QUANTUM MECHANICS
(NONRELATIVISTIC THEORY)

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CHAPTER   I

THE BASIC CONCEPTS OF QUANTUM MECHANICS

§ 1. The uncertainty principle

When we attempt to apply classical mechanics and electrodynamics to explain atomic phenomena, they lead to results which are in obvious conflict with experiment. This is very clearly seen from the contradiction obtained on applying ordinary electrodynamics to a model of an atom in which the electrons move round the nucleus in classical orbits. During such motion, as in any accelerated motion of charges, the electrons would have to emit electromagnetic waves continually. By this emission, the electrons would lose their energy, and this would eventually cause them to fall into the nucleus. Thus, according to classical electrodynamics, the atom would be unstable, which does not at all agree with reality.

This marked contradiction between theory and experiment indicates that the construction of a theory applicable to atomic phenomena—that is, phenomena occurring in particles of very small mass at very small distances—demands a fundamental modification of the basic physical concepts and laws.

As a starting-point for an investigation of these modifications, it is convenient to take the experimentally observed phenomenon known as *electron diffraction*.[1] It is found that, when a homogeneous beam of electrons passes through a crystal, the emergent beam exhibits a pattern of alternate maxima and minima of intensity, wholly similar to the diffraction pattern observed in the diffraction of electromagnetic waves. Thus, under certain conditions, the behaviour of material particles—in this case, the electrons—displays features belonging to wave processes.

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[1] The phenomenon of electron diffraction was in fact discovered after quantum mechanics was invented. In our discussion, however, we shall not adhere to the historical sequence of development of the theory, but shall endeavour to construct it in such a way that the connection between the basic principles of quantum mechanics and the experimentally observed phenomena is most clearly shown.

How markedly this phenomenon contradicts the usual ideas of motion is best seen from the following imaginary experiment, an idealization of the experiment of electron diffraction by a crystal. Let us imagine a screen impermeable to electrons, in which two slits are cut. On observing the passage of a beam of electrons[2] through one of the slits, the other being covered, we obtain, on a continuous screen placed behind the slit, some pattern of intensity distribution; in the same way, by uncovering the second slit and covering the first, we obtain another pattern. On observing the passage of the beam through both slits, we should expect, on the basis of ordinary classical ideas, a pattern which is a simple superposition of the other two: each electron, moving in its path, passes through one of the slits and has no effect on the electrons passing through the other slit. The phenomenon of electron diffraction shows, however, that in reality we obtain a diffraction pattern which, owing to interference, does not at all correspond to the sum of the patterns given by each slit separately. It is clear that this result can in no way be reconciled with the idea that electrons move in paths.

Thus the mechanics which governs atomic phenomena—*quantum mechanics* or *wave mechanics*—must be based on ideas of motion which are fundamentally different from those of classical mechanics. In quantum mechanics there is no such concept as the path of a particle. This forms the content of what is called the uncertainty principle, one of the fundamental principles of quantum mechanics, discovered by W. Heisenberg in 1927.[3]

In that it rejects the ordinary ideas of classical mechanics, the uncertainty principle might be said to be negative in content. Of course, this principle in itself does not suffice as a basis on which to construct a new mechanics of particles. Such a theory must naturally be founded on some positive assertions, which we shall discuss below (§2). However, in order to formulate these assertions, we must first ascertain the statement of the problems which confront quantum mechanics. To do so, we first examine the special nature of the interrelation between quantum mechanics and classical mechanics. A more general theory can usually be formulated in a logically complete manner, independently of a less general theory which forms a limiting case of it. Thus, relativistic mechanics can be constructed on the basis of its own fundamental principles, without any reference to Newtonian mechanics. It is in principle impossible, however, to formulate the basic concepts of quantum

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[2] The beam is supposed so rarefied that the interaction of the particles in it plays no part.

[3] It is of interest to note that the complete mathematical formalism of quantum mechanics was constructed by W. Heisenberg and E. Schrödinger in 1925–6, before the discovery of the uncertainty principle, which revealed the physical content of this formalism.

mechanics without using classical mechanics. The fact that an electron[4] has no definite path means that it has also, in itself, no other dynamical characteristics[5] . Hence it is clear that, for a system composed only of quantum objects, it would be entirely impossible to construct any logically independent mechanics. The possibility of a quantitative description of the motion of an electron requires the presence also of physical objects which obey classical mechanics to a sufficient degree of accuracy. If an electron interacts with such a "classical object", the state of the latter is, generally speaking, altered. The nature and magnitude of this change depend on the state of the electron, and therefore may serve to characterize it quantitatively.

In this connection the "classical object" is usually called *apparatus*, and its interaction with the electron is spoken of as *measurement*. However, it must be emphasized that we are here not discussing a process of measurement in which the physicist-observer takes part. By *measurement*, in quantum mechanics, we understand any process of interaction between classical and quantum objects, occurring apart from and independently of any observer. The importance of the concept of measurement in quantum mechanics was elucidated by N. Bohr.

We have defined "apparatus" as a physical object which is governed, with sufficient accuracy, by classical mechanics. Such, for instance, is a body of large enough mass. However, it must not be supposed that apparatus is necessarily macroscopic. Under certain conditions, the part of apparatus may also be taken by an object which is microscopic, since the idea of "with sufficient accuracy" depends on the actual problem proposed. Thus, the motion of an electron in a Wilson chamber is observed by means of the cloudy track which it leaves, and the thickness of this is large compared with atomic dimensions; when the path is determined with such low accuracy, the electron is an entirely classical object.

Thus quantum mechanics occupies a very unusual place among physical theories: it contains classical mechanics as a limiting case, yet at the same time it requires this limiting case for its own formulation.

We may now formulate the problem of quantum mechanics. A typical problem consists in predicting the result of a subsequent measurement from the known results of previous measurements. Moreover, we shall see later that, in comparison with classical mechanics, quantum mechanics, generally speaking, restricts the range of values which can be taken by various physical

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[4] In this and the following sections we shall, for brevity, speak of "an electron", meaning in general any object of a quantum nature, i.e. a particle or system of particles obeying quantum mechanics and not classical mechanics.

[5] We refer to quantities which characterize the motion of the electron, and not to those, such as the charge and the mass, which relate to it as a particle; these are parameters.

quantities (for example, energy): that is, the values which can be obtained as a result of measuring the quantity concerned. The methods of quantum mechanics must enable us to determine these admissible values.

The measuring process has in quantum mechanics a very important property: it always affects the electron subjected to it, and it is in principle impossible to make its effect arbitrarily small, for a given accuracy of measurement. The more exact the measurement, the stronger the effect exerted by it, and only in measurements of very low accuracy can the effect on the measured object be small. This property of measurements is logically related to the fact that the dynamical characteristics of the electron appear only as a result of the measurement itself. It is clear that, if the effect of the measuring process on the object of it could be made arbitrarily small, this would mean that the measured quantity has in itself a definite value independent of the measurement.

Among the various kinds of measurement, the measurement of the coordinates of the electron plays a fundamental part. Within the limits of applicability of quantum mechanics, a measurement of the coordinates of an electron can always be performed[6]) with any desired accuracy.

Let us suppose that, at definite time intervals Δt, successive measurements of the coordinates of an electron are made. The results will not in general lie on a smooth curve. On the contrary, the more accurately the measurements are made, the more discontinuous and disorderly will be the variation of their results, in accordance with the non-existence of a path of the electron. A fairly smooth path is obtained only if the coordinates of the electron are measured with a low degree of accuracy, as for instance from the condensation of vapour droplets in a Wilson chamber.

If now, leaving the accuracy of the measurements unchanged, we diminish the intervals Δt between measurements, then adjacent measurements, of course, give neighbouring values of the coordinates. However, the results of a series of successive measurements, though they lie in a small region of space, will be distributed in this region in a wholly irregular manner, lying on no smooth curve. In particular, as Δt tends to zero, the results of adjacent measurements by no means tend to lie on one straight line.

This circumstance shows that, in quantum mechanics, there is no such concept as the velocity of a particle in the classical sense of the word, i.e. the limit to which the difference of the coordinates at two instants, divided by the interval Δt between these instants, tends as Δt tends to zero. However,

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[6]) Once again we emphasize that, in speaking of "performing a measurement", we refer to the interaction of an electron with a classical "apparatus", which in no way presupposes the presence of an external observer.

we shall see later that in quantum mechanics, nevertheless, a reasonable definition of the velocity of a particle at a given instant can be constructed, and this velocity passes into the classical velocity as we pass to classical mechanics. But whereas in classical mechanics a particle has definite coordinates and velocity at any given instant, in quantum mechanics the situation is entirely different. If, as a result of measurement, the electron is found to have definite coordinates, then it has no definite velocity whatever. Conversely, if the electron has a definite velocity, it cannot have a definite position in space. For the simultaneous existence of the coordinates and velocity would mean the existence of a definite path, which the electron has not. Thus, in quantum mechanics, the coordinates and velocity of an electron are quantities which cannot be simultaneously measured exactly, i.e. they cannot simultaneously have definite values. We may say that the coordinates and velocity of the electron are quantities which do not exist simultaneously. In what follows we shall derive the quantitative relation which determines the possibility of an inexact measurement of the coordinates and velocity at the same instant.

A complete description of the state of a physical system in classical mechanics is effected by stating all its coordinates and velocities at a given instant; with these initial data, the equations of motion completely determine the behaviour of the system at all subsequent instants. In quantum mechanics such a description is in principle impossible, since the coordinates and the corresponding velocities cannot exist simultaneously. Thus a description of the state of a quantum system is effected by means of a smaller number of quantities than in classical mechanics, i.e. it is less detailed than a classical description.

A very important consequence follows from this regarding the nature of the predictions made in quantum mechanics. Whereas a classical description suffices to predict the future motion of a mechanical system with complete accuracy, the less detailed description given in quantum mechanics evidently cannot be enough to do this. This means that, even if an electron is in a state described in the most complete manner possible in quantum mechanics, its behaviour at subsequent instants is still in principle uncertain. Hence quantum mechanics cannot make completely definite predictions concerning the future behaviour of the electron. For a given initial state of the electron, a subsequent measurement can give various results. The problem in quantum mechanics consists in determining the probability of obtaining various results on performing this measurement. It is understood, of course, that in some cases the probability of a given result of measurement may be equal to unity, i.e. certainty, so that the result of that measurement is unique.

All measuring processes in quantum mechanics may be divided into two

classes. In one, which contains the majority of measurements, we find those which do not, in any state of the system, lead with certainty to a unique result. The other class contains measurements such that for every possible result of measurement there is a state in which the measurement leads with certainty to that result. These latter measurements, which may be called *predictable*, play an important part in quantum mechanics. The quantitative characteristics of a state which are determined by such measurements are what are called *physical quantities* in quantum mechanics. If in some state a measurement gives with certainty a unique result, we shall say that in this state the corresponding physical quantity has a definite value. In future we shall always understand the expression "physical quantity" in the sense given here.

We shall often find in what follows that by no means every set of physical quantities in quantum mechanics can be measured simultaneously, i.e. can all have definite values at the same time. We have already mentioned one example, namely the velocity and coordinates of an electron. An important part is played in quantum mechanics by sets of physical quantities having the following property: these quantities can be measured simultaneously, but if they simultaneously have definite values, no other physical quantity (not being a function of these) can have a definite value in that state. We shall speak of such sets of physical quantities as *complete sets*.

Any description of the state of an electron arises as a result of some measurement. We shall now formulate the meaning of a *complete description* of a state in quantum mechanics. Completely described states occur as a result of the simultaneous measurement of a complete set of physical quantities. From the results of such a measurement we can, in particular, determine the probability of various results of any subsequent measurement, regardless of the history of the electron prior to the first measurement.

From now on (except in §14) we shall understand by the states of a quantum system just these completely described states.

§ 2. The principle of superposition

The radical change in the physical concepts of motion in quantum mechanics as compared with classical mechanics demands, of course, an equally radical change in the mathematical formalism of the theory. We must therefore consider first of all the way in which states are described in quantum mechanics.

We shall denote by q the set of coordinates of a quantum system, and by $\mathrm{d}q$ the product of the differentials of these coordinates. This $\mathrm{d}q$ is called an

element of volume in the *configuration space* of the system; for one particle, dq coincides with an element of volume dV in ordinary space.

The basis of the mathematical formalism of quantum mechanics lies in the proposition that the state of a system can be described by a definite (in general complex) function $\Psi(q)$ of the coordinates. The square of the modulus of this function determines the probability distribution of the values of the coordinates: $|\Psi|^2 dq$ is the probability that a measurement performed on the system will find the values of the coordinates to be in the element dq of configuration space. The function Ψ is called the *wave function* of the system.[7]

A knowledge of the wave function allows us, in principle, to calculate the probability of the various results of any measurement (not necessarily of the coordinates) also. All these probabilities are determined by expressions bilinear in Ψ and Ψ^*. The most general form of such an expression is

$$\iint \Psi(q)\Psi^*(q')\varphi(q,q')dq dq', \tag{2.1}$$

where the function $\varphi(q,q)$ depends on the nature and the result of the measurement, and the integration is extended over all configuration space. The probability $\Psi\Psi^*$ of various values of the coordinates is itself an expression of this type.[8]

The state of the system, and with it the wave function, in general varies with time. In this sense the wave function can be regarded as a function of time also. If the wave function is known at some initial instant, then, from the very meaning of the concept of complete description of a state, it is in principle determined at every succeeding instant. The actual dependence of the wave function on time is determined by equations which will be derived later.

The sum of the probabilities of all possible values of the coordinates of the system must, by definition, be equal to unity. It is therefore necessary that the result of integrating $|\Psi|^2$ over all configuration space should be equal to unity:

$$\int |\Psi|^2 dq = 1. \tag{2.2}$$

This equation is what is called the *normalization condition* for wave functions. If the integral of $|\Psi|^2$ converges, then by choosing an appropriate

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[7] It was first introduced into quantum mechanics by Schrödinger in 1926.

[8] It is obtained from (2.1) when $\varphi(q,q) = \delta(q-q_0)\delta(q-q_0)$, where δ denotes the delta function, defined in §5 below; q_0 denotes the value of the coordinates whose probability is required.

constant coefficient the function Ψ can always be, as we say, *normalized*. However, we shall see later that the integral of $|\Psi|^2$ may diverge, and then Ψ cannot be normalized by the condition (2.2). In such cases $|\Psi|^2$ does not, of course, determine the absolute values of the probability of the coordinates, but the ratio of the values of $|\Psi|^2$ at two different points of configuration space determines the relative probability of the corresponding values of the coordinates.

Since all quantities calculated by means of the wave function, and having a direct physical meaning, are of the form (2.1), in which Ψ appears multiplied by Ψ^*, it is clear that the normalized wave function is determined only to within a constant *phase factor* of the form $e^{i\alpha}$ (where α is any real number). This indeterminacy is in principle irremovable; it is, however, unimportant, since it has no effect upon any physical results.

The positive content of quantum mechanics is founded on a series of propositions concerning the properties of the wave function. These are as follows.

Suppose that, in a state with wave function $\Psi_1(q)$, some measurement leads with certainty to a definite result (result 1), while in a state with $\Psi_2(q)$ it leads to result 2. Then it is assumed that every linear combination of Ψ_1 and Ψ_2, i.e. every function of the form $c_1\Psi_1(q) + c_2\Psi_2(q)$ (where c_1 and c_1 are constants), gives a state in which that measurement leads to either result 1 or result 2. Moreover, we can assert that, if we know the time dependence of the states, which for the one case is given by the function $\Psi_1(q,t)$, and for the other by $\Psi_2(q,t)$, then any linear combination also gives a possible dependence of a state on time. These propositions constitute what is called the *principle of superposition of states*, the chief positive principle of quantum mechanics. In particular, it follows from this principle that all equations satisfied by wave functions must be linear in Ψ.

Let us consider a system composed of two parts, and suppose that the state of this system is given in such a way that each of its parts is completely described.[9]) Then we can say that the probabilities of the coordinates q_1 of the first part are independent of the probabilities of the coordinates q_2 of the second part, and therefore the probability distribution for the whole system should be equal to the product of the probabilities of its parts. This means that the wave function $\Psi_{12}(q_1, q_2)$ of the system can be represented in the

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[9]) This, of course, means that the state of the whole system is completely described also. However, we emphasize that the converse statement is by no means true: a complete description of the state of the whole system does not in general completely determine the states of its individual parts (see also §14).

form of a product of the wave functions $\Psi_1(q_1)$ and $\Psi_2(q_2)$ of its parts:

$$\Psi_{12}(q_1, q_2) = \Psi_1(q_1)\Psi_2(q_2). \tag{2.3}$$

If the two parts do not interact, then this relation between the wave function of the system and those of its parts will be maintained at future instants also, i.e. we can write

$$\Psi_{12}(q_1, q_2, t) = \Psi_1(q_1, t)\Psi_2(q_2, t). \tag{2.4}$$

§ 3. Operators

Let us consider some physical quantity f which characterizes the state of a quantum system. Strictly, we should speak in the following discussion not of one quantity, but of a complete set of them at the same time. However, the discussion is not essentially changed by this, and for brevity and simplicity we shall work below in terms of only one physical quantity.

The values which a given physical quantity can take are called in quantum mechanics its *eigenvalues*, and the set of these is referred to as the *spectrum of eigenvalues* of the given quantity. In classical mechanics, generally speaking, quantities run through a continuous series of values. In quantum mechanics also there are physical quantities (for instance, the coordinates) whose eigenvalues occupy a continuous range; in such cases we speak of a *continuous spectrum of eigenvalues.* As well as such quantities, however, there exist in quantum mechanics others whose eigenvalues form some discrete set; in such cases we speak of a *discrete spectrum.*

We shall suppose for simplicity that the quantity f considered here has a discrete spectrum; the case of a continuous spectrum will be discussed in §5. The eigenvalues of the quantity f are denoted by f_n, where the suffix n takes the values $0, 1, 2, 3, \ldots$. We also denote the wave function of the system, in the state where the quantity f has the value f_n, by Ψ_n. The wave functions Ψ_n are called the *eigenfunctions* of the given physical quantity f. Each of these functions is supposed normalized, so that

$$\int |\Psi_n|^2 \mathrm{d}q = 1. \tag{3.1}$$

If the system is in some arbitrary state with wave function Ψ, a measurement of the quantity f carried out on it will give as a result one of the eigenvalues f_n. In accordance with the principle of superposition, we can assert that the wave function Ψ must be a linear combination of those eigenfunctions Ψ_n which correspond to the values f_n that can be obtained, with probability

different from zero, when a measurement is made on the system and it is in the state considered. Hence, in the general case of an arbitrary state, the function Ψ can be represented in the form of a series

$$\Psi = \sum a_n \Psi_n, \tag{3.2}$$

where the summation extends over all n, and the a_n are some constant coefficients.

Thus we reach the conclusion that any wave function can be, as we say, expanded in terms of the eigenfunctions of any physical quantity. A set of functions in terms of which such an expansion can be made is called a *complete* (or *closed*) set.

The expansion (3.2) makes it possible to determine the probability of finding (i.e. the probability of getting the corresponding result on measurement), in a system in a state with wave function Ψ, any given value f_n of the quantity f. For, according to what was said in the previous section, these probabilities must be determined by some expressions bilinear in Ψ and Ψ^*, and therefore must be bilinear in a_n and a_n^*. Furthermore, these expressions must, of course, be positive. Finally, the probability of the value f_n must become unity if the system is in a state with wave function $\Psi = \Psi_n$, and must become zero if there is no term containing Ψ_n in the expansion (3.2) of the wave function Ψ. The only essentially positive quantity satisfying these conditions is the square of the modulus of the coefficient a_n. Thus we reach the result that the squared modulus $|a_n|^2$ of each coefficient in the expansion (3.2) determines the probability of the corresponding value f_n of the quantity f in the state with wave function Ψ. The sum of the probabilities of all possible values f_n must be equal to unity; in other words, the relation

$$\sum_n |a_n|^2 = 1 \tag{3.3}$$

must hold.

If the function Ψ were not normalized, then the relation (3.3) would not hold either. The sum $\sum |a_n|^2$ would then be given by some expression bilinear in Ψ and Ψ^*, and becoming unity when Ψ was normalized. Only the integral $\int \Psi \Psi^* \mathrm{d}q$ is such an expression. Thus the equation

$$\sum_n a_n a_n^* = \int \Psi \Psi^* \mathrm{d}q \tag{3.4}$$

must hold.

On the other hand, multiplying by Ψ the expansion of the function Ψ^* (the complex conjugate of Ψ), and integrating, we obtain

$$\int \Psi \Psi^* \mathrm{d}q = \sum_n a_n^* \int \Psi_n^* \Psi \mathrm{d}q.$$

Comparing this with (3.4), we have

$$\sum_n a_n a_n^* = \sum_n a_n^* \int \Psi_n^* \Psi \mathrm{d}q,$$

from which we derive the following formula determining the coefficients a_n in the expansion of the function Ψ in terms of the eigenfunctions Ψ_n:

$$a_n = \int \Psi \Psi_n^* \mathrm{d}q. \tag{3.5}$$

If we substitute here from (3.2), we obtain

$$a_n = \sum_m a_m \int \Psi_m \Psi_n^* \mathrm{d}q$$

from which it is evident that the eigenfunctions must satisfy the conditions

$$\int \Psi_m \Psi_n^* \mathrm{d}q = \delta_{nm} \tag{3.6}$$

where $\delta_{nm} = 1$ for $n = m$ and $\delta_{nm} = 0$ for $n \neq m$. The fact that the integrals of the products $\Psi_m \Psi_n^*$ with $n \neq m$ vanish is called the *orthogonality* of the functions Ψ_n. Thus the set of eigenfunctions Ψ_n forms a complete set of normalized and orthogonal (or, for brevity, *orthonormal*) functions.

We shall now introduce the concept of the mean value $\overline{f}$ of the quantity f in the given state. In accordance with the usual definition of mean values, we define $\overline{f}$ as the sum of all the eigenvalues f_n of the given quantity, each multiplied by the corresponding probability $|a_n|^2$. Thus

$$\overline{f} = \sum_n f_n |a_n|^2. \tag{3.7}$$

We shall write $\overline{f}$ in the form of an expression which does not contain the coefficients a_n in the expansion of the function Ψ, but this function itself. Since the products $a_n a_n*$ appear in (3.7), it is clear that the required expression must be bilinear in Ψ and Ψ^*. We introduce a mathematical operator,

which we denote[10] by $\widehat{f}$ and define as follows. Let $(\widehat{f}\Psi)$ denote the result of the operator $\widehat{f}$ acting on the function Ψ. We define $\widehat{f}$ in such a way that the integral of the product of $(\widehat{f}\Psi)$ and the complex conjugate function Ψ^* is equal to the mean value $\overline{f}$:

$$\overline{f} = \int \Psi^*(\widehat{f}\Psi)\mathrm{d}q. \tag{3.8}$$

It is easily seen that, in the general case, the operator $\widehat{f}$ is a linear[11] integral operator. For, using the expression (3.5) for a_n, we can rewrite the definition (3.7) of the mean value in the form

$$\overline{f} = \sum_n f_n a_n a_n^* = \int \Psi^*(\sum_n a_n f_n \Psi_n)\mathrm{d}q.$$

Comparing this with (3.8), we see that the result of the operator $\widehat{f}$ acting on the function Ψ has the form

$$(\widehat{f}\Psi) = \sum_n a_n f_n \Psi_n. \tag{3.9}$$

If we substitute here the expression (3.5) for a_n, we find that $\widehat{f}$ is an integral operator of the form

$$(\widehat{f}\Psi) = \int K(q, q')\Psi(q')\mathrm{d}q', \tag{3.10}$$

where the function $K(q, q')$ (called the *kernel* of the operator) is

$$K(q, q') = \sum_n f_n \Psi_n^*(q')\psi_n(q). \tag{3.11}$$

Thus, for every physical quantity in quantum mechanics, there is a definite corresponding linear operator.

It is seen from (3.9) that, if the function Ψ is one of the eigenfunctions Ψ_n(so that all the an except one are zero), then, when the operator $\widehat{f}$ acts on it, this function is simply multiplied by the corresponding eigenvalue f_n:

$$\widehat{f}\Psi_n = f_n \Psi_n. \tag{3.12}$$

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[10] By convention, we shall always denote operators by letters with circumflexes.

[11] An operator is said to be linear if it has the properties

$$\widehat{f}(\Psi_1 + \Psi_2) = \widehat{f}(\Psi_1) + \widehat{f}(\Psi_2) \text{ and } \widehat{f}(a\Psi) = a\widehat{f}\Psi$$

where Ψ_1 and Ψ_2 are arbitrary functions and a is an arbitrary constant.

(In what follows we shall always omit the parentheses in the expression $(\widehat{f}\Psi)$, where this cannot cause any misunderstanding; the operator is taken to act on the expression which follows it.) Thus we can say that the eigenfunctions of the given physical quantity f are the solutions of the equation

$$\widehat{f}\Psi = f\Psi,$$

where f is a constant, and the eigenvalues are the values of this constant for which the above equation has solutions satisfying the required conditions. As we shall see below, the form of the operators for various physical quantities can be determined from direct physical considerations, and then the above property of the operators enables us to find the eigenfunctions and eigenvalues by solving the equations $\widehat{f}\Psi = f\Psi$.

Both the eigenvalues of a real physical quantity and its mean value in every state are real. This imposes a restriction on the corresponding operators. Equating the expression (3.8) to its complex conjugate, we obtain the relation

$$\int \Psi^*(\widehat{f}\Psi)\mathrm{d}q = \int \psi(\widehat{f}^*\Psi^*)\mathrm{d}q, \tag{3.13}$$

where $\widehat{f}^*$ denotes the operator which is the complex conjugate of $\widehat{f}$.[12] This relation does not hold in general for an arbitrary linear operator, so that it is a restriction on the form of the operator $\widehat{f}$. For an arbitrary operator $\widehat{f}$ we can find what is called the *transposed operator* $\widetilde{f}$, defined in such a way that

$$\int \Phi(\widehat{f}^*\Psi)\mathrm{d}q = \int \Psi(\widetilde{\widehat{f}}\Phi)\mathrm{d}q \tag{3.14}$$

where Ψ and Φ are two different functions. If we take, as the function Φ, the function Ψ^* which is the complex conjugate of Ψ, then a comparison with (3.13) shows that we must have

$$\widetilde{\widehat{f}} = \widehat{f}^* \tag{3.15}$$

Operators satisfying this condition are said to be *Hermitian*.[13] Thus the operators corresponding, in the mathematical formalism of quantum mechanics, to real physical quantities must be Hermitian.

We can formally consider complex physical quantities also, i.e. those whose eigenvalues are complex. Let f be such a quantity. Then we can

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[12] By definition, if for the operator $\widehat{f}$ we have $\widehat{f}\Psi = \varphi$, then the complex conjugate operator $\widehat{f}^*$ is that for which we have $\widehat{f}^*\Psi^* = \varphi^*$.

[13] For a linear integral operator of the form (3.10), the Hermitian condition means that the kernel of the operator must be such that $K(q,q) = K^*(q,q)$.

introduce its complex conjugate quantity f^*, whose eigenvalues are the complex conjugates of those of f. We denote by $\widehat{f}^\dagger$ the operator corresponding to the quantity f^*. It is called the *Hermitian conjugate* of the operator $\widehat{f}$ and, in general, will be different from the definition of the operator $\widehat{f^*}$: the mean value of the quantity f^* in a state Ψ is

$$\overline{f^*} = \int \Psi^* \widehat{f}^\dagger \Psi \mathrm{d}q.$$

We also have

$$\left(\overline{f}\right)^* = \left[\int \Psi^* \widehat{f} \Psi \mathrm{d}q\right]^*$$

$$= \int \Psi \widehat{f}^* \Psi^* \mathrm{d}q$$

$$= \int \Psi^* \widetilde{\widehat{f}}^* \Psi \mathrm{d}q.$$

Equating these two expressions gives

$$\widehat{f}^\dagger = \widetilde{\widehat{f}}^*, \tag{3.16}$$

from which it is clear that $\widehat{f}^\dagger$ is in general not the same as $\widehat{f^*}$.

The condition (3.15) can now be written

$$\widehat{f} = \widehat{f}^\dagger, \tag{3.17}$$

i.e. the operator of a real physical quantity is the same as its Hermitian conjugate (Hermitian operators are also called *self-conjugate*).

We shall show how the orthogonality of the eigenfunctions of an Hermitian operator corresponding to different eigenvalues can be directly proved. Let f_n and f_m be two different eigenvalues of the real quantity f, and Ψ_n, Ψ_m the corresponding eigenfunctions:

$$\widehat{f}\Psi_n = f_n \Psi_n, \widehat{f}\Psi_m = f_m \Psi_m.$$

Multiplying both sides of the first of these equations by Ψ_m^*, and both sides of the complex conjugate of the second by Ψ_n, and subtracting corresponding terms, we find

$$\Psi_m^* \widehat{f} \Psi_n - \Psi_n \widehat{f}^* \Psi_m^* = (f_n - f_m)\Psi_n \Psi_m^*.$$

We integrate both sides of this equation over q. Since $\widehat{f^*} = \widetilde{\widehat{f}}$, by (3.14) the integral on the left-hand side of the equation is zero, so that we have

$$(f_n - f_m) \int \Psi_n \Psi_m^* \mathrm{d}q = 0$$

whence, since $f_n \neq f_m$, we obtain the required orthogonality property of the functions Ψ_n and Ψ_m.

We have spoken here of only one physical quantity f, whereas, as we said at the beginning of this section, we should have spoken of a complete set of simultaneously measurable physical quantities. We should then have found that to each of these quantities $f, g, \ldots$ there corresponds its operator $\widehat{f}, \widehat{g}, \ldots$. The eigenfunctions Ψ_n then correspond to states in which all the quantities concerned have definite values, i.e. they correspond to definite sets of eigenvalues $f_n, g_n, \ldots$, and are simultaneous solutions of the system of equations

$$\widehat{f}\Psi = f\Psi, \quad \widehat{g}\Psi = g\Psi, \ldots.$$

§ 4. Addition and multiplication of operators

If $\widehat{f}$ and $\widehat{g}$ are the operators corresponding to two physical quantities f and g, the sum $f + g$ has a corresponding operator $\widehat{f} + \widehat{g}$. However, the significance of adding different physical quantities in quantum mechanics depends considerably on whether the quantities are or are not simultaneously measurable. If f and g are simultaneously measurable, the operators $\widehat{f}$ and $\widehat{g}$ have common eigenfunctions, which are also eigenfunctions of the operator $\widehat{f}+\widehat{g}$, and the eigenvalues of the latter operator are equal to the sums f_n+g_n. But if f and g cannot simultaneously take definite values, their sum $f + g$ has a more restricted significance. We can assert only that the mean value of this quantity in any state is equal to the sum of the mean values of the separate quantities:

$$\overline{f + g} = \overline{f} + \overline{g}. \tag{4.1}$$

The eigenvalues and eigenfunctions of the operator $\widehat{f}+\widehat{g}$ will not, in general, now bear any relation to those of the quantities f and g. It is evident that, if the operators $\widehat{f}$ and $\widehat{g}$ are Hermitian, the operator $\widehat{f} + \widehat{g}$ will be so too, so that its eigenvalues are real and are equal to those of the new quantity $f + g$ thus defined.

The following theorem should be noted. Let f_0 and g_0 be the smallest eigenvalues of the quantities f and g, and $(f+g)_0$ that of the quantity $f+g$. Then

$$(f + g)_0 \geqslant f_0 + g_0 \tag{4.2}$$

The equality holds if f and g can be measured simultaneously. The proof follows from the obvious fact that the mean value of a quantity is always greater than or equal to its least eigenvalue. In a state in which the quantity

$f + g$ has the value $(f + g)_0$ we have $\overline{f + g} = (f + g)_0$, and since, on the other hand, $\overline{f + g} = \overline{f} + \overline{g} \geqslant f_0 + g_0$, we arrive at the inequality (4.2).

Next, let f and g once more be quantities that can be measured simultaneously. Besides their sum, we can also introduce the concept of their *product* as being a quantity whose eigenvalues are equal to the products of those of the quantities f and g. It is easy to see that, to this quantity, there corresponds an operator whose effect consists of the successive action on the function of first one and then the other operator. Such an operator is represented mathematically by the product of the operators $\widehat{f}$ and $\widehat{g}$. For, if Ψ_n are the eigenfunctions common to the operators $\widehat{f}$ and $\widehat{g}$, we have

$$\widehat{f}\widehat{g}\Psi_n = \widehat{f}(\widehat{g}\Psi_n) = \widehat{f}g_n\Psi_n = g_n\widehat{f}\Psi_n = g_n f_n \Psi_n$$

(the symbol $\widehat{f}\widehat{g}$ denotes an operator whose effect on a function Ψ consists of the successive action first of the operator $\widehat{g}$ on the function Ψ and then of the operator $\widehat{f}$ on the function $\widehat{g}\Psi$). We could equally well take the operator $\widehat{g}\widehat{f}$ instead of $\widehat{f}\widehat{g}$, the former differing from the latter in the order of its factors. It is obvious that the result of the action of either of these operators on the functions Ψ_n will be the same. Since, however, every wave function Ψ can be represented as a linear combination of the functions Ψ_n, it follows that the result of the action of the operators $\widehat{f}\widehat{g}$ and $\widehat{g}\widehat{f}$ on an arbitrary function will also be the same. This fact can be written in the form of the symbolic equation $\widehat{f}\widehat{g} = \widehat{g}\widehat{f}$ or

$$\widehat{f}\widehat{g} - \widehat{g}\widehat{f} = 0 \tag{4.3}$$

Two such operators $\widehat{f}$ and $\widehat{g}$ are said to be *commutative*, or to *commute* with each other. Thus we arrive at the important result: if two quantities f and g can simultaneously take definite values, then their operators commute with each other.

The converse theorem can also be proved (§11): if the operators $\widehat{f}$ and $\widehat{g}$ commute, then all their eigenfunctions can be taken common to both; physically, this means that the corresponding physical quantities can be measured simultaneously. Thus the commutability of the operators is a necessary and sufficient condition for the physical quantities to be simultaneously measurable.

A particular case of the product of operators is an operator raised to some power. From the above discussion we can deduce that the eigenvalues of an operator $\widehat{f}^p$ (where p is an integer) are equal to the pth powers of the eigenvalues of the operator $\widehat{f}$. Any function $\varphi(\widehat{f})$ of an operator can be defined as an operator whose eigenvalues are equal to the same function $\varphi(f)$ of the eigenvalues of the operator $\widehat{f}$. If the function $\varphi(f)$ can be expanded

as a Taylor series, this expresses the effect of the operator $\varphi(\widehat{f})$ in terms of those of various powers $\widehat{f}^p$.

In particular, the operator $\widehat{f}^{-1}$ is called the inverse of the operator $\widehat{f}$. It is evident that the successive action of the operators $\widehat{f}$ and $\widehat{f}^{-1}$ on any function leaves the latter unchanged, i.e. $\widehat{f}\widehat{f}^{-1} = \widehat{f}^{-1}\widehat{f} = 1$.

If the quantities f and g cannot be measured simultaneously, the concept of their product does not have the same direct meaning. This appears in the fact that the operator $\widehat{fg}$ is not Hermitian in this case, and hence cannot correspond to any real physical quantity. For, by the definition of the transpose of an operator we can write

$$\int \Psi \widehat{fg}\Phi \mathrm{d}q = \int \Psi \widehat{f}(\widehat{g}\Phi)\mathrm{d}q = \int (\widehat{g}\Phi)(\widetilde{\widehat{f}}\Psi)\mathrm{d}q.$$

Here the operator $\widetilde{\widehat{f}}$ acts only on the function Ψ, and the operator $\widehat{g}$ on Φ, so that the integrand is a simple product of two functions $\widehat{g}\Phi$ and $\widetilde{\widehat{f}}\Psi$. Again using the definition of the transpose of an operator, we can write

$$\int \Psi \widehat{fg}\Phi \mathrm{d}q = \int (\widetilde{\widehat{f}}\Psi)(\widehat{g}\Phi)\mathrm{d}q = \int \Phi \widetilde{\widehat{g}}\widetilde{\widehat{f}}\Phi \mathrm{d}q.$$

Thus we obtain an integral in which the functions Ψ and Φ have changed places as compared with the original one. In other words, the operator $\widetilde{\widehat{g}}\widetilde{\widehat{f}}$ is the transpose of $\widehat{fg}$, and we can write

$$\widetilde{\widehat{fg}} = \widetilde{\widehat{g}}\widetilde{\widehat{f}} \tag{4.4}$$

i.e. the transpose of the product $\widehat{fg}$ is the product of the transposes of the factors written in the opposite order. Taking the complex conjugate of both sides of equation (4.4), we have

$$(\widehat{fg})^{\dagger} = \widehat{g}^{\dagger}\widehat{f}^{\dagger} \tag{4.5}$$

If each of the operators $\widehat{f}$ and $\widehat{g}$ is Hermitian, then $(\widehat{fg})^{\dagger} = \widehat{g}\widehat{f}$. It follows from this that the operator $\widehat{fg}$ is Hermitian if and only if the factors $\widehat{f}$ and $\widehat{g}$ commute.

We note that, from the products $\widehat{fg}$ and $\widehat{g}\widehat{f}$ of two non-commuting Hermitian operators, we can form an Hermitian operator, the *symmetrized product*

$$\frac{1}{2}(\widehat{fg} + \widehat{g}\widehat{f}) \tag{4.6}$$

It is easy to see that the difference $\widehat{f}\widehat{g} - \widehat{g}\widehat{f}$ is an *anti-Hermitian* operator (i.e. one for which the transpose is equal to the complex conjugate taken with the opposite sign). It can be made Hermitian by multiplying by i; thus

$$\mathrm{i}(\widehat{f}\widehat{g} - \widehat{g}\widehat{f}) \tag{4.7}$$

is again an Hermitian operator.

In what follows we shall sometimes use for brevity the notation

$$\{\widehat{f}, \widehat{g}\} = \widehat{f}\widehat{g} - \widehat{g}\widehat{f} \tag{4.8}$$

called the commutator of these operators. It is easily seen that

$$\{\widehat{f}\widehat{g}, \widehat{h}\} = \{\widehat{f}, \widehat{h}\}\widehat{g} + \widehat{f}\widehat{g}, \widehat{h} \tag{4.9}$$

We notice that, if $\{\widehat{f}, \widehat{h}\} = 0$ and $\{\widehat{g}, \widehat{h}\} = 0$, it does not in general follow that $\widehat{f}$ and $\widehat{g}$ commute.

§ 5. The continuous spectrum

All the relations given in §3 and 4, describing the properties of the eigenfunctions of a discrete spectrum, can be generalized without difficulty to the case of a continuous spectrum of eigenvalues.

Let f be a physical quantity having a continuous spectrum. We shall denote its eigenvalues by the same letter f simply, and the corresponding eigenfunctions by Ψ_f. Just as an arbitrary wave function Ψ can be expanded in a series (3.2) of eigenfunctions of a quantity having a discrete spectrum, it can also be expanded (this time as an integral) in terms of the complete set of eigenfunctions of a quantity with a continuous spectrum. This expansion has the form

$$\Psi(q) = \int a_f \Psi_f(q) \mathrm{d}f \tag{5.1}$$

where the integration is extended over the whole range of values that can be taken by the quantity f.

The subject of the normalization of the eigenfunctions of a continuous spectrum is more complex than in the case of a discrete spectrum. The requirement that the integral of the squared modulus of the function should be equal to unity cannot here be satisfied, as we shall see below. Instead, we try to normalize the functions Ψ_f in such a way that $|a_f|^2 \mathrm{d}f$ is the probability that the physical quantity concerned, in the state described by the

wave function Ψ, has a value between f and $f + \mathrm{d}f$. Since the sum of the probabilities of all possible values of f must be equal to unity, we have

$$\int |a_f|^2 \mathrm{d}f = 1 \tag{5.2}$$

(similarly to the relation (3.3) for a discrete spectrum).

Proceeding in exactly the same way as in the derivation of formula (3.5), and using the same arguments, we can write, firstly,

$$\int \Psi\Psi^* \mathrm{d}q = \int |a_f|^2 \mathrm{d}f$$

and, secondly,

$$\int \Psi\Psi^* \mathrm{d}q = \iint a_f^* \Psi_f^* \Psi \mathrm{d}f \mathrm{d}q.$$

By comparing these two expressions we find the formula which determines the expansion coefficients,

$$a_f = \int \Psi(q)\Psi_f^*(q)\mathrm{d}q, \tag{5.3}$$

in exact analogy to (3.5).

To derive the normalization condition, we now substitute (5.1) in (5.3), and obtain

$$a_f = \int a_{f'} \left(\int \Psi_{f'}\Psi_f^* \mathrm{d}q \right) \mathrm{d}f'$$

This relation must hold for arbitrary a_f, and therefore must be satisfied identically. For this to be so, it is necessary that, first of all, the coefficient of a_f, in the integrand (i.e. the integral $\int \Psi_{f'}\Psi_f^* \mathrm{d}q$) should be zero for all $f \neq f$. For $f = f$, this coefficient must become infinite (otherwise the integral over f would vanish). Thus the integral $\int \Psi_{f'}\Psi_f^* \mathrm{d}q$ is a function of the difference $f' - f$, which becomes zero for values of the argument different from zero and is infinite when the argument is zero. We denote this function by $\delta(f' - f)$:

$$\int \Psi_{f'}\Psi_f^* \mathrm{d}q = \delta(f' - f) \tag{5.4}$$

The manner in which the function $\delta(f' - f)$ becomes infinite for $f' - f = 0$ is determined by the fact that we must have

$$\int \delta(f' - f)a_{f'}\mathrm{d}f' = a_f$$

It is clear that, for this to be so, we must have

$$\int \delta(f' - f)\mathrm{d}f' = 1$$

The function thus defined is called a *delta function*, and was first used in theoretical physics by P. A. M. Dirac. We shall write out once more the formulae which define it. They are

$$\delta(x) = 0 \text{ for } x \neq 0, \qquad \delta(0) = \infty, \qquad (5.5)$$

while

$$\int_{-\infty}^{+\infty} \delta(x)\mathrm{d}x = 1. \qquad (5.6)$$

We can take as limits of integration any numbers such that $x = 0$ lies between them. If $f(x)$ is some function continuous at $x = 0$, then

$$\int_{-\infty}^{+\infty} \delta(x)f(x)\mathrm{d}x = f(0) \qquad (5.7)$$

This formula can be written in the more general form

$$\int \delta(x - a)f(x)\mathrm{d}x = f(a) \qquad (5.8)$$

where the range of integration includes the point $x = a$, and $f(x)$ is continuous at $x = a$. It is also evident that

$$\delta(-x) = \delta(x) \qquad (5.9)$$

i.e. the delta function is even. Finally, writing

$$\int_{-\infty}^{+\infty} \delta(\alpha x)\mathrm{d}x = \int_{-\infty}^{+\infty} \delta(y)\frac{\mathrm{d}y}{|\alpha|} = \frac{1}{|\alpha|}$$

we can deduce that

$$\delta(\alpha x) = \frac{1}{|\alpha|}\delta(x) \qquad (5.10)$$

where α is any constant.

The formula (5.4) gives the normalization rule for the eigenfunctions of a continuous spectrum; it replaces the condition (3.6) for a discrete spectrum. We see that the functions Ψ_f and $\Psi_{f'}$ with $f \neq f'$ are, as before, orthogonal. However, the integrals of the squared moduli $|\Psi_f|^2$ of the functions diverge for a continuous spectrum.

The functions $\Psi_f(q)$ satisfy still another relation similar to (5.4). To derive this, we substitute (5.3) in (5.1), which gives

$$\Psi(q) = \int \Psi(q') \left(\int \Psi_f^*(q')\Psi_f(q)\mathrm{d}f \right) \mathrm{d}q'$$

whence we can at once deduce that we must have

$$\int \Psi_f^*(q')\Psi_f(q)\mathrm{d}f = \delta(q' - q) \tag{5.11}$$

There is, of course, an analogous relation for a discrete spectrum:

$$\sum_n \Psi_n^*(q')\Psi_n(q) = \delta(q' - q) \tag{5.12}$$

Comparing the pair of formulae (5.1), (5.4) with the pair (5.3), (5.11), we see that, on the one hand, the function $\Psi(q)$ can be expanded in terms of the functions $\Psi_f(q)$ with expansion coefficients a_f and, on the other hand, formula (5.3) represents an entirely analogous expansion of the function $a_f \equiv a(f)$ in terms of the functions $\Psi_f^*(q)$, while the $\Psi(q)$ play the part of expansion coefficients. The function $a(f)$, like $\Psi(q)$, completely determines the state of the system; it is sometimes called a wave function *in the f representation* (while the function $\Psi(q)$ is called a wave function in the *q representation*). Just as $|\Psi(q)|^2$ determines the probability for the system to have coordinates lying in a given interval $\mathrm{d}q$, so $|a(f)|^2$ determines the probability for the values of the quantity f to lie in a given interval $\mathrm{d}f$. On the one hand, the functions $\Psi_f(q)$ are the eigenfunctions of the quantity f in the q representation; on the other hand, their complex conjugates are the eigenfunctions of the coordinate q in the f representation.

Let $\varphi(f)$ be some function of the quantity f, such that φ and f are related in a one-to-one manner. Each of the functions $\Psi_f(q)$ can then be regarded as an eigenfunction of the quantity φ. Here, however, the normalization of these functions must be changed: the eigenfunctions $\Psi_\varphi(q)$ of the quantity φ must be normalized by the condition

$$\int \Psi_{\varphi(f')}\Psi_{\varphi(f)}^*\mathrm{d}q = \delta\left[\varphi(f') - \varphi(f)\right],$$

whereas the functions Ψ_f, are normalized by the condition (5.4). The argument of the delta function becomes zero only for $f' = f$. As f' approaches f, we have

$$\varphi(f') - \varphi(f) = \frac{\mathrm{d}\varphi(f)}{\mathrm{d}f}(f' - f).$$

By (5.10) we can therefore write[14])

$$\delta\left[\varphi(f') - \varphi(f)\right] = \frac{1}{|\mathrm{d}\varphi(f)/\mathrm{d}f|}\delta(f' - f) \qquad (5.13)$$

Comparing this with (5.4), we see that the functions Ψ_φ and Ψ_f are related by

$$\Psi_{\varphi(f)} = \frac{1}{\sqrt{|\mathrm{d}\varphi(f)/\mathrm{d}f|}}\Psi_f \qquad (5.14)$$

There are also physical quantities which in one range of values have a discrete spectrum, and in another a continuous spectrum. For the eigenfunctions of such a quantity all the relations derived in this and the previous sections are, of course, true. It need only be noted that the complete set of functions is formed by combining the eigenfunctions of both spectra. Hence the expansion of an arbitrary wave function in terms of the eigenfunctions of such a quantity has the form

$$\Psi(q) = \sum_n a_n \Psi_n(q) + \int a_f \Psi_f(q)\mathrm{d}f \qquad (5.15)$$

where the sum is taken over the discrete spectrum and the integral over the whole continuous spectrum.

The coordinate q itself is an example of a quantity having a continuous spectrum. It is easy to see that the operator corresponding to it is simply multiplication by q. For, since the probability of the various values of the coordinate is determined by the square $|\Psi(q)|^2$, the mean value of the coordinate is

$$\bar{q} = \int q|\Psi|^2\mathrm{d}q = \int \Psi^* q \Psi \mathrm{d}q.$$

Comparison of this with the definition (3.8) of an operator shows that[15])

$$\widehat{q} = q. \qquad (5.16)$$

The eigenfunctions of this operator must be determined, according to the usual rule, by the equation $q\Psi_{q_0} = q_0\Psi_{q_0}$, where q_0 temporarily denotes the

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[14]) In general, if $\varphi(x)$ is some one-valued function (the inverse function need not be one-valued), we have

$$\delta\left[\varphi(x)\right] = \sum_i \frac{1}{|\varphi'(\alpha_i)|}\delta(x - \alpha_i) \qquad (5.13a)$$

where α_i are the roots of the equation $\varphi(x) = 0$.

[15]) In future we shall always, for simplicity, write operators which amount to multiplication by some quantity in the form of that quantity itself.

actual values of the coordinate as distinct from the variable q. Since this equation can be satisfied either by $\Psi_{q_0} = 0$ or by $q = q_0$, it is clear that the eigenfunctions which satisfy the normalization condition are[16]

$$\Psi_{q_0} = \delta(q - q_0) \qquad (5.17)$$

§ 6. The passage to the limiting case of classical mechanics

Quantum mechanics contains classical mechanics in the form of a certain limiting case. The question arises as to how this passage to the limit is made.

In quantum mechanics an electron is described by a wave function which determines the various values of its coordinates; of this function we so far know only that it is the solution of a certain linear partial differential equation. In classical mechanics, on the other hand, an electron is regarded as a material particle, moving in a path which is completely determined by the equations of motion. There is an interrelation, somewhat similar to that between quantum and classical mechanics, in electrodynamics between wave optics and geometrical optics. In wave optics, the electromagnetic waves are described by the electric and magnetic field vectors, which satisfy a definite system of linear differential equations, namely Maxwell's equations. In geometrical optics, however, the propagation of light along definite paths, or rays, is considered. Such an analogy enables us to see that the passage from quantum mechanics to the limit of classical mechanics occurs similarly to the passage from wave optics to geometrical optics.

Let us recall how this latter transition is made mathematically (see Fields, §53). Let u be any of the field components in the electromagnetic wave. It can be written in the form $u = ae^{i\varphi}$ (with a and φ real), where a is called the amplitude and φ the phase of the wave (called in geometrical optics the eikonal). The limiting case of geometrical optics corresponds to small wavelengths; this is expressed mathematically by saying that φ varies by a large amount over short distances; this means, in particular, that it can be

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[16] The expansion coefficients for an arbitrary function Ψ in terms of these eigenfunctions are

$$a_{q_0} = \int \Psi(q)\delta(q - q_0)\mathrm{d}q = \Psi(q_0).$$

The probability that the value of the coordinate lies in a given interval $\mathrm{d}q_0$ is

$$|a_{q_0}|^2 \mathrm{d}q_0 = |\Psi(q_0)|^2 \mathrm{d}q_0,$$

as it should be.

supposed large in absolute value.

Similarly, we start from the hypothesis that, to the limiting case of classical mechanics, there correspond in quantum mechanics wave functions of the form $\Psi = a\mathrm{e}^{\mathrm{i}\varphi}$, where a is a slowly varying function and φ takes large values. As is well known, the path of a particle can be determined in mechanics by means of the variational principle, according to which what is called the action S of a mechanical system must take its least possible value (the principle of least action). In geometrical optics the path of the rays is determined by what is called Fermat's principle, according to which the optical path length of the ray, i.e. the difference between its phases at the beginning and end of the path, must take its least (or greatest) possible value.

On the basis of this analogy, we can assert that the phase φ of the wave function, in the limiting (classical) case, must be proportional to the mechanical action S of the physical system considered, i.e. we must have $S = \mathrm{const}\,\varphi$. The constant of proportionality is called Planck's constant[17] and is denoted by $\hbar$. It has the dimensions of action (since φ is dimensionless) and has the value

$$\hbar = 1.054 \times 10^{-27} \mathrm{erg} \cdot \mathrm{s}$$

Thus, the wave function of an "almost classical" (or, as we say, *quasi-classical*) physical system has the form

$$\Psi = a\mathrm{e}^{\mathrm{i}S/\hbar} \tag{6.1}$$

Planck's constant $\hbar$ plays a fundamental part in all quantum phenomena. Its relative value (compared with other quantities of the same dimensions) determines the "extent of quantization" of a given physical system. The transition from quantum mechanics to classical mechanics, corresponding to large phase, can be formally described as a passage to the limit $\hbar \to 0$ (just as the transition from wave optics to geometrical optics corresponds to a passage to the limit of zero wavelength, $\lambda \to 0$).

We have ascertained the limiting form of the wave function, but the question still remains how it is related to classical motion in a path. In general, the motion described by the wave function does not tend to motion in a definite path. Its connection with classical motion is that, if at some initial instant the wave function, and with it the probability distribution of the coordinates, is given, then at subsequent instants this distribution will change according to the laws of classical mechanics (for a more detailed discussion of this, see the end of §17).

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[17] It was introduced into physics by M. Planck in 1900. The constant $\hbar$ which we use everywhere in this book, is, strictly speaking, Planck's constant divided by 2π; this is Dirac's notation.

In order to obtain motion in a definite path, we must start from a wave function of a particular form, which is perceptibly different from zero only in a very small region of space (what is called a wave packet); the dimensions of this region must tend to zero with $\hbar$. Then we can say that, in the quasi-classical case, the wave packet will move in space along a classical path of a particle.

Finally, quantum-mechanical operators must reduce, in the limit, simply to multiplication by the corresponding physical quantity.

§ 7. The wave function and measurements

Let us again return to the process of measurement, whose properties have been qualitatively discussed in §1; we shall show how these properties are related to the mathematical formalism of quantum mechanics.

We consider a system consisting of two parts: a classical apparatus and an electron (regarded as a quantum object). The process of measurement consists in these two parts' coming into interaction with each other, as a result of which the apparatus passes from its initial state into some other; from this change of state we draw conclusions concerning the state of the electron. The states of the apparatus are distinguished by the values of some physical quantity (or quantities) characterizing it—the "readings of the apparatus". We conventionally denote this quantity by g, and its eigenvalues by g_n; these take in general, in accordance with the classical nature of the apparatus, a continuous range of values, but we shall—merely in order to simplify the subsequent formulae—suppose the spectrum discrete. The states of the apparatus are described by means of quasi-classical wave functions, which we shall denote by $\Psi_n(\xi)$, where the suffix n corresponds to the "reading" g_n of the apparatus, and ξ denotes the set of its coordinates. The classical nature of the apparatus appears in the fact that, at any given instant, we can say with certainty that it is in one of the known states Ψ_n with some definite value of the quantity g; for a quantum system such an assertion would, of course, be unjustified.

Let $\Phi_0(\xi)$ be the wave function of the initial state of the apparatus (before the measurement), and $\Psi(q)$ some arbitrary normalized initial wave function of the electron (q denoting its coordinates). These functions describe the state of the apparatus and of the electron independently, and therefore the initial wave function of the whole system is the product

$$\Psi(q)\Phi_0(\xi) \tag{7.1}$$

Next, the apparatus and the electron interact with each other. Applying the

equations of quantum mechanics, we can in principle follow the change of the wave function of the system with time. After the measuring process it may not, of course, be a product of functions of ξ and q. Expanding the wave function in terms of the eigenfunctions Φ_n of the apparatus (which form a complete set of functions), we obtain a sum of the form

$$\sum_n A_n(q)\Psi_n(\xi) \tag{7.2}$$

where the $A_n(q)$ are some functions of q.

The classical nature of the apparatus, and the double role of classical mechanics as both the limiting case and the foundation of quantum mechanics, now make their appearance. As has been said above, the classical nature of the apparatus means that, at any instant, the quantity g (the "reading of the apparatus") has some definite value. This enables us to say that the state of the system apparatus + electron after the measurement will in actual fact be described, not by the entire sum (7.2), but by only the one term which corresponds to the "reading" gn of the apparatus,

$$A_n(q)\Psi_n(\xi) \tag{7.3}$$

It follows from this that $A_n(q)$ is proportional to the wave function of the electron after the measurement. It is not the wave function itself, as is seen from the fact that the function $A_n(q)$ is not normalized. It contains both information concerning the properties of the resulting state of the electron and the probability (determined by the initial state of the system) of the occurrence of the nth "reading" of the apparatus.

Since the equations of quantum mechanics are linear, the relation between $A_n(q)$ and the initial wave function of the electron $\Psi(q)$ is in general given by some linear integral operator:

$$A_n(q) = \int K_n(q, q')\Psi(q')\mathrm{d}q' \tag{7.4}$$

with a kernel $K_n(q, q')$ which characterizes the measurement process concerned.

We shall suppose that the measurement concerned is such that it gives a complete description of the state of the electron. In other words (see §1), in the resulting state the probabilities of all the quantities must be independent of the previous state of the electron (before the measurement). Mathematically, this means that the form of the functions $A_n(q)$ must be determined by the measuring process itself, and does not depend on the initial wave function $\Psi(q)$ of the electron. Thus the A_n must have the form

$$A_n(q) = a_n\varphi_n(q) \tag{7.5}$$

where the φ_n are definite functions, which we suppose normalized, and only the constants a_n depend on $\Psi(q)$. In the integral relation (7.4) this corresponds to a kernel $K_n(q, q')$ which is a product of a function of q and a function of q':

$$K_n(q, q') = \varphi_n(q)\Psi_n^*(q') \tag{7.6}$$

then the linear relation between the constants an and the function $\Psi(q)$ is

$$a_n = \int \Psi(q)\Psi_n^*(q)\mathrm{d}q \tag{7.7}$$

where the $\Psi_n(q)$ are certain functions depending on the process of measurement.

The functions $\varphi_n(q)$ are the normalized wave functions of the electron after measurement. Thus we see how the mathematical formalism of the theory reflects the possibility of finding by measurement a state of the electron described by a definite wave function.

If the measurement is made on an electron with a given wave function $\Psi(q)$, the constants a_n have a simple physical meaning: in accordance with the usual rules, $|a_n|^2$ is the probability that the measurement will give the nth result. The sum of the probabilities of all results is equal to unity:

$$\sum_n |a_n|^2 = 1 \tag{7.8}$$

In order that equations (7.7) and (7.8) should hold for an arbitrary normalized function $\Psi(q)$, it is necessary (cf. §3) that an arbitrary function $\Psi(q)$ can be expanded in terms of the functions $\Psi_n(q)$. This means that the functions $\Psi_n(q)$ form a complete set of normalized and orthogonal functions.

If the initial wave function of the electron coincides with one of the functions $\Psi_n(q)$, then the corresponding constant a_n is evidently equal to unity, while all the others are zero. In other words, a measurement made on an electron in the state $\Psi_n(q)$ gives with certainty the nth result.

All these properties of the functions $\Psi_n(q)$ show that they are the eigenfunctions of some physical quantity (denoted by f) which characterizes the electron, and the measurement concerned can be spoken of as a measurement of this quantity.

It is very important to notice that the functions $\Psi_n(q)$ do not, in general, coincide with the functions $\varphi_n(q)$; the latter are in general not even mutually orthogonal, and do not form a set of eigenfunctions of any operator. This expresses the fact that the results of measurements in quantum mechanics cannot be reproduced. If the electron was in a state $\Psi_n(q)$, then a measurement of the quantity f carried out on it leads with certainty to the value f_n.

After the measurement, however, the electron is in a state $\varphi_n(q)$ different from its initial one, and in this state the quantity f does not in general take any definite value. Hence, on carrying out a second measurement on the electron immediately after the first, we should obtain for f a value which did not agree with that obtained from the first measurement.[18] To predict (in the sense of calculating probabilities) the result of the second measurement from the known result of the first, we must take from the first measurement the wave function $\varphi_n(q)$ of the state in which it resulted, and from the second measurement the wave function $\Psi_n(q)$ of the state whose probability is required. This means that from the equations of quantum mechanics we determine the wave function $\varphi_n(q, t)$ which, at the instant when the first measurement is made, is equal to $\varphi_n(q)$; the probability of the mth result of the second measurement, made at time t, is then given by the squared modulus of the integral $\int \varphi_n(q, t)\Psi_m^*(q)dq$.

We see that the measuring process in quantum mechanics has a "two-faced" character: it plays different parts with respect to the past and future of the electron. With respect to the past, it "verifies" the probabilities of the various possible results predicted from the state brought about by the previous measurement. With respect to the future, it brings about a new state (see also §44). Thus the very nature of the process of measurement involves a far-reaching principle of irreversibility.

This irreversibility is of fundamental significance. We shall see later (at the end of §18) that the basic equations of quantum mechanics are in themselves symmetrical with respect to a change in the sign of the time; here quantum mechanics does not differ from classical mechanics. The irreversibility of the process of measurement, however, causes the two directions of time to be physically non-equivalent, i.e. creates a difference between the future and the past.

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[18] There is, however, an important exception to the statement that results of measurements cannot be reproduced: the one quantity the result of whose measurement can be exactly reproduced is the coordinate. Two measurements of the coordinates of an electron, made at a sufficiently small interval of time, must give neighbouring values; if this were not so, it would mean that the electron had an infinite velocity. Mathematically, this is related to the fact that the coordinate commutes with the operator of the interaction energy between the electron and the apparatus, since this energy is (in non-relativistic theory) a function of the coordinates only.

CHAPTER II

ENERGY AND MOMENTUM

§ 8. The Hamiltonian operator

The wave function Ψ completely determines the state of a physical system in quantum mechanics. This means that, if this function is given at some instant, not only are all the properties of the system at that instant described, but its behaviour at all subsequent instants is determined (only, of course, to the degree of completeness which is generally admissible in quantum mechanics). The mathematical expression of this fact is that the value of the derivative $\partial\Psi/\partial t$ of the wave function with respect to time at any given instant must be determined by the value of the function itself at that instant, and, by the principle of superposition, the relation between them must be linear. In the most general form we can write

$$i\hbar\frac{\partial\Psi}{\partial t} = \widehat{H}\Psi \tag{8.1}$$

where $\widehat{H}$ is some linear operator; the factor $i\hbar$ is introduced here for a reason that will become apparent.

Since the integral $\int \Psi^*\Psi \mathrm{d}q$ is a constant independent of time, we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\int|\Psi|^2\mathrm{d}q = \int\frac{\partial\Psi^*}{\partial t}\Psi\mathrm{d}q + \int\Psi^*\frac{\partial\Psi}{\partial t}\mathrm{d}q = 0$$

Substituting here (8.1) and using in the first integral the definition of the transpose of an operator, we can write (omitting the common factor $i/\hbar$)

$$\int\Psi\widehat{H}^*\Psi^*\mathrm{d}q - \int\Psi^*\widehat{H}\Psi\mathrm{d}q = \int\Psi^*\widetilde{\widehat{H}}^*\Psi\mathrm{d}q - \int\Psi^*\widehat{H}\Psi\mathrm{d}q$$

$$= \int\Psi^*\left(\widetilde{\widehat{H}}^* - \widehat{H}\right)\Psi\mathrm{d}q = 0.$$

Since this equation must hold for an arbitrary function Ψ, it follows that we must have identically $\widehat{H}^\dagger = \widehat{H}$; the operator $\widehat{H}$ is therefore Hermitian. Let

us find the physical quantity to which it corresponds. To do this, we use the limiting expression (6.1) for the wave function and write

$$\frac{\partial \Psi}{\partial t} = \frac{i}{\hbar} \frac{\partial S}{\partial t} \Psi;$$

the slowly varying amplitude a need not be differentiated. Comparing this equation with the definition (8.1), we see that, in the limiting case, the operator $\widehat{H}$ reduces to simply multiplying by $-\partial S/\partial t$. This means that $-\partial S/\partial t$ is the physical quantity into which the Hermitian operator $\widehat{H}$ passes.

The derivative $-\partial S/\partial t$ is just Hamilton's function H for a mechanical system. Thus the operator $\widehat{H}$ is what corresponds in quantum mechanics to Hamilton's function; this operator is called the *Hamiltonian operator* or, more briefly, the *Hamiltonian* of the system. If the form of the Hamiltonian is known, equation (8.1) determines the wave functions of the physical system concerned. This fundamental equation of quantum mechanics is called the *wave equation.*

§ 9. The differentiation of operators with respect to time

The concept of the derivative of a physical quantity with respect to time cannot be defined in quantum mechanics in the same way as in classical mechanics. For the definition of the derivative in classical mechanics involves the consideration of the values of the quantity at two neighbouring but distinct instants of time. In quantum mechanics, however, a quantity which at some instant has a definite value does not in general have definite values at subsequent instants; this was discussed in detail in §1.

Hence the idea of the derivative with respect to time must be differently defined in quantum mechanics. It is natural to define the *derivative* $\dot{f}$ of a quantity f as the quantity whose mean value is equal to the derivative, with respect to time, of the mean value . Thus we have the definition

$$\overline{\dot{f}} = \dot{\overline{f}} \tag{9.1}$$

Starting from this definition, it is easy to obtain an expression for the quantum-mechanical operator $\widehat{\dot{f}}$ corresponding to the quantity $\widehat{f}$:

$$\overline{\dot{f}} = \dot{\overline{f}} = \frac{d}{dt} \int \Psi^* \widehat{f} \Psi \, dq = \int \Psi^* \frac{\partial \widehat{f}}{\partial t} \Psi \, dq + \int \frac{\partial \Psi^*}{\partial t} \widehat{f} \Psi \, dq + \int \Psi^* \widehat{f} \frac{\partial \Psi}{\partial t} \, dq.$$

Here $\partial f/\partial t$ is the operator obtained by differentiating the operator f with respect to time; $\widehat{f}$ may depend on the time as a parameter. Substituting for $\partial\Psi/\partial t$, $\partial\Psi^*/\partial t$ their expressions according to (8.1), we obtain

$$\overline{\dot{f}} = \int \Psi^* \frac{\partial\widehat{f}}{\partial t}\Psi\mathrm{d}q + \frac{\mathrm{i}}{\hbar}\int (\widehat{H}^*\Psi^*)\widehat{f}\Psi\mathrm{d}q - \frac{\mathrm{i}}{\hbar}\int \Psi^*\widehat{f}(\widehat{H}\Psi)\mathrm{d}q.$$

Since the operator $\widehat{H}$ is Hermitian, we have

$$\int (\widehat{H}^*\Psi^*)(\widehat{f}\Psi)\mathrm{d}q = \int \Psi^*\widehat{H}\widehat{f}\Psi\mathrm{d}q;$$

thus

$$\overline{\dot{f}} = \int \Psi^* \left(\frac{\partial\widehat{f}}{\partial t} + \frac{\mathrm{i}}{\hbar}\widehat{H}\widehat{f} - \frac{\mathrm{i}}{\hbar}\widehat{f}\widehat{H} \right) \Psi\mathrm{d}q.$$

Since, on the other hand, we must have, by the definition of mean values, $\overline{\dot{f}} = \int \Psi^*\widehat{\dot{f}}\Psi\mathrm{d}q$, it is seen that the expression in parentheses in the integrand is the required operator $\widehat{\dot{f}}$:[1]

$$\widehat{\dot{f}} = \frac{\partial f}{\partial t} + \frac{\mathrm{i}}{\hbar}(\widehat{H}\widehat{f} - \widehat{f}\widehat{H}) \qquad (9.2)$$

---

[1] In classical mechanics we have for the total derivative, with respect to time, of a quantity f which is a function of the generalized coordinates q_i and momenta p_i of the system

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\partial f}{\partial t} + \sum_i \left(\frac{\partial f}{\partial q_i}\dot{q}_i + \frac{\partial f}{\partial p_i}\dot{p}_i \right).$$

Substituting, in accordance with Hamilton's equations, $\dot{q}_i = \frac{\partial H}{\partial p_i}$ and $\dot{p}_i = -\frac{\partial H}{\partial q_i}$, we obtain

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\partial f}{\partial t} + [H, f],$$

where

$$[H, f] \equiv \sum_i \left(\frac{\partial f}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial H}{\partial q_i} \right)$$

is what is called the *Poisson bracket* for the quantities f and H (see Mechanics, §42). On comparing with the expression (9.2), we see that, as we pass to the limit of classical mechanics, the operator $\mathrm{i}(\widehat{H}\widehat{f} - \widehat{f}\widehat{H})$ reduces in the first approximation to zero, as it should, and in the second approximation (with respect to $\hbar$) to the quantity $\hbar[H, f]$. This result is true also for any two quantities f and g; the operator $\mathrm{i}(\widehat{f}\widehat{g} - \widehat{g}\widehat{f})$ tends in the limit to the quantity $\hbar[f, g]$, where $[f, g]$ is the Poisson bracket

$$[f, g] \equiv \sum_i \left(\frac{\partial g}{\partial q_i}\frac{\partial f}{\partial p_i} - \frac{\partial g}{\partial p_i}\frac{\partial f}{\partial q_i} \right)$$

This follows from the fact that we can always formally imagine a system whose Hamiltonian is $\widehat{g}$.

If the operator $\widehat{f}$ is independent of time, $\dot{\widehat{f}}$ reduces, apart from a constant factor, to the commutator of the operator $\widehat{f}$ and the Hamiltonian.

A very important class of physical quantities is formed by those whose operators do not depend explicitly on time, and also commute with the Hamiltonian, so that $\dot{\widehat{f}} = 0$. Such quantities are said to be *conserved*. For these $\dot{\overline{f}} = \overline{\dot{f}} = 0$, that is, is constant. In other words, the mean value of the quantity remains constant in time. We can also assert that, if in a given state the quantity f has a definite value (i.e. the wave function is an eigenfunction of the operator $\widehat{f}$), then it will have a definite value (the same one) at subsequent instants also.

§ 10. Stationary states

The Hamiltonian of a closed system (and of a system in a *constant* external field) cannot contain the time explicitly. This follows from the fact that, for such a system, all times are equivalent. Since, on the other hand, any operator of course commutes with itself, we reach the conclusion that Hamilton's function is conserved for systems which are not in a varying external field. As is well known, a Hamilton's function which is conserved is called the *energy*. The law of conservation of energy in quantum mechanics signifies that, if in a given state the energy has a definite value, this value remains constant in time.

States in which the energy has definite values are called *stationary states* of a system. They are described by wave functions Ψ_n which are the eigenfunctions of the Hamiltonian operator, i.e. which satisfy the equation $\widehat{H}\Psi_n = E_n\Psi_n$, where E_n are the eigenvalues of the energy. Correspondingly, the wave equation (8.1) for the function Ψ_n,

$$i\hbar\frac{\partial\Psi_n}{\partial t} = \widehat{H}\Psi_n = E_n\Psi_n$$

can be integrated at once with respect to time and gives

$$\Psi_n = \exp\left(-\frac{i}{\hbar}E_n t\right)\psi_n(q) \tag{10.1}$$

where Ψ_n is a function of the coordinates only. This determines the relation between the wave functions of stationary states and the time.

We shall denote by the small letter ψ the wave functions of stationary states without the time factor. These functions, and also the eigenvalues of the energy, are determined by the equation

$$\widehat{H}\psi = E\psi \tag{10.2}$$

The stationary state with the smallest possible value of the energy is called the *normal* or *ground state* of the system.

The expansion of an arbitrary wave function Ψ in terms of the wave functions of stationary states has the form

$$\Psi = \sum_n a_n \exp\left(-\frac{\mathrm{i}}{\hbar}E_n t\right)\psi_n(q) \tag{10.3}$$

The squared moduli $|a_n|^2$ of the expansion coefficients, as usual, determine the probabilities of various values of the energy of the system.

The probability distribution for the coordinates in a stationary state is determined by the squared modulus $|\Psi_n|^2 = |\psi_n|2$ we see that it is independent of time. The same is true of the mean values

$$\overline{f} = \int \Psi_n^* \widehat{f} \Psi_n \mathrm{d}q = \int \psi_n^* \widehat{f} \psi_n \mathrm{d}q$$

of any physical quantity f (whose operator does not depend explicitly on the time).

As has been said, the operator of any quantity that is conserved commutes with the Hamiltonian. This means that any physical quantity that is conserved can be measured simultaneously with the energy.

Among the various stationary states, there may be some which correspond to the same value of the energy (the same *energy level* of the system), but differ in the values of some other physical quantities. Such energy levels, to which several different stationary states correspond, are said to be *degenerate*. Physically, the possibility that degenerate levels can exist is related to the fact that the energy does not in general form by itself a complete set of physical quantities.

If there are two conserved physical quantities f and g whose operators do not commute, then the energy levels of the system are in general degenerate. For, let ψ be the wave function of a stationary state in which, besides the energy, the quantity f also has a definite value. Then we can say that the function $\widehat{g}\psi$ does not coincide (apart from a constant factor) with ψ; if it did, this would mean that the quantity g also had a definite value, which is impossible, since f and g cannot be measured simultaneously. On the other hand, the function $\widehat{g}\psi$ is an eigenfunction of the Hamiltonian, corresponding to the same value E of the energy as ψ:

$$\widehat{H}(\widehat{g}\psi) = \widehat{g}\widehat{H}\psi = E(\widehat{g}\psi)$$

Thus we see that the energy E corresponds to more than one eigenfunction, i.e. the energy level is degenerate.

It is clear that any linear combination of wave functions corresponding to the same degenerate energy level is also an eigenfunction for that value of the energy. In other words, the choice of eigenfunctions of a degenerate energy level is not unique. Arbitrarily selected eigenfunctions of a degenerate energy level are not, in general, orthogonal. By a proper choice of linear combinations of them, however, we can always obtain a set of orthogonal (and normalized) eigenfunctions (and this can be done in infinitely many ways; for the number of independent coefficients in a linear transformation of n functions is n^2, while the number of normalization and orthogonality conditions for n functions is $n(n+1)/2$, i.e. less than n^2).

These statements concerning the eigenfunctions of a degenerate energy level relate, of course, not only to eigenfunctions of the energy, but also to those of any operator. Only those functions are automatically orthogonal which correspond to different eigenvalues of the operator concerned; functions which correspond to the same degenerate eigenvalue are not in general orthogonal.

If the Hamiltonian of the system is the sum of two (or more) parts, $\widehat{H} = \widehat{H}_1 + \widehat{H}_2$, one of which contains only the coordinates q_1 and the other only the coordinates q_2, then the eigenfunctions of the operator $\widehat{H}$ can be written down as products of the eigenfunctions of the operators $\widehat{H}_1$ and $\widehat{H}_2$, and the eigenvalues of the energy are equal to the sums of the eigenvalues of these operators.

The spectrum of eigenvalues of the energy may be either discrete or continuous. A stationary state of a discrete spectrum always corresponds to a finite motion of the system, i.e. one in which neither the system nor any part of it moves off to infinity. For, with eigenfunctions of a discrete spectrum, the integral $\int |\Psi|^2 \mathrm{d}q$, taken over all space, is finite. This certainly means that the squared modulus $|\Psi|^2$ decreases quite rapidly, becoming zero at infinity. In other words, the probability of infinite values of the coordinates is zero; that is, the system executes a finite motion, and is said to be in a *bound state*.

For wave functions of a continuous spectrum, the integral $\int |\Psi|^2 \mathrm{d}q$ diverges. Here the squared modulus $|\Psi|^2$ of the wave function does not directly determine the probability of the various values of the coordinates, and must be regarded only as a quantity proportional to this probability. The divergence of the integral $\int |\Psi|^2 \mathrm{d}q$ is always due to the fact that $|\Psi|^2$ does not become zero at infinity (or becomes zero insufficiently rapidly). Hence we can say that the integral $\int |\Psi|^2 \mathrm{d}q$, taken over the region of space outside any arbitrarily large but finite closed surface, will always diverge. This means that, in the state considered, the system (or some part of it) is at infinity.

For a wave function which is a superposition of the wave functions of various stationary states of a continuous spectrum, the integral $\int |\Psi|^2 \mathrm{d}q$ may converge, so that the system lies in a finite region of space. However, in the course of time, this region moves unrestrictedly, and eventually the system moves off to infinity. This can be seen as follows. Any superposition of wave functions of a continuous spectrum has the form

$$\Psi = \int a_E \exp\left(-\frac{\mathrm{i}}{\hbar}Et\right)\psi_E(q)\mathrm{d}E$$

The squared modulus of Ψ can be written in the form of a double integral:

$$|\Psi|^2 = \iint a_E a_{E'}^* \exp\left(\frac{\mathrm{i}}{\hbar}(E'-E)t\right)\psi_E(q)\psi_{E'}^*(q)\mathrm{d}E\mathrm{d}E'.$$

If we average this expression over some time interval T, and then let T tend to infinity, the mean values of the oscillating factors $\exp\{\mathrm{i}(E'-E)t/\hbar\}$, and therefore the whole integral, tend to zero in the limit. Thus the mean value, with respect to time, of the probability of finding the system at any given point of configuration space tends to zero. This is possible only if the motion takes place throughout infinite space.[2] Thus the stationary states of a continuous spectrum correspond to an infinite motion of the system.

§ 11. Matrices

We shall suppose for convenience that the system considered has a discrete energy spectrum; all the relations obtained below can be generalized at once to the case of a continuous spectrum. Let $\Psi = \sum a_n \Psi_n$ be the expansion of an arbitrary wave function in terms of the wave functions Ψ_n of the stationary states. If we substitute this expansion in the definition (3.8) of the mean value of some quantity f, we obtain

$$\overline{f} = \sum_n \sum_m a_n^* a_m f_{nm}(t) \tag{11.1}$$

---

[2] Note that, for a function which is a superposition of functions of a discrete spectrum, we should have

$$\overline{|\Psi|^2} = \sum_n \sum_m a_n a_m^* \overline{\exp\left\{\frac{\mathrm{i}}{\hbar}(E_m - E_n)t\right\}}\psi_n\psi_m^* = \sum_n |a_n\psi_n(q)|^2,$$

i.e. the probability density remains finite on averaging over time.

where $f_{nm}(t)$ denotes the integral

$$f_{nm}(t) = \int \Psi_n^* \widehat{f} \Psi_m \mathrm{d}q \qquad (11.2)$$

The set of quantities $f_{nm}(t)$ with all possible n and m is called the *matrix* of the quantity f, and each of the $f_{nm}(t)$ is called the *matrix element* corresponding to the *transition* from state m to state n.[3]

The dependence of the matrix elements $f_{nm}(t)$ on time is determined (if the operator does not contain the time explicitly) by the dependence of the functions Ψ_n on time. Substituting for them the expressions (10.1), we find that

$$f_{nm}(t) = f_{nm}\mathrm{e}^{\mathrm{i}\omega_{nm}t}, \qquad (11.3)$$

where

$$\omega_{nm} = \frac{E_n - E_m}{\hbar} \qquad (11.4)$$

is what is called the *transition frequency* between the states n and m, and the quantities

$$f_{nm} = \int \psi_n^* \widehat{f} \psi_m \mathrm{d}q \qquad (11.5)$$

form the matrix of the quantity f which is independent of time, and which is commonly used.[4]

The matrix elements of the derivative are obtained by differentiating the matrix elements of the quantity f with respect to time; this follows directly from the fact that

$$\overline{\dot{f}} = \dot{\overline{f}} = \sum_m \sum_n a_n^* a_m \dot{f}_{nm}(t). \qquad (11.6)$$

From (11.3) we thus have for the matrix elements of $\dot{f}$

$$\dot{f}_{nm}(t) = \mathrm{i}\omega_{nm} f_{nm}(t) \qquad (11.7)$$

or (cancelling the time factor $\exp(\mathrm{i}\omega_{nm}t)$ from both sides) for the matrix elements independent of time

$$\left(\dot{f}\right)_{nm} = \mathrm{i}\omega_{nm} f_{nm} = \frac{\mathrm{i}}{\hbar}(E_n - E_m) f_{nm} \qquad (11.8)$$

---

[3] The matrix representation of physical quantities was introduced by Heisenberg in 1925, before Schrödinger's discovery of the wave equation. "Matrix mechanics" was later developed by M. Born, W. Heisenberg and P. Jordan.

[4] Because of the indeterminacy of the phase factor in normalized wave functions (see §2), the matrix elements f_{nm} (and $f_{nm}(t)$) also are determined only to within a factor of the form $\exp\left[\mathrm{i}(\alpha_m - \alpha_n)\right]$. Here again this indeterminacy has no effect on any physical results.

To simplify the notation in the formulae, we shall derive all our relations below for the matrix elements independent of time; exactly similar relations hold for the matrices which depend on the time.

For the matrix elements of the complex conjugate f^* of the quantity f we obtain, taking into account the definition of the Hermitian conjugate operator,

$$(f^*)_{nm} = \int \psi_n^* \widehat{f}^{\dagger} \psi_m \mathrm{d}q = \int \psi_n^* \widetilde{\widehat{f}^*} \psi_m \mathrm{d}q = \int \psi_m \widehat{f}^* \psi_n^* \mathrm{d}q$$

or

$$(f^*)_{nm} = (f_{mn})^* \tag{11.9}$$

For real physical quantities, which are the only ones we usually consider, we consequently have

$$f_{nm} = f_{mn}^* \tag{11.10}$$

(f_{mn}^* stands for $(f_{mn})^*$). Such matrices, like the corresponding operators, are said to be *Hermitian*.

Matrix elements with $n = m$ are called diagonal elements. These are independent of time, and (11.10) shows that they are real. The element f_{nn} is the mean value of the quantity f in the state Ψ_n.

It is not difficult to obtain the multiplication rule" for matrices. To do so, we first observe that the formula

$$\widehat{f}\psi_n = \sum_m f_{mn}\psi_m \tag{11.11}$$

holds. This is simply the expansion of the function in terms of the functions ψ_m, the coefficients being determined in accordance with the general formula (3.5). Remembering this formula, let us write down the result of the product of two operators acting on the function ψ_n:

$$\widehat{f}\widehat{g}\psi_n = \widehat{f}(\widehat{g}\psi_n) = \widehat{f}\sum_k g_{kn}\psi_k = \sum_k g_{kn}\widehat{f}\psi_k = \sum_{k,m} g_{kn}f_{mk}\psi_m.$$

Since, on the other hand, we must have

$$\widehat{f}\widehat{g}\psi_n = \sum_m (fg)_{mn}\psi_m,$$

we arrive at the result that the matrix elements of the product fg are determined by the formula

$$(fg)_{mn} = \sum_k f_{mk}g_{kn} \tag{11.12}$$

This rule is the same as that used in mathematics for the multiplication of matrices: the rows of the first matrix in the product are multiplied by the columns of the second matrix.

If the matrix is given, then so is the operator itself. In particular, if the matrix is given, it is in principle possible to determine the eigenvalues of the physical quantity concerned and the corresponding eigenfunctions.

We shall now consider the values of all quantities at some definite instant, and expand an arbitrary wave function Ψ (at that instant) in terms of the eigenfunctions of the Hamiltonian, i.e. of the wave functions ψ_m of the stationary states (these wave functions are independent of time).

$$\Psi = \sum_m c_m \psi_m \tag{11.13}$$

where the expansion coefficients are denoted by c_m. We substitute this expansion in the equation $\widehat{f}\Psi = f\Psi$ which determines the eigenvalues and eigenfunctions of the quantity f. We have

$$\sum_m c_m(\widehat{f}\psi_m) = f \sum_m c_m \psi_m$$

We multiply both sides of this equation by ψ_n^* and integrate over q. Each of the integrals on the left-hand side of the equation is the corresponding matrix element f_{nm}. On the right-hand side, all the integrals $\int \psi_n^* \psi_m \mathrm{d}q$ with $m \neq n$ vanish by virtue of the orthogonality of the functions ψ_m, and $\int \psi_n^* \psi_n \mathrm{d}q = 1$ by virtue of their normalization.[5] Thus

$$\sum_m f_{nm} c_m = f c_n, \tag{11.14}$$

or

$$\sum_m (f_{nm} - f\delta_{nm}) c_m = 0,$$

where

$$\delta_{nm} = \begin{cases} 0, & n \neq m; \\ 1, & n = m. \end{cases}$$

---

[5] In accordance with the general rule (§5), the set of coefficients c_n in the expansion (11.13) can be considered as the wave function in the "energy representation" (the variable being the suffix n that gives the number of the energy eigenvalue). The matrix f_{nm} here acts as the operator in this representation, the action of which on the wave function is given by the left-hand side of (11.14). The formula then corresponds to the general expression for the mean value of a quantity in terms of its operator and the wave function of the state concerned.

Thus we have obtained a system of homogeneous algebraic equations of the first degree (with the c_m as unknowns). As is well known, such a system has solutions different from zero only if the determinant formed by the coefficients in the equations vanishes, i.e. only if

$$|f_{nm} - f\delta_{nm}| = 0 \tag{11.15}$$

The roots of this equation (in which f is regarded as the unknown) are the possible values of the quantity f. The set of values c_m satisfying the equations (11.14) when f is equal to any of these values determines the corresponding eigenfunction.

If, in the definition (11.5) of the matrix elements of the quantity f, we take as ψ_n the eigenfunctions of this quantity, then from the equation $\widehat{f}\psi_n = f_n\psi_n$ we have

$$f_{nm} = \int \psi_n^* \widehat{f}\psi_m \mathrm{d}q = f_m \int \psi_n^* \psi_m \mathrm{d}q.$$

By virtue of the orthogonality and normalization of the functions ψ_m, this gives $f_{nm} = 0$ for $n \neq m$ and $f_{mm} = f_m$. Thus only the diagonal matrix elements are different from zero, and each of these is equal to the corresponding eigenvalue of the quantity f. A matrix with only these elements different from zero is said to be put in *diagonal form.* In particular, in the usual representation, with the wave functions of the stationary states as the functions ψ_n, the energy matrix is diagonal (and so are the matrices of all other physical quantities having definite values in the stationary states). In general, the matrix of a quantity f, defined with respect to the eigenfunctions of some operator $\widehat{g}$, is said to be the matrix of f *in a representation in which g is diagonal.* We shall always, except where the subject is specially mentioned, understand in future by the matrix of a physical quantity its matrix in the usual representation, in which the energy is diagonal. Everything that has been said above regarding the dependence of matrices on time refers, of course, only to this usual representation.[6])

By means of the matrix representation of operators we can prove the theorem mentioned in §4: if two operators commute with each other, they have their entire sets of eigenfunctions in common. Let $\widehat{f}$ and $\widehat{g}$ be two such operators. From $\widehat{f}\widehat{g} = \widehat{g}\widehat{f}$ and the matrix multiplication rule (11.12), it follows that

$$\sum_k f_{mk}g_{kn} = \sum_k g_{mk}f_{kn}.$$

---

[6]) Bearing in mind the diagonality of the energy matrix, it is easy to see that equation (11.8) is the operator relation (9.2) written in matrix form.

If we take the eigenfunctions of the operator $\widehat{f}$ as the set of functions ψ_n with respect to which the matrix elements are calculated, we shall have $f_{mk} = 0$ for $m \neq k$, so that the above equation reduces to $f_{mm}g_{mn} = g_{mn}f_{nn}$, or

$$g_{mn}(f_m - f_n) = 0$$

If all the eigenvalues f_n of the quantity f are different, then for all $m \neq n$ we have $f_m f_n \neq 0$, so that we must have $g_{mn} = 0$. Thus the matrix g_{mn} is also diagonal, i.e. the functions ψ_n are eigenfunctions of the physical quantity g also. If, among the values f_n, there are some which are equal (i.e. if there are eigenvalues to which several different eigenfunctions correspond), then the matrix elements g_{mn} corresponding to each such group of functions ψ_n are, in general, different from zero. However, linear combinations of the functions ψ_n which correspond to a single eigenvalue of the quantity f are evidently also eigenfunctions of f; one can always choose these combinations in such a way that the corresponding non-diagonal matrix elements g_{mn} are zero, and thus, in this case also, we obtain a set of functions which are simultaneously the eigenfunctions of the operators $\widehat{f}$ and $\widehat{g}$.

The following formula is useful in applications:

$$\left(\frac{\partial H}{\partial \lambda}\right)_{nn} = \frac{\partial E_n}{\partial \lambda} \tag{11.16}$$

where λ is a parameter on which the Hamiltonian $\widehat{H}$ (and therefore the energy eigenvalues E_n) depends. It is proved as follows. Differentiating the equation $(\widehat{H} - E_n)\psi_n = 0$ with respect to λ and then multiplying on the left by ψ_n^*, we obtain

$$\psi_n^*(\widehat{H} - E_n)\frac{\partial \psi_n}{\partial \lambda} = \psi_n^*\left(\frac{\partial E_n}{\partial \lambda} - \frac{\partial \widehat{H}}{\partial \lambda}\right)\psi_n$$

On integration with respect to q, the left-hand side gives zero, since

$$\int \psi_n^*(\widehat{H} - E_n)\frac{\partial \psi_n}{\partial \lambda}\mathrm{d}q = \int \frac{\partial \psi_n}{\partial \lambda}(\widehat{H} - E_n)^*\psi_n^*\mathrm{d}q,$$

the operator $\widehat{H}$ being Hermitian. The right-hand side gives the required equation.

A widely used notation (introduced by Dirac) in recent literature is that which denotes the matrix elements f_{nm} by[7]

$$\langle n|f|m\rangle \tag{11.17}$$

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[7] Both notations are used in the present book. The form (11.17) is especially convenient when each suffix has to be written as several letters.

This symbol is written so that it may be regarded as "consisting" of the quantity f and the symbols $|m\rangle$ and $\langle n|$ which respectively stand for the initial and final states as such (independently of the representation of the wave functions of the states). With the same symbols we can construct notations for the expansion coefficients of wave functions: if there is a complete set of wave functions corresponding to the states $|n_1\rangle, |n_2\rangle, \ldots$, the coefficients in the expansion in terms of these of the wave function of a state $|m\rangle$ are denoted by

$$\langle n_i|m\rangle = \int \psi_{n_i}^* \psi_m \mathrm{d}q. \tag{11.18}$$

§ 12. Transformation of matrices

The matrix elements of a given physical quantity can be defined with respect to various sets of wave functions, for example the wave functions of stationary states described by various sets of physical quantities, or the wave functions of stationary states of the same system in various external fields. The problem therefore arises of the transformation of matrices from one representation to another.

Let $\psi_n(q)$ and $\psi_n'(q)$ $(n = 1, 2, \ldots)$ be two complete sets of orthonormal functions, related by some linear transformation:

$$\psi_n' = \sum_m S_{mn} \psi_m \tag{12.1}$$

which is simply an expansion of the function ψ_n' in terms of the complete set of functions ψ_n. This transformation may be conventionally written in the operator form

$$\psi_n' = \widehat{S} \psi_n \tag{12.2}$$

The operator $\widehat{S}$ must satisfy a certain condition in order that the functions ψ_n' should be orthonormal if the functions ψ_n are. Substituting (12.2) in the condition

$$\int \psi_m'^* \psi_n' \mathrm{d}q = \delta_{nm}$$

and using the definition of the transposed operator (3.14), we have

$$\int (\widehat{S}\psi_n)\widehat{S}^* \psi_m^* \mathrm{d}q = \int \psi_m^* \widetilde{\widehat{S}^*}\widehat{S}\psi_n \mathrm{d}q = \delta_{nm}$$

If these equations hold for all m and n, we must have $\widetilde{\widehat{S}^*}\widehat{S} = 1$, or

$$\widetilde{\widehat{S}^*} \equiv \widehat{S}^\dagger = \widehat{S}^{-1} \tag{12.3}$$

i.e. the inverse operator is equal to the Hermitian conjugate operator. Operators having this property are said to be unitary. Owing to this property, the transformation $\psi_n = \widehat{S}^{-1}\psi'_n$ inverse to (12.1) is given by

$$\psi_n = \sum_m S^*_{nm}\psi'_m \tag{12.4}$$

Writing the equations $\widehat{S}^\dagger\widehat{S} = 1$ and $\widehat{S}\widehat{S}^\dagger = 1$ in matrix form, we obtain the following forms of the *unitarity* condition:

$$\sum_l S^*_{lm}S_{ln} = \delta_{mn} \tag{12.5}$$

$$\sum_l S^*_{ml}S_{nl} = \delta_{mn} \tag{12.6}$$

Let us now consider some physical quantity f and write down its matrix elements in the "new" representation, i.e. with respect to the functions ψ'_n. These are given by the integrals

$$\int \psi'^*_m \widehat{f}\psi'_n \mathrm{d}q = \int (\widehat{S}^*\psi^*_m)(\widehat{f}\widehat{S}\psi_n)\mathrm{d}q$$

$$= \int \psi^*_m \widetilde{\widehat{S}^*}\widehat{f}\widehat{S}\psi_n \mathrm{d}q = \int \psi^*_m \widehat{S}^{-1}\widehat{f}\widehat{S}\psi_n \mathrm{d}q.$$

Hence we see that the matrix of the operator in the new representation is equal to the matrix of the operator

$$\widehat{f}' = \widehat{S}^{-1}\widehat{f}\widehat{S} \tag{12.7}$$

in the old representation.[8]

The sum of the diagonal elements of a matrix is called the *trace* or *spur*[9] of the matrix and denoted by $\mathrm{tr}f$:

$$\mathrm{tr}f = \sum_n f_{nn} \tag{12.8}$$

---

[8] If $\{\widehat{f}, \widehat{g}\} = -\mathrm{i}\hbar\widehat{c}$ is the commutation rule for two operators $\widehat{f}$ and $\widehat{g}$, the transformation (12.7) gives $\{\widehat{f}', \widehat{g}'\} = -\mathrm{i}\hbar\widehat{c}'$, i.e. the rule is unchanged. We have shown in the footnote in §9 that is the quantum analogue of the classical Poisson bracket $[f, g]$. In classical mechanics, however, the Poisson brackets are invariant under canonical transformations of the variables (generalized coordinates and momenta); see Mechanics, §45. In this sense we can say that unitary transformations in quantum mechanics play a role analogous to that of canonical transformations in classical mechanics.

[9] From the German word *Spur*. The notation $\mathrm{sp}f$ is also used. The trace can be defined, of course, only if the sum over n is convergent.

It may be noted first of all that the trace of a product of two matrices is independent of the order of multiplication:

$$\text{tr}(fg) = \text{tr}(gf) \tag{12.9}$$

since the rule of matrix multiplication gives

$$\text{tr}(fg) = \sum_n \sum_n f_{nk}g_{kn} = \sum_k \sum_n g_{kn}f_{nk} = \text{tr}(gf).$$

Similarly we can easily see that, for a product of several matrices, the trace is unaffected by a cyclic permutation of the factors; for example,

$$\text{tr}(fgh) = \text{tr}(hfg) = \text{tr}(ghf) \tag{12.10}$$

An important property of the trace is that it does not depend on the choice of the set of functions with respect to which the-matrix elements are defined, since

$$(\text{tr} f)' = \text{tr}(S^{-1}fS) = \text{tr}(S^{-1}Sf) = \text{tr} f \tag{12.11}$$

A unitary transformation leaves unchanged the sum of the squared moduli of the functions that are transformed: from (12.6) we have

$$\sum_i |\psi_i'|^2 = \sum_{k,l,i} S_{ki}\psi_k S_{li}^*\psi_l^* = \sum_{k,l} \psi_k \psi_l^* \delta_{kl} = \sum_k |\psi_k|^2. \tag{12.12}$$

Any unitary operator may be written-as

$$\widehat{S} = e^{i\widehat{R}} \tag{12.13}$$

where $\widehat{R}$ is an Hermitian operator: since $\widehat{R}^\dagger = \widehat{R}$, we have

$$\widehat{S}^\dagger = e^{-i\widehat{R}^\dagger} = e^{-i\widehat{R}} = \widehat{S}^{-1}$$

The expansion

$$\widehat{f'} = \widehat{S}^{-1}\widehat{f}\widehat{S} = \widehat{f} + \{\widehat{f}, i\widehat{R}\} + \frac{1}{2}\{\{\widehat{f}, i\widehat{R}\}, i\widehat{R}\} + \ldots \tag{12.14}$$

is easily verified by a direct expansion of the factors $\exp(\pm i\widehat{R})$ in powers of $\widehat{R}$. This expansion may be useful when $\widehat{R}$ is proportional to a small parameter, so that (12.14) becomes an expansion in powers of the parameter.

§ 13. The Heisenberg representation of operators

In the mathematical formalism of quantum mechanics described here, the operators corresponding to various physical quantities act on functions of the coordinates and do not usually depend explicitly on time. The time dependence of the mean values of physical quantities is due only to the time dependence of the wave function of the state, according to the formula

$$\overline{f}(t) = \int \Psi^*(q,t)\widehat{f}\Psi(q,t)\mathrm{d}q. \tag{13.1}$$

The quantum-mechanical treatment can, however, be formulated also in a somewhat different but equivalent form, in which the time dependence is transferred from the wave functions to the operators. Although we shall not use this *Heisenberg representation* (as opposed to the *Schrödinger representation*) of operators in the present volume, a statement of it is given here with a view to applications in the relativistic theory.

We define the operator (which is unitary; see (12.13))

$$\widehat{S} = \exp\left(-\frac{\mathrm{i}}{\hbar}\widehat{H}t\right), \tag{13.2}$$

where $\widehat{H}$ is the Hamiltonian of the system. By definition, its eigenfunctions are the same as those of the operator $\widehat{H}$, i.e. the stationary-state wave functions $\psi_n(q)$, where

$$\widehat{S}\psi_n(q) = \exp(-\frac{\mathrm{i}}{\hbar}E_n t)\psi_n(q). \tag{13.3}$$

Hence it follows that the expansion (10.3) of an arbitrary wave function Ψ in terms of the stationary-state wave functions can be written in the operator form

$$\Psi(q,t) = \widehat{S}\Psi(q,0), \tag{13.4}$$

i.e. the effect of the operator $\widehat{S}$ is to convert the wave function of the system at some initial instant into the wave function at an arbitrary instant.

Defining, as in (12.7), the time-dependent operator

$$\widehat{f}(t) = \widehat{S}^{-1}\widehat{f}\widehat{S} \tag{13.5}$$

we have

$$\overline{f}(t) = \int \Psi^*(q,0)\widehat{f}(t)\Psi(q,0)\mathrm{d}q, \tag{13.6}$$

and thus obtain the formula (3.8) for the mean value of the quantity f in a form in which the time dependence is entirely transferred to the operator (for our definition of an operator rests on formula (3.8)).

It is evident that the matrix elements of the operator (13.5) with respect to the stationary-state wave functions are the same as the time-dependent matrix elements $f_{nm}(t)$ defined by formula (11.3).

Finally, differentiating the expression (13.5) with respect to time (assuming that the operators $\widehat{f}$ and $\widehat{H}$ do not themselves involve t), we obtain

$$\frac{\partial}{\partial t}\widehat{f}(t) = \frac{\mathrm{i}}{\hbar}\left[\widehat{H}\widehat{f}(t) - \widehat{f}(t)\widehat{H}\right],\tag{13.7}$$

which is similar in form to (9.2) but has a somewhat different significance: the expression (9.2) defines the operator $\widehat{\dot{f}}$ corresponding to the physical quantity $\dot{f}$, while the left-hand side of equation (13.7) is the time derivative of the operator of the quantity f itself.

§ 14. The density matrix

The description of a system by means of a wave function is the most complete description possible in quantum mechanics, in the sense indicated at the end of §1.

States that do not allow such a description are encountered if we consider a system that is part of a larger closed system. We suppose that the closed system as a whole is in some state described by the wave function $\Psi(q, x)$, where x denotes the set of coordinates of the system considered, and q the remaining coordinates of the closed system. This function in general does not fall into a product of functions of x and of q alone, so that the system does not have its own wave function.[10]

Let f be some physical quantity pertaining to the system considered. Its operator therefore acts only on the coordinates x, and not on q. The mean value of this quantity in the state considered is

$$\overline{f} = \iint \Psi^*(q, x)\widehat{f}\Psi(q, x)\mathrm{d}q\mathrm{d}x.\tag{14.1}$$

---

[10] In order that $\Psi(q, x)$ should (at a given instant) fall into such a product, the measurement as a result of which this state was brought about must completely describe the system considered and the remainder of the closed system separately. In order that $\Psi(q, x)$ should continue to have this form at subsequent instants, it is necessary in addition that these parts of the closed system should not interact (see §2). Neither of these conditions is now assumed.

We introduce the function $\rho(x, x')$ defined by

$$\rho(x, x') = \int \Psi(q, x)\Psi^*(q, x')\mathrm{d}q \qquad (14.2)$$

where the integration is extended only over the coordinates q; this function is called the *density matrix* of the system. From the definition (14.2) it is evident that the function is "Hermitian":

$$\rho^*(x, x') = \rho(x', x) \qquad (14.3)$$

The "diagonal elements" of the density matrix

$$\rho(x, x) = \int |\Psi(q, x)|^2 \mathrm{d}q$$

determine the probability distribution for the coordinates of the system.

Using the density matrix, we can write the mean value f in the form

$$\overline{f} = \int \left[\widehat{f}\rho(x, x')_{x'=x}\mathrm{d}x \right] \qquad (14.4)$$

Here $\widehat{f}$ acts only on the variables x in the function $\rho(x, x')$; after calculating the result of its action, we put $x' = x$. We see that, if we know the density matrix, we can calculate the mean value of any quantity characterizing the system. It follows from this that, by means of $\rho(x, x')$, we can also determine the probabilities of various values of the physical quantities in the system. Thus the state of a system which does not have a wave function can be described by means of a density matrix. This does not contain the coordinates q which do not belong to the system concerned, though, of course, it depends essentially on the state of the closed system as a whole.

The description by means of the density matrix is the most general form of quantum-mechanical description of the system. The description by means of the wave function, on the other hand, is a particular case of this, corresponding to a density matrix of the form $\rho(x, x') = \Psi(x)\Psi^*(x')$. The following important difference exists between this particular case and the general one.[11] For a state having a wave function there is always a complete set of measuring processes such that they lead with certainty to definite results (mathematically, this means that Ψ is an eigenfunction of some operator). For states having only a density matrix, on the other hand, there is no complete set of measuring processes whose result can be uniquely predicted.

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[11] States having a wave function are called "pure" states, as distinct from "mixed" states, which are described by a density matrix.

Let us now suppose that the system is closed, or became so at some instant. Then we can derive an equation giving the change in the density matrix with time, similar to the wave equation for the Ψ function. The derivation can be simplified by noticing that the required linear differential equation for $\rho(x, x', t)$ must be satisfied in the particular case where the system has a wave function, i.e.

$$\rho(x, x', t) = \Psi(x, t)\Psi^*(x, t).$$

Differentiating with respect to time and using the wave equation (8.1), we have

$$i\hbar\frac{\partial\rho}{\partial t} = i\hbar\Psi^*(x', t)\frac{\partial\Psi(x, t)}{\partial t} + i\hbar\Psi(x, t)\frac{\partial\Psi^*(x', t)}{\partial t} =$$
$$= \Psi^*(x', t)\widehat{H}\Psi(x, t) - \Psi(x, t)\widehat{H}'^*\Psi^*(x', t),$$

where $\widehat{H}$ is the Hamiltonian of the system, acting on a function of x, and $\widehat{H}'$ is the same operator acting on a function of x'. The functions $\Psi^*(x', t)$ and $\Psi(x, t)$ can obviously be placed behind the respective operators $\widehat{H}$ and $\widehat{H}'$, and we thus obtain the required equation:

$$i\hbar\frac{\partial\rho(x, x', t)}{\partial t} = (\widehat{H} - \widehat{H}'^*)\rho(x, x', t). \tag{14.5}$$

Let $\Psi_n(x, t)$ be the wave functions of the stationary states of the system, i.e. the eigenfunctions of its Hamiltonian. We expand the density matrix in terms of these functions; the expansion consists of a double series in the form

$$\rho(x, x', t) = \sum_m \sum_n a_{mn}\Psi_n^*(x', t)\Psi_m(x, t)$$
$$= \sum_m \sum_n \psi_n^*(x')\psi_m(x)\exp\left(\frac{i}{\hbar}(E_n - E_m)t\right). \tag{14.6}$$

For the density matrix, this expansion plays a part analogous to that of the expansion (10.3) for wave functions. Instead of the set of coefficients a_n, we have here the double set of coefficients a_{mn}. These clearly have the property of being "Hermitian", like the density matrix itself:

$$a_{nm}^* = a_{mn}. \tag{14.7}$$

For the mean value of some quantity f we have, substituting (14.6) in (14.4),

$$\overline{f} = \sum_m \sum_n a_{mn}\int\Psi_n^*(x, t)\widehat{f}\Psi_m(x, t)\mathrm{d}x,$$

or

$$\overline{f} = \sum_m \sum_n a_{mn} f_{nm}(t) = \sum_m \sum_n a_{mn} f_{nm} \exp\left(\frac{\mathrm{i}}{\hbar}(E_n - E_m)t\right), \quad (14.8)$$

where f_{nm} are the matrix elements of the quantity f. This expression is similar to formula (11.1).[12]

The quantities a_{mn} must satisfy certain inequalities. The "diagonal elements" $\rho(x, x)$ of the density matrix, which determine the probability distribution for the coordinates, must obviously be positive quantities. It therefore follows from the expression (14.6) (with $x' = x$) that the quadratic form

$$\sum_n \sum_m a_{mn} \xi_n^* \xi_m$$

constructed with the coefficients a_{mn} (where the ξ_n are arbitrary complex quantities) must be positive. This places certain conditions, known from the theory of quadratic forms, on the quantities a_{nm}. In particular, all the "diagonal" quantities must clearly be positive:

$$a_{nm} \geqslant 0 \qquad (14.9)$$

and any three quantities a_{nn}, a_{mm} and a_{mn} must satisfy the inequality

$$a_{nn} a_{mm} \geqslant |a_{mn}|^2 \qquad (14.10)$$

To the "pure" case, where the density matrix reduces to a product of functions, there evidently corresponds a matrix a_{mn} of the form

$$a_{mn} = a_m a_n^*. \qquad (14.11)$$

We shall indicate a simple criterion which enables us to decide, from the form of the matrix a_{mn}, whether we are concerned with a "pure" or a "mixed" state. In the pure case we have

$$(a^2)_{mn} = \sum_k a_{mk} a_{kn} = \sum_k a_k^* a_m a_n^* a_k = a_m a_n^* \sum_k |a_k|^2 = a_m a_n^*,$$

or

$$(a^2)_{mn} = a_{mn}, \qquad (14.12)$$

i.e. the density matrix is equal to its own square.

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[12] The quantities a_{mn} form the density matrix in the energy representation. The description of the states of a system by means of this matrix was introduced independently by L. Landau and F. Bloch in 1927.

§ 15. Momentum

Let us consider a closed system of particles not in an external field. Since all positions in space of such a system as a whole are equivalent, we can say, in particular, that the Hamiltonian of the system does not vary when the system undergoes a parallel displacement over any distance. It is sufficient that this condition should be fulfilled for an arbitrary small displacement.

An infinitely small parallel displacement over a distance $\delta\boldsymbol{r}$ signifies a transformation under which the radius vectors $\boldsymbol{r}_a$ of all the particles (a being the number of the particle) receive the same increment $\delta\boldsymbol{r} : \boldsymbol{r}_a \to \boldsymbol{r}_a + \delta\boldsymbol{r}$. An arbitrary function $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots)$ of the coordinates of the particles, under such a transformation, becomes the function

$$\psi(\boldsymbol{r_1} + \delta\boldsymbol{r}, \boldsymbol{r_2} + \delta\boldsymbol{r}, \dots) = \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots) + \delta\boldsymbol{r} \cdot \sum_a \nabla_a \psi$$

$$= (1 + \delta\boldsymbol{r} \cdot \nabla_a)\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots)$$

(∇_a denotes the operator of differentiation with respect to $\boldsymbol{r}_a$). The expression

$$1 + \delta\boldsymbol{r} \cdot \nabla_a$$

is the operator of an infinitely small displacement, which converts the function $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots)$ into the function

$$\psi(\boldsymbol{r}_1 + \delta\boldsymbol{r}, \boldsymbol{r}_2 + \delta\boldsymbol{r}, \dots).$$

The statement that some transformation does not change the Hamiltonian means that, if we make this transformation on the function $\widehat{H}\psi$, the result is the same as if we make it only on the function ψ and then apply the operator $\widehat{H}$. Mathematically, this can be written as follows. Let $\widehat{\ }$ be the operator which effects the transformation in question. Then we have $\widehat{O}(\widehat{H}\psi) = \widehat{H}(\widehat{O}\psi)$, whence

$$\widehat{O}\widehat{H} - \widehat{H}\widehat{O} = 0$$

i.e. the Hamiltonian must commute with the operator $\widehat{O}$.

In the case considered, the operator $\widehat{O}$ is the operator of an infinitely small displacement. Since the unit operator (the operator of multiplying by unity) commutes, of course, with any operator, and the constant factor $\delta\boldsymbol{r}$ can be taken in front of $\widehat{H}$, the condition $\widehat{O}\widehat{H} - \widehat{H}\widehat{O} = 0$ reduces here to

$$\left(\sum_a \nabla_a\right)\widehat{H} - \widehat{H}\left(\sum_a \nabla_a\right) = 0 \tag{15.1}$$

As we know, the commutability of an operator (not containing the time explicitly) with $\widehat{H}$ means that the physical quantity corresponding to that operator is conserved. The quantity whose conservation for a closed system follows from the homogeneity of space is the momentum of the system (cf. Mechanics, §7). Thus the relation (15.1) expresses the law of conservation of momentum in quantum mechanics; the operator $\sum_a \nabla_a$ must correspond, apart from a constant factor, to the total momentum of the system, and each term ∇_a of the sum to the momentum of an individual particle.

The coefficient of proportionality between the operator $\widehat{\boldsymbol{p}}$ of the momentum of a particle and the operator ∇ can be determined by means of the passage to the limit of classical mechanics, and is $-\mathrm{i}\hbar$:

$$\widehat{\boldsymbol{p}} = -\mathrm{i}\hbar\nabla \tag{15.2}$$

or, in components,

$$\widehat{p}_x = -\mathrm{i}\hbar\frac{\partial}{\partial x}, \quad \widehat{p}_y = -\mathrm{i}\hbar\frac{\partial}{\partial y}, \quad \widehat{p}_z = -\mathrm{i}\hbar\frac{\partial}{\partial z}$$

Using the limiting expression (6.1) for the wave function, we have

$$\widehat{\boldsymbol{p}} = \mathrm{i}\hbar\frac{\mathrm{i}}{\hbar}\Psi\nabla\boldsymbol{S} = \Psi\nabla\boldsymbol{S}$$

i.e. in the classical approximation the effect of the operator reduces to multiplication by $\nabla\boldsymbol{S}$. The gradient $\nabla\boldsymbol{S}$ of the action is the classical momentum p of the particle (see Mechanics, §43).

It is easy to see that the operator (15.2) is Hermitian, as it should be. For, with arbitrary functions $\psi(x)$ and $\varphi(x)$ which vanish at infinity, we have

$$\int \varphi\widehat{p}_x\psi\,\mathrm{d}x = -\mathrm{i}\hbar\int \varphi\frac{\partial\psi}{\partial x}\,\mathrm{d}x = \mathrm{i}\hbar\int \psi\frac{\partial\varphi}{\partial x}\,\mathrm{d}x = \int \psi\widehat{p}_x^*\varphi\,\mathrm{d}x,$$

and this is the condition that the operator should be Hermitian.

Since the result of differentiating functions with respect to two different variables is independent of the order of differentiation, it is clear that the operators of the three components of momentum commute with one another:

$$\widehat{p}_x\widehat{p}_y - \widehat{p}_y\widehat{p}_x = 0, \quad \widehat{p}_x\widehat{p}_z - \widehat{p}_z\widehat{p}_x = 0 \quad \widehat{p}_y\widehat{p}_z - \widehat{p}_z\widehat{p}_y = 0 \tag{15.3}$$

This means that all three components of the momentum of a particle can simultaneously have definite values.

Let us find the eigenfunctions and eigenvalues of the momentum operators. They are determined by the vector equation

$$\mathrm{i}\hbar\nabla\psi = \boldsymbol{p}\psi \tag{15.4}$$

The solutions are of the form

$$\psi = \mathrm{C} \cdot \mathrm{e}^{\mathrm{i}\boldsymbol{pr}/\hbar} \tag{15.5}$$

where C is a constant. If all three components of the momentum are given simultaneously, we see that this completely determines the wave function of the particle. In other words, the quantities p_x, p_y, p_z form one of the possible complete sets of physical quantities for a particle. Their eigenvalues form a continuous spectrum extending from $-\infty$ to $+\infty$.

According to the rule (5.4) for normalizing the eigenfunctions of a continuous spectrum, the integral $\int \psi_{\boldsymbol{p'}}^* \psi_{\boldsymbol{p}} \mathrm{d}V$ taken over all space $(\mathrm{d}V = \mathrm{d}x\mathrm{d}y\mathrm{d}z)$ must be equal to the delta function $\delta(\boldsymbol{p'} - \boldsymbol{p})$.[13] However, for reasons that will become clear from subsequent applications, it is more natural to normalize the eigenfunctions of the particle momentum by the delta function of the momentum difference divided by $2\pi\hbar$:

$$\int \psi_{\boldsymbol{p'}}^* \psi_{\boldsymbol{p}} \mathrm{d}V = \left(\frac{\boldsymbol{p'} - \boldsymbol{p}}{2\pi\hbar} \right)$$

or, equivalently,

$$\int \psi_{\boldsymbol{p'}}^* \psi_{\boldsymbol{p}} \mathrm{d}V = (2\pi\hbar)^3 \delta(\boldsymbol{p'} - \boldsymbol{p}) \tag{15.6}$$

(since each of the three factors in the three-dimensional delta function is $\delta[(p_x' - p_x)/2\pi\hbar] = 2\pi\hbar\delta(p_x'p_x)$, and so on).

The integration is effected by means of the formula[14]

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{e}^{\mathrm{i}\alpha\xi} \mathrm{d}\xi = \delta(\alpha) \tag{15.7}$$

This shows that the constant in (15.5) is equal to unity if the normalization is according to (15.6):[15]

$$\psi_{\boldsymbol{p}} = \mathrm{e}^{\mathrm{i}\boldsymbol{pr}/\hbar} \tag{15.8}$$

---

[13] The three-dimensional function $\delta(\boldsymbol{a})$ of a vector $\boldsymbol{a}$ is defined as a product of delta functions of the components of the vector $\boldsymbol{a}$: $\delta(\boldsymbol{a}) = \delta(a_x)\delta(a_y)\delta(a_z)$.

[14] The conventional meaning of this formula is that the function on the left-hand side has the property (5.8) of the delta function. Substituting $\delta(x - a)$ in the form (15.7), we obtain from (5.8) the well-known Fourier integral formula

$$f(a) = \iint_{-\infty}^{\infty} f(x)\mathrm{e}^{\mathrm{i}\xi(x-a)}\mathrm{d}x\frac{\mathrm{d}\xi}{2\pi}$$

[15] Note that with this normalization the probability density $|\Psi|^2 = 1$, i.e. the function is normalised to "one particle per unit volume". This agreement of normalizations is, of course, no accident; see the last footnote to §48.

The expansion of an arbitrary wave function $\psi(\boldsymbol{r})$ of a particle in terms of the eigenfunctions $\psi_{\boldsymbol{p}}$ of its momentum operator is simply the expansion as a Fourier integral:

$$\psi(\boldsymbol{r}) = \int a(\boldsymbol{p})\psi_{\boldsymbol{p}}(\boldsymbol{r})\frac{\mathrm{d}^3 p}{(2\pi\hbar)^3} = \int a(\boldsymbol{p})\mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}\frac{\mathrm{d}^3 p}{(2\pi\hbar)^3} \qquad (15.9)$$

(where $\mathrm{d}^3 p = \mathrm{d}p_x \mathrm{d}p_y \mathrm{d}p_z$). The expansion coefficients $a(\boldsymbol{p})$ are, according to formula (5.3),

$$a(\boldsymbol{p}) = \int \psi(\boldsymbol{r})\psi_{\boldsymbol{p}}^*(\boldsymbol{r})\mathrm{d}V = \int \psi(\boldsymbol{r})\mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}\mathrm{d}V \qquad (15.10)$$

The function $a(\boldsymbol{p})$ can be regarded (see §5) as the wave function of the particle in the "momentum representation";

$$|a(\boldsymbol{p})|^2 \frac{\mathrm{d}^3 p}{(2\pi\hbar)^3}$$

is the probability that the momentum has a value in the interval $\mathrm{d}^3 p$.

Just as the operator $\widehat{\boldsymbol{p}}$ corresponds to the momentum, determining its eigenfunctions in the coordinate representation, we can introduce the operator $\widehat{\boldsymbol{r}}$ of the coordinates of the particle in the momentum representation. It must be defined so that the mean value of the coordinates can be represented in the form

$$\overline{\boldsymbol{r}} = \int a^*(\boldsymbol{p})\widehat{\boldsymbol{r}}a(\boldsymbol{p})\frac{\mathrm{d}^3 p}{(2\pi\hbar)^3} \qquad (15.11)$$

On the other hand, this mean value is determined from the wave function $\psi(\boldsymbol{r})$ by

$$\overline{\boldsymbol{r}} = \int \psi^* \boldsymbol{r}\psi\mathrm{d}V.$$

Substituting $\psi(\boldsymbol{r})$ in the form (15.9) we have (integrating by parts)

$$\boldsymbol{r}\psi(\boldsymbol{r}) = \int \boldsymbol{r}a(\boldsymbol{p})\mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}\frac{\mathrm{d}^3 p}{(2\pi\hbar)^3} = \int \mathrm{i}\hbar\mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}\frac{\partial a(\boldsymbol{p})}{\partial\boldsymbol{p}}\frac{\mathrm{d}^3 p}{(2\pi\hbar)^3}$$

Using this expression and (15.10), we find

$$\overline{\boldsymbol{r}} = \iint \psi^*(\boldsymbol{r})\mathrm{i}\hbar\frac{\partial a(\boldsymbol{p})}{\partial\boldsymbol{p}}\mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}\mathrm{d}V\frac{\mathrm{d}^3 p}{(2\pi\hbar)^3} = \int \mathrm{i}\hbar a^*(\boldsymbol{p})\frac{\partial a(\boldsymbol{p})}{\partial\boldsymbol{p}}\frac{\mathrm{d}^3 p}{(2\pi\hbar)^3}$$

Comparing with (15.11), we see that the radius vector operator in the momentum representation is

$$\widehat{\boldsymbol{r}} = \mathrm{i}\hbar\frac{\partial}{\partial\boldsymbol{p}} \qquad (15.12)$$

The momentum operator in this representation reduces simply to multiplication by $\boldsymbol{p}$.

Finally, we shall express in terms of $\widehat{\boldsymbol{p}}$ the operator of a parallel displacement in space over any finite (not only infinitesimal) distance $\boldsymbol{a}$. By the definition of this operator $(\widehat{T}_{\boldsymbol{a}})$ we must have

$$\widehat{T}_{\boldsymbol{a}}\psi(\boldsymbol{r}) = \psi(\boldsymbol{r} + \boldsymbol{a}).$$

Expanding the function $\psi(\boldsymbol{r} + \boldsymbol{a})$ in a Taylor series, we have

$$\psi(\boldsymbol{r} + \boldsymbol{a}) = \psi(\boldsymbol{r}) + \boldsymbol{a} \cdot \frac{\partial\psi(\boldsymbol{r})}{\partial\boldsymbol{r}} + \dots,$$

or, introducing the operator $\widehat{\boldsymbol{p}} = \mathrm{i}\hbar\nabla$,

$$\psi(\boldsymbol{r} + \boldsymbol{a}) = \left[1 + \frac{\mathrm{i}}{\hbar}\boldsymbol{a} \cdot \widehat{\boldsymbol{p}} + \frac{1}{2}\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{a} \cdot \widehat{\boldsymbol{p}}\right)^2 + \dots\right]\psi(\boldsymbol{r}).$$

The expression in brackets is the operator

$$\widehat{T}_{\boldsymbol{a}} = \exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{a} \cdot \widehat{\boldsymbol{p}}\right) \tag{15.13}$$

This is the required operator of the *finite displacement.*

§ 16. Uncertainty relations

Let us derive the rules for commutation between momentum and coordinate operators. Since the result of successively differentiating with respect to one of the variables x, y, z and multiplying by another of them does not depend on the order of these operations, we have

$$\widehat{p}_x y - y\widehat{p}_x = 0, \quad \widehat{p}_x z - z\widehat{p}_x = 0 \tag{16.1}$$

and similarly for $\widehat{p}_y, \widehat{p}_z$.

To derive the commutation rule for $\widehat{p}_x$ and x, we write

$$(\widehat{p}_x x - x\widehat{p}_x)\psi = -\mathrm{i}\hbar\frac{\partial}{\partial x}(x\psi) + \mathrm{i}\hbar x\frac{\partial\psi}{\partial x} = \mathrm{i}\hbar\psi$$

We see that the result of the action of the operator $\widehat{p}_x x - x\widehat{p}_x$ reduces to multiplication by $\mathrm{i}\hbar$; the same is true, of course, of the commutation of $\widehat{p}_y$ with y and $\widehat{p}_z$ with z. Thus we have[16]

$$\widehat{p}_x - x\widehat{p}_x = -\mathrm{i}\hbar, \qquad \widehat{p}_y - y\widehat{p} = -\mathrm{i}\hbar, \qquad \widehat{p}_x x - x\widehat{p}_x = -\mathrm{i}\hbar \tag{16.2}$$

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[16] These relations, discovered in matrix form by Heisenberg in 1925, formed the genesis of quantum mechanics.

All the relations (16.1) and (16.2) can be written jointly in the form

$$\widehat{p}_i x_k - x_k \widehat{p}_i = -i\hbar\delta_{ik}, \qquad (i, k = x, y, z) \tag{16.3}$$

Before going on to examine the physical significance of these relations and their consequences, we shall set down two formulae which will be useful later. Let $f(\boldsymbol{r})$ be some function of the coordinates. Then

$$\widehat{\boldsymbol{p}}f(\boldsymbol{r}) - f(\boldsymbol{r})\widehat{\boldsymbol{p}} = -i\hbar\nabla f \tag{16.4}$$

For

$$(\widehat{\boldsymbol{p}}f - f\widehat{\boldsymbol{p}})\psi = -i\hbar[\nabla(f\psi) - f\nabla\psi] = -i\hbar\psi\nabla f$$

A similar relation holds for the commutator of $\boldsymbol{r}$ with a function of the momentum operator:

$$f(\widehat{\boldsymbol{p}})\boldsymbol{r} - \boldsymbol{r}f(\widehat{\boldsymbol{p}}) = -i\hbar\frac{\partial f}{\partial \boldsymbol{p}} \tag{16.5}$$

It can be derived in the same way as (16.4) if we calculate in the momentum representation, using the expression (15.12) for the coordinate operators.

The relations (16.1) and (16.2) show that the coordinate of a particle along one of the axes can have a definite value at the same time as the components of the momentum along the other two axes; the coordinate and momentum component along the same axis, however, cannot exist simultaneously. In particular, the particle cannot be at a definite point in space and at the same time have a definite momentum $\boldsymbol{p}$.

Let us suppose that the particle is in some finite region of space, whose dimensions along the three axes are (of the order of magnitude of) Δx, Δy, Δz. Also, let the mean value of the momentum of the particle be $\boldsymbol{p}_0$. Mathematically, this means that the wave function has the form $\psi = u(\boldsymbol{r})e^{i\boldsymbol{p}_0\boldsymbol{r}/\hbar}$, where $u(\boldsymbol{r})$ is a function which differs considerably from zero only in the region of space concerned. We expand the function ψ in terms of the eigenfunctions of the momentum operator (i.e. as a Fourier integral). The coefficients $a(\boldsymbol{p})$ in this expansion are determined by the integrals (15.10) of functions of the form $u(\boldsymbol{r})e^{i(\boldsymbol{p}_0-\boldsymbol{p})\boldsymbol{r}/\hbar}$. If this integral is to differ considerably from zero, the periods of the oscillatory factor $e^{i(\boldsymbol{p}_0-\boldsymbol{p})\boldsymbol{r}/\hbar}$ must not be small in comparison with the dimensions Δx, Δy, Δz of the region in which the function $u(\boldsymbol{r})$ is different from zero. This means that $a(\boldsymbol{p})$ will be considerably different from zero only for values of $\boldsymbol{p}$ such that $(p_{0x} - p_x)\Delta x/\hbar \lesssim 1$, etc. Since $|a(\boldsymbol{p})|^2$ determines the probability of the various values of the momentum, the ranges of values of p_x, p_y, p_z in which $a(\boldsymbol{p})$ differs from zero are just those

in which the components of the momentum of the particle may be found, in the state considered. Denoting these ranges by Δp_x, Δp_y, Δp_z, we thus have

$$\Delta p_x \Delta x \sim \hbar, \qquad \Delta p_y \Delta y \sim \hbar, \qquad \Delta p_z \Delta z \sim \hbar \qquad (16.6)$$

These relations, known as the *uncertainty relations*, were obtained by Heisenberg in 1927.

We see that, the greater the accuracy with which the coordinate of the particle is known (i.e. the less Δx), the greater the uncertainty Δp_x in the component of the momentum along the same axis, and *vice versa*. In particular, if the particle is at some completely definite point in space ($\Delta x = \Delta y = \Delta z = 0$), then $\Delta p_x = \Delta p_y = \Delta p_z = \infty$. This means that all values of the momentum are equally probable. Conversely, if the particle has a completely definite momentum $\boldsymbol{p}$, then all positions of it in space are equally probable (this is seen directly from the wave function (15.8), whose squared modulus is quite independent of the coordinates).

If the uncertainties of the coordinates and momenta are specified by the standard deviations

$$\delta x = \sqrt{\overline{(x - \overline{x})^2}}, \quad \delta p_x = \sqrt{\overline{(x - \overline{x})^2}},$$

we can specify exactly the least possible value of their product (H. Weyl). Let us consider the one-dimensional case of a wave packet with wave function $\psi(x)$ depending on only one coordinate, and assume for simplicity that the mean values of x and p_x in this state are zero. We consider the obvious inequality

$$\int_{-\infty}^{\infty} \left| \alpha x \psi + \frac{\mathrm{d}\psi}{\mathrm{d}x} \right|^2 \mathrm{d}x \geqslant 0$$

where α is an arbitrary real constant. On calculating this integral, noticing that

$$\int_{-\infty}^{\infty} x^2 |\psi|^2 \mathrm{d}x = (\delta x)^2,$$

$$\int \left(x \frac{\mathrm{d}\psi^*}{\mathrm{d}x} \psi + x \psi^* \frac{\mathrm{d}\psi}{\mathrm{d}x} \right) \mathrm{d}x = \int x \frac{\mathrm{d}|\psi|^2}{\mathrm{d}x} \mathrm{d}x = -\int |\psi|^2 \mathrm{d}x = -1,$$

$$\int \frac{\mathrm{d}\psi^*}{\mathrm{d}x} \frac{\mathrm{d}\psi}{\mathrm{d}x} \mathrm{d}x = -\int \psi^* \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} \mathrm{d}x = \frac{1}{\hbar^2} \int \psi^* \widehat{p}_x^2 \psi \mathrm{d}x = \frac{1}{\hbar^2} (\delta p_x)^2,$$

we obtain

$$\alpha^2 (\delta x)^2 - \alpha + \frac{(\delta p_x)^2}{\hbar^2} \geqslant 0$$

If this quadratic (in α) trinomial is positive for all α, its discriminant must be negative, which gives the inequality

$$\delta x \delta p_x \geqslant 0 \tag{16.7}$$

The least possible value of the product is $\hbar/2$, and occurs for wave packets with wave functions of the form

$$\psi = \frac{1}{(2\pi)^{1/4}\sqrt{\delta x}} \exp\left(\frac{i}{\hbar}p_0 x - \frac{x^2}{4(\delta x)^2}\right) \tag{16.8}$$

where p_0 and δx are constants. The probabilities of the various values of the coordinates in such a state are

$$|\psi|^2 = \frac{1}{\sqrt{2\pi}\delta x} \exp\left(-\frac{x^2}{2(\delta x)^2}\right)$$

and thus have a Gaussian distribution about the origin (the mean value $\overline{x} = 0$) with standard deviation δx. The wave function in the momentum representation is

$$a(p_x) = \int_{-\infty}^{\infty} \psi(x) \exp\left(-i\frac{p_x x}{\hbar}\right) dx$$

Calculation of the integral gives

$$a(p_x) = \text{const} \cdot \exp\left(-\frac{(\delta x)^2(p_x - p_0)^2}{\hbar^2}\right).$$

The distribution of probabilities of values of the momentum, $|a(p_x)|^2$, is also Gaussian about the mean value $\overline{p_x} = p_0$, with standard deviation $\delta p_x = \hbar/2\delta x$, so that the product $\delta p_x \delta x$ is indeed $\hbar/2$.

Finally, we shall derive another useful relation. Let f and g be two physical quantities whose operators obey the commutation rule

$$\widehat{f}\widehat{g} - \widehat{g}\widehat{f} = -i\hbar\widehat{c} \tag{16.9}$$

where $\widehat{c}$ is the operator of some physical quantity c. On the right-hand side of the equation the factor $\hbar$ is introduced in accordance with the fact that in the classical limit (i.e. as $\hbar \to 0$) all operators of physical quantities reduce to multiplication by these quantities and commute with one another. Thus, in the "quasi-classical" case, we can, to a first approximation, regard the right-hand side of equation (16.9) as being zero. In the next approximation,

the operator   can be replaced by the operator of simple multiplication by the quantity c. We then have

$$\widehat{f}\widehat{g} - \widehat{g}\widehat{f} = -\mathrm{i}\hbar c.$$

This equation is exactly analogous to the relation $\widehat{p}_x x - x\widehat{p}_x = -\mathrm{i}\hbar$, the only difference being that, instead of the constant $\hbar$, we have[17] the quantity $\hbar c$. We can therefore conclude, by analogy with the relation $\Delta x \Delta p_x \sim \hbar$, that in the quasi-classical case there is an uncertainty relation

$$\Delta f \Delta g \sim \hbar c \qquad (16.10)$$

for the quantities f and g.

In particular, if one of these quantities is the energy $(\widehat{f} \equiv \widehat{H})$ and the operator $(\widehat{g})$ of the other does not depend explicitly on the time, then by 9.2 $c = \dot{g}$, and the uncertainty relation in the quasi-classical case is

$$\Delta E \Delta g \sim \hbar \dot{g}. \qquad (16.11)$$

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[17] The classical quantity c is the Poisson bracket of the quantities f and g; see the footnote in §9.

CHAPTER III

SCHRÖDINGER'S EQUATION

§ 17. Schrödinger's equation

The form of the wave equation of a physical sysytem is detemined by its Hamiltonian, which is therefore of fundamental significance in the whole mathematical fomulation of quantum mechanics.

The form of the Hamiltonian for a free particle is established by the general requirements imposed by the homogeneity and isotropy of space and by Galileo's relativity principle. In classical mechanics, these requirements lead to a quadratic dependence of the energy of the particle on its momentum: $E = p^2/2m$, where the constant m is called the mass of the particle (see Mechanics, §4). In quantum mechanics, the same requirements lead to a corresponding relation for the energy and momentum eigenvalues, these quantities being conserved and simultaneously measurable (for a free particle).

If the relation $E = p^2/2m$ holds for every eigenvalue of the energy and momentum, the same relation must hold for their operators also:

$$\widehat{H} = \frac{1}{2m} \left(\widehat{p}_x^2 + \widehat{p}_y^2 + \widehat{p}_z^2 . \right) \tag{17.1}$$

Substituting here from (15.2), we obtain the Hamiltonian of a freely moving particle in the form

$$\widehat{H} = -\frac{\hbar}{2m} \Delta \tag{17.2}$$

where $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ is the Laplacian operator.

The Hamiltonian of a system of non-interacting particles is equal to the sum of the Hamiltonians of the separate particles:

$$\widehat{H} = -\frac{\hbar^2}{2} \sum_a \frac{\Delta_a}{m_a} \tag{17.3}$$

(the suffix a is the number of the particle; Δ_a is the Laplacian operator in which the differentiation is with respect to the coordinates of the ath particle).

In classical (non-relativistic) mechanics, the interaction of particles is described by an additive term in the Hamiltonian, the potential energy of the interaction $U(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots)$, which is a function of the coordinates of the particles. By adding a similar function to the Hamiltonian of the system, the interaction of particles can be represented in quantum mechanics[1] :

$$\widehat{H} = -\frac{\hbar^2}{2} \sum_a \frac{\Delta_a}{m_a} + U(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots). \qquad (17.4)$$

The first term can be regarded as the operator of the kinetic energy and the second as that of the potential energy. In particular, the Hamiltonian for a single particle in an external field is

$$\widehat{H} = \frac{\widehat{p}^2}{2m} + U(x, y, z) = -\frac{\hbar^2}{2m}\Delta + U(x, y, z), \qquad (17.5)$$

where $U(x, y, z)$ is the potential energy of the particle in the external field.

Substituting the expressions (17.2) to (17.5) in the general equation (8.1), we obtain the wave equations for the corresponding systems. We shall write out here the wave equation for a particle in an external field:

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\Delta\Psi + U(x, y, z) \qquad (17.6)$$

The equation (10.2), which determines the stationary states, takes the form

$$\frac{\hbar^2}{2m}\Delta\psi + [E - U(x, y, z)]\,\psi = 0 \qquad (17.7)$$

The equations (17.6) and (17.7) were obtained by Schrödinger in 1926 and are called *Schrödinger's equations.*

For a free particle, equation (17.7) has the form

$$\frac{\hbar^2}{2m}\Delta\psi + E\psi = 0 \qquad (17.8)$$

This equation has solutions finite in all space for any positive value of the energy E. For states with definite directions of motion, these solutions are

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[1] This statement is, of course, not a logical consequence of the basic principles of quantum mechanics, and is to be regarded as a deduction from experiment.

eigenfunctions of the momentum operator, with $E = p^2/2m$. The complete (time-dependent) wave functions of such stationary states are

$$\Psi = \text{const} \cdot \exp\left(\frac{\text{i}}{\hbar}\left(Et - \boldsymbol{pr}\right)\right). \tag{17.9}$$

Each such function, a *plane wave*, describes a state in which the particle has a definite energy E and momentum $\boldsymbol{p}$. The angular frequency of this wave is $E/\hbar$ and its wave vector $\boldsymbol{k} = \boldsymbol{p}/\hbar$; the corresponding wavelength $2\pi\hbar/p$ is called the *de Broglie wavelength* of the particle.[2]

The energy spectrum of a freely moving particle is thus found to be continuous, extending from zero to $+\infty$. Each of these eigenvalues (except $E = 0$) is degenerate, and the degeneracy is infinite. For there corresponds to every value of E, different from zero, an infinite number of eigenfunctions (17.9), differing in the direction of the vector $\boldsymbol{p}$, which has a constant absolute magnitude.

Let us enquire how the passage to the limit of classical mechanics occurs in Schrödinger's equation, considering for simplicity only a single particle in an external field. Substituting in Schrödinger's equation (17.6) the limiting expression (6.1) for the wave function,$\Psi = ae^{\text{i}S/\hbar}$, we obtain, on performing the differentiation,

$$a\frac{\partial S}{\partial t} - \text{i}\hbar\frac{\partial a}{\partial t} + \frac{a}{2m}(\nabla S)^2 - \frac{\text{i}\hbar}{2m}a\Delta S - \frac{\text{i}\hbar}{m}\nabla S\nabla a - \frac{\hbar^2}{2m}\Delta a + Ua = 0.$$

In this equation there are purely real and purely imaginary terms (we recall that S and a are real); equating each separately to zero, we obtain two equations

$$\frac{\partial S}{\partial t} + \frac{1}{2m}(\nabla S)^2 + U - \frac{\hbar^2}{2ma}\Delta a = 0,$$

$$\frac{\partial a}{\partial t} + \frac{a}{2m}\Delta S + \frac{1}{m}\nabla S\nabla a = 0.$$

Neglecting the term containing $\hbar$ in the first of these equations, we obtain

$$\frac{\partial S}{\partial t} + \frac{1}{2m}(\nabla S)^2 + U = 0, \tag{17.10}$$

that is; the classical Hamilton—Jacobi equation for the action S of a particle, as it should be. We see, incidentally, that, as $\hbar \to 0$, classical mechanics is valid as far as quantities of the first (and not only the zero) order in $\hbar$ inclusive.

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[2] The idea of a wave related to a particle was first introduced by L. de Broglie in 1924.

The second equation obtained above, on multiplication by $2a$, can be rewritten in the form

$$\frac{\partial a^2}{\partial t} + \text{div}\left(a^2 \frac{\nabla S}{m}\right) = 0 \tag{17.11}$$

This equation has an obvious physical meaning: a^2 is the probability density for finding the particle at some point in space($|\Psi|^2 = a^2$);$\nabla S/m = \boldsymbol{p}/m$ is the classical velocity $\boldsymbol{v}$ of the particle. Hence equation (17.11) is simply the equation of continuity, which shows that the probability density "moves" according to the laws of classical mechanics with the classical velocity $\boldsymbol{v}$ at every point.

PROBLEM

Find the transformation law for the wave function in a Galilean transformation.

SOLUTION.Let us apply the transformation to the wave function for free motion of a particle (a plane wave). Since any function Ψ can be expanded in plane waves, this will also give the transformation law for any wave function.

The plane waves in the frames of reference K and K' (K' moving with velocity V relative to K) are

$$\Psi(\boldsymbol{r}, t) = \text{const} \cdot \exp\left[\text{i}(\boldsymbol{p}\boldsymbol{r} - Et)/\hbar\right],$$

$$\Psi'(\boldsymbol{r}', t) = \text{const} \cdot \exp\left[\text{i}(\boldsymbol{p}'\boldsymbol{r}' - E't)/\hbar\right],$$

where $\boldsymbol{r} = \boldsymbol{r}' + \boldsymbol{V}t$; the particle momenta and energies in the two frames are related by

$$\boldsymbol{p} = \boldsymbol{p}' + m\boldsymbol{V}, E = E' + \boldsymbol{V}\boldsymbol{p}' + mV^2/2$$

(see Mechanics, §8). Substitution of these expressions in Ψ gives

$$\Psi(\boldsymbol{r}, t) = \Psi'(\boldsymbol{r}', t)\exp\left[\frac{\text{i}}{\hbar}\left(m\boldsymbol{V}\boldsymbol{r}' + \frac{mV^2}{2}t\right)\right] =$$

$$= \Psi'(\boldsymbol{r} - \boldsymbol{V}t, t)\exp\left[\frac{\text{i}}{\hbar}\left(m\boldsymbol{V}\boldsymbol{r} - \frac{mV^2}{2}t\right)\right]. \tag{1}$$

This formula does not contain the parameters of the free motion of the particle, and gives the required general transformation law for the wave function of any state of the particle. For a system of particles, the exponent in (1) contains a summation over the particles.

§ 18. The fundamental properties of Schrödinger's equation

The conditions which must be satisfied by solutions of Schrödinger's equation are very general in character. First of all, the wave function must be

single-valued and continuous in all space. The requirement of continuity is maintained even in cases where the field $U(x, y, z)$ itself has a surface of discontinuity. At such a surface both the wave function and its derivatives must remain continuous. The continuity of the derivatives, however, does not hold if there is some surface beyond which the potential energy U becomes infinite. A particle cannot penetrate at all into a region of space where $U = \infty$, i.e. we must have $\psi = 0$ everywhere in this region. The continuity of ψ means that ψ vanishes at the boundary of this region; the derivatives of ψ, however, in general are discontinuous in this case.

If the field $U(x, y, z)$ nowhere becomes infinite, then the wave function also must be finite in all space. The same condition must hold in cases where U becomes infinite at some point but does so only as $1/r^s$ with $s < 2$ (see also §35).

Let $U_{\min}$ be the least value of the function $U(x, y, z)$. Since the Hamiltonian of a particle is the sum of two terms, the operators of the kinetic energy $\widehat{T}$ and of the potential energy, the mean value $\overline{E}$ of the energy in any state is equal to the sum $\overline{T} + \overline{U}$. But all the eigenvalues of the operator $\widehat{T}$(which is the Hamiltonian of a free particle) are positive; hence the mean value $\overline{T} \geqslant 0$. Recalling also the obvious inequality $\overline{U} > U_{\min}$, we find that $\overline{E} > U_{\min}$. Since this inequality holds for any state, it is clear that it is valid for all the eigenvalues of the energy:

$$E_n > U_{\min} \tag{18.1}$$

Let us consider a particle moving in an external field which vanishes at infinity; we define the function $U(x, y, z)$, in the usual way, so that it vanishes at infinity. It is easy to see that the spectrum of negative eigenvalues of the energy will then be discrete, i.e. all states with $E < 0$ in a field which vanishes at infinity are bound states. For, in the stationary states of a continuous spectrum, which correspond to infinite motion, the particle reaches infinity (see §10); however, at sufficiently large distances the field may be neglected, the motion of the particle may be regarded as free, and the energy of a freely moving particle can only be positive.

The positive eigenvalues, on the other hand, form a continuous spectrum and correspond to an infinite motion; for $E > 0$, Schrödinger's equation in general has no solutions (in the field concerned) for which the integral $\int |\psi|^2 \mathrm{d}V$ converges.[3]

Attention must be drawn to the fact that, in quantum mechanics, a particle in a finite motion may be found in those regions of space where $E < U$; the

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[3] However, it must be mentioned that, for some particular mathematical forms of the function U (x, y, z) (which have no physical significance), a discrete set of values may be absent from the otherwise continuous spectrum.

probability $|\psi|^2$ of finding the particle tends rapidly to zero as the distance into such a region increases, yet it differs from zero at all finite distances. Here there is a fundamental difference from classical mechanics, in which a particle cannot penetrate into a region where $U > E$. In classical mechanics the impossibility of penetrating into this region is related to the fact that, for $E < U$, the kinetic energy would be negative, that is, the velocity would be imaginary. In quantum mechanics, the eigenvalues of the kinetic energy are likewise positive; nevertheless, we do not reach a contradiction here, since, if by a process of measurement a particle is localized at some definite point of space, the state of the particle is changed, as a result of this process, in such a way that it ceases in general to have any definite kinetic energy.

If $U(x, y, z) > 0$ in all space(and $U \to 0$ at infinity), then, by the inequality (18.1), we have $E_n > 0$. Since, on the other hand, for E > 0 the spectrum must be continuous, we conclude that, in this case, the discrete spectrum is absent altogether, i.e. only an infinite motion of the particle is possible.

Let us suppose that, at some point (which we take as origin), U tends to $-\infty$ in the manner

$$U \approx -\alpha r^{-s}, \quad \alpha > 0. \tag{18.2}$$

We consider a wave function finite in some small region (of radius r_0) about the origin, and equal to zero outside this region. The uncertainty in the values of the coordinates of a particle in such a wave packet is of the order of r_0; hence the uncertainty in the value of the momentum is $\sim \hbar/r_0$. The mean value of the kinetic energy in this state is of the order of $\hbar^2/mr_0^2$, and the mean value of the potential energy is $\sim -\alpha/r_0^s$. Let us first suppose that s < 2. Then the sum

$$h^2/mr_0^2 - \alpha/r_0^s$$

takes arbitrarily larpe negative values for sufficiently small r_0. If, however, the mean energy can take such values, this always means that the energy has negative eigenvalues which are arbitrarily large in absolute value. The motion of the particle in a very small region of space near the origin corresponds to the energy levels with large $|E|$. The "normal" state corresponds to a particle at the origin itself, i.e. the particle "falls" to the point $r = 0$.

If, however, s < 2, the energy cannot take arbitrarily large negative values. The discrete spectrum begins at some finite negative value. In this case the particle does not fall to the centre. It should be mentioned that, in classical mechanics, the fall of a particle to the centre would be possible in principle in any attractive field (i.e. for any positive s). The case $s = 2$ will be specially considered in §35.

Next, let us investigate how the nature of the energy spectrum depends on the behaviour of the field at large distances. We suppose that, as $r \to \infty$, the

potential energy, which is negative, tends to zero according to the power law (18.2) (r is now large in this formula), and consider a wave packet "filling" a spherical shell of large radius r_0 and thickness $\Delta r \ll r_0$. Then the order of magnitude of the kinetic energy is again $\hbar^2/m(\Delta r)^2$, and of the potential energy, $-\alpha/r_0^s$. We increase r_0, at the same time increasing Δr, in such a way that Δr increases proportionally to r_0. If $s < 2$, then the sum becomes negative for sufficiently large r_0. Hence it follows that there are stationary states of negative energy, in which the particle may be found, with a fair probability, at large distances from the origin. This, however, means that there are levels of arbitrarily small negative energy (it must be recalled that the wave functions rapidly tend to zero in the region of space where $U > E$). Thus, in this case, the discrete spectrum contains an infinite number of levels, which become denser and denser towards the level $E = 0$.

If the field diminishes as $-1/r^s$ at infinity, with $s > 2$, then there are not levels of arbitrarily small negative energy. The discrete spectrum terminates at a level with a non-zero absolute value, so that the total number of levels is finite.

Schrödinger's equation for the wave functions ψ of stationary states is real, as are the conditions imposed on its solution. Hence its solutions can always be taken as real.[4] The eigenfunctions of non-degenerate values of the energy are automatically real, apart from the unimportant phase factor. For ψ^* satisfies the same equation as ψ, and therefore must also be an eigenfunction for the same value of the energy; hence, if this value is not degenerate, ψ and ψ^* must be essentially the same, i.e. they can differ only by a constant factor (of modulus unity). The wave functions corresponding to the same degenerate energy level need not be real, however, but by a suitable choice of linear combinations of them we can always obtain a set of real functions.

The complete (time-dependent) wave functions Ψ are determined by an equation in whose coefficients i appears. This equation, however, retains the same form if we replace t in it by $-t$ and at the same time take the complex conjugate.[5] Hence we can always choose the functions Ψ in such a way that Ψ and Ψ^* differ only by the sign of the time.

As is well known, the equations of classical mechanics are unchanged by time reversal, i.e. when the sign of the time is reversed. In quantum mechanics, the symmetry with respect to the two directions of time is expressed, as we see, in the invariance of the wave equation when the sign of t is changed and Ψ is simultaneously replaced by Ψ^*. However, it must be recalled that

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[4] These assertions are not valid for systems in a magnetic field.

[5] It is assumed that the potential energy U does not depend explicitly on the time: the system is either closed or in a constant (non-magnetic) field.

this symmetry here relates only to the equation, and not to the concept of measurement itself, which plays a fundamental part in quantum mechanics (as we have explained in detail in §7).

§ 19. The current density

In classical mechanics the velocity $\boldsymbol{v}$ of a particle is related to its momentum by $\boldsymbol{p} = m\boldsymbol{v}$. A similar relation holds between the corresponding operators in quantum mechanics, as we should expect. This is easily shown by calculating the operator by the general rule (9.2) for the differentiation of operators with respect to time:

$$\widehat{\boldsymbol{v}} = \frac{\mathrm{i}}{\hbar} \left(\widehat{H}\boldsymbol{r} - \boldsymbol{r}\widehat{H} \right).$$

Using the expression (17.5) for $\widehat{H}$ and formula (16.5), we obtain

$$\widehat{\boldsymbol{v}} = \boldsymbol{p}/m \tag{19.1}$$

Similar relations will clearly hold between the eigenvalues of the velocity and momentum, and between their mean values in any state.

The velocity, like the momentum of a particle, cannot have a definite value simultaneously with the coordinates. But the velocity multiplied by an infinitely short time interval $\mathrm{d}t$ gives the displacement of the particle in the time $\mathrm{d}t$. Hence the fact that the velocity cannot exist at the same time as the coordinates means that, if the particle is at a definite point in space at some instant, it has no definite position at an infinitely close subsequent instant.

We may notice a useful formula for the operator $\widehat{\dot{f}}$ of the derivative, with respect to time, of some quantity $f(r)$ which is a function of the radius vector of the particle. Bearing in mind that f commutes with $U(r)$, we find

$$\widehat{\dot{f}} = \frac{\mathrm{i}}{\hbar} \left(\widehat{H}f - f\widehat{H} \right) = \frac{\mathrm{i}}{2m\hbar} \left(\widehat{\boldsymbol{p}}^2 f - f\widehat{\boldsymbol{p}}^2 \right).$$

Using (16.4), we can write

$$\widehat{\boldsymbol{p}}^2 f = \widehat{\boldsymbol{p}}(f\widehat{\boldsymbol{p}} - \mathrm{i}\hbar\nabla f), \quad f\widehat{\boldsymbol{p}}^2 = (\widehat{\boldsymbol{p}}f - \mathrm{i}\hbar\nabla f)\widehat{\boldsymbol{p}}$$

Thus we obtain the required expression:

$$\widehat{\dot{f}} = \frac{1}{2m} \left(\widehat{\boldsymbol{p}}\nabla f + \nabla f \cdot \widehat{\boldsymbol{p}} \right) \tag{19.2}$$

Next, let us find the acceleration operator. We have

$$\widehat{\boldsymbol{v}} = \frac{\mathrm{i}}{\hbar}\left(\widehat{H}\widehat{\boldsymbol{v}} - \widehat{\boldsymbol{v}}\widehat{H}\right) = \frac{\mathrm{i}}{m\hbar}\left(\widehat{H}\widehat{\boldsymbol{p}} - \widehat{\boldsymbol{p}}\widehat{H}\right) = \frac{\mathrm{i}}{m\hbar}\left(U\widehat{\boldsymbol{p}} - \widehat{\boldsymbol{p}}U\right)$$

Using formula (16.4), we find

$$m\widehat{\dot{\boldsymbol{v}}} = -\nabla U. \tag{19.3}$$

This operator equation is exactly the same in form as the equation of motion (Newton's equation) in classical mechanics.

The integral $\int|\Psi|^2\mathrm{d}V$, taken over some finite volume V, is the probability of finding the particle in this volume. Let us calculate the derivative of this probability with respect to time. We have

$$\frac{\mathrm{d}}{\mathrm{d}t}\int|\Psi|^2\mathrm{d}V = \int\left(\Psi\frac{\partial\Psi^*}{\partial t} + \Psi^*\frac{\partial\Psi}{\partial t}\right)\mathrm{d}V = \frac{\mathrm{i}}{\hbar}\int\left(\Psi\widehat{H}^*\Psi^* - \Psi^*\widehat{H}\Psi\right)\mathrm{d}V.$$

Substituting here

$$\widehat{H} = \widehat{H}^* = -\frac{\hbar^2}{2m}\Delta + U(x,y,z)$$

and using the identity

$$\Psi\Delta\Psi^* - \Psi^*\Delta\Psi = \mathrm{div}\left(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi\right)$$

we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\int|\Psi|^2\mathrm{d}V = -\int\mathrm{div}\boldsymbol{j}\,\mathrm{d}V$$

where $\boldsymbol{j}$ denotes the vector[6])

$$\boldsymbol{j} = \frac{\mathrm{i}\hbar}{2m}(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi) = \frac{1}{2m}(\Psi\widehat{\boldsymbol{p}}^*\Psi^* + \Psi^*\widehat{\boldsymbol{p}}\Psi). \tag{19.4}$$

The integral of $\mathrm{div}\boldsymbol{j}$ can be transformed by Gauss's theorem into an integral over the closed surface which bounds the volume V:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int|\Psi|^2\mathrm{d}V = -\oint\boldsymbol{j}\,\mathrm{d}\boldsymbol{f} \tag{19.5}$$

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[6]) If ψ is written as $|\psi|\mathrm{e}^{\mathrm{i}\alpha}$, then

$$\boldsymbol{j} = \frac{\hbar}{m}|\psi|^2\nabla\alpha \tag{19.4a}$$

It is seen from this that the vector $\boldsymbol{j}$ may be called the *probability current density* vector, or simply the *current density*. The integral of this vector over a surface is the probability that the particle will cross the surface during unit time. The vector $\boldsymbol{j}$ and the probability density $|\Psi|^2$ satisfy the equation

$$\frac{\partial|\Psi|^2}{\partial t} + \mathrm{div}\,\boldsymbol{j} = 0 \tag{19.6}$$

which is analogous to the classical equation of continuity.

The wave function of free motion (the plane wave (17.9)) can be normalized so as to describe a flow of particles with unit current density (in which, on average, one particle crosses a unit cross-section of the flow per unit time). This function is then

$$\Psi = \frac{1}{\sqrt{v}} \exp\left[-\frac{\mathrm{i}}{\hbar}(Et - \boldsymbol{pr})\right], \tag{19.7}$$

where v is the velocity of the particle, since substitution of this in (19.4) gives $\boldsymbol{j} = \boldsymbol{p}/mv$, i.e. a unit vector in the direction of the motion.

It is useful to show how the orthogonality of the wave functions of states with different energies follows immediately from Schrödinger's equation. Let ψ_m and ψ_n be two such functions; they satisfy the equations

$$-\frac{\hbar^2}{2m}\Delta\psi_m + U\psi_m = E_m\psi_m,$$
$$-\frac{\hbar^2}{2m}\Delta\psi_n^* + U\psi_n^* = E_n\psi_n^*.$$

We multiply the first of these by ψ_n^* and the second by ψ_m and subtract corresponding terms; this gives

$$(E_m - E_n)\psi_m\psi_n^* = \frac{\hbar^2}{2m}(\psi_m\Delta\psi_n^* - \psi_n^*\Delta\psi_m) = \frac{\hbar^2}{2m}\mathrm{div}(\psi_m\nabla\psi_n^* - \psi_n^*\nabla\psi_m).$$

If we now integrate both sides of this equation over all space, the right-hand side, on transformation by Gauss's theorem, reduces to zero, and we obtain

$$(E_m - E_n)\int\psi_m\psi_n^*\mathrm{d}V = 0,$$

whence, by the hypothesis $E_m \neq E_n$, there follows the required orthogonality relation

$$\int\psi_m\psi_n^*\mathrm{d}V = 0.$$

§ 20. The variational principle

SchrÖdinger's equation, in the general form $\widehat{H}\psi = E\psi$, can be obtained from, the variational principle

$$\delta \int \psi^*(\widehat{H} - E)\psi \mathrm{d}q = 0 \tag{20.1}$$

Since ψ is complex, we can vary ψ and ψ^* independently. Varying ψ^*, we have

$$\int \delta\psi^*(\widehat{H} - E)\psi \mathrm{d}q = 0$$

whence, because $\delta\psi^*$ is arbitrary, we obtain the required equation $\widehat{H}\psi = E\psi$. The variation of ψ gives nothing different. For, varying ψ and using the fact that the operator $\widehat{H}$ is Hermitian, we have

$$\int \psi^*(\widehat{H} - E)\delta\psi \mathrm{d}q = \int \delta\psi(\widehat{H}^* - E)\psi^* \mathrm{d}q = 0$$

from which we obtain the complex conjugate equation $\widehat{H}^*\psi^* = E\psi^*$.

The variational principle (20.1) requires an unconditional extremum of the integral. It can be stated in a different form by regarding E as a Lagrangian multiplier in a problem with the conditional extremum requirement

$$\delta \int \psi^*\widehat{H}\psi \mathrm{d}q = 0 \tag{20.2}$$

the condition being

$$\int \psi\psi^* \mathrm{d}q = 1 \tag{20.3}$$

The least value of the integral in (20.2) (with the condition (20.3)) is the first eigenvalue of the energy, i.e. the energy E_0 of the normal state. The function ψ which gives this minimum is accordingly the wave function ψ_0 of the normal state.[7]) The wave functions $\psi_n(n > 0)$ of the other stationary states correspond only to an extremum, and not to a true minimum of the integral.

In order to obtain, from the condition that the integral in (20.2) is a minimum, the wave function ψ_1 and the energy E_1 of the state next to the normal one, we must restrict our choice to those functions ψ which satisfy not only the normalization condition (20.3) but also the condition of orthogonality

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[7]) In the rest of this section we shall suppose the wave functions ψ to be real; they can always be so chosen (if there is no magnetic field).

with the wave function ψ_0 of the normal state: $\int \psi\psi_0 \mathrm{d}q = 0$. In general, if the wave functions $\psi_0, \psi_1, \ldots, \psi_{n-1}$ of the first n states (arranged in order of increasing energy) are known, the wave function of the next state gives a minimum of the integral in (20.2) with the additional conditions

$$\int \psi^2 \mathrm{d}q = 1, \quad \int \psi\psi_m \mathrm{d}q = 0 \quad m = 0, 1, 2, \ldots, n-1. \tag{20.4}$$

We shall give here some general theorems which can be proved from the variational principle.[8]

The wave function ψ_0 of the normal state does not become zero (or, as we say, has no *nodes*) for any finite values of the coordinates.[9] In other words, it has the same sign in all space. Hence, it follows that the wave functions $\psi_n (n > 0)$ of the other stationary states, being orthogonal to ψ_0, must have nodes (if ψ_n is also of constant sign, the integral $\int \psi_0\psi_n \mathrm{d}q$ cannot vanish).

Next, from the fact that ψ_0 has no nodes, it follows that the normal energy level cannot be degenerate. For, suppose the contrary to be true, and let ψ_0, ψ_0' be two different eigenfunctions corresponding to the level E_0. Any linear combination $c\psi_0 + c'\psi_0'$ will also be an eigenfunction; but by choosing the appropriate constants c, c', we can always make this function vanish at any given point in space, i.e. we can obtain an eigenfunction with nodes.

If the motion takes place in a bounded region of space, we must have $\psi = 0$ at the boundary of this region (see §18). To determine the energy levels, it is necessary to find, from the variational principle, the minimum value of the integral in (20.2) with this boundary condition. The theorem that the wave function of the normal state has no nodes means in this case that ψ_0 does not vanish anywhere inside this region.

We notice that, as the dimensions of the region containing the motion increase, all the energy levels E_n decrease; this follows immediately from the fact that an extension of the region increases the range of functions which can make the integral a minimum, and consequently the least value of the integral can only diminish.

The expression

$$\int \psi\widehat{H}\psi\mathrm{d}q = \int \left[-\sum_a \frac{\hbar^2}{2m_a} \psi\Delta_a\psi + U\psi^2 \right] \mathrm{d}q$$

---

[8] The proof of theorems concerning the zeros of eigenfunctions (see also §21) is given by M. A. Lavrent'ev and L. A. Lyusternik, *The Calculus of Variations (Kurs variatsionnogo ischislemya)*, 2nd edition, chapter IX, Moscow, 1950; R. Courant and D. Hilbert, *Methods of Mathematical Physics*, volume I, chapter VI, Interscience, New York, 1953.

[9] This theorem and its consequences are not in general valid for the wave functions of systems consisting of several identical particles (see the end of §63).

for the states of the discrete spectrum of a particle system may be transformed into another expression which is more convenient in practice. In the first term of the integrand we write

$$\psi \Delta_a \psi = \mathrm{div}_a(\psi \nabla_a \psi) - (\nabla_a \psi)^2.$$

The integral of $\mathrm{div}_a(\psi \nabla_a \psi)$ over all space is transformed into an integral over an infinitely distant closed surface, and since the wave functions of the states of a discrete spectrum tend to zero sufficiently rapidly at infinity, this integral vanishes. Thus

$$\int \psi \widehat{H} \psi \mathrm{d}q = \int \left[\sum_a \frac{\hbar^2}{2m_a} (\nabla_a \psi)^2 + U\psi^2 \right] \mathrm{d}q. \tag{20.5}$$

§ 21. General properties of motion in one dimension

If the potential energy of a particle depends on only one coordinate (x), then the wave function can be sought as the product of a function of y and z and a function of x only. The former of these is determined by Schrödinger's equation for free motion, and the second by the one-dimensional Schrödinger's equation

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{2m}{\hbar^2}[E - U(x)]\psi = 0 \tag{21.1}$$

Similar one-dimensional equations are evidently obtained for the problem of motion in a field whose potential energy is $U(x, y, z) = U_1(x) + U_2(y) + U_3(z)$, i.e. can be written as a sum of functions each of which depends on only one of the coordinates. In §§22–24 we shall discuss a number of actual examples of such "one-dimensional" motion. Here we shall obtain some general properties of the motion.

We shall show first of all that, in a one-dimensional problem, none of the energy levels of a discrete spectrum is degenerate. To prove this, suppose the contrary to be true, and let ψ_1 and ψ_2 be two different eigenfunctions corresponding to the same value of the energy. Since both of these satisfy the same equation (21.1), we have

$$\frac{\psi_1''}{\psi_1} = \frac{2m}{\hbar^2}(U - E) = \frac{\psi_2''}{\psi_2}$$

or $\psi_1'' \psi_2 - \psi_1 \psi_2'' = 0$ (the prime denotes differentiation with respect to x). Integrating this relation, we find

$$\psi_1' \psi_2 - \psi_1 \psi_2' = \mathrm{const.} \tag{21.2}$$

Since $\psi_1 = \psi_2 = 0$ at infinity, the constant must be zero, and so

$$\psi_1' \psi_2 - \psi_1 \psi_2' = 0,$$

or $\psi_1'/\psi_1 = \psi_2'/\psi_2$. Integrating again, we obtain $\psi_1 = \text{const} \cdot \psi_2$, i.e. the two functions are essentially identical.

The following theorem (called the *oscillation theorem*) may be stated for the wave functions $\psi_n(x)$ of a discrete spectrum. The function $\psi_n(x)$ corresponding to the $(n+1)$th eigenvalue E_n (the eigenvalues being arranged in order of magnitude), vanishes n times (for finite[10] values of x).

We shall suppose that the function $U(x)$ tends to finite limiting values as $x \to \pm\infty$ (though it need not be a monotonic function). We take the limiting value $U(+\infty)$ as the zero of energy (i.e. we put $U(+\infty) = 0$), and we denote $U(-\infty)$ by U_0, supposing that $U_0 > 0$. The discrete spectrum lies in the range of energy values for which the particle cannot move off to infinity; for this to be so, the energy must be less than both limiting values $U(\pm\infty)$, i.e. it must be negative:

$$E < 0, \tag{21.3}$$

and we must, of course, have in any case $E > U_{\min}$, i.e. the function $U(x)$ must have at least one minimum with $U_{\min} < 0$.

Let us now consider the range of positive energy values less than U_0:

$$0 < E < U_0 \tag{21.4}$$

In this range the spectrum will be continuous, and the motion of the particle in the corresponding stationary states will be infinite, the particle moving off towards $x = +\infty$. It is easy to see that none of the eigenvalues of the energy in this part of the spectrum is degenerate either. To show this, it is sufficient to notice that the proof given above (for the discrete spectrum) still holds if the functions ψ_1, ψ_2 are zero at only one infinity (in the present case they tend to zero as $x \to -\infty$).

For sufficiently large positive values of x, we can neglect $U(x)$ in Schrödinger's equation (21.1):

$$\psi'' + \frac{2m}{\hbar^2} E\psi = 0$$

This equation has real solutions in the form of a stationary plane wave

$$\psi = a\cos(kx + \delta) \tag{21.5}$$

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[10] If the particle can be found only on a limited segment of the x-axis, we must consider the zeros of $\psi_n(x)$ within that segment.

where a and δ are constants, and the *wave number* $k = p/\hbar = \sqrt{2mE}/\hbar$. This formula determines the asymptotic form (for $x \to +\infty$) of the wave functions of the non-degenerate energy levels in the range (21.4) of the continuous spectrum. For large negative values of x, Schrödinger's equation is

$$\psi'' - \frac{2m}{\hbar^2}(U_0 - E)\psi = 0$$

The solution which does not become infinite as $x \to -\infty$ is

$$\psi = be^{\varkappa x}, \quad \varkappa = \frac{1}{2m}\sqrt{U_0 - E}. \tag{21.6}$$

This is the asymptotic form of the wave function as $x \to \infty$. Thus the wave function decreases exponentially in the region where $E < U$.

Finally, for

$$E > U_0 \tag{21.7}$$

the spectrum will be continuous, and the motion will be infinite in both directions. In this part of the spectrum all the levels are doubly degenerate. This follows from the fact that the corresponding wave functions are determined by the second-order equation (21.1), and both of the two independent solutions of this equation satisfy the necessary conditions at infinity (whereas, for instance, in the previous case one of the solutions became infinite as $x \to -\infty$, and therefore had to be rejected). The asymptotic form of the wave function as $x \to +\infty$ is

$$\psi = a_1 e^{ikx} + a_2 e^{-ikx} \tag{21.8}$$

and similarly for $x \to -\infty$. The term e^{ikx} corresponds to a particle moving to the right, and e^{-ikx} corresponds to one moving to the left.

Let us suppose that the function $U(x)$ is even $[U(x) = U(x)]$. Then Schrödinger's equation (21.1) is unchanged when the sign of the coordinate is reversed. It follows that, if $\psi(x)$ is some solution of this equation, then $\psi(-x)$ is also a solution, and coincides with $\psi(x)$ apart from a constant factor: $\psi(-x) = c\psi(x)$. Changing the sign of x again, we obtain $\psi(x) = c^2\psi(x)$, whence $c = \pm 1$. Thus, for a potential energy which is symmetrical (relative to $x = 0$), the wave functions of the stationary states must be either even $[\psi(-x) = \psi(x)]$ or odd $[\psi(-x) = -\psi(x)]$.[11] In particular, the wave function

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[11] In this discussion it is assumed that the stationary state is not degenerate, i.e. the motion is not infinite in both directions. Otherwise, when the sign of x is changed, two wave functions belonging to the energy level concerned may be transformed into each other. In this case, however, although the wave functions of the stationary states need not be even or odd, they can always be made so (by choosing appropriate linear combinations of the original functions).

of the ground state is even, since it cannot have a node, while an odd function always vanishes for $x = 0$ $[\psi(0) = -\psi(0) = 0]$.

To normalize the wave functions of one-dimensional motion (in a continuous spectrum), there is a simple method of determining the normalization coefficient directly from the asymptotic expression for the wave function for large values of $|x|$.

Let us consider the wave function of a motion infinite in one direction, $x \to +\infty$. The normalization integral diverges as $x \to \infty$ (as $x \to -\infty$, the function decreases exponentially, so that the integral rapidly converges). Hence, to determine the normalization constant, we can replace ψ by its asymptotic value (for large positive x), and perform the integration, taking as the lower limit any finite value of x, say zero; this amounts to neglecting a finite quantity in comparison with an infinite one. We shall show that the wave function normalized by the condition

$$\int \psi_p^* \psi_{p'} \mathrm{d}x = \delta\left(\frac{p - p'}{2\pi\hbar}\right) = 2\pi\hbar\delta(p - p'), \qquad (21.9)$$

where p is the momentum of the particle at infinity, must have the asymptotic form (21.5) with $a = 2$:

$$\psi_p \approx 2\cos(kx + \delta) = \mathrm{e}^{\mathrm{i}(kx+\delta)} + \mathrm{e}^{-\mathrm{i}(kx+\delta)} \qquad (21.10)$$

Since we do not intend to verify the orthogonality of the functions corresponding to different p, on substituting the functions (21.10) in the normalization integral we shall suppose the momenta p and p' to be arbitrarily close; we can therefore put $\delta = \delta'$ (in general δ is a function of p). Next, we retain in the integrand only those terms which diverge for $p = p'$; in other words, we omit terms containing the factor $\mathrm{e}^{\pm\mathrm{i}(k+k')x}$. Thus we obtain

$$\int \psi_p^* \psi_{p'} \mathrm{d}x = \int_0^{+\infty} \mathrm{e}^{\mathrm{i}(k'-k)x}\mathrm{d}x + \int_0^{+\infty} \mathrm{e}^{-\mathrm{i}(k'-k)x}\mathrm{d}x = \int_{-\infty}^{+\infty} \mathrm{e}^{\mathrm{i}(k'-k)x}\mathrm{d}x$$

which, from (15.7), is the same as (21.9).

The change to normalization by the delta function of energy is effected, in accordance with (5.14), by multiplying ψ_p by

$$\left(\frac{\mathrm{d}(p/2\pi\hbar)}{\mathrm{d}E}\right)^{1/2} = \frac{1}{\sqrt{2\pi\hbar v}}$$

where v is the velocity of the particle at infinity. Thus

$$\psi_E = \frac{1}{\sqrt{2\pi\hbar v}}\psi_p = \frac{1}{\sqrt{2\pi\hbar v}}(\mathrm{e}^{\mathrm{i}(kx+\delta)} + \mathrm{e}^{-\mathrm{i}(kx+\delta)}) \qquad (21.11)$$

The current density is $1/(2\pi\hbar)$ in each of the travelling waves that make up the stationary wave (21.11). Thus we can formulate the following rule for the normalization of the wave function for a motion infinite in one direction by the delta function of energy: having represented the asymptotic expression for the wave function in the form of a sum of two plane waves travelling in opposite directions, we must choose the normalization coefficient in such a way that the current density in the wave travelling towards (or away from) the origin is $1/(2\pi\hbar)$.

Similarly, we can obtain an analogous rule for normalizing the wave functions of a motion infinite in both directions. The wave function will be normalized by the delta function of energy if the sum of the probability currents in the waves travelling towards the origin from $x = +\infty$ and $x = -\infty$ is $1/(2\pi\hbar)$.

§ 22. The potential well

As a simple example of one-dimensional motion, let us consider motion in a square potential well, i.e. in a field where $U(x)$ has the form shown in FIG.1: $U(x) = 0$ for $0 < x < a$, $U(x) = U_0$ for $x < 0$ and $x > a$. It is evident a priori that for $E < U_0$ the spectrum will be discrete, while for $E > U_0$ we have a continuous spectrum of doubly degenerate levels.

In the region $0 < x < a$ we have Schrödinger's equation

$$\psi'' + \frac{2m}{\hbar^2} E \psi = 0 \qquad (22.1)$$

(the prime denotes differentiation with respect to x), while in the region outside the well

$$\psi'' + \frac{2m}{\hbar^2}(E - U_0)\psi = 0 \qquad (22.2)$$

FIG.1

For $x = 0$ and $x = a$ the solutions of these equations must be continuous together with their derivatives, while for $x = \pm\infty$ the solution of equation (22.2) must remain finite (for the discrete spectrum when $E < U_0$, it must vanish).

For $E < U_0$, the solution of equation (22.2) which vanishes at infinity is $\psi = \text{const} \cdot e^{\mp \varkappa x}$, where

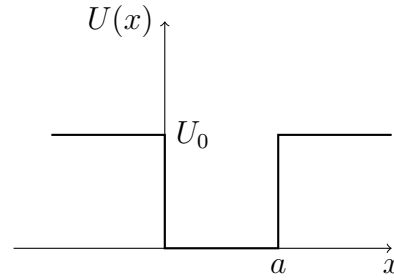$$\varkappa = \frac{1}{\hbar}\sqrt{2m(U_0 - E)}; \qquad (22.3)$$

the signs $-$ and $+$ in the exponent refer to the regions $x > a$ and $x < 0$ respectively. The probability $|\psi|^2$ of finding the particle decreases exponentially in the region where $E < U(x)$. Instead of the continuity of ψ and ψ' at the edge of the potential well, it is convenient to require the continuity of ψ and of its logarithmic derivative ψ'/ψ. Taking account of (22.3), we obtain the boundary condition in the form

$$|\psi'|/\psi = \mp\varkappa \tag{22.4}$$

We shall not pause here to determine the energy levels in a well of arbitrary depth U_0 (see Problem 2), and shall analyse fully only the limiting case of infinitely high walls ($U_0 \to \infty$).

For $U_0 = \infty$, the motion takes place only between the points $x = 0$ and $x = a$ and, as was pointed out in §18, the boundary condition at these points is

$$\psi = 0 \tag{22.5}$$

(It is easy to see that this condition is also obtained from the general condition (22.4). For, when $U_0 \to \infty$, we have also $\varkappa \to \infty$ and hence $\psi'/\psi \to \infty$; since ψ' cannot become infinite, it follows that $\psi = 0$.) We seek a solution of equation (22.1) inside the well in the form

$$\psi = c\sin(kx + \delta), \quad k = \frac{\sqrt{2mE}}{\hbar}. \tag{22.6}$$

The condition $\psi = 0$ for $x = 0$ gives $\delta = 0$, and then the same condition for $x = a$ gives $\sin ka = 0$, whence $ka = n\pi$, n being a positive integer,[12] or

$$E_n = \frac{\pi^2\hbar^2}{2ma^2}n^2, \quad n = 1, 2, 3, \ldots \tag{22.7}$$

This determines the energy levels of a particle in a potential well. The normalized wave functions of the stationary states are

$$\psi_n = \sqrt{\frac{2}{n}}\sin\left(\frac{\pi n}{a}x\right). \tag{22.8}$$

From these results we can immediately write down the energy levels for a particle in a rectangular "potential box", i.e. for three-dimensional motion in a field whose potential energy $U = 0$ for $0 < x < a$, $0 < y < b$, $0 < z < c$ and $U = \infty$ outside this region. In fact, these levels are given by the sums

$$E_{n_1 n_2 n_3} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right), \quad n_1, n_2, n_3 = 1, 2, 3, \ldots, \tag{22.9}$$

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[12] For $n = 0$ we should have $\psi = 0$ identically.

and the corresponding wave functions by the products

$$\psi_{n_1 n_2 n_3} = \sqrt{\frac{8}{abc}} \sin\left(\frac{\pi n_1}{a}x\right) \sin\left(\frac{\pi n_2}{b}y\right) \sin\left(\frac{\pi n_3}{c}z\right). \qquad (22.10)$$

It may be noted that the energy E_0 of the ground state is, by (22.7) or (22.9), of the order of $\hbar^2/ml^2$, where l is the linear dimension of the region in which the particle moves. This result is in accordance with the uncertainty relation; when the uncertainty in the coordinate is $\sim l$, the uncertainty in the momentum, and therefore the order of magnitude of the momentum itself, is $\sim \hbar/l$. The corresponding energy is $\sim (\hbar/l)^2/m$.

PROBLEMS

1. Determine the probability distribution for various values of the momentum for the normal state of a particle in an infinitely deep square potential well.

SOLUTION. The coefficients $a(p)$ in the expansion of the function ψ_1 (22.8) in terms of the eigenfunctions of the momentum are

$$a(p) = \int \psi_p^* \psi_1 dx = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{\pi}{a}x\right) \exp\left(-i\frac{px}{\hbar}\right) dx.$$

Calculating the integral and squaring its modulus, we obtain the required probability distribution:

$$|a(p)|^2 \frac{dp}{2\pi\hbar} = \frac{4\pi\hbar^3 a}{(p^2a^2 - \pi^2\hbar^2)^2} \cos^2\frac{pa}{2\hbar} dp.$$

2. Determine the energy levels for the potential well shown in FIG.2.

SOLUTION. The spectrum of energy values $E < U_1$, which we shall consider, is discrete. In the region $x < 0$ the wave function is
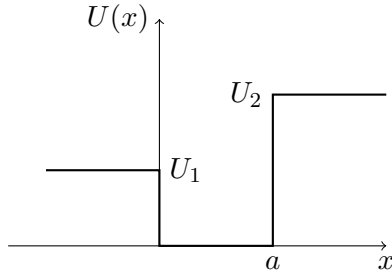

FIG.2

$$\psi = c_1 e^{\varkappa_1 x}, \quad \varkappa_1 = (1/\hbar)\sqrt{2m(U_1 - E)},$$

while in the region $x > a$

$$\psi = c_2 e^{-\varkappa_2 x}, \quad \varkappa_2 = (1/\hbar)\sqrt{2m(U_2 - E)}.$$

Inside the well $(0 < x < a)$ we look for ψ in the form

$$\psi = c\sin(kx + \delta), \quad k = \sqrt{2mE}/\hbar.$$

The condition of the continuity of ψ'/ψ at the edges of the well gives the equations

$$k\cot\delta = \varkappa_1 = \sqrt{\frac{2m}{\hbar^2}U_1 - k^2}, \quad k\cot(ka + \delta) = -\varkappa_2 = -\sqrt{\frac{2m}{\hbar^2}U_2 - k^2},$$

or

$$\sin \delta = \frac{k\hbar}{\sqrt{2mU_1}}, \quad \sin(ka + \delta) = -\frac{k\hbar}{\sqrt{2mU_2}}.$$

Eliminating δ, we obtain the transcendental equation

$$ka = n\pi - \arcsin \frac{k\hbar}{\sqrt{2mU_1}} - \arcsin \frac{k\hbar}{\sqrt{2mU_2}} \tag{1}$$

(where $n = 1, 2, 3, \ldots$, and the values of the inverse sine are taken between 0 and $\pi/2$), whose roots determine the energy levels $E = k^2\hbar^2/2m$. For each n there is in general one root; the values of n number the levels in order of increasing energy.

Since the argument of the inverse sine cannot exceed unity, it is clear that the values of k can lie only in the range from 0 to $\sqrt{2mU_1}/\hbar$. The left-hand side of equation (1) increases monotonically with k, and the right-hand side decreases monotonically. Hence it is necessary, for a root of equation (1) to exist, that for the right-hand side should be less than the left-hand side. In particular, the inequality

$$a\frac{\sqrt{2mU_1}}{\hbar} \geqslant \frac{\pi}{2} - \arcsin \sqrt{\frac{U_1}{U_2}}, \tag{2}$$

which is obtained for $n = 1$, is the condition that at least one energy level exists in the well. We tee that for given and unequal $U_1 \neq U_2$, there are always widths a of the well which are so small that there is no discrete energy level. For $U_1 = U_2$, the condition (2) is evidently always satisfied.

For $U_1 = U_2 = U_0$ (a symmetrical well), equation (1) reduces to

$$\arcsin \frac{\hbar k}{\sqrt{2mU_0}} \frac{n\pi - ka}{2}. \tag{3}$$

Introducing the variable $\xi = ka/2$, we obtain for odd n the equation

$$\cos \xi = \pm \gamma \xi, \quad \gamma = \frac{\hbar}{a}\sqrt{\frac{2}{mU_0}}, \tag{4}$$

and those roots of this equation must be taken for which $\tan \xi > 0$. For even n we obtain the equation

$$\sin \xi = \pm \gamma \xi, \tag{5}$$

and we must take those roots for which $\tan \xi < 0$. The roots of these two equations determine the energy levels $E = 2\xi^2\hbar^2/ma^2$. The number of levels is finite when $\gamma \neq 0$.

In particular, for a shallow well in which $U_0 \ll \hbar^2/ma^2$, we have $\gamma \gg 1$ and equation (5) has no root. Equation (4) has one root (with the upper sign on the right-hand side), $\xi \approx (1/\gamma)(1 - 1/2\gamma^2)$. Thus the well contains only one energy level,

$$E_0 \approx U_0 - \frac{ma^2}{2\hbar^2}U_0^2$$

which is near the top of the well.

3. Determine the pressure exerted on the walls of a rectangular "potential box" by a particle inside it.

SOLUTION. The force on the the wall perpendicular to the x-axis is the mean value of the derivative $-\partial H/\partial a$ of the Hamilton's function of the particle with respect to the length of the box in the direction of the x-axis. The pressure is obtained by dividing this force by the area bc of the wall. According to the formula (11.16), the required mean value is found by differentiating the eigenvalue (22.9) of the energy. The result is

$$p^{(x)} = \frac{\pi^2 \hbar^2}{ma^3 bc} n_1^2.$$

§ 23. The linear oscillator

Let us consider a particle executing small oscillations in one dimension (what is called a *linear oscillator*). The potential energy of such a particle is $m\omega^2 x^2/2$, where ω is, in classical mechanics, the characteristic (angular) frequency of the oscillations. Accordingly, the Hamiltonian of the oscillator is

$$\widehat{H} = \frac{\widehat{p}^2}{2m} + \frac{m\omega^2 x^2}{2}. \tag{23.1}$$

Since the potential energy becomes infinite for $x = \pm\infty$, the particle can have only a finite motion, and the energy eigenvalue spectrum is entirely discrete.

Let us determine the energy levels of the oscillator, using the matrix method[13] . We shall start from the equations of motion in the form (19.3); in this case they give

$$\widehat{\ddot{x}} + \omega^2 x = 0. \tag{23.2}$$

In matrix form, this equation reads

$$(\ddot{x})_{mn} + \omega^2 x_{mn} = 0.$$

For the matrix elements of the acceleration we have, according to (11.8), $(\ddot{x})_{mn} = \mathrm{i}\omega_{mn}(\dot{x})_{mn} = -\omega_{mn}^2 x_{mn}$. Hence we obtain

$$(\omega_{mn}^2 - \omega^2) x_{mn} = 0.$$

Hence it is evident that all the matrix elements x_{mn} vanish except those for which $\omega_{mn} = \omega$ or $\omega_{mn} = -\omega$. We number all the stationary states so that

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[13] This was done by Heisenberg in 1925, before Schrödinger's discovery of the wave equation.

the frequencies $\pm\omega$ correspond to transitions $n \to n \mp 1$, i.e. $\omega_{n,n\mp 1} = \pm\omega$. Then the only non-zero matrix elements are $x_{n,n\pm 1}$.

We shall suppose that the wave functions ψ_n are taken real. Since x is a real quantity, all the matrix elements x_{mn} are real. The Hermitian condition (11.10) now shows that the matrix x_{mn} is symmetrical:

$$x_{mn} = x_{nm}.$$

To calculate the matrix elements of the coordinate which are different from zero, we use the commutation rule

$$\widehat{\dot{x}}\widehat{x} - \widehat{x}\widehat{\dot{x}} = -\mathrm{i}\frac{\hbar}{m},$$

written in the matrix form

$$(\dot{x}x)_{mn} - (x\dot{x})_{mn} = -\frac{\mathrm{i}\hbar}{m}\delta_{mn}$$

By the matrix multiplication rule (11.12) we hence have for $m = n$

$$\mathrm{i}\sum_l(\omega_{nl}x_{nl}x_{ln} - x_{nl}\omega_{ln}x_{ln}) = 2\mathrm{i}\sum_l\omega_{nl}x_{nl}^2 = -\mathrm{i}\frac{\hbar}{m}.$$

In this sum, only the terms with $l = n \pm 1$ are different from zero, so that we have

$$(x_{n+1,n})^2 - (x_{n,n-1})^2 = \frac{\hbar}{2m\omega}. \tag{23.3}$$

From this equation we deduce that the quantities $(x_{n+1,n})^2$ form an arithmetic progression, which is unbounded above, but is certainly bounded below, since it can contain only positive terms. Since we have as yet fixed only the relative positions of the numbers n of the states, but not their absolute values, we can arbitrarily choose the value of n corresponding to the first (normal) state of the oscillator, and put this value equal to zero. Accordingly $x_{0,1}$ must be regarded as being zero identically, and the application of equations (23.3) with $n = 0, 1, \cdots$ successively leads to the result

$$(x_{n,n-1})^2 = \frac{n\hbar}{2m\omega}.$$

Thus we finally obtain the following expression for the matrix elements of the coordinate which are different from zero:[14]

$$x_{n,n-1} = x_{n-1,n} = \sqrt{\frac{n\hbar}{2m\omega}} \tag{23.4}$$

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[14] We choose the indeterminate phases α_n (see the second footnote to §11) so as to obtain the plus sign in front of the radical in all the matrix elements (23.4). Such a choice is always possible for a matrix in which only those elements are different from zero which correspond to transitions between states with adjacent numbers.

The matrix of the operator $\widehat{H}$ is diagonal, and the matrix elements H_{nn} are the required eigenvalues E_n of the energy of the oscillator. To calculate them, we write

$$H_{nn} = E_n = \frac{m}{2}\left[\left(\dot{x}^2\right)_{nn} + \omega^2(x^2)_{nn}\right] =$$

$$= \frac{m}{2}\left[\sum_l i\omega_{nl}x_{nl}i\omega_{ln}x_{ln} + \omega^2\sum_l x_{nl}x_{ln}\right] = \frac{m}{2}\left(\omega^2 + \omega_{nl}^2\right)x_{ln}^2.$$

In the sum over l, only the terms with $l = n \pm 1$ are different from zero; substituting (23.4), we obtain

$$E_n = (n + 1/2)\hbar\omega, \quad n = 0, 1, 2, \ldots \tag{23.5}$$

Thus the energy levels of the oscillator lie at equal intervals of $\hbar\omega$ from one another. The energy of the normal state $(n = 0)$ is $\hbar\omega/2$; we call attention to the fact that it is not zero.

The result (23.5) can also be obtained by solving Schrödinger's equation. For an oscillator, this has the form

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{m\omega^2 x^2}{2}\right)\psi = 0 \tag{23.6}$$

Here it is convenient to introduce, instead of the coordinate x, the dimensionless variable ξ by the relation

$$\xi = \sqrt{\frac{m\omega}{\hbar}}x. \tag{23.7}$$

Then we have the equation

$$\psi'' + \left(\frac{2E}{\hbar\omega} - \xi^2\right)\psi = 0; \tag{23.8}$$

here the prime denotes differentiation with respect to ξ.

For large ξ, we can neglect $2E/\hbar\omega$ in comparison with ξ^2; the equation $\psi'' = \xi^2\psi$ has the asymptotic integrals $\psi = e^{\pm\xi^2/2}$(for differentiation of this function gives $\psi'' = \xi^2\psi$ on neglecting terms of order less than that of the term retained). Since the wave function ψ must remain finite as $\xi \to \pm\infty$, the index must be taken with the minus sign. It is therefore natural to make in equation (23.8) the substitution

$$\psi = e^{-\xi^2/2}\chi(\xi). \tag{23.9}$$

For the function we obtain the equation (with the notation $2E/1 = 2n$; since we already know that $E > 0$, we have $n > -1/2$)

$$\chi'' - 2\xi\chi' + 2n\chi = 0, \qquad (23.10)$$

where the function must be finite for all finite ξ, and for $\xi \to \pm\infty$ must not tend to infinity more rapidly than every finite power of ξ (in order that the function ψ should tend to zero).

Such solutions of equation (23.10) exist only for positive integral (and zero) values of n (see §a of the Mathematical Appendices); this gives the eigenvalues (23.5) for the energy, which we know already. The solutions of equation (23.10) corresponding to various integral values of n are

$$\chi = \text{const} \cdot H_n(\xi),$$

where $H_n(\xi)$ are what are called *Hermite polynomials*; these are polynomials of the nth degree in ξ, defined by the formula

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n e^{-\xi^2}}{d\xi^n} \qquad (23.11)$$

Determining the constants so that the functions ψ_n satisfy the normalization condition

$$\int_{-\infty}^{+\infty} \psi_n^2(x) dx = 1$$

we obtain (see (a.7))

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} \exp\left(-\frac{m\omega}{2\hbar}x^2\right) H_n\left(x\sqrt{\frac{m\omega}{\hbar}}\right). \qquad (23.12)$$

Thus the wave function of the normal state is

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar}x^2\right). \qquad (23.13)$$

It has no zeros for finite x, which is as it should be.

By calculating the integrals $\int_{-\infty}^{+\infty} \psi_n\psi_m \xi d\xi$, we can determine the matrix elements of the coordinate; this calculation leads, of course, to the same values (23.4).

Finally, we shall show how the wave functions ψ_n may be calculated by the matrix method. We notice that, in the matrices of the operators $\widehat{\dot{x}} \pm i\omega\widehat{x}$, the only elements different from zero are

$$(\dot{x} - i\omega x)_{n,n-1} = -(\dot{x} + i\omega)_{n,n-1} - i\sqrt{\frac{2\omega\hbar n}{m}} \qquad (23.14)$$

Using the general formula (11.11), and taking into account the fact that $_1 \equiv 0$, we conclude that

$$\frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar} x \psi_0,$$

After substituting the expression $\widehat{x} = -i\frac{\hbar}{m}\frac{d}{dx}$, we obtain the equation

$$\frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar} x \psi_0$$

whose normalized solution is (23.13). And, since

$$(\widehat{\dot{x}} + i\omega\widehat{x})\psi_{n-1} = (\dot{x} + i\omega x)_{n,n-1}\psi_n = i\sqrt{\frac{2\omega\hbar n}{m}}\psi_n,$$

we obtain the recurrence formula

$$\psi_n = \sqrt{\frac{m}{2\omega\hbar n}}\left(-\frac{\hbar}{m}\frac{d}{dx} + \omega x\right)\psi_{n-1} = \frac{1}{\sqrt{2n}}\left(-\frac{d}{d\xi} + \xi\right)\psi_{n-1} =$$

$$= -\frac{1}{\sqrt{2n}}\exp\frac{\xi^2}{2}\frac{d}{d\xi}\left(\exp\left(-\frac{\xi^2}{2}\right)\psi_{n-1}\right),$$

when this is applied n times to the function (23.13), we obtain the expression (23.12) for the normalized functions ψ_n.

PROBLEMS

1. Determine the probability distribution of the various values of the momentum for an oscillator.

SOLUTION. Instead of expanding the wave function of the stationary state in terms of the eigenfunctions of momentum, it is simpler in the case of the oscillator to start directly from Schrödinger's equation in the momentum representation. Substituting in (23.1) the coordinate operator (15.12), we obtain the Hamiltonian in the p representation,

$$\widehat{H} = \frac{p^2}{2m} - \frac{m\omega^2\hbar}{2}\frac{d^2}{dp^2}.$$

The corresponding Schrödinger's equation $\widehat{H}a(p) = Ea(p)$ for the wave function $a(p)$ in the momentum representation is

$$\frac{d^2a(p)}{dp^2} + \frac{2}{m\omega^2\hbar^2}\left(E - \frac{p^2}{2m}\right)a(p) = 0.$$

This equation is of exactly the same form as (23.6); hence its solutions can be written down at once by analogy with (23.12). Thus we find the required probability distribution to be

$$|a(p)|^2\frac{dp}{2\pi\hbar} = \frac{1}{2^n n!\sqrt{\pi m\omega\hbar}}\exp\left(-\frac{p^2}{m\omega\hbar}\right)H_n^2\left(\frac{p}{\sqrt{m\omega\hbar}}\right).$$

2. Determine the lower limit of the possible values of the energy of an oscillator, using the uncertainty relation (16.7).

SOLUTION. Since $\overline{x^2} = \overline{x}^2 + (\delta x)^2, \overline{p^2} = \overline{p}^2 + (\delta p)^2$, (16.7) gives for the mean value of the energy of the oscillator

$$\overline{E} = \frac{m\omega^2}{2}\overline{x^2} + \frac{\overline{p^2}}{2m} \geqslant \frac{m\omega^2}{2}\overline{(\delta x)^2} + \frac{\overline{(\delta p)^2}}{2m} \geqslant \frac{m\omega^2\hbar^2}{8(\delta p)^2} + \frac{(\delta p)^2}{2m}.$$

On determining the minimum value of this expression (regarded as a function of δp), we find the lower limit of the mean values of the energy, and therefore that of all possible values: $E \geqslant \hbar\omega/2$.

3. Find the wave functions of the states of a linear oscillator that minimize the uncertainty relation, i.e. in which the standard deviations of the coordinate and momentum in the wave packet are related by $\delta p\,\delta x = \hbar/2$ (E. Schrödinger 1926).[15]

SOLUTION. The required wave functions must have the form

$$\Psi(x,t) = \frac{1}{(2\pi)^{1/4}(\delta x)^{1/2}} \exp\left\{ i\frac{\overline{p}x}{\hbar} - \frac{(x - \overline{x})^2}{4(\delta x)^2} - i\varphi(t) \right\}. \qquad (1)$$

Their dependence on the coordinate at any instant is in accordance with (16.8), $\overline{x} = \overline{x}(t)$ and $\overline{p} = \overline{p}(t) = m\dot{\overline{x}}(t)$ being the mean values of the coordinate and the momentum; according to (19.3), we have, for a linear oscillator ($U = m\omega^2x^2/2$), $\widehat{\dot{p}} = -m\omega^2 x$, and therefore for the mean value $\dot{\overline{p}} = -m\omega^2\overline{x}$ or

$$\ddot{\overline{x}} + \omega^2\overline{x} = 0 \qquad (2)$$

i.e. the function satisfies the classical equation of motion. The constant factor in (1) is determined by the normalization condition $\int_{-\infty}^{+\infty}|\Psi|^2\mathrm{d}x = 1$ in addition to this factor, Ψ may contain a phase factor with a time-dependent phase $\varphi(t)$. The unknown constant δx and the unknown function $\varphi(t)$ are found by substituting (1) in the wave equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + \frac{m\omega^2x^2}{2}\Psi = i\hbar\frac{\partial\Psi}{\partial t}.$$

With (2), the substitution gives

$$\left(\frac{x^2}{2} - x\overline{x}\right)\left(\frac{m^2\omega^2}{\hbar^2} - \frac{1}{4(\delta x)^4}\right) + \left[\frac{m^2\dot{\overline{x}}^2}{2\hbar^2} - \frac{\overline{x}^2}{8(\delta x)^4} + \frac{1}{4(\delta x)^2} - \frac{m}{\hbar}\dot{\varphi}(t)\right] = 0.$$

Hence $(\delta x)^2 = \hbar/(2m)$ and

$$\dot{\varphi} = \frac{m}{2\hbar}(\dot{\overline{x}}^2 - \omega^2\overline{x}^2) + \frac{\omega}{2}, \quad \varphi = \frac{1}{2\hbar}\overline{p}x + \frac{\omega}{2}t.$$

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[15] These are called *coherent states.*

Thus we have finally

$$\Psi(x,t) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left\{\frac{\mathrm{i}\overline{p}x}{\hbar} - \frac{m\omega(x-\overline{x})^2}{2\hbar}\right\} \exp\left\{-\frac{\mathrm{i}\omega t}{2} - \frac{\mathrm{i}\overline{p}\overline{x}}{2\hbar}\right\} \tag{3}$$

When $\overline{x} = 0$ and $\overline{p} = 0$, this becomes $\psi_0(x)\mathrm{e}^{\mathrm{i}\omega t/2}$, the wave function of the oscillator ground state.

The mean energy of the oscillator in a coherent state is

$$\overline{E} = \frac{\overline{p^2}}{2m} + \frac{m\omega^2\overline{x^2}}{2} = \frac{\overline{p}^2}{2m} + \frac{m\omega^2\overline{x}^2}{2} + \frac{\hbar\omega}{2} \equiv \hbar\omega\left(\overline{n} + \frac{1}{2}\right); \tag{4}$$

the quantity $\overline{n}$ is the mean "number" of quanta $\hbar\omega$ in the state. We see that the coherent state is completely specified by the function $\overline{x}(t)$ satisfying the classical equation (2). The general form of this function may be given as

$$\frac{m\omega\overline{x} + \mathrm{i}\overline{p}}{\sqrt{2m\hbar\omega}} a\mathrm{e}^{\mathrm{i}\omega t}, \quad |a|^2 = \overline{n}. \tag{5}$$

The function (3) can be expanded in wave functions of the stationary states of the oscillator:

$$\Psi = \sum_{n=0}^{\infty} a_n\Psi_n, \quad \Psi_n(x,t) = \psi_n(x)\exp\left\{-\mathrm{i}\left(n + \frac{1}{2}\right)\omega t\right\}.$$

The coefficients in this expansion are (cf. §41, Problem 1)

$$a_n = \int_{-\infty}^{+\infty} \Psi_n^*\Psi\,\mathrm{d}x. \tag{6}$$

The probability for the oscillator to be in the nth state is therefore

$$\omega_n = |a_n|^2 = \mathrm{e}^{-\overline{n}}\frac{\overline{n}^n}{n!} \tag{7}$$

the Poisson distribution.

4. Determine the energy levels for a particle moving in a field of potential energy (Fig. 3; P. M. Morse)

$$U(x) = A\left(\mathrm{e}^{-2\alpha x} - 2\mathrm{e}^{-\alpha x}\right).$$

SOLUTION. The spectrum of positive eigenvalues of the energy is continuous (and the levels are not degenerate), while the spectrum of negative eigenvalues is discrete.

Schrödinger's equation reads

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{2m}{\hbar^2}\left(E - A\mathrm{e}^{-2\alpha x} + 2A\mathrm{e}^{-\alpha x}\right)\psi = 0.$$

We introduce a new variable

$$\xi = \frac{2\sqrt{2mA}}{\alpha\hbar}\mathrm{e}^{-\alpha x}$$

(taking values from 0 to ∞) and the notation (we consider the discrete spectrum, so that $E < 0$)

$$s = \frac{\sqrt{-2mE}}{\alpha\hbar}, \quad n = \frac{\sqrt{2mA}}{\alpha\hbar} + \left(s + \frac{1}{2}\right) \tag{1}$$

Schrödinger's equation then takes the form

$$\psi'' + \frac{1}{\xi}\psi' + \left(-\frac{1}{4} + \frac{n + s + 1/2}{\xi} - \frac{s^2}{\xi^2}\right)\psi = 0$$

As $\xi \to \infty$, the function ψ behaves asymptotically as $e^{\pm\xi/2}$, while as $\xi \to 0$ it is proportional to $\xi \pm s$. From considerations of finiteness we must choose the solution which behaves as $e^{-\xi/2}$ as $\xi \to \infty$ and as ξ^s as $\xi \to 0$. We make the substitution

$$\psi = \mathrm{e}^{-\xi/2}\xi^s\omega(\xi)$$

and obtain for ω the equation

$$\xi\omega'' + (2s + 1 - \xi)\omega' + n\omega = 0, \tag{2}$$

which has to be solved with the conditions that ω is finite as $\xi \to 0$, while as $\xi \to \infty$, ω tends to infinity not more rapidly than every finite power of ξ. Equation (2) is the equation for a confluent hypergeometric function (see §d of the Mathematical Appendices):

FIG. 3

$$\omega = F(-n, 2s + 1, \xi).$$

A solution satisfying the required conditions is obtained for non-negative integral n (when the function F reduces to a polynomial). According to the definitions (1), we thus obtain for the energy levels the values

$$-E_n = \left[1 - \frac{\alpha\hbar}{\sqrt{2mA}}\left(n + \frac{1}{2}\right)\right]^2.$$

where n takes positive integral values from zero to the greatest value for which (so that the parameter s is positive in accordance with its definition). Thus the discrete spectrum contains only a limited number of levels. If

$$\frac{\sqrt{2mA}}{\alpha\hbar} < \frac{1}{2},$$

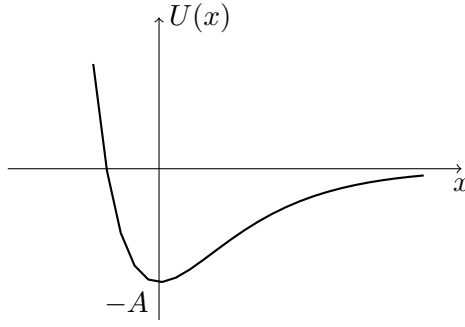there is no discrete spectrum at all.

5. The same as Problem 4, but with $U = -\dfrac{U_0}{\cosh^2 \alpha x}$ (Fig. 4).

SOLUTION. The spectrum of positive eigenvalues of the energy is continuous, while that of negative values is discrete; we shall consider the latter. Schrödinger's equation is

$$\frac{\mathrm{d}^2 \psi}{\mathrm{d}x^2} + \frac{2m}{\hbar}\left(E + \frac{U_0}{\cosh^2 \alpha x}\right)\psi = 0.$$

We put $\xi = \tanh \alpha x$ and use the notation

$$\varepsilon = \frac{\sqrt{-2mE}}{\hbar \alpha}, \quad \frac{2mU_0}{\alpha^2 \hbar^2} = s(s+1), \quad s = \frac{1}{2}\left(-1 + \sqrt{1 + \frac{8mU_0}{\alpha^2 \hbar^2}}\right),$$

obtaining

$$\frac{\mathrm{d}}{\mathrm{d}\xi}\left[(1 - \xi^2)\frac{\mathrm{d}\psi}{\mathrm{d}\xi}\right] + \left[s(s+1) - \frac{\varepsilon^2}{1 - \xi^2}\right]\psi = 0.$$

This is the equation of the associated Legendre polynomials; it can be brought to hypergeometric form by making the substitution
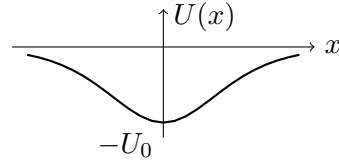
FIG. 4

$$\psi = (1\xi^2)^{\varepsilon/2}w(\xi)$$

and temporarily changing the variable to $\frac{1}{2}(1) = u$:

$$u(1 - u)w'' + (\varepsilon + 1)(1 - 2u)w' - (\varepsilon - s)(\varepsilon + s + 1)w = 0.$$

The solution finite for $\xi = 1$ (i.e. for $x = \infty$) is

$$\psi = (1\xi^2)^{\varepsilon/2}w(\xi)F[\varepsilon - s, \varepsilon + s + 1, \varepsilon - 1, (1 - \xi)/2].$$

If ψ remains finite for $\xi = 1$ (i.e. for $x = -\inf$), we must have $\varepsilon - s = -n$ where $n = 0, 1, 2, \ldots$; then F is a polynomial of degree n, which is finite for $\xi = 1$.

Thus the energy levels are determined by $\varepsilon - s = -n$, or

$$E_n = -\frac{\hbar^2 \alpha^2}{8m}\left[-(2n+1) + \sqrt{1 + \frac{8mU_0}{\alpha^2 \hbar^2}}\right]^2.$$

There is a finite number of levels, determined by the condition $\varepsilon > 0$, i.e. $n < s$.

§ 24. Motion in a homogeneous field

Let us consider the motion of a particle in a homogeneous external field. We take the direction of the field as the axis of x; let F be the force acting

on the particle in this field. In an electric field of intensity E, this force is $F = eE$, where e is the charge on the particle.

The potential energy of the particle in the homogeneous field is of the form $U = Fx +$ const; choosing the constant so that $U = 0$ for $x = 0$, we have $U = -Fx$. Schrödinger's equation for this problem is

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{2m}{\hbar}(E + Fx)\psi = 0. \tag{24.1}$$

Since U tends to $+\infty$ as $x \to -\infty$, and vice versa, it is clear that the energy levels form a continuous spectrum occupying the whole range of energy values E from $-\infty$ to $+\infty$. None of these eigenvalues is degenerate, and they correspond to motion which is finite towards $x = -\infty$ and infinite towards $x = +\infty$.

Instead of the coordinate x, we introduce the dimensionless variable

$$\xi = \left(x + \frac{E}{F}\right)\left(\frac{2mF}{\hbar}\right)^{1/3}. \tag{24.2}$$

Equation (24.1) then takes the form

$$\psi'' + \xi\psi = 0. \tag{24.3}$$

This equation does not contain the energy parameter. Hence, if we obtain a solution of it which satisfies the necessary conditions of finiteness, we at once have the eigenfunction for arbitrary values of the energy.

The solution of equation (24.3) which is finite for all x has the form (see §b of the Mathematical Appendices)

$$\psi(\xi) = A\Phi(-\xi), \tag{24.4}$$

where

$$\Phi(\xi) = \frac{1}{\sqrt{\pi}} \int_0^\infty \cos\left(\frac{1}{3}u^3 + u\xi\right) \mathrm{d}u$$

is called the *Airy function*, while A is a normalization factor which we shall determine below.

As $\xi \to -\infty$, the function $\psi(\xi)$ tends exponentially to zero. The asymptotic expression which determines $\psi(\xi)$ for large negative values of ξ is (see (b.4))

$$\psi(\xi) \approx \frac{A}{2|\xi|^{1/4}} \exp\left(-\frac{2}{3}|\xi|^{3/2}\right) \tag{24.5}$$

For large positive values of ξ, the asymptotic expression for $\psi(\xi)$ is (see (b.5))[16]

$$\psi(\xi) = \frac{A}{\xi^{1/4}} \sin\left(\frac{2}{3}\xi^{3/2} + \frac{\pi}{4}\right). \tag{24.6}$$

Using the general rule (5.4) for the normalization of eigenfunctions of a continuous spectrum, let us reduce the function (24.4) to the form normalized by the delta function of energy, for which

$$\int_{-\infty}^{+\infty} \psi(\xi)\psi(\xi')\mathrm{d}x\delta(E' - E). \tag{24.7}$$

In §21 we gave a simple method of determining the normalization coefficient by means of the asymptotic expression for the wave functions. Following this method, we represent the function (24.6) as the sum of two travelling waves:

$$\psi(\xi) \approx \frac{A}{2\xi^{1/4}} \left\{ \exp\left[\mathrm{i}\left(\frac{2}{3}\xi^{3/2} - \frac{\pi}{4}\right)\right] + \exp\left[-\mathrm{i}\left(\frac{2}{3}\xi^{3/2} - \frac{\pi}{4}\right)\right] \right\}.$$

The current density, calculated from each of these two terms, is

$$v\left(\frac{A}{2\xi^{1/4}}\right)^2 = \sqrt{\frac{2}{m}(E + Fx)}\left(\frac{A}{2\xi^{1/4}}\right)^2 = A^2\frac{(2\hbar F)^{1/3}}{4m^{2/3}}.$$

and equating this to $1/2\pi\hbar$ we find

$$A = \frac{(2m)^{1/3}}{\pi^{1/2}F^{1/6}\hbar^{2/3}}. \tag{24.8}$$

PROBLEM

Determine the wave functions in the momentum representation for a particle in a homogeneous field.

SOLUTION. The Hamiltonian in the momentum representation is

$$\widehat{H} = \frac{p^2}{2m} - \mathrm{i}\hbar F\frac{\mathrm{d}}{\mathrm{d}p},$$

so that Schrödinger's equation for the wave function $a(p)$ has the form

$$-\mathrm{i}\hbar F\frac{\mathrm{d}a}{\mathrm{d}p} + \left(\frac{p^2}{2m} - E\right)a.$$

---

[16] It may be noted, by way of anticipation, that the asymptotic expressions (24.5) and (24.6) correspond to the quasi-classical expressions for the wave function in the classically inaccessible and accessible regions (§47).

Solving this equation, we find the required functions

$$a_E(p) = \frac{1}{\sqrt{2\pi\hbar F}} \exp\left\{\frac{i}{\hbar F} F\left(Ep - \frac{p^3}{6m}\right)\right\}.$$

These functions are normalized by the condition

$$\int_{-\infty}^{+\infty} a_E^*(p) a_{E'}(p)\mathrm{d}p = \delta(E' - E).$$

§ 25. The transmission coefficient

Let us consider the motion of particles in a field of the type shown in Fig. 5: $U(x)$ increases monotonically from one constant limit ($U = 0$ as $x \to -\infty$) to another ($U = U_0$ as $x \to +\infty$). According to classical mechanics, a particle of energy $E < U_0$ moving in such a field from left to right, on reaching such a "potential wall", is reflected from it, and begins to move in the opposite direction; if, however, $E > U_0$, the particle continues to move in its original direction, though with diminished velocity. In quantum mechanics, a new phenomenon appears: even for $E > U_0$, the particle may be reflected from the potential wall. The probability of reflection must in principle be calculated as follows.
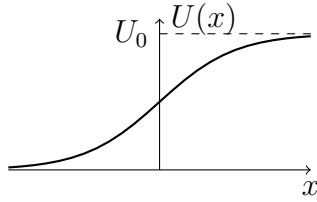
FIG. 5

Let the particle be moving from left to right. For large positive values of x, the wave function must describe a particle which has passed "above the wall" and is moving in the positive direction of x, i.e. it must have the asymptotic form

$$\text{for } x \to \infty: \quad \psi \approx A\mathrm{e}^{ik_2 x}, \quad k_2 = \frac{1}{\hbar}\sqrt{2m(E - U_0)} \qquad (25.1)$$

and A is a constant. To find the solution of Schrödinger's equation which satisfies this boundary condition, we calculate the asymptotic expression for $x \to -\infty$; it is a linear combination of the two solutions of the equation of free motion, i.e. it has the form

$$\text{for } x \to -\infty: \quad \psi \approx \mathrm{e}^{ik_1 x} + B\mathrm{e}^{-k_1 x}, \quad k_1 = \frac{1}{\hbar}\sqrt{2mE}. \qquad (25.2)$$

The first term corresponds to a particle incident on the wall (we suppose ψ normalized so that the coefficient of this term is unity); the second term

represents a particle reflected from the wall. The probability current density in the incident wave is k_1, in the reflected wave $k_1|B|^2$, and in the transmitted wave $k_2|A|^2$. We define the *transmission coefficient* D of the particle as the ratio of the probability current density in the transmitted wave to that in the incident wave:

$$D = \frac{k_2}{k_1}|A|^2. \tag{25.3}$$

Similarly we can define the reflection coefficient R as the ratio of the density in the reflected wave to that in the incident wave. Evidently $R = 1D$:

$$R = |B|^2 = 1 - \frac{k_2}{k_1}|A|^2 \tag{25.4}$$

(this relation between A and B is automatically satisfied).

If the particle moves from left to right with energy $E < U_0$, then k_2 is purely imaginary, and the wave function decreases exponentially as $x \to +\infty$. The reflected current is equal to the incident one, i.e. we have "total reflection" of the particle from the potential wall. We emphasize, however, that in this case the probability of finding the particle in the region where $E < U$ is still different from zero, though it diminishes rapidly as x increases.

In the general case of an arbitrary stationary state (with energy $E > U_0$), the asymptotic form of the wave function is given, both for $x \to -\infty$ and for $x \to +\infty$, by a sum of waves propagated in each direction:

$$\begin{aligned}
\psi &= A_1 e^{ik_1x} + B_1 e^{-ik_1x} \quad \text{for} \quad x \to -\infty, \\
\psi &= A_2 e^{ik_2x} + B_2 e^{-ik_2x} \quad \text{for} \quad x \to +\infty.
\end{aligned} \tag{25.5}$$

Since these expressions are asymptotic forms of the same solution of a linear differential equation, there must be a linear relation between the coefficients A_1, B_1 and A_2, B_2. Let $A_2 = \alpha A_1 + \beta B_1$, where α, β are constants (in general complex) which depend on the specific form of the field $U(x)$. The corresponding relation for B_2 can then be written down from the fact that Schrödinger's equation is real. This shows that, if ψ is a solution of a given Schrödinger's equation, the complex conjugate function ψ^* is also a solution. The asymptotic forms

$$\begin{aligned}
\psi^* &= A_1^* e^{-ik_1x} + B_1^* e^{ik_1x} \quad \text{for} \quad x \to -\infty, \\
\psi^* &= A_2^* e^{-ik_2x} + B_2^* e^{ik_2x} \quad \text{for} \quad x \to +\infty
\end{aligned}$$

differ from (25.5) only in the nomenclature of the constant coefficients; we therefore have $B_2^* = \alpha B_1^* + \beta A_1^*$ or $B2 = \alpha^* B_1 + \beta^* A_1$. Thus the coefficients in (25.5) are related by equations of the form

$$A_2 = \alpha A_1 + \beta B_1, \quad B_2 = \beta^* A_1 + \alpha^* B_1. \tag{25.6}$$

The condition of constant current along the x-axis leads to the relation

$$k_1(|A_1|^2 - |B_1|^2) = k_2(|A_2|^2 - |B_2|^2).$$

Expressing A_2, B_2 in terms of A_1, B_1 by (25.6), we find

$$|\alpha|^2 - |\beta|^2 = \frac{k_1}{k_2}. \tag{25.7}$$

Using the relation (25.6), we can show, in particular, that the reflection coefficients are equal (for a given energy $E > U_0$) for particles moving in the positive and negative directions of the x-axis; the former case corresponds to putting $B_2 = 0$ in (25.5), and the latter case to $A_1 = 0$. In these two cases, $B_1/A_1 = \beta^*/\alpha^*$ and $A_2/B_2 = \beta/\alpha^*$ respectively. The corresponding reflection coefficients are

$$R_1 = \left|\frac{B_1}{A_1}\right|^2 = \left|\frac{\beta^*}{\alpha^*}\right|^2, \quad R_2 = \left|\frac{A_2}{B_2}\right|^2 = \left|\frac{\beta}{\alpha^*}\right|^2$$

whence it is clear that $R_1 = R_2$.

It is natural to call $B_1/A_1 = -\beta^*/\alpha^*$ and $A_2/B_2 = \beta/\alpha^*$ the *reflection amplitudes* for motion in the positive and negative directions respectively. They are equal in modulus but may have different phase factors.

PROBLEMS

1. Determine the reflection coefficient of a particle from a rectangular potential wall (Fig. 6); the energy of the particle $E > U_0$.
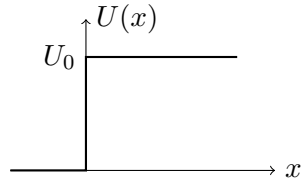
SOLUTION. Throughout the region $x > 0$, the wave function has the form (25.1), while in the region $x < 0$ its form is (25.2). The constants A and B are determined from the condition that ψ and $\mathrm{d}\psi/\mathrm{d}x$ are continuous at $x = 0$:

$$1 + B = A, \quad k_1(1 - B) = k_2 A,$$

whence

$$A = \frac{2k_1}{k_1 + k_2}, \quad B = \frac{k_1 - k_2}{k_1 + k_2}.$$

FIG. 6

The reflection coefficient[17]) is (25.4)

$$R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2 \left(\frac{p_1 - p_2}{p_1 + p_2}\right)^2$$

---

[17]) In the limiting case of classical mechanics, the reflection coefficient must become zero. The expression obtained here, however, does not contain the quantum constant at all. This apparent contradiction is explained as follows. The classical limiting case is that in which the de Broglie wavelength of the particle $\lambda \sim \hbar/p$ is small in comparison with the characteristic dimensions of the problem, i.e. the distances over which the field $U(x)$ changes noticeably. In the schematic example considered, however, this distance is zero (at the point $x = 0$), so that the passage to the limit cannot be effected.

For $E = U_0$ $(k_2 = 0)$, R becomes unity, while for $E \to \infty$ it tends to zero as $R = (U_0/4E)^2$.

2. Determine the transmission coefficient for a rectangular potential barrier (Fig. 7).

SOLUTION. Let E be greater than U_0, and suppose that the incident particle is moving from left to right. Then we have for the wave function in the different regions expressions of the form

$$\psi = \mathrm{e}^{ik_1x} + A\mathrm{e}^{-ik_1x} \qquad\qquad \text{for } x < 0,$$
$$\psi = B\mathrm{e}^{ik_2x} + B'\mathrm{e}^{-ik_2x} \qquad\qquad \text{for } 0 < x < a,$$
$$\psi = C\mathrm{e}^{ik_1x} \qquad\qquad \text{for } x > a.$$

(on the side $x > a$ there can be only the transmitted wave, propagated in the positive direction of x). The constants A, B, B' and C are determined from the conditions of continuity of ψ and $\mathrm{d}\psi/\mathrm{d}x$ at the points $x = 0$ and a. The transmission coefficient is determined as $D = k_1|C|^2/k_1 = |C|^2$. On calculating this, we obtain

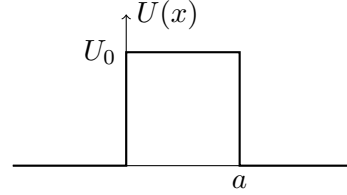$$D = \frac{4k_1^2 k_2^2}{(k_1^2 - k_2^2)^2 \sin^2 ak_2 + 4k_1^2 k_2^2}$$

FIG. 7

For $E < U_0$, k_2 is a purely imaginary quantity; the corresponding expression for D is obtained by replacing k_2 by $i\varkappa_2$ where $\hbar\varkappa_2 = \sqrt{2m(U_0 - E)}$:

$$D = \frac{4k_1^2 \varkappa_2^2}{(k_1^2 - \varkappa_2^2)^2 \sin^2 a\varkappa_2 + 4k_1^2 \varkappa_2^2}$$

3. Determine the reflection coefficient for a potential wall defined by the formula

$$U(x) = U_0/(1 + \mathrm{e}^{-\alpha x})$$

(Fig. 5); the energy of the particle is $E > U_0$.

SOLUTION. Schrödinger's equation is

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{2m}{\hbar^2}\left(E - \frac{U_0}{1 + \mathrm{e}^{-\alpha x}}\right)\psi = 0.$$

We have to find a solution which, as $x \to +\infty$, has the form

$$\psi = \mathrm{const} \cdot \mathrm{e}^{ik_2}.$$

We introduce a new variable

$$\xi = -\mathrm{e}^{-\alpha x}.$$

(which takes values from $-\infty$ to 0), and seek a solution of the form

$$\psi = \xi^{-ik_2/\alpha}w(\xi),$$

where $w(\xi)$ tends to a constant as $\xi \to 0$ (i.e. as $x \to \infty$). For $w(\xi)$ we find an equation of hypergeometric type:

$$\xi(1-\xi)w'' + \left(1 - \frac{2i}{\alpha}k_2\right)(1-\xi)w' + \frac{1}{\alpha^2}(k_2^2 - k_1^2)w = 0,$$

which has as its solution the hypergeometric function

$$w = F\left[\frac{i}{\alpha}(k_1 - k_2), -\frac{i}{\alpha}(k_1 + k_2), -\frac{2i}{\alpha}k_2 + 1, \xi\right]$$

(we omit a constant factor). As $\xi \to 0$, this function tends to 1, i.e. it satisfies the condition imposed.

The asymptotic form of the function ψ as $\xi \to -\infty$ (i.e. $x \to -\infty$) is[18]

$$\psi \approx \xi^{-ik_2/\alpha}\left[C_1(-\xi)^{i(k_2-k_1)/\alpha} + C_2(-\xi)^{i(k_1+k_2)/\alpha}\right] =$$
$$= (-1)^{ik_2/\alpha}\left[C_1e^{ik_1x} + C_2e^{-ik_2x}\right],$$

where

$$C_1 = \frac{\Gamma(-(2i/\alpha)k_1)\Gamma(-(2i/\alpha)k_2 + 1)}{\Gamma(-(i/\alpha)(k_1 + k_2))\Gamma(-(i/\alpha)(k_1 + k_2) + 1)},$$
$$C_2 = \frac{\Gamma((2i/\alpha)k_1)\Gamma(-(2i/\alpha)k_2 + 1)}{\Gamma((i/\alpha)(k_1 - k_2))\Gamma((i/\alpha)(k_1 - k_2) + 1)}.$$

The required reflection coefficient is $R = |C_2/C_1|^2$ on calculating it by means of the well known formula
$$\Gamma(x)\Gamma(1-x) = \frac{\pi}{\sin \pi x},$$
we have
$$R = \left\{\frac{\sinh[(\pi/\alpha)(k_1 - k_2)]}{\sinh[(\pi/\alpha)(k_1 + k_2)]}\right\}^2.$$

For $E = U_0$ ($k_2 = 0$), R becomes unity, while for $E \to \infty$ it tends to zero as

$$R = \left(\frac{\pi U_0}{\alpha\hbar}\right)^2 \frac{2m}{E}\exp\left(-\frac{4\pi}{\alpha\hbar}\sqrt{2mE}\right).$$

In the limiting case of classical mechanics. R becomes zero, as it should.

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[18] See formula (e.6), in each of whose two terms we must take only the first term of the expansion, i.e. replace the hypergeometric functions of $1/z$ by unity.
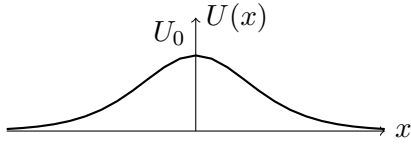
$U_0 \uparrow U(x)$

FIG. 8

4. Determine the transmission coefficient for a potential barrier defined by the formula

$$U(x) = \frac{U_0}{\cosh^2 \alpha x}$$

(Fig. 8); the energy of the particle is $E < U_0$.

SOLUTION. The Schrödinger's equation is the same as that obtained in the solution of Problem 5, §23; it is necessary merely to alter the sign of U_0 and to regard the energy E now as positive. A similar calculation gives the solution

$$\psi = (1 - \xi^2)^{-\frac{ik}{2\alpha}} F\left(-\frac{ik}{\alpha} - s, -\frac{ik}{\alpha} + s + 1, -\frac{ik}{\alpha} + 1, \frac{1 - \xi}{2}\right), \tag{1}$$

where

$$\xi = \tanh \alpha x, \quad k = \frac{1}{\hbar}\sqrt{2mE}, \quad s = \frac{1}{2}\left(-1 + \sqrt{1 - \frac{8mU_0}{\alpha^2 \hbar^2}}\right).$$

This solution satisfies the condition that, as $x \to \infty$ (i.e. as $\xi \to 1$, $(1 - \xi) \approx 2e^{-2\alpha x}$), the wave function should include only the transmitted wave ($\sim e^{ikx}$). The asymptotic form of the wave function as $x \to -\infty (\xi \to 1)$ is found by transforming the hypergeometric function with the aid of formula (e.7):

$$\psi \sim e^{ikx}\frac{\Gamma(ik/\alpha)\Gamma(1 - ik/\alpha)}{\Gamma(-s)\Gamma(1 + s)} + e^{ikx}\frac{\Gamma(-ik/\alpha)\Gamma(1 - ik/\alpha)}{\Gamma(-ik/\alpha - s)\Gamma(-ik/\alpha + s + 1)}. \tag{2}$$

Taking the squared modulus of the ratio of coefficients in this function, we obtain the following expression for the transmission coefficient $D = 1R$:

$$D = \frac{\sinh^2 \frac{\pi k}{\alpha}}{\sinh^2 \frac{\pi k}{\alpha} + \cos^2\left(\frac{\pi}{2}\sqrt{1 - \frac{8mU_0}{\hbar^2\alpha^2}}\right)} \quad \text{if} \quad \frac{8mU_0}{\hbar^2\alpha^2} < 1,$$

$$D = \frac{\sinh^2 \frac{\pi k}{\alpha}}{\sinh^2 \frac{\pi k}{\alpha} + \cosh^2\left(\frac{\pi}{2}\sqrt{\frac{8mU_0}{\hbar^2\alpha^2} - 1}\right)} \quad \text{if} \quad \frac{8mU_0}{\hbar^2\alpha^2} > 1.$$

The first of these formulae holds also for the case $U_0 < 0$, i.e. when the particle is passing over a potential well instead of a potential barrier. It is interesting to note that in that case $D = 1$ if $1 + 8m|U_0|/\hbar^2\alpha^2 = (2n + 1)^2$; thus, for certain values of the depth $|U_0|$ of the well, particles passing over it are not reflected. This is evident from equation (2), where the term in e^{ikx} vanishes for positive integral s.

5. Determine how the transmission coefficient tends to zero as $E \to 0$, assuming that the potential energy $U(x)$ decreases rapidly at distances $|x| \gg a$, where a is the dimension of the interaction region.

SOLUTION. For distances $k|x| \ll 1$, E can be neglected in Schrödinger's equation. If also $|x| \gg a$, the potential energy can also be neglected, and the equation becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = 0,$$

the solution of this may be written as

$$\psi = a_1 + b_1 x, \quad x < 0, \qquad \psi = a_2 + b_2 x, \quad x > 0. \tag{1}$$

The relation between a_1, b_1 and a_2, b_2 can be found by solving the equation at distances $|x| \sim a$. It is linear:

$$a_1 = \rho a_2 + \mu b_2, \quad b_1 = \nu a_1 + \tau b_2. \tag{2}$$

The coefficients ρ, μ, ν and τ are real and independent of the energy, which does not appear in the equation.[19] The solution (1) must be the same as the first two terms in the expansion of (25.1) and (25.2) in powers of x, so that

$$a_1 = B + 1, \quad b_1 = \mathrm{i}k(1 - B), \quad a_2 = A, \quad b_2 = \mathrm{i}kA.$$

Substituting these in (2) and solving for A, we get, for small k: $A \approx 2\mathrm{i}k/\nu$, whence

$$D \approx \frac{4k^2}{\nu^2} \sim E$$

The transmission coefficient thus tends to zero in proportion to the particle energy. This is of course true for the examples in Problems 2 and 4.

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[19] Since the flux is constant, $\rho\tau - \mu\nu = 1$.