}$; the function $\psi_x(x') = \delta(x' - x)$. Consequently,

$$S(p_x, x) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} e^{-(i/\hbar)p_x x'} \delta(x' - x) dx' = (2\pi\hbar)^{-1/2} e^{-(i/\hbar)p_x x}$$

Using this expression in (18.1) and taking into account that by (17.3) we have $c(x) = \psi_\alpha(x)$, we obtain

$$c_\alpha(p_x) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} e^{-(i/\hbar)p_x x} \psi_\alpha(x) dx \quad (18.3)$$

(we have used the subscript α on c to stress the circumstance that this function describes the same state as ψ_α). This result can also be obtained with the aid of formula (12.7), substituting p_x for q in it.

Formula (18.3) is written in a three-dimensional form as follows:

$$c_\alpha(\mathbf{p}) = (2\pi\hbar)^{-3/2} \int e^{-(i/\hbar)\mathbf{p}\mathbf{r}} \psi_\alpha(\mathbf{r}) dV \quad (18.4)$$

(the integral is evaluated over the entire infinite volume).

Formula (18.3) gives the transformation from $\psi_\alpha(x)$ (i.e. the psi-function in the coordinate representation) to $c_\alpha(p_x)$ (i.e. the psi-function in the momentum representation). The inverse transformation (i.e. the transformation from the momentum representation

to the coordinate one) can be obtained by expanding $\psi_\alpha(x)$ by the eigenfunctions (17.8) of the operator \hat{p}_x :

$$\psi_\alpha(x) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} c(p_x) e^{(i/\hbar)p_x x} dp_x \quad (18.5)$$

A comparison of formulas (18.5) and (18.3) leads us to the conclusion that they are in essence (within the insignificant factor \hbar) direct and inverse Fourier transforms [see Vol. 1, formulas (XIV.21) and (XIV.22)]. We can therefore say that the function $c(p_x)$ is the Fourier image of the function $\psi_\alpha(x)$.

Introducing the function $\psi_{x'}(x) = \delta(x - x')$ into formula (18.3), we obtain the eigenfunction of the coordinate in the momentum representation (for a value of the coordinate equal to x'):

$$\begin{aligned} c_{x'}(p_x) &= (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} e^{-(i/\hbar)p_x x} \delta(x - x') dx \\ &= (2\pi\hbar)^{-1/2} e^{-(i/\hbar)x' p_x} \end{aligned} \quad (18.6)$$

This formula differs from (17.8) in that p_x and x have exchanged roles; in addition, the sign of the exponent has changed.

Now let us take the eigenfunction of the momentum operator $\psi_{p'_x}(x)$ corresponding to the value $p_x = p'_x$ as $\psi_\alpha(x)$.

Substitution of this function into (18.3) yields

$$\begin{aligned} c_{p'_x}(p_x) &= (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} \exp\left(-\frac{i}{\hbar}p_x x\right) \left[(2\pi\hbar)^{-1/2} \exp\left(\frac{i}{\hbar}p'_x x\right)\right] dx \\ &= (2\pi\hbar)^{-1} \int_{-\infty}^{+\infty} \exp\left[\frac{i}{\hbar}(p'_x - p_x)x\right] dx = (2\pi\hbar)^{-1} 2\pi\hbar \delta(p'_x - p_x) \end{aligned}$$

[see (17.7)]. Hence, with a view to the fact that $\delta(-x) = \delta(x)$, we obtain

$$c_{p'_x}(p_x) = \delta(p_x - p'_x) \quad (18.7)$$

[compare with (17.2)].

Consider the psi-function in the energy representation. Assume that the Hamiltonian \hat{H} has a discrete spectrum of eigenvalues: E_1, E_2, \dots . Let us designate the relevant eigenfunctions by $\psi_1^{(E)}, \psi_2^{(E)}, \dots$. We expand $\psi_\alpha(x)$ into a series in these functions:

$$\psi_\alpha(x) = \sum_m c_m^{(E)} \psi_m^{(E)}(x)$$

According to (14.1), the coefficients $c_m^{(E)}$ are determined by the expression

$$c_m^{(E)} = \langle \psi_m^{(E)} | \psi_\alpha \rangle = \int_{-\infty}^{+\infty} [\psi_m^{(E)}(x)]^* \psi_\alpha(x) dx \quad (18.8)$$

The set of coefficients $c_m^{(E)}$ is the psi-function of state α in the energy representation. In the Dirac notation

$$c_m^{(E)} = \langle E_m | \alpha \rangle \quad (18.9)$$

[compare with (13.12)].

Now let us establish the form of the operators \hat{x} and \hat{p}_x in the p -representation. We know [see (15.1) and (15.7)] that in the x -representation these operators have the form

$$\hat{x} = x, \quad \hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad (18.10)$$

We shall proceed from formula (7.14) for the mean values of physical quantities. For one dimension, this formula is written as

$$\langle q \rangle = \int_{-\infty}^{+\infty} \psi^*(x) \hat{Q} \psi(x) dx \quad (18.11)$$

We remind our reader that when using this formula, we must take the psi-function and the operator in the same representation. The result (i.e. the value of $\langle q \rangle$) does not depend on the form of the representation.

By formula (12.3), we have

$$\langle p_x \rangle = \int_{-\infty}^{+\infty} |c(p_x)|^2 p_x dp_x = \int_{-\infty}^{+\infty} [c(p_x)]^* p_x c(p_x) dp_x$$

On the other hand, by formula (18.11), we have

$$\langle p_x \rangle = \int_{-\infty}^{+\infty} [c(p_x)]^* \hat{p}_x c(p_x) dp_x$$

where \hat{p}_x is the momentum operator in the p -representation. A comparison of the last two expressions for $\langle p_x \rangle$ shows that the action of the momentum operator in its eigenrepresentation on $c(p_x)$ consists in multiplication of $c(p_x)$ by p_x so that

$$\hat{p}_x = p_x \quad (18.12)$$

Similarly in a coordinate representation, $\hat{x} = x$

The mean value of the coordinate x is determined in the coordinate representation by the formula

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^*(x) x \psi(x) dx \quad (18.13)$$

and in the momentum representation, by the formula

$$\langle x \rangle = \int_{-\infty}^{+\infty} c^*(p_x) \hat{x} c(p_x) dp_x \quad (18.14)$$

where \hat{x} is the coordinate operator in the momentum representation. We shall show that if we assume

$$\hat{x} = i\hbar \frac{\partial}{\partial p_x} \quad (18.15)$$

expression (18.14) transforms into (18.13), i.e. we obtain the correct value of $\langle x \rangle$.

Let us introduce expression (18.3) for $c(p_x)$ and expression (18.15) for \hat{x} into (18.14):

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{+\infty} \left\{ (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} e^{(i/\hbar)p_x \xi} \psi^*(\xi) d\xi \right\} \\ &\times i\hbar \frac{\partial}{\partial p_x} \left\{ (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} e^{-(i/\hbar)p_x \eta} \psi(\eta) d\eta \right\} dp_x \end{aligned}$$

Recall that $\psi^*(\xi)$ and $\psi(\eta)$ are psi-functions in a coordinate representation. To avoid confusion, we have designated the integration variable in the expression for $c^*(p_x)$ by the letter ξ , and in the expression for $c(p_x)$ by the letter η . Let us perform differentiation with respect to the parameter p_x in the integral over the variable η . As a result, the factor $-i\eta/\hbar$ will appear, which together with $i\hbar$ gives η . Now we shall write the expression obtained as follows:

$$\langle x \rangle = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \psi^*(\xi) d\xi \int_{-\infty}^{+\infty} \psi(\eta) \eta d\eta \int_{-\infty}^{+\infty} \exp \left[i \frac{p_x}{\hbar} (\xi - \eta) \right] d(p_x/\hbar)$$

By (VIII.12), the integral over the variable p_x/\hbar equals $2\pi\delta(\xi - \eta)$. Hence,

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^*(\xi) d\xi \int_{-\infty}^{+\infty} \psi(\eta) \eta \delta(\xi - \eta) d\eta = \int_{-\infty}^{+\infty} \psi^*(\xi) \xi \psi(\xi) d\xi$$

which differs from expression (18.13) only in the designation of the integration variable (ξ instead of x).

We have thus proved that the coordinate operator in the momentum representation has the form of (18.15). In the three-dimensional form, this operator is determined by the expression

$$\hat{\mathbf{r}} = i\hbar \nabla_{\mathbf{p}} \quad (18.16)$$

(the subscript \mathbf{p} signifies that differentiation is performed over p_x, p_y, p_z). In the coordinate representation,

$$\hat{\mathbf{p}} = -i\hbar \nabla_{\mathbf{r}} \quad (18.17)$$

A comparison of (18.16) with (18.17) shows that when we go over from one of these formulas to the other, \mathbf{p} and \mathbf{r} exchange roles, as it were. In addition, these formulas differ in the sign [compare with (17.2) and (18.7)].

19. Eigenvalues and Eigenfunctions of the Angular Momentum Operator

In Sec. 17, we found the eigenfunctions of the coordinate and momentum operators and established that these operators have continuous spectra of eigenvalues. The energy operator \hat{H} includes the potential U as an addend [see (15.4)]. Therefore, the form of the eigenfunctions and the spectrum of the energy values depend on the nature of the force field in which a particle moves. In the following, we solve the problem of finding the eigenvalues and eigenfunctions of the energy operator for some typical force fields. In the present section, we shall find the eigenvalues and eigenfunctions of the operator of the angular momentum projection onto a direction that we shall call the z -axis, and of the operator of the square of the angular momentum.

We shall conduct our treatment in spherical coordinates. Let us write Eq. (7.3) for M_z , taking (15.11) into account:

$$-i\hbar \frac{\partial \psi}{\partial \varphi} = M_z \psi \quad (19.1)$$

The following function will be a solution of this equation:

$$\psi = C e^{i(M_z/\hbar)\varphi} \quad (19.2)$$

For this function to be single-valued, the condition $\psi(\varphi + 2\pi) = \psi(\varphi)$ must be observed, i.e.

$$\exp \left[i \frac{M_z}{\hbar} (\varphi + 2\pi) \right] = \exp \left(i \frac{M_z}{\hbar} \varphi \right)$$

This condition will be satisfied if we assume that $M_z = m\hbar$, where m is a positive or negative integer, or zero. Consequently, M_z can take on only discrete values:

$$M_z = m\hbar \quad (m = 0, \pm 1, \pm 2, \dots) \quad (19.3)$$

so that the operator \hat{M}_z has a discrete spectrum. For reasons that will be revealed on a later page, m is called the **magnetic quantum number**.

Introducing $M_z = m\hbar$ into (19.2), we obtain the eigenfunctions of the operator \hat{M}_z :

$$\psi_m = Ce^{im\varphi} \quad (19.4)$$

Let us normalize these functions to unity. The square of the magnitude of ψ_m equals $|C|^2$. Consequently,

$$\langle \psi_m | \psi_m \rangle = \int_0^{2\pi} \psi_m^* \psi_m d\varphi = \int_0^{2\pi} |C|^2 d\varphi = 2\pi |C|^2$$

This expression shows that for the function (19.4) to be normalized to unity, we must assume that $C = (1/\sqrt{2\pi})e^{i\alpha}$. Omitting the phase factor $e^{i\alpha}$, we obtain the following expression for the normalized eigenfunctions:

$$\psi_m = (2\pi)^{-1/2} e^{im\varphi} \quad (19.5)$$

It is not at all difficult to verify that the functions (19.5) are mutually orthogonal so that the following condition is observed for them:

$$\langle \psi_{m'} | \psi_{m''} \rangle = \int_0^{2\pi} \psi_{m'}^* \psi_{m''} d\varphi = \delta_{m'm''} \quad (19.6)$$

Now let us turn to the eigenvalues and eigenfunctions of the operator \hat{M}^2 . Substitution of expression (15.12) for the operator into Eq. (7.3) yields

$$-\hbar^2 \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial \psi}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 \psi}{\partial \varphi^2} \right] = M^2 \psi$$

Dividing this equation by \hbar^2 and transferring all terms to one side of the equation, we arrive at a differential equation of spherical functions [see formula (II.1)]

$$\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial \psi}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 \psi}{\partial \varphi^2} + \alpha \psi = 0 \quad (19.7)$$

in which the parameter $\alpha = M^2/\hbar^2$.

It is shown in Appendix II that the eigenvalues of the parameter α are

$$\alpha = \frac{M^2}{\hbar^2} = l(l+1) \quad (l=0, 1, 2, \dots) \quad (19.8)$$

[see (II.37)], while the following spherical functions are the eigenfunctions:

$$Y_{lm} = (-1)^{\frac{m+|m|}{2}} \frac{1}{\sqrt{2\pi}} \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} e^{im\varphi} P_l^{|m|}(\cos \vartheta) \quad (19.9)$$

[see (II.35)].

Examination of the condition (19.8) shows that the square of the angular momentum has a discrete spectrum:

$$M^2 = \hbar^2 l(l+1) \quad (l=0, 1, 2, \dots) \quad (19.10)$$

The quantum number l is known as the **azimuthal** (or **orbital**) **quantum number**. To each eigenvalue of the square of the angular momentum (i.e. to each value of l) there correspond $2l+1$ different functions Y_{lm} differing in the values of the magnetic quantum number m .

The function (19.9) can be written as $C_\vartheta e^{im\varphi}$, where C_ϑ is a coefficient depending only on ϑ . Hence, it is a simple matter to conclude that the functions Y_{lm} satisfy Eq. (19.1), i.e. are simultaneously eigenfunctions of the operator \hat{M}_z . The functions Y_{lm} are non-zero only when $|m| \leq l$ [see the text following formula (II.28)]. Therefore, the operators \hat{M}_z and \hat{M}^2 have non-zero eigenfunctions at

$$\begin{aligned} l &= 0, 1, 2, \dots \\ m &= -l, -l+1, \dots, -1, 0, 1, \dots, l-1, l \end{aligned} \quad (19.11)$$

The azimuthal quantum number l determines the magnitude of the square of the angular momentum by formula (19.10), and the magnetic quantum number m determines the projection of the angular momentum onto the z -axis by formula (19.3). We must note that there can never be values of M^2 and M_z other than (19.10) and (19.3). Consequently, the angular momenta of macroscopic bodies also obey the rules (19.10) and (19.3). True, owing to the smallness of \hbar , the discreteness of the angular momenta of macroscopic bodies is virtually not detected, in the same way as owing to the smallness of the elementary charge e , the discreteness of macroscopic electric charges is not detected.

In concluding, we shall give the expressions for several first functions Y_{lm} determined by formula (II.35):

$$\begin{aligned} Y_{00} &= 1/\sqrt{4\pi}, \\ Y_{10} &= \sqrt{3/4\pi} \cos \vartheta, & Y_{1, \pm 1} &= \mp \sqrt{3/8\pi} \sin \vartheta e^{\pm i\varphi} \\ Y_{20} &= \sqrt{5/16\pi} (3 \cos^2 \vartheta - 1), & Y_{2, \pm 1} &= \mp \sqrt{15/8\pi} \sin \vartheta \cos \vartheta e^{\pm i\varphi} \\ & & Y_{2, \pm 2} &= \sqrt{15/32\pi} \sin^2 \vartheta e^{\pm i2\varphi} \end{aligned} \quad (19.12)$$

20. Parity

Parity is a purely quantum-mechanical quantity having no classical analogue. To arrive at the concept of parity, let us consider the behaviour of the psi-function upon the inversion of the coordinate axes.

Inversion consists in reversing the direction of all the axes. It is not difficult to see that inversion transforms a right-handed coordinate system into a left-handed one and, conversely, a left-handed system into a right-handed one. Inversion results in the signs of all the coordinates changing and, consequently, the function $\psi(x, y, z)$ transforms into $\psi(-x, -y, -z)$. This transition can be considered as a result of the action of the inversion operator \hat{P} on the psi-function:

$$\psi(-x, -y, -z) = \hat{P}\psi(x, y, z) \quad (20.1)$$

By again acting with the operator \hat{P} on relation (20.1), we obtain the initial function on the left, i.e. we arrive at the relation

$$\psi(x, y, z) = \hat{P}^2\psi(x, y, z)$$

from which it follows that the square of the operator \hat{P} equals unity.

To determine the eigenvalues of the inversion operator, we must solve the equation

$$\hat{P}\psi(x, y, z) = P\psi(x, y, z) \quad (20.2)$$

Let us act on this equation with the inversion operator:

$$\hat{P}^2\psi(x, y, z) = P\hat{P}\psi(x, y, z)$$

Taking into account that $\hat{P}^2 = 1$ and $\hat{P}\psi = P\psi$, we obtain

$$\psi(x, y, z) = P^2\psi(x, y, z)$$

whence it follows that $P^2 = 1$, i.e. $P = \pm 1$.

Hence, the eigenvalues of the inversion operator are +1 and -1. With a view to this circumstance, we can write Eq. (20.2) as follows:

$$\hat{P}\psi(x, y, z) = \pm\psi(x, y, z) \quad (20.3)$$

Finally, introducing the obtained value of $\hat{P}\psi$ into (20.1), we arrive at the relation

$$\psi(-x, -y, -z) = \pm\psi(x, y, z) \quad (20.4)$$

The quantity depicted by the operator \hat{P} is known as the parity. The result we have obtained, expressed by formulas (20.3) and (20.4), signifies that psi-functions of states with a definite parity

value can be divided into two classes: (1) functions $\psi_{(+)}$ that do not change when the inversion operator acts on them, and (2) functions $\psi_{(-)}$ that change their sign when the inversion operator acts on them.

The functions $\psi_{(+)}$ and $\psi_{(-)}$ satisfy the relations

$$\hat{P}\psi_{(+)} = \psi_{(+)}, \quad \hat{P}\psi_{(-)} = -\psi_{(-)} \quad (20.5)$$

States corresponding to the functions $\psi_{(+)}$ are said to be **even**, and those corresponding to the functions $\psi_{(-)}$ are said to be **odd**. The parity of a state described by the function $\psi = c_1\psi_{(+)} + c_2\psi_{(-)}$ is indeterminate.

Let us determine the parity of a state with the azimuthal quantum number l . In spherical coordinates, the operation of inversion means the substitution of $\pi - \vartheta$ for ϑ and $\varphi + \pi$ for φ . The cosine of ϑ changes its sign. The change in the sign of $\cos \vartheta$ in formula (II.35) leads to the appearance of the factor $(-1)^{l+|m|}$ [recall that $P_l(-x) = (-1)^l P_l(x)$; see (II.21)]. In addition, $e^{im\varphi}$ transforms into $e^{im(\varphi+\pi)} = (e^{i\pi})^m e^{im\varphi} = (-1)^m e^{im\varphi}$. We finally obtain that in inversion, the spherical function (19.9) is multiplied by $(-1)^{l+|m|+m} = (-1)^l$.

Hence, states with even l 's have a positive parity, and states with odd l 's, a negative parity.

In addition to the parity considered above, which is determined by the behaviour of the psi-function describing the motion of particles in inversion, there also exists the **intrinsic parity** of particles¹. For example, a proton, neutron, and electron have a positive intrinsic parity, their antiparticles have a negative intrinsic parity, and all pi-mesons (π^+ , π^- , π^0) have a negative intrinsic parity.

The parity of a system of particles is evaluated as the product of the intrinsic parities of the particles in a system and the parity of the psi-function describing the motion of the particles.

¹ Similarly, in addition to the orbital angular momentum, particles have an intrinsic angular momentum—a spin.

Chapter IV

TIME DEPENDENCE OF PHYSICAL QUANTITIES

21. The Time Derivative of an Operator

In classical mechanics, the finding of the time derivative of a physical quantity is associated with consideration of the values of the quantity at two close instants. In quantum mechanics, however, a quantity having a definite value at a certain instant no longer has a definite value at the following instant. Indeed, as we noted in Sec. 2, a dynamical characteristic of a microobject appears only as a result of measurement (this is what we called, for brevity's sake, the interaction of a microobject with a macroscopic body). A measurement, however, results in an uncontrollable change in the state of the microobject. Therefore, measurements of a quantity performed for the same system in equal time intervals yield results that cannot be plotted on a smooth curve, but will occupy absolutely chaotic positions.

It follows from the above that in quantum mechanics the classical concept of the time derivative of a physical quantity loses its meaning. But this concept can be applied to the mean values of physical quantities. Let us determine the time derivative \hat{Q} of the quantity Q as a quantity whose mean value equals the time derivative of the mean value of the quantity Q . This definition can be written analytically as follows:

$$\left\langle \frac{dQ}{dt} \right\rangle = \frac{d}{dt} \langle q \rangle, \text{ or } \dot{\langle q \rangle} = \frac{d}{dt} \langle q \rangle \quad (21.1)$$

Let us find an expression for the operator \hat{Q} (the operator of the time derivative of the quantity Q) satisfying the condition (21.1). By formula (7.14), we have

$$\langle q \rangle = \int \psi^* \hat{Q} \psi dV \quad (21.2)$$

$$\dot{\langle q \rangle} = \int \psi^* \hat{Q} \psi dV \quad (21.3)$$

Let us differentiate expression (21.2) with respect to time, assuming that both the function ψ and the operator \hat{Q} may depend explicitly on t :

$$\frac{d}{dt} \langle q \rangle = \frac{d}{dt} \int \psi^* \hat{Q} \psi dt$$

If the time were not contained explicitly in ψ and \hat{Q} , the integral on the right-hand side would be simply a number whose derivative with respect to t is zero. If the time is contained in the integrand explicitly, however, it plays the role of the parameter with respect to which differentiation is being performed. Consequently,

$$\frac{d}{dt} \langle q \rangle = \int \frac{\partial \psi^*}{\partial t} \hat{Q} \psi dV + \int \psi^* \frac{\partial \hat{Q}}{\partial t} \psi dV + \int \psi^* \hat{Q} \frac{\partial \psi}{\partial t} dV \quad (21.4)$$

The Schrödinger equation (5.1) can be written as

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (21.5)$$

whence

$$\frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} \hat{H}\psi \quad (21.6)$$

Taking the complex conjugate expression of (21.6), we obtain

$$\frac{\partial \psi^*}{\partial t} = \frac{i}{\hbar} \hat{H}^* \psi^* \quad (21.7)$$

Let us replace the time derivatives of the psi-function in the first and third integrals of formula (21.4) with their expressions (21.6) and (21.7):

$$\frac{d}{dt} \langle q \rangle = \frac{i}{\hbar} \int (\hat{H}^* \psi^*) \hat{Q} \psi dV + \int \psi^* \frac{\partial \hat{Q}}{\partial t} \psi dV - \frac{i}{\hbar} \int \psi^* \hat{Q} (\hat{H} \psi) dV \quad (21.8)$$

Owing to the Hermitian character, the operator \hat{H} satisfies the condition (8.13). Therefore,

$$\int (\hat{H}^* \psi^*) \hat{Q} \psi dV = \int (\hat{Q} \psi) \hat{H}^* \psi^* dV = \int \psi^* \hat{H} (\hat{Q} \psi) dV$$

(the second integral is obtained by simply transposing the cofactors). Performing such a replacement in the first integral of expression (21.8) and then combining all three integrals into a single one, we obtain

$$\frac{d}{dt} \langle q \rangle = \int \psi^* \left(\frac{i}{\hbar} \hat{H} \hat{Q} + \frac{\partial \hat{Q}}{\partial t} - \frac{i}{\hbar} \hat{Q} \hat{H} \right) \psi dV \quad (21.9)$$

Finally, let us introduce expressions (21.3) and (21.9) into the condition (21.1):

$$\int \psi^* \hat{Q} \hat{\psi} dV = \int \psi^* \left(\frac{i}{\hbar} \hat{H} \hat{Q} + \frac{\partial \hat{Q}}{\partial t} - \frac{i}{\hbar} \hat{Q} \hat{H} \right) \psi dV$$

It thus follows that

$$\hat{\dot{Q}} = \frac{\partial \hat{Q}}{\partial t} + \frac{i}{\hbar} (\hat{H}\hat{Q} - \hat{Q}\hat{H}) = \frac{\partial \hat{Q}}{\partial t} + \frac{i}{\hbar} [\hat{H}, \hat{Q}] \quad (21.10)$$

where $[\hat{H}, \hat{Q}]$ is the commutator of the operators \hat{H} and \hat{Q} [see formula (10.22)].

A glance at (21.10) shows that if the operator \hat{Q} does not depend explicitly on the time and, in addition, commutes with the Hamiltonian, we have $\hat{\dot{Q}} = 0$, and, consequently, the mean value of the quantity Q remains constant: $\langle q \rangle = \text{const}$ [to verify this statement, formulas (21.3) and (21.4) must be considered]. Quantities having such a property are said to be conserved.

In Sec. 31 of Vol. 1, we obtained the following expression for the time derivative of the function $f(q_h, p_h, t)$ of the canonical variables q_h, p_h and the time t [see formula (31.5) of Vol. 1]:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \{H, f\} \quad (21.11)$$

where

$$\{H, f\} = \sum_k \left(\frac{\partial H}{\partial p_k} \frac{\partial f}{\partial q_k} - \frac{\partial f}{\partial p_k} \frac{\partial H}{\partial q_k} \right)$$

is what is called the Poisson bracket for the functions f and H (here H is a Hamiltonian function).

Formulas (21.10) and (21.11) are similar in appearance. For this reason, the expression

$$\{\hat{H}, \hat{Q}\} = \frac{i}{\hbar} [\hat{H}, \hat{Q}] = \frac{i}{\hbar} [\hat{H}\hat{Q} - \hat{Q}\hat{H}] \quad (21.12)$$

is called the Poisson quantum bracket.

Let us find an expression for the operator of the velocity of a particle, limiting ourselves for simplicity to one dimension. By (21.10), we have

$$\hat{v}_x = \hat{\dot{x}} = \frac{\partial x}{\partial t} + \frac{i}{\hbar} (\hat{H}x - x\hat{H}) = \frac{i}{\hbar} (\hat{H}x - x\hat{H})$$

(recall that $\hat{x} = x$). Introduction of the expression for \hat{H} leads to the formula

$$\hat{\dot{x}} = \frac{i}{\hbar} \left\{ \left[-\frac{\hbar^2}{2m_0} \frac{\partial^2}{\partial x^2} + U(x) \right] x - x \left[-\frac{\hbar^2}{2m_0} \frac{\partial^2}{\partial x^2} + U(x) \right] \right\}$$

Elementary calculations show that

$$\frac{\partial^2}{\partial x^2} (x\psi) - x \frac{\partial^2 \psi}{\partial x^2} = 2 \frac{\partial \psi}{\partial x}$$

Consequently,

$$\hat{\dot{x}} = \frac{i}{\hbar} \left(-\frac{\hbar^2}{2m_0} \right) 2 \frac{\partial}{\partial x} = -\frac{i\hbar}{m_0} \frac{\partial}{\partial x} = \frac{\hat{p}_x}{m_0}$$

Hence,

$$\hat{v}_x = \hat{\dot{x}} = \frac{\hat{p}_x}{m_0} \quad (21.13)$$

In three dimensions, we have

$$\hat{\mathbf{v}} = \frac{\hat{\mathbf{p}}}{m_0} \quad (21.14)$$

We see that the relation between the velocity and momentum operators has the same form as that between these quantities themselves in classical mechanics.

Now we can find the operator of the acceleration of a particle. By (21.10) and (21.13), we have

$$\begin{aligned} \hat{\ddot{x}} &= \frac{\partial \hat{\dot{x}}}{\partial t} + \frac{i}{\hbar} (\hat{H} \hat{\dot{x}} - \hat{\dot{x}} \hat{H}) = \frac{i}{\hbar m_0} (\hat{H} \hat{p}_x - \hat{p}_x \hat{H}) \\ &= \frac{i}{\hbar m_0} \left\{ \left[-\frac{\hbar^2}{2m_0} \frac{\partial^2}{\partial x^2} + U(x) \right] \left(-i\hbar \frac{\partial}{\partial x} \right) \right. \\ &\quad \left. - \left(-i\hbar \frac{\partial}{\partial x} \right) \left[-\frac{\hbar^2}{2m_0} \frac{\partial^2}{\partial x^2} + U(x) \right] \right\} \\ &= \frac{i}{\hbar m_0} \left\{ U(x) \left(-i\hbar \frac{\partial}{\partial x} \right) - \left(-i\hbar \frac{\partial}{\partial x} \right) U(x) \right\} = -\frac{1}{m_0} \frac{\partial U}{\partial x} \end{aligned}$$

Hence,

$$\hat{\ddot{x}} = -\frac{1}{m_0} \frac{\partial U}{\partial x} \quad (21.15)$$

or for the three-dimensional case

$$\hat{\mathbf{v}} = -\frac{1}{m_0} \nabla U \quad (21.16)$$

The operator equation we have obtained coincides in form with the equation of Newton's second law in classical mechanics.

22. Time Dependence of Matrix Elements

For stationary states, the time dependence of the psi-function is determined by an exponential factor [see formula (5.6)]:

$$\psi_n(x, y, z, t) = \varphi_n(x, y, z) e^{-i(E_n/\hbar)t}$$

Let us introduce this function into expression (9.9) determining the matrix elements of the quantity \hat{Q} :

$$Q_{mn}(t) = \int \varphi_m^* e^{i(E_m/\hbar)t} \hat{Q} \varphi_n e^{-i(E_n/\hbar)t} dV$$

If the operator \hat{Q} contains no time derivative, the exponent can be put outside the operator symbol. The result is

$$Q_{mn}(t) = e^{i[(E_m - E_n)/\hbar]t} \int \varphi_m^* \hat{Q} \varphi_n dV = e^{i\omega_{mn}t} Q_{mn}$$

where

$$\omega_{mn} = \frac{E_m - E_n}{\hbar} \quad (22.1)$$

is a quantity known as the transition frequency between the states m and n , while

$$Q_{mn} = \int \varphi_m^* \hat{Q} \varphi_n dV \quad (22.2)$$

is a time-independent matrix element. When the time dependence of the matrix elements is immaterial, only matrices with the elements (22.2) are considered. Particularly, we proceeded in this way in Sec. 9, using the letter ψ for the function $\varphi_n(x, y, z)$.

Hence,

$$Q_{mn}(t) = e^{i\omega_{mn}t} Q_{mn} \quad (22.3)$$

Let us write expression (9.25) for the mean value of the quantity Q :

$$\langle q \rangle = \sum_{m,n} c_m^* Q_{mn}(t) c_n \quad (22.4)$$

(the coefficients c_m^* and c_n determine ψ^* and ψ of the state for which $\langle q \rangle$ is being calculated).

The mean value of the quantity Q in the same state is determined by expression (22.4) in which \dot{Q} must be substituted for Q :

$$\langle \dot{q} \rangle = \sum_{m,n} c_m^* (\dot{Q})_{mn}(t) c_n \quad (22.5)$$

and in the same way as for Q

$$(\dot{Q})_{mn}(t) = e^{i\omega_{mn}t} (\dot{Q})_{mn} \quad (22.6)$$

[see (22.3)].

Let us differentiate expression (22.4) with respect to t , remembering that c_m^* and c_n are numbers:

$$\frac{d}{dt} \langle q \rangle = \sum_{m,n} c_m^* \left[\frac{d}{dt} Q_{mn}(t) \right] c_n \quad (22.7)$$

In the preceding section, we determined the derivative of a physical quantity with the aid of relation (21.1), i.e. assuming the quantities (22.5) and (22.7) to be equal. Consequently, the following equality must be observed:

$$(\dot{Q})_{mn}(t) = \frac{d}{dt} Q_{mn}(t) \quad (22.8)$$

A matrix element of the quantity \dot{Q} is on the left, and the time derivative of a matrix element of the quantity Q is on the right.

With a view to formula (22.3), we find that

$$(\dot{Q})_{mn}(t) = i\omega_{mn} e^{i\omega_{mn} t} Q_{mn} = i\omega_{mn} Q_{mn}(t)$$

Finally, introducing expression (22.6) for $(\dot{Q})_{mn}(t)$ into the left-hand side of the relation obtained and cancelling the time factor on both sides, we arrive at the formula

$$(\dot{Q})_{mn} = i\omega_{mn} Q_{mn} \quad (22.9)$$

Using relation (21.1) twice, we can write that

$$\ddot{\langle q \rangle} = \frac{d}{dt} \dot{\langle q \rangle} = \frac{d}{dt} \left(\frac{d}{dt} \langle q \rangle \right) = \frac{d^2}{dt^2} \langle q \rangle \quad (22.10)$$

Double differentiation of expression (22.4) with account taken of (22.3) yields

$$\frac{d^2}{dt^2} \langle q \rangle = \sum_{m,n} c_m^* \left[\frac{d^2}{dt^2} Q_{mn}(t) \right] c_n = \sum_{m,n} c_m^* [-\omega_{mn}^2 Q_{mn}(t)] c_n \quad (22.11)$$

At the same time,

$$\ddot{\langle q \rangle} = \sum_{m,n} c_m^* (\ddot{Q})_{mn}(t) c_n \quad (22.12)$$

[compare with (22.4) and (22.5)].

By (22.10), expressions (22.11) and (22.12) equal each other. Hence,

$$(\ddot{Q})_{mn}(t) = -\omega_{mn}^2 Q_{mn}(t) \quad (22.13)$$

or, after cancelling the time factor,

$$(\ddot{Q})_{mn} = -\omega_{mn}^2 Q_{mn} \quad (22.14)$$

Formulas (22.9) and (22.14) allow us, if we know the matrix of the quantity Q , to find the matrices of the quantities \dot{Q} and \ddot{Q} . Recall that all the calculations have been performed assuming that the state in which $\langle q \rangle$, $\dot{\langle q \rangle}$, and $\ddot{\langle q \rangle}$ were determined is stationary.

Chapter V

MOTION OF A PARTICLE IN FORCE FIELDS

23. A Particle in a Central Force Field

The potential energy of a particle in a centrally symmetric force field depends only on the distance from the particle to the force-centre: $U = U(r)$. Consequently, the Hamiltonian of the particle has the form

$$\hat{H} = -\frac{\hbar^2}{2m_0} \nabla^2 + U(r) \quad (23.1)$$

To avoid confusing the mass of a particle with the magnetic quantum number m , we have designated this mass by m_0 .

Owing to the central symmetry of the force field, it is expedient to solve the problem in spherical coordinates. An expression for the Laplacian operator ∇^2 in spherical coordinates is given in Appendix XI of Vol. 1 [see formula (XI.88)]. Substituting this expression into (23.1), we obtain

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m_0} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) \right. \\ & \left. + \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right\} + U(r) \end{aligned} \quad (23.2)$$

A comparison with expression (15.12) shows that the second and third terms in braces are identical with the operator of the square of the angular momentum \hat{M}^2 divided by $-\hbar^2 r^2$. Therefore, the Hamiltonian (23.2) can be written as follows:

$$\hat{H} = -\frac{\hbar^2}{2m_0 r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{M}^2}{2m_0 r^2} + U(r) \quad (23.3)$$

It is not difficult to see that the operator (23.3) commutes both with the operator \hat{M}^2 and with the operator \hat{M}_z . Indeed, the sum of the first and last terms of expression (23.3) is the operator $\hat{Q}(r, \partial/\partial r)$ that contains only r and $\partial/\partial r$ and does not contain the angles ϑ , φ , nor derivatives with respect to the angles. We can thus write that

$$\hat{H} = \hat{Q} \left(r, \frac{\partial}{\partial r} \right) + \frac{1}{2m_0 r^2} \hat{M}^2$$

The operator \hat{M}^2 contains only the angle ϑ and derivatives with respect to the angles ϑ and φ . Therefore, \hat{M}^2 commutes with $\hat{Q}(r, \partial/\partial r)$ and does not act on the factor $1/r^2$. It thus follows that \hat{M}^2 commutes with the operator (23.3).

The operator \hat{M}_z contains only the derivative with respect to the angle φ [see (15.11)]. It therefore commutes with the operator $\hat{Q}(r, \partial/\partial r)$ and does not act on the factor $1/r^2$. In addition, \hat{M}_z is known to commute with the operator \hat{M}^2 [see formula (16.14)]. It follows from this that \hat{M}_z also commutes with the operator (23.3).

Hence, the operators \hat{M}^2 and \hat{M}_z commute with the operator \hat{H} of a particle in the field of central forces. This shows (see Sec. 10) that such a particle can simultaneously have definite values of the energy, the square of the angular momentum, and of the projection of this momentum onto the selected direction z . By formulas (19.3), (19.10), and (19.11), the square and the projection of the angular momentum can have the values

$$M^2 = \hbar^2 l(l+1) \quad (l = 0, 1, 2, \dots), \quad (23.4)$$

$$M_z = m\hbar \quad (n = -l, -l+1, \dots, -1, 0, +1, \dots, l-1, l) \quad (23.5)$$

To find the values of the energy of a particle, we must solve the equation

$$-\frac{\hbar^2}{2m_0r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{2m_0r^2} \hat{M}^2 \psi + U(r) \psi = E \psi \quad (23.6)$$

[see (7.3) and (23.3)]. We shall try to seek the solution of this equation in the form of the product of two functions, one of which depends only on r , and the other only on the angles ϑ and φ :

$$\psi(r, \vartheta, \varphi) = R(r) \cdot Y(\vartheta, \varphi) \quad (23.7)$$

Substitution of expression (23.7) into Eq. (23.6) yields

$$-\frac{\hbar^2}{2m_0r^2} Y \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{1}{2m_0r^2} R \hat{M}^2 Y + U(r) RY = ERY$$

We have written the symbol of the total derivative with respect to r because the function R depends only on r . Recall that the operator \hat{M}^2 does not contain differentiation with respect to r .

Multiplying the relation obtained by r^2/RY , we reduce it to the form

$$\frac{\hbar^2}{2m_0R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + r^2 [E - U(r)] = \frac{1}{2m_0Y} \hat{M}^2 Y \quad (23.8)$$

We can see that the introduction of (23.7) resulted in separation of the variables: the left-hand side of relation (23.8) contains only

the variable r , and the right-hand side only the variables ϑ and φ . Relation (23.8) must be observed at any values of the variables r , ϑ , φ . This is possible only if the right-hand and the left-hand sides of the relation are separately equal to the same constant quantity C . Consequently, instead of Eq. (23.8) we can write two equations:

$$\frac{\hbar^2}{2m_0} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + r^2 [E - U(r)] R - CR = 0 \quad (23.9)$$

$$\hat{M}^2 Y = 2m_0 CY \quad (23.10)$$

Equation (23.10) belongs to the type of (7.3). The eigenfunctions of the operator \hat{M}^2 , i.e. the spherical functions $Y_{lm}(\vartheta, \varphi)$ [see (19.9)] are its solutions, and the quantities (19.10) are its eigenvalues. Therefore, the constant C must satisfy the condition

$$2m_0 C = \hbar^2 l(l+1) \quad (l = 0, 1, 2, \dots)$$

whence

$$C = (\hbar^2/2m_0) l(l+1) \quad (l = 0, 1, 2, \dots) \quad (23.11)$$

Thus, the angular part of the psi-function (23.7) coincides with the eigenfunctions of the square of the angular momentum.

In accordance with the properties of the solution of Eq. (23.10), we shall be interested only in the solutions of Eq. (23.9) that are obtained at the values of C determined by formula (23.11). We therefore rewrite Eq. (23.9), replacing C in it with its value from (23.11):

$$\frac{\hbar^2}{2m_0} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + r^2 [E - U(r)] R - \frac{\hbar^2}{2m_0} l(l+1) R = 0$$

We transform this equation by differentiating with respect to r the expression in the first parentheses and dividing the entire equation by $\hbar^2/2m_0$. The result is the following differential equation for $R(r)$:

$$r^2 \frac{d^2 R}{dr^2} + 2r \frac{dR}{dr} + \frac{2m_0 r^2}{\hbar^2} [E - U(r)] R - l(l+1) R = 0 \quad (23.12)$$

To solve this equation, we must set the form of the function $U(r)$. Hence, the radial part of the psi-function (23.7) is determined by the nature of the force field. The angular part of the psi-function, however, does not depend on the form of $U(r)$. It is determined by the values of the quantum numbers l and m , i.e. by the magnitude of the angular momentum and of its projection onto the z -axis.

By solving Eq. (23.12), we can find the eigenvalues of the energy E and the functions R corresponding to them. These functions depend on the quantum number l and, consequently, must be written in the form $R_l(r)$. Hence, the solution of Eq. (23.6) is

$$\psi(r, \vartheta, \varphi) = R_l(r) Y_{lm}(\vartheta, \varphi) \quad (23.13)$$

Superposition of functions of the form of (23.13) will be the most general solution of Eq. (23.6):

$$\psi(r, \theta, \phi) = \sum_{l, m} C_{lm} R_l(r) Y_{lm}(\theta, \phi) \quad (23.14)$$

Equation (23.12) does not contain the quantum number m . Consequently, the values of E do not depend on m . This signifies that states with different values of m (there are altogether $2l + 1$ such values) have the same energy. This phenomenon is known as **degeneracy**. Therefore, for a particle in a central field of forces, degeneracy occurs with respect to the quantum number m , the degree of degeneracy being $2l + 1$.

Degeneracy with respect to m is due to the spherical symmetry of the force field. Owing to this symmetry, the energy does not depend on the orientation of the angular momentum in space, i.e. on the magnitude of its projection onto an arbitrarily chosen direction.

It is customary practice to designate states having different values of the angular momentum (i.e. different values of the quantum number l) by Roman letters:

value of l	0	1	2	3	4	5	6	7	\dots
symbol of state	s	p	d	f	g	h	i	k	\dots

Let us see how the radial function $R_l(r)$ behaves near the origin of coordinates and at very great distances from the force centre. It will be more convenient to do this by writing the function as

$$R_l(r) = \frac{1}{r} \chi(r) \quad (23.15)$$

(to make our notation simpler, we shall not write the subscript l on χ). Substitution of expression (23.15) into (23.12) yields the following equation for $\chi(r)$:

$$\frac{d^2\chi}{dr^2} + \left[\frac{2m_0}{\hbar^2} (E - U) - \frac{l(l+1)}{r^2} \right] \chi = 0 \quad (23.16)$$

This equation is simpler than Eq. (23.12). This justifies the representation of the radial function in the form of (23.15).

We must note that Eq. (23.16) coincides formally with the Schrödinger equation for the one-dimensional motion of a particle in a force field:

$$U_l(r) = U(r) + \frac{\hbar^2}{2m_0} \frac{l(l+1)}{r^2} \quad (23.17)$$

Here the term

$$\frac{\hbar^2}{2m_0} \frac{l(l+1)}{r^2} = \frac{M_l^2}{2m_0 r^2}$$

can be called the **centrifugal energy**.

Let us first establish the form of the radial function at very small r 's. Assume that the potential energy near the origin of coordinates behaves so that

$$\lim_{r \rightarrow 0} U(r) r^2 = 0 \quad (23.18)$$

This condition, particularly, is observed for a particle in a Coulomb field, i.e. in a field of the form $U = \alpha/r$.

Examination of (23.18) reveals that $U(r)$ grows at a slower rate than $1/r^2$ when r shrinks to zero. For this reason in Eq. (23.16), we may disregard the term $2m_0(E - U)/\hbar^2$ in comparison with the term $l(l+1)/r^2$. Hence, at small r 's, the function $\chi(r)$ is a solution of the equation

$$\frac{d^2\chi}{dr^2} - \frac{l(l+1)}{r^2} \chi = 0 \quad (23.19)$$

The circumstance that the coefficients of the equation are proportional to 1 and $1/r^2$ suggests the idea of trying to seek the solution in the form of $\chi = Cr^s$, where C is a constant and s is an integer. Substitution of this expression into Eq. (23.19) results in a quadratic equation for s :

$$s(s-1) = l(l+1)$$

The roots of this equation are

$$s = l + 1 \text{ and } s = -l$$

The second root cannot be used because when $s = -l$ we find that $R \propto r^{-(l+1)}$ and, consequently, at any l the function R would become equal to infinity at $r = 0$ (recall that $l \geq 0$). Hence, near the origin of coordinates, $\chi \propto r^{l+1}$, and the radial function is determined by the formula

$$R(r) = Cr^l \quad (23.20)$$

Now let us establish the form of the radial function at very great r 's. If, as is usually done, the value of the potential energy at infinity is taken equal to zero, we have

$$\lim_{r \rightarrow \infty} U(r) = 0 \quad (23.21)$$

Therefore at large r 's, the term $-2m_0U\chi/\hbar^2$ in Eq. (23.16), as well as the term $l(l+1)\chi/r^2$, may be disregarded in comparison with $2m_0E\chi/\hbar^2$. The equation will now become simplified as follows:

$$\frac{d^2\chi}{dr^2} + k^2\chi = 0 \quad (23.22)$$

where

$$k^2 = \frac{2m_0E}{\hbar^2} \quad (23.23)$$

The general solution of this equation is

$$\chi = A_1 e^{ikr} + A_2 e^{-ikr} \quad (23.24)$$

Accordingly, the asymptotic (at $r \rightarrow \infty$) expression for $R(r)$ is determined by the formula

$$R_l(r) = A_1 \frac{e^{ikr}}{r} + A_2 \frac{e^{-ikr}}{r} \quad (23.25)$$

When the energy E is positive, the parameter k will be real. Therefore, (23.25) is a superposition of a diverging and converging spherical waves. If we demand that $R_l(r)$ be real, the function (23.25) for $E > 0$ can be written as

$$R_l(r) := \frac{a_l \sin(kr + \beta_l)}{r} \quad (23.26)$$

Hence, at very small r 's, the asymptotic expression of the radial function is determined by formula (23.20), while at very large r 's and at $E < 0$, by formula (23.25). We must note that these asymptotic expressions do not depend on the form of the function $U(r)$. It is only essential that this function satisfy the conditions (23.18) and (23.21).

The asymptotic form of the function $R(r)$ at very large r 's and at $E < 0$ will be considered in the following section.

24. An Electron in a Coulomb Field. The Hydrogen Atom

A Coulomb field is a central one. Therefore, all the results obtained in the preceding section also relate to the given problem. Limiting ourselves to attraction, we can write the potential energy of an electron as

$$U = -\frac{Ze^2}{r} \quad (24.1)$$

where e is the elementary charge, and Z is an integer. When $Z = 1$, expression (24.1) is the potential energy of an electron in a hydrogen atom, when $Z > 1$, it is the potential energy of an electron in a hydrogen-like ion. We must note that the function (24.1) satisfies the conditions (23.18) and (23.21).

Substitution of the function (24.1) into (23.12) yields the equation

$$r^2 \frac{d^2 R}{dr^2} + 2r \frac{dR}{dr} + \frac{2m_e r^2}{\hbar^2} \left[E + \frac{Ze^2}{r} \right] R - l(l+1)R = 0 \quad (24.2)$$

(m_e is the mass of an electron). To get rid of the cumbersome coefficients in this equation, it is customary practice to go over to what we call atomic units of physical quantities.

In atomic units, it is assumed that $m_e = 1$, $e = 1$, and $\hbar = 1$. Combinations of m_e , e , and \hbar having the relevant dimension are

taken as the units of other quantities. For instance, the unit of length is the quantity

$$r_0 = \frac{\hbar^2}{m_e e^2} = 0.529 \text{ \AA} \quad (24.3)$$

coinciding with the Bohr radius (the radius of the first Bohr orbit). The unit of energy is

$$E_0 = \frac{m_e e^4}{\hbar^2} = \frac{e^2}{r_0} = 27.2 \text{ eV} = 2 \text{ rydbergs}^1 \quad (24.4)$$

The unit of time is

$$t_0 = \frac{\hbar^3}{m_e e^4} = 2.42 \times 10^{-17} \text{ s} \quad (24.5)$$

and so on.

Let us perform the following substitutions in Eq. (24.2):

$$r = r_0 \rho = \frac{\hbar^2}{m_e e^2} \rho, \quad E = E_0 \epsilon = \frac{m_e e^4}{\hbar^2} \epsilon \quad (24.6)$$

We shall take into account here that, as follows from (24.6), we have $r (\partial/\partial r) = \rho (\partial/\partial \rho)$ and $r^2 (\partial^2/\partial r^2) = \rho^2 (\partial^2/\partial \rho^2)$. These substitutions yield

$$\rho^2 \frac{d^2 R}{d\rho^2} + 2\rho \frac{dR}{d\rho} + \frac{2m_e r_0^2 \rho^2}{\hbar^2} \left[E_0 \epsilon + \frac{Ze^2}{r_0 \rho} \right] R - l(l+1) R = 0.$$

Taking into account the values of r_0 and E_0 and dividing the equation by ρ^2 , we finally obtain

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left[2\epsilon + \frac{2Z}{\rho} - \frac{l(l+1)}{\rho^2} \right] R = 0 \quad (24.7)$$

Recall that ρ is the distance from an electron to the force centre measured in the units (24.3), and ϵ is the energy of the electron measured in the units (24.4).

We must note that if in Eq. (24.2) we assumed m_e , e , and \hbar to be unity, and substituted ρ for r and ϵ for E , we would also arrive at Eq. (24.7).

We established in Sec. 23 that at very small values of r , the radial function is proportional to r^l [see (23.20)]. Accordingly,

$$R(\rho) \propto \rho^l \text{ when } \rho \rightarrow 0 \quad (24.8)$$

At very large values of ρ , we may drop all the terms in Eq. (24.7) that contain ρ or ρ^2 in their denominator (owing to the standard

¹ The rydberg (Ry) is defined to be a unit of energy equal to the energy of the ground state of a hydrogen atom taken with the opposite sign.

conditions, $dR/d\rho$ must be finite; see the end of Sec. 6). Equation (24.7) thus becomes simplified as follows:

$$\frac{d^2R}{d\rho^2} + 2\epsilon R = 0 \quad (24.9)$$

This is a well-known equation. Its solution depends on the sign of the energy ϵ . It was established in Sec. 11 of Volume 1 that when $\epsilon > 0$, the motion of a particle in a field of central forces of attraction is infinite, and when $\epsilon < 0$, it is finite. The same relation also holds in quantum mechanics. We shall be interested only in bound states of an electron, i.e. in finite motion. Let us therefore consider the case when $\epsilon < 0$. We shall introduce the notation

$$\alpha^2 = -2\epsilon > 0 \quad (24.10)$$

Equation (24.9) will now be written as

$$\frac{d^2R}{d\rho^2} - \alpha^2 R = 0$$

The general solution of such an equation is

$$R(\rho) = A e^{-\alpha\rho} + B e^{\alpha\rho}$$

To satisfy the standard conditions (R must be finite everywhere), we must assume that $B = 0$. Hence, the behaviour of $R(\rho)$ at very great distances from the force centre is shown by the function

$$R(\rho) = A e^{-\alpha\rho} \quad (24.11)$$

The function

$$R(\rho) = e^{-\alpha\rho} \sum_{k=0}^{\infty} a_k \rho^k \quad (24.12)$$

will behave as required both when $\rho \rightarrow 0$ (because of the factor ρ^k) and when $\rho \rightarrow \infty$ (because of the factor $e^{-\alpha\rho}$). We shall therefore seek the solution of Eq. (24.7) in the form of (24.12). We meanwhile leave an indefinite number of addends in the sum. We write expression (24.12) as follows:

$$R(\rho) = e^{-\alpha\rho} \sum_{k=0}^{\infty} a_k \rho^{k+l} \quad (24.13)$$

Differentiation of this function with respect to ρ yields

$$\frac{dR}{d\rho} = -\alpha e^{-\alpha\rho} \sum_{k=0}^{\infty} a_k \rho^{k+l} + e^{-\alpha\rho} \sum_{k=0}^{\infty} a_k (k+l) \rho^{k+l-1} \quad (24.14)$$

Repeated differentiation leads to the expression

$$\frac{d^2R}{d\rho^2} = \alpha^2 e^{-\alpha\rho} \sum_{k=0} a_k \rho^{k+l} - 2\alpha e^{-\alpha\rho} \sum_{k=0} a_k (k+l) \rho^{k+l-1} + e^{-\alpha\rho} \sum_{k=0} a_k (k+l)(k+l-1) \rho^{k+l-2} \quad (24.15)$$

Introducing expressions (24.13)-(24.15) into Eq. (24.7) and combining similar sums [recall that by (24.10), we have $\alpha^2 + 2e = 0$], we obtain the following relation:

$$e^{-\alpha\rho} \left\{ \sum_{k=0} 2 [Z - \alpha(k+l+1)] a_k \rho^{k+l-1} + \sum_{k=0} [(k+l+1)(k+l) - l(l+1)] a_k \rho^{k+l-2} \right\} = 0$$

For the obtained relation to be observed at any values of ρ , the coefficients at all the powers of ρ must be zero. An identical power of ρ is obtained if in the first sum we take the term with the number k , and in the second sum the term with the number $k+1$. Consequently, at any k , the following condition must be observed:

$$2[Z - \alpha(k+l+1)] a_k + [(k+l+2)(k+l+1) - l(l+1)] a_{k+1} = 0$$

Hence we obtain a recurrence formula for the coefficients a_k :

$$a_{k+1} = \frac{2[\alpha(k+l+1)-Z]}{(k+l+2)(k+l+1)-l(l+1)} a_k \quad (24.16)$$

With the aid of this formula, knowing the value of a_0 , we can calculate a_1 , then a_2 , etc. The value of a_0 is determined from the condition of normalization of the psi-function. We must note that to each value of α (i.e. of the energy) there corresponds its own set of coefficients a_k .

At large values of k , we may disregard Z in the numerator and $l(l+1)$ in the denominator of formula (24.16). The recurrence formula now becomes

$$a_{k+1} = \frac{2\alpha}{k+l+2} a_k \quad (24.17)$$

Although relation (24.17) has been obtained for large values of k , we shall extend it to small values. Here we shall introduce no appreciable error into the values of the function (24.12) at large values of ρ because when $\rho \gg 1$ the first terms of the series introduce a negli-

gibly small contribution. Using formula (24.17) to consecutively calculate the coefficients, we obtain the following values:

$$\begin{aligned} a_1 &= \frac{2\alpha}{1+2} a_0 = \frac{2\alpha}{1+l+1} a_0, \\ a_2 &= \frac{2\alpha}{1+l+2} a_1 = \frac{(2\alpha)^2}{(1+l+1)(2+l+1)} a_0, \\ &\dots \dots \dots \dots \dots \dots \dots \\ a_k &= \frac{(2\alpha)^k}{(1+l+1)(2+l+1)\dots(k+l+1)} a_0 = \frac{(l+1)!}{(2\alpha)^{l+1}} \frac{(2\alpha)^{k+l+1}}{(k+l+1)!} a_0, \\ &\dots \dots \dots \dots \dots \dots \dots \end{aligned}$$

Hence, at large values of ρ with a high degree of accuracy, we have

$$\begin{aligned} \sum_{k=0} a_k \rho^k &\approx \frac{(l+1)!}{(2\alpha)^{l+1}} \sum_{k=0} \frac{(2\alpha)^{k+l+1}}{(k+l+1)!} \rho^k \\ &= \frac{(l+1)!}{(2\alpha)^{l+1}} \rho^{-(l+1)} \sum_{k=0} \frac{(2\alpha)^{k+l+1}}{(k+l+1)!} \rho^{k+l+1} \end{aligned}$$

Let us introduce the notation $s = k + l + 1$. Therefore,

$$\sum_{k=0} a_k \rho^k \approx \frac{(l+1)!}{(2\alpha)^{l+1}} \rho^{-(l+1)} \sum_{s=l+1} \frac{(2\alpha)^s}{s!} \rho^s \quad (24.18)$$

The Maclaurin series for the function $e^{2\alpha\rho}$ has the form

$$e^{2\alpha\rho} = \sum_{s=0}^{\infty} \frac{(2\alpha)^s}{s!} \rho^s$$

In comparison with this series, the sum (24.18) lacks the first $l + 1$ addends that play no appreciable role at large values of ρ . Consequently, within the constant factor $(l + 1)!/(2\alpha)^{l+1}$ we can write that

$$\sum_{k=0}^{\infty} a_k \rho^k \propto \rho^{-(l+1)} e^{2\alpha\rho}$$

Substitution of this expression into formula (24.12) yields

$$R(\rho) \propto e^{-\alpha\rho} \rho^l \rho^{-(l+1)} e^{2\alpha\rho} = \rho^{-1} e^{\alpha\rho}$$

This function becomes equal to infinity when $\rho \rightarrow \infty$. We can thus arrive at the following conclusion: if the number of addends in the sum in expression (24.12) were infinite, the function $R(\rho)$ would not satisfy the requirement of being finite at any distance from the force centre. Hence, $R(\rho)$ will satisfy the standard conditions only if the series $\sum a_k \rho^k$ terminates at a term with the number n_r . For

this to occur, it is necessary that the coefficient a_k with the number $n_r + 1$ be zero. As a result, owing to the recurrence formula (24.16), all the following coefficients will also be zero.

Assume that $a_{n_r} \neq 0$, and $a_{n_r+1} = 0$. This will occur if at $k = n_r$ the numerator in formula (24.16) vanishes. This condition is written analytically as follows:

$$\alpha(n_r + l + 1) - Z = 0 \quad (24.19)$$

Recalling that the constant α is associated with the energy of state by the relation $\alpha^2 = -\varepsilon$ [see (24.10)], we obtain the energy values at which the psi-function satisfies the standard conditions. These values are

$$\varepsilon_n = -\frac{Z^2}{2n^2} \quad (24.20)$$

where n is an integer determined by the relation

$$n = n_r + l + 1 \quad (24.21)$$

It is called the **principal quantum number**. The number n_r is called the **radial quantum number**. Since n_r cannot be negative, the condition

$$n \geqslant l + 1$$

must be observed. It thus follows that the maximum possible value of the azimuthal quantum number l at a given n is $n - 1$, i.e. that

$$l \leqslant n - 1 \quad (24.22)$$

Formula (24.20) determines the energy of an electron in atomic units. To express the energy in ergs, we must multiply ε_n by $E_0 = m_e e^4 / \hbar^2$ [see (24.4) and (24.6)]. The result is the value

$$E_n = -\frac{m_e e^4 Z^2 / \hbar^2}{2n^2} \quad (24.23)$$

coinciding with the value obtained by N. Bohr in his theory of the hydrogen atom.

The energy of a particle in a Coulomb field was found to depend only on the principal quantum number n . Consequently, in a Coulomb field, there is degeneracy not only with respect to m , but also with respect to l . The latter degeneracy is a specific property of a Coulomb field, whereas degeneracy with respect to m , as we established in Sec. 23, is observed in a spherically symmetric field of any kind (with any dependence on r). The greater a field differs from a Coulomb one, the more do the energies of states with different values of l differ (at identical n 's).

According to formulas (24.19) and (24.21), the parameter α can have discrete values:

$$\alpha_n = \frac{Z}{n} \quad (n = 1, 2, \dots) \quad (24.24)$$

Let us introduce this value into expression (24.12). In addition, we shall take account of the fact that beginning from $k = n_r + 1 = n - l$, all the coefficients a_k equal zero. As a result, we obtain the following expression for the radial part of the psi-function:

$$R_{nl}(\rho) = e^{-Z\rho/n} \rho^l \sum_{k=0}^{n-l-1} a_k \rho^k \quad (24.25)$$

(we have used the subscripts n and l on R because the expression for this function is determined by the values of these quantum numbers). The coefficients a_k in formula (24.25) can be calculated by the recurrence formula

$$a_{k+1} = \frac{2Z}{n} \cdot \frac{(k+l+1-n)}{(k+l+2)(k+l+1)-l(l+1)} a_k \quad (24.26)$$

We obtained this formula by substituting the value (24.24) for α into expression (24.16).

We must note that polynomials with coefficients satisfying formula (24.26) coincide to within a constant factor with what are called the **Laguerre polynomials**. We shall not stop to consider them in detail.

The total psi-function of a hydrogen-like atom has the form

$$\psi_{nlm} = R_{nl}(\rho) \cdot Y_{lm}(\theta, \varphi) \quad (24.27)$$

Let us find R_{nl} for the ground state (i.e. for the state with the lowest possible energy). In this state, $n = 1$, $l = 0$ [see (24.22)], and $n - l - 1 = 0$ so that the sum contains only one addend corresponding to $k = 0$. Consequently,

$$R_{10}(\rho) = a_0 e^{-Z\rho} \quad (24.28)$$

For $n = 2$ and $l = 0$, formulas (24.25) and (24.26) give the expression

$$R_{20}(\rho) = a_0 e^{-Z\rho/2} \left(1 - \frac{Z\rho}{2} \right) \quad (24.29)$$

For $n = 2$ and $l = 1$, we obtain

$$R_{21}(\rho) = a_0 e^{-Z\rho/2} Z\rho \quad (24.30)$$

and so on.

The coefficient a_0 in the expressions we have obtained can be found from the normalization condition for the psi-function:

$$\int \psi^* \psi dV = \int (RY)^* (RY) \rho^2 \sin \vartheta d\rho d\vartheta d\varphi = 1$$

Let us write this condition as follows:

$$\int_0^\infty R_{nl}^2 \rho^2 d\rho \int Y_{lm}^* Y_{lm} \sin \vartheta d\vartheta d\varphi = 1$$

(the function R_{nl} is real). The spherical functions are normalized to unity. We thus arrive at the normalization condition for R_{nl} :

$$\int_0^\infty R_{nl}^2 \rho^2 d\rho = 1 \quad (24.31)$$

Calculations by this formula give the following values for the coefficient a_0 : $2Z^{3/2}$ for R_{10} , $Z^{3/2}/\sqrt{2}$ for R_{20} , and $Z^{3/2}/2\sqrt{6}$ for R_{21} ¹.

A volume element in spherical coordinates is determined by the expression $dV = \rho^2 \sin \vartheta d\rho d\vartheta d\varphi = \rho^2 d\rho d\Omega$ (here $d\Omega$ is an element of a solid angle; dV is the volume cut out from a spherical layer of radius ρ and thickness $d\rho$ by the solid angle $d\Omega$). The probability of an electron being detected within this volume is

$$dP_{\rho, \vartheta, \varphi} = |\psi|^2 dV = |Y_{lm}|^2 d\Omega \cdot R_{nl}^2 \rho^2 d\rho \quad (24.32)$$

Integration of this probability over the angles yields

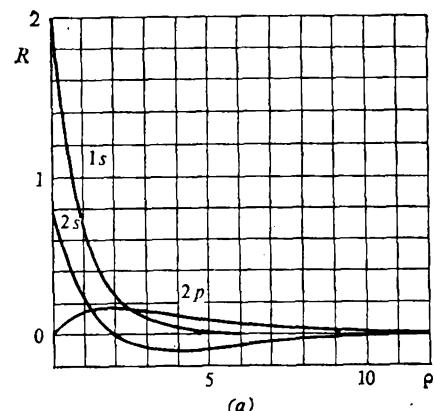
$$dP_\rho = R_{nl}^2 \rho^2 d\rho$$

determining the probability of detecting an electron in a spherical layer of thickness $d\rho$, i.e. at a distance from the nucleus ranging from ρ to $\rho + d\rho$. Accordingly, the expression $R_{nl}^2 \rho^2$ is the density of the probability that the electron is at a distance ρ from the nucleus. For the ground state of a hydrogen atom ($n = 1$, $l = 0$, $Z = 1$), the function $R_{10}^2 \rho^2 = a_0^2 e^{-2\rho} \rho^2$. It is not difficult to see that the maximum of this function is achieved when $\rho = 1$. Thus, the Bohr radius is the distance from the nucleus at which the probability of detecting the electron is the greatest in the ground state of a hydrogen atom.

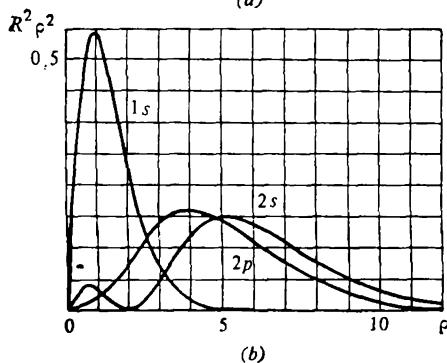
¹ If we introduce $\rho = r/r_0$ [see (24.6)] into (24.31), the factor $1/r_0^3$ will appear in front of the integral. Accordingly, the above values of a_0 must be multiplied by $(1/r_0)^{3/2}$.

Figure 24.1a shows plots of the functions R_{nl} we have found above for the states $1s$ ($n = 1, l = 0$), $2s$ ($n = 2, l = 0$), and $2p$ ($n = 2, l = 1$); Z has been taken equal to unity. We must note that the radial quantum number $n_r = n - l - 1$ gives the number of nodes of the function R_{nl} , i.e. the number of intersections of the plot of this function with the ρ -axis (except for the origin of coordinates). Figure 24.1b shows plots of the probability density $R_{nl}^2 \rho^2$ for the same states.

If we integrate expression (24.32) with respect to ρ from 0 to ∞ , we obtain the probability of finding the electron within the limits of the solid angle $d\Omega$ (at any distance from the force centre). In view of (24.31), this probability is



(a)



(b)

Fig. 24.1

The expression $|Y_{lm}|^2$ is the density of the probability that the electron will be detected in a direction determined by the angles θ and φ . It follows from the form of the function $Y_{lm}(\theta, \varphi)$ [see formula (19.9)] that the square of its magnitude does not depend on the angle φ . Therefore, the density of the probability of detecting the electron in a certain direction is symmetric relative to the z -axis.

Figure 24.2 contains polar diagrams characterizing the distribution of the probability depending on the angle θ for the s - and p -states of an electron. The values of $|Y_{lm}|^2$ are determined by the length of the segment cut off by the diagram on a ray drawn from the origin of

coordinates at the angle θ . To obtain a spatial distribution of the probability, we must rotate the diagrams depicted in the figure about the z -axis. It must be noted that the form of the diagrams of $|Y_{lm}|^2$ does not depend on the quantum number n . Moreover, these diagrams have the same appearance for both a Coulomb field and a non-Coulomb centrally symmetric field.

Using formulas (19.12) and (24.28)-(24.30), we shall write several first psi-functions of a hydrogen-like ion:

$$\left. \begin{aligned} \psi_{100} &= \left(\frac{Z}{r_0} \right)^{3/2} \frac{1}{\sqrt{\pi}} e^{-Zr/r_0} \\ \psi_{200} &= \left(\frac{Z}{r_0} \right)^{3/2} \frac{1}{4\sqrt{2\pi}} e^{-Zr/2r_0} \left(2 - \frac{r}{r_0} \right) \\ \psi_{211} &= - \left(\frac{Z}{r_0} \right)^{3/2} \frac{1}{8\sqrt{\pi}} e^{-Zr/2r_0} \left(\frac{r}{r_0} \right) e^{i\varphi} \sin \theta \\ \psi_{210} &= \left(\frac{Z}{r_0} \right)^{3/2} \frac{1}{4\sqrt{2\pi}} e^{-Zr/2r_0} \left(\frac{r}{r_0} \right) \cos \theta \\ \psi_{21-1} &= \left(\frac{Z}{r_0} \right)^{3/2} \frac{1}{8\sqrt{\pi}} e^{-Zr/2r_0} \left(\frac{r}{r_0} \right) e^{-i\varphi} \sin \theta \end{aligned} \right\} \quad (24.33)$$

To obtain the psi-functions for a hydrogen atom, we must assume that $Z = 1$ in these formulas.

Up to now, we have treated the motion of an electron in the field of a stationary nucleus. Actually, however, both the electron and

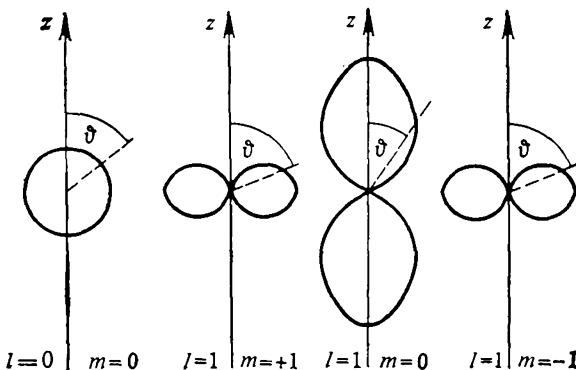


Fig. 24.2

the nucleus move about the centre of mass of the system. We shall show that in quantum mechanics, as in classical mechanics, the problem of two interacting particles (the two-body problem) reduces to a problem of a particle moving in a central force field, the mass of this particle being taken equal to the reduced mass $m_{\text{red}} = m_1 m_2 / (m_1 + m_2)$.

In classical mechanics, the energy of a system consisting of two interacting particles is

$$E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + U(r)$$

Here m_1 and m_2 are the masses of the particles, \mathbf{p}_1 and \mathbf{p}_2 are their momenta, $U(r)$ is the energy of interaction, and r is the distance between the particles. Accordingly, the Hamiltonian of the system has the form

$$\hat{H} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + U(r) \quad (24.34)$$

where $\nabla_1^2 = \Delta_1$ is the sum of the second partial derivatives with respect to the coordinates of the first particle, and $\nabla_2^2 = \Delta_2$ is the sum of similar derivatives with respect to the coordinates of the second particle.

Let us introduce instead of the position vectors \mathbf{r}_1 and \mathbf{r}_2 of the particles the vector \mathbf{r} of the mutual arrangement of the particles and the position vector \mathbf{r}_C of the centre of mass of the system. The vectors we have introduced are related to \mathbf{r}_1 and \mathbf{r}_2 by the expressions

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1, \quad \mathbf{r}_C = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}$$

or in Cartesian coordinates

$$\begin{aligned} x &= x_2 - x_1, \quad x_C = \frac{m_1 x_1}{m_1 + m_2} + \frac{m_2 x_2}{m_1 + m_2} \\ &\dots \dots \dots \dots \dots \dots \dots \end{aligned} \quad (24.35)$$

By relations (24.35), we have

$$\begin{aligned} \frac{\partial}{\partial x_1} &= \frac{\partial}{\partial x} \frac{\partial x}{\partial x_1} + \frac{\partial}{\partial x_C} \frac{\partial x_C}{\partial x_1} = -\frac{\partial}{\partial x} + \frac{m_1}{m_1 + m_2} \frac{\partial}{\partial x_C} \\ \frac{\partial^2}{\partial x_1^2} &= \left(\frac{\partial}{\partial x_1} \right)^2 = \left(-\frac{\partial}{\partial x} + \frac{m_1}{m_1 + m_2} \frac{\partial}{\partial x_C} \right)^2 \\ &= \frac{\partial^2}{\partial x^2} - \frac{2m_1}{m_1 + m_2} \frac{\partial^2}{\partial x \partial x_C} + \left(\frac{m_1}{m_1 + m_2} \right)^2 \frac{\partial^2}{\partial x_C^2} \end{aligned} \quad (24.36)$$

Similarly

$$\begin{aligned} \frac{\partial}{\partial x_2} &= \frac{\partial}{\partial x} \frac{\partial x}{\partial x_2} + \frac{\partial}{\partial x_C} \frac{\partial x_C}{\partial x_2} = \frac{\partial}{\partial x} + \frac{m_2}{m_1 + m_2} \frac{\partial}{\partial x_C} \\ \frac{\partial^2}{\partial x_2^2} &= \left(\frac{\partial}{\partial x_2} \right)^2 = \left(\frac{\partial}{\partial x} + \frac{m_2}{m_1 + m_2} \frac{\partial}{\partial x_C} \right)^2 \\ &= \frac{\partial^2}{\partial x^2} + \frac{2m_2}{m_1 + m_2} \frac{\partial^2}{\partial x \partial x_C} + \left(\frac{m_2}{m_1 + m_2} \right)^2 \frac{\partial^2}{\partial x_C^2} \end{aligned} \quad (24.37)$$

Dividing (24.36) by m_1 and (24.37) by m_2 and summatting the expressions obtained, we arrive at the relation

$$\frac{1}{m_1} \frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2} \frac{\partial^2}{\partial x_2^2} = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial x^2} + \frac{1}{m_1 + m_2} \frac{\partial^2}{\partial x_C^2}$$

The same relations are obtained for the derivatives with respect to y and z . We thus conclude that

$$\frac{1}{m_1} \nabla_1^2 + \frac{1}{m_2} \nabla_2^2 = \frac{1}{m_{\text{red}}} \nabla_r^2 + \frac{1}{m_1 + m_2} \nabla_C^2$$

where $m_{\text{red}} = m_1 m_2 / (m_1 + m_2)$, ∇_r^2 is the Laplacian operator with respect to the components of the vector \mathbf{r} , and ∇_C^2 is the Laplacian operator with respect to the components of the vector \mathbf{r}_C .

Substitution into (24.34) yields

$$\hat{H} = -\frac{\hbar^2}{2(m_1 + m_2)} \nabla_C^2 - \frac{\hbar^2}{2m_{\text{red}}} \nabla_r^2 + U(r) \quad (24.38)$$

The Hamiltonian thus breaks up into the sum of two independent Hamiltonians, one of which contains the total mass of the system and the position vector of the centre of mass, and the second contains the reduced mass and the vector of the mutual arrangement of the particles.

We write the Schrödinger equation:

$$-\frac{\hbar^2}{2(m_1 + m_2)} \nabla_C^2 \psi - \frac{\hbar^2}{2m_{\text{red}}} \nabla_r^2 \psi + U(r) \psi = E \psi$$

We shall seek its solution in the form of the product of two functions

$$\psi = \psi_C \cdot \psi_r$$

where ψ_C is a function of \mathbf{r}_C , and ψ_r is a function of \mathbf{r} . Substitution into the equation yields

$$-\frac{\hbar^2}{2(m_1 + m_2)} \psi_r \nabla_C^2 \psi_C - \frac{\hbar^2}{2m_{\text{red}}} \psi_C \nabla_r^2 \psi_r + U(r) \psi_C \psi_r = E \psi_C \psi_r$$

Dividing by $\psi_C \psi_r$, we obtain

$$\left\{ -\frac{\hbar^2}{2(m_1 + m_2)} \frac{1}{\psi_C} \nabla_C^2 \psi_C \right\} + \left\{ -\frac{\hbar^2}{2m_{\text{red}}} \frac{1}{\psi_r} \nabla_r^2 \psi_r + U(r) \right\} = E$$

The expression in the first braces depends only on \mathbf{r}_C , and that in the second braces only on \mathbf{r} . The sum of these expressions at any values of \mathbf{r}_C and \mathbf{r} must equal the constant quantity E . This is possible only if each of the expressions equals its own constant, and the sum of these constants is E . Consequently, we arrive at two differential equations:

$$-\frac{\hbar^2}{2(m_1 + m_2)} \nabla_C^2 \psi_C = E_C \psi_C \quad (24.39)$$

$$-\frac{\hbar^2}{2m_{\text{red}}} \nabla_r^2 \psi_r + U(r) \psi_r = E_r \psi_r \quad (24.40)$$

(here $E_C + E_r = E$).

Equation (24.39) is the Schrödinger equation for a free particle having the mass $m_1 + m_2$. It is evident that E_C is the kinetic energy

of motion of the system as a whole. Equation (24.40) differs from the Schrödinger equation for an electron in a central force field only in containing the reduced mass of the electron and the nucleus instead of the mass of the electron. The quantity E_r is the internal energy of the system (atom).

Consequently, when we take into consideration the motion of a nucleus, we must write m_{red} instead of m_e in all the formulas, particularly in expression (24.23), for E_n . Otherwise, the results we have obtained remain unchanged.

25. The Harmonic Oscillator

A harmonic oscillator is defined to be a particle with one degree of freedom whose potential energy is expressed by the formula

$$U(x) = \frac{kx^2}{2} = \frac{m_0\omega^2 x^2}{2} \quad (25.1)$$

where m_0 is the mass of the particle, k is the quasielastic force coefficient, and ω is the natural (classical) frequency of the oscillator equal to $\sqrt{k/m_0}$.

The Schrödinger equation [see (5.8)] in the given case is as follows:

$$\frac{d^2\psi}{dx^2} + \frac{2m_0}{\hbar^2} \left(E - \frac{m_0\omega^2 x^2}{2} \right) \psi = 0 \quad (25.2)$$

To simplify the form of Eq. (25.2), let us go over to the dimensionless variable

$$\xi = x \sqrt{\frac{m_0\omega}{\hbar}} \quad (25.3)$$

The result is the differential equation

$$\frac{d^2\psi}{d\xi^2} + \left(\frac{2E}{\hbar\omega} - \xi^2 \right) \psi = 0 \quad (25.4)$$

At very great values of ξ , the quantity $2E/\hbar\omega$ may be disregarded in comparison with ξ^2 . Equation (25.4) is therefore simplified as follows:

$$\psi'' - \xi^2\psi = 0 \quad (25.5)$$

The asymptotic solutions of this equation at $\xi \rightarrow \infty$ have the form $e^{\pm\xi^2/2}$. Indeed,

$$\frac{d^2}{d\xi^2} e^{\pm\xi^2/2} = (\xi^2 \pm 1) e^{\pm\xi^2/2} \approx \xi^2 e^{\pm\xi^2/2}$$

so that Eq. (25.5) is satisfied. Since we are seeking finite solutions, the exponent with the plus sign must be discarded.

Hence, the solution of Eq. (25.4) behaves at $\xi \rightarrow \infty$ as $e^{-\xi^2/2}$. We shall therefore seek the solution in the form

$$\psi(\xi) = e^{-\xi^2/2} f(\xi) \quad (25.6)$$

Substitution of expression (25.6) into Eq. (25.4) leads to the following differential equation for $f(\xi)$:

$$f''(\xi) - 2\xi f'(\xi) + \left(\frac{2E}{\hbar\omega} - 1\right) f(\xi) = 0 \quad (25.7)$$

Solutions of equations of this kind are found in Appendix III. In formula (III.1), the coefficient at $f(\xi)$ is designated by the letter λ . Consequently, when using the results obtained in this Appendix, we must have in view that

$$\frac{2E}{\hbar\omega} - 1 = \lambda \quad (25.8)$$

By formula (III.8), the eigenvalues of the parameter λ equal $2n$. Hence follows the condition

$$\frac{2E}{\hbar\omega} - 1 = 2n \quad (n = 0, 1, 2, \dots)$$

determining the possible values of the oscillator's energy:

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right) \quad (n = 0, 1, 2, \dots) \quad (25.9)$$

We must note that the energy of a harmonic oscillator cannot be zero. The minimum value $E_0 = \hbar\omega/2$ is said to be the zero energy.

The Chebyshev-Hermite polynomials determined by formula (III.11)

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} (e^{-\xi^2}) \quad (n = 0, 1, 2, \dots) \quad (25.10)$$

are the eigenfunctions of Eq. (25.7). To obtain the eigenfunctions of an oscillator, we must multiply the polynomials (25.10) by the exponent $e^{-\xi^2/2}$ [see (25.6)]. Hence,

$$\psi_n(\xi) = A_n e^{-\xi^2/2} H_n(\xi) \quad (25.11)$$

The coefficient A_n must be determined from the normalization condition. By formula (III.20), we have

$$\int_{-\infty}^{+\infty} \psi_n^* \psi_n d\xi = A_n^2 \int_{-\infty}^{+\infty} e^{-\xi^2} [H_n(\xi)]^2 d\xi = A_n^2 n! 2^n \sqrt{\pi} \quad (25.12)$$

Therefore, for the functions $\psi_n(\xi)$ to be normalized to unity, we must assume that $A_n = [n! 2^n \sqrt{\pi}]^{-1/2}$, so that

$$\psi_n(\xi) = [n! 2^n \sqrt{\pi}]^{-1/2} e^{-\xi^2/2} H_n(\xi) \quad (25.13)$$

By formula (III.19) when $n \neq m$, we have

$$\int_{-\infty}^{+\infty} \psi_n^* \psi_m d\xi = A_n A_m \int_{-\infty}^{+\infty} e^{-\xi^2} H_n(\xi) H_m(\xi) d\xi = 0$$

Consequently, the system of functions (25.13) is orthonormal.

Only one function $\psi_n(\xi)$ corresponds to each value of the energy E_n (to each value of n). Hence, the energy levels of an oscillator are not degenerate.

The eigenfunctions (25.13) are expressed in terms of the dimensionless variable ξ . To go over to the variable x , we must replace ξ in accordance with (25.3). Such a substitution in the formula expressing the condition of normalization of the function (25.12) yields

$$\begin{aligned} & \int_{-\infty}^{+\infty} [\psi_n(x)]^2 dx \\ &= [n! 2^n \sqrt{\pi}]^{-1} \int_{-\infty}^{+\infty} e^{-m_0\omega x^2/\hbar} [H_n(x \sqrt{m_0\omega/\hbar})]^2 \sqrt{m_0\omega/\hbar} dx = 1 \end{aligned}$$

From a comparison of the integrands, we obtain the following expression for $\psi_n(x)$:

$$\psi_n(x) = \alpha^{1/2} [n! 2^n \sqrt{\pi}]^{-1/2} e^{-\alpha^2 x^2/2} H_n(\alpha x) \quad (25.14)$$

where

$$\alpha = \sqrt{\frac{m_0\omega}{\hbar}} \quad (25.15)$$

Using formulas (III.24)-(III.27), we shall write expressions for the first four functions $\psi_n(x)$:

$$\psi_0(x) = \alpha^{1/2} [\sqrt{\pi}]^{-1/2} e^{-\alpha^2 x^2/2} \quad (25.16)$$

$$\psi_1(x) = \alpha^{1/2} [2 \sqrt{\pi}]^{-1/2} e^{-\alpha^2 x^2/2} 2\alpha x \quad (25.17)$$

$$\psi_2(x) = \alpha^{1/2} [8 \sqrt{\pi}]^{-1/2} e^{-\alpha^2 x^2/2} (4\alpha^2 x^2 - 2) \quad (25.18)$$

$$\psi_3(x) = \alpha^{1/2} [48 \sqrt{\pi}]^{-1/2} e^{-\alpha^2 x^2/2} (8\alpha^3 x^3 - 12\alpha x) \quad (25.19)$$

Figure 25.1a shows plots of these functions, and Fig. 25.1b, plots of the functions $[\psi_n(x)]^2$. The latter plots determine the density of the probability of detecting an oscillator at a point with the coordinate x .

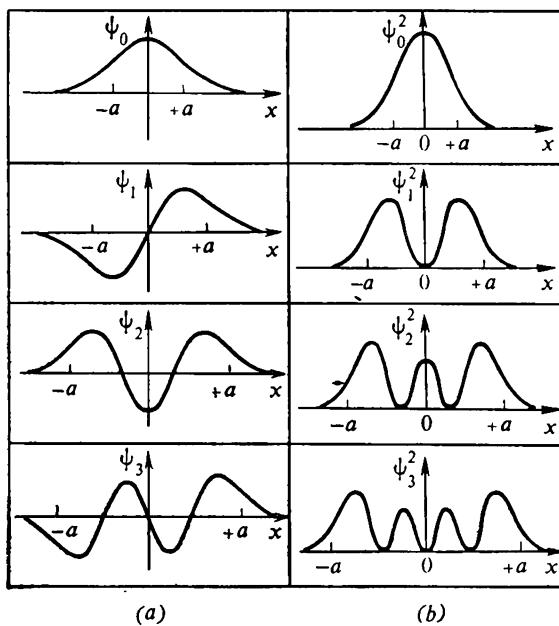


Fig. 25.1

The points $-a$ and $+a$ indicated on the x -axis correspond to the maximum deflections (amplitudes) of a classical oscillator. The values of a are obtained from the relation $E_n = m_0 a^2 \omega^2 / 2$.

26. Solution of the Harmonic Oscillator Problem in the Matrix Form

In quantum electrodynamics, an electromagnetic field is represented in the form of the superposition of independent quantum oscillators. In this connection, the harmonic oscillator problem is very important. We shall therefore consider its solution in the matrix form. Moreover, this problem was solved for the first time by W. Heisenberg in 1925 with the aid of the matrix method.

The potential energy of an oscillator is determined by the expression $U = m_0 \omega^2 x^2 / 2$. Let us write the equation of motion of an oscillator in the form of (21.15). Taking into account that $\partial U / \partial x = m_0 \omega^2 x$, we obtain the operator equation

$$\hat{x} + \omega^2 x = 0 \quad (26.1)$$

This equation is identical in form with the classical equation for an oscillator (recall that $\hat{x} = x$).

Designating the functions of the stationary states of an oscillator (i.e. the eigenfunctions of the operator \hat{H}) by the symbol ψ_n [$\psi_n = \psi_n(x)$], we can write by (26.1)

$$\int_{-\infty}^{+\infty} \psi_m^* (\ddot{\hat{x}} + \omega^2 x) \psi_n dx = \int_{-\infty}^{+\infty} \psi_m^* \ddot{x} \psi_n dx + \omega^2 \int_{-\infty}^{+\infty} \psi_m^* x \psi_n dx = 0$$

The first integral is a matrix element of the acceleration, i.e. $(\ddot{x})_{mn}$, the second integral is the matrix element of the coordinate, i.e. x_{mn} . We have thus arrived at an equation of motion in the matrix form:

$$(\ddot{x})_{mn} + \omega^2 x_{mn} = 0 \quad (26.2)$$

By formula (22.14), $(\ddot{x})_{mn} = -\omega_{mn}^2 x_{mn}$. Substitution of this expression into (26.2) yields

$$(\omega^2 - \omega_{mn}^2) x_{mn} = 0 \quad (26.3)$$

Since the eigenfunctions of the operator \hat{H} were used to calculate the matrix elements, we shall solve the problem in the energy representation. In this representation, the energy matrix is diagonal, and the diagonal elements of the matrix equal the eigenvalues of the energy. The Hamiltonian of an oscillator is

$$\hat{H} = \frac{\hat{p}_x^2}{2m_0} + \frac{m_0 \omega^2 x^2}{2} = \frac{m_0 \dot{x}^2}{2} + \frac{m_0 \omega^2 x^2}{2} \quad (26.4)$$

To any operator equation there corresponds an analogous matrix equation. This can be verified readily by premultiplying [as we did in deriving Eq. (26.2)] the operator equation by ψ_m^* , postmultiplying it by ψ_n , and integrating the relation obtained. The equation

$$H_{mn} = E_{mn} = \frac{m_0}{2} (\dot{x})_{mn} + \frac{m_0 \omega^2}{2} (x^2)_{mn}$$

corresponds to Eq. (26.4). With a view to formula (10.31), we obtain

$$E_{mn} = \frac{m_0}{2} \sum_k (\dot{x})_{mk} (\dot{x})_{kn} + \frac{m_0 \omega^2}{2} \sum_k x_{mk} x_{kn}$$

Finally, making the substitution $(\dot{x})_{mn} = i\omega_{mn} x_{nn}$ [see (22.9)] and combining the two sums into a single one, we arrive at the following formula:

$$E_{mn} = \frac{m_0}{2} \sum_k (\omega^2 - \omega_{mk} \omega_{kn}) x_{mk} x_{kn} \quad (26.5)$$

Hence, to find the eigenvalues of the energy, we must calculate the frequencies ω_{mn} and the matrix elements x_{mn} .

A glance at formula (26.3) shows that only those elements x_{mn} can be non-zero for which

$$\omega_{mn} = \pm \omega \quad (26.6)$$

By (22.1), the "frequency of the transition" between the states ψ_m and ψ_n is related to the energies of the states by the expression

$$\omega_{mn} = \frac{E_m - E_n}{\hbar} \quad (26.7)$$

Consequently, condition (26.6) signifies that only those x_{mn} 's are non-zero that correspond to "transitions" between states with energies differing by $\hbar\omega$. Let us number the stationary states (i.e. the functions ψ_n and the energy values E_n) so that the subscripts for the states with energies differing by $\hbar\omega$ differ by unity, the energies of the states increasing with the number n . In accordance with (26.7), this signifies that the numbering must be chosen so that

$$\omega_{n+1, n} = \omega, \quad \omega_{n-1, n} = -\omega \quad (26.8)$$

Hence, only the elements $x_{n+1, n}$ and $x_{n-1, n}$ will be non-zero. To find these elements we shall use rule (16.1) for commutation of the operators $\hat{x} = x$ and $\hat{p}_x = m_0 \dot{x}$, according to which $[\hat{x}, \hat{p}_x] = \hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar$. Therefore,

$$\hat{x}\hat{x} - \hat{x}\hat{x} = \frac{i\hbar}{m_0} \quad (26.9)$$

Going over in the way indicated above from the operator relation (26.9) to the matrix one, we obtain

$$(\dot{xx})_{mn} - (\dot{xx})_{mn} = \frac{i\hbar}{m_0} \delta_{mn}$$

Particularly, when $m = n$, we have

$$(\dot{xx})_{nn} - (\dot{xx})_{nn} = \frac{i\hbar}{m_0}$$

Using formula (10.30), we can write that

$$\sum_k x_{nk} (\dot{x})_{kn} - \sum_k (\dot{x})_{nk} x_{kn} = \frac{i\hbar}{m_0}$$

Let us make the substitution $(\dot{x})_{mn} = i\omega_{mn}x_{mn}$ [see (22.9)]:

$$i \sum_k x_{nk} \omega_{kn} x_{kn} - i \sum_k \omega_{nk} x_{nk} x_{kn} = \frac{i\hbar}{m_0}$$

Cancelling imaginary unity and taking into account that $x_{mn} = x_{nm}^*$ because of the Hermitian nature of the matrix, we arrive at the formula

$$\sum_k \omega_{kn} x_{kn}^* x_{kn} - \sum_k \omega_{nk} x_{kn}^* x_{kn} = \frac{\hbar}{m_0}$$

Finally, taking into account that $\omega_{nk} = -\omega_{kn}$ [see (26.7)], we obtain

$$2 \sum_k \omega_{kn} |x_{kn}|^2 = \frac{\hbar}{m_0}$$

In this sum, only two addends are non-zero. In one of them, $k = n + 1$ and, consequently, $\omega_{kn} = \omega_{n+1,n} = \omega$, and in the other $k = n - 1$ and $\omega_{kn} = \omega_{n-1,n} = -\omega$ [see (26.8)]. Hence,

$$2(\omega |x_{n+1,n}|^2 - \omega |x_{n-1,n}|^2) = \frac{\hbar}{m_0} \quad (26.10)$$

Since $x_{n-1,n} = x_{n,n-1}^*$, we have $|x_{n-1,n}|^2 = |x_{n,n-1}|^2$. Making such a substitution in (26.10), we arrive at the relation

$$|x_{n+1,n}|^2 = |x_{n,n-1}|^2 + \frac{\hbar}{2m_0\omega} \quad (26.11)$$

Inspection of formula (26.11) shows that the squares of the magnitudes of the matrix elements form an arithmetic progression with no upper limit. The lower limit of the progression is determined by the requirement that all its terms be greater than zero. The first term of the progression is the square of the magnitude of the matrix element whose smaller subscript coincides with the number of the ground state (the state with the lowest energy). We have meanwhile imposed only one restriction on the numbering of the states—we have arranged the psi-functions in a series of increasing numbers so that the condition $\omega_{mn} = \pm\omega$ is satisfied for a pair of functions whose numbers differ by unity and, in addition, so that an increase in the number of a state is attended by a growth in its energy E_n . But we shall meanwhile leave the question of what number should be assigned to the ground state open. In principle, this number can be assumed to equal, say, -12 or $+8$. It is natural, however, to assign the number zero or unity to the ground state. It is customary practice to assign the number zero to it.

With this choice of the number of the ground state, all the psi-functions with negative numbers will be identically equal to zero (no corresponding states exist). Therefore, say,

$$x_{0,-1} = \int_{-\infty}^{+\infty} \psi_0^* x \psi_{-1} dx = 0$$

Similarly, all $x_{n,n-1}$'s with negative values of n will be zero.

Introducing the values $x_{0,-1} = 0$ into the right-hand side of relation (26.11), we obtain $|x_{10}|^2 = \hbar/2m_0\omega$. Next, introducing this value into the right-hand side, we obtain $|x_{21}|^2 = 2\hbar/2m_0\omega$, and so on. We thus arrive at the formula

$$|x_{n,n-1}|^2 = |x_{n-1,n}|^2 = \frac{n\hbar}{2m_0\omega} \quad (26.12)$$

Let us assume that the matrix elements $x_{n,n-1}$ are real. The correctness of this assumption will be confirmed by the fact that it will not lead us to any contradictions. We thus obtain the following expression¹ from (26.12) for the matrix elements of the coordinate:

$$x_{n,n-1} = x_{n-1,n} = \sqrt{\frac{n\hbar}{2m_0\omega}} \quad (26.13)$$

The matrix of the coordinate of a harmonic oscillator has the form

$$(x_{mn}) = \sqrt{\frac{\hbar}{2m_0\omega}} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \dots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & \dots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \dots \\ 0 & 0 & \sqrt{3} & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (26.14)$$

By (22.9), we have $(\dot{x})_{mn} = i\omega_{mn}x_{mn}$. The matrix x_{mn} is symmetric; the factor ω_{mn} in transposition of the subscripts reverses its sign. Therefore, $(\dot{x})_{mn} = -(\dot{x})_{nm}$, i.e. the velocity matrix is anti-symmetric. With a view to (26.8) and (26.13), we obtain

$$(\dot{x})_{n,n-1} = i\sqrt{\frac{n\hbar\omega}{2m_0}}, \quad (\dot{x})_{n-1,n} = -i\sqrt{\frac{n\hbar\omega}{2m_0}} \quad (26.15)$$

Multiplying expression (26.15) by the mass of an oscillator m_0 , we can find the matrix elements of the momentum. The momentum matrix is as follows:

$$((p_x)_{mn}) = i\sqrt{\frac{m_0\hbar\omega}{2}} \begin{pmatrix} 0 & -\sqrt{1} & 0 & 0 & \dots \\ \sqrt{1} & 0 & -\sqrt{2} & 0 & \dots \\ 0 & \sqrt{2} & 0 & -\sqrt{3} & \dots \\ 0 & 0 & \sqrt{3} & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (26.16)$$

¹ Upon introducing negative values of n into formula (26.13), we obtain a non-zero imaginary quantity. This would seem to contradict the above statement that the $x_{n,n-1}$'s with negative n 's equal zero. It must be remembered, however, that expression (26.13) has been obtained from formula (26.12) which holds only when $n \geq 0$, so that the introduction of negative values of n into formula (26.13) is illegitimate.

Now let us find the matrix of the energy of an oscillator with the aid of formula (26.5). We shall first see what the values of E_{mn} are for $m \neq n$. When $m - n > 2$ and $n - m > 2$, all the addends of the sum (26.5) will be zero either because of the factor x_{mk} or because of the factor x_{kn} . The same occurs when $m - n = 1$ and $n - m = 1$. When $m - n = 2$, only the product $x_{mk}x_{kn}$ in which $m - 1 = k = n + 1$ is non-zero, but in this condition the factor in parentheses is $(\omega^2 - \omega_{m,m-1}\omega_{n+1,n}) = 0$ [see (26.8)], so that $E_{mn} = 0$. We can see in a similar way that when $n - m = 2$, expression (26.5) also becomes equal to zero. All the results we have obtained could have been foreseen because the energy matrix in its eigenrepresentation must be diagonal.

Let us calculate the diagonal elements of the matrix. Assuming in (26.5) that $m = n$, we obtain

$$\begin{aligned} E_{nn} &= (m_0/2) \sum_k (\omega^2 - \omega_{nk}\omega_{kn}) x_{nk}x_{kn} \\ &= (m_0/2) \sum_k (\omega^2 + \omega_{nk}^2) x_{nk}^2 = m_0\omega^2 \sum_k x_{nk}^2 \end{aligned}$$

(recall that $\omega_{nk} = -\omega_{kn}$, $\omega_{nk}^2 = \omega^2$, $x_{nk} = x_{kn}$). In the sum we have obtained, only the addends with $k = n - 1$ and $k = n + 1$ are non-zero. Consequently,

$$E_{nn} = m_0\omega^2 [(x_{n,n-1})^2 + (x_{n,n+1})^2]$$

Let us introduce into this equation the values of the matrix elements determined by formula (26.13):

$$E_{nn} = m_0\omega^2 \left[\frac{n\hbar}{2m_0\omega} + \frac{(n+1)\hbar}{2m_0\omega} \right] = \frac{\hbar\omega}{2} (2n+1)$$

The diagonal matrix elements equal the eigenvalues of the energy operator. We can therefore write that

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) \quad (n = 0, 1, 2, \dots) \quad (26.17)$$

[compare with formula (25.9)]. The energy matrix has the form

$$(E_{mn}) = \hbar\omega \begin{pmatrix} 1/2 & 0 & 0 & 0 & \dots \\ 0 & 3/2 & 0 & 0 & \dots \\ 0 & 0 & 5/2 & 0 & \dots \\ 0 & 0 & 0 & 7/2 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (26.18)$$

To find the eigenfunctions of an oscillator, we shall take advantage of the circumstance that the formula

$$\hat{Q}\psi_n = \sum_m Q_{mn} \psi_m \quad (26.19)$$

[see (10.5)] holds for any operator. Let us take as \hat{Q} the operators $(\dot{x} + i\omega x)$ and $(\dot{x} - i\omega x)$. All the matrix elements of these operators are clearly equal to zero except those having the subscripts $n - 1$, n , and $n + 1$, n . Therefore, formula (26.19) for these operators is as follows:

$$\left. \begin{aligned} \hat{(\dot{x} + i\omega x)} \psi_n &= (\dot{x} + i\omega x)_{n-1, n} \psi_{n-1} + (\dot{x} + i\omega x)_{n+1, n} \psi_{n+1} \\ \hat{(\dot{x} - i\omega x)} \psi_n &= (\dot{x} - i\omega x)_{n-1, n} \psi_{n-1} + (\dot{x} - i\omega x)_{n+1, n} \psi_{n+1} \end{aligned} \right\} \quad (26.20)$$

To simplify writing of the expressions, we shall introduce the symbol

$$\beta = \frac{\hbar\omega}{2m_0} \quad (26.21)$$

Hence, by formulas (26.13) and (26.15), we have

$$(\dot{x} + i\omega x)_{n-1, n} = (\dot{x})_{n-1, n} + i\omega x_{n-1, n} = -i\sqrt{n\beta} + i\sqrt{n\beta} = 0$$

$$(\dot{x} + i\omega x)_{n+1, n} = i\sqrt{(n+1)\beta} + i\sqrt{(n+1)\beta} = 2i\sqrt{(n+1)\beta}$$

Reversing the sign in front of i in these formulas, we obtain

$$\begin{aligned} (\dot{x} - i\omega x)_{n-1, n} &= -2i\sqrt{n\beta} \\ (\dot{x} - i\omega x)_{n+1, n} &= 0 \end{aligned}$$

Introducing into formulas (26.20) the expression for the velocity operator, i.e. $\dot{x} = (-i\hbar/m_0) \partial/\partial x$ and the found values of the matrix elements, we arrive at the differential equations

$$\left[-\left(\frac{\hbar}{m_0} \right) \frac{\partial}{\partial x} + \omega x \right] \psi_n = 2\sqrt{(n+1)\beta} \psi_{n+1} \quad (26.22)$$

$$\left[-\left(\frac{\hbar}{m_0} \right) \frac{\partial}{\partial x} - \omega x \right] \psi_n = -2\sqrt{n\beta} \psi_{n-1} \quad (26.23)$$

Equation (26.23) can be used to find the function ψ_0 . Since $\psi_{-1} \equiv 0$, we obtain the equation

$$\left(\frac{\hbar}{m_0} \right) \frac{\partial \psi_0}{\partial x} + \omega x \psi_0 = 0$$

Writing this equation in the form

$$\frac{\psi'_0}{\psi_0} = -\frac{m_0\omega}{\hbar} x$$

we easily obtain the expression

$$\psi_0 = A \exp \left(-\frac{m_0\omega x^2}{2\hbar} \right) \quad (26.24)$$

that coincides with (25.16). Taking into consideration the value of the Poisson integral

$$\int_{-\infty}^{+\infty} e^{-\gamma x^2} dx = \sqrt{\pi/\gamma}$$

we can see that the constant A has the same value as in formula (25.15).

Equation (26.22) can be used as a recurrence formula. For this purpose, we can rewrite it as follows:

$$\psi_{n+1} = \frac{1}{\sqrt{2(n+1)}} \left(-\sqrt{\frac{\hbar}{m_0\omega}} \frac{\partial}{\partial x} + \sqrt{\frac{m_0\omega}{\hbar}} x \right) \psi_n$$

Finally, going over to the dimensionless variable $\xi = x \sqrt{m_0\omega/\hbar}$ [see (25.3)] and decreasing the numbers of the functions by unity (i.e. replacing n with $n - 1$), we obtain the formula

$$\psi_n = \frac{1}{\sqrt{2n}} \left(-\frac{\partial}{\partial \xi} + \xi \right) \psi_{n-1}$$

that can be represented in the form

$$\psi_n = -\frac{1}{\sqrt{2n}} e^{\xi^2/2} \frac{d}{d\xi} (e^{-\xi^2/2} \psi_{n-1}) \quad (26.25)$$

Substituting the value (26.22) for ψ_0 into this formula, we can find ψ_1 , then ψ_2 , and so on.

The eigenfunctions were found to be real. Therefore, the matrix elements $x_{n,n-1} = \int \psi_n^* x \psi_{n-1} dx = \int \psi_n x \psi_{n-1} dx$ will also be real. This confirms the correctness of our assumption that $x_{n,n-1}$ is real.

27. Annihilation and Creation Operators

The problem of a harmonic oscillator can be solved very elegantly by introducing the adjoint operators \hat{a} and \hat{a}^+ determined with the aid of the following relations:

$$\left. \begin{aligned} \hat{a} &= \frac{1}{\sqrt{2}} \left(\sqrt{\frac{m_0\omega}{\hbar}} \hat{x} + \frac{i}{\sqrt{m_0\hbar\omega}} \hat{p}_x \right) \\ \hat{a}^+ &= \frac{1}{\sqrt{2}} \left(\sqrt{\frac{m_0\omega}{\hbar}} \hat{x} - \frac{i}{\sqrt{m_0\hbar\omega}} \hat{p}_x \right) \end{aligned} \right\} \quad (27.1)$$

The adjoint character of these operators follows from the circumstance that the operators \hat{x} and \hat{p}_x are self-adjoint. Consequently, $\hat{x}^+ = \hat{x}$, and $\hat{p}_x^+ = \hat{p}_x$. In addition, $(i\hat{p}_x)^+ = -i\hat{p}_x^+$ [see (10.13)].

The form of the operators (27.1) is greatly simplified if we introduce instead of the coordinate x the dimensionless variable ξ determined by the relation $\xi = x \sqrt{m_0\omega/\hbar}$ [see (25.3)]. Making this substitution in expressions (27.1) and taking into account that

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} = -i\hbar \sqrt{m_0\omega/\hbar} \frac{\partial}{\partial \xi}$$

we arrive at the formulas

$$\hat{a} = \frac{1}{\sqrt{2}} \left(\xi + \frac{\partial}{\partial \xi} \right) \quad (27.2)$$

$$\hat{a}^+ = \frac{1}{\sqrt{2}} \left(\xi - \frac{\partial}{\partial \xi} \right) \quad (27.3)$$

As applied to the operators designated by the letter a (lower-case), we shall treat the sign “+” of an adjoint operator simply as a superscript allowing us to distinguish the operators (27.2) and (27.3). In this connection, we shall not adhere to the rule according to which an adjoint operator is written at the right of the function on which it acts. Accordingly, we shall write the condition for these operators to be adjoint in the form

$$\langle \varphi | \hat{a} \psi \rangle = \langle \hat{a}^+ \varphi | \psi \rangle \quad (27.4)$$

[see (8.4)], and not in the form of (8.5).

We shall show below that by acting on the psi-functions of a harmonic oscillator, the operator \hat{a} transforms the function ψ_n into ψ_{n-1} :

$$\hat{a} \psi_n = \sqrt{n} \psi_{n-1} \quad (27.5)$$

that is, diminishes the energy of an oscillator, as it were, by a “quantum” $\hbar\omega$. It is therefore called the **annihilation operator**. The operator \hat{a}^+ transforms the function ψ_n into ψ_{n+1} :

$$\hat{a}^+ \psi_n = \sqrt{n+1} \psi_{n+1} \quad (27.6)$$

i.e. increases, as it were, the oscillator energy by $\hbar\omega$, and in this connection it is called the **creation operator**¹.

Let us find the commutator of the operators \hat{a} and \hat{a}^+ :

$$\begin{aligned} [\hat{a}, \hat{a}^+] &= \hat{a}\hat{a}^+ - \hat{a}^+\hat{a} = \frac{1}{2} [(\xi + \partial/\partial\xi)(\xi - \partial/\partial\xi) - (\xi - \partial/\partial\xi)(\xi + \partial/\partial\xi)] \\ &= \frac{1}{2} [(\xi^2 + \partial/\partial\xi \cdot \xi - \xi \cdot \partial/\partial\xi - \partial^2/\partial\xi^2) \\ &\quad - (\xi^2 - \partial/\partial\xi \cdot \xi + \xi \cdot \partial/\partial\xi - \partial^2/\partial\xi^2)] = \partial/\partial\xi \cdot \xi - \xi \cdot \partial/\partial\xi = 1 \end{aligned} \quad (27.7)$$

¹ We shall disclose the meaning of the terms “creation operator” and “annihilation operator” completely when dealing with second quantization (see Sec. 50).

(compare with the commutator of the operators $\partial/\partial x$ and x , p. 43). The commutator thus equals unity:

$$[\hat{a}, \hat{a}^+] = \hat{a}\hat{a}^+ - \hat{a}^+\hat{a} = 1 \quad (27.8)$$

Substituting plus for minus in the brackets of expression (27.7), we find that

$$\hat{a}\hat{a}^+ + \hat{a}^+\hat{a} = \xi^2 - \frac{\partial^2}{\partial \xi^2}$$

It is not difficult to see that the operator we have obtained is proportional to the Hamiltonian of an oscillator expressed in terms of the variable ξ . Indeed,

$$\hat{H} = \frac{\hat{p}_\xi^2}{2m_0} + \frac{m_0\omega^2 x^2}{2} = -\frac{\hbar^2}{2m_0} \frac{\partial^2}{\partial x^2} + \frac{m_0\omega^2 x^2}{2}$$

Making the substitution $\xi = x\sqrt{m_0\omega/\hbar}$, we arrive at the expression

$$\hat{H} = \frac{\hbar\omega}{2} \left(\xi^2 - \frac{\partial^2}{\partial \xi^2} \right)$$

from which it follows that

$$\hat{H} = \frac{\hbar\omega}{2} (\hat{a}\hat{a}^+ + \hat{a}^+\hat{a}) \quad (27.9)$$

Taking into account the commutation rule (27.8), we can write the Hamiltonian as

$$\hat{H} = \hbar\omega \left(\hat{a}\hat{a}^+ - \frac{1}{2} \right) \quad (27.10)$$

or as

$$\hat{H} = \hbar\omega \left(\hat{a}^+\hat{a} + \frac{1}{2} \right) \quad (27.11)$$

In accordance with the meaning of the Hamiltonian, we have

$$\hat{H}\psi_n = E_n\psi_n \quad (27.12)$$

where ψ_n is the eigenfunction of the oscillator, and E_n is its energy. Let us attempt to act with the operator \hat{H} on the function $\hat{a}\psi_n$ obtained as a result of the action of the operator \hat{a} on the function ψ_n . Taking the Hamiltonian in the form of (27.10), we obtain

$$\begin{aligned} \hat{H}(\hat{a}\psi_n) &= \hbar\omega \left(\hat{a}\hat{a}^+ - \frac{1}{2} \right) (\hat{a}\psi_n) = \hbar\omega \left(\hat{a}\hat{a}^+\hat{a}\psi_n - \frac{1}{2} \hat{a}\psi_n \right) \\ &= \hat{a}\hbar\omega \left[\left(\hat{a}^+\hat{a} + \frac{1}{2} \right) - 1 \right] \psi_n \end{aligned}$$

We have given the expression this form to allow us to write, using formula (27.11),

$$\hat{H}(\hat{a}\psi_n) = \hat{a}(\hat{H} - \hbar\omega)\psi_n = \hat{a}(\hat{H}\psi_n) - \hbar\omega\hat{a}\psi_n$$

Finally, performing the substitution (27.12), we arrive at the relation

$$\hat{H}(\hat{a}\psi_n) = \hat{a}(E_n\psi_n) - \hbar\omega\hat{a}\psi_n = E_n\hat{a}\psi_n - \hbar\omega\hat{a}\psi_n$$

from which we obtain the equation

$$\hat{H}(\hat{a}\psi_n) = (E_n - \hbar\omega)(\hat{a}\psi_n)$$

The result we have arrived at signifies that the function $\hat{a}\psi_n$ is the eigenfunction ψ_m of an oscillator corresponding to the eigenvalue of the energy $E_m = E_n - \hbar\omega$. Having numbered the states of the oscillator in the order of the growth in their energy and assuming that there are no other allowed energy values between E_n and E_m , we must assume that $m = n - 1$. As a result, we find that

$$\hat{a}\psi_n = C\psi_{n-1}, \quad E_{n-1} = E_n - \hbar\omega \quad (27.13)$$

The coefficient C must be determined so that the functions ψ_n and ψ_{n-1} are normalized to unity. We have thus proved the correctness of the statement that the action of the operator \hat{a} transforms the function ψ_n into ψ_{n-1} [see (27.5)].

Now let us attempt to act with the operator \hat{H} on the function $\hat{a}^+\psi_n$. We shall take the operator in the form of (27.11):

$$\begin{aligned} \hat{H}(\hat{a}^+\psi_n) &= \hbar\omega \left(\hat{a}^+\hat{a} + \frac{1}{2} \right) (\hat{a}^+\psi_n) = \hat{a}^+ \hbar\omega \left[\left(\hat{a}\hat{a}^+ - \frac{1}{2} \right) + 1 \right] \psi_n \\ &= \hat{a}^+ (\hat{H} + \hbar\omega) \psi_n = \hat{a}^+ (E_n + \hbar\omega) \psi_n = (E_n + \hbar\omega)(\hat{a}^+\psi_n) \end{aligned}$$

The result obtained signifies that

$$\hat{a}^+\psi_n = C'\psi_{n+1}, \quad E_{n+1} = E_n + \hbar\omega \quad (27.14)$$

We have thus proved the statement contained in formula (27.6).

Let us evaluate a diagonal matrix element of the operator \hat{H} , taking this operator in the form of (27.11):

$$\begin{aligned} H_{nn} &= \hbar\omega \left\langle \psi_n \mid \left(\hat{a}^+\hat{a} + \frac{1}{2} \right) \psi_n \right\rangle = \hbar\omega \langle \psi_n \mid \hat{a}^+ (\hat{a}\psi_n) \rangle \\ &+ \frac{\hbar\omega}{2} \langle \psi_n \mid \psi_n \rangle = \hbar\omega \langle \hat{a}\psi_n \mid \hat{a}\psi_n \rangle + \frac{\hbar\omega}{2} = \hbar\omega \int_{-\infty}^{+\infty} |\hat{a}\psi_n|^2 d\xi + \frac{\hbar\omega}{2} \end{aligned}$$

[see formulas (10.3) and (27.4)]. We have thus arrived at the relation

$$E_n = H_{nn} = \hbar\omega \int_{-\infty}^{+\infty} |\hat{a}\psi_n|^2 d\xi + \frac{\hbar\omega}{2} \quad (27.15)$$

inspection of which shows that the energy of an oscillator cannot be less than $\hbar\omega/2$.

Let us assign the subscript $n = 0$ to the state with the lowest energy. The function corresponding to it will be ψ_0 . There are no states with a lower energy. Hence, for all negative \hbar 's, the functions $\psi_h \equiv 0$. Particularly, ψ_{-1} also identically equals zero. Let us write Eq. (27.13) for $n = 0$:

$$\hat{a}\psi_0 = C\psi_{-1} \equiv 0 \quad (27.16)$$

Substitution of the value (27.16) for $\hat{a}\psi_0$ into (27.15) yields the value $\hbar\omega/2$ for $E_0 = H_{00}$. We have established that the interval between adjacent levels is $\hbar\omega$. Consequently,

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega \quad (27.17)$$

A comparison of expressions (27.15) and (27.17) leads us to the conclusion that

$$\int_{-\infty}^{+\infty} |\hat{a}\psi_n|^2 d\xi = n$$

Replacing, according to (27.13), $\hat{a}\psi_n$ with $C\psi_{n-1}$, we obtain the relation

$$|C|^2 \int_{-\infty}^{+\infty} |\psi_{n-1}|^2 d\xi = n$$

If we assume that ψ_{n-1} is normalized to unity, we obtain a value equal to \sqrt{n} for $|C|$. Owing to the arbitrary nature of the phase factor, we assume that C equals \sqrt{n} . Substitution of this value into (27.13) leads to formula (27.5).

To find the value of the coefficient C' in formula (27.14), let us introduce into the expression for H_{nn} the operator \hat{H} in the form of (27.10):

$$\begin{aligned} H_{nn} &= \hbar\omega \left\langle \psi_n \left| \left(\hat{a}\hat{a}^\dagger - \frac{1}{2} \right) \psi_n \right. \right\rangle = \hbar\omega \langle \psi_n | \hat{a} (\hat{a}^\dagger \psi_n) \rangle - \frac{\hbar\omega}{2} \\ &= \hbar\omega \langle \hat{a}^\dagger \psi_n | \hat{a}^\dagger \psi_n \rangle - \frac{\hbar\omega}{2} \end{aligned}$$

Hence,

$$H_{nn} = \hbar\omega \int_{-\infty}^{+\infty} |\hat{a}^+ \psi_n|^2 d\xi - \frac{\hbar\omega}{2}$$

A comparison of this expression with (27.17) yields

$$\int_{-\infty}^{+\infty} |\hat{a}^+ \psi_n|^2 d\xi = n + 1$$

whence with a view to (27.14), we have

$$|C'|^2 \int_{-\infty}^{+\infty} |\psi_{n+1}|^2 d\xi = n + 1$$

Consequently, we obtain the value $\sqrt{n+1}$ for the constant C' in formula (27.14), and we arrive at relation (27.6).

Introducing expression (27.2) for \hat{a} into Eq. (27.16), we obtain the following differential equation:

$$\frac{\partial \psi_0}{\partial \xi} + \xi \psi_0 = 0, \quad \text{or} \quad \frac{\psi'_0}{\psi_0} = -\xi$$

The solution of this equation is

$$\psi_0 = A e^{-\xi^2/2}$$

From the normalization condition

$$\int_{-\infty}^{+\infty} |\psi_0|^2 d\xi = |A|^2 \int_{-\infty}^{+\infty} e^{-\xi^2} d\xi = |A|^2 \sqrt{\pi} = 1$$

we find that $A = \pi^{-1/4}$ (we drop the factor of the form $e^{i\alpha}$). Hence,

$$\psi_0 = \pi^{-1/4} e^{-\xi^2/2}$$

[compare with $\psi_0(\xi)$ obtained from formula (25.12) when $n = 0$].

The other functions can be obtained from ψ_0 by the consecutive action of the operator \hat{a}^+ . From (27.6), we obtain the formula

$$\psi_{n+1} = \frac{1}{\sqrt{n+1}} \hat{a}^+ \psi_n$$

with the aid of which we find that

$$\psi_1 = \frac{1}{\sqrt{0+1}} \hat{a}^+ \psi_0 = \frac{1}{\sqrt{1!}} \hat{a}^+ \psi_0$$

$$\psi_2 = \frac{1}{\sqrt{1+1}} \hat{a}^+ \psi_1 = \frac{1}{\sqrt{2!}} \hat{a}^+ (\hat{a}^+ \psi_0) = \frac{1}{\sqrt{2!}} (\hat{a}^+)^2 \psi_0$$

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$$\psi_n = \cdot = \frac{1}{\sqrt{n!}} (\hat{a}^+)^n \psi_0$$

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The procedure we have used to find the functions ψ_n coincides in essence with the method used to determine ψ_n in Sec. 26. Notwithstanding their similarity, however, we have considered it expedient to set out both methods.

Chapter VI

PERTURBATION THEORY

28. Introduction

An exact solution of Schrödinger's equation is possible only for a small number of very simple force fields. Most problems in quantum mechanics allow only an approximate solution. We often find, however, that real physical systems do not differ very greatly from idealized systems allowing an exact solution. In these cases, the approximate solution of the problem on the eigenfunctions and eigenvalues consists in finding corrections to the exact solution of the idealized problem. The general method of calculating these corrections is known as the **perturbation theory**.

Hence, the perturbation theory is one of the ways of approximately solving quantum-mechanical problems. It is used when the deviation of the system being considered from the system allowing an exact solution can be represented as a small correction (perturbation) to the Hamiltonian of the unperturbed system.

The corrections to the eigenfunctions and eigenvalues are represented as the sum of quantities of different orders of smallness, next the corrections of the same order of smallness as the perturbation are evaluated, then the corrections that are quadratic with respect to the perturbation, and so on. Consequently, the method of the perturbation theory is in essence a method of successive approximations.

The perturbation theory is divided into **stationary** and **non-stationary** theory. The former (also called the perturbation theory for stationary states) deals with time-independent perturbations. The non-stationary theory (also called the **variation method**) deals with systems whose Hamiltonian depends explicitly on the time.

29. Time-Independent Perturbations

In this section, we shall set out the fundamentals of the perturbation theory for stationary problems with a discrete energy spectrum. For the states of a physical system being considered to be stationary, its Hamiltonian \hat{H} must not contain the time explicitly.

The perturbation theory can be used to solve a given problem if the Hamiltonian \hat{H} allows breaking up into two terms:

$$\hat{H} = \hat{H}_0 + \hat{V} \quad (29.1)$$

where \hat{H}_0 is the Hamiltonian of the problem allowing an exact solution, and \hat{V} is a small correction known as the **perturbation operator** (the exact meaning of the definition "small" will be revealed in the following). We shall call the operator \hat{H}_0 an **unperturbed Hamiltonian**. By our assumption, both terms do not depend explicitly on the time.

The eigenfunctions of the operator \hat{H}_0 will be designated by the symbol $\psi_n^{(0)}$, and its eigenvalues, by the symbol $E_n^{(0)}$. These eigenvalues are assumed to be non-degenerate. The following relation holds:

$$\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \quad (29.2)$$

We shall designate the eigenfunctions and eigenvalues of the operator \hat{H} by ψ_n and E_n , respectively. With a view to (29.1), we can write that

$$(\hat{H}_0 + \hat{V}) \psi_n = E_n \psi_n \quad (29.3)$$

According to our assumption, Eq. (29.2) has an exact solution, whereas Eq. (29.3) does not allow an exact solution. We shall seek an approximate solution of Eq. (29.3) in the form of the series

$$E_n = E_n^{(0)} + \Delta E_n^{(1)} + \Delta E_n^{(2)} + \dots \quad (29.4)$$

$$\psi_n = \psi_n^{(0)} + \Delta \psi_n^{(1)} + \Delta \psi_n^{(2)} + \dots \quad (29.5)$$

where $\Delta E_n^{(1)}$ and $\Delta \psi_n^{(1)}$ are corrections of the same order of smallness as the perturbation, $\Delta E_n^{(2)}$ and $\Delta \psi_n^{(2)}$ are quadratic with respect to the perturbation, etc.

Let us expand the function ψ_n in the eigenfunctions $\psi_k^{(0)}$ of the unperturbed operator \hat{H}_0 :

$$\psi_n = \sum_k c_{nk} \psi_k^{(0)} \quad (n = 1, 2, \dots) \quad (29.6)^1$$

The task of finding the functions (29.5) consists in determining the coefficients c_{nk} . We shall also seek the approximate values of these coefficients in the form of the series

$$c_{nk} = c_{nk}^{(0)} + \Delta c_{nk}^{(1)} + \Delta c_{nk}^{(2)} + \dots \quad (29.7)$$

Substitution of expression (29.7) into formula (29.6) yields

$$\psi_n = \sum_k c_{nk}^{(0)} \psi_k^{(0)} + \sum_k \Delta c_{nk}^{(1)} \psi_k^{(0)} + \sum_k \Delta c_{nk}^{(2)} \psi_k^{(0)} + \dots \quad (29.8)$$

¹ It must be borne in mind that the quantities c_{nk} cannot be treated as elements of a square matrix. The set of coefficients c_{nk} forms a multitude of column matrices differing from one another in the values of n .

In the zero approximation, we have $\psi_n = \psi_n^{(0)}$ [see (29.5)]. To obtain this result, we must assume that $c_{nk}^{(0)} = \delta_{nk}$. Therefore, the series (29.7) is as follows:

$$c_{nk} = \delta_{nk} + \Delta c_{nk}^{(1)} + \Delta c_{nk}^{(2)} + \dots \quad (29.9)$$

To make the order of each approximation more obvious, we introduce the notation

$$\hat{V} = \lambda \hat{W} \quad (29.10)$$

where \hat{W} is an operator of the same order of magnitude as \hat{H}_0 , and λ is a small dimensionless parameter. With such notation, the expressions containing λ to the first power will be of the same order of smallness as the perturbation; the expressions containing λ^2 will be quadratic with respect to the perturbation, etc. In the final formulas, we shall pass over from the auxiliary operator \hat{W} to the perturbation operator \hat{V} , replacing $\lambda \hat{W}$ with \hat{V} .

Accordingly, let us write the series (29.4) and (29.9) in the form

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (29.11)$$

$$c_{nk} = \delta_{nk} + \lambda c_{nk}^{(1)} + \lambda^2 c_{nk}^{(2)} + \dots \quad (29.12)$$

where $E_n^{(0)}$, $E_n^{(2)}$, ... are quantities of the same order as $E_n^{(0)}$, and $c_{nk}^{(1)}$, $c_{nk}^{(2)}$ are quantities of the order of unity.

The substitution of the series (29.12) into formula (29.6) leads to the expression

$$\psi_n = \psi_n^{(0)} + \lambda \sum_k c_{nk}^{(1)} \psi_k^{(0)} + \lambda^2 \sum_k c_{nk}^{(2)} \psi_k^{(0)} + \dots \quad (29.13)$$

[compare with (29.5)].

The introduction of expression (29.10) instead of the operator \hat{V} gives Eq. (29.3) the form

$$(\hat{H}_0 + \lambda \hat{W}) \psi_n = E_n \psi_n \quad (29.14)$$

Let us substitute into this equation expressions (29.11) and (29.13) for E_n and ψ_n . We obtain

$$\begin{aligned} (\hat{H}_0 + \lambda \hat{W}) (\psi_n^{(0)} + \lambda \sum_k c_{nk}^{(1)} \psi_k^{(0)} + \lambda^2 \sum_k c_{nk}^{(2)} \psi_k^{(0)} + \dots) \\ = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) \\ \times (\psi_n^{(0)} + \lambda \sum_k c_{nk}^{(1)} \psi_k^{(0)} + \lambda^2 \sum_k c_{nk}^{(2)} \psi_k^{(0)} + \dots) \end{aligned}$$

Opening the parentheses, we collect together terms of the same order of smallness:

$$\begin{aligned}
 & \hat{H}_0 \psi_n^{(0)} + \lambda \left(\sum_k c_{nk}^{(1)} \hat{H}_0 \psi_k^{(0)} + \hat{W} \psi_n^{(0)} \right) \\
 & + \lambda^2 \left(\sum_k c_{nk}^{(2)} \hat{H}_0 \psi_k^{(0)} + \sum_k c_{nk}^{(1)} \hat{W} \psi_k^{(0)} \right) + \dots \\
 & = E_n^{(0)} \psi_n^{(0)} + \lambda \left(E_n^{(0)} \sum_k c_{nk}^{(1)} \psi_k^{(0)} + E_n^{(1)} \psi_n^{(0)} \right) \\
 & + \lambda^2 \left(E_n^{(0)} \sum_k c_{nk}^{(2)} \psi_k^{(0)} + E_n^{(1)} \sum_k c_{nk}^{(1)} \psi_k^{(0)} + E_n^{(2)} \psi_n^{(0)} \right) + \dots
 \end{aligned}$$

Let us substitute, in accordance with (29.2), $E_l^{(0)} \psi_l^{(0)}$ for expressions of the kind $\hat{H}_0 \psi_l^{(0)}$ (as a result of which the first terms will cancel out), and then perform scalar multiplication of both sides of the equation by $\psi_m^{(0)}$:

$$\begin{aligned}
 & \lambda \left(\sum_k c_{nk}^{(1)} E_k^{(0)} \langle \psi_m^{(0)} | \psi_k^{(0)} \rangle + \langle \psi_m^{(0)} | \hat{W} \psi_n^{(0)} \rangle \right) \\
 & + \lambda^2 \left(\sum_k c_{nk}^{(2)} E_k^{(0)} \langle \psi_m^{(0)} | \psi_k^{(0)} \rangle + \sum_k c_{nk}^{(1)} \langle \psi_m^{(0)} | \hat{W} \psi_k^{(0)} \rangle \right) + \dots \\
 & = \lambda \left(E_n^{(0)} \sum_k c_{nk}^{(1)} \langle \psi_m^{(0)} | \psi_k^{(0)} \rangle + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle \right) \\
 & + \lambda^2 \left(E_n^{(0)} \sum_k c_{nk}^{(2)} \langle \psi_m^{(0)} | \psi_k^{(0)} \rangle + E_n^{(1)} \sum_k c_{nk}^{(1)} \langle \psi_m^{(0)} | \psi_k^{(0)} \rangle \right. \\
 & \quad \left. + E_n^{(2)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle \right) + \dots \quad (29.15)
 \end{aligned}$$

The expression

$$W_{mk} = \langle \psi_m^{(0)} | \hat{W} \psi_k^{(0)} \rangle \quad (29.16)$$

is a matrix element of the operator \hat{W} in the " $E^{(0)}$ -representation". Using the notation (29.16) and taking into account that $\langle \psi_r^{(0)} | \psi_s^{(0)} \rangle = \delta_{rs}$, we give formula (29.15) the form

$$\begin{aligned}
 & \lambda \left(\sum_k c_{nk}^{(1)} E_k^{(0)} \delta_{mk} + W_{mn} \right) + \lambda^2 \left(\sum_k c_{nk}^{(2)} E_k^{(0)} \delta_{mk} + \sum_k c_{nk}^{(1)} W_{mk} \right) + \dots \\
 & = \lambda \left(E_n^{(0)} \sum_k c_{nk}^{(1)} \delta_{mk} + E_n^{(1)} \delta_{mn} \right) \\
 & + \lambda^2 \left(E_n^{(0)} \sum_k c_{nk}^{(2)} \delta_{mk} + E_n^{(1)} \sum_k c_{nk}^{(1)} \delta_{mk} + E_n^{(2)} \delta_{mn} \right) + \dots
 \end{aligned}$$

In the sums containing δ_{mk} , only the addend with $k = m$ is non-zero. Hence,

$$\begin{aligned} & \lambda(c_{nm}^{(1)}E_m^{(0)} + W_{mn}) + \lambda^2(c_{nm}^{(2)}E_m^{(0)} + \sum_k c_{nk}^{(1)}W_{mk}) + \dots \\ & = \lambda(E_n^{(0)}c_{nm}^{(1)} + E_n^{(1)}\delta_{mn}) + \lambda^2(E_n^{(0)}c_{nm}^{(2)} + E_n^{(1)}c_{nm}^{(1)} + E_n^{(2)}\delta_{mn}) + \dots \end{aligned} \quad (29.17)$$

Equating the coefficients of identical powers of λ on the left-hand and right-hand sides of Eq. (29.17), we obtain a series of algebraic equations:

$$W_{mn} = (E_n^{(0)} - E_m^{(0)})c_{nm}^{(1)} + E_n^{(1)}\delta_{nm} \quad (29.18)$$

$$\sum_k c_{nk}^{(1)}W_{mk} = (E_n^{(0)} - E_m^{(0)})c_{nm}^{(2)} + E_n^{(1)}c_{nm}^{(1)} + E_n^{(2)}\delta_{nm} \quad (29.19)$$

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Assuming in Eq. (29.18) that $m = n$, we find that

$$E_n^{(1)} = W_{nn} \quad (29.20)$$

whence it follows that in the first approximation

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} = E_n^{(0)} + \lambda W_{nn} = E_n^{(0)} + V_{nn} \quad (29.21)$$

[see (29.11) and (29.10)]. We must note that the first-order correction to $E_n^{(0)}$ equal to

$$\Delta E_n^{(1)} = V_{nn} = \langle \psi_n^{(0)} | \hat{V} \psi_n^{(0)} \rangle \quad (29.22)$$

is exactly the mean value of the perturbation in the state described by the unperturbed function $\psi_n^{(0)}$.

Assuming in (29.18) that $m \neq n$, we arrive at the relation $W_{mn} = (E_n^{(0)} - E_m^{(0)})c_{nm}^{(1)}$, from which

$$c_{nm}^{(1)} = \frac{W_{mn}}{E_n^{(0)} - E_m^{(0)}} \quad (m \neq n) \quad (29.23)$$

Consequently, in the first approximation

$$c_{nm} = c_{nm}^{(0)} + \lambda c_{nm}^{(1)} = \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} \quad (m \neq n) \quad (29.24)$$

This formula gives the values of all the coefficients c_{nm} except c_{nn} . The latter coefficient must be chosen so that the function ψ_n is normalized to within the terms of the order of λ .

Substitution of (29.24) into expression (29.6) yields

$$\psi_n = c_{nn}\psi_n^{(0)} + \sum_m' \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \quad (29.25)$$

(the prime on the sum symbol indicates that only addends for which $m \neq n$ are taken). Let us calculate the scalar square of the function (29.25), representing V_{mn} in the form $V_{mn} = \lambda W_{mn}$:

$$\begin{aligned}\langle \psi_n | \psi_n \rangle &= \left\langle \left(c_{nn} \psi_n^{(0)} + \lambda \sum_m' \frac{W_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \right) \middle| \left(c_{nn} \psi_n^{(0)} \right. \right. \\ &\quad \left. \left. + \lambda \sum_k' \frac{W_{kn}}{E_n^{(0)} - E_k^{(0)}} \psi_k^{(0)} \right) \right\rangle \\ &= \langle c_{nn} \psi_n^{(0)} | c_{nn} \psi_n^{(0)} \rangle + \lambda \sum_h' \left\langle c_{nn} \psi_n^{(0)} \middle| \frac{W_{hn}}{E_n^{(0)} - E_h^{(0)}} \psi_h^{(0)} \right\rangle \\ &\quad + \lambda \sum_m' \left\langle \frac{W_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \middle| c_{nn} \psi_n^{(0)} \right\rangle \\ &\quad + \lambda^2 \sum_{m,k}' \left\langle \frac{W_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \middle| \frac{W_{kn}}{E_n^{(0)} - E_k^{(0)}} \psi_k^{(0)} \right\rangle \quad (29.26)\end{aligned}$$

The first term in the expression we have obtained is equal to $\langle c_{nn} \psi_n^{(0)} | c_{nn} \psi_n^{(0)} \rangle = c_{nn}^* c_{nn} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = c_{nn}^* c_{nn} = |c_{nn}|^2$. The second term can be transformed to

$$\lambda \sum_k' c_{nn}^* \frac{W_{kn}}{E_n^{(0)} - E_k^{(0)}} \langle \psi_n^{(0)} | \psi_k^{(0)} \rangle$$

Since in summation the value $k = n$ is excluded, all the addends of the last sum vanish (because of δ_{nn}). Similarly, we can show that the sum \sum_m' in expression (29.26) also vanishes.

We want to normalize the function ψ_n to within terms of the order of λ . We may therefore disregard the term in (29.26) that is proportional to λ^2 . We thus arrive at the conclusion that with the required accuracy, $\langle \psi_n | \psi_n \rangle = |c_{nn}|^2$. Consequently, for the function ψ_n to be normalized, the magnitude of c_{nn} must equal unity: $|c_{nn}|^2 = 1$. Since the psi-function is determined to within an arbitrary phase factor, we can assume¹ that $c_{nn} = 1$. We must note that in accordance with (29.12), the equality of c_{nn} to unity signifies that

$$c_{nn}^{(1)} = 0 \quad (29.27)$$

Assuming in (29.25) that $c_{nn} = 1$, we obtain the final expression for ψ_n in the first approximation:

$$\psi_n = \psi_n^{(0)} + \sum_m' \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \quad (29.28)$$

¹ We assume that $c_{nn} = e^{-i\alpha}$. Then, multiplying ψ_n by the phase factor $e^{i\alpha}$, we make c_{nn} equal unity.

Hence, in the first approximation, the eigenvalues and eigenfunctions of the operator (29.1) are calculated by formulas (29.21) and (29.28).

Let us go over to finding the energy in the second approximation. Assuming in Eq. (29.19) that $m = n$, we find that

$$\sum_k c_{nk}^{(1)} W_{nk} = E_n^{(1)} c_{nn}^{(1)} + E_n^{(2)}$$

whence

$$E_n^{(2)} = -E_n^{(1)} c_{nn}^{(1)} + c_{nn}^{(1)} W_{nn} + \sum'_k c_{nk}^{(1)} W_{nk}$$

(we have separated the term with $k = n$ from the sum). But $c_{nn}^{(1)} = 0$ [see (29.27)]. Therefore,

$$E_n^{(2)} = \sum'_k c_{nk}^{(1)} W_{nk}$$

Substitution of the value (29.23) for $c_{nk}^{(1)}$ yields

$$E_n^{(2)} = \sum'_k \frac{W_{nk} W_{kn}}{E_n^{(0)} - E_k^{(0)}}$$

By (29.11), the correction to the energy quadratic with respect to the perturbation is

$$\Delta E_n^{(2)} = \lambda^2 E_n^{(2)} = \sum'_k \frac{(\lambda W_{nk})(\lambda W_{kn})}{E_n^{(0)} - E_k^{(0)}} = \sum'_k \frac{V_{nk} V_{kn}}{E_n^{(0)} - E_k^{(0)}} = \sum'_k \frac{|V_{nk}|^2}{E_n^{(0)} - E_k^{(0)}}$$

(owing to the Hermitian nature, $V_{kn} = V_{nk}^*$). Consequently,

$$\Delta E_n^{(2)} = \sum'_m \frac{|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}} \quad (29.29)$$

[we have used the letter m instead of k for the dummy index to make the notation in formulas (29.28) and (29.29) coincide]. By adding the correction found to expression (29.21), we determine the energy in the second approximation:

$$E_n = E_n^{(0)} + V_{nn} + \sum'_m \frac{|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}} \quad (29.30)$$

The energy of the ground state is minimum. Therefore, if the subscript n takes on a value corresponding to the ground state, in all the terms of expression (29.29) $E_n^{(0)} < E_m^{(0)}$. It thus follows that a second-order correction to the energy of the ground state is always negative.

We shall not calculate the psi-functions in the second approximation because it is customary practice to evaluate the energy in the second approximation, and the psi-functions in the first approxi-

mation. It is sometimes necessary, however, to resort to approximations of higher orders.

The above method can lead to a correct result if the series of successive approximations will be converging¹. A necessary condition for convergence is the smallness of each higher-order correction in comparison with the preceding one. It is not difficult to conclude from formula (29.30) that for $\Delta E_n^{(2)}$ to be much smaller than $\Delta E_n^{(1)}$, the inequality

$$|V_{nm}| \ll |E_n^{(0)} - E_m^{(0)}| \quad (29.31)$$

must hold for all $m \neq n$. Consequently, a condition for perturbation theory applicability is the requirement that the non-diagonal elements of the matrix V be small in comparison with the differences of the relevant values of the unperturbed energy.

When degeneracy is present, the same energy value is realized in several different states, for instance, in the n -th and m -th ones [$E_n^{(0)} = E_m^{(0)}$]. Therefore, infinitely large terms appear in formulas (29.28) and (29.30). Consequently, the method of calculation set out in this section cannot be used when degeneracy is present.

Let us consider as an illustration to the method of calculation treated above the perturbation of the energy levels of a harmonic oscillator when a small addend quadratic in x is imparted to the potential energy. This example, in particular, is interesting in that it allows us to obtain exact values of the energy in a perturbation problem and compare them with the approximate values obtained by the method of the perturbation theory.

Recall that the levels of an oscillator are not degenerate so that all the formulas of the present section hold. In the example being considered

$$\begin{aligned}\hat{H}_0 &= \frac{\hbar}{2m_0} \frac{d^2}{dx^2} + \frac{ax^2}{2} \quad (a = m_0\omega^2) \\ \hat{V} &= \frac{bx^2}{2} \quad (b \ll a), \\ E_n^{(0)} &= \left(n + \frac{1}{2}\right) \hbar\omega\end{aligned}$$

(see Sec. 25).

The matrix elements V_{nm} can be written as

$$V_{nm} = \frac{b}{2} (x^2)_{nm} = \frac{b}{2} \sum_k x_{nk} x_{km} \quad (9.32)$$

¹ Sometimes, the first approximations of the perturbation theory also give good results when the series diverges.

[see formula (10.31)]. We established in Sec. 26 that only those matrix elements x_{nm} are non-zero whose subscripts differ by unity, and $x_{n,n-1} = x_{n-1,n} = \sqrt{n\hbar/2m_0\omega}$ [see (26.14) and (26.12)]. Hence, only those addends in (29.32) will be non-zero in which k satisfies one of the following relations:

$$k = n + 1 = m + 1, \quad k = n + 1 = m - 1,$$

$$k = n - 1 = m + 1, \quad k = n - 1 = m - 1$$

The first and fourth relations are realized when $m = n$, the second when $m = n + 2$, and the third when $m = n - 2$. Hence, only the following three matrix elements are non-zero:

$$V_{n,n-2} = (b/2)x_{n,n-1}x_{n-1,n-2} = \alpha\sqrt{n(n-1)}$$

$$V_{n,n} = (b/2)(x_{n,n-1}x_{n-1,n} + x_{n,n+1}x_{n+1,n}) = \alpha(2n+1)$$

$$V_{n,n+2} = (b/2)x_{n,n+1}x_{n+1,n+2} = \alpha\sqrt{(n+1)(n+2)}$$

where $\alpha = (b/2)(\hbar/2m_0\omega) = \hbar\omega(b/a)$.

The substitution of these values of the matrix elements into formulas (29.22) and (29.29) gives the following value of the energy [recall that $E_n^{(0)} - E_m^{(0)} = (n - m)\hbar\omega$]:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega + \alpha(2n+1) + \frac{\alpha^2 n(n-1)}{2\hbar\omega} - \frac{\alpha^2(n+1)(n+2)}{2\hbar\omega}$$

Introduction of the value of α and transformation yield

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \left(1 + \frac{b}{2a} - \frac{b^2}{8a^2}\right) \quad (29.33)$$

At the same time, the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V} = \frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} + \frac{(a+b)x^2}{2}$$

describes an oscillator having the frequency $\omega' = \sqrt{(a+b)/m_0}$, so that the exact value of the energy of the "perturbed" system is

$$\begin{aligned} E_n &= \left(n + \frac{1}{2}\right)\hbar\omega \sqrt{\frac{a+b}{m_0}} = \left(n + \frac{1}{2}\right)\hbar\omega \sqrt{\left(\frac{a}{m_0}\right)\left(1 + \frac{b}{a}\right)} \\ &= \left(n + \frac{1}{2}\right)\hbar\omega \sqrt{1 + \frac{b}{a}} \end{aligned}$$

Expanding this expression in powers of the small quantity b/a , we arrive at the formula

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \left(1 + \frac{b}{2a} - \frac{b^2}{8a^2} + \frac{b^3}{16a^3} - \dots\right)$$

A comparison with (29.33) shows that the value of the energy obtained by the method of the perturbation theory is the expansion of the exact expression for the energy in powers of b/a taken to within the terms of the second order of smallness.

30. Case of Two Close Levels

When among the eigenvalues of the operator \hat{H}_0 there is at least one value of $E_m^{(0)}$ close to $E_n^{(0)}$, the condition (29.31) is not obeyed, the corrections to $\psi_n^{(0)}$ and $E_n^{(0)}$ calculated by formulas (29.28) and (29.29) are large, and these formulas cannot be used. If the number of levels $E_m^{(0)}$ close to $E_n^{(0)}$ is not large, however, it is possible to change the method of calculations so as to prevent the appearance of large corrections. We shall show this on the example of two close levels.

Assume that the levels $E_1^{(0)}$ and $E_2^{(0)}$ are close to each other, and all the other levels are far from them. In this case, the contribution of the function $\psi_2^{(0)}$ to the first-order correction to the function $\psi_1^{(0)}$ will be large [see (29.28)]. The contribution of the function $\psi_1^{(0)}$ to the correction to $\psi_2^{(0)}$ will also be large. It is therefore expedient already in the zero approximation to seek the solution in the form

$$\psi = a\psi_1^{(0)} + b\psi_2^{(0)} \quad (30.1)$$

Introducing this value into the equation $\hat{H}\psi = E\psi$ (where $\hat{H} = \hat{H}_0 + \hat{V}$), we obtain

$$a\hat{H}\psi_1^{(0)} + b\hat{H}\psi_2^{(0)} = aE\psi_1^{(0)} + bE\psi_2^{(0)}$$

We perform scalar multiplication of this relation first by $\psi_1^{(0)}$ and then by $\psi_2^{(0)}$. As a result, we obtain two equations:

$$aH_{11} + bH_{12} = aE, \quad aH_{21} + bH_{22} = bE \quad (30.2)$$

where

$$H_{mn} = \langle \psi_m^{(0)} | \hat{H}\psi_n^{(0)} \rangle = \langle \psi_m^{(0)} | \hat{H}_0\psi_n^{(0)} \rangle + \langle \psi_m^{(0)} | \hat{V}\psi_n^{(0)} \rangle = E_n^{(0)}\delta_{mn} + V_{mn} \quad (30.3)$$

We transform Eqs. (30.2) as follows:

$$\left. \begin{aligned} (H_{11} - E)a + H_{12}b &= 0 \\ H_{21}a + (H_{22} - E)b &= 0 \end{aligned} \right\} \quad (30.4)$$

For this system to have non-zero solutions, its determinant must be zero. Hence we obtain a quadratic equation for E :

$$(H_{11} - E)(H_{22} - E) - H_{12}H_{21} = 0, \quad \text{or}$$

$$E^2 - (H_{11} + H_{22})E + (H_{11}H_{22} - H_{12}H_{21}) = 0$$

The roots of this equation are

$$\left. \begin{aligned} E_1 &= \frac{1}{2} [(H_{11} + H_{22}) + \sqrt{(H_{11} - H_{22})^2 + 4|H_{12}|^2}] \\ E_2 &= \frac{1}{2} [(H_{11} + H_{22}) - \sqrt{(H_{11} - H_{22})^2 + 4|H_{12}|^2}] \end{aligned} \right\} \quad (30.5)$$

(owing to the Hermitian nature, $H_{12} = H_{21}^*$).

Let us investigate expression (30.5) in two limiting cases.

1. We assume that

$$|H_{11} - H_{22}| \gg |H_{12}| \quad (30.6)$$

In accordance with (30.3), this signifies that

$$|(E_1^{(0)} + V_{11}) - (E_2^{(0)} + V_{22})| \approx |E_1^{(0)} - E_2^{(0)}| \gg |V_{12}|$$

i.e. the condition (29.31) for the applicability of the conventional perturbation theory treated in Sec. 29 is observed. In the roughest approximation, we may drop $4|H_{12}|^2$ in the radical in (30.5). The result is

$$E_1 = H_{11} = E_1^{(0)} + V_{11}, \quad E_2 = H_{22} = E_2^{(0)} + V_{22}$$

i.e. the values of the energy in the first approximation of the conventional perturbation theory. In a less rough approximation, i.e. employing the formula $\sqrt{1+x} \approx 1+x/2$ ($x \ll 1$), we obtain

$$\begin{aligned} E_1 &= \frac{1}{2} \left[(H_{11} + H_{22}) + (H_{11} - H_{22}) + \frac{2|H_{12}|^2}{H_{11} - H_{22}} \right] = H_{11} + \frac{|H_{12}|^2}{H_{11} - H_{22}} \\ &= E_1^{(0)} + V_{11} + \frac{|V_{12}|^2}{E_1^{(0)} - E_2^{(0)}} \end{aligned} \quad (30.7)$$

where $E_n^{(1)} = E_n^{(0)} + V_{nn}$.

Similarly

$$E_2 = E_2^{(0)} + V_{22} + \frac{|V_{21}|^2}{E_1^{(0)} - E_2^{(0)}} \quad (30.8)$$

The found values of E_1 and E_2 virtually coincide with those obtained in the second order by the formulas of the conventional perturbation theory. A distinction is that the denominator contains the difference of the energies of the first approximation instead of the zero one and, in addition, that the terms with $m > 2$ are absent. By assumption, however, all other levels are far from $E_1^{(0)}$ and $E_2^{(0)}$ so that their contribution to the sum may be disregarded.

2. We assume that

$$|H_{11} - H_{22}| \ll |H_{12}| \quad (30.9)$$

In this case to within the terms of the first order of smallness, we have

$$E_{1,2} = \frac{H_{11} + H_{22}}{2} \pm \left\{ |H_{12}| + \frac{(H_{11} - H_{22})^2}{|H_{12}|} \right\}$$

Let us investigate the relation between the difference of the energy values determined by formulas (30.5) and the difference $H_{11} - H_{22}$. For this purpose, we assume that

$$H_{11} = H_0 + \gamma x, \quad H_{22} = H_0 - \gamma x \quad (30.10)$$

where γ is a constant coefficient, and x is an independent variable. Consequently,

$$H_{11} - H_{22} = 2\gamma x, \quad H_{11} + H_{22} = 2H_0$$

The relevant substitutions in formulas (30.5) yield

$$E_1 = H_0 + \sqrt{4\gamma^2 x^2 + |H_{12}|^2}, \quad E_2 = H_0 - \sqrt{4\gamma^2 x^2 + |H_{12}|^2} \quad (30.11)$$

Figure 30.1 shows plots of the functions (30.11) (solid lines) and of the functions (30.10) (dashed lines) for a fixed value of $|H_{12}|$. The

difference of the ordinates of the solid and the closest dashed line gives the second-order correction to the energy values. We must note that second-order corrections always increase the distance between levels. In this connection, we sometimes speak of the "repulsion of levels", understanding this to signify the increase in the distance between two close levels appearing because of account being taken in the Hamiltonian of the terms that were dropped in the more simplified problem.

A glance at Fig. 30.1 shows that even when the difference

$H_{11} - H_{22}$ vanishes, there is a difference between E_1 and E_2 equal to $2|H_{12}| = 2|V_{12}|$.

Let us find the psi-functions corresponding to the energy values E_1 and E_2 . For this purpose, we must determine the values of the coefficients a and b in formula (30.1). By the first¹ of equations (30.4), we have

$$\frac{a}{b} = \frac{H_{12}}{E - H_{11}}$$

¹ The same result is obtained if we express the ratio a/b from the second equation.

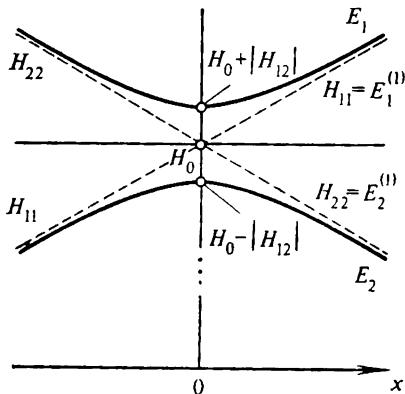


Fig. 30.1

Introducing E_1 and E_2 determined by expressions (30.5) into this equation, we obtain two values of the ratio a/b :

$$\left(\frac{a}{b}\right)_{1,2} = \frac{2H_{12}}{(H_{11}-H_{22})\{-1 \pm \sqrt{1+[2H_{12}/(H_{11}-H_{22})]^2}\}} \quad (30.12)$$

The plus sign in front of the radical corresponds to the subscript 1 on a/b , and the minus sign to the subscript 2. If we introduce the notation

$$\tan 2\alpha = \frac{2H_{12}}{H_{11}-H_{22}} \quad (30.13)$$

formula (30.12) becomes

$$\left(\frac{a}{b}\right)_{1,2} = \frac{\tan 2\alpha}{-1 \pm \sqrt{1+\tan^2 2\alpha}}$$

Simplification of this expression with the aid of trigonometric transformations yields

$$\left(\frac{a}{b}\right)_1 = \cot \alpha, \quad \left(\frac{a}{b}\right)_2 = -\tan \alpha \quad (30.14)$$

For the function (30.1) to be normalized, the relation

$$a^2 + b^2 = 1 \quad (30.15)$$

must be satisfied. It is evident that the conditions (30.14) and (30.15) will be satisfied if we assume that

$$a_1 = \cos \alpha, \quad b_1 = \sin \alpha; \quad a_2 = -\sin \alpha, \quad b_2 = \cos \alpha$$

Substituting these values into formula (30.1), we obtain normalized psi-functions corresponding to the energy values E_1 and E_2 :

$$\begin{aligned} \psi_1 &= \psi_1^{(0)} \cos \alpha + \psi_2^{(0)} \sin \alpha \\ \psi_2 &= -\psi_1^{(0)} \sin \alpha + \psi_2^{(0)} \cos \alpha \end{aligned} \quad \left. \right\} \quad (30.16)$$

By (30.13), when inequality (30.6) holds, we have $\tan 2\alpha \approx 0$, and, consequently, $\psi_1 = \psi_1^{(0)}$ and $\psi_2 = \psi_2^{(0)}$, i.e. the new functions coincide with the initial ones. When inequality (30.9) holds, we have $\tan 2\alpha \approx \infty$, i.e. $\alpha = \pi/4$ and, consequently, the functions $\psi_1^{(0)}$ and $\psi_2^{(0)}$ are contained in ψ_1 and ψ_2 with the same weight.

It follows from what has been said above that among the energy values

$$E_1, E_2, E_3^{(0)}, E_4^{(0)}, \dots$$

none will be close to one another. Hence, these values and the functions

$$\psi_1, \psi_2, \psi_3^{(0)}, \psi_4^{(0)}, \dots$$

corresponding to them can be used as the zero approximation in evaluating the psi-functions in the first approximation and the corrections to the energies in the second approximation by formulas (29.28) and (29.29).

The same procedure can be used if $E_1 = E_2$, i.e. if there is a doubly degenerate level with the functions $\psi_{11}^{(0)}$ and $\psi_{12}^{(0)}$. All the formulas of this section hold if by $\psi_1^{(0)}$ in them we understand $\psi_{11}^{(0)}$ and by $\psi_2^{(0)}$, the function $\psi_{12}^{(0)}$.

31. Degenerate Case

The method set out in the preceding section is also used when all the levels are degenerate, the degree of degeneracy exceeding two.

Assume that the unperturbed level $E_n^{(0)}$ has a degeneracy equal to s_n^1 (different levels may have different degeneracies). This signifies that the energy $E_n^{(0)}$ is realized in s_n different states described by the functions

$$\psi_{n1}^{(0)}, \psi_{n2}^{(0)}, \dots, \psi_{nk}^{(0)}, \dots, \psi_{ns_n}^{(0)} \quad (31.1)$$

We shall designate the system of functions (31.1) by the symbol $\psi_{nk}^{(0)}$ ($k=0, 1, \dots, s_n$) and consider it as the initial one in the present problem. A drawback of these functions is that they change very greatly under the influence of a small perturbation [because of the zeros appearing in the denominator of formula (29.28)].

Owing to the superposition principle, instead of the functions (31.1), we can take any s_n independent linear combinations of these functions, i.e. s_n expressions of the form

$$\psi_{ni}^{(0)} = \sum_{k=1}^s c_{ni}^{(0)} \psi_{nk}^{(0)} \quad (i=1, 2, \dots, s_n) \quad (31.2)$$

[compare with (30.1)]. Let us attempt to choose these expressions so that the values of the perturbed energy corresponding to them do not coincide². The set of functions (31.2) satisfying this requirement is said to be regular. Regular functions are characterized by a small change under the influence of a small perturbation.

The initial functions (31.1) belong to the energy value $E_n^{(0)}$ and therefore satisfy the equation

$$\hat{H}_0 \psi_{nk}^{(0)} = E_n^{(0)} \psi_{nk}^{(0)} \quad (k=1, 2, \dots, s_n) \quad (31.3)$$

where \hat{H}_0 is the unperturbed Hamiltonian. The regular functions (31.2) also belong to the energy value $E_n^{(0)}$ and satisfy the similar equation

$$\hat{H}_0 \psi_{ni}^{(0)} = E_n^{(0)} \psi_{ni}^{(0)} \quad (i=1, 2, \dots, s_n) \quad (31.4)$$

¹ To simplify our notation, we shall not always write the subscript n on s .

² All the s_n functions (31.2), like the functions (31.1), satisfy the equation $\hat{H}_0 \psi = E \psi$ so that the unperturbed values of the energy coincide for them.

We must note that the failure of the energy of the state $\psi_{ni}^{(0)}$ to depend on the subscript i can be considered as degeneracy with respect to the "quantum number" i .

One of the problems we are confronted with is to find the regular functions of the zero approximation, i.e. such values of the coefficient's $c_{nkh}^{(0)}$ at which the functions (31.2) will change only slightly under the action of a perturbation. In the absence of degeneracy, such a problem did not appear—the initial functions $\psi_n^{(0)}$ (see Sec. 29) were regular and could be taken as the zero approximation.

The first step which we can undertake is to find the functions of the zero approximation [i.e. the regular functions $\psi_{ni}^{(0)}$] and the first-order corrections $\Delta E_n^{(1)}$ to the energy values $E_n^{(0)}$. For this purpose, let us introduce into the Schrödinger equation written for the operator $\hat{H} = \hat{H}_0 + \hat{V}$ the psi-functions in the zero approximation and the energy values taken in the first approximation. The result is the relation

$$(\hat{H}_0 + \hat{V}) \psi_{ni}^{(0)} = (E_n^{(0)} + \Delta E_n^{(1)}) \psi_{ni}^{(0)} \quad (i = 1, 2, \dots, s_n)$$

that with a view to (31.4) is simplified as follows:

$$\hat{V} \psi_{ni}^{(0)} = \Delta E_n^{(1)} \psi_{ni}^{(0)} \quad (i = 1, 2, \dots, s_n) \quad (31.5)$$

Introducing expression (31.2) for $\psi_{ni}^{(0)}$ into (31.5), we obtain the equation

$$\sum_{k=1}^s c_{nkh}^{(0)} \hat{V} \psi_{nk}^{(0)} = \sum_{k=1}^s \Delta E_n^{(1)} c_{nkh}^{(0)} \psi_{nk}^{(0)} \quad (i = 1, 2, \dots, s_n)$$

Scalar multiplication of both sides of this equation by the initial function $\psi_{nm}^{(0)}$ [the m -th function of the set (31.1)] yields

$$\begin{aligned} & \sum_{k=1}^s c_{nkh}^{(0)} \langle \psi_{nm}^{(0)} | \hat{V} \psi_{nk}^{(0)} \rangle \\ &= \sum_{k=1}^s \Delta E_n^{(1)} c_{nkh}^{(0)} \langle \psi_{nm}^{(0)} | \psi_{nk}^{(0)} \rangle \\ & \quad (i, m = 1, 2, \dots, s_n) \end{aligned}$$

The functions $\psi_{nk}^{(0)}$ are assumed to be normalized: $\langle \psi_{nm}^{(0)} | \psi_{nk}^{(0)} \rangle = \delta_{mk}$. Consequently, the relation obtained can be written as

$$\sum_{k=1}^s c_{nkh}^{(0)} V_{nm, nk} = \sum_{k=1}^s \Delta E_n^{(1)} c_{nkh}^{(0)} \delta_{mk} \quad (i, m = 1, 2, \dots, s_n) \quad (31.6)$$

where

$$V_{nm, nk} = \langle \psi_{nm}^{(0)} | \hat{V} \psi_{nk}^{(0)} \rangle \quad (m, k = 1, 2, \dots, s_n) \quad (31.7)$$

is the matrix element of the perturbation operator calculated with the aid of the initial functions (31.1).

Transferring all the terms of relation (31.6) to the left-hand side of the equation, we obtain a set of s_n^2 equations:

$$\sum_{h=1}^{s_n} (V_{nm,nh} - \delta_{mh} \Delta E_n^{(1)}) c_{nih}^{(0)} = 0 \quad (i, m = 1, 2, \dots, s_n) \quad (31.8)$$

differing from one another in the values of the subscripts i and m . Selecting all the equations with an identical value of the subscript i from this set ($i = \text{const}$, $m = 1, 2, \dots, s_n$), we obtain a system of s_n linear homogeneous equations in s_n unknowns $c_{ni}^{(0)}$ ($i = \text{const}$, $k = 1, 2, \dots, s_n$). These unknowns are the coefficients in expression (31.2) for $\psi_{ni}^{(0)}$ with a given value of i . Consequently, solving such a system, we find the regular function $\psi_{ni}^{(0)}$. By solving all the s_n systems (for $i = 1, 2, \dots, s_n$), we find all the s_n functions $\psi_{ni}^{(0)}$ ($i = 1, 2, \dots, s_n$).

Let us fix i and write s_n equations of the form of (31.8) (for $m = 1, 2, \dots, s_n$) in the extended form:

$$\begin{aligned} (V_{n1, n1} - \Delta E_n^{(1)}) c_{n11}^{(0)} + V_{n1, n2} c_{n12}^{(0)} + \dots + V_{n1, ns} c_{n1s}^{(0)} &= 0 \\ V_{n2, n1} c_{n11}^{(0)} + (V_{n2, n2} - \Delta E_n^{(1)}) c_{n12}^{(0)} + \dots + V_{n2, ns} c_{n1s}^{(0)} &= 0 \\ \dots &\dots \\ V_{ns, n1} c_{n11}^{(0)} + & \quad V_{ns, n2} c_{n12}^{(0)} + \dots + (V_{ns, ns} - \Delta E_n^{(1)}) c_{n1s}^{(0)} = 0 \end{aligned} \quad (31.9)$$

For the system of linear homogeneous equations to have non-zero solutions, the determinant of the system must be zero:

$$\left| \begin{array}{cccc} V_{n1, n1} - \Delta E_n^{(1)} & V_{n1, n2} & \dots & V_{n1, ns} \\ V_{n2, n1} & V_{n2, n2} - \Delta E_n^{(1)} & \dots & V_{n2, ns} \\ \dots & \dots & \dots & \dots \\ V_{ns, n1} & V_{ns, n2} & \dots & V_{ns, ns} - \Delta E_n^{(1)} \end{array} \right| = 0 \quad (31.10)$$

Evaluating the determinant, we obtain an algebraic equation of the s_n -th degree in the unknown $\Delta E_n^{(1)}$. This equation is called secular¹.

The secular equation has, generally speaking, s_n different real roots: $\Delta E_{ni}^{(1)}$ ($i = 1, 2, \dots, s_n$). In a particular case, some of the roots may be multiple. In the absence of multiple roots, the unperturbed s_n -fold degenerate level $E_n^{(0)}$ splits under the action of the perturbation \hat{V} into s_n non-coinciding sublevels

$$E_{ni}^{(0)} = E_n^{(0)} + \Delta E_{ni}^{(1)} \quad (i = 1, 2, \dots, s_n) \quad (31.11)$$

Hence, the perturbation removes the degeneracy with respect to the "quantum number" i [see the text following formula (31.4)]. When the secular equation has multiple roots, the degeneracy will be removed partially.

¹ The name has been taken from celestial mechanics.

Using in (31.9) the value of $\Delta E_n^{(1)}$ equal to $\Delta E_{n1}^{(1)}$ ($i = 1$), we obtain a system of equations having non-zero solutions $c_{n1k}^{(0)}$ (where $k = 1, 2, \dots, s_n$). The substitution of these values into (31.2) yields the function $\psi_{n1}^{(0)}$ —the function of a perturbed state having the energy $E_{n1}^{(0)}$ in the zero approximation. By introducing consecutively $\Delta E_{n2}^{(1)}$, $\Delta E_{n3}^{(1)}$, etc. into (31.9), we obtain the remaining functions $\psi_{ni}^{(0)}$.

Having determined in the way described above the zero-approximation regular functions $\psi_{ni}^{(0)}$, we can go over to finding the form of the psi-functions in the first approximation.

We must note first of all that the matrix $V_{nm, nk}$ calculated with the aid of regular functions [see (31.7)] will be diagonal. Indeed, regular functions satisfy Eq. (31.5), i.e. $\hat{V}\psi_{nk}^{(0)} = \Delta E_{nk}^{(1)}\psi_{nk}^{(0)}$. Consequently,

$$V_{nm, nk} = \langle \psi_{nm}^{(0)} | \hat{V} \psi_{nk}^{(0)} \rangle = \langle \psi_{nm}^{(0)} | \Delta E_{nk}^{(1)} \psi_{nk}^{(0)} \rangle = \Delta E_{nk}^{(1)} \delta_{nm, nk} \quad (31.12)$$

whence it follows that the off-diagonal matrix elements are zero, while the diagonal ones are the relevant first-order corrections to the energy levels:

$$\Delta E_{nm}^{(1)} = V_{nm, nm} \quad (m = 1, 2, \dots, s_n) \quad (31.13)$$

The determinant (31.10) in this case becomes

$$(V_{n1, n1} - \Delta E_{n1}^{(1)}) (V_{n2, n2} - \Delta E_{n2}^{(1)}) \dots (V_{ns, ns} - \Delta E_{ns}^{(1)}) = 0$$

Now we shall follow the procedure adopted in Sec. 29. We shall reduce the evaluation of the functions ψ_{ni} to finding the coefficients of the expansion of these functions in the regular zero-approximation functions $\psi_{kp}^{(0)}$:

$$\psi_{ni} = \sum_{kp} c_{ni, kp} \psi_{kp}^{(0)} \quad (n = 1, 2, \dots, i = 1, 2, \dots, s_n) \quad (31.14)$$

[compare with (29.6)]. In this sum, the subscript k takes on the values $1, 2, \dots, n, \dots$, and the subscript p at the given k —the values $1, 2, \dots, s_k$. The total number of addends is $s_1 + s_2 + \dots + s_n + \dots$.

We shall represent the eigenvalues of the energy and the coefficients $c_{ni, kp}$ in the form of series similar to (29.11) and (29.12):

$$E_{ni} = E_{ni}^{(0)} + \lambda E_{ni}^{(1)} + \lambda^2 E_{ni}^{(2)} + \dots \quad (31.15)$$

$$c_{ni, kp} = \delta_{ni, kp} + \lambda c_{ni, kp}^{(1)} + \lambda^2 c_{ni, kp}^{(2)} + \dots \quad (31.16)$$

The Kronecker delta is non-zero provided that $n = k$ and $i = p$.

We next introduce expression (31.15) for E_{ni} and (31.14) for ψ_{ni} [in the latter we must replace the coefficients with the series (31.16)] into the Schrödinger equation for the operator $\hat{H} = \hat{H}_0 + \hat{V} = \hat{H}_0 + \lambda \hat{W}$, then multiply the relation obtained by $\psi_{ni}^{(0)}$, etc.

It is evident from what has been said above that the formulas which we shall arrive at will differ from those obtained in Sec. 29 only in that the double subscript ni will appear instead of the subscript n , the subscript kp instead of k , and ml instead of m . Particularly, the substitution of ni for n in (29.21) leads to the equation

$$E_{ni} = E_{ni}^{(0)} + V_{ni, ni} \quad (31.17)$$

that coincides with (31.13). The requirement that ψ_{ni} be normalized to within the terms of the order of λ leads to the condition

$$c_{ni, ni}^{(1)} = 0 \quad (31.18)$$

[see (29.27)].

Let us write the analogues of formulas (29.18) and (29.19):

$$W_{ml, ni} = (E_{ni}^{(0)} - E_{ml}^{(0)}) c_{ni, ml}^{(1)} + E_{ni}^{(1)} \delta_{ni, ml} \quad (31.19)$$

$$\sum_{kp} c_{ni, kp}^{(1)} W_{ml, kp} = (E_{ni}^{(0)} - E_{ml}^{(0)}) c_{ni, ml}^{(2)} + E_{ni}^{(1)} c_{ni, ml}^{(1)} + E_{ni}^{(2)} \delta_{ni, ml} \quad (31.20)$$

Assuming in formula (31.19) that $m \neq n$, we obtain

$$c_{ni, ml}^{(1)} = \frac{W_{ml, ni}}{E_{ni}^{(0)} - E_{ml}^{(0)}} \quad (m \neq n) \quad (31.21)$$

[compare with (29.23)]. Now let us write (31.20) for $m = n$ and $l \neq i$:

$$\sum_{kp} c_{ni, kp}^{(1)} W_{nl, kp} = E_{ni}^{(1)} c_{ni, nl}^{(1)} \quad (31.22)$$

[owing to degeneracy, $E_{ni}^{(0)} = E_{nl}^{(0)}$].

By (31.13), we have $E_{ni}^{(1)} = W_{ni, ni}$ [recall that $\Delta E^{(1)} = \lambda E^{(1)}$ and $\hat{V} = \lambda \hat{W}$]. Let us perform such a substitution in (31.22) and, in addition, separate from the sum over the subscripts k and p the addends in which $k = n$:

$$\sum_p c_{ni, np}^{(1)} W_{nl, np} + \sum_{\substack{kp \\ (k \neq n)}} c_{ni, kp}^{(1)} W_{nl, kp} = W_{ni, ni} c_{ni, nl}^{(1)}$$

The matrix $W_{nl, np}$, like the matrix $V_{nl, np}$, is diagonal [see (31.12)]. Therefore in the sum over p , only one addend is non-zero (in which $p = l$), and it equals $c_{ni, nl}^{(1)} W_{nl, nl}$. With a view to this circumstance, we can write that

$$c_{ni, nl}^{(1)} = \frac{1}{W_{ni, ni} - W_{nl, nl}} \sum_{\substack{kp \\ (k \neq n)}} c_{ni, kp}^{(1)} W_{nl, kp}$$

Finally, substituting for $c_{ni, kp}^{(1)}$ its value following from (31.21), we obtain the formula

$$c_{ni, nl}^{(1)} = \frac{1}{W_{ni, ni} - W_{nl, nl}} \sum_{\substack{kp \\ (k \neq n)}} \frac{W_{nl, kp} W_{kp, ni}}{E_{ni}^{(0)} - E_{kp}^{(0)}} \quad (i \neq l) \quad (31.23)$$

Formulas (31.21) and (31.23) give the values of all the coefficients $c_{ni, ml}^{(1)}$ except $c_{ni, ni}^{(1)}$, but we know the latter to be zero [see (31.18)]. We can thus write an expression for the psi-function in the first approximation:

$$\begin{aligned} \psi_{ni} &= \psi_{ni}^{(0)} + \sum_{\substack{ml \\ (m \neq n)}} \frac{V_{ml, ni}}{E_{ni}^{(0)} - E_{ml}^{(0)}} \psi_{ml}^{(0)} \\ &+ \sum_l \frac{1}{V_{ni, ni} - V_{nl, nl}} \sum_{\substack{kp \\ (h \neq n)}} \frac{V_{nl, kp} V_{kp, ni}}{E_{ni}^{(0)} - E_{kp}^{(0)}} \psi_{nl}^{(0)} \end{aligned} \quad (31.24)$$

[compare with (29.28)].

Let us find the correction to the energy in the second approximation. To do this, we shall use relation (31.20), assuming in it that $m = n$ and $l = i$:

$$\sum_{kp} c_{ni, kp}^{(1)} W_{ni, kp} = E_{ni}^{(1)} c_{ni, ni}^{(1)} + E_{ni}^{(2)} \quad (31.25)$$

Hence, with a view to (31.18), we find that

$$E_{ni}^{(2)} = \sum_p c_{ni, np}^{(1)} W_{ni, np} + \sum_{\substack{kp \\ (k \neq n)}} c_{ni, kp}^{(1)} W_{ni, kp}$$

[we have broken up the sum on the left in (31.25) into two sums]. All the addends of the first sum are zero: when $p = i$ because of $c_{ni, ni}^{(1)}$, and when $p \neq i$ because of the diagonal nature of the matrix $W_{ni, np}$. Therefore, introducing the values (31.21) for the coefficients $c_{ni, kp}^{(1)}$ into the second sum, we obtain the following formula for the correction to the energy in the second approximation:

$$\Delta E_{ni}^{(2)} = \lambda^2 E_{ni}^{(2)} = \sum_{\substack{kp \\ (k \neq n)}} \frac{V_{ni, kp} V_{kp, ni}}{E_{ni}^{(0)} - E_{kp}^{(0)}} \quad (31.26)$$

32. Examples of Application of the Stationary Perturbation Theory

We shall consider the Zeeman effect for a particle having no spin and the Stark effect for a hydrogen atom as examples of stationary perturbation theory application.

Let us begin with the Zeeman effect. Consider a particle differing from an electron only in that it has no spin. Let the particle move

in the Coulomb field of an atomic nucleus. The Hamiltonian of the particle thus has the form

$$\hat{H}_0 = \frac{1}{2m_e} \hat{\mathbf{p}}^2 - \frac{Ze^2}{r} \quad (32.1)$$

It was found in Sec. 24 that the eigenvalues of such an operator are determined by expression (24.23), while the eigenfunctions have the form

$$\psi_{nlm} = R_{nl}(r) \cdot Y_{lm}(\theta, \varphi)$$

[see (24.27)].

Let us find how the values of the energy will change if we act on the nucleus-particle system with the homogeneous constant magnetic field \mathbf{B} . For this purpose, we must know the expression of the Hamiltonian for a charged particle moving in an electromagnetic field. It was established in Sec. 70 of Vol. 1 that the Hamiltonian function for a particle having the charge e (and not $-e$, as our particle has) is determined by the expression

$$H = \frac{1}{2m_e} \left(\mathbf{P} - \frac{e}{c} \mathbf{A} \right)^2 + e\varphi \quad (32.2)$$

where \mathbf{P} is the generalized momentum of the particle, and \mathbf{A} and φ are the vector and the scalar potentials of the field at the point where the particle is [see Vol. 1, formula (70.12)].

The same operator $-i\hbar\nabla$ is associated with the generalized momentum \mathbf{P} as with the conventional momentum \mathbf{p} . We therefore write $\hat{\mathbf{p}}$ instead of $\hat{\mathbf{P}}$. In the coordinate representation, the operator $\hat{\mathbf{A}} = \mathbf{A}$ is associated with the vector potential, as with any other position function. Accordingly, the Hamiltonian is determined by the expression

$$\hat{H} = \frac{1}{2m_e} \left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A} \right)^2 + e\varphi \quad (32.3)$$

Opening the parentheses, we obtain

$$\hat{H} = \frac{1}{2m_e} \hat{\mathbf{p}}^2 - \frac{e}{2m_ec} \hat{\mathbf{p}}\mathbf{A} - \frac{e}{2m_ec} \mathbf{A}\hat{\mathbf{p}} + \frac{e^2}{2m_ec^2} \mathbf{A}^2 + e\varphi \quad (32.4)$$

It is not difficult to find that the commutator of the operators $\hat{\mathbf{p}}$ and \mathbf{A} is

$$[\hat{\mathbf{p}}, \mathbf{A}] = \hat{\mathbf{p}}\mathbf{A} - \mathbf{A}\hat{\mathbf{p}} = -i\hbar\nabla\mathbf{A} \quad (32.5)$$

Consequently, replacing $\hat{\mathbf{p}}\mathbf{A}$ with $\mathbf{A}\hat{\mathbf{p}} - i\hbar\nabla\mathbf{A}$, we can write (32.4) as

$$\hat{H} = \frac{1}{2m_e} \hat{\mathbf{p}}^2 - \frac{e}{m_ec} \hat{\mathbf{A}}\mathbf{p} + i\hbar\nabla\mathbf{A} + \frac{e^2}{2m_ec^2} \mathbf{A}^2 + e\varphi \quad (32.6)$$

Recall that this expression of the Hamiltonian has been obtained for a particle having the charge e . We are considering the motion of a particle having the charge $-e$. For such a particle, the Hamiltonian must be written as follows:

$$\hat{H} = \frac{1}{2m_e} \hat{\mathbf{p}}^2 + \frac{e}{mc} \hat{\mathbf{A}} \hat{\mathbf{p}} + i\hbar \nabla \mathbf{A} + \frac{e^2}{2m_e c^2} \mathbf{A}^2 - e\varphi \quad (32.7)$$

It was shown in Sec. 47 of Vol. 1 that the vector potential of a homogeneous constant field \mathbf{B} directed along the z -axis can be represented by the formulas

$$A_x = -\frac{1}{2} By, \quad A_y = \frac{1}{2} Bx, \quad A_z = 0 \quad (32.8)$$

Let us determine the form of the Hamiltonian (32.7) for the given case. It is not difficult to see that for a potential with the components (32.8), we have $\nabla \mathbf{A} = 0$. Consequently, the third term in (32.7) vanishes. Further, by (32.8)

$$\hat{\mathbf{A}} \hat{\mathbf{p}} = -\frac{1}{2} By \cdot \hat{p}_x + \frac{1}{2} Bx \cdot \hat{p}_y = \frac{1}{2} B(x\hat{p}_y - y\hat{p}_x) = \frac{1}{2} B \hat{M}_z \propto B \quad (32.9)$$

[see (15.11)],

$$\mathbf{A}^2 = \frac{1}{4} B^2 (x^2 + y^2) \propto B^2 \quad (32.10)$$

If we limit ourselves to a consideration of weak fields, in formula (32.7) the fourth term proportional to B^2 may be disregarded in comparison with the second term proportional to B .

Dropping the third and fourth terms in formula (32.7), and also replacing φ with its value for the field of a nucleus, we arrive at the following expression:

$$\hat{H} = \frac{1}{2m_e} \hat{\mathbf{p}}^2 - \frac{Ze^2}{r} + \frac{e}{mc} \hat{\mathbf{A}} \hat{\mathbf{p}} = \hat{H}_0 + \frac{e}{mc} \hat{\mathbf{A}} \hat{\mathbf{p}} \quad (32.11)$$

[see (32.1)]. Hence, the Hamiltonian broke up into the sum of the unperturbed Hamiltonian \hat{H}_0 and the perturbation operator

$$\hat{V} = \frac{e}{mc} \hat{\mathbf{A}} \hat{\mathbf{p}} = \frac{eB}{2m_e c} \hat{M}_z \quad (32.12)$$

[we have taken advantage of relation (32.9)].

The energy values for the unperturbed states are determined by formula (24.23), and the eigenfunctions $\psi_{nlm}^{(0)}$, by formula (24.27), $\sum_{l=0}^{n-1} (2l+1) = n^2$ functions differing in the values of the quantum numbers l and m (there is degeneracy with respect to l and m) corresponding to the n -th energy value.

When there is degeneracy, the corrections to the energy in the first approximation are found from the solution of the secular equation (31.10). These corrections cannot be calculated directly by formulas (31.13) and (31.12) with the aid of the functions (24.27) because these functions may be "irregular" [recall that the functions in formula (31.12) are assumed to be "regular"].

To compile a secular equation, we must know the matrix elements

$$V_{nlm, nl'm'} = \langle \psi_{nlm}^{(0)} | \hat{V} | \psi_{nl'm'}^{(0)} \rangle \quad (32.13)$$

It was established in Sec. 23 that the operator (32.1) commutes with the operator \hat{M}_z . Therefore, the functions ψ_{nlm} are simultaneously the eigenfunctions of the operator \hat{M}_z , i.e. satisfy the equation

$$\hat{M}_z \psi_{nlm}^{(0)} = m\hbar \psi_{nlm}^{(0)}$$

Consequently, $\hat{V} \psi_{nl'm'}^{(0)} = (eB/2m_e c) \hat{M}_z \psi_{nl'm'}^{(0)} = (eB/2m_e c) m\hbar \psi_{nl'm'}^{(0)}$. Substitution of this expression into (32.13) yields

$$V_{nlm, nl'm'} = \frac{eB}{2m_e c} m\hbar \delta_{nlm, nl'm'} \quad (32.14)$$

Hence, at any value of n , the matrix V is diagonal. This signifies [see the text preceding formula (31.12)] that with respect to the perturbation (32.12), the functions (24.27) are "regular". In this case, the corrections to the energy in the first approximation equal the diagonal matrix elements (32.14), i.e.

$$\Delta E_{nlm}^{(1)} = \frac{e\hbar}{2m_e c} B m = \mu_B B m \quad (32.15)$$

where μ_B is the Bohr magneton.

We have established that when a magnetic field acts on an atom (with a spinless electron), the energy of the atom becomes dependent on the quantum number m (which is why it is called the magnetic quantum number). The magnetic field thus removes the degeneracy with respect to m . But since the correction to the energy does not depend on the quantum number l , the degeneracy with respect to l remains so that in the given case the perturbation removes the degeneracy only partially.

Now let us consider the Stark effect. Assume that a hydrogen atom is acted upon by a weak constant and homogeneous electric field of strength E directed along the z -axis. The potential of this field is $\varphi = -Ex = -Er \cos \vartheta$. Consequently, the perturbation operator has the form

$$\hat{V} = eEr \cos \vartheta \quad (32.16)$$

The matrix elements of the operator (32.15) evaluated with the aid of the functions (24.27) are as follows:

$$V_{nlm, nl'm'} = \langle \Psi_{nlm}^{(0)} | eEr \cos \vartheta \Psi_{nl'm'}^{(0)} \rangle \\ = eE \int Y_{lm}^* Y_{l'm'} \cos \vartheta \sin \vartheta d\vartheta d\phi \int_0^\infty R_{nl} R_{nl'} r \cdot r^2 dr \quad (32.17)$$

The ground state is not degenerate. Hence, the function ψ_{100} is regular and by (31.13) [and also by (29.22)], we have

$$\Delta E_1^{(1)} = V_{100, 100} = \langle \Psi_{100} | eEr \cos \vartheta \Psi_{100} \rangle$$

Substituting for ψ_{100} in this equation its value from (24.33), we obtain ($Z = 1$)

$$\Delta E_1^{(1)} = \frac{1}{\pi r_0^3} \int e^{-2r/r_0} eEr \cos \vartheta r^2 \sin \vartheta dr d\vartheta d\phi$$

Since $\int_0^{2\pi} d\phi \int_0^\pi \cos \vartheta \sin \vartheta d\vartheta = 0$, we find that $\Delta E_1^{(1)} = 0$. Consequently, for the ground state of a hydrogen atom, the first-order Stark effect is absent.

The first excited state of a hydrogen atom ($n = 2$) is four-fold degenerate—the following functions correspond to the energy E_2 [see (24.33)]:

$$\left. \begin{aligned} \Psi_{200} &= \frac{1}{r_0^{5/24} \sqrt{2\pi}} e^{-r/2r_0} \left(2 - \frac{r}{r_0} \right) \\ \Psi_{211} &= -\frac{1}{r_0^{5/28} \sqrt{\pi}} e^{-r/2r_0} r e^{i\varphi} \sin \vartheta \\ \Psi_{210} &= \frac{1}{r_0^{5/24} \sqrt{2\pi}} e^{-r/2r_0} r \cos \vartheta \\ \Psi_{21-1} &= \frac{1}{r_0^{5/28} \sqrt{\pi}} e^{-r/2r_0} r e^{-i\varphi} \sin \vartheta \end{aligned} \right\} \quad (32.18)$$

Of the 16 matrix elements $V_{2lm, 2l'm'}$ that can be obtained with the aid of the functions (32.18), only the two corresponding to $l \neq l'$ and $m = m'$ are non-zero. This can be seen by direct verification. But this result also ensues from the following considerations. It was shown in Sec. 20 that the parity of the function $Y_{lm}(\vartheta, \varphi)$ coincides with that of the quantum number l —this signifies that when we substitute $\pi - \vartheta$ for ϑ and $\varphi + \pi$ for φ , the function Y_{lm} is multiplied by $(-1)^l$. The radial function $R_{nl}(r)$ is even (in inversion, r does not change). The function $\cos \vartheta$ is odd. Consequently, the parity of the

integrand in (32.17) is $l + l' + 1$. Integration of an odd function of the angles over $d\Omega = \sin \vartheta d\vartheta d\varphi$ within the limits of the round solid angle 4π yields zero. The integral is thus non-zero only for even values of $l + l' + 1$, i.e. for $l \neq l'$. Further, when $m \neq m'$, expression (32.17) contains the factor

$$\int_0^{2\pi} e^{i(m-m')\varphi} d\varphi = 0$$

Hence, only the elements $V_{200, 210}$ and $V_{210, 200}$ are non-zero. They have the value

$$\begin{aligned} V_{200, 210} &= V_{210, 200} \\ &= \frac{1}{r_0^3 32\pi} \int_0^\infty \int_0^\pi e^{-r/r_0} \frac{r}{r_0} \left(2 - \frac{r}{r_0} \right) \cos \vartheta eEr \cos \vartheta \cdot 2\pi r^2 \sin \vartheta dr d\vartheta \\ &= -3eEr_0 \quad (32.19) \end{aligned}$$

We must note that in the given case the matrix V is not diagonal so that the functions (32.18) are not regular with respect to the perturbation (32.16) [recall that with respect to the perturbation (32.12) they were regular].

Having chosen the sequence of the subscripts: 200, 210, 211, 21-1, we write the secular equation [see (31.10)]

$$\begin{vmatrix} 0 - \Delta E & -3eEr_0 & 0 & 0 \\ -3eEr_0 & 0 - \Delta E & 0 & 0 \\ 0 & 0 & 0 - \Delta E & 0 \\ 0 & 0 & 0 & 0 - \Delta E \end{vmatrix} = 0$$

Expanding the determinant, we obtain

$$(-\Delta E)^2 [(-\Delta E)^2 - (-3eEr_0)^2] = 0$$

The roots of this equation are:

$$\Delta E_1 = 3eEr_0, \quad \Delta E_2 = -3eEr_0, \quad \Delta E_3 = \Delta E_4 = 0 \quad (32.20)$$

Having taken ΔE_1 , we obtain a system of equations for determining the coefficients c_{2lm} [see (31.9)]:

$$\left. \begin{array}{l} -3eEr_0 \cdot c_1 - 3eEr_0 \cdot c_2 = 0 \\ -3eEr_0 \cdot c_1 - 3eEr_0 \cdot c_2 = 0 \\ -3eEr_0 \cdot c_3 = 0 \\ -3eEr_0 \cdot c_4 = 0 \end{array} \right\} \quad (32.21)$$

Hence, $c_1 = -c_2$, and $c_3 = c_4 = 0$. Consequently, the following function corresponds to the level $E_0 + \Delta E_1$ in the zero approximation:

$$\begin{aligned}\psi_1 &= c(\psi_{200} - \psi_{210}) = \frac{1}{\sqrt{\frac{1}{2}}} (\psi_{200} - \psi_{210}) \\ &= \frac{1}{r_0^{3/2} 8 \sqrt{\pi}} e^{-r/r_0} \left[2 - \frac{r}{r_0} (1 + \cos \vartheta) \right] \quad (32.22)\end{aligned}$$

Forming a system similar to (32.21) for $\Delta E_2 = -3eEr_0$, we find that $c_1 = c_2$, and $c_3 = c_4 = 0$. Consequently, the following function corresponds to the level $E_0 + \Delta E_2$:

$$\psi_2 = \frac{1}{\sqrt{\frac{1}{2}}} (\psi_{200} + \psi_{210}) = \frac{1}{r_0^{3/2} 8 \sqrt{\pi}} e^{-r/r_0} \left[2 - \frac{r}{r_0} (1 - \cos \vartheta) \right] \quad (32.23)$$

Introduction of the value $\Delta E = 0$ into the system (31.9) yields $c_1 = c_2 = 0$; the other coefficients remain indeterminate. We can therefore assume that

$$\psi_3 = \psi_{211}, \quad \psi_4 = \psi_{21-1} \quad (32.24)$$

The set of functions (32.22)-(32.24) forms a regular system of zero-approximation functions when the perturbation operator has the form of (32.16). With the aid of these functions, the first-approximation corrections to the energies can be calculated by formula (31.13). Substituting, for example, the function (32.22) into this formula, we obtain

$$\begin{aligned}\Delta E &= \frac{eE}{r_0^3 64\pi} \int_0^\infty \int_0^\pi e^{-r/r_0} \left[2 - \frac{r}{r_0} (1 + \cos \vartheta) \right]^2 \\ &\quad \times r \cos \vartheta \cdot 2\pi r^2 \sin \vartheta dr d\vartheta = 3eEr_0\end{aligned}$$

which coincides with ΔE_1 from (32.20). It is not difficult to see that

$$\langle \psi_3 | \hat{V} \psi_3 \rangle = \langle \psi_4 | \hat{V} \psi_4 \rangle = 0$$

where ψ_3 and ψ_4 are determined by formulas (32.24). This result also agrees with (32.20).

Summarizing, we can say that of the four degenerate states corresponding to $n=2$, in the first approximation two states do not change under the action of a weak electric field. The other two states described by the functions (32.22) and (32.23) acquire the additional energy $3eEr_0$ and $-3eEr_0$. This can be interpreted to signify that a hydrogen atom in the first excited state behaves like a dipole having the moment $3er_0$ and capable of orienting itself parallel to the field (one state), antiparallel to the field (one state), and normally to the field (two states).

33. Time-Dependent Perturbations

Assume that the perturbation operator \hat{V} depends on the time explicitly. Consequently, the Hamiltonian of the problem being considered

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \quad (33.1)$$

also contains the time explicitly. In this case, we cannot speak about corrections to the eigenvalues of the energy of the unperturbed states because stationary perturbed states (i.e. states with a constant energy) do not exist. Our task will therefore consist in approximately evaluating the psi-functions of the perturbed states.

For this purpose, we assume that originally (at $t < 0$) the system being considered was in one of the stationary states described by the function $\psi_n^{(0)}$ of the unperturbed operator \hat{H}_0 [this signifies that $\hat{V}(t) = 0$ when $t < 0$]. At the instant $t = 0$, a weak perturbation begins to act on the system. Owing to the smallness of this perturbation, we can consider that the psi-function of the perturbed state changes only slightly with time.

The psi-functions of the unperturbed system, with a view to their time dependence, are as follows:

$$\psi_n^{(0)}(x, t) = \psi_n^{(0)}(x) e^{-(i/\hbar)E_n t} \quad (n = 1, 2, \dots) \quad (33.2)$$

[see (5.6); by x is meant the set of coordinates of the particles in the system]. Recall that the functions $\psi_n^{(0)}(x)$ satisfy the equation

$$\hat{H}_0 \psi_n^{(0)}(x) = E_n \psi_n^{(0)}(x)$$

and the functions $\psi_n(x, t)$ — the equation

$$\hat{H}_0 \psi_n^{(0)}(x, t) = i\hbar \frac{\partial \psi_n^{(0)}(x, t)}{\partial t} \quad (33.3)$$

Unlike Sec. 32, now only unperturbed states are stationary ones (i.e. states with a definite energy). Hence, there is no need to use the superscript “(0)” on the energy values.

Since a perturbed state is not stationary, its psi-function cannot be represented in a form similar to (33.2). But owing to the completeness of the system of functions (33.2), the function $\psi(x, t)$ can for any instant be expanded into a series in these functions, i.e. written in the form

$$\psi(x, t) = \sum_k c_{nk}(t) \psi_k^{(0)}(x, t) = \sum_k c_{nk}(t) \psi_k^{(0)}(x) e^{-(i/\hbar)E_k t} \quad (33.4)$$

where the coefficients $c_{nk}(t)$ depend only on t . If, as we assumed, the system was originally in the stationary state $\psi_n^{(0)}(x, t)$, at the

instant $t = 0$ the condition $\psi(x, 0) = \psi_n^{(0)}(x, 0)$ must be observed. By (33.4), this condition will be satisfied if

$$c_{nk}(0) = \delta_{nk} \quad (33.5)$$

The function $\psi(x, t)$ is a solution of the equation

$$[\hat{H}_0 + \hat{V}(t)]\psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t} \quad (33.6)$$

Let us introduce the expression (33.4) for $\psi(x, t)$ into Eq. (33.6):

$$[\hat{H}_0 + \hat{V}(t)] \sum_k c_{nk}(t) \psi_k^{(0)}(x, t) = i\hbar \frac{\partial}{\partial t} \sum_k c_{nk}(t) \psi_k^{(0)}(x, t)$$

The time is not contained explicitly in \hat{H}_0 , and is contained as a parameter in $\hat{V}(t)$. Consequently, the operators \hat{H}_0 and $\hat{V}(t)$ do not act on the coefficients $c_{nk}(t)$. Therefore, the equation we have obtained can be transformed as follows:

$$\begin{aligned} & \sum_k c_{nk}(t) \hat{H}_0 \psi_k^{(0)}(x, t) + \sum_k c_{nk}(t) \hat{V}(t) \psi_k^{(0)}(x, t) \\ &= \sum_k c_{nk}(t) i\hbar \frac{\partial \psi_k^{(0)}(x, t)}{\partial t} + i\hbar \sum_k \frac{dc_{nk}(t)}{dt} \psi_k^{(0)}(x, t) \end{aligned}$$

Owing to (33.3), the first sum on the left-hand and right-hand sides of the equation can be dropped. We multiply the remaining equation scalarly by $\psi_m^{(0)}(x, t)$:

$$\begin{aligned} & \sum_k c_{nk}(t) \langle \psi_m^{(0)}(x, t) | \hat{V}(t) | \psi_k^{(0)}(x, t) \rangle \\ &= i\hbar \sum_k \frac{dc_{nk}(t)}{dt} \langle \psi_m^{(0)}(x, t) | \psi_k^{(0)}(x, t) \rangle \end{aligned}$$

Finally, introducing the notation

$$V_{mk}(t) = \langle \psi_m^{(0)}(x, t) | \hat{V}(t) | \psi_k^{(0)}(x, t) \rangle \quad (33.7)$$

and having in view that $\langle \psi_m^{(0)}(x, t) | \psi_k^{(0)}(x, t) \rangle = \delta_{mk}$, we can write

$$i\hbar \frac{dc_{nm}(t)}{dt} = \sum_k V_{mk}(t) c_{nk}(t) \quad (33.8)$$

We must note that the perturbation matrix element determined by formula (33.7) can be written as follows:

$$\begin{aligned} V_{mk}(t) &= \langle \psi_m^{(0)}(x) e^{-(i/\hbar)E_m t} | \hat{V}(t) | \psi_k^{(0)}(x) e^{-(i/\hbar)E_k t} \rangle \\ &= e^{(i/\hbar)(E_m - E_k)t} \langle \psi_m^{(0)}(x) | \hat{V}(t) | \psi_k^{(0)}(x) \rangle = e^{i\omega_{mk}t} v_{mk}(t) \end{aligned} \quad (33.9)$$

where

$$\omega_{mk} = \frac{E_m - E_k}{\hbar} \quad (33.10)$$

$$v_{mk}(t) = \langle \psi_m^{(0)}(x) | \hat{V}(t) | \psi_k^{(0)}(x) \rangle \quad (33.11)$$

Using the notations (33.10) and (33.11), we can write

$$V_{mk}(t) = v_{mk}(t) e^{i\omega_{mk}t} \quad (33.12)$$

Let us return to Eq. (33.8). We shall seek its solution in the form

$$c_{nm}(t) = c_{nm}^{(0)}(t) + \lambda c_{nm}^{(1)}(t) + \lambda^2 c_{nm}^{(2)}(t) + \dots$$

If we take the unperturbed function $\psi_n^{(0)}(x, t)$ as the zero approximation, we have $c_{nm}^{(0)}(t) = \delta_{nm}$ [see (33.5)]. Consequently,

$$\begin{aligned} c_{nm}(t) &= \delta_{nm} + \lambda c_{nm}^{(1)}(t) + \lambda^2 c_{nm}^{(2)}(t) + \dots \\ &= \delta_{nm} + \Delta c_{nm}^{(1)}(t) + \Delta c_{nm}^{(2)}(t) + \dots \end{aligned} \quad (33.13)$$

We shall write the matrix elements $V_{mk}(t)$ as $\lambda W_{mk}(t)$. Equation (33.8) will therefore be written as follows:

$$\begin{aligned} i\hbar\lambda \frac{dc_{nm}^{(1)}(t)}{dt} + i\hbar\lambda^2 \frac{dc_{nm}^{(2)}(t)}{dt} + \dots \\ = \lambda \sum_k W_{mk}(t) \delta_{nk} + \lambda^2 \sum_k W_{mk}(t) c_{nk}^{(1)}(t) + \dots \end{aligned}$$

Equating the coefficients of identical powers of λ , we obtain a series of equations

$$i\hbar \frac{dc_{nm}^{(1)}(t)}{dt} = W_{mn}(t)^1 \quad (33.14)$$

$$i\hbar \frac{dc_{nm}^{(2)}(t)}{dt} = \sum_k W_{mk}(t) c_{nk}^{(1)}(t) \quad (33.15)$$

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¹ $\sum_k W_{mk}\delta_{nk} = W_{mn}$.

Integration of these equations yields the following values for the corrections to the coefficients $c_{nm}^{(0)}(t) = \delta_{nm}$

$$\Delta c_{nm}^{(1)} = \lambda c_{nm}^{(1)} = -\frac{i}{\hbar} \int_0^t V_{mn}(t') dt = -\frac{i}{\hbar} \int_0^t v_{mn}(t') e^{i\omega_{mn} t'} dt \quad (33.16)$$

$$\begin{aligned} \Delta c_{nm}^{(2)} = \lambda^2 c_{nm}^{(2)} &= -\frac{i}{\hbar} \sum_k \int_0^t V_{mk}(t') \Delta c_{nk}^{(1)}(t') dt' \\ &= \left(-\frac{i}{\hbar}\right)^2 \sum_k \int_0^t V_{mk}(t') \left\{ \int_0^{t'} V_{kn}(t'') dt'' \right\} dt' \\ &= \left(-\frac{i}{\hbar}\right)^2 \sum_k \int_0^t v_{mk}(t') e^{i\omega_{mk} t'} \left\{ \int_0^{t'} v_{kn}(t'') e^{i\omega_{kn} t''} dt'' \right\} dt' \end{aligned} \quad (33.17)$$

.

(to avoid confusion, we have designated the integration variable in one case by t' , and in the other by t'' instead of t). Recall that n in these formulas signifies the index of the initial, unperturbed state.

Introducing the corrections evaluated in this way into formula (33.13), we find the expansion coefficients $c_{nm}(t)$ and, consequently, the perturbed function (33.4) itself. Hence, solution of the problem consists in finding the matrix elements (33.7) and in calculating the integrals (33.16), (33.17), etc.

Therefore, with account taken of formulas (33.5), (33.16), and (33.17), we have

$$\begin{aligned} c_{nm}(t) &= \delta_{nm} - \frac{i}{\hbar} \int_0^t v_{mn}(t') e^{i\omega_{mn} t'} dt' \\ &\quad + \left(-\frac{i}{\hbar}\right)^2 \sum_k \int_0^t v_{mk}(t') e^{i\omega_{mk} t'} \left\{ \int_0^{t'} v_{kn}(t'') e^{i\omega_{kn} t''} dt'' \right\} dt' + \dots \end{aligned} \quad (33.18)$$

Assume that at the instant τ the perturbation stops its action. Beginning from this instant, the coefficients of the expansion take on the constant values $c_{nk}(\tau)$. Consequently, when $t > \tau$, the state ψ of the system will be a superposition of the stationary states

$$\psi := \sum_k c_{nk}(\tau) \psi_k^{(0)}(x) e^{-(i/\hbar)E_k t}$$

[see (33.4)]. In this case, the probability P_{nm} of the system being in a stationary state with the energy E_m is determined by the square

of the magnitude of the coefficient $c_{nm}(\tau)$. If we limit ourselves to the first approximation, by (33.18) we have

$$c_{nm}(\tau) = -\frac{i}{\hbar} \int_0^\tau v_{mn}(t) e^{i\omega_{mn} t} dt \quad (m \neq n) \quad (33.19)$$

Accordingly

$$P_{nm} = |c_{nm}(\tau)|^2 = \frac{1}{\hbar^2} \left| \int_0^\tau v_{mn}(t) e^{i\omega_{mn} t} dt \right|^2 \quad (m \neq n) \quad (33.20)$$

Expression (33.20) determines the probability of transition of a system from the stationary state $\psi_n^{(0)}(x)$ to the stationary state $\psi_m^{(0)}(x)$ ($m \neq n$) during the time of action of a perturbation.

We must note that the expression we have obtained for P_{nm} holds only if the matrix elements $V_{mn}(t)$ and the perturbation time τ are sufficiently small for the corrections $\Delta c_{nm}(\tau)$ to be small in comparison with unity.

If $\hat{V}(0) = \hat{V}(\tau) = 0$ [accordingly, $v_{mn}(0)$ and $v_{mn}(\tau)$ are also zero] formula (33.20) can be transformed by taking the integral by parts:

$$\int_0^\tau v_{mn}(t) e^{i\omega_{mn} t} dt = \frac{1}{i\omega_{mn}} v_{mn}(t) e^{i\omega_{mn} t} \Big|_0^\tau - \frac{1}{i\omega_{mn}} \int_0^\tau \frac{dv_{mn}}{dt} e^{i\omega_{mn} t} dt$$

The first term vanishes upon substitution of the integration limits. We can therefore write that

$$P_{nm} = \frac{1}{\hbar^2 \omega_{mn}^2} \left| \int_0^\tau \frac{dv_{mn}}{dt} e^{i\omega_{mn} t} dt \right|^2 \quad (33.21)$$

Up to now, we have considered the very simple case when the operator \hat{H}_0 has a discrete spectrum of eigenvalues. Accordingly, expression (33.20) gives the probability of a transition between states belonging to a discrete spectrum. Of great interest is a transition from a state belonging to a discrete spectrum to one belonging to a continuous spectrum. Such transitions are possible when the spectrum of the operator \hat{H}_0 contains both discrete and continuous regions. In this case instead of (33.4), we obtain the formula

$$\psi(x, t) = \sum_k c_k(t) \psi_k^{(0)}(x, t) + \int c_v(t) \psi_v^{(0)}(x, t) dv \quad (33.22)$$

where the index v characterizes the state belonging to the continuous part of the spectrum [see (12.1)]. After introduction of this expression into Eq. (33.6) and simplifications, we arrive at the relation

$$\sum_k c_k(t) \hat{V} \psi_k^{(0)}(x, t) + \int c_v(t) \hat{V} \psi_v^{(0)}(x, t) dv \\ = i\hbar \sum_k \frac{dc_k(t)}{dt} \psi_k^{(0)}(x, t) + i\hbar \int \frac{dc_v(t)}{dt} \psi_v^{(0)}(x, t) dv \quad (33.23)$$

Performing scalar multiplication of (33.23) by $\psi_m^{(0)}(x, t)$ and taking into account that owing to the orthogonal nature of the eigenfunctions $\langle \psi_m^{(0)} | \psi_v^{(0)} \rangle = 0$, we obtain an analogue of Eq. (33.8):

$$i\hbar \frac{dc_m(t)}{dt} = \sum_k V_{mk}(t) c_k(t) + \int V_{mv}(t) c_v(t) dv \quad (33.24)$$

where

$$V_{mv}(t) = \langle \psi_m^{(0)}(x, t) | \hat{V} \psi_v^{(0)}(x, t) \rangle \quad (33.25)$$

while $V_{mk}(t)$ is determined by formula (33.7). Representing in (33.24) the required coefficients in the form

$$\left. \begin{aligned} c_k(t) &= \delta_{nk} + \lambda c_k^{(1)}(t) + \lambda^2 c_k^{(2)}(t) + \dots \\ c_v(t) &= \lambda c_v^{(1)}(t) + \lambda^2 c_v^{(2)}(t) + \dots \end{aligned} \right\} \quad (33.26)$$

[we assume that $\psi(x, 0) = \psi_n^{(0)}(x, 0)$, therefore all $c_v^{(0)}(t) \equiv 0$], and next equating the coefficients at identical powers of λ , we arrive at equations similar to (33.14) and (33.15):

$$i\hbar \frac{dc_m^{(1)}}{dt} = W_{mn}(t) \quad (33.27)$$

$$i\hbar \frac{dc_m^{(2)}}{dt} = \sum_k W_{mk}(t) c_k^{(1)}(t) + \int W_{mv}(t) c_v^{(1)}(t) dt \quad (33.28)$$

• • • • • • • • • • • • • • • • • • • • •

($W_{mn} = V_{mn}/\lambda$, etc.). Their solutions have the form

$$\Delta c_m^{(1)} = \lambda c_m^{(1)} = -\frac{i}{\hbar} \int_0^t V_{mn}(t) dt = -\frac{i}{\hbar} \int_0^t v_{mn}(t) e^{i\omega_{mn} t} dt \quad (33.29)$$

$$\Delta c_m^{(2)} = \lambda^2 c_m^{(2)}$$

$$= -\frac{i}{\hbar} \left\{ \sum_k \int_0^t V_{mk}(t) c_k^{(1)}(t) dt + \int dv \int_0^t V_{mv}(t) c_v^{(1)}(t) dt \right\} \quad (33.30)$$

• • • • • • • • • • • • • • • • • • • • •

[compare with (33.16) and (33.17)].

By multiplying (33.23) scalarly by $\psi_{v'}^{(0)}(x, t)$ and performing similar calculations¹, we arrive at the equations

$$i\hbar \frac{dc_{v'}^{(1)}}{dt} = W_{v'n}(t) \quad (33.31)$$

$$i\hbar \frac{dc_v^{(2)}}{dt} = \sum_k W_{v'k}(t) c_k^{(1)}(t) + \int W_{vv}(t) c_v^{(1)}(t) dv \quad (33.32)$$

where

$$W_{v'n}(t) = \langle \psi_{v'}^{(0)}(x, t) | \hat{W}(t) \psi_n^{(0)}(x, t) \rangle \quad (33.33)$$

$$W_{vv}(t) = \langle \psi_v^{(0)}(x, t) | \hat{W}(t) \psi_v^{(0)}(x, t) \rangle \quad (33.34)$$

Solving Eq. (33.31), we find the coefficient $c_{v'}$ in the first approximation:

$$c_{v'} = \Delta c_{v'}^{(1)} = \lambda c_v^{(1)}$$

$$= -\frac{i}{\hbar} \int_0^t V_{v'n}(t) dt = -\frac{i}{\hbar} \int_0^t v_{v'n}(t) e^{i\omega_{v'n} t} dt \quad (33.35)$$

where

$$v_{v'n}(t) = \langle \psi_{v'}^{(0)}(x) | \hat{V}(t) \psi_n^{(0)}(x) \rangle; \quad \omega_{v'n} = (E_{v'} - E_n)/\hbar \quad (33.36)$$

Formula (33.20) determines the probability of the transition from the definite state n to the definite state m . Unlike this, for transitions into a continuous spectrum, we must consider the probability of a transition from the state n into one of the states belonging to the interval from v to $v + dv$. The expression for this probability is (we have discarded the prime on v)

$$dP_{nv} = |c_v|^2 dv = \frac{1}{\hbar^2} \left| \int_0^\tau v_{vn}(t) e^{i\omega_{vn} t} dt \right|^2 dv \quad (33.37)$$

We shall consider two limiting cases of the behaviour of the perturbation $\hat{V}(t)$: (1) the case when the perturbation, having appeared at the instant $t = 0$, slowly grows from zero to a certain value, and then slowly diminishes to zero at the moment $t = \tau$. During the entire interval from 0 to τ , the derivative $d\hat{V}/dt$ is very small. Such a perturbation is said to be adiabatic; (2) the case of a very rapid,

¹ In performing these calculations, we must take into account that $\langle \psi_{v'}^{(0)}(x, t) | \psi_v^{(0)}(x, t) \rangle = \delta(v' - v)$ [see (12.6)].

"sudden", switching on of the interaction. Having grown in a very short interval Δt from zero to a certain value, the perturbation then changes adiabatically and by the instant $t = \tau$ vanishes adiabatically. In this case, the derivative $d\hat{V}/dt$ is very large in the interval from 0 to Δt , and is very small all the other time.

We shall consider that the eigenvalues of the unperturbed operator are discrete and not degenerate. To assess the probabilities of a transition, we shall use formula (33.21). Assume that

$$\left| \frac{dv_{mn}}{dt} \right| \ll \hbar \omega_{mn}^2 \quad (33.38)$$

(the adiabatic change in the perturbation). During the time τ , the exponential factor in (33.21) performs many oscillations. Therefore, the comparatively slowly changing factor dv_{mn}/dt may be put outside the integral, taking a mean value within the interval $[0, \tau]$ for it. We may thus state that

$$\begin{aligned} P_{nm} &\approx \frac{1}{\hbar^2 \omega_{mn}^2} \left| \frac{dv_{mn}}{dt} \right|^2 \left| \int_0^\tau e^{i\omega_{mn}t} dt \right|^2 \\ &= \frac{1}{\hbar^2 \omega_{mn}^2} \left| \frac{dv_{mn}}{dt} \right|^2 \left| \frac{e^{i\omega_{mn}\tau/2} (e^{i\omega_{mn}\tau/2} - e^{-i\omega_{mn}\tau/2})}{i\omega_{mn}} \right|^2 \\ &= \frac{4}{\hbar^2 \omega_{mn}^4} \left| \frac{dv_{mn}}{dt} \right|^2 \sin^2 \frac{\omega_{mn}\tau}{2} \end{aligned}$$

Taking the condition (33.38) into account, we find that $P_{nm} \ll 1$. This signifies that a system, which before a perturbation satisfying the condition (33.38) begins to act was in the non-degenerate state ψ_n , remains in this state after the perturbation stops acting.

When a perturbation begins to act suddenly, the contribution to the integral (33.21) will be appreciable only during the time Δt needed to switch on the perturbation. We shall consider this time to be much smaller than $1/\omega_{mn}$. All the other time, the perturbation changes adiabatically so that it cannot make an appreciable contribution to the probability of a transition, as was established above. During the very small time Δt , the exponential factor changes slightly ($\omega_{mn} \Delta t \ll 1$), therefore it can be put outside the integral and assumed to equal unity. The result is

$$P_{nm} \approx \frac{1}{\hbar^2 \omega_{mn}^2} \left| \int_0^{\Delta t} \frac{dv_{mn}}{dt} dt \right|^2 = \frac{1}{\hbar^2 \omega_{mn}^2} |v_{mn}(\Delta t)|^2 \quad (33.39)$$

It is obvious that $v_{mn}(\Delta t)$ is determined by the magnitude of the suddenly switched on perturbation.

34. Perturbations Varying Harmonically with Time

Let a perturbation within the interval $0 \leq t \leq \tau$ have the form

$$\hat{V}(t) = \hat{V}(e^{i\omega t} + e^{-i\omega t}) = \frac{1}{2} \hat{V} \cos \omega t \quad (34.1)$$

and when $t < 0$ and $t > \tau$, it is zero. Here \hat{V} is an operator not containing the time explicitly.

Consider a transition from a discrete spectrum to a continuous one occurring under the influence of such a perturbation. In this case, the matrix element $V_{vn}(t)$ [equal to the product of λ and expression (33.33)] can be written as

$$\begin{aligned} V_{vn}(t) &= \langle \psi_v^{(0)}(x) e^{-(i/\hbar)E_v t} | \hat{V}(e^{i\omega t} + e^{-i\omega t}) \psi_n^{(0)}(x) e^{-(i/\hbar)E_n t} \rangle \\ &= \langle \psi_v^{(0)}(x) | \hat{V} \psi_n^{(0)}(x) \rangle e^{i\omega_{vn} t} (e^{i\omega t} + e^{-i\omega t}) \\ &= V_{vn} [e^{i(\omega_{vn} + \omega)t} + e^{i(\omega_{vn} - \omega)t}] \end{aligned} \quad (34.2)$$

where V_{vn} is simply a number, and $\omega_{vn} = (E_v - E_n)/\hbar$.

Integration of expression (34.2) with respect to time yields

$$\int_0^\tau V_{vn}(t) dt = V_{vn} \left\{ \frac{e^{i(\omega_{vn} + \omega)\tau} - 1}{i(\omega_{vn} + \omega)} + \frac{e^{i(\omega_{vn} - \omega)\tau} - 1}{i(\omega_{vn} - \omega)} \right\} \quad (34.3)$$

The result obtained indicates that there is an especially high probability of transitions to states that are within the interval from v to $v + dv$ for which $\omega_{vn} \approx \omega$, i.e.

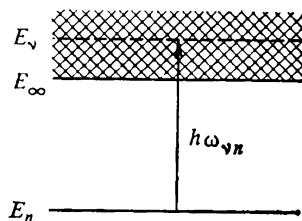


Fig. 34.1

$$\hbar\omega_{vn} = E_v - E_n \approx \hbar\omega \quad (34.4)$$

For this condition to be observed, the perturbation frequency ω must satisfy the requirement

$$\hbar\omega > E_\infty - E_n \quad (34.5)$$

where E_∞ is the boundary between the discrete and the continuous regions of the spectrum (Fig. 34.1). We shall assume in the following that the condition (34.5) holds. We must note that, as follows from Fig. 34.1, we have $\omega_{vn} > 0$.

At a frequency ω close to ω_{vn} ($\omega \approx \omega_{vn}$), the second term in (34.3) will be much larger than the first one. We therefore drop the

first term, and (34.3) becomes

$$\begin{aligned} \int_0^{\tau} V_{vn}(t) dt &\approx V_{vn} \frac{\exp[i(\omega_{vn} - \omega)\tau] - 1}{i(\omega_{vn} - \omega)} = V_{vn} \exp\left[i(\omega_{vn} - \omega)\frac{\tau}{2}\right] \\ &\times \frac{\exp[i(\omega_{vn} - \omega)\tau/2] - \exp[-i(\omega_{vn} - \omega)\tau/2]}{2i(\omega_{vn} - \omega)/2} \\ &= V_{vn} \exp\left[i(\omega_{vn} - \omega)\frac{\tau}{2}\right] \frac{\sin[(\omega_{vn} - \omega)\tau/2]}{(\omega_{vn} - \omega)/2} \end{aligned}$$

Squaring the magnitude of this expression and introducing it into (33.37), we obtain

$$dP_{nv} = \frac{1}{\hbar^2} |V_{vn}|^2 \frac{\sin^2[(\omega_{vn} - \omega)\tau/2]}{[(\omega_{vn} - \omega)/2]^2} d\nu = \frac{1}{\hbar^2} |V_{vn}|^2 f(\xi, \tau) d\nu \quad (34.6)$$

where $\xi = \xi(\nu) = (\omega_{vn} - \omega)/2$ is the argument, and τ is a parameter (dP_{nv} is a function of ν).

Figure 34.2 depicts the function

$$f(\xi, \tau) = \frac{\sin^2 \tau \xi}{\xi^2} \quad (34.7)$$

contained in (34.6). A glance at the figure shows that the probability is the highest for the transitions for which the values of $\xi =$

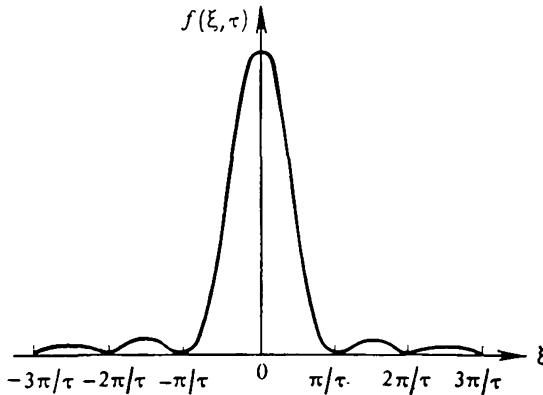


Fig. 34.2

$= (\omega_{vn} - \omega)/2 = (E_v - E_n - \hbar\omega)/2\hbar$ are confined within the limits of $\sim \pm 1/\tau$, i.e. the magnitude of the difference between E_v and $E_n + \hbar\omega$ does not exceed $\sim \hbar/\tau$:

$$E_v - (E_n + \hbar\omega) \leq \frac{\hbar}{\tau} \quad (34.8)$$

The indeterminacy of the energy of the final state also satisfies this condition

$$\Delta E_v \sim \frac{\hbar}{\tau} \quad (34.9)$$

[compare with (16.5)].

Examination of (34.9) reveals that when $\tau \rightarrow \infty$, we have $\Delta E_v \rightarrow 0$ so that only transitions to a state with a quite definite energy $E_{v'}$, satisfying the condition

$$E_{v'} - E_n = \hbar\omega \quad (34.10)$$

have a non-zero probability.

We can arrive at the same result in a different way. Let us write expression (34.6) in the form

$$dP_{nv} = \frac{1}{\hbar^2} |V_{vn}|^2 F(\xi, \tau) \pi \tau dv$$

where

$$F(\xi, \tau) = \frac{1}{\pi \tau} f(\xi, \tau) = \frac{\sin^2 \tau \xi}{\pi \tau \xi^2} \quad (34.11)$$

We shall show that

$$\lim_{\tau \rightarrow \infty} F(\xi, \tau) = \lim_{\tau \rightarrow \infty} \frac{\sin^2 \tau \xi}{\pi \tau \xi^2} = \delta(\xi) \quad (34.12)$$

Indeed, since $\lim_{\alpha \rightarrow 0} (\sin^2 \alpha / \alpha^2) = 1$, when $\xi = 0$ expression (34.12) equals τ/π , i.e. in the limit expands to infinity. Further, at any $\xi \neq 0$, the limit (34.12) is zero. Finally,

$$\int_{-\infty}^{+\infty} \frac{\sin^2 \tau \xi}{\pi \tau \xi^2} d\xi = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\sin^2 u}{u^2} du = 1$$

Hence, expression (34.12) has all the properties of a δ -function. Consequently, at very large values of τ , formula (34.6) can be written as

$$\begin{aligned} dP_{nv} &= \frac{\pi}{\hbar^2} |V_{vn}|^2 \delta\left(\frac{\omega_{vn} - \omega}{2}\right) \tau dv \\ &= \frac{\pi}{\hbar^2} |V_{vn}|^2 \delta\left(\frac{E_v - E_n - \hbar\omega}{2\hbar}\right) \tau dv \\ &= \frac{2\pi}{\hbar} |V_{vn}|^2 \delta(E_v - E_n - \hbar\omega) \tau dv \end{aligned} \quad (34.13)$$

[we have taken advantage of the property (VIII.7)].

Integration of (34.13) over v yields the probability of the system passing from the n -th discrete state to one of the states of the continuous spectrum:

$$\begin{aligned} P = \int dP_{nv} &= \frac{2\pi}{\hbar} \int |V_{vn}|^2 \delta(E_v - E_n - \hbar\omega)\tau dv \\ &= \frac{2\pi}{\hbar} |V_{vn}|^2 g_{v'\tau} \end{aligned} \quad (34.14)$$

Here $g_{v'}$ is the degree of degeneracy of the level with the energy $E_{v'}$ satisfying the condition (34.10). We have thus again arrived at the conclusion that when $\tau \rightarrow \infty$, only transitions to states with the energy $E_{v'}$ that satisfies the condition (34.10) have a non-zero probability.

The formulas we have obtained hold when the changes in the initial function $\psi_n^{(0)}$ are relatively small. For this requirement to be obeyed, the total probability of a transition, i.e. the quantity (34.14), must be much smaller than unity:

$$\frac{2\pi}{\hbar} |V_{vn}|^2 g_{v'\tau} \ll 1 \quad (34.15)$$

Since the left-hand side of this inequality is proportional to τ , the time of action of the perturbation must not be too great. The limitation of τ leads, in accordance with (34.9), to the interval ΔE_v being finite.

By (34.13), dP_{nv} is proportional to the time τ of action of the perturbation. Therefore, dividing expression (34.13) by τ , we obtain the probability of a transition to a state within the interval from v to $v + dv$ in unit time:

$$dP_{nv} |_{\Delta t=1} = \frac{2\pi}{\hbar} |V_{vn}|^2 \delta(E_v - E_n - \hbar\omega) dv \quad (34.16)$$

The index v characterizing the states of the continuous spectrum includes a set of parameters among which may be the energy E of a state. Several states differing in the values of other parameters may correspond to the same value of E . Therefore, to the interval dE of energy values there corresponds the interval of the values of the index v equal to

$$dv = g(E) dE \quad (34.17)$$

where $g(E)$ is a function known as the density of states. Introducing (34.17) into (34.16) and substituting E for v accordingly, we obtain

$$dP_{nE} |_{\Delta t=1} = \frac{2\pi}{\hbar} |V_{En}|^2 \delta(E - E_n - \hbar\omega) g(E) dE \quad (34.18)$$

Integration over E yields the total probability of a transition

$$P |_{\Delta t=1} = \frac{2\pi}{\hbar} |V_{E'n}|^2 g(E') \quad (34.19)$$

where E' satisfies the same condition as E_v in (34.10) [compare with (34.14)].

The results we have obtained cannot be applied to transitions between the states of a discrete spectrum because in the resonance case (i.e. when $\omega = \omega_{nm}$) the corrections to $\psi_n^{(0)}$ become large and the conditions of applicability of the derived formulas are violated. Therefore, a different approach is needed in solving problems on transitions in a discrete spectrum under the influence of a perturbation of the form of (34.1).

We shall proceed from the exact equation (33.8) for the coefficients $c_m(t)$

$$i\hbar \frac{dc_m(t)}{dt} = \sum_k V_{mk}(t) c_k(t) \quad (34.20)$$

Substitution into (33.7) of expression (34.1) for $\hat{V}(t)$ results in a value of $V_{mk}(t)$ differing from (34.2) only in containing the indices mk instead of vn . Introducing this value into (34.20), we arrive at the equation

$$i\hbar \frac{dc_m(t)}{dt} = \sum_k V_{mk} [e^{i(\omega_{mk} + \omega)t} + e^{i(\omega_{mk} - \omega)t}] c_k(t) \quad (34.21)$$

The greatest role in this equation is played by the terms that oscillate with the lowest of the frequencies. This can be understood by turning to formula (34.3): the largest term in this formula is the one with the smaller denominator, i.e. the term oscillating with the lower frequency. We must note that in (34.3) all the ω_{vn} 's are greater than zero. Formula (34.21), on the other hand, contains terms with both positive and negative values of ω_{mk} .

Let us choose from the entire set of unperturbed states two states m and n for which $\omega_{mn} = (E_m - E_n)/\hbar$ differs from ω by the very small quantity ϵ :

$$\omega_{mn} - \omega = \frac{E_m - E_n - \hbar\omega}{\hbar} = \epsilon \quad (34.22)$$

We must note that when the levels are not spaced equally, this choice can be made, generally speaking, in a single way.

In accordance with the above, the coefficients $c_m(t)$ and $c_n(t)$ will change the most noticeably with time. It is exactly the equations (34.21) written for these coefficients that will contain a very slowly oscillating term. The variation of the other coefficients with time may be disregarded.

Assume that $E_m > E_n$, so that $\omega_{mn} > 0$. It is evident that $\omega_{nm} = -\omega_{mn} < 0$. Consequently, in Eq. (34.21) written for c_m , we must retain only the term with the exponential $e^{i(\omega_{mn} - \omega)t} = e^{iet}$ on the right. In Eq. (34.21), written for c_n , on the other hand, we must retain

the term with the exponential $e^{i(\omega_{nm} + \omega)t} = e^{-i\epsilon t} [(\omega_{nm} + \omega) = -(-\omega_{nm} - \omega) = -(\omega_{mn} - \omega)]$. We thus arrive at the following system of equations of the form of (34.21):

$$i\hbar \frac{dc_m(t)}{dt} = V_{mn} e^{i\epsilon t} c_n(t) \quad (34.23)$$

$$i\hbar \frac{dc_n(t)}{dt} = V_{nm} e^{-i\epsilon t} c_m(t) \quad (34.24)$$

$$i\hbar \frac{dc_l(t)}{dt} \approx 0 \text{ (for all } l\text{'s not equal to } m \text{ and } n\text{)}$$

To find the coefficients $c_m(t)$ and $c_n(t)$, we must solve the system of two differential equations (34.23) and (34.24). Let us introduce instead of $c_n(t)$ the auxiliary function

$$u_n(t) = e^{i\epsilon t} c_n(t) \quad (34.25)$$

Differentiation of this function yields

$$\dot{c}_n(t) = [\dot{u}_n(t) - i\epsilon u_n(t)] e^{-i\epsilon t} \quad (34.26)$$

With a view to (34.25) and (34.26), Eqs. (34.23) and (34.24) acquire the form

$$\begin{aligned} i\hbar \dot{c}_m &= V_{mn} u_n \\ i\hbar [\dot{u}_n - i\epsilon u_n] &= V_{nm} c_m \end{aligned}$$

We can delete the function $c_m(t)$ from these equations by preliminarily differentiating the second equation with respect to t . As a result, we obtain the following differential equation for $u_n(t)$:

$$\ddot{u}_n - i\epsilon \dot{u}_n + \frac{|V_{mn}|^2}{\hbar^2} u_n = 0 \quad (34.27)$$

(owing to the Hermitian nature of the operator \hat{V} , the relation $V_{nm} = V_{mn}^*$ holds).

Solving Eq. (34.27) by introducing $u_n = e^{i\lambda t}$, we obtain two values for λ :

$$\lambda_1 = \frac{\epsilon}{2} + \omega_0, \quad \lambda_2 = \frac{\epsilon}{2} - \omega_0 \quad (\omega_0 = \sqrt{\frac{\epsilon^2}{4} + \frac{|V_{mn}|^2}{\hbar^2}}) \quad (34.28)$$

Consequently, the general solution of Eq. (34.27) has the form

$$u_n(t) = A e^{i\lambda_1 t} + B e^{i\lambda_2 t}$$

In accordance with (34.25), we have

$$c_n(t) = e^{-i\epsilon t} u_n(t) = A e^{i\alpha_1 t} + B e^{-i\alpha_2 t} \quad (34.29)$$

where

$$\alpha_1 = \lambda_1 - \epsilon = \omega_0 - (\epsilon/2), \quad \alpha_2 = \epsilon - \lambda_2 = \omega_0 + (\epsilon/2) \quad (34.30)$$

Introducing the derivative of the function (34.29) into the left-hand side of Eq. (34.24), we obtain the following expression for $c_m(t)$:

$$c_m(t) = \frac{\hbar}{V_{nm}} (\alpha_2 B e^{-i\alpha_1 t} - \alpha_1 A e^{i\alpha_1 t}) \quad (34.31)$$

We have thus obtained the formulas (34.29) and (34.31) for the coefficients $c_m(t)$ and $c_n(t)$. The constants A and B are determined from the condition of normalization and the initial conditions.

Assume that at the instant when the perturbation begins to act (i.e. when $t = 0$), the system is in the state $\psi_n^{(0)}$. Then at the instant t , the psi-function of the system will be [see (34.4)]:

$$\begin{aligned} \psi(x, t) = c_n(t) \psi_n^{(0)}(x, t) + c_m(t) \psi_m^{(0)}(x, t) &= (A e^{i\alpha_1 t} + B e^{-i\alpha_1 t}) \psi_n^{(0)} \\ &\quad + (\hbar / V_{nm}) (\alpha_2 B e^{-i\alpha_1 t} - \alpha_1 A e^{i\alpha_1 t}) \psi_m^{(0)} \end{aligned}$$

From the initial condition $\psi(x, 0) = \psi_n^{(0)}(x, 0)$, we obtain the following relations:

$$A + B = 1, \quad \alpha_2 B - \alpha_1 A = 0$$

From these relations, with a view to (34.30), we find that

$$A = \frac{\alpha_2}{2\omega_0}, \quad B = \frac{\alpha_1}{2\omega_0}$$

Replacing α_1 and α_2 with their values from (34.30), and also taking into account that $\alpha_1 \alpha_2 = \omega_0^2 - \varepsilon^2/4 = |V_{mn}|^2/\hbar^2 = V_{mn} V_{nm}/\hbar^2$, we can write

$$\begin{aligned} \psi(x, t) &= \frac{1}{2\omega_0} \left[\left(\omega_0 + \frac{\varepsilon}{2} \right) e^{i(\omega_0 - \varepsilon/2)t} + \left(\omega_0 - \frac{\varepsilon}{2} \right) e^{-i(\omega_0 + \varepsilon/2)t} \right] \psi_n^{(0)} \\ &\quad + \frac{V_{mn}}{2\hbar\omega_0} [e^{-i(\omega_0 - \varepsilon/2)t} - e^{i(\omega_0 + \varepsilon/2)t}] \psi_m^{(0)} \\ &= e^{-i\varepsilon t/2} \left[\cos \omega_0 t + \frac{i\varepsilon}{2\omega_0} \sin \omega_0 t \right] \psi_n^{(0)} \\ &\quad - e^{i\varepsilon t/2} \frac{iV_{mn}}{\hbar\omega_0} \sin \omega_0 t \cdot \psi_m^{(0)} \quad (34.32) \end{aligned}$$

It is not difficult to see that the sum of the squares of the magnitudes of the coefficients at $\psi_n^{(0)}$ and $\psi_m^{(0)}$ equals unity.

The square of the magnitude of the coefficient at $\psi_m^{(0)}$ is

$$|c_m(t)|^2 = \frac{|V_{mn}|^2}{\hbar^2 \omega_0^2} \sin^2 \omega_0 t = \frac{|V_{mn}|^2}{2\hbar^2 \omega_0^2} (1 - \cos 2\omega_0 t) \quad (34.33)$$

Consequently, the probability of the fact that the system at the instant t will be in the state $\psi_m^{(0)}(x, t)$ varies with the frequency $2\omega_0$ within the limits from zero to $|V_{mn}|^2/\hbar^2 \omega_0^2$. Recall that [see (34.28) and (34.22)]

$$\omega_0 = \sqrt{\frac{\varepsilon^2}{4} + \frac{|V_{mn}|^2}{\hbar^2}} = \frac{1}{2} \hbar \sqrt{(E_m - E_n - \hbar\omega)^2 + 4|V_{mn}|^2}$$

In exact resonance (i.e. when $\epsilon = 0$), we have $\omega_0 = |V_{mn}|/\hbar$, and (34.33) becomes

$$|c_m(t)|^2 = \frac{1}{2} \left[1 - \cos \frac{2|V_{mn}|}{\hbar} t \right] \quad (34.34)$$

Examination of (34.34) shows that the system periodically passes from the state n to the state m and back. The frequency of this transition grows with increasing $|V_{mn}|$, i.e. when the perturbation becomes more intensive.

We must stress the circumstance that all the results obtained hold only if at the instant when the periodic perturbation begins to act, the system is on one of the levels E_n or E_m satisfying the condition (34.22).

It can be shown that if a discrete spectrum is equidistant (as, for instance, in a harmonic oscillator), when condition (34.22) is observed, the system will pass to higher and higher levels. This corresponds to the buildup of a classical oscillator under the action of an external force varying with the resonance frequency.

35. Transitions in a Continuous Spectrum

Assuming in formula (34.1) that $\omega = 0$, we obtain the perturbation operator \hat{V} that does not contain the time explicitly [it is equivalent to $2\hat{V}$ in (34.1)]. Accordingly, the expression (34.2) for the matrix elements will be

$$V_{vn}(t) = V_{vn} e^{i\omega_{vn}t} \quad (35.1)$$

Integration of a matrix element over t yields

$$\int_0^\tau V_{vn}(t) dt = V_{vn} \frac{e^{i\omega_{vn}\tau} - 1}{i\omega_{vn}} = V_{vn} e^{i\omega_{vn}\tau/2} \frac{\sin(\omega_{vn}\tau/2)}{\omega_{vn}/2}$$

And, further,

$$dP_{nv} = \frac{1}{\hbar^2} |V_{vn}|^2 \frac{\sin^2(\omega_{vn}\tau/2)}{(\omega_{vn}/2)^2} d\tau \quad (35.2)$$

By analogy with (34.16), we can write that

$$dP_{nv} |_{\Delta t=1} = \frac{\pi}{\hbar^2} |V_{vn}|^2 \delta\left(\frac{\omega_{vn}}{2}\right) d\tau = \frac{2\pi}{\hbar} |V_{vn}|^2 \delta(E_v - E_n) dv \quad (35.3)$$

A glance at (35.3) shows that a time-independent perturbation may cause transitions only between degenerate states. The levels of a continuous spectrum are always degenerate (for instance, for a free particle the energy E is realized in a multitude of states differing in the direction of the momentum p). For this reason, the action of

a constant perturbation is of interest mainly as applied to the states of a continuous spectrum. Having this in view, let us rewrite (35.3) as follows:

$$dP_{v_0 v} |_{\Delta t=1} = \frac{2\pi}{\hbar} | V_{vv_0} |^2 \delta(E_v - E_{v_0}) dv \quad (35.4)$$

Here v_0 is the index of the initial state which we now assume to belong to a continuous spectrum, and v is the index of the final state.

We write by analogy with (34.17) that

$$dv = \frac{d\mathbf{v}}{dE} dE = g(E) dE \quad (35.5)$$

Let us perform such a replacement in (35.4) after which we shall integrate over E . The result is the total probability of a transition from the state v_0 to other states having the same energy E :

$$P_{v_0} |_{\Delta t=1} = \frac{2\pi}{\hbar} | V_{Ev_0} |^2 g(E) \quad (35.6)$$

Let the role of the index v be played by the momentum \mathbf{p} of a particle. Hence

$$dv = dp_x dp_y dp_z = p^2 dp d\Omega = pm_0 d\Omega dE = g(E) dE$$

where $d\Omega$ is a solid angle element, and $E = p^2/2m_0$ is the energy of the final states of the particle. Substitution of the found value of $g(E)$ into (34.6) yields

$$P |_{\Delta t=1} = \frac{2\pi}{\hbar} | V_{pp_0} |^2 pm_0 d\Omega \quad (35.7)$$

This formula gives the probability of the fact that a particle having the momentum p_0 will pass in unit time to one of the states, the directions of whose momenta are within the solid angle $d\Omega$.

36. Potential Energy as a Perturbation

Let us consider the case when the potential energy of a particle in an external field can be dealt with as a perturbation. Here the unperturbed Schrödinger equation is an equation of the freely moving particle:

$$-\frac{\hbar^2}{2m_0} \nabla^2 \psi^{(0)} = E^{(0)} \psi^{(0)} \quad (36.1)$$

If we introduce the notation

$$k^2 = \frac{2m_0 E^{(0)}}{\hbar^2} = \frac{p^2}{\hbar^2} \quad (36.2)$$

(p is the momentum of the particle), Eq. (36.1) can be given the form

$$(\nabla^2 + k^2) \psi^{(0)} = 0 \quad (36.3)$$

A plane wave is the solution of this equation, namely,

$$\Psi^{(0)} = e^{ikr} \quad (36.4)$$

($\mathbf{k} = \mathbf{p}/\hbar$).

Adding the perturbation operator \hat{V} , whose role is played by the potential energy U , to the operator $\hat{H}_0 = -(\frac{\hbar^2}{2m_0}) \nabla^2$ in Eq. (36.1), we obtain the equation

$$\left(-\frac{\hbar^2}{2m_0} \nabla^2 + U \right) \psi = E\psi \quad (36.5)$$

To find the psi-function in the first approximation, we introduce $\psi = \psi^{(0)} + \Delta\psi^{(1)}$ and $E = E^{(0)}$ into (36.5):

$$\left(-\frac{\hbar^2}{2m_0} \nabla^2 + U \right) (\psi^{(0)} + \Delta\psi^{(1)}) = E^{(0)} (\psi^{(0)} + \Delta\psi^{(1)}) \quad (36.6)$$

Opening the parentheses and taking into account (36.1), we obtain

$$-\frac{\hbar^2}{2m_0} \nabla^2 \Delta\psi^{(1)} + U\psi^{(0)} + U\Delta\psi^{(1)} = E^{(0)} \Delta\psi^{(1)}$$

Owing to the smallness of the quantities U and $\Delta\psi^{(1)}$, we may disregard their product. The equation remaining after this has been done can be reduced to the following form with the aid of relation (36.2):

$$\nabla^2 \Delta\psi^{(1)}(\mathbf{r}) + k^2 \Delta\psi^{(1)}(\mathbf{r}) = \frac{2m_0}{\hbar^2} U(\mathbf{r}) \psi^0(\mathbf{r}) \quad (36.7)$$

Let us leave this equation for a while and turn to the d'Alembert equation for the scalar potential $\varphi(\mathbf{r}, t)$ produced by charges of the density $\rho(\mathbf{r}, t)$, known from electrodynamics:

$$\nabla^2 \varphi(\mathbf{r}, t) - \frac{1}{c^2} \frac{\partial^2 \varphi(\mathbf{r}, t)}{\partial t^2} = -4\pi\rho(\mathbf{r}, t) \quad (36.8)$$

The retarded potential

$$\varphi(\mathbf{r}, t) = \int \frac{\rho(\mathbf{r}', t-R/c)}{R} dV' \quad (36.9)$$

is the solution of this equation. We have introduced the notation

$$R = |\mathbf{r} - \mathbf{r}'| \quad (36.10)$$

[see Vol. 1, formulas (76.1) and (76.11)].

Consider the case when the charge density at each point varies according to a harmonic law:

$$\rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) e^{-i\omega t} \quad (36.11)$$

Formula (36.9) in this case becomes

$$\varphi(\mathbf{r}, t) = \int \frac{\rho_0(\mathbf{r}') e^{-i\omega(t-R/c)}}{R} dV' = \varphi_0(\mathbf{r}) e^{-i\omega t} \quad (36.12)$$

where

$$\varphi_0(\mathbf{r}) = \int \frac{\rho_0(\mathbf{r}') e^{i\omega R/c}}{R} dV' \quad (36.13)$$

Introducing the functions (36.12) and (36.11) into (36.8) and cancelling the factor $e^{-i\omega t}$ in all terms, we obtain a differential equation for $\varphi_0(\mathbf{r})$:

$$\nabla^2 \varphi_0(\mathbf{r}) + \frac{\omega^2}{c^2} \varphi_0(\mathbf{r}) = -4\pi\rho_0(\mathbf{r}) \quad (36.14)$$

The function (36.13) is a solution of this equation.

Equation (36.7) which we are interested in is similar to Eq. (36.14). Consequently, its solution can be obtained by replacing in formula (36.13) ω/c with k and $\rho_0(\mathbf{r}')$ with $-(m_0/2\pi\hbar^2) U(\mathbf{r}') \psi^{(0)}(\mathbf{r}') = -(m_0/2\pi\hbar^2) U(\mathbf{r}') e^{ikr' \cos \vartheta}$ [see (36.4); ϑ is the angle between the vectors \mathbf{k} and \mathbf{r}']. As a result, we obtain

$$\Delta\psi^{(1)}(\mathbf{r}) = -\frac{m_0}{2\pi\hbar^2} \int \frac{1}{|\mathbf{r}-\mathbf{r}'|} U(\mathbf{r}') e^{ik(r' \cos \vartheta + |\mathbf{r}-\mathbf{r}'|)} dV' \quad (36.15)$$

[we have replaced R with $|\mathbf{r}-\mathbf{r}'|$; see (36.10)]. Recall that this function is a first-order correction to the unperturbed functions $\psi^{(0)}(\mathbf{r})$ due to the perturbation $\hat{V} = U(\mathbf{r})$.

Let us find the conditions in which the potential $U(\mathbf{r})$ can be considered as a perturbation. We shall proceed from the fact that the condition for the applicability of the perturbation theory consists in the requirement $|\Delta\psi^{(1)}| \ll |\psi^{(0)}|$. Since the magnitude of the unperturbed function (36.4) is unity, we arrive at the condition $|\Delta\psi^{(1)}| \ll 1$, i.e.

$$\left| \frac{m_0}{2\pi\hbar^2} \left| \int \frac{1}{|\mathbf{r}-\mathbf{r}'|} U(\mathbf{r}') e^{ik(r' \cos \vartheta + |\mathbf{r}-\mathbf{r}'|)} dV' \right| \right| \ll 1 \quad (36.16)$$

Let the function $U(\mathbf{r})$ noticeably differ from zero only when $r \leqslant a$ (the wavy line signifies that we are dealing not with exact values, but with the orders of magnitude of the relevant quantities). Hence, the main contribution to expression (36.16) is made by the part of the integral that relates to the volume of radius a . It thus follows that $\Delta\psi^{(1)}$ diminishes with r so that if the condition (36.16) is observed at $r = 0$, it will be observed at any r . The condition (36.16) can thus be replaced with the condition

$$\frac{m_0}{2\pi\hbar^2} \left| \int_{r' \leqslant a} \frac{1}{r'} U(\mathbf{r}') e^{ikr'(\cos \vartheta + 1)} dV' \right| \ll 1 \quad (36.17)$$

Let us assess the integral in two limiting cases:

1. At such small energies that $ka \ll 1$. Accordingly,

$$E \ll \frac{\hbar^2}{m_0 a^3} \quad (36.18)$$

(we have dropped the unimportant factor two in the denominator).

2. At such great energies that $ka \gg 1$. Accordingly,

$$E \gg \frac{\hbar^2}{m_0 a^2} \quad (36.19)$$

We must note that the expression $\hbar^2/m_0 a^2$ gives the order of magnitude of the kinetic energy that, in accordance with the uncertainty relation, a particle confined in a volume with a radius of the order of a would have (the momentum of such a particle would be of the order of \hbar/a). It can also be shown that this expression equals the minimum depth of a spherical potential well of radius a at which a bound state of a particle with a discrete energy level appears.

In the first case, the exponential factor in the integrand in the entire region of integration virtually equals unity so that (36.17) transforms into

$$\frac{m_0}{2\pi\hbar^2} \left| \int_{r' \leq a} \frac{U(r') dV'}{r'} \right| \approx \frac{m_0}{2\pi\hbar^2} |\langle U \rangle| \int_{r' \leq a} \frac{dV'}{r'} = \frac{m_0}{2\pi\hbar^2} |\langle U \rangle| 2\pi a^2 \ll 1$$

where $\langle U \rangle$ is the value of the potential energy averaged over the region of radius a . The inequality obtained leads to the condition

$$|\langle U \rangle| \ll \frac{\hbar^2}{m_0 a^2} \quad (36.20)$$

Remember that this condition must be observed for energies satisfying relation (36.18).

In the second case, the exponential factor in (36.17) varies very rapidly and in integration over the region $r' \leq a$ it completes many cycles of change. Consequently, we replace the comparatively slowly varying factor $U(r')$ with its mean value $\langle U \rangle$ and put it outside the integral. As a result, the condition (36.17) becomes

$$\frac{m_0}{\hbar^2} |\langle U \rangle| \left| \int_{r' \leq a} e^{i\hbar r'(\cos\theta+1)} \sin\theta d\theta r' dr' \right| \ll 1 \quad (36.21)$$

(we have substituted $2\pi \sin\theta d\theta r'^2 dr'$ for dV' and cancelled 2π in the numerator and denominator; here θ is the angle between the

vectors \mathbf{k} and \mathbf{r}' measured from the fixed vector \mathbf{k}). Evaluation of the integral yields

$$\int_0^a r' dr' \int_0^\pi e^{ikr'(\cos\theta+1)} \sin\theta d\theta \\ = \frac{1}{ik} \int_0^a (e^{2ika} - 1) dr' = \frac{1}{ik} \left[\frac{e^{2ika} - 1}{2ik} - a \right] \approx -\frac{a}{ik}$$

(we have disregarded the first term in the brackets because by our condition k is very large).

Introducing the found value of the integral into inequality (36.21), we obtain

$$\frac{m_0}{\hbar^2} |\langle U \rangle| \frac{a}{k} \ll 1$$

whence

$$|\langle U \rangle| \ll \frac{k\hbar^2}{m_0 a} \quad (36.22)$$

We remind our reader that the function U must satisfy this condition at energy values determined by relation (36.19). We must note that the condition (36.22) is weaker than (36.20). Indeed, the right-hand side of (36.22) is ka times larger than the right-hand side of (36.20), and in case 2 the product ka is very large. Hence, if U can be considered as a perturbation at low energies of a particle, this is also possible at high energies.

The condition (36.22) can be represented in the form

$$|\langle U \rangle| \ll \frac{\hbar v}{a} \quad (36.23)$$

where $v = \hbar k/m_0 = p/m_0$ is the velocity of a particle.

For a Coulomb field, the potential $U = \alpha/r$ diminishes so slowly that we cannot introduce the concept of the effective radius a of the region of interaction. Taking arbitrarily a certain quantity a , let us find the value of the Coulomb potential averaged over a sphere of radius a :

$$\langle U \rangle = \frac{1}{\frac{4}{3} \pi a^3} \int_0^a \frac{\alpha}{r} 4\pi r^2 dr \approx \frac{\alpha}{a}$$

Hence, the product $\langle U \rangle a$ does not depend on the choice of a and equals α . The condition (36.23) for a Coulomb field can thus be written as

$$\alpha \ll \hbar v \quad (36.24)$$

Particularly, if the potential is set up by a nucleus having the charge Ze , while the particle has the charge e , the condition (36.24) is as follows:

$$Ze^2 \ll \hbar v \quad (36.25)$$

THE QUASICLASSICAL APPROXIMATION

37. The Classical Limit

The behaviour of microobjects quite often differs only slightly from the classical behaviour. An example is the motion of an electron in a cathode-ray tube. In such cases, an approximate method of solving quantum-mechanical problems known as the **quasiclassical approximation**¹ is helpful. This method is based on the expansion of a psi-function in powers of \hbar and the dropping of the terms of higher degrees of smallness relative to \hbar .

In the same way as we write a complex number in the form $\rho e^{i\alpha}$ (ρ is the modulus, and α is the phase or argument of the number), we can write the psi-function of a particle as

$$\psi(\mathbf{r}, t) = \varphi(\mathbf{r}, t, \hbar) \exp\{if(\mathbf{r}, t, \hbar)\} \quad (37.1)$$

To emphasize the circumstance that the psi-function may include \hbar , we have introduced this constant into φ and f as a parameter.

Let us transform the function (37.1) as follows:

$$\psi(\mathbf{r}, t) = \exp\{i[f(\mathbf{r}, t, \hbar) - i \ln \varphi(\mathbf{r}, t, \hbar)]\}$$

Finally, designating the function in brackets by $(1/\hbar) S(\mathbf{r}, t, \hbar)$, we obtain

$$\psi(\mathbf{r}, t) = \exp\left\{\frac{i}{\hbar} S(\mathbf{r}, t, \hbar)\right\} \quad (37.2)$$

When considering a quasiclassical approximation, it is very convenient to represent the psi-function in the form of (37.2). In the following, we shall write the designation of the function S as $S(\mathbf{r}, t)$, dropping the parameter \hbar .

Introducing the function (37.2) into the Schrödinger equation (5.1), we obtain

$$-\frac{\hbar^2}{2m_0} \nabla^2 e^{(i/\hbar)S} + U e^{(i/\hbar)S} = i\hbar \frac{\partial}{\partial t} e^{(i/\hbar)S}$$

¹ It is also known as the Wentzel-Kramers-Brillouin (WKB) approximation, or the WKB method.

Performing differentiation¹ and cancelling the common factor $e^{(i/\hbar)S}$, we arrive at an equation for the function $S(\mathbf{r}, t)$

$$\frac{1}{2m_0} (\nabla S)^2 - \frac{i\hbar}{2m_0} \nabla^2 S + U = -\frac{\partial S}{\partial t} \quad (37.3)$$

Performing the formal limiting process $\hbar \rightarrow 0$ in (37.3), we obtain the equation

$$\frac{1}{2m_0} (\nabla S)^2 + U = -\frac{\partial S}{\partial t}$$

that coincides with the Hamilton-Jacobi equation known from classical mechanics [see Vol. 1, formula (32.15)]. It is exactly this circumstance that is had in mind when the equations of quantum mechanics are said to transform into those of classical mechanics at $\hbar \rightarrow 0$.

But we are interested in the quasiclassical case when the quantum effects, although very small, are nevertheless non-zero. For this reason, we must investigate Eq. (37.3). To simplify our task, we shall write it for stationary states and, in addition, limit ourselves to a treatment of one-dimensional motions. The time enters the psi-function of stationary states through the factor $e^{-(i/\hbar)Et}$. Therefore, the function $S(\mathbf{r}, t)$ in (37.2) has the following form for stationary states:

$$S(\mathbf{r}, t) = S(\mathbf{r}) - Et \quad (37.4)$$

Substitution of (37.4) into Eq. (37.3) leads to the following equation for the function $S(\mathbf{r})$:

$$\frac{1}{2m_0} (\nabla S)^2 - \frac{i\hbar}{2m_0} \nabla^2 S + U = E \quad (37.5)$$

or for one dimension

$$\frac{1}{2m_0} \left(\frac{dS}{dx} \right)^2 - \frac{i\hbar}{2m_0} \frac{d^2S}{dx^2} + U = E \quad (37.6)$$

By S in (37.6) and in all the following formulas is meant the function $S(x)$.

Let us attempt to find the solution of Eq. (37.6) in the form of the series

$$S = S_0 + \frac{\hbar}{i} S_1 + \left(\frac{\hbar}{i} \right)^2 S_2 + \dots \quad (37.7)$$

¹ $\nabla^2 e^{kf(r)} = \nabla(\nabla e^{kf}) = \nabla(e^{kf} k \nabla f) = e^{kf} [k^2 (\nabla f)^2 + k \nabla^2 f]$ (here k is a constant).

where the quantities S_0, S_1, S_2 , etc. no longer contain \hbar . Substitution into (37.6) yields

$$\begin{aligned} & \frac{1}{2m_0} \left[\frac{dS_0}{dx} + \frac{\hbar}{i} \frac{dS_1}{dx} + \left(\frac{\hbar}{i} \right)^2 \frac{dS_2}{dx} + \dots \right]^2 \\ & - \frac{i\hbar}{2m_0} \left[\frac{d^2S_0}{dx^2} + \frac{\hbar}{i} \frac{d^2S_1}{dx^2} + \left(\frac{\hbar}{i} \right)^2 \frac{d^2S_2}{dx^2} + \dots \right] + U = E \end{aligned} \quad (37.8)$$

We open the parentheses and brackets, writing only the terms containing \hbar/i to a power not higher than the first:

$$\frac{1}{2m_0} \left(\frac{dS_0}{dx} \right)^2 + \frac{1}{2m_0} 2 \frac{dS_0}{dx} \frac{\hbar}{i} \frac{dS_1}{dx} + \dots - \frac{i\hbar}{2m_0} \frac{d^2S_0}{dx^2} - \dots + U = E$$

Equating the coefficients at identical powers of \hbar , we obtain a series of equations

$$\left. \begin{aligned} & \frac{1}{2m_0} \left(\frac{dS_0}{dx} \right)^2 + U = E \\ & 2 \frac{dS_0}{dx} \frac{dS_1}{dx} + \frac{d^2S_0}{dx^2} = 0 \\ & \dots \dots \dots \end{aligned} \right\} \quad (37.9)$$

The first equation is a one-dimensional Hamilton-Jacobi equation for contracted action [see Vol. 1, Eq. (32.16)]. Solution of this equation relative to dS_0/dx yields

$$\frac{dS_0}{dx} = \pm \sqrt{2m_0 [E - U(x)]} = \pm p(x) \quad (37.10)$$

where

$$p_x = \sqrt{2m_0 [E - U(x)]} \quad (37.11)$$

When $E > U$, the quantity $p(x)$ is real, when $E < U$, it is imaginary. In the latter case, we shall designate it by $i |p(x)|$.

Integration of Eq. (37.10) yields

$$S_0(x) = \pm \int_{x_0}^x p(x) dx \quad (37.12)$$

(the choice of the lower integration limit will be treated below).

Differentiating (37.10) with respect to x , we find that

$$\frac{d^2S_0}{dx^2} = \pm \frac{dp}{dx} \quad (37.13)$$

Let us solve the second of Eqs. (37.9) relative to dS_1/dx and introduce into the result the values of the derivatives of S_0 with respect to x from (37.10) and (37.13). We obtain the differential equation

$$\frac{dS_1}{dx} = -\frac{1}{2p} \frac{dp}{dx} \quad (37.14)$$

Integration of (37.14) yields the function $S_1(x)$:

$$S_1(x) = -\frac{1}{2} \ln p + \text{const} \quad (37.15)$$

Hence, with an accuracy to within the terms of the order of \hbar/i , the function (37.7) becomes

$$S(x) = \pm \int_{x_0}^x p(x) dx - \frac{1}{2} \frac{\hbar}{i} \ln p + \text{const}' \quad (37.16)$$

To take into account both signs in (37.16), we shall write the expression for the psi-function in the form of two addends:

$$\begin{aligned} \psi(x) = & A \exp \left\{ \frac{i}{\hbar} \left[\int_{x_0}^x p(x) dx - \frac{1}{2} \frac{\hbar}{i} \ln p + \text{const}' \right] \right\} \\ & + B \exp \left\{ \frac{i}{\hbar} \left[- \int_{x_0}^x p(x) dx - \frac{1}{2} \frac{\hbar}{i} \ln p + \text{const}' \right] \right\} \end{aligned}$$

Introducing the notation $C_1 = A e^{(i/\hbar)\text{const}'}$, $C_2 = B e^{(i/\hbar)\text{const}'}$, we obtain the following expressions for the psi-function:

$$\begin{aligned} \psi(x) = & C_1 \frac{1}{\sqrt{p(x)}} \exp \left\{ \frac{i}{\hbar} \int_{x_0}^x p(x) dx \right\} \\ & + C_2 \frac{1}{\sqrt{p(x)}} \exp \left\{ - \frac{i}{\hbar} \int_{x_0}^x p(x) dx \right\} \quad (E > U) \quad (37.17) \end{aligned}$$

$$\begin{aligned} \psi(x) = & C'_1 \frac{1}{\sqrt{|p(x)|}} \exp \left\{ \frac{1}{\hbar} \int_{x_0}^x |p(x)| dx \right\} \\ & + C'_2 \frac{1}{\sqrt{|p(x)|}} \exp \left\{ - \frac{1}{\hbar} \int_{x_0}^x |p(x)| dx \right\} \quad (E < U) \quad (37.18) \end{aligned}$$

We can now see that only the values of the coefficients C and C' depend on the choice of the lower integration limit; the nature of the psi-functions does not depend on this choice.

The two solutions obtained differ appreciably from each other. When a particle travels in the classically allowed region ($E > U$, the momentum is real), the psi-function has an oscillating character, whereas in motion that cannot be realized from the classical viewpoint ($E < U$, the momentum is imaginary), the psi-function is the sum of two exponents.

At points where $E = U$, known as turning points, the momentum vanishes, and expressions (37.17) and (37.18) lose their meaning. Consequently, the method we have developed cannot be applied near the turning points. The behaviour of the psi-functions near the turning points, however, must be known to determine the coefficients C_1 , C_2 , C'_1 and C'_2 in the expressions for the psi-functions, i.e. to "link" the psi-functions at the turning point. It is evident from the above that the lower integration limit in (37.17) and (37.18) must be chosen so that the interval $[x_0, x]$ in which integration is being performed contains no turning points.

We must note that the factor $1/V \bar{p} \propto 1/\sqrt{v}$ in the expressions for the psi-functions has a simple meaning. Owing to this factor, the probability of a particle being within the interval from x to $x + dx$ equal to $|\psi(x)|^2 dx$ is mainly proportional to $dx/v = dt$, i.e. to the time interval during which a "classical" particle is within dx .

Let us establish the conditions of applicability of the quasiclassical approximation. The role of the quantum effects is characterized by the relative magnitude of the term $(-\imath\hbar/2m_0) \nabla^2 S$ in Eq. (37.5) (when this term vanishes, we obtain a purely classical equation). We must therefore take the requirement that the magnitude of this term be much smaller than the first term in (37.5) as the condition for the quasiclassical character, i.e.

$$\hbar |\nabla^2 S| \ll (\nabla S)^2$$

For one dimension, this inequality is

$$\hbar \left| \frac{d^2S}{dx^2} \right| \ll \left(\frac{dS}{dx} \right)^2 \quad (37.19)$$

The derivative of the action with respect to the coordinate gives the component of the momentum corresponding to this coordinate [see Vol. 1, formula (32.6); this also follows from (37.12)]. Consequently, (37.19) signifies that the following relation must be observed:

$$\hbar \left| \frac{dp}{dx} \right| \ll p^2 \quad (37.20)$$

Examination of (37.11) shows that

$$\left| \frac{dp}{dx} \right| = \frac{m_0}{p} \left| \frac{dU}{dx} \right|$$

Substitution of this expression into (37.20) leads to the condition of the applicability of the quasiclassical approximation

$$\hbar m_0 \left| \frac{dU}{dx} \right| \ll p^3 \quad (37.21)$$

Hence, the quasiclassical approximation holds for sufficiently rapid particles (a large value of p) moving in a field that does not vary too much from point to point (a small value of dU/dx).

The condition (37.20) can be expressed in terms of the de Broglie wavelength. For this purpose, we replace p in accordance with the equation $\lambda = \hbar/p^1$. The result is

$$\frac{d\lambda}{dx} \ll 1 \quad (37.22)$$

or

$$\frac{d\lambda}{dx} \lambda \ll 1$$

The left-hand side of the last inequality is the change in λ occurring when a particle moves over the distance $\Delta x = \lambda$. Consequently, the condition for the quasiclassical character can be formulated as the requirement that the change in the wavelength over the length λ be much smaller than λ itself.

From condition (37.21), it is easy to gauge the distance to the turning point over which we may still use the quasiclassical approximation. Let the coordinate of the turning point be a . At this point, the potential energy equals the total energy: $U(a) = E$. Let us expand the potential energy into a series in the vicinity of the point a and take only the first two terms

$$U(x) = U(a) + \frac{dU}{dx}(x-a) = E + \frac{dU}{dx}(x-a)$$

Introducing this expansion into (37.11), we obtain

$$p^2 = 2m_0 \left| \frac{dU}{dx} \right| |x-a|$$

Finally, deleting $|dU/dx|$ from this expression and from (37.21), we arrive at the relation

$$|x-a| \gg \frac{\hbar}{2p(x)} = \frac{\lambda(x)}{2} = \frac{\lambda(x)}{4\pi} \quad (37.23)$$

where $\lambda(x)$ is the de Broglie wavelength which a particle has at the point x . This relation determines the distance $|x-a|$ to the turning point at which the quasiclassical approximation still holds.

38. Boundary Conditions at a Turning Point

Figure 38.1 shows a turning point with the coordinate $x = a$. To the left of the hatched region, the psi-function is determined by expression (37.18) (we designate it by ψ_1), and to the right, by expression (37.17) (we designate it by ψ_2). To link these two functions into a

¹ The quantity λ is $1/2\pi$ of the de Broglie wavelength λ determined by the relation $\lambda = 2\pi\hbar/p$.

single one, i.e. to establish the relations between the coefficients C_1 , C_2 and C'_1 , C'_2 , we must know how the psi-function behaves in the hatched region. In this region, the quasiclassical approximation cannot be applied, therefore, we shall have to find an approximate solution of the exact Schrödinger equation for it. This solution will be used as an intermediate unit in linking the functions ψ_1 and ψ_2 . This task is facilitated by the fact that owing to the relative smallness of the size of the hatched region, the potential energy in this region can be considered to vary linearly with x .

Hence, we expand $U(x)$ into a series, taking only the zero- and first-order terms:

$$U(x) = U(a) + U'(a)(x - a) \quad (38.1)$$

Having in view that $U(a) = E$ and $-U'(a)$ equals the force F_x acting on a particle, we can write (38.1) as

$$U(x) = E - F_x \cdot (x - a) \quad (38.2)$$

We must note that in the vicinity of the point $x = a$, the force $F_x > 0$ (see Fig. 38.1). For simplification, we shall drop the subscript "x" on F in the following.

From (38.2), we obtain

$$E - U(x) = F \cdot (x - a) \quad (38.3)$$

Introducing this value of $E - U(x)$ into the Schrödinger equation (5.8), we have

$$\frac{d^2\psi}{dx^2} + \frac{2m_0F}{\hbar^2}(x - a)\psi = 0 \quad (38.4)$$

Let us pass from the variable x to a new variable ξ associated with x by the relation

$$\beta\xi = x - a \quad (38.5)$$

We choose the constant β so that the coefficients at $d^2\psi/d\xi^2$ and at $\xi\psi$ in the equation obtained become the same. Substitution of (38.5) into (38.4) yields

$$\frac{1}{\beta^2} \frac{d^2\psi}{d\xi^2} + \frac{2m_0F}{\hbar^2} \beta\xi\psi = 0$$

We find from the condition $1/\beta^2 = 2m_0F\beta/\hbar^2$ that we must take

$$\beta = \left(\frac{\hbar^2}{2m_0F} \right)^{1/3} \quad (38.6)$$

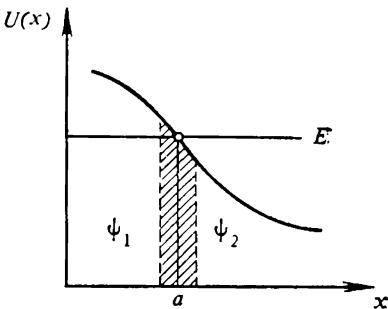


Fig. 38.1

At the right-hand boundary of the hatched region, the functions (37.17) and (38.17) must coincide. If $x_0 = a$, this occurs provided that

$$C'_1 = \frac{A}{2i} e^{i\pi/4}, \quad C'_2 = -\frac{A}{2i} e^{-i\pi/4} \quad (38.19)$$

as a result of which (37.17) transforms into (38.17).

Formulas (38.18) and (38.19) determine the boundary conditions at a turning point of the type depicted in Fig. 38.1.

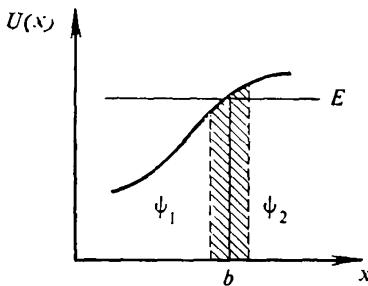


Fig. 38.2

Hence, the functions of a quasiclassical approximation in the region of their applicability have the form of (38.15) to the left of $x = a$ and of (38.17) to the right of $x = a$.

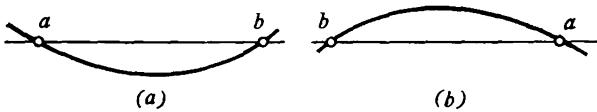


Fig. 38.3

The same reasoning for a turning point of the type depicted in Fig. 38.2 gives the following formulas for the functions of a quasiclassical approximation:

$$\psi(x) = \frac{B}{2\sqrt{|p(x)|}} \exp \left\{ -\frac{1}{\hbar} \int_b^x |p(x)| dx \right\} \quad (x > b, E < U) \quad (38.20)$$

$$\psi(x) = \frac{B}{\sqrt{p(x)}} \sin \left\{ -\frac{1}{\hbar} \int_b^x p(x) dx + \frac{\pi}{4} \right\} \quad (x < b, E > U) \quad (38.21)$$

Let us summarize the rules for linking functions at the boundaries of a potential well (Fig. 38.3a) or a potential hump (Fig. 38.3b):

to the left of a

$$\psi = \frac{A}{2\sqrt{|p(x)|}} \exp \left\{ \frac{1}{\hbar} \int_a^x |p(x)| dx \right\} \quad \left. \begin{array}{l} \\ \end{array} \right\} \quad (38.22)$$

to the right of a

$$\psi = \frac{A}{\sqrt{p(x)}} \sin \left\{ \frac{1}{\hbar} \int_a^x p(x) dx + \frac{\pi}{4} \right\} \quad \left. \begin{array}{l} \\ \end{array} \right\}$$

to the left of b

$$\psi = \frac{B}{\sqrt{p(x)}} \sin \left\{ -\frac{1}{\hbar} \int_b^x p(x) dx - \frac{\pi}{4} \right\} \quad \left. \begin{array}{l} \\ \end{array} \right\} \quad (38.23)$$

to the right of b

$$\psi = \frac{B}{2\sqrt{|p(x)|}} \exp \left\{ -\frac{1}{\hbar} \int_b^x |p(x)| dx \right\} \quad \left. \begin{array}{l} \\ \end{array} \right\}$$

We must note that, say, the function determined by expression (38.22) contains only one arbitrary constant, A [the same holds with respect to the function determined by expression (38.23)]. Consequently, it cannot be a general solution of a second-order differential equation as the Schrödinger equation is. A general solution can be obtained in the form of the sum of two linearly independent solutions. The method of linking functions with the aid of the asymptotic expressions for the Airy function allows us to find only one of such solutions. To find the second one, we have to invent other methods.

To find the second solution, we need a relation which we shall now derive. Let $\psi_1(x)$ and $\psi_2(x)$ be two non-coinciding solutions of the Schrödinger equation. Each of them satisfies the equation $\psi'' + (2m_0/\hbar^2)(E - U)\psi = 0$, or $\psi''/\psi = (2m_0/\hbar^2)(U - E)$. We can therefore write

$$\frac{1}{\psi_1} \frac{d^2\psi_1}{dx^2} = \frac{1}{\psi_2} \frac{d^2\psi_2}{dx^2} = \frac{2m_0}{\hbar^2} (U - E)$$

whence

$$\frac{\psi_1''}{\psi_1} - \frac{\psi_2''}{\psi_2} = 0$$

Reducing this expression to a common denominator and dropping the latter because it is not identical to zero, we obtain

$$\psi_1''\psi_2 - \psi_1\psi_2'' = (\psi_1'\psi_2 - \psi_1\psi_2')' = 0$$

or

$$\psi_1'\psi_2 - \psi_1\psi_2' = \text{const} \quad (38.24)$$

This is just the relation we need.

Let us take the function (38.22) as ψ_1 and attempt to construct the function ψ_2 that is linearly independent of ψ_1 and that together with ψ_1 would satisfy relation (38.24). We can therefore be confident that ψ_2 is a solution of the Schrödinger equation and, consequently, can be used to obtain a general solution. It is natural to take the following function for the expression to the left of a that is independent of (38.22):

$$\psi = \frac{A'}{2\sqrt{|p(x)|}} \exp \left\{ -\frac{1}{\hbar} \int_a^x |p(x)| dx \right\} \quad (x < a) \quad (38.25)$$

(the functions e^x and e^{-x} are linearly independent). In the same way, it is natural to take the following function for the expression to the right of a :

$$\psi = \frac{A''}{\sqrt{p(x)}} \sin \left\{ -\frac{1}{\hbar} \int_a^x p(x) dx + \alpha \right\} \quad (x > a) \quad (38.26)$$

where $\alpha \neq -\pi/4$. Let us verify whether the function (38.22), considered as ψ_1 , and the function ψ_2 , determined by expressions (38.25) and (38.26), satisfy relation (38.24). We have:

to the left of a

$$\begin{aligned} \frac{d}{dx} \left\{ \frac{A}{2\sqrt{|p|}} \exp \left[\frac{1}{\hbar} \int_a^x |p| dx \right] \right\} \left\{ \frac{A'}{2\sqrt{|p|}} \exp \left[-\frac{1}{\hbar} \int_a^x |p| dx \right] \right\} \\ - \left\{ \frac{A}{2\sqrt{|p|}} \exp \left[\frac{1}{\hbar} \int_a^x |p| dx \right] \right\} \\ \times \frac{d}{dx} \left\{ \frac{A'}{2\sqrt{|p|}} \exp \left[-\frac{1}{\hbar} \int_a^x |p| dx \right] \right\} = \frac{AA'}{2\hbar} \end{aligned} \quad (38.27)$$

to the right of a

$$\begin{aligned} \frac{d}{dx} \left\{ \frac{A}{\sqrt{p}} \sin \left[\frac{1}{\hbar} \int_a^x p dx + \frac{\pi}{4} \right] \right\} \left\{ \frac{A''}{\sqrt{p}} \sin \left[-\frac{1}{\hbar} \int_a^x p dx + \alpha \right] \right\} \\ - \left\{ \frac{A}{\sqrt{p}} \sin \left[\frac{1}{\hbar} \int_a^x p dx + \frac{\pi}{4} \right] \right\} \frac{d}{dx} \left\{ \frac{A''}{\sqrt{p}} \sin \left[-\frac{1}{\hbar} \int_a^x p dx + \alpha \right] \right\} \\ = \frac{AA''}{\hbar} \sin \left(\alpha + \frac{\pi}{4} \right) \end{aligned} \quad (38.28)$$

Hence, for the functions being considered, relation (38.24) is observed both to the left and to the right of the point a . Since we are

considering the psi-function of the same state to the left and to the right, the constants (38.27) and (38.28) must be identical. It thus follows that

$$\frac{A'}{2} = A'' \sin \left(\alpha + \frac{\pi}{4} \right)$$

It is the simplest to satisfy this condition by assuming that

$$A'' = \frac{A'}{2} \quad \text{and} \quad \alpha = \frac{\pi}{4} \quad (38.29)$$

Consequently, the solution linearly independent of (38.22) has the form

$$\psi = \frac{A'}{2 \sqrt{|p(x)|}} \exp \left\{ -\frac{1}{\hbar} \int_a^x |p(x)| dx \right\} \quad (x < a) \quad (38.30)$$

$$\psi = \frac{A'}{2 \sqrt{p(x)}} \sin \left\{ -\frac{1}{\hbar} \int_a^x p(x) dx + \frac{\pi}{4} \right\} \quad (x > a) \quad (38.31)$$

Similar reasoning gives the following formulas for the function linearly independent of (38.23):

$$\psi = \frac{B'}{2 \sqrt{|p(x)|}} \exp \left\{ \frac{1}{\hbar} \int_b^x |p(x)| dx \right\} \quad (x > b) \quad (38.32)$$

$$\psi = \frac{B'}{2 \sqrt{p(x)}} \sin \left\{ \frac{1}{\hbar} \int_b^x p(x) dx + \frac{\pi}{4} \right\} \quad (x < b) \quad (38.33)$$

Hence, the general solution of the Schrödinger equation in the quasiclassical approximation has the form:

to the left of a

$$\begin{aligned} \psi = & \frac{1}{2 \sqrt{|p(x)|}} \left\{ A \exp \left[\frac{1}{\hbar} \int_a^x |p(x)| dx \right] \right. \\ & \left. + A' \exp \left[-\frac{1}{\hbar} \int_a^x |p(x)| dx \right] \right\} \quad (x < a) \end{aligned} \quad (38.34)$$

to the right of a

$$\begin{aligned} \psi = & \frac{1}{\sqrt{p(x)}} \left\{ A \sin \left[\frac{1}{\hbar} \int_a^x p(x) dx + \frac{\pi}{4} \right] \right. \\ & \left. + \frac{A'}{2} \sin \left[-\frac{1}{\hbar} \int_a^x p(x) dx + \frac{\pi}{4} \right] \right\} \quad (x > a) \end{aligned} \quad (38.35)$$

to the left of b

$$\Psi = \frac{1}{\sqrt{p(x)}} \left\{ B \sin \left[-\frac{1}{\hbar} \int_b^x p(x) dx + \frac{\pi}{4} \right] + \frac{B'}{2} \sin \left[\frac{1}{\hbar} \int_b^x p(x) dx + \frac{\pi}{4} \right] \right\} \quad (x < b) \quad (38.36)$$

to the right of b

$$\Psi = \frac{1}{2 \sqrt{|p(x)|}} \left\{ B \exp \left[-\frac{1}{\hbar} \int_b^x |p(x)| dx \right] + B' \exp \left[\frac{1}{\hbar} \int_b^x |p(x)| dx \right] \right\} \quad (x > b) \quad (38.37)$$

The function (38.35), like the function (38.36), is the superposition of two plane waves running in opposite directions [compare with formulas (5.13) and (5.14)]. Let us set out these waves, expressing the sines in terms of exponents. After simple transformations, we obtain

$$\Psi = \frac{1}{\sqrt{p(x)}} \left\{ C_1 \exp \left[\frac{i}{\hbar} \int_a^x p(x) dx \right] + C_2 \exp \left[-\frac{i}{\hbar} \int_a^x p(x) dx \right] \right\} \quad (38.38)$$

where

$$C_1 = \frac{2Ae^{i\pi/4} - A'e^{-i\pi/4}}{4i}, \quad C_2 = \frac{A'e^{i\pi/4} - 2Ae^{-i\pi/4}}{4i} \quad (38.39)$$

The factor of C_1 in (38.38) is a wave running to the right along the x -axis, and the factor of C_2 is a wave running to the left along this axis. It is not difficult to understand this by assuming that $p(x) = \text{const}$. Now the first factor becomes e^{ikx} ($k = p/\hbar$), and the second becomes e^{-ikx} [compare with formula (5.13)].

It is quite simple to verify that when

$$A' = -2iA \quad (38.40)$$

the coefficient C_2 vanishes, and the coefficient C_1 becomes equal to $Ae^{-i\pi/4}$. In this case, the quasiclassical psi-function to the right of the point $x = a$ has the form

$$\begin{aligned}\psi &= \frac{1}{\sqrt{p(x)}} Ae^{-i\pi/4} \exp \left\{ \frac{i}{\hbar} \int_a^x p(x) dx \right\} \\ &= \frac{A}{\sqrt{p(x)}} \exp \left\{ i \left[\frac{1}{\hbar} \int_a^x p(x) dx - \frac{\pi}{4} \right] \right\} \quad (38.41)\end{aligned}$$

i.e. is a wave running to the right along the x -axis.

Substitution of the value (38.40) for A' into formula (38.34) leads to the following expression for the psi-function to the left of the point $x = a$:

$$\begin{aligned}\psi &= \frac{A}{2\sqrt{|p(x)|}} \left\{ \exp \left[\frac{1}{\hbar} \int_a^x |p(x)| dx \right] \right. \\ &\quad \left. - 2i \exp \left[- \frac{1}{\hbar} \int_a^x |p(x)| dx \right] \right\} \quad (38.42)\end{aligned}$$

Expressing the sines in terms of the exponentials in formula (38.36), we can write the psi-function to the left of the point $x = b$ as

$$\begin{aligned}\psi &= \frac{1}{\sqrt{p(x)}} \left\{ \frac{B'e^{i\pi/4} - 2Be^{-i\pi/4}}{4i} \exp \left[\frac{i}{\hbar} \int_b^x p(x) dx \right] \right. \\ &\quad \left. + \frac{2Be^{i\pi/4} - B'e^{-i\pi/4}}{4i} \exp \left[- \frac{i}{\hbar} \int_b^x p(x) dx \right] \right\} \\ &= \frac{1}{4\sqrt{p(x)}} \left\{ (2B - iB') \exp \left\{ i \left[\frac{1}{\hbar} \int_b^x p(x) dx + \frac{\pi}{4} \right] \right\} \right. \\ &\quad \left. + (2B + iB') \exp \left\{ - i \left[\frac{1}{\hbar} \int_b^x p(x) dx + \frac{\pi}{4} \right] \right\} \right\} \quad (38.43)\end{aligned}$$

The first term in this formula corresponds to the wave running from the left to the right, and the second, to the wave running from the right to the left.

39. Bohr-Sommerfeld Quantization Rule

Consider the motion of a particle in a potential well (Fig. 39.1) in the quasiclassical approximation. We shall assume that apart from this potential well, there are no allowed regions of motion of the particle. We designate the total energy of the particle by E_n .

We can represent the psi-function of the particle within the confines of the well in two ways [see (38.22) and (38.23)]:

$$\left. \begin{aligned} \psi &= \frac{A}{\sqrt{p(x)}} \sin \left\{ \frac{1}{\hbar} \int_a^x p(x) dx + \frac{\pi}{4} \right\} \\ \psi &= \frac{B}{\sqrt{p(x)}} \sin \left\{ \frac{1}{\hbar} \int_x^b p(x) dx + \frac{\pi}{4} \right\} \end{aligned} \right\} \quad (39.1)$$

(in the second expression, we have gotten rid of the minus in front of the integral by interchanging the integration limits). Both expressions must have the same value at every point of the interval $[a, b]$.

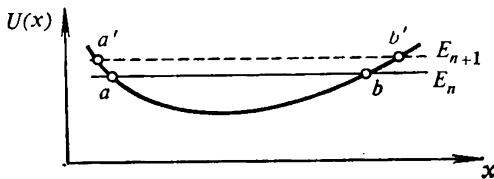


Fig. 39.1

This requirement sets the relations between the coefficients A and B , and also between the arguments of the sine in both formulas. We choose the last relation so that it includes the integral $\int p dx$ evaluated within the limits from a to b . For this purpose, we use the formula¹ $\sin \alpha = (-1)^n \sin [(n + 1)\pi - \alpha]$. According to this formula, both expressions (39.1) will coincide if we assume that $B = (-1)^n A$ and

$$\int_a^b p(x) dx = \left(n + \frac{1}{2} \right) \pi \hbar \quad (n = 0, 1, 2, \dots) \quad (39.2)$$

[since within the limits of the well $p(x) > 0$ and $b > a$, the integral (39.2) can have only positive non-zero values].

¹ The simplest way of verifying the correctness of this formula is to consider the cases $n = 0, \pm 1, \pm 2$, etc. using a "trigonometric circle".

We must therefore take the expression

$$\psi_n(x) = \frac{A}{\sqrt{p(x)}} \sin \left\{ \frac{1}{\hbar} \int_a^x p(x) dx + \frac{\pi}{4} \right\} \quad (39.3)$$

as the quasiclassical psi-function describing the behaviour of a particle in a potential well. The index n on $\psi(x)$ indicates¹ that the argument of the sine varies from $\pi/4$ at the point a to $[(n + 1/2)\pi + \pi/4]$ at the point b , i.e. receives an increment equal to $(n + 1/2)\pi$. It is not difficult to see that here the sine becomes equal to zero n times. Consequently, the function ψ_n has n nodes.

Let x_0 and $x_0 + \Delta x$ be the coordinates of adjacent points at which $\psi_n(x)$ vanishes. The phases of the sine at these points differ by π . Consequently,

$$\pi = \frac{1}{\hbar} \int_{x_0}^{x_0 + \Delta x} p(x) dx \approx \frac{1}{\hbar} p(x) \Delta x$$

whence we have $\Delta x \approx \pi [\hbar/p(x)] = \pi \lambda(x)$. Therefore, the distance between adjacent zeros of the psi-function has the order of magnitude of the de Broglie wavelength. We established in Sec. 37 that the formulas of the quasiclassical approximation hold beginning with distances from a turning point of the order of several de Broglie wavelengths [see inequality (37.23)]. At the same time, when $n \sim 10$, the middle of a potential well is at this distance from the points a and b . It thus follows that formula (39.3) holds only for very large n 's, and the results obtained with the aid of the quasiclassical approximation will be more accurate when n grows.

Let us determine the coefficient A in formula (39.3) from the condition of normalization. The psi-function diminishes rapidly to the left of the point a and to the right of the point b . For this reason, the contribution of these intervals to the normalizing integral may be disregarded. The normalization condition will thus be as follows:

$$\int_a^b |\psi_n(x)|^2 dx = A^2 \int_a^b \frac{dx}{p(x)} \sin^2 \left\{ \frac{1}{\hbar} \int_a^x p(x') dx' + \frac{\pi}{4} \right\} = 1 \quad (39.4)$$

Since the square of the sine oscillates very rapidly in the interval $[a, b]$ (n is very large), it may be replaced with the mean value equal to 1/2. As a result, the condition (39.4) becomes

$$\frac{A^2}{2} \int_a^b \frac{dx}{p(x)} = 1 \quad (39.5)$$

¹ Now it is clear why we used the symbol E_n for the total energy (see Fig. 39.1). The index underlines that we have in view the energy of a particle in the state ψ_n .

Let us transform the integral in (39.5) as follows:

$$\int_a^b \frac{dx}{p(x)} = \frac{1}{m_0} \int_a^b \frac{dx}{v(x)} = \frac{1}{m_0} \int_a^b dt = \frac{1}{2m_0} \tau = \frac{\pi}{m_0 \omega} \quad (39.6)$$

where τ is the period of motion¹ of a classical particle in the potential well (the time needed for a "round trip" between the points a and b), and ω is the cyclic frequency of a classical particle. The introduction of (39.6) into (39.5) leads to the following value of the coefficient A :

$$A = \sqrt{\frac{2m_0\omega}{\pi}} \quad (39.7)$$

Hence, the normalized quasiclassical psi-function for a particle in a potential well is determined by the formula

$$\psi_n(x) = \sqrt{\frac{2\omega_n}{\pi v(x)}} \sin \left\{ \frac{1}{\hbar} \int_a^x p(x) dx + \frac{\pi}{4} \right\} \quad (39.8)$$

[we have inserted (39.7) into (39.3) and taken into account that $p = m_0 v$]. In connection with the fact that the frequency depends on the energy of the state [through $p(x)$ and the integration limits; see (39.6) and Fig. 39.1] we have used the subscript n on ω .

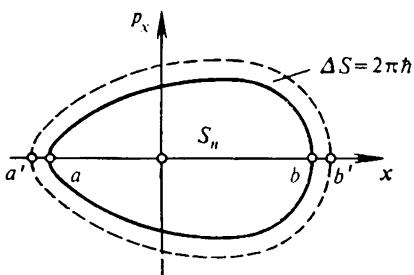


Fig. 39.2

If within the confines of the entire well $U(x) \propto x^2$, the phase trajectory has the shape of an ellipse. We must note that p_x in Fig. 39.2 stands for the projection of the momentum onto the x -axis, whereas $p(x)$ in the integral of (39.8) stands for the magnitude of the momentum at the point x .

The area enclosed by the phase trajectory is

$$S = \oint p_x dx = 2 \int_a^b p(x) dx \quad (39.9)$$

¹ A classical particle having a non-zero total energy will perform oscillating motion between the points a and b when it is in a potential well.

With a view to formula (39.2), we find that

$$\oint p_x dx = \left(n + \frac{1}{2} \right) 2\pi\hbar \quad (n = 0, 1, 2, \dots) \quad (39.10)$$

Relation (39.10) determines the stationary states of a particle in the quasiclassical case. It corresponds to the Bohr-Sommerfeld quantization rule in the old quantum theory (in this theory the addend 1/2 was absent at n).

Inspection of formulas (39.9) and (39.10) reveals that upon a transition from the n -th to the $(n + 1)$ -th state, the area enclosed by the phase trajectory grows by $2\pi\hbar$ (see Fig. 39.2). By (39.9), for this purpose, it is necessary that the values of the function $p(x)$ (i.e. the difference $E - U$) increase, or that the integration interval $[a, b]$ grow. A glance at Fig. 39.1 shows that these two processes are related. The energy level corresponding to the $(n + 1)$ -th state is depicted by a dashed straight line. Therefore, an increase in n is attended by a growth in the energy of the state.

From the fact that in a transition from the n -th to the $(n + 1)$ -th state the area enclosed by the phase trajectory grows by $2\pi\hbar$, it also follows that a cell having an area equal to $2\pi\hbar$ corresponds to each quantum state on the phase plane. Generalizing this result for motion in three-dimensional space, we find that a cell with a volume of $(2\pi\hbar)^3$ corresponds to each state in the phase space. Hence, the number of states corresponding to the phase volume $\Delta\Omega = \Delta x \Delta y \Delta z \times \Delta p_x \Delta p_y \Delta p_z$ is

$$\Delta N = \frac{\Delta\Omega}{(2\pi\hbar)^3} = \frac{\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z}{(2\pi\hbar)^3} \quad (39.11)$$

Formula (39.11) is a fundamental one in statistical physics.

Finally, let us gauge the distance ΔE between adjacent energy levels, i.e. $E_{n+1} - E_n$ (naturally, for large n 's). Since for large n 's the inequality $\Delta E \ll E_n$ is observed, we may consider that

$$p_{n+1}(x) - p_n(x) \approx \frac{\partial p}{\partial E} \Delta E$$

Integrating this relation over the period of motion of a particle and taking into account (39.10), we find that

$$2\pi\hbar = \Delta E \oint \frac{\partial p}{\partial E} dx \approx \Delta E \oint \frac{dx}{(\partial E / \partial p)}$$

From the expression $E = p^2/2m_0 + U(x)$, we have $\partial E/\partial p = p/m_0 = v$. Consequently,

$$2\pi\hbar = \Delta E \oint \frac{dx}{v} = \Delta E \tau = \frac{2\pi\Delta E}{\omega}$$

whence

$$\Delta E = \hbar\omega_n \quad (39.12)$$

At large n 's, the inequality $(\Delta E/E) \ll 1$ holds, and accordingly $(\Delta\omega/\omega) \ll 1$; therefore the frequencies ω_n for a group of adjacent levels may be considered to be approximately identical. It thus follows that within the limits of small regions of the quasiclassical part of the spectrum, the levels are virtually equidistant.

The formulas obtained in this section hold, generally speaking, only for large n 's. For a harmonic oscillator, formula (39.12) is exact for any n , and ω does not depend on n [see (25.9)].

40. Penetration of a Potential Barrier

A potential barrier is defined to be a region on which the potential energy $U(x)$ exceeds the total energy E of a particle (Fig. 40.1).

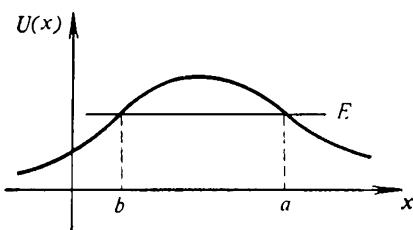


Fig. 40.1

A classical particle cannot penetrate such a barrier. A quantum-mechanical particle, on the other hand, has a non-zero probability of getting to the other side of the barrier, i.e. to pass, as it were, through a tunnel in the barrier (the tunnel effect). For observing the conditions of applicability of the quasiclassical approximation, the barrier must be broad and not too steep [see (37.21)].

Let a particle approach the barrier from the left. Behind the barrier (i.e. at $x > a$), there can exist only a wave propagating to the right along the x -axis. Such a wave is described by the formula

$$\psi = \frac{A}{\sqrt{p(x)}} \exp \left\{ i \left[\frac{1}{\hbar} \int_a^x p(x) dx - \frac{\pi}{4} \right] \right\} \quad (40.1)$$

[see (38.41)]. In the region $b \leq x \leq a$, the psi-function has the form

$$\begin{aligned} \psi = \frac{A}{2 \sqrt{|p(x)|}} & \left\{ \exp \left[\frac{1}{\hbar} \int_a^x |p(x)| dx \right] \right. \\ & \left. - 2i \exp \left[- \frac{1}{\hbar} \int_a^x |p(x)| dx \right] \right\} \quad (40.2) \end{aligned}$$

[see (38.42)]. The same function, according to (38.37), can be written as

$$\begin{aligned} \Psi = \frac{1}{2\sqrt{|p(x)|}} & \left\{ B \exp \left[-\frac{1}{\hbar} \int_b^x |p(x)| dx \right] \right. \\ & \left. + B' \exp \left[\frac{1}{\hbar} \int_b^x |p(x)| dx \right] \right\} \quad (40.3) \end{aligned}$$

To bring expressions (40.2) and (40.3) into agreement, we shall take into account that

$$\int_b^x = \int_b^a + \int_a^x$$

Hence, introducing the notation

$$\gamma = \frac{1}{\hbar} \int_b^a |p(x)| dx \quad (40.4)$$

we can write formula (40.3) as follows:

$$\begin{aligned} \Psi = \frac{1}{2\sqrt{|p(x)|}} & \left\{ Be^{-\gamma} \exp \left[-\frac{1}{\hbar} \int_a^x |p(x)| dx \right] \right. \\ & \left. + B'e^\gamma \exp \left[\frac{1}{\hbar} \int_a^x |p(x)| dx \right] \right\} \quad (40.5) \end{aligned}$$

Expressions (40.2) and (40.5) coincide provided that $Be^{-\gamma} = -2iA$ and $B'e^\gamma = A$, i.e.

$$B = -2iAe^\gamma, \quad B' = Ae^{-\gamma}$$

Introducing these values of the coefficients B and B' into formula (38.43), we find the psi-function ahead of the potential barrier (for $x < b$):

$$\begin{aligned} \Psi = \frac{A}{4i\sqrt{p(x)}} & \left\{ (4e^\gamma + e^{-\gamma}) \exp \left\{ i \left[\frac{1}{\hbar} \int_b^x p(x) dx + \frac{\pi}{4} \right] \right\} \right. \\ & \left. + (4e^\gamma - e^{-\gamma}) \exp \left\{ -i \left[\frac{1}{\hbar} \int_b^x p(x) dx + \frac{\pi}{4} \right] \right\} \right\} \quad (40.6) \end{aligned}$$

Assume that a beam of particles is incident on a potential barrier. Part of them are reflected from the barrier, after which they move in the opposite direction, and part of them pass "through" the barrier

and continue to move in the initial direction. In this case, the incident particles are described by the first term in (40.6), the reflected particles, by the second term in (40.6), and the transmitted particles, by the function (40.1). The density of the probability flux j determined by formula (6.5) can be associated with each particle flux. The ratio of $|j_{\text{trans}}|$ to $|j_{\text{inc}}|$ determines the **transmission coefficient** of particles, which we shall designate by the symbol D :

$$D = \frac{j_{\text{trans}}}{j_{\text{inc}}} \quad (40.7)$$

Similarly,

$$R = \frac{j_{\text{refl}}}{j_{\text{inc}}} \quad (40.8)$$

is the **reflection coefficient** of particles.

Let us calculate the flux densities at a sufficiently great distance from the barrier, where the momentum of a particle and, consequently, the factor $1/\sqrt{p(x)}$ may be considered constant in calculations.

By formula (6.5), for one dimension, we have

$$j = \left| \frac{\hbar}{2m_0 i} \left(\psi^* \frac{d\psi}{dx} - \psi \frac{d\psi^*}{dx} \right) \right| \quad (40.9)$$

All the functions by means of which we shall calculate the fluxes and the derivatives of these functions have the form

$$\begin{aligned} \psi &= \frac{C}{\sqrt{p}} \exp \left\{ \pm i \left[\frac{1}{\hbar} \int_{x_0}^x p dx + \alpha \right] \right\} \\ \frac{d\psi}{dx} &= \psi \left(\pm i \frac{p}{\hbar} \right) \end{aligned} \quad (40.10)$$

Consequently,

$$\begin{aligned} \left(\psi^* \frac{d\psi}{dx} - \psi \frac{d\psi^*}{dx} \right) &= \psi^* \psi \left(\pm i \frac{p}{\hbar} \right) - (\psi \psi^*) \left(\mp i \frac{p}{\hbar} \right) \\ &= \pm \psi \psi^* 2i \frac{p}{\hbar} = \pm 2i \frac{|C|^2}{\hbar} \end{aligned}$$

Substitution of this value into (40.9) yields

$$j = \frac{|C|^2}{m_0} \quad (40.11)$$

Calculation of the flux density thus consists in finding the square of the magnitude of the coefficient in the function (40.10).

For the transmitted flux, by (40.1), $|C|^2 = |A|^2$, for the incident flux [the first term in (40.6)], $|C|^2 = |A|^2 (e^\gamma + e^{-\gamma}/4)^2$, and,

finally, for the reflected flux, $|C|^2 = |A|^2 (e^\gamma - e^{-\gamma}/4)^2$. With account taken of these values, we have

$$D = \frac{1}{\left(e^\gamma + \frac{1}{4} e^{-\gamma}\right)^2} = \frac{e^{-2\gamma}}{\left(1 + \frac{1}{4} e^{-2\gamma}\right)^2} \quad (40.12)$$

$$R = \frac{\left(e^\gamma - \frac{1}{4} e^{-\gamma}\right)^2}{\left(e^\gamma + \frac{1}{4} e^{-\gamma}\right)^2} = \frac{\left(1 - \frac{1}{4} e^{-2\gamma}\right)^2}{\left(1 + \frac{1}{4} e^{-2\gamma}\right)^2} \quad (40.13)$$

It is not difficult to see that $D + R = 1$.

We have already noted that the quasiclassical approximation holds only for a sufficiently wide potential barrier. In this case, the quantity γ determined by formula (40.4) is large, and $e^{-2\gamma} \ll 1$. Therefore, the denominator in formula (40.12) can be considered equal to unity, so that

$$D \approx e^{-2\gamma} = \exp \left[-\frac{2}{\hbar} \int_b^a |p(x)| dx \right] \quad (40.14)$$

Formula (40.14) determines the probability of a particle penetrating a potential barrier. Remember that this formula holds only when the conditions of applicability of a quasiclassical approximation are observed. These conditions, in addition to a great width of the barrier, provide for a sufficiently smooth, not too steep path of the function $U(x)$. In practice, one often has to do with barriers for which $U(x)$ at one side is so steep that the quasiclassical approximation is not applicable. The relevant calculations give in this case an expression for D that apart from exactly the same exponential function as in (40.14) also contains a preexponential factor.

Chapter VIII

SEMIEMPIRICAL THEORY OF PARTICLES WITH SPIN

41. Psi-Function of a Particle with Spin

A number of experimental facts (the fine structure of spectral lines, the anomalous Zeeman effect, etc.) show that microparticles have a specific internal degree of freedom. The intrinsic angular momentum M_s of a particle called the spin is associated with this degree of freedom.

Spin has a purely quantum character. When going over to classical mechanics (at $\hbar \rightarrow 0$), the spin vanishes. This is why it has no classical analogue.

The existence and the magnitude of the spin of an electron strictly follow from relativistic quantum mechanics. A number of properties of particles having spin can be obtained, however, even without involving the relativistic theory, on the basis of general quantum-mechanical considerations and a small number of experimental facts. The present chapter deals with the semiempirical theory of particles with spin.

The psi-function of a particle with spin depends not only on its space coordinates, but also on a fourth coordinate σ characterizing the internal state of the particle:

$$\psi = \psi(x, y, z, \sigma, t) \quad (41.1)$$

The magnitude of the projection of the spin M_{sz} onto the arbitrary axis z expressed in units of \hbar ($M_{sz} = \sigma\hbar$) is taken as the coordinate σ . The latter takes on $2s + 1$ discrete values differing from one another by unity:

$$\sigma = s, s - 1, \dots, -s + 1, -s \quad (41.2)$$

where s is a quantum number determining the magnitude of the square of the spin by a formula similar to (19.10):

$$M_s^2 = \hbar^2 s(s + 1) \quad (41.3)$$

Owing to the discreteness of the variable σ , its values can be assigned to the psi-function as a subscript. Consequently, the function (41.1) can be considered as a set of several different functions of space

coordinates differing in the value of the subscript σ . This set can be written as a column matrix with $2s + 1$ rows:

$$\psi = \begin{pmatrix} \psi_{\sigma_1} \\ \psi_{\sigma_2} \\ \vdots \\ \psi_{\sigma_{2s+1}} \end{pmatrix} \quad (41.4)$$

The expression $|\psi_{\sigma_i}(x, y, z, t)|^2 dV$ determines the probability of the fact that at a given instant a particle is in the volume element dV , the projection of its spin onto the z -axis being $\hbar\sigma_i$. The quantity

$$P_i := \int |\psi_{\sigma_i}(x, y, z, t)|^2 dV$$

gives the probability of the fact that at a given instant a particle at a point in space has a spin projection equal to $\hbar\sigma_i$. The sum of such probabilities must be unity. Consequently, the normalization condition for the function (41.4) has the form

$$\sum_i \int |\psi_{\sigma_i}(x, y, z, t)|^2 dV = 1 \quad (41.5)$$

In the following, we shall consider mainly particles with a spin equal to $1/2$ ($s = 1/2$). In this case, the coordinate σ can take on only two values: $\sigma_1 = +1/2$, and $\sigma_2 = -1/2$, so that

$$\psi = \begin{pmatrix} \psi_{+1/2} \\ \psi_{-1/2} \end{pmatrix} \quad (41.6)$$

If the probabilities for the spin projections do not depend on the coordinates of a particle, i.e. the probability of having a certain value of the spin projection and the probability of being at different points of space do not depend on each other, the function (41.1) can be written as the product of two functions:

$$\psi(x, y, z, \sigma, t) = \psi(x, y, z, t) \cdot \varphi(\sigma) \quad (41.7)$$

The factor $\psi(x, y, z, t)$ is a conventional (position) psi-function, and the factor $\varphi(\sigma)$ is a spin psi-function that can take on only two¹ values:

$$\varphi\left(+\frac{1}{2}\right) = a_1 \text{ and } \varphi\left(-\frac{1}{2}\right) = a_2$$

¹ In the general case, $2s + 1$ values.

Upon substituting expression (41.7) into (41.6), the position function can be put outside the matrix symbol, as a result of which we obtain the following expression for ψ :

$$\psi(x, y, z, \sigma, t) = \psi(x, y, z, t) \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \quad (41.8)$$

Consequently,

$$\varphi(\sigma) = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \quad (41.9)$$

where a_1 and a_2 are, generally speaking, complex numbers. The quantities $|a_1|^2$ and $|a_2|^2$ give the probabilities of the spin projections M_{sz} having values of $+\hbar/2$ and $-\hbar/2$, respectively. For a normalized psi-function, the condition

$$|a_1|^2 + |a_2|^2 = 1 \quad (41.10)$$

must be satisfied.

If

$$\varphi(\sigma) = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (41.11)$$

i.e. $a_1 = 1$, and $a_2 = 0$, the projection of the spin has a definite value equal to $+\hbar/2$. If

$$\varphi(\sigma) = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (41.12)$$

the projection of the spin has a definite value equal to $-\hbar/2$. If both numbers, a_1 and a_2 , are non-zero, the particle will be in a state in which the projection of the spin has no definite value.

42. Spin Operators

Let us find the form of the linear operators \hat{Q} that can act on spin functions. Their action on a spin function $\varphi(\sigma)$ must transform it into another, also spin function $f(\sigma)$:

$$f(\sigma) = \hat{Q}\varphi(\sigma) \quad (42.1)$$

By (41.9), the functions $\varphi(\sigma)$ and $f(\sigma)$ are column matrices:

$$\varphi(\sigma) = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}, \quad f(\sigma) = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} \quad (42.2)$$

It thus follows that the operator \hat{Q} must have the form of a two-row [in the general case, of a $(2s + 1)$ -row] square matrix:

$$\hat{Q} = \begin{pmatrix} Q_{11} & Q_{12} \\ Q_{21} & Q_{22} \end{pmatrix} \quad (42.3)$$

Substitution of the matrices (42.2) and (42.3) into Eq. (42.1) yields

$$\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} Q_{11} & Q_{12} \\ Q_{21} & Q_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} Q_{11}a_1 + Q_{12}a_2 \\ Q_{21}a_1 + Q_{22}a_2 \end{pmatrix}$$

(we have multiplied the matrices Q and a). Hence, the action of the operator \hat{Q} on a function with the components a_1 and a_2 transforms it into a function with the components

$$b_1 = Q_{11}a_1 + Q_{12}a_2 \text{ and } b_2 = Q_{21}a_1 + Q_{22}a_2$$

the above process can be written as

$$\hat{Q}\psi = \begin{pmatrix} Q_{11} & Q_{12} \\ Q_{21} & Q_{22} \end{pmatrix} \begin{pmatrix} \psi_{\sigma_1} \\ \psi_{\sigma_2} \end{pmatrix} = \begin{pmatrix} Q_{11}\psi_{\sigma_1} + Q_{12}\psi_{\sigma_2} \\ Q_{21}\psi_{\sigma_1} + Q_{22}\psi_{\sigma_2} \end{pmatrix} \quad (42.4)$$

If it is impossible to break up the psi-function into a coordinate and spin components, formula (42.4) must be modified as follows:

$$\hat{Q}\psi = \begin{pmatrix} Q_{11} & Q_{12} \\ Q_{21} & Q_{22} \end{pmatrix} \begin{pmatrix} \psi_{\sigma_1} \\ \psi_{\sigma_2} \end{pmatrix} = \begin{pmatrix} Q_{11}\psi_{\sigma_1} + Q_{12}\psi_{\sigma_2} \\ Q_{21}\psi_{\sigma_1} + Q_{22}\psi_{\sigma_2} \end{pmatrix} \quad (42.5)$$

Hence, any operator acting on the spin function (41.6) must have the form of (42.3). Particularly, the operator of the square of the spin \hat{s}^2 and those of the spin projections onto the coordinate axes \hat{s}_x , \hat{s}_y , \hat{s}_z must have such a form. The same transposition relations hold for these operators as for those of the orbital angular momentum [see (16.12) and (16.15)], namely:

$$\hat{s}_x\hat{s}_y - \hat{s}_y\hat{s}_x = i\hbar\hat{s}_z, \quad \hat{s}_y\hat{s}_z - \hat{s}_z\hat{s}_y = i\hbar\hat{s}_x, \quad \hat{s}_z\hat{s}_x - \hat{s}_x\hat{s}_z = i\hbar\hat{s}_y \quad (42.6)$$

$$\hat{s}^2\hat{s}_x - \hat{s}_x\hat{s}^2 = 0, \quad \hat{s}^2\hat{s}_y - \hat{s}_y\hat{s}^2 = 0, \quad \hat{s}^2\hat{s}_z - \hat{s}_z\hat{s}^2 = 0 \quad (42.7)$$

The operators of the square of the spin and of its projections are related by the expression [see (15.10)]

$$\hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2 = \hat{s}^2 \quad (42.8)$$

It follows from the commutation rules that the square of the spin and, say, the projection of the spin onto the z -axis can simultaneously have definite values so that their matrices can be simultaneously reduced to the diagonal form. The other two spin projections will be indefinite, and their matrices will be non-diagonal.

If we consider the operators \hat{s}^2 and \hat{s}_z in their eigenrepresentation, the diagonal elements of the relevant matrices will equal the eigenvalues of the operators, while the non-diagonal elements will be zero. The eigenvalues of the operator \hat{s}^2 are $\hbar^2 s(s+1) = \hbar^2 (1/2)(1+1/2) = = 3\hbar^2/4$. The eigenvalues of the operator \hat{s}_z are $+\hbar/2$ and $-\hbar/2$. Consequently,

$$\hat{s}^2 = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (42.9)$$

$$\hat{s}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (42.10)$$

The square of the operator (42.10) is

$$\hat{s}_z^2 = \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{3} \hat{s}^2 \quad (42.11)$$

To find the operators \hat{s}_x and \hat{s}_y , we first determine the form of the auxiliary operators:

$$\hat{s}_+ = \hat{s}_x + i\hat{s}_y \text{ and } \hat{s}_- = \hat{s}_x - i\hat{s}_y \quad (42.12)$$

[compare with (I.3)]. Like the operators \hat{s}_x and \hat{s}_y , these auxiliary operators are square two-row matrices. Having established the form of the operators \hat{s}_+ and \hat{s}_- and taken their sum, we obtain \hat{s}_x , whereas their difference yields \hat{s}_y .

Let us find the commutators of the operators (42.12) with the operator \hat{s}_z . Using formulas (42.6), we obtain

$$\begin{aligned} [\hat{s}_+, \hat{s}_z] &= (\hat{s}_x + i\hat{s}_y) \hat{s}_z - \hat{s}_z (\hat{s}_x + i\hat{s}_y) \\ &= (\hat{s}_x \hat{s}_z - \hat{s}_z \hat{s}_x) + i (\hat{s}_y \hat{s}_z - \hat{s}_z \hat{s}_y) = (-i\hbar \hat{s}_y) + i(i\hbar \hat{s}_x) \\ &= -\hbar (\hat{s}_x + i\hat{s}_y) = -\hbar \hat{s}_+ \end{aligned}$$

Hence,

$$[\hat{s}_+, \hat{s}_z] = \hat{s}_+ \hat{s}_z - \hat{s}_z \hat{s}_+ = -\hbar \hat{s}_+ \quad (42.13)$$

Similar calculations yield

$$[\hat{s}_-, \hat{s}_z] = \hat{s}_- \hat{s}_z - \hat{s}_z \hat{s}_- = \hbar \hat{s}_- \quad (42.14)$$

Designating the eigenvalue of the operator \hat{s}_z by the symbol $\sigma\hbar$, we can write

$$\hat{s}_z \psi_\sigma = \sigma\hbar \psi_\sigma \quad (42.15)$$

where ψ_σ is the eigenfunction of the operator \hat{s}_z corresponding to the eigenvalue $\sigma\hbar^1$. Let us act with the operator \hat{s}_+ on Eq. (42.15):

$$\hat{s}_+ \hat{s}_z \psi_\sigma = \sigma \hbar \hat{s}_+ \psi_\sigma$$

Transforming the left-hand side with the aid of relation (42.13), we obtain

$$\hat{s}_z \hat{s}_+ \psi_\sigma - \hbar \hat{s}_+ \psi_\sigma = \sigma \hbar \hat{s}_+ \psi_\sigma$$

which can be written as follows:

$$\hat{s}_z (\hat{s}_+ \psi_\sigma) = (\sigma + 1) \hbar (\hat{s}_+ \psi_\sigma) \quad (42.16)$$

The result obtained signifies that the function $\hat{s}_+ \psi_\sigma$ within the arbitrary constant factor λ coincides with the eigenfunction of the operator \hat{s}_z corresponding to the eigenvalue $(\sigma + 1)\hbar$. Consequently, the operator \hat{s}_+ acting on the function ψ_σ transforms it into $\lambda \psi_{\sigma+1}$:

$$\hat{s}_+ \psi_\sigma = \lambda \psi_{\sigma+1}$$

The dimension of \hat{s}_+ coincides with that of \hbar [see (42.12) and (42.10)], the dimensions of \hat{s}_x , \hat{s}_y , and \hat{s}_z are the same. The constant λ can therefore be written as $\lambda = \hbar c_1$, where c_1 is a dimensionless constant. As a result, we obtain the relation

$$\hat{s}_+ \psi_\sigma = \hbar c_1 \psi_{\sigma+1} \quad (42.17)$$

Acting on Eq. (42.15) with the operator \hat{s}_- and using relation (42.14), it is not difficult to see that

$$\hat{s}_- \psi_\sigma = \hbar c_2 \psi_{\sigma-1} \quad (42.18)$$

We can now find the matrix elements of the operators \hat{s}_+ and \hat{s}_- in the s_z -representation. For \hat{s}_+ , we have

$$(s_+)_{\sigma\sigma'} = \langle \psi_\sigma | \hat{s}_+ | \psi_{\sigma'} \rangle = \langle \psi_\sigma | \hbar c_1 \psi_{\sigma+1} \rangle = \hbar c_1 \delta_{\sigma, \sigma'+1} \quad (42.19)$$

The subscripts σ and σ' take on two values: $+\frac{1}{2}$ and $-\frac{1}{2}$. Only the matrix element for which $\sigma = \sigma' + 1$ is non-zero (and equal $\hbar c_1$). Consequently,

$$\hat{s}_+ = \begin{pmatrix} (s_+)_{+\frac{1}{2}, +\frac{1}{2}} & (s_+)_{+\frac{1}{2}, -\frac{1}{2}} \\ (s_+)_{-\frac{1}{2}, +\frac{1}{2}} & (s_+)_{-\frac{1}{2}, -\frac{1}{2}} \end{pmatrix} = \hbar c_1 \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad (42.20)$$

¹ The operators \hat{s}^2 , \hat{s}_z , and \hat{H} commute and, consequently, have common eigenfunctions. Accordingly, the matrices of these operators can be reduced simultaneously to a diagonal form. By ψ_σ in (42.15) is meant the common eigenfunction of the three operators. In particular, it is also the eigenfunction of the operator \hat{s}_z . The function ψ_σ , in addition to (42.15), satisfies two other equations:

$$\hat{H} \psi_\sigma = E \psi_\sigma, \quad \hat{s}^2 \psi_\sigma = M_s^2 \psi_\sigma$$

[we arranged the values of the subscript σ in the series (41.2) so that its numerical values diminish from left to right].

Let us find the elements of the matrix of \hat{s}_- . By (42.18),

$$(s_-)_{\sigma, \sigma'} = \langle \psi_\sigma | \hat{s}_- | \psi_{\sigma'} \rangle = \langle \psi_\sigma | \hbar c_2 \psi_{\sigma'-1} \rangle = \hbar c_2 \delta_{\sigma, \sigma'-1} \quad (42.21)$$

In this matrix, only the element for which $\sigma = \sigma' - 1$ is non-zero. Therefore,

$$\hat{s}_- = \begin{pmatrix} (s_-)_{1/2, 1/2} & (s_-)_{1/2, -1/2} \\ (s_-)_{-1/2, 1/2} & (s_-)_{-1/2, -1/2} \end{pmatrix} = \hbar c_2 \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \quad (42.22)$$

Operators, like psi-functions, are determined to within an arbitrary phase factor. The constants c_1 and c_2 in (42.20) and (42.22) can thus be considered as real.

There is a relation between the elements of the matrices (42.20) and (42.22) that allows us to establish the relation between the constants c_1 and c_2 .

To find this relation, let us write the following two equations in accordance with formulas (42.12):

$$(s_+)_\sigma, \sigma' = (s_x)_\sigma, \sigma' + i (s_y)_\sigma, \sigma' \quad (42.23)$$

$$(s_-)_\sigma, \sigma' = (s_x)_\sigma, \sigma' - i (s_y)_\sigma, \sigma' \quad (42.24)$$

Inspection of (42.24) shows that $(s_-)_{\sigma', \sigma}^* = (s_x)_{\sigma', \sigma}^* + i (s_y)_{\sigma', \sigma}^*$. But owing to the Hermitian nature of the operators s_x and s_y , the conditions $(s_x)_{\sigma', \sigma}^* = (s_x)_{\sigma, \sigma'}$ and $(s_y)_{\sigma', \sigma}^* = (s_y)_{\sigma, \sigma'}$ are satisfied. Consequently,

$$(s_-)_{\sigma', \sigma}^* = (s_x)_{\sigma, \sigma'} + i (s_y)_{\sigma, \sigma'} = (s_+)_\sigma, \sigma' \quad (42.25)$$

This is exactly the required relation.

It follows from (42.20) and (42.22) that $(s_+)_{{1/2}, {-1/2}} = \hbar c_1$, and $(s_-)_{{-1/2}, {1/2}}^* = (s_-)_{{-1/2}, {1/2}} = \hbar c_2$. According to (42.25), we have $(s_-)_{{-1/2}, {1/2}}^* = (s_+)_{{1/2}, {-1/2}}$, whence we find that $c_1 = c_2 = c$. Therefore, the subscripts 1 and 2 on c in the matrices (42.20) and (42.22) may be dropped.

By (42.12), the operator \hat{s}_x equals the half-sum of the matrices (42.20) and (42.22), i.e.

$$\hat{s}_x = c \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (42.26)$$

Dividing the difference of the matrices (42.20) and (42.22) by $2i$ (which is equivalent to multiplying it by $-i/2$), we find that

$$\hat{s}_y = c \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (42.27)$$

Squaring the matrices (42.26) and (42.27), we obtain

$$\left. \begin{aligned} \hat{s}_x^2 &= c^2 \frac{\hbar^2}{4} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = c^2 \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ \hat{s}_y^2 &= c^2 \frac{\hbar^2}{4} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = c^2 \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{aligned} \right\} \quad (42.28)$$

Let us find the sum of the matrices (42.28) and (42.11):

$$\begin{aligned} \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2 &= c^2 \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + c^2 \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ &= \frac{\hbar^2}{4} \begin{pmatrix} 1 + 2c^2 & 0 \\ 0 & 1 + 2c^2 \end{pmatrix} \end{aligned}$$

According to (42.8), the matrix we have obtained must coincide with the matrix (42.9). For this purpose, we must assume that $c = 1$. Introducing this value into (42.26) and (42.27), we finally obtain

$$\hat{s}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (42.29)$$

$$\hat{s}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (42.30)$$

By formulas (42.11) and (42.28) (we must assume that $c^2 = 1$ in the latter), we find that

$$\hat{s}_x^2 = \hat{s}_y^2 = \hat{s}_z^2 \quad (42.31)$$

The matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (42.32)$$

are known as the **Pauli spin matrices**. Using these matrices, we can write expressions (42.29), (42.30), and (42.10) as follows:

$$\hat{s}_x = \frac{\hbar}{2} \sigma_x, \quad \hat{s}_y = \frac{\hbar}{2} \sigma_y, \quad \hat{s}_z = \frac{\hbar}{2} \sigma_z \quad (42.33)$$

Let us find the products of the matrices σ_x and σ_y :

$$\sigma_x \sigma_y = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} = i \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = i \sigma_z$$

$$\sigma_y \sigma_x = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = -i \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = -i \sigma_z$$

Similar formulas are also obtained for other pairs of matrices. Consequently,

$$\sigma_x \sigma_y = -\sigma_y \sigma_x = i\sigma_z, \quad \sigma_y \sigma_z = -\sigma_z \sigma_y = i\sigma_x, \quad \sigma_z \sigma_x = -\sigma_x \sigma_z = i\sigma_y \quad (42.34)$$

It is not difficult to obtain the commutation rules for the Pauli spin matrices from relations (42.34):

$$\sigma_x \sigma_y - \sigma_y \sigma_x = 2i\sigma_z, \quad \sigma_y \sigma_z - \sigma_z \sigma_y = 2i\sigma_x, \quad \sigma_z \sigma_x - \sigma_x \sigma_z = 2i\sigma_y \quad (42.35)$$

It also follows from (42.34) that

$$\sigma_x \sigma_y + \sigma_y \sigma_x = 0, \quad \sigma_y \sigma_z + \sigma_z \sigma_y = 0, \quad \sigma_z \sigma_x + \sigma_x \sigma_z = 0 \quad (42.36)$$

Equations (42.36) signify that the Pauli spin matrices anticommute [see (10.21)]. It is evident that similar rules of anticommutation also hold for the operators of the spin projections:

$$\hat{s}_x \hat{s}_y + \hat{s}_y \hat{s}_x = 0, \quad \hat{s}_y \hat{s}_z + \hat{s}_z \hat{s}_y = 0, \quad \hat{s}_z \hat{s}_x + \hat{s}_x \hat{s}_z = 0 \quad (42.37)$$

It is a simple matter to see that the squares of the Pauli spin matrices equal a unit matrix:

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (42.38)$$

It thus follows with a view to (42.33) that

$$\hat{s}_x^2 = \hat{s}_y^2 = \hat{s}_z^2 = \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (42.39)$$

which agrees with (42.8) and (42.9).

We have obtained expressions of the operators for the case when the spin of a particle equals one-half. For other spin values, the operators are found in a similar way. For instance, if the spin equals unity, the eigenvalue of the operator \hat{s}^2 is $\hbar^2 \cdot 1 (1 + 1) = 2\hbar^2$, while the eigenvalues of \hat{s}_z equal +1, 0, and -1. Consequently,

$$\hat{s}^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (42.40)$$

(the spin function in this case has three components), and

$$\hat{s}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (42.41)$$

Formulas (42.19) and (42.21) were obtained without specifying the value of the spin. Consequently, they also hold for $s = 1$. Using these formulas, we obtain¹

$$\hat{s}_+ = \begin{pmatrix} (s_+)_{1,1} & (s_+)_{1,0} & (s_+)_{1,-1} \\ (s_+)_{0,1} & (s_+)_{0,0} & (s_+)_{0,-1} \\ (s_+)_{-1,1} & (s_+)_{-1,0} & (s_+)_{-1,-1} \end{pmatrix} = \hbar c \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \quad (42.42)$$

$$\hat{s}_- = \begin{pmatrix} (s_-)_{1,1} & (s_-)_{1,0} & (s_-)_{1,-1} \\ (s_-)_{0,1} & (s_-)_{0,0} & (s_-)_{0,-1} \\ (s_-)_{-1,1} & (s_-)_{-1,0} & (s_-)_{-1,-1} \end{pmatrix} = \hbar c \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \quad (42.43)$$

Taking first the half-sum of these matrices, and then their difference divided by $2i$, we find that

$$\hat{s}_x = c \frac{\hbar}{2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \hat{s}_y = c \frac{\hbar}{2} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \quad (42.44)$$

The squares of the matrices (42.44) and (42.41) are

$$\hat{s}_x^2 = \frac{\hbar^2 c^2}{4} \begin{pmatrix} 1 & 0 & 1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{pmatrix}, \quad \hat{s}_y^2 = \frac{\hbar^2 c^2}{4} \begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{pmatrix}, \quad \hat{s}_z^2 = \hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (42.45)$$

Their summation yields

$$\hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2 = \hbar^2 \begin{pmatrix} 1 + c^2/2 & 0 & 0 \\ 0 & c^2 & 0 \\ 0 & 0 & 1 + c^2/2 \end{pmatrix}$$

To make this expression agree with (42.10), we must assume that $c^2 = 2$. Hence, $c = \sqrt{2}$. Substituting this value into (42.44), we obtain

$$\hat{s}_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \hat{s}_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \quad (42.46)$$

We must note that according to (42.45), when $s = 1$ the squares of the operators of the spin projections do not coincide ($\hat{s}_x^2 \neq \hat{s}_y^2 \neq \hat{s}_z^2$) as they did for $s = 1/2$ [see (42.31)]. For the matrices (42.46) and (42.41), there are also no relations similar to (42.37). The commutation rules (42.6) and (42.7) are naturally observed, which can be seen by direct verification.

¹ We can show in the same way as for $s = 1/2$ that the coefficient c in the matrices (42.42) and (42.43) is the same.

43. Eigenvalues and Eigenfunctions of Spin Operators

Equation (7.3) for the operators \hat{s}_x , \hat{s}_y , \hat{s}_z has the form

$$\hat{s}_i \varphi_i = s_i \varphi_i \quad (i = x, y, z) \quad (43.1)$$

where φ_i is a column with two rows [see (41.9)]. Introducing expression (42.29) for \hat{s}_x , we obtain the equation

$$\frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = s_x \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

Multiplication of the matrices on the left yields

$$\frac{\hbar}{2} \begin{pmatrix} a_2 \\ a_1 \end{pmatrix} = s_x \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}, \quad \text{whence } \begin{pmatrix} \hbar a_2 / 2 \\ \hbar a_1 / 2 \end{pmatrix} = \begin{pmatrix} s_x a_1 \\ s_x a_2 \end{pmatrix}$$

In equal matrices, the corresponding elements are equal. We thus obtain two linear homogeneous equations with the unknowns a_1 and a_2 :

$$\left. \begin{array}{l} s_x a_1 - \frac{\hbar}{2} a_2 = 0 \\ \frac{\hbar}{2} a_1 - s_x a_2 = 0 \end{array} \right\} \quad (43.2)$$

For this system to have non-zero solutions, its determinant must be zero:

$$\begin{vmatrix} s_x & -\hbar/2 \\ \hbar/2 & -s_x \end{vmatrix} = 0$$

whence $-s_x^2 + (\hbar/2)^2 = 0$. This equation has the solutions

$$s_x = +\frac{\hbar}{2} \text{ and } s_x = -\frac{\hbar}{2} \quad (43.3)$$

These are exactly the eigenvalues of the spin projection onto the x -axis.

Introducing $s_x = \hbar/2$ into (43.2) and cancelling $\hbar/2$ lead to the system

$$\begin{aligned} a_1 - a_2 &= 0 \\ a_2 - a_1 &= 0 \end{aligned}$$

from which we find that $a_1 = a_2 = a$. Therefore,

$$\varphi_{s_x=\hbar/2} = \begin{pmatrix} a \\ a \end{pmatrix}$$

Examination of the normalization condition (41.10) shows that $2 |a|^2 = 1$, whence $a = (1/\sqrt{2}) e^{i\alpha_1}$. Hence,

$$\Psi_{s_x=\hbar/2} = \frac{1}{\sqrt{2}} e^{i\alpha_1} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad (43.4)$$

Using $s_x = -\hbar/2$ in (43.2) and solving the system obtained lead to the second eigenfunction of the operator \hat{s}_x :

$$\Psi_{s_x=-\hbar/2} = \frac{1}{\sqrt{2}} e^{i\alpha_2} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (43.5)$$

Now let us write Eq. (43.1) for \hat{s}_y . With a view to (42.30), we have

$$\frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = s_y \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}$$

Multiplying the matrices and equating the relevant elements, we obtain the system

$$\left. \begin{array}{l} s_y b_1 + i \frac{\hbar}{2} b_2 = 0 \\ i \frac{\hbar}{2} b_1 - s_y b_2 = 0 \end{array} \right\} \quad (43.6)$$

Assuming that the determinant of the system is zero, we obtain the equation

$$-s_y^2 + \left(\frac{\hbar}{2} \right)^2 = 0$$

Its solutions

$$s_y = +\frac{\hbar}{2} \quad \text{and} \quad s_y = -\frac{\hbar}{2} \quad (43.7)$$

are eigenvalues of the operator \hat{s}_y .

Introducing $s_y = \hbar/2$ into (43.6), we obtain the following system of equations after cancelling $\hbar/2$:

$$\begin{aligned} b_1 + i b_2 &= 0 \\ i b_1 - b_2 &= 0 \end{aligned}$$

from which it follows that $b_2 = i b_1$ and, therefore, $|b_2| = |b_1|$. According to the normalization condition, $1 = |b_1|^2 + |b_2|^2 = 2 |b_1|^2 = 2 |b_2|^2$. Hence

$$b_1 = \frac{1}{\sqrt{2}} e^{i\alpha_3}, \quad b_2 = \frac{i}{\sqrt{2}} e^{i\alpha_3}$$

We thus obtain

$$\Psi_{s_y=\hbar/2} = \frac{1}{\sqrt{2}} e^{i\alpha_s} \begin{pmatrix} 1 \\ i \end{pmatrix} \quad (43.8)$$

Similar calculations show that

$$\Psi_{s_y=-\hbar/2} = \frac{1}{\sqrt{2}} e^{i\alpha_s} \begin{pmatrix} 1 \\ -i \end{pmatrix} \quad (43.9)$$

Using expression (42.10) for \hat{s}_z in (43.1) and solving the system of equations obtained, we get an already known result:

$$s_z = +\frac{\hbar}{2}, \quad s_z = -\frac{\hbar}{2} \quad (43.10)$$

$$\Psi_{s_z=\hbar/2} = e^{i\alpha_s} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \Psi_{s_z=-\hbar/2} = e^{i\alpha_s} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (43.11)$$

[see (41.11) and (41.12)].

We must note that the eigenvalues of all three spin projections are identical and equal $\pm\hbar/2$, while the eigenfunctions are different (recall that our treatment is being conducted in the s_z -representation). The arbitrary phase factors of the form $e^{i\alpha}$ in expressions (43.4), (43.5), (43.8), (43.9), and (43.11) may naturally be assumed equal to unity (i.e. we may assume that $\alpha = 0$).

Equation (7.3) for the operator \hat{s}^2 has the following form:

$$\frac{3\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = s^2 \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

[see (42.9)]. After multiplication of the matrices, we obtain the relation

$$\frac{3\hbar^2}{4} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = s^2 \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

from which we can see that the eigenvalue of the operator \hat{s}^2 is $s^2 = 3\hbar^2/4$, while its eigenfunction is any column of the kind

$$\Psi_{s^2} = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

whose elements satisfy the normalization condition $|a_1|^2 + |a_2|^2 = 1$.

44. Spinors

We shall show in the present section that the spin psi-functions are spinors.

A spinor is defined to be a multicomponent mathematical quantity that transforms in a special way (differing, particularly, from that of tensor transformation) upon changes in the system of coordinates. A spinor of rank one is the simplest example. It has two components—the complex quantities z_1 and z_2 transforming according to the law

$$\begin{pmatrix} z'_1 \\ z'_2 \end{pmatrix} = \begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix} \begin{pmatrix} z_1 \\ z_2 \end{pmatrix} \quad (44.1)$$

where z_1, z_2 are the spinor components in the coordinate system K ; z'_1, z'_2 are the spinor components in the coordinate system K' ; and $\alpha, \beta, \gamma, \delta$ are the elements of the transformation matrix satisfying

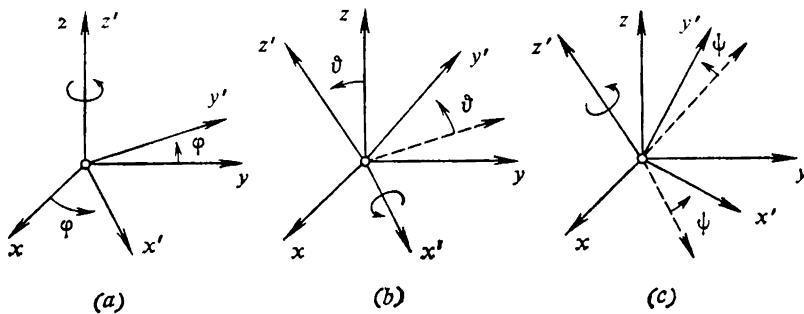


Fig. 44.1

the condition $D = \alpha\delta - \beta\gamma = 1$ (D is the determinant of the matrix).

A spinor of rank two is defined to be a set of four complex quantities that transform like the products of the components of two spinors of rank one (similarly, the components of a tensor of rank two transform like the products of the components of two tensors of rank one, i.e. vectors). Spinors of higher ranks are defined in a similar way.

An arbitrary rotation of the coordinate system K' relative to the system K can be characterized with the aid of the Euler angles $\varphi, \vartheta, \psi^1$ (see Vol. 1, Sec. 22). Rotation is performed in three steps (Fig. 44.1):

¹ Although the letters φ and ψ are also used to designate psi-functions, we have used the standard symbols for the Euler angles. This cannot cause any ambiguity because the Euler angles will be encountered in the formulas only preceded by trigonometric functions.

- (a) rotation about the coinciding axes z and z' through the angle φ ;
- (b) rotation about the new position of the x -axis (about the nodal line) through the angle ϑ ;
- (c) rotation about the z' -axis through the angle ψ .

When the change in the coordinate system consists of rotation about the origin of coordinates, the transformation matrix in (44.1) has the form

$$\begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix} = \begin{pmatrix} e^{i(\varphi+\psi)/2} \cos \vartheta/2 & ie^{-i(\varphi-\psi)/2} \sin \vartheta/2 \\ ie^{i(\varphi-\psi)/2} \sin \vartheta/2 & e^{-i(\varphi+\psi)/2} \cos \vartheta/2 \end{pmatrix} \quad (44.2)$$

(it is quite simple to see that the determinant of this matrix is unity). The difference in the ways of transforming spinors and tensors can be revealed especially clearly if we consider rotation about the y -axis through the angle ϑ . Such rotation can be performed by means of consecutive rotations through the angles $\varphi = \pi/2$, $\vartheta = \vartheta$, and $\psi = -\pi/2$. Introducing these values into (44.2), we obtain the matrix

$$\begin{pmatrix} \cos \vartheta/2 & \sin \vartheta/2 \\ -\sin \vartheta/2 & \cos \vartheta/2 \end{pmatrix} \quad (44.3)$$

that differs from the matrix of a similar transformation of tensors of rank one (i.e. vectors) in containing half the angle of rotation ϑ instead of the complete one. For this reason, spinors are also known as semivectors.

Now let us turn to establishing the formulas for transformation of the spin operators and spin functions upon rotations of the coordinate system. Consider two coordinate systems: the system K with the axes x , y , z and the system K' with the axes x' , y' , z' turned relative to it. The spin function of the physical system being considered can be written either in the system K : $\varphi^{(K)}$, or in the system K' : $\varphi^{(K')}$. These functions define the same state in two different representations: the first in the K -representation, and the second in the K' -representation.

It was established in Sec. 14 that the transformation of functions and operators in a transition from one representation to another is accomplished with the aid of a unitary operator. In the given case, the rotation operator \hat{R} (see the end of Sec. 15) is this operator. Since it is unitary, its Hermitian conjugate equals the inverse operator:

$$\hat{R}^+ = \hat{R}^{-1} \quad (44.4)$$

[see (14.15)]. By (14.24) and (14.25), we have

$$\varphi^{(K')} = \hat{R}\varphi^{(K)} \quad (44.5)$$

$$\hat{s}_m^{(K')} = \hat{R}\hat{s}_m^{(K)}\hat{R}^+ = \hat{R}\hat{s}_m^{(K)}\hat{R}^{-1} \quad (m=x, y, z) \quad (44.6)$$

The components of any vector in a transition from one coordinate system to another are transformed by the formulas

$$b'_m = \sum_n \alpha_{mn} b_n, \quad b_m = \sum_n \alpha_{nm} b'_n \quad (44.7)$$

where $\alpha_{mn} = e'_m e_n = \cos(x'_m, x_n)$ (see Vol. 1, Appendix VI). Particularly, when the system K' is turned relative to the system K about the z -axis through the angle φ , the matrix of the transformation coefficients α_{mn} has the form

$$(\alpha_{mn}) = \begin{pmatrix} \cos \varphi & \sin \varphi & 0 \\ -\sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and by formulas (44.7)

$$b'_x = b_x \cos \varphi + b_y \sin \varphi, \quad b'_y = -b_x \sin \varphi + b_y \cos \varphi, \quad b'_z = b_z \quad (44.8)$$

$$b_x = b'_x \cos \varphi - b'_y \sin \varphi, \quad b_y = b'_x \sin \varphi + b'_y \cos \varphi, \quad b_z = b'_z \quad (44.9)$$

The angular momentum, particularly the spin, is a pseudovector, therefore its components are transformed by formulas (44.8) and (44.9). The same relations exist between operators as between the quantities they depict. We thus conclude that the operators \hat{s}_x , \hat{s}_y , \hat{s}_z must transform in rotation of the coordinate system according to formulas (44.8) and (44.9), it being possible to write these formulas in both the K -representation and the K' -representation.

Let us agree to understand by \hat{s}_x , \hat{s}_y , \hat{s}_z the operators of the spin projections onto the axes of the system K , and by \hat{s}'_x , \hat{s}'_y , \hat{s}'_z , the operators of the spin projections onto the axes of the system K' [in formulas (44.7), the components b_m correspond to \hat{s}_x , \hat{s}_y , \hat{s}_z , and the components b'_m correspond to \hat{s}'_x , \hat{s}'_y , \hat{s}'_z]. Let us write formulas (44.9) in the K -representation:

$$\left. \begin{aligned} \hat{s}_x^{(K)} &= \hat{s}'_x^{(K)} \cos \varphi - \hat{s}'_y^{(K)} \sin \varphi \\ \hat{s}_y^{(K)} &= \hat{s}'_x^{(K)} \sin \varphi + \hat{s}'_y^{(K)} \cos \varphi \\ \hat{s}_z^{(K)} &= \hat{s}'_z^{(K)} \end{aligned} \right\} \quad (44.10)$$

In the K' -representation, they have the same form:

$$\left. \begin{aligned} \hat{s}_x^{(K')} &= \hat{s}_{x'}^{(K')} \cos \varphi - \hat{s}_{y'}^{(K')} \sin \varphi \\ \hat{s}_y^{(K')} &= \hat{s}_{x'}^{(K')} \sin \varphi + \hat{s}_{y'}^{(K')} \cos \varphi \\ \hat{s}_z^{(K')} &= \hat{s}_{z'}^{(K')} \end{aligned} \right\} \quad (44.11)$$

The two coordinate systems are absolutely equivalent. Therefore, say, the operator $\hat{s}_{x'}^{(K')}$ has exactly the same form as $\hat{s}_x^{(K)}$ [both are determined by formula (42.29)]. The same relates to the other two operators. Consequently,

$$\hat{s}_{x'}^{(K')} = \hat{s}_x^{(K)}, \quad \hat{s}_{y'}^{(K')} = \hat{s}_y^{(K)}, \quad \hat{s}_{z'}^{(K')} = \hat{s}_z^{(K)} \quad (44.12)$$

With a view to these relations, formulas (44.11) can be altered as follows:

$$\left. \begin{aligned} \hat{s}_x^{(K')} &= \hat{s}_x^{(K)} \cos \varphi - \hat{s}_y^{(K)} \sin \varphi \\ \hat{s}_y^{(K')} &= \hat{s}_x^{(K)} \sin \varphi + \hat{s}_y^{(K)} \cos \varphi \\ \hat{s}_z^{(K')} &= \hat{s}_z^{(K)} \end{aligned} \right\} \quad (44.13)$$

We have obtained formulas for transforming the operators of the spin projections from the K -representation to the K' -representation. By (44.6), these formulas can be written with the aid of the unitary rotation operator \hat{R}_z :

$$\left. \begin{aligned} \hat{s}_x^{(K')} &= \hat{R}_z \hat{s}_x^{(K)} \hat{R}_z^{-1} \\ \hat{s}_y^{(K')} &= \hat{R}_z \hat{s}_y^{(K)} \hat{R}_z^{-1} \\ \hat{s}_z^{(K')} &= \hat{R}_z \hat{s}_z^{(K)} \hat{R}_z^{-1} \end{aligned} \right\} \quad (44.14)$$

(to underline that we have in view rotation about the z -axis, we have used the subscript z on \hat{R}).

A comparison of formulas (44.13) and (44.14) allows us to find the operator \hat{R}_z . By comparing the last of the formulas (44.13) with the last of the formulas (44.14), we find that

$$\hat{s}_z^{(K)} = \hat{R}_z \hat{s}_z^{(K)} \hat{R}_z^{-1}$$

Postmultiplying both sides of the equation by \hat{R}_z , we obtain

$$\hat{s}_z^{(K)} \hat{R}_z = \hat{R}_z \hat{s}_z^{(K)}$$

$(\hat{R}_z^{-1}\hat{R}_z = 1)$, whence it follows that the operators $\hat{s}_z^{(K)}$ and \hat{R}_z commute. The matrices of commuting operators can be reduced simultaneously to the diagonal form (see the last paragraph of Sec. 9). The operator \hat{s}_z is represented by the diagonal matrix (42.10). Therefore, the matrix of the operator \hat{R}_z must also be diagonal, i.e. have the form

$$\hat{R}_z = \begin{pmatrix} \kappa_1 & 0 \\ 0 & \kappa_2 \end{pmatrix} \quad (44.15)$$

The Hermitian conjugate operator is determined by the matrix

$$\hat{R}_z^* = \begin{pmatrix} \kappa_1^* & 0 \\ 0 & \kappa_2^* \end{pmatrix} \quad (44.16)$$

[see (9.19)]. Owing to unitarity, the product of the matrices (44.15) and (44.16) must equal a unit matrix:

$$\begin{pmatrix} \kappa_1 & 0 \\ 0 & \kappa_2 \end{pmatrix} \begin{pmatrix} \kappa_1^* & 0 \\ 0 & \kappa_2^* \end{pmatrix} = \begin{pmatrix} |\kappa_1|^2 & 0 \\ 0 & |\kappa_2|^2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Hence, $|\kappa_1|^2 = |\kappa_2|^2 = 1$. With this in view, let us write the matrix (44.15) in the form

$$\hat{R}_z = \begin{pmatrix} e^{i\alpha_1} & 0 \\ 0 & e^{i\alpha_2} \end{pmatrix} \quad (44.17)$$

where α_1 and α_2 are real.

We have meanwhile used only the third equations of (44.13) and (44.14). To find the relation between the phases α_1 and α_2 , let us use the remaining equations. Postmultiplying the first of the equations (44.14) by \hat{R}_z , we arrive at the relation

$$\hat{s}_x^{(K')} \hat{R}_z = \hat{R}_z \hat{s}_x^{(K)}$$

Let us substitute $\hat{s}_x^{(K')}$ in it in accordance with the first of the equations (44.13). The result is

$$\hat{s}_x^{(K)} \hat{R}_z \cos \varphi - \hat{s}_y^{(K)} \hat{R}_z \sin \varphi = \hat{R}_z \hat{s}_x^{(K)} \quad (44.18)$$

In the following, we shall have to do only with operators of the spin projections in the K -representation. We shall therefore suppress the superscript (K) . Let us substitute into (44.18) the matrix (42.29) for \hat{s}_x , the matrix (42.30) for \hat{s}_y , and the matrix (44.17) for \hat{R}_z :

$$\begin{aligned} \frac{\hbar}{2} \cos \varphi \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} e^{i\alpha_1} & 0 \\ 0 & e^{i\alpha_2} \end{pmatrix} - \frac{\hbar}{2} \sin \varphi \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} e^{i\alpha_1} & 0 \\ 0 & e^{i\alpha_2} \end{pmatrix} \\ = \frac{\hbar}{2} \begin{pmatrix} e^{i\alpha_1} & 0 \\ 0 & e^{i\alpha_2} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \end{aligned}$$

Multiplication of the matrices yields (we cancel $\hbar/2$)

$$\cos \varphi \begin{pmatrix} 0 & e^{i\alpha_2} \\ e^{i\alpha_1} & 0 \end{pmatrix} - i \sin \varphi \begin{pmatrix} 0 & -e^{i\alpha_2} \\ e^{i\alpha_1} & 0 \end{pmatrix} = \begin{pmatrix} 0 & e^{i\alpha_1} \\ e^{i\alpha_2} & 0 \end{pmatrix}$$

(give attention to the fact that the operators \hat{s}_x and \hat{R}_z do not commute). Equating the relevant matrix elements, we obtain two equations:

$$\left. \begin{aligned} \cos \varphi e^{i\alpha_2} + i \sin \varphi e^{i\alpha_1} &= e^{i\alpha_1} \\ \cos \varphi e^{i\alpha_1} - i \sin \varphi e^{i\alpha_2} &= e^{i\alpha_2} \end{aligned} \right\} \quad (44.19)$$

Expressing $\sin \varphi$ and $\cos \varphi$ in them in terms of the exponentials, we arrive at the relations

$$e^{i(\alpha_2+\varphi)} = e^{i\alpha_1}, \quad e^{i(\alpha_1-\varphi)} = e^{i\alpha_2} \quad (44.20)$$

We must note that if we had taken the second of the equations (44.14) and performed the same transformations, we would also have arrived at Eqs. (44.19).

The simplest condition in which relations (44.20) are satisfied states that $\alpha_1 - \alpha_2 = \varphi$. Let us assume that $\alpha_1 = \alpha_0 + \varphi/2$, $\alpha_2 = \alpha_0 - \varphi/2$, and introduce these values into (44.17). The result is

$$\hat{R}_z = e^{i\alpha_0} \begin{pmatrix} e^{i\varphi/2} & 0 \\ 0 & e^{-i\varphi/2} \end{pmatrix}$$

The arbitrary phase factor $e^{i\alpha_0}$ may be dropped. Consequently, the operator of rotation of the coordinate system about the z-axis through the angle φ has the form

$$\hat{R}_z(\varphi) = \begin{pmatrix} e^{i\varphi/2} & 0 \\ 0 & e^{-i\varphi/2} \end{pmatrix} \quad (44.21)$$

This operator can be written as follows:

$$\begin{aligned} \hat{R}_z(\varphi) &= \begin{pmatrix} \cos \varphi/2 + i \sin \varphi/2 & 0 \\ 0 & \cos \varphi/2 - i \sin \varphi/2 \end{pmatrix} \\ &= \cos \varphi/2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + i \sin \varphi/2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{aligned}$$

The multiplier of $\cos \varphi/2$ is the unit matrix I , and that of $i \sin \varphi/2$ is the Pauli spin matrix σ_z [see (42.32)]. Hence,

$$\hat{R}_z(\varphi) = \left(\cos \frac{\varphi}{2} \right) I + i \left(\sin \frac{\varphi}{2} \right) \sigma_z \quad (44.22)$$

In expressions of this kind, the symbol I may be suppressed. Since the second term contains a two-row square matrix, the first term

must also contain a two-row square matrix, which, if not indicated, can be only an identity one. Hence, (44.22) can be abbreviated to

$$\hat{R}_z(\varphi) = \cos \frac{\varphi}{2} + i \left(\sin \frac{\varphi}{2} \right) \sigma_z \quad (44.23)$$

If the angle of rotation is infinitely small, expression (44.23) becomes

$$\hat{R}_z(\delta\varphi) = 1 + i \frac{\delta\varphi}{2} \sigma_z = 1 + \frac{i}{\hbar} \delta\varphi \cdot \hat{s}_z \quad (44.24)$$

[compare with (15.20)].

The operator of rotation about any other axis has the same form as (44.23), it being necessary only to replace σ_z with the Pauli spin matrix for the relevant axis. Consequently,

$$\hat{R}_x(\vartheta) = \cos \frac{\vartheta}{2} + i \sigma_x \sin \frac{\vartheta}{2} \quad (44.25)$$

$$\hat{R}_y(\vartheta) = \cos \frac{\vartheta}{2} + i \sigma_y \sin \frac{\vartheta}{2} \quad (44.26)$$

Introducing the matrices I , σ_x , and σ_y into expressions (44.25) and (44.26), we obtain

$$\hat{R}_x(\vartheta) = \cos \frac{\vartheta}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + i \sin \frac{\vartheta}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} \cos \frac{\vartheta}{2} & i \sin \frac{\vartheta}{2} \\ i \sin \frac{\vartheta}{2} & \cos \frac{\vartheta}{2} \end{pmatrix} \quad (44.27)$$

$$\hat{R}_y(\vartheta) = \cos \frac{\vartheta}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + i \sin \frac{\vartheta}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \begin{pmatrix} \cos \frac{\vartheta}{2} & \sin \frac{\vartheta}{2} \\ -\sin \frac{\vartheta}{2} & \cos \frac{\vartheta}{2} \end{pmatrix} \quad (44.28)$$

A comparison of (44.28) with (44.3) shows that upon rotation about the y -axis, the matrix of transformation of spin functions coincides with the matrix of transformation of a spinor. Let us convince ourselves that this also occurs in an arbitrary rotation of the coordinate system.

An arbitrary rotation, as was indicated at the beginning of this section, can be performed with the aid of three consecutive rotations through the angles φ , ϑ , and ψ . The first rotation is described by the operator $\hat{R}_z(\varphi)$, the second by the operator $\hat{R}_x(\vartheta)$, and the third by the operator $\hat{R}_z(\psi)$ ¹. The operator of the resultant rotation equals the product of these three operators:

$$\hat{R}(\psi, \vartheta, \varphi) = \hat{R}_z(\psi) \hat{R}_x(\vartheta) \hat{R}_z(\varphi)$$

¹ We have omitted the prime on the subscript z because $\sigma_{z'} = \sigma_z$ and, consequently, in accordance with (44.23) we have $\hat{R}_{z'} = \hat{R}_z$.

Introducing expression (44.21) for \hat{R}_z and (44.27) for \hat{R}_x , we obtain

$$\begin{aligned}\hat{R}(\psi, \vartheta, \varphi) &= \begin{pmatrix} e^{i\psi/2} & 0 \\ 0 & e^{-i\psi/2} \end{pmatrix} \begin{pmatrix} \cos \frac{\vartheta}{2} & i \sin \frac{\vartheta}{2} \\ i \sin \frac{\vartheta}{2} & \cos \frac{\vartheta}{2} \end{pmatrix} \begin{pmatrix} e^{i\varphi/2} & 0 \\ 0 & e^{-i\varphi/2} \end{pmatrix} \\ &= \begin{pmatrix} e^{i(\varphi+\psi)/2} \cos \frac{\vartheta}{2} & i e^{-i(\varphi-\psi)/2} \sin \frac{\vartheta}{2} \\ i e^{i(\varphi-\psi)/2} \sin \frac{\vartheta}{2} & e^{-i(\varphi+\psi)/2} \cos \frac{\vartheta}{2} \end{pmatrix} \quad (44.29)\end{aligned}$$

[compare with (44.2)].

The spin function of a particle with a spin of $1/2$ has the form of the column $\varphi = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$ [see (41.9)]. Consequently, the formula for the transformation of this function upon rotation of the coordinate system is as follows:

$$\begin{pmatrix} a'_1 \\ a'_2 \end{pmatrix} = \hat{R}(\psi, \vartheta, \varphi) \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \quad (44.30)$$

where $\hat{R}(\psi, \vartheta, \varphi)$ is the matrix (44.29) coinciding with the matrix of transformation of a spinor of rank one. We have thus proved that a spin function is a spinor. The spin function of a system of two particles with a spin of $1/2$ is a spinor of rank two.

For any spinor $\varphi = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$, we can always find an operator $\hat{R}(\psi, \vartheta, \varphi)$ such that transforms φ into $\varphi' = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$. Now, the angles φ, ϑ, ψ determine the direction in which the spin of a particle is "oriented" (i.e. the direction for which the projection of the spin is +1).

Introducing the matrix (44.27) into (44.30) and performing multiplication, we find that¹

$$a'_1 = a_1 \cos \frac{\vartheta}{2} + a_2 \sin \frac{\vartheta}{2}, \quad a'_2 = -a_1 \sin \frac{\vartheta}{2} + a_2 \cos \frac{\vartheta}{2}$$

Let us perform rotation through $\vartheta = 2\pi$. Here $a'_1 = -a_1$ and $a'_2 = -a_2$, i.e. the spinor reverses its sign. The same evidently holds in rotation through 2π about an arbitrary axis (the y -axis does not differ in any way from any other axis). It thus follows that a spinor cannot have a direct physical meaning (any physical quantity upon

¹ Transformations of such a kind, i.e. transformations of the kind $a'_1 = \alpha a_1 + \beta a_2$, are called *binary*.

rotation through 2π transforms into itself). This is not surprising—we know that a spinor is a psi-function, and the latter has no direct physical meaning.

Only bilinear expressions of the kind $a_1 b_2 - a_2 b_1$, where $\begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$ and $\begin{pmatrix} b_1 \\ b_2 \end{pmatrix}$ are two spinors, can have a physical meaning. In rotation through 2π , both spinors reverse their sign, but their product remains unchanged.

Chapter IX

SYSTEMS CONSISTING OF IDENTICAL PARTICLES

45. Principle of Indistinguishability of Identical Particles

In classical mechanics, particles of an identical nature (for instance, electrons) can be distinguished in principle. Numbering them at a certain initial instant t_0 , we can observe each of them as it moves in its trajectory and at any instant t indicate the number that was assigned to a definite particle.

In quantum mechanics, matters are radically different. Owing to the uncertainty principle, the concept of the trajectory of a particle loses its meaning. Even if the position of a particle has been determined at a certain instant, already after an infinitely small time interval elapses, the coordinates of the particle are absolutely indeterminate. Therefore, even if we have localized all the particles at the instant t_0 and have numbered them, we will not be able to indicate which of the particles will be localized at the instant t at a definite point of space. Consequently, it is impossible to watch every one of identical particles and thus distinguish them. Hence, in quantum mechanics, particles of an identical nature completely lose their "individuality"—such particles are absolutely indistinguishable. This statement is known as the **principle of indistinguishability of identical particles**.

The impossibility in principle of distinguishing between identical particles leads to deep-seated physical consequences. It plays the main role in considering systems consisting of identical particles.

Assume that we have a system of N identical particles. Let us designate the set of coordinates and the projection of the spin of the i -th particle by the symbol ξ_i . The psi-function of the system will therefore be

$$\psi(\xi_1, \xi_2, \dots, \xi_i, \dots, \xi_k, \dots, \xi_N, t)$$

Let us interchange the i -th and k -th particles, i.e. replace in the psi-function the coordinates and the projection of the spin of the i -th particle with the coordinates and the projection of the spin of the k -th particle and vice versa. Owing to the principle of indistinguishability of the particles, the state of the system cannot change as

a result of this replacement, and, consequently, the psi-function can change only by an insignificant phase factor:

$$\begin{aligned}\psi(\xi_1, \xi_2, \dots, \xi_k, \dots, \xi_i, \dots, \xi_N, t) \\ = e^{i\alpha} \psi(\xi_1, \xi_2, \dots, \xi_i, \dots, \xi_k, \dots, \xi_N, t)\end{aligned}$$

If we interchange the i -th and the k -th particles once more, the psi-function will again be multiplied by $e^{i\alpha}$, and at the same time it must take on its original form. We can therefore write that

$$\begin{aligned}\psi(\xi_1, \xi_2, \dots, \xi_i, \dots, \xi_k, \dots, \xi_N, t) \\ = e^{i\alpha} \psi(\xi_1, \xi_2, \dots, \xi_k, \dots, \xi_i, \dots, \xi_N, t) \\ = e^{2i\alpha} \psi(\xi_1, \xi_2, \dots, \xi_i, \dots, \xi_k, \dots, \xi_N, t)\end{aligned}$$

whence we can see that $e^{2i\alpha} = 1$ and $e^{i\alpha} = \pm 1$.

Hence, in the transposition of two identical particles, the psi-function of the system can behave in one of two ways: either remain unchanged, or reverse its sign. Psi-functions of the first kind are said to be **symmetric**, and of the second, **antisymmetric**.

Let us introduce the exchange operator \hat{P}_{ik} determined by the relation

$$\begin{aligned}\hat{P}_{ik}\psi(\xi_1, \xi_2, \dots, \xi_i, \dots, \xi_k, \dots, \xi_N, t) \\ = \psi(\xi_1, \xi_2, \dots, \xi_k, \dots, \xi_i, \dots, \xi_N, t)\end{aligned}$$

As a result of the fact that $\psi(\dots, \xi_k, \dots, \xi_i, \dots) = \pm \psi(\dots, \xi_i, \dots, \xi_k, \dots)$, we have

$$\hat{P}_{ik}\psi = \pm 1 \cdot \psi \quad (45.1)$$

It thus follows that the eigenvalues of the exchange operator are ± 1 . The symmetric functions of a system of particles are the eigenfunctions of the operator \hat{P}_{ik} corresponding to the eigenvalue $+1$, while the antisymmetric functions are the eigenfunctions corresponding to the eigenvalue -1 .

The Hamiltonian of a system of particles has the form

$$\hat{H} = \sum_{i=1}^N \left[-\frac{\hbar^2}{2m_0} \nabla_i^2 + U(\xi_i, t) \right] + U(\xi_1, \xi_2, \dots, \xi_N) \quad (45.2)$$

where $U(\xi_i, t)$ is the potential corresponding to the interaction of a particle with the external field, and $U(\xi_1, \xi_2, \dots, \xi_N)$ is the energy of interaction of the particles with one another. It is evident that this Hamiltonian does not change in the transposition of two

particles. Consequently, $\hat{P}_{ik} (\hat{H}\psi) = \hat{H} (\hat{P}_{ik}\psi)$, whence it can be seen that the exchange operator commutes with the Hamiltonian:

$$\hat{H}\hat{P}_{ik} - \hat{P}_{ik}\hat{H} = 0$$

It was shown in Sec. 21 that if an operator of a quantity does not depend explicitly on the time and, in addition, commutes with the Hamiltonian, this quantity is conserved. The properties of symmetry of the psi-function of a system of given particles are thus conserved in time (are an integral of motion). In this connection, we can assume that the type of symmetry of the psi-function is determined by the nature of the particles forming a system. It is proved in relativistic quantum mechanics that particles with an integral (particularly, zero) spin are described by symmetric functions; particles with a half-integral spin are described by antisymmetric functions.

Particles with an integral (and zero) spin are called bosons, and particles with a half-integral spin, fermions.

The type of the symmetry of the psi-function describing a collection of identical compound particles (for example, nuclei or atoms) depends on the magnitude of the resultant spin of a given compound particle. With an integral (and zero) resultant spin, the psi-function is symmetric, with a half-integral one, it is antisymmetric.

46. Psi-Functions for Systems of Particles. The Pauli Principle

The Hamiltonian of a system of non-interacting (or very weakly interacting) identical particles in a stationary external field is determined by the expression

$$\hat{H} = \sum_{i=1}^N \left[-\frac{\hbar^2}{2m_0} \nabla_i^2 + U(\xi_i) \right] \quad (46.1)$$

[compare with (45.2); we have disregarded the energy of interaction of the particles owing to its smallness]. Consequently, the eigenfunctions of the system can be found by solving the equation

$$\sum_{i=1}^N \left[-\frac{\hbar^2}{2m_0} \nabla_i^2 + U(\xi_i) \right] \psi(\xi_1, \xi_2, \dots, \xi_N) = E\psi(\xi_1, \xi_2, \dots, \xi_N) \quad (46.2)$$

Let us attempt to find the solution of this equation in the form

$$\psi(\xi_1, \xi_2, \dots, \xi_N) = \psi_1(\xi_1)\psi_2(\xi_2)\dots\psi_N(\xi_N) \quad (46.3)$$

where $\psi_i(\xi_i)$ is the function of the coordinates and the projection of the spin of only the i -th particle. Substitution into (46.2) yields

$$\sum_{i=1}^N \psi_1(\xi_1) \psi_2(\xi_2) \dots \psi_{i-1}(\xi_{i-1}) \psi_{i+1}(\xi_{i+1}) \dots \psi_N(\xi_N) \times \left[-\frac{\hbar^2}{2m_0} \nabla_i^2 + U(\xi_i) \right] \psi_i(\xi_i) = E \psi$$

Dividing both sides of the equation by ψ , we obtain

$$\sum_{i=1}^N \frac{1}{\psi_i(\xi_i)} \left[-\frac{\hbar^2}{2m_0} \nabla_i^2 + U(\xi_i) \right] \psi_i(\xi_i) = E$$

The left-hand side of this relation is the sum of expressions, each of which depends on its own variable ξ_i . For such a sum to equal the constant quantity E at arbitrary values of the variables ξ_i , each of the addends must equal its own constant E_i . Hence follow the conditions

$$-\frac{\hbar^2}{2m_0} \nabla_i^2 \psi_i(\xi_i) + U(\xi_i) \psi_i(\xi_i) = E_i \psi_i(\xi_i) \quad (46.4)$$

$$(i = 1, 2, \dots, N)$$

$$\sum_{i=1}^N E_i = E \quad (46.5)$$

Owing to the identity of the particles, the function $U(\xi_i)$ and Eq. (46.4) have an identical form for all the particles. By solving this equation, we find the functions $\psi_i(\xi_i)$ corresponding to E_i . Next, multiplying the functions $\psi_i(\xi_i)$, we obtain the solution of Eq. (46.2). The quantity E_i is the energy of the i -th particle.

The functions $\psi_i(\xi_i)$ are different eigenfunctions of the operator

$$-\frac{\hbar^2}{2m_0} \nabla^2 + U(\xi) \quad (46.6)$$

Therefore, the subscript i on ψ_i indicates what stationary state of the operator (46.6) the i -th particle is in. Each stationary state is characterized by a set of certain quantum numbers. Designating this set of numbers by the symbol m_i , we shall write ψ_{m_i} instead of ψ_i in the following.

The solutions of Eq. (46.2) are thus

$$\psi(\xi_1, \xi_2, \dots, \xi_N) = \psi_{m_1}(\xi_1) \psi_{m_2}(\xi_2) \dots \psi_{m_N}(\xi_N) \quad (46.7)$$

Any superposition of functions of the form of (46.7) differing in the values of m_i on each of the factors will also be a solution.

Since, generally speaking,

$$\psi_{m_i}(\xi_h)\psi_{m_k}(\xi_i) \neq \pm \psi_{m_i}(\xi_i)\psi_{m_k}(\xi_h)^1$$

the function (46.7) in a general case will be neither symmetric nor antisymmetric. A function, the nature of whose symmetry corresponds to the nature of the particles forming the system, can be obtained in the form of a properly selected superposition of solutions of the form of (46.7).

We shall explain the above on the example of a system of two particles. The following two functions are solutions of Eq. (46.2) corresponding to the energy $E = E_1 + E_2$:

$$\left. \begin{aligned} \psi_1(\xi_1, \xi_2) &= \psi_1(\xi_1)\psi_2(\xi_2) \\ \psi_2(\xi_1, \xi_2) &= \psi_2(\xi_1)\psi_1(\xi_2) \end{aligned} \right\} \quad (46.8)$$

where ψ_1 is the eigenfunction of the operator (46.6) corresponding to the energy of a particle equal to E_1 , and ψ_2 is a similar function corresponding to the energy E_2 . Both functions (46.8) correspond to the same energy E of the system.

We can use the functions (46.8) to form a symmetric ψ_s and anti-symmetric ψ_a functions of the system:

$$\psi_s = c_1 [\psi_1(\xi_1)\psi_2(\xi_2) + \psi_2(\xi_1)\psi_1(\xi_2)] \quad (46.9)$$

$$\psi_a = c_2 [\psi_1(\xi_1)\psi_2(\xi_2) - \psi_2(\xi_1)\psi_1(\xi_2)] \quad (46.10)$$

It is not difficult to see that the transposition of the coordinates ξ_1 and ξ_2 leaves the function (46.9) unchanged, while the sign of the function (46.10) changes. The coefficients c_1 and c_2 are determined from the normalization conditions, which in the given case are as follows:

$$\int |\psi_s|^2 dV_1 dV_2 = 1, \quad \int |\psi_a|^2 dV_1 dV_2 = 1$$

¹ Such a transposition signifies that the k -th particle transfers to a state with the set m_i of quantum numbers, and the i -th particle to a state with the set m_k of quantum numbers.

Assuming that the functions $\psi_i(\xi_i)$ are normalized to unity, we obtain

$$\begin{aligned}
 1 &= \int \psi_s^* \psi_s dV_1 dV_2 = c_1^* c_1 \int [\psi_1^*(\xi_1) \psi_2^*(\xi_2) + \psi_2^*(\xi_1) \psi_1^*(\xi_2)] \\
 &\quad \times [\psi_1(\xi_1) \psi_2(\xi_2) + \psi_2(\xi_1) \psi_1(\xi_2)] dV_1 dV_2 \\
 &= c_1^* c_1 \left\{ \int \psi_1^*(\xi_1) \psi_1(\xi_1) dV_1 \int \psi_2^*(\xi_2) \psi_2(\xi_2) dV_2 \right. \\
 &\quad + \int \psi_1^*(\xi_1) \psi_2(\xi_1) dV_1 \int \psi_2^*(\xi_2) \psi_1(\xi_2) dV_2 \\
 &\quad + \int \psi_2^*(\xi_1) \psi_1(\xi_1) dV_1 \int \psi_1^*(\xi_2) \psi_2(\xi_2) dV_2 \\
 &\quad \left. + \int \psi_2^*(\xi_1) \psi_2(\xi_1) dV_1 \int \psi_1^*(\xi_2) \psi_1(\xi_2) dV_2 \right\} \\
 &= c_1^* c_1 \{1 \cdot 1 + 0 \cdot 0 + 0 \cdot 0 + 1 \cdot 1\} = 2 |c_1|^2 \quad (46.11)
 \end{aligned}$$

(the second and third terms are zero owing to the orthogonality of the functions ψ_1 and ψ_2). Hence, $c_1 = 1/\sqrt{2}$ with an accuracy to the phase factor. Similar calculations show that c_2 in (46.10) has the same value as c_1 .

Introducing the values of the coefficients obtained into (46.9) and (46.10), we get the normalized functions of the symmetric and antisymmetric states:

$$\psi_s = \frac{1}{\sqrt{2}} [\psi_1(\xi_1) \psi_2(\xi_2) + \psi_2(\xi_1) \psi_1(\xi_2)] \quad (46.12)$$

$$\psi_a = \frac{1}{\sqrt{2}} [\psi_1(\xi_1) \psi_2(\xi_2) - \psi_2(\xi_1) \psi_1(\xi_2)] \quad (46.13)$$

Let us generalize the results obtained for a system of N non-interacting particles. If the latter are bosons, the psi-function of the system must be symmetric. The following superposition of the functions (46.3) will have such a property:

$$\psi_s = c_1 \sum_{[m_1, m_2, \dots, m_N]} \psi_{m_1}(\xi_1) \psi_{m_2}(\xi_2) \dots \psi_{m_N}(\xi_N) \quad (46.14)$$

Summation is performed over all possible permutations of the subscripts m_1, m_2, \dots, m_N ¹. If all these subscripts have different values, the number of permutations and, consequently, the number of addends in the sum (46.14) will be $N!$. It must be taken into account, however, that some particles may be in identical single-particle states.

¹ Permutation of the indices corresponds to permutations of states with different quantum numbers among particles arranged in the order of an increase in their numbers, or, which is the same, to permutations of the particles among states with different quantum numbers.

Assume that two particles—a first and a second one—are in the state with the set m_1 of quantum numbers. Now the indices m_1 and m_2 coincide, and all the permutations in which m_1 and m_2 exchange places correspond to identical addends. Since in superposition, each state is taken only once, the number of addends in (46.14) will be $N!/2$ in the case being considered.

If there are n_i particles in the state m_i , then $n_i!$ permutations of these particles correspond to one addend in (46.14), so that the number of addends in (46.14) will be $N!/n_i!$. Assume that n_1 particles are in the state m_1 , n_2 particles are in the state m_2 , and so on (the sum of these numbers must equal the total number of particles: $n_1 + n_2 + \dots = N$). Hence, the number of addends in (46.14) will be $N!/n_1!n_2! \dots$ ¹.

The coefficient c_1 in (46.14) is determined from the normalization condition:

$$1 = \int \psi_s^* \psi_s dV_1 dV_2 \dots dV_N = c_1^* c_1 \int \left[\sum \psi_{m_1}^*(\xi_1) \dots \psi_{m_N}^*(\xi_N) \right] \times \left[\sum \psi_{m_1}(\xi_1) \dots \psi_{m_N}(\xi_N) \right] dV_1 \dots dV_N$$

Owing to the orthogonality of the functions ψ_{m_i} , only the squares of the magnitude of each term of the sum (46.14) will make a non-zero (and equal to unity) contribution to the normalization integral

¹ We must note that when $n_i > 1$, the sets of quantum numbers corresponding to n_i particles will be identical, for example $m_i = m_k = m_l = \dots$. In this case in the product inside the sum (46.14), the set m_i will be in the form of an index on n_i factors, whereas the sets m_k , m_l , etc. will be absent. We shall explain this using the example of three particles. First assume that these particles are in different states. The sum (46.14) will now contain six addends corresponding to permutations of the indices 1, 2, 3:

$$\psi_1(\xi_1) \psi_2(\xi_2) \psi_3(\xi_3) \quad (1)$$

$$\psi_2(\xi_1) \psi_1(\xi_2) \psi_3(\xi_3) \quad (2)$$

$$\psi_1(\xi_1) \psi_3(\xi_2) \psi_2(\xi_3) \quad (3)$$

$$\psi_2(\xi_1) \psi_3(\xi_2) \psi_1(\xi_3) \quad (4)$$

$$\psi_3(\xi_1) \psi_1(\xi_2) \psi_2(\xi_3) \quad (5)$$

$$\psi_3(\xi_1) \psi_2(\xi_2) \psi_1(\xi_3) \quad (6)$$

Now assume that the particles 1 and 2 are in the same state: $\psi_1 \equiv \psi_2$. In this case, the pairs of addends (1) and (2), (3) and (4), (5) and (6) will be identical. The symmetric function therefore has the form

$$\psi_s = c_1 \{ \psi_1(\xi_1) \psi_1(\xi_2) \psi_3(\xi_3) + \psi_1(\xi_1) \psi_3(\xi_2) \psi_1(\xi_3) + \psi_3(\xi_1) \psi_1(\xi_2) \psi_1(\xi_3) \}$$

i.e. contains only three addends instead of six (the number of addends is $N!/n_1! = 3!/2!$).

If all three particles are in the same state (i.e. $\psi_1 \equiv \psi_2 \equiv \psi_3$), the function $\psi_1(\xi_1) \psi_1(\xi_2) \psi_1(\xi_3)$ will be symmetric itself, so that expression (46.14) will contain only one addend (the number of addends is $N!/n_1! = 3!/3!$).

[compare with (46.11)]. Therefore, the normalization integral will equal the number of addends in this sum. Consequently, $1 = c_1^* c_1 N! / n_1! n_2! \dots$, and for c_1 we obtain the value

$$c_1 = \left(\frac{n_1! n_2! \dots}{N!} \right)^{1/2}$$

The introduction of this value into (46.14) leads to a normalized symmetric psi-function of a system of N bosons:

$$\Psi_s = \left(\frac{n_1! n_2! \dots}{N!} \right)^{1/2} \sum_{[m_1, m_2, \dots, m_N]} \psi_{m_1}(\xi_1) \psi_{m_2}(\xi_2) \dots \psi_{m_N}(\xi_N) \quad (46.15)$$

Recall that, for example, we may have $m_1 = m_7 = m_N$. Hence, an exchange of the places of m_1 and m_7 , or of m_1 and m_N , or of m_7 and m_N does not result in a new permutation and, consequently, in an additional term in (46.15).

For a system of N fermions, the psi-function must be antisymmetric. Such a function can be obtained by multiplying each addend in a sum similar to (46.14) by the skew-symmetric Kronecker symbol $\varepsilon_{m_1 m_2 \dots m_N}$:

$$\Psi_a = c_2 \sum_{[m_1, m_2, \dots, m_N]} \varepsilon_{m_1 m_2 \dots m_N} \psi_{m_1}(\xi_1) \psi_{m_2}(\xi_2) \dots \psi_{m_N}(\xi_N) \quad (46.16)$$

Indeed, the transposition of any two indices on ε changes its sign so that expression (46.16) will be antisymmetric. In the given case, addends with coinciding values of at least two indices m_i and m_k are absent because the corresponding value of ε is zero¹. The number of addends in (46.16) is thus $N!$. Therefore, from the normalization condition, we obtain the value $1/\sqrt{N!}$ for c_2 . Expression (46.16) can be written as a determinant [see Vol. 1, formula (VIII.3)]:

$$\Psi_a = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{m_1}(\xi_1) & \psi_{m_1}(\xi_2) & \dots & \psi_{m_1}(\xi_N) \\ \psi_{m_2}(\xi_1) & \psi_{m_2}(\xi_2) & \dots & \psi_{m_2}(\xi_N) \\ \dots & \dots & \dots & \dots \\ \psi_{m_N}(\xi_1) & \psi_{m_N}(\xi_2) & \dots & \psi_{m_N}(\xi_N) \end{vmatrix} \quad (46.17)$$

The transposition of two columns of the determinant (46.17) corresponds to the transposition of two particles, and the result, as is known, is that the determinant changes its sign.

The quantum numbers m_i play the role of the row numbers of the determinant (46.17). When the values of two quantum numbers, say

¹ For example, for two particles when $\psi_1 \equiv \psi_2$, expression (46.13) vanishes.

m_i and m_k , coincide, two rows will be identical in the determinant, and the latter becomes identically equal to zero—the state of the system will be absent [this also follows, as we have noted, from expression (46.16)].

We have thus arrived at a very important result: *in a system of identical fermions, there can never be more than one particle in the same single-particle state.* This statement is known as the **Pauli** (or **Pauli exclusion**) principle.

47. Summation of Angular Momenta

Assume that a system being considered can be represented as two subsystems, the interaction between which may be ignored. Let the first subsystem have the angular momentum M_1 characterized by the quantum number J_1 , and the second subsystem—the angular momentum M_2 characterized by the quantum number J_2 .

In the general case, the subsystems consist of several particles so that M_1 and M_2 are the resultant angular momenta of the subsystems which, generally speaking, are formed by the summation of both the orbital and the spin angular momenta of the individual particles. It is customary practice to designate the quantum number of the resultant “mixed” angular momentum by the letter J . If the resultant angular momentum is formed by the summation of orbital momenta, the letter L is used, and of spin momenta, the letter S . Finally, as applied to the sum of the orbital and spin angular momenta of an individual particle, the quantum number is designated by the letter j . We shall consider the most general case, and have therefore designated the quantum numbers by the letter J .

Let us find the possible values of the angular momentum M of a system, which is equal to the sum of the angular momenta of the subsystems: $M = M_1 + M_2$. Since the interaction between the subsystems is negligibly small, the operators \hat{M}_1 and \hat{M}_2 act on variables relating to different subsystems and, consequently, commute: $\hat{M}_1 \hat{M}_2 = \hat{M}_2 \hat{M}_1$. Each of the operators \hat{M}_1 and \hat{M}_2 satisfies the permutation relations

$$\begin{aligned} \hat{M}_x \hat{M}_y - \hat{M}_y \hat{M}_x &= i\hbar \hat{M}_z, & \hat{M}_y \hat{M}_z - \hat{M}_z \hat{M}_y &= i\hbar \hat{M}_x, \\ \hat{M}_z \hat{M}_x - \hat{M}_x \hat{M}_z &= i\hbar \hat{M}_y \end{aligned} \quad (47.1)$$

[see (16.11)]. Let us write the permutation relations for the resultant angular momentum \hat{M} , taking into account that the relations between the operators \hat{M} , \hat{M}_1 , and \hat{M}_2 must be similar to those between

the quantities themselves, i.e. that $\hat{M} = \hat{M}_1 + \hat{M}_2$, $\hat{M}_x = \hat{M}_{x1} + \hat{M}_{x2}$, etc.:

$$\begin{aligned}\hat{M}_x \hat{M}_y - \hat{M}_y \hat{M}_x &= (\hat{M}_{x1} + \hat{M}_{x2})(\hat{M}_{y1} + \hat{M}_{y2}) - (\hat{M}_{y1} + \hat{M}_{y2})(\hat{M}_{x1} + \hat{M}_{x2}) \\ &= (\hat{M}_{x1}\hat{M}_{y1} - \hat{M}_{y1}\hat{M}_{x1}) + (\hat{M}_{x2}\hat{M}_{y2} - \hat{M}_{y2}\hat{M}_{x2}) \\ &\quad + [\hat{M}_{x1}\hat{M}_{y2} - \hat{M}_{y2}\hat{M}_{x1}] + [\hat{M}_{x2}\hat{M}_{y1} - \hat{M}_{y1}\hat{M}_{x2}] \\ &= i\hbar(\hat{M}_{z1} + \hat{M}_{z2}) = i\hbar\hat{M}_z\end{aligned}$$

(the terms in brackets vanish because the operators \hat{M}_1 and \hat{M}_2 commute). Similar results are also obtained for the other two commutators. Hence, the operator \hat{M} also satisfies relations (47.1).

The state of the system (as regards its angular momentum) can be characterized by setting the magnitudes and the projections onto an arbitrary z -axis of the angular momenta \hat{M}_1 and \hat{M}_2 , i.e. the quantum numbers J_1 , J_2 , and m_1 , m_2 . Since with given values of J_1 and J_2 , the quantum numbers m_1 and m_2 can take on, independently of each other, $(2J_1 + 1)$ and $(2J_2 + 1)$ different values, there are $(2J_1 + 1) \times (2J_2 + 1)$ states of the system differing from one another in the value of at least one of the numbers m_1 and m_2 .

Before considering the case of arbitrary values of J_1 and J_2 , let us examine the case when $J_1 = 2$ and $J_2 = 1$. Here, we obtain 15 different states (see Table 47.1). To characterize these states, we can use the numbers J_1 , J_2 , J , and m instead of the quantum numbers J_1 , J_2 , m_1 , and m_2 , where J is the quantum number of the system's angular momentum, and m is the quantum number of its projection onto the z -axis. This substitution signifies a transition from the representation (J_1, J_2, m_1, m_2) to the representation (J_1, J_2, J, m) . The number of different states in the new representation naturally remains the same, i.e. equal to $(2J_1 + 1) \times (2J_2 + 1)$, the states differing from one another in the value of at least one of the numbers J and m .

Since $M_z = M_{z1} + M_{z2}$, the quantum number m equals the sum of the numbers m_1 and m_2 :

$$m = m_1 + m_2 \tag{47.2}$$

The values of m obtained by this formula are given in columns 6, 7, and 8 of Table 47.1. Inspection of this table reveals that, say, the value $m = +2$ is observed in two different states—the second and third, while $m = +1$ is observed in three states—the fourth,

Table 47.1

State number	J_1	J_2	m_1	m_2	m			J
1	2	3	4	5	6	7	8	9
1	2	1	+2	+1	+3			3
2	2	1	+2	0	+2			3
3	2	1	+1	+1		+2		2
4	2	1	+2	-1	+1			3
5	2	1	+1	0		+1		2
6	2	1	0	+1			+1	1
7	2	1	+1	-1		0		3
8	2	1	0	0			0	2
9	2	1	-1	+1			0	1
10	2	1	0	-1	-1			3
11	2	1	-1	0		-1		2
12	2	1	-2	+1			-1	1
13	2	1	-1	-1	-2			3
14	2	1	-2	0		-2		2
15	2	1	-2	-1	-3			3

fifth, and sixth. It is evident that these states differ in the value of the number J .

A glance at Table 47.1 shows that all the possible states of the system can be divided into three groups indicated in columns 6, 7, and 8 of the table. The greatest value of m in these groups is 3, 2, and 1, respectively. At a given J , the quantum number m can take on all the values from $+J$ to $-J$. Consequently, J coincides with the maximum value of the quantum number m possible at a given J . It is thus not difficult to conclude that in the case being considered, the angular momenta M_1 and M_2 of the subsystems can be summated in three ways leading to the values of the resultant angular momentum M characterized by $J = 3, 2$, and 1 . We must note that the values of J change from $J_1 + J_2$ to $J_1 - J_2$ (here $J_1 > J_2$).

Now let us turn to the case of arbitrary values of J_1 and J_2 , assuming only that $J_1 > J_2$. Let us consider the possible values of the number m . The maximum values of the numbers m_1 and m_2 are J_1 and J_2 . Therefore, the maximum value of m is $J_1 + J_2$. The next value is less by unity, i.e. is $J_1 + J_2 - 1$. This value is obtained for two different states, in one of which $m_1 = J_1$, $m_2 = J_2 - 1$, and in the other $m_1 = J_1 - 1$, $m_2 = J_2$. The number m in these states is the same, therefore they differ in the value of J . For one of the states, $m = J_1 + J_2 - 1$ is the value following $m_{\max} = J_1 + J_2$ (in this state $J = J_1 + J_2$), and for the other state $m = J_1 + J_2 - 1$ is the maximum value m_{\max} (in this state $J = J_1 + J_2 - 1$).

The following value of m equal to $J_1 + J_2 - 2$ is obtained in three different states: (1) $m_1 = J_1$, $m_2 = J_2 - 2$; (2) $m_1 = J_1 - 1$, $m_2 = J_2 - 1$; and (3) $m_1 = J_1 - 2$, $m_2 = J_2$. For one of them, this value is the one after $J_1 + J_2$ and $J_1 + J_2 - 1$ (in this state $J = J_1 + J_2$), for the second one it is the value after $m_{\max} = J_1 + J_2 - 1$ (in this state $J = J_1 + J_2 - 1$) and, finally, for the third state the value $m = J_1 + J_2 - 2$ is maximum (in this state $J = J_1 + J_2 - 2$).

Matters will continue in this way until the diminishing of m by unity results in an increase in the number of states by unity. This will occur until the number of different states corresponding to a given m becomes equal to the number of possible values of the number m_2 , i.e. $2J_2 + 1$ (see Table 47.1).

The maximum number of different states that can correspond to the same value of m is $2J_2 + 1$. This will be precisely the number of different values of J , i.e. the number of ways in which we can summate the angular momenta M_1 and M_2 to get the resultant angular momentum M . Since the largest value of J is $J_1 + J_2$, and each following value is less than the preceding one by unity, the smallest value of J will be $(J_1 + J_2) - 2J_2 = J_1 - J_2$.

If $J_1 < J_2$, by the same reasoning, exchanging the places of J_1 and J_2 , we arrive at the conclusion that the number of possible values of J is $2J_1 + 1$, and $J_{\min} = J_2 - J_1$.

We have thus arrived at the following rule for the summation of two angular momenta determined by the quantum numbers J_1 and J_2 : the quantum number J of the resultant momentum can have $2J_2 + 1$ (if $J_2 < J_1$) or $2J_1 + 1$ (if $J_1 < J_2$) different values equal to

$$J_1 + J_2, \quad J_1 + J_2 - 1, \quad J_1 + J_2 - 2, \dots, |J_1 - J_2| \quad (47.3)$$

To each J there correspond $2J + 1$ different states conforming to different values of the quantum number m . Consequently, the total number of states differing in the values of at least one of the numbers J and m is determined by the expression

$$\sum_{J=|J_1-J_2|}^{J_1+J_2} (2J + 1) = (2J_1 + 1)(2J_2 + 1)$$

This number coincides with the previously found number of states considered in the (J_1, J_2, m_1, m_2) -representation.

48. Psi-Function of System of Two Particles Having a Spin of $\frac{1}{2}$

Consider a system consisting of two identical particles with a spin of one-half. The psi-function of such a system depends on the space coordinates, i.e. on r_1 and r_2 , and also on the spin projec-

tions σ_1 and σ_2 of the two particles. Assume that the interaction between the particles does not depend on their spins¹, and also that a magnetic field is absent. Now the Hamiltonian of the system will not contain the spin operators of the particles, owing to which the psi-function breaks up into two factors:

$$\psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) = \psi(\mathbf{r}_1, \mathbf{r}_2) \cdot \varphi(\sigma_1, \sigma_2) \quad (48.1)$$

[see (41.7)].

The function (48.1) must be antisymmetric (we are considering a particle with a spin of $1/2$). Therefore, if the factor $\varphi(\sigma_1, \sigma_2)$ is symmetric (or antisymmetric), the coordinate function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ must be antisymmetric (or symmetric, accordingly).

The resultant spin S of a system can have two values: 0 (when the spins of the particles are antiparallel) and 1 (when the spins of the particles are parallel). In the first case, the quantum number σ of the projection of the summary spin is zero; in the second case, σ takes on three values: 1, 0, -1. The state of a system of two particles with $S = 0$ is called a parastate, and the state with $S = 1$, an orthostate.

Let us find the general form of the functions $\varphi(\sigma_1, \sigma_2)$ for states with different S 's and σ 's. Each of these functions satisfies two equations simultaneously:

$$(\hat{s}_1 + \hat{s}_2)^2 \varphi = \hbar^2 S(S+1) \varphi \quad (48.2)$$

$$(\hat{s}_{z1} + \hat{s}_{z2}) \varphi = \hbar \sigma \varphi \quad (48.3)$$

where \hat{s}_1 and \hat{s}_{z1} are the operators of the first particle, \hat{s}^2 and \hat{s}_{z2} are the operators of the second particle, $S = 0$ or 1, and accordingly $\sigma = 0$ or 1, 0, -1.

The common eigenfunctions of the operators \hat{s}_k^2 and \hat{s}_{zk} of a separately taken k -th particle are determined by the expressions

$$\varphi_{+1/2}(k) = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \varphi_{-1/2}(k) = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (48.4)$$

[see (43.11)]. In the following for brevity's sake, we shall write these functions in the form $\varphi_+(k)$ and $\varphi_-(k)$. Using formulas (42.10), (42.29), and (42.30), let us find the result of the action of the operators \hat{s}_{xk} , \hat{s}_{yk} , and \hat{s}_{zk} on the functions (48.4):

$$\hat{s}_{xk} \varphi_+(k) = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \varphi_-(k) \quad (48.5)$$

$$\hat{s}_{yk} \varphi_+(k) = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 \\ i \end{pmatrix} = i \frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = i \frac{\hbar}{2} \varphi_-(k) \quad (48.6)$$

¹ This holds in a non-relativistic approximation.

$$\hat{s}_{z\hbar}\varphi_+(k) = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \varphi_+(k) \quad (48.7)$$

$$\hat{s}_{x\hbar}\varphi_-(k) = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \varphi_+(k) \quad (48.8)$$

$$\hat{s}_{y\hbar}\varphi_-(k) = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} -i \\ 0 \end{pmatrix} = -i \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = -i \frac{\hbar}{2} \varphi_+(k) \quad (48.9)$$

$$\hat{s}_{z\hbar}\varphi_-(k) = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 \\ -1 \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2} \varphi_-(k) \quad (48.10)$$

Consider four functions obtained from the functions (48.4):

$$\varphi_1(1, 2) = \varphi_+(1) \varphi_+(2) \quad (48.11)$$

$$\varphi_2(1, 2) = \varphi_-(1) \varphi_-(2) \quad (48.12)$$

$$\varphi_3(1, 2) = \frac{1}{\sqrt{2}} [\varphi_+(1) \varphi_-(2) + \varphi_-(1) \varphi_+(2)] \quad (48.13)$$

$$\varphi_4(1, 2) = \frac{1}{\sqrt{2}} [\varphi_+(1) \varphi_-(2) - \varphi_-(1) \varphi_+(2)] \quad (48.14)$$

The first three of these functions are evidently symmetric, the last one is antisymmetric. The functions $\varphi_+(1)$ and $\varphi_+(2)$ are normalized to unity, therefore the function (48.11) is normalized too; the same can be said about the function (48.12). The functions (48.13) and (48.14) are the superposition of the functions (48.11) and (48.12). The normalization condition in this case has the form $\sum |c_m|^2 = 1$, where c_m are the expansion coefficients [see (7.5)]. It follows from what has been said above that all four functions are normalized [compare with (46.12) and (46.13)].

Let us act on the function (48.11) with the operator $(\hat{s}_{z1} + \hat{s}_{z2})$. We shall take into account that the operator \hat{s}_{z1} acts only on $\varphi_+(1)$, and \hat{s}_{z2} only on $\varphi_+(2)$:

$$\begin{aligned} (\hat{s}_{z1} + \hat{s}_{z2}) \varphi_+(1) \varphi_+(2) &= \hat{s}_{z1} \varphi_+(1) \varphi_+(2) + \hat{s}_{z2} \varphi_+(1) \varphi_+(2) \\ &= \varphi_+(2) \hat{s}_{z1} \varphi_+(1) + \varphi_+(1) \hat{s}_{z2} \varphi_+(2) \end{aligned}$$

With a view to relation (48.7), we obtain

$$\begin{aligned} (\hat{s}_{z1} + \hat{s}_{z2}) \varphi_+(1) \varphi_+(2) &= \varphi_+(2) \frac{\hbar}{2} \varphi_+(1) + \varphi_+(1) \frac{\hbar}{2} \varphi_+(2) \\ &= \hbar \varphi_+(1) \varphi_+(2) \end{aligned}$$

A comparison with Eq. (48.3) shows that (48.11) is an eigenfunction of the operator $(\hat{s}_{z1} + \hat{s}_{z2})$ corresponding to the eigenvalue $\sigma = 1$.

We can show in a similar way that the functions (48.12)-(48.14) are also eigenfunctions of the operator $(\hat{s}_{z_1} + \hat{s}_{z_2})$; here (48.12) corresponds to $\sigma = -1$, while (48.13) and (48.14) correspond to $\sigma = 0$.

We shall show that the functions (48.11)-(48.14) are simultaneously eigenfunctions of the operator $(\hat{s}_1 + \hat{s}_2)^2$ [see (48.2)]. For this purpose, we express this operator in terms of the operators of the projections of the spins of individual particles:

$$\begin{aligned} (\hat{s}_1 + \hat{s}_2)^2 &= (\hat{s}_{x_1} + \hat{s}_{x_2})^2 + (\hat{s}_{y_1} + \hat{s}_{y_2})^2 + (\hat{s}_{z_1} + \hat{s}_{z_2})^2 \\ &= (\hat{s}_{x_1}^2 + 2\hat{s}_{x_1}\hat{s}_{x_2} + \hat{s}_{x_2}^2) + (\hat{s}_{y_1}^2 + 2\hat{s}_{y_1}\hat{s}_{y_2} + \hat{s}_{y_2}^2) \\ &\quad + (\hat{s}_{z_1}^2 + 2\hat{s}_{z_1}\hat{s}_{z_2} + \hat{s}_{z_2}^2) \end{aligned} \quad (48.15)$$

We remind our reader that each operator of the form of \hat{s}_{x_k} acts on the psi-functions of only its own, k -th particle; therefore, for example, the operators \hat{s}_{x_1} and \hat{s}_{x_2} commute.

To facilitate further calculations, we shall give the following relations obtained from formulas (48.5)-(48.10):

$$\left. \begin{array}{l} \hat{s}_{xk}^2 \varphi_+(k) = (\hbar^2/4) \varphi_+(k) \\ \hat{s}_{yk}^2 \varphi_+(k) = (\hbar^2/4) \varphi_+(k) \\ \hat{s}_{zk}^2 \varphi_+(k) = (\hbar^2/4) \varphi_+(k) \\ \hat{s}_{xk}^2 \varphi_-(k) = (\hbar^2/4) \varphi_-(k) \\ \hat{s}_{yk}^2 \varphi_-(k) = (\hbar^2/4) \varphi_-(k) \\ \hat{s}_{zk}^2 \varphi_-(k) = (\hbar^2/4) \varphi_-(k) \end{array} \right\} \quad (48.16)$$

Let us act with the operator (48.15) on the function (48.11):

$$\begin{aligned} &(\hat{s}_1 + \hat{s}_2)^2 \varphi_+(1) \varphi_+(2) \\ &= [\varphi_+(2) \hat{s}_{x_1}^2 \varphi_+(1) + 2\hat{s}_{x_1} \varphi_+(1) \hat{s}_{x_2} \varphi_+(2) + \varphi_+(1) \hat{s}_{x_2}^2 \varphi_+(2)] \\ &\quad + [\varphi_+(2) \hat{s}_{y_1}^2 \varphi_+(1) + 2\hat{s}_{y_1} \varphi_+(1) \hat{s}_{y_2} \varphi_+(2) + \varphi_+(1) \hat{s}_{y_2}^2 \varphi_+(2)] \\ &\quad + [\varphi_+(2) \hat{s}_{z_1}^2 \varphi_+(1) + 2\hat{s}_{z_1} \varphi_+(1) \hat{s}_{z_2} \varphi_+(2) + \varphi_+(1) \hat{s}_{z_2}^2 \varphi_+(2)] \\ &= (\hbar^2/4) \{[\varphi_+(1) \varphi_+(2) + 2\varphi_-(1) \varphi_-(2) + \varphi_+(1) \varphi_+(2)] \\ &\quad + [\varphi_+(1) \varphi_+(2) - 2\varphi_-(1) \varphi_-(2) + \varphi_+(1) \varphi_+(2)] \\ &\quad + [\varphi_+(1) \varphi_+(2) + 2\varphi_+(1) \varphi_+(2) + \varphi_+(1) \varphi_+(2)]\} \\ &= (\hbar^2/4) 8\varphi_+(1) \varphi_+(2) = 2\hbar^2 \varphi_+(1) \varphi_+(2) \end{aligned}$$

[we have used relations (48.5)-(48.7) and (48.16)]. A comparison with Eq. (48.2) shows that (48.11) is the eigenfunction of the operator $(\hat{s}_1 + \hat{s}_2)^2$ corresponding to $S = 1$.

Similar calculations show that the functions (48.12)-(48.14) are also eigenfunctions of the operator $(\hat{s}_1 + \hat{s}_2)^2$; here (48.12) and (48.13) correspond to $S = 1$, and (48.14) corresponds to $S = 0$.

In summarizing, we can say that the spin function of a system of two particles with a spin of $1/2$ is symmetric when $S = 1$, and depending on the value of σ (1, 0, or -1) it has the form of (48.11), (48.13), or (48.12). When $S = 0$, the spin function is antisymmetric and has the form of (48.14). To facilitate subsequent references, we shall write out these functions once more:

$$\sigma = 1 \quad \varphi_{1,1} = \varphi_{+1/2}(1) \varphi_{-1/2}(2) \quad (48.17)$$

$$S = 1, \quad \left\{ \begin{array}{l} \sigma = 0 \quad \varphi_{1,0} = \frac{1}{\sqrt{2}} [\varphi_{+1/2}(1) \varphi_{-1/2}(2) + \varphi_{-1/2}(1) \varphi_{+1/2}(2)] \\ \sigma = -1 \quad \varphi_{1,-1} = \varphi_{-1/2}(1) \varphi_{-1/2}(2) \end{array} \right. \quad (48.18)$$

$$\sigma = -1 \quad \varphi_{1,-1} = \varphi_{-1/2}(1) \varphi_{-1/2}(2) \quad (48.19)$$

$$S = 0, \quad \sigma = 0 \quad \varphi_{0,0} = \frac{1}{\sqrt{2}} [\varphi_{+1/2}(1) \varphi_{-1/2}(2) - \varphi_{-1/2}(1) \varphi_{+1/2}(2)] \quad (48.20)$$

49. Exchange Interaction

The indistinguishability of identical particles underlies the existence of a particular, specifically quantum interaction between particles known as **exchange interaction**.

Consider a system of two particles with a spin of $1/2$ between which there is interaction not associated with the interaction between the spins of the particles. Assume that this interaction is weak enough to be treated as the perturbation of a system of non-interacting particles. Let us characterize the perturbation by the operator $\hat{V}(r_{12})$, where r_{12} is the distance between the particles. We must note that the operator $\hat{V}(r_{12})$ does not act on the spin variables of the particles.

The mean energy of interaction in a first approximation can be calculated by a formula similar to the formula

$$\Delta E_n^{(1)} = V_{nn} = \langle \psi_n^{(0)} | \hat{V} \psi_n^{(0)} \rangle = \int (\psi_n^{(0)})^* \hat{V} \psi_n^{(0)} dV$$

[see (29.22)]. This formula has been written for one particle without a spin. In our case, there are two particles with a spin. The formula must therefore be taken in the form

$$\Delta E^{(1)} = \sum \int (\psi^{(0)})^* \hat{V} \psi^{(0)} dV_1 dV_2 \quad (49.1)$$

where summation is performed over all the values of the spin variables (we have dropped the subscript n as superfluous).

The function $\psi^{(0)}$ describes the unperturbed state, i.e. the state of the non-interacting particles. The form of this function depends on the summary spin of the system. It was revealed in Sec. 48 that when $S = 0$, the spin function is antisymmetric, and accordingly the position function must be symmetric, i.e. have the form

$$\psi(1, 2) = \frac{1}{\sqrt{2}} [\psi_{m_1}(1) \psi_{m_2}(2) + \psi_{m_2}(1) \psi_{m_1}(2)] \quad (49.2)$$

where ψ_{m_1} and ψ_{m_2} are two arbitrary psi-functions of single-particle states [see (46.12)]. The numbers 1 and 2 in parentheses stand for the set of space coordinates of the first and second particles, respectively. At $S = 1$, the spin function is symmetric so that

$$\psi(1, 2) = \frac{1}{\sqrt{2}} [\psi_{m_1}(1) \psi_{m_2}(2) - \psi_{m_2}(1) \psi_{m_1}(2)] \quad (49.3)$$

[see (46.13)].

At $S = 0$, the spin function equals 1, at $S = 1$

$$\varphi(\sigma) = \begin{pmatrix} a_1 \\ a_0 \\ a_{-1} \end{pmatrix}$$

where σ is the quantum number of the projection of the summary spin ($\sum_i |a_i|^2 = 1$).

Let us introduce into (49.1) the psi-function for the case when $S = 1$. Since the operator \hat{V} does not act on the spin function, the latter can be removed from the sign of the operator. As a result, we obtain [see the text preceding formula (9.24)]

$$\begin{aligned} \Delta E^{(1)} &= (a_1^* a_0^* a_{-1}^*) \begin{pmatrix} a_1 \\ a_0 \\ a_{-1} \end{pmatrix} \int [\psi(1, 2)]^* \hat{V} \psi(1, 2) dV_1 dV_2 \\ &= \sum_i |a_i|^2 \int \psi^* \hat{V} \psi dV_1 dV_2 = \int \psi^* \hat{V} \psi dV_1 dV_2 \end{aligned}$$

Thus, the summation sign in formula (49.1) may be omitted, and $\psi^{(0)}$ understood to be the coordinate part of the psi-function. Taking

this into account, we shall write expression (49.1) as follows:

$$\begin{aligned}\Delta E^{(1)} &= \frac{1}{2} \int [\psi_{m_1}(1) \psi_{m_2}(2) \pm \psi_{m_1}(2) \psi_{m_2}(1)]^* \hat{V} [\psi_{m_1}(1) \psi_{m_2}(2) \\ &\pm \psi_{m_1}(2) \psi_{m_2}(1)] dV_1 dV_2 = \frac{1}{2} \left\{ \int \psi_{m_1}^*(1) \psi_{m_2}^*(2) \hat{V} \psi_{m_1}(1) \psi_{m_2}(2) dV_1 dV_2 \right. \\ &+ \int \psi_{m_1}^*(2) \psi_{m_2}^*(1) \hat{V} \psi_{m_1}(2) \psi_{m_2}(1) dV_1 dV_2 \\ &\pm \int \psi_{m_1}^*(1) \psi_{m_2}^*(2) \hat{V} \psi_{m_1}(2) \psi_{m_2}(1) dV_1 dV_2 \\ &\left. \pm \int \psi_{m_1}^*(2) \psi_{m_2}^*(1) \hat{V} \psi_{m_1}(1) \psi_{m_2}(2) dV_1 dV_2 \right\}\end{aligned}$$

The plus sign corresponds to the case when $S = 0$, the minus sign, to $S = 1$.

It is not difficult to comprehend that the first two integrals in the braces are identical. Indeed, they differ only in that the particle designated in the first integral by the number 1 is designated in the second integral by the number 2, and vice versa. Owing to the indistinguishability of the particles, such a change of the symbols cannot affect the value of the integral. The same relates to the third and fourth integrals in the braces. Therefore, combining the integrals in pairs, we can write:

$$\begin{aligned}\Delta E^{(1)} &= \int \psi_{m_1}^*(1) \psi_{m_2}^*(2) \hat{V} \psi_{m_1}(1) \psi_{m_2}(2) dV_1 dV_2 \\ &\pm \int \psi_{m_1}^*(1) \psi_{m_2}^*(2) \hat{V} \psi_{m_1}(2) \psi_{m_2}(1) dV_1 dV_2 = Q \pm A \quad (49.4)\end{aligned}$$

The result obtained shows that the first-order correction to the energy of two particles with a spin of $1/2$ consists of two parts. The first part, Q , is in no way related to the presence of spin in the particles and has a classical analogue. The sign of the second part, A , depends on the mutual orientation of the particles' spins (on the total spin of the system), although the interaction between the spins was not taken into account by the operator \hat{V} . This second part A is called the **exchange energy**. The term is due to the fact that in the functions in the integrand in front of the operator \hat{V} and in the functions behind it the particles exchange places. It thus follows that each particle, as it were, is simultaneously in both states. We must note that the exchange energy is also obtained when the operator $\hat{V}(r_{12})$ takes into account the interaction between the spin magnetic moments, i.e. acts on the spin parts of the psi-function.

We must stress that the exchange "interaction" is not due to any "force". It is a consequence of the uncertainty relation and the Pauli principle. We shall explain this by the following consider-

ations. Assume that there is in general no interaction between two particles with a spin of $1/2$. One of the particles has the coordinates x, y, z with the indeterminacies $\Delta x, \Delta y, \Delta z$ of the order of a , and the momenta p_x, p_y, p_z with the indeterminacies $\Delta p_x, \Delta p_y, \Delta p_z$ of the order of Δp . According to the uncertainty relation

$$\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z \sim a^3 (\Delta p)^3 \sim (2\pi\hbar)^3$$

In accordance with formula (39.11), a phase volume of such a magnitude contains only one quantum state (without taking into account the spin of the particle). The Pauli principle allows two particles with antiparallel spins to be in such a state and does not allow two particles with parallel spins to be in it. Hence, two particles with a given momentum p can approach each other to the distance a when their spins are antiparallel, and cannot approach each other to such a distance if their spins are in the same direction. There appears, as it were, a "repelling force" that keeps the particles from approaching to the distance a .

When the interaction between the particles is Coulombian, we have $\hat{V}(r_{12}) = e^2/r_{12}$. Accordingly [see (49.4)]

$$Q = \int |\psi_{m_1}(1) \psi_{m_2}(2)|^2 \frac{e^2}{r_{12}} dV_1 dV_2 \quad (49.5)$$

$$A = \int \psi_{m_1}^*(1) \psi_{m_2}^*(2) \frac{e^2}{r_{12}} \psi_{m_1}(2) \psi_{m_2}(1) dV_1 dV_2 \quad (49.6)$$

The first integral, known as a **Coulomb** integral, has a simple physical meaning that becomes especially clear if we write it in the form

$$Q = \int \frac{(|\psi_{m_1}(1)|^2 e) dV_1 \cdot (|\psi_{m_2}(2)|^2 e) dV_2}{r_{12}} = \int \frac{\rho_1 dV_1 \cdot \rho_2 dV_2}{r_{12}}$$

where ρ_1 and ρ_2 are the mean densities of the charge set up by the first and second charged particles, respectively. It can thus be seen that the Coulomb integral determines the "classical" part of the energy of electrostatic interaction of the particles.

The integral (49.6) is called an **exchange** one. As already noted, it has no classical analogue. When the operator \hat{V} takes into account only the electrostatic interaction between particles, the exchange energy is the part of the Coulomb energy of particle interaction that owes its appearance to the correlation of the motion of the two particles due to the symmetry of the psi-functions.

In concluding, we shall indicate that in all systems for which the relevant calculations were performed, Q and A were found to be positive. This shows that the energy of parastates ($S = 0$, see Sec. 48) is greater than the energy of orthostates ($S = 1$).

We must note that the results obtained in this section relate to the case when the single-particle states ψ_{m_1} and ψ_{m_2} are not identical.

If these states coincide, however ($\psi_m \equiv \psi_n \equiv \psi$), we must take $\psi(1, 2) = \psi(1)\psi(2)$ instead of the function (49.2), while the function (49.3) is identically equal to zero (see the footnote on page 221). In this case

$$\Delta E^{(1)} = \int \psi^*(1)\psi^*(2)\hat{V}\psi(1)\psi(2)dV_1dV_2 \quad (49.7)$$

which coincides with Q in formula (49.4). The exchange integral A is absent in this case.

50. Second Quantization

Second quantization is the name given to a method of calculations employed in the quantum mechanics of systems consisting of a large number of arbitrarily interacting identical particles. To understand the essence of this method, let us first consider a method that can be used to describe such a system in a conventional coordinate representation.

Let us take an auxiliary system consisting of N non-interacting particles in an external potential field U_0 . The eigenfunctions of the stationary states of such a system can be used to expand the psi-function of a system of N interacting particles in an external arbitrary field U .

Let us designate by

$$\psi_1(\xi), \psi_2(\xi), \dots, \psi_k(\xi), \dots \quad (50.1)$$

the psi-functions of the stationary states of one particle in the field U_0 (one-particle functions). The letter ξ stands for the set of coordinates and spin projections of a particle. We shall assume that the system (50.1) is orthonormalized and complete.

We shall use the one-particle functions (50.1) to construct all possible functions describing the stationary states of a system of N non-interacting particles in the field U_0 . Let us designate these functions by

$$\psi_l^{(0)}(\xi_1, \xi_2, \dots, \xi_N) \quad (l = 1, 2, \dots) \quad (50.2)$$

where ξ_i is the set of coordinates and spin projections of the i -th particle. We shall also consider the system (50.2) to be orthonormalized and complete. The way of constructing the functions (50.2) from the one-particle functions depends on what particles we have to do with: for bosons this construction is performed in one way, and for fermions in another.

Now consider a system of N arbitrarily interacting particles in an external field U that does not coincide with U_0 . The psi-function of such a system

$$\psi(\xi_1, \xi_2, \dots, \xi_N, t) \quad (50.3)$$

can be expanded in the functions (50.2), i.e. written as

$$\Psi = \sum_l c_l(t) \psi_l^{(0)} \quad (50.4)$$

The functions (50.3) and (50.4) are the psi-functions of a system of particles in a coordinate representation.

Unlike the above scheme, the method of second quantization uses a different approach. Each of the particles of the auxiliary system (see above) is in one of the states (50.1). The numbers

$$n_1, n_2, \dots, n_k, \dots \quad (50.5)$$

indicating what number of particles are in the corresponding one-particle states at a given instant are known as **occupation numbers**. It is obvious that the sum of the occupation numbers equals the total number of particles:

$$\sum_k n_k = N \quad (50.6)$$

It is not difficult to see that the assignment of the set (50.5) of occupation numbers completely determines the state of the auxiliary system, i.e. it is equivalent to setting the function (50.2). We can thus go over from a coordinate representation to a representation of the occupation numbers, and instead of the functions (50.2) consider the functions

$$\psi^{(0)}(n_1, n_2, \dots, n_k, \dots) \quad (50.7)$$

We have not used the index l on $\psi^{(0)}$ because the set of numbers $n_1, n_2, \dots, n_k, \dots$ itself determines uniquely the stationary state of the system, i.e. plays the role of a state index.

Substitution of the functions (50.7) instead of (50.2) into (50.4) leads to the following expression:

$$\Psi = \sum_{[n_1, n_2, \dots]} c(n_1, n_2, \dots, t) \psi^{(0)}(n_1, n_2, \dots) \quad (50.8)$$

Summation is performed over all the possible sets of the numbers n_1, n_2, \dots , compatible with the requirement (50.6) and with the properties of the particles.

In accordance with the main principles of quantum mechanics, the quantity

$$|c(n_1, n_2, \dots, t)|^2 \quad (50.9)$$

gives the probability of the fact that at the instant t there will be n_1 particles in the first state, n_2 in the second, etc.

The transition to the occupation number representation makes it necessary to introduce operators that can act on these numbers. It is customary practice to designate these operators by the letter a ;

by \hat{a}_k we designate an operator which when acting on the psi-function diminishes the number n_k by one, and by \hat{a}_k^\dagger an operator that increases n_k by one. Accordingly, \hat{a}_k is said to be an **annihilation (or destruction) operator** (for particles in the k -th state), and \hat{a}_k^\dagger is said to be a **creation operator** (compare with Sec. 27). Since the operators \hat{a}_k and \hat{a}_k^\dagger act only on a variable n_k , their matrix elements must be written as follows:

$$\langle n_1, n_2, \dots, n_k - 1, \dots | \hat{a}_k | n_1, n_2, \dots, n_k, \dots \rangle \quad (50.10)$$

$$\langle n_1, n_2, \dots, n_k + 1, \dots | \hat{a}_k^\dagger | n_1, n_2, \dots, n_k, \dots \rangle \quad (50.11)$$

We can express the operator of any physical quantity in terms of the operators \hat{a}_k and \hat{a}_k^\dagger and thus go over to an occupation number representation.

We must note that the method of second quantization may also be applied to systems with a varying total number N of particles, for instance to an assembly of photons. In this case, the terms "annihilation operator" and "creation operator" acquire a literal meaning.

In the present section, we have treated the general ideas of second quantization. In the following two sections, we shall develop them as applied to bosons and fermions.

51. Second Quantization Applied to Bosons

By (46.15), for bosons, the function (50.2) acquires the form

$$\psi_{n_1, n_2, \dots, n_s} = A \sum \psi_{m_1}(\xi_1) \psi_{m_2}(\xi_2) \dots \psi_{m_N}(\xi_N) \quad (51.1)$$

where

$$A = \left(\frac{n_1! n_2! \dots n_s!}{N!} \right)^{1/2} \quad (51.2)$$

m_k is the number of the state in which the particle numbered k is, and n_k is the number of particles in the state numbered m_k . The sum is taken over all the non-coinciding permutations of the numbers m_1, m_2, \dots, m_N . Consequently, the number of addends is $N!/(n_1! n_2! \dots n_s!)$. The value of s is generally less than N and is determined by the relation

$$n_1 + n_2 + \dots + n_s = N \quad (51.3)$$

Of the N functions ψ_{m_i} that are factors in (51.1), only s are not identical.

Let us introduce an operator $\hat{Q}_k^{(1)}$ acting only on functions of the coordinates of the k -th particle. From N identical (i.e. relating

to the same physical quantity) operators $\hat{Q}_k^{(1)}$, it is possible to construct the operator

$$\hat{Q}_1 = \sum_{k=1}^N \hat{Q}_k^{(1)} \quad (51.4)$$

that is symmetric with respect to all the particles. Similarly, from the operators $\hat{Q}_{kl}^{(2)}$ acting on the coordinates ξ_k and ξ_l of two particles, it is possible to construct the operator

$$\hat{Q}_2 = \sum_{k, l=1}^N \hat{Q}_{kl}^{(2)} \quad (51.5)$$

etc.

Let us establish the form of the matrix elements of the operator (51.4) evaluated with the aid of the functions (51.1). Since

$$\langle \psi_\alpha | \hat{Q}_1 \psi_\beta \rangle = \left\langle \psi_\alpha \left| \sum_{k=1}^N \hat{Q}_k^{(1)} \psi_\beta \right. \right\rangle = \sum_{k=1}^N \langle \psi_\alpha | \hat{Q}_k^{(1)} \psi_\beta \rangle \quad (51.6)$$

we shall first find the matrix element of the operator $\hat{Q}_k^{(1)}$. This element can be written as follows in Dirac notation:

$$\begin{aligned} & \langle n'_1, n'_2, \dots | \hat{Q}_k^{(1)} | n_1, n_2, \dots \rangle \\ &= A' A \left\langle \sum' \psi_{m'_1}(\xi_1) \dots \psi_{m'_k}(\xi_k) \dots \psi_{m'_N}(\xi_N) \left| \sum \psi_{m_1}(\xi_1) \dots \right. \right. \\ & \quad \times [\hat{Q}_k^{(1)} \psi_{m_k}(\xi_k)] \dots \psi_{m_N}(\xi_N) \rangle \quad (51.7) \end{aligned}$$

where

$$A' = \left(\frac{n'_1! n'_2! \dots! n'_p!}{N!} \right)^{1/2} \quad (51.8)$$

$(n'_1 + n'_2 + \dots + n'_p = N)$, the coefficient A is determined by formula (51.2). The primed sum (\sum') is taken over all the non-coinciding permutations of the numbers m'_1, m'_2, \dots, m'_N , and the unprimed sum (\sum) over all the non-coinciding permutations of the numbers m_1, m_2, \dots, m_N . Both permutations are performed independently of each other.

Before continuing our treatment, let us determine the properties of a scalar product of the products of functions. Assume that $\varphi(x_1, x_2) = \varphi_1(x_1) \varphi_2(x_2)$, and $\psi(x_1, x_2) = \psi_1(x_1) \psi_2(x_2)$. Hence, by (7.7), we have

$$\begin{aligned} & \langle \varphi_1(x_1) \varphi_2(x_2) | \psi_1(x_1) \psi_2(x_2) \rangle = \int \varphi_1^*(x_1) \varphi_2^*(x_2) \psi_1(x_1) \psi_2(x_2) dx_1 dx_2 \\ &= \int \varphi_1^*(x_1) \psi_1(x_1) dx_1 \int \varphi_2^*(x_2) \psi_2(x_2) dx_2 \\ &= \langle \varphi_1(x_1) | \psi_1(x_1) \rangle \langle \varphi_2(x_2) | \psi_2(x_2) \rangle \quad (51.9) \end{aligned}$$

The same result is evidently obtained with any number of factors.

With account taken of the property (51.9), expression (51.7) can be given the form

$$\begin{aligned} \langle n'_1, n'_2, \dots, n'_p | \hat{Q}_k^{(1)} | n_1, n_2, \dots, n_s \rangle &= A' A \sum' \sum \langle \psi_{m_1}'(\xi_1) | \psi_{m_1}(\xi_1) \rangle \dots \\ &\times \langle \psi_{m_k'}(\xi_k) | \hat{Q}_k^{(1)} \psi_{m_k}(\xi_k) \rangle \dots \langle \psi_{m_N'}(\xi_N) | \psi_{m_N}(\xi_N) \rangle \\ &= A' A \sum' \sum \delta_{m_1', m_1} \dots Q_{m_k', m_k}^{(1)} \dots \delta_{m_N', m_N} \quad (51.10) \end{aligned}$$

where

$$Q_{m_k', m_k}^{(1)} = \langle \psi_{m_k'}(\xi_k) | \hat{Q}_k^{(1)} \psi_{m_k}(\xi_k) \rangle \quad (51.11)$$

We have taken advantage of the orthonormalized nature of the functions $\psi_m(\xi)$. In calculating scalar products, integration is performed over space coordinates, and summation, over a spin variable.

Expression (51.11) is a number whose value is determined not by the number of the operator and of the variable ξ , but by the values of the indices m'_k and m_k . Indeed, the structure of all the $\hat{Q}_k^{(1)}$'s, by assumption, is the same, so that, for example, the functions $\hat{Q}_1^{(1)} \psi_{m_k}(\xi_1)$ and $\hat{Q}_2^{(1)} \psi_{m_k}(\xi_2)$ differ only in the designation of the independent variable. The scalar product of the functions is the integral

$$\langle \psi_{m_k'}(\xi_k) | \hat{Q}_k^{(1)} \psi_{m_k}(\xi_k) \rangle = \int \psi_{m_k'}^*(\xi_k) \hat{Q}_k^{(1)} \psi_{m_k}(\xi_k) d\xi_k$$

whose value does not depend on the designation of the integration variable. Consequently, no matter what the number of the operator and the coordinate is, the value of the number (51.11) is determined only by the values of the state indices m'_k and m_k [generally speaking, $\psi_1(\xi)$, $\psi_2(\xi)$, etc. are different functions]. Formula (51.11) can thus be written as

$$Q_{m_k', m_k}^{(1)} = \langle \psi_{m_k'}(\xi) | \hat{Q}^{(1)} \psi_{m_k}(\xi) \rangle \quad (51.12)$$

If we also introduce the notation $m'_k = i$ and $m_k = j$, we arrive at the formula

$$Q_{ij}^{(1)} = \langle \psi_i(\xi) | \hat{Q}^{(1)} \psi_j(\xi) \rangle \quad (51.13)$$

We must stress that k is the number of a particle and of an operator, whereas i and j are numbers of states.

It follows from expression (51.10) that only the addends of the double sum in which $m'_1 = m_1, \dots, m'_{k-1} = m_{k-1}, m'_{k+1} = m_{k+1}, \dots, m'_N = m_N$ will be non-zero. As regards the k -th factor, it may be non-zero both when $m'_k = m_k$ and when $m'_k \neq m_k$. What has been said above signifies that the matrix element (51.10) will be non-zero only when the 1st, 2nd, ..., ($k - 1$)-th, ($k + 1$)-th, ..., N -th particles do not experience a transition to other states, whereas the k -th particle either remains in its initial state ($m'_k = m_k$) or passes from the state m_k to the state $m'_k = m_l \neq m_k$. In the first case, all the numbers $n_1, n_2, \dots, n_k, \dots, n_l, \dots, n_s$ remain unchanged, and in the second case, the number n_k diminishes by one, the number n_l grows by one, and the remaining numbers remain unchanged.

Hence, only matrix elements for transitions without a change in the numbers n_1, n_2, \dots (diagonal elements) and for transitions in which one of these numbers diminishes and the other grows by one (here only one particle changes its state) can be non-zero.

In accordance with the above, for diagonal elements only those addends of the double sum (51.10) will be non-zero in which all the primed indices coincide with the unprimed ones. If we retain only such addends, the double sum transforms into a single one, and we arrive at an expression for a diagonal matrix element (D.M.E.)

$$\begin{aligned} \text{D.M.E.} &= \langle n_1, n_2, \dots, n_s | \hat{Q}_k^{(1)} | n_1, n_2, \dots, n_s \rangle \\ &= A^2 \sum \delta_{m_1, m_1} \dots Q_{m_k, m_k}^{(1)} \dots \delta_{m_N, m_N} \quad (51.14) \end{aligned}$$

(it is not difficult to see that in this case $A' = A$). The sum is evaluated over all the non-coinciding permutations of the pairs of indices.

We must note that when performing the permutations, each particle figuring in expression (51.1) remains in its place, and only the indices m_i exchange places. The same relates to expression (51.14). The operator $\hat{Q}_k^{(1)}$ is "bound" to the particle numbered k , therefore in all the addends, the factor $Q_{m_k, m_k}^{(1)}$ is in the k -th place. Among the addends of the function (51.1) that are to the right of $\hat{Q}_k^{(1)}$ in (51.10), there are addends including the factor $\psi_{m_k}(\xi_k)$ with all possible values of the subscript m_k . Accordingly, the sum (51.14) also contains addends with all possible values of the indices m_k, m_k . This signifies that the indices which are on $Q^{(1)}$ in (51.14) participate in the permutations.

Assume that among the N values of the indices m_1, m_2, \dots, m_N there are n_1 of them that equal 1, there are n_2 that equal 2, and so

on. Hence, in a more expanded form, expression (51.14) can be written as follows:

$$\begin{aligned} \text{D.M.E.} = & \left\{ A^2 \sum \delta_{m_1, m_1} \dots Q_{11}^{(1)} \dots \delta_{m_N, m_N} \right. \\ & + A^2 \sum \delta_{m_1, m_1} \dots Q_{22}^{(1)} \dots \delta_{m_N, m_N} + \\ & \left. \dots + A^2 \sum \delta_{m_1, m_1} \dots Q_{ss}^{(1)} \dots \delta_{m_N, m_N} \right\} \quad (51.15) \end{aligned}$$

[recall that the value of s is determined by relation (51.3)]. In each of the sums, the factor $Q_{11}^{(1)}$, $Q_{22}^{(1)}$, etc. is in the k -th place.

Let us find the number of addends in each of the s sums. We shall begin with the first sum in which all the addends equal $Q_{11}^{(1)}$. One of the n_1 pairs of indices 11 is "bound" to $Q_{11}^{(1)}$ (it can exchange places only with another pair of the same kind at one of the δ_{11} 's, but such an exchange does not result in a new permutation). The remaining $n_1 - 1$ pairs of such indices participate in the permutations (say, one of the factors δ_{11} exchanges places with δ_{22} or δ_{33} , etc.). Altogether, $N - 1$ pairs of indices participate in the permutations. We thus conclude that the number of addends in the first sum is $(N - 1)! / [(n_1 - 1)! n_2! \dots n_s!]$. All the addends are identical and equal $Q_{11}^{(1)}$. Hence, the first term in (51.15) with account taken of the value of A^2 is

$$\frac{n_1! n_2! \dots n_s!}{N!} \frac{(N-1)!}{(n_1-1)! n_2! \dots n_s!} Q_{11}^{(1)} = \frac{n_1}{N} Q_{11}^{(1)}$$

Similar reasoning leads to the conclusion that the second term is

$$\frac{n_1! n_2! \dots n_s!}{N!} \frac{(N-1)!}{n_1! (n_2-1)! \dots n_s!} Q_{22}^{(1)} = \frac{n_2}{N} Q_{22}^{(1)}$$

etc.

Therefore, the diagonal matrix element determined by expression (51.14) is

$$\langle n_1, n_2, \dots, n_s | \hat{Q}_k^{(1)} | n_1, n_2, \dots, n_s \rangle = \frac{1}{N} \sum_{i=1}^s n_i Q_{ii}^{(1)} \quad (51.16)$$

This element does not depend on the index k . Consequently, all N addends in (51.16) are identical, so that to obtain a diagonal matrix element of the operator (51.4), it is necessary to simply multiply (51.16) by N :

$$\langle n_1, n_2, \dots, n_s | \hat{Q}_1 | n_1, n_2, \dots, n_s \rangle = \sum_{i=1}^s n_i Q_{ii}^{(1)} \quad (51.17)$$

Now let us pass over to evaluating the matrix elements corresponding to the transitions of one particle. In such a transition, n_k

diminishes by one, and n_l grows by one. Therefore, a matrix element (M.E.) has the form [see (51.10)]

$$\text{M.E.} = \langle n_1, \dots, n_k - 1, \dots, n_l + 1, \dots, n_s | \hat{Q}_k^{(1)} | n_1, \dots, n_k, \dots, n_l, \dots, n_s \rangle = A' A \sum' \sum \delta_{m'_l, m_k} \dots Q_{m_l, m_k}^{(1)} \dots \delta_{m'_N, m_N} \quad (51.18)$$

where, by (51.13),

$$Q_{m_l, m_k}^{(1)} = \langle \psi_{m_l}(\xi) | \hat{Q}^{(1)} \psi_{m_k}(\xi) \rangle = Q_{lk}^{(1)} \quad (m_l \neq m_k) \quad (51.19)$$

Let us determine which of the addends in the double sum (51.18) are non-zero. Assume that in the function to the right of the operator in the matrix element, n_1 factors have the index 1, n_2 —the index 2, ..., \dots, n_k —the index k , \dots, n_l —the index l , \dots, n_s —the index s . Consequently, in the function to the left of the operator there are n_1 factors with the index 1, n_2 with the index 2, $\dots, n_k - 1$ with the index k , $\dots, n_l + 1$ with the index l , \dots, n_s with the index s . Let us consider such addends in which as a result of the permutations, the indices m_l and m_k acquire identical values, for instance, the factor $Q_{11}^{(1)}$ or $Q_{22}^{(1)}$, etc. was obtained (remember that m_l is equivalent to m'_k). Hence, among the other factors there will be

$$\underbrace{\delta_{kk} \dots \delta_{kk}}_{n_k - 1} \underbrace{\delta_{ik} \dots \delta_{il}}_{n_l} \dots \underbrace{\delta_{ll} \dots \delta_{lj}}_{n_j} \quad (51.20)$$

where $i \neq k$ and $j \neq l$. This is due to the circumstance that among the first indices in δ_{ij} only $n_k - 1$ have the value k , whereas among the second indices in it n_k have the value k . Similarly, among the first indices in δ_{ij} , $n_l + 1$ have the value l , whereas among the second indices in it n_l have the value l . The symbols δ_{ik} and δ_{lj} equal zero, so that the corresponding addends of the double sum must be discarded.

Let us consider the addends containing, for example, the factor $Q_{12}^{(1)}$. These addends, in addition to the factors (51.20), also include factors of the form δ_{i1} and δ_{2j} (here $i \neq 1$ and $j \neq 2$). These addends will also vanish. We conclude from the above that only the addends of the double sum in which the first index on $Q^{(1)}$ is l and the second is k can be non-zero. But in this case, the addend, for example, will have the form

$$\underbrace{\delta_{11} \dots \delta_{11}}_{n_1} \dots \underbrace{\delta_{kk} \dots \delta_{kk}}_{n_k - 1} \dots Q_{lk} \dots \underbrace{\delta_{ll} \dots \delta_{ll}}_{n_l} \dots \underbrace{\delta_{ss} \dots \delta_{ss}}_{n_s}$$

Hence, if we retain only the non-zero addends, expression (51.18) becomes

$$\text{M.E.} = A' A \sum \delta_{m_1, m_1} \dots Q_{m_l, m_k}^{(1)} \dots \delta_{m_N, m_N} \quad (51.21)$$

The sum is taken over all the non-coinciding permutations of the pairs of indices on the factors δ . The total number of these pairs is $N - 1$; among them are n_1 pairs of indices 11, n_2 pairs of indices 22, $n_k - 1$ pairs of indices kk , ..., n_l pairs of indices ll , and n_s pairs of indices ss . Consequently, the number of addends in the sum (51.21) is $(N - 1)!/[n_1! \dots (n_k - 1)! \dots n_l! \dots n_s!]$. All the addends are identical and equal $Q_{m_l, m_k}^{(1)} = Q_{lk}^{(1)}$. Taking into account that $A' = [n_1! \dots (n_k - 1)! \dots (n_l + 1)! \dots n_s!] / N!^{1/2}$, and $A = [n_1! \dots n_h! \dots n_l! \dots n_s!] / N!^{1/2}$, we obtain the following value for the matrix element (51.18) (for brevity, we shall indicate only the occupation numbers that undergo a change):

$$\begin{aligned} & \langle n_k - 1, n_l + 1 | \hat{Q}_k^{(1)} | n_k, n_l \rangle \\ &= \left[\frac{n_1! \dots (n_k - 1)! \dots (n_l + 1)! \dots n_s!}{N!} \right]^{1/2} \left[\frac{n_1! \dots n_k! \dots n_l! \dots n_s!}{N!} \right]^{1/2} \\ & \quad \times \frac{(N - 1)!}{n_1! \dots (n_k - 1)! \dots n_l! \dots n_s!} Q_{lk}^{(1)} = \frac{1}{N} \sqrt{n_k (n_l + 1)} Q_{lk}^{(1)} \end{aligned}$$

Recall that the value of $Q_{lk}^{(1)}$ does not depend on the number of the operator $\hat{Q}^{(1)}$; it is determined by the state indices l and k [see (51.13)]. The latter, in turn, are determined by the values of the occupation numbers that undergo a change in a transition. Consequently, as for diagonal elements, all the addends in (51.6) are identical and for a matrix element of the operator (51.4) we obtain the expression

$$\langle n_k - 1, n_l + 1 | \hat{Q}_1 | n_k, n_l \rangle = \sqrt{n_k (n_l + 1)} Q_{lk}^{(1)}$$

This formula can be given a symmetric form by replacing n_l with $n_l - 1$ (this signifies that we designate the number of particles which were in the state m_l before the transition by $n_l - 1$):

$$\langle n_k - 1, n_l | \hat{Q}_1 | n_k, n_l - 1 \rangle = \sqrt{n_k n_l} Q_{lk}^{(1)} \quad (51.22)$$

Our next task is the evaluation of the matrix elements (51.17) and (51.22) for the annihilation and creation operators acting not on functions of the coordinates (like $\hat{Q}_k^{(1)}$ and \hat{Q}_1), but on the occupation numbers n_1, n_2, \dots (see Sec. 50). We define these operators with the aid of the following relations:

$$\hat{a}_k \psi_{n_1, \dots, n_k, \dots} = \sqrt{n_k} \psi_{n_1, \dots, n_k - 1, \dots} \quad (51.23)$$

$$\hat{a}_k^\dagger \psi_{n_1, \dots, n_k, \dots} = \sqrt{n_k + 1} \psi_{n_1, \dots, n_k + 1, \dots} \quad (51.24)$$

[compare with (27.5) and (27.6)]. The operator \hat{a}_k , by acting on a function, replaces the index n_k with $n_k - 1$, i.e. reduces the number of particles in the state k (previously we said in the state m_k) by one (in addition, it multiplies the function by $\sqrt{n_k}$). It is therefore called

the operator of particle annihilation in the k -th state. The operator \hat{a}_k^\dagger replaces the index n_k with $n_k + 1$, i.e. increases the number of particles in the state k by one (in addition, it multiplies the function by $\sqrt{n_k + 1}$). This is why it is called the operator of particle creation in the k -th state.

The consecutive application of these operators yields

$$\begin{aligned}\hat{a}_k^\dagger (\hat{a}_k \psi_{n_1, \dots, n_k, \dots}) &= \sqrt{n_k} \hat{a}_k^\dagger \psi_{n_1, \dots, n_k - 1, \dots} \\ &= \sqrt{n_k} \sqrt{n_k} \psi_{n_1, \dots, n_k, \dots}\end{aligned}$$

Hence,

$$\hat{a}_k^\dagger \hat{a}_k \psi_{n_1, \dots, n_k, \dots} = n_k \psi_{n_1, \dots, n_k, \dots} \quad (51.25)$$

This signifies that the consecutive application of the operators \hat{a}_k and \hat{a}_k^\dagger does not change the number of particles in the k -th state, while the function is multiplied by n_k . On the basis of (51.25), we obtain the following value for the product of the operators:

$$\hat{a}_k^\dagger \hat{a}_k = n_k \quad (51.26)$$

Accordingly, the operator $\hat{a}_k^\dagger \hat{a}_k$ is called the operator of the number of particles in the k -th state.

We can show in a similar way that

$$\hat{a}_k \hat{a}_k^\dagger = n_k + 1 \quad (51.27)$$

Inspection of (51.26) and (51.27) shows that the commutator of the operators \hat{a}_k and \hat{a}_k^\dagger equals unity:

$$\hat{a}_k \hat{a}_k^\dagger - \hat{a}_k^\dagger \hat{a}_k = 1 \quad (51.28)$$

[compare with (27.8)].

It is quite simple to convince ourselves that the following relations are correct:

$$\hat{a}_k \hat{a}_l^\dagger - \hat{a}_l^\dagger \hat{a}_k = 0 \quad (k \neq l) \quad (51.29)$$

$$\left. \begin{array}{l} \hat{a}_k \hat{a}_l - \hat{a}_l \hat{a}_k = 0 \\ \hat{a}_k^\dagger \hat{a}_l^\dagger - \hat{a}_l^\dagger \hat{a}_k^\dagger = 0 \end{array} \right\} \text{for any } k \text{ and } l \quad (51.30)$$

$$(51.31)$$

Expressions (51.28) and (51.29) can be combined into a single expression

$$\hat{a}_k \hat{a}_l^\dagger - \hat{a}_l^\dagger \hat{a}_k = \delta_{kl} \quad (51.32)$$

From the definition (51.23), we obtain the following formula for the matrix elements of the operator \hat{a}_k (in the designation of the matrix element we indicate only the numbers that undergo a change):

$$\begin{aligned}\langle n_k - 1 | \hat{a}_k | n_k \rangle &= \langle \psi_{\dots n_{k-1} \dots} | \hat{a}_k \psi_{\dots n_k \dots} \rangle \\ &= \langle \psi_{\dots n_{k-1} \dots} | \sqrt{n_k} \psi_{\dots n_{k-1} \dots} \rangle = \sqrt{n_k} \delta_{n_{k-1}, n_{k-1}} = \sqrt{n_k}\end{aligned}$$

Using a different designation of the matrix elements, we can write

$$(\hat{a}_k)_{n_{k-1}, n_k} = \langle n_k - 1 | \hat{a}_k | n_k \rangle = \sqrt{n_k} \quad (51.33)$$

Similarly

$$(\hat{a}_k^*)_{n_k+1, n_k} = \langle n_k + 1 | \hat{a}_k^* | n_k \rangle = \sqrt{n_k + 1} \quad (51.34)$$

It is not difficult to verify that the matrix elements of the operator (51.26) equal

$$(a_k^* a_k)_{n'_k, n_k} = n_k \delta_{n'_k, n_k} \quad (51.35)$$

It can be seen from (51.33) and (51.34) that the operators \hat{a}_k and \hat{a}_k^* are Hermitian conjugates of each other. Indeed, by (51.33), we have $(a_k)_{n_k, n_k+1} = \sqrt{n_k + 1}$. A comparison with (51.34) shows that

$$(a_k^*)_{n_k+1, n_k} = (a_k)_{n_k, n_k+1}$$

Since both matrices are real, they satisfy the condition (9.21) for Hermitian matrices.

The consecutive application of the operators \hat{a}_l^* and \hat{a}_k to the function $\psi_{n_1, \dots, n_k, \dots, n_{l-1}, \dots}$ yields, by (51.23) and (51.24), the expression $\sqrt{n_k n_l} \psi_{n_1, \dots, n_{k-1}, \dots, n_l, \dots}$. Consequently,

$$\begin{aligned}\langle n_k - 1, n_l | \hat{a}_l^* \hat{a}_k | n_k, n_l - 1 \rangle &= \sqrt{n_k n_l} \langle \psi_{n_1, \dots, n_{k-1}, \dots, n_l, \dots} | \psi_{n_1, \dots, n_{k-1}, \dots, n_l, \dots} \rangle \\ &= \sqrt{n_k n_l} \quad (51.36)\end{aligned}$$

The consecutive application of the operators $\hat{a}_r^* \hat{a}_p$ and $\hat{a}_l^* \hat{a}_k$ to the function $\psi_{n_1, \dots, n_k, \dots, n_{l-1}, \dots, n_p, \dots, n_{r-1}, \dots}$ yields the expression $\sqrt{n_k n_l n_p n_r} \psi_{n_1, \dots, n_{k-1}, \dots, n_l, \dots, n_{p-1}, \dots, n_r, \dots}$. Hence,

$$\begin{aligned}\langle n_k - 1, n_l, n_p - 1, n_r | \hat{a}_r^* \hat{a}_p \hat{a}_l^* \hat{a}_k | n_k, n_l - 1, n_p, n_r - 1 \rangle &= \sqrt{n_k n_l n_p n_r} \quad (51.37)\end{aligned}$$

We must note that in view of (51.29)-(51.31), the operators in (51.37) may be written in any sequence.

We have brought to light the properties of the operators \hat{a}_k and

\hat{a}_k^+ that we shall need in the following. To complete the transition to the representation of the occupation numbers, we must learn how to express the operators of any physical quantities in terms of the annihilation and creation operators.

Let us begin with the operator (51.4). We shall show that it can be represented in the form

$$\hat{Q}_1 = \sum_{i,j} Q_{ij}^{(1)} \hat{a}_i^+ \hat{a}_j, \quad (51.38)$$

where $Q_{ij}^{(1)}$ is a number determined by formula (51.13). Summation is performed over the indices i and j within the limits from 1 to N so that the sum consists of N^2 addends.

We find the matrix element of the operator inside the sum sign in (51.38). Having in view that $Q_{ij}^{(1)}$ are simple numbers, we obtain

$$\begin{aligned} \text{M.E.} &= \langle n_k - 1, n_l | \sum_{i,j} Q_{ij}^{(1)} \hat{a}_i^+ \hat{a}_j | n_k, n_l - 1 \rangle \\ &= \sum_{i,j} Q_{ij}^{(1)} \langle n_k - 1, n_l, n_i - 1, n_j | \hat{a}_i^+ \hat{a}_j | n_k, n_l - 1, n_i - 1, n_j \rangle \end{aligned} \quad (51.39)$$

Since the operators \hat{a}_i^+ and \hat{a}_j act on n_i and n_j , we have indicated these numbers in the state indices. We are calculating the matrix element for transitions with a change in only the numbers n_k and n_l . Therefore, the occupation numbers with the indices i and j on the right and the left have been taken the same. For convenience, the number of particles in the state i has been taken equal to $n_i - 1$. We transform the expression obtained with a view to (51.36):

$$\begin{aligned} \text{M.E.} &= \sum_{i,j} Q_{ij}^{(1)} \sqrt{n_i n_j} \langle n_k - 1, n_l, n_i - 1, n_j | n_k, n_l - 1, n_i, n_j - 1 \rangle \\ &= \sum_{i,j} Q_{ij}^{(1)} \sqrt{n_i n_j} \delta_{(n_k - 1, n_l, n_i - 1, n_j), (n_k, n_l - 1, n_i, n_j - 1)} \end{aligned}$$

Of the N^2 addends of the last sum, only the one for which $i = l$ and $j = k$ is non-zero¹. Consequently,

$$\text{M.E.} = \sqrt{n_l n_k} Q_{lk}^{(1)} \quad (51.40)$$

This result coincides with (51.22).

Now let us calculate the diagonal matrix element:

$$\begin{aligned} \text{D.M.E.} &= \langle n_1, \dots, n_i - 1, \dots, n_j, \dots | \sum_{i,j} Q_{ij}^{(1)} \hat{a}_i^+ \hat{a}_j | n_1, \\ &\quad \dots, n_i - 1, \dots, n_j, \dots \rangle = \sum_{i,j} Q_{ij}^{(1)} \sqrt{n_i n_j} \langle n_1, \dots, n_i - 1, \dots, n_j, \dots | \end{aligned}$$

¹ On the face of it, the quantity $\delta_{(n_k - 1, n_l, n_i - 1, n_j), (n_k, n_l - 1, n_i, n_j - 1)}$ must be zero because formally the "indices" differ in the sequence in which the numbers forming the index on δ are arranged. But a change in the sequence of these numbers signifies only a change in the sequence of arrangement of the factors in formula (51.1), which evidently does not change the function ψ itself.

$$\dots, n_j, \dots | n_1, \dots, n_t, \dots, n_{j-1}, \dots \rangle \\ = \sum_{i,j} Q_{ij}^{(1)} \sqrt{n_i n_j} \delta_{(n_i-1, n_j), (n_j, n_{j-1})}$$

In the last sum, only those addends are non-zero for which $j = t$. Therefore,

$$\text{D.M.E.} = \sum_i n_i Q_{ii}^{(1)}$$

that coincides with (51.17).

It can be seen that the matrix elements corresponding to the transitions of two and more particles are zero.

We have thus convinced ourselves that the matrix elements of the operator (51.38) coincide with those of the operator (51.4). Consequently, it is legitimate to represent the operator \hat{Q}_1 in the form of (51.38).

We shall give the expression for the operator (51.5) in the occupation number representation without a proof:

$$\hat{Q}_2 = \sum_{i, p, j, r} Q_{(ip), (jr)}^{(2)} \hat{a}_i^\dagger \hat{a}_p^\dagger \hat{a}_j \hat{a}_r \quad (51.41)$$

where

$$Q_{(ip), (jr)}^{(2)} := \langle \psi_{m_i}(\xi') \psi_{m_p}(\xi'') | \hat{Q}^{(2)} \psi_{m_j}(\xi') \psi_{m_r}(\xi'') \rangle \quad (51.42)$$

(ξ' and ξ'' are two independent variables, and $\hat{Q}^{(2)}$ acts on both these variables).

Now we can express the Hamiltonian of a system of N identical particles in terms of the operators \hat{a}_i^\dagger and \hat{a}_j . If the particles do not interact with one another, the Hamiltonian is determined by the expression

$$\hat{H} = \sum_{k=1}^N \left[-\frac{\hbar^2}{2m_0} \nabla_k^2 + U(\xi_k) \right] = \sum_{k=1}^N \hat{H}_k^{(1)} \quad (51.43)$$

[see (46.1)]. Here $U(\xi_k)$ is the potential energy of the k -th particle in an external stationary field. This operator belongs to the type of (51.4). In our case

$$\hat{Q}_k^{(1)} = \hat{H}_k^{(1)} = -\frac{\hbar^2}{2m_0} \nabla_k^2 + U(\xi_k) \quad (51.44)$$

In accordance with formulas (51.38) and (51.13), we have

$$\hat{H} = \sum_{i,j} H_{ij}^{(1)} \hat{a}_i^\dagger \hat{a}_j \quad (51.45)$$

where

$$H_{ij}^{(1)} = \langle \psi_{m_i}(\xi) | \hat{H}^{(1)} \psi_{m_j}(\xi) \rangle$$

Expression (51.45) is exactly the Hamiltonian of a system of non-interacting particles in the occupation number representation.

If we take as the functions $\psi_{m_k}(\xi_k)$ the eigenfunctions of the operator (51.44), i.e. functions satisfying the equations

$$\hat{H}_k^{(1)} \psi_{m_k}(\xi_k) = E_{m_k} \psi_{m_k}(\xi_k)$$

then

$$H_{ij}^{(1)} = E_{m_j} \langle \psi_{m_i} | \psi_{m_j} \rangle = E_{m_j} \delta_{m_i, m_j}$$

Introducing this value into formula (51.45), we obtain

$$\hat{H} = \sum_{i,j} E_{m_j} \delta_{m_i, m_j} \hat{a}_i^\dagger \hat{a}_j = \sum_j E_{m_j} \hat{a}_j^\dagger \hat{a}_j.$$

Recall that E_{m_j} is the energy of the state which the j -th particle is in; the operators \hat{a}_j^\dagger and \hat{a}_j act on the coordinates ξ_j of this particle. With a view to (51.26), we can write that

$$\hat{H} = \sum_j E_{m_j} n_j = E$$

where E is the total energy of the system. We have obtained a trivial result: the action of the operator \hat{H} on its eigenfunction consists in multiplication of this function by E . If we had selected the functions ψ_{m_k} in a different way, we would not have obtained such a result. For instance, by taking as ψ_{m_k} the eigenfunctions of the operator $-(\hbar^2/2m_0) \nabla_k^2$, i.e. the functions satisfying the equation

$$-\frac{\hbar^2}{2m_0} \nabla^2 \psi_{m_k} = E'_{m_k} \psi_{m_k}$$

we arrive, as can readily be verified, at the following expression for the Hamiltonian:

$$\hat{H} = \sum_j E'_{m_j} \hat{a}_j^\dagger \hat{a}_j + \sum_{i,j} \langle \psi_{m_j}(\xi) | U(\xi) \psi_{m_i}(\xi) \rangle \hat{a}_i^\dagger \hat{a}_j$$

For a system of particles between which there is pairwise interaction, the Hamiltonian has the form

$$\hat{H} = \sum_k \hat{H}_k^{(1)} + \frac{1}{2} \sum_{k \neq l} U_{kl}^{(2)}(\xi_k, \xi_l) = \hat{H}_1 + \hat{H}_2, \quad (51.46)$$

[see (51.43)]. The first term has the form of (51.4), the second, of (51.5). We have already obtained expression (51.45) for the first term. For the second term, by formulas (51.41) and (51.42), we have

$$\hat{H}_2 = \frac{1}{2} \sum_{i, p, j, r} U_{(ip), (jr)}^{(2)} \hat{a}_i^{\dagger} \hat{a}_p^{\dagger} \hat{a}_j \hat{a}_r \quad (51.47)$$

where

$$U_{(ip), (jr)}^{(2)} = \langle \psi_{m_i}(\xi') \psi_{m_p}(\xi'') | U^{(2)} \psi_{m_j}(\xi') \psi_{m_r}(\xi'') \rangle \quad (51.48)$$

[the condition $k \neq l$ written in (51.46) under the sum sign is taken into account by the fact that integration in calculating (51.48) is performed over the two independent variables ξ' and ξ''].

Hence, for pairwise interactions, the Hamiltonian is the sum of expressions (51.45) and (51.47). If we want to take into account the energy of triple interactions, we must add the operator \hat{H}_3 , which will be represented by the sum of the products of six operators \hat{a} , and so on.

The formulas we have obtained can be written more compactly with the aid of the following formal procedure. We introduce the operators

$$\hat{\psi}(\xi) = \sum_j \psi_{m_j}(\xi) \hat{a}_j \quad \text{and} \quad \hat{\psi}^*(\xi) = \sum_i \psi_{m_i}^*(\xi) \hat{a}_i^{\dagger} \quad (51.49)$$

where the variables ξ are treated as parameters. Let us act with the operator $\hat{\psi}(\xi)$ on a certain function $\psi_{n_1, n_2, \dots, n_s}$ (recall that the sum of the indices is $n_1 + n_2 + \dots + n_s = N$). The result is a new function determined by the expression

$$\sum_i \psi_{m_i}(\xi) \hat{a}_i \psi_{n_1, \dots, n_i, \dots, n_s} = \sum_i \psi_{m_i}(\xi) \sqrt{n_i} \psi_{n_1, \dots, n_{i-1}, \dots, n_s}$$

The sum of the indices on ψ in each of the addends will be less by one than the sum of the indices on the initial function. Consequently, the new function describes a system of $N - 1$ particles. The operator $\hat{\psi}(\xi)$ thus diminishes the total number of particles in a system by one. We can convince ourselves in a similar way that the operator $\hat{\psi}^*(\xi)$ increases the number of particles in a system by one.

Let us form the expression

$$\hat{Q}_1 = \int \hat{\psi}^*(\xi) \hat{Q}^{(1)} \hat{\psi}(\xi) d\xi \quad (51.50)$$

[the operator $\hat{Q}^{(1)}$ is understood to act on the parameter ξ]. Substitution of expression (51.49) into (51.50) yields

$$\begin{aligned}\hat{Q}_1 &= \int \left\{ \sum_i \psi_{m_i}^*(\xi) \hat{a}_i^\dagger \right\} \hat{Q}^{(1)} \left\{ \sum_j \psi_{m_j}(\xi) \hat{a}_j \right\} d\xi \\ &= \sum_{i,j} \hat{a}_i^\dagger \hat{a}_j \int \psi_{m_i}^*(\xi) \hat{Q}^{(1)} \psi_{m_j}(\xi) d\xi \\ &= \sum_{i,j} \hat{a}_i^\dagger \hat{a}_j \langle \psi_{m_i} | \hat{Q}^{(1)} \psi_{m_j} \rangle = \sum_{i,j} Q_{ij}^{(1)} \hat{a}_i^\dagger \hat{a}_j\end{aligned}$$

A comparison with (51.38) shows that expression (51.50) is equivalent to the operator \hat{Q}_1 in the occupation number representation.

The operators \hat{Q}_2 , \hat{Q}_3 , etc. can also be expressed in terms of the operators (51.49). For example,

$$\hat{Q}_2 = \frac{1}{2} \int \int \hat{\psi}^+(\xi') \hat{\psi}^+(\xi'') \hat{Q}^{(2)} \hat{\psi}(\xi'') \hat{\psi}(\xi') d\xi' d\xi'' \quad (51.51)$$

Using formulas (51.50) and (51.51), we can write expression (51.46) of the Hamiltonian in the representation of the second quantization:

$$\begin{aligned}\hat{H} &= \int \hat{\psi}^+(\xi) \hat{H}^{(1)} \hat{\psi}(\xi) d\xi \\ &\quad + \frac{1}{2} \int \int \hat{\psi}^+(\xi') \hat{\psi}^+(\xi'') U^{(2)} \hat{\psi}(\xi'') \hat{\psi}(\xi') d\xi' d\xi'' \quad (51.52)\end{aligned}$$

To understand the origin of the term "second quantization", let us consider the following example. Assume that a system of N pairwise interacting bosons is in a state in which all the particles are in the same one-particle state $\psi_m(\xi)$ [this signifies that all the m_i 's in the function (51.1) are the same and equal m]. We shall consider that the functions ψ_m are normalized as follows:

$$\langle \psi_m | \psi_m \rangle = N \quad (51.53)$$

[it was assumed in (51.1) that the ψ_m 's are normalized to unity!]. To determine the coefficient A in (51.1), we equate the scalar square of the psi-function to unity:

$$\begin{aligned}1 &= A^2 \langle \psi_m(\xi_1) \psi_m(\xi_2) \dots \psi_m(\xi_N) | \psi_m(\xi_1) \psi_m(\xi_2) \dots \psi_m(\xi_N) \rangle \\ &= A^2 \langle \psi_m(\xi_1) | \psi_m(\xi_1) \rangle \langle \psi_m(\xi_2) | \psi_m(\xi_2) \rangle \dots \langle \psi_m(\xi_N) | \psi_m(\xi_N) \rangle = A^2 N^N\end{aligned}$$

[by (51.53), each of the N factors equals N]. Hence, $A = 1/\sqrt{N^N}$.

The Hamiltonian of the system is determined by expression (51.46). Let us find the mean value of the system's energy:

$$\begin{aligned}
 \langle E \rangle &= \langle \psi | \hat{H} \psi \rangle \\
 &= \frac{1}{N^N} \left\{ \sum_i \langle \psi_m(\xi_1) \dots \psi_m(\xi_i) \dots | \hat{H}_i^{(1)} \psi_m(\xi_1) \dots \psi_m(\xi_i) \dots \rangle \right. \\
 &\quad + \frac{1}{2} \sum_{i,j} \langle \psi_m(\xi_1) \dots \psi_m(\xi_i) \dots \psi_m(\xi_j) \\
 &\quad \dots | U_{ij}(\xi_i, \xi_j) \psi_m(\xi_1) \dots \psi_m(\xi_i) \dots \psi_m(\xi_j) \dots \rangle \Big\} \\
 &= \frac{1}{N^N} \left\{ \sum_i \langle \psi_m(\xi_1) | \psi_m(\xi_1) \rangle \dots \langle \psi_m(\xi_i) | \hat{H}_i^{(1)} \psi_m(\xi_i) \rangle \dots \right. \\
 &\quad + \frac{1}{2} \sum_{i,j} \langle \psi_m(\xi_1) | \psi_m(\xi_1) \rangle \dots \\
 &\quad \times \langle \psi_m(\xi_i) \psi_m(\xi_j) | U_{ij}(\xi_i, \xi_j) \psi_m(\xi_i) \psi_m(\xi_j) \rangle \dots \Big\} \\
 &= \frac{1}{N^N} \left\{ \sum_i N^{N-1} \langle \psi_m(\xi_i) | \hat{H}_i^{(1)} \psi_m(\xi_i) \rangle \right. \\
 &\quad + \frac{1}{2} \sum_{i,j} N^{N-2} \langle \psi_m(\xi_i) \psi_m(\xi_j) | U_{ij}(\xi_i, \xi_j) \psi_m(\xi_i) \psi_m(\xi_j) \rangle \Big\}.
 \end{aligned}$$

All the addends of the sum over i are identical, their total number is N . Similarly, all the addends of the double sum over i and j are also identical, their total number is N^2 . We thus arrive at the expression

$$\begin{aligned}
 \langle E \rangle &= \langle \psi_m(\xi) | \hat{H}^{(1)} \psi_m(\xi) \rangle \\
 &+ \frac{1}{2} \langle \psi_m(\xi_i) \psi_m(\xi_j) | U_{ij}(\xi_i, \xi_j) \psi_m(\xi_i) \psi_m(\xi_j) \rangle = \int \psi^*(\xi) \hat{H}^{(1)} \psi(\xi) d\xi \\
 &+ \frac{1}{2} \int \int \psi^*(\xi') \psi^*(\xi'') U(\xi', \xi'') \psi(\xi'') \psi(\xi') d\xi' d\xi'' \quad (51.54)
 \end{aligned}$$

(we have dropped the index m on ψ as superfluous).

Expressions (51.52) and (51.54) are very similar to each other in their appearance. If in (51.54) we replace the energy with its operator, the function ψ with the operator $\hat{\psi}$, and the function ψ^* with the operator $\hat{\psi}^+$, this expression will transform into (51.52). Hence there follows a useful rule for finding the Hamiltonian in the representation of second quantization: one must write the expression for the mean energy in terms of the psi-function ψ of an individual particle [nor-

alized in accordance with (51.53)], and then perform the replacements:

$$\psi(\xi) \rightarrow \hat{\psi}(\xi), \quad \psi^*(\xi) \rightarrow \hat{\psi}^*(\xi)$$

where $\hat{\psi}(\xi)$ and $\hat{\psi}^*(\xi)$ are determined by formulas (51.49).

Replacement of the function ψ with the operator $\hat{\psi}$ underlies the term "second quantization". In conventional ("first") quantization, physical quantities are replaced with operators, in second quantization, psi-functions are replaced with operators.

52. Second Quantization Applied to Fermions

In accordance with (46.16), for fermions, the function (50.2) has the form

$$\psi_{n_1, n_2, \dots} = A \sum \epsilon_{m_1, m_2, \dots, m_N} \psi_{m_1}(\xi_1) \psi_{m_2}(\xi_2) \dots \psi_{m_N}(\xi_N) \quad (52.1)$$

where

$$A = \frac{1}{\sqrt{N!}} \quad (52.2)$$

The sum is taken over all the permutations of the numbers m_1, m_2, \dots, m_N . Among these numbers, there are no identical ones because if even two indices are identical, the symbol $\epsilon_{m_1, m_2, \dots, m_N}$ is zero (this signifies that there cannot be more than one particle in a state with the given m). The sign of ϵ depends on the number of disorders in the permutation of the indices (a disorder means that a greater number is ahead of a smaller one). With an even number of disorders, $\epsilon = +1$, with an odd number, $\epsilon = -1$. Remember that disorders are absent when the inequalities $m_1 < m_2 < \dots < m_N$ are observed.

The occupation numbers can now have only two values: 0 and 1. Values greater than 1 are forbidden by the Pauli principle.

Let us use the functions (52.1) to find the form of the matrix elements of the operator

$$\hat{Q}_1 = \sum_{k=1}^N \hat{Q}_k^{(1)} \quad (52.3)$$

[see (51.4)]. As for bosons,

$$(Q_1)_{\alpha\beta} = \sum_{k=1}^N (Q_k^{(1)})_{\alpha\beta} \quad (52.4)$$

[see (51.6)]. We therefore first calculate the matrix elements of the operator $\hat{Q}_k^{(1)}$. They are

$$\begin{aligned}
 & \langle n'_1, n'_2, \dots | \hat{Q}_k^{(1)} | n_1, n_2, \dots \rangle \\
 &= A^2 \sum' \sum \epsilon_{m'_1, m'_2, \dots, m'_N} \epsilon_{m_1, m_2, \dots, m_N} \langle \psi_{m'_1}(\xi_1) | \psi_{m_1}(\xi_1) \rangle \\
 &\quad \dots \langle \psi_{m'_k}(\xi_k) | \hat{Q}_k^{(1)} \psi_{m_k}(\xi_k) \rangle \dots \langle \psi_{m'_N}(\xi_N) | \psi_{m_N}(\xi_N) \rangle \\
 &= A^2 \sum' \sum \epsilon_{m'_1, m'_2, \dots, m'_N} \epsilon_{m_1, m_2, \dots, m_N} \delta_{m'_1, m_1} \dots Q_{m'_k, m_k}^{(1)} \dots \delta_{m'_N, m_N}
 \end{aligned} \tag{52.5}$$

where $Q_{m_k, m_k}^{(1)}$ is determined by formula (51.12). In the given case, the coefficient A' always equals the coefficient A [see (52.2)].

The expression we have obtained differs from (51.10) only in the presence of the factors ϵ . For the same reasons that were revealed in Sec. 51 in discussing formula (51.10), the matrix elements (52.5) can be non-zero only for transitions without a change in the occupation numbers (diagonal elements) and for transitions in which only one particle changes its state. One of the occupation numbers, say n_k , diminishes from 1 to 0, and another one, say n_l , grows from 0 to 1.

For diagonal elements, expression (52.5) has the form

$$\text{D.M.E.} = A^2 \sum (\epsilon_{m_1, m_2, \dots, m_N})^2 \delta_{m_1, m_1} \dots Q_{m_k, m_k}^{(1)} \dots \delta_{m_N, m_N} \tag{52.6}$$

Since $(\epsilon \dots)^2$ with any permutation of the indices equals +1, expression (52.6) coincides with (51.14). Consequently, the final result will also be the same, i.e. the diagonal matrix elements are determined by the formula [see (51.17)]

$$\langle n_1, n_2, \dots | \hat{Q}_1 | n_1, n_2, \dots \rangle = \sum_i n_i Q_{ii}^{(1)} \tag{52.7}$$

(since the numbers n_i now equal 1 or 0, the sum may be extended to all possible single-particle states).

Consider a matrix element corresponding to a transition of one of the particles from the state m_k to the state m_l . We shall consider for determinacy that $m_l > m_k$. In such a transition, n_k changes its value from 1 to 0, and n_l from 0 to 1. Consequently, the matrix

element has the form

$$\begin{aligned} & \langle n_k = 0, n_l = 1 | \hat{Q}_k^{(1)} | n_k = 1, n_l = 0 \rangle \\ &= A^2 \sum \varepsilon_{m_1, \dots, m_{k-1}, m_{k+1}, \dots, m_{l-1}, m_l, m_{l+1}, \dots} \\ & \times \varepsilon_{m_1, \dots, m_{k-1}, m_k, m_{k+1}, \dots, m_{l-1}, m_{l+1}, \dots} \delta_{m_1, m_1} \dots \\ & \times \langle \psi_{m_l} (\xi_k) | \hat{Q}_k^{(1)} \psi_{m_k} (\xi_k) \rangle \dots \delta_{m_N, m_N} \quad (52.8) \end{aligned}$$

In the function to the right of the operator in (52.8), the factor $\psi_{m_k} (\xi_k)$ is present, but the factor $\psi_{m_l} (\xi_k)$ is absent. In the function to the left of the operator, the factor $\psi_{m_k} (\xi_k)$ is absent, but the factor $\psi_{m_l} (\xi_k)$ is present (the k -th particle passes from the state ψ_{m_k} to the state ψ_{m_l} , in which no particle has been before this).

Assume that the initial permutation of the indices in the function to the right of the operator contains no disorders, i.e.

$$\begin{aligned} m_1 < m_2 < \dots < m_{k-1} < m_k < m_{k+1} < \\ & \dots < m_{l-1} < m_{l+1} < \dots \quad (52.9) \end{aligned}$$

Now in the initial permutation of the indices in the function to the left of the operator,

$$m_1, m_2, \dots, m_{k-1}, m_l, m_{k+1}, \dots, m_{l-1}, m_{l+1}, \dots \quad (52.10)$$

disorders appear because $m_l > m_k$. The number m_l is greater than $m_{k+1}, m_{k+2}, \dots, m_{l-2}, m_{l-1}$. Consequently, the number of appearing disorders equals the number of indices in the permutations having values greater than m_k and smaller than m_l . This number evidently equals the sum of the occupation numbers of all the states from the $(k+1)$ -th to the $(l-1)$ -th, inclusively:

$$v = \sum_{s=k+1}^{l-1} n_s \quad (52.11)$$

(if an intermediate index is absent, the corresponding occupation number vanishes).

Hence, if the second factor ε_{\dots} in (52.8) is +1, the first factor ε_{\dots} has the value $(-1)^v$, where v is determined by formula (52.11). It follows that the product of the symbols ε in (52.8) at any permutation of similar pairs of indices has the same value equal to

$$(-1)^v = (-1)^{\sum_{s=k+1}^{l-1} n_s} \quad (52.12)$$

The number (52.12) can be written in a more convenient form:

$$(-1)^v = \prod_{s=k+1}^{l-1} (1 - 2n_s) \quad (52.13)$$

Indeed, the factors for which $n_s = 0$ are +1, and those for which $n_s = 1$ are -1. Consequently, expression (52.13) will contain the same number of factors equal to -1 as expression (52.12) does.

Hence, the product $\epsilon_{...}\epsilon_{...}$ in (52.8) for each of the addends has a value equal to (52.13). Putting this factor outside the sum sign, we obtain

$$\begin{aligned} & \langle n_k = 0, n_l = 1 | \hat{Q}_k^{(1)} | n_k = 1, n_l = 0 \rangle \\ &= A^2 \prod_{s=k+1}^{l-1} (1 - 2n_s) \sum \delta_{m_1, m_1} \delta_{m_2, m_2} \dots Q_{lk}^{(1)} \dots \delta_{m_N, m_N} \end{aligned} \quad (52.14)$$

[compare with (51.18)]. The sum is taken over all the permutations of the pairs of indices, among which there are now no coinciding ones. Only the indices on $Q^{(1)}$ do not participate in the permutations. The number of indices that do participate in them is therefore $N - 1$. Hence, the sum in (52.14) consists of $(N - 1)!$ identical addends equal to $Q_{lk}^{(1)}$. Taking into account the value (52.2) for A , we thus conclude that

$$\begin{aligned} & \langle n_k = 0, n_l = 1 | \hat{Q}_k^{(1)} | n_k = 1, n_l = 0 \rangle \\ &= \frac{1}{N!} \prod_{s=k+1}^{l-1} (1 - 2n_s) (N - 1)! Q_{lk}^{(1)} \end{aligned} \quad (52.15)$$

Recall that the number $Q_{lk}^{(1)}$ does not depend on the number of the operator $\hat{Q}_k^{(1)}$ and is determined only by the indices of the initial and final states [see (51.13)]. This is why we obtain a matrix element of the operator (52.3) by simply multiplying (52.15) by N :

$$\langle n_k = 0, n_l = 1 | \hat{Q}_1 | n_k = 1, n_l = 0 \rangle = \prod_{s=k+1}^{l-1} (1 - 2n_s) Q_{lk}^{(1)} \quad (52.16)$$

We have assumed that $m_l > m_k$. If $m_l < m_k$, the coefficient in (52.16) must be taken in the form $\prod_{s=l+1}^{k-1} (1 - 2n_s)$.

Let us establish how the annihilation and creation operators must be determined for fermions if we want the operator (52.3), being expressed in terms of these operators, to have the same form as for bosons, i.e. if the equation

$$\hat{Q}_1 = \sum_{i,j} Q_{ij}^{(1)} \hat{a}_i^\dagger \hat{a}_j \quad (52.17)$$

see (51.38)] is to be observed.

Since $Q_{ij}^{(1)}$ are simply numbers, a matrix element of the operator (52.17) has the following form:

$$\begin{aligned} \langle n_k=0, n_l=1 | \sum_{i,j} Q_{ij}^{(1)} \hat{a}_i^\dagger \hat{a}_j | n_k=1, n_l=0 \rangle \\ = \sum_{i,j} Q_{ij}^{(1)} \langle n_k=0, n_l=1 | \hat{a}_i^\dagger \hat{a}_j | n_k=1, n_l=0 \rangle \quad (52.18) \end{aligned}$$

The expression obtained coincides with (52.14) if we assume that

$$\begin{aligned} \langle n_k=0, n_l=1 | \hat{a}_i^\dagger \hat{a}_j | n_k=1, n_l=0 \rangle \\ = \begin{cases} \prod_{s=k+1}^{l-1} (1 - 2n_s) & \text{when } i = l, j = k \\ 0 & \text{when } i \neq l \text{ or } j \neq k \end{cases} \quad (52.19) \end{aligned}$$

Hence, the operators must satisfy the condition

$$\langle n_k=0, n_l=1 | \hat{a}_l^\dagger \hat{a}_k | n_k=1, n_l=0 \rangle = \prod_{s=k+1}^{l-1} (1 - 2n_s) \quad (52.20)$$

This condition will be observed if we determine the operators with the aid of the following relations:

$$\hat{a}_k \psi_{n_1, n_2, \dots, n_k, \dots} = \prod_{s=1}^{k-1} (1 - 2n_s) \psi_{n_1, n_2, \dots, n_{k-1}, \dots} \quad (52.21)$$

$$\hat{a}_k^\dagger \psi_{n_1, n_2, \dots, n_k, \dots} = \prod_{s=1}^{k-1} (1 - 2n_s) \psi_{n_1, n_2, \dots, n_{k+1}, \dots} \quad (52.22)$$

where n_s stands for the occupation numbers of the function which the operator acts on. Indeed, by consecutively applying the operators determined by these relations to the function ψ for which $n_k = 1$ and $n_l = 0$, we obtain a train of transformations

$$\begin{aligned} \hat{a}_l^\dagger \hat{a}_k \psi_{n_k=1, n_l=0} &= \hat{a}_l^\dagger \prod_{s=1}^{k-1} (1 - 2n_s) \psi_{n_k=0, n_l=0} \\ &= \prod_{s=1}^{k-1} (1 - 2n_s) \prod_{s=1}^{l-1} (1 - 2n_s) \psi_{n_k=0, n_l=1} \quad (52.23) \end{aligned}$$

The factor numbered k in the second product \prod_s equals $+1$ so that the psi-function which the operator \hat{a}_l^\dagger acts on corresponds to the state

with $n_k = 0$. The right-hand side of relation (52.23) can therefore be transformed as follows:

$$\begin{aligned} \prod_{s=1}^{k-1} (1 - 2n_s) \prod_{s=1}^{l-1} (1 - 2n_s) \\ = \prod_{s=1}^{k-1} (1 - 2n_s)^2 \prod_{s=k+1}^{l-1} (1 - 2n_s) = \prod_{s=k+1}^{l-1} (1 - 2n_s). \end{aligned}$$

[we have discarded the factor $(1 - 2n_k)$ equal to unity]. Introducing this result into (52.23), we obtain

$$\hat{a}_k^\dagger \hat{a}_k \psi_{n_k=1, n_l=0} = \prod_{s=k+1}^{l-1} (1 - 2n_s) \psi_{n_k=0, n_l=1} \quad (52.24)$$

Finally, performing scalar multiplication of both sides of (52.24) by $\psi_{n_k=0, n_l=1}$, we arrive at expression (52.20) (the scalar product of a normalized function with itself is unity).

Let us find the commutation rules for the operators determined by relations (52.21) and (52.22). We act consecutively with the operators \hat{a}_k and \hat{a}_k^\dagger on the function $\psi_{n_k=1}$:

$$\begin{aligned} \hat{a}_k^\dagger \hat{a}_k \psi_{n_k=1} &= \hat{a}_k^\dagger \left\{ \prod_{s=1}^{k-1} (1 - 2n_s) \psi_{n_k=0} \right\} \\ &= \prod_{s=1}^{k-1} (1 - 2n_s) \prod_{s=1}^{k-1} (1 - 2n_s) \psi_{n_k=1} = \psi_{n_k=1} \quad (52.25) \end{aligned}$$

We must note that the action of the operator \hat{a}_k on the function $\psi_{n_k=0}$ gives zero. Indeed, let us write purely formally in accordance with (52.21) the following equation:

$$\hat{a}_k \psi_{n_k=0} = \prod_{s=1}^{k-1} (1 - 2n_s) \psi_{n_k=-1} \quad (52.26)$$

But there cannot be a state with $n_k = -1$. A non-realized state has $\psi \equiv 0$ (the equality of the psi-function to zero signifies the absence of a state, see p. 13). Hence, the expression on the right in (52.26) equals zero. In a similar way, we arrive at the conclusion that $\hat{a}_k^\dagger \psi_{n_k=1}$ is also zero (states with $n_k = 2$ cannot exist). It follows from what has been said above that

$$\hat{a}_k \hat{a}_k^\dagger \psi_{n_k=1} = 0 \quad (52.27)$$

Relations (52.25) and (52.27) signify that as applied to the function $\psi_{n_k=1}$, we have

$$\hat{a}_k^\dagger \hat{a}_k = 1, \quad \hat{a}_k \hat{a}_k^\dagger = 0 \quad (52.28)$$

Similar calculations show that as applied to the function $\psi_{n_k=0}$, we have

$$\hat{a}_k^\dagger \hat{a}_k = 0, \quad \hat{a}_k \hat{a}_k^\dagger = 1 \quad (52.29)$$

The first equations in (52.28) and (52.29) allow us to write that the operator

$$\hat{a}_k^\dagger \hat{a}_k = n_k \quad (52.30)$$

Indeed, the action of this operator on a psi-function is equivalent to multiplication by unity when the function describes a state with $n_k = 1$, and it gives zero when the function describes a state with $n_k = 0$.

Equations (52.28) and (52.29) satisfy the general relation

$$\hat{a}_k \hat{a}_k^\dagger + \hat{a}_k^\dagger \hat{a}_k = 1 \quad (52.31)$$

A comparison of the relation obtained with (51.28) shows that the rules for commuting the operators \hat{a}_k and \hat{a}_k^\dagger differ for bosons and for fermions. This difference is due to the following reasons. For bosons, the operators acting on different occupation numbers n_i are absolutely independent: each of them acts only on its own occupation number, the result of this action not depending on the values of the other occupation numbers. For fermions, on the other hand, the result of the action of the operator \hat{a}_i depends not only on the number n_i , but also on the occupation numbers of all the preceding states [on the numbers n_s with $s < i$, see (52.21)]. Consequently, the action of the arbitrarily taken operators \hat{a}_i and \hat{a}_j cannot be considered as independent.

The correctness of the following relations is quite evident:

$$\hat{a}_k \hat{a}_l^\dagger + \hat{a}_l^\dagger \hat{a}_k = 0 \quad (k \neq l) \quad (52.32)$$

$$\hat{a}_k \hat{a}_l + \hat{a}_l \hat{a}_k = 0 \quad \left. \right\} \text{for any } k \text{ and } l \quad (52.33)$$

$$\hat{a}_k^\dagger \hat{a}_l^\dagger + \hat{a}_l^\dagger \hat{a}_k^\dagger = 0 \quad (52.34)$$

[compare with (51.29)-(51.31)]. Hence, the operators \hat{a}_k and \hat{a}_l (like \hat{a}_k^\dagger and \hat{a}_l^\dagger) when $k \neq l$ are anticommuting [see (10.21)], whereas for bosons, they commute.

We can combine relations (52.31) and (52.32) as follows:

$$\hat{a}_k \hat{a}_l^\dagger + \hat{a}_l^\dagger \hat{a}_k = \delta_{kl} \quad (52.35)$$

[compare with (51.32)].

Let us convince ourselves that when determining the operators \hat{a}_k and \hat{a}_k^\dagger with the aid of relations (52.21) and (52.22), the diagonal

matrix elements of the operator \hat{Q}_1 are also correct. Changing the designations of the indices in (52.24), we obtain

$$\hat{a}_i^\dagger \hat{a}_j \psi_{n_j=1, n_i=0} = \prod_{s=j+1}^{i-1} (1 - 2n_s) \psi_{n_j=0, n_i=1} \quad (52.36)$$

It is obvious that

$$\hat{a}_i^\dagger \hat{a}_j \psi_{n_j=0, n_i=0} = 0, \quad \hat{a}_i^\dagger \hat{a}_j \psi_{n_j=1, n_i=1} = 0, \quad \hat{a}_i^\dagger \hat{a}_j \psi_{n_j=0, n_i=1} = 0 \quad (52.37)$$

We write an expression for a diagonal matrix element of the operator (52.17):

$$\begin{aligned} \text{D.M.E.} &= \langle n_1, n_2, \dots | \sum_{i,j} Q_{ij}^{(1)} \hat{a}_i^\dagger \hat{a}_j | n_1, n_2, \dots \rangle \\ &= \sum_{i,j} Q_{ij}^{(1)} \langle n_1, n_2, \dots | \hat{a}_i^\dagger \hat{a}_j | n_1, n_2, \dots \rangle \end{aligned} \quad (52.38)$$

In the sum obtained, all the addends with $i \neq j$ are zero. Indeed, when one of the situations (52.37) occurs, the addend vanishes because the multiplicand in the scalar product of the functions equals zero. When (52.36) occurs, the addend will be proportional to the scalar product of functions with non-coinciding values of n_j , which owing to the orthogonality of the functions being multiplied is zero. Hence, we must retain only the addends for which $j = i$. As a result, (52.38) becomes

$$\text{D.M.E.} = \sum_i Q_{ii}^{(1)} \langle n_1, n_2, \dots | \hat{a}_i^\dagger \hat{a}_i | n_1, n_2, \dots \rangle$$

Finally, taking into account formula (52.30), we arrive at the expression

$$\text{D.M.E.} = \sum_i Q_{ii}^{(1)} n_i \langle n_1, n_2, \dots | n_1, n_2, \dots \rangle = \sum_i n_i Q_{ii}^{(1)}$$

that coincides with (52.17).

We have thus shown that if for fermions we determine the operators \hat{a}_k and \hat{a}_k^\dagger with the aid of relations (52.21) and (52.22), for the operator \hat{Q}_1 in the occupation number representation we obtain the same expression as for bosons [see (52.17) and (51.38)]. Correspondingly, all the other formulas will be the same. We have in view formulas (51.41), (51.44), (51.46)-(51.48). Formulas (51.50)-(51.52) expressing the operators of physical quantities in terms of the operators $\hat{\psi}(\xi)$ and $\hat{\psi}^+(\xi)$ [see (51.49)] also remain correct.

Chapter X

ATOMS AND MOLECULES

53. Methods of Calculating Atomic Systems

If the relativistic effects are comparatively small (as is usually the case), the Hamiltonian of an atomic system can be written as

$$\hat{H} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{r_i} \right) + \frac{1}{2} \sum_{i \neq k} \frac{e_i e_k}{r_{ik}} + \hat{V}_{LS} \quad (53.1)$$

(N is the number of electrons in an atom). Each addend in the first sum is the Hamiltonian of an individual electron moving in the Coulomb field of the stationary nucleus; the second sum takes the Coulomb interaction between the electrons into account; the operator \hat{V}_{LS} , which can be considered as a small perturbation, takes into account the interaction between the spins of the electrons, and also the interaction between the orbital and spin magnetic moments (the spin-orbit interaction).

A system of electrons in an atom is characterized by the orbital quantum number L (determining the total orbital angular momentum of the atom) and the spin quantum number S (determining the resultant spin of the atom). The angular momenta (orbital and spin) of the individual electrons are added to form the resultant angular momenta according to the rules established in Sec. 47. When no account is taken of the spin-orbit interaction, the energy of an atom does not depend on the orientation in space and the mutual orientation of the total orbital and total spin angular momenta. The energy levels of the atom are therefore $(2L + 1)(2S + 1)$ -fold degenerate.

The taking into account of the spin-orbit interaction leads to the energy depending on the mutual orientation of the orbital and spin angular momenta. Consequently, under the influence of the perturbation \hat{V}_{LS} , each of the degenerate levels splits up into a number of closely arranged levels differing in the values of the total angular momentum J . Altogether, there will be $2S + 1$ such values (when $S \leq L$), or $2L + 1$ (when $L \leq S$). Such splitting of the levels is called multiplet splitting, and the set of levels obtained is called fine structure.

The non-relativistic theory of the simplest single-electron atom was treated in Sec. 24. Spin-orbit interaction leads to the fact that

each of the levels we found there (except for the S -levels) splits into two close sublevels corresponding to $j = l \pm 1/2$. In the following sections, we shall briefly consider the theory of many-electron atoms, and also of the hydrogen molecule. We shall not deal with a number of matters treated in sufficient detail in general courses of physics (the designation and systematization of terms, electron configurations, D. Mendeleev's Periodic Table).

Even if we discard the term \hat{V}_{LS} in the Hamiltonian (53.1), the corresponding problem does not lend itself to exact solution. This is why a number of approximate methods are used in the theory of the atom, such as the perturbation theory, the variation method, the method of self-consistent field (the Hartree-Fock method), and the Thomas-Fermi statistical model. These methods are discussed in the following sections.

54. The Helium Atom

In the simplest theory of a two-electron atom, spin-orbit interaction is disregarded, and the energy of the Coulomb interaction of the electrons is treated as a perturbation. In this case, the Hamiltonian can be written as

$$\hat{H} = \hat{H}_0 + \hat{V}_e$$

where

$$\begin{aligned}\hat{H}_0 &= \left(-\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{2e^2}{r_1} \right) + \left(-\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{r_2} \right) \\ \hat{V}_e &= \frac{e^2}{r_{12}}\end{aligned}\quad (54.1)$$

[see formula (53.1)].

In the zero approximation, we solve the equation

$$\hat{H}_0 \psi^{(0)} = E^{(0)} \psi^{(0)} \quad (54.2)$$

similar to Eq. (46.1). According to the results obtained in Sec. 46 [see (46.7)], we have

$$\psi^{(0)} = \psi_1(r_1) \psi_2(r_2), \quad E^{(0)} = E_1 + E_2$$

where $\psi_i(r_i)$ and E_i are determined by the equation

$$\left(-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{2e^2}{r_i} \right) \psi_i(r_i) = E_i \psi_i(r_i)$$

We found the solution of such an equation in Sec. 24. By formulas (24.23) and (24.27) (we assume that $Z = 2$), we have

$$E^{(0)} = -\frac{\alpha}{n_1^2} - \frac{\alpha}{n_2^2} \quad (54.3)$$

$(\alpha = 2m_e e^4/\hbar^2 = 2e^2/r_0; r_0 \text{ is the Bohr radius})$

$$\psi^{(0)} = \psi_{n_1, l_1, m_1} (1) \psi_{n_2, l_2, m_2} (2) \quad (54.4)$$

The smallest value of the energy (i.e. the energy of the ground state) is obtained when $n_1 = n_2 = 1$. It is

$$E_0^{(0)} = -2\alpha = -\frac{4m_e e^4}{\hbar^2} = -\frac{4e^2}{r_0} \quad (54.5)$$

Both electrons are in the state $1s$ ($n = 1, l = 0$). According to the Pauli principle, the spins of the electrons in this case must be directed oppositely so that the total spin is zero. Consequently, the ground state of the helium atom is the parastate (see the beginning of Sec. 48). The total orbital angular momentum is also zero. Hence, the term of the ground state must be written¹ as 1S_0 .

The first-order correction to the energy (54.5) is calculated by the formula

$$\Delta E_0^{(1)} = \int \psi_{1, 0, 0}^2 (1) \psi_{1, 0, 0}^2 (2) \frac{e^2}{r_{12}} dV_1 dV_2 \quad (54.6)$$

[compare with (49.1), the function $\psi_{1, 0, 0}$ is real]. Expression (54.6) is just the mean energy of electrostatic interaction of the electrons, which in Sec. 49 was designated by the letter Q [see (49.5)].

We obtain an expression for $\psi_{1, 0, 0}$ by assuming that $Z = 2$ in the first of the formulas (24.33). Substitution of this expression into (54.6) yields

$$\Delta E_0^{(1)} = Q = \left(\frac{2}{r_0} \right)^6 \frac{1}{\pi^2} \int e^{-4(r_1+r_2)/r_0} \frac{e^2}{r_{12}} dV_1 dV_2$$

Calculations that we have omitted give the value

$$Q = \frac{5e^2}{4r_0}$$

(we must note that $Q > 0$). Hence, we obtain the following expression for the energy of the ground state of the helium atom in the first approximation of the perturbation theory:

$$E_0^{(1)} = E_0^{(0)} + Q = -\frac{4e^2}{r_0} + \frac{5e^2}{4r_0} = -\frac{11e^2}{4r_0} \quad (54.7)$$

¹ Recall that the term of an atom is written symbolically in the form ${}^{2S+1}L_J$, where S is the quantum number of the total spin, J is the quantum number of the total angular momentum (obtained by adding the orbital and spin angular momenta), and " L " is the symbol of the quantum number of the total orbital angular momentum (the value $L = 0$ is designated by the letter S , $L = 1$ by P , $L = 2$ by D , etc.).

The ionization energy of a helium atom equals the difference of the ground state energy of a singly charged helium ion ($-2e^2/r_0$) and the energy given by (54.7):

$$E_{\text{ioniz}} = -\frac{2e^2}{r_0} + \frac{11}{4} \frac{e^2}{r_0} = \frac{3}{4} \frac{e^2}{r_0} = 0.75 \text{ atomic unit}$$

The experimentally obtained value of the ionization energy is 0.90 atomic unit. Such a great discrepancy indicates that the perturbation (54.1) is not sufficiently small for the strict application of the perturbation theory.

Now let us consider the first excited state of the helium atom. The electron configuration $1s2s$ ($n_1 = 1, l_1 = 0, n_2 = 2, l_2 = 0$) corresponds to this state. The Pauli principle does not forbid the parallel spin of the electrons now, so that both the parastate ($S = 0$, term 1S_0) and the orthostate ($S = 1$, term 3S_1) are possible.

Equation (54.2) for no perturbation has two solutions:

$$\psi_1 = \psi_{1,0,0}(1)\psi_{2,0,0}(2) \text{ and } \psi_2 = \psi_{2,0,0}(1)\psi_{1,0,0}(2) \quad (54.8)$$

differing in the transposition of the electrons (the numbers 1 and 2 stand for the sets of space coordinates of the first and second electrons). Both solutions correspond to the same energy $E = E_1 + E_2$. Consequently, we have to do with what is called **exchange degeneracy** that doubles the number of states. As a result, the parastate ($S = 0, \sigma = 0$) and each of the three orthostates ($S = 1, \sigma = 1, 0, -1$) are doubly degenerate. Therefore, to calculate the energy of the excited states of the helium atom, we must use the theory set out in Sec. 31.

For two-fold degeneracy, the secular equation (31.10) has the form

$$\begin{vmatrix} V_{11} - \Delta E^{(1)} & V_{12} \\ V_{21} & V_{22} - \Delta E^{(1)} \end{vmatrix} = 0$$

where

$$V_{11} = \int \psi_{100}^*(1)\psi_{200}^*(2) \frac{e^2}{r_{12}} \psi_{100}(1)\psi_{200}(2) dV_1 dV_2$$

$$V_{12} = \int \psi_{100}^*(1)\psi_{200}^*(2) \frac{e^2}{r_{12}} \psi_{200}(1)\psi_{100}(2) dV_1 dV_2$$

$$V_{21} = \int \psi_{200}^*(1)\psi_{100}^*(2) \frac{e^2}{r_{12}} \psi_{100}(1)\psi_{200}(2) dV_1 dV_2$$

$$V_{22} = \int \psi_{200}^*(1)\psi_{100}^*(2) \frac{e^2}{r_{12}} \psi_{200}(1)\psi_{100}(2) dV_1 dV_2$$

The expressions for V_{11} and V_{22} differ only in the designations of the integration variables. The same relates to V_{12} and V_{21} . Consequently, $V_{11} = V_{22}$ and $V_{12} = V_{21}$. In addition, a comparison with

formulas (49.5) and (49.6) shows that $V_{11} = V_{22} = Q$, and $V_{12} = V_{21} = A$.

The secular equation thus becomes

$$\begin{vmatrix} Q - \Delta E^{(1)} & A \\ A & Q - \Delta E^{(1)} \end{vmatrix} = 0$$

Expanding the determinant, we obtain $[Q - \Delta E^{(1)}]^2 = A^2$, whence $Q - \Delta E^{(1)} = \pm A$. Correspondingly for $\Delta E^{(1)}$, we obtain the values

$$\Delta E_1^{(1)} = Q + A, \quad \Delta E_2^{(1)} = Q - A$$

where Q is the Coulomb integral (49.5), and A is the exchange integral (49.6). The plus sign relates to the parastate ($S = 0$), and the minus sign to the orthostate ($S = 1$).

By (24.33), for $Z = 2$ we have

$$\begin{aligned} \psi_{1,0,0} &= \left(\frac{2}{r_0}\right)^{3/2} \frac{1}{\sqrt{\pi}} e^{-2r/r_0}, \quad \psi_{2,0,0} = \left(\frac{2}{r_0}\right)^{3/2} \\ &\quad \times \frac{1}{4\sqrt{2\pi}} e^{-r/r_0} \left(2 - \frac{r}{r_0}\right) \end{aligned}$$

Introducing these functions into formulas (49.5) and (49.6) instead of ψ_m , and ψ_{m_s} , we can evaluate the quantities Q and A . They are both found to be positive. Consequently, in the first approximation of the perturbation theory, the energy of the parastate

$$E_{\text{para}}^{(1)} = -\frac{5}{2} \frac{e^2}{r_0} + Q + A$$

is greater by $2A$ than the energy of the orthostate

$$E_{\text{ortho}}^{(1)} = -\frac{5}{2} \frac{e^2}{r_0} + Q - A$$

A similar result is also obtained for other excited states.

Let us write the total psi-functions for the excited para- and ortho-states:

$$\psi_{\text{para}} = \psi_s(1, 2) \varphi_{0,0}(1, 2)$$

where the first factor is determined by formula (49.2), and the second by formula (48.20);

$$\psi_{\text{ortho},1} = \psi_a(1, 2) \varphi_{1,1}(1, 2)$$

$$\psi_{\text{ortho},2} = \psi_a(1, 2) \varphi_{1,0}(1, 2)$$

$$\psi_{\text{ortho},3} = \psi_a(1, 2) \varphi_{1,-1}(1, 2)$$

where the first factor is determined by formula (49.3), and $\varphi_{1,1}$, $\varphi_{1,0}$, and $\varphi_{1,-1}$ by formulas (48.17)-(48.19).

It can be seen from the above that the energy levels of the helium atom are divided into two systems: levels of parastates, which are singlets, and levels of orthostates, which are triplets. In an approximation taking no account of spin-orbit interaction, transitions between singlet and triplet states with the emission and absorption of light are forbidden. Therefore, in this approximation, the singlet and triplet states of the helium atom are independent. For this reason, the lowest triplet state is metastable. A helium atom getting into such a state will remain in it for a very long time (of the order of months). Helium atoms in singlet and triplet states can thus be considered as two different types of atoms known as **parahelium** and **orthohelium**.

Parahelium atoms have no magnetic moment and form a diamagnetic gas. Orthohelium atoms have a magnetic moment and form a paramagnetic gas. The spectral lines of parahelium atoms are singlets. The orthohelium lines consist of three close lines (triplets). This is due to the fact that in states corresponding to the electron configuration $1s2p$ and in other states with $L \neq 0$, the degeneracy of the levels corresponding to the orthostates is removed owing to spin-orbit interaction.

55. The Variation Method

The variation method allows us to obtain approximate values of the energy and psi-functions of the ground and first excited states of quantum systems without resorting to the perturbation theory. The method is based on a number of inequalities, the first of which is

$$E_0 \leq \langle \psi | \hat{H} \psi \rangle \quad (55.1)$$

where E_0 is the energy of the ground state, \hat{H} is the Hamiltonian of the system, and ψ is an arbitrary function satisfying the normalization condition

$$\langle \psi | \psi \rangle = 1 \quad (55.2)$$

To prove relation (55.1), let us expand ψ in the eigenfunctions ψ_m of the operator \hat{H} :

$$\psi = \sum_{m=0}^{\infty} a_m \psi_m, \text{ where } \sum_{m=0}^{\infty} |a_m|^2 = 1 \quad (55.3)$$

Introduction of this expansion into the factor on the right in (55.1) yields

$$\begin{aligned} \langle \psi | \hat{H} \psi \rangle &= \sum_{m,n=0}^{\infty} a_m^* a_n \langle \psi_m | \hat{H} \psi_n \rangle = \sum_{m,n=0}^{\infty} a_m^* a_n E_n \langle \psi_m | \psi_n \rangle \\ &= \sum_{m,n=0}^{\infty} a_m^* a_n E_n \delta_{mn} = \sum_{m=0}^{\infty} |a_m|^2 E_m \geq E_0 \sum_{m=0}^{\infty} |a_m|^2 = E_0 \end{aligned}$$

which coincides with (55.1). An equality sign may be obtained when of all the addends of the sum $\sum |a_m|^2 E_m$ only the one corresponding to $m = 0$ is non-zero. This will happen if we take ψ_0 as ψ in (55.1).

Hence, calculation of the energy E_0 of the ground state of the system consists in evaluating the minimum of the expression $\mathcal{J}_0 = \langle \psi | \hat{H} \psi \rangle$ by variation of the normalized function ψ :

$$E_0 = \min \mathcal{J}_0 = \min \langle \psi | \hat{H} \psi \rangle \quad (\langle \psi | \psi \rangle = 1) \quad (55.4)$$

In practice, calculation of E_0 consists in choosing, on the basis of physical considerations or experimental data, the trial function $\psi_{0, \text{tr}}(x, y, z, \alpha, \beta, \dots)$ containing a certain number of unknown parameters α, β, \dots and satisfying the condition (55.2). Calculation of the product

$$\mathcal{J}_0 = \langle \psi_{0, \text{tr}}(x, y, z, \alpha, \beta, \dots) | \hat{H} \psi_{0, \text{tr}}(x, y, z, \alpha, \beta, \dots) \rangle \quad (55.5)$$

leads to the function $\mathcal{J}_0(\alpha, \beta, \dots)$ that depends on the parameters α, β, \dots . Next we find the minimum of this function by solving the system of equations

$$\frac{\partial \mathcal{J}_0}{\partial \alpha} = \frac{\partial \mathcal{J}_0}{\partial \beta} = \dots = 0$$

as a result of which we obtain the values α_0, β_0, \dots . With a good choice of the trial function, the value of $\mathcal{J}_0(\alpha_0, \beta_0, \dots)$ is close to the true value of E_0 even with a small number of the parameters used (one or two). The expression

$$\psi_{0, \text{tr}}(x, y, z, \alpha_0, \beta_0, \dots) \quad (55.6)$$

will be an approximate one for the psi-function of the ground state.

To obtain an approximate value of the energy and the psi-function for the first excited level, we shall proceed from the relation

$$E_1 \leq \langle \psi | \hat{H} \psi \rangle \quad (55.7)$$

where E_1 is the energy of the first excited state, and ψ is an arbitrary function satisfying the conditions

$$\langle \psi | \psi \rangle = 1, \quad \langle \psi_0 | \psi \rangle = 0 \quad (55.8)$$

(ψ_0 is the psi-function of the ground state). To prove relation (55.7), let us expand the function ψ in the eigenfunctions ψ_m of the operator \hat{H} :

$$\psi = \sum_{m=1}^{\infty} b_m \psi_m, \quad \text{where} \quad \sum_{m=1}^{\infty} |b_m|^2 = 1 \quad (55.9)$$

Unlike (55.3), there is no addend with $m = 0$ in these sums. This is due to the fact that owing to the condition $\langle \psi_0 | \psi \rangle = 0$, the coefficient $b_0 = 0$. Introduction of the expansion (55.9) into the factor on the right in (55.7) yields

$$\begin{aligned}\langle \psi | \hat{H} \psi \rangle &= \sum_{m, n=1}^{\infty} b_m^* b_n \langle \psi_m | \hat{H} \psi_n \rangle \\ &= \sum_{m=1}^{\infty} |b_m|^2 E_m \geq E_1 \sum_{m=1}^{\infty} |b_m|^2 = E_1\end{aligned}$$

which coincides with (55.7).

On the basis of (55.7), we take a trial function $\psi_{1, \text{tr}}(x, y, z, \gamma, \delta, \dots)$ satisfying the conditions (55.8) [we use the function (55.6) as ψ_0]. Having calculated $\mathcal{J}_1(\gamma, \delta, \dots)$, we find the minimum of this expression (obtained at values of the parameters equal to $\gamma_0, \delta_0, \dots$). Next we assume that $E_1 \approx \mathcal{J}_1(\gamma_0, \delta_0, \dots)$ and $\psi_1 \approx \psi_{1, \text{tr}}(x, y, z, \gamma_0, \delta_0, \dots)$.

The second excited level is determined as the minimum of the expression $\langle \psi_{2, \text{tr}} | \hat{H} \psi_{2, \text{tr}} \rangle$, where the conditions

$$\langle \psi_{2, \text{tr}} | \psi_{2, \text{tr}} \rangle = 1, \quad \langle \psi_0 | \psi_{2, \text{tr}} \rangle = 0, \quad \langle \psi_1 | \psi_{2, \text{tr}} \rangle = 0$$

are imposed onto $\psi_{2, \text{tr}}$, and so on.

The drawbacks of the variation method include the circumstance that the error of the results it gives remains indeterminate.

The method of calculation set out above is called the **direct variation method** or the **Ritz method**. We shall illustrate this method by using it to evaluate the energy of the ground state of a harmonic oscillator. In this case

$$\hat{H} = -\frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} + \frac{m_0 \omega^2 x^2}{2} \quad (55.10)$$

Let us take a very simple function that shrinks to zero when x tends to $\pm\infty$ as the trial function. Such a function has the form

$$\psi(x, \alpha) = A e^{-\alpha x^2/2} \quad (55.11)$$

($1/2$ has been introduced into the exponent for convenience). Its scalar square is

$$\langle \psi | \psi \rangle = A^2 \int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = A^2 \sqrt{\pi/\alpha}$$

(the Poisson integral). Consequently, the condition (55.2) will be satisfied if we assume that $A = (\alpha/\pi)^{1/4}$.

We evaluate expression (55.5):

$$\begin{aligned} \mathcal{J}(\alpha) = \langle \psi_{\text{tr}} | \hat{H} \psi_{\text{tr}} \rangle &= (\alpha/\pi)^{1/2} \int_{-\infty}^{+\infty} e^{-\alpha x^2/2} \left(-\frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} + \frac{m_0 \omega^2 x^2}{2} \right) e^{-\alpha x^2/2} dx \\ &= \frac{\hbar^2 \alpha}{4m_0} + \frac{m_0 \omega^2}{4\alpha} \quad (55.12) \end{aligned}$$

Let us differentiate this expression with respect to α and equate the derivative to zero:

$$\frac{\hbar^2}{4m_0} - \frac{m_0 \omega^2}{4\alpha^2} = 0$$

Hence, $\alpha_0 = m_0 \omega / \hbar$. Substitution of this value into (55.11) and (55.12) yields

$$E_0 = \mathcal{J}(\alpha_0) = \frac{\hbar \omega}{2}, \quad \psi_0(x) = \left(\frac{m_0 \omega}{\pi \hbar} \right)^{1/4} \exp \left(-\frac{m_0 \omega x^2}{2\hbar} \right)$$

A comparison with (25.9) and (25.15) shows that the trial function was chosen so successfully that the variation method gave exact values of the energy and the psi-function of the ground state.

In addition to the direct variation method set out above, in which the parameters of the trial function are varied, there is a more general variation method in which the form itself of the psi-function is varied. This more general method is equivalent to solving the Schrödinger equation. Indeed, the condition for the minimum of the quantity $\langle \psi | \hat{H} \psi \rangle$ reduces to the equation

$$\langle \delta \psi | \hat{H} \psi \rangle + \langle \psi | \hat{H} \delta \psi \rangle = 0 \quad (55.13)$$

Let us write the function ψ in the form $\psi = \psi_1 + i\psi_2$. Hence, $\psi^* = \psi_1 - i\psi_2$, $\delta \psi = \delta \psi_1 + i\delta \psi_2$, $\delta \psi^* = \delta \psi_1 - i\delta \psi_2$ and, consequently, $(\delta \psi)^* = \delta \psi^*$.

Taking advantage of the Hermitian character of the operator \hat{H} , let us transform the second term of formula (55.13) as follows:

$$\langle \psi | \hat{H} \delta \psi \rangle = \langle \hat{H} \psi | \delta \psi \rangle = \langle \delta \psi | \hat{H} \psi \rangle^* = \langle \delta \psi^* | \hat{H}^* \psi^* \rangle$$

As a result, (55.13) becomes

$$\langle \delta \psi | \hat{H} \psi \rangle + \langle \delta \psi^* | \hat{H}^* \psi^* \rangle = 0 \quad (55.14)$$

From the additional condition $\langle \psi | \psi \rangle = 1$, it follows that

$$\langle \delta \psi | \psi \rangle + \langle \psi | \delta \psi \rangle = \langle \delta \psi | \psi \rangle + \langle \delta \psi^* | \psi^* \rangle = 0 \quad (55.15)$$

According to the rules for finding a potential extremum, we must add relations (55.14) and (55.15), multiplying the latter by an indeterminate Lagrangian multiplier which we designate by $-E$. Hence,

the following equation is the condition for the minimum of the expression $\langle \psi | \hat{H} \psi \rangle$ with the additional condition that $\langle \psi | \psi \rangle = 1$:

$$\langle \delta\psi | \hat{H} \psi \rangle + \langle \delta\psi^* | \hat{H}^* \psi^* \rangle - E (\langle \delta\psi | \psi \rangle + \langle \delta\psi^* | \psi^* \rangle) = 0$$

Taking advantage of the distributivity of the scalar product of the functions, let us rewrite the equation obtained as follows:

$$\langle \delta\psi | (\hat{H}\psi - E\psi) \rangle + \langle \delta\psi^* | (\hat{H}^*\psi^* - E\psi^*) \rangle = 0$$

Introducing $\delta\psi = \delta\psi_1 + i\delta\psi_2$ and $\delta\psi^* = \delta\psi_1 - i\delta\psi_2$ and performing simple transformations, we obtain

$$\langle \delta\psi_1 | [(\hat{H}\psi - E\psi) + (\hat{H}^*\psi^* - E\psi^*)] \rangle$$

$$+ i \langle \delta\psi_2 | [(\hat{H}\psi - E\psi) - (\hat{H}^*\psi^* - E\psi^*)] \rangle = 0 \quad (55.16)$$

The real and the imaginary parts of the function ψ can be varied independently of each other. Therefore, Eq. (55.16) must be obeyed upon arbitrary and independent variations of $\delta\psi_1$ and $\delta\psi_2$. This is possible only if the following two equations are observed:

$$(\hat{H}\psi - E\psi) + (\hat{H}^*\psi^* - E\psi^*) = 0$$

$$(\hat{H}\psi - E\psi) - (\hat{H}^*\psi^* - E\psi^*) = 0$$

By summatting these two equations, we arrive at the Schrödinger equation: $\hat{H}\psi = E\psi$. Subtracting them from each other, we obtain an equation that is the complex conjugate to the Schrödinger equation.

The variation method in which not the parameters, but the form itself of the function ψ is varied, is thus indeed equivalent to the solution of the Schrödinger equation.

In this way, we obtain $E = E_0$ and $\psi = \psi_0$ for the ground state of the system being considered. To obtain the following stationary states, we must perform variation by imposing on ψ the additional condition $\langle \psi_0 | \psi \rangle = 0$, where ψ_0 is the function found above, then the additional condition $\langle \psi_1 | \psi \rangle = 0$, and so on.

We shall note in concluding that the Schrödinger equation is also obtained by equating to zero the variation of the expression $\mathcal{J} = \langle \psi | \hat{H} \psi \rangle$ when the functions ψ and ψ^* are considered to be formally independent and only one of them, say ψ^* , is varied. To show this, we shall write \mathcal{J} as

$$\mathcal{J} = \int \psi^* \hat{H} \psi \, dV \quad \left(\int \psi^* \psi \, dV = 1 \right)$$

Having varied ψ^* , we write the condition for an extremum

$$\int \delta\psi^* \hat{H} \psi \, dV - E \int \delta\psi^* \psi \, dV = \int \delta\psi^* (\hat{H}\psi - E\psi) \, dV = 0 \quad (55.17)$$

($-E$ is a Lagrangian multiplier). Owing to the arbitrariness of $\delta\psi^*$, the equation $\hat{H}\psi - E\psi = 0$ must hold.

56. The Method of the Self-Consistent Field

The idea of the method of calculating atomic systems developed by D. Hartree and V. Fock consists in that every electron of an atom is treated as moving in a "self-consistent" field set up by the nucleus and all the other electrons. The electrons are considered to move independently of one another in the sense that each of them is described by its own psi-function $\psi_k(\mathbf{r}_k)$ satisfying the equation¹

$$\left[-\frac{\hbar^2}{2m_e} \nabla_k^2 - \frac{Ze^2}{r_k} \sum_j' \int |\psi_j(\mathbf{r}_j)|^2 \frac{e^2}{r_{jk}} dV_j \right] \psi_k(\mathbf{r}_k) = E_k \psi_k(\mathbf{r}_k) \quad (k = 1, 2, \dots, Z). \quad (56.1)$$

The sum in the Hamiltonian is the mean energy of interaction of the k -th electron with all the other electrons in the states $\psi_j(\mathbf{r}_j)$. Equation (56.1) takes no account of spin-spin and spin-orbit interactions.

Equation (56.1) can be obtained with the aid of the variation method. For this purpose, let us take the trial function in the form

$$\psi_{\text{tr}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z) = \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \dots \psi_Z(\mathbf{r}_Z). \quad (56.2)$$

When the spin-orbit interaction is disregarded, the Hamiltonian has the form

$$\hat{H} = \sum_k \left(-\frac{\hbar^2}{2m_e} \nabla_k^2 - \frac{Ze^2}{r_k} \right) + \frac{1}{2} \sum_{j, k}' \frac{e^2}{r_{jk}} = \sum_k \hat{H}_k + \frac{1}{2} \sum_{j, k}' \hat{H}_{jk} \quad (56.3)$$

Substitution of (56.2) and (56.3) into (55.5) yields the expression

$$\begin{aligned} \mathcal{J} &= \int \psi_1^*(\mathbf{r}_1) \dots \psi_Z^*(\mathbf{r}_Z) \left[\sum_k \hat{H}_k \right. \\ &\quad \left. + \frac{1}{2} \sum_{j, k}' \hat{H}_{jk} \right] \psi_1(\mathbf{r}_1) \dots \psi_Z(\mathbf{r}_Z) dV_1 \dots dV_Z \\ &= \sum_k \int \psi_1^* \psi_1 dV_1 \dots \int \psi_k^* \hat{H}_k \psi_k dV_k \dots \int \psi_Z^* \psi_Z dV_Z \\ &\quad + \frac{1}{2} \sum_{j, k}' \int \psi_1^* \psi_1 dV_1 \dots \int \psi_j^* \psi_k^* \hat{H}_{jk} \psi_j \psi_k dV_j dV_k \dots \int \psi_Z^* \psi_Z dV_Z \\ &= \sum_k \int \psi_k^* \hat{H}_k \psi_k dV_k + \frac{1}{2} \sum_{j, k}' \int \psi_j^* \psi_k^* \hat{H}_{jk} \psi_j \psi_k dV_j dV_k \quad (56.4) \end{aligned}$$

¹ Here and in all the following sums, the prime signifies that the values $j \neq k$ are excluded.

Let us find the variation of expression (56.4) provided that only ψ_{tr}^* is varied [see (55.17)]:

$$\begin{aligned}\delta\mathcal{J} = \sum_k \int \delta\psi_k^* \hat{H}_k \psi_k dV_k + \frac{1}{2} \sum'_{j, k} \left[\int \delta\psi_j^* \psi_k^* \hat{H}_{jk} \psi_j \psi_k dV_j dV_k \right. \\ \left. + \int \psi_j^* \delta\psi_k^* \hat{H}_{jk} \psi_j \psi_k dV_j dV_k \right]\end{aligned}$$

Exchanging the places of the dummy indices j and k in the first integral in the brackets and taking into account that $\hat{H}_{kj} = \hat{H}_{jk}$ [see (56.3)], we obtain an expression coinciding with the second term. Consequently,

$$\begin{aligned}\delta\mathcal{J} = \sum_k \delta\psi_k^* \hat{H}_k \psi_k dV_k + \sum'_{j, k} \int \delta\psi_k^* \psi_j^* \hat{H}_{jk} \psi_j \psi_k dV_j dV_k \\ = \sum_k \int \delta\psi_k^* \left[\hat{H}_k + \sum'_{j} \int \psi_j^* \hat{H}_{jk} \psi_j dV_j \right] \psi_k dV_k \quad (56.5)\end{aligned}$$

Each of the ψ_k 's obeys the condition $\int \psi_k^* \psi_k dV_k = 1$. By varying ψ_k^* , we obtain

$$\int \delta\psi_k^* \psi_k dV_k = 0 \quad (k = 1, 2, \dots, Z) \quad (56.6)$$

To find an extremum, we multiply each of the expressions (56.6) by its indeterminate Lagrangian multiplier $-E_k$ and, after summatting all the products with the variation (56.5), we equate the expression obtained to zero. The result is

$$\sum_k \int \delta\psi_k^* \left[\hat{H}_k + \sum'_{j} \int \psi_j^* \hat{H}_{jk} \psi_j dV_j - E_k \right] \psi_k dV_k = 0 \quad (56.7)$$

The variations $\delta\psi_k^*$ are independent of one another. Therefore, Eq. (56.7) will be observed only provided that

$$\left[\hat{H}_k + \sum'_{j} \int \psi_j^* \hat{H}_{jk} \psi_j dV_j \right] \psi_k = E_k \psi_k \quad (k = 1, 2, \dots, Z) \quad (56.8)$$

Introducing $\hat{H}_{jk} = e^2/r_{jk}$ into (56.8), we arrive at the system of equations (56.1).

Expression (56.8) is a system of Z non-linear integro-differential equations with whose aid, in principle, we can find Z functions $\psi_k(\mathbf{r}_k)$. The direct solution of these equations is impossible, and

in this connection we have to use the method of successive approximations.

In the zero approximation, we adopt the psi-functions $\psi_j^{(0)}$ of a hydrogen-like atom as the functions $\psi_j(\mathbf{r}_j)$. With their aid, we calculate the expression

$$U_k^{(0)}(\mathbf{r}_k) = \sum_j' \int |\psi_j^{(0)}|^2 \frac{e^2}{r_{jk}} dV_j$$

Introducing it into (56.8), we obtain a system of independent equations for determining the functions ψ_k and the energies E_k in the first approximation:

$$[\hat{H}_k + U_k^{(0)}(\mathbf{r}_k)] \psi_k^{(1)} = E_k^{(1)} \psi_k^{(1)} \quad (56.9)$$

Having solved this system and found the functions $\psi_k^{(1)}$, we evaluate

$$U_k^{(1)}(\mathbf{r}_k) = \sum_j' \int |\psi_j^{(1)}|^2 \frac{e^2}{r_{jk}} dV_j$$

Next we solve the system

$$[\hat{H}_k + U_k^{(1)}(\mathbf{r}_k)] \psi_k^{(2)} = E_k^{(2)} \psi_k^{(2)} \quad (56.10)$$

and so on. This process is continued until a new approximation results in virtually the same functions ψ_k that were obtained in the preceding approximation. The field

$$\varphi_k(\mathbf{r}_k) = \sum_j' \int |\psi_j^{(0)}|^2 \frac{e}{r_{jk}} dV_j \quad (56.11)$$

calculated with the aid of such functions is called **self-consistent** (the symbol φ stands for the potential of an electric field).

In performing the calculations, we transform the expressions $U_k(\mathbf{r}_k)$ into spherically symmetric functions $U_k(r_k)$ by averaging over the directions of the position vector \mathbf{r}_k . This allows us to seek the solutions of Eqs. (56.9), (56.10), etc. in the form of products of spherical functions and functions depending only on r_k .

The one-particle zero-approximation functions are chosen with a view to the electron configuration of the state of the atom being considered. The electron configuration is not the same for the ground and excited states of an atom, correspondingly, the self-consistent field and the energy of the atom are also different.

According to the variation principle, the energy of an atom equals the minimum value of expression (56.4). The minimum value is

obtained when we introduce functions determined from equations (56.8) into (56.4). Let us write (56.4) in the form

$$\begin{aligned} \mathcal{J} &= \sum_k \int \psi_k^* \hat{H}_k \psi_k dV_k + \sum'_{j, k} \int \psi_j^* \psi_k^* \hat{H}_{jk} \psi_j \psi_k dV_j dV_k \\ &\quad - \frac{1}{2} \sum'_{j, k} \int \psi_j^* \psi_k^* \hat{H}_{jk} \psi_j \psi_k dV_j dV_k \\ &= \sum_k \int \psi_k^* \left[\hat{H}_k + \sum_j' \int \psi_j^* \hat{H}_{jk} \psi_j dV_j \right] \psi_k dV_k \\ &\quad - \frac{1}{2} \sum'_{j, k} \int \psi_j^* \psi_k^* \hat{H}_{jk} \psi_j \psi_k dV_j dV_k \end{aligned}$$

If we introduce functions satisfying Eqs. (56.8), the first sum transforms into $\sum \int \psi_k^* E_k \psi_k dV_k = \sum E_k$ (the quantity \mathcal{J} transforms into the energy E of an atom). Hence,

$$\begin{aligned} E &= \sum_k E_k - \frac{1}{2} \sum'_{j, k} \int \psi_j^* \psi_k^* \hat{H}_{jk} \psi_j \psi_k dV_j dV_k \\ &= \sum_k E_k - \frac{1}{2} \sum'_{j, k} \int |\psi_j|^2 |\psi_k|^2 \frac{e^2}{r_{jk}} dV_j dV_k \quad (56.12) \end{aligned}$$

The result obtained signifies that the energy of an atom is less than the sum of the energies of the one-particle states by the energy of the electrostatic interaction of the electrons. The explanation is that the interaction energy is taken into account twice in $\sum E_k$. For example, E_1 includes the energy of interaction of the first electron with all the others, including the second one, E_2 includes the energy of interaction of the second electron with all the others, including the first one, and so on.

The method set out above was developed by Hartree. Equation (56.1) was derived from the variation principle by Fock. Hartree's method does not take the symmetry properties of the psi-functions into consideration. Fock improved the method, using a trial function that takes a correct account of the symmetry relative to the transposition of the electrons.

Let us use Fock's method to calculate the self-consistent field for the very simple case of a helium atom. In this case [see (56.3)], we have

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12} \quad (56.13)$$

We assume that the one-particle states do not coincide. With this assumption, the trial function must have the form

$$\psi_{\text{tr}} = \frac{1}{\sqrt{2}} [\psi_{m_1}(1) \psi_{m_2}(2) \pm \psi_{m_1}(1) \psi_{m_2}(2)]$$

where the plus sign relates to parastates and the minus to ortho-states [see (49.2) and (49.3)]. Accordingly,

$$\begin{aligned} \mathcal{J} &= \int \psi_{\text{tr}}^* \hat{H} \psi_{\text{tr}} dV_1 dV_2 \\ &= \frac{1}{2} \int [\psi_{m_1}^*(1) \psi_{m_2}^*(2) \pm \psi_{m_1}^*(1) \psi_{m_2}^*(2)] \hat{H}_1 [\psi_{m_1}(1) \psi_{m_2}(2) \\ &\quad \pm \psi_{m_1}(1) \psi_{m_2}(2)] dV_1 dV_2 + \frac{1}{2} \int [\psi_{m_1}^*(1) \psi_{m_2}^*(2) \pm \psi_{m_1}^*(1) \psi_{m_2}^*(2)] \\ &\quad \times \hat{H}_2 [\psi_{m_1}(1) \psi_{m_2}(2) \pm \psi_{m_1}(1) \psi_{m_2}(2)] dV_1 dV_2 \\ &\quad + \frac{1}{2} \int [\psi_{m_1}^*(1) \psi_{m_2}^*(2) \pm \psi_{m_1}^*(1) \psi_{m_2}^*(2)] \\ &\quad \times \hat{H}_{12} [\psi_{m_1}(1) \psi_{m_2}(2) \pm \psi_{m_1}(1) \psi_{m_2}(2)] dV_1 dV_2 \\ &= \mathcal{J}_1 + \mathcal{J}_2 + \mathcal{J}_{12} \quad (56.14) \end{aligned}$$

We calculate the first of the three terms:

$$\begin{aligned} \mathcal{J}_1 &= \frac{1}{2} \left\{ \int \psi_{m_1}^*(1) \psi_{m_2}^*(2) \hat{H}_1 \psi_{m_1}(1) \psi_{m_2}(2) dV_1 dV_2 \right. \\ &\quad + \int \psi_{m_2}^*(1) \psi_{m_1}^*(2) \hat{H}_1 \psi_{m_2}(1) \psi_{m_1}(2) dV_1 dV_2 \\ &\quad \pm \int \psi_{m_1}^*(1) \psi_{m_2}^*(2) \hat{H}_1 \psi_{m_2}(1) \psi_{m_1}(2) dV_1 dV_2 \\ &\quad \left. \pm \int \psi_{m_2}^*(1) \psi_{m_1}^*(2) \hat{H}_1 \psi_{m_1}(1) \psi_{m_2}(2) dV_1 dV_2 \right\} \\ &= \frac{1}{2} \left\{ \int \psi_{m_1}^*(1) \hat{H}_1 \psi_{m_1}(1) dV_1 + \int \psi_{m_2}^*(1) \hat{H}_1 \psi_{m_2}(1) dV_1 \right\} \quad (56.15) \end{aligned}$$

(the remaining two integrals vanish owing to the orthogonality of the functions ψ_{m_1} and ψ_{m_2}). Similar calculations yield

$$\mathcal{J}_2 = \frac{1}{2} \left\{ \int \psi_{m_2}^*(2) \hat{H}_2 \psi_{m_2}(2) dV_2 + \int \psi_{m_1}^*(2) \hat{H}_2 \psi_{m_1}(2) dV_2 \right\} \quad (56.16)$$

A comparison of (56.15) and (56.16) shows that the corresponding integrals in them differ only in the designation of the integration variable. For example,

$$\int \psi_{m_1}^*(1) \hat{H}_1 \psi_{m_1}(1) dV_1 = \int \psi_{m_1}^*(2) \hat{H}_2 \psi_{m_1}(2) dV_2$$

Consequently, the sum of expressions (56.15) and (56.16) can be written as

$$\mathcal{J}_1 + \mathcal{J}_2 = \int \psi_{m_1}^*(1) \hat{H}_1 \psi_{m_1}(1) dV_1 + \int \psi_{m_2}^*(2) \hat{H}_2 \psi_{m_2}(2) dV_2 \quad (56.17)$$

Now let us calculate the third term in (56.14):

$$\begin{aligned} \mathcal{J}_{12} &= \frac{1}{2} \left\{ \int \psi_{m_1}^*(1) \psi_{m_2}^*(2) \hat{H}_{12} \psi_{m_1}(1) \psi_{m_2}(2) dV_1 dV_2 \right. \\ &\quad + \int \psi_{m_2}^*(1) \psi_{m_1}^*(2) \hat{H}_{12} \psi_{m_2}(1) \psi_{m_1}(2) dV_1 dV_2 \\ &\pm \int \psi_{m_1}^*(1) \psi_{m_2}^*(2) \hat{H}_{12} \psi_{m_2}(1) \psi_{m_1}(2) dV_1 dV_2 \\ &\quad \left. \pm \int \psi_{m_2}^*(1) \psi_{m_1}^*(2) \hat{H}_{12} \psi_{m_1}(1) \psi_{m_2}(2) dV_1 dV_2 \right\} \end{aligned}$$

Since $\hat{H}_{12} = \hat{H}_{21}$, the first and second, and also the third and fourth integrals differ only in the transposition of the integration variables 1 and 2. The integrals can therefore be combined pairwise. Adding the expression obtained to (56.17), we find that

$$\begin{aligned} \mathcal{J} &= \int \psi_{m_1}^*(1) \hat{H}_1 \psi_{m_1}(1) dV_1 + \int \psi_{m_2}^*(2) \hat{H}_2 \psi_{m_2}(2) dV_2 \\ &\quad + \int \psi_{m_1}^*(1) \psi_{m_2}^*(2) \hat{H}_{12} \psi_{m_1}(1) \psi_{m_2}(2) dV_1 dV_2 \\ &\pm \int \psi_{m_1}^*(1) \psi_{m_2}^*(2) \hat{H}_{12} \psi_{m_2}(1) \psi_{m_1}(2) dV_1 dV_2 \end{aligned}$$

Variation of the functions $\psi_{m_1}^*$ and $\psi_{m_2}^*$ yields

$$\begin{aligned} \delta \mathcal{J} &= \int \delta \psi_{m_1}^*(1) \hat{H}_1 \psi_{m_1}(1) dV_1 + \int \delta \psi_{m_2}^*(2) \hat{H}_2 \psi_{m_2}(2) dV_2 \\ &\quad + \int \delta \psi_{m_1}^*(1) \psi_{m_2}^*(2) \hat{H}_{12} \psi_{m_1}(1) \psi_{m_2}(2) dV_1 dV_2 \\ &\quad + \int \delta \psi_{m_2}^*(2) \psi_{m_1}^*(1) \hat{H}_{12} \psi_{m_1}(1) \psi_{m_2}(2) dV_1 dV_2 \\ &\pm \int \delta \psi_{m_1}^*(1) \psi_{m_2}^*(2) \hat{H}_{12} \psi_{m_2}(1) \psi_{m_1}(2) dV_1 dV_2 \\ &\quad \pm \int \delta \psi_{m_2}^*(2) \psi_{m_1}^*(1) \hat{H}_{12} \psi_{m_2}(1) \psi_{m_1}(2) dV_1 dV_2 \\ &= \int \delta \psi_{m_1}^*(1) \left\{ \hat{H}_1 \psi_{m_1}(1) + \left[\int \psi_{m_2}^*(2) \hat{H}_{12} \psi_{m_2}(2) dV_2 \right] \psi_{m_1}(1) \right\} dV_1 \\ &\quad \pm \left[\int \psi_{m_2}^*(2) \hat{H}_{12} \psi_{m_1}(2) dV_2 \right] \psi_{m_1}(1) dV_1 \\ &\quad + \int \delta \psi_{m_2}^*(2) \left\{ \hat{H}_2 \psi_{m_2}(2) + \left[\int \psi_{m_1}^*(1) \hat{H}_{12} \psi_{m_1}(1) dV_1 \right] \psi_{m_2}(2) \right\} dV_2 \end{aligned}$$

$$\begin{aligned} & \pm \left[\int \psi_{m_1}^*(1) \hat{H}_{12} \psi_{m_1}(1) dV_1 \right] \psi_{m_1}(2) \} dV_2 \\ & = \int \delta\psi_{m_1}^*(1) \{ [\hat{H}_1 + U_{m_2, m_1}] \psi_{m_1}(1) \pm U_{m_1, m_1} \psi_{m_1}(1) \} dV_1 \\ & \quad + \int \delta\psi_{m_1}^*(2) \{ [\hat{H}_2 + U_{m_1, m_1}] \psi_{m_1}(2) \pm U_{m_1, m_1} \psi_{m_1}(2) \} dV_2 \end{aligned}$$

where

$$U_{m_1, m_1} = \int \psi_{m_1}^*(1) \hat{H}_{12} \psi_{m_1}(1) dV_1 = \int |\psi_{m_1}(1)|^2 \frac{e^2}{r_{12}} dV_1 \quad (56.18)$$

is an integral taking into account the energy of the second electron in the averaged field of the first one,

$$U_{m_2, m_2} = \int \psi_{m_2}^*(2) \hat{H}_{12} \psi_{m_2}(2) dV_2 = \int |\psi_{m_2}(2)|^2 \frac{e^2}{r_{12}} dV_2 \quad (56.19)$$

is an integral taking into account the energy of the first electron in the averaged field of the second one, and

$$\begin{aligned} U_{m_1, m_2} &= \int \psi_{m_1}^*(1) \hat{H}_{12} \psi_{m_2}(1) dV_1 \\ U_{m_2, m_1} &= \int \psi_{m_2}^*(2) \hat{H}_{12} \psi_{m_1}(2) dV_2 \end{aligned} \quad (56.20)$$

are exchange integrals taking into account the correlation between the motion of the electrons due to the symmetry of position functions. Any integration variable may be taken in all four integrals.

The conditions $\int \psi_{m_1}^*(1) \psi_{m_1}(1) dV_1 = 1$ and $\int \psi_{m_2}^*(2) \psi_{m_2}(2) dV_2 = 1$ show that $\int \delta\psi_{m_1}^*(1) \psi_{m_1}(1) dV_1 = 0$ and $\int \delta\psi_{m_2}^*(2) \psi_{m_2}(2) dV_2 = 0$. Multiplying each of these variations by its Lagrangian multiplier (we designated these multipliers by $-E_1$ and $-E_2$) and adding the products to $\delta\mathcal{J}$, we obtain the condition for an extremum

$$\begin{aligned} & \int \delta\psi_{m_1}^*(1) \{ [\hat{H}_1 + U_{m_2, m_1} - E_1] \psi_{m_1}(1) \pm U_{m_1, m_1} \psi_{m_1}(1) \} dV_1 \\ & + \int \delta\psi_{m_2}^*(2) \{ [\hat{H}_2 + U_{m_1, m_1} - E_2] \psi_{m_2}(2) \pm U_{m_1, m_1} \psi_{m_2}(2) \} dV_2 = 0 \end{aligned}$$

With the arbitrary variations $\delta\psi_{m_1}^*$ and $\delta\psi_{m_2}^*$, the above condition will be observed only when both expressions in the braces are zero. We thus obtain a system of two equations

$$\begin{aligned} & [\hat{H}_1 + U_{m_2, m_1}] \psi_{m_1}(1) \pm U_{m_1, m_1} \psi_{m_1}(1) = E_1 \psi_{m_1}(1) \\ & ... [\hat{H}_2 + U_{m_1, m_1}] \psi_{m_2}(2) \pm U_{m_1, m_1} \psi_{m_2}(2) = E_2 \psi_{m_2}(2) \end{aligned} \quad (56.21)$$

Fock's equations (56.21) differ from Hartree's equations (56.8) only in the exchange terms. Fock's method gives different results for para- and orthostates. Hartree's method gives the same energy value for the para- and orthostates.

The Hartree-Fock system of integro-differential equations can be solved only using numerical methods (with the aid of computers). The time needed for the calculations grows very rapidly with an increase in the number of electrons. This is why the Thomas-Fermi method treated in the following section has come into great favour for heavy atoms.

57. The Thomas-Fermi Method

The Thomas-Fermi method is based on the circumstance that most of the electrons in heavy atoms have large quantum numbers, and as a result the quasiclassical approximation can be used.

In this approximation, the momentum can be assumed approximately to be a position function. Each phase-space cell with a volume of $(2\pi\hbar)^3$ can be occupied by not more than two electrons with opposite spins [see (39.10)].

In a stationary state of an atom, each volume element dV contains a non-time-varying number of electrons dN . Their total kinetic energy will be minimum if these electrons fill pairwise all the phase-space cells corresponding to the volume dV and to the values of the momentum from zero to a certain p_{\max} determined by the expression

$$(2\pi\hbar)^3 \frac{dN}{2} = \frac{4}{3}\pi p_{\max}^3 dV \quad (57.1)$$

The quotient dN/dV is the density n of the electrons at the place where the volume dV was taken. Considering the distribution of the electrons in an atom to be centrally symmetric, we write, on the basis of (57.1),

$$n(r) = \frac{8\pi [p_{\max}(r)]^3}{3(2\pi\hbar)^3} \quad (57.2)$$

where r is the distance from the centre of the atom (from its nucleus).

The maximum total energy of an electron at the distance r from the nucleus is

$$E_{\max}(r) = \frac{[p_{\max}(r)]^2}{2m_e} - e\varphi(r) = -e\varphi_0 \quad (57.3)$$

where $-e\varphi(r)$ is the potential energy of the electron, and φ_0 is a quantity having the dimension of potential. In a stationary state, the maximum total energy of an electron must be the same at all distances from the nucleus, otherwise the electrons would be redistrib-

uted, passing from places where the maximum total energy is larger to places where it is smaller. Consequently, φ_0 in (57.3) is a constant.

Excluding $p_{\max}(r)$ from Eqs. (57.2) and (57.3), we obtain an expression relating the density of the electrons and the potential at each point of an atom:

$$n(r) = \frac{1}{3\pi^2\hbar^3} (2m_e e)^{3/2} [\varphi(r) - \varphi_0]^{3/2} \quad (57.4)$$

It follows from the nature of charge distribution in an atom that the potential $\varphi(r)$, being positive, must diminish with increasing r and vanish at the atom's boundary. Hence, $\varphi(R) = 0$, where R is the distance corresponding to the atom's boundary. The density of the electrons also vanishes at the atom's boundary. These considerations show that the constant φ_0 in (57.4) can only be zero. With this in view, let us write (57.4) as follows:

$$n(r) = \frac{1}{3\pi^2\hbar^3} (2m_e e)^{3/2} [\varphi(r)]^{3/2} \quad (57.5)$$

Multiplying $n(r)$ by $-e$, we obtain the mean charge density inside an atom. The potential $\varphi(r)$ is related to the charge density by Poisson's equation $\nabla^2\varphi = -4\pi\rho$ [see Vol. 1, formula (42.4)]. When φ depends only on r , we have $\nabla^2\varphi = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\varphi}{dr} \right)$. Consequently, assuming that $\rho = -en(r)$, where $n(r)$ is determined by formula (57.5), we arrive at the equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\varphi}{dr} \right) = \frac{4e}{3\pi\hbar^3} (2m_e e)^{3/2} \varphi^{3/2} \quad (57.6)$$

known as the Thomas-Fermi equation. The solution of this equation characterizes the potential inside atoms with a large Z .

The solution must satisfy the following boundary conditions: when $r \rightarrow 0$, the field must transform into the Coulomb field of the nucleus

$$\varphi(r) \rightarrow \frac{Ze}{r} \quad \text{when } r \rightarrow 0 \quad (57.7)$$

and at the boundary of an atom, the derivative $d\varphi/dr$ must vanish:

$$\varphi'(R) = 0 \quad (57.8)$$

[recall that $\varphi(R)$ also equals zero].

Let us represent Eq. (57.6) in the form

$$\frac{d^2\varphi}{dr^2} + \frac{2}{r} \frac{d\varphi}{dr} = C\varphi^{3/2} \quad (57.9)$$

When $r = R$, the potential φ and its derivative φ' vanish. In accordance with (57.9), the second derivative $\varphi''(R)$ also vanishes. Differentiation of (57.9) with respect to r yields

$$\frac{d^3\varphi}{dr^3} + \frac{2}{r} \frac{d^2\varphi}{dr^2} - \frac{2}{r^2} \frac{d\varphi}{dr} = C \frac{3}{2} \varphi^{1/2} \frac{d\varphi}{dr}$$

Taking into account that $\varphi(R) = \varphi'(R) = \varphi''(R) = 0$, we find that $\psi'''(R) = 0$, etc. We thus arrive at the conclusion that both φ and all its derivatives vanish when $r = R$.

The equality to zero of a function and all its derivatives at a point that is not infinitely remote is possible only if the function identically equals zero. Hence, Eq. (57.6) in combination with the boundary condition (57.8) has a non-zero solution only when $R = \infty$. Consequently, according to the Thomas-Fermi equation, the radius of a neutral atom is infinitely great.

Owing to the spherically symmetric distribution of the mean electron charge, the potential at the distance r from the nucleus has the magnitude

$$\varphi(r) = \frac{Ze - q(r)}{r}$$

where $-q(r)$ is the total electron charge confined in a sphere of radius r . When $r \rightarrow \infty$, the charge $-q(r)$ tends to $-Ze$. Consequently, $\varphi(r)$ tends to zero more rapidly than $1/r$, i.e.

$$r\varphi(r) \rightarrow 0 \quad \text{when } r \rightarrow \infty \quad (57.10)$$

The solution of Eq. (57.6) must thus satisfy the boundary conditions (57.7) and (57.10).

It is customary practice to write Eq. (57.6) in the dimensionless form, introducing instead of φ the new function χ and instead of r the variable x , it being assumed that

$$r = xbZ^{-1/3}, \quad \varphi = \frac{\chi Ze}{r} = \frac{\chi Z^{4/3} e}{bx} \quad (57.11)$$

where

$$b = \frac{1}{2} \left(\frac{3\pi}{4} \right)^{2/3} r_0 \approx 0.8853 r_0 \quad (57.12)$$

(r_0 is the Bohr radius). The result is the equation

$$\sqrt{x} \frac{d^2\chi}{dx^2} = \chi^{3/2} \quad (57.13)$$

In accordance with (57.11), we have $\chi = \varphi r / Ze$. The variable x tends to zero together with r . Therefore, the boundary condition (57.7) in the new notation has the form

$$\chi \rightarrow 1 \quad \text{when } x \rightarrow 0 \quad (57.14)$$

We obtain from (57.11) that

$$\chi \rightarrow 0 \quad \text{when} \quad x \rightarrow \infty \quad (57.15)$$

Equation (57.13) was solved with account taken of the boundary conditions (57.14) and (57.15) using numerical methods. Asymptotic expressions of the solution were also found for small and large values of x . The Thomas-Fermi method is more approximate than that of Hartree and Fock. It does not take into account the individual properties of atoms and does not reveal the structure of the electron shells and the distribution of the density of the comparatively weakly bound valence electrons. An advantage of the Thomas-Fermi method is its comparative mathematical simplicity. In addition, this method is successfully applied to other systems consisting of a large number of particles—atomic nuclei, molecules, and crystals.

58. The Zeeman Effect

Consider an atom in a weak homogeneous magnetic field with the magnetic induction B . For a Russel-Saunders coupling¹, the Hamiltonian of an atom is

$$\hat{H} = \frac{1}{2m_e} \sum_k \left(\hat{\mathbf{p}}_k + \frac{e}{c} \mathbf{A}_k \right)^2 + U + \hat{W}_{LS} + \frac{e\hbar}{m_e c} \mathbf{B} \hat{\mathbf{S}}$$

[compare with (32.3)], where U is the energy of interaction of the electrons with the nucleus and with one another, \hat{W}_{LS} is the operator of spin-orbit interaction, $\hat{\mathbf{S}} = \sum_k \hat{\mathbf{s}}_k$ is the operator of the total spin of the atom. Summation is performed over all the electrons. Assuming the vector potential to be gauged so that $\nabla \mathbf{A} = 0^2$, let us transform the expression of the Hamiltonian as follows:

$$\begin{aligned} \hat{H} = & \left\{ \frac{1}{2m_e} \sum_k \hat{\mathbf{p}}_k^2 + U + \hat{W}_{LS} \right\} + \frac{e}{m_e c} \sum_k \mathbf{A}_k \hat{\mathbf{p}}_k \\ & + \frac{e^2}{2m_e c^2} \sum_k \mathbf{A}_k^2 + \frac{e\hbar}{m_e c} \mathbf{B} \hat{\mathbf{S}} \end{aligned} \quad (58.1)$$

The expression in braces is the Hamiltonian of the atom in the absence of a magnetic field, i.e. the unperturbed Hamiltonian \hat{H}_0 .

¹ A coupling is said to be of the Russel-Saunders type if the orbital angular momenta of the electrons add up into the total orbital angular momentum of the atom characterized by the quantum number L , the spin angular momenta add up into the total spin angular momentum characterized by the quantum number S , and then the total orbital and spin angular momenta combine to form the total angular momentum of the atom characterized by the quantum number J .

² In this case, the operators $\hat{\mathbf{p}}$ and \mathbf{A} commute [see (32.5)].

The vector potential of a homogeneous field can be written as $\mathbf{A} = \frac{e}{2m_e c} [\mathbf{Br}]$ [compare with (32.8)]. Introduction of this expression into (58.1) yields

$$\hat{H} = \hat{H}_0 + \frac{e}{2m_e c} \mathbf{B} \sum_k [\mathbf{r}_k, \hat{\mathbf{p}}_k] + \frac{e^2}{8m_e c^2} \sum_k [\mathbf{B}, \mathbf{r}_k]^2 + \frac{e\hbar}{m_e c} \mathbf{B} \hat{\mathbf{S}} \quad (58.2)$$

(we have performed the cyclic transposition $[\mathbf{B}, \mathbf{r}_k] \hat{\mathbf{p}}_k = \mathbf{B} [\mathbf{r}_k, \hat{\mathbf{p}}_k]$).

The expression $[\mathbf{r}_k, \hat{\mathbf{p}}_k]$ is the operator of the orbital angular momentum of the k -th electron [see (15.10)], and the sum of such expressions is the operator of the total orbital angular momentum of the atom, which we shall designate by the symbol $\hbar \hat{\mathbf{L}}$. Combining the second and fourth terms of expression (58.2) and taking into account that $e\hbar/2m_e c$ equals the Bohr magneton μ_B , we obtain

$$\hat{H} = \hat{H}_0 + \mu_B \mathbf{B} (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) + \frac{e^2}{8m_e c^2} \sum_k [\mathbf{B}, \mathbf{r}_k]^2 \quad (58.3)$$

We must note that the operator

$$\hat{\mu} = -\mu_B (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) = -\mu_B (\hat{\mathbf{J}} + \hat{\mathbf{S}}) \quad (58.4)$$

can be considered as the operator of the magnetic moment of an atom (which the atom has in the absence of a field).

For a weak field, the term quadratic in \mathbf{B} in (58.3) may be ignored in comparison with the term linear in \mathbf{B} . Hence

$$\hat{H} = \hat{H}_0 - B \hat{\mu} \quad (58.5)$$

and we may consider the second term as a perturbation.

In the absence of a field, the energy levels of an atom are degenerate with respect to the quantum number m_J that determines the projection of the total angular momentum of the atom onto the z -axis. The magnetic field removes the degeneracy in m_J , and as a result the level with the given J splits into $2J + 1$ sublevels. The magnitude of the splitting is determined by the matrix elements of the perturbation operator $\hat{V} = -B \hat{\mu} = -B \hat{\mu}_z$ (because \mathbf{B} is a constant vector directed along the z -axis) calculated with the aid of the unperturbed functions ψ_{L, S, J, m_J} , i.e. of the expressions

$$\langle \psi_{L, S, J, m'_J} | -B \hat{\mu}_z \psi_{L, S, J, m_J} \rangle \quad (58.6)$$

Let us represent the relation between the operators of the magnetic moment $\hat{\mu}$ and the mechanical angular momentum $\hat{\mathbf{M}}_J = \hbar \hat{\mathbf{J}}$ with the aid of the auxiliary operator \hat{G} :

$$\hat{\mu} = -\frac{e}{2m_e c} \hat{G} \hat{\mathbf{M}}_J = -\frac{e}{2m_e c} \hat{G} (\hbar \hat{\mathbf{J}}) = -\mu_B \hat{G} \hat{\mathbf{J}} \quad (58.7)$$

Correspondingly

$$\hat{\mu}_z = -\frac{e}{2m_e c} \hat{G} \hat{M}_z \quad (58.8)$$

A comparison of expressions (58.4) and (58.7) shows that

$$\hat{G} \hat{\mathbf{J}} = \hat{\mathbf{J}} + \hat{\mathbf{S}}$$

Let us perform scalar multiplication of this equation by $\hat{\mathbf{J}}$:

$$\hat{G} \hat{\mathbf{J}}^2 = \hat{\mathbf{J}}^2 + \hat{\mathbf{J}} \hat{\mathbf{S}}$$

whence

$$\hat{G} = 1 + \frac{\hat{\mathbf{J}} \hat{\mathbf{S}}}{\hat{\mathbf{J}}^2} \quad (58.9)$$

Squaring the relation $\hat{\mathbf{L}} = \hat{\mathbf{J}} - \hat{\mathbf{S}}$, we obtain $\hat{\mathbf{L}}^2 = \hat{\mathbf{J}}^2 - 2\hat{\mathbf{J}}\hat{\mathbf{S}} + \hat{\mathbf{S}}^2$, whence $2\hat{\mathbf{J}}\hat{\mathbf{S}} = \hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2$. Substitution of this value into (58.9) yields

$$\hat{G} = 1 + \frac{\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2}{2\hat{\mathbf{J}}^2} \quad (58.10)$$

The operator \hat{G} commutes with \hat{M}_z and, consequently, has common eigenfunctions with it. We are considering unperturbed states of an atom with definite values of \mathbf{J}^2 , \mathbf{L}^2 , and \mathbf{S}^2 . In these states, the quantity described by the operator \hat{G} has the value

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (58.11)$$

This expression is called the Lande g -factor. It is clear from above that g is the eigenvalue of the operator \hat{G} .

Introducing expression (58.8) for $\hat{\mu}_z$ into (58.6), we get the matrix elements of the perturbation operator \hat{V} :

$$\begin{aligned} & \langle \psi_{L', s', J', m'_J} | \hat{V} | \psi_{L, s, J, m_J} \rangle \\ &= \left\langle \psi_{L', s', J, m'_J} \left| \frac{Be}{2m_e c} \hat{G} \hat{M}_z \right| \psi_{L, s, J, m_J} \right\rangle \\ &= \frac{Be}{2m_e c} g \hbar m_J \langle \psi_{L', s', J', m'_J} | \psi_{L, s, J, m_J} \rangle \\ &= \mu_B B g m_J \delta_{(L', s', J', m'_J), (L, s, J, m_J)} \end{aligned} \quad (58.12)$$

[compare with formula (32.14)]. [The eigenvalues of the product of commuting operators equal the products of the eigenvalues of the multipliers, see (10.27)]. The eigenvalues of the operators \hat{G} and \hat{M}_z equal g and $\hbar m_J$, respectively.

The matrix of the operator \hat{V} evaluated with the aid of functions describing the unperturbed states of an atom is diagonal. This signifies [see the text preceding formula (31.12)] that although the unperturbed functions are degenerate, the first-order corrections to the energy equal the diagonal matrix elements (58.12). Hence,

$$\Delta E = \mu_B B g m_J \quad (m_J = -J, -J + 1, \dots, J - 1, J) \quad (58.13)$$

The result obtained signifies that a $(2J + 1)$ -fold degenerate level under the action of a weak magnetic field splits up into $2J + 1$ equidistant levels arranged symmetrically relative to the unperturbed level E_L . Consequently, a magnetic field removes degeneracy with respect to the quantum number m_J .

Splitting of the levels determined by formula (58.13) (with $g \neq 1$) is called the complicated (or anomalous) Zeeman effect. When $S = 0$ (particularly, for particles without a spin), the Lande g -factor becomes equal to unity [see (58.11)], and formula (58.13) acquires the form

$$\Delta E = \mu_B B m_J \quad (58.14)$$

coinciding with (32.15). Splitting described by formula (58.14) is called the simple (or normal) Zeeman effect.

59. The Theory of Molecules in the Adiabatic Approximation

The mass of a nucleus is three or four orders of magnitude larger than that of an electron. For this reason, the nuclei in a molecule move considerably slower than the electrons. This circumstance gives us grounds to consider the nuclei to be at rest in the zero approximation, and in the following approximations to consider the motion of the nuclei as a perturbation. This method of calculations is known as the adiabatic approximation.

In a non-relativistic approximation, the Hamiltonian of a system consisting of nuclei and electrons has the form

$$\hat{H} = - \sum_i \frac{\hbar^2}{2M_i} \nabla_{\mathbf{R}_i}^2 - \frac{\hbar^2}{2m_e} \sum_k \nabla_{\mathbf{r}_k}^2 + U(\mathbf{r}_k, \mathbf{R}_i) = \hat{T}_{\text{nuc}} + \hat{T}_e + U \quad (59.1)$$

Here M_i and \mathbf{R}_i are the masses and position vectors of the nuclei, \mathbf{r}_k are the position vectors of the electrons, $U(\mathbf{r}_k, \mathbf{R}_i)$ is the potential energy of interaction between all the particles, \hat{T}_{nuc} is the operator of the kinetic energy of the nuclei, and \hat{T}_e is the operator of the kinetic energy of the electrons. The adiabatic approximation pro-

ceeds from the assumption that the operator of the kinetic energy of the nuclei can be considered as a small perturbation:

$$\hat{V} = \hat{T}_{\text{nuc}} = - \sum_i \frac{\hbar^2}{2M_i} \nabla_{R_i}^2 \quad (59.2)$$

The unperturbed Hamiltonian will then consist of the second and third terms of expression (59.1):

$$\hat{H}_0(\mathbf{R}_i) = \hat{T}_e + U = - \frac{\hbar^2}{2m_e} \sum_k \nabla_{r_k}^2 + U(\mathbf{r}_k, \mathbf{R}_i) \quad (59.3)$$

The position vectors \mathbf{R}_i play the role of parameters in this expression.

In the zero approximation, the energies and psi-functions of the stationary states are determined from the solution of the equation

$$\hat{H}_0(\mathbf{R}_i) \psi_n^{(0)}(\mathbf{r}_k, \mathbf{R}_i) = E_n^{(0)}(\mathbf{R}_i) \psi_n^{(0)}(\mathbf{r}_k, \mathbf{R}_i) \quad (59.4)$$

The index n stands for the set of quantum numbers characterizing the stationary state of the system. The values of the energy and the psi-function depend on the position vectors of the nuclei as on parameters. The functions $\psi_n^{(0)}(\mathbf{r}_k, \mathbf{R}_i)$ characterize the state of motion of the electrons with fixed positions of the nuclei determined by the values of \mathbf{R}_i .

Let us attempt to find a solution of the equation $\hat{H}\psi = E\psi$ [where $\hat{H} = \hat{H}_0 + \hat{T}_{\text{nuc}}$ is the operator (59.1)] in the form of an expansion¹ in the functions $\psi_n^{(0)}(\mathbf{r}_k, \mathbf{R}_i)$; we shall designate the coefficients of the expansion by $\Psi_n(\mathbf{R}_i)$:

$$\psi(\mathbf{r}_k, \mathbf{R}_i) = \sum_n \Psi_n(\mathbf{R}_i) \psi_n^{(0)}(\mathbf{r}_k, \mathbf{R}_i) \quad (59.5)$$

Substitution into the equation yields

$$(\hat{H}_0 + \hat{T}_{\text{nuc}}) \sum_n \Psi_n \psi_n^{(0)} = E \sum_n \Psi_n \psi_n^{(0)}$$

Opening the parentheses and taking into account (59.4), we obtain

$$\sum_n \Psi_n E_n^{(0)} \psi_n^{(0)} + \hat{T}_{\text{nuc}} \sum_n \Psi_n \psi_n^{(0)} = E \sum_n \Psi_n \psi_n^{(0)}$$

Let us perform scalar premultiplication of this relation by $\psi_m^{(0)}$ (in calculating the scalar product, integration is performed over

¹ If the spectrum of the operator \hat{H}_0 has continuous regions, the right-hand side of formula (59.5), in addition to the sum over the discrete states, will contain an integral over the continuous states.

the coordinates of the electrons, therefore the functions of R_i may be put outside the symbol $\langle \cdot | \cdot \rangle$:

$$\sum_n \Psi_n E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle + \sum_n \langle \psi_m^{(0)} | \hat{T}_{\text{nuc}} (\Psi_n \psi_n^{(0)}) \rangle \\ = E \sum_n \Psi_n \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle$$

Owing to orthogonality of the functions $\psi_i^{(0)}$, the first sum on the left equals $\Psi_m E_m^{(0)}$, and the sum on the right equals $E \Psi_m$. We thus arrive at the equation

$$\Psi_m (R_i) E_m^{(0)} + \sum_n \langle \psi_m^{(0)} (r_k, R_i) | \hat{T}_{\text{nuc}} (R_i) [\Psi_n (R_i) \psi_n^{(0)} (r_k, R_i)] \rangle \\ = E \Psi_m (R_i) \quad (59.6)$$

We calculate the expression inside the summation sign¹:

$$\langle \psi_m^{(0)} | \hat{T}_{\text{nuc}} (\Psi_n \psi_n^{(0)}) \rangle = \left\langle \psi_m^{(0)} \left| \left(- \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 \right) (\Psi_n \psi_n^{(0)}) \right. \right\rangle \\ = -\hbar^2 \sum_i \frac{1}{M_i} \langle \psi_m^{(0)} | (\nabla_i \Psi_n) (\nabla_i \psi_n^{(0)}) \rangle \\ + \left\langle \psi_m^{(0)} \left| \left(- \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 \right) \psi_n^{(0)} \right. \right\rangle \Psi_n + \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle \left(- \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 \right) \Psi_n \\ = -\hbar^2 \sum_i \frac{1}{M_i} \langle \psi_m^{(0)} | \nabla_i \psi_n^{(0)} \rangle \nabla_i \Psi_n \\ + \langle \psi_m^{(0)} | \hat{T}_{\text{nuc}} \psi_n^{(0)} \rangle \Psi_n + \delta_{mn} \hat{T}_{\text{nuc}} \Psi_n \quad (59.7)$$

If we introduce an operator acting on the function of R_i :

$$\hat{\Lambda}_{mn} = \hbar^2 \sum_i \frac{1}{M_i} \langle \psi_m^{(0)} | \nabla_i \psi_n^{(0)} \rangle \nabla_i - \langle \psi_m^{(0)} | \hat{T}_{\text{nuc}} \psi_n^{(0)} \rangle \quad (59.8)$$

expression (59.7) can be given the form

$$-\hat{\Lambda}_{mn} \Psi_n + (\hat{T}_{\text{nuc}} \Psi_n) \delta_{mn}$$

Substitution of this value into (59.6) yields

$$\Psi_m (R_i) E_m^{(0)} - \sum_n \Lambda_{mn} \Psi_n (R_i) + \sum_n [\hat{T}_{\text{nuc}} \Psi_n (R_i)] \delta_{mn} = E \Psi_m (R_i)$$

whence we obtain the relation

$$[\hat{T}_{\text{nuc}} + E_m^{(0)} (R_i) - E] \Psi_m (R_i) = \sum_n \hat{\Lambda}_{mn} \Psi_n (R_i) \quad (59.9)$$

¹ $\nabla^2 (\varphi f) = \nabla (\varphi \nabla f + f \nabla \varphi) = 2\nabla \varphi \nabla f + \varphi \nabla^2 f + f \nabla^2 \varphi.$

Assigning the values 1, 2, ... to the index m in (59.9), we obtain a system of equations for finding the values of E and the functions $\Psi_n(\mathbf{R}_i)$. This system is exact, but its exact solution is impossible.

If the operator \hat{T}_{nuc} may be treated as a small perturbation, the system can be solved by the method of successive approximations. In the zero (adiabatic) approximation, the right-hand side in (59.9) is assumed to equal zero. The system (59.9) in this case breaks up into a set of independent equations

$$[\hat{T}_{\text{nuc}} + E_m^{(0)}(\mathbf{R}_i)] \Psi_m^{(0)}(\mathbf{R}_i) = E \Psi_m^{(0)}(\mathbf{R}_i) \quad (59.10)$$

The equation with the number m determines the function $\Psi_m^{(0)}$ describing the motion of the nuclei when the state of motion of the electrons is determined by the set of quantum numbers m . Since there may be several states of motion of the nuclei in this case, we shall provide the function $\Psi_m^{(0)}$ with an additional index v designating the set of quantum numbers characterizing the state of motion of the nuclei. To underline the fact that E in (59.10) is the energy of the state in which the motion of the electrons is characterized by the set of quantum numbers m , and the motion of the nuclei by the set of quantum numbers v , we shall use both these indices on E . As a result, Eq. (59.10) becomes

$$[\hat{T}_{\text{nuc}} + E_m^{(0)}(\mathbf{R}_i)] \Psi_{mv}^{(0)}(\mathbf{R}_i) = E_{mv} \Psi_{mv}^{(0)}(\mathbf{R}_i) \quad (59.11)$$

A comparison with the equation $(\hat{T} + U)\psi = E\psi$ shows that the energy $E_m^{(0)}(\mathbf{R}_i)$ of the electrons plays the role of the potential energy of the nuclei in Eq. (59.11).

Hence, in the adiabatic approximation, the psi-function of a molecule is

$$\psi_{\text{mol}, mv} = \Psi_{mv}^{(0)}(\mathbf{R}_i) \psi_m^{(0)}(\mathbf{r}_k, \mathbf{R}_i) \quad (59.12)$$

i.e. it breaks up into two factors, one of which describes the motion of the electrons, and the other the motion of the nuclei. The function $\psi_m^{(0)}$ is found by solving Eq. (59.4), the function $\Psi_{mv}^{(0)}$, by solving Eq. (59.11).

The energy $E_n^{(0)}$ obtained from Eq. (59.4) is (to within a constant factor) the electron term of a molecule. The energy E_{mv} obtained from Eq. (59.11) includes, in addition to the electron energy $E_n^{(0)}$, the energy of motion of the nuclei (the vibrational and rotational energy of a molecule).

60. The Hydrogen Molecule

For a hydrogen molecule, the operator (59.3) has the form

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) + e^2 \left[\frac{1}{r_{12}} + \frac{1}{R} - \frac{1}{r_{A1}} - \frac{1}{r_{B1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B2}} \right] \quad (60.1)$$

The subscripts *A* and *B* relate to nuclei, the subscripts 1 and 2—to electrons, *R* is the internuclear distance.

The equation

$$\hat{H}_0 \psi(1, 2, R) = E^{(0)}(R) \psi(1, 2, R) \quad (60.2)$$

[see (59.4)] was first solved by W. Heitler and F. London by the method of successive approximations. The psi-function of two isolated atoms was taken as the zero-order psi-function.

Let us consider the limit (when $R \rightarrow \infty$) expression for the Hamiltonian (60.1). Assume that when one of the atoms is removed to infinity, the electron 1 is found near the nucleus *A*, and the electron 2 near the nucleus *B*. The limiting value of the Hamiltonian therefore has the form

$$\hat{H}'_\infty = \hat{H}_{A1} + \hat{H}_{B2}, \quad (60.3)$$

where

$$\hat{H}_{A1} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{e^2}{r_{A1}}, \quad \hat{H}_{B2} = -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{r_{B2}}$$

The equation $\hat{H}'_\infty \psi = E \psi$ will have as its solution the function

$$\psi_1 = \psi_{A1}(r_{A1}) \psi_{B2}(r_{B2}) \quad (60.4)$$

whose factors satisfy the equations

$$\hat{H}_{A1} \psi_{A1}(r_{A1}) = E_{A1} \psi_{A1}(r_{A1}), \quad \hat{H}_{B2} \psi_{B2}(r_{B2}) = E_{B2} \psi_{B2}(r_{B2})$$

Indeed, the function (60.4) satisfies the equation

$$\hat{H}_{A1} \psi_1 + \hat{H}_{B2} \psi_1 = E \psi_1 \quad (60.5)$$

provided that $E = E_{A1} + E_{B2}$ [the operator \hat{H}_{A1} does not act on $\psi_{B2}(r_{B2})$, and the operator \hat{H}_{B2} does not act on $\psi_{A1}(r_{A1})$].

Owing to the indistinguishability of the electrons in the atoms infinitely far from each other, the first electron may be found near the nucleus *B*, and the second near the nucleus *A*. The limiting value of the Hamiltonian (60.1) will therefore be

$$\hat{H}'_\infty = \hat{H}_{B1} + \hat{H}_{A2} \quad (60.6)$$

where

$$\hat{H}_{B1} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{e^2}{r_{B1}}, \quad \hat{H}_{A2} = -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{r_{A2}}$$

The equation $\hat{H}_\infty \psi = E\psi$ will have as its solution the function

$$\psi_2 = \psi_{B1}(r_{B1}) \psi_{A2}(r_{A2}) \quad (60.7)$$

whose factors satisfy the equations

$$\hat{H}_{B1}\psi_{B1}(r_{B1}) = E_{B1}\psi_{B1}(r_{B1}), \quad \hat{H}_{A2}\psi_{A2}(r_{A2}) = E_{A2}\psi_{A2}(r_{A2}).$$

The energy corresponding to the state (60.7) is $E = E_{B1} + E_{A2}$.

In the following, we shall limit ourselves to considering the ground state of the hydrogen molecule. Accordingly, in the limit, isolated atoms are obtained that are in the ground state with the energy E_0 . Therefore

$$E_{A1} = E_{B2} = E_{B1} = E_{A2} = E_0 \quad (60.8)$$

so that the energy of the states described by the functions (60.4) and (60.7) is the same and equals $2E_0$.

Hence, in the zero approximation we have used, the ground state of the hydrogen molecule is doubly degenerate (exchange degeneracy). A feature of the problem being considered is that the functions ψ_1 and ψ_2 describing degenerate states are eigenfunctions of different operators [the function (60.7) does not satisfy Eq. (60.5), and the function (60.4) does not satisfy the equation $\hat{H}_\infty \psi = E\psi$]. Therefore, we cannot assert that ψ_1 and ψ_2 are mutually orthogonal.

Let us use as zero-approximation psi-functions the linear combinations of the functions ψ_1 and ψ_2 that take into account the requirements of symmetry which a system of two particles with a spin of $1/2$ must meet. The following two types of position functions correspond to the two possible spin states ($S = 0$ and $S = 1$):

$$\Psi_s^{(0)} = C_1 [\psi_A(1) \psi_B(2) + \psi_A(2) \psi_B(1)] \quad (60.9)$$

$$\Psi_a^{(0)} = C_2 [\psi_A(1) \psi_B(2) - \psi_A(2) \psi_B(1)]. \quad (60.10)$$

To simplify writing, we have used the notation

$$\psi_{A1}(r_{A1}) = \psi_A(1), \quad \psi_{B2}(r_{B2}) = \psi_B(2)$$

$$\psi_{A2}(r_{A2}) = \psi_A(2), \quad \psi_{B1}(r_{B1}) = \psi_B(1)$$

The functions ψ_A and ψ_B are psi-functions of the ground state of a hydrogen atom. By the first of formulas (24.33), we have

$$\left. \begin{aligned} \psi_A(1) &= Ce^{-r_{A1}/r_0}, & \psi_B(2) &= Ce^{-r_{B2}/r_0}, \\ \psi_A(2) &= Ce^{-r_{A2}/r_0}, & \psi_B(1) &= Ce^{-r_{B1}/r_0} \end{aligned} \right\} \quad (60.11)$$

where $C = (1/r_0)^{3/2}/\sqrt{\pi}$. All these functions are real.

Let us find values of the coefficients C_1 and C_2 in (60.9) and (60.10) from the normalization condition. We write the normalization condition for $\psi_s^{(0)}$:

$$1 = \int [\psi_s^{(0)}]^2 dV_1 dV_2 = C_1^2 \left\{ \int [\psi_A(1)]^2 dV_1 \int [\psi_B(2)]^2 dV_2 \right. \\ \left. + 2 \int \psi_A(1) \psi_B(1) dV_1 \int \psi_A(2) \psi_B(2) dV_2 \right. \\ \left. + \int [\psi_A(2)]^2 dV_2 \int [\psi_B(1)]^2 dV_1 \right\}.$$

The first and third terms equal unity. The factors in the second term differ only in the designation of the integration variable. We therefore arrive at the relation

$$1 = 2C_1^2 \{1 + S^2\} \quad (60.12)$$

where

$$S = \int \psi_A(1) \psi_B(1) dV_1 = \frac{1}{\pi r_0^3} \int e^{-(r_{A1}+r_{B1})/r_0} dV_1 \quad (60.13)$$

is a quantity known as the **overlap integral of psi-functions**. It characterizes the degree of non-orthogonality of the functions (60.4) and (60.7). If these functions were orthogonal, the coefficient C_1 in (60.9) would be $1/\sqrt{2}$, which is obtained when $S = 0$ [see (60.12)]. A glance at (60.12) shows that

$$C_1 = \frac{1}{\sqrt{2(1+S^2)}} \quad (60.14)$$

Similar calculations give the following value for the coefficient C_2 in (60.10):

$$C_2 = \frac{1}{\sqrt{2(1-S^2)}} \quad (60.15)$$

By formula (7.14), we have

$$\langle E \rangle = \int \psi^* \hat{H} \psi dV$$

If in the state ψ , the energy has the definite value E , then $\langle E \rangle$ equals this value, so that for stationary states we have

$$E = \int \psi^* \hat{H} \psi dV \quad (60.16)$$

Heitler and London used formula (60.16) for calculating the energy of the ground state of the hydrogen molecule. They took the functions (60.9) and (60.10) as ψ , and the operator \hat{H}_0 determined by formula (60.4) as \hat{H} .

For the parastate, we have

$$\begin{aligned}
 E_s &= \int \psi_s \hat{H}_0 \psi_s dV_1 dV_2 \\
 &= \frac{1}{2(1+S^2)} \int [\psi_A(1) \psi_B(2) + \psi_A(2) \psi_B(1)] \\
 &\quad \times \hat{H}_0 [\psi_A(1) \psi_B(2) + \psi_A(2) \psi_B(1)] dV_1 dV_2 \\
 &= \frac{1}{2(1+S^2)} \left\{ \int \psi_A(1) \psi_B(2) \hat{H}_0 \psi_A(1) \psi_B(2) dV_1 dV_2 \right. \\
 &\quad + \int \psi_A(1) \psi_B(2) \hat{H}_0 \psi_A(2) \psi_B(1) dV_1 dV_2 \\
 &\quad + \int \psi_A(2) \psi_B(1) \hat{H}_0 \psi_A(1) \psi_B(2) dV_1 dV_2 \\
 &\quad \left. + \int \psi_A(2) \psi_B(1) \hat{H}_0 \psi_A(2) \psi_B(1) dV_1 dV_2 \right\}
 \end{aligned}$$

The first and fourth integrals differ only in the designations of the integration variables, consequently they equal each other. The same relates to the second and third integrals. We can therefore write

$$\begin{aligned}
 E_s &= \frac{1}{1+S^2} \left\{ \int \psi_A(1) \psi_B(2) \hat{H}_0 \psi_A(1) \psi_B(2) dV_1 dV_2 \right. \\
 &\quad \left. + \int \psi_A(1) \psi_B(2) \hat{H}_0 \psi_A(2) \psi_B(1) dV_1 dV_2 \right\}
 \end{aligned}$$

In calculating the integrals, we have in view that

$$\left(-\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{e^2}{r_{A1}} \right) \psi_A(1) = E_0 \psi_A(1)$$

$$\left(-\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{r_{A2}} \right) \psi_A(2) = E_0 \psi_A(2)$$

$$\left(-\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{e^2}{r_{B1}} \right) \psi_B(1) = E_0 \psi_B(1)$$

$$\left(-\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{r_{B2}} \right) \psi_B(2) = E_0 \psi_B(2)$$

[see (60.8)]. With account taken of these relations, we have

$$\begin{aligned}
 E_s &= \frac{1}{1+S^2} \left\{ 2 \int \psi_A(1) \psi_B(2) E_0 \psi_A(1) \psi_B(2) dV_1 dV_2 \right. \\
 &\quad + \int \psi_A(1) \psi_B(2) \left[e^2 \left(\frac{1}{r_{12}} + \frac{1}{R} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} \right) \right] \\
 &\quad \times \psi_A(1) \psi_B(2) dV_1 dV_2 + 2 \int \psi_A(1) \psi_B(2) E_0 \psi_A(2) \psi_B(1) dV_1 dV_2 \\
 &\quad + \int \psi_A(1) \psi_B(2) \left[e^2 \left(\frac{1}{r_{12}} + \frac{1}{R} - \frac{1}{r_{A1}} - \frac{1}{r_{B2}} \right) \right] \\
 &\quad \times \psi_A(2) \psi_B(1) dV_1 dV_2 \left. \right\}
 \end{aligned}$$

Since the functions ψ_A (1) and ψ_B (2) are normalized to unity, the first integral equals E_0 . In accordance with (60.13), the third integral equals $S^2 E_0$. We can therefore write that

$$E_s = \frac{1}{1+S^2} \{ 2E_0 + 2S^2 E_0 + Q + A \} = 2E_0 + \frac{Q+A}{1+S^2} \quad (60.17)$$

where

$$\begin{aligned} Q &= \int \psi_A^2 (1) \psi_B^2 (2) \left[e^2 \left(\frac{1}{r_{12}} + \frac{1}{R} - \frac{1}{r_{A_2}} - \frac{1}{r_{B_1}} \right) \right] dV_1 dV_2 \\ &= \frac{e^2}{R} + \int \psi_A^2 (1) \frac{e^2}{r_{12}} \psi_B^2 (2) dV_1 dV_2 \\ &\quad - \int \psi_A^2 (1) \frac{e^2}{r_{B_1}} dV_1 - \int \psi_B^2 (2) \frac{e^2}{r_{A_2}} dV_2 \end{aligned} \quad (60.18)$$

$$\begin{aligned} A &= \int \psi_A (1) \psi_B (2) \left[e^2 \left(\frac{1}{r_{12}} + \frac{1}{R} - \frac{1}{r_{A_1}} - \frac{1}{r_{B_2}} \right) \right] \\ &\quad \times \psi_A (2) \psi_B (1) dV_1 dV_2 \\ &= \frac{e^2}{R} S^2 + \int \psi_A (1) \psi_B (2) \frac{e^2}{r_{12}} \psi_A (2) \psi_B (1) dV_1 dV_2 \\ &\quad - S \int \psi_A (1) \frac{e^2}{r_{A_1}} \psi_B (1) dV_1 - S \int \psi_B (2) \frac{e^2}{r_{B_2}} \psi_A (2) dV_2 \end{aligned} \quad (60.19)$$

Similar calculations give the following expression for the energy of the orthostate:

$$E_a = 2E_0 + \frac{Q-A}{1-S^2} \quad (60.20)$$

The quantity Q determined by expression (60.18) is known as the **Coulomb interaction integral**. The first term of this expression gives the energy of the Coulomb interaction of the nuclei, the second term determines the mean value of the energy of the Coulomb interaction of the electrons (without account taken of the correlation due to the symmetry of the psi-functions), the third term is the mean energy of Coulomb interaction of the electron 1 in the atom A with the nucleus of the atom B (also without account taken of correlation), and the fourth term is the similar energy for the electron 2 and the nucleus A . The third and fourth terms coincide numerically.

The quantity A determined by expression (60.19) is called the **exchange energy** because it corresponds to the part of the Coulomb interaction between the electrons and nuclei associated with the correlation in the motion of the electrons appearing owing to symmetrization of the psi-functions in accordance with the Pauli exclusion principle [compare with (49.5) and (49.6)].

The quantities Q and A are functions of the internuclear distance R . Figure 60.1 shows how the energies E_s and E_a depend on the internuclear distance R . The quantities Q and A are evaluated with the aid of the functions (60.10). The dashed line shows the experimentally obtained curve for the parastate. Examination of the figure shows that the results of Heitler and London do not agree very well

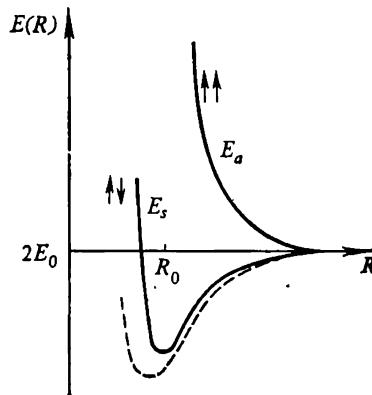


Fig. 60.1

with experimental data, but qualitatively, the features of interaction between hydrogen atoms in the para- and orthostate are described by the theoretical curves correctly.

These features consist in the following. When hydrogen atoms with antiparallel spins of their electrons approach each other, the energy of the system diminishes up to the distance R_0 equal to about 0.80 Å (the experimental value is 0.74 Å). When the nuclei continue to approach each other, a sharp increase in the energy occurs. The presence of a minimum on the energy curve makes the formation of a molecule possible. The curve of E_a has no minimum, as a result of which two hydrogen atoms with parallel spins of their electrons cannot form bound states (at any R the atoms repel each other). Hence, a hydrogen molecule can be formed only in the singlet spin state.

We have already noted that the theory advanced by Heitler and London leads to unsatisfactory quantitative agreement with experimental data. Employment of the variation method made it possible to obtain more accurate results.

Chapter XI

RADIATION THEORY

61. Quantization of an Electromagnetic Field

It was shown in Sec. 67 of Vol. 1 that an electromagnetic field in a vacuum (we shall call such a field a free one) can be characterized with the aid of the Lagrangian whose density is

$$L_0 = \frac{1}{8\pi} (\mathbf{E}^2 - \mathbf{B}^2) \quad (61.1)$$

[see Vol. 1, formula (67.8)]. Let us go over from \mathbf{E} and \mathbf{B} to the field potentials \mathbf{A} and φ . For a free field, these potentials can always be chosen so that the scalar potential φ is zero, and the vector potential satisfies the condition $\nabla \mathbf{A} = 0$. We shall assume in the following that both these conditions are observed.

By formulas (56.1) and (56.3) of Vol. 1, we have

$$\mathbf{B} = [\nabla \mathbf{A}], \quad \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}$$

($\varphi = 0$). Introducing these values into formula (61.1), we arrive at the following expression for the density of the Lagrangian of an electromagnetic field:

$$L_0 = \frac{1}{8\pi} \left\{ \frac{1}{c^2} \left(\frac{\partial \mathbf{A}}{\partial t} \right)^2 - [\nabla \mathbf{A}]^2 \right\} \quad (61.2)$$

In mechanics, the Lagrangian is defined to be a function of the generalized coordinates q_i , the generalized velocities \dot{q}_i , and the time t , that is $L = L(q_i, \dot{q}_i, t)$. A comparison with (61.2) shows that an electromagnetic field can be considered as a "mechanical system" whose generalized coordinates are the values of the potential \mathbf{A} at various points of space:

$$q_i(t) \rightarrow \mathbf{A}(x, y, z, t) \quad (61.3)$$

Hence, the coordinates of points in space number, as it were, the degrees of freedom of the field. It thus follows that an electromagnetic field is a system with an infinitely large number of degrees of freedom.

In mechanics, the generalized momentum is determined as

$$P_i = \frac{\partial L}{\partial \dot{q}_i}$$

and the energy as

$$E = \sum_i \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i - L = \sum_i P_i \dot{q}_i - L$$

[see Vol. 1, formulas (4.19) and (5.1)]. Accordingly for the generalized momentum and energy of a field, we obtain the expressions

$$P = \frac{\partial L}{\partial (\partial \mathbf{A} / \partial t)} = \frac{1}{4\pi c^2} \frac{\partial \mathbf{A}}{\partial t} \quad (61.4)$$

$$\begin{aligned} E &= \int \left(\frac{1}{4\pi c^2} \frac{\partial \mathbf{A}}{\partial t} \right) \frac{\partial \mathbf{A}}{\partial t} dV - \int L_0 dV \\ &= \int \left\{ \frac{1}{4\pi c^2} \left(\frac{\partial \mathbf{A}}{\partial t} \right)^2 - \frac{1}{8\pi c^2} \left(\frac{\partial \mathbf{A}}{\partial t} \right)^2 + \frac{1}{8\pi} [\nabla \mathbf{A}]^2 \right\} dV \\ &= \int \left\{ \frac{1}{8\pi c^2} \left(\frac{\partial \mathbf{A}}{\partial t} \right)^2 + \frac{1}{8\pi} [\nabla \mathbf{A}]^2 \right\} dV \end{aligned} \quad (61.5)$$

[in accordance with (61.3), summation over i is replaced with integration over the coordinates].

We obtain the Hamiltonian function for an electromagnetic field by expressing E in terms of the generalized momenta $\mathbf{P}(x, y, z, t)$ determined by formula (61.4) and the generalized coordinates $\mathbf{A}(x, y, z, t)$. Substitution of \mathbf{P} for $\partial \mathbf{A} / \partial t$ in (61.5) yields

$$H(\mathbf{P}, \mathbf{A}) = \int \left\{ 2\pi c^2 \mathbf{P}^2 + \frac{1}{8\pi} [\nabla \mathbf{A}]^2 \right\} dV \quad (61.6)$$

The transition from a classical description to a quantum one is accomplished, as for conventional mechanical systems, by replacing \mathbf{P} and \mathbf{A} with operators. It is especially convenient to express these operators in terms of the creation operator \hat{a}^\dagger and the annihilation operator \hat{a} treated in Secs. 27 and 51. But before making such a replacement, let us impose certain conditions of periodicity onto a field and represent it as the superposition of plane waves, i.e. let us carry out a Fourier transformation of \mathbf{A} and \mathbf{P} .

Assume that a field is confined in a large cubic box with mirror walls and an edge of length a . The field in this box will have the same properties as that in the entire space, which obeys the following conditions:

$$\begin{aligned} \mathbf{A}(x, y, z) &= \mathbf{A}(x + a, y, z) = \mathbf{A}(x, y + a, z) \\ &= \mathbf{A}(x, y, z + a) \end{aligned} \quad (61.7)$$

In these conditions, the potential can be expanded in a Fourier series instead of a Fourier integral. In this way, we shall ensure that the number of degrees of freedom, although being infinitely large, will be countable.

Let us write the Fourier transform for the vector potential:

$$\mathbf{A}(\mathbf{r}, t) = \frac{1}{\sqrt{a^3}} \sum_{\mathbf{k}} C_{\mathbf{k}}(t) e^{i\mathbf{kr}} \quad (61.8)$$

Introducing the notation $C_{\mathbf{k}}(t) = c \sqrt{\frac{4\pi}{a^3}} A_{\mathbf{k}}(t)$ (c is the speed of light), we can write (61.8) in the form

$$\mathbf{A}(\mathbf{r}, t) = c \sqrt{\frac{4\pi}{a^3}} \sum_{\mathbf{k}} A_{\mathbf{k}}(t) e^{i\mathbf{kr}} \quad (61.9)$$

(the factor $c\sqrt{\frac{4\pi}{a^3}}$ has been introduced for simplification of the following formulas). Summation is performed over the entire k -space. Each of the addends must satisfy the periodicity condition (61.7):

$$e^{i\mathbf{kr}} = e^{i\mathbf{k}(\mathbf{r} + a\mathbf{e}_x)} = e^{i\mathbf{k}(\mathbf{r} + a\mathbf{e}_y)} = e^{i\mathbf{k}(\mathbf{r} + a\mathbf{e}_z)}$$

Hence,

$$e^{ik_x a} = e^{ik_y a} = e^{ik_z a} = 1$$

Consequently, the components of the wave vector can take on only discrete values:

$$k_x = \frac{2\pi}{a} n_1, \quad k_y = \frac{2\pi}{a} n_2, \quad k_z = \frac{2\pi}{a} n_3 \quad (61.10)$$

where n_1, n_2, n_3 are integers. Three numbers n_1, n_2 , and n_3 correspond to each addend in (61.8). Since summation is performed over the entire k -space, each of these numbers takes on the values $0, \pm 1, \pm 2, \dots$.

For observation of the condition $\nabla \mathbf{A} = 0$, it is necessary that each addend of the sum (61.9) separately satisfy this condition. Consequently,

$$\nabla(A_{\mathbf{k}} e^{i\mathbf{kr}}) = \mathbf{A}_{\mathbf{k}} \nabla e^{i\mathbf{kr}} = \mathbf{A}_{\mathbf{k}} i \mathbf{k} e^{i\mathbf{kr}} = i (\mathbf{A}_{\mathbf{k}} \mathbf{k}) e^{i\mathbf{kr}} = 0$$

It thus follows that $\mathbf{A}_{\mathbf{k}} \mathbf{k} = 0$, i.e. that the vector $\mathbf{A}_{\mathbf{k}}$ is perpendicular to the vector \mathbf{k} (the waves are transverse). Having chosen two fixed directions of polarization perpendicular to the vector \mathbf{k} , we can represent $\mathbf{A}_{\mathbf{k}}$ as the sum of two components along these directions: $\mathbf{A}_{\mathbf{k}} = \mathbf{e}_{\mathbf{k}1} A_{\mathbf{k}1} + \mathbf{e}_{\mathbf{k}2} A_{\mathbf{k}2}$ ($\mathbf{e}_{\mathbf{k}1}$ and $\mathbf{e}_{\mathbf{k}2}$ are the unit vectors of the directions forming a right-handed system with \mathbf{k}).

Expression (61.9) can thus be written as

$$\mathbf{A}(\mathbf{r}, t) = c \sqrt{\frac{4\pi}{a^3}} \sum_{\mathbf{k}, \alpha} \mathbf{e}_{\mathbf{k}\alpha} A_{\mathbf{k}\alpha}(t) e^{i\mathbf{kr}} \quad (61.11)$$

(α takes on the values 1 and 2). For the vector potential to be real, expression (61.11) must equal its complex conjugate. Taking advantage of this circumstance, we write the expression for $\mathbf{A}(\mathbf{r}, t)$ as the half-sum of expression (61.11) and its complex conjugate:

$$\mathbf{A}(\mathbf{r}, t) = c \sqrt{\frac{\pi}{a^3}} \sum_{\mathbf{k}, \alpha} \mathbf{e}_{\mathbf{k}\alpha} [A_{\mathbf{k}\alpha}(t) e^{i\mathbf{k}\mathbf{r}} + A_{\mathbf{k}\alpha}^*(t) e^{-i\mathbf{k}\mathbf{r}}] \quad (61.12)$$

When written in this way, the potential is real automatically, without any stipulations on the properties of the quantities $A_{\mathbf{k}\alpha}(t)$.

The vector potential for a field in a vacuum satisfies the equation

$$\nabla^2 \mathbf{A} = \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2}$$

Introducing the function $\mathbf{e}_{\mathbf{k}\alpha} A_{\mathbf{k}\alpha}(t) e^{i\mathbf{k}\mathbf{r}}$ into this equation and cancelling $\mathbf{e}_{\mathbf{k}\alpha} e^{i\mathbf{k}\mathbf{r}}$, we obtain

$$\frac{\partial^2 A_{\mathbf{k}\alpha}}{\partial t^2} + k^2 c^2 A_{\mathbf{k}\alpha} = 0$$

whence

$$A_{\mathbf{k}\alpha}(t) = A_{\mathbf{k}\alpha} e^{-i\omega_{\mathbf{k}} t} \quad (61.13)$$

(of the two possible exponent signs, we have taken the minus sign). Here $A_{\mathbf{k}\alpha}$ is a constant, generally speaking, complex quantity, while the frequency is determined by the formula

$$\omega_{\mathbf{k}}^2 = \mathbf{k}^2 c^2 \quad (61.14)$$

Correspondingly

$$A_{\mathbf{k}\alpha}^*(t) = A_{\mathbf{k}\alpha}^* e^{i\omega_{\mathbf{k}} t} \quad (61.15)$$

Hence, in performing a Fourier transformation, we have in essence expanded the potential in plane waves of the form $e^{\pm i(\omega_{\mathbf{k}} t - \mathbf{k}\mathbf{r})}$.

By formula (61.4), we can obtain the expansion of a generalized momentum in plane waves by differentiating expression (61.12) with respect to t . With a view to (61.13) and (61.15), we obtain

$$\mathbf{P}(\mathbf{r}, t) = \frac{1}{4\pi c^2} c \sqrt{\frac{\pi}{a^3}} \sum_{\mathbf{k}, \alpha} \mathbf{e}_{\mathbf{k}\alpha} [-i\omega_{\mathbf{k}} A_{\mathbf{k}\alpha}(t) e^{i\mathbf{k}\mathbf{r}} + i\omega_{\mathbf{k}} A_{\mathbf{k}\alpha}^*(t) e^{-i\mathbf{k}\mathbf{r}}]$$

Introducing the notation

$$P_{\mathbf{k}\alpha}(t) = \omega_{\mathbf{k}} A_{\mathbf{k}\alpha}(t) \quad (61.16)$$

we give the above expression the form

$$\mathbf{P}(\mathbf{r}, t) = \frac{-i}{4c} \sqrt{\frac{\pi}{a^3}} \sum_{\mathbf{k}, \alpha} \mathbf{e}_{\mathbf{k}\alpha} [P_{\mathbf{k}\alpha}(t) e^{i\mathbf{k}\mathbf{r}} - P_{\mathbf{k}\alpha}^*(t) e^{-i\mathbf{k}\mathbf{r}}] \quad (61.17)$$

It is not difficult to see that expression (61.17) coincides with its complex conjugate and, consequently, is real.

Substituting (61.12) and (61.17) into expression (61.6), we obtain the classical Hamiltonian function for an electromagnetic field:

$$\begin{aligned}
 H(P, A) = & -\frac{1}{8a^3} \int \sum_{k, \alpha, k', \alpha'} e_{k\alpha} e_{k'\alpha'} \{ P_{k\alpha} P_{k'\alpha'} e^{i(k+k')r} \\
 & - P_{k\alpha} P_{k'\alpha'}^* e^{i(k-k')r} - P_{k\alpha}^* P_{k'\alpha'} e^{-i(k-k')r} + P_{k\alpha}^* P_{k'\alpha'}^* e^{-i(k+k')r} \} dV \\
 & + \frac{1}{8a^3} \int c^2 \sum_{k, \alpha, k', \alpha'} \{ A_{k\alpha} A_{k'\alpha'} [\nabla, e_{k\alpha} e^{ikr}] \\
 & \times [\nabla, e_{k'\alpha'} e^{ik'r}] + A_{k\alpha} A_{k'\alpha'}^* [\nabla, e_{k\alpha} e^{ikr}] [\nabla, e_{k'\alpha'} e^{-ik'r}] \\
 & + A_{k\alpha}^* A_{k'\alpha'} [\nabla, e_{k\alpha} e^{ikr}] [\nabla, e_{k'\alpha'} e^{ik'r}] \\
 & + A_{k\alpha}^* A_{k'\alpha'}^* [\nabla, e_{k\alpha} e^{-ikr}] [\nabla, e_{k'\alpha'} e^{-ik'r}] \} dV = \mathcal{J}_1 + \mathcal{J}_2 \quad (61.18)
 \end{aligned}$$

The quantities $P_{k\alpha}$ and $A_{k\alpha}$ are functions of t ; this is not indicated explicitly so as not to make the formulas more complicated.

Let us first calculate the integral \mathcal{J}_1 . After changing the sequence of integration and summation, \mathcal{J}_1 transforms into the sum of addends that contain integrals of the form

$$\mathcal{J} = \int e^{\pm i(k \pm k')r} dV \quad (61.19)$$

With a view to (61.10), we have

$$\begin{aligned}
 \mathcal{J} = & \int_0^a \exp [\pm i(2\pi/a)(n_1 \pm n'_1)x] dx \\
 & \times \int_0^a \exp [\pm i(2\pi/a)(n_2 \pm n'_2)y] dy \int_0^a \exp [\pm i(2\pi/a)(n_3 \pm n'_3)z] dz
 \end{aligned}$$

This expression is non-zero (and equals a^3) only if $n_1 \pm n'_1 = n_2 \pm n'_2 = n_3 \pm n'_3 = 0$, i.e. $k \pm k' = 0$. Correspondingly in the sums in which the exponent contains $k + k'$, only the addends with $k' = -k$ will be non-zero, and in the sums in which the exponent contains $k - k'$, the addends with $k' = k$ will be non-zero. Therefore

$$\begin{aligned}
 \mathcal{J}_1 = & \frac{-1}{8} \sum_{k, \alpha, \alpha'} \{ e_{k\alpha} e_{-k\alpha'} P_{k\alpha} P_{-k\alpha'} \\
 & - e_{k\alpha} e_{k\alpha'} P_{k\alpha} P_{k\alpha'}^* - e_{k\alpha} e_{k\alpha'} P_{k\alpha}^* P_{k\alpha'} + e_{k\alpha} e_{-k\alpha'} P_{k\alpha}^* P_{-k\alpha'}^* \} \\
 (\text{a^3 was cancelled.})
 \end{aligned}$$

Now let us take advantage of the fact that $e_{k\alpha} e_{k\alpha'} = \delta_{\alpha\alpha'}$, and $e_{k\alpha} e_{-k\alpha'} = -\delta_{\alpha\alpha'}$. As a result, the expression for \mathcal{J}_1 is simplified as

follows [we return to the complete writing of the functions $P_{k\alpha}(t)$ and $A_{k\alpha}(t)$]:

$$\mathcal{J}_1 = \frac{1}{8} \sum_{k, \alpha} \{ P_{k\alpha}(t) P_{-k\alpha}(t) + 2P_{k\alpha}(t) P_{k\alpha}^*(t) + P_{k\alpha}^*(t) P_{-k\alpha}^*(t) \} \quad (61.20)$$

Before beginning to evaluate the integral \mathcal{J}_2 , we shall find the values of the vector products contained in the integrand. By formula (XI.28) of Vol. 1, we find that

$$[\nabla, e_{k\alpha} e^{\pm ikr}] = [\nabla e^{\pm ikr}, e_{k\alpha}] = \pm ie^{\pm ikr} [k, e_{k\alpha}]$$

Accordingly

$$[\nabla, e_{k\alpha} e^{\pm ikr}] [\nabla, e_{k'\alpha'} e^{\mp ik'r}] = -e^{\pm i(k+k')r} [k, e_{k\alpha}] [k', e_{k'\alpha'}] \quad (61.21)$$

$$[\nabla, e_{k\alpha} e^{\pm ikr}] [\nabla, e_{k'\alpha'} e^{\mp ik'r}] = e^{\pm i(k-k')r} [k, e_{k\alpha}] [k', e_{k'\alpha'}] \quad (61.22)$$

After substitution of these values into (61.18) and changing the sequence of integration and summation, in the expression for \mathcal{J}_2 integrals of the form of (61.19) will appear. These integrals are non-zero (and are equal to a^3) for products of the type of (61.21) when $k' = -k$, and for products of the type of (61.22) when $k' = k$. Consequently, we obtain the following expression for \mathcal{J}_2 :

$$\begin{aligned} \mathcal{J}_2 = & \frac{c^2}{8} \sum_{k, \alpha, \alpha'} \{ -A_{k\alpha} A_{-k\alpha'} [k, e_{k\alpha}] [-k, e_{-k\alpha'}] \\ & + A_{k\alpha} A_{k\alpha'}^* [k, e_{k\alpha}] [k, e_{k\alpha'}] + A_{k\alpha}^* A_{k\alpha'} [k, e_{k\alpha}] [k, e_{k\alpha'}] \\ & - A_{k\alpha}^* A_{-k\alpha'}^* [k, e_{k\alpha}] [-k, e_{-k\alpha'}] \} \end{aligned} \quad (61.23)$$

When $\alpha' \neq \alpha$, the vector products are mutually perpendicular so that their scalar product is zero. For this reason, we must retain only the terms in which $\alpha' = \alpha$ in (61.23). Taking into account that $e_{-k\alpha} = -e_{k\alpha}$, we obtain

$$[k, e_{k\alpha}] [\pm k, e_{\pm k\alpha}] = [k, e_{k\alpha}]^2 = k^2 e_{k\alpha}^2 - (ke_{k\alpha})^2 = k^2$$

[see Vol. 1, formula (VI.6), $e_{k\alpha}$ is perpendicular to k].

Hence, all the non-zero products of the vector products in (61.23) have the same value equal to k^2 . With a view to the fact that $c^2 k^2 = \omega_k^2$ [see (61.14)], we shall represent \mathcal{J}_2 in the form

$$\begin{aligned} \mathcal{J}_2 = & \frac{1}{8} \sum_{k, \alpha} \omega_k^2 \{ -A_{k\alpha}(t) A_{-k\alpha}(t) + 2A_{k\alpha}(t) A_{k\alpha}^*(t) \\ & - A_{k\alpha}^*(t) A_{-k\alpha}^*(t) \} \end{aligned} \quad (61.24)$$

To obtain the function (61.18), we must add expressions (61.20) and (61.24). The first and third terms in these sums cancel each other [this follows from (61.16)]. Consequently,

$$H(\mathbf{P}, \mathbf{A}) = \frac{1}{4} \sum_{\mathbf{k}, \alpha} \{ P_{\mathbf{k}\alpha}(t) P_{\mathbf{k}\alpha}^*(t) + \omega_{\mathbf{k}}^2 A_{\mathbf{k}\alpha}(t) A_{\mathbf{k}\alpha}^*(t) \} \quad (61.25)$$

Let us correlate the following real variables with the complex quantities $A_{\mathbf{k}\alpha}(t)$ and $P_{\mathbf{k}\alpha}(t)$:

$$q_{\mathbf{k}\alpha}(t) = \frac{1}{2} [A_{\mathbf{k}\alpha}(t) + A_{\mathbf{k}\alpha}^*(t)] \quad (61.26)$$

$$p_{\mathbf{k}\alpha}(t) = \frac{-i}{2} [P_{\mathbf{k}\alpha}(t) - P_{\mathbf{k}\alpha}^*(t)] \quad (61.27)$$

It is evident that $q_{\mathbf{k}\alpha}(t)$ is the real part of $A_{\mathbf{k}\alpha}(t)$, and $p_{\mathbf{k}\alpha}(t)$ is the imaginary part of $P_{\mathbf{k}\alpha}(t)$. Such a definition of $p_{\mathbf{k}\alpha}(t)$ is due to the circumstance that expression (61.17) contains the quantities $P_{\mathbf{k}\alpha}(t)$ multiplied by $-i$. Therefore, the imaginary part of $P_{\mathbf{k}\alpha}(t)$ plays the same role with respect to the generalized momentum $\mathbf{P}(\mathbf{r}, t)$ of the field that the real part of $A_{\mathbf{k}\alpha}(t)$ plays with respect to the generalized coordinate $\mathbf{A}(\mathbf{r}, t)$ of the field.

Since $P_{\mathbf{k}\alpha}(t) = \omega_{\mathbf{k}} A_{\mathbf{k}\alpha}(t)$ [see (61.16)], expression (61.27) can be written as

$$p_{\mathbf{k}\alpha}(t) = -i\omega_{\mathbf{k}} [A_{\mathbf{k}\alpha}(t) - A_{\mathbf{k}\alpha}^*(t)] \quad (61.28)$$

Examination of (61.26) and (61.28) shows that

$$A_{\mathbf{k}\alpha}(t) = q_{\mathbf{k}\alpha} + i \frac{p_{\mathbf{k}\alpha}}{\omega_{\mathbf{k}}}, \quad A_{\mathbf{k}\alpha}^*(t) = q_{\mathbf{k}\alpha} - i \frac{p_{\mathbf{k}\alpha}}{\omega_{\mathbf{k}}} \quad (61.29)$$

Multiplication of these expressions by $\omega_{\mathbf{k}}$ yields

$$P_{\mathbf{k}\alpha}(t) = \omega_{\mathbf{k}} q_{\mathbf{k}\alpha} + i p_{\mathbf{k}\alpha}, \quad P_{\mathbf{k}\alpha}^*(t) = \omega_{\mathbf{k}} q_{\mathbf{k}\alpha} - i p_{\mathbf{k}\alpha} \quad (61.30)$$

Expressing P , P^* , A , and A^* in (61.25) in terms of q and p in accordance with (61.29) and (61.30) and performing simple transformations, we arrive at the formula

$$H(p_{\mathbf{k}\alpha}, q_{\mathbf{k}\alpha}) = \frac{1}{2} \sum_{\mathbf{k}, \alpha} (p_{\mathbf{k}\alpha}^2 + \omega_{\mathbf{k}}^2 q_{\mathbf{k}\alpha}^2) \quad (61.31)$$

It follows from (61.31) that the classical Hamiltonian function for an electromagnetic field is the sum of independent addends of the form

$$H_{\mathbf{k}\alpha} = \frac{1}{2} (p_{\mathbf{k}\alpha}^2 + \omega_{\mathbf{k}}^2 q_{\mathbf{k}\alpha}^2) \quad (61.32)$$

coinciding with the Hamiltonian function for a harmonic oscillator with unit mass. We thus arrive at the conclusion that an electromag-

netic field can be represented as a set of an infinitely great number of harmonic oscillators.

The transition from the classical description to the quantum one is performed by replacing the quantities $p_{k\alpha}(t)$ and $q_{k\alpha}(t)$ with the operators $\hat{p}_{k\alpha}(t)$ and $\hat{q}_{k\alpha}(t)$ that obey the same commutation relations as the operators of conventional coordinates and momenta do:

$$\{\hat{q}_{k\alpha}, \hat{q}_{k'\alpha'}\} = 0, \quad [\hat{p}_{k\alpha}, \hat{p}_{k'\alpha'}] = 0, \quad [\hat{q}_{k\alpha}, \hat{p}_{k'\alpha'}] = i\hbar\delta_{kk'}\delta_{\alpha\alpha'} \quad (61.33)$$

[compare with (16.3)]. In accordance with (61.29) and (61.30), the quantities A and P transform into the operators

$$\hat{A}_{k\alpha}(t) = \hat{q}_{k\alpha}(t) + i \frac{\hat{p}_{k\alpha}(t)}{\omega_k} \quad (61.34)$$

$$\hat{P}_{k\alpha}(t) = \omega_k \hat{q}_{k\alpha}(t) + i \hat{p}_{k\alpha}(t) \quad (61.35)$$

Hermitian conjugation of operators corresponds to complex conjugation of quantities. For this reason, the quantities $A_{k\alpha}^*(t)$ and $P_{k\alpha}^*(t)$ must be replaced with the operators

$$\hat{A}_{k\alpha}^*(t) = \hat{q}_{k\alpha}^*(t) - i \frac{\hat{p}_{k\alpha}^*(t)}{\omega_k} \quad (61.36)$$

$$\hat{P}_{k\alpha}^*(t) = \omega_k \hat{q}_{k\alpha}^*(t) - i \hat{p}_{k\alpha}^*(t) \quad (61.37)$$

[see (10.13)]. We must note that formulas (61.36) and (61.37) are obtained by substituting operators for the variables q and p in expression (61.29) for $A_{k\alpha}^*(t)$ and in expression (61.30) for $P_{k\alpha}^*(t)$ (with subsequent consideration of the fact that $\hat{q} = \hat{q}^*$ and $\hat{p} = \hat{p}^*$).

To simplify writing of the formulas, we shall not always indicate the explicit time dependence of the operators $\hat{A}_{k\alpha}(t)$, $\hat{P}_{k\alpha}(t)$, $\hat{q}_{k\alpha}(t)$, and $\hat{p}_{k\alpha}(t)$ in the following. It must be remembered, however, that this dependence exists.

We have already noted that it is expedient to transform the Hamiltonian (61.31) to the occupation number representation (see Sec. 50), i.e. express it in terms of the particle annihilation and creation operators (see Secs. 27 and 51). These operators are determined by expressions similar to (27.1):

$$\begin{aligned} \hat{a}_{k\alpha}(t) &= \frac{1}{\sqrt{2}} \left\{ \sqrt{\frac{\omega_k}{\hbar}} \hat{q}_{k\alpha}(t) + \frac{i}{\sqrt{\hbar\omega_k}} \hat{p}_{k\alpha}(t) \right\} \\ \hat{a}_{k\alpha}^*(t) &= \frac{1}{\sqrt{2}} \left\{ \sqrt{\frac{\omega_k}{\hbar}} \hat{q}_{k\alpha}(t) - \frac{i}{\sqrt{\hbar\omega_k}} \hat{p}_{k\alpha}(t) \right\} \end{aligned} \quad (61.38)$$

It is obvious that all the commutation relations obtained in Sec. 27 for the operators (27.1) also hold for the operators (61.38). Particularly,

$$[\hat{a}_{\mathbf{k}\alpha}, \hat{a}_{\mathbf{k}\alpha}^+] = \hat{a}_{\mathbf{k}\alpha} \hat{a}_{\mathbf{k}\alpha}^+ - \hat{a}_{\mathbf{k}\alpha}^+ \hat{a}_{\mathbf{k}\alpha} = 1 \quad (61.39)$$

$$\frac{1}{2} (\hat{a}_{\mathbf{k}\alpha} \hat{a}_{\mathbf{k}\alpha}^+ + \hat{a}_{\mathbf{k}\alpha}^+ \hat{a}_{\mathbf{k}\alpha}) = \hat{a}_{\mathbf{k}\alpha}^+ \hat{a}_{\mathbf{k}\alpha} + \frac{1}{2} \quad (61.40)$$

A comparison of expressions (61.34) and (61.36) with formulas (61.38) shows that

$$\left. \begin{aligned} \hat{A}_{\mathbf{k}\alpha}(t) &= \sqrt{2\hbar/\omega_{\mathbf{k}}} \hat{a}_{\mathbf{k}\alpha}(t) \\ \hat{A}_{\mathbf{k}\alpha}^+(t) &= \sqrt{2\hbar/\omega_{\mathbf{k}}} \hat{a}_{\mathbf{k}\alpha}^+(t) \end{aligned} \right\} \quad (61.41)$$

Introducing these values into (61.12), we obtain the operator of the vector potential of a field in the occupation number representation:

$$\hat{\mathbf{A}}(\mathbf{r}, t) = c \sqrt{\frac{2\pi\hbar}{a^3}} \sum_{\mathbf{k}, \alpha} \frac{e_{\mathbf{k}\alpha}}{\sqrt{\omega_{\mathbf{k}}}} \{ \hat{a}_{\mathbf{k}\alpha}(t) e^{i\mathbf{k}\mathbf{r}} + \hat{a}_{\mathbf{k}\alpha}^+(t) e^{-i\mathbf{k}\mathbf{r}} \} \quad (61.42)$$

Solving the system of equations (61.38) relative to $\hat{q}_{\mathbf{k}\alpha}$ and $\hat{p}_{\mathbf{k}\alpha}$, we obtain expressions of these operators in the occupation number representation:

$$\left. \begin{aligned} \hat{q}_{\mathbf{k}\alpha} &= \sqrt{\hbar/2\omega_{\mathbf{k}}} (\hat{a}_{\mathbf{k}\alpha}^+ + \hat{a}_{\mathbf{k}\alpha}) \\ \hat{p}_{\mathbf{k}\alpha} &= i \sqrt{\hbar\omega_{\mathbf{k}}/2} (\hat{a}_{\mathbf{k}\alpha}^+ - \hat{a}_{\mathbf{k}\alpha}) \end{aligned} \right\} \quad (61.43)$$

Replacing the quantities p and q with operators in (61.31), we obtain the following expression for the Hamiltonian of a free electromagnetic field:

$$\hat{H} = \frac{1}{2} \sum_{\mathbf{k}, \alpha} (\hat{p}_{\mathbf{k}\alpha}^2 + \omega_{\mathbf{k}}^2 \hat{q}_{\mathbf{k}\alpha}^2)$$

Introducing expressions (61.43) for \hat{p} and \hat{q} into this equation, we obtain the Hamiltonian of a field in the occupation number representation:

$$\begin{aligned} \hat{H} &= \sum_{\mathbf{k}, \alpha} \frac{\hbar\omega_{\mathbf{k}}}{4} [(\hat{a}_{\mathbf{k}\alpha}^+ + \hat{a}_{\mathbf{k}\alpha})(\hat{a}_{\mathbf{k}\alpha}^+ + \hat{a}_{\mathbf{k}\alpha}) - (\hat{a}_{\mathbf{k}\alpha}^+ - \hat{a}_{\mathbf{k}\alpha})(\hat{a}_{\mathbf{k}\alpha}^+ - \hat{a}_{\mathbf{k}\alpha})] \\ &= \sum_{\mathbf{k}, \alpha} \frac{\hbar\omega_{\mathbf{k}}}{2} (\hat{a}_{\mathbf{k}\alpha} \hat{a}_{\mathbf{k}\alpha}^+ + \hat{a}_{\mathbf{k}\alpha}^+ \hat{a}_{\mathbf{k}\alpha}) \end{aligned}$$

Using relation (61.40), let us write the Hamiltonian in the form

$$\hat{H} = \sum_{\mathbf{k}, \alpha} \hbar\omega_{\mathbf{k}} \left(\hat{a}_{\mathbf{k}\alpha}^+ \hat{a}_{\mathbf{k}\alpha} + \frac{1}{2} \right) \quad (61.44)$$

Recall that summation is performed over all the values of the wave vector \mathbf{k} and two values of the polarization.

The operator (61.44) differs from the Hamiltonian (51.45) for a system of bosons obtained in Sec. 51 only in a constant term equal to $\hbar\omega_{\mathbf{k}}/2$. We thus conclude that a free electromagnetic field is a system of bosons. The latter are called **photons**.

Introducing expression (61.44) for \hat{H} into the equation $\hat{H}\psi = E\psi$, we obtain

$$\sum_{\mathbf{k}, \alpha} \hbar\omega_{\mathbf{k}} \hat{a}_{\mathbf{k}\alpha}^{\dagger} \hat{a}_{\mathbf{k}\alpha} \psi + \frac{1}{2} \sum_{\mathbf{k}, \alpha} \hbar\omega_{\mathbf{k}} \psi = E\psi \quad (61.45)$$

According to (51.26), $\hat{a}_{\mathbf{k}\alpha}^{\dagger} \hat{a}_{\mathbf{k}\alpha} \psi = n_{\mathbf{k}\alpha} \psi$, where $n_{\mathbf{k}\alpha}$ is the number of photons with given values of \mathbf{k} and α . With this in view, we obtain from (61.45) the following expression for the energy of an electromagnetic field:

$$E = \sum_{\mathbf{k}, \alpha} n_{\mathbf{k}\alpha} \hbar\omega_{\mathbf{k}} + \sum_{\mathbf{k}, \alpha} \frac{\hbar\omega_{\mathbf{k}}}{2} \quad (61.46)$$

We conclude from (61.46) that the energy of a photon is $\hbar\omega_{\mathbf{k}}$. In addition, it follows from (61.46) that even in the absence of photons (i.e. if all the $n_{\mathbf{k}\alpha}$'s equal zero), the energy of a field has a non-zero value equal to

$$E_0 = \sum_{\mathbf{k}, \alpha} \frac{\hbar\omega_{\mathbf{k}}}{2} \quad (61.47)$$

The quantity (61.47) is called the **zero-point energy** of an electromagnetic field, and the state of a field in which all the $n_{\mathbf{k}\alpha}$'s are zero is called a **vacuum**. Since the number of addends in (61.47) is infinitely large, E_0 is infinitely large too. For the majority of processes of interaction of a field with a substance, only the difference of the energies for two states of the substance-field system is of significance. Therefore, the presence of an infinitely great constant quantity in the energy does not manifest itself in these processes. The existence of zero-point oscillations, however, affects some processes and results in effects that, although very small, are observable.

Let us find the operator of the momentum of an electromagnetic field. It is known from classical electrodynamics that the momentum of a plane wave $e^{i\mathbf{k}\mathbf{r}}$ with the polarization α is

$$\mathbf{p}_{\mathbf{k}\alpha} = \frac{\mathbf{k}}{k} \frac{E_{\mathbf{k}\alpha}}{c} = \mathbf{k} \frac{E_{\mathbf{k}\alpha}}{\omega_{\mathbf{k}}}$$

where $E_{k\alpha}$ is the energy of the wave. Consequently, the total momentum of a field is determined by the expression

$$\mathbf{p} = \sum_{\mathbf{k}, \alpha} \frac{\mathbf{k}}{\omega_{\mathbf{k}}} E_{\mathbf{k}\alpha}$$

Going over to operators, we obtain

$$\hat{\mathbf{p}} = \sum_{\mathbf{k}, \alpha} \frac{\mathbf{k}}{\omega_{\mathbf{k}}} \hat{H}_{\mathbf{k}\alpha} = \sum_{\mathbf{k}, \alpha} \hbar \mathbf{k} \left(\hat{a}_{\mathbf{k}\alpha}^* \hat{a}_{\mathbf{k}\alpha} + \frac{1}{2} \right) \quad (61.48)$$

From the equation $\hat{\mathbf{p}}\psi = \mathbf{p}\psi$, we obtain [compare with (61.45)] the following expression for the momentum of a field:

$$\mathbf{p} = \sum_{\mathbf{k}, \alpha} n_{\mathbf{k}\alpha} \hbar \mathbf{k} + \sum_{\mathbf{k}, \alpha} \frac{\hbar \mathbf{k}}{2}$$

from which it follows that the momentum of a photon is $\hbar \mathbf{k}$.

Bosons, which include photons, have an integral (or zero) spin. The spin of a photon is unity. The concept of spin as the angular momentum of a particle at rest cannot obviously be applied to a photon. Therefore, the spin of a photon is defined to be the smallest of the possible values of its angular momentum. It is just this smallest value that equals unity.

The psi-function of an electromagnetic field (or, as is customarily said, the amplitude of the field state) has the following form in the occupation number representation:

$$\psi = \psi(n_{\mathbf{k}_11}, n_{\mathbf{k}_12}, n_{\mathbf{k}_21}, n_{\mathbf{k}_22}, \dots) \quad (61.49)$$

62. Interaction of an Electromagnetic Field with a Charged Particle

Consider that the velocity of a particle is small in comparison with c . In this case, the particle is described by the non-relativistic Hamiltonian (32.6). If we gauge the field so that the conditions

$$\varphi = 0, \quad \nabla \mathbf{A} = 0$$

are observed, expression (32.6) becomes

$$\hat{H} = \frac{1}{2m_0} \hat{\mathbf{p}}^2 - \frac{e}{m_0 c} \hat{\mathbf{p}} \hat{\mathbf{A}} + \frac{e^2}{2m_0 c} \hat{\mathbf{A}}^2 \quad (62.1)$$

Recall that with this gauging, the operators $\hat{\mathbf{p}}$ and $\hat{\mathbf{A}}$ commute:

$$[\hat{\mathbf{p}}, \hat{\mathbf{A}}] = 0 \quad (62.2)$$

[see (32.5)]. For this reason, the sequence of the factors in the second term of expression (62.1) is immaterial.

The Hamiltonian of the system "field + particle" will be written as follows:

$$\hat{H} = \frac{1}{2m_0} \hat{\mathbf{p}}^2 - \frac{e}{m_0 c} \hat{\mathbf{p}} \hat{\mathbf{A}} + \frac{e^2}{2m_0 c^2} \hat{\mathbf{A}}^2 + \hat{H}_{\text{field}} \quad (62.3)$$

The first term in this expression contains only quantities characterizing a particle, therefore we can designate it by $\hat{H}_{\text{particle}}$. The last term contains only quantities characterizing a field. The second and third terms contain both quantities characterizing a particle (e, m_0, \mathbf{p}) and a quantity characterizing a field (\mathbf{A}). Hence, these two addends are the operator of particle-field interaction

$$\hat{V} = -\frac{e}{m_0 c} \hat{\mathbf{p}} \hat{\mathbf{A}} + \frac{e^2}{2m_0 c^2} \hat{\mathbf{A}}^2 = \hat{V}_1 + \hat{V}_2 \quad (62.4)$$

The operator \hat{V} determines the processes of particle-field interaction that may consist either in the creation of photons (i.e. in the emission of photons by the particle) or in the annihilation of photons (i.e. in the absorption of photons by the particle).

Considering \hat{V} as a weak perturbation, let us use the perturbation theory for studying the processes of emission and absorption of photons. Accordingly, the evaluation of the probabilities of these processes will be reduced to evaluation of the matrix elements of the operator (62.4).

The unperturbed Hamiltonian breaks up into two independent terms:

$$\hat{H}_0 = \hat{H}_{\text{particle}} + \hat{H}_{\text{field}}$$

Therefore, the psi-functions of the unperturbed problem can be represented as the product of two functions, the first of which describes the particle, and the second, the field:

$$\psi^{(0)} = \psi_{\text{particle}}^{(0)} \cdot \psi_{\text{field}}^{(0)} \quad (62.5)$$

[compare with (46.2) and (46.3)].

By (61.42), the operator $\hat{\mathbf{A}}(\mathbf{r}, t)$ in the occupation number representation is determined by the expression

$$\begin{aligned} \hat{\mathbf{A}} &= c \sqrt{\frac{2\pi\hbar}{a^3}} \sum_{\mathbf{k}, \alpha} \frac{e_{\mathbf{k}\alpha}}{\sqrt{\omega_{\mathbf{k}}}} (\hat{a}_{\mathbf{k}\alpha} e^{i\mathbf{k}\mathbf{r}} + \hat{a}_{\mathbf{k}\alpha}^* e^{-i\mathbf{k}\mathbf{r}}) \\ &= \sum_{\mathbf{k}, \alpha} (C_{\mathbf{k}\alpha} \hat{a}_{\mathbf{k}\alpha} + C_{\mathbf{k}\alpha}^* \hat{a}_{\mathbf{k}\alpha}^*) \end{aligned} \quad (62.6)$$

where

$$C_{k\alpha} = c \sqrt{\frac{2\pi\hbar}{a^3}} \frac{e_{k\alpha}}{\sqrt{\omega_k}} e^{ikr} \quad (62.7)$$

For a system of bosons, only the matrix elements

$$\langle \dots, n_{k\alpha} - 1, \dots | \hat{a}_{k\alpha} | \dots, n_{k\alpha}, \dots \rangle = \sqrt{n_{k\alpha}} \quad (62.8)$$

$$\langle \dots, n_{k\alpha} + 1, \dots | \hat{a}_{k\alpha}^\dagger | \dots, n_{k\alpha}, \dots \rangle = \sqrt{n_{k\alpha} + 1} \quad (62.9)$$

are non-zero [see formulas (51.33) and (51.34)]. The corresponding matrices are as follows:

$$\hat{a}_{k\alpha} = \begin{pmatrix} 0 & 1 & 0 & 0 & \dots \\ 0 & 0 & \sqrt{2} & 0 & \dots \\ 0 & 0 & 0 & \sqrt{3} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} \quad (62.10)$$

$$\hat{a}_{k\alpha}^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 & \dots \\ 1 & 0 & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & 0 & \dots \\ 0 & 0 & \sqrt{3} & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} \quad (62.11)$$

In these matrices, the row number coincides with the number of particles in the final state, and the column number with the number of particles in the initial state. Consequently, the non-zero elements of the matrix $\hat{a}_{k\alpha}$ correspond to the transitions

1 particle \rightarrow 0 particles, 2 particles \rightarrow 1 particle, etc.

and the non-zero elements of the matrix $\hat{a}_{k\alpha}^\dagger$, to the transitions

0 particles \rightarrow 1 particle, 1 particle \rightarrow 2 particles, etc.

Hence, the operator \hat{V}_1 [see (62.4)] in the first approximation describes single-photon transitions, i.e. processes of the emission or absorption of one photon. The operator \hat{A}^2 has the form [see (62.6)]

$$\begin{aligned} \hat{A}^2 &= \sum_{k, \alpha} (C_{k\alpha} \hat{a}_{k\alpha} + C_{k\alpha}^* \hat{a}_{k\alpha}^\dagger) \sum_{k', \alpha'} (C_{k'\alpha'} \hat{a}_{k'\alpha'} + C_{k'\alpha'}^* \hat{a}_{k'\alpha'}^\dagger) \\ &= \sum_{k, \alpha, k', \alpha'} (C_{k\alpha} C_{k'\alpha'}^* \hat{a}_{k\alpha} \hat{a}_{k'\alpha'} + C_{k\alpha} C_{k'\alpha'}^* \hat{a}_{k\alpha} \hat{a}_{k'\alpha'}^\dagger \\ &\quad + C_{k\alpha}^* C_{k'\alpha'} \hat{a}_{k\alpha}^\dagger \hat{a}_{k'\alpha'} + C_{k\alpha}^* C_{k'\alpha'}^* \hat{a}_{k\alpha}^\dagger \hat{a}_{k'\alpha'}^\dagger) \quad (62.12) \end{aligned}$$

The matrices of the operators $\hat{a}_{k'\alpha'}$ and $\hat{a}_{k'\alpha'}^\dagger$ have the same form as the matrices of the operators $\hat{a}_{k\alpha}$ and $\hat{a}_{k\alpha}^\dagger$. Multiplication of the matrices (62.10) and (62.11) yields

$$\hat{a}\hat{a} = \begin{pmatrix} 0 & 0 & \sqrt{1 \cdot 2} & 0 & 0 & \dots \\ 0 & 0 & 0 & \sqrt{2 \cdot 3} & 0 & \dots \\ 0 & 0 & 0 & 0 & \sqrt{3 \cdot 4} & \dots \\ \vdots & \ddots & \ddots & \ddots & \ddots & \ddots \\ \vdots & \ddots & \ddots & \ddots & \ddots & \ddots \\ \vdots & \ddots & \ddots & \ddots & \ddots & \ddots \end{pmatrix} \quad (62.13)$$

$$\hat{a}^+\hat{a}^+ = \begin{pmatrix} 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & \dots \\ \sqrt{1 \cdot 2} & 0 & 0 & \dots \\ 0 & \sqrt{2 \cdot 3} & 0 & \dots \\ 0 & 0 & \sqrt{3 \cdot 4} & \dots \\ \vdots & \ddots & \ddots & \ddots & \ddots & \ddots \end{pmatrix}$$

$$\hat{a}\hat{a}^+ = \begin{pmatrix} 1 & 0 & 0 & \dots \\ 0 & 2 & 0 & \dots \\ 0 & 0 & 3 & \dots \\ \vdots & \ddots & \ddots & \ddots \end{pmatrix}, \quad \hat{a}^+\hat{a} = \begin{pmatrix} 0 & 0 & 0 & 0 & \dots \\ 0 & 1 & 0 & 0 & \dots \\ 0 & 0 & 2 & 0 & \dots \\ 0 & 0 & 0 & 3 & \dots \\ \vdots & \ddots & \ddots & \ddots & \ddots \end{pmatrix} \quad (62.14)$$

We must note that from (62.14), the difference $\hat{a}\hat{a}^+ - \hat{a}^+\hat{a}$ equals a unit matrix [see (61.39)].

Recall that the number of a row equals the number of particles in the final state, and the number of a column—the number of particles in the initial state. Consequently, the non-zero elements of the matrix $\hat{a}\hat{a}$ correspond to the transitions

2 particles \rightarrow 0 particles, 3 particles \rightarrow 1 particle, etc.,
the elements of the matrix $\hat{a}^+\hat{a}^+$ —to the transitions

0 particles \rightarrow 2 particles, 1 particle \rightarrow 3 particles, etc.,
the elements of the matrix $\hat{a}\hat{a}^+$ —to the transitions

0 particles \rightarrow 0 particles, 1 particle \rightarrow 1 particle, etc.,
and, finally, the elements of the matrix $\hat{a}^+\hat{a}$ —to the transitions

1 particle \rightarrow 1 particle, 2 particles \rightarrow 2 particles, etc.

Therefore, the matrix \hat{A}^2 and, consequently, the operator \hat{V}_2 too [see (62.4)] describe two-photon transitions: the simultaneous emission or absorption of two photons [the terms in (62.12) corresponding

to the matrices (62.13)], and also processes involving the simultaneous emission of one photon and the absorption of another, as a result of which the number of photons remains unchanged [the terms corresponding to the matrices (62.14)].

We have seen above that the operator \hat{V}_1 in a first approximation describes one-photon processes. Only in the second approximation of the perturbation theory, when the squares of the matrix elements begin to play a role, does the operator \hat{V}_1 contribute to two-photon transitions. The operator \hat{V}_2 , on the other hand, gives a non-zero probability of two-photon transitions already in the first approximation.

The operator (62.4) may be considered as a weak perturbation only when A is small. Consequently, $|A^2| \ll |A|$. We thus conclude that the probability of two-photon transitions is low in comparison with that of one-photon transitions.

63. One-Photon Processes

Let us investigate the one-photon processes occurring in the system "electron-field". The charge of an electron is $-e$, therefore the operator responsible for one-photon transitions [see \hat{V}_1 in (62.4)] has the form

$$\hat{V} = \frac{e}{m_e c} \hat{p} \hat{A} \quad (63.1)$$

According to (62.5), the psi-function of an unperturbed system breaks up into two factors:

$$\psi^{(0)} = \psi_{\text{electron}}^{(0)} \cdot \psi_{\text{field}}^{(0)} \quad (63.2)$$

We take the function $\psi_{\text{electron}}^{(0)}$ in the coordinate representation, and the function $\psi_{\text{field}}^{(0)}$ in the occupation number representation. We must accordingly take the operator \hat{p} in the coordinate representation, and the operator \hat{A} in the occupation number representation.

In evaluating the matrix element $\langle \psi_1^{(0)} | \hat{V} \psi_2^{(0)} \rangle$, we shall have to perform both integration over the coordinates and operations with the occupation numbers. We shall first perform the operations with the occupation numbers, and then evaluate the integral over the coordinates.

Consider a process attended by the emission of a photon of the frequency ω_k and the polarization α , and also by the transition of

an electron from the state 2 to the state 1. The following matrix element corresponds to this process:

$$\langle 1, n_{k\alpha} + 1 | \hat{V} | 2, n_{k\alpha} \rangle = \left\langle \Psi_{el, 1}^{(0)} \Psi_{field}^{(0)} (n_{k\alpha} + 1) \left| \frac{e}{m_e c} \hat{\mathbf{p}} \hat{\mathbf{A}} \right| \Psi_{el, 2}^{(0)} \Psi_{field}^{(0)} (n_{k\alpha}) \right\rangle \quad (63.3)$$

Having performed the operations with the occupation numbers, we obtain a factor that by (62.6) and (62.11) is

$$\begin{aligned} & \left\langle \dots, n_{k\alpha} + 1, \dots \left| c \sqrt{\frac{2\pi\hbar}{a^3\omega_k}} \mathbf{e}_{k\alpha} e^{-ikr} \hat{a}_{k\alpha}^\dagger \right| \dots, n_{k\alpha}, \dots \right\rangle \\ &= c \sqrt{\frac{2\pi\hbar(n_{k\alpha} + 1)}{a^3\omega_k}} \mathbf{e}_{k\alpha} e^{-ikr} \end{aligned}$$

Introducing this expression into (63.3) and writing the scalar product of the functions in the form of an integral, we obtain

$$\begin{aligned} & \langle 1, n_{k\alpha} + 1 | \hat{V} | 2, n_{k\alpha} \rangle \\ &= \frac{e}{m_e} \sqrt{\frac{2\pi\hbar(n_{k\alpha} + 1)}{a^3\omega_k}} \int [\Psi_{el, 1}^{(0)}]^* \mathbf{e}_{k\alpha} \hat{\mathbf{p}} e^{-ikr} \Psi_{el, 2}^{(0)} dV \quad (63.4) \end{aligned}$$

Similar calculations for a process attended by the absorption of a photon and the transition of an electron from the state 1 to the state 2 yield

$$\begin{aligned} & \langle 2, n_{k\alpha} - 1 | \hat{V} | 1, n_{k\alpha} \rangle \\ &= \frac{e}{m_e} \sqrt{\frac{2\pi\hbar n_{k\alpha}}{a^3\omega_k}} \int [\Psi_{el, 2}^{(0)}]^* \mathbf{e}_{k\alpha} \hat{\mathbf{p}} e^{ikr} \Psi_{el, 1}^{(0)} dV \quad (63.5) \end{aligned}$$

The probabilities of the processes are proportional to the squares of the magnitudes of the relevant matrix elements [see the text following formula (9.18)]. A glance at formula (63.4) shows that the probability of emitting a photon is proportional to $n_{k\alpha} + 1$, where $n_{k\alpha}$ is the number of photons present before the process of emission:

$$P_{emis} \propto n_{k\alpha} + 1 \quad (63.6)$$

The probability of emission can thus be divided into two parts:

$$P_{emis} = P_{stim} + P_{spont} \quad (63.7)$$

where $P_{stim} \propto n_{k\alpha}$, and $P_{spont} \propto 1$, i.e. does not depend on $n_{k\alpha}$.

The part of the radiation corresponding to P_{stim} is due to the electromagnetic field present. This field, acting on an electron, causes its transition to a new state with the emission of an additional photon of the same frequency and polarization. The radiation appearing in this way is said to be **stimulated** (or **induced**).

The part of the radiation corresponding to P_{spont} does not depend on the field already present. In this case, an electron emits a photon not under the action of external factors, but spontaneously. Such emission is called spontaneous¹. [3pɔn' + eŋj əɔʃ]

Inspection of formula (63.5) reveals that the probability of absorption of a photon is proportional to $n_{k\alpha}$:

$$P_{\text{abs}} \propto n_{k\alpha} \quad (63.8)$$

Taking into account the Hermitian nature of the matrix elements (63.4) and (63.5), we can assert that

$$P_{\text{stim}} = P_{\text{abs}} \quad (63.9)$$

Hence, the probabilities of absorption and stimulated emission are the same.

Assume that an electron interacting with an electromagnetic field does not experience any other actions, i.e. is free. Therefore, $\Psi_{\text{electron}}^{(0)}$ in (63.2) has the form

$$\psi_1^{(0)} = C \exp\left(\frac{i}{\hbar} \mathbf{p}_1 \mathbf{r}\right), \quad \psi_2^{(0)} = C \exp\left(\frac{i}{\hbar} \mathbf{p}_2 \mathbf{r}\right)$$

In this case, the integral, for example, in (63.4) appears as follows:

$$\begin{aligned} & \int \psi_1^* (-e_{k\alpha} i\hbar \nabla) \exp(i\mathbf{k}\mathbf{r}) \psi_2 dV \\ &= -i\hbar |C|^2 \int \exp\left[-\frac{i}{\hbar} \mathbf{p}_1 \mathbf{r}\right] e_{k\alpha} \nabla \exp\left[\frac{i}{\hbar} (\mathbf{p}_2 - \hbar\mathbf{k}) \mathbf{r}\right] dV \\ &= |C|^2 e_{k\alpha} (\mathbf{p}_2 - \hbar\mathbf{k}) \int \exp\left[-\frac{i}{\hbar} (\mathbf{p}_1 - \mathbf{p}_2 + \hbar\mathbf{k}) \mathbf{r}\right] dV \\ &= |C|^2 e_{k\alpha} \mathbf{p}_2 \hbar (2\pi)^3 \delta(\mathbf{p}_1 - \mathbf{p}_2 + \hbar\mathbf{k}) \end{aligned}$$

[we have taken into account that $e_{k\alpha} \mathbf{k} = 0$ and have used formulas (VIII.13) and (VIII.7)]. We must note that if we had put the factor $\exp(i\mathbf{k}\mathbf{r})$ in front of the operator ∇ in the integrand, the result would have remained the same.

Hence, the probability of a free electron emitting a photon could be non-zero only provided that

$$\mathbf{p}_2 = \mathbf{p}_1 + \hbar\mathbf{k} \quad (63.10)$$

(momentum conservation). At the same time, however, the following condition must be observed:

$$E_2 = E_1 + \hbar\omega_k \quad (63.11)$$

¹ The spontaneous emission of radiation is due to the interaction of an atom with the zero-point oscillations of the electromagnetic field.

(energy conservation). For a free non-relativistic electron, we have $E = p^2/2m_e$ so that (63.11) can be represented as

$$\mathbf{p}_s^2 = \mathbf{p}_i^2 + 2m_e\hbar\omega_k \quad (63.12)$$

Equations (63.10) and (63.12) are incompatible. We thus conclude that a free electron cannot emit photons. A similar result is obtained for absorption.

For both conservation laws (energy and momentum) to be obeyed simultaneously, the participation of a third body is required, which the surplus momentum is transmitted to.

64. Dipole Radiation [rei dī' eisəh]

Consider the emission of a photon by a valence electron of an atom (we ignore the spin of the electron). The energy of an outer (valence) electron in its order of magnitude is Z^*e^2/a , where Z^* is a quantity of the order of unity, and a is the effective radius of the atom. The change in the energy of an atom in a transition will be of the same order, i.e. the energy $\hbar\omega$ of an emitted photon approximately equals

$$\hbar\omega \approx \frac{e^2}{a}$$

Accordingly, the length of an emitted wave is $\lambda \approx c/\omega \approx \hbar c/e^2$. Hence

$$\frac{a}{\lambda} \approx \frac{e^2}{\hbar c} = \frac{1}{137}$$

Assuming that $a \approx 10^{-8}$ cm and $\lambda \approx 10^{-6}$ cm (ultraviolet radiation), we obtain the same result. For visible light, the ratio a/λ will be still smaller ($\sim 10^{-4}$).

The psi-functions of discrete states of an atom differ appreciably from zero only in a region of the order of the effective dimensions of the atom. Within this region, the exponent in the factor $\exp(-ikr)$ in (63.4) does not exceed in magnitude the quantity

$$\frac{2\pi}{\lambda} a \approx \frac{a}{\lambda}$$

i.e. is much smaller than unity ($a \ll \lambda$). Therefore, this factor can be expanded into a series:

$$\exp(-ikr) = 1 - ikr + \dots \quad (64.1)$$

Limiting ourselves only to the first term of the expansion (i.e. replacing the exponential with unity), we obtain what is called the long-wave approximation. If a matrix element calculated in this approxi-

mation is zero, the next term in the expansion (64.1) is taken into consideration.

Replacing in (63.4) the exponential with unity, we obtain the following expression for the matrix element of a transition:

$$\text{M.E.} = \langle 1, n_{k\alpha} + 1 | \hat{V} | 2, n_{k\alpha} \rangle = \frac{e}{m_e} \sqrt{\frac{2\pi\hbar(n_{k\alpha} + 1)}{a^3\omega_k}} (\mathbf{e}_{k\alpha} \mathbf{p})_{12} \quad (64.2)$$

where $(\mathbf{e}_{k\alpha} \mathbf{p})_{12}$ is a matrix element of the operator of the projection of the electron's momentum onto the direction of polarization of the emitted photon.

Generalizing formulas (21.13) and (22.9), we obtain

$$\hat{\mathbf{p}} = m_e \hat{\mathbf{r}}, \quad (\hat{\mathbf{r}})_{12} = i\omega_k (\mathbf{r})_{12}$$

With a view to these relations, we can write

$$\begin{aligned} (\mathbf{e}_{k\alpha} \mathbf{p})_{12} &= m_e (\mathbf{e}_{k\alpha} \dot{\mathbf{r}})_{12} = im_e \omega_k (\mathbf{e}_{k\alpha} \mathbf{r})_{12} \\ &= i \left(-\frac{m_e}{e} \right) \omega_k \{ \mathbf{e}_{k\alpha} (-e\mathbf{r}) \}_{12} = -i \frac{m_e}{e} \omega_k (\mathbf{e}_{k\alpha} \hat{\mathbf{d}})_{12} \end{aligned} \quad (64.3)$$

Here $\hat{\mathbf{d}} = -\hat{e}\mathbf{r}$ is the operator of the dipole moment of an electron (the charge of an electron is $-e$). For a many-electron atom, we must treat $\hat{\mathbf{d}}$ as the operator of the dipole moment of all the electrons (i.e. the dipole moment of the atom as a whole).

Hence, in the long-wave approximation, the matrix element (64.2) can be written as

$$\text{M.E.} = -i \sqrt{\frac{2\pi\hbar\omega_k(n_{k\alpha} + 1)}{a^3}} (\mathbf{e}_{k\alpha} \mathbf{d})_{12} \quad (64.4)$$

The initial state of the system is discrete. Since the frequency of a photon changes continuously, the final state belongs to a continuous spectrum. It was established in Sec. 34 that the probability of the transition of a system in unit time from a state belonging to a discrete spectrum to a state belonging to a continuous spectrum under the action of a perturbation varying with time according to a harmonic law is determined by the formula

$$P = \frac{2\pi}{\hbar} | V_{E', E_1} |^2 g(E') \quad (64.5)$$

[see (34.19)], where the energy of the final state $E' = E_1 + \hbar\omega_k$ satisfies the condition

$$E' = E_1 + \hbar\omega_k = E_2 \quad (64.6)$$

[we must replace $\delta(E_v - E_n - \hbar\omega)$ in formula (34.14) with $\delta(E_1 + \hbar\omega_k - E_2)$]. We have substituted the index E_2 for the

index n in formula (34.19). Remember that E_2 is the energy of the initial state of an atom.

The function $g(E')$ in (64.5) determines the number of states per unit interval of final energy (the density of states):

$$g(E') = \frac{dN}{dE'}$$

To find $g(E')$, let us calculate the number of states dN of the electromagnetic field falling within the interval dk of values of the magnitude of the wave vector and within the interval of directions of the vector \mathbf{k} corresponding to the solid angle $d\Omega$. In k -space, the volume $k^2 dk d\Omega$ corresponds to these intervals. By (61.10), a volume equal to $(2\pi/a)^3$ corresponds to each state (one polarization). Consequently, the number of states we are interested in is

$$dN = \frac{a^3 k^2 dk d\Omega}{(2\pi)^3} \quad (64.7)$$

The interval of values of the final energy is

$$dE' = d(E_1 + \hbar\omega_k) = d(\hbar\omega_k) = d(\hbar ck) = \hbar c dk$$

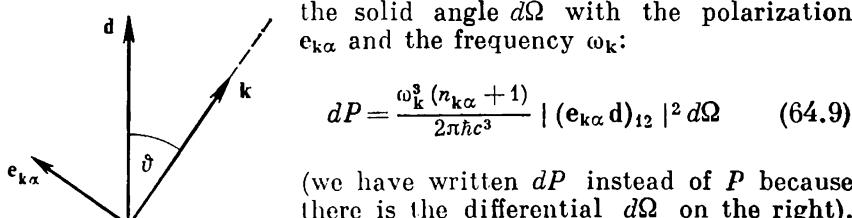
whence $dk = dE'/\hbar c$. The square of the wave vector is $k^2 = \omega_k^2/c^2$. Having in view this expression, we can write (64.7) as follows:

$$dN = \frac{a^2 \omega_k^2 d\Omega}{(2\pi c)^3 \hbar} dE'$$

whence

$$g(E') = \frac{dN}{dE'} = \frac{a^3 \omega_k^2}{(2\pi c)^3 \hbar} d\Omega \quad (64.8)$$

Introducing into formula (64.5) expression (64.4) for a matrix element and expression (64.8) for $g(E')$, we obtain the probability of the emission of a photon in unit time in the solid angle $d\Omega$ with the polarization $e_{k\alpha}$ and the frequency ω_k :



(we have written dP instead of P because there is the differential $d\Omega$ on the right).

The vectors e_k and $e_{k\alpha}$ are chosen arbitrarily, it is only necessary that they be normal to the vector \mathbf{k} and to each other.

Let us choose the direction of the unit vector $e_{k\alpha}$ so that it is in the plane \mathbf{d}, \mathbf{k} (Fig. 64.1). Hence,

$$(e_{k\alpha} d_{12}) = |d_{12}| \sin \theta$$

where ϑ is the angle between the direction of the dipole electric moment and the vector \mathbf{k} . Consequently, expression (64.9) can be written as

$$dP = \frac{\omega_k^3 (n_{k\alpha} + 1)}{2\pi\hbar c^3} |\mathbf{d}_{12}|^2 \sin^2 \vartheta d\Omega \quad (64.10)$$

Multiplying this expression by $\hbar\omega_k$, we obtain the energy emitted per second into an element of the solid angle $d\Omega$:

$$dJ = \frac{\omega_k^4 (n_{k\alpha} + 1)}{2\pi c^3} |\mathbf{d}_{12}|^2 \sin^2 \vartheta d\Omega \quad (64.11)$$

Of this energy, a portion equal to

$$dJ_{\text{spont}} = \frac{\omega_k^4}{2\pi c^3} |\mathbf{d}_{12}|^2 \sin^2 \vartheta d\Omega \quad (64.12)$$

falls to the share of spontaneous emission. We must note that expression (64.12) determines the total radiation of a dipole because with the directions of polarization we have chosen (see Fig. 64.1) the projection of the vector \mathbf{d} onto the second unit vector is zero.

Integration of expression (64.12) over $d\Omega$ yields the total energy emitted in unit time, i.e. the power of dipole radiation

$$J_{\text{spont}} = \frac{\omega_k^4}{2\pi c^3} |\mathbf{d}_{12}|^2 \int_0^\pi \sin^2 \vartheta 2\pi \sin \vartheta d\vartheta = \frac{4\omega_k^4}{3c^3} |\mathbf{d}_{12}|^2 \quad (64.13)$$

The quantum expression for the power of dipole radiation differs from the classical one only in that it contains the matrix element of the dipole moment instead of the dipole moment itself.

The matrix element $\mathbf{d}_{12} = \langle \psi_1^{(0)} | \hat{\mathbf{d}} \psi_2^{(0)} \rangle$ may equal zero. The transitions for which this occurs are said to be forbidden. This term must not be understood literally because when $\mathbf{d}_{12} = 0$, the probability of emission, although very low, is nevertheless non-zero. In this case, we must take into account the second term of the expansion (64.1). Instead of the matrix element \mathbf{d}_{12} , Eq. (64.10) will contain the expression $\langle \psi_1^{(0)} | \mathbf{e}_{k\alpha} \hat{\mathbf{p}} (-ikr) \psi_2^{(0)} \rangle$, which can be considered as a matrix element of the product of the operators $(\mathbf{e}_{k\alpha} \hat{\mathbf{p}})$ and $(-ikr)$. The matrix of the product of two quantities equals the product of the matrices of the quantities being multiplied (see the last paragraph of Sec. 10). A matrix element can therefore be represented in the form $-i \{(\mathbf{e}_{k\alpha} \hat{\mathbf{p}})(kr)\}_{12}$. Replacing $(\mathbf{e}_{k\alpha} \hat{\mathbf{p}})$ with $im_e \omega_k (\mathbf{e}_{k\alpha} \mathbf{r})$ in accordance with (64.3), we obtain the element $m_e \omega_k \{(\mathbf{e}_{k\alpha} \mathbf{r})(kr)\}_{12}$. This element must be introduced into (64.9) instead of $-i(m_e/e) \times \omega_k (\mathbf{e}_{k\alpha} \mathbf{d})_{12}$ [see (64.3)]. As a result, formula (64.12) becomes

$$dJ_{\text{spont}} = \frac{e^2 \omega_k^4}{2\pi c^3} \{(\mathbf{e}_{k\alpha} \mathbf{r})(kr)\}_{12}^2 \sin^2 \vartheta d\Omega \quad (64.14)$$

The radiation characterized by formula (64.14) is a combination of magnetic dipole and quadrupole radiations.

Let us compare the intensities (64.12) and (64.14). To do this, we take into consideration that $e^2 r^2 \sim d^2$, and $(kr)^2 \sim (ka)^2 \sim (a/\lambda)^2$ (a is the effective radius of an atom). We thus find that for visible light, for instance, the intensity of the magnetic dipole and quadrupole radiations is $1/10^6$ of that of dipole radiation. This is just what gives us the grounds to call the relevant transitions forbidden.

65. Selection Rules

We established in the preceding section that the probability of dipole emission is determined by the matrix element of the projection of an atom's dipole moment onto the direction of polarization of a photon:

$$(e_{k\alpha} d)_{12} = -e (e_{k\alpha} r)_{12} \quad (65.1)$$

The numerical value of this element depends on the form of the psi-functions $\psi_1^{(0)}$ and $\psi_2^{(0)}$ of the electron performing a transition. For the matrix element to be non-zero, the psi-functions must satisfy definite requirements known as the **selection rules** for dipole radiation. There are also selection rules for magnetic dipole and quadrupole radiations, but we shall limit ourselves to treating only the selection rules for dipole radiation.

Consider that the radiating electron is moving in a central force field. We disregard the spin-orbit interaction. In these conditions, the psi-function of the electron is

$$\psi_{nlm}(r, \vartheta, \varphi) = Y_{lm}(\vartheta, \varphi) R_{nl}(r)$$

Let us first deal with the case when the photon being emitted is polarized along the z -axis. In this case, $e_{k\alpha} r = z = r \cos \vartheta$. The matrix element (65.1) therefore breaks up into two factors:

$$\text{M.E.} = \langle Y_{l_1 m_1} | \cos \vartheta | Y_{l_2 m_2} \rangle \langle R_{n_1 l_1} | -er | R_{n_2 l_2} \rangle \quad (65.2)$$

The second factor cannot be zero in any conditions. Consequently, the transition probability is determined by the factor

$$\langle Y_{l_1 m_1} | \cos \vartheta | Y_{l_2 m_2} \rangle = \int_0^{\pi} \int_0^{2\pi} Y_{l_1 m_1}^* Y_{l_2 m_2} \cos \vartheta \sin \vartheta d\vartheta d\varphi$$

By (II.33), this factor is proportional to the expression

$$I_1 \cdot I_2 = \int_0^{\pi} P_{l_1}^{m_1}(\cos \vartheta) P_{l_2}^{m_2}(\cos \vartheta) \sin \vartheta d\vartheta \int_0^{2\pi} e^{i(m_2 - m_1)\varphi} d\varphi \quad (65.3)$$

The integral I_2 is non-zero only when $m_2 = m_1$. In the integral I_1 , we go over to the variable $x = \cos \vartheta$:

$$I_1 = \int_{-1}^{+1} P_{l_1}^{m_1}(x) P_{l_2}^{m_2}(x) x dx$$

In accordance with formula (II.30), we have

$$x P_{l_2}^{m_2}(x) = AP_{l_2+1}^{m_2}(x) + BP_{l_2-1}^{m_2}(x)$$

where A and B are constant non-zero coefficients. Hence,

$$\mathcal{J}_1 = A \int_{-1}^{+1} P_{l_1}^{m_1}(x) P_{l_2+1}^{m_2}(x) dx + B \int_{-1}^{+1} P_{l_1}^{m_1}(x) P_{l_2-1}^{m_2}(x) dx$$

Owing to the orthogonality of the associated Legendre polynomials [see (II.29)], for $m_1 = m_2$ this expression is non-zero in two cases: when $l_1 = l_2 + 1$ and when $l_1 = l_2 - 1$. Therefore, we obtain the following selection rules for radiation polarized along the z -axis:

$$\Delta l = \pm 1, \quad \Delta m = 0 \quad (65.4)$$

A photon emitted in the direction of the z -axis is polarized in the plane xy . Instead of radiation polarized along the x - or the y -axis, it is more convenient to consider radiation polarized circularly. Motion in a circle in the plane xy can be represented as the superposition of two mutually perpendicular oscillations shifted in phase by $\pi/2$, i.e. as $\cos \varphi \pm i \sin \varphi$ ($\varphi = \omega t$). Accordingly, the probability of a transition with the emission of a circularly polarized photon is determined by the matrix element of the quantity $x \pm iy$. The latter can be written as

$$x \pm iy = r \sin \vartheta \cos \varphi \pm ir \sin \vartheta \sin \varphi = r \sin \vartheta e^{\pm i\varphi}$$

Hence, the factor, similar to (65.3), that determines the probability of a transition is as follows:

$$I_1 \cdot I_2 = \int_0^\pi P_{l_1}^{m_1}(\cos \vartheta) P_{l_2}^{m_2}(\cos \vartheta) \sin \vartheta \sin \vartheta d\vartheta \int_0^{2\pi} e^{i(m_2 - m_1 \pm 1)\varphi} d\varphi$$

The integral I_2 is non-zero when $m_2 = m_1 \pm 1$. Let us consider each case separately. Assuming that $m_2 = m_1 + 1$ and passing over to the variable $x = \cos \vartheta$, we obtain

$$I_1 \cdot I_2 \propto \int_{-1}^{+1} P_{l_1}^{m_1}(x) P_{l_2}^{m_1+1}(x) \sqrt{1-x^2} dx \quad (65.5)$$

By formula (II.31), we have

$$P_{l_2}^{m_1+1}(x) \sqrt{1-x^2} = AP_{l_2+1}^{m_1}(x) + BP_{l_2-1}^{m_1}(x)$$

where A and B are non-zero coefficients. Substitution into (65.5) yields

$$I_1 \cdot I_2 \propto A \int_{-1}^{+1} P_{l_1}^{m_1}(x) P_{l_2+1}^{m_1}(x) dx + B \int_{-1}^{+1} P_{l_1}^{m_1}(x) P_{l_2-1}^{m_1}(x) dx$$

This expression is non-zero when $l_1 = l_2 \pm 1$.

Assuming that $m_2 = m_1 - 1$, we obtain

$$I_1 \cdot I_2 \propto \int_{-1}^{+1} P_{l_1}^{m_1}(x) P_{l_2}^{m_1-1}(x) \sqrt{1-x^2} dx \quad (65.6)$$

By formula (II.31), we have

$$P_{l_1}^{m_1}(x) \sqrt{1-x^2} = CP_{l_1+1}^{m_1-1}(x) + DP_{l_1-1}^{m_1-1}(x)$$

where C and D are constants. Substitution into (65.6) leads to the expression

$$I_1 \cdot I_2 \propto C \int_{-1}^{+1} P_{l_1+1}^{m_1-1}(x) P_{l_2}^{m_1-1}(x) dx + D \int_{-1}^{+1} P_{l_1-1}^{m_1-1}(x) P_{l_2}^{m_1-1}(x) dx$$

The latter is non-zero when $l_2 = l_1 \pm 1$.

Hence, for radiation polarized at right angles to the z -axis, we obtain the selection rules

$$\Delta l = \pm 1, \quad \Delta m = \pm 1 \quad (65.7)$$

Combining formulas (65.4) and (65.7), we obtain the following selection rules for dipole radiation:

$$\Delta l = \pm 1, \quad \Delta m = 0, \pm 1 \quad (65.8)$$

Transitions with $\Delta m = 0$ lead to the emission of radiation polarized along the z -axis; transitions with $\Delta m = \pm 1$ lead to the emission of radiation polarized in the plane xy .

We must note that the selection rules (65.8) agree with the requirements of the momentum and parity conservation laws.

Chapter XII

SCATTERING THEORY

66. Scattering Cross Section

Scattering is defined to be the deviation of a particle from its original direction of motion caused by its interaction with another particle (the scatterer). In connection with the fact that scattering is caused by the interaction (collision) of two particles, the scattering theory is also known as the **collision theory**.

The proceeding of a scattering process in time consists in that two initially infinitely remote particles move towards each other, next, upon approaching, they interact, and, finally, fly away in different directions. Instead of considering how a scattering process goes on in time, it is often convenient to deal with an equivalent stationary picture. The transition from a temporal to a stationary description is performed with the aid of the assumption that there is a continuous flux of particles flying from infinity that because of interaction with a scattering centre¹ transforms into a flux of scattered particles flying away from this centre in different directions. The density of the particles in the flux must be sufficiently low for the interaction between the incident particles to be negligibly small. In the stationary treatment, the scattering problem consists in calculation of the flux of scattered particles (at an infinitely great distance from the scattering centre) as a function of the incident particle flux when we know the scattering force field.

Scattering is characterized by the **differential scattering cross section**

$$d\sigma(\vartheta, \varphi) = \frac{dN_{\text{scat}}(\vartheta, \varphi)}{j_{\text{inc}}} \quad (66.1)$$

where $dN_{\text{scat}}(\vartheta, \varphi)$ is the number of particles scattered in unit time within the solid angle $d\Omega$ taken in the direction (ϑ, φ) , and j_{inc} is the density of the incident particle flux [see Vol. 1, formula (14.2)].

Let us introduce the density of the scattered particle flux at large distances r from the scattering centre, and designate this density by $j_{\text{scat}}(r, \vartheta, \varphi)$. We can therefore write that

$$dN_{\text{scat}}(\vartheta, \varphi) = j_{\text{scat}}(r, \vartheta, \varphi) r^2 d\Omega$$

¹ Or with a collection of scattering centres, the distance between which is so great that each of the incident particles interacts only with one of the centres.

Substitution of this expression into (66.1) yields

$$d\sigma(\vartheta, \varphi) = \frac{j_{\text{scat}}(r, \vartheta, \varphi)}{j_{\text{inc}}} r^2 d\Omega \quad (66.2)$$

In quantum mechanics, j_{scat} and j_{inc} are understood to be the relevant densities of the probability fluxes [see (6.5)].

Integrating expression (66.2) over all the angles, we obtain the quantity

$$\sigma = \frac{1}{j_{\text{inc}}} \oint j_{\text{scat}}(r, \vartheta, \varphi) dS_r = \frac{\Phi_{\text{scat}}}{j_{\text{inc}}} \quad (66.3)$$

which is called the **total effective scattering cross section**. In formula (66.3), $dS_r = r^2 d\Omega$ is the area of an elementary surface at the distance r from the scattering centre and corresponding to the solid angle $d\Omega$, and Φ_{scat} is the scattered particle flux through the closed surface enveloping the scattering centre. The surface over which the integral is evaluated is assumed to be at a great distance from the centre. We may therefore consider that at each point of this surface the scattered particles fly in a radial direction.

According to (66.3), the total scattering cross section is the ratio of the total probability of scattering of a particle (in unit time) to the density of the probability flux in the incident beam.

We distinguish elastic and inelastic scattering. In **elastic scattering**, the internal states and composition of the colliding particles do not change. In **inelastic scattering**, the internal state of one or both particles changes.

It was shown at the end of Sec. 24 that when the interaction between particles depends only on the distance between them, the problem of the motion of two particles can be reduced to two one-particle problems. One of them deals with the motion of a particle having the mass $m_{\text{red}} = m_1 m_2 / (m_1 + m_2)$ relative to the centre of mass, and the second one deals with the free motion of the centre of mass. The solution of the first problem gives the scattering angle ϑ in the CMS (centre-of-mass system). The transition from the CMS to the LS (laboratory system) is accomplished with the aid of the formulas

$$\tan \theta_1 = \frac{m_2 \sin \vartheta}{m_1 + m_2 \cos \vartheta}, \quad \theta_2 = \frac{\pi - \vartheta}{2} \quad (66.4)$$

where θ_1 is the scattering angle of the first particle, θ_2 is the recoil angle of the second particle determined in the LS, and ϑ is the angle of deflection of the first particle in the CMS [see Vol. 1, formulas (13.5) and (13.6); in these formulas the angle ϑ is designated by the letter χ].

In the following, we shall deal only with what happens in the centre-of-mass system of the colliding particles.

67. Scattering Amplitude

Let us consider a stationary scattering problem. The motion of the particle being scattered is infinite. Consequently, the energy of a system consisting of the particle being scattered and the one scattering it is always positive and, consequently, is not quantized. We thus have to do with a continuous energy spectrum in the scattering theory.

Let us place the origin of coordinates at a fixed scattering centre. Now the interaction of a particle with this centre can be described with the aid of the potential function $U(r)$. Assume that this function is non-zero only in a limited part of space with $r \leq a$ that we shall call the range of force.

Within the range of force, the motion of the particle being considered obeys the Schrödinger equation

$$-\frac{\hbar^2}{2m_0} \nabla^2 \psi(r) + U(r) \psi(r) = E \psi(r) \quad (67.1)$$

(m_0 is the mass of the scattered particle). Introducing the notation

$$\mathbf{k}^2 = \frac{2m_0}{\hbar^2} E = \frac{\mathbf{p}^2}{\hbar^2} \quad (67.2)$$

we can write Eq. (67.1) in the form

$$(\nabla^2 + \mathbf{k}^2) \psi(r) = \frac{2m_0}{\hbar^2} U(r) \psi(r) \quad (67.3)$$

Beyond the range of force, the particle moves freely, and its state is described by a plane wave. Adopting the direction of motion of the incident particle as the z -axis, we obtain the following expression for the psi-function describing the state of the particle before its interaction with the scattering centre:

$$\psi_{\text{inc}} = e^{ikz} \quad (67.4)$$

It is not difficult to see that this function is one of the possible solutions of Eq. (67.3) when the right-hand side vanishes.

After passing through the range of force, the scattered particles again move like free ones. At large distances from this region, the scattered particles move in radial directions from the scattering centre. Consequently, the motion of the scattered particles will be described by a diverging spherical wave:

$$\psi_{\text{scat}} = A(\theta, \varphi) \frac{e^{ikr}}{r} \quad (67.5)$$

where r , θ , and φ are spherical coordinates.

We must note that in elastic scattering, the quantity k in formulas (67.4) and (67.5) is the same and is determined by relation (67.2).

The function $A(\vartheta, \varphi)$ is called the scattering amplitude. It depends, generally speaking, on both angles, ϑ and φ . When $U(\mathbf{r}) = U(r)$, the scattering amplitude evidently depends only on the angle ϑ .

It can be shown (see Appendix VII) that the solution of Eq. (67.3) for large distances from the scattering centre (when $r \gg a$) equals the sum of the functions (67.4) and (67.5):

$$\psi = e^{i\hbar z} + A(\vartheta, \varphi) \frac{e^{i\hbar r}}{r} \quad (67.6)$$

We must note that the first term in this expression is written in Cartesian coordinates, and the second in spherical ones.

Let us find the densities of the incident and scattered fluxes of particles [i.e. the densities of the probability fluxes corresponding to the functions (67.5) and (67.6)]. By formula (6.5), we have

$$\mathbf{j}_{\text{inc}} = \frac{\hbar}{2m_0 i} (\psi_{\text{inc}}^* \nabla \psi_{\text{inc}} - \psi_{\text{inc}} \nabla \psi_{\text{inc}}^*)$$

Having in view that ψ_{inc} depends only on z [see (67.4)], we obtain the following expression for the magnitude of \mathbf{j}_{inc} :

$$j_{\text{inc}} = \frac{\hbar}{2m_0 i} \left(\psi_{\text{inc}}^* \frac{d\psi_{\text{inc}}}{dz} - \psi_{\text{inc}} \frac{d\psi_{\text{inc}}^*}{dz} \right) = \frac{\hbar k}{m_0} = \frac{p}{m_0} = v \quad (67.7)$$

where v is the velocity of an incident particle. Hence, the function (67.4) is normalized so that the density of the flux of incident particles numerically equals the velocity of the scattered particle at infinity.

The gradient in spherical coordinates is determined by the expression

$$\nabla \psi = \frac{\partial \psi}{\partial r} \mathbf{e}_r + \frac{1}{r} \frac{\partial \psi}{\partial \vartheta} \mathbf{e}_\vartheta + \frac{1}{r \sin \vartheta} \frac{\partial \psi}{\partial \varphi} \mathbf{e}_\varphi \quad (67.8)$$

[see Vol. 1, formula (XI.78)]. We are interested in the radial component j_r of the flux of scattered particles. It can be found by replacing $\nabla \psi$ in formula (6.5) with the radial component which, by (67.8), equals $\partial \psi / \partial r$. Consequently,

$$j_r = \frac{\hbar}{2m_0 i} \left(\psi_{\text{scat}}^* \frac{\partial \psi_{\text{scat}}}{\partial r} - \psi_{\text{scat}} \frac{\partial \psi_{\text{scat}}^*}{\partial r} \right)$$

The introduction of expression (67.5) for ψ_{scat} results in the formula

$$j_r = \frac{\hbar k}{m_0 r^2} |A(\vartheta, \varphi)|^2 \quad (67.9)$$

Substitution of (67.7) and (67.9) into formula (66.2) yields the following expression for the differential scattering cross section:

$$d\sigma (\vartheta, \varphi) = |A(\vartheta, \varphi)|^2 d\Omega \quad (67.10)$$

Hence, the determination of the differential scattering cross section consists in finding the scattering amplitude.

68. Born Approximation

One of the methods for the approximated calculation of the scattering amplitude is that developed by M. Born and based on the representation of a scattering field as a perturbation (see Sec. 36). In this case, the psi-function describing the state of a scattered particle can be written as

$$\psi = \psi^{(0)} + \Delta\psi^{(1)} \quad (68.1)$$

where $\psi^{(0)}$ is the psi-function of the unperturbed problem; it describes the behaviour of the particle before it interacts with the scattering centre; it is a plane wave, namely

$$\psi^{(0)} = e^{ik_0 r} \quad (68.2)$$

(the vector $k_0 = p_0/\hbar$ has the direction of the incident beam, in Sec. 36 this vector was designated simply by \mathbf{k}).

The additional term $\Delta\psi^{(1)}$ due to the scattering field $U(r)$, by formula (36.15), is

$$\Delta\psi^{(1)}(r) = -\frac{m_0}{2\pi\hbar^2} \int \frac{1}{R} U(r') e^{i(k_0 r' + k_0 R)} dV' \quad (68.3)$$

where R is the magnitude of the vector $\mathbf{R} = \mathbf{r} - \mathbf{r}'$. We are interested in an asymptotic expression for $\Delta\psi^{(1)}(r)$, i.e. in the form of the function for large distances r from the scattering centre. The integral, on the other hand, is evaluated over the range of force, i.e. for $r' \leq a$. Consequently, $r \gg r'$. We must also note that at large distances a particle flies in a radial direction from the scattering centre so that its wave vector \mathbf{k} coincides in direction with \mathbf{r} .

Taking into account the inequality $r \gg r'$, we obtain

$$R^2 = (\mathbf{r} - \mathbf{r}')^2 = r^2 - 2\mathbf{r}\mathbf{r}' + r'^2 \approx r^2 \left(1 - 2\frac{\mathbf{r}\mathbf{r}'}{r^2}\right)$$

(we have disregarded r'^2 in comparison with the other terms). Owing to the smallness of r'/r , we can write that

$$R \approx r \left(1 - \frac{\mathbf{r}\mathbf{r}'}{r^2}\right) = r - \frac{\mathbf{k}\mathbf{r}'}{k} \quad (68.4)$$

(we have taken advantage of the fact that $\mathbf{r}/r = \mathbf{k}/k$).

Let us replace R in the exponential of (68.3) with its approximate value from (68.4), and in the fractional factor use simply r instead of R . As a result (with a view to the fact that $k = k_0$), we obtain

$$\Delta\psi^{(1)}(\mathbf{r}) = -\frac{m_0}{2\pi\hbar^2 r} e^{ikr} \int U(r') e^{i(k_0 - \mathbf{k}) \cdot \mathbf{r}'} dV'$$

A comparison with (67.6) leads us to the conclusion that the scattering amplitude in the Born approximation is determined by the formula

$$A(\vartheta, \phi) = -\frac{m_0}{2\pi\hbar^2} \int U(r') e^{iq\mathbf{r}'} dV' \quad (68.5)$$

The vector

$$\mathbf{q} = \mathbf{k}_0 - \mathbf{k} \quad (68.6)$$

sometimes called the collision vector, has a magnitude equal to

$$q = 2k \sin \frac{\vartheta}{2} \quad (68.7)$$

where ϑ is the angle between the vectors \mathbf{k}_0 and \mathbf{k} , i.e. scattering angle. Recall that the vector \mathbf{k}_0 is directed along the incident beam, and the vector \mathbf{k} —along the position vector drawn from the scattering centre to the point of observation of the scattered particles.

If the function $U(\mathbf{r}')$ is spherically symmetrical, i.e. $U(\mathbf{r}') = U(r')$, in (68.5) we can perform integration over the angles θ and ϕ (whereas the angle ϑ is measured from the direction of the vector \mathbf{k}_0 , the angle θ is measured from the direction of the vector \mathbf{q}). In this case, as we have already noted, the scattering amplitude does not depend on ϕ . Integration yields

$$\begin{aligned} A(\vartheta) &= -\frac{m_0}{2\pi\hbar^2} \int_0^\infty U(r') r'^2 dr' \int_0^\pi e^{iqr'} \cos \theta 2\pi \sin \theta d\theta \\ &= -\frac{2m_0}{\hbar^2} \int_0^\infty U(r') \frac{\sin qr'}{qr'} r'^2 dr' \end{aligned} \quad (68.8)$$

The momentum of the particles being scattered and the scattering angle ϑ are in this formula in terms of q [see (68.7)].

Introducing expression (68.8) into formula (67.9), we obtain the following value of the differential scattering cross section:

$$d\sigma = \frac{4m_0^2}{\hbar^4} \left| \int_0^\infty U(r') \frac{\sin qr'}{qr'} r'^2 dr' \right|^2 d\Omega \quad (68.9)$$

Expression (68.9) is known as **Born's formula**. We remind our reader that the Born approximation holds when the conditions (36.20) or (36.22) are satisfied.

69. Method of Partial Waves

In the preceding section, we considered the approximate scattering theory for an arbitrary field $U(\mathbf{r})$. For the case when the scattering field is centrally symmetric, i.e. $U(\mathbf{r}) = U(r)$, a theory has been developed that uses what is known as the **method of partial waves**. This theory starts from the fact that at large distances from the scattering centre, the psi-function of a scattered particle has the form

$$\psi = e^{ikz} + A(\vartheta) \frac{e^{ikr}}{r} \quad (69.1)$$

[compare with (67.6)]. Since the scattering field is centrally symmetric, the scattering amplitude cannot depend on the angle φ . Accordingly, the function (69.1) also does not depend on φ .

Since $U(\mathbf{r}) = U(r)$, the theory being considered is associated with the solution of the problem on the motion of a particle in a central force field. The approach to the solution, however, must be different than in Sec. 24. There we were interested in finite motion with negative energy values. Now, on the other hand, we are considering infinite motion, and we need solutions satisfying definite boundary conditions. These conditions consist in that the asymptotic form of the solution (for $r \rightarrow \infty$) must be determined by formula (69.1).

It was shown in Sec. 23 that the following expression is the most general solution of the Schrödinger equation for a centrally symmetric field [see (23.14)]:

$$\psi(r, \vartheta, \varphi) = \sum_{l, m} b_{lm} R_l(r) Y_{lm}(\vartheta, \varphi) \quad (69.2)$$

where b_{lm} are constant coefficients determined by the boundary conditions and the conditions of normalization. We are interested in solutions that do not depend on the angle φ [see (69.1)]. Therefore, in the sum (69.2), we must retain only the terms not containing φ , i.e. the terms corresponding to $m = 0$. By formula (II.35), the spherical function for $m = 0$ is

$$Y_{l, 0} = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \vartheta) \quad (69.3)$$

where P_l is the Legendre polynomial determined by the formula

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} [(x^2 - 1)^l] \quad (69.4)$$

[see (II.12)]. For this reason, formula (69.2) in the case we are interested in becomes

$$\psi(r, \vartheta) = \sum_{l=0}^{\infty} b_l R_l(r) P_l(\cos \vartheta) \quad (69.5)$$

[we have included the coefficient of P_l in (69.3) in b_l].

We can obtain an asymptotic form of the function (69.5) (when $r \rightarrow \infty$) by introducing into (69.5) the asymptotic expression (23.25) for R_l :

$$\psi_{(r \rightarrow \infty)} \approx \sum_{l=0}^{\infty} b_l P_l(\cos \vartheta) \frac{a_l \sin(kr + \delta_l - l\pi/2)}{r}$$

(for reasons that will be revealed in the following, we have taken the phase β_l in the form of $\delta_l - l\pi/2$). Introducing the notation: $b_l a_l = c_l/k$, we can give the formula obtained the following form:

$$\psi_{(r \rightarrow \infty)} = \sum_{l=0}^{\infty} c_l P_l(\cos \vartheta) \frac{\sin(kr + \delta_l - l\pi/2)}{kr} \quad (69.6)$$

We can represent the asymptotic solution of any problem on the motion of a particle in a centrally symmetric field, including the function (69.1), in such a form. To find the expression of the scattering amplitude $A(\vartheta)$ in terms of the coefficients c_l and the phases δ_l , we must give (69.1) the form of (69.6). To do this, we have to expand expression (69.1) into a series in the Legendre polynomials (69.4) (the Legendre polynomials form a complete system). We must note that the final expression for the amplitude will include the values of the coefficients c_l satisfying the boundary conditions.

Let us find the form of the expansion in Legendre polynomials of the first term in (69.1), i.e. of the function e^{ikz} . For this purpose, we write it as

$$e^{ikz} = e^{ikr \cos \vartheta} = \sum_{l=0}^{\infty} f_l(r) P_l(\cos \vartheta) \quad (69.7)$$

where the expansion coefficients $f_l(r)$ are the functions r whose form we are to establish. To simplify the formulas, let us go over from the variable ϑ to the variable $x = \cos \vartheta$. Relation (69.7) therefore becomes

$$e^{ikrx} = \sum_{l=0}^{\infty} f_l(r) P_l(x) \quad (69.8)$$

To find the coefficients $f_l(r)$, we shall use a conventional procedure, namely, we shall multiply Eq. (69.8) by $P_{l'}(x)$ and integrate over x from -1 to $+1$ (here ϑ varies from π to 0):

$$\int_{-1}^{+1} e^{ikrx} P_{l'}(x) dx = \sum_{l=0}^{\infty} f_l(r) \int_{-1}^{+1} P_l(x) P_{l'}(x) dx$$

By formulas (II.19) and (II.20), we have

$$\int_{-1}^{+1} P_l(x) P_{l'}(x) dx = \frac{2}{2l+1} \delta_{l,l'} \quad (69.9)$$

Consequently, in the sum over l only one addend, equal to $f_{l'}(r) \times 2/(2l'+1)$, is non-zero. We thus obtain the following formula for the expansion coefficients (we have omitted the prime on l):

$$f_l(r) = \frac{2l+1}{2} \int_{-1}^{+1} e^{ikrx} P_l(x) dx \quad (69.10)$$

To find the form of $f_l(r)$ for large values of r , let us perform integration by parts on the right-hand side of formula (69.10):

$$\begin{aligned} f_l(r) &= \frac{2l+1}{2} \left\{ \frac{e^{ikrx}}{ikr} P_l(x) \Big|_{x=-1}^{x=+1} - \int_{-1}^{+1} \frac{e^{ikrx}}{ikr} P'_l(x) dx \right\} \\ &= \frac{2l+1}{2} \left\{ \frac{e^{ikr} - (-1)^l e^{-ikr}}{ikr} - \frac{1}{ikr} \int_{-1}^{+1} e^{ikrx} P'_l(x) dx \right\} \quad (69.11) \end{aligned}$$

We have taken into account that according to (II.22) and (II.23), $P_l(1) = 1$, and $P_l(-1) = (-1)^l$. The obtained integral differs from the integral in (69.10) only in containing $P'_l(x)$ instead of $P_l(x)$. Recall that $P_l(x)$ is a polynomial of degree l ; consequently, $P'_l(x)$ will be a polynomial of degree $l-1$.

Again performing integration by parts in (69.11), we obtain a term similar to the first term in (69.11) whose denominator will contain $(ikr)^2$, and an integral similar to (69.10) that will contain $P''_l(x)$, i.e. a polynomial of degree $l-2$, instead of $P_l(x)$. Hence, integrating by parts l times, we obtain a series of terms in which the denominator of each following one contains r to a power that is greater by one than that in the preceding term. We are interested in the form of $f_l(r)$ at large r 's. We can therefore limit ourselves to the first term in (69.11), i.e. assume that

$$f_l(r) = \frac{2l+1}{2} \frac{e^{ikr} - (-1)^l e^{-ikr}}{ikr} \quad (69.12)$$

To simplify this expression, let us write $(-1)^l$ in the form

$$(-1)^l = (e^{i\pi})^l = e^{il\pi/2} \cdot e^{il\pi/2}$$

Now (69.12) will appear as follows:

$$f_l(r) = \frac{2l+1}{2} e^{il\pi/2} \frac{e^{i(kr-l\pi/2)} - e^{-i(kr-l\pi/2)}}{ikr}$$

The factor $e^{il\pi/2}$ can be written as $(e^{i\pi/2})^l = i^l$. The difference of the exponentials divided by $2i$ gives the sine. We therefore finally obtain

$$f_l(r) = i^l (2l+1) \frac{\sin(kr-l\pi/2)}{kr} \quad (69.13)$$

Now it is clear why we wrote the phase β_l in the form of $\delta_l - l\pi/2$ in formula (69.6).

Substitution of (69.13) into (69.7) gives the following asymptotic expression for the first term of the function (69.1):

$$e^{ihz} = \sum_{l=0}^{\infty} i^l (2l+1) P_l(\cos \vartheta) \frac{\sin(kr-l\pi/2)}{kr} \quad (69.14)$$

In the second term of (69.1), let us expand the coefficient $A(\vartheta)$ into a series in Legendre polynomials. This expansion has the form

$$A(\vartheta) = \sum_{l=0}^{\infty} g_l P_l(\cos \vartheta) \quad (69.15)$$

where g_l are numbers.

The substitution of expressions (69.14) and (69.15) into (69.1) gives the following asymptotic formula for the psi-function of a scattered particle:

$$\begin{aligned} \psi = & \sum_{l=0}^{\infty} i^l (2l+1) P_l(\cos \vartheta) \frac{\sin(kr-l\pi/2)}{kr} \\ & + \sum_{l=0}^{\infty} g_l P_l(\cos \vartheta) \frac{e^{ihr}}{r} \end{aligned} \quad (69.16)$$

At the same time, as we have revealed above, this function can be represented in the form of (69.6). We therefore equate expressions (69.6) and (69.16). We first express the sines in terms of the differ-

ence of the exponentials, and i^l in the form $e^{il\pi/2}$. As a result, we obtain

$$\begin{aligned} & \sum_{l=0}^{\infty} \frac{1}{2ikr} c_l [e^{i(kr+\delta_l-l\pi/2)} - e^{-i(kr+\delta_l-l\pi/2)}] P_l(\cos \vartheta) \\ & = \sum_{l=0}^{\infty} \frac{1}{r} \left\{ e^{il\pi/2} (2l+1) \frac{1}{2ik} [e^{i(kr-l\pi/2)} - e^{-i(kr-l\pi/2)}] + g_l e^{ihr} \right\} P_l(\cos \vartheta) \end{aligned}$$

For the equality obtained to be obeyed at any values of ϑ , it is necessary that the coefficients to the right and left of each P_l be the same. Let us equate the coefficients, separating the factors e^{ihr} and e^{-ihr} and cancelling r in the denominator:

$$\begin{aligned} & \frac{1}{2ik} c_l [e^{ihr} \cdot e^{i(\delta_l-l\pi/2)} - e^{-ihr} \cdot e^{-i(\delta_l-l\pi/2)}] \\ & = \frac{2l+1}{2ik} [e^{ihr} - e^{-ihr} \cdot e^{il\pi}] + g_l e^{ihr} \end{aligned}$$

For the equality to be obeyed at any values of r , it is necessary that the coefficients to the left and right of e^{ihr} and e^{-ihr} be the same. Equating these coefficients, we obtain two relations:

$$\frac{1}{2ik} c_l e^{i(\delta_l-l\pi/2)} = \frac{2l+1}{2ik} + g_l, \quad -\frac{1}{2ik} c_l e^{-i(\delta_l-l\pi/2)} = -\frac{2l+1}{2ik} e^{il\pi}$$

We find from the second relation that

$$c_l = (2l+1) e^{i(\delta_l+l\pi/2)} \quad (69.17)$$

Introduction of this value into the first relation leads to the following expression for g_l :

$$g_l = \frac{2l+1}{2ik} (e^{2i\delta_l} - 1)$$

Finally, introducing this expression into (69.15), we obtain a formula for the scattering amplitude:

$$A(\vartheta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) (e^{2i\delta_l} - 1) P_l(\cos \vartheta) \quad (69.18)$$

In accordance with (67.10), we have

$$d\sigma(\vartheta) = \frac{1}{4k^2} \left| \sum_{l=0}^{\infty} (2l+1) (e^{2i\delta_l} - 1) P_l(\cos \vartheta) \right|^2 d\Omega \quad (69.19)$$

Inspection of this formula reveals that the differential scattering cross section is determined by the set of phases δ_l .

We obtain the total scattering cross section by integrating (69.19) over the total solid angle 4π . The square of the modulus of a complex number equals the product of this number and its complex conjugate. A solid angle element in the given case can be taken in the form $d\Omega = 2\pi \sin \vartheta d\vartheta = -2\pi d(\cos \vartheta)$. With this in view, we can write:

$$\begin{aligned}\sigma &= \int d\sigma(\vartheta) = \frac{1}{4k^2} \int \left\{ \sum_{l=0}^{\infty} (2l+1)(e^{2i\delta_l} - 1) P_l(\cos \vartheta) \right\} \\ &\quad \times \left\{ \sum_{l'=0}^{\infty} (2l'+1)(e^{-2i\delta_{l'}} - 1) P_{l'}(\cos \vartheta) \right\} 2\pi [-d(\cos \vartheta)] \\ &= \frac{1}{4k^2} \sum_{l, l'} (2l+1)(2l'+1)(e^{2i\delta_l} - 1) \\ &\quad \times (e^{-2i\delta_{l'}} - 1) (-2\pi) \int_{+1}^{-1} P_l(x) P_{l'}(x) dx\end{aligned}$$

(integration over $x = \cos \vartheta$ from $+1$ to -1 corresponds to integration over ϑ from 0 to π). Taking into account (69.9), we obtain

$$\begin{aligned}\sigma &= \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1)(e^{2i\delta_l} - 1)(e^{-2i\delta_l} - 1) \\ &= \frac{(2i)^2}{k^2} \pi \sum_{l=0}^{\infty} (2l+1) \frac{e^{i\delta_l}(e^{i\delta_l} - e^{-i\delta_l}) e^{-i\delta_l}(e^{-i\delta_l} - e^{i\delta_l})}{(2i)^2} \quad (69.20)\end{aligned}$$

Going over to sines, we arrive at the formula

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l \quad (69.21)$$

A glance at this formula shows that the total cross section σ can be written as the sum of the partial sections σ_l

$$\sigma = \sum_{l=0}^{\infty} \sigma_l \quad (69.22)$$

where

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \delta_l \quad (69.23)$$

Each of the partial cross sections corresponds to scattering of a particle with a definite angular momentum (determined by the quantum number l).

The maximum value of the scattering cross section of a particle with the angular momentum l is evidently equal to

$$(\sigma_l)_{\max} = \frac{4\pi}{k^2} (2l + 1) \quad (69.24)$$

The calculation of the phases δ_l , as a rule, is a very difficult problem. The practical value of formulas (69.19) and (69.21) grows when the number of terms of the series that play a significant role diminishes, i.e. when the relevant series converge more rapidly.

We must note that upon introducing the value (69.17) for c_l into formula (69.6), we obtain the following asymptotic (at $r \rightarrow \infty$) expression for the psi-function:

$$\psi = \sum_{l=0}^{\infty} (2l + 1) e^{i(\delta_l + l\pi/2)} P_l(\cos \vartheta) \frac{\sin(kr + \delta_l - l\pi/2)}{kr}$$

Expressing the sine in terms of exponentials and dropping the phase factor equal to i , we can give this expression the form

$$\psi = \frac{1}{2k} \sum_{l=0}^{\infty} (2l + 1) P_l(\cos \vartheta) \left[(-1)^l \frac{e^{-ikr}}{r} - S_l \frac{e^{ikr}}{r} \right] \quad (69.25)$$

where

$$S_l = e^{2i\delta_l} \quad (69.26)$$

We shall need formula (69.25) in the following.

The first term in the brackets in formula (69.25) is a converging spherical wave with the amplitude $(-1)^l$, and the second term is a diverging spherical wave with the amplitude S_l . The absolute value of both amplitudes is unity. Consequently, the psi-function describing elastic scattering has the form of a standing wave formed by the superposition of a converging and a diverging spherical waves.

By formula (6.5), the probability flux density corresponding to a converging wave is

$$\begin{aligned} \mathbf{j}_{\text{conv}} &= \frac{\hbar}{2m_0 i} |(-1)^l|^2 \left\{ \frac{e^{ikr}}{r} \nabla \left(\frac{e^{-ikr}}{r} \right) - \frac{e^{-ikr}}{r} \nabla \left(\frac{e^{ikr}}{r} \right) \right\} \\ &= -\frac{\hbar k}{m_0 r^2} \mathbf{e}_r \end{aligned} \quad (69.27)$$

where \mathbf{e}_r is the unit vector of the position vector \mathbf{r} .

Similar calculations give the following value for the probability flux density corresponding to a diverging wave:

$$\mathbf{j}_{\text{div}} = |S_l|^2 \frac{\hbar k}{m_0 r^2} \mathbf{e}_r \quad (69.28)$$

Since $|S_l|^2 = 1$, the vectors (69.27) and (69.28) differ only in their direction. Therefore, the probability flux through any surface, including a sphere of radius R , corresponding to the function (69.25) is zero. This agrees with the fact that in elastic scattering the number of particles flying from a scattering centre equals the number of particles flying towards this centre.

70. Inelastic Scattering

The term **inelastic** is applied to processes in which the internal state of the particles taking part in them changes (particularly, the type of the particles may change). Examples of such processes are the excitation of atoms or nuclei, the ionization of atoms, the decay of nuclei, and the decay or creation of particles.

Each of the processes that can take place in collisions of particles is called a **reaction channel**. Particles whose internal states do not change as a result of collision are considered to remain in the inlet channel. The latter evidently corresponds to elastic scattering. If a process is compatible with conservation laws, the relevant channel is said to be **open**.

If there are several different reaction channels, the asymptotic expression of the psi-function of the colliding particles is the sum of terms each of which corresponds to one of the reaction channels. These channels also include an inlet channel corresponding to elastic scattering. We shall begin with a consideration of the term corresponding to the inlet channel.

As in elastic scattering, the psi-function corresponding to the inlet channel can be represented as the sum of a converging and a diverging spherical waves [see (69.25)]

$$\Psi = \frac{1}{2k} \sum_{l=0}^{\infty} (2l+1) P_l(\cos \vartheta) \left[(-1)^l \frac{e^{-ikr}}{r} - S_l \frac{e^{ikr}}{r} \right] \quad (70.1)$$

Now the S_l 's, however, are no longer determined by formula (69.26), but are certain, generally speaking, complex quantities with moduli less than unity. Accordingly, the flux of particles in the inlet channel flying from the scattering centre is less than the flux of particles incident on the centre [see formulas (69.27) and (69.28)].

Calculations similar to those which led us to formula (69.18) give the following expression for the scattering amplitude:

$$A(\vartheta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1)(S_l - 1) P_l(\cos \vartheta) \quad (70.2)$$

It differs from (69.18) in containing the quantity S_l with an absolute value less than unity instead of $e^{2i\delta_l}$ [compare with (69.26)]. Introducing this expression into formula (67.10), we obtain the differential cross section of elastic scattering:

$$d\sigma_{el} = |A(\vartheta)|^2 d\Omega$$

$$= -\frac{1}{4k^2} \sum_{l, l'} (2l+1)(2l'+1)(S_l^* - 1)(S_{l'} - 1) P_l P_{l'} d\Omega.$$

Integration of this expression over the angles results, with a view to (69.9), in the following value of the total elastic scattering cross-section [compare with (69.20)]:

$$\begin{aligned} \sigma_{el} &= -\frac{1}{4k^2} \sum_{l, l'} (2l+1)(2l'+1)(S_l^* - 1)(S_{l'} - 1) 2\pi \frac{2}{2l+1} \delta_{l, l'} \\ &= \frac{\pi}{k^2} \sum_l (2l+1) |S_l - 1|^2 = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) |1 - S_l|^2 \end{aligned} \quad (70.3)$$

The partial elastic scattering cross section is

$$\sigma_{l, el} = \frac{\pi}{k^2} (2l+1) |1 - S_l|^2 \quad (70.4)$$

To find the inelastic scattering cross section, let us surround the scattering centre with an imaginary spherical surface having a large radius R and evaluate the particle flux Φ , determined by the function (70.1), through this surface. By formula (6.5), we have

$$\Phi = \frac{1}{2m_0 i} \oint \left(\psi^* \frac{\partial \psi}{\partial r} - \psi \frac{\partial \psi^*}{\partial r} \right)_R R^2 d\Omega \quad (70.5)$$

(we take the radial component of the gradient at the distance R from the centre). Disregarding terms of the order of $1/r^2$ in comparison with terms of the order of $1/r$ (R is large), we obtain the following expression for the derivative of the function (70.1) with respect to r :

$$\frac{\partial \psi}{\partial r} = \frac{1}{2kr} \sum_{l=0}^{\infty} (2l+1) P_l(\cos \vartheta) [-ik(-1)^l e^{-ihr} - ikS_l e^{ihr}]$$

The derivative $\partial\psi^*/\partial r$ differs from the above only in the signs in front of i . Substitution into (70.5) of these expressions for the derivatives and of expression (70.1) for ψ yields

$$\begin{aligned}\Phi &= \frac{\hbar}{2m_0 i} \frac{1}{4k^2} \sum_{l=0}^{\infty} (2l+1)^2 (-2ik)(1-|S_l|^2) \oint P_l^2 d\Omega \\ &= -\frac{\hbar}{4m_0 k} \sum_{l=0}^{\infty} (2l+1)^2 (1-|S_l|^2) 2\pi \frac{2}{2l+1} \\ &= -\frac{\pi\hbar}{m_0 k} \sum_{l=0}^{\infty} (2l+1) (1-|S_l|^2)\end{aligned}\quad (70.6)$$

The flux is negative because $|S_l| < 1$. Seeing that a certain number of particles experiences inelastic scattering or absorption, the flux of elastically scattered particles is less than that of particles incident on the scattering centre.

The flux of particles experiencing inelastic scattering is evidently equal to the flux (70.6) taken with the opposite sign:

$$\Phi_{\text{inel}} = \frac{\pi\hbar}{m_0 k} \sum_{l=0}^{\infty} (2l+1) (1-|S_l|^2) \quad (70.7)$$

Dividing this flux by the flux density of the incident particles [which equals $v = p/m_0 = \hbar k/m_0$, see (67.7)], we obtain, according to (66.3), the total inelastic scattering cross section (the total over all the inelastic channels). Hence,

$$\sigma_{\text{inel}} = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) (1-|S_l|^2) \quad (70.8)$$

Each addend of this sum is a partial inelastic scattering cross section:

$$\sigma_{l, \text{inel}} = \frac{\pi}{k^2} (2l+1) (1-|S_l|^2) \quad (70.9)$$

When $S_l = 1$, expression (70.9) vanishes—inelastic scattering of particles with a given l is absent. The case $S_l = 0$ corresponds to the complete “absorption” of particles with the given l . In this case, by formulas (70.4) and (70.8), we have

$$\sigma_{l, \text{el}} = \sigma_{l, \text{inel}} = \frac{\pi}{k^2} (2l+1) \quad (70.10)$$

When the cross section (70.9) is non-zero, the section (70.4) is also non-zero. Hence, the existence of inelastic reaction channels always leads to elastic scattering.

APPENDICES

1. Angular Momentum Operators in Spherical Coordinates

The following formulas are used for a transition from Cartesian to spherical coordinates:

$$r^2 = x^2 + y^2 + z^2, \quad \cos \vartheta = \frac{z}{r}, \quad \tan \varphi = \frac{y}{x}$$

The reverse transformations have the form

$$x = r \sin \vartheta \cos \varphi, \quad y = r \sin \vartheta \sin \varphi, \quad z = r \cos \vartheta$$

With the aid of these formulas, we can find that

$$\begin{aligned} \frac{\partial}{\partial x} &= \frac{\partial}{\partial r} \frac{\partial r}{\partial x} + \frac{\partial}{\partial \vartheta} \frac{\partial \vartheta}{\partial x} + \frac{\partial}{\partial \varphi} \frac{\partial \varphi}{\partial x} \\ &= \sin \vartheta \cos \varphi \frac{\partial}{\partial r} + \frac{\cos \vartheta \cos \varphi}{r} \frac{\partial}{\partial \vartheta} - \frac{\sin \varphi}{r \sin \vartheta} \frac{\partial}{\partial \varphi} \\ \frac{\partial}{\partial y} &= \frac{\partial}{\partial r} \frac{\partial r}{\partial y} + \frac{\partial}{\partial \vartheta} \frac{\partial \vartheta}{\partial y} + \frac{\partial}{\partial \varphi} \frac{\partial \varphi}{\partial y} \\ &= \sin \vartheta \sin \varphi \frac{\partial}{\partial r} + \frac{\cos \vartheta \sin \varphi}{r} \frac{\partial}{\partial \vartheta} - \frac{\cos \varphi}{r \sin \vartheta} \frac{\partial}{\partial \varphi} \\ \frac{\partial}{\partial z} &= \frac{\partial}{\partial r} \frac{\partial r}{\partial z} + \frac{\partial}{\partial \vartheta} \frac{\partial \vartheta}{\partial z} + \frac{\partial}{\partial \varphi} \frac{\partial \varphi}{\partial z} = \cos \vartheta \frac{\partial}{\partial r} - \frac{\sin \vartheta}{r} \frac{\partial}{\partial \vartheta} \end{aligned}$$

Introducing these expressions into the formula

$$\hat{M}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

[see (15.11)], we obtain

$$\begin{aligned} \hat{M}_z &= -i\hbar \left\{ (r \sin \vartheta \cos \varphi) \left[\sin \vartheta \sin \varphi \frac{\partial}{\partial r} + \frac{\cos \vartheta \sin \varphi}{r} \frac{\partial}{\partial \vartheta} \right. \right. \\ &\quad \left. \left. + \frac{\cos \varphi}{r \sin \vartheta} \frac{\partial}{\partial \varphi} \right] - (r \sin \vartheta \sin \varphi) \left[\sin \vartheta \cos \varphi \frac{\partial}{\partial r} \right. \right. \\ &\quad \left. \left. + \frac{\cos \vartheta \cos \varphi}{r} \frac{\partial}{\partial \vartheta} - \frac{\sin \varphi}{r \sin \vartheta} \frac{\partial}{\partial \varphi} \right] \right\} = -i\hbar \frac{\partial}{\partial \varphi} \end{aligned}$$

Hence,

$$\hat{M}_z = -i\hbar \frac{\partial}{\partial \varphi} \tag{I.1}$$

Similar calculations lead to the formulas

$$\hat{M}_x = i\hbar \left(\sin \vartheta \frac{\partial}{\partial \varphi} + \cot \vartheta \cos \varphi \frac{\partial}{\partial \varphi} \right)$$

$$\hat{M}_y = -i\hbar \left(\cos \vartheta \frac{\partial}{\partial \varphi} - \cot \vartheta \sin \varphi \frac{\partial}{\partial \varphi} \right)$$

Substitution of the obtained expressions into the formula $\hat{M}^2 = \hat{M}_x^2 + \hat{M}_y^2 + \hat{M}_z^2$ [see (15.10)] yields after simplifications¹

$$\hat{M}^2 = -\hbar^2 \left\{ \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right\} \quad (I.2)$$

The following auxiliary operators are also useful:

$$\begin{aligned} \hat{M}_x + i\hat{M}_y &= \hbar e^{i\varphi} \left[\frac{\partial}{\partial \vartheta} + i \cot \vartheta \frac{\partial}{\partial \varphi} \right] \\ \hat{M}_x - i\hat{M}_y &= \hbar e^{-i\varphi} \left[-\frac{\partial}{\partial \vartheta} + i \cot \vartheta \frac{\partial}{\partial \varphi} \right] \end{aligned} \quad (I.3)$$

II. Spherical Functions

Let us find the function $\psi(\vartheta, \varphi)$ satisfying the differential equation

$$\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial \psi}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 \psi}{\partial \varphi^2} + \alpha \psi = 0 \quad (II.1)$$

where α is a real parameter, and of all the solutions let us choose only those that are finite and single-valued. The latter signifies that they meet the requirement

$$\psi(\vartheta, \varphi + 2\pi) = \psi(\vartheta, \varphi) \quad (II.2)$$

We shall attempt to separate the variables ϑ and φ . To do this, we shall try to seek the solution in the form

$$\psi(\vartheta, \varphi) = \Theta(\vartheta) \cdot \Phi(\varphi) \quad (II.3)$$

Introduction of the function (II.3) into Eq. (II.1) yields

$$\Phi \frac{1}{\sin \vartheta} \frac{d}{d\vartheta} \left(\sin \vartheta \frac{d\Theta}{d\vartheta} \right) + \frac{1}{\sin^2 \vartheta} \Theta \frac{d^2 \Phi}{d\varphi^2} + \alpha \Theta \Phi = 0$$

¹ It must be borne in mind that, for example,

$$\begin{aligned} \hat{M}_x^2 &= i\hbar \left(\sin \vartheta \frac{\partial}{\partial \vartheta} + \cot \vartheta \cos \varphi \frac{\partial}{\partial \varphi} \right) i\hbar \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \cot \vartheta \cos \varphi \frac{\partial}{\partial \varphi} \\ &= -\hbar^2 \left[\sin^2 \vartheta \frac{\partial^2}{\partial \vartheta^2} + \sin \vartheta \cos \varphi \frac{\partial}{\partial \vartheta} \left(\cot \vartheta \frac{\partial}{\partial \varphi} \right) \right. \\ &\quad \left. + \cot \vartheta \cos \varphi \frac{\partial}{\partial \varphi} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \cot^2 \vartheta \cos \varphi \frac{\partial}{\partial \varphi} \left(\cos \varphi \frac{\partial}{\partial \varphi} \right) \right] \end{aligned}$$

The quantity \hat{M}_y^2 is calculated similarly.

Dividing the equation obtained by $\Theta\Phi$ and multiplying by $\sin^2 \vartheta$, we obtain

$$\frac{1}{\Theta} \sin \vartheta \frac{d}{d\vartheta} \left(\sin \vartheta \frac{d\Theta}{d\vartheta} \right) + \frac{1}{\Phi} \frac{d^2\Phi}{d\varphi^2} + \alpha \sin^2 \vartheta = 0$$

or

$$\frac{1}{\Theta} \sin \vartheta \frac{d}{d\vartheta} \left(\sin \vartheta \frac{d\Theta}{d\vartheta} \right) + \alpha \sin^2 \vartheta = - \frac{1}{\Phi} \frac{d^2\Phi}{d\varphi^2} \quad (\text{II.4})$$

The left-hand side of Eq. (II.4) depends only on ϑ , and its right-hand side only on φ . For the equation to hold at arbitrary values of ϑ and φ , it is necessary that both sides of it be equal to the same constant quantity¹, which we have designated β^2 . We thus arrive at two differential equations:

$$-\frac{1}{\Phi} \frac{d^2\Phi}{d\varphi^2} = \beta^2, \text{ or } \frac{d^2\Phi}{d\varphi^2} + \beta^2\Phi = 0 \quad (\text{II.5})$$

$$\sin \vartheta \frac{d}{d\vartheta} \left(\sin \vartheta \frac{d\Theta}{d\vartheta} \right) + \alpha \sin^2 \vartheta \cdot \Theta - \beta^2\Theta = 0 \quad (\text{II.6})$$

The following function is a solution of Eq. (II.5):

$$\Phi = Ce^{i\beta\varphi}$$

For the condition (II.2) to be satisfied, β must be a real quantity having an integral positive or negative value (particularly, β may equal zero). Designating this integer by m , we obtain

$$\Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \quad (m = 0, \pm 1, \pm 2, \dots) \quad (\text{II.7})$$

We have assumed that $C = 1/\sqrt{2\pi}$ for the system of functions to be orthonormalized, i.e. for the condition

$$\int_0^{2\pi} \Phi_{m'}^* \Phi_{m''} d\varphi = \delta_{m'm''} \quad (\text{II.8})$$

to be observed [see (19.6)].

Introducing m^2 instead of β^2 into Eq. (II.6), we write it as follows:

$$\frac{1}{\sin \vartheta} \frac{d}{d\vartheta} \left(\sin \vartheta \frac{d\Theta}{d\vartheta} \right) + \left(\alpha - \frac{m^2}{\sin^2 \vartheta} \right) \Theta = 0 \quad (\text{II.9})$$

Let us go over to the new variable

$$\eta = \cos \vartheta \quad (\text{II.10})$$

¹ This quantity is known as the separation constant.

The substitution of $(d/d\eta) (d\eta/d\vartheta) = -\sin \vartheta (d/d\eta)$ for $d/d\vartheta$ in (II.9) yields

$$\frac{1}{\sin \vartheta} \left(-\sin \vartheta \frac{d}{d\eta} \right) \left[\sin \vartheta \left(-\sin \vartheta \frac{d\Theta}{d\eta} \right) \right] + \left(\alpha - \frac{m^2}{\sin^2 \vartheta} \right) \Theta = 0$$

Finally, substituting $1 - \cos^2 \vartheta = 1 - \eta^2$ for $\sin^2 \vartheta$, we arrive at the equation

$$\frac{d}{d\eta} \left[(1 - \eta^2) \frac{d\Theta}{d\eta} \right] + \left(\alpha - \frac{m^2}{1 - \eta^2} \right) \Theta = 0 \quad (\text{II.11})$$

We must note that the function $\Theta(\eta)$ in Eq. (II.11) has a different analytic form than the function $\Theta(\vartheta)$ in Eq. (II.9). Therefore, strictly speaking, the function $\Theta(\eta)$ ought to be designated by a different letter.

Let us leave Eq. (II.11) alone for a while and consider n -degree polynomials that are determined by the formula

$$P_n(x) = \frac{1}{2^n n!} \frac{d^n}{dx^n} [(x^2 - 1)^n] \quad (\text{II.12})$$

They are known as **Legendre polynomials**. Assuming consecutively in formula (II.12) that $n = 0$, $n = 1$, $n = 2$, we can obtain expressions for the first three polynomials:

$$P_0 = 1, \quad P_1 = x, \quad P_2 = \frac{1}{2} (3x^2 - 1) \quad (\text{II.13})$$

Assuming that $n = 4, 5$, etc., we can also calculate the relevant polynomials. These polynomials can be found in a simpler way, however, by using the recurrence formula which we shall give without a proof. This formula relates three consecutive polynomials and is as follows:

$$P_{n+1}(x) = \frac{2n+1}{n+1} x P_n(x) - \frac{n}{n+1} P_{n-1}(x) \quad (\text{II.14})$$

It is simple to find with the aid of this formula that

$$P_3 = \frac{1}{2} (5x^3 - 3x), \quad P_4 = \frac{1}{8} (35x^4 - 30x^2 + 3), \quad \text{etc.} \quad (\text{II.15})$$

Let us find a differential equation having Legendre polynomials as its solutions. For this purpose, consider the auxiliary function

$$w = (x^2 - 1)^n$$

Differentiating this function with respect to x , we obtain the identity

$$w' \equiv n (x^2 - 1)^{n-1} 2x \equiv \frac{2nwx}{x^2 - 1}$$

whence

$$w' (x^2 - 1) - 2nwx = 0$$

Let us differentiate this identity $n + 1$ times with respect to x , taking into account that

$$(uv)^{(n+1)} = u^{(n+1)}v + (n+1)u^{(n)}v' + \frac{(n+1)n}{2}u^{(n-1)}v'' + \dots$$

As a result, we obtain the relation

$$\begin{aligned} w^{(n+2)}(x^2 - 1) + (n+1)w^{(n+1)}2x + \frac{(n+1)n}{2}w^{(n)}2 \\ - 2nw^{(n+1)}x - 2n(n+1)w^{(n)} = 0 \end{aligned}$$

which is simplified as follows:

$$w^{(n+2)}(x^2 - 1) + w^{(n+1)}2x - n(n+1)w^{(n)} = 0$$

From this expression, we obtain a differential equation for the function $w^{(n)}$:

$$(x^2 - 1)(w^{(n)})'' + 2x(w^{(n)})' - n(n+1)w^{(n)} = 0 \quad (\text{II.16})$$

The function $w^{(n)} = \frac{d^n}{dx^n}[(x^2 - 1)^n]$ differs from $P_n(x)$ only in the factor $1/2^n n!$ [see (II.12)]. Consequently, $P_n(x)$ also satisfies relation (II.16). We thus conclude that the Legendre polynomials are solutions of the differential equation

$$(x^2 - 1)y'' + 2xy' - \gamma y = 0 \quad (\text{II.17})$$

that correspond to values of the parameter γ equal to $n(n+1)$.

Equation (II.17) can be written in the form

$$\frac{d}{dx}[(1-x^2)y'] + \gamma y = 0 \quad (\text{II.18})$$

Equation (II.17), like (II.18), is known as the **Legendre equation**.

It can be proved that the Legendre polynomials are orthogonal over the interval $[-1, +1]$. This signifies that¹

$$\int_{-1}^{+1} P_n^*(x) P_l(x) dx = \int_{-1}^{+1} P_n(x) P_l(x) dx = 0 \quad \text{when } n \neq l \quad (\text{II.19})$$

What we call the square of the norm of a polynomial has the following value:

$$\int_{-1}^{+1} P_n^*(x) P_n(x) dx = \int_{-1}^{+1} P_n(x) P_n(x) dx = \frac{2}{2n+1} \quad (\text{II.20})$$

¹ Legendre polynomials are real, therefore $P_n^*(x) = P_n(x)$.

Let us establish two other important properties of the Legendre polynomials. First, we shall prove that $P_n(x)$ is an even function at an even n and an odd function at an odd n . For this purpose, we shall replace x with $-x$ in formula (II.12) and correspondingly dx with $-dx = (-1) dx$. The result is

$$\begin{aligned} P_n(-x) &= \frac{1}{2^n n!} \frac{d^n}{(-1)^n dx^n} \{[(-x)^2 - 1]^n\} \\ &= \frac{1}{2^n n!} \frac{1}{(-1)^n} \frac{d^n}{dx^n} \{[x^2 - 1]^n\} = \frac{1}{(-1)^n} P_n(x) = (-1)^n P_n(x) \end{aligned}$$

Hence,

$$P_n(-x) = (-1)^n P_n(x) \quad (\text{II.21})$$

Q.E.D.

Now let us calculate the value of $P_n(x)$ for $x = 1$. To do this, we shall go over from x in formula (II.12) to the new variable ε related to x by the expression $x = 1 + \varepsilon$, and then find the limit of the expression obtained when ε shrinks to zero. In going over from x to ε , we shall take into account that $dx = d\varepsilon$ and, consequently, $d/dx = d/d\varepsilon$. Hence, substitution of $1 + \varepsilon$ for x in (II.12) yields

$$\begin{aligned} P_n(1 + \varepsilon) &= \frac{1}{2^n n!} \frac{d^n}{d\varepsilon^n} [\varepsilon^n (2 + \varepsilon)^n] = \frac{1}{2^n n!} \left\{ \left(\frac{d^n}{d\varepsilon^n} \varepsilon^n \right) (2 + \varepsilon)^n \right. \\ &\quad \left. + n \left(\frac{d^{n-1}}{d\varepsilon^{n-1}} \varepsilon^n \right) \left[\frac{d}{d\varepsilon} (2 + \varepsilon)^n \right] + \dots + (\varepsilon^n) \left[\frac{d^n}{d\varepsilon^n} (2 + \varepsilon)^n \right] \right\} \\ &= \frac{1}{2^n n!} \{n! (2 + \varepsilon)^n + n(n!)\varepsilon [n(2 + \varepsilon)^{n-1}] + \dots + \varepsilon^n n!\} \end{aligned}$$

All the terms in the braces except the first one contain the factor ε to a power from 1 to n . Consequently, when $\varepsilon \rightarrow 0$, we find that

$$P_n(1) = 1 \quad (\text{II.22})$$

It follows from formulas (II.21) and (II.22) that

$$P_n(-1) = (-1)^n P_n(1) = (-1)^n \quad (\text{II.23})$$

Now we shall turn to the differential equation (II.11) and write it, substituting x for η and y for Θ :

$$\frac{d}{dx} [(1 - x^2) y'] + \left(\alpha - \frac{m^2}{1 - x^2} \right) y = 0 \quad (\text{II.24})$$

We shall attempt to find a solution of this equation in the form

$$y = (1 - x^2)^{\frac{|m|}{2}} u(x) \quad (\text{II.25})$$

Recall that the number m can take on either positive or negative values [see (II.7)]. In expression (II.25), we have used the magnitude of m .

Substitution of the function (II.25) into Eq. (II.24) leads, after simple transformations, to the following differential equation for $u(x)$:

$$(x^2 - 1) u'' + 2(|m| + 1)xu' + [|m|(|m| + 1) - \alpha]u = 0 \quad (\text{II.26})$$

We shall prove that when $\alpha = n(n + 1)$, this equation is satisfied by the function

$$u(x) = \frac{d^{|m|}}{dx^{|m|}} P_n(x)$$

where $P_n(x)$ is a Legendre polynomial. To do this, we write Eq. (II.17), assuming in it that $\gamma = n(n + 1)$ and $y = P_n(\hat{x})$:

$$(x^2 - 1) P_n'' + 2xP_n' - n(n + 1)P_n = 0$$

Differentiating this equation $|m|$ times with respect to x , we obtain

$$\begin{aligned} & \left(\frac{d^{|m|} P_n}{dx^{|m|}} \right)'' (x^2 - 1) + |m| \left(\frac{d^{|m|} P_n}{dx^{|m|}} \right)' 2x \\ & + \frac{|m|(|m| - 1)}{2} \left(\frac{d^{|m|} P_n}{dx^{|m|}} \right) 2 + \left(\frac{d^{|m|} P_n}{dx^{|m|}} \right)' 2x \\ & + |m| \left(\frac{d^{|m|} P_n}{dx^{|m|}} \right) 2 - n(n + 1) \left(\frac{d^{|m|} P_n}{dx^{|m|}} \right) = 0 \end{aligned}$$

or after transformations

$$\begin{aligned} & (x^2 - 1) \left(\frac{d^{|m|} P_n}{dx^{|m|}} \right)'' + 2(|m| + 1)x \left(\frac{d^{|m|} P_n}{dx^{|m|}} \right)' \\ & + [|m|(|m| + 1) - n(n + 1)] \left(\frac{d^{|m|} P_n}{dx^{|m|}} \right) = 0 \quad (\text{II.27}) \end{aligned}$$

A comparison of Eqs. (II.26) and (II.27) shows that the function $u(x) = d^{|m|} P_n / dx^{|m|}$ satisfies Eq. (II.26) provided that $\alpha = n(n + 1)$. Taking into account (II.25), we can assert that when $\alpha = n(n + 1)$, Eq. (II.24) has as its solution the function

$$P_n^m(x) = (1 - x^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{dx^{|m|}} P_n(x) \quad (\text{II.28})$$

The functions $P_n^m(x)$ are called associated Legendre polynomials. Since the $(n + 1)$ -th derivative of an n -th degree polynomial is zero, the functions (II.28) differ from zero only when $|m| \leq n$.

We must note that the only finite solutions of Eq. (II.24) in the interval $[-1, +1]$ are the associated Legendre polynomials. Con-

sequently, the latter are eigenfunctions of differential equation (II.24), and the numbers n ($n + 1$) are the eigenvalues of this equation ($n = 0, 1, 2, \dots$).

The following relation is observed for the functions (II.28):

$$\int_{-1}^{+1} P_n^m(x) P_l^m(x) dx = \frac{2}{2n+1} \frac{(n+|m|)!}{(n-|m|)!} \delta_{nl} \quad (\text{II.29})$$

Hence, the polynomials P_n^m are mutually orthogonal.

Recurrence formulas exist for the associated Legendre polynomials, namely,

$$x P_n^m(x) = \frac{n-|m|+1}{2n+1} P_{n+1}^m(x) + \frac{n+|m|}{2n+1} P_{n-1}^m(x) \quad (\text{II.30})$$

and

$$\begin{aligned} \sqrt{1-x^2} P_n^{m+1}(x) &= \frac{(n-|m|)(n-|m|+1)}{2n+1} P_{n+1}^m(x) \\ &\quad - \frac{(n+|m|)(n+|m|+1)}{2n+1} P_{n-1}^m(x) \end{aligned} \quad (\text{II.31})$$

Equation (II.11) thus has finite solutions only when $\alpha = l(l+1)$, where $l = 0, 1, 2, \dots$ ¹, the functions $P_l^m(\eta)$ being these solutions. To make the system of these solutions orthonormalized, we shall write them in accordance with (II.29) as follows:

$$\begin{aligned} \Theta_{lm}(\eta) &= \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} P_l^m(\eta) \\ &= \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} (1-\eta^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{dx^{|m|}} P_l(\eta) \end{aligned}$$

Substituting $\cos \vartheta$ for η [see (II.10)], we obtain an orthonormalized system of solutions of Eq. (II.9):

$$\begin{aligned} \Theta_{lm}(\vartheta) &= \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} P_l^m(\cos \vartheta) \\ &= \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} \sin^{|m|} \vartheta \frac{d^{|m|}}{d(\cos \vartheta)^{|m|}} P_l(\cos \vartheta) \end{aligned} \quad (\text{II.32})$$

[we have taken advantage of the fact that $(1 - \cos^2 \vartheta)^{\frac{|m|}{2}} = \sin^{|m|} \vartheta$].

¹ Having in view the physical applications, we have written l instead of n .

Finally, multiplying the functions (II.7) and (II.32), we arrive at a solution of Eq. (II.1):

$$\begin{aligned} Y_{lm}(\vartheta, \varphi) &= \frac{1}{\sqrt{2\pi}} \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} e^{im\varphi} P_l^m(\cos \vartheta) \\ &= \frac{1}{\sqrt{2\pi}} \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} e^{im\varphi} \sin^{|m|} \vartheta \\ &\quad \times \frac{d^{|m|}}{d(\cos \vartheta)^{|m|}} P_l(\cos \vartheta) \quad (\text{II.33}) \end{aligned}$$

The functions $Y_{lm}(\vartheta, \varphi)$ defined by formula (II.29) are called **spherical**. Since the systems of functions (II.7) and (II.32) are orthonormalized, the spherical functions (II.33) are also orthonormalized. This signifies that

$$\begin{aligned} &\int_{-1}^{+1} \int_0^{2\pi} Y_{l'm'}^*(\vartheta, \varphi) Y_{l''m''}(\vartheta, \varphi) d(\cos \vartheta) d\varphi \\ &= \int_0^{\pi} \int_0^{2\pi} Y_{l'm'}^*(\vartheta, \varphi) Y_{l''m''}(\vartheta, \varphi) \sin \vartheta d\vartheta d\varphi = \delta_{l'l''} \delta_{m'm''} \quad (\text{II.34}) \end{aligned}$$

When $l' \neq l''$, the integral vanishes because of the factor $\Theta(\vartheta)$ [see (II.29)], and when $m' \neq m''$, it vanishes because of the factor $\Phi(\varphi)$ [see (II.8)].

We know that psi-functions are determined to within a phase factor of the form of $e^{i\alpha}$. For this reason, the functions (II.33) may be multiplied by any complex (particularly, real) number with a modulus equal to unity. In this case, they as previously will satisfy Eq. (II.1) and retain the property (II.34). In quantum mechanics, it is more convenient to write the solution of Eq. (II.1) in the form

$$\begin{aligned} Y_{lm}(\vartheta, \varphi) &= (-1)^{\frac{m+|m|}{2}} \frac{1}{\sqrt{2\pi}} \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} e^{im\varphi} P_l^m(\cos \vartheta) \\ &= (-1)^{\frac{m+|m|}{2}} \frac{1}{\sqrt{2\pi}} \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} e^{im\varphi} \\ &\quad \times \sin^{|m|} \vartheta \frac{d^{|m|}}{d(\cos \vartheta)^{|m|}} P_l(\cos \vartheta) \quad (\text{II.35}) \end{aligned}$$

In practice, this signifies that for $m \leq 0$ the solutions are taken in the form of (II.33), and for $m > 1$ the functions (II.33) are multiplied by $(-1)^m$.

The factor i^l is sometimes introduced into the function (II.35). The function (II.35), like (II.33), is called spherical. We must note

that as a rule only spherical functions for $m \geq 0$ are treated in courses of calculus.

It is not difficult to see that the following relation holds for the function (II.35):

$$Y_{l,-m}(\vartheta, \varphi) = (-1)^m Y_{lm}^*(\vartheta, \varphi) \quad (\text{II.36})$$

where m stands for a positive number.

Summary. Equation (II.1) has single-valued and finite solutions at values of the parameter α equal to

$$\alpha = l(l+1), \text{ where } l = 0, 1, 2, \dots \quad (\text{II.37})$$

The spherical functions Y_{lm} whose orthonormalized expressions are given by formula (II.35) are solutions of this equation. To each eigenvalue of the parameter α there belong $2l+1$ eigenfunctions Y_{lm} differing in the values of the number m , which at a given l can equal

$$m = -l, -l+1, \dots, -1, 0, 1, \dots, l-1, l \quad (\text{II.38})$$

III. Chebyshev-Hermite Polynomials

Consider the differential equation

$$f''(x) - 2xf'(x) + \lambda f(x) = 0 \quad (\text{III.1})$$

Let us attempt to find the solutions of this equation that remain finite at any values of x . We shall try to find such a solution in the form of the series

$$f(x) = \sum_{k=0} a_k x^k \quad (\text{III.2})$$

We meanwhile leave the number of terms in the series indeterminate. The first two derivatives of the function (III.2) are

$$f'(x) = \sum_{k=0} ka_k x^{k-1} \quad (\text{III.3})$$

$$\begin{aligned} f''(x) &= \sum_{k=0} k(k-1)a_k x^{k-2} = \sum_{k=2} k(k-1)a_k x^{k-2} \\ &= \sum_{k=0} (k+2)(k+1)a_{k+2} x^k \end{aligned} \quad (\text{III.4})$$

We have discarded the terms equal to zero that correspond to $k=0$ and $k=1$ in the sum (III.4) and have then replaced k with $k+2$ in this sum.

Let us substitute the function (III.2) and its derivatives (III.3) and (III.4) into Eq. (III.1):

$$\sum_{k=0} (k+2)(k+1)a_{k+2} x^k - 2x \sum_{k=0} ka_k x^{k-1} + \lambda \sum_{k=0} a_k x^k = 0$$

Introducing x inside the second sum and then combining all three sums into one, we obtain the relation

$$\sum_{k=0} [(k+2)(k+1)a_{k+2} - (2k-\lambda)a_k] x^k = 0$$

The latter must be obeyed at any values of x . This is possible if the coefficients of x at all its powers are zero. Consequently, the following condition must be observed:

$$(k+2)(k+1)a_{k+2} - (2k-\lambda)a_k = 0 \quad (k = 0, 1, 2, \dots)$$

Hence follows a recurrence formula for the coefficients a_k :

$$a_{k+2} = \frac{2k-\lambda}{(k+2)(k+1)} a_k \quad (\text{III.5})$$

Since the recurrence formula determines the coefficient a_{k+2} in terms of a_k , the sum (III.2) contains terms only with even or only with odd powers of x .

We shall show that the infinite series (III.2) with coefficients satisfying relation (III.5) behaves like $\exp(x^2)$ when x tends to infinity. At large values of k , the recurrence formula (III.5) can be simplified as follows:

$$a_{k+2} \approx \frac{2}{k+2} a_k \quad (\text{III.6})$$

Extending this formula to any k 's, we obtain

$$a_2 \approx \frac{2}{0+2} a_0 = \frac{1}{1} a_0 = \frac{1}{1!} a_0$$

$$a_4 \approx \frac{2}{2+2} a_2 \approx \frac{1}{2} \frac{1}{1} a_0 = \frac{1}{2!} a_0$$

$$a_6 \approx \frac{2}{4+2} a_4 \approx \frac{1}{3} \frac{1}{2} \frac{1}{1} a_0 = \frac{1}{3!} a_0$$

• • • • • • • • • • • • •

$$a_{2k} \approx \dots = \frac{1}{k!} a_0$$

• • • • • • • • • • • • •

Substitution of these values into (III.2) yields

$$f(x) = \sum_{k=0} a_{2k} x^{2k} \approx a_0 \sum_{k=0} \frac{x^{2k}}{k!} \quad (\text{III.7})$$

The circumstance that we have calculated the first coefficients of the series by formula (III.6), which holds only for large k 's, does not play an appreciable role because the contribution of the first terms of the series at large x 's is insignificant.

It is quite simple to verify that the expansion of the function $\exp(x^2)$ into Maclaurin's series has the form

$$e^{x^2} = \sum_{k=0}^{\infty} \frac{x^{2k}}{k!}$$

A comparison of this formula with (III.7) shows that the infinite series (III.2) with coefficients satisfying formula (III.5) behaves like $\exp(x^2)$ when x tends to infinity, i.e. grows unlimitedly. We have given the proof assuming that the coefficients a_k with even numbers k are non-zero. In a similar way, we can conduct the proof assuming that the coefficients with odd k 's are non-zero.

Consequently, the sum (III.2) can be a finite solution of Eq. (III.1) at all values of x only if the number of addends in it is finite. For this to occur, the coefficients a_k beginning with a certain value of k must be zero.

Assume that $a_n \neq 0$ and $a_{n+2} = 0$. Therefore, in accordance with (III.5), all the subsequent coefficients will be zero too. By (III.5), the coefficient a_{n+2} will vanish when $a_n \neq 0$ if $2n - \lambda = 0$. Hence we obtain the values of the parameter λ at which the solutions of Eq. (III.1) expressed by the sum (III.5) are finite:

$$\lambda = 2n \quad (n = 0, 1, 2, \dots) \quad (\text{III.8})$$

The numbers (III.8) are the eigenvalues of Eq. (III.1). At these values of the parameter λ , Eq. (III.1) becomes

$$f''(x) - 2xf'(x) + 2nf(x) = 0 \quad (\text{III.9})$$

The eigenfunctions of this equation are polynomials of degree n :

$$H_n(x) = \sum_{k=0}^n a_k x^k$$

whose coefficients satisfy the condition

$$a_{k+2} = \frac{2(k-n)}{(k+2)(k+1)} a_k \quad (\text{III.10})$$

[we have introduced (III.8) into formula (III.5)]. Such polynomials are called **Chebyshev-Hermite polynomials**.

The last non-zero coefficient of the polynomial $H_n(x)$ will be a_n . Consequently, when n is even, the polynomial contains only even powers of x , and when n is odd—only odd ones. Indeed, let us take an even n equal, for instance, to 4. Assume that the coefficients a_1 and a_3 are non-zero. Hence, according to (III.10), all the subsequent a_k 's with odd k 's will be non-zero, and the series will be infinite. Similarly, with an odd n , all the a_k 's with even k 's must be zero.

Formula (III.10) allows us to express the coefficients a_k in terms of a_0 (with an even n) or in terms of a_1 (with an odd n). The values of a_0 or a_1 for each $H_n(x)$ are determined from the normalization condition.

The Chebyshev-Hermite polynomials can be written as

$$H_n(x) = (-1)^n \exp(x^2) \frac{d^n}{dx^n} \exp(-x^2) \quad (n = 0, 1, 2, \dots) \quad (\text{III.11})$$

To prove this, we shall show that the functions (III.11) satisfy differential equation (III.9). For this purpose, we introduce the auxiliary function

$$w = \exp(-x^2) \quad (\text{III.12})$$

Taking into account (III.11), we can write that

$$H_n(x) = (-1)^n \exp(x^2) w^{(n)}$$

whence it follows that the n -th derivative of the function (III.12) is

$$w^{(n)} = (-1)^n \exp(-x^2) H_n(x) \quad (\text{III.13})$$

Let us evaluate the first and second derivatives of the function (III.13):

$$[w^{(n)}]' = (-1)^n \exp(-x^2) (H'_n - 2xH_n) \quad (\text{III.14})$$

$$[w^{(n)}]'' = (-1)^n \exp(-x^2) (H''_n - 4xH'_n + 4x^2H_n - 2H_n) \quad (\text{III.15})$$

Now we differentiate the function (III.12) with respect to x :

$$w' = -2x \exp(-x^2) = -2xw$$

We have arrived at the identity

$$w' + 2xw \equiv 0$$

Let us differentiate this identity $n+1$ times with respect to x :

$$(w')^{(n+1)} + (2xw)^{(n+1)} \equiv 0 \quad (\text{III.16})$$

The n -order derivative of the product of two functions u and v is calculated by the formula

$$(uv)^{(n)} = \sum_{k=0}^n \frac{n!}{k!(n-k)!} u^{(n-k)}v^{(k)} \quad (\text{III.17})$$

According to this formula, we have

$$(2x \cdot w)^{(n+1)} = \sum_{k=0}^{n+1} \frac{(n+1)!}{k!(n+1-k)!} (2x)^{(n+1-k)} w^{(k)}$$

In this expression, only the last two terms equal to $(n+1) 2w^{(n)} + 2xw^{(n+1)}$ are non-zero. Substitution of them into (III.16) yields

$$(w')^{(n+1)} + 2(n+1)w^{(n)} + 2xw^{(n+1)} \equiv 0$$

Let us rewrite this identity as follows:

$$[w^{(n)}]'' + 2x[w^{(n)}]' + 2(n+1)w^{(n)} \equiv 0$$

Finally, introducing instead of $w^{(n)}$, $[w^{(n)}]'$, and $[w^{(n)}]''$ their values from (III.13), (III.14), and (III.15) and dividing the relation obtained by $(-1)^n \exp(-x^2)$, we arrive at the equation

$$H_n'' - 2xH_n' + 2nH_n = 0 \quad (\text{III.18})$$

A comparison with (III.9) shows that the polynomials determined by formula (III.11) satisfy Eq. (III.9) and, consequently, are identical with the Chebyshev-Hermite polynomials.

It can be proved that the polynomials $H_n(x)$ determined by the formula (III.11) are orthogonal with the weight $\exp(-x^2)$. This signifies that

$$\int_{-\infty}^{+\infty} H_n(x) H_m(x) \exp(-x^2) dx = 0 \quad (n \neq m) \quad (\text{III.19})$$

When $n = m$, the integral (III.19) is non-zero and has the following value:

$$\int_{-\infty}^{+\infty} [H_n(x)]^2 \exp(-x^2) dx = n! 2^n \sqrt{\pi} \quad (\text{III.20})$$

Let us differentiate the function (III.11) with respect to x :

$$\begin{aligned} H_n' &= \frac{d}{dx} \left\{ (-1)^n \exp(x^2) \frac{d^n}{dx^n} [\exp(-x^2)] \right\} \\ &= (-1)^n 2x \exp(x^2) \frac{d^n}{dx^n} [\exp(-x^2)] \\ &\quad - (-1)^{n+1} \exp(x^2) \frac{d^{n+1}}{dx^{n+1}} [\exp(-x^2)] \end{aligned}$$

[instead of $(-1)^n$ we have written $-(-1)^{n+1}$. The expression we have obtained can be written as follows:

$$H_n' = 2xH_n - H_{n+1} \quad (\text{III.21})$$

We differentiate this relation once more with respect to x :

$$H_n'' = 2H_n + 2xH_n' - H_{n+1}'$$

Let us replace H_n' and H_{n+1}' in accordance with (III.21). The result is

$$H_n'' = 2H_n + 2x[2xH_n - H_{n+1}] - [2xH_{n+1} - H_{n+2}]$$

$$= (2+4x^2)H_n - 4xH_{n+1} + H_{n+2} \quad (\text{III.22})$$

Substitution of expressions (III.21) and (III.22) into Eq. (III.18) leads to the following recurrence relation between the functions H_n , H_{n+1} , and H_{n+2} :

$$H_{n+2}(x) - 2xH_{n+1}(x) + 2(n+1)H_n(x) = 0 \quad (\text{III.23})$$

With the aid of this relation, knowing $H_0(x)$ and $H_1(x)$, we can calculate all the higher-degree polynomials. It is easy to calculate the first two polynomials directly by formula (III.11):

$$H_0(x) = (-1)^0 e^{x^2} \frac{d^0}{dx^0}(e^{-x^2}) = e^{x^2} \cdot e^{-x^2} = 1 \quad (\text{III.24})$$

$$H_1(x) = (-1)^1 e^{x^2} \frac{d}{dx}(e^{-x^2}) = -e^{x^2}(-2xe^{-x^2}) = 2x \quad (\text{III.25})$$

Next, we use relation (III.23):

$$\begin{aligned} H_2(x) &= 2xH_1(x) - 2(0+1)H_0(x) = 2x \cdot 2x - 2 \cdot 1 \\ &= 4x^2 - 2 \end{aligned} \quad (\text{III.26})$$

$$\begin{aligned} H_3(x) &= 2xH_2(x) - 2(1+1)H_1(x) \\ &= 2x(4x^2 - 2) - 4 \cdot 2x = 8x^3 - 12x \end{aligned} \quad (\text{III.27})$$

and so on.

IV. Some Information from the Theory of Functions of a Complex Variable

The function of a complex variable $z = x + iy$ is defined to be the expression

$$f(z) = u(x, y) + iv(x, y) \quad (\text{IV.1})$$

where $u(x, y)$ and $v(x, y)$ are real functions of the real variables x and y .

The function (IV.1) is defined in a certain range of the variable z (i.e. in a certain region or domain on the plane x, y). This region may be **singly connected** or **multiply connected**. A region is said to be singly connected if any closed curve in the region includes only points belonging to this region. A region not complying with this condition is said to be multiply connected. A singly connected region contains no "holes". In Fig. IV.1, the region R_1 is singly connected, and R_2 is multiply connected.

The function $f(z)$ is said to be differentiable in a region if at each point of the region there exists the limit

$$\frac{df}{dz} = \lim_{\Delta z \rightarrow 0} \frac{f(z + \Delta z) - f(z)}{\Delta z} = \lim_{\Delta z \rightarrow 0} \frac{\Delta f(z)}{\Delta z} \quad (\text{IV.2})$$

whose value does not depend on how Δz tends to zero.

A function that is single-valued, finite, and differentiable in a region is called **analytic** in this region. The point $z = z_s$, at which the function $f(z)$ has no derivative is called a **singular point** or **singularity**.

If $f(z)$ is analytic in the singly connected region R , the integral of this function around any contour Γ in R is zero:

$$\oint_{\Gamma} f(z) dz = 0 \quad (\text{IV.3})$$

This statement is known as the **Cauchy integral theorem**.

It follows from the Cauchy integral theorem that the value of a linear integral of an analytic function taken around a closed contour containing a hole in a multiply connected region is identical for all such contours:

$$\oint_{\Gamma_1} f(z) dz = \oint_{\Gamma_2} f(z) dz$$

Upon a change in the direction of circumvention of a contour, the sign of the integral changes. For this reason, we have to come to an agreement on what direction of circumvention will be considered

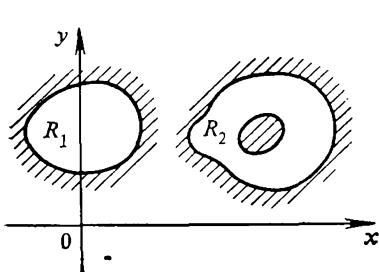


Fig. IV.1

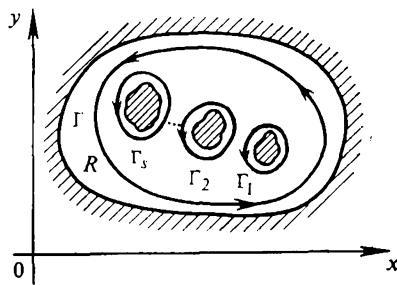


Fig. IV.2

positive and what negative. It is customary practice in the theory of the functions of a complex variable to consider the anticlockwise direction of circumvention to be positive. This has been done to have the azimuth angle φ grow in positive circumvention of a contour containing the origin of coordinates. In accordance with this choice, the symbol \oint in the following will always designate an integral evaluated with a positive direction of circumvention.

Assume that the region R in which the function $f(z)$ has been defined has s holes: R_1, R_2, \dots, R_s (Fig. IV.2). We can prove

with the aid of the Cauchy integral theorem that in this case the following relation holds:

$$\oint_{\Gamma} f(z) dz = \sum_{k=1}^s \oint_{\Gamma_k} f(z) dz \quad (\text{IV.4})$$

where Γ is a contour containing all the holes, and Γ_k is a contour containing only the k -th hole.

The function of a complex variable can be expanded into a Taylor series:

$$f(z) = \sum_{n=0}^{\infty} \frac{f^{(n)}(z_0)}{n!} (z - z_0)^n \quad (\text{IV.5})$$

Here z_0 is a fixed point in whose vicinity the expansion is performed. The representation of a function in the form of (IV.5) is legitimate for all z 's satisfying the condition $|z - z_0| < |z_s - z_0|$, where z_s is the closest singular point to z_0 .

Analytic Continuation. We can prove the following statement: assume that a continuous function $f(x)$ of a real variable is set on the segment $[a, b]$ of the real axis x ; now in a certain region R of a complex plane (Fig. IV.3) containing the segment $[a, b]$ of a real axis there can exist only one analytic function $f(z)$ of the complex variable z taking on the given values $f(x)$ on the segment $[a, b]$. This single function $f(z)$ is called the **analytic continuation** of the function $f(x)$ of the real variable x in the complex region R .

Laurent Expansion. Assume that the function $f(z)$ is analytic in the entire region $|z - z_0| < R$ except for the point z_0 that is a singular one. In this case for z satisfying the condition $0 < |z - z_0| < R$, the function can be written as

$$f(z) = \sum_{n=-\infty}^{+\infty} a_n (z - z_0)^n \quad (\text{IV.6})$$

where

$$a_n = \frac{1}{2\pi i} \oint_{\Gamma} \frac{f(z') dz'}{(z' - z_0)^{n+1}} \quad (\text{IV.7})$$

Integration in (IV.7) is performed around an arbitrary contour including the point z_0 and not extending beyond the limits of the region $|z - z_0| < R$.

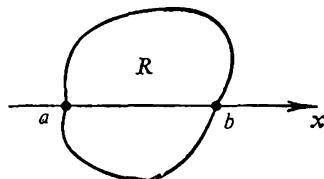


Fig. IV.3

Expression (IV.6) is called the **Laurent expansion** or **Laurent series**. It differs from the Taylor series in having terms with negative powers of $z - z_0$.

We can use the Laurent expansion to classify isolated singular points. This classification is established depending on the number of terms with negative values of n in the Laurent expansion (IV.6). Three cases are possible.

1. Terms with negative n 's are absent so that the expansion begins with the term equal to a_0 . If the initially set value of $f(z_0)$ does not coincide with a_0 or $f(z)$ has not been defined for the point z_0 , the latter is called a **removable singular point**. By assuming that $f(z_0) = a_0$, we eliminate the discontinuity of the function at the point z_0 and make the function analytic over the entire neighbourhood of z_0 , including the point z_0 itself.

2. The number of terms in (IV.6) with negative values of n is not zero, but is finite; all the a_{-n} 's with $n > N \neq 0$ are zero, and the coefficient $a_{-N} \neq 0$, i.e.

$$f(z) = \sum_{n=-N}^{+\infty} a_n (z - z_0)^n \quad (\text{IV.8})$$

In this case, the point z_0 is called a **pole of order N** of the function $f(z)$. The expansion of the function in the neighbourhood of the N -order pole begins with the term

$$\frac{a_{-N}}{(z - z_0)^N} \quad (\text{IV.9})$$

A first-order pole is called a **simple pole**.

It can be proved that when $z \rightarrow z_0$ (the latter is a pole), the modulus of the function (IV.8) grows unlimitedly regardless of how z tends to the pole z_0 . The function $\varphi(z)$, which is the reciprocal of the function $f(z)$ that has a pole of order N at z_0 , has at z_0 a zero of order N^1 .

3. The number of terms with negative values of n in the Laurent expansion is infinitely large. In this case, the point z_0 is called an **essential singular point**.

The following main distinctions exist between a pole of order N and an essential singular point. The former can be removed by multiplying the function $f(z)$ by $(z - z_0)^N$. An essential singular

¹ The function $\varphi(z)$ has a zero of the order N at the point z_0 if for this point the first N coefficients of the expansion of $\varphi(z)$ into a Taylor series are zero. In this case, the expansion begins with the term

$$\frac{1}{N!} f^{(N)}(z_0) (z - z_0)^N$$

$[f^{(N)}(z_0) \neq 0]$.

point cannot be eliminated in this way. When z tends to a pole of any order N , the function has a definite limit equal to infinity. When z tends to an essential singular point, the function has neither a finite nor an infinite limit. Depending on how z tends to z_0 , sequences of values of $f(z)$ are obtained that converge to different limits.

Theory of Residues. The residue of the analytic function $f(z)$ at the isolated singular point z_0 is defined to be

$$\text{Res}[f(z), z_0] = \frac{1}{2\pi i} \oint_{\Gamma} f(z') dz' \quad (\text{IV.10})$$

where Γ is an arbitrary contour including only the given singular point z_0 . The integral is evaluated in the positive direction of circumvention. We must note that for a contour not including singular points, expression (IV.10), according to (IV.3), vanishes.

A comparison of (IV.10) with (IV.7) shows that the residue coincides with the coefficient of the Laurent expansion for $n = -1$:

$$\text{Res}[f(z), z_0] = a_{-1} \quad (\text{IV.11})$$

Consider the contour Γ including several isolated singular points z_1, z_2, \dots, z_s (Fig. IV.4). We surround these points with the contours $\Gamma_1, \Gamma_2, \dots, \Gamma_s$. By formula (IV.4), we have

$$\oint_{\Gamma} f(z) dz = \sum_{k=1}^s \oint_{\Gamma_k} f(z) dz = 2\pi i \sum_{k=1}^s \text{Res}[f(z), z_k] \quad (\text{IV.12})$$

We have arrived at the basic theorem of the theory of residues, according to which the integral of an analytic function evaluated around a contour including several singular points equals the product of $2\pi i$ and the sum of the residues of the function at all the points.

Isolated singular points are sometimes located on the integration contour itself (Fig. IV.5). In this case, the contour must be deformed so that it circumvents the given point along a semicircle of an infinitely small radius. The point may either be excluded from (the point A in Fig. IV.5) or included (the point B in Fig. IV.5) in the region included by the contour.

In the infinitely small neighbourhood of the point, the function may be considered as virtually constant. Therefore, the integral around the semicircle can be assumed to equal half the residue of the

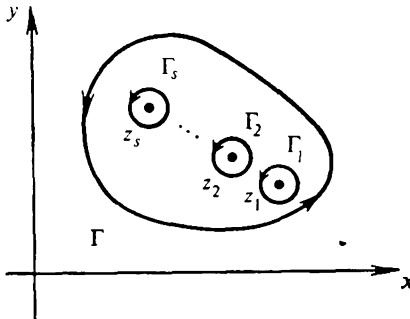


Fig. IV.4

function at the given point taken with the minus sign at the point *A* (clockwise integration) and with the plus sign at the point *B* (anti-clockwise integration). This half with its sign must be added to the left-hand side or, which is the same, subtracted from the right-hand side of formula (IV.12). Further, for *A*, the residue at the given point is not included in the sum of the residues on the right-hand side of the formula so that in the long run an additional term appears on the right equal to half the residue at the point under consideration. For *B*, the point makes a contribution to the right-hand side



Fig. IV.5

equal to the residue at this point, but at the same time half of the same residue is subtracted so that in the long run the result is the same—an additional term appears on the right equal to half the residue. Consequently, the final result does not depend on how we circumvent a point (*A* or *B*). In all cases, a singular point on a contour introduces into the right-hand side of formula (IV.12) half the contribution which it would have introduced if it were inside the contour.

When an isolated singular point is on the integration contour, another procedure is also used. It consists in displacing the singular point from the contour over the distance ϵ , and upon completion of calculations the limiting process $\epsilon \rightarrow 0$ is performed.

By formula (IV.10), to determine residues, it is necessary to calculate the contour integrals of the function $f(z)$. If the singular point z_0 is a simple pole (i.e. a first-order pole), the residue can be calculated in a simpler way. In this case, the expansion of the function in the neighbourhood of z_0 has the form

$$f(z) = a_{-1}(z - z_0)^{-1} + a_0 + a_1(z - z_0) + \dots$$

Let us multiply both sides by $(z - z_0)$ and perform the limiting process $z \rightarrow z_0$. As a result, we find that

$$\text{Res}[f(z), z_0] = a_{-1} = \lim_{z \rightarrow z_0} (z - z_0) f(z) \quad (\text{IV.13})$$

Evaluation of Definite Integrals with the Aid of Residues. The theory of residues is very helpful in evaluating many integrals of functions of a real variable. We shall give a few examples.

Let us calculate the integral

$$\int_{-\infty}^{+\infty} \frac{dx}{x^2+1} \quad (\text{JV.14})$$

For this purpose, we consider the integral

$$\mathcal{J} = \oint_{\Gamma} \frac{dz}{z^2+1} \quad (\text{IV.15})$$

where Γ has the form shown in Fig. IV.6 ($R > 1$). Writing the integrand in the form

$$f(z) = \frac{1}{z^2+1} = \frac{1}{(z+i)(z-i)}$$

it is not difficult to see that it has two simple poles at the points $z_1 = +i$ and $z_2 = -i$. Using formula (IV.13), we find that

$$\text{Res}[f(z), i] = \lim_{z \rightarrow i} (z - i) f(z) = \lim_{z \rightarrow i} \frac{1}{z+i} = \frac{1}{2i} \quad (\text{IV.16})$$

The residue at the point $-i$ is $-1/2i$.

Let us represent the integral (IV.15) as two integrals, one of which is evaluated over a segment of the x -axis, and the other around a

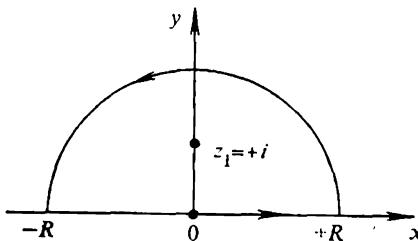


Fig. IV.6

semicircle. In the second integral, we shall go over to polar coordinates in accordance with the formula $z = Re^{i\varphi}$. In addition, we shall take advantage of formula (IV.12). As a result, we obtain

$$\mathcal{J} = \int_{-R}^{+R} \frac{dx}{x^2+1} + \int_0^\pi \frac{iRe^{i\varphi} d\varphi}{R^2 e^{2i\varphi} + 1} = 2\pi i \text{Res}[f(z), i] = 2\pi i \frac{1}{2i} = \pi$$

Now let R tend to infinity. The second integral vanishes because it has a magnitude of the order of $1/R$, and we obtain the result we are interested in:

$$\int_{-\infty}^{+\infty} \frac{dx}{x^2+1} = \pi \quad (\text{IV.17})$$

We invite our reader to convince himself that by taking a segment of the x -axis and the lower semicircle as the contour, we would obtain the same result.

In evaluating the integral (IV.15), we obtained the possibility of using the theory of residues by closing the real axis with a semicircle of an infinitely large radius, the contribution introduced by this semicircle into the integral being zero. For the integral (IV.14), the latter circumstance could be seen, so to say, with the naked eye. Whether or not we may use a similar procedure in more complicated cases can be determined by means of Jordan's lemma.

Jordan's Lemma. Assume that the function $\psi(z)$ is analytic in the upper half-plane except for a finite number of isolated singular points, and when $|z| \rightarrow \infty$ it tends to zero uniformly over all the directions of φ ($0 \ll \varphi \ll \pi$). Hence, when $\alpha > 0$,

$$\lim_{R \rightarrow \infty} \int_{\Gamma_R} e^{i\alpha z} \psi(z) dz = 0 \quad (\text{IV.18})$$

where Γ_R is the arc of a semicircle of radius R in the upper half-plane.

When $\alpha < 0$, the assertion of the lemma remains in force if the upper half-plane is replaced with the lower one in its statement. If $\alpha = \pm i\beta$ ($\beta > 0$), similar statements hold when integrating in the right and left half-planes, respectively.

Let us use Jordan's lemma to evaluate the integral

$$\mathcal{J} = \int_{-\infty}^{+\infty} e^{i\alpha x} \frac{x}{k^2 - x^2} dx \quad (\text{IV.19})$$

Consider the integral

$$\mathcal{J}_1 = \oint_{\Gamma} e^{i\alpha z} \frac{z}{k^2 - z^2} dz \quad (\text{IV.20})$$

The integrand has simple poles at the points $z = \pm k$. The function $\psi(z) = z/(k^2 - z^2)$ tends to zero when $|z| \rightarrow \infty$. Consequently, the requirements of Jordan's lemma are satisfied.

Let us take a real axis and a semicircle of radius R in the upper half-plane as the integration contour Γ . When $R \rightarrow \infty$, the integral around the semicircle, according to (IV.18), vanishes, so that the integral (IV.20) transforms into (IV.19).

The poles are on the integration contour. We can therefore assert that the integral (IV.19) will equal the half-sum of the residues of the function at the poles multiplied by $2\pi i$ [see formula (IV.12) and the text following it]. The poles are simple, and we may there-

fore use formula (IV.13) to calculate the residues. For the point $z = k$, we have

$$\begin{aligned}\text{Res}[f(z), k] &= \lim_{z \rightarrow k} (z - k) f(z) = \lim_{z \rightarrow k} e^{i\alpha z} \frac{(z - k) z}{k^3 - z^2} \\ &= - \lim_{z \rightarrow k} e^{i\alpha z} \frac{z}{z + k} = - \frac{1}{2} e^{i\alpha k} \quad (\text{IV.21})\end{aligned}$$

Similar calculations for $z = -k$ yield

$$\text{Res}[f(z), -k] = - \frac{1}{2} e^{-i\alpha k} \quad (\text{IV.22})$$

Consequently, for \mathcal{J} we obtain the value

$$\mathcal{J} = 2\pi i \frac{1}{2} \left(- \frac{1}{2} e^{i\alpha k} - \frac{1}{2} e^{-i\alpha k} \right) = -\pi i \cos \alpha k \quad (\text{IV.23})$$

Let us attempt to evaluate the integral (IV.19) in a different way—we displace the poles, replacing k with $k + i\varepsilon$, where ε is a small

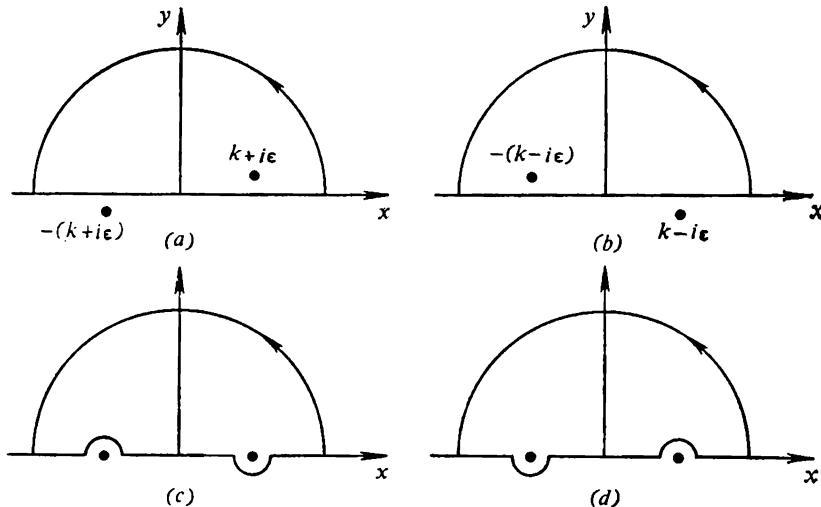


Fig. IV.7

positive quantity (Fig. IV.7a). Accordingly, $-k$ transforms into $-(k + i\varepsilon)$. As a result, the pole $z = k$ gets inside the integration contour, and the pole $z = -k$ leaves it.

Now the integral \mathcal{J} is equal to the limit (when $\varepsilon \rightarrow 0$) of the value of the residue at the point $k + i\varepsilon$. This residue is determined by the expression

$$\begin{aligned}\text{Res} &= -\lim_{z \rightarrow k+i\varepsilon} e^{iz\alpha} \frac{(z-k-i\varepsilon) z}{(z+k+i\varepsilon)(z-k-i\varepsilon)} = \lim_{z \rightarrow k+i\varepsilon} e^{iz\alpha} \frac{z}{z+k+i\varepsilon} \\ &= -e^{i\alpha(k+i\varepsilon)} \frac{k+i\varepsilon}{2(k+i\varepsilon)} = -\frac{1}{2} e^{i\alpha(k+i\varepsilon)}\end{aligned}$$

Hence

$$\mathcal{J} = \lim_{\varepsilon \rightarrow 0} \{2\pi i \text{Res}\} = -\lim_{\varepsilon \rightarrow 0} \{\pi i e^{i\alpha(k+i\varepsilon)}\} = -\pi i e^{i\alpha k} \quad (\text{IV.24})$$

The same result is evidently obtained if, without displacing the pole, we deform the contour as shown in Fig. IV.7c.

The value of \mathcal{J} we have obtained differs from (IV.23). Before discussing this difference, let us evaluate the integral once more, displacing the poles by the substitution $k \rightarrow k - i\varepsilon$ (Fig. IV.7b). Performing calculations similar to those that led us to formula (IV.24), we find that

$$\mathcal{J} = -\pi i e^{-i\alpha k} \quad (\text{IV.25})$$

The same result is obtained if instead of displacing the poles, we deform the contour as shown in Fig. IV.7d.

Hence, depending on how we chose the contour for the integral (IV.19), we obtain different results. This is due to the fact that the given integral is *improper*¹. It cannot be evaluated uniquely until additional limiting conditions are introduced.

We must note that expression (IV.23) is the arithmetical mean of expressions (IV.24) and (IV.25). It is the principal value of the integral (IV.19).

V. Airy Function

Consider the differential equation

$$y'' - xy = 0 \quad (\text{V.1})$$

One of the solutions of this equation can be written as

$$\Phi(x) = \frac{1}{\sqrt{\pi}} \int_0^{\infty} \cos \left(x\xi + \frac{\xi^3}{3} \right) d\xi \quad (\text{V.2})$$

A function determined by expression (V.2) is called an Airy function.

¹ The term improper is applied to an integral in which either the domain of integration or the integrand is unbounded.

For applications, it is important to know the asymptotic expression of the function $\Phi(x)$ at large values of $|x|$. At large positive values of x , the asymptotic expression of the function has the form

$$\Phi(x) \approx \frac{1}{2x^{1/4}} \exp\left(-\frac{2}{3}x^{3/2}\right) \quad (\text{V.3})$$

i.e. $\Phi(x)$ attenuates exponentially. At large negative values of x

$$\Phi(x) \approx \frac{1}{|x|^{1/4}} \sin\left(\frac{2}{3}|x|^{3/2} + \frac{\pi}{4}\right) \quad (\text{V.4})$$

i.e. $\Phi(x)$ oscillates. The first (greatest) maximum is $\Phi(-1.02) = 0.95$.

We must note that when the sign of x changes, Eq. (V.1) becomes

$$y'' + xy = 0 \quad (\text{V.5})$$

It is evident that an Airy function will also be a solution of this equation. The functions

$$\left. \begin{array}{l} \Phi(x) \approx \frac{1}{x^{1/4}} \sin\left(\frac{2}{3}x^{3/2} + \frac{\pi}{4}\right) \quad \text{when } x > 0 \\ \Phi(x) \approx \frac{1}{2|x|^{1/4}} \exp\left(-\frac{2}{3}|x|^{3/2}\right) \quad \text{when } x < 0 \end{array} \right\} \quad (\text{V.6})$$

will be asymptotic solutions of Eq. (V.5).

VI. Method of Green's Functions

The method of Green's functions is one of the methods of solving differential equations in partial derivatives. To understand the essence of this method, let us consider the following example. Let a differential equation have the form

$$\hat{Q}\varphi(\mathbf{r}) = f(\mathbf{r}) \quad (\text{VI.1})$$

where \hat{Q} is a linear differential operator, $f(\mathbf{r})$ is a set function, and $\varphi(\mathbf{r})$ is the required function.

To each function $f(\mathbf{r})$ there corresponds its own solution $\varphi(\mathbf{r})$. Such a correspondence can be represented in the form of the operator relation

$$\varphi(\mathbf{r}) = \hat{L}f(\mathbf{r}) \quad (\text{VI.2})$$

in which \hat{L} is an operator determined by the form of the operator \hat{Q} . With such a representation, the function $f(\mathbf{r})$ can be treated as an action, or influence, and $\varphi(\mathbf{r})$ as the result of this action, or as the response to the action.

We introduce the function $G(\mathbf{r}, \mathbf{r}')$ that is a solution of the equation

$$\hat{Q}G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (\text{VI.3})$$

[compare with (VI.1)]. The function $G(\mathbf{r}, \mathbf{r}')$ is called Green's function corresponding to the problem being considered¹ [i.e. to the problem characterized by Eq. (VI.1)]. It is the response to the action described by a delta function with a singularity at the point \mathbf{r}' :

$$G(\mathbf{r}, \mathbf{r}') = L\delta(\mathbf{r} - \mathbf{r}') \quad (\text{VI.4})$$

[compare with (VI.2)].

Using the Green's function, we can represent the solution of Eq. (VI.1) in the form

$$\varphi(\mathbf{r}) = \int G(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') dV' \quad (\text{VI.5})$$

Indeed, let us act on relation (VI.5) with the operator \hat{Q} , taking into account that this operator acts on the variable \mathbf{r} and does not act on the integration variable \mathbf{r}' . With a view to (VI.3), we obtain

$$\hat{Q}\varphi(\mathbf{r}) = \int [\hat{Q}G(\mathbf{r}, \mathbf{r}')] f(\mathbf{r}') dV' = \int \delta(\mathbf{r} - \mathbf{r}') f(\mathbf{r}') dV' = f(\mathbf{r})$$

We have arrived at the initial equation (VI.1) and have thus proved that the function (VI.5) satisfies this equation.

Now let us consider an equation differing from (VI.1) in containing 0 on the right-hand side instead of $f(\mathbf{r})$:

$$\hat{Q}\varphi(\mathbf{r}) = 0 \quad (\text{VI.6})$$

This equation may be called a homogeneous one corresponding to the non-homogeneous equation (VI.1). Let the general solution of Eq. (VI.6) be the function $\varphi_0(\mathbf{r})$, i.e.

$$\hat{Q}\varphi_0(\mathbf{r}) = 0 \quad (\text{VI.7})$$

Now the general solution of Eq. (VI.1) can be written as

$$\varphi(\mathbf{r}) = \varphi_0(\mathbf{r}) + \int G(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') dV' \quad (\text{VI.8})$$

endeed, owing to the linear character of the operator \hat{Q} , we have

$$\hat{Q}\varphi = \hat{Q}\left(\varphi_0 + \int \right) = \hat{Q}\varphi_0 + \hat{Q}\int = 0 + f(\mathbf{r}) = f(\mathbf{r})$$

The introduction of Green's function makes it possible to reduce the solution of Eq. (VI.1) to the solution of two simpler ones: (VI.3) and (VI.6).

¹ Every problem has its own Green's function. There is no single expression for Green's function.

Let us explain what has been said above using an example from electrostatics. The potential of an electrostatic field satisfies Poisson's equation

$$\nabla^2\varphi(\mathbf{r}) = -4\pi\rho(\mathbf{r}) \quad (\text{VI.9})$$

[see Vol. 1, formula (42.4)]. This equation corresponds to Eq. (VI.1) (in the given case $\hat{Q} = \nabla^2$). The equation

$$\nabla^2G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (\text{VI.10})$$

corresponds to Eq. (VI.5). Let us write (VI.10) in the form

$$\nabla^2G(\mathbf{r}, \mathbf{r}') = -4\pi \left[-\frac{1}{4\pi} \delta(\mathbf{r} - \mathbf{r}') \right] \quad (\text{VI.11})$$

It follows from (VI.9) that $G(\mathbf{r}, \mathbf{r}')$ is (to within a dimensional factor numerically equal to unity) the potential of the field of a point charge of the magnitude $-(1/4\pi)$ placed at the point \mathbf{r}' . Consequently,

$$G(\mathbf{r}, \mathbf{r}') = \frac{-(1/4\pi)}{|\mathbf{r} - \mathbf{r}'|} \quad (\text{VI.12})$$

Now let us use formula (VI.4), taking into consideration that in the given case $f(\mathbf{r}) = -4\pi\rho(\mathbf{r})$:

$$\begin{aligned} \varphi(\mathbf{r}) &= \int G(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') dV' \\ &= \int \frac{-(1/4\pi)}{|\mathbf{r} - \mathbf{r}'|} [-4\pi\rho(\mathbf{r}')] dV' = \int \frac{\rho(\mathbf{r}') dV'}{|\mathbf{r} - \mathbf{r}'|} \end{aligned} \quad (\text{VI.13})$$

We have obtained the known expression for the potential produced by a charge distributed with the density $\rho(\mathbf{r})$ [see Vol. 1, formula (42.7)].

Hence, in the example considered above, the physical meaning of Green's function consists in that it numerically coincides with the potential produced by a point charge of the magnitude $-(1/4\pi)$. We can also say that Green's function describes the influence of the charge $\rho(\mathbf{r}') dV'$ perceived at the point \mathbf{r} .

We must note that in the given case the solution of the homogeneous equation

$$\nabla^2\varphi_0(\mathbf{r}) = 0$$

[see (VI.7) and (VI.9)] is a homogeneous constant field of strength $\mathbf{E}_0 = -\nabla\varphi_0 = \text{const}$ imposed onto the field described by the function (VI.13).

VII. Solution of the Fundamental Equation of the Scattering Theory by the Method of Green's Functions

In the scattering theory, it is often necessary to solve the equation

$$(\nabla^2 + k^2) \psi(r) = \frac{2m_0}{\hbar^2} U(r) \psi(r) \quad (\text{VII.1})$$

where

$$k^2 = \frac{2m_0 E}{\hbar^2} = \text{const} \quad (\text{VII.2})$$

and $U(r)$ is a function that is non-zero only in the restricted part of space where $r \leq a$ [see Eq. (67.3)].

Assuming that $(\nabla^2 + k^2) = \hat{Q}$ and $(2m_0/\hbar^2) U(r) \psi(r) = f(r)$ ¹, we reduce Eq. (VII.1) to the form of (VI.1). Consequently, we can write an expression similar to (VI.8) for $\psi(r)$:

$$\psi(r) = \psi_0(r) + \int G(r, r') \left[\frac{2m_0}{\hbar^2} U(r') \psi(r') \right] dV' \quad (\text{VII.3})$$

where $\psi_0(r)$ is the solution of Eq. (VII.1) without the right-hand side:

$$(\nabla^2 + k^2) \psi_0(r) = 0$$

To satisfy the boundary conditions, we take as $\psi_0(r)$ the function

$$\psi_0(r) = \exp(i\mathbf{k}_{\text{inc}} \cdot \mathbf{r}) = \exp(ikz) \quad (\text{VII.4})$$

where \mathbf{k}_{inc} is a vector determining the direction of motion of the incident particles. In Sec. 67, we assumed the z -axis to be this direction (the magnitudes of vectors of different directions are identical and equal to k).

Green's function $G(r, r')$ in expression (VII.3) is a solution of the equation

$$(\nabla^2 + k^2) G(r, r') = \delta(r - r') \quad (\text{VII.5})$$

[see (VI.3)]. Let us transform this equation, acting on both of its sides with the operator $(\nabla^2 + k^2)^{-1}$ that is the reciprocal of the operator $(\nabla^2 + k^2)$. As a result, we obtain

$$G(r, r') = (\nabla^2 + k^2)^{-1} \delta(r - r') \quad (\text{VII.6})$$

By formula (VIII.13), we have

$$\delta(r - r') = \frac{1}{(2\pi)^3} \int e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} dV_q \quad (\text{VII.7})$$

where dV_q is a volume element in q -space. We have designated the integration variable by \mathbf{q} instead of \mathbf{k} because we have already used

¹ With such a treatment, the function $f(r)$ includes the required function $\psi(r)$ as a factor. Formally, however, Eq. (VI.1) remains correct.

k to designate the wave vector with a magnitude determined by (VII.2). In formula (VII.7), on the other hand, the magnitude of the vector q takes on all values from 0 to ∞ upon integration.

Introducing (VII.7) into Eq. (VII.6), we obtain

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{(2\pi)^3} \int (\nabla^2 + \mathbf{k}^2)^{-1} e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} dV_q \quad (\text{VII.8})$$

To calculate the integrand, we shall proceed from the relation

$$\begin{aligned} (\nabla^2 + \mathbf{k}^2) e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} &= \nabla^2 e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} + \mathbf{k}^2 e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} \\ &= -\mathbf{q}^2 e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} + \mathbf{k}^2 e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} = (\mathbf{k}^2 - \mathbf{q}^2) e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} \end{aligned}$$

Acting on this relation with the operator $(\nabla^2 + \mathbf{k}^2)^{-1}$, we arrive at the equation

$$e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} = (\mathbf{k}^2 - \mathbf{q}^2) (\nabla^2 + \mathbf{k}^2)^{-1} e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}$$

whence

$$(\nabla^2 + \mathbf{k}^2)^{-1} e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} = \frac{1}{\mathbf{k}^2 - \mathbf{q}^2} e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}$$

Substitution of this expression into (VII.8) yields

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{(2\pi)^3} \int \frac{1}{\mathbf{k}^2 - \mathbf{q}^2} e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} dV_q$$

Let us go over to the spherical coordinates q, θ, φ in q -space; we shall measure the angle θ from the direction of the vector $\mathbf{r} - \mathbf{r}'$ whose magnitude we shall designate by the letter α :

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}') &= \frac{1}{(2\pi)^3} \int \frac{1}{\mathbf{k}^2 - q^2} e^{iq\alpha \cos \theta} q^2 dq \sin \theta d\theta d\varphi \\ &= \frac{1}{(2\pi)^3} \int_0^\infty \frac{q^2}{\mathbf{k}^2 - q^2} dq \cdot 2\pi \int_0^\pi e^{iq\alpha \cos \theta} \sin \theta d\theta \\ &= \frac{1}{(2\pi)^2} \int_0^\infty \frac{q^2}{\mathbf{k}^2 - q^2} \frac{e^{i\alpha q} - e^{-i\alpha q}}{i\alpha q} dq \\ &= \frac{1}{4\pi^2 i\alpha} \left\{ \int_0^\infty e^{i\alpha q} \frac{q dq}{\mathbf{k}^2 - q^2} - \int_0^\infty e^{-i\alpha q} \frac{q dq}{\mathbf{k}^2 - q^2} \right\} \end{aligned}$$

Let us replace the integration variable q in the second integral with $-q$. The result is

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}') &= \frac{1}{4\pi^2 i\alpha} \left\{ \int_0^\infty e^{i\alpha q} \frac{q dq}{k^2 - q^2} - \int_0^{-\infty} e^{i\alpha q} \frac{q dq}{k^2 - q^2} \right\} \\ &= \frac{1}{4\pi^2 i\alpha} \int_{-\infty}^{+\infty} e^{i\alpha q} \frac{q dq}{k^2 - q^2} \quad (\text{VII.9}) \end{aligned}$$

We conclude from the form of the function (VII.9) that $G(\mathbf{r}, \mathbf{r}') = G(\alpha) = G(|\mathbf{r} - \mathbf{r}'|)$.

The integral (VII.9) was evaluated in Appendix IV with the aid of the theory of residues (the integrand is analytically continued onto a complex plane). The result of the calculations depends on the choice of the rules of circumvention of the poles $q = \pm k$. These rules are determined from the boundary conditions imposed on the function $G(\alpha)$ when $\alpha \rightarrow \infty$. To obtain a solution corresponding to waves diverging from the scattering centre, it is necessary to choose the integration path shown in Fig. IV.7c. Hence, by (IV.24), the integral equals $-\pi i e^{i\alpha k}$. Introducing this value into (VII.9), we obtain

$$G(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|} e^{ik|\mathbf{r} - \mathbf{r}'|} \quad (\text{VII.10})$$

($\alpha = |\mathbf{r} - \mathbf{r}'|$).

Adopting the function (VII.4) as $\psi_0(\mathbf{r})$ and introducing expression (VII.10) for $G(\mathbf{r}, \mathbf{r}')$ into (VII.3), we obtain the following formula for $\psi(\mathbf{r})$:

$$\psi(\mathbf{r}) = e^{ikz} - \frac{m_0}{2\pi\hbar^2} \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} e^{ik|\mathbf{r} - \mathbf{r}'|} U(\mathbf{r}') \psi(\mathbf{r}') dV' \quad (\text{VII.11})$$

The function $U(\mathbf{r}')$ is non-zero only in a small region for which $r' \leqslant \alpha$. Therefore for $r \gg a$, we can assume in (VII.11) that $|\mathbf{r} - \mathbf{r}'| \approx r$ in the denominator, and perform in the exponent the expansion

$$|\mathbf{r} - \mathbf{r}'| = \sqrt{(\mathbf{r} - \mathbf{r}')^2} \approx \sqrt{r^2 - 2\mathbf{r}\cdot\mathbf{r}'} \approx r - \mathbf{e}_r \cdot \mathbf{r}'$$

where \mathbf{e}_r is the unit vector of the vector \mathbf{r} . The result is

$$\begin{aligned} \psi(\mathbf{r}) &= e^{ikz} - \frac{m_0}{2\pi\hbar^2 r} e^{ikr} \int e^{-ik\mathbf{e}_r \cdot \mathbf{r}'} U(\mathbf{r}') \psi(\mathbf{r}') dV' \\ &= e^{ikz} + A(\vartheta, \varphi) \frac{e^{ikr}}{r} \quad (\text{VII.12}) \end{aligned}$$

where

$$A(\vartheta, \varphi) = A(\mathbf{e}_r) = -\frac{m_0}{2\pi\hbar^2} \int e^{-ik\mathbf{e}_r \cdot \mathbf{r}'} U(\mathbf{r}') \psi(\mathbf{r}') dV' \quad (\text{VII.13})$$

[ϑ and φ are angles determining the direction of the vector \mathbf{r} , i.e. the direction to the point, remote from the scattering centre, for which $\psi(\mathbf{r})$ is being calculated].

Formula (VII.12) coincides with formula (67.6). Expression (VII.13) determines the scattering amplitude. Taking into account that the function

$$\psi_{\mathbf{p}_r}(\mathbf{r}') = e^{i\mathbf{p}_r \cdot \mathbf{r}'/\hbar} = e^{i\mathbf{k}_r \cdot \mathbf{r}'}$$

is the psi-function of a particle moving freely in the direction of the position vector \mathbf{r} (to indicate this, we have used the subscript r on \mathbf{p}), we can write the expression for the scattering amplitude as follows:

$$A(\vartheta, \varphi) = -\frac{m_0}{2\pi\hbar^2} \langle \psi_{\mathbf{p}_r} | U \psi \rangle \quad (\text{VII.14})$$

[compare with (68.5)].

VIII. The Dirac Delta Function

To normalize the psi-functions belonging to a continuous spectrum, Dirac introduced the delta function (δ function), which is determined as follows:

(1) The function $\delta(x - a)$ equals zero for all $x \neq a$ and becomes equal to infinity when $x = a$;

(2) when $x = a$, the delta function becomes equal to infinity so that

$$\int_{x_1}^{x_2} \delta(x - a) dx = 1 \quad (\text{VIII.1})$$

provided that the domain of integration includes the point $x = a$, i.e. $x_1 < a < x_2$ [if point $x = a$ is outside the domain of integration, the integral (VIII.1) evidently vanishes].

The most important property of the delta function consists in that

$$\int_{-\infty}^{+\infty} f(x) \delta(x - a) dx = f(a) \quad (\text{VIII.2})$$

(for the proof of this relation, see Appendix XIII of Vol. 1).

The three-dimensional delta function is defined similarly:

$$\delta(\mathbf{r}) = \delta(x) \cdot \delta(y) \cdot \delta(z) \quad (\text{VIII.3})$$

It has the property

$$\int f(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_0) dV = f(\mathbf{r}_0) \quad (\text{VIII.4})$$

Some properties of the delta function are given below:

$$\delta(-x) = \delta(x) \quad (\text{VIII.5})$$

$$x\delta(x) = 0 \quad (\text{VIII.6})$$

$$\delta(ax) = \frac{1}{|a|} \delta(x) \quad (\text{VIII.7})$$

The meaning of these relations is that if an integrand contains one side of an equation as a factor, it may be replaced with the other side without the integral changing.

The property (VIII.5) is obvious. It signifies that $\delta(x)$ is an even function.

To prove the property (VIII.6), let us take a continuous function $\varphi(x)$ and form the expression

$$\int_{-\infty}^{+\infty} \varphi(x) x\delta(x) dx$$

Introducing the notation $f(x) = \varphi(x)x$ and taking advantage of the property (VIII.2), we obtain

$$\int_{-\infty}^{+\infty} \varphi(x) x\delta(x) dx = \int_{-\infty}^{+\infty} f(x) \delta(x) dx = f(0) = \varphi(0) \cdot 0 = 0$$

whence (VIII.6) follows.

Relation (VIII.7) is proved in a similar way. Let us form the expression

$$\int_{-\infty}^{+\infty} \varphi(x) \delta(ax) dx = \int_{-\infty}^{+\infty} \varphi(x) \delta(|a|x) dx \quad (\text{VIII.8})$$

[we have used the property (VIII.5)]. Let us go over from the variable x to the variable y related to x by the expression

$$y = |a|x, dy = |a|dx$$

(we have taken $|a|$ for dy and dx to have the same sign). The integral (VIII.8) now becomes

$$\int_{-\infty}^{+\infty} \varphi\left(\frac{y}{|a|}\right) \delta(y) \frac{dy}{|a|} = \frac{1}{|a|} \int_{-\infty}^{+\infty} \varphi\left(\frac{y}{|a|}\right) \delta(y) dy \quad (\text{VIII.9})$$

We introduce the function $f(y)$ defined by the relation

$$f(y) = \varphi\left(\frac{y}{|a|}\right)$$

that when $y = 0$ transforms into the equation $f(0) = \varphi(0)$. As a result, (VIII.9) transforms as follows:

$$\frac{1}{|a|} \int_{-\infty}^{+\infty} \varphi\left(\frac{y}{|a|}\right) \delta(y) dy = \frac{1}{|a|} \int_{-\infty}^{+\infty} f(y) \delta(y) dy = \frac{1}{|a|} f(0) = \frac{1}{|a|} \varphi(0)$$

We would have arrived at the same result if we had taken as the initial expression not (VIII.8), but the integral

$$\int_{-\infty}^{+\infty} \varphi(x) \left\{ \frac{1}{|a|} \delta(x) \right\} dx$$

Hence follows the property (VIII.7).

Let us write the Fourier transform

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-ikx} dk \int_{-\infty}^{+\infty} \delta(\xi) e^{ik\xi} d\xi$$

[see Vol. 1, formula (XIV.20)] for the delta function. In accordance with (VIII.2), the integral over $d\xi$ equals $e^0 = 1$. Consequently

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-ikx} dk \quad (\text{VIII.10})$$

Taking relation (VIII.5) into account, we can write that

$$\delta(x) = \delta(-x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx} dk \quad (\text{VIII.11})$$

From relation (VIII.11), we obtain the formula

$$\int_{-\infty}^{+\infty} e^{ikx} dk = 2\pi \delta(x) \quad (\text{VIII.12})$$

In accordance with (VIII.3) and (VIII.11), we have

$$\begin{aligned} \delta(r) &= \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} e^{ik_x x} dk_x \int_{-\infty}^{+\infty} e^{ik_y y} dk_y \int_{-\infty}^{+\infty} e^{ik_z z} dk_z \\ &= \frac{1}{(2\pi)^3} \int e^{ikr} dV_k \quad (\text{VIII.13}) \end{aligned}$$

where dV_k is a volume element in k -space. A glance at (VIII.13) shows that

$$\int e^{ikr} dV_k = (2\pi)^3 \delta(r) \quad (\text{VIII.14})$$

Integration is performed over the entire k -space. Formula (VIII.14) is a three-dimensional analogue of formula (VIII.12).

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