

THE
PHYSICAL REVIEW
SUPPLEMENT

THE GENERAL PRINCIPLES OF QUANTUM
MECHANICS. PART I

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SECTION 1. ELEMENTARY PRINCIPLES OF WAVE MECHANICS

1. HISTORICAL INTRODUCTION

FROM the empirical standpoint the most striking features in the development of twentieth-century physics have been (a) the discovery and exploitation of the corpuscular characteristics of radiation; (b) the discovery and exploitation of the existence of discrete atomic and molecular energy levels, bringing into mechanics a new kind of atomicity superposed on the atomicity of electron and proton; (c) the discovery of the wave-like characteristics of matter as exhibited in the now famous experiments of Davisson and Germer. The quantum mechanics is the fruit of the efforts of theoretical physicists to provide a concise and unified description of these new experimental facts and of the great mass of empirical data on which the "classical" physics of the nineteenth century was built.

Roughly speaking we may divide the history of twentieth-century theoretical physics into two periods. In the first period, extending from the initial discovery of the Planck radiation formula until 1925, the leaders in theoretical physics were Planck, Einstein, Bohr, and Sommerfeld. Einstein led the way in the formulation of the corpuscular theory of radiation which proved so stimulating to experimental physicists. The many successes of this point of view culminating in its interpretation of the Compton effect served to place it on an equal footing with the classical wave theory. The older theory was not completely overthrown, however, as it gave the only natural interpretation of the facts regarding interference and diffraction. In practice physicists were led to the adoption of a dualistic mode of thought in which they treated light as waves in the discussion of one class of experiments and as corpuscles in the discussion of another.

In parallel with the development of the corpuscular theory of radiation went the formulation of the Bohr quantum theory of atomic structure with its marvelously useful interpretation of line and band spectra and of the collision experiments of Franck, Hertz, K. T. Compton, and others. This theory performed most admirably the function of correlating the

empirical facts in the field which it covered and through the correspondence principle laid the foundation for the matrix mechanics of Heisenberg, Born, and Jordan. It was at all times, however, confessedly incomplete and in many respects inaccurate.

The second period witnessed the simultaneous development of the matrix mechanics and of the wave mechanics of de Broglie and Schrödinger. These theories, now fused together into what we call quantum mechanics, correct the deficiencies of the Bohr theory as a tool for investigating the structure of matter, remove its restriction to periodic motions, relate the diffraction of electrons to the problem of atomic structure, and throw a great deal of new light on the dilemma regarding the nature of radiation.

In the form of quantum mechanics now most widely used, the dualistic nature of radiation is accepted as a brute fact to be described rather than explained or exorcised. A similar dualistic nature is ascribed to matter and thus a unification in the treatment of matter and radiation is attained. The discovery of the fundamental similarity between matter and radiation is one of the most striking features of present physical theory. Differences, of course, remain and we can by no stretch of the imagination identify these two fundamental modes of existence, but the analogy is far-reaching enough to permit the use of observations regarding the characteristics of radiation as guides in the formulation of a theory of matter. The de Broglie-Schrödinger theory was the result of a conscious attempt to follow such guides and this method of approach to the quantum mechanics seems to the present writer to be more natural than any other.

2. THE DUALISTIC THEORY OF RADIATION

The importance of optical analogy in the development of quantum mechanics lies primarily in the fact that the dualistic nature of light is much more obvious than the dualistic nature of matter. In the region of long waves the wave-like characteristics of radiation are strongly predominant, while in the x-ray region the corpuscular characteristics are predominant. As the transition from the one part of the spectrum to the other is continuous, the dualism is inescapable.

Let us then begin our survey of the quantum mechanics with a brief preliminary examination of the problem of radiation. What is the upshot of the battle between the wave theory of light and the corpuscular theory? The answer is, "A deadlock."¹ The wave theory gives a simple and accurate account of interference, diffraction, and dispersion besides making proper connection with quasi-static electromagnetic phenomena in the limiting region of very long waves. The corpuscular theory gives a simple and accurate account of the fundamental laws of the photo-electric effect and the Compton effect; it is a logical corollary of the fundamental law of spectro-

¹ Here we explicitly ignore the recent "double quantization" theory of Jordan and his collaborators which achieves a genuine fusion of the two theories by treating the electromagnetic vectors E and H as matrix quantities. This development should logically follow that of the quantum mechanics.

scopy $E' - E'' = h\nu$; and it accounts for the abrupt changes in momentum experienced by emitting and absorbing atoms and molecules in a radiation field. Neither point of view gives a satisfactory description of the whole field of optics. In the case of a few phenomena, notably the Doppler effect, the predictions of the two theories are identical and agree with experiment. In other cases the two theories supplement each other. For example, in the case of the inverse photo-electric effect or the production of the continuous x-ray spectrum, the corpuscular theory is needed to account for the sharply defined limit to the spectrum, but must be supplemented by the wave theory in order to take into account the polarization phenomenon. Either point of view gives a qualitative explanation of the variation in hardness with direction of emission, which is, in fact, a kind of Doppler effect.

Evidently we need a fusion of these two theories. Perhaps the most obvious mode of procedure for uniting the two points of view is to assume that light consists of "wave packets" or wave disturbances occupying a small volume in space. Such a fusion of the two theories meets insuperable difficulty, however, in the fact that wave packets except under very special circumstances spread out indefinitely as they progress, instead of remaining small. Moreover, the facts regarding interference and diffraction require spreading wave fields rather than wave packets. To see this, we observe first that to account for the passage of light through small holes and for the basic phenomena which have given rise to the corpuscular conception, we must assume that the wave packets are very small. Interference would have to be accounted for as due to the overlapping of different packets. But the experiments on interference in weak light show clearly that interference fringes are perfectly formed even when the photons are so far apart that such overlapping is out of the question.

A more successful way of uniting the two theories is to adopt a frankly dualistic point of view by assuming that light consists of *both* spreading waves and corpuscles. The familiar fundamental formulas of Einstein for the energy and momentum of a light corpuscle, i.e.

$$E = h\nu \tag{1}$$

$$p = h\nu/c = h/\lambda \tag{2}$$

point directly to such a dualism, since they are really merely a basic lexicon for translating wave language into corpuscle language. If we postulate such a dualism, we can suppose that the electromagnetic waves of Maxwell's theory act as guides to the corpuscles and thus produce interference phenomena,² while the localization of energy and momentum in the photons accounts for the photo-electric effect, etc.

Of course, the existence of two apparently conflicting sets of characteristics for radiation has been a commonplace for many years and to many physicists the adoption of a dualistic point of view as the starting point for a fresh attack on the fundamental problems of physics will seem an evasion

² Cf. W. F. G. Swann, *Science*, **61**, p. 433 (1925).

of the fundamental question, “*Why* does light act in some respects like an assemblage of corpuscles and in other respects like a spreading wave phenomenon?” We assert, however, that in the last analysis the function of theoretical physics is to describe rather than to explain. Science seeks to interpret the infinitely complex world of direct experience as the outcome of fundamentally simple laws. The reduction of complexity to simplicity is the goal, and when it is attained, we prove that order underlies chaos and leave the question, “*Why*” still essentially untouched. Hence, discarding this question as ultimately unanswerable, we may address ourselves to the task of describing what we observe in the most compact manner possible. If the behavior of radiation can be at least approximately described by means of the dualistic point of view, its temporary adoption will be a step in advance. No claim of ultimate validity is made for the theory, however.

An apparently essential feature of any such fusion of the wave and corpuscle theories is its statistical character. As the corpuscles are discontinuously distributed in space while the waves are continuous, it is evident that if the waves are to determine the positions of the corpuscles, they can only do so statistically. In other words we must regard the intensity of light of frequency ν in any small volume G as a measure of the probable number of photons of energy $h\nu$ in G . This mode of correlating the positions of waves and corpuscles we will carry over directly from the radiation problem to the matter problem.

3. AN ANALOGY BETWEEN GEOMETRICAL OPTICS AND CLASSICAL MECHANICS

The wave or “optical” theory of matter has its roots in the formulation of the principles of least time for geometrical optics and of least action for Newtonian mechanics by Fermat and Maupertuis, respectively. The principle of least time states that the path of a ray of light (wave-front normal) from a point A to a point B is always such as to make the integral

$$\int_A^B \frac{ds}{w}$$

an extremal (usually a minimum) with respect to all other conceivable paths for rays of the same color or frequency. w in this formula denotes the phase velocity of light and is a function of the frequency and of the space coordinates x, y, z . As the frequency ν is treated as a constant in varying the integral, and as the wave-length λ is equal to w/ν , the principle may equally well be stated in the form

$$\delta \int_A^B \frac{ds}{\lambda} = 0. \quad (\nu \text{ unvaried}) \quad (3)$$

This means that the path length measured in wave-lengths is an extremal. As the spreading of light waves in space is fully determined by the “wave equation”

$$\nabla^2\psi = \frac{1}{w^2(x, y, z, \nu)} \frac{\partial^2\psi}{\partial t^2} \quad (4)$$

we may conclude that Fermat's principle is deducible under suitable conditions from this equation. The proof is very simple in the case of plane waves moving in homogeneous media bounded by plane surfaces of discontinuity. The generalization to non-homogeneous media is not given in the classical treatises on optics, but de Broglie³ has shown how to carry it through. For this purpose it is necessary to assume that the wave whose rays are to be determined is progressive and only slightly curved.⁴ Also the fractional change in the phase velocity w or in the wave-length λ in the distance λ must be small. These restrictions create no difficulty in the formulation of a wave theory of matter.

Let us now compare Fermat's principle in the form of Eq. (3) with the principle of least action. In case of a single particle of total energy E , kinetic energy T , and mass μ , moving through a force field with potential energy $V(x, y, z)$ the latter principle requires that the action integral

$$S = \int_A^B 2T dt = \int_A^B [2\mu(E - V)]^{1/2} ds \quad (5)$$

over the natural or mechanical path between two points A and B shall be an extremal as compared with its value for all adjacent paths using the same value of E . For such a particle the integrand $[2\mu(E - V)]^{1/2}$ is identical with the absolute value of the instantaneous momentum p which the particle would assume at x, y, z so that the principle may be stated in the form

$$\delta \int_A^B p(E, x, y, z) ds = 0. \quad (E \text{ unvaried}) \quad (6)$$

The analogy between these two principles was seized upon by Sir William Hamilton in the early part of the nineteenth century and used as a guide in the development of dynamical and optical theory. Hamilton regarded it as an analogy only, however, and it remained for de Broglie and Schrödinger to show that in view of this analogy Newtonian mechanics may be regarded as a limiting case of a suitably defined wave problem.

A comparison of equations (3) and (6) shows that the paths of particles in the Newtonian dynamics may be identified with the "rays" in a wave problem in which the index of refraction and phase velocity are made suitable functions of x, y, z , and the energy E . To be exact, the condition imposed on the wave problem is that

$$\frac{C}{\lambda} = \frac{C\nu}{w} = p(E, x, y, z) = (2\mu[E - V(x, y, z)])^{1/2}, \quad (7)$$

where C is an arbitrary constant.

³ L. de Broglie, Journ. de Physique 7, p. 321 (1926).

⁴ Radius of curvature large compared with the wave-length.

4. WAVE PACKETS AND GROUP VELOCITY

We have set out to develop a theory of mechanics parallel to our theory of light. Hence we must demand *ab initio* that the relation between the motion of photons in optics and the motion of the associated optical waves shall be duplicated in the relation between the motions of large scale bodies and the associated "mechanical waves." Now the nearest that we can come to observing the motion of an individual photon is to form a "wave packet" or localized disturbance of an approximately monochromatic nature. To this end we may shine plane parallel monochromatic light on a small aperture provided with a shutter. If this be opened for a brief interval of time, it will allow a short train of waves to pass through. Such a train is called a wave packet, since it is a localized bundle of energy which may be resolved into a superposition of plane waves spread over a narrow range of directions and frequencies. The path of such a train may be approximately mapped out and its velocity can be approximately measured. In theory, at any rate, there is nothing to prevent the observation of the orbit of such a train even in an inhomogeneous dispersive medium. Of course, such a train will ordinarily contain more than one photon, but since the behavior of such packets is known to be independent of the light intensity, it is clear that the result would be the same if only one photon were involved. Diffraction will make trouble if we try to define the path too accurately by using an excessively small aperture, but diffraction will be minimized by using x-ray wave-lengths. We will return to this question later on.

Clearly if we are to associate a wave motion with the orbital motion of a large scale body such as a golf ball, the wave function must be of the same nature as that of the optical wave packets just described. Otherwise we could not interpret the observed properties of our golf ball (simultaneous position and velocity) by means of waves. Hence if the analogy between Fermat's principle and the principle of least action really means anything, it must be possible to show from it that the orbit and orbital velocity of a large scale "particle"⁵ are identical with the orbit and orbital velocity of a wave packet in a suitably defined wave problem. We must then show (a) that wave packets travel along the rays of geometric optics and (b) that the speed of the packet is the same as the speed of the corresponding mechanical particle.

The first of these two propositions is commonly assumed without proof. Professor Slater has worked out a simple elementary proof (unpublished) for the general case of a non-homogeneous medium, but we shall not reproduce the argument here. Consider then the second of these two propositions. The speed of the packet is the same as the group velocity of the waves, v_g . According to a well-known formula

$$\frac{1}{v_g} = \frac{\partial}{\partial \nu} \left(\frac{1}{\lambda} \right). \quad (8)$$

⁵ Of course, a large scale body is an assemblage of many particles. The justification for treating it as a single particle in the wave mechanics follows from a center of gravity theorem as in Newtonian mechanics.

If this is to be the same as the velocity of the particle v , Eq. (7) gives

$$\frac{1}{v} = \frac{\partial}{\partial v} \left(\frac{p}{C} \right) = \frac{\partial}{\partial v} \left\{ \frac{[2\mu(E-V)]^{1/2}}{C} \right\} = \frac{\mu}{Cp} \frac{\partial E}{\partial v}. \quad (9)$$

As p is equal to μv , this reduces to

$$C = \partial E / \partial v, \quad (10)$$

a relation which immediately suggests the assumption that the Einstein energy-frequency relation (1) holds for matter as well as for radiation. If we accept (1) as an hypothesis for matter, Eq. (10) is satisfied and we see that the required relations between the motion of the particle and the packet will be fulfilled if

$$p \equiv \mu v = [2\mu(E-V)]^{1/2} = h/\lambda. \quad (11)$$

This equation has been confirmed experimentally by the electron diffraction experiments of Davisson and Germer,⁶ Thompson⁷, and Rupp.⁸ The wave-lengths involved are almost inconceivably small when (11) is applied to bodies of microscopic dimensions. In the case of a golf ball weighing 47 grams the ratio h/μ is 1.4×10^{-28} . If the ball moves with a speed as low as a millimeter in 10 seconds, the wave-length is 1.4×10^{-26} centimeters! This means that diffraction effects are hopelessly beyond the reach of experiment in the case of large scale bodies. On the other hand, the computed wave-length is not inappreciable when Eq. (11) is applied to atomic and molecular problems. For example, the wave-length of an oxygen molecule with a speed corresponding to the mean thermal energy at 300°K is approximately 1.45×10^{-8} cm, while that for an electron with a 10-volt kinetic energy is 5.3×10^{-8} cm. As these wave-lengths are of the order of magnitude of atomic diameters, it is clear that diffraction effects must play a prominent part in atomic dynamical problems.

It is important to note that by introducing a vector δ having the magnitude $1/\lambda$ and the direction of the wave normal, we can throw equation (11) into the vector form

$$\mathbf{p} = h\delta. \quad (12)$$

We shall call δ the vector wave number. Its components $\sigma_x, \sigma_y, \sigma_z$ denote the number of waves per centimeter crossed by lines parallel to the x, y , and z axes.

5. THE SCHRÖDINGER WAVE EQUATION

In view of the above results we may assume that the differential equation (4) is valid for matter waves if we set

⁶ C. Davisson and L. H. Germer, Phys. Rev. **30**, p. 705 (1927); Proc. Nat. Acad. **14**, p. 317 (1928).

⁷ G. P. Thomson, Proc. Roy. Soc. **117(A)**, p. 600 (1928); **119(A)**, p. 651 (1928).

⁸ E. Rupp, Ann. d. Physik **85**, p. 981 (1928).

$$w(x, y, z, \nu) = \lambda \nu = \frac{E}{p} = \frac{E}{[2\mu(E-V)]^{1/2}} = \frac{h\nu}{[2\mu(h\nu-V)]^{1/2}}. \quad (13)$$

As in the optical case the differential equation holds for monochromatic or "monoenergetic" wave functions only, it being assumed that all possible wave forms can be built up from monochromatic waves.

This restriction means that all solutions of Eq. (4) are to be of the form

$$\psi = u(x, y, z)T(t) \quad (14)$$

where $T(t)$ is of the form

$$T(t) = \cos 2\pi(\nu t + \epsilon) \text{ or } e^{\pm 2\pi i(\nu t + \epsilon)}.$$

Then substitution from Eqs. (13) and (14) into Eq. (4) and elimination of T yields

$$\nabla^2 u + \frac{8\pi^2\mu}{h^2}(E-V)u = 0. \quad (15)$$

This latter equation is quite as general as (4). The factor $u(x, y, z)$ is sometimes called the amplitude. The term "space factor" is also appropriate and will be used in this review.

For many purposes Eqs. (4) and (15) are adequate, but we frequently have to do with problems in which ψ is made up of a sum of terms of the type of Eq. (14) and for which we need a more general differential equation which does not contain the parameter E or its equivalent ν . Such a differential equation becomes a necessity when we have to do with problems in which the potential energy depends on the time, or in which for any reason the energy of the system is not conserved. A most important example is the perturbation of an atom by an external light wave which is the basis of the theory of dispersion. Here the assumption that we have to do with a single monochromatic wave function or a fixed combination of such functions breaks down completely.

The obvious procedure for deriving a differential equation applicable directly to a wave packet, or to the sum of several monochromatic waves is to eliminate ν from Eq. (4) by differentiation. Schrödinger⁹ has shown that in this way one obtains the rather awkward fourth order equation

$$\left[\nabla^2 - \frac{8\pi^2}{h^2} \mu V \right]^2 \psi + \frac{16\pi^2\mu^2}{h^2} \frac{\partial^2 \psi}{\partial t^2} = 0. \quad (16)$$

This equation is correct for any monochromatic ψ function which obeys Eq. (4) or Eq. (14), or for any linear combination of such functions. A simpler equation of the second order, however, is adequate for our needs. Again following Schrödinger we observe that if we specialize $T(t)$ [Eq. (14)] making the assumption that the basic monochromatic functions have the form

$$\psi = u(x, y, z)e^{+2\pi iEt/h} \quad (17)$$

⁹ E. Schrödinger, *Ann. d. Physik* (4) **81**, p. 109 (1926).

we can replace $E \psi$ by $(h/2\pi i)(\partial\psi/\partial t)$ thus converting Eqs. (4) and (15) into

$$\boxed{\nabla^2\psi - \frac{8\pi^2\mu}{h^2}V\psi - \frac{4\pi\mu i}{h} \frac{\partial\psi}{\partial t} = 0.} \quad (18)$$

This latter equation⁹ is much easier to handle than (16) and is equally adequate for the description of the physical facts. The specialization of the function $T(t)$ involved in Eq. (17) is of the nature of a convention. It is justified by its convenience, and by the fact that waves of this type have all the characteristics needed for our physical problem.

Eq. (18) also makes a simple connection with the Hamiltonian function of the classical mechanics which is of great importance when we come to extrapolate our formulas to non-conservative systems where wave functions of the form (17) do not exist.

Of course the convention (17) could not be used for optical problems since the electric and magnetic vectors which obey the optical differential equation have an intrinsic physical meaning which requires them to be real. Our freedom to adopt Eq. (17) comes from the fact that while $|\psi|^2$ has a direct physical meaning, ψ has not.

6. APPLICATION OF RESTRICTED RELATIVITY PRINCIPLE TO FREE PARTICLE

Historically the first step in the development of wave mechanics was the application of the restricted relativity principle to the problem of the correlation of waves and free particles by de Broglie.¹⁰ Symmetry demands that a stationary particle be associated with a stationary wave system. In other words the wave function for a free particle must be of the form

$$\psi = f(x_0, y_0, z_0)e^{2\pi i\nu_0 t} \quad (19)$$

when referred to a system of coordinates x_0, y_0, z_0 with respect to which the particle is at rest. To get the form of the wave for an electron moving in the direction of the z axis de Broglie applies the Lorentz transformation,

$$z_0 = \frac{z - vt}{[1 - v^2/c^2]^{1/2}}; \quad t_0 = \frac{t - vz/c^2}{[1 - v^2/c^2]^{1/2}}; \quad x_0, y_0 = x, y$$

which yields

$$\psi = f\left(x, y, \frac{z - vt}{[1 - v^2/c^2]^{1/2}}\right) \exp \left\{ \frac{2\pi\nu_0}{[1 - v^2/c^2]^{1/2}} \left(t - \frac{vz}{c^2}\right) \right\}. \quad (20)$$

This expression may be made to describe either an infinite plane wave system or a wave packet according to the hypothesis regarding the amplitude $f(x_0, y_0, z_0)$. In either case the frequency defined by the phase factor is

¹⁰ L. de Broglie, *Nature*, **112**, p. 540 (1923); Thesis, Paris (1924); *Ann de Physique*, (10) **3**, p. 22 (1925).

$$\frac{\nu_0}{[1-v^2/c^2]^{1/2}}$$

If the zero level of energy is fixed in accordance with the usual relativity expression

$$E = \mu c^2 = \frac{\mu_0 c^2}{[1-v^2/c^2]^{1/2}} \quad (21)$$

E and ν transform in the same way so that the fundamental relation (1) is invariant of a Lorentz transformation. This fact is the first great contribution of de Broglie. The wave-length required by Eq. (20) is

$$\lambda = \frac{c^2}{v} \frac{[1-v^2/c^2]^{1/2}}{\nu_0} = \frac{c^2 h}{E v} = \frac{h}{\mu v},$$

in agreement with Eq. (11). The phase velocity is c^2/v as may be read directly from (20) or deduced from Eq. (1), the above expression for λ , and the relation $w = \lambda\nu$.

The variation in mass with velocity can also be taken into account when the particle moves in a force field of potential energy V . The action integral in this case takes the form

$$S = \int_A^B (F + E - V) dt = \int_A^B p ds \quad (22)$$

where $F = \mu_0 c^2 [1-v^2/c^2]^{1/2}$ and $p = \mu v = \mu_0 v / [1-v^2/c^2]^{1/2}$. A comparison of (18) and (3) shows that as in the Newtonian theory the rays defined by Fermat's principle and the mechanical orbits agree if $C/\lambda = p$. In this case the expression for the momentum in terms of the energy is

$$p = \frac{1}{c} [(E - V)^2 - E_0^2]^{1/2} \quad (23)$$

but as before we find that

$$\frac{\partial p}{\partial \nu} = \frac{\mu}{p} \frac{\partial E}{\partial \nu} = \frac{1}{v} \frac{\partial E}{\partial \nu},$$

so that the group velocity of the waves is equal to the velocity of the particle if we identify C with $\partial E / \partial \nu$ or h .

7. THE PROBLEM OF n PARTICLES

Eqs. (15) and (18) can be generalized without difficulty to include the case of a system of n particles moving under the influence of conservative forces. It is convenient for this purpose to introduce the idea of a many-dimensional "coordinate space" similar to that used in the classical statistical mechanics. We need a number of dimensions equal to the number of coordinates of the system, i.e. $3n$, rather than twice that number, as in statistical mechanics. Let the Cartesian coordinates of the particles be x_1, x_2, \dots, x_{3n} and let the

corresponding masses be $\mu_1, \mu_2, \dots, \mu_{3n}$ where, of course, the three masses associated with the coordinates of any one individual particle will be the same. Then any point in our coordinate space will represent a possible configuration of the system and the complete motion of the system is represented by the orbit of a representative point in configuration space. We shall show that the motion of this representative point may be identified with the motion of a wave packet derived from a suitably defined wave equation operating in the coordinate space. To this end the principle of least action is conveniently stated in the form

$$\delta S = \int_A^B 2T dt = \delta \int_A^B \sum_{k=1}^{3n} p_k dx_k = 0 \quad (E \text{ unvaried}) \quad (24)$$

where A and B are the initial and final configurations and p_k denotes the momentum $\mu_k \dot{x}_k$ (or $\partial T / \partial \dot{x}_k$) associated with the coordinate x_k . Fermat's principle for waves derived from the $3n$ -dimensional equation

$$\sum_{k=1}^{3n} \frac{\partial^2 \psi}{\partial x_k^2} = \frac{1}{w^2(x_1 \dots x_{3n})} \frac{\partial^2 \psi}{\partial t^2} \quad (25)$$

would be

$$\delta \int_A^B \sum_{k=1}^{3n} \frac{\alpha_k dx_k}{\lambda(x_1 \dots x_{3n})} = 0, \quad (26)$$

where $\lambda = w/\nu$ and the α 's are direction cosines subject to the condition

$$\sum_{k=1}^{3n} \alpha_k^2 = 1. \quad (27)$$

In order to throw Eq. (24) into the form (26), it is necessary to introduce slightly different variables, viz.:

$$X_k = \mu_k^{1/2} x_k. \quad k = 1, 2, \dots, 3n. \quad (28)$$

Then the momentum associated with X_k is

$$P_k = \frac{\partial T}{\partial \dot{X}_k} = \frac{\partial}{\partial \dot{X}_k} \left(\sum_{k=1}^{3n} \frac{1}{2} \dot{X}_k^2 \right) = \dot{X}_k, \quad (29)$$

and the principle of least action becomes

$$\delta \int_A^B \sum_k P_k dX_k = 0. \quad (30)$$

The energy equation yields

$$\sum_k (P_k)^2 = 2T = 2(E - V) \quad (31)$$

and (30) can be written in the form

$$\delta \int_A^B \sum_k g_k [2(E-V)]^{1/2} dX_k = 0 \quad (32)$$

if we define the g_k 's by

$$g_k = P_k / [2(E-V)]^{1/2}. \quad (33)$$

This definition and (31) show that the g 's are of the nature of direction cosines being subject to the same condition as the α 's, viz.,

$$\sum_{k=1}^{3n} g_k^2 = 1.$$

The g 's [cf. (33)] are clearly determined by the path of the representative point of the system in configuration space and are independent of the speed with which the path is traversed.

Equation (32) states the principle of least action in a form entirely analogous to the generalized Fermat's principle (26), and the problem of identifying the solutions of the two problems is solved if we first assume that equations (25) and (26) are valid only if we replace the x_k 's by X_k 's and then fix the form of the hitherto arbitrary function w to agree with

$$\frac{C\nu}{w} = \frac{C}{\lambda} = [2(E-V)]^{1/2}. \quad (34)$$

As before we may identify $[2(E-V)]^{1/2}$ with the resultant momentum or resultant velocity of the representative point in X_1, \dots, X_{3n} space and can show that this velocity is equal to the group velocity or packet velocity of the waves if $C = \partial E / \partial \nu$. Introducing the assumption that $E = h\nu$, we find that the motion of wave packets in configuration space is in agreement with the Newtonian mechanics if the wave equation has the form

$$\sum_{k=1}^{3n} \frac{\partial^2 \psi}{\partial X_k^2} = \frac{1}{w^2(X_1, \dots, X_{3n})} \frac{\partial^2 \psi}{\partial t^2} \quad (35)$$

and

$$w^2 = \frac{h^2 \nu^2}{2[h\nu - V]} = \frac{E^2}{2[E - V]}. \quad (36)$$

Returning to our original coordinates and adopting the assumption (17), we derive from Eq. (35) the familiar Schrödinger equation

$$\sum_{i=1}^n \frac{1}{\mu_i} \nabla_i^2 u + \frac{8\pi^2}{h^2} (E - V) u = 0 \quad (37)$$

where

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

and i is a particle index replacing the coordinate index k of Eq. (35). Eliminating the energy as before we obtain

$$\sum_{i=1}^n \frac{1}{\mu_i} \nabla_i^2 \psi - \frac{8\pi^2}{h^2} V\psi - \frac{4\pi i}{h} \frac{\partial \psi}{\partial t} = 0. \quad (38)$$

While the above discussion clearly reveals the possibility of developing a wave mechanics of which the classical mechanics is an appropriate limiting case it brings out one important distinction between radiation waves and matter waves. The latter must be thought of as functions of as many independent variables as there are coordinates in the mechanical system under consideration, whereas the former are functions of only three independent variables. We may say, if we like, that the matter waves are waves in a $3n$ -dimensional space, but this is only one way of describing the fact that there are more than three independent variables in Eq. (27) and Eq. (28). The idea of a many-dimensional space is by no means essential to these equations or to their application. The reason for this difference between matter waves and light waves lies in the fact that matter corpuscles exert forces on each other, while photons do not. Consider the two-body problem of astronomy. If we try to describe the orbital motion of the two bodies by two independent wave packets in three-dimensional space, we confront immediate difficulty in that the behavior of each packet is affected by the instantaneous position of the other. Then the index of refraction for the waves of one packet must be a function of the coordinates of the other packet. Thus the waves of each packet must be functions of six independent variables instead of three.

In special cases, however, such as streams of electrons or atomic rays, we have to deal with assemblages of particles under circumstances which permit us to neglect the forces between them. Such streams can be treated like photons by means of three-dimensional waves.

8. THE STATISTICAL INTERPRETATION OF THE WAVE THEORY OF MATTER

Let us now return to the three-dimensional waves of Eqs. (4), (15) and (18) and consider their interpretation in somewhat greater detail. Our assumptions up to this point comprise the following:

- (a) Matter, like radiation, is both waves and corpuscles.
- (b) In the case of a single particle in a conservative force field all the waves are to be built up out of monochromatic solutions of the wave equation (18).
- (c) The behavior of large scale bodies as described by the Newtonian mechanics is to be interpreted in wave language by means of wave packets compounded from elementary approximately plane† waves with a variety of frequencies and wave normals.

† That is, plane over the volume of the packet.

(d) The energy of a particle and the frequency of the associated waves are related according to the optical rule

$$E = h\nu. \quad (1)$$

(e) The vector momentum of the particle and the vector wave-number δ are related according to the rule

$$\mathbf{p} = h\delta. \quad (12)$$

(f) The “intensity” of the wave function in any element of volume $dx dy dz$ at the time t is to determine the probability that the particle lies in that element just as the intensity of light waves in an element $dx dy dz$ determines the probability that any given photon lies in the corresponding element.

This last assumption requires some clarification. In the case of radiation the intensity is given by the sum of the squares of the electric and magnetic vectors. For simplicity we shall regard the wave function ψ for matter as a complex scalar quantity for the present, however, since such a scalar is adequate to describe all that we know of the wave characteristics of matter. The term “intensity” is accordingly identified with $|\psi|^2$ or with $\psi\psi^*$ where ψ^* is the complex conjugate to ψ .

To give precision to the relation between $\psi\psi^* dx dy dz$ and the probability that the associated particle lies in $dx dy dz$ we note that in the case of a complex radiation field the intensity ($\mathfrak{E}^2 + \mathfrak{H}^2$) determines the probable energy density of the photons rather than the “number density.” If, however, we have given a wave function ϕ such that $\phi\phi^* dx dy dz$ measures probable energy density, we can always set up a second function ψ which obeys the same differential equation and such that $\psi\psi^* dx dy dz$ is at least a plausible measure of the desired number density of the particles. To do so we have merely to analyse ϕ into monochromatic constituents, divide the amplitude of each by $(h\nu)^{1/2}$ and sum up again. This statement will be justified in the discussion of the Fourier analysis of wave packets which follows. Since number density rather than energy density is fundamental in the theory of matter waves we assume that the wave functions we are dealing with are so formed that we may identify $\psi\psi^* dx dy dz$ with the former type of density at least to a constant of proportionality. If we have to do with a single particle we may fix the absolute magnitude of ψ by means of the normalization condition

$$\int \int \int_{\infty} \psi\psi^* dx dy dz = 1, \quad (39)$$

in which case $\psi\psi^* dx dy dz$ gives directly the probability that the particle lies in the volume element $dx dy dz$.¹¹

¹¹ It is easily proven by the aid of Green's theorem that if ψ is any solution of Eq. (18) which vanishes at infinity

$$\frac{\partial}{\partial t} \int \int \int_{\infty} \psi\psi^* dx dy dz = 0.$$

It is but a short step from these assumptions to the formulation of the Heisenberg uncertainty principle which forbids the assignment of precise simultaneous values to the coordinates of a particle and to the corresponding momenta. In order to develop this principle, we observe first of all that the frequency ν and the vector wave-number δ are uniquely defined only for infinite plane monochromatic waves. A wave packet, like an experimental spectrum line, contains a narrow continuous spectrum of frequencies and also a continuous "spectrum" of wave normals. Hence the right hand members of Eq. (1) and Eq. (12) are to a certain extent ambiguous. Conceivably we may interpret the symbols ν and δ as mean values over the packets under consideration, or we may assume that the range of values of ν and δ contained within a wave packet is to be correlated with a corresponding uncertainty in the energy and momentum of the associated particle. The former assumption, however, is readily shown to be untenable. To prove this let us consider the case of a wave function composed of the sum of two disturbances ψ_1 and ψ_2 each of which is a typical wave packet having a fairly well defined frequency and direction of motion. In the optical case such a disturbance could be obtained experimentally by allowing a beam of plane parallel monochromatic radiation to fall on an aperture covered by a shutter. Opening and closing the shutter momentarily would form a primary packet which could be split into two parts with different wave-lengths and directions of motion by suitable reflection from a moving half-silvered glass mirror. If a disturbance of this kind is associated with a single particle, whether electron or photon, hypothesis (*f*) requires that the particle have a certain probability of moving with packet No. 1 with its corresponding velocity and a certain complementary probability of moving with packet No.2 with its velocity. But these two possible positions are correlated with two different momenta whose probabilities are determined by hypothesis (*f*). Hence in this case the correlation of a single energy and single momentum with the wave function is impossible, and since no dividing line can be drawn between such a case as this and the case of the typical single packet we conclude that it is equally impossible for a single packet. In fact we know by direct experiment in the optical case that such a single packet always contains a range of possible energies and momenta. If the packet be formed with the aid of an aperture and shutter as suggested above, diffraction will cause the radiation to diverge by an amount varying inversely with the dimensions of the aperture. If the intensity is large and the aperture is small compared with the wave-length, photons will proceed in all directions from the slit carrying with them momentum directed along the radius vector from the slit. At the same time the interruption of the primary beam by the shutter will destroy its monochromatic character and scatter the photons over a narrow continuous spectrum. Diffraction experiments involving prolonged photographic exposures and very low intensities show that the distribution of energy over the pattern is independent of the intensity. We infer that if the intensity of the radiation in the packet under consideration is so low that only one or

two photons pass through the aperture during its formation, the relative probability of each energy and direction of motion is the same as if the intensity were very large.

The determination of the relative probabilities of the different momenta associated with a wave packet moving in a field free space is fundamental for our theory. As a first step in the derivation of a formula for this purpose we observe that the usual elementary theory of Fraunhofer diffraction phenomena in which one sums up the contributions of Huygens' wavelets from different parts of the aperture is equivalent to an analysis of the radiation emerging from it into plane waves having different wave normals. At large distances from the aperture where the Fraunhofer theory applies, the energy of the radiation in any elementary cone of solid angle $d\Omega$ is equal to the energy of a corresponding set of plane waves in what we may call the "plane wave spectrum" of the complete wave system at the aperture. Hence to find the probability that any particular photon in a monochromatic diffracted train has a momentum vector lying in the solid angle $d\Omega$ we have to analyse the beam emergent from the aperture into plane waves and compute the ratio of the sum of the intensities of all elementary waves having normals in $d\Omega$ to the intensity of the entire beam. Similarly if we have radiation which is not monochromatic, (whether due to a finite length of train or not) we can find the probability that any photon has an energy in the interval between $h\nu$ and $h(\nu+d\nu)$ by a Fourier analysis of the wave function into rigorously monochromatic constituents. The complete analysis of a finite wave group or packet into a three-dimensional system of plane waves characterized by the three independent parameters $\sigma_x, \sigma_y, \sigma_z$, will then serve to determine the relative probability of the three components of the momentum and of the different energies of the associated particle or particles.

The formulas for this analysis are simpler for matter waves than for radiation since in the former case the waves are described in terms of complex numbers. The normal form for the description of a plane matter wave is then

$$\psi = C e^{2\pi i [v t - (x\sigma_x + y\sigma_y + z\sigma_z)]} = C e^{(2\pi i/h) [E t - (x p_x + y p_y + z p_z)]} \quad (40)$$

where C is a complex constant. This expression is a solution of the wave equation (18) for a homogeneous medium (zero force field) if the frequency satisfies the relation

$$\frac{v^2}{w^2} = \frac{1}{\lambda^2} = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = h^{-2}(p_x^2 + p_y^2 + p_z^2). \quad (41)$$

The desired analysis is accomplished by the aid of Fourier's integral which permits us to resolve any wave packet into exponential components by the use of the formulas

$$\psi(t, x, y, z) = \frac{1}{h^{3/2}} \int \int \int_{-\infty}^{\infty} Q(t, p_x, p_y, p_z) e^{-(2\pi i/h)(x p_x + y p_y + z p_z)} dp_x dp_y dp_z, \quad (42)$$

$$Q(t, p_x, p_y, p_z) = \frac{1}{h^{3/2}} \int \int \int_{-\infty}^{\infty} \psi(t, x, y, z) e^{+(2\pi i/h)(x p_x + y p_y + z p_z)} dx dy dz. \quad (43)$$

The packet may be defined either by ψ or by Q . If the latter function has the form

$$Q(t, p_x, p_y, p_z) = G(p_x, p_y, p_z) e^{-2\pi i \nu t} \tag{44}$$

where ν is defined by Eq. (41), the expression (42) for ψ becomes a solution of the wave equation (18) for the case of a free particle where $V=0$. It can be fitted to arbitrary initial conditions provided only that at $t=0$ ψ vanishes at infinity, and so will represent any wave packet. Moreover, it may be proved that¹²

$$\int \int \int_{-\infty}^{\infty} \psi \psi^* dx dy dz = \int \int \int_{-\infty}^{\infty} Q Q^* dp_x dp_y dp_z \tag{45}$$

and we conclude that as $\psi \psi^* dx dy dz$ measures the probability that the particle lies in the volume element $dx dy dz$ in ordinary space, so $Q Q^* dp_x dp_y dp_z$, or $G G^* dp_x dp_y dp_z$, measures the probability that its momentum vector terminates in the element $dp_x dp_y dp_z$ of "momentum space."¹³ Q describes a stationary wave motion in momentum space and satisfies a differential equation that is closely related to that of ψ . Jordan calls $\psi(t, x, y, z)$ the *probability amplitude* for the positional coordinates and $Q(t, p_x, p_y, p_z)$ the probability amplitude for the momentum.

In case we have to do with the motion of a particle in a force field the momentum varies with t and the plane wave (40) is not a solution of the wave equation, though it may approximate to a solution in a suitable small neighborhood. Hence $\psi(t, x, y, z)$ as defined by Eq. (42) does not describe the movement of the packet in time if p_x, p_y, p_z are treated as independent of t , but we can still use equations (41) and (43) to determine the instantaneous probability distribution for the momentum components of the particle. This extension of equations (42) and (43) to the more general case is justified by our initial correlation of wave-length and momentum through the principles of least time and least action.

¹² This is a limiting case (in three dimensions) of the well-known theorem that if

$$f(x) = \sum_{\tau} c_{\tau} e^{2\pi i \tau x / T}, \quad a < x < a + T,$$

$$\sum_{\tau} c_{\tau} c_{\tau}^* = \int_a^{a+T} f(x) f^*(x) dx$$

Cf. Schuster, *Phil. Mag.* **37**, p. 509 (1894); Schuster and Nicholson, *Theory of Optics*, 3rd Ed. 1924, p. 334.

¹³ If $Q Q^* dp_x dp_y dp_z$ gives the probability that the momentum vector terminates in the element $dp_x dp_y dp_z$, it is clear that $h\nu Q Q^* dp_x dp_y dp_z$ gives the energy associated with that element. Then if $\phi(t, x, y, z)$ is defined by

$$\phi = \frac{1}{h^{3/2}} \int \int \int_{-\infty}^{\infty} (h\nu)^{1/2} Q \exp \left[-\frac{2\pi i}{h} (x p_x + y p_y + z p_z) \right] dp_x dp_y dp_z$$

$\phi \phi^* dx dy dz$ must give the energy associated with the volume element $dx dy dz$ in ordinary space. Conversely, given ϕ we can pass to ψ as stated on p. 170.

9. HEISENBERG'S UNCERTAINTY PRINCIPLE¹⁴

The qualitative discussion in the preceding article shows clearly that a reduction in the size of a wave packet to *increase* the precision with which it locates the associated particle in space is always accompanied by a *decrease* in the precision with which its momentum is defined. The question immediately arises "Is the impossibility of forming a wave packet which will describe a particle with a perfectly definite position and momentum a weakness of the wave mechanics or does it correspond to an inherent experimental difficulty in making precise simultaneous observations of position and momentum?" Heisenberg has shown that the second of these alternatives is correct and on this basis formulates the principle: *Under ideal conditions the product of the experimental uncertainty in the value of any coordinate q and the experimental uncertainty in the value of the corresponding momentum p has a minimum value of the order of magnitude of Plank's constant h .*¹⁵

If we grant for the moment that the minimum experimental uncertainties are those inherent in our wave packet theory we may deduce Heisenberg's principle from equations (42) and (43). Consider the case of a packet bounded at $t=0$ by a rectangular box such that in the region S defined by the inequalities $-a < x < +a$; $-b < y < +b$; $-c < z < +c$, ψ_0 has the value

$$\psi_0 = A e^{-(2\pi i/h) x p_0}$$

whereas outside S , ψ_0 vanishes. In this case we may identify the uncertainties in x , y , and z with a , b , and c respectively. The momentum of the packet is as sharply defined as is possible for a packet of this size, the mean values of the components being p_0 , 0, 0. Applying Eq. (42) we have

$$Q(0, p_x, p_y, p_z) = G(p_x, p_y, p_z) = \frac{8abc}{h^{3/2}} G_1(p_x) G_2(p_y) G_3(p_z)$$

where

$$G_1(p_x) = \frac{1}{2a} \int_{-a}^{+a} e^{-(2\pi i/h)x(p_0 - p_x)} dx = \frac{\sin \{2\pi a(p_0 - p_x)/h\}}{2\pi a(p_0 - p_x)/h},$$

$$G_2(p_y) = \frac{\sin 2\pi b p_y/h}{2\pi b p_y/h}; \quad G_3(p_z) = \frac{\sin 2\pi c p_z/h}{2\pi c p_z/h}$$

($|A|$ takes on the value $(8abc)^{1/2}$ if adjusted to satisfy the normalizing condition Eq. (39)). The probability that p_x lies in the interval dp_x is then proportional to

$$G_1^2(p_x) dp_x = \frac{\sin^2 2\pi a(p_0 - p_x)/h}{[2\pi a(p_0 - p_x)/h]^2}.$$

¹⁴ W. Heisenberg, *Zeits. f. Physik* **43**, 172 (1927); N. Bohr, *Nature* **121**, 580 (1928).

¹⁵ The uncertainty postulated is, of course, quite unimportant for the dynamics of large scale bodies. If the uncertainty in any one of the positional coordinates of the golf ball of p. 163 is of the order of magnitude of an atomic diameter the corresponding minimum uncertainty in velocity is of the order of magnitude of 10^{-20} cm/sec!

This distribution function is the familiar one met with in the theory of diffraction by a single slit and illustrated by Fig. 1. The half spacing of the central pair of minima ($\xi = \pm \pi$ in Fig. 1) gives a fair measure of the uncertainty in the value of p_x . Hence $\delta p_x = h/2a$ and

$$\delta x \delta p_x (= \delta y \delta p_y = \delta z \delta p_z) = h/2 \tag{46}$$

in agreement with Heisenberg's principle.†

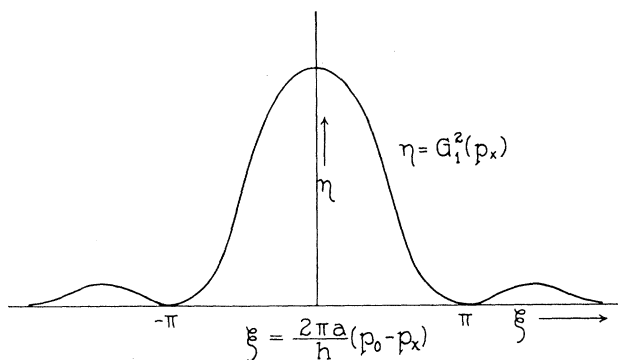


Fig. 1

The same type of formula may be used to relate the uncertainty in the energy of the particle and the uncertainty in the time at which it takes on a certain coordinate value. For example, the above wave packet will cross the plane $x=0$ in the time $2\delta t$ given by

$$2\delta t = 2a/v = 2a \frac{\partial \sigma_x}{\partial v} = \frac{2a}{h} \frac{\partial p_x}{\partial v} .$$

Hence the product of the uncertainties in t and E is

$$\delta E \delta t = h \delta v \frac{a}{h} \frac{\partial p_x}{\partial v} = a \delta p_x = h/2 .$$

In the Hamiltonian theory of classical dynamics t and $-E$ are canonically conjugate variables like x and p_x . Hence a plausible extrapolation would lead us to expect the same relation between the uncertainties in any two canonically conjugate dynamical variables.

Heisenberg justifies the conclusion that these uncertainty relations are experimental as well as theoretical by an analysis of the various possible experimental means for determining simultaneous values of coordinate and momentum. We may determine the position of a particle, for example, by observing the direction of motion of photons or electrons which have been scattered by collision with it or by allowing it to pass through a slit or small aperture. In each case, however, if one assumes the validity of the ordinary theory of the Compton effect and also the applicability to matter

† In the one-dimensional case if the packet is defined to give $\psi\psi^*$ the form of a Gauss error curve GG^* has the same form and $\delta x \delta p_x = h/2\pi$. Cf. W. Heisenberg, reference 14.

of the optical theory of diffraction by apertures, one finds that the observation of any positional coordinate introduces an uncontrollable alteration in the corresponding component of momentum such that even if the latter were uniquely known before the position was observed, Heisenberg's uncertainty relation would hold true after the observation of position. Conversely if one measures the positional coordinate first and the momentum afterward, the measurement of momentum introduces an uncontrollable alteration in position with the same ultimate result regarding the minimum values of the uncertainties.¹⁶ This savors of arguing in a circle since we assume the diffraction of matter in order to derive from a conceptual experiment a relation previously obtained directly from the theory of diffraction. The point is, however, that there is no way of sidestepping the diffraction effect if it is real—a qualification which need hardly be considered.

As Bridgman¹⁷ has shown, the uncertainty relation is bound up with our inability to trace out the details of collisions between photons, electrons, and apertures. This inability, in turn, is due to the absence of tools finer than complete collisions for making the measurements necessary to give reality to such details.

The perfect harmony which exists between our dualistic theory and the experimental limit of the uncertainty product $\delta q \delta p$ is a strong indication that the former is on the right track. It shows that the theory is marvelously adapted to the description of observable magnitudes without introducing others which are unobservable as did the Bohr theory. The desirability of eliminating unobservable quantities from the theory was in fact one of the basic ideas in Heisenberg's original development of the matrix mechanics.

It is hardly necessary to dwell here on the philosophical significance of the uncertainty principle which gives final precise form to the hypothesis of indeterminism in physics. This hypothesis may be said to have originated in the discovery of the law of radioactive decay. It received important support in Einstein's speculations on the transition probabilities which govern the jumps of atoms from one energy level to another and now seems permanently enthroned in the quantum mechanics. To be sure, many physicists still regard the indeterminism of the quantum theory as a temporary phase in the development of the science and look for a return to determinism later on. To the writer, however, it seems quite clear that such a return is impossible unless some wholly revolutionary discoveries of an experimental character give us tools which we now lack for the detailed investigation of collisions. Moreover, the quantum mechanics has so many of the characteristics of ultimate perfection in theory that the possibility of unlimited revolutions in the future can no longer be granted without question. If the

¹⁶ For a detailed discussion of the various possible types of experiment the reader is referred to the original papers of Heisenberg and Bohr (note 12). It is perhaps desirable to note here that we always observe pairs of coordinates and not single coordinates. Thus the "simultaneous" measurement of a coordinate q and conjugate momentum p means the correlation of the values of q and p with the same value of some third variable x , which may be either some independent space coordinate or the time.

¹⁷ P. W. Bridgman, *Harper's Magazine*, March, 1929, p. 443.

purpose of science is to reveal the orderliness and inner simplicity of nature, scientific theory is to be judged by the extent to which it reduces chaos to a single formula or group of formulas. If we look back over the history of science and forward to the future with this criterion in mind, we can hardly resist the conviction that we are within sight of the goal. The past has seen the reduction of existence to the two modes, matter and radiation, the reduction of matter to the 92 chemical elements and their isotopes, the reduction of the various atomic species to electrons and protons, and most recently the lowering of the barrier between matter and radiation through the discovery of their common dualistic nature and of the possibility of transmuting one into the other.¹⁸ Many problems have yet to be solved before the territory already within our grasp shall have been fully consolidated, but in view of the uncanny power of the tools now available the discrepancy between the present state of physical theory and the ideal is almost uncomfortably small.

SECTION 2. THE CHARACTERISTIC VALUE PROBLEM OF THE WAVE MECHANICS

1. THE LINEAR OSCILLATOR

It is a well-known empirical fact that each species of atom has a characteristic set of discrete energy levels. From the wave mechanics point of view these levels are to be identified with a corresponding set of standing wave monochromatic solutions of the equation (38) for the atom in question. In order to obtain such a set of solutions Schrödinger has introduced the hypothesis¹⁹ that the only solutions of the wave equation having physical meaning are those which are finite, single-valued and twice differentiable over the whole of coordinate space.²⁰ The hypothesis is justified by its results and by the fact that infinite or multiple-valued functions would be hard to interpret physically. It is equivalent to a boundary condition (and will be referred to hereafter as such) since in many cases ψ must either become infinite at singular points of the differential equation or satisfy typical homogeneous boundary conditions there.

The problem thus presented is of the familiar type known to the mathematicians as the characteristic value problem (Eigenwertproblem).²¹ Solutions are obtainable only for certain characteristic values (Eigenwerte) of an adjustable parameter involved in the differential equation—in this case the parameter E or its equivalent ν . The solutions of the equation which satisfy the boundary conditions are called characteristic functions (Eigen-

¹⁸ The evidence for transmutation is primarily astronomical.

¹⁹ E. Schrödinger, *Ann. d. Physik* (4) **79**, p. 361 (1927).

²⁰ It now seems necessary to modify the first part of this hypothesis in certain cases to permit the wave function to become infinite at isolated points provided that $\int \psi \psi^* d\tau$ is finite when extended over small regions surrounding and including these points. Cf. A. H. Wilson, *Proc. Roy. Soc.* **A118**, p. 635 (1928).

²¹ For a comprehensive mathematical discussion the reader is referred to Courant-Hilbert "Methoden der Mathematischen Physik I," Berlin 1924, or to Riemann-Webers "Differentialgleichungen der Physik I," 7th ed. Braunschweig, 1925.

funktionen). The normal modes of vibration of various elastic systems are familiar examples of such characteristic functions.

As a first example of the characteristic value problem of the wave mechanics let us consider the case of a particle of mass μ vibrating in one dimension under the influence of a potential energy function $V(x)$ which for simplicity we assume to have the form shown in Figure 2 with a single minimum at x_0 , a pole of the second or higher order at $x=0$, and an asymptotic finite limit at $x = \infty$.²² (The potential energy V is defined only for the range of values $0 < x < \infty$ since the discontinuity in V at $x=0$ would in any

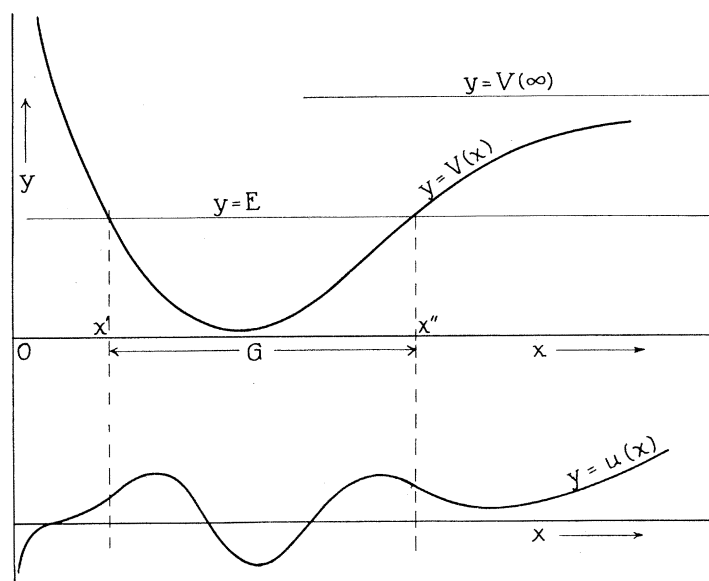


Fig. 2. Potential energy function for one-dimensional oscillator and typical integral curve for Eq. (48).

case destroy the continuity of the solutions $u(x)$ at that point. In the general case of a differential equation to be solved subject to boundary conditions the region defined by the boundaries is called the *fundamental region*. In the applications to wave mechanics values of the independent variable outside the fundamental region have no physical meaning). The wave-length is

$$\lambda(x) = \frac{w(x)}{v} = \frac{h}{[2\mu(E-V)]^{1/2}} \quad (47)$$

and the wave equation for the space factor u reduces to the form

$$\frac{d^2u}{dx^2} + \frac{8\pi^2\mu}{h^2}(E-V)u = 0. \quad (48)$$

²² This is the characteristic type of potential energy function for the problem of the vibrations of a diatomic molecule.

λ has a minimum value at x_0 and if $E < V(\infty)$ λ becomes infinite at two points x' and x'' where $E = V$. The classical motion is confined to the region G between x' and x'' if $E < V(\infty)$ (Case I) and extending from x' to infinity if $E \geq V(\infty)$ (Case II). Outside this region the kinetic energy, defined in the wave mechanics by

$$T = E - V = - \left(\frac{h^2}{8\pi^2\mu} \right) \frac{1}{\psi} \frac{d^2\psi}{dx^2},$$

is negative, while the momentum and wave-length are imaginary. Such negative values of the kinetic energy have no meaning in the classical mechanics but in the present theory they play an important rôle. The wave functions of the linear oscillator problem under discussion are spread out over the whole of the positive x axis including the part outside of G . Since $\psi\psi^*dx$ ($=uu^*dx$) gives the probability that the particle is in the elemental region dx , it is clear that it must spend a definite fraction of its time in the region of negative kinetic energy. This fraction is small, however, especially for the higher modes of vibration or upper energy levels.

2. GRAPHICAL DISCUSSION OF THE INTEGRAL CURVES²³

As the coefficients of Eq. (48) are real, the real and imaginary parts of $u(x)$ must be solutions of the equation which satisfy the boundary conditions. Real solutions are readily shown to be unique except for a constant multiplicative factor and hence any characteristic function $u(x)$ may be resolved into the product of a real function of x and a complex constant. Obviously it suffices to search for real solutions. Each will be characterized by two constants of integration α and β of which one (say α) is multiplicative. An "integral curve" representing a solution of the equation will pass through any predetermined point of the u, x plane with any predetermined slope, but in general these curves will not fit the boundary conditions. Clearly each curve will be concave to the x axis if

$$\frac{1}{u} \frac{d^2u}{dx^2} \text{ or } \frac{8\pi^2\mu}{h^2}(V-E)$$

is negative and convex to the axis if it is positive. Consequently each curve (Cf. Fig. 3) is of an oscillatory character like a distorted sine curve inside G , while outside G it is convex to the axis and acts as if repelled from the axis by a force proportional to $V-E$ and to its own absolute value. x' and x'' are points of inflection.

It is easy to show that if V becomes infinite at $x=0$ as $1/x^2$, or more rapidly, as we shall suppose, $u(x)$ can remain finite at the origin only by vanishing there. Similarly in Case I, where $E < V(\infty)$, $u(x)$ must vanish at $x = \infty$ in order to remain finite there. Moreover, as u is convex to the axis outside of G , it cannot have more than one nodé on either side of G . The boundary conditions are satisfied and u becomes a characteristic function

²³ Cf. F. Hund, *Zeits. f. Physik* **40**, 742 (1927).

if the two possible nodes outside G occur at the limiting points $x=0$ and $x=\infty$.

Consider now the adjustment of the parameters α , β , E which must be made in order to locate a characteristic function and characteristic value. The multiplicative parameter α is useless since a variation in its value does not affect the "zero's" of the function u . The condition at the origin can be met by the adjustment of β only. In Case II this is the only boundary condition and every value of E is a characteristic value. In this case the classical motion of the particle would be aperiodic and the continuous "spectrum" of energy values permitted by the wave mechanics corresponds to the continuous spectrum of E values permitted for an aperiodic motion by the Bohr theory. On the other hand in Case I the classical motion is periodic and in the wave mechanics the additional boundary condition at $x=\infty$ can be met only by a suitable adjustment of E .

It is of interest to note the exact way in which the variation in E affects the integral curves and makes it possible to meet the boundary conditions. Starting with any initial value, let E be increased by a small amount ΔE . Let β be adjusted for each value of E to fit the boundary condition $u=0$ at the origin. The increase in E makes the curves less convex to the axis outside G and more concave to the axis inside G . Hence it may be proved either graphically or analytically that all the nodes are shifted to the left.²⁴ As E increases continuously new nodes appear at $x=\infty$, then move to the left, and finally enter the region G where they accumulate. The first appearance of each node at $x=\infty$ marks a corresponding characteristic function and characteristic value of E . The minimum number of nodes between the boundary points is zero, and the characteristic function having no nodes except those at the boundary points is associated with the lowest characteristic value of E . Two characteristic functions having the same value of E must have the same zeros and can differ only in the multiplicative constant α . For our present purpose they may be identified with one another. Thus we have the rule that the n th characteristic function, or wave function, divides the region between the boundary points into exactly n parts. The number of nodes plays the rôle of the quantum number in the Bohr theory. It is an integer which defines the characteristic function and characteristic value, giving the ordinal number of the latter in a series arranged according to magnitude. Conventional practise counts only the nodes between the boundary points so that the quantum number for the lowest state is zero.²⁵

Figure 3 shows the qualitative form of the characteristic functions u for the lowest energy levels.

The general appearance of these lowest wave functions is unaffected by considerable changes in $V(x)$. Suppose, for example, that V remains finite from $x=+\infty$ to $x=-\infty$, with a single minimum between. As before there will be a continuous spectrum of E values for Case II and a discrete

²⁴ Cf. Courant-Hilbert, p. 367 or Riemann-Weber, p. 281.

²⁵ Half-integral quantum numbers do not appear except in connection with the electron spin which we ignore for the present.

spectrum for Case I. The lower wave functions for Case I will be qualitatively unchanged in character. If V becomes infinite at $x = \pm \infty$, as in the case of the ideal linear oscillator where $V = 1/2 kx^2$, the continuous spectrum disappears, but the lower wave functions are substantially unchanged. This remark holds good also if V has two poles of the second or higher order at finite points x_0 and x_1 with a single minimum between them.

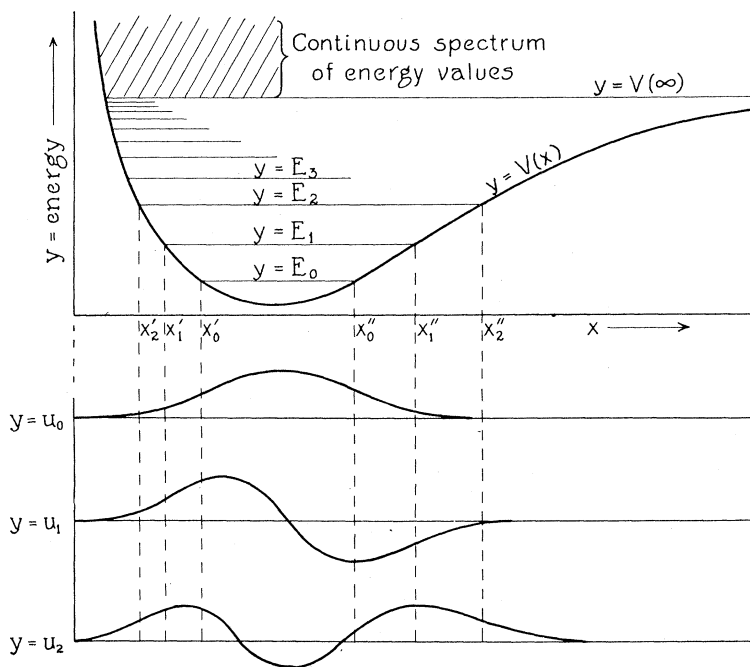


Fig. 3. Energies and wave functions for one-dimensional oscillator.

3. THE STURM-LIOUVILLE PROBLEM

All the above mentioned variations in the linear oscillator problem and also most if not all of the exactly solved characteristic value problems of the wave mechanics are ultimately referable to one-dimensional equations of the Sturm-Liouville type

$$\frac{d}{dx} \left[p(x) \frac{dy}{dx} \right] - q(x)y + \lambda \rho(x)y = 0 \tag{49}$$

in which λ is the variable parameter playing the rôle of E in Eq. (48).^{25a} Solutions of this equation subject to the homogeneous boundary conditions

$$y(a) + \gamma y'(a) = 0 ; \quad y(b) + \eta y'(b) = 0 \tag{50}$$

have been studied in detail and shown to have the characteristics described

^{25a}In Eq. (49) we have adhered to the notation of Courant-Hilbert despite the fact that p and λ are used in a different sense throughout most of this review.

in the preceding paragraph.²⁶ (It is possible to show that if Schrödinger's requirement that the wave functions remain finite at the boundary points leads to any boundary condition at all, it will lead to one of the type (50).) The characteristic functions also satisfy an "orthogonality" condition to which we will return later on.

4. CORRELATION OF CHARACTERISTIC VALUES WITH ENERGY LEVELS OF THE BOHR THEORY

The possibility of deriving the experimental energy levels of atoms from the wave theory was first indicated by de Broglie²⁷ who showed that the Bohr quantum condition for circular orbits in hydrogen is identical with the condition that the "optical path" around the orbit is an integral number of wave-lengths. Later Schrödinger²⁸ showed that in a number of important special cases the energy values given by appropriate solutions of the wave equation are in substantial agreement with the Bohr theory and with experiment.

A more general proof of the agreement between the Bohr theory and the wave mechanics is due to the work of Brillouin, Wentzel, and Kramers.²⁹ The oscillatory character of the wave functions in the range of the classical vibration G suggests the possibility of describing them approximately by means of a cosine function with a variable amplitude and wave-length. This type of approximation is of no value outside the range G but that fact does not destroy its usefulness. Substitution shows that the formula

$$u = A\lambda^{1/2} \cos \left\{ 2\pi \int \frac{dx}{\lambda} \right\}. \quad (51)$$

[λ is defined by Eq. (47)] describes the integral curves very well at points not too close to the boundaries of the range G . At each of the points x' and x'' the oscillatory portion of each of the characteristic functions must make a smooth junction with the exponential-like curve outside of G which then approaches the axis monotonically as one moves away from G . Thus the boundary conditions determine the phase angle of the cosine function in Eq. (51) at the points x' and x'' . The exact phase will vary with $V(x)$ but Kramers has shown that normally we obtain a good approximation if we give it the values $-\pi/4$ or $-5\pi/4$ at x' and $\pi/4$ or $5\pi/4$ at x'' . Hence the phase difference between the points x' and x'' is an odd multiple of $\pi/2$ or

$$2\pi \int_{x'}^{x''} \frac{dx}{\lambda} = \frac{2\pi}{h} \int_{x'}^{x''} p dx = (2n+1) \frac{\pi}{2}, \quad n = 0, 1, 2, \dots \quad (52)$$

²⁶ Courant-Hilbert, Kap. VI, esp. pp. 366-7; Riemann-Weber, Kap. VII.

²⁷ L. de Broglie, Thesis, Chap. III; J. de Physique **7**, p. 327 (1926). Cf., however, M. Brillouin, Comptes Rendus **168**, p. 1318 (1919); **169**, p. 48 (1919); **171**, p. 1000 (1920); J. de Phys. **3**, p. 65 (1922).

²⁸ E. Schrödinger, l. c. and Ann. d. Physik (4) **79**, 489 (1929).

²⁹ L. Brillouin, Comptes Rendus **183**, p. 24 (1926); J. de Physique **7**, p. 353 (1926); G. Wentzel, Zeits. f. Physik **38**, p. 518 (1926); H. A. Kramers, Zeits. f. Physik **39**, p. 828 (1926).

which is the Wilson-Sommerfeld quantum condition for the problem with the quantum number made a "half-integer." As this quantum condition with half-integral quantum numbers is known to give a satisfactory expression for the energy of a vibrating molecule, we conclude that the characteristic values of E given by the wave equation may be identified with the corresponding experimental energy values.

5. THE PLANCK IDEAL LINEAR OSCILLATOR

The characteristic values and characteristic functions have been worked out exactly for a number of special cases of the linear oscillator problem among which we may mention here the Planck case where $V = \frac{1}{2}kx^2$. The corresponding wave equation and boundary value problem were well known to mathematicians before the advent of the wave mechanics.³⁰ The characteristic functions are the Hermitian orthogonal functions

$$u_n = A_n e^{-\alpha x^2/2} H_n(\alpha^{1/2} x) \quad (53)$$

where A_n is an arbitrary constant amplitude factor, α is the constant $(2\pi/\hbar)(k\mu)^{1/2}$ and H_n is the n th Hermitian polynomial

$$H_n(\xi) = (2\xi)^n - \frac{n(n-1)}{1!} (2\xi)^{n-2} + \frac{n(n-1)(n-2)(n-3)}{2!} (2\xi)^{n-4} - \dots \quad (54)$$

If we determine A_n in accordance with the normalization condition (39) it takes the value $2^{-n/2}(n!)^{-1/2}$. The energy levels are identical with those of the Bohr theory using half-integral quantum numbers, viz.,

$$E_n = (n + \frac{1}{2}) h\nu_0 \quad n = 0, 1, 2, \dots \quad (55)$$

ν_0 denoting the classical vibration frequency $(1/2\pi)(k/\mu)^{1/2}$. The wave functions are alternately even and odd as may be proved directly from the differential equation.

The polynomial method described by Sommerfeld³¹ gives a valuable direct mode of attack on this and other exactly solvable Sturm-Liouville characteristic value problems. It does not work in all cases but has a wide range of applicability.

6. THE TWO BODY PROBLEM

This is one of the most important characteristic value problems of the theory. We assume that the potential energy V depends only on the distance r between the particles. Let M denote the total mass $\mu_1 + \mu_2$ and let μ be a mass coefficient defined by the relation

$$\frac{1}{\mu} = \frac{1}{\mu_1} + \frac{1}{\mu_2} \quad (56)$$

Let ξ, η, ζ denote the coordinates of the center of gravity and let x, y, z

³⁰ E. Schrödinger, *Ann. d. Physik* (4) **79**, p. 489 (1926); Courant-Hilbert, p. 261.

³¹ A. Sommerfeld, "Atombau und Spektrallinien Wellenmechanischer Ergänzungsband," Braunschweig, 1929, Kap. I, 2.

denote the projections of r along the three axes. Then the space factor equation (37) takes the form

$$\frac{1}{M} \left(\frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2} + \frac{\partial^2}{\partial \zeta^2} \right) u + \frac{1}{\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) u + \frac{8\pi^2}{h^2} (E - V) u = 0. \quad (57)$$

Let us seek particular solutions of the form

$$u = u_1(\xi, \eta, \zeta) u_2(x, y, z). \quad (58)$$

Substitution of this expression into Eq. (57) breaks the equation into the two parts

$$\left(\frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2} + \frac{\partial^2}{\partial \zeta^2} \right) u_1 + \frac{8\pi^2 M}{h^2} E_1 u_1 = 0, \quad (59)$$

and

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) u_2 + \frac{8\pi^2 \mu}{h^2} (E_2 - V) u_2 = 0 \quad (60)$$

where $E_1 + E_2 = E$. Clearly E_1 is the energy of the translational motion of the center of gravity and E_2 is the internal energy of the system. Equation (59) is the amplitude equation for a free particle. Its solution is a plane wave or superposition of plane waves. A packet may be built up from such solutions to locate the center of gravity in space if desired.

In order to solve the wave equation for the internal motion one may make another change of variables introducing the spherical coordinates r, θ, ϕ . We repeat the process of splitting the differential equation or "separating the variables" by seeking for particular solutions of the type

$$u_2 = R(r) Y(\theta, \phi). \quad (61)$$

Eq. (60) then breaks into two parts with the separation constant α , viz.,

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{8\pi^2 \mu}{h^2} \left[E_2 - V(r) + \frac{\alpha h^2}{8\pi^2 \mu r^2} \right] R = 0, \quad (62)$$

$$\frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial Y}{\partial \theta} \right] - \alpha Y = 0. \quad (63)$$

The latter equation is familiar from potential theory³² where it must be solved in such a way that Y is single valued and continuous over the entire sphere. The variables in (63) may be separated in turn and a solution of the problem is then

$$Y = \Phi(\phi) \Theta(\theta) \times \text{const.} \quad (64)$$

where the values of Φ and Θ are

$$\Phi_m(\phi) = e^{im\phi} \quad m = 0, \pm 1, \pm 2, \dots \quad (65)^{33}$$

$$\Theta_{l,m}(\theta) = P_l^{|m|}(\cos \theta) \quad l = |m|, |m| + 1, \dots \quad (66)$$

³² Courant-Hilbert, p. 265, p. 420.

³³ The functions $\sin m\phi, \cos m\phi$ ($m = 0, 1, 2, \dots$) are equally valid.

Here $P_l^k(x)$ is the associated Legendre spherical harmonic

$$P_l^k(x) = (1-x^2)^{k/2} \frac{d^k}{dx^k} P_l(x), \quad (67)$$

$P_l(x)$ being the Legendre polynomial of degree l . α has the characteristic values

$$\alpha = -l(l+1) \quad l = 0, 1, 2, 3, \dots \quad (68)$$

Inserting this expression for α into Eq. (62), dropping the subscript in the symbol E_2 , and changing the dependent variable from R to $\mathfrak{R} = rR$, we obtain

$$\frac{d^2 \mathfrak{R}}{dr^2} + \frac{8\pi^2 \mu}{h^2} \left[E - V(r) - \frac{l(l+1)h^2}{8\pi^2 \mu r^2} \right] \mathfrak{R} = 0, \quad (69)$$

an equation identical in form with Eq. (48). Comparing this with the energy equation of the classical theory for the radial motion

$$\left(\frac{dr}{dt} \right)^2 + 2\mu \left[E - V(r) - \frac{M^2}{2\mu r^2} \right] = 0 \quad (70)$$

where M is the angular momentum, we see that in the wave mechanics $(h/2\pi)[l(l+1)]^{1/2}$ plays the rôle of angular momentum. This interpretation will be justified later from another point of view.

The solution of Eq. (69) depends on the form assigned to $V(r)$. In the special case of the atomic Kepler problem $V = -Ze^2/r$ where Z is the atomic number of the nucleus. V vanishes at ∞ and if E is negative (Case I, p. 35) there is a discrete set of energy values given by the familiar Bohr formula

$$E_n = -\frac{2\pi^2 \mu e^4 Z^2}{h^2 n^2}. \quad (71)$$

Here $n-1$ is the sum of the nodes in $R(r)$, $\Theta(\theta)$, and the real part of $\Phi(\phi)$. If E is positive (Case II) we have a continuous spectrum of E values.

The wave functions R may be expressed in terms of a complex integral in both cases.¹⁹ In Case I they may also be written in the form

$$R_{n,l}(r) = \rho^l L_{n+l}^{(2l+1)}(\rho) e^{-\rho/2} \times \text{const.} \quad (72)$$

where

$$\rho = \left(\frac{8\pi^2 \mu e^2 Z}{h^2 n} \right) r = \frac{2Z}{na_1} r \quad (73)$$

and $L_k^{(\tau)}(x)$ is the τ^{th} derivative of the Laguerre polynomial of degree k . a_1 is the radius of the innermost Bohr orbit for hydrogen.

In contrast to the linear oscillator problem we have here a multiplicity of characteristic functions for each energy level paralleling the multiplicity of orbital types which exist for each level in the Bohr theory. This multiplicity is called *degeneracy* and is of a two-fold character. Due to the spherical sym-

metry of the force field each of the characteristic values of α (i.e., each value of l) is associated with $2l+1$ wave functions of the type of Eq. (64) and characterized by the values $0, \pm 1, \dots, \pm l$ for the quantum number m . This degeneracy is destroyed by the application of an external magnetic or electric field to the atom. In the former case each of the wave functions given by Eqs. (64), (65), and (66) is associated with a separate energy level. Hence m is frequently called the magnetic quantum number. In the absence of disturbing influences the most general solution of Eq. (63) for any given characteristic value α_l is

$$Y_l = \sum_m C_{l,m} \Theta_{l,m} \Phi_m.$$

Such a function is called a tesseral harmonic.

A more special type of degeneracy is exhibited by the radial Eq. (62) in the special case of a Coulomb force field. The energy depends only on the "total quantum number" n and is independent of the "azimuthal quantum number" l . As l takes on all values between 0 and $n-1$ there are in all $\sum_{l=0}^{n-1} (2l+1)$ or n^2 different sets of values of l and m for each energy level. The most general possible wave function for the energy level E_n may be proved to be an arbitrary linear combination of terms of the type $R_{n,l} \Theta_{l,m} \Phi_m$.

7. ORTHOGONALITY AND THE EXPANSION PROBLEM

The last statement of the preceding article leads us to the question of orthogonality and series expansion which is one of the most important aspects of the characteristic value problem.

Consider first the case of a one-dimensional motion where the differential equation for the space factor $u(x)$ has the form of Eq. (49). Let us assume that there is no continuous spectrum of energy values. A very general solution of Eq. (18) will then be given by the series

$$\psi(t, x) = \sum_{n=0}^{\infty} c_n u_n(x) e^{(2\pi i/\hbar) E_n t} \quad (74)$$

in which $u_n(x)$ is the n^{th} characteristic function of the space factor equation and E_n the corresponding value of E . The c 's are arbitrary constants which must be so chosen to insure the convergence of the series. Now Eq. (18) shows that $\psi(t, x)$ is in the most general case fully determined by its value at $t=0$. Thus Eq. (74) does give the most general solution of the problem provided that it can be fitted to an arbitrary complex initial function $f(x)$ which meets the boundary conditions. Hence it must be proved that such a function can always be expanded into the infinite series

$$f(x) = \sum_{n=0}^{\infty} c_n u_n(x). \quad (75)$$

Such an expansion is most easily carried out in the case of a *normalized*

orthogonal system of functions $u_n(x)$.³⁴ Here we use the word *normalized* in the sense of Eq. (39) to indicate that for every value of n

$$\int_a^b u_n(x)u_n^*(x)dx = 1, \quad (76)$$

where $x = a, b$ are the boundaries of the region of definition of the functions. This equation can always be satisfied by suitable adjustment of the arbitrary multiplicative constant α . The term *orthogonal*³⁵ is applied to the series of functions $u_n(x)$ when

$$\int_a^b u_n(x)u_m^*(x)dx = 0, \quad n \neq m. \quad (77)$$

If the given wave functions form such a set, the coefficients in Eq. (75) may be determined like those in a Fourier series.† Multiplication of the equation by $u_\tau^*(x)$ and integration yields

$$c_\tau = \int_a^b f(x)u_\tau^*(x)dx; \quad \tau = 0, 1, 2, \dots \quad (78)$$

A slightly more general case is that in which the given set of functions is not orthogonal as it stands, but may be converted into such a set through multiplication by a suitable real common factor $[\bar{p}(x)]^{1/2}$. The condition that the modified functions form a normalized orthogonal system is then

$$\int_a^b \bar{p}(x)u_n(x)u_m^*(x)dx = \delta_{nm}, \quad (79)$$

where the symbol δ_{nm} stands for unity if $m = n$ and zero if $m \neq n$. Eq. (78) becomes

$$c_\tau = \int_a^b \bar{p}(x)f(x)u_\tau^*(x)dx. \quad (80)$$

The characteristic functions of the Sturm-Liouville problem are readily proved³⁶ to have this modified type of orthogonality, the function \bar{p} being

³⁴ Cf. Courant-Hilbert, Chapter II; Riemann-Weber, Chapter VIII, 1, Chapter XII, 3.

³⁵ A continuous function of x may be regarded as a vector in a space of infinitely many dimensions and Eq. (77) is a limiting case of the condition for the orthogonality of two complex vectors U_n, U_m in a space of many dimensions. Cf. pp. 210, 211 below.

† Obviously if the expansion (75) is to be valid, the series of functions $u_n(x)$ must be *complete*, i.e., no function can exist not identically zero which is not in the series and is orthogonal to all members of the series. Cf. Courant-Hilbert, pp. 35-38.

³⁶ If λ_1 and λ_2 are two different characteristic values of Eq. (49), y_1, y_2 being the characteristic functions,

$$(\lambda_1 - \lambda_2) \int_a^b \rho y_1 y_2^* dx + \int_a^b \frac{d}{dx} (\rho [y_1' y_2^* - y_1 y_2'^*]) dx = 0.$$

The second expression vanishes due to the boundary conditions and since $\lambda_1 \neq \lambda_2$, the orthogonality condition follows at once. Cf. Courant-Hilbert, p. 239; Riemann-Weber, p. 366.

identical to a constant factor with the $\rho(x)$ of Eq. (49).[‡] Moreover, the development of Eq. (75) is valid in every case³⁷ so that the series (74) does give the most general solution of the one-dimensional wave equation which meets the boundary conditions.

In the case of the linear oscillator equation (48) under consideration, ρ is a constant and we may normalize the wave functions in accordance with Eqs. (76) and (39) to preserve our original simple physical interpretation of $\psi\psi^*dx$ for the case where ψ has the monochromatic form $\psi = u_n e^{+(2\pi i/\hbar)E_n t}$

8. CONTINUOUS SPECTRUM

The above results have been generalized to include the case where there is a continuous as well as a discrete spectrum. In this case one of the boundaries is at infinity and a part of the series expansion (75) goes over into an integral analogous to the Fourier integral. Thus if $f(x)$ is a function which, together with its second derivative is continuous and quadratically integrable over the fundamental region $a < x < \infty$, it can be expanded in the absolutely and uniformly convergent representation³⁸

$$f(x) = \sum_n c_n u_n(x) + \int_{\epsilon}^{\infty} c(E) u(x, E) dE. \quad (81)$$

Here $u(x, E)$ is the space factor for the energy E and ϵ is the minimum energy value for the continuous spectrum. (We assume that the constant of integration β (p. 179) is determined by the boundary condition at one end of the fundamental region so that, except for the multiplicative constant α , $u(x, E)$ depends on x and E only.)

The discrete functions $u_n(x)$ are normalized and their coefficients c_n determined as before. The normalization-orthogonality relation Eq. (79) does not apply to the characteristic functions of the continuous spectrum, however, since the integrals do not converge. This difficulty is met by the use of the modified condition that³⁹

$$\int_a^{\infty} dx \bar{\rho}(x) u^*(x, \lambda) \int_{E_1}^{E_2} u(x, E) dE = F(\lambda) \quad \text{or} \quad 0 \quad (82)$$

according as $E_1 < \lambda < E_2$, or not. Then the formula for determining the coefficients $c(E)$ of the continuous spectrum is

$$c(E') = \frac{1}{F(E')} \frac{d}{dE'} \int_a^{\infty} dx \bar{\rho}(x) f(x) \int_{\epsilon}^{E'} u^*(x, \lambda) d\lambda. \quad (83)$$

For our present purpose $F(E')$ is arbitrary and Schrödinger sets it equal to

[‡] ρ can always be eliminated by an appropriate change of the dependent variable as in Eq. 69.

³⁷ Courant-Hilbert, p. 278; Riemann-Weber VII §4, XIII, §1.

³⁸ H. Weyl, Math. Ann. **68**, 220 (1910).

³⁹ Cf. E. Fues, Ann. d. Physik (4) **81**, p. 281 (1926); E. Schrödinger, Ann. d. Physik (4) **81**, p. 109 (1926). Other forms of this condition are used by Oppenheimer, Zeits. f. Physik **41**, p. 268 (1927); Phys. Rev. **31**, p. 66 (1928).

unity. Oppenheimer, on the other hand, finds it convenient from the standpoint of statistical weights to give this function the constant value \hbar .

The following heuristic procedure will serve to make the above formulas plausible. If we should try to determine the coefficients $c(E)$ by the same method as that used for the c_n 's we would multiply Eq. (81) by $\bar{\rho}(x)u^*(x, E')$ and integrate formally over all values of x . It may happen, however, that the integral $\int_a^\infty \bar{\rho}(x)f(x)u^*(x, E')dx$ does not exist. Hence we must replace $u^*(x, E')$ by the "wave packet" $\int_\epsilon^{E'} u^*(x, \lambda) d\lambda$ which approaches zero rapidly for large values of x due to interference of its elements. The resulting equation is

$$\int_a^\infty dx \bar{\rho}(x)f(x) \int_\epsilon^{E'} u^*(x, \lambda) d\lambda = \sum_n c_n \int_a^\infty dx \bar{\rho}(x)u_n(x) \int_\epsilon^{E'} u^*(x, \lambda) d\lambda + \int_a^\infty \bar{p}(x)dx \int_\epsilon^{E'} u^*(x, \lambda) d\lambda \int_\epsilon^\infty c(E)u(x, E)dE. \quad (84)$$

Due to difficulty about interchanging the order of integrations in the right hand side of Eq. (84) we make use of the fact that the characteristic functions of the continuous spectrum may be regarded as limiting cases of discrete characteristic functions obtained by a suitable modification of the potential energy function. [E.g., if the potential energy $V_0(x)$ has the form indicated in Fig. 2 with a continuous spectrum, we may consider a modified problem in which

$$V = V_0(x) + V_1(x)$$

where V_1 vanishes if $x < x_1$ and has the value $V_1 = a(x - x_1)$ if $x > x_1$. Then the modified problem has no continuous spectrum since $V(\infty) = \infty$, but if x_1 is allowed to increase without limit the energy levels above the critical value $V_0(\infty)$ become indefinitely close together and the wave functions approximate more and more closely to those of the original problem.] On this basis we may prove (a) that the sum which forms the first term of the right hand member is zero, and (b) that $\int_a^\infty dx \bar{\rho}u^*(x, \lambda) \int_{E_1}^{E_2} c(E)u(x, E)dE$ vanishes unless $E_1 < \lambda < E_2$ and is independent of $E_2 - E_1$. The value of the integral is then proportional to $c(\lambda)$ and by the introduction of a suitable normalization factor can be reduced to $c(\lambda)F(\lambda)$ where F is arbitrary [Cf. Eq. (82)]. Then Eq. (84) yields

$$\int_a^\infty dx \bar{p}f(x) \int_\epsilon^{E'} u^*(x, \lambda) d\lambda = \int_\epsilon^{E'} c(\lambda)F(\lambda) d\lambda.$$

Differentiating with respect to E' we obtain Eq. (83).

An important auxiliary relation similar to Eq. (45) is

$$\int_a^\infty ff^* dx = \sum_n c_n c_n^* + \int_\epsilon^\infty c(E)c^*(E)dE. \quad (85)$$

From the above development it follows that the most general solution of the one-dimensional wave equation for $\psi(x, t)$, viz.,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{\hbar^2} \left[\frac{\hbar}{2\pi i} \frac{\partial}{\partial t} - V \right] \psi = 0, \quad (86)$$

in harmony with the boundary condition is

$$\psi(x, t) = \sum_n c_n u_n e^{(2\pi i/\hbar)E_n t} + \int_\epsilon^\infty c(E)u(x, E)e^{(2\pi i/\hbar)E t} dE. \quad (87)$$

9. ORTHOGONALITY AND EXPANSION PROPERTIES OF THE CHARACTERISTIC FUNCTIONS OF THE TWO-BODY PROBLEM

By means of Green's theorem one may prove that any two characteristic functions of the Schrödinger equation (60) corresponding to different energy levels are orthogonal to one another and to any packet formed from characteristic functions belonging to the continuous spectrum.⁴⁰ Furthermore, if the variables are separated, mutual orthogonality relations are readily established which, when combined with a suitable normalization, are expressed by the formulas

$$\begin{aligned} \int_0^{2\pi} \Phi_m \Phi_{m'}^* d\phi = \delta_{m,m'} : \int_0^\pi \Theta_{l,m} \Theta_{l',m'} \sin \theta d\theta = \delta_{l,l'} \\ \int_0^\infty R_{n,l} R_{n',l'} r^2 dr = \int_0^\infty \mathfrak{R}_{n,l} \mathfrak{R}_{n',l'} dr = \delta_{n,n'}. \end{aligned} \quad (88)$$

Hence

$$\begin{aligned} \int_\infty^\infty \int_\infty^\infty u_{n,l,m} u_{n',l',m'}^* dx dy dz = \int_\infty^\infty \int_\infty^\infty R_{n,l} \Theta_{l,m} \Phi_m R_{n',l'} \Theta_{l',m'} \Phi_{m'}^* r^2 \sin \theta dr d\theta d\phi \\ = \delta_{n,n'} \delta_{l,l'} \delta_{m,m'}. \end{aligned} \quad (89)$$

It can also be proved that an arbitrary function of θ and ϕ which, together with its first and second derivatives, is continuous over the entire sphere may be developed into an absolutely and uniformly convergent series of spherical harmonics⁴¹ $\Theta_{l,m} \Phi_m$. Combining this fact with the corresponding theorem for $R(r)$ which follows from the Sturm-Liouville character of the differential equation (62), we conclude that a suitably continuous arbitrary function of x, y, z or of r, θ, ϕ may be expanded in the form

$$\begin{aligned} f(x, y, z) = \sum_{n=l+1}^\infty \sum_{l=|m|}^\infty \sum_{m=-\infty}^{+\infty} c_{n,l,m} R_{n,l} \Theta_{l,m} \Phi_m \\ + \int_0^\infty dE \left\{ \sum_{l=|m|}^\infty \sum_{m=-\infty}^{+\infty} c_{l,m}(E) R_l(E, r) \Theta_{l,m} \Phi_m \right\}. \end{aligned} \quad (90)$$

As in the simpler case of the one-dimensional oscillator, we have only to insert appropriate time factors in the right hand member of Eq. (90) to obtain the most general solution of the wave equation for the internal motion of the two-body problem in the form (18).

Similar orthogonality relations and expansion properties hold, no doubt, for most, if not all, of the characteristic value problems of the wave mechan-

⁴⁰ Cf. Courant-Hilbert, p. 255. Two functions u_n, u_m of the space coordinates x, y, z are by definition orthogonal in the region consisting of all space if

$$\iiint_\infty u_n u_m^* dx dy dz = 0, \quad n \neq m.$$

⁴¹ Cf. Courant-Hilbert, p. 422.

ics, though the writer knows of no comprehensive and rigorous discussion of the subject. The plausibility of these relations may be made evident in various ways which lie outside the scope of this review and is so great that they have been assumed without question by most theoretical physicists. They are of the greatest importance not only for expressing the most general solution of the basic wave equation (38) in terms of characteristic functions defined by the space factor equation (37), but also in the development of perturbation theory and in the study of the problem of the emission of radiation by matter.

SECTION 3. OPERATORS AND MOMENTA IN THE WAVE MECHANICS

1. MEAN VALUES OF FUNCTIONS OF THE COORDINATES

Mean values play an important rôle in any statistical theory. In fact we may say that the function of any statistical theory is to determine mean values of one kind and another. For example, $\psi\psi^*d\tau$ may be regarded as a mean value for the number of particles in the volume element $d\tau$.

To find the mean value of any function of the coordinates $f(q)$ we have to multiply the probability that the system lies in any particular element in coordinate space by the corresponding value of $f(q)$ and sum. Thus

$$\overline{f(q)} = \int f(q)\psi\psi^*d\tau. \quad (91)$$

As an example of the use of this type of mean value we may cite the rigorous derivation of Newton's laws of motion for wave packets in the form

$$\mu\ddot{x} = -\frac{\partial\overline{V}}{\partial x} \quad (92)$$

by Ehrenfest.^{41a}

2. THE LINEAR MOMENTUM OPERATOR

Consider next the average values of the components of momentum. In the case of a single particle we have already shown that by analysing $\psi(t, x, y, z)$ into plane waves we may derive a wave function $Q(t, p_x, p_y, p_z)$ such that $QQ^*dp_xdp_ydp_z$ gives the probability that the momentum vector terminates in the element of volume $dp_xdp_ydp_z$ in momentum space. Then clearly the mean value of any component of momentum, say p_x is

$$\overline{p_x} = \iiint_{\infty} p_x QQ^*dp_xdp_ydp_z. \quad (93)$$

By means of the operator $(-h/2\pi i)\partial/\partial x$ we can replace the above mode of averaging by a more direct one which does not involve the evaluation of the Q function. When applied to a wave function corresponding to a single

^{41a} P. Ehrenfest, *Zeits. f. Physik* **45**, p. 455 (1927). Ehrenfest's proof for the one-dimensional case has been extended to the general case of a conservative system composed of n particles by Ruark, *Phys. Rev.* **31**, p. 533 (1928). Cf. also Sommerfeld "Ergänzungsband," pp. 287-9.

definite value of p_x [and hence of the form $f(t, y, z)e^{-(2\pi i/h)xp_x}$] the operator yields the relation

$$-\frac{h}{2\pi i} \frac{\partial \psi}{\partial x} = p_x \psi. \quad (94)$$

Hence, differentiating Eq. (42) with respect to x , we have

$$-\frac{h}{2\pi i} \frac{\partial \psi}{\partial x} = \frac{1}{h^{3/2}} \int \int \int p_x Q e^{(2\pi i/h)(xp_x + yp_y + zp_z)} dp_x dp_y dp_z \quad (96)$$

Now by a slight extension of the theorem of Eq. (45)⁴² we may show that if $\psi_1, Q_1; \psi_2, Q_2$ are two pairs of functions which satisfy the relations of Eqs. (42) and (43)

$$\int \int \int \psi_1 \psi_2^* dx dy dz = \int \int \int Q_1 Q_2^* dp_x dp_y dp_z. \quad (97)$$

Hence, identifying ψ_1 with $-(h/2\pi i)\partial\psi/\partial x$ and ψ_2 with ψ , we obtain

$$\int \int \int \psi^* \left(-\frac{h}{2\pi i} \frac{\partial}{\partial x} \right) \psi dx dy dz = \int \int \int Q^* p_x Q dp_x dp_y dp_z = \bar{p}_x. \quad (98)$$

Thus the mean value of each of the components of momentum may be evaluated by a rule formally the same as that used for $f(q)$ but with the substitution of the operator $-(h/2\pi i)\partial/\partial q$ for the momentum p conjugate to the coordinate q . Similarly we may determine the mean value of p^n by the rule

$$\bar{p}^n = \int \int \int \psi^* \left(-\frac{h}{2\pi i} \frac{\partial}{\partial q} \right)^n \psi dx dy dz. \quad (99)$$

The above mean value formulas are valid for a particle moving in a force field as well as for a free particle and are readily extended to cover a system of particles. In the latter case the Fourier analysis may be applied to one coordinate only as follows.⁴³

$$\left. \begin{aligned} \psi(t, x_1, x_2, \dots, x_{3n}) &= h^{-1/2} \int_{-\infty}^{+\infty} \phi(t, x_1, \dots, p_k, \dots, x_{3n}) e^{-(2\pi i/h)x_k p_k} dp_k \\ \phi(t, x_1, \dots, p_k, \dots, x_{3n}) &= h^{-1/2} \int_{-\infty}^{+\infty} \psi(t, x_1, \dots, x_k, \dots, x_{3n}) e^{(2\pi i/h)x_k p_k} dx_k \end{aligned} \right\} (100)$$

$$\begin{aligned} & \int_{-\infty}^{\infty} \psi^* \left(-\frac{h}{2\pi i} \frac{\partial}{\partial x_k} \right) \psi dx_1 \dots dx_{3n} \\ &= \int_{-\infty}^{\infty} \phi^* p_k \phi dx_1 \dots dp_k \dots dx_{3n} = \bar{p}_k. \end{aligned} \quad (101)$$

⁴² The mode of procedure is suggested in Riemann-Weber, p. 299 in connection with the proof of Eq. (16).

⁴³ It follows from the analysis of Sect. 1, that the fundamental formula (12) can be used to correlate the components of the momentum of the individual particles in such a system with the corresponding components of the wave-number in configuration space.

Evidently the total momentum in the direction of the x axis may be averaged by similar use of the operator $\sum_{i=1}^n (-\hbar/2\pi i)\partial/\partial x_i$.

As Sommerfeld⁴⁴ has pointed out, the use of the operator $(-\hbar/2\pi i)\partial/\partial q_k$ for the momentum p_k conjugate the coordinate q_k is intimately related to a fundamental theorem derived by Schrödinger⁴⁵ and interpreted by him as a statement of the law of the conservation of electricity. In its simplest form for a single particle in three dimensions using Cartesian coordinates this theorem is

$$\frac{\partial}{\partial t}(\psi\psi^*) = \frac{\hbar}{4\pi\mu i} \operatorname{div} [\psi \operatorname{grad} \psi^* - \psi^* \operatorname{grad} \psi]. \quad (102)$$

Multiplying through by the charge e and interpreting $e\psi\psi^*$ as the charge density (statistical mean), Eq. (102) takes the form of the equation of continuity with the vector current density \mathbf{S} defined by

$$\mathbf{S} = \frac{e\hbar}{4\pi\mu i} [\psi \operatorname{grad} \psi^* - \psi^* \operatorname{grad} \psi]. \quad (103)$$

Multiplication of \mathbf{S} by μ/e should give the vector momentum per unit volume, and integration over all coordinate space should give the total average momentum. In this way we find

$$\overline{p_x} = \frac{\hbar}{4\pi i} \iiint_{\infty} \left[\psi \frac{\partial \psi^*}{\partial x} - \psi^* \frac{\partial \psi}{\partial x} \right] dx dy dz. \quad (104)$$

The equivalence of Eq. (104) and our previous expression for $\overline{p_x}$ [Eq. (98)] may be proved by partial integration of Eq. (104) or by reference to Eqs. (94) and (95).

The theorem of Eq. (102) is given by Schrödinger in a general form applicable to a system of n particles described by means of any sort of generalized coordinates. Sommerfeld has used it to resolve Eq. (92) into the pair of equations

$$\overline{p_x} = \mu \dot{\overline{x}} \quad (105); \quad \dot{\overline{p_x}} = -\overline{\partial V / \partial x}. \quad (106)$$

3. THE ANGULAR MOMENTUM OPERATOR

The angular momentum of a system of particles is defined in the classical mechanics by the vector formula

$$\mathbf{M} = \sum_{k=1}^n \mathbf{r}_k \times \mathbf{p}_k. \quad (107)$$

As this formula when expressed in terms of a Cartesian coordinate system involves all the coordinates and all the momenta it might appear at first glance that the above methods of computing the mean value of \mathbf{M} would

⁴⁴ Sommerfeld "Ergänzungsband," pp. 284-5.

⁴⁵ E. Schrödinger, Ann. d. Physik (4) **81**, p. 136 (1926).

break down due to the impossibility of assigning exact simultaneous values to the coordinates and conjugate momenta. Ignoring this possible difficulty for the moment, however, we observe that by means of the Cartesian expressions for the components of \mathbf{M} in terms of the components of the linear momentum we may write out operators to be associated with M_x , M_y , M_z , respectively. Thus, in the case of a single particle

$$M_z = xp_y - yp_x \rightarrow -\frac{h}{2\pi i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \quad (108)$$

Now the definition of \mathbf{M} given in Eq. (107) is, of course restricted to wave packets in the limiting case where the uncertainties in coordinates and momenta can be ignored. Outside this special realm of the classical mechanics we are at liberty to define the components of angular momentum as we please, provided only that our definitions are in agreement with Eq. (107) in cases where the latter is valid. Hence, in harmony with Eq. (94) we define M_z for ψ functions which give it a unique numerical value by means of the equation

$$-\frac{h}{2\pi i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \psi = \alpha \psi. \quad (109)$$

If the quantity α is independent of x , y , z , we identify it with M_z . Otherwise we assign no definite value of M_z to the wave function under consideration but assume that it has a certain probability of taking on any one of a variety of values like the components of linear momentum for a wave packet. As a means for determining the probability amplitude for M_z in such cases we adopt the scheme of analyzing the wave function into a linear combination of functions which satisfy Eq. (109) and the usual boundary conditions for some value of α independent of the space coordinates. Thus Eq. (109) is to be made the basis of a characteristic value problem like the Schrödinger equation (15). The characteristic values of α are the possible values of M_z . The characteristic functions are the types of wave function which have definite angular momenta along the z axis.

Before formulating a mean value theorem for M_z we must give the differential equation (109) a brief examination. If we introduce the same spherical coordinates as in the two body problem [Sect. 1, 6] the operator $(h/2\pi i) [x(\partial/\partial y) - y(\partial/\partial x)]$ becomes $(h/2\pi i)\partial/\partial\phi$ and our differential equation takes the simple form

$$\frac{h}{2\pi i} \frac{\partial\psi}{\partial\phi} + M_z\psi = 0. \quad (110)$$

Its solution is

$$\psi = \chi(t, r, \theta) e^{-(2\pi i/h)M_z\phi}. \quad (111)$$

Continuity of ψ regarded as a function of x , y , and z requires that $2\pi M_z/h$ be restricted to integral characteristic values. M_z has no continuous spectrum

This is the origin of the quantization of angular momentum as it occurs in the Bohr theory. From our present point of view non-integral values of $2\pi M_z/h$ have no meaning.

As an arbitrary continuous function of x, y, z expressed in terms of the spherical coordinates r, θ, ϕ has the period 2π in ϕ , it follows that such a function can be expanded into the series of characteristic functions

$$\psi(t, r, \theta, \phi) = \sum_{m=-\infty}^{+\infty} \chi_m(t, r, \theta) e^{-im\phi}. \quad (112)$$

$\chi_m(t, r, \theta)$ plays the rôle of probability amplitude for the three independent variables r, θ, M_z . To get the mean value of M_z for the given ψ function we use the same procedure as for \bar{p}_z .

$$\bar{M}_z = \sum_m \int \chi_m^* M_z \chi_m d\tau = \int \psi^* \left(-\frac{h}{2\pi i} \frac{\partial}{\partial \phi} \right) \psi d\tau \quad (113)$$

where $d\tau$ is the element of volume $dx dy dz$ or $r^2 \sin \theta dr d\theta d\phi$.

The definition of M_z involved in equation (110) can now be justified by applying it to a wave packet having a precisely defined position and momentum as required by the classical mechanics. In the case of such a packet one can readily prove that

$$\overline{x p_y} = \int \psi^* \left(-x \frac{h}{2\pi i} \frac{\partial}{\partial y} \right) \psi d\tau \cong \bar{x} \bar{p}_y.$$

Hence \bar{M}_z is approximately equal to $\bar{x} \bar{p}_y - \bar{y} \bar{p}_x$. As the classical values of coordinates and momenta are identical with the mean values for the packet, this shows that our definition reduces to the classical one in the realm of validity of the older theory.

Sommerfeld⁴⁶ has proved the additional theorem that

$$\vec{M} = \mathbf{r} \times \text{grad } V = \text{mean applied torque}. \quad (114)$$

This he calls the integral form of the angular momentum law for the wave mechanics.

The possibility of assigning an exact value to M_z and hence also to M_x or to M_y , does not carry with it the possibility of assigning an exact value to the vector angular momentum \vec{M} , for simultaneous solutions of Eq. (110) and the corresponding equations for M_x and M_y do not exist. On the other hand, unique values for $M^2 = M_x^2 + M_y^2 + M_z^2$ are possible. The corresponding operator is

$$-\frac{h^2}{4\pi^2} \left[\left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)^2 + \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)^2 + \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)^2 \right].$$

Introducing spherical coordinates, applying the above operator to ψ , and identifying the resulting expression with $-M^2\psi$, we obtain the differential equation

⁴⁶ Sommerfeld "Ergänzungsband," p. 290.

$$\frac{\hbar^2}{4\pi^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] - \mathbf{M}^2 \psi = 0. \quad (115)$$

This is identical with the differential equation (63) whose solutions are the tesseral spherical harmonics. Thus one of the differential equations obtained on separating the variables in the two-body problem is identical with the condition that the wave functions for the various energy levels in that problem shall have definite values of \mathbf{M}^2 or of $|\mathbf{M}|$.⁴⁷ The characteristic values of \mathbf{M}^2 for the one-body problem or for the two-body problem are given by the formula

$$\mathbf{M}^2 = \frac{\hbar^2}{4\pi^2} l(l+1) \quad l=0, 1, 2, \dots \quad (116)$$

first derived by the matrix mechanics.⁴⁸ The extension of this formula to the problem of n particles presents no difficulty.

As Eqs. (110) and (111) are also valid for the special solutions of the two-body characteristic value problem of Sect. 2, 6 in which the variables are separated, we see that these solutions have unique values of M_z as well as of \mathbf{M}^2 . As previously noted, M_x and M_y cannot have unique values for functions which make M_z unique. Their mean values are zero for the special solutions under consideration and the sum of the mean squares is

$$\overline{M_x^2} + \overline{M_y^2} = \overline{\mathbf{M}^2} - \overline{M_z^2} = \frac{\hbar^2}{4\pi^2} [l(l+1) - m^2]. \quad (117)$$

4. THE ENERGY OPERATORS

The entire theory developed up to this point is based on the hypothesis that all ψ functions are linear combinations of functions of the form $u(t, q)e^{(2\pi i/\hbar)Et}$. Hence if any particular wave function is monochromatic (i.e., has a unique energy value)

$$\frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t} = E\psi. \quad (118)$$

⁴⁷ It is hardly necessary to note that if we start from the definition

$$M_x = \sum_{k=1,2} [y_k(p_z)_k - z_k(p_y)_k]$$

and introduce the coordinates of the center of gravity ξ, η, ζ together with the relative coordinates x, y, z as in Sect 2, 6, the operator for M_x splits into two parts, one of which is

$$-\frac{\hbar}{2\pi i} \left(\eta \frac{\partial}{\partial \zeta} - \zeta \frac{\partial}{\partial \eta} \right)$$

and gives the angular momentum of the center of gravity, while the other is formally identical with the operator used in Eq. (110) for a single particle and gives the angular momentum of the two bodies about their center of gravity. Applying the same procedure to the other components of \mathbf{M} we justify the direct application to the two-body problem of the operators developed above for a single particle.

⁴⁸ Born, Heisenberg, and Jordan, *Zeits. f. Physik* **35**, p. 557 (1925).

The mean value of E for any normalized wave function is readily shown to be

$$\bar{E} = \int_{-\infty}^{\infty} \psi^* \left(\frac{\hbar}{2\pi i} \frac{\partial}{\partial t} \right) \psi d\tau. \quad (119)$$

Thus the operator $(\hbar/2\pi i)\partial/\partial t$ bears the same relation to the numerical values of E as $-(\hbar/2\pi i)\partial/\partial x$ bears to the numerical values of p_x . [Classically E and $-t$ are canonically conjugate variables like p_x and x].

There is another operator, however, associated with the energy and derivable from the classical Hamiltonian function. In the case of a set of n particles moving in a conservative force field the expression for the energy in terms of coordinates and momenta (classical Hamiltonian) is

$$H = \sum_{k=1}^{3n} \frac{p_k^2}{2\mu_k} + V(x_1, \dots, x_{3n}).$$

If we replace the p_k 's by the corresponding operators we obtain a new operator which we will designate as $H(x_k, -\partial/\partial x_k)$. Thus⁴⁹

$$H\left(x_k, -\frac{\partial}{\partial x_k}\right) = -\sum_{k=1}^{3n} \frac{\hbar^2}{8\pi^2\mu_k} \frac{\partial^2}{\partial x_k^2} + V. \quad (120)$$

If this operator is applied to ψ and the resulting expression is equated to $-(\hbar/2\pi i)\partial\psi/\partial t$ one obtains

$$\left[\sum_{k=1}^{3n} \frac{1}{\mu_k} \frac{\partial^2}{\partial x_k^2} - \frac{8\pi^2 V}{\hbar^2} + \frac{4\pi}{\hbar i} \frac{\partial}{\partial t} \right] \psi = 0. \quad (121)$$

This is the basic equation of the Schrödinger theory (36). Eq. (36) is therefore equivalent to a statement of the identity of the two operators for E when applied to physically permissible wave functions. In view of this relation between the fundamental wave equation and the Hamiltonian function it is customary to write the differential equation in the symbolic form

$$H\psi = \frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t}. \quad (122)$$

The disclosure of the intimate relation between the Hamiltonian function of classical theory and the operator H of Eq. (122) when Cartesian coordinates are used immediately raises the question of the relation between these expressions in other coordinates. This problem has been investigated by Schrödinger⁵⁰ and by Podolsky⁵¹ who find that given the Hamiltonian func-

⁴⁹ V as an operator is interpreted to mean "multiply by the numerical value of the function V ."

⁵⁰ E. Schrödinger, *Ann. d. Physik* (4) **79**, pp. 747, 748 (1926).

⁵¹ B. Podolsky, *Phys. Rev.* **32**, p. 812 (1928). Cf. also P. A. M. Dirac, *Proc. Roy. Soc. A* **113**, p. 621 (1927). Schrödinger's method gives what Podolsky calls ψ_x , i.e. the ψ function of Eqs. (18) and (36) with the physical interpretation " $\psi_x \psi_x^* dx_1 \cdots dx_{3n}$ = probability of configuration in the element $dx_1 \cdots dx_{3n}$ of Cartesian coordinate space." Dirac's transformation theory introduces a different function, ψ_q , for the generalized coordinates q_1, \dots, q_{3n} such

tion in any system of coordinates one can deduce the corresponding operator H without the intermediate step of reverting to a Cartesian system. The operator H is frequently written as $H(q, \partial/\partial q)$ suggesting that it can be formed in any set of coordinates by the mere substitution of $-(\hbar/2\pi i)\partial/\partial q$ for the component of momentum conjugate to q in the classical Hamiltonian. The problem is not quite so direct and simple as that, however, since the suggested procedure is ambiguous. Consider, for example, the kinetic energy term $p_r^2/2\mu$ of the classical Hamiltonian in spherical coordinates which goes over into the operator

$$\frac{-\hbar^2}{8\pi^2\mu r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)$$

So long as p_r is a number the factor p_r^2 can be replaced by $[1/f(r)]p_r f(r)p_r$ with $f(r)$ arbitrary, but when we convert p_r into an operator we must use the definite form $r^{-2}p_r r^2 p_r$. Hence a rule is needed for choosing that particular way of writing the classical Hamiltonian which will yield the correct operator when one makes the substitution $p_k \rightarrow (-\hbar/2\pi i)\partial/\partial q_k$.

The converse step of deducing the classical Hamiltonian function $H(q, p)$ from the wave equation in generalized coordinates involves no such difficulty.

Incidentally the possibility of deducing the wave equation in any set of coordinates from $H(q, p)$ and the above operator substitution suggests that we define numerical values of the generalized component of momentum conjugate to any coordinate q as we defined the numerical values of M_x in Eq. (110), i.e. that we ascribe the value α to p_k when ψ satisfies the differential equation

$$-\frac{\hbar}{2\pi i} \frac{\partial}{\partial q_k} \psi(t, q_1, \dots, q_{3n}) = \alpha \psi(t, q_1, \dots, q_{3n}) \quad (123)$$

and fix the probability of various values of p_k for a normalized ψ function by an analysis of the function into a linear combination of the solutions

$$\psi = \chi(t, q_1, \dots, q_{k-1}, q_{k+1}, \dots, q_{3n}) e^{-(2\pi i/\hbar)q_k p_k}.$$

5. CONSERVATION OF ENERGY AND MOMENTUM.

In the classical mechanics the law of the conservation of energy ascribes to every conservative system a function of its coordinates and momenta which is called its energy and which is constant in time as the motion progresses. In the wave mechanics we have in general no single definite energy, but in general a distribution function giving the probability of various possible energy values. By "conservation of energy" we may therefore imply the constancy of this distribution function in time, or, what comes to the same thing, the constancy of the mean values of E and its various powers.

that $\psi_q^* \psi_q dq_1 \dots dq_{3n}$ is the probability that the configuration lies in the element $dq_1 \dots dq_{3n}$ of the corresponding coordinate space and Podolsky gives a method of writing out the Hamiltonian function such that the substitution of $-(\hbar/2\pi i)\partial/\partial q_k$ for p_k yields directly the wave equation for ψ_q . ψ_q is equal to ψ_x multiplied by the square root of the Jacobian of the transformation from the Cartesian coordinate system to the system q_1, \dots, q_{3n} .

In deriving this law it will be sufficient to deal with the special case of the linear oscillator. Eq. (87) shows that the most general physically admissible solution of the wave equation is a linear combination of monochromatic solutions. The relative probabilities of the different discrete energy values and the different elementary intervals of the continuous spectrum are given by the squares of the absolute values of the coefficients c_n and $c(E)$ respectively [Cf. Eq. (85)]. As these coefficients are constants the theorem is proved.

Defining the laws of the conservation of linear and angular momentum in the same way, we note that a sufficient condition for the conservation of any mechanical quantity α associated with an operator O_α is that ψ shall be expansible into a linear combination of orthogonal functions each of which is monochromatic and also a characteristic solution of the equation

$$O_\alpha \psi = \alpha \psi. \quad (124)$$

This means that every non-degenerate solution of the wave equation (37) must also be a solution of Eq. (124). In the case of an energy level exhibiting r -fold degeneracy there exist an infinite number of sets of r mutually orthogonal solutions of Eq. (37) for the given energy. Each of these sets is derivable from any other by a suitable change of axes or by taking suitable linear combinations of the other solutions. In this case the conservation law holds for α if there exists some one set of r orthogonal solutions of Eq. (37) each member of which is also a solution of Eq. (124). In the case of a free particle the plane waves of Eq. (40) have the required characteristics for the conservation of linear momentum. In the case of the two-body problem referred to its center of gravity as origin, the solutions obtained in Sect. 2, 6 by separation of the variables in spherical coordinates have the required characteristics to prove the conservation of the z component of angular momentum. Evidently a rotation of axes will suffice to give new solutions exhibiting the conservation of M_x and M_y .

Sommerfeld⁵² defines what he calls the differential form of the "surface law" or law of the conservation of angular momentum by the equation

$$(H - E)\mathbf{M}\psi = 0. \quad (125)$$

in which \mathbf{M} is the operator $iM_x + jM_y + kM_z$. This equation is derivable from Eq. (37) if the operators H and \mathbf{M} commute, i.e., if $MH\psi = HM\psi$. It shows that if ψ is a solution of Eq. (37), $\mathbf{M}\psi$ is also a solution. Then if Eq. (37) has the r mutually orthogonal solutions $\psi_1, \psi_2, \dots, \psi_r$

$$\mathbf{M}\psi_n = \sum_{k=1}^r c_{nk} \psi_k. \quad (126)$$

Sommerfeld's form of the conservation law reduces to that given above if the operators M_x, M_y, M_z , or \mathbf{M}^2 are substituted for the vector operator \mathbf{M} . In each of these cases the required set of simultaneous solutions of Eq.

⁵² Sommerfeld "Ergänzungsband," p. 295.

(37) and Eq. (124) are derivable from the relation (126). In the case of the vector operator \mathbf{M} , however, the equation (124) has no solutions except the trivial one where α is zero. Hence the above statement of the conservation law in terms of the distribution function applies to \mathbf{M} only in so far as it is true for each of the components of \mathbf{M} taken separately.

The constancy in time of the mean value of the quantity α may be proved if the operator O_α commutes with $H(q_k, -\partial/\partial q_k)$.

SECTION 4.* PERTURBATION THEORY

1. THE CHARACTERISTIC VALUE PROBLEM AND PERTURBATIONS WHICH DO NOT INVOLVE THE TIME.

In the quantum mechanics as in the Bohr theory, perturbation methods are of fundamental importance due to the fact that so few problems can be rigorously solved by direct attack. The fundamental idea of these methods is that by starting from an approximate solution of the problem in hand one may compute by "hammer and tongs" a series of corrections designed to improve the degree of approximation. The procedure is easy or difficult according to one's success in choosing a happy starting point. The successive approximations may not converge on an exact solution of the problem in hand, but usually the first few steps do yield an appreciable improvement on the initial wave functions.

Consider first the solution of a typical Schrödinger characteristic value problem by the perturbation method. The best type of initial approximation consists in a complete⁵³ orthogonal function system in which one may expand any solution of the actual problem. Such a system may be obtained by the rigorous solution of a simplified related characteristic value problem⁵⁴ whose equation we write in the symbolic form

$$(H_0 - E)u = 0. \quad (127)$$

We call this the unperturbed equation and designate the corresponding unperturbed characteristic functions and characteristic values by u_k^0 and E_k^0 respectively. Let the differential equation to be solved (the perturbed differential equation) be of the form

$$(H - E)u \equiv (H_0 + H_1 - E)u = 0. \quad (128)$$

A formal solution of this equation can be obtained by the expansion of u in terms of the u_k^0 's as follows:

$$u = \sum_n c_n u_n^0 + \int_\epsilon^\infty c(E) u_E^0 dE. \quad (129)$$

Here u_E^0 is a wave function associated with the continuous spectrum of Eq. (127). Due to degeneracy in the wave functions of the continuous spectrum the integrand of the above integral will usually be a sum as in Eq. (90) but to avoid undue complication we use the above simplified

* Mostly machinery—a necessary evil!

⁵³ Cf. Note †, p. 187.

⁵⁴ Cf. Section 2.

form of expansion. In fact we shall omit the integral entirely in carrying through the detailed application of Eq. (129) to the solution of Eq. (128). This is permissible in view of the fact that in some cases Eqs. (127) and (128) have no continuous spectrum while in other cases a good approximation to the lower characteristic forms of u can be obtained without considering the continuous spectrum.

Let the function Hu_n^0 have the corresponding expansion

$$Hu_n^0 = \sum_m H(n, m)u_m^0 + \int_\epsilon^\infty H(n, E) u_E^0 dE. \quad (130)$$

The two-dimensional array of coefficients $H(n, m)$ forms a matrix which we designate by $\{H(n, m)\}$. The elements of this matrix are given by the formula

$$H(n, m) = \int_\infty u_m^{0*} Hu_n^0 d\tau. \quad (131)$$

$\{H(n, m)\}$ has what is called the Hermitian character, i.e., the symmetrical elements $H(m, n)$ and $H(n, m)$ are conjugate complex quantities. The proof of this statement will be given in §3 of this section. Since the operator $H(q, -\partial/\partial q)$ is real, it follows that

$$H(m, n) = H^*(n, m) = \int_\infty u_m^0 Hu_n^{0*} d\tau. \quad (132)$$

A matrix is a function of two independent variables (sometimes two sets of independent variables) which take on only discrete values. The coefficients $H(n, E)$ appearing in Eq. (130) and the additional coefficients $H(E', m)$, $H(E', E)$ obtained from the expansion of $Hu_{E'}^0$ may be combined with the $H(n, m)$'s to form a single function of two sets of independent variables, which take on discrete values in certain regions and continuous ones in others. Each set must of course be just sufficient to pick out one member of the complete orthogonal set of wave functions under consideration. Consider, for example, the important case where H_0 is the Hamiltonian operator for the central force field problem of Eq. (60). The arbitrary ordinal number n used above can then be replaced by the three variables M_z, M^2, E , or, using the quantum numbers for the first two variables, by m, l, E . The function $H(n, m)$ then merges with $H(n, E)$, $H(E', m)$ and $H(E', E)$ above to form a single function $H(m', l', E'; m'', l'', E'')$ in which m', l', m'', l'' take on only discrete values while E' and E'' take on either real or discrete values according to the region under consideration. Such functions form the stock in trade of Dirac's q -number theory. Due to the manner in which they are used and to their symmetrical Hermitian character expressed by the relation

$$H^*(m'', l'', E''; m', l', E') = H(m', l', E'; m'', l'', E''),$$

such functions may be regarded as generalized matrices.

Introducing the expansion (129) into the wave equation (128) and neglecting the continuous spectrum, we have

$$\sum_n c_n (Hu_n^0 - Eu_n^0) = 0.$$

Expanding Hu_n in turn by Eq. (130), and neglecting the continuous spectrum again we obtain

$$\sum_n c_n \left[\sum_m H(n, m)u_m^0 - Eu_n^0 \right] = 0.$$

In this equation the coefficient of each individual function u_k^0 must vanish. To prove this we multiply the equation by u_k^{0*} and integrate over all coordinate space. This yields the set of equations

$$\sum_n c_n [H(n, k) - E\delta_{n, k}] = 0. \quad (134)$$

Written out in full for the successive values 1, 2, 3, \dots of k these equations are

$$\left. \begin{aligned} c_1[H(1, 1) - E] + c_2H(2, 1) + c_3H(3, 1) + \dots &= 0 \\ c_1H(1, 2) + c_2[H(2, 2) - E] + c_3H(3, 2) + \dots &= 0 \\ c_1H(1, 3) + c_2H(2, 3) + c_3[H(3, 3) - E] + \dots &= 0 \\ \dots & \dots \end{aligned} \right\} \quad (135)$$

The solution of this infinite set of equations with its infinite set of unknowns⁵⁵ gives the values of the c_n 's and in case there is no continuous spectrum fully determines the character of the perturbed wave functions. If there is a continuous spectrum it may still give a good approximate description of the wave functions for the lower energy levels. A similar set of equations is derived in the matrix theory of Heisenberg, Born, and Jordan.⁵⁶

Such a set of equations forms an obvious extrapolation of the familiar case of a set of r homogeneous linear equations in r unknowns whose theory is so familiar.⁵⁷ According to this theory a solution of the equations different from the trivial one where all the c 's vanish exists only if the determinant of the coefficients vanishes, i.e., if

$$|H(n, k) - E\delta_{nk}| = 0. \quad (136)$$

If we limit the expansion of Eq.(129) to the first r characteristic functions this determinant is a polynomial of degree r in E . Hence Eq. (136) has r roots.⁵⁸ The limiting values of these roots as r approaches infinity are the

⁵⁵ If there is no continuous spectrum the number of discrete characteristic functions of Eq. (127) is infinite. Otherwise it may be either finite or infinite.

⁵⁶ A set of equations of the form (134) holds for each characteristic function of Eq. (128). The totality of these equations is equivalent to the single matrix equation (20) given by Born, Heisenberg and Jordan in *Zeits. f. Physik* **35**, p. 557 (1926).

It will be observed that the use of the expansion (129) and replacement of the differential equation (128) by the set of equations (134, 5) does not depend on the assumption that the u^0 's are solutions of the approximate differential equation (127). That assumption is of importance, however, for the practical problem of solving Eqs. (134) by successive approximations.

⁵⁷ The solution of these equations is equivalent to finding the principal axis transformation for the infinite quadratic form $Q \equiv \sum_n \sum_m c_n c_m^* H(n, m)$ as explained in Sect. 4, 2 below. The theory

of this transformation for infinite forms has been carried through for an important class of cases (limited forms) by Hilbert [*Nachr. d. K. Ges. d. W. zu Göttingen, Math. Phys. Kl.* pp. 154 and 439 (1906)] and Hellinger [*Crelle's Journal* **136**, p. 210 (1909)]. It shows that in some cases the transformation cannot be carried through without the use of the continuous spectrum.

⁵⁸ These roots are all real due to the Hermitian character of the matrix $H(n, k)$ Cf. Madelung, "Math. Hilfsmittel des Physikers" First Ed. p. 6. An equation of the form of (136) is called a "secular" equation as a consequence of the important rôle of this type of equation

energy levels of Eq. (128) if the unperturbed equation (127) has no continuous spectrum. In other cases they may give good approximations to the energy levels in question. Corresponding to each simple root E_k there is a set of c 's, say c_{kn} , uniquely determined except for an arbitrary common factor. If the perturbed wave function u_k is to be normalized like the unperturbed functions, the common factor is fixed by the resulting condition

$$\sum_n c_{kn}^2 = 1. \tag{137}$$

Any two sets of c 's, say c_{kn}, c_{ln} belonging to *different* roots of Eq. (136) will automatically satisfy the orthogonality condition

$$\sum_n c_{kn}c_{ln} = \int_{-\infty}^{\infty} u_k u_l d\tau = 0. \tag{138}$$

If two or more roots are equal, the c_{kn} 's are not uniquely determined and we have a case of degeneracy in the wave functions similar to that of Section 2, 6. Different sets of c 's associated with the same root need not be orthogonal in the sense of Eq. (138) but it may be proved that if n roots fall together one can (in an infinite number of ways) choose n mutually orthogonal sets of c 's such that any other set is necessarily a linear combination of them. In other words, in the case of an n -tuple root there exist exactly n linearly independent corresponding solutions of the wave equation.

In practice the solution of the secular equation (136) and the evaluation of the c 's is impracticable except by a method of successive approximations such as that described below.

The matrix of the Hamiltonian of the unperturbed equation in terms of an orthogonal system of its own solutions, i.e.,

$$\{H_0(n, m)\} \equiv \left\{ \int_{-\infty}^{\infty} u_n^{0*} H_0 u_m^0 d\tau \right\},$$

is *diagonal*. In other words, all elements vanish except those for which $n = m$. (As H_0 is any Hamiltonian operator which we happen to choose as the starting point of our perturbation theory this means that the matrix of any Hamiltonian is diagonal when referred to an orthogonal system of its own characteristic functions.) Since $H_0 u_n^0 = E_n^0 u_n^0$, this matrix has the explicit form

$$\{H_0(n, m)\} = \{E_n^0 \delta_{nm}\}.$$

Consequently

$$H(n, m) = E_n^0 \delta_{nm} + H_1(n, m)$$

and we may express the system of equations (134) in the modified form

$$\sum_n c_{kn} [H_1(n, m) - (E_k - E_n^0) \delta_{nm}] = 0. \quad m = 1, 2, 3, \dots \tag{139}$$

which is particularly convenient for solution by successive approximations.

in the astronomical theory of secular perturbations. The roots are called the characteristic values of the matrix $H(n, k)$. If the matrix is brought to diagonal form by a suitable transformation these characteristic values will form its diagonal terms.

As the next step in the development of the perturbation theory we write the Hamiltonian of the perturbed equation in the form

$$H = H_0 + \lambda h_1 \quad (140)$$

where λ is a parameter which we arbitrarily introduce into the problem if necessary and which may eventually be given the value unity. The wave functions and energy values will then depend upon λ and by allowing this parameter to approach zero we can carry the perturbed problem over into the unperturbed problem. It is now plausible to assume that the energy values and the coefficients c_{kn} which determine the wave functions are expandable in power series in λ .

$$\begin{aligned} E_k &= E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots, \\ c_{kn} &= c_{kn}^{(0)} + \lambda c_{kn}^{(1)} + \lambda^2 c_{kn}^{(2)} + \dots. \end{aligned} \quad (141)$$

These expansions need not be valid but we proceed on the hopeful assumption that they are permissible.⁵⁹

The first step in the evaluation of the coefficients in the above expansions is to note that the $E_k^{(0)}$'s must be the energy levels of the unperturbed system. If the perturbed energy levels are numbered in the same way as the unperturbed, we may identify $E_k^{(0)}$ with E_k^0 . Also the limiting value of the perturbed wave function in the case where λ becomes equal to zero, i.e., $\sum_n c_{kn}^{(0)} u_n^0$ must be a solution of the unperturbed equation for the characteristic value E_k^0 . If E_k^0 is non-degenerate, as we shall assume for the present, the above expression has the unique value u_k^0 and we conclude that $c_{kn}^{(0)} = \delta_{kn}$.

Using the values thus obtained for $E_k^{(0)}$ and $c_{kn}^{(0)}$, inserting the series (141) into Eqs. (139), replacing $H_1(n, m)$ by $\lambda h_1(n, m)$, and equating the coefficients of the first and second powers of λ to zero, one obtains

$$\lambda E_k^{(1)} = \lambda h_1(k, k) = H_1(k, k); \quad (142)$$

$$c_{kk}^{(1)} = 0; \quad \lambda c_{kn}^{(1)} = \frac{H_1(k, n)}{E_k^0 - E_n^0}, \quad n \neq k; \quad (143)$$

$$\lambda^2 E_k^{(2)} = \lambda^2 \sum_n c_{kn}^{(1)} h_1(n, k) = \sum_n \frac{H_1(k, n) H_1^*(k, n)}{E_k^0 - E_n^0}. \quad (144)$$

These equations carry the approximation far enough for most purposes.

⁵⁹ As an example of an instance in which the above expansions are not rigorously valid the case of the Stark effect as worked out by Schrödinger may be mentioned. If one assumes a uniform electric field extending to infinity in all directions the perturbing potential is infinite at infinite points in the direction of the negative electric force and no monochromatic solutions of the perturbed problem exist. Nevertheless the solutions obtained by Schrödinger using the above series do agree with the experimental observations. Evidently the mathematical difficulty here is introduced by an excessive idealization of the experimental conditions for observing the Stark effect.

The form of perturbation theory developed in this article is due to Schrödinger, though he does not separate the two steps, expansion in terms of the unperturbed wave functions and development in terms of the parameter, as we do. Cf. E. Schrödinger, *Ann. d. Physik* (4) **80**, p. 437, (1926). The conditions for the convergence of the series (141) have been worked out by A. H. Wilson. Cf. Wilson's papers, *Proc. Roy. Soc.* **A122**, p. 589 and **A124**, p. 176 (1929).

Eq. (142) states that in first approximation the change in the energy due to the perturbing Hamiltonian operator H_1 is equal to the "mean value of H_1 " averaged over the unperturbed function u_k^0 . This is the wave mechanical equivalent of a familiar corresponding theorem of the classical mechanics.⁶⁰ Eqs. (143) and (144) may be interpreted as the description of an interaction between the unperturbed wave functions and the unperturbed energy levels produced by the operator H_1 . This interaction is small for widely separated energy levels both on account of the energy difference $E_k^0 - E_n^0$ in the denominators and on account of the fact that the matrix elements $H_1(k,n)$ for widely separated wave functions are normally quite small. This result justifies our previous statement that the lower energy levels of the discrete spectrum will be very slightly affected by interaction with the continuous spectrum.

The second order energy correction $\lambda^2 E_k^{(2)}$ is wholly due to interaction between the primary level E_k^0 under consideration and the other energy levels. The contribution of any other level E_n^0 is positive if the latter lies lower than E_k^0 and vice versa. Moreover, the perturbing effect of E_n^0 on E_k^0 is exactly equal and opposite to that of E_k^0 on E_n^0 . Hence one may say that the perturbative Hamiltonian introduces a set of repulsive forces between the different energy levels.

Consider next the case where *the energy level E_k^0 is degenerate*. Let the $r+1$ energy levels $E_k^0, E_{k+1}^0, \dots, E_{k+r}^0$ associated with the wave functions u_k^0, \dots, u_{k+r}^0 fall together. Any perturbed wave function u_k such that

$$\lim_{\lambda \rightarrow 0} E_k = E_k^0$$

must reduce to the form

$$u_k^{(0)} = \sum_{n=k}^{k+r} c_{kn}^{(0)} u_n^0$$

when λ becomes equal to zero. Due to the degeneracy, however, the above sum does not reduce to a single term. The values of the $c_{kn}^{(0)}$'s and of the first order correction to the energy may be deduced from Eqs. (139) if the coefficients of the first power terms in λ are set equal to zero. By this means one obtains the $r+1$ equations

$$\left. \begin{aligned} &c_{k,k}^{(0)} [h_1(k,k) - E_k^{(1)}] + c_{k,k+1}^{(0)} h_1(k,k+1) + \dots + c_{k,k+r}^{(0)} h_1(k,k+r) = 0 \\ &c_{k,k}^{(0)} h_1(k+1,k) + c_{k,k+1}^{(0)} [h_1(k+1,k+1) - E_k^{(1)}] \\ &\qquad \qquad \qquad + \dots + c_{k,k+r}^{(0)} h_1(k+1,k+r) = 0 \\ &\dots \\ &c_{k,k}^{(0)} h_1(k+r,k) + c_{k,k+1}^{(0)} h_1(k+r,k+1) \\ &\qquad \qquad \qquad + \dots + c_{k,k+r}^{(0)} [h_1(k+r,k+r) - E_k^{(1)}] = 0. \end{aligned} \right\} (145)$$

These equations admit of a solution different from zero only in case the determinant of the coefficients vanishes. The corresponding secular equation for $E_k^{(1)}$ has $r+1$ real roots. If they are all different, the primary energy

⁶⁰ Cf. M. Born, "Vorlesungen über Atommechanik," Springer, Berlin, 1925, p. 287.

level E_k^0 is split into $r+1$ sublevels by the perturbing operator H_1 and the initial degeneracy is completely removed. In this case the $c^{(0)}$'s are uniquely determined by Eqs. (145) and the normalization condition. The $u_k^{(0)}$'s form a second complete orthogonal set of solutions of the unperturbed differential equation.⁶¹

As an opposite extreme to the case where all the roots of the secular equation are different comes the case where all are equal due to the fact that the diagonal elements of the $(r+1)$ -rowed matrix $\{h_1(k, n)\}$ are all equal while the off-diagonal elements vanish. The initial degeneracy remains unaffected by the perturbation and the $c^{(0)}$'s from $c_{k, k}^{(0)}$ to $c_{k, k+r}^{(0)}$ are arbitrary except for the normalization condition. It is then convenient to give one of them the value unity while equating the others to zero.

Intermediate cases in which the degeneracy is partly removed by the perturbation are of practical importance but need not receive detailed consideration here. Neither shall we take up the computation of the first order corrections to the characteristic functions for the case where E_k^0 is degenerate. For a discussion of this question, of the relation of the continuous spectrum to the perturbation theory, and of many other related questions the reader is referred to the original papers of Schrödinger.^{61a}

2. THE VARIATION METHOD AND ITS APPLICATION TO THE PERTURBATION PROBLEM.

A very different and instructive derivation of the fundamental equations (134) can be worked out from a variation principle equivalent to the Schrödinger wave equation and boundary condition. In its more general form this variational principle constitutes a wave-mechanical equivalent of Hamilton's principle in the classical dynamics. In a less general form it gives a valuable formulation of the characteristic value problem of Eqs. (15) and (37). The possibility of reducing the boundary value problems of the classical physics to calculus of variations form has long been recognized by mathematicians and has been of fundamental importance in the development of the general theory of these characteristic value problems. In the wave mechanics the variational method is as old as the differential equation method, for Schrödinger's first contribution to the subject begins with a deduction of the wave equation from an assumed variational principle.⁶²

To set up the variational equivalent of the wave equation for a single particle in the general form (18) one may proceed as follows.⁶³ Let the wave equation be reduced to the simple form $L\psi=0$ by the introduction of the operator

$$L = H - \frac{\hbar}{2\pi i} \frac{\partial}{\partial t} = -\frac{\hbar^2}{8\pi^2\mu} \nabla^2 + V(x, y, z) - \frac{\hbar}{2\pi i} \frac{\partial}{\partial t}, \quad (146)$$

⁶¹ The problem of Eqs. (145) is identical with that of the principal axis transformation of the quadratic form having the matrix $\{h_1(k, n)\}$ as explained in Sect. 4, 2. The orthogonality of the $u_k^{(0)}$'s is a simple corollary on the theory of such transformations.

^{61a} E. Schrödinger, Ann. d. Physik (4) **80**, 437 (1926); **81**, 109 (1926); **83**, 556 (1927).

⁶² E. Schrödinger, Ann. d. Physik (4) **79**, 361 (1926).

⁶³ Our discussion of this subject is a modification of that given by Sommerfeld in his "Ergänzungsband," Kap. I 9d.

and let M denote the conjugate operator $H + (\hbar/2\pi i)\partial/\partial t$. By Green's theorem applied to any pair of suitably continuous functions $u(x, y, z)$, $v(x, y, z)$ defined throughout a volume G enclosed by a surface S

$$\begin{aligned} \iiint_G vLu d\tau = \iiint_G \left[\frac{\hbar^2}{8\pi^2\mu} \left\{ \frac{\partial u}{\partial x} \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \frac{\partial v}{\partial y} + \frac{\partial u}{\partial z} \frac{\partial v}{\partial z} \right\} + uvV \right. \\ \left. - \frac{\hbar}{2\pi i} \cdot v \frac{\partial u}{\partial t} \right] d\tau - \iint_S \frac{\partial u}{v} dS. \end{aligned} \quad (147)$$

$$\begin{aligned} \iiint_G uMv d\tau = \iiint_G \left[\frac{\hbar^2}{8\pi^2\mu} \left\{ \frac{\partial u}{\partial x} \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \frac{\partial v}{\partial y} + \frac{\partial u}{\partial z} \frac{\partial v}{\partial z} \right\} + uvV \right. \\ \left. + \frac{\hbar}{2\pi i} \cdot u \frac{\partial v}{\partial t} \right] d\tau - \frac{\hbar^2}{8\pi^2\mu} \iint_S u \frac{\partial v}{\partial n} dS. \end{aligned} \quad (148)$$

Subtraction yields

$$\begin{aligned} \iiint_G [vLu - uMv] d\tau = -\frac{\hbar}{2\pi i} \frac{\partial}{\partial t} \iiint_G uv d\tau \\ + \frac{\hbar^2}{8\pi^2\mu} \iint_S \left(u \frac{\partial v}{\partial n} - v \frac{\partial u}{\partial n} \right) dS. \end{aligned} \quad (149)$$

Let v be the complex conjugate of u and let the region G be a sphere whose radius approaches infinity. If $\iiint_{\infty} uu^* d\tau$ exists, the surface integral will vanish in the limit. Mu^* is the complex conjugate of Lu and must vanish if the latter quantity does. Hence Eq. (149) may be used to prove the constancy of $\iiint_{\infty} uu^* d\tau$ for functions which are quadratically integrable and satisfy the differential equation (18).⁶⁴

Consider now the integral K defined by

$$K = \int_{t_0}^{t_1} dt \iiint_G \psi^* L\psi dx dy dz. \quad (150)$$

Its first variation is

$$\delta K = \iiint_{G,T} [\delta\psi^* L\psi + \psi^* L(\delta\psi)] d\tau dt. \quad (151)$$

where T denotes the time interval $t_0 < t < t_1$. Using the theorem of Eq. (149) with u and v set equal to $\delta\psi$ and ψ^* respectively, we obtain

$$\begin{aligned} \delta K = \iiint_{G,T} [\delta\psi^* L\psi + \delta\psi M\psi^*] d\tau dt \\ - \frac{\hbar}{2\pi i} \iint_G [(\psi^* \delta\psi)_{t_1} - (\psi^* \delta\psi)_{t_0}] d\tau \\ + \frac{\hbar^2}{8\pi^2\mu} \iint_{S,T} \left[\delta\psi \frac{\partial \psi^*}{\partial n} - \psi^* \frac{\partial (\delta\psi)}{\partial n} \right] dS dt. \end{aligned} \quad (152)$$

⁶⁴ Cf. foot-note on p. 170; also p. 193.

Then if δK vanishes for all variations in $\delta\psi$ which reduce the last two integrals of the above equation to zero, we may conclude that ψ satisfies the wave equation (18) [$L\psi=0$] in the region G, T .

To prove the above statement it is convenient to separate ψ and $L\psi$ into real and imaginary parts as follows

$$\begin{aligned}\psi &= \psi_1 + i\psi_2, & \psi^* &= \psi_1 - i\psi_2, \\ L\psi &= \phi_1 + i\phi_2, & M\psi^* &= \phi_1 - i\phi_2.\end{aligned}$$

Then Eq. (152) reduces to

$$\delta K = 2 \iiint_{G,T} [\delta\psi_1\phi_1 + \delta\psi_2\phi_2] d\tau dt.$$

$\delta\psi_1$ and $\delta\psi_2$ are independent and arbitrary except at the boundaries of the space-time region G, T . Hence, if $\delta K=0$, ϕ_1 , ϕ_2 , and $\phi_1+i\phi_2$ must vanish. This proves the theorem.

Now let the region G take the form of a sphere whose radius approaches infinity. Let K approach a finite limit K_∞ . If $\delta K_\infty=0$ for arbitrary variations in ψ which vanish at infinity and for which

$$\iint_{\infty} [(\psi^*\delta\psi)_{t_1} - (\psi^*\delta\psi)_{t_0}] d\tau = 0 \quad (154)$$

we may conclude that Eq. (18) holds over all space and through the time interval T . This theorem (I) is a wave-mechanical analogue of Hamilton's principle.

By means of Eq. (147) we may give the principle a slightly different form (II) in which K_∞ is replaced by the integral K'_∞ defined by

$$\begin{aligned}K'_\infty &= \int_{t_0}^{t_1} dt \iiint_{\infty} \left\{ \frac{h^2}{8\pi^2\mu} \left[\frac{\partial\psi^*}{\partial x} \frac{\partial\psi}{\partial x} + \frac{\partial\psi^*}{\partial y} \frac{\partial\psi}{\partial y} + \frac{\partial\psi^*}{\partial z} \frac{\partial\psi}{\partial z} \right] \right. \\ &\quad \left. + \psi^*\psi V - \frac{h}{2\pi i} \psi^* \frac{\partial\psi}{\partial t} \right\} d\tau.\end{aligned} \quad (155)$$

A restricted form of the principle (III) is obtained if one seeks to fulfill the variation principle (I) by means of a monochromatic function

$$\psi = ue^{2\pi iEt/h}$$

Then K_∞ can be replaced by

$$J = \iiint_{\infty} u^*(H-E)u \, dx dy dz \quad (156)$$

where H is the Hamiltonian operator. The requirement that δJ vanish for all variations in u which vanish at infinity and for which $\delta E=0$ is equivalent to the requirement that u satisfy the wave equation (15) or that

$$Hu = Eu. \quad (157)$$

The variational principle (III) may be written

$$\delta J = \delta Q - E \delta \int_{\infty} u^* u d\tau = 0 \tag{158}$$

where

$$Q = \int_{\infty} u^* H u d\tau. \tag{159}$$

If E is fixed in the proper manner, Eq. (158) is the same as the pair of equations

$$\delta Q = 0 ; \delta N = \delta \int_{\infty} u^* u d\tau = 0. \tag{160}$$

From Eqs. (156) and (157) it is clear that the desired characteristic value of E is given by

$$E = [Q/N]_m ; N = \int_{\infty} u^* u d\tau. \tag{161}$$

if the subscript m be used to denote the “extremalized” value of the bracketed ratio. This last form of the variation principle (as stated in Eqs. (160) and (161)) we call (IV). It presupposes the existence of the integrals Q and N^* , and is therefore restricted to energy levels belonging to the discrete spectrum, but is of great importance in the approximate theoretical determination of these levels and of their wave functions.

The variational principles (III) and (IV) can be modified like (I) through the substitution of the quantity $\Lambda = (\hbar^2/8\pi^2\mu) (\text{grad } u^* \text{ grad } u) + u^* u V$ for $u^* H u$ in the integrands of the integrals to be varied. It is in these last forms that the variational principles are stated by Schrödinger⁶⁵ and Sommerfeld (l.c.). The extension of these principles to the n -body problem is obvious.

In the classical mechanics one of the most important uses of the variational principles is in deriving the differential equations of motion in generalized coordinates. To change from one coordinate system to another one has only to transform the integrand of the integral to be varied from the old system to the new and then write down Euler’s equations for the minimization of the integral using the transformed integrand. The same use is made of the variational principles in the wave mechanics.⁶⁶

After this rather lengthy introduction, we turn to the application of the variational method in the form (III) to the perturbation problem. To this end we use the Ritz direct method of attack on the variational problem.⁶⁷ Let $u_1^0, u_2^0, \dots, u_n^0, \dots$ denote as before a complete normalized orthogonal system of discrete functions in terms of which we can expand any suitably continuous quadratically integrable comparison function u to be considered in connection with our variational problem. Let the expansion be

$$u = \sum_{n=1}^{\infty} c_n u_n^0 \tag{162}$$

⁶⁵ E. Schrödinger, l.c. and Ann. d. Physik **82**, 265 (1927). Cf. also W. Gordon, Zeits. f. Physik **40**, 117 (1926).

⁶⁶ E. Schrödinger, Ann. d. Physik (4) **79**, 734 (1926); V. Fock, Zeits. f. Physik **38**, 242 (1926).

the c_n 's being arbitrary except for the fact that the sum of their squares must converge to a definite limit. Let Hu_n^0 have the expansion

$$Hu_n^0 = \sum_{m=1}^{\infty} H(n, m)u_m^0. \quad (163)$$

Then term by term integration of J converts it into the infinite quadratic form.

$$J = \sum_n \sum_m c_n c_m^* [H(n, m) - E\delta_{nm}]. \quad (164)$$

In order to minimize J we differentiate with respect to the real and imaginary parts of c_n and equate the derivatives to zero. By adding the two equations for each value of n one obtains the infinite set of equations (134, 5).⁶⁸

The coefficients $c_1, c_2, \dots, c_n, \dots$ may be regarded as an infinite set of complex coordinates which determine the function u . In the special case that these coefficients are real they may be interpreted as the orthogonal components of a vector in a space of infinitely many dimensions (function space).⁶⁹ In the more general case where the c 's are complex it is still helpful to use a geometrical language based on the above-mentioned possibility to describe the characteristic value problem. As indicated in Eq. (138) the orthogonality of two functions U, V with components a_n and b_n , respectively, is equivalent to the statement that

$$\sum_n a_n b_n^* = 0.$$

As this is a generalization of the formula for the orthogonality of two vectors in three dimensions we may say that when two functions are orthogonal in the sense of Eq. (77) the corresponding vectors in function space are mutually perpendicular. Normalized functions are correlated with points on the unit hypersphere

$$N(c_n) \equiv \sum_n c_n c_n^* = 1.$$

If we express the integral $Q = \int_{\infty} u^* H u \, d\tau$ in terms of the components of u it becomes a homogeneous quadratic form and the equation

$$Q(c_n) = \sum_n \sum_m c_n c_m^* H(n, m) = E$$

represents an infinite family of similar "ellipsoids" in function space. In extremalizing J and Q we determine the directions in which the unit hypersphere is tangent to one of these ellipsoids, i.e., the principal axes of the family. The lengths of these principal axes for any fixed ellipsoid are inversely proportional to the square roots of the characteristic values E_1, E_2, \dots . Hence the *lowest* characteristic value E_1 is the absolute minimum of Q for any point on the unit hypersphere or the absolute minimum of Q/N . The other values are minima with respect to displacements in certain directions and maxima with respect to others. It is possible, however, to set up a restricted variation problem for which any particular characteristic value, say E_r , is an absolute minimum. To do so we must find all linearly independent characteristic functions u_1, u_2, \dots, u_{r-1} for the energy levels below E_r . Then E_r is the absolute minimum of Q/N for comparison functions which are orthogonal to u_1, u_2, \dots, u_{r-1} .⁷⁰

The process of minimizing or extremalizing J and Q and the location of a complete normalized orthogonal set of solutions u_n of Eq. (128) is the equivalent of performing the

⁶⁷ W. Ritz, *J. reine angew. Math.* **135**, 1 (1909); Courant-Hilbert, p. 157.

⁶⁸ For a more rigorous discussion with due emphasis on the dangers of the procedure see Courant-Hilbert, l.c.

⁶⁹ Cf. Courant-Hilbert, pp. 38, 39, 40.

⁷⁰ Cf. Courant-Hilbert, Kap. VI, § 1, 2.

principal axis transformation upon the quadratic forms $J(c_n)$ and $Q(c_n)$.⁷¹ In the expansion

$$u_n = \sum_m \xi_{nm} u_m^0$$

for a normalized orthogonal set of u_n 's the coefficients ξ_{nm} must constitute a normalized orthogonal solution of Eqs. (134). If we describe the comparison function u of Eq. (162) in terms of the u_n 's instead of the u_n^0 's the expansion becomes

$$u = \sum_n d_n u_n$$

where

$$c_m = \sum_n \xi_{mn} d_n. \tag{165}$$

This equation describes an orthogonal linear transformation of coordinates in function space. If J is expressed in terms of the d 's by means of this transformation it takes the normal form

$$J = \sum_n d_n d_n^* (E_n - E). \tag{166}$$

By analogy with the analytic geometry of the conic sections we call this the "principal axis transformation". Such a geometrical interpretation is of course equivalent to saying that the matrices $\{H(n,m)\}$ and $\{H(n,m) - E\delta_{nm}\}$ of Q and J are reduced to diagonal form when referred to the correct characteristic functions of the problem in hand.

It seems probable that the variational method of deriving the perturbational equations (134) can be extended to cases where continuous as well as discontinuous spectra are involved but so far as the writer is aware the details have not been worked out.

The variation principle suggests an important method of attack on the problem of securing an approximate theoretical determination of the lower energy levels of a given system and their characteristic functions which does not involve the conventional expansion in powers of λ . In the case of the lowest energy level, for example, let an expression $u(q)$ be given, perhaps by the solution of one or more related problems, which constitutes a reasonable first approximation to the wave function desired. $u(q)$ can be generalized by the insertion of one or more parameters $\alpha_1, \alpha_2, \dots, \alpha_r$ in order to give $u(q, \alpha_1, \dots, \alpha_r)$ maximum flexibility consistent with reasonable mathematical simplicity. It is then plausible to suppose that by a proper choice of the parameters $\alpha_1, \dots, \alpha_r$ we shall obtain a much better approximation than the original $u(q)$. To get the best values of the α 's and also an approximate energy value one may insert $u(q, \alpha)$ into Eq. (159) and determine Q/N as a function of the α 's. Minimization with respect to these parameters fixes the best values of the α 's and at the same time locates the best energy values obtainable by this method. It is, of course, impossible to predict in advance the success of such a procedure, but the computed energy is sure to give an upper limit to the correct value (Cf. p. 81) and comparison with experimental data usually permits an estimation of the error after the completion of the calculation. In practice the uncertainty of this method is usually shared by the λ -series procedure owing to the excessive labor involved in working out the higher terms in the series.

The method just described can be applied to a few of the upper energy levels in case the wave functions have suitable symmetry characteristics.

⁷¹ Cf. Madelung, "Math. Hilfsmittel" pp. 2, 3; Riemann-Weber I, Kap. 2, 2; Courant-Hilbert, Kap. I, § 3.

Thus if the lowest wave function is known to have a certain type of symmetry it may be possible to insure the orthogonality of this lowest function and a flexible comparison function $u(q, \alpha)$ by giving the latter a different type of symmetry. Then in accordance with the theory of p. 81 minimization of $Q(\alpha)/N(\alpha)$ yields an approximate energy value and wave function for the lowest of the energy levels having the corresponding type of symmetry.⁷²

A quite distinct method of successive approximations has been developed by Brillouin who expands $\log \psi$ as a power series in \hbar . The first approximation to the energy levels is then given by the Bohr theory with half-integral quantum numbers. Cf. Sect. 2, 4 and the references in footnote 29, p. 182.

3. PERTURBATIONS INVOLVING THE TIME

The problem of perturbations involving the time has been treated by Schrödinger,⁷³ Dirac,⁷⁴ Born,⁷⁵ and Slater.⁷⁶ It is of fundamental importance for the discussion of the absorption, dispersion, and emission of radiation by matter—a problem to be considered in Section 5.

The most general form of wave equation derived up to this point is Eq. (38) in which V denotes a function of the coordinates only. We assume the possibility of modifying this equation, however, to include an interaction between the atom and a variable external electromagnetic field. Anticipating a result to be justified in the next section we write the modified equation in the symbolic form

$$\left(H - \frac{\hbar}{2\pi i} \frac{\partial}{\partial t} \right) \psi = \left(H_0 + H_1 - \frac{\hbar}{2\pi i} \frac{\partial}{\partial t} \right) \psi = 0. \quad (167)$$

Here H_0 represents the unperturbed Hamiltonian operator of Eq. (120) or an equivalent in generalized coordinates. H_1 is a perturbing operator which in the simplest case is merely a potential V_1 , depending on t as well as on the coordinates.

Following Born (l.c.) we assume that H_1 vanishes outside the time interval $0 < t < T$. For negative values of t any permissible wave function must then reduce to the form

$$\psi = \sum_n c_n u_n e^{2\pi i E_n t / \hbar} + \int_{\epsilon}^{\infty} c(E) u_E e^{2\pi i E t / \hbar} dE \quad (168)$$

⁷² The first application of the variation method to the characteristic value problem was the computation of the energy of normal He and normal Li^+ by Kellner (Zeits. f. Physik **44**, 91 and 110 (1927)). The most conspicuous success is that attained by Hylleraas in his recent recomputation of the energy of normal He (Zeits. f. Physik **54**, 347 (1929)). The well-known computation of the energy of normal H_2 by Heitler and London, although carried through along lines closely paralleling the usual λ -series procedure for degenerate systems, is perhaps best justified as an example of the variation method. An excellent example of the application of the method to an excited state is contained in the paper on the B state of the H_2 molecule by Zener and Guillemin (Phys. Rev.—in press).

⁷³ E. Schrödinger, Ann. d. Physik (4) **81**, 109 (1926); **83**, 956 (1927).

⁷⁴ P. A. M. Dirac, Proc. Roy. Soc. **A112**, 661 (1926).

⁷⁵ M. Born, Zeits. f. Physik **40**, 109 (1926).

⁷⁶ J. C. Slater, Proc. Nat. Acad. Sci. **13**, 7 and 104 (1927).

where u_n and u_E are characteristic functions of the unperturbed problem (Eq. (127)) with the characteristic values E_n and E respectively. (We drop the superscript "0" for the unperturbed wave functions used in Sect 4, 1 as no other characteristic functions appear in our present discussion). In case the energy levels E_n are degenerate, we assume the u_n 's form a complete normalized orthogonal set of characteristic functions.

As the expansion (168) is valid for any continuous function of the coordinates which behaves properly at infinity, it will hold for all values of t if the c 's are made suitable functions of the time. As in the preceding articles we give formulas for the c 's only in the idealized case where there is no continuous spectrum. The general case is discussed by Schrödinger. (l.c.).

Replacing H_1 by $\lambda F\{q, (\hbar/2\pi i)\partial/\partial q, t\}$ in accordance with Born's notation and following the procedure of Sect. 4, 1 we find

$$\dot{H}u_n = \sum_m H(n, m)u_m = E_{\dots n} + \lambda \sum_m F_{nm}(t)u_m. \quad (169)$$

with

$$F_{nm}(t) = \int_{-\infty}^{\infty} u_m^* F u_n d\tau$$

Introducing the expansions (168) and (169) into Eq. (167) one obtains the following infinite set of homogeneous differential equations for the c 's

$$\frac{\hbar}{2\pi i} \dot{c}_n = \lambda \sum_m c_m F_{mn}(t) e^{2\pi i(E_m - E_n)t/\hbar} \quad n = 1, 2, 3, \dots \quad (170)$$

These relations take the place of Eqs. (134), (139) of Sect. 4, 1. For negative values of t the right hand members vanish as they should. The corresponding arbitrary constant initial values of the c 's we indicate by the symbols c_n^0 .

In order to retain our fundamental hypothesis regarding the physical interpretation of $\psi\psi^*$ it is necessary that any generalization of the wave equation such as Eq. (167) shall conform to the theorem of foot-note 11, p. 170 ($\partial/\partial t \int_{-\infty}^{\infty} \psi\psi^* d\tau = 0$). In view of the discussion on p. 207 it follows that the basic operator H must satisfy the relation

$$\int_{-\infty}^{\infty} [\psi^* H \psi - \psi H^* \psi^*] d\tau = 0. \quad (171)$$

If this important restriction is obeyed, we can reverse an argument due to Dirac (l.c.) to prove that the matrices $\{H(n, m)\}$ and $\{F_{nm}(t)\}$ are Hermitian. Then by hypothesis

$$\frac{\partial}{\partial t} \int_{-\infty}^{\infty} \psi^* \psi d\tau = \frac{\partial}{\partial t} \left(\sum_n c_n c_n^* \right) = \sum_n (\dot{c}_n^* c_n + c_n^* \dot{c}_n) = 0. \quad (172)$$

By the aid of Eq. (170) we can throw the above equation into the form

$$\begin{aligned} & \frac{2\pi i \lambda}{\hbar} \left\{ \sum_{n, m} [c_n^* c_m F_{mn}(t) e^{2\pi i(E_m - E_n)t/\hbar} - c_n c_m^* F_{mn}^*(t) e^{2\pi i(E_n - E_m)t/\hbar}] \right\} \\ & = \frac{2\pi i \lambda}{\hbar} \sum_{n, m} c_n^* c_m [F_{mn}(t) - F_{nm}^*(t)] e^{2\pi i(E_m - E_n)t/\hbar} = 0. \end{aligned} \quad (173)$$

Since this quadratic form vanishes for arbitrary values of all the variables (subject only to the normalization condition) it follows that all the coefficients must vanish or that

$$F_{mn}(t) = F_{nm}^*(t). \quad (176)$$

This proves the theorem for $\{F_{nm}(t)\}$. As $\{H(n, m)\} = \{E_n \delta_{nm} + \lambda F_{nm}\}$ it is true also for $\{H(n, m)\}$.

The approximate solutions of Eqs. (170) given by other authors are contained in the following complete power series expansion due to Born (l.c.).

$$c_n = \sum_m c_m^0 f_{mn}(t). \quad (177)$$

Here

$$f_{mn}(t) = \sum_{p=0}^{\infty} f_{mn}^{(p)}(t) \lambda^p \quad (178)$$

with

$$\left. \begin{aligned} f_{mn}^{(p)}(t) &= \frac{2\pi i}{\hbar} \int_0^t \sum_k f_{mk}^{(p-1)}(t') F_{kn}(t') dt' ; \\ f_{mn}^{(0)}(t) &= \delta_{mn}. \end{aligned} \right\} \quad (179)$$

For values of t greater than T (i.e., after the perturbation is over) Eq. (177) becomes

$$c_n = \sum_m c_m^0 f_{mn}(T). \quad (180)$$

The effect of the perturbation is thus expressible as a linear transformation of the c 's with coefficients depending on the time. This transformation is *orthogonal*, for by Eq. (172)

$$\sum_n (c_n c_n^* - c_n^0 c_n^{0*}) = \sum_{m,k} c_m^0 c_k^{0*} \left[\left(\sum_n f_{mn} f_{kn}^* \right) - \delta_{mk} \right] = 0. \quad (181)$$

As the above statement is true for all values of the c 's, we conclude that

$$\sum_n f_{mn} f_{kn}^* = \sum_n f_{mn} f_{nk} = \delta_{mk}. \quad (182)$$

Born bases his physical interpretation of these results on the postulate that an atomic system cannot occupy two energy levels at once. On this view the wave functions are to be used as the basis of a statistical mechanics dealing with ensembles of identical independent systems like the classical statistical mechanics of Gibbs.⁷⁷ Since $\sum_n c_n c_n^* = 1$, $c_n c_n^*$ is interpreted as the probability that an arbitrary system chosen from the ensemble is in the n^{th} state, or will occupy the n^{th} state if the perturbation is removed at the instant in question. It follows from Eq. (180) that if initially all the atoms are in the m^{th} state the final probability that any one of them will be in the n^{th} state is

$$\Phi_{mn} = f_{mn}(T) f_{mn}^*(T). \quad (183)$$

Born interprets the induced changes in the c 's as quantum jumps and calls Φ_{mn} the transition probability for jumps from the n^{th} state to the m^{th} . The quantum jumps are not independent, however, since $c_n c_n^* = \left| \sum_m c_m^0 f_{mn}(T) \right|^2$.

⁷⁷ Cf. J. C. Slater, J. Franklin Inst. **207**, 449 (1929).

Born derives the Ehrenfest adiabatic theorem in the wave mechanics as a special consequence of Eqs. (177)–(179). He also treats perturbations involving the time in which the applied field is not removed after the time T . For details the reader is referred to the original paper (l.c.).

Foot-note added at reading of proof: All formulas in this article are based on the assumption of Eq. (17) that the sign of the exponent in the frequency factor of a monochromatic ψ function is *positive*. While this sign convention has been much used, notably in Sommerfeld's "Ergänzungsband," the author is inclined to the opinion that the opposite choice is preferable. The formulas for this alternative convention are obtained from those given above by replacing the symbol $i[(-1)^{1/2}]$ by $-i$ throughout. The operators used above are replaced by their conjugates which may be obtained direct from the appropriate classical formulas by the substitution $p_k \rightarrow +(\hbar/2\pi i)\partial/\partial q_k$.