# Contemporary Advances in Physics. XIV. Introduction to Wave-Mechanics

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IN a period when a limited domain of physical phenomena is exciting wide fervent interest and commanding intensive study, and continues for years to monopolize the attention of many brilliant theorists, sometimes it is the fortune of an ingenious mind to express or interpret or picture the already-discovered laws in a new way which makes so greatly favourable an impression, that in a moment it sweeps its rivals from the field. The new theory may not lead to more or better agreements with experience than did its predecessors; it need not make predictions which they were incapable of making; its mathematical processes may be identical with theirs, the old symbols reappearing with new names in the old equations. Contrariwise it may be born well endowed with these advantages which normally decide the contest between old theories and new, yet owe its victory not to them at all. It triumphs because it seems natural or sensible or reasonable or elegant or beautiful—words said of a theory which fulfils some deep-seated demand or evades some deep-rooted prejudice in the minds of its judges. Later its vogue may pass, not through the disclosure of any intrinsic defect, but because the physicists of the rising generation do not share the prejudices and the predilections of those who first applauded it. The kinetic theory of gases was welcomed by a generation which wished to believe in atoms; the electromagnetic theory by people prejudiced against the notion of action at a distance; the quantum-theory has always had to do battle against those who yearn for continuity in their images of Nature, and the theory to which these pages are devoted has captivated the world of physics in a few brief months because it seems to promise a fulfilment of that long-baffled and insuppressible desire.

Wave-mechanics being a new way of interpreting a vast field of well-known phenomena, it is unnecessary as indeed it would be impossible for me to recite in this place everything which the new theory is meant to explain. A few years hence, indeed, we may recognize in certain phenomena only newly or not yet discovered the securest basis for the new conceptions; but for the present, any adequate description of the facts on which Bohr's atom-model is based is nearly sufficient. I will recall only that the cardinal and dominant facts of the field which is the hunting-ground of the present generation of theorists are these: atoms exist in Stationary States—they emit or absorb radiation in passing from one of these States to another—the frequency of the radiation is proportional to the energy-difference between the two States from one to the other of which the atom passes. Moreover, for certain kinds of atoms and molecules there are empirical formulæ which express known interrelations among the energy-values of the various Stationary States. These in brief are the major facts to be explained.

Bohr proved that the energy-values of the Stationary States of the hydrogen atom could be reproduced by affirming, *first*, that the atom consists of an electron and a nucleus of known masses and equal and opposite known charges; *second*, that these revolve around their common centre of mass according to the classical laws of mechanics and without radiating energy; *third*, that among all the conceivable orbits which such particles might describe there are certain ellipses, distinguished by certain especial and peculiar features, which alone the particles are permitted to choose—to each "permitted" ellipse there corresponds a Stationary State, and each Stationary State may be visualized as a permitted ellipse.

The first of these assumptions has never since departed from the physicists' world-pictures. In wave-mechanics it is still implicit, though easily overlooked. The second and third have not so firm a foothold. As I have elsewhere remarked, they are and always will be as good as they ever really were. If we make the first two of Bohr's assumptions, then it follows as a matter of course that whichever Stationary State of the hydrogen atom we may wish to consider or may hereafter discover, we shall always be able to find an elliptic orbit with the proper energy-value to serve as its picture. Yet this alone is not an important fact; the serious question is, whether the family of all permitted elliptic orbits is set apart from the vast multitude of forbidden ones by some simple and striking distinction which they all share and none of the rest possesses, whether they rejoice in some intrinsic patent of aristocracy. At first it seemed so; now, however, it turns out that the distinctive feature which originally was supposed to ennoble just the orbits required to account for the Stationary States, and no others, is not perfectly suited to every case. This weakened the prestige of the elliptic orbits; and though the introduction of the Spinning Electron has done much to save the situation, it has not done enough to preserve them from the crescent disparagement of those who never really liked them.

With other atoms and with molecules, the situation is much the same. Bohr and his successors visualized atoms as groups of electrons surrounding nuclei; diatomic molecules, as paired nuclei surrounded by their jointly shared electron-family, capable of revolving like a dumbbell around their centre of mass and of vibrating like the two ends of a spring along their line of centres. These pictures persist in wave-mechanics; but the permitted vibration-amplitudes, the permitted rotation-speeds, and the permitted electron-orbits adduced to symbolize the Stationary States languish for the moment in the same discredit as the permitted elliptic orbits of the hydrogen atom.

Meanwhile, the humiliation of the electron-orbits accentuates the grave defect of the original atom-model of Bohr. That model offered nothing to interpret the fact that when an atom passes between two Stationary States of energy-values (let me say) $E_i$ and $E_j$, it emits (or absorbs) radiation of the precise frequency $(E_i - E_j)/h$, the quotient of the energy-difference by the notorious constant of Planck. Neither in the initial State nor in the final State are the constituent parts of the atom-model vibrating with this frequency (except in occasional untypical cases). The frequencies of the waves streaming out from the atom do not agree with the frequencies of the motions assumed to exist inside the atom—a very uncomfortable idea, altogether discordant with all our experience of sound and electrical circuits.

If it should be found possible to incorporate into the atom-model something vibratory, having for its vibration-frequency the quotient of the energy-value of the then-existing Stationary State by Planck's constant: then in the foregoing case this "something" would be vibrating initially with frequency $E_i/h$ and finally with frequency $E_j/h$, and the frequency of the emitted radiation would be the heterodyne or beat-frequency of these two. This is an agreeable idea; and wave-mechanics offers it. If then it should be found possible to arrive at the energy-values of the Stationary States by imposing conditions upon this vibrating entity instead of the electron-orbits, we should achieve as much as the electron-orbits enable us to achieve, and have the foregoing advantage also, and perhaps others as well. This is what wave-mechanics promises.

To this introduction I wish to join two warnings before plunging into the exposition. In the first place, wave-mechanics has several aspects, and may be approached from several directions; the one which I have chosen for this article is not the one which de Broglie elected nor the one which Schroedinger prefers.[1] In the second place, wave-

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[1] I suspect that the method of exposition which I shall follow is the one which Schroedinger meant when he wrote "I had originally the intention of establishing the new formulation of the quantum-conditions in this more visualizable (*anschaulich*) way, but preferred a neutral mathematical form, because it makes the essence clearer." Schroedinger himself stresses the formal likeness between ordinary me-

mechanics is yet incomplete. It has been applied with success to many problems, but there are situations—those involving the Spinning Electron, for instance—in which the way to apply it is not yet clear, and many theorists are groping. The new theory is still plastic; many minds, perhaps the hands of many experimenters, have yet to work upon it before it is molded into its final shape.

## Classical Mechanics and Wave-Mechanics

The underlying principles of "classical" or "Newtonian" mechanics may be stated in several alternative ways, each of which is especially well adapted to certain particular classes of problems. The most familiar of the statements is Newton's own. Unfortunately, it is another and less current which is the most expedient for the problems with which we have to deal. This formulation I will derive from Newton's, by imagining a particular extremely simple mechanical system and using Cartesian coordinates.

Conceive then a particle of mass $m$ and charge $e$, moving in an electrostatic field of which the potential is a function $U(x, y, z)$ of the coordinates.[2] Its momentum is a vector of which the components are $m\dot{x}$, $m\dot{y}$, $m\dot{z}$. These are called the *momenta with respect to the coordinates* $x$, $y$, $z$, and are designated by $p_x$, $p_y$, $p_z$. The force upon the particle is the negative of the product of $e$ into the gradient of the potential, a vector of which the components are $dU/dx$, $dU/dy$, $dU/dz$.

Newton's way of stating the underlying principles of mechanics then gives:

$$dp_x/dt = \dot{p}_x = -\,e dU/dx; \qquad \dot{p}_y = -\,e dU/dy, \qquad \dot{p}_z = -\,e dU/dz. \quad (1)$$

Multiplying the members of these three equations by $\dot{x}$, $\dot{y}$ and $\dot{z}$ respectively, and adding, we find:

$$\frac{d}{dt}\frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) = -\,e\left(\frac{dU}{dx}\frac{dx}{dt} + \frac{dU}{dy}\frac{dy}{dt} + \frac{dU}{dz}\frac{dz}{dt}\right). \quad (2)$$

On the left we have the rate of change of the kinetic energy $T$ of the particle as it travels along its path. To interpret the right-hand

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chanics and geometrical optics on the one hand and wave-mechanics and diffraction-theory on the other. I have not yet found this comparison helpful, and therefore cannot present it in a convincing manner.

I wish to acknowledge the valuable assistance of my colleague Mr. L. A. MacColl in preparing the mathematical portions of this paper.

[2] The reader will doubtless recognize that I am leading up to the case of the electron traveling in the field of a nucleus; I must therefore recall that in the case of the electron the charge $e$ is intrinsically negative, and that according to the classical electromagnetic theory equation (1) should contain a term describing the reaction of the emitted radiation upon the electron—a term which is omitted in all contemporary atomic theories.

member, introduce a symbol $V$ to designate the value of $U$ at the locality where at any moment the particle actually is, multiplied by $+e$; this is the potential-energy-function of the particle, and the right-hand member of (2) is its rate of change. Therefore:

$$\frac{d}{dt}(T + V) = 0,$$

$$T + V = \text{constant} = E. \tag{3}$$

The constant $E$ is (by definition) the energy. As the behavior of the particle depends upon the field, the ensemble of particle and field should be considered as one entity, the *system*, of which kinetic energy $T$ and potential-energy-function $V$ and total energy $E$ are properties.

To bring out the next feature, I take the still more specific case of a particle of charge $e$ and mass $m$ moving in the inverse-square central field of a "nucleus," an immobile point-charge equal in magnitude and opposite in sign to the electron-charge. Using Cartesian coordinates with the origin at the nucleus, we have $V = -e^2/\sqrt{x^2 + y^2 + z^2}$; using polar coordinates,[3] we have $V = -e^2/r$. It is obvious that polar coordinates permit a much simpler expression for $V$ than do Cartesians; on the other hand, they entail a distinctly more complicated expression for $T$. The proper choice of coordinates is often a vital question. For a few paragraphs I will carry along the reasoning in both coordinate-systems. The underlying equation (3) becomes, in the one and in the other:

$$\tfrac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) - e^2/\sqrt{x^2 + y^2 + z^2} = E, \tag{4a}$$

$$\tfrac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2 \sin^2 \theta \cdot \dot{\varphi}^2) - e^2/r = E. \tag{4b}$$

In these equations, we have the potential-energy-function expressed as a function of the *coordinates* ($x$, $y$, $z$ or $r$, $\theta$, $\varphi$) and the kinetic energy expressed in terms of the coordinates and the *velocities* ($\dot{x}$, $\dot{y}$, $\dot{z}$ or $\dot{r}$, $\dot{\theta}$, $\dot{\varphi}$). It is desirable to express the kinetic energy in terms of the coordinates and the *momenta*. We have already met the momenta in Cartesian coordinates, the quantities $m\dot{x}$, $m\dot{y}$, $m\dot{z}$. It is obvious that they are the derivatives of the expression for the kinetic energy with respect to the velocities, always in Cartesian coordinates:

$$p_x = dT/d\dot{x}; \qquad p_y = dT/d\dot{y}; \qquad p_z = dT/d\dot{z}. \tag{5}$$

The momenta in any other coordinate-system are defined in the same

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[3] The equations of transformation are: $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$, $z = r \cos\theta$.

way; first the kinetic energy is expressed as a function of the velocities, then differentiated with respect to these. In polar coordinates

$$\begin{gathered} p_r = dT/d\dot{r} = m\dot{r}; \qquad p_\theta = dT/d\dot{\theta} = mr^2\dot{\theta}; \\ p_\varphi = dT/d\dot{\varphi} = mr^2 \sin^2\theta \cdot \dot{\varphi}. \end{gathered} \tag{6}$$

Expressing in the equations (4a) and (4b) the kinetic energy in terms of the coordinates and momenta, we have

$$\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) - e^2/\sqrt{x^2 + y^2 + z^2} = E, \tag{7a}$$

$$\frac{1}{2m}\left(p_r^2 + \frac{1}{r^2}p_\theta^2 + \frac{1}{r^2\sin^2\theta}p_\varphi^2\right) - e^2/r = E. \tag{7b}$$

*Whenever in any problem the kinetic energy and the potential energy of the system are given as functions of coordinates and momenta, the problem is prepared for treatment by the methods of classical mechanics.*

To make the next step, we consider the function $L = T - V$, the difference between the kinetic energy and the potential-energy-function of the particle, a function of the particle as it travels along its path in the force-field:

$$L = T - V = 2T - E \tag{8}$$

and the time-integral of this function

$$W = \int L dt = \int 2T dt - Et. \tag{9}$$

Into the expression for $W$, insert explicitly the expression for kinetic energy in Cartesian or in polar (or in any other) coordinates:

$$W = m\int(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)dt - Et = m\int(\dot{x}dx + \dot{y}dy + \dot{z}dz) - Et, \tag{10a}$$

$$\begin{aligned} W &= m\int(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta \cdot \dot{\varphi}^2)dt - Et \\ &= m\int(\dot{r}dr + r^2\dot{\theta}d\theta + r^2\sin^2\theta \cdot \dot{\varphi}d\varphi) - Et. \end{aligned} \tag{10b}$$

From all of this it follows that

$$p_x = dW/dx, \qquad p_y = dW/dy, \qquad p_z = dW/dz, \tag{11a}$$

$$p_r = dW/dr, \qquad p_\theta = dW/d\theta, \qquad p_\varphi = dW/d\varphi, \tag{11b}$$

and in general, *the momenta belonging to any coordinate-system are the derivatives of the function W with respect to the coordinates.*

Into the fundamental equation (7a) substitute these expressions for the momenta, and obtain:

$$\frac{1}{2m}\left[\left(\frac{\partial W}{\partial x}\right)^2 + \left(\frac{\partial W}{\partial y}\right)^2 + \left(\frac{\partial W}{\partial z}\right)^2\right] + V(x, y, z) = E \tag{12}$$

or, seeing that the quantity $\sqrt{(\partial W/\partial x)^2 + (\partial W/\partial y)^2 + (\partial W/\partial z)^2}$ is the magnitude $|\nabla W|$ of the *gradient* of the function $W$, the gradient of a function being a vector well known in vector-analysis and denoted by prefixing the sign $\nabla$ or the abbreviation *grad* to the symbol of the function:

$$|\nabla W|^2 = 2m(E - V). \tag{13}$$

This equation governs the space-derivatives of the function $W$; it is complemented by the equation derived from (9) which governs the time-derivative of $W$:

$$\partial W/\partial t = -E. \tag{13a}$$

At this point the procedure of classical mechanics and the procedure of wave-mechanics diverge from one another.

Were we to follow the classical procedure, we should perform certain integrations and other processes, and arrive in the end at equations describing trajectories or orbits—in the particular case of an inverse-square central force-field, at equations describing elliptical orbits. The particular elliptical orbit to which the reasoning would conduct us would be determined by the value which had originally been assigned to the energy $E$, and the values which we attributed to the various constants of integration supervening in the course of the working-out. The function $W$, having served its purpose, would have vanished from the scene, leaving with us the electron swinging in its orbit within the atom or the planet in its orbit across the heavens.

The procedure of wave-mechanics, however, is based upon the observation that the equations (13) and (13a) together are *the description of a family of wave-fronts, traveling with the speed* $E/\sqrt{2m(E-V)}$ *through space.*

To display this aspect of the equation, let it be supposed at some prescribed time-instant $t_0$ the function $W$ has a certain prescribed constant value $W_0$ at every point of a surface $S_0$; for instance, that at time $t_0 = 1$ it is equal to unity all over the sphere of unit radius centered at the origin. It is to be shown that at a slightly later instant $t_0 + dt$ there is again a surface everywhere over which the value of $W$ is $W_0$, this not however being the same surface $S_0$, but another—a surface $S_1$ so placed that from any point $P_0$ on $S_0$ the shortest line to $S_1$ is perpendicular to $S_0$ and its length is $(E/\sqrt{2m(E-V)}dt)$.

This is easily shown. Imagine a vehicle[4] which at the instant $t_0$

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[4] I use this word instead of "particle" lest this entity be confused with the moving electron to which the foregoing equations relate. The electron does travel along a curve normal to the surfaces of constant $W$, not however with the speed $u$ about to be defined, but with a different speed related to $u$ in a curious and significant way (cf. the allusion on p. 695).

is traveling through $P_0$, along the line normal to $S_0$, with a speed to be designated by $u$. At the instant $t_0 + dt$ it occupies a locality where the value of $W$ is given by the formula:

$$\begin{aligned} W_0 + dW &= W_0 + |\nabla W| ds + \left(\frac{\partial W}{\partial t}\right) dt \\ &= W_0 + u|\nabla W| dt - E dt, \end{aligned} \tag{14}$$

for in the time-interval $dt$ it travels over a distance $ds = udt$ along the normal to the surface $S_0$, and along this normal the slope of the function $W$ is equal to $|\nabla W|$, and meanwhile at each point of space $W$ is varying directly with time by virtue of the term $-Et$ occurring in the equation (9) which defines it. Now if the imaginary vehicle happens to be moving with just the speed defined by the equation

$$u = E/\nabla W = E/\sqrt{2m(E - V)}, \tag{15}$$

the coefficient of $dt$ in equation (14) vanishes; that is, the vehicle as it moves outward keeps up with the prescribed value of $W$; but this is the same thing as saying that the value given for $u$ in (15) is the speed of the wave-front.

At this (if not an earlier) stage of the argument, one begins to wonder what $W$ "really is"; one turns back to seek the original definition of this artfully constructed function, so suddenly advanced from an auxiliary to the central rôle of the theory; one tries to grasp it, to form an image of it. I can do little to satisfy this very human craving. I can point out that $W$ is that quantity "action" with which the Principle of Least Action has to do; this feature scarcely makes it more conceivable, but at least enhances its prestige. I can point out that since no one has ever seen what moves or is inside an atom, the conception of waves in an intangible medium curling and flowing around a centre is no more far-fetched than the conception of intangible particles sailing in ellipses around a nucleus. (To this one can reply that the planets in their courses supply a visible analogue for the notion of revolving electrons, but no one has seen in the sky the wave-fronts of the function $W$.) I can point out that for some important purposes, notably the prediction of the Stationary States, it makes no difference what the function $W$ "really is"—no more difference than it makes to the solver of a quadratic equation whether the variable be called $x$ or $t$, whether in the mind of the propounder of the equation it stood for distance or for time. One might in fact begin with the forthcoming equation (20) as foundation, laying it down without introduction or apology; yet there must be deep-lying interconnections between the classical mechanics and the new, which such a procedure might mask. I can refer the reader to Schroedinger's own attempts to interpret $W$, some of which will figure in the last section of this article; or I can invite him to grow his own conception of $W$. This last in fact is what I will do.

Now if it is proposed to regard the fundamental dynamical equation (13) as the description of a family of wave-fronts perpetually wandering through space with the speed $E/\sqrt{2m(E-V)}$—and this is precisely what is proposed—then the description is obviously incomplete; for it omits to state the wave-length of these waves or the frequency of whatever be the vibrating thing which manifests itself by the waves, and indeed if the frequency were separately stated there would be no place for it in such an equation as (13). That equation, in fact, may be compared with the bare statement that the ripples traveling over the water of a pond from the place where a stone fell in are circles expanding at a given speed, or that the sound-waves proceeding through air from a distant source are plane waves traveling about 340 metres per second. To describe the ripples or the sound-waves completely it is essential to discover some ampler equation; a like extension is necessary here.

In treating familiar vibrating mechanical systems, stretched strings and tensed membranes and the like, it is customary to employ the general Wave-Equation

$$u^2\left(\frac{d^2\Psi}{dx^2}+\frac{d^2\Psi}{dy^2}+\frac{d^2\Psi}{dz^2}\right) \equiv u^2\nabla^2\Psi = \frac{d^2\Psi}{dt^2} \tag{16}$$

in which $\nabla^2$ stands for the Laplacian differential operator (page 671); $\Psi$ stands for the sidewise displacement of the string or distortion of the membrane or whatever it is that is transmitted as a wave; and $u$ for the speed of propagation of the wave. It is furthermore customary to supplement this by the equation

$$d^2\Psi/dt^2 = -4\pi^2\nu^2\Psi, \tag{17}$$

in which $\nu$ stands for the frequency of the vibration; combining which with (16), one obtains

$$\nabla^2\Psi + k^2\Psi \equiv \nabla^2\Psi + \frac{4\pi^2\nu^2}{u^2}\Psi \equiv \nabla^2\Psi + \frac{4\pi^2}{\lambda^2}\Psi = 0, \tag{18}$$

in which $\lambda = u/\nu$ stands for the wave-length of the wave-motion.

All of these matters will be developed at length in the following section. At this point it is necessary only to return to the description of the wave-motion partially but only partially described by (13), and complete it by the assertion—not an inevitable nor a self-evident assumption, but an original and daring hypothesis—that it is indeed a wave-motion endowed with a frequency, and this the frequency

$$\nu = E/h. \tag{19}$$

This manner of introducing into every mechanical system a vibration-frequency linked with its energy by the vital quantum-relation (19) was the invention of Louis de Broglie.

The wave-equation to which this hypothesis leads us then is:

$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0. \tag{20}$$

This is a particular form of the wave-equation of de Broglie and Schroedinger. It is the form which I will use throughout this article, for it is adequate to the first steps in the processes of atom-design—adequate, for instance, to supply a theory of the major features of the spectrum of atomic hydrogen, though not of its fine-structure; adequate also to interpret the data of the experiment of Davisson and Germer, and sufficient for an introduction to the ways of thinking which constitute wave-mechanics. Nevertheless it is certainly not the general wave-equation, for it is subject to at least two limitations.

The first of these is, that equation (20) is based upon Newtonian, not upon relativistic mechanics. We should therefore expect it to be valid only for slow-moving particles, to be the limiting form of a relativistic wave-equation appropriate to all velocities. Such an equation, indeed, was the first propounded by de Broglie. The past history of atomic theory suggests that we should need it when embarking upon the enterprise of explaining the fine-structure of the hydrogen spectrum. The latest developments in that history, however, indicate that the mere replacement of equation (20) by its relativistic analogue would not suffice for that enterprise; due allowance must be made in addition for the "spin" of the electron.[5] Wave-mechanics being yet too young to have furnished an answer to this twofold problem, the relativistic equation still wants what may in the end turn out to be its main experimental support. Yet it can scarcely be doubted that relativity must figure in the general wave-equation.

The second limitation upon equation (20) is due to its origin in

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[5] For the application of the relativistic equation to the hydrogen atom without allowance for the spinning electron, see V. Fock, *Zs. f. Phys.*, **38**, pp. 262–269 (1926). See also the first footnote on p. 688.

equation (13), and to a peculiar feature of that equation—to the fact that in it the magnitude of the gradient of $W$ stands equated to a function of the coordinates. This indeed is the feature which rendered it possible to imagine flowing waves. Now this feature occurs because the system to which equation (13) relates—the particle voyaging in a force-field—has a *kinetic-energy-function which is the sum of the squares of the momenta* (multiplied by a constant). Had we presupposed a system possessing a kinetic-energy-function not capable of being so expressed—two particles of different masses voyaging in a force-field, or a rigid rotating body of irregular shape, for example—the equation which we should have obtained in lieu of (13) would not have had the peculiar feature aforesaid; the wave-picture would not have offered itself, much less the equation (20) which was superposed upon the wave-picture. It is precisely at this obstacle that the mode of thought known as *non-Euclidean geometry* proves itself useful. It proposes equations of a general type, which can be written down for every system of which the kinetic-energy-function is preassigned, and which for the single particle floating in a force-field become the equation (13) and (20). In the language of non-Euclidean geometry, even the words and the symbols for *wave* and *wave-speed* and *gradient* and *Laplacian* are preserved; but whether they are advantageous to anyone not already versed in this subject may well be doubted. Suffice it to say, that non-Euclidean geometry provides a general equation [6] of which (20) is a special case, and that the general equation has already justified its existence by its successes in dealing with certain atom-models and molecule-models such as the rigid rotator used in the study of band-spectra. But the question as to what the waves "really are" becomes in these cases all the darker and more perplexing.

One further step, and we attain to the idea on which the calculation of the energy-values of the Stationary States reposes.

It is very well known that a medium capable of transmitting waves, and *bounded* in certain ways, may develop what are variously known as standing waves—stationary wave-patterns—the phenomena of resonance. Air enclosed in a box, a string pinched at the ends, a membrane clamped around its circumference, the mobile electricity in

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[6] Let the kinetic-energy-function of the system, expressed in terms of the coordinates and velocities, be written

$$T = \sum_i \sum_j Q_{ij}\dot{q}_i\dot{q}_j$$

and let $\Delta$ stand for the Laplacian operator in the non-Euclidean configuration-space of which the metric is $ds^2 = \Sigma\Sigma Q_{ij}dq_idq_j$; then the general wave-equation of de Broglie and Schroedinger is:

$$h^2\Delta\psi + 8\pi^2(E - V)\psi = 0.$$

a tuned circuit—each of these vibrates in a wave-pattern of "nodes" and "loops" if the frequency of vibration imposed upon it conforms to one of its own "natural frequencies" or "resonance frequencies." To each of these natural frequencies corresponds a particular pattern of loops and nodes; when one of them is impressed upon the medium, its corresponding wave-pattern springs into existence, and would continue forever were it not for friction internal or external. When any frequency not agreeing with one of the resonances is imposed upon the bounded medium, the resulting motion is very much more complicated. The calculation of these natural frequencies, the mapping of these vibration-patterns, is performed by using the methods of one of the great divisions of mathematical physics—the methods underlying the Theory of Acoustics.

May the Stationary States, then, of a natural atomic system be visualized as stationary wave-patterns such as these, and their energy-values as the products of the natural frequencies by the constant of Planck? Are the problems of atomic theory to be solved by devising atom-models imitated after familiar resonant bodies or tuned circuits, and applying to these "acoustic models" the mathematical technique of the Theory of Acoustics? This idea was developed by E. Schroedinger.[7]

## FAMILIAR EXAMPLES OF STATIONARY WAVE-PATTERNS

To display the laws governing wave-patterns, I will develop three examples: the stretched string, the tensed membrane, the ball of fluid confined in a spherical shell. The first of these is the simplest and most familiar of all instances; excursions into the theory of vibrating systems commence always at the wire of the piano and the string of the violin. Physically, this is a case of one dimension (distance, measured along the length of the string); mathematically, it is a case of two variables (that distance, and the time). The example of the tensed membrane is not unfamiliar in the practice of telephony, though many of the diaphragms of actual instruments are too thick to be considered such; for a membrane is, by definition, infinitely thin. It is a case of two dimensions and three variables. It will reveal to us the desirability of choosing for each specific problem its appropriate set of coordinates; and we shall observe what happens when one of the chosen coordinates is cyclic, being an angle which for all practical purposes returns to its original value when increased by $2\pi$; and we

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[7] Since the present article is based henceforth chiefly on Schroedinger's publications, I wish to make particular reference here to works embodying de Broglie's contributions: his own *Ondes et mouvements* (Paris, Gauthier-Villars, 1926) and article in *Jour. de Phys.* (6), **7**, pp. 321–337 (1926); L. Brillouin, *ibid.*, pp. 353–368.

shall encounter functions not so widely known as the simple sine and cosine which suffice for the case of the stretched string. The little-known example of the ball of fluid, with its three dimensions and four variables, will repeat these lessons, and will serve as the final stepping-stone to the wave-motions imagined by de Broglie and by Schroedinger. To proceed to these, it will suffice to imagine strings and fluids not uniform like those of the simple theory of vibrating systems and sound, but varying from point to point in a curious and artificial way.

### *Example of the Stretched String*

Imagine a stretched string, infinitely long, extended along the $x$-axis of a system of coordinates. Designate the tension in the string by $T$, the (linear) density of the string by $\rho$. To derive the differential equation governing the motion, conceive the string as a succession of short straight segments (Figure 1). Each segment exerts upon its neighbors a force, which is the tension in the string. When the string lies straight along the axis of $x$, each segment lies in equilibrium between the equal and opposite forces which its neighbors exert upon it. When however the string is drawn sidewise (remaining, we shall suppose, in the $xy$-plane) the neighbors of each segment are oblique to it and to one another, the forces which they exert upon it have components along the $y$-direction. These components are in general unequal, and their algebraic sum is a force urging the segment along the $y$-direction. Denote by $dx$ the length of such a segment, by $y$ its lateral displacement, by $\theta$ the angle between it and the axis of $x$; so that $dy/dx = \tan\theta$, and $\rho dx$ stands for the mass of the segment. The resultant force upon the segment is given by:

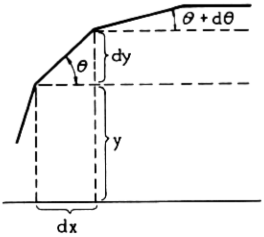

Fig. 1

$$\begin{aligned} F &= T[\sin(\theta + d\theta) - \sin\theta] = T[\tan(\theta + d\theta) - \tan\theta] \\ &= T\cdot d(\tan\theta/dx)dx = T(d^2y/dx^2)dx \qquad (101) \end{aligned}$$

to the degree of approximation to which the difference between $\sin\theta$ and $\tan\theta$ may be neglected.[8]

Equating this to the product of mass by acceleration, we obtain:

$$\rho d^2y/dt^2 = T(d^2y/dx^2) \qquad (102)$$

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[8] This is the degree of approximation all but universal in the theory of vibrating systems and sound. The conclusions from this theory are therefore strictly valid only in the limit of infinitesimal displacements or distortions.

or using dots to symbolize differentiation with respect to time, and dashes to represent differentiation with respect to space:

$$\ddot{y} = \sqrt{T/\rho}\cdot y''. \tag{103}$$

This equation, a linear combination of a second derivative with respect to time and a second derivative with respect to space, is the first and simplest of our wave-equations.

It is called a wave-equation, because it may represent—it does not necessarily represent, but it may—a shape or a figure or a distortion of the string (whichever one may choose to call it) which travels continually and indefinitely along the string with a constant speed.

To illustrate this possibility, let us suppose that at the time $t = 0$ the string is distorted into a sinusoidal curve described by the equation:

$$y = A \sin mx \quad \text{at} \quad t = 0 \tag{104}$$

and that its points are moving parallel to the $y$-axis with speeds described by the equation:

$$\dot{y} = nA \cos mx \quad \text{at} \quad t = 0. \tag{105}$$

At any other moment $t$, the configuration of the string is described by the equations:

$$y = A \sin (nt + mx), \qquad \dot{y} = nA \cos (nt + mx), \tag{106}$$

for these satisfy the differential equation which underlies the whole theory, and they satisfy also the "initial conditions" specified by (104) and (105). They satisfy these equations, that is to say, provided that a certain relation is fulfilled among the constants $n$ and $m$, and the quantities $T$ and $\rho$ which describe the physical nature of the stretched string; this relation being:

$$n/m = \sqrt{T/\rho}. \tag{107}$$

If this relation is fulfilled, the condition of the string throughout all time is described by the equations (106).

Examining these equations, we perceive that they signify that the values of displacement and speed, which at the time $t = 0$ existed at any point $x_0$ on the string, are at any other time $t$ to be found at the point $x_1 = x_0 - (n/m)t$. These values are moving steadily along the string; the whole configuration of the string, its sinusoidal shape and its transverse velocities, is slipping steadily lengthwise in the direction of decreasing $x$—the shape of the string is being transmitted as a wave, with the ratio of the constants $n/m$ for its speed of propagation $u$:

$$u = n/m = \sqrt{T/\rho}. \tag{108}$$

This result justifies the title *wave-equation* for the differential equation (103), and the meaning *speed of propagation* for its coefficient $\sqrt{T/\rho}$.

The reader will scarcely have failed to notice, however, that the result was obtained only by prescribing very sharply defined physical conditions. The string was supposed infinitely long; it was supposed distorted into the form of a sine-wave; the transverse speeds of its successive particles at the instant $t = 0$ were preassigned as rigorously as their positions. Were we to alter this last specification, we should arrive at very different results. If for instance we should make the assumption that at $t = 0$ the string is distorted into a sine-wave *and is stationary*, the equations (106) would not be adequate to describe what happens. We should then be forced to have recourse to a more general solution of the differential equation:

$$y = C \sin (nt + mx) + D \sin (nt - mx) \tag{109}$$

and to adjust the constants $C$ and $D$ so as to conform to the newly prescribed initial conditions, which are:

$$y = A \sin mx, \qquad \dot{y} = 0 \quad \text{at} \quad t = 0. \tag{110}$$

The adjustment is attained by making $C = D = \frac{1}{2}A$, whereupon we get:

$$y = A \sin nt \cos mx, \tag{111}$$

an equation which describes not a wave advancing perpetually along the string, but a stationary oscillation with nodes and loops of vibration, like those which a violin-string properly bowed exhibits, those in the air-column of Kundt's tube which the hillocks of dust reveal. One would hardly detect by instinct in this stationary wave-pattern the superposition of two oppositely gliding wave-trains each traveling with the speed $u = n/m = \sqrt{T/\rho}$. Yet the one is always equivalent to the other, and in the equation (111), the coefficients $n$ and $m$ are linked to one another through the wave-speed characterizing the string, and the equation may be written

$$y = A \sin umt \cos mx, \qquad u = \sqrt{T/\rho}. \tag{112}$$

Although the tension and the density of the string thus determine $n$ when $m$ is preassigned (or vice versa), nothing so far brought upon the scene compels any limitations upon the coefficient $m$. The infinitely long wire can sustain vibrations of any wave-length, or vibrations of two or any number of wave-lengths simultaneously, with any interrelation whatever among their several amplitudes and phases. On this fact rests our freedom to impose any initial conditions whatsoever on such a wire (subject to the usual restrictions of continuity and finiteness). For, if it be demanded that at $t = 0$ the displacement $y$ shall vary along the wire according to any totally arbitrary function $f(x)$, and the transverse speed $y$ according to any totally arbitrary function $g(x)$, then we have only to expand these functions $f$ and $g$ into Fourier series, or if need be, Fourier integrals; and each term in such an expansion corresponds to such a solution as (109), with a specific value of $m$ and such specific values of $C$ and $D$ as the initial conditions require; and the configuration of the wire forever before and after is described by the sum of all these solutions. In such a case we should not see an unchanging distortion of the wire slipping steadily along its length with a constant speed, nor a stationary pattern of nodes and loops. All the obvious features of wave-motions would be blotted out; and yet the infinitely complicated and variable figure of the string would be equivalent, in the last analysis, to a multitude of sinusoidal wave-trains perpetually gliding to and fro with the same uniform speed.

As soon, however, as we impose *boundary-conditions*, the vibrations which the string can execute are severely restricted.

As a simple and familiar example of boundary-conditions, I will assume that the string is clamped at the points $x = 0$ and $x = L$, and concern myself only with the finite length of string, $L$, comprised between these two fixed extremities.

As a preparation for future developments, it is advisable to restate the underlying differential equation, and solve it *ab initio*. We have:

$$\ddot{y} = u^2 y'', \tag{113}$$

in which $u$ stands for the speed of propagation of a sine-wave along an infinite wire. We essay a tentative solution, in the form of a product of a function of $t$ only by a function of $x$ only:

$$y = g(t) \cdot f(x). \tag{114}$$

The differential equation subjects the functions $g$ and $f$ to the condition:

$$f''/f = \ddot{g}/u^2 g = -m^2, \tag{115}$$

for, since the first member of this triple equation does not depend on $t$, and the second does not depend on $x$, each of the two must be independent of both $t$ and $x$, and equal to a constant which (for the sake of consistency with prior notation) I denote by $-m^2$. Solutions of these differential equations into which the underlying one was broken up are these:

$$f = A \cos mx + B \sin mx, \qquad g = C \cos mut + D \sin mut. \tag{116}$$

So far, there is no limitation upon $m$.

Now come the boundary-conditions, formulated thus:

$$f(0) = f(L) = 0. \tag{117}$$

We have now encountered, in its simplest example, the peculiar and characteristic problem of the Theory of Acoustics, which is also the peculiar and characteristic problem of the type of Atomic Theory which is inherent in wave-mechanics. This is not the question which we meet in the theory of moving particles, where we are asked what path a particle will follow through all future time if its position and velocity at a single moment are given. A similar question will indeed presently be asked and answered; but this peculiar problem intrudes itself at the beginning.

To adjust the function $f(x)$ to the boundary conditions, it is evident that we must set $A = 0$ and $\sin mL = 0$; therefore we must assume that $m$ has one of the values:

$$m = k\pi/L \qquad k = 1, 2, 3, 4 \cdots. \tag{118}$$

*The boundary-conditions have compelled the coefficient m to choose among a rigidly defined series of values.* The wave-lengths, and consequently the frequencies, of the permitted vibrations are strictly determined.

The permitted values of $m$ are known in German as the *Eigenwerte* of the differential equation for the boundary-conditions in question. The English term would be "characteristic values"; but it is long and has many meanings, and I think it preferable to borrow the German word as a foreshadowing of the application which Schroedinger has made peculiarly his own. To each *Eigenwert* of $m$ there corresponds a value of the vibration-frequency $mu/2\pi$, which in German is called an *Eigenfrequenz;* but here we may as well keep to the English term *natural frequency.*

To each *Eigenwert* there corresponds a solution of the differential equation, an *Eigenfunktion.* In the present instance the *Eigenfunktion* corresponding to the *Eigenwert* $m = k\pi/L$ is:

$$y_k = \sin \frac{k\pi}{L} x \left( C_k \cos \frac{k\pi u}{L} t + D_k \sin \frac{k\pi u}{L} t \right). \tag{119}$$

It represents a sinusoidal stationary oscillation of the wire, with nodes at the ends and at $(k - 1)$ points spaced evenly between the ends—a case not difficult to realize with a violin-string, if $k$ be not too great. The constants $C$ and $D$ specify the amplitude of the oscillation, and its phase at any given instant.

It is of course not necessary that the motion of the wire should conform to a single *Eigenfunktion*. Any number of *Eigenfunktionen*, corresponding to different permitted values of $m$—different integer values of $k$—might coexist simultaneously, each with its particular values of $C_k$ and $D_k$; the actual distortion of the wire would be the superposition of all. It would in fact be necessary to adjust the initial distortion of the wire and the initial velocities of its points with infinite accuracy, to cause its future motion to conform exactly to a single *Eigenfunktion*. On the other hand, any choice whatever of initial distortion and initial velocities would entail a future motion compounded out of the various *Eigenfunktionen* with suitable values of $C_k$ and $D_k$, which could be computed. This process corresponds to that of determining the future orbit of a particle of which the position and the velocity at a given instant are preassigned.[9] Both in acoustics and in wave-mechanics it is, as a rule, much more laborious than the determination of natural frequencies; and happily it is often less important, though not always to be neglected.

### *Example of the Tensed Membrane*

The differential equation of the tensed membrane is:

$$\nabla^2 z = \frac{d^2 z}{dx^2} + \frac{d^2 z}{dy^2} = \frac{1}{u^2}\frac{d^2 z}{dt^2}\,. \tag{120}$$

The coordinate-axes of $x$ and $y$ lie in the equilibrium plane of the membrane, and $z$ stands for the displacement of any point of the membrane normally from this plane. The symbol $u$ stands for the speed of a sine-wave traveling in an infinite membrane of the same tension $T$ and surface-density $\rho$ as the actual one, and is determined by the equation:

$$u^2 = T/\rho, \tag{121}$$

which is derived by an obvious extension of the method employed in deriving the like equation for a stretched string. In an actual bounded membrane the motion may be tremendously complicated, but it can

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[9] Inversely, the imposition of quantum-conditions upon orbits corresponds to the determination of natural frequencies; here is the bridge between the atom-models with electron-orbits and the atom-models of wave-mechanics.

be analyzed into a multitude of wave-trains traveling to and fro with the speed $u$.

The symbol $\nabla^2$ (to be read *del* or *nabla-squared*) stands for the Laplacian operator which in rectangular coordinates is $d^2/dx^2$, or $(d^2/dx^2 + d^2/dy^2)$, or $(d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$, according as we are dealing with one, two or three dimensions. In other coordinates than rectangular, it naturally assumes other forms. Now in these problems of two and three dimensions, the choice of coordinate-system and the imposition of boundary-conditions are two decisions which cannot be separated from one another. Were we to decree that the membrane should be square or rectangular with its edges clamped, the suitable coordinate-system would be the rectangular. The problem would then be extremely simple (the reader can easily solve it for himself by using the method adopted for the stretched string, and will arrive at very similar results) but not so instructive to us as the problem of the circular membrane with clamped edge. For this we must adopt polar coordinates (with the origin at the centre of the membrane, naturally). In these, the Laplacian operator assumes the form:

$$\nabla^2 = \frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr} + \frac{1}{r^2}\frac{d^2}{d\theta^2}\,. \tag{122}$$

We restate the fundamental differential equation (120) in this fashion; we essay a tentative solution in the form of a product of a function $f(r)$ of $r$ exclusively, a function $F(\theta)$ of $\theta$ exclusively, and a function $g(t)$ of $t$ exclusively; and we discover as before that each of these functions is subjected to a differential equation of its own. The procedure is like that already used in the case of the stretched string clamped at its ends. First we have

$$\frac{1}{f}\frac{d^2f}{dr^2} + \frac{1}{rf}\frac{df}{dr} + \frac{1}{r^2F}\frac{d^2F}{d\theta^2} = \frac{1}{u^2g}\frac{d^2g}{dt^2} = -\,m^2, \tag{123}$$

for, since the first member of this triplet does not depend on $t$, the second not on $r$ nor on $\theta$, both must be independent of all three variables and equal to a constant which, as before, I denote by $-\,m^2$. The differential equation for the factor dependent on $t$ has the solution:

$$g(t) = A\cos mut + B\sin mut. \tag{124}$$

Our experience with the stretched string suggests that $m$ will be restricted to certain *Eigenwerte*, derived from the boundary-conditions; and this is true; but before arriving at these, we must attend to the differential equation governing the functions $f$ and $F$. This assumes the form:

$$\frac{r^2}{f}\frac{d^2f}{dr^2} + \frac{r}{f}\frac{df}{dr} + m^2r^2 = -\frac{1}{F}\frac{d^2F}{d\theta^2} = \lambda^2, \tag{125}$$

both members of the equation being, by the familiar reasoning, equal to a constant which I denote by $\lambda^2$. It follows that the function $F(\theta)$ is of the form:

$$F(\theta) = C\cos\lambda\theta + D\sin\lambda\theta \tag{126}$$

and the coefficient $\lambda$ thus far seems to be unrestricted. But it carries its own restrictions in itself; for the coordinate $\theta$ is a cyclic coordinate, like longitude on the earth; whenever it is altered by $2\pi$, we are back at the same place. The function $F(\theta)$ must therefore repeat itself whenever $\theta$ is altered by $2\pi$; but this will not occur, unless $\lambda$ is an integer:

$$\lambda = 0, 1, 2, 3 \cdots. \tag{126a}$$

These are the *Eigenwerte*, and the functions (126) with one or another of these values assigned to $\lambda$ are the *Eigenfunktionen*, of the equation (125). In this case we have obtained *Eigenwerte* for the parameter and *Eigenfunktionen* for the solutions of a differential equation, not out of boundary conditions but out of the simple fact that the independent variable is by its nature cyclic. Such cases will occur in the undulatory mechanics.

We arrive at the third and last step of the problem: the determination of the function $f(r)$. It is governed by the differential equations:

$$\frac{d^2f}{dr^2} + \frac{1}{r}\frac{df}{dr} + \left(m^2 - \frac{\lambda^2}{r^2}\right)f = 0, \tag{127}$$

a distinct equation for each of the permitted integer values of $\lambda$. As the solution of such an equation as (115) is a sine-function of the variable $mx$, so the solution of such an equation as (127) is a function of the variable $mx$; not however a sine-function, but a Bessel function. For the values 0, 1, 2, $\cdots$ of $\lambda$, the solutions of (127) are the Bessel functions of order 0, 1, 2, $\cdots$, denoted by $J_0(mr)$, $J_1(mr)$, $J_2(mr)$, and so forth.

Like the sine-function of $mx$, the Bessel functions of $mr$ oscillate back and forth between negative and positive values as their variable increases from zero to infinity, and pass through zero at an infinite number of discrete values of $mr$. These do not lie at equal intervals, as do the values of $mx$ at which $\sin mx$ vanishes. Their values may be found in the tables; I shall designate them as $b^1$, $b^2$, $b^3$, $\cdots$ in order of increasing magnitude, using the superscripts not as exponents, but as ordinal numbers so that I may reserve the subscripts to distinguish the various Bessel functions from one another. The function

$$Z = J_\lambda(mr)(C \cos \lambda\theta + D \sin \lambda\theta)(A \cos mut + B \sin mut) \quad (129)$$

represents a stationary oscillation of an infinitely extended membrane, in which $\lambda$ lines intersecting one another at the origin are nodal lines, and an infinity of concentric circles centred at the origin are nodal circles. These lines and circles are motionless while the sections of the membrane which they delimit vibrate with the frequency $mu/2\pi$. The $\lambda$ lines are spaced uniformly in angle; the radii $r_1$, $r_2$, $\cdots$ of the infinity of circles are obtained by dividing $m$ into the roots $b_\lambda^1$, $b_\lambda^2$, $b_\lambda^3$, $\cdots$ of the Bessel function of order $\lambda$, $J_\lambda(mr)$.

How then does the boundary-condition upon the finite membrane enter in? Obviously, if a membrane of radius $R$ be clamped at its edge, and if it is vibrating in the manner described by (129), then the edge must coincide with one of the nodal circles; the radius $R$ must be equal to one of the quantities $b_\lambda^i/m$. Or rather, since the nodal circles are to be adjusted to the size of the diaphragm and not the size of the diaphragm to the nodal circles, the coefficient $m$ must conform to one of the equations:

$$m = b_\lambda^1/R, \quad \text{or} \quad b_\lambda^2/R, \quad \text{or} \quad b_\lambda^3/R, \quad \cdots. \quad (130)$$

*These equations define Eigenwerte of the parameter* m *in the differential equation of the tensed membrane.* There is a double infinity of these—an infinite series of them for each of the *Eigenwerte* of the parameter $\lambda$. To each corresponds a natural frequency of the membrane, and to each corresponds an *Eigenfunktion,* the one written down in (129) with the proper value of $m$ taken from (130). The constants $A$, $B$, $C$, and $D$ in the *Eigenfunktionen* specify the amplitude of the oscillation, the phase of the vibrations at any given instant, and the orientation of the nodal lines with respect to any given axis. Any number of *Eigenfunktionen* may coexist simultaneously; the actual distortion of the membrane will be the superposition of all. Any initial conditions imposed on $z$ and $\dot{z}$ (and not involving discontinuities or infinities) could be satisfied by adjusting the constants.

### *Example of the Ball of Fluid*

Among the familiar vibrating systems the ball of fluid presents the closest analogy to the atom-model for the hydrogen atom in wave-mechanics, the wave-patterns in the two cases being strikingly alike.

In three dimensions and in polar coordinates (those appropriate to the boundary-conditions which we shall impose) the wave-equation assumes the somewhat alarmingly intricate form:

$$\ddot{\Psi} = u^2\nabla^2\Psi = u^2\frac{\operatorname{cosec}\theta}{r^2}\left[\frac{d}{dr}\left(r^2\sin\theta\frac{d\Psi}{dr}\right) + \frac{d}{d\varphi}\left(\operatorname{cosec}\theta\frac{d\Psi}{d\varphi}\right) + \frac{d}{d\theta}\left(\sin\theta\frac{d\Psi}{d\theta}\right)\right]. \tag{131}$$

The argument $\Psi$ can no longer be visualized as a displacement perpendicular to the equilibrium-position of the undistorted medium, since all three dimensions are already used up. The reader may visualize it, if he will, as a condensation or a rarefaction, after the fashion of sound-waves. Perhaps not to visualize it at all would be a better preparation for the study of wave-mechanics.

In the familiar way, we essay a solution in the form of a product of a function of time $g(t)$, a function of radius $f(r)$, a function $\Phi(\phi)$ of the longitude-angle $\phi$ and a function $\Theta(\theta)$ of the colatitude-angle $\theta$. As before, we find that the time-function is of the form:

$$g(t) = A\cos mut + B\sin mut \tag{132}$$

and, as before, we shall find that the boundary-conditions confine the coefficient $m$ and the frequency $mu/2\pi$ to certain "permitted" values. The angle-functions and the radius-function are governed by the differential equations:

$$\frac{1}{f}\left[\frac{d}{dr}\left(r^2\frac{df}{dr}\right) + m^2r^2f\right] = -\frac{1}{Y}\operatorname{cosec}\theta\left[\frac{d}{d\varphi}\left(\operatorname{cosec}\theta\frac{dY}{d\varphi}\right) + \frac{d}{d\theta}\left(\sin\theta\frac{dY}{d\theta}\right)\right] = \lambda, \tag{133}$$

in which $Y$ stands for the product of $\Theta$ and $\Phi$, and $\lambda$ for a constant which seems to be arbitrary, but as a matter of fact is constrained by the same circumstance as arose in the case of the membrane; for, whenever $\varphi$ is altered by $2\pi$ and $\theta$ by $\pi$, we are back at the same place as before, and the function $Y$ must have the same value as before; and this will occur only if

$$\lambda = n(n+1), \qquad n = 0, 1, 2, 3, \cdots, \tag{134}$$

these being the *Eigenwerte* for the differential equation in (133) for the angle-function.[10] The corresponding *Eigenfunktionen* are spherical

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[10] This and the following statements about the functions $Y_n$ are proved by writing $Y$ in the second of equations (133) as the product of a function of $\theta$ and a function of $\phi$, and so dissolving the equation into two in the manner which I have already

harmonics. To each value of $n$ belongs a "spherical harmonic of order $n$," which itself is a sum of $(2n+1)$ terms, each multiplied by a constant which is at our disposal and can be adjusted to fit initial conditions or to emphasize particular modes of vibration. These terms are products of sine-functions of $\varphi$ by peculiar functions, the *Legendrian functions* $P_{n,s}$, of the variable $\theta$; so that the *Eigenfunktion* for a permitted value $n(n+1)$ of the parameter $\lambda$ has this for its most general form:

$$Y_n(\theta,\varphi)=a_{n,0}P_{n,0}(\cos\theta)+\sum_{s=1}^{n}a_{n,s}\cos(s\varphi)P_{n,s}(\cos\theta)+\sum_{s=1}^{n}b_{n,s}\sin(s\varphi)P_{n,s}(\cos\theta). \tag{135}$$

Each term by itself describes a particular mode of vibration of the fluid; the sum represents a superposition of divers modes of vibration. If we isolate one of these modes by giving to $n$ some particular value $n_1$, and to $s$ some particular value $s_1$, and causing all the constants $a$ and $b$ in (135) to vanish except $a_{n_1,s_1}$ and $b_{n_1,s_1}$; we then find that $Y$, and consequently $\Psi$, and consequently the motion altogether, vanishes at $s_1$ values of $\varphi$ and at $n_1-s_1$ values of $\theta$. If we draw a sphere centred at the origin, we find that its surface bears $s_1$ nodal meridian-circles, and $n_1-s_1$ nodal latitude-circles, along which there is perpetual rest. If we consider all the spheres at once—if, that is to say, we consider the entire volume of the fluid medium—we see that when the fluid is vibrating in the mode distinguished by the integers (I had almost said "quantum-numbers"!) $n_1$ and $s_1$, it is divided into compartments by $s_1$ nodal planes intersecting along the axis $\theta=0°$, and $n_1-s_1$ double-cones having that axis for their axis and the origin for this apex.

We have not yet considered the dependence of the wave-motion on the radius $r$; but the close analogy between this and the corresponding stage of the problem of the tensed membrane will make the task easy. The differential equation (133) for $f(r)$ resembles Bessel's equation (127), and has the somewhat similar solution

$$f(r)=\frac{1}{\sqrt{r}}J_{n+\frac{1}{2}}(mr). \tag{136}$$

used five or six times; the values of the constant $s$ in equation (135) are the *Eigenwerte* of the latter of these two. I thought it desirable not to overload the exposition by carrying through all stages of the process of solution, especially as the splitting of $Y_n(\theta,\phi)$ into the two functions is of secondary importance in the atom-model to which all this leads up; nevertheless the reader may find it advantageous to supply the lack.

This function vanishes, entailing the vanishing of the wave-motion, at an infinity of discrete values of the variable $mr$:—the roots of the function, which I denote in order of increasing magnitude by $B^1$, $B^2$, $B^3$, $\cdots$. In an infinite medium we could assign any value whatever to $r$, and then there would be an infinity of nodal spheres, their radii given by $B^1/m$, $B^2/m$, $B^3/m$, $\cdots$. If the medium is bounded by a rigid spherical wall of radius $R$, the coefficient $m$ must possess one of the values $B^i/R$, so that one of the nodal spheres may coincide with the wall. These are the *Eigenwerte* of the constant $m$, and the natural frequencies of the corresponding vibrations are given by $B^i u/2\pi R$. The *Eigenfunktionen* are given by the equation (136) with the various values $B^i/R$ substituted for the parameter $m$.

The *Eigenfunktionen* of the fundamental differential equation for the fluid sphere are, therefore, each a product of a radius-function given by (136), with a "permitted" value for the constant $m$ determined by the boundary-condition; an angle-function given by (135), with "permitted" values for the constants $n$ and $s$, determined by the fact that the angles are cyclic variables; and a time-function given by (132), with a "permitted" vibration-frequency determined by the boundary-condition. Each *Eigenfunktion* with the indices $m$, $n$, $s$ describes a mode of vibration, in which the fluid sphere is divided into compartments by $s$ meridian planes, $(n - s)$ double-cones, and a certain number of spheres, upon each of which the fluid is perpetually at rest; within the compartments, it vibrates with a prescribed frequency.

## Atom-Models in Wave-Mechanics

### *Case of a "String" for which the Wave-Speed is Variable, or even Imaginary*

Thus far I have used the images of the stretched string, the tensed membrane, and the elastic fluid to illustrate the behavior of the differential equation

$$u^2\nabla^2\Psi = d^2\Psi/dt^2, \tag{151}$$

when the coefficient $u^2$ is a positive constant. In these examples $u^2$ is interpreted as the ratio of the intrinsically positive quantities "tension" (or "pressure") and "density," and turns out to be equal to the square of the speed of propagation of sine-waves in the string, membrane, or fluid. In certain problems of undulatory mechanics we encounter just such an equation. In some of the most important applications of Schroedinger's theory, however, one meets with differential equations of the type of (151), in which however the coefficient $u^2$ depends on the coordinates and even assumes negative values! Such equations need not be more difficult to solve than the conventional wave-equation in which $u^2$ stands for a positive constant; but the image of the elastic medium becomes unsatisfying. In the one-dimensional case, so long as $u^2$ remains a positive function of $x$, one can visualize a string of which the density varies along its length; but when $u^2$ passes through zero and becomes negative, the wave-speed attains zero and is superseded by an imaginary quantity. One may speak, in such a case, of a "string" or a "fluid" characterized by an "imaginary wave-speed." So speaking, one comes perilously close to the verge of using words devoid of physical meaning; but otherwise, there is no verbal language with which to relieve the monotony of the procession of equations.

The differential equation of the type of (151), with a constant negative value of the coefficient $u^2$, is not a difficult one. Confining ourselves to one dimension, we find for one of the solutions of the equation for a "string with constant imaginary wave-speed" this expression:

$$\Psi = (A \cos mUt + B \sin mUt)(Ce^{mx} + De^{-mx}), \qquad (152)$$

in which $U$ stands for the (real) square root of $-u^2$. This is a much less tractable function than the product of sine-functions which serves when $u^2$ is positive. One cannot, for instance, find *Eigenwerte* for the constant $m$ whereby the function can be made to vanish at all times at two distinct points upon the "string"; or rather, one can find only the value $m = 0$, which fulfils this familiar boundary-condition by destroying the function. Similarly, one cannot force $\Psi$ to remain finite everywhere except by annulling either $m$ or else both $A$ and $B$, again destroying the function. Vibrations which are sine-functions of time are, however, permitted by the differential equation.

Consider now the equation

$$d^2y/dx^2 = (a - bx^2)d^2y/dt^2, \qquad (153)$$

which may be regarded as the wave-equation of a string of which the wave-speed varies with $x$ along its length as the function $(a - bx^2)^{-1/2}$, being therefore real over the central part from $x = -\sqrt{a/b}$ to $x = +\sqrt{a/b}$, and imaginary from each extremity of this central range outward to infinity. In the usual way, we derive the equations:

$$y = f(x)g(t), \qquad g = A \cos \nu t + B \sin \nu t,$$
$$d^2f/dx^2 + \nu^2(a - bx^2)f = d^2f/dx^2 + (C - x^2)f = 0, \qquad (154)$$

and it is incumbent upon us to solve the equation[11] for $f(x)$.

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[11] The constant $\nu^2 b$ has been equated to unity, which entails no loss of generality.

Essay a solution in the form of a power-series, multiplied by $e^{-(1/2)x^2}$:

$$f(x) = e^{-(1/2)x^2} \sum_{n=0}^{\infty} a_n x^n. \tag{155}$$

Substitute this into the differential equation, and group all the terms involving the same power of $x$. For each such group, we have

$$a_{n+2}(n + 1)(n + 2)x^n - a_n(2n + 1 - C)x^n, \tag{156}$$

and equating each group separately to zero, we arrive at the relation

$$a_{n+2}/a_n = (2n + 1 - C)/(n + 1)(n + 2). \tag{157}$$

Put $a_0 = 0$, thus causing all the even-numbered coefficients to vanish; assign any arbitrary value to $a_1$, and calculate the odd-numbered coefficients $a_3$, $a_5$, $a_7$, and so onward. Or, put $a_1$ and all the odd-numbered coefficients equal to zero, assign any arbitrary value to $a_0$, and calculate the even-numbered coefficients $a_2$, $a_4$, $a_6$, and so onward. Either way we shall get a solution of (154), whatever the value of the parameter $C$; but there are certain specific values of $C$ which admit a peculiar sort of solution. It is, in fact, evident from (156) that we shall arrive at two entirely distinct results, according as $C$ is or is not equal to some value of $(2n + 1)$—according, that is to say, as $C$ is or is not an odd integer. For, if $C$ is equal to an odd integer $(2n + 1)$, the chain of coefficients will come to an abrupt end at the member having that particular value of $n$; it and all the succeeding members will be zero; the power-series in the tentative (and adequate) expression (155) for the unknown function $f(x)$ will consist of a finite number of terms. But, if $C$ is not equal to an odd integer, the power-series will go on forever.

Here we have a new kind of *Eigenwert*. If the parameter $C$, in the differential equation for the curious kind of "string" which I have just defined, has for its value one of the numbers:

$$C = 2n + 1, \qquad n = 0, 1, 2, 3, 4, \cdots, \tag{158}$$

the equation enjoys a special sort of solution. If the parameter does not have one of these *Eigenwerte*, the solution of the differential equation is altogether different.

Let us see what difference these *Eigenwerte* make in the general solution (155) of the differential equation. If the parameter $C$ has some other value than one of these, the series $a_n x^n$ goes on forever; and as $x$ approaches infinity, the value of its summation increases at such a rate as to overwhelm the steadily declining factor $e^{-(1/2)x^2}$, so that the function $f(x)$ is infinite at both ends of the range $-\infty < x < \infty$.

If however $C$ is equal to one of the *Eigenwerte*, the series $a_n x^n$ comes to an abrupt end; and as $x$ approaches infinity, the decline of the factor $e^{-(1/2)x^2}$ overpowers the increase of the summation, and $f(x)$ remains finite at infinity. The values 1, 3, 5, $\cdots$ of the constant $C$ are therefore the *Eigenwerte* which permit solutions *which remain finite all through the range of values of the independent variable from positive to negative infinity.* This condition replaces the boundary-conditions applied to the ordinary stretched string.

The *Eigenfunktionen* are:

$$f_m(x) = e^{-(1/2)x^2} H_m(x), \tag{159}$$

the symbol $H_m(x)$ standing for the finite series $\sum a_n x^n$ constructed according to the rules of the foregoing paragraphs, and terminating at the $m$th term. These are known as the *polynomials of Hermite.*[12]

### *Interpretation of the Simple-Harmonic Linear Oscillator by Wave-Mechanics*

The foregoing section contains all that is necessary to Schroedinger's theory[13] of the linear simple-harmonic oscillator—an object, or a concept, famous in the history of the quantum-theory; for it was the linear oscillator which Planck first "quantized"—of which, that is to say, Planck first proposed that it be endowed with the power of receiving and retaining and disbursing energy only in fixed finite amounts; thereby arriving at an explanation of the black-body radiation-law, and founding the quantum theory.

Conceive a particle of mass $m$, constrained to move along the $x$-axis, attracted to the origin by a force $-k^2x$ proportional to its displacement, and consequently prone to oscillate to and fro across the origin with frequency $\nu_0 = k/2\pi\sqrt{m}$. Its potential energy is the following function of $x$:

$$V = \tfrac{1}{2}k^2x^2 = 2\pi^2 m\nu_0^2 x^2. \tag{160}$$

The wave-equation assumes the form

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - 2\pi^2 m\nu_0^2 x^2)\Psi = 0. \tag{161}$$

A simple change of variable $(q = x \cdot 2\pi\sqrt{m\nu_0/h})$ transforms this into the equation (154):

$$d^2\Psi/dq^2 + (C - q^2)\Psi = 0; \qquad C = 2E/h\nu_0. \tag{162}$$

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[12] The first five are written down by Schroedinger, *Ann. d. Phys.*, **79**, p. 515 (1927). An arbitrary numerical multiplier remains at disposal.

[13] Schroedinger, *Ann. d. Phys.*, **79**, pp. 514–519 (1926); for the general case in which the restoring-force is not supposed to vary as the displacement, consult H. A. Kramers, *ZS. f. Phys.*, **39**, pp. 828–840 (1926).

According to Schroedinger *the Stationary States of the linear oscillator are distinguished by the energy-values which cause this equation to have a solution finite at all values of the variable, infinity included.*

These are the values of the constant $C$ which cause the parameter $C$ to take one of the *Eigenwerte* set down in (158).

The energy-values of the Stationary States should therefore be

$$\begin{aligned} E_n &= \frac{h\nu_0}{2}(2n+1) \\ &= \frac{1}{2}h\nu_0,\ \frac{3}{2}h\nu_0,\ \frac{5}{2}h\nu_0,\ \cdots. \end{aligned} \tag{163}$$

The successive permitted energy-values of the linear simple-harmonic oscillator of frequency $\nu_0$, the energy-values of its consecutive Stationary States, are therefore specified by wave-mechanics as the products of the fundamental factor $h\nu_0$ by the consecutive "half-integers" 1/2, 3/2, 5/2, and so onward.

The linear simple-harmonic oscillator thus furnishes an instance of "half-quantum-numbers." In most of the earlier theories it was either assumed or inferred that this "Planck" oscillator displayed "whole quantum-numbers"—that its permitted energy-values were the products of $h\nu_0$ by the successive integers 1, 2, 3, 4, $\cdots$. However, in the interpretation of certain features of band-spectra by the assumption that the two atoms of a diatomic molecule vibrate as linear oscillators along their line of centres, the half-quantum-numbers sometimes led to better agreement with experience than did the whole-quantum-numbers.

The *Eigenfunktionen* corresponding to the consecutive Stationary States are these:

$$\Psi_n(x) = \text{const}\cdot e^{-2\pi^2 m\nu_0 x^2/h} H_n(2\pi x\sqrt{m\nu_0/h}). \tag{164}$$

The first five of these *Eigenfunktionen* are exhibited in Fig. 2. These curves may be regarded, if the reader so chooses, as the stationary-wave patterns of "loops" and "nodes," exhibited by five resonating strings along which the wave-speed varies according to the five laws obtained by assigning the first five values given by (163) to the constant $E$ in the equation:

$$u = \frac{E}{\sqrt{2m(E - 2\pi^2 m\nu_0^2 x^2)}}\cdot \tag{165}$$

The various Stationary States of a linear oscillator are therefore imaged not as the fundamental and the overtones of one and the same string, but as the fundamental (and exclusive) nodes of vibration of distinct strings. It is important to realize this. Schroedinger's way of thinking provides not a single atom-model for each sort of atom, but as many distinct models as there are Stationary States.*

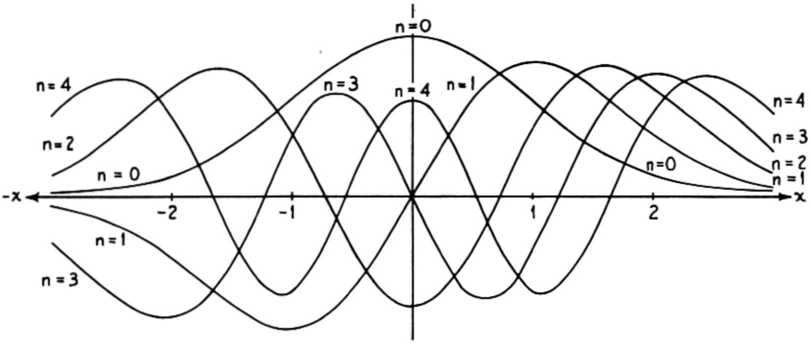

Fig. 2 (after Schroedinger).

## *Interpretation of the Hydrogen Atom by Wave-Mechanics*

The hydrogen atom is conceived as a system endowed with the potential energy $V = -e^2/r$. This form for the potential energy, I recall, is obtained by imagining an electron and a nucleus, or more precisely two point-charges $+e$ and $-e$, separated by a distance denoted by $r$. The image of the electron and the nucleus does not come over explicitly into the new theory; but in spirit it does come over, for the potential-energy-function derived from that image is the basis for the new theory.

Polar coordinates for the wave-equation are imperiously suggested by a potential-energy-function of this form, and consequently it is thus expressed:

$$\frac{E^2}{2m(E+e^2/r)}\nabla^2\Psi = \frac{d^2\Psi}{dt^2}, \qquad (171)$$

and putting $E/h$ for the vibration-frequency, we attain

$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)\Psi = 0. \qquad (172)$$

The resemblance of these equations to those laid down for the ball of fluid is as unmistakable as the resemblance of the wave-equation for a linear oscillator to that of a stretched string. Here we have the case of a fluid in which the wave-speed varies from point to point, according to the law

$$u^2 = E^2/2m(E+e^2/r), \qquad (173)$$

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* Some may find satisfaction in conceiving, as my colleague Dr. T. C. Fry suggests, a "string" so constructed that the speed of propagation of waves along it is a function of their frequency.

and we meet the problem of finding modes of vibration and stationary wave-patterns.

If $E$ is supposed positive, the wave-speed is everywhere real. Boundary-conditions of the usual sorts (*e.g.*, the prescription that the fluid shall be confined within a rigid spherical wall of given radius) might be imposed, and then *Eigenwerte* of the constant $E$ could be calculated, and from these the wave-patterns and natural frequencies of the fluid. If no such boundary-conditions were prescribed, the equation (172) could be solved with any value of $E$.

If $E$ is supposed negative, the whole state of affairs is changed. The wave-speed is now real within the sphere of radius $-e^2/E$, zero over this sphere and imaginary beyond it. This recalls the case of the "string" proposed as an analogy for the linear oscillator, for which the wave-speed was real along its central segment and imaginary from each end of its central segment onwards to infinity. There are important differences: in the present case, the variable $r$ assumes positive values only, and the wave-speed at $r = 0$ is infinite though real.

In the case of the "string" with variable and at some points imaginary wave-speed, we found that the law of variation of wave-speed could be so chosen that the "string" enjoys a natural mode of vibration with a stationary wave-pattern and a natural resonance-frequency. This was done by selecting any of a series of *Eigenwerte* for a parameter of the differential equation. Here we shall do likewise.

Essaying for the function $\Psi$ in (172) a solution in the form of a product of a function of $\theta$ and $\varphi$ exclusively by a function of $r$ exclusively, we arrive in the familiar way at differential equations:

$$\operatorname{cosec}\theta\left\{\frac{d}{d\theta}\left(\sin\theta\frac{dY}{d\theta}\right)+\frac{d}{d\varphi}\left(\operatorname{cosec}\theta\frac{dY}{d\varphi}\right)\right\} = -\lambda Y. \qquad (175)$$

$$\frac{d}{dr}\left(r^2\frac{df}{dr}\right)+\frac{8\pi^2 mr^2}{h^2}\left(E+\frac{e^2}{r}\right)f = +\lambda f, \qquad (174)$$

The equation (175) is the identical one which we encountered in the case of the ball of fluid. Here, as there, the fact that the variables $\theta$ and $\varphi$ are cyclic requires *Eigenwerte* of the constant $\lambda$:

$$\lambda = l(l+1), \qquad l = 0, 1, 2, 3, 4, \cdots \qquad (176)$$

Equation (174), however, is not the same as the corresponding equation (133) of the prior case; here we find the difference between the fluids of actual experience and the "imaginary fluid" which is to serve as material for the atom-model supplied by wave-mechanics for hydrogen.

If in that equation (174) one were to assign an arbitrarily chosen negative value to the parameter $E$, one would in general not be able to find a solution which is finite both at the origin and at infinity. This is the same situation as occurred in the theory of the linear oscillator, where an arbitrary choice of a value for the parameter there called $C$ would in general have led to a solution implying infinite amplitude at both ends of the "string."

Schroedinger however discovered [14] that there is a series of *Eigenwerte* for the parameter $E$, each of which (subject to a limitation to be introduced below) entails a solution which is single-valued, continuous and finite over the entire range of the variable $r$.

These *Eigenwerte* are the following:

$$E_n = -2\pi^2 me^2/h^2n^2; \qquad n = 1, 2, 3, 4, \cdots. \tag{177}$$

*The consecutive permitted energy-values of the system of potential-energy-function* $-e^2/r$, *the Stationary States of the model for the hydrogen atom, are therefore specified by wave-mechanics as the quotients of the fundamental factor* $-2\pi^2 me^4/h^2$ *by the squares of the consecutive integers from unity onward.*

These agree with experiment. The formula (177) is in fact the renowned formula of Bohr, from which the whole contemporary theory of spectra sprang; a formula so successful that it is scarcely conceivable that any alternative theory should ever win acceptance unless by presenting the identical equation over again.

Schroedinger's models for the hydrogen atom in its various Stationary States thus are imaginary fluids each pervading the whole of space, and in each of which the wave-speed depends on the distance $r$ from a centre, according to a peculiar law—the law obtained by inserting into the formula (173) the appropriate value for $E$, chosen from the sequence given in (177). If into (173) we were to put any value chosen at random for the energy-constant $E$, we should be inventing an imaginary fluid; but, in general, this fluid would not be capable of sustaining a continuous stationary wave-pattern of finite amplitude. Only when one of Bohr's sequence of energy-values is chosen do we get a fluid able to resonate as a ball of actual physical substance can.

The next task is to enquire into the wave-patterns in the imaginary fluids corresponding to these various permitted energy-values. This is much more difficult than the same problem for the imaginary strings corresponding to the various permitted energy-values of the linear oscillator, and the new complexities are not altogether due to the fact that we now have three dimensions to deal with instead of one; they

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[14] Schroedinger, *Ann. d. Phys.*, **79**, pp. 361–376 (1926). For an alternative method of proof see A. S. Eddington, *Nature*, **120**, p. 117 (1927).

are due chiefly to the fact that the system is mathematically "degenerate." Owing to this circumstance there are more than one possible mode of vibration, more than one stationary wave-pattern, for each (except the first) of the permitted energy-values. To describe these it is necessary to consider both of the equations (174) and (175).

Since the equation (175) is identical with the corresponding equation derived for balls of actual physical fluids, the modes of vibration for Schroedinger's atom-model are identical with the modes of vibration of actual fluid spheres *insofar as the dependence on angle is concerned.* The imaginary fluid is divided into compartments by nodal planes, nodal double-cones and nodal spheres; and the division by planes and double-cones is identically such as we should find in the corresponding mode of vibration of an actual fluid ball; it is only the division by nodal spheres which differs.

To the first *Eigenwert*, $E_1$ ($n = 1$) there corresponds a single *Eigenfunktion* of equation (174); to the second, $E_2$, a pair; to the third, three; and so forth. This multiplicity is linked with the limitation upon the *Eigenwerte* which was foreshadowed above. In the expression for the function $\Psi$ as a product of functions of the individual variables

$$\Psi(r, \theta, \varphi) = F(r) Y_l(\theta, \varphi), \tag{178}$$

if we assign an *Eigenwert* $E_n$ to the parameter $E$ in the first factor according to (174), we have still a choice of values to assign to the parameter $l$ in the second factor according to (176). This choice however is limited. We must not take any value of $l$ as great as or greater than the value adopted for $n$; otherwise the value of $E_n$ would not be an *Eigenwert* in the sense adopted. Thus for $n = 1$ we are restricted to the choice $l = 0$; for $n = 2$ we have the alternative of $l = 0$ or $l = 1$; for $n = 3$ the option of $n = 0, 1,$ or $2$, and so forth. Each *Eigenwert* $E_n$ thus admits $(n - 1)$ distinct spherical harmonics $Y_1(\theta, \varphi), Y_2(\theta, \varphi) \cdots Y_{n-1}(\theta, \varphi)$ as solutions of equation (175); and to each of these there corresponds, with each of these there goes, a distinct *Eigenfunktion* $F_{n,\,l}(r)$ of the equation (174), which is expressed as follows in terms of a variable $\rho = \dfrac{2\pi\sqrt{-2mE_n}}{h}\,r = \dfrac{4\pi^2 me^2}{nh^2}\,r \equiv \dfrac{1}{na_0}\,r$ instead of $r$ to make the function seem less intricate:[15]

$$X_{n,\,l}(\rho) = \text{const. } \rho^{+l} e^{-\rho} \sum_{k=0}^{n-l-1} \frac{(-2\rho)^k}{k!} \binom{n+l}{n-l-1-k}, \tag{180}$$

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[15] The factor in parentheses in equation (180) stands for the "number of combinations of $(n + l)$ quantities taken $(n - l - 1 - k)$ at a time," which is the $(n - l - 1 - k)$th coefficient in the binomial expansion of $(a + b)^{l+n}$.

The function $X_{n,\,l}(\rho)$ has $(n - l - 1)$ roots, so that the corresponding mode of vibration has $(n - l - 1)$ nodal spheres. To each permitted energy-value $E_n$ there consequently correspond $n$ different solutions of the general equation (172), differing from one another in respect of the number of nodal spheres:

$$\Psi_{n,\,l}(r,\,\theta,\,\phi) = X_{n,\,l}(\rho)\,Y_1(\theta,\,\phi); \qquad l = 0,\,1,\,2\,\cdots\,(n-1). \quad (181)$$

Each of these describes a permitted class of modes of vibration, owing to the subdivision of the spherical harmonic $Y_1$ into terms according to (135).

Allowing for the subdivision of the spherical harmonics, there are $(1 + 2 + 3 + \cdots n) = n(n + 1)/2$ modes of vibration for the $n$th permitted energy-value $E_n$.

The equation (181) exhibits the various modes of vibration of which our imaginary "fluid," the model for the hydrogen atom, is capable. It would be possible to describe these with a wealth of verbal detail. I hesitate to do so; for vast amounts of industry and ink have been expended during the last twelve years in tracing and describing electron-orbits, which are now quite out of fashion; and who dares affirm that in another five years the vibrating imaginary fluid will not be *dêmodé*? Yet it is altogether probable that for some years to come, if not for all time, the image of the vibrating fluid will furnish the customary symbolism for expressing the data of experiment. Therefore let me point out some features of the vibrations corresponding to the first (or "lowest," or "deepest") three states of the hydrogen atom:

*Normal State*, $n = 1$. One *Eigenfunktion*, $X_{1,\,0}(\rho)$; an exponential function of $r$, decreasing steadily from the origin to infinity, with no nodal spheres. Corresponding spherical harmonic $Y_0(\theta,\,\varphi)$,—a constant. The vibration consequently is described by

$$\Psi(r) = \text{const. } e^{-r/a_0} \quad (a_0 = h^2/4\pi^2 me^2) \qquad (182)$$

and is endowed with perfect spherical symmetry.

*First Excited State*, $n = 2$ (the state into which the atom relapses after emitting any line of the Balmer series). Two *Eigenfunktionen* $X_{2,\,0}$ and $X_{2,\,1}$; the first represents a vibration with a single nodal sphere, the second a vibration diminishing steadily in amplitude from the origin outward. The first is to be multiplied by $Y_0(\theta,\,\varphi)$ to obtain the complete description of the vibration; $Y_0$ being a constant, this mode is endowed with perfect spherical symmetry. The second is to be multiplied by $Y_1$, which is a combination of terms written out in equation (135); the permissible mode, or rather modes, of vibration involve nodal planes and double-cones, which the reader may work out for himself with the aid of (135).

*Second Excited State*, $n = 3$ (the state from which the atom departs when it emits the line *H*-alpha). Three *Eigenfunktionen* $X_{3,0}$, $X_{3,1}$ and $X_{3,2}$. The first corresponds to a vibration with two nodal spheres, and perfect spherical symmetry. The second and third correspond to vibrations with one nodal sphere, and with a steady diminution of amplitude from the centre outward, respectively; but being multiplied with the spherical harmonics $Y_1$ and $Y_2$, they describe modes which are not endowed with spherical symmetry, and involve nodal double-cones and nodal planes.

*Generally:* the state distinguished by the numeral $n$ enjoys $n$ distinct *Eigenfunktionen*, describing vibrations having respectively $0, 1, 2, 3 \cdots (n-1)$ nodal spheres; to the *Eigenfunktion* with the maximum number of nodal spheres corresponds a single mode of vibration which is spherically symmetric, to the others various modes with varying members of nodal double-cones and planes.

If this is destined to be the "language of the future" for describing the data of experiment, it will be necessary to have dictionaries for translating it out of (or into) the "language of the present," the vocabulary of the Bohr-Sommerfeld atom-model in which Stationary States are represented by electron-orbits. They will contain definitions such as these: the numeral $n$ is the total-quantum-number of the electron-orbits—the numeral $l$ is one unit smaller than the azimuthal quantum-number $k$ of the electron-orbit—the numeral $(n - l - 1)$, to which the number of nodal spheres is equal, is the radial quantum-number of the electron-orbit. To elucidate these "definitions" of the future dictionary, I recall that the Bohr-Sommerfeld atom-model provided, for the hydrogen atom in its state of energy-values $E_n$, a family of $n$ distinct electron-orbits, of which one is circular while the other $(n - 1)$ are ellipses of varying degrees of eccentricity.[16] These ellipses were selected by laying down the conditions, that the integral $\int p_{\varphi} d\varphi$ of the angular momentum $p_{\varphi}$ around the orbit shall be equal to the product of $h$ by some integer $k$ equal to or less than the prescribed $n$; and the integral $\int p_r dr$ of the radial momentum $\int p_r dr$ shall be equal to the product of $h$ by the integer $(n - k)$; so that the sum of the integrals $\int p_{\varphi} d\varphi$ and $\int p_r dr$ shall be equal to the product of $h$ by $n$. The quantities $n$, $k$ and $n - k$ were given the names *total, azimuthal, radial quantum-number.* "Defini-

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[16] The introduction some twenty months ago of the "spinning electron" caused a modification of this picture; for those who accept the modification, it is the "language of antiquity" which is compared in this paragraph with the "language of the future."

tions" such as those above (which are not necessarily the only self-consistent nor the best ones) make it possible to translate orbits of the orbit-model into modes of vibration of the wave-model, and vice versa; and to devise definitions for these three kinds of quantum-numbers from the qualities of the vibrations themselves.

### *Perturbations*

Inasmuch as the wave-mechanics indicates $n$ different *Eigenfunktionen* with $n$ different collections of nodal spheres (not to speak of the still more greatly varied possibilities of nodal planes and double-cones) for the Stationary State having the *Eigenwert* and energy-value $E_n$, one may well ask whether there is any chance of distinguishing which of these, or which linear combination of these (for the differential equation will permit any) is actually adopted by a hydrogen atom.

Translating into the language of the Bohr-Sommerfeld atom-model, we find the question in this form: is there any way of distinguishing which of the $n$ permitted elliptical electron-orbits is actually adopted?

When the question was asked in this form, it was answered by pointing out that if the force exerted upon the electron were not the pure inverse-square force ascribed to the nucleus, but the sum of this and a *perturbing force*, the energy-values of the $n$ permitted ellipses would cease to coincide exactly. If for instance the atom under examination were composed of a nucleus of charge $11e$, a group of ten electrons very close to it and an "outer" electron relatively far out (the conventional model for a sodium atom in certain states); then the group of ten inner electrons would act upon the outer one with a perturbing force, and the $n$ permitted ellipses of the outer one would be endowed with distinct energy-values—the single Stationary State of the outer electron would be dissolved into $n$ distinguishable states. Even in the hydrogen atom, the dependence of the mass of the electron upon its speed should separate the energy-values of the various ellipses which but for this fact would share a common energy $E_n$, and produce the fine-structure of the hydrogen lines.

The very same thing occurs in wave-mechanics; and from the effect of a perturbing force, allowance for which is made in the potential-energy-function introduced into the wave-equation, we may expect to be able to distinguish the different modes of vibration attributed to a single *Eigenwert* and a single Stationary State of the unperturbed hydrogen atom.[17]

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[17] In the language of the mathematicians, the perturbing forces remove the degeneracy of the problem; some kinds of perturbation remove it completely, others in part.

The results are, in fact, just like those obtained with the Bohr-Sommerfeld atom-model; and this is somewhat embarrassing. For, in order to perfect the Bohr-Sommerfeld model and establish a complete analogy between (for instance) the sodium spectrum on the one hand and the fine-structure of the hydrogen lines on the other hand, it was necessary to introduce a new feature—the "spinning electron." Something of the sort must evidently be done again—the "spinning electron" must be imported into the undulatory mechanics; but the exact way to do it seems as yet to elude the virtuosi of mathematical physics.[18]

In one case—when the perturbing force is an impressed electric field—the results obtained by the method of Bohr and Sommerfeld and those obtained by the method of Schroedinger agree to first approximation with each other and with the data of experience, without the introduction of a "spinning electron." As this case of the "Stark Effect" furnishes a convenient transition to the last section of the article, I will quote the results.[19]

### *The Stark Effect*

Imagine a hydrogen atom, upon which an electric field $F$ parallel to some arbitrary direction which we call the $z$-direction is acting. Owing to this field, the electron at the point $x$, $y$, $z$ and the nucleus at the origin (we are still using the concept of the nucleus and the electron!) possess a potential energy composed of the "intrinsic" term $-e^2/r$ and the "perturbation" $+eFz$. The wave-equation takes the form:

$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r} - eFz\right) = 0. \tag{183}$$

Paraboloidal coordinates are indicated for this problem. Instead of the planes, double-cones and spheres of the polar coordinate-system which we earlier used, it is desirable to employ planes and two families of paraboloids of rotation; the planes intersect one another along the line through the nucleus parallel to the field (hitherto called the $z$-axis), and the two families of paraboloids have their common foci at the nucleus and their noses pointing opposite ways along that axis. The transformation is made by the equations:

$$x = \sqrt{\xi\eta}\cos\varphi, \qquad y = \sqrt{\xi\eta}\sin\varphi, \qquad z = \tfrac{1}{2}(\xi - \eta) \tag{184}$$

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[18] Unless the problem has been solved by C. F. Richter (cf. preliminary note in *Proc. Nat. Acad. Sci.*, **13**, pp. 476–479; 1927).

[19] Schroedinger, *Ann. d. Phys.*, **80**, pp. 457–464 (1926); P. S. Epstein, *Phys. Rev.* (2), **28**, pp. 695–710 (1926).

and the wave-equation appears in this guise:

$$\frac{d}{d\xi}\left(\xi\frac{d\Psi}{d\xi}\right)+\frac{d}{d\eta}\left(\eta\frac{d\Psi}{d\eta}\right)+\frac{1}{4}\left(\frac{1}{\xi}+\frac{1}{\eta}\right)\frac{d^2\Psi}{d\varphi^2} + \frac{2\pi^2m}{h^2}[E(\xi+\eta)+2e^2-\tfrac{1}{2}eF(\xi^2-\eta^2)]\Psi = 0. \tag{185}$$

Essaying as tentative solution a product of a function of $\varphi$ by a function of $\xi$ and a function of $\eta$, we obtain as usual three differential equations, involving $E$ and two other parameters, to which specific *Eigenwerte* must be assigned either because the variable $\varphi$ is cyclic, or because for values other than these *Eigenwerte* the solutions become infinite for certain values of the variable.

Suppose that we set $F = 0$, and ascertain these *Eigenwerte*, and insert them into the equations: we then find the imaginary fluid vibrating in a stationary wave-pattern, oscillating in compartments divided from one another by nodal planes and by nodal paraboloids pointing up or down the field. To each of the energy-values $E_n$ there correspond $(1 + 2 + 3 + \cdots n)$ distinct wave-patterns, each having a distinctive number $k_1$ of nodal paraboloids of the one family, a distinctive number $k_2$ of nodal paraboloids of the other family, and a distinctive number $s$ of nodal planes; the values of $k_1$ and $k_2$ and $s$ are limited by the conditions that they must be integers, that they cannot be less than zero nor greater than $n$, and that their sum must be equal to $(n - 1)$: that is,

$$k_1 + k_2 + s + 1 = n. \tag{186}$$

(Translating into the language of the electron-orbits, we find that $s$ becomes the equatorial quantum-number which represents the angular momentum of the electron around the direction of the field (in terms of the unit $h/2\pi$) and $k_1$ and $k_2$ become the parabolic quantum-numbers.)

Introducing now the impressed electric field $F$, we find that among the $(1 + 2 + 3 + \cdots n)$ modes of vibration which originally shared the energy-value $E_n$, those for which $k_1 = k_2$ retain this energy-value, while the rest are displaced by varying amounts given by the celebrated Epstein formula:

$$\Delta E = \frac{3Fh^2n}{8\pi^2me}(k_1 - k_2). \tag{187}$$

The Stationary State of energy-value $E_n$ is thus "resolved" or "split" into several—not, however, into the full number $(1 + 2 + 3 + \cdots n)$ corresponding to the total number of modes of vibration, for some of these still share identical energy-values. The line resulting from the transition between two States, $E_3$ and $E_2$ for instance, is thus resolved into a set of lines lying close together. These individual "Stark-effect components" testify to the individual existence of the several distinct modes of vibration which, when there is no impressed electric field, should share a common energy-value $E_n$ and be indistinguishable from one another.[20]

In the closing section we shall consider another aspect of these Stark-effect components. At this point I wish only to allude to a quaint little paradox which may already have disconcerted the reader. I have just said that the imaginary "fluid" executes stationary vibrations in which it is divided into compartments by nodal planes and nodal paraboloids, even when the impressed field $F$ is made equal to zero; but earlier I said that the "fluid" representing the unperturbed hydrogen atom executes vibrations in which it is divided into compartments by nodal planes, nodal double-cones and nodal spheres. There is no actual contradiction between these two assertions; for a mode of vibration of the one kind can be obtained by superposing two or more modes of vibration of the other kind, with a proper distribution of relative amplitudes. Take the specific case of the "first excited state" of the hydrogen atom, $n = 2$. By the earlier process, we find three wave-patterns: ($a$) with one nodal sphere, ($b$) with one nodal double-cone, ($c$) with one nodal plane. By the later process, we find three wave-patterns: ($\alpha$) with one nodal paraboloid facing one way; ($\beta$) with one nodal paraboloid facing the other way; ($\gamma$) with one nodal plane. The wave-patterns ($c$) and ($\gamma$) are evidently the same, while either ($\alpha$) or ($\beta$) can be reproduced by superposing ($a$), ($b$) and ($c$) with the proper relative amplitudes.[21] If the field $F$ acting upon a hydrogen atom in the first excited state were to be gradually reduced to zero, it would leave the atom, or to speak more carefully the "imaginary fluid," vibrating in a manner which would be one of the modes ($\alpha$), ($\beta$) or ($\gamma$), hence a cleverly adjusted superposition of the three modes ($a$), ($b$) and ($c$). Suppose however that a very small field $F$ were to be applied to a hitherto unperturbed atom; why should it necessarily find ready for it a vibration with precisely the proper relative adjustment of the modes ($a$), ($b$) and ($c$)? or if it did not, if it should find the atom vibrating say in mode ($\alpha$), how would it persuade the "fluid" to change over into the manner of vibration suitable for its own operations to begin?[22]

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[20] A couple of "contour maps" of the wave-patterns for two of these paraboloidal modes of vibration are given by F. G. Slack (*Ann. d. Phys.*, **82**, pp. 576–584; 1927).

[21] I have not actually proved this, but believe that it must follow from Schroedinger's general theorem.

[22] This same curious thing occurs in a somewhat different guise when the electron-orbit theory is adopted.

### *Interpretation of the Rotator by Wave-Mechanics*

The rotator or rotating body, the "spinning-top" as the Germans often call it, is a very important object in the workshop of the builder of atom-models. It is the accepted molecule-model used in theorizing about the polarization of gases by electric and magnetic fields, and the basis of the accepted molecule-model used in explaining the band-spectra of diatomic and polyatomic gases. Most models devised for the latter purpose combine the features of the rotator and the linear oscillator; but for the present purpose it is sufficient to view these separately, conceiving the rotator as a perfectly rigid whirling body.

The treatment of the rotator by wave-mechanics is in one respect admirably simple, but eventually we are led into the mazes of the General Equation with its non-Euclidean geometry. One can however avoid the complexity long enough to benefit by the intelligible feature, by considering first a rotator such as was invented more than fifty years ago to account for the specific heats of diatomic gases such as hydrogen—a dumbbell not permitted to spin around its own axis-of-figure or line-of-centres, but revolving around some axis passing through its center-of-mass perpendicular to its line-of-centres. The orientation of such a dumbbell is specified by the angles $\theta$ and $\phi$ which define, in a polar coordinate-system, the direction in which its axis-of-figure is pointing. The energy is exclusively kinetic, so that the term containing $V$ vanishes from the wave-equation, a circumstance which is very helpful. Representing by $A$ the moment of inertia of the dumbbell about the axis of revolution, we find the wave-equation in the form:[23]

$$\nabla^2\psi + \frac{8\pi^2 EA}{h^2}\,\psi = 0. \qquad (190)$$

In this equation the Laplacian operator is to be expressed in the polar coordinates $\theta$ and $\phi$, as it was expressed in equation (131), but without the terms involving the third and missing coordinate $r$. We have before us, therefore, the second of equations (133), with a specific value for the constant there called $\lambda$:

$$-\operatorname{cosec}\theta\left[\frac{d}{d\phi}\left(\operatorname{cosec}\theta\,\frac{d\psi}{d\phi}\right)+\frac{d}{d\theta}\left(\sin\theta\,\frac{d\psi}{d\theta}\right)\right]=\frac{8\pi^2 EA}{h^2}\,\psi. \qquad (191)$$

Here, as there, the function $\psi$ must repeat itself whenever $\theta$ is altered by any multiple of $\pi$ and $\phi$ by any multiple of $2\pi$; for then we are back at the same place, i.e. at the same orientation of the rotator.

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[23] Schroedinger, *Ann. d. Phys.*, **79**, pp. 520–522 (1926).

Here, as there, this necessity imposes of itself a certain condition upon the coefficient of $\psi$ in the right-hand member, which is tantamount to this condition imposed on $E$:

$$E=n(n+1)\frac{h^2}{8\pi^2A}=(n+\tfrac{1}{2})^2\frac{h^2}{8\pi^2A}+\text{const.},\qquad n=0,1,2,3\cdots. \tag{192}$$

The energy of the rotator is thus *by the mere fact that the variables are cyclic* limited to a single sequence of permitted values, furnishing incidentally another example of half-quantum-numbers.

The *Eigenwerte*, the permitted energy-values, are thus for the rotator determined by an exceptionally lucid condition; yet the complications of the General Equation already appear on the horizon. Equation (190) differs from the wave-equation which I have hitherto used by virtue of the substitution of moment-of-inertia $A$ for mass $m$. This replacement seems sensible enough; one might rely on intuition in this particular case; but strictly it is caused by the form preassumed for the General Wave-Equation and by the specific form of the kinetic-energy-function for this specially restricted kind of rotator. If now we remove the restriction, and permit the rotator to spin about its axis-of-figure at the same time as it whirls about some axis normal to that—if we pose the general problem of the rigid rotator unrestricted save by the conditions which the wave-equation imposes, it is necessary to invoke the General Equation with the non-Euclidean geometry. The problem is soluble, and has been solved;[24] the utility of the results for the interpretation of band-spectra gives valuable support to the form selected by de Broglie and Schroedinger for the General Equation.

The polarization of a gas by an electric (or magnetic) field may be treated by supposing that each atom is an electric (or magnetic) doublet. The treatment is simplest if we may assume that the electric (or magnetic) axis of the doublet coincides with the axis-of-figure of a dumbbell-molecule, not allowed to spin around its axis-of-figure. Let $M$ stand for the moment of such a doublet, and suppose the field $H$ to be parallel to the direction from which the angle $\theta$ of the foregoing paragraphs is measured. The field supplies the potential-energy term to be added to the left-hand member of equation (190); this new term is:

$$-V\psi=(MH\cos\theta)\psi. \tag{193}$$

It is easy to see that the wave-equation has *Eigenwerte*, so that the atoms are in effect limited to certain "permitted" orientations in the

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[24] F. Reiche, *ZS. f. Phys.*, **39**, pp. 444–464 (1926); R. de L. Kronig, I. I. Rabi, *Phys. Rev.* (2), **29**, pp. 262–269 (1927).

field—a conclusion from the earlier atomic theory, which for magnetic fields has become a fact of experience through the experiments of Gerlach and Stern and others. To calculate the polarization of a gas, it is necessary to make a further assumption concerning the relative probabilities of these various orientations in a gas in thermal equilibrium; having done so, one obtains a formula for the polarization, or the dielectric constant, or the susceptibility of the gas as function of applied field and temperature. The customary assumption leads to a formula which, in the limiting case of high temperature and low field, agrees with the celebrated equation of Langevin for the polarization of a paramagnetic gas by a magnetic field:[25]

$$\text{Susceptibility} = I/H = NM^2/3kT. \tag{194}$$

### *Interpretation of the Free Electron in Wave-Mechanics*

We now depart from the calculation of *Eigenwerte* and Stationary States, and return to the original ideas of de Broglie.

For a free electron moving in a field-free region—or any particle moving in a region where no force acts upon it—with a constant speed $v$ along a direction which I will take as the $x$-direction, the (non-relativistic) wave-equation assumes the form:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 mE}{h^2}\psi = 0 \qquad (E = \tfrac{1}{2}mv^2). \tag{195}$$

This equation admits a sine-function as its solution whatever the value of the constant $E$ and consequently does not restrict the energy-values which the electron is allowed to take (a contrary result would have been hard to swallow!). Assigning the value $E/h$ to the frequency of the sine-wave and the value $E/\sqrt{2mE}$ to its speed, we obtain for the wave-length of the wave-train, "associated with" a free electron (or free particle) of mass $m$ and speed $v$, this value:

$$\lambda = \frac{E/\sqrt{2mE}}{E/h} = \frac{h}{\sqrt{2mE}} = \frac{h}{mv}\,. \tag{196}$$

For electrons of such speeds as ordinarily occur in discharge-tubes, these wave-lengths are of the magnitude of X-ray wave-lengths; for instance, a 150-volt electron is associated with a wave-length of very nearly one Angstrom unit.

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[25] C. Manneback, *Phys. ZS.*, **28**, pp. 72–84 (1927); J. H. Van Vleck, *Phys. Rev.* (2), **29**, pp. 727–744; **30**, pp. 31–54 (1927). For the classical derivation of formula (194) and meaning of the symbols cf. my article "Ferromagnetism," this Journal, **6** (1927), pp. 351–353.

This coincidence makes one wonder whether, if a stream of such electrons were projected against a crystal such as is used for diffracting X-rays, there would be a semblance of diffraction. Nothing yet said about the waves leads inevitably to such an inference. On the contrary, it might well be argued that we have no greater justification for expecting to observe them in the ordinary world of space and time than for expecting the $x$ and the $y$ of an algebraic equation to come to life before our eyes. It might forcibly be pointed out that while in this instance and the instance of the hydrogen atom the "waves" are defined in ordinary space, there are other instances—supplied for instance by rotators—in which the wave-equation is formally similar to (195) and the theory quite as effective, and yet the alleged "waves" exist only in the configuration-space and indeed in non-Euclidean configuration-space, which is much the same as saying that they do not exist at all. Nevertheless it appears that there is indeed a diffraction of electrons by crystals, and that the wave-length indicated by the diffraction-angles is in accordance with the value given by de Broglie! The first evidence for this amazing and portentous effect will be narrated by its discoverers Davisson and Germer in the following issue of this Journal.[26]

Notice that the speed of the associated wave-train is not the same as that of the flying particle; it is $\sqrt{E/2m}$, that of the particle is $\sqrt{2E/m}$. It is, however, the wave-length of the wave-train which is measured by the diffraction-experiments; not the speed, and not the frequency. This is important; for it is the wave-length which is exempt from the consequences of the essential uncertainty in the value of $E$. In classical mechanics, energy-differences alone are definite, but the absolute values of the "energy" of a system are not defined; the definition of energy involves an arbitrary additive constant. If now we were to add an arbitrary constant to the kinetic energy of the free electron, and call $E$ the sum of the two, we should alter the frequency and alter the speed assigned to the wave-train; but we should not alter the wave-length, for the wave-length is strictly equal to $h/\sqrt{2m(E - V)}$ with $V$ standing for the potential energy of the free electron, and the added constant would enter into $V$ and vanish by subtraction. Returning to the preceding sections of this

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[26] Consult meanwhile their note in *Nature*, **119**, pp. 558–560; 1927. The prediction was first published by W. Elsasser (*Naturwiss.*, **13**, p. 711; 1925). For additional intimations of evidence for undulatory qualities in matter cf. G. P. Thomson, A. Reid (*Nature*, **119**, p. 890; 1927); T. H. Johnson, *Nature*, **120**, p. 191 (1927); E. G. Dymond, *Phys. Rev.* (2), **29**, pp. 433–441 (1927). Schroedinger's elegant treatment of the Compton effect is based upon the conception of electrons as wave-trains (*Ann. d. Phys.*, **82**, pp. 257–264; 1927); for a more elaborate treatment of Compton effect cf. W. Gordon (*ZS. f. Phys.*, **40**, pp. 117–133).

article, we see that Schroedinger calculated the energy-values of the Stationary States by conditions imposed upon the wave-lengths of the waves, not upon their frequencies; the wave-patterns depend only upon the wave-lengths, and the frequency of the light which an atom emits in passing between two Stationary States depends only on the difference between their energy-values. In relativistic mechanics, energy is defined absolutely, and this difficulty never even threatens to arise; yet it is worth while to note that the ambiguity of the concept "energy" in classical mechanics does not interfere with, nor is it resolved by, anything which has been observed in Nature and interpreted by wave-mechanics.

In relativistic mechanics, the wave-equation for the free-flying particle assumes the form:

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{h^2c^2}(E - m_0{}^2c^4) = 0 \qquad \left(E = \frac{m_0c^2}{\sqrt{1 - v^2/c^2}}\right). \tag{197}$$

The wave-length has the value $h\sqrt{1 - v^2c^2}/m_0v = h/mv$; the frequency is $m_0c^2/h\sqrt{1 - v^2/c^2}$; the speed of propagation of the waves is $c^2/v$, superior to the speed of light.

I can no more than allude to the strangely suggestive fact, that in general as well as in this special case the speed of the particle and the speed of the associated waves are related to one another in the same way as group-speed and wave-speed in ordinary optics.

## ATTEMPT TO FIND A MEANING FOR THE SYMBOL $\Psi$

Thirty-three years ago the Earl of Salisbury, invited by reason of his eminence as a statesman to be the President of the British Association for the Advancement of Science, observed the physicists of his day involved in their fervent speculations over the nature of the æther; and of an address brilliant with felicitous phrases the best-remembered words are those by which he described the outcome of their travail: *The main, if not the only, function of the word* aether *has been to furnish a nominative case to the verb 'to undulate.'* Quite the same thing could now be said of the symbol $\Psi$, insofar as it serves to determine the energy-values of the Stationary States of the systems devised to represent atoms. When it is used for this purpose, it vanishes just as the final triumph is achieved. Like the variable under the sign of integration in a definite integral, it drops out of sight when the calculations which it proposes are actually performed. Indeed it might be discarded altogether during the process of calculating *Eigenwerte* and energy-values; one might speak exclusively of the "differential operator" $\nabla^2 - 8\pi^2m(E - V)/h^2$; many mathematicians do so.

Schroedinger however conceived the daring, the admittedly tentative and still incomplete but very alluring, idea of seeking in $\Psi$ some measure of the density of electric charge. Specifically, it occurred to him to define the square of the amplitude of the oscillations of $\Psi$, which the *Eigenfunktionen* prescribe as function of the coordinates—to define this squared amplitude as the density of the electric charge, spreading the electron as it were throughout space.

Let us examine this idea, and see whither it leads.

To avoid avoidable complexities as far as possible, I take the simplest of all cases: the linear oscillator, represented by the imaginary "string" stretched along the $x$-axis, possessed of a wave-speed varying as $\sqrt{1 - x^2/L^2}$, real from the origin both ways as far as the points $x = \pm L$ and imaginary thenceforward. I will also refer to the still simpler "actual" case which served as an introduction to this one: the problem of the stretched string, clamped at its extremities at $x = \pm L$, possessed of a uniform real wave-speed $u$ at all points between.

In both these cases of the imaginary and the real string, the search for the *Eigenwerte* and the *Eigenfunktionen* leads us to diverse natural modes of vibration, executed with various frequencies $\nu_0, \nu_1, \nu_2, \nu_3 \cdots$ and displaying stationary wave-patterns described by the *Eigenfunktionen:*

$$y_i = f_i(x)(A_i \cos 2\pi\nu_i t + B_i \sin 2\pi\nu_i t); \quad i = 0, 1, 2, 3 \cdots \qquad (201)$$

For the real string the functions $f_i(x)$ are sine-functions; for the imaginary strings which are the model of the linear oscillator, they are given by (155). I recall once more that in the latter case we have, not distinct modes of oscillation of one string, but the fundamental modes of as many strings as there are Stationary States.

When the real string is vibrating in the $i$th mode, or when we are dealing with the $i$th imaginary string, the function $f_i(x)$ is proportional to its vibration-amplitude. The form of equation (201) shows that this amplitude at any fixed point remains constant in time.

If the square of the vibration-amplitude is to be regarded as the density of electric charge along the string, it follows that when the oscillator is in one of its stationary states, and the string therefore vibrating in one of its modes, the density and the distribution of charge remain everywhere constant. There would be no to-and-fro motion of charges, and no tendency to radiation.

Suppose now that the real string is vibrating simultaneously in two modes, the $i$th and the $j$th; or that we have both the $i$th and the $j$th imaginary string coexisting (this is where the model is clumsiest!).

The vibrations are described by the following formula (I have put $A_i = A_j = 1$ and $B_i = B_j = 0$, which simplifies without injury to the generality of the result):

$$y = y_i + y_j = f_i(x) \cos 2\pi\nu_i t + f_j(x) \cos 2\pi\nu_j t, \qquad (202)$$

which is easily transformed thus:

$$y = C \cos (2\pi\nu_i t - \alpha), \qquad (203)$$

in which

$$C^2 = f_i^2 + f_j^2 + 2f_i f_j \cos 2\pi(\nu_i - \nu_j)t, \qquad (204)$$

and $\alpha$ = a constant not important for our purpose.

Here we have a vibration in which the amplitude at any fixed point varies with time; the square of the amplitude is the sum of a constant term and a sine-function of time, and the frequency of the sine-function is the difference between the frequencies of the two coexisting modes of vibration.

Identifying the square of the amplitude with the density of electric charge, we see that this charge-density varies at each point with the frequency $(\nu_i - \nu_j)$. We might therefore expect radiation of this frequency.

Now the vibration-frequencies $\nu_i$ and $\nu_j$ corresponding to the modes of vibration, that is to the Stationary States $i$ and $j$ having energy-values $E_i$ and $E_j$, are respectively $E_i/h$ and $E_j/h$.

If therefore—to speak in a vague but suggestive fashion—the linear oscillator were simultaneously in two Stationary States, their energy-values being $E_i$ and $E_j$, then the square of the amplitude of the oscillations of $\Psi$ would be fluctuating at each point of the "imaginary string" with the frequency $(E_i - E_j)/h$; and if this squared amplitude were to be identified with charge-density, then the system might be expected to emit radiation of the frequency $(E_i - E_j)/h$.

*Transition* between two states would then signify *coexistence* of the two states.[27]

We proceed a step further in the development of this idea, by forming the following integral:

$$M = \int_{-\infty}^{\infty} xC^2dx = \int_{-\infty}^{\infty} xf_i^2dx + \int_{-\infty}^{\infty} xf_j^2dx + \left\{ 2\int_{-\infty}^{\infty} xf_if_jdx \right\} \cos 2\pi(\nu_i - \nu_j)t. \qquad (205)$$

This integral represents the *electric moment* of the supposed distribu-

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[27] I should again recall that in the picture we have, not two distinct coexisting modes of vibration of the same elastic string; but the fundamental (and solitary) modes of vibration of two distinct elastic strings.

tion of "electric charge" along the imaginary string, relatively to its centre at the origin. If it should turn out zero, there would be equal amounts of charge to left and to right of the centre; if it should turn out positive or negative, there would be more charge to the right of the centre than to the left, or more to the left than to the right; if it should turn out variable, if for instance the coefficient of the cosine-term should differ from zero, there would be a *surging of the charge* to and fro across the origin.

The functions $f_i(x)$ have been written down in equation (155), near which it was shown that they are alternately even and odd functions of $x$; $f_0, f_2, f_4 \cdots$ are even, $f_1, f_3, f_5 \cdots$ are odd. Their squares are consequently even, the products of their squares by $x$ are odd, functions of $x$; and the first two integrals in the expression (205) for $M$ vanish. As for the integral $\int_{-\infty}^{\infty} xf_if_jdx$, its integrand is an odd function of $x$ if $i$ and $j$ are both even or both odd, and in either case it vanishes; so that if two wave-patterns corresponding both to even-numbered or both to odd-numbered Stationary States coexist, there is no surging of charge to and fro, and the electric moment of the system remains constant. If $i$ is even and $j$ odd, or vice versa, the conclusion is not so immediate. It follows however from the general properties of the Hermite polynomials [28] that the integral $\int_{-\infty}^{\infty} xf_if_jdx$ always vanishes unless $i$ and $j$ differ by one unit, so that in every case but this the electric moment is continually zero. This leads us to the rule:

*If two modes of vibration i and j coexist, the electric moment of the "imaginary string" representing the linear harmonic oscillator varies sinusoidally with the frequency* $(\nu_i - \nu_j)$, *if and only if* $i = j \pm 1$; *otherwise the electric moment is and remains zero.*

This may be interpreted as meaning physically that radiation occurs only when two "adjacent" states—two states for which the quantum-number differs by one unit—coexist; that *transitions are possible only between adjacent states.*

This is a Principle of Selection. It is the principle of selection predicted for the linear harmonic oscillator in the earlier versions of atomic theory, and sustained by observations on those features of band spectra which are attributed to simple-harmonic vibrations of molecules.

Thus in the case of the linear oscillator, the idea of interpreting the square of the amplitude of the Ψ-vibrations as density of electric charge is twice successful. When the oscillator is in one of its sta-

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[28] Courant-Hilbert, *Methoden der math. Physik*, p. 76.

tionary states, the distribution of "charge" along the imaginary string which represents it is stationary; when the vibrations corresponding to two distinct Stationary States coexist, the distribution of the "charge" fluctuates, with precisely the frequency which experiment teaches us to expect from a transition between the states in question; when and only when the two coexisting stationary states are adjacent in the ordering, when and only when experiment teaches us to expect transitions, the fluctuation assumes the emphatic character of a bodily surging of the charge to and fro across the centre of the string.[29]

One further desirable result of identifying square of amplitude of $\Psi$ with density of electric charge appears when from one dimension we go over to systems of two or three dimensions. As illustration I take the example of an hydrogen atom exposed to an electric field, represented by an imaginary fluid in three dimensions, the stationary wave-patterns of which correspond to the stationary states of the perturbed atom. If two of these stationary wave-patterns coexist, there may be a bodily surging of charge to and fro, with the frequency belonging to the transition between the stationary states which the wave-patterns represent. If in particular two wave-patterns sharing a common value of the quantum-number $s$ (the "equatorial quantum-number," equation 186) coexist, there is a surging of the "charge," and its to-and-fro motion is parallel to the applied electric field; there is no component of the motion normal to the field. With this result agrees well the fact of experience, that the light emitted by virtue of transitions between stationary states differing only in the quantum-numbers $k_1$ and $k_2$, and sharing the same value of $s$, is polarized with its electric vector parallel to the field. Again, if two wave-patterns for which the values of $s$ differ by one unit coexist, the resultant surging of the charge is perpendicular to the electric field; and it is a fact of experience that the light due to transitions between stationary states having values of $s$ one unit apart is polarized with electric vector normal to the field. Finally, if two wave-patterns for which the values of $s$ differ by two or more units coexist, there is no far-sweeping dis-

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[29] Schroedinger has shown that if we conceive a great number of Stationary States with high values of $i$ and artfully chosen relative "amplitudes" (i.e. values of $A_i$ and $B_i$ in equation 201) to exist simultaneously, we find the "charge-density" concentrated into a small region, a sort of knot or bundle which oscillates back and forth across the centre of the string with frequency $\nu_0$ and with approximately the same amplitude of vibration as the original particle (the particle with mass $m$ and restoring-force $-4\pi^2 m\nu_0^2 x$ of which the string is our image in wave-mechanics) would have if its energy were the same as that of the Stationary State which was made most prominent in the summation (*Naturwiss.*, **14**, pp. 664–666; 1926). This is a promising result, suggesting as it does that atoms in highly excited states may be groups of particles which, as the system returns to normalcy, spread out into a sort of fluid haze. The idea can be generalized widely, and merits a thorough analysis.

placement of charge; and in the spectra, the lines which such transitions should cause are missing.

Thus in the case of the hydrogen atom exposed to an electric field, and in other two- and three-dimensional systems as well, the identification of the square of the amplitude of the $\Psi$-vibrations with density of electric charge is thrice successful. In the picture, we see the electric charge stationary when the system is in a stationary state, fluctuating with the proper frequency when two states coexist; we see it surging back and forth *en masse* when the coexisting states are two between which a transition is "permitted," and otherwise not; we see it surging back and forth along the proper direction to explain the polarization of the light which results from the transition. As a device for picturing the radiation-process, Schroedinger's model is certainly unrivalled. In the earlier atom-models, even the frequencies of the emitted rays of light and the frequencies of the intra-atomic vibrations did not agree. Here at last they do, and when a tube full of hydrogen atoms is pouring out the light of the red Balmer line with its frequency of $4.57 \cdot 10^{14}$, it is permissible at last to imagine each of them as a mechanism, within which something is vibrating $4.57 \cdot 10^{14}$ times in a second.

Even the relative intensities of spectrum lines may fall within the scope of wave-mechanics. We have seen that in the case of the linear oscillator, the vanishing of the integral $\int x f_i f_j dx$ for all pairs of Stationary States for which $i$ and $j$ differ by more than one unit entails the non-occurrence of the corresponding transitions, the inability to emit or absorb the corresponding radiation. May it not be that the intensity of the radiation emitted by reason of the transition between any two states of any system, and polarized parallel to any direction $x$, is governed by the value of the integral $\int x \psi_i \psi_j dx$ involving the *Eigenfunktionen* $\psi_i$ and $\psi_j$ of the states in question? To develop this idea more assumptions must be introduced than I have yet mentioned, since every *Eigenfunktion* which I have thus far written down might be multiplied by any constant factor without ceasing to be an *Eigenfunktion*, and some rule must be laid down to fix these constant factors. To predict the relative intensities of the components into which certain hydrogen-atom lines are split by electric field, Schroedinger made a simple and natural assumption about these factors; and the results turned out to be in good agreement with the data.[30] I cannot enter further into this topic, except to remark that the point of contact between wave-mechanics and the matrix-mechanics of Heisenberg lies here; for the integrals in question figure as matrix-

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[30] Schroedinger, *Ann. d. Phys.*, **80**, pp. 464–478 (1926); *Phys. Rev.* (2), **28**, pp. 1049–1070 (1926).

elements in the latter theory, which indeed appears to be an alternative way of thinking to reach the same conclusions as emerge from the speculations of de Broglie and Schroedinger.[31]

Nevertheless the image is still far from perfect; there is certainly something still lacking, something still to be discovered and added. Radiation may flow forth from the atom when two stationary states coexist, but it does not flow forever; one or the other of the wave-patterns must therefore die out, soon after the radiation commences; yet no agency has thus far been provided to effect the extinction of either. It may not be difficult to insert such an agency into the theory, in the form perhaps of an interaction between the $\Psi$-waves and the outflowing electromagnetic waves. It may be much more troublesome to extricate ourselves from the paradox into which the identification of square-of-amplitude-of-the-$\Psi$-vibration with density-of-electric-charge has led us. All of the numerical agreements between this theory of the hydrogen atom and the features of the hydrogen spectrum are obtained by putting $-e^2/r$ for the potential-energy-function of the atom-model. This is the potential-energy-function for a point-nucleus and a point-electron. If we dissolve the electron, spread it out like a cloud in space around the centre of the atom, how can we consistently retain the potential-energy-function derived from the picture of a point-charge? How is it defensible to define electric charge in one way in order to lay the cornerstone of the new theory, and then redefine it in a contrasting way in order to raise the superstructure?

Wave-mechanics, striking as are the pictures which it offers of certain of the processes within the atom, still abounds in conceptual difficulties of which the last is a fair instance; and those who share the view of Lessing that it is more desirable to be approaching truth perpetually than ever to attain it may still find satisfaction in physics. Wave-mechanics still is tentative, not definitive; a plan of campaign, rather than a conquest. The outcome cannot now be foreseen. Yet we may reflect that twenty-five years ago it was universally supposed that light possesses only the qualities of a wave-motion; and then experiment was piled upon experiment which showed that in addition it behaves in many situations as though it were a stream of corpuscles. Perhaps we stand at the beginning of an equally imposing series of experiments, which will show that matter with equal inconsistency partakes of the qualities of particles and of the qualities of waves.

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[31] Schroedinger, *Ann. d. Phys.*, **79**, pp. 734–756 (1926); C. Eckart, *Phys. Rev.* (2), **28**, pp. 711–726 (1926).