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Atomic and Molecular Theory Since Bohr: Historical Survey

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THE revolution in man's conception of the physical universe which has occurred during the last two decades is comparable, both in magnitude of philosophic conception and in pragmatic fertility, to the upheaval that took place during the sixteenth and seventeenth centuries. The earlier period witnessed what may be called an emancipation of physical doctrine from the scholastic presuppositions of ontology: The Aristotelian conception of motion in conformity with the principle of being gave way to an epistemological description in terms of perceptible and measurable qualities, such as mass and acceleration.

The famous treatise on gunnery, contained in Tartaglia's great work *La Nova Scientia* (Venice, 1537; second volume, 1546) exemplifies the problem at issue. In the first volume he endeavors to describe the trajectory of a cannon ball in accordance with Aristotle's teachings. The path consists first of a straight-line portion in which the projectile rises and hence departs from the place destined for it by ontological conditions, for its natural place is the element "earth." This departure is termed "violent motion;" according to Aristotle, its occurrence requires "force." The straight-line portion of the trajectory is followed by a part in which the motion is downward, hence "natural," and proceeds without application of force. Motion, in Tartaglia's early conception, reflects the categories of being.

Painstaking empirical investigations, however, caused the same author to abandon this classification of motions in the second volume of his work, which contains nearly correct diagrams of trajectories and more emphatic reference to the observable properties of the path. The new conception reached its full development in the work of Galileo and Newton, who succeeded in extracting the crucial elements of explanation from the empirical features presented by motion itself, rather than from the supposedly external and invariable structural conditions antecedent to the motion.

If the sketched transformation of thought can be characterized as the passage from an ontological to an epistemological explanation of nature, the recent conceptual changes have led the physicist from a descriptive toward a symbolic understanding of his universe. The precise sense of this statement will, we hope, reveal itself in the subsequent pages; but a preliminary exposition of its qualitative meaning may be helpful to the reader at once.

Bohr's theory of the atom represents the last great attempt to unravel the workings of the microcosm with the use of perceptible elements of discourse, called models. We shall see how this attempt has failed. The theory was descriptive in the sense that it attributes to the unperceived entity "atom" certain qualities as being possessed by it in the same way as sensible qualities are

assigned to things when they are described. In the later quantum theories, qualities—such as position, velocity, and so forth—are assigned to atomic objects not possessively but through a less intimate sort of correspondence. We may no longer say that an electron *has* position under all circumstances. Nevertheless, position remains a valid quality with respect to the entity *electron* insofar as it can be revealed by measurement and insofar as it enters the theory as an observable. This loosening of the possessive relation required by modern quantum theory we have here chosen to call the transition from descriptive to symbolic understanding of nature.

The term *symbolic* should not be construed as implying a judgment of lessened reality of the qualities which it affects; nor should it convey the impression that the qualities of classical models are not also symbols. It is used as a ready label for what is sometimes called nonmechanistic or noncausal—words we wish to avoid because they have led to serious fallacies.

In presenting a survey of the history of ideas since Bohr we disclaim all pretension of completeness and of finality. The goal of the present movement is still too distant to be seen. Present theories are certainly not complete. But they exhibit a uniformity of logical structure which suggests an unmistakable trend, and their success is so astounding as to make them memorable even if they are wrong.

DECLINE OF BOHR'S ATOMIC THEORY

The reason for the abandonment of the Bohr theory is twofold: First, there occurred an accumulation of material discrepancies between the theory and experimental observations which called for more and more radical revisions of Bohr's postulates; second, there came about a gradual recognition of certain basic impossibilities, that is, inconsistencies of a logical kind, residing in the very purpose the theory was hoping to achieve. We first consider the technical difficulties which the Bohr theory, while eminently successful in a vast domain, ultimately failed to master. Knowledge of the essentials of the theory will be taken for granted.[1]

[1] See, for example, C. E. Behrens, Am. J. Phys. **11**, 60, 135, 272 (1943).

The quantum number k, which arose in the quantization of angular momentum in the atomic problem, was subject to slight suspicion from the very start. For clearly the linear orbits corresponding to $k=0$ did not correspond to reality. At first they were excluded for extraneous reasons, chiefly by saying that on these orbits the electron would collide with the nucleus, and this nature would not permit. Thus the quantum number k enjoyed the distinction, above all the others, of never being zero. But soon it became apparent that the situation was in need of more radical revision. The magnetic behavior of atoms (Lande's g formula) and other matters suggested strongly that $k-1$ rather than k was of fundamental significance. Why, then, should the Bohr theory yield k as quantum number?

The disease which befell the quantum number k was contagious. Observations on the spacing of lines in band spectra indicated clearly that only half-integral quantum numbers could render account of the facts. Moreover, in many cases where theory demanded the square of a quantum number such as j^2, observation insisted on $j(j+1)$. Could it be true, then, that quantum numbers are sometimes integral, sometimes half-integral, and sometimes irrational?

The formula that represents the fine structure of the spectral lines of atomic hydrogen has had a most peculiar history. It sprang with perfection from the fertile mind of *Sommerfeld*, who derived it in 1916 by applying relativity theory to Bohr's electronic orbits. But its perfection was the source of considerable embarrassment. Experiment confirmed it so completely that no room was left for accommodating within the formula any effects other than the relativity corrections, although such other effects soon demanded consideration. Goudsmit and Uhlenbeck, in 1925, called attention to the perplexing circumstance that the electron spin, without regard to relativity considerations, produces a fine structure of the hydrogen lines identical with Sommerfeld's except for minor details, and these minor details favored the interpretation of Uhlenbeck and Goudsmit. Yet relativity corrections were certainly called for, and the spin was needed for other reasons. Both effects, however, literally "overexplained" the phenomena.

Introduction of the spin hypothesis had other disintegrating effects, if not on the Bohr theory, then at least on the ideas regarding the structure of an electron which were implied by it. Both value of the angular momentum of a spinning electron and its magnetic moment were known from spectroscopic and other observations. To produce them, a (Lorentz) electron would have to revolve about its axis so fast that a point on its circumference would have a linear velocity 300 times that of light. (The rigid-sphere electron of Abraham failed altogether to give the correct ratio of spin to magnetic moment.) This, while possibly not a point of great importance—since the Bohr theory did not pretend to explain the structure of an electron anyway—indicated a weakness in the conceptions underlying the atomic hypothesis.

Perhaps the most damaging of the theory's failures was its inability to account quantitatively for the spectra of atoms having more than one electron. Notable attempts were made to apply Bohr's reasoning to the helium atom: The two electrons were tentatively located in a single fixed plane, then in space; their motions were described with all conceivable relations of phase between them; they were made to move in the same sense and in opposite senses; but the correct ionization potential could not be obtained. In judging this result, it must be remembered that calculations involving more than two bodies are never exact, but the discrepancies incurred were larger than could reasonably be ascribed to unwarranted approximations. Furthermore, in the helium problem the difficulty of complexity, of top-heaviness on the part of the theory, became apparent for the first time; it took form in the question: Are the constructs with which the theory operates (sense of revolution of electrons, relative phase of the motion) germane to the problem at hand? What experiment could ever lead to their determination?

A very similar state of affairs prevailed in the account which the Bohr theory gave of molecular structure. As early as 1913 Bohr proposed a model of the hydrogen molecule, the details of which were elaborated by Epstein in 1916. The model placed the two electrons in the equatorial plane relative to the two protons as poles, and considered them as revolving in a circle at opposite ends of a diameter. By assigning the proper speed of revolution, several empirical facts could be reproduced; for example, the dispersion of light and the magneto-rotation of the plane of polarized light in hydrogen gas came out correctly. But the predicted heat of dissociation of the molecule was not in agreement with experiment, and its magnetic behavior was palpably wrong since two electrons revolving in the same sense make the molecule paramagnetic, whereas hydrogen is known to be diamagnetic.

All of the aforementioned inconsistencies appear as minor ills in comparison with the cancer which began to develop within the whole system of descriptive explanation—the wave-particle dualism. Its earliest symptoms, though incompletely diagnosed at the time, were the light quanta of Planck (blackbody radiation) and Einstein (photoelectric effect). These discoveries hinted at the corpuscular character of light through the relation $E=h\nu$ which they established. In the so-called Ramsauer effect, nature gave the first inkling of the converse to the former proposition, that is, of the wave properties of matter. For Ramsauer, and almost simultaneously Townsend and Bailey, showed in 1921 that electrons moving with small velocities may pass through matter almost without obstruction, just as light of certain wavelengths passes through a transparent medium without absorption. The issue could no longer be evaded when Arthur Compton, in 1923, discovered the effect named after him. X-rays could change their frequency on collision with electrons, and change it precisely in the manner of a particle which, when possessing kinetic energy $h\nu$, collides elastically with an electron. Again, waves exhibited particle behavior. It was at this stage that physicists began to feel uneasy, for phenomena were shaking their faith in the consistency of nature.

During the next few years, facts were discovered that made the dualism more pronounced. But the embarrassment was progressively lightened because new theories sprang up which dealt constructively with the situation. Before discussing them, let us return to the Bohr theory and analyze it briefly from a methodological point of view.

It is often said that Bohr's postulates leading to quantization of the electron's motion are some-

how *ad hoc*, or man-made, or artificial. This view, which is difficult to phrase clearly, reflects a prevalent judgment upon the circumstance that the theory in question is unrelated to other familiar theories. It hardly amounts to a valid criticism, for the element of strangeness attaches to all new departures and wears off when they become successful.

There is, however, a more important inconsistency, perhaps rarely mentioned but pointing directly at the core of the later quantum theories. It was, in fact, to remedy this fault that statistical reasoning was subsequently adopted. Bohr's theory, as well as every other of the type we have called descriptive, represents motions by correlating momentary positions in space, that is, points, with instants of time. Now the constructs *point* and *instant* are fraught with difficulties not of a mathematical, but of a physical sort. It is all very well to define an instant as the limit to which a time interval may be conceived to shrink. Nor should any one object to this, or any other, limiting, ideal definition merely because it is *operationally* impossible, for who is to determine what operations will be possible in the future? But if the limiting process contradicts the *known laws of nature*, then we must reject it so long as we believe in these laws of nature. Unfortunately, the passage to the limit "instant" encounters an obstacle of this essential kind.

Let us say for definiteness that our knowledge of temporal duration is gained by receiving a light signal sustained during the interval. Any other kind of signal would serve equally well in this argument. What happens to the light signal as the interval shrinks to zero? The spectral range of the signal broadens until finally it includes *all* frequencies with constant amplitude. (The Fourier transform of a "unit impulse" is a constant.) Now if, in accordance with Bohr's theory, $E=h\nu$, the presence in the light signal of infinite frequencies involves an infinite energy, and this means that knowledge of an instant is not attainable. This difficulty is not restricted to the Bohr theory, for even in classical mechanics and electrodynamics a wave of infinite frequency possesses an infinite energy.

What about the geometric point? Again the same trouble appears in an even more obvious way. No signal can transmit the exact location of anything that is smaller than the wavelength of the signal. To locate a point would therefore require a signal of zero wavelength, and hence of infinite frequency, and hence again of infinite energy. Thus one might well expect that the classical descriptive method of representing motion by specifying an *equation of motion*, which is a relation between space points and corresponding instants, must ultimately fail. Even when the objects are not regarded as points but as extended bodies the trouble remains; in fact it remains unless the boundaries of the objects are made hazy in both space and time. One way, and indeed the one adopted later, is to replace the classical equation of motion $x=x(t)$ by a probability relation $P\Delta x=P(x)\Delta x$, where P is the probability density, or probability, per unit range, of finding the system within the range Δx. This solution would not deprive points and instants of logical meaning, but it would render the description of motion in terms of them physically objectionable.

The philosopher will find an interesting parallelism between these considerations and the theory of primary qualities. These, in Locke's terminology, are the properties which attach to matter itself, in contradistinction to the secondary qualities which spring from the interaction of matter with mind and are incidental to the process of perception. Typical among primary qualities are size, shape and position, while color, warmth and odor are secondary. In modern terminology this distinction is more frequently expressed by the words *objective* and *subjective*. Subsequent philosophies, most notably those of Hume and Berkeley, have effected a progressive conversion of primary qualities into secondary ones, and the process is apparently still operative. In Bohr's theory size and shape of electron orbits are primary qualities. Modern quantum theories, as will be seen, deprive them of this status.

In view of this, the dualism between waves and particles takes on a different significance. If size and shape can no longer be ascribed to subatomic systems, perhaps the concepts of particle and of wave lose their obvious meaning with respect to such systems. We are gradually learning that to speak of the wave or particle nature of an electron is as empty as a reference to its color.

The crisis of causality has often been discussed in connection with modern quantum theories, though rarely in connection with Bohr's hypotheses where it was much more threatening indeed. The principle of causality requires that a given state of a physical system shall determine, or permit a prediction of, its future state at any time. If the principle is to have significance, a state must be completely describable. But a description by means of models, with respect to which instants of time and points of space have relevance, can never be complete because the state of the model at every point must be given. Causal inquiry becomes impotent because it is forced to proceed under the crushing burden of a state defined by an infinity of variables. So long as the electron was regarded as a point or a sphere the structure of which was a matter of creed, the failure of causality did not become apparent; any further development of the Bohr theory, however, would have brought it to light relentlessly.

It is the purpose of the next few sections to give a semihistorical treatment of the essential ideas of the new quantum theories. It is hoped that this will throw light on why they were originally introduced, a thing often hard to ascertain from the final form in which they appear in the finished theory. In a later article the complete theory will be developed from the logical point of view.

THE CORRESPONDENCE PRINCIPLE

Perhaps the most appropriate subject with which to introduce the ideas of the new quantum theories is Bohr's correspondence principle, for historically it was, and indeed is even now, a most suggestive doctrine. Although it was more often a name for the incisive intuition which guided the founders of quantum mechanics than an articulate statement, it can be formulated more or less precisely in the following two ways:

(*i*) There is a one-to-one correspondence between the calculated classical frequencies of a multiply periodic system (for example, the frequencies of the periodic motions of the electrons in an atom) on the one hand, and the frequencies obtained from possible energy transitions between empirical states according to the Bohr equation,

$$(E_1-E_2)/h=\nu \qquad (1)$$

on the other. For high energy values E_1 and E_2 and small energy differences, this correspondence approaches identity.

(*ii*) There must be a general formal equivalence of quantum and classical theory in those regions of application in which the classical theory has already been verified.

In the form (*i*) the correspondence principle has led to important results such as selection rules for atomic and molecular transitions, approximate intensities of spectral lines and polarization rules. Its fruitfulness continues in regions where the quantum theory is not yet complete, such as quantum electrodynamics. The vaguer and more generally methodic form (*ii*) has been less pregnant with specific discoveries. Aside from stating the trivial fact that well-substantiated classical theory cannot be wrong, it expresses a dogma and an attitude which has proved psychologically useful in the extension of theories.

While historically the correspondence principle has played a most dominant role, its logical function is somewhat difficult to analyze. Among the founders of quantum mechanics, Bohr, Heisenberg and Jordan ascribe to it the exalted status of a general scientific directive, of a methodological postulate. To quote Jordan (*Anschauliche Quantenmechanik*):

> Bohr's so-called correspondence principle is without doubt the most important idea of the whole quantum theory. Every attempt to penetrate the world of quanta, which is so foreign to . . . customary concepts and modes of reasoning, must aim above all at the attainment of a thorough and practiced understanding of the idea of correspondence.

The tenor of such pronouncements is clearly positivistic in the sense that any artefact which leads to practical discovery is to be conceded a methodological rank commensurate with its fruitfulness; it reflects an important sentiment of our time.

Realists, on the other hand, who see in every valid theory a fundamentally significant counterpart of the workings of nature, are inclined to minimize the importance of the correspondence principle. Their argument might run as follows. All accepted theories of classical physics are

constructed in direct reliance upon experiment; their starting points lie in the material of immediate observation. The principle under discussion is not of this kind. For it juxtaposes not one theory with nature, but one man-made set of constructions (classical physics) with another (quantum mechanics). The relevance to nature thus becomes less direct, and quantum mechanics is converted into a kind of superstructure reared upon other ideal devices rather than an edifice built upon the solid rock of primary experience. From a philosophical point of view this argument may be disastrous. But instead of indulging in further speculations upon this debated theme, it seems preferable in this summary to record the further development of ideas which has indeed solved the problem satisfactorily by permitting an attitude that makes the fundamental claims of this principle dispensable, while leaving it intact as a heuristic device.

MATRIX MECHANICS

It was an inductive correspondence consideration that led Heisenberg in 1925 to the matrix mechanics, the first form of the quantum theory to make possible a unified, self-sustained attack on atomic problems. Heisenberg assumed[2]

(*a*) the existence of stationary states of atomic systems;

(*b*) the Bohr frequency equation (1);

(*c*) the Ritz combination principle; this says that if $\nu_{nm}=(E_n-E_m)/h$ and $\nu_{ml}=(E_m-E_l)/h$ are emitted frequencies, then ν_{nl}, if it occurs at all, will be $(E_n-E_l)/h=\nu_{nm}+\nu_{nl}$.

He noted that in the classical theory of multiply periodic systems the coordinates could be represented by a Fourier series

$$q_k=\sum_{n_1\cdots n_f=-\infty}^{\infty} q^{(k)}_{n_1\cdots n_f}\exp\left[2\pi i(n_1\nu_1+\cdots n_f\nu_f)t\right],$$

where $\nu_1\cdots\nu_f$ are the fundamental frequencies of the motion, and that the amplitudes $q^{(k)}_{n_1\cdots n_f}$ were sufficient to characterize the motion. Now in the classical theory the frequencies of emitted radiation were identified with $(n_1\nu_1+\cdots n_f\nu_f)$, the amplitudes with $q^{(k)}_{n_1\cdots n_f}$ and therefore with a single state of motion. However, in the Bohr equation (1) a frequency of emitted radiation is associated with a transition *between two states*. If quantum-mechanical systems were to be characterized by Fourier amplitudes, those amplitudes would also have to refer to two states and therefore have two sets of subindices. Further, since the Fourier series of the classical theory could in general be added, multiplied and differentiated term by term, the quantum-mechanical analogs of these operations had to be found. In other words, a new kinematics of the microcosm was needed before the problem of dynamics could be attacked.

The following considerations guided Heisenberg in solving the kinematical problem. He arranged the Fourier amplitudes and their exponential time factors in the form of a square array

$$\{q_{nm}\exp(2\pi i\nu_{nm}t)\},$$

a natural procedure since now there were two subscripts, the first, n, referring to the assemblage of numbers $n_1, n_2, \cdots n_f$ characterizing the state before transition, and the second, m, the numbers $m_1, m_2, \cdots m_f$ labeling the state after. When two Fourier series are added the amplitudes of corresponding terms add; when a series is differentiated with respect to time its amplitudes are multiplied by $2\pi i\nu$. The same rules are assumed to hold for quantum kinematics:

$$\{q_{nm}\exp 2\pi i\nu_{nm}t\}+\{r_{nm}\exp 2\pi i\nu_{nm}t\}=\{(q_{nm}+r_{nm})\exp 2\pi i\nu_{nm}t\},$$

$$\frac{d}{dt}\{q_{nm}\exp 2\pi i\nu_{nm}t\}=\{2\pi i\nu_{nm}q_{nm}\exp 2\pi i\nu_{nm}t\}.$$

To obtain the analog of multiplication the procedure is to multiply only pairs of terms whose time factors, $\exp 2\pi i\nu_{kj}t$, contain frequencies in their exponents that add according to the Ritz combination principle to give the required frequency. Thus, suppose we have two arrays $\mathbf{p}$ and $\mathbf{q}$ and we wish to obtain the array which corresponds to the product $\mathbf{pq}$. To get the n,m element of $\mathbf{pq}$ we must add all products $p_{ij}q_{kl}$ whose associated frequencies yield ν_{nm}. Since, for every l,

$$p_{nl}q_{lm}\exp 2\pi i(\nu_{nl}+\nu_{lm})t=p_{nl}q_{lm}\exp 2\pi i\nu_{nm}t,$$

[2] Zeits. f. Physik **33**, 879 (1925); *Physical principles of the quantum theory* (Univ. of Chicago Press), p. 105.

we see that

$$(\mathbf{pq})_{nm}=\sum_l p_{nl}q_{lm}.$$

This means that the laws of addition and multiplication are exactly those of the matrix theory which mathematicians have studied since Cayley's time. Heisenberg's square arrays, therefore, are matrices.

This completes the kinematics of the theory; for now if there be a system of n degrees of freedom which in classical mechanics would be described by n numbers p_j (momentums) and n numbers q_k (coordinates), then it will be represented in matrix mechanics by $2n$ matrices $\mathbf{p}_j$ and $\mathbf{q}_k$, where $j, k=1, \cdots n$, and if the analog of any classical function of the dynamical variables p_j, q_k is desired it can be found by substituting the matrices. The ambiguity caused by the fact that often $\mathbf{pq}\neq\mathbf{qp}$ for matrices can be eliminated by substituting the symmetrized matrix $\frac{1}{2}(\mathbf{pq}+\mathbf{qp})$ for $\mathbf{pq}$ when this product occurs in the function desired.

The next question is that of the development of dynamics. Here we must find the analogs of the equations of motion of the classical theory. The latter can be stated in the form[3]

$$p_k=\sum_{j=1}^{n}\left(\frac{\partial H}{\partial p_j}\frac{\partial p_k}{\partial q_j}-\frac{\partial H}{\partial q_j}\frac{\partial p_k}{\partial p_j}\right),$$

$$\dot{q}_k=\sum_{j=1}^{n}\left(\frac{\partial H}{\partial p_j}\frac{\partial q_k}{\partial q_j}-\frac{\partial H}{\partial q_j}\frac{\partial q_k}{\partial p_j}\right).$$

The right-hand member of the equation for p_k is often symbolized by (Hp_k), the right-hand member of that for $\dot{q}_k$ by (Hq_k). The symbols themselves are called *Poisson brackets*. The passage from classical to quantum dynamics can most easily be made by using the Poisson bracket as the point of departure. It was first shown by Dirac[4] that the quantum-mechanical analog of the Poisson bracket (xy) is the expression $(xy-yx)(2\pi i/h)$, for which we shall use the symbol $[xy]2\pi i/h)$. Quantities appearing within the square brackets—that is, within the "quantum Poisson bracket"—are of course matrices. Thus the dynamics of a quantum-mechanical system is completely expressed by the equations

$$\dot{\mathbf{p}}_k=\frac{2\pi i}{h}[\mathbf{Hp}_k], \qquad \dot{\mathbf{q}}_k=\frac{2\pi i}{h}[\mathbf{Hq}_k], \quad (2a)$$

$$[\mathbf{p}_j\mathbf{q}_k]=\frac{h}{2\pi i}\delta_{jk}, \qquad [\mathbf{p}_j\mathbf{p}_k]=[\mathbf{q}_j\mathbf{q}_k]=0. \quad (2b)$$

The last three equations are the analogs of classical identities resulting from the independence of p_j and q_j as variables.

Now to give the solution to any problem of quantum dynamics we need only find $2n$ matrices $\mathbf{p}_j$, $\mathbf{q}_j$ that satisfy the foregoing relations. Note that if a set of $\mathbf{p}_j$ and $\mathbf{q}_j$ independent of the time can be found which makes the energy matrix diagonal and satisfies the exchange relations (2b), then the dynamical problem is solved. For if we provide these p_j and q_j with time factors $\exp(2\pi i/h)(H_n-H_m)t$, where H_n and H_m are the diagonal elements of $\mathbf{H}$, they will automatically satisfy the equations of motion, Eqs. (2a). This is, in fact, the usual method of solving a problem in matrix mechanics.

In order to interpret the matrix solution of a problem one must again use the correspondence principle. On the classical theory, where the Fourier amplitudes are amplitudes of motion, their squares are proportional to the *intensity* of emitted radiation. It seems reasonable to introduce transition probabilities as the matrix correlates to the intensities since, according to the old quantum theory, they should be proportional to the intensities of emitted radiation. Thus the elements of the matrix $\{q_{nm}\exp 2\pi i\nu_{nm}t\}$ become "probability amplitudes" whose squares measure the probability of transition between the states of their subindices. Further, it seems reasonable to assume that those elements of matrices which are independent of the time (the diagonal elements) represent time averages of the matrix quantity since this is true for the corresponding Fourier series. Finally, if there are no elements of the matrix that depend on the time, the matrix will represent a quantity that is stationary. Thus the aforementioned diagonal form of the $\mathbf{H}$ matrix has as diagonal elements the possible stationary values of the energy.

[3] See Lindsay and Margenau, *Foundations of physics* (Wiley), p. 148.

[4] Proc. Roy. Soc. **109**, 642 (1925).

Matrix mechanics constituted an advance over the Bohr theory in the following respects. First, it was self-contained in the sense that it made no appeal other than to its own axioms in the prediction of phenomena. Of course the correspondence principle was still of practical importance in the choice of a Hamiltonian function for the theory of a given system, but such a choice could be regarded as empirical in any case. Second, it gave correct results in the cases previously mentioned in which the Bohr theory failed, and was sufficiently powerful to give many more. Third, from a positivistic point of view, it was more satisfying in that it operated with observable quantities, frequencies and transition probabilities, eliminating the "unmeasurable observables"[5] previously mentioned. Admittedly it did this by introducing probability into the theory in a way that demanded a re-examination of the meaning of a physical state and of the doctrine of physical causality. This will be discussed in more detail later.

WAVE MECHANICS

In the same years in which matrix mechanics was being discovered and applied, another important method of attack on quantum phenomena was developed which received its impetus from a somewhat different set of physical ideas. To introduce these it is appropriate to make some further remarks on the wave-particle dualism.

The great success of particle mechanics and electromagnetic theory in accounting for phenomena in terms of atomic particles and electromagnetic waves can lead easily to the attitude of mind which regards any elementary entity as either a particle or a wave. There would seem to be little possibility of getting the two ideas together since their descriptions are so sharply distinct. The state of the particle is given by six numbers—its position and velocity components with respect to some axes; whereas the electromagnetic wave must be specified by six point functions, defined throughout space—the three components of the electric and the three components of the magnetic field intensities. The wave-particle distinction began to face great difficulties early in the twentieth century. First light, formerly considered a wave, turned out to have particle-like properties, and then electrons, formerly considered as particles, were found to have wave-like properties. This was beyond the powers of explanation of both the classical wave and particle theories, as well as of the Bohr theory.

The earliest successful attempt to incorporate wave-like properties into the theory of particles was made by de Broglie.[6] He represented a free electron, for instance, by means of a set of progressive waves traveling with *phase* velocity c^2/v (greater than the velocity of light), but with *group* velocity v, the observed velocity of the particle. He proposed to associate with the particle of mass m a wavelength

$$\lambda = h/mv. \tag{3}$$

de Broglie was led to these suppositions by two considerations. First, he noted that if one started with a *standing* wave

$$\psi(x_0, y_0, z_0) \exp 2\pi i \nu_0 t$$

of constant phase throughout space, then a Lorentz transformation, demanded by restricted relativity, would cause an observer moving with the velocity v along x to perceive the altered phenomenon:

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

Since the frequency transforms as $1/\mathrm{d}t_0$, it follows that $\nu = \nu_0/[1-(v^2/c^2)]^{\frac{1}{2}}$ and hence that the last expression takes the form

$$\psi\left\{\frac{x-vt}{[1-(v^2/c^2)]^{\frac{1}{2}}}\ y, z\right\} \exp\left(2\pi i \nu t - 2\pi i \frac{\nu v x}{c^2}\right).$$

This is a progressive wave with phase velocity c^2/v. de Broglie found that he could superimpose a set of these waves in such a way as to get a group velocity v. This he chose as the representation of a moving particle. Now the restricted theory of relativity associates with a particle of

[5] Indeed, the foregoing exposition scarcely indicates the aversion which several of the founders of quantum mechanics had for the use of "unobserved quantities."

[6] Ann. d. Physik **3**, 22 (1925); Thesis (1924).

rest mass m a rest energy mc^2, and from the Bohr equation, $E=h\nu$, one might be inclined to set

$$h\nu=mc^2.$$

This gives, provided there is a phase velocity c^2/v as previously noted,

$$\lambda=(c^2/v)/\nu=h/mv.$$

Secondly, there is a much deeper analogy between particle and wave motion which was already known to W. R. Hamilton in 1834. In his famous paper on geometrical optics of 1824[7] Hamilton had developed analytic methods for describing in the approximation of geometrical optics the propagation of light as the gradual unfolding of a wave front normal at every point to the rays of light. His paper of 1834 on mechanics[8] showed that there was an analogy between geometrical optics and mechanics. This is due to the fact that by a suitable definition of a "refractive index" in terms of potential energy a problem dealing with the motion of a particle in classical dynamics can be transformed into one of geometrical optics, the possible trajectories of the particle becoming optical rays. More generally, since the solution of a classical problem of n degrees of freedom consists in expressions for the $2n$ coordinates and momentums p_i and q_j as functions of the time, and since these represent possible trajectories of the system in n-dimensional q_j space, the possible motion of the system along such trajectories can equally well be represented as the expansion of an $(n-1)$-dimensional wave surface, orthogonal to the trajectories, which obeys the laws of (n-dimensional) geometrical optics, provided that the refractive index be properly defined in terms of the potential energy of the system. Now geometrical optics is adequate as a description of the phenomena of light only when the wavelength of the light may be neglected in comparison with the length of its path. Of course when diffraction, interference or polarization are to be considered, account must be taken of the wave properties. It was de Broglie's idea that just as geometrical optics had to be abandoned for physical optics whenever phenomena of the order of magnitude of the wavelength of light were to be explained, so for domains of atomic order of magnitude (that is, of the order of magnitude of the aforementioned wavelengths of electrons when they have velocities such as those which occur in Bohr orbits), classical mechanics would have to be abandoned for a wave mechanics of particles. It should be noted that except for the case of one particle in which the matter waves have a direct analogy to the light waves of three-dimensional physical optics, the analogy is between a wave mechanics for matter of n-dimensional configuration space and a hypothetical "physical optics" for an n-dimensional space.

de Broglie did not at first write down the wave equation for his matter waves. This was done by Schrödinger,[9] who was thereby led to another formulation of quantum mechanics, usually referred to as *wave mechanics*. He starts with the wave equation

$$\nabla^2 u-\frac{1}{v^2}\frac{\partial^2 u}{\partial t^2}=0.$$

For the case of monochromatic waves, for which

$$u=\psi(x, y, z)\exp 2\pi i\nu t,$$

the equation becomes, since $\lambda\nu=v$,

$$\nabla^2\psi+\frac{4\pi^2}{\lambda^2}\psi=0. \tag{4}$$

If now a solution of the form

$$\psi=a\exp\left[-2\pi i\varphi(x, y, z)\right]$$

be assumed and the derivatives of a be neglected in comparison with those of φ, the equation takes on a form well known in geometrical optics:

$$(\nabla\varphi)^2-\frac{1}{\lambda^2}=0. \tag{5}$$

But Hamilton's theory of the equations of mechanics leads to the Hamilton-Jacobi equation, which reads

$$(\nabla S)^2-2m(E-V)=0, \tag{6}$$

[7] Trans. Roy. Irish Acad. **15**, 69 (1828); supplements **16**, 4, 93 (1830); **17**, 1 (1837).

[8] Phil. Trans. (1834), p. 247; (1835), p. 95.

[9] *Collected papers on wave mechanics* (Blackie and Son), p. 27.

where E is the total energy, V the potential energy, m the mass of the particle and S is the "action" function. The similarity of form of Eqs. (5) and (6) is a mathematical expression of the previously developed analogy. We therefore assume $S=h\varphi$, h being the Planck constant (which has the dimensions of action since φ is dimensionless). Then from Eqs. (5) and (6),

$$\lambda=h/[2m(E-V)]^{\frac{1}{2}}$$

which will be recognized immediately as a generalization of Eq. (3). If now we substitute this expression for the wavelength of the matter waves in Eq. (4), we have

$$\nabla^2\psi+\frac{8\pi^2m}{h^2}(E-V)\psi=0,$$

which is Schrödinger's equation for the wave mechanics of a particle.

The set of ordinary differential equations of classical mechanics has now been replaced by a partial differential equation. This might lead to misgivings regarding the number of possible solutions obtainable. For in the classical theory the solutions were too numerous, and Bohr's quantum conditions had to be applied to pick the correct ones. For a *partial* differential equation the set of solutions is far more inclusive. Nevertheless, more stringent quantum conditions are not needed. Indeed no quantum conditions at all are needed if certain restrictions are made with respect to the boundary values of the solutions. It is characteristic of partial differential equations such as the wave equation that they possess solutions satisfying given boundary conditions only for special values (eigenvalues, or proper values) of the parameters they contain. For example, the usual states of vibration of a vibrating string result from the imposition of the condition that the ends of the string be fixed. In the case of the Schrödinger equation the eigenvalues of the energy are determined from the condition that $\int|\psi|^2d\tau$ shall be finite, where $d\tau$ is the volume element of configuration space over which the integral is extended. The functions or function ψ which satisfy the differential equation for the eigenvalue E_k of the parameter E are called the eigenfunctions belonging to E_k. The justification of the imposition of this condition is more easily made later when a physical meaning has been given to $|\psi|^2$. At present, suffice it to say that one desires that the integral of the intensity of the wave over the whole configuration space be finite.

The results of the calculation of eigenvalues of the Schrödinger equation for various different potential energy functions V were in general in accord with experiment and, what was surprising at the time of their first calculation, were in complete agreement with the results of matrix mechanics at those points where it departed from the classical theory. The reason for this was made clear by Schrödinger[10] and by Eckart,[11] who proved the mathematical equivalence of the two theories.

The basis for the proof is the following. In the matrix theory the fundamental *matrices* are the $\mathfrak{p}_i$ and $\mathfrak{q}_i$ that satisfy the exchange relations (2). In the Schrödinger theory there are *operators* that correspond to the p's and q's and satisfy the same relations,

$$p_j\rightarrow\frac{h}{2\pi i}\frac{\partial}{\partial q_j},\quad q_j\rightarrow q_j,$$

$$\frac{h}{2\pi i}\frac{\partial}{\partial q_j}(q_jf)-q_j\frac{h}{2\pi i}\frac{\partial}{\partial q_j}(f)=\frac{h}{2\pi i}f.$$

This is true because the Schrödinger equation can be obtained directly from the classical expression for the energy,

$$H=\frac{1}{2m}(p_x^2+p_y^2+p_z^2)+V(x,y,z),$$

by substituting the foregoing operators and then letting the resulting operator,

$$-\frac{h^2}{8\pi^2m}\nabla^2+V(x,y,z)\equiv H,$$

act on ψ:

$$H\psi=E\psi.$$

From the operators q_j and $(h/2\pi i)(\partial/\partial q_j)$ we can form the operator corresponding to any function $f(p_j, q_j)$ that can be expanded in a power series.

[10] *Collected papers*, p. 45.
[11] Phys. Rev. **28**, 711 (1926).

The correspondence between matrices and operators is

$$F_{jk}=\int \psi_j^* F\left(q_l \frac{h}{2\pi i}\frac{\partial}{\partial q_l}\right)\psi_k \mathrm{d}\tau,$$

where ψ_j and ψ_k are eigenfunctions of some arbitrary operator and the asterisk indicates the complex conjugate. The proof shows that addition or multiplication of operators inside the integral sign gives the sum or product of *matrices* on the left-hand side of the equation; that is, the algebra of matrices is isomorphic to the algebra of operators under this correspondence. Further, the problem of diagonalization of a given matrix by the proper choice of $\mathbf{p}_j$ and $\mathbf{q}_j$ matrices is exactly equivalent to the problem of finding the eigenfunctions of the Schrödinger equation.

At this point, a difficulty of interpretation appears. For in matrix mechanics $|q_{jk}|^2$ is interpreted as a transition probability, and therefore, according to the foregoing statements,

$$\left|\int \psi_j^* q \psi_k \mathrm{d}\tau\right|^2$$

should be a transition probability from state j to state k. No such interpretation has been made so far, and indeed it might at first be plausible to consider a solution of the matter-wave equation as defining a state of an electron which is "smeared" over all space with density $|\psi|^2$. One might then interpret $e\int q|\psi|^2 \mathrm{d}\tau$ as the electric dipole moment of a classical charge distribution, which would radiate if the dipole moment contained oscillating terms. That this is only a rude analogy will be seen in the next article, where the interpretation of wave mechanics will be made to coincide with that of matrix mechanics.

STATISTICAL INTERPRETATION OF QUANTUM MECHANICS

It has been rather characteristic of the theories of quantum phenomena that formal results in agreement with experiment have been obtained but without a satisfying interpretation. This was the case with the wave mechanics, as will be seen later in this section. Let us first, however, go farther back in history for another rather striking example.

Some of the earliest successes of the quantum theory had been concerned with situations in which waves appeared to act like particles. The photoelectric effect, for example, was explained by Einstein with the aid of the light-quantum hypothesis which assumes that light is transmitted in bundles of energy $h\nu$, ν being the frequency and h the Planck constant. This hypothesis completely contradicts the classical electromagnetic theory. It leads to difficulties, for example, in so simple a phenomenon as the variation of intensity of polarized light under examination by means of an analyzer. For suppose that light is made up of photons, each with its own position, velocity, frequency and plane of polarization, but otherwise indistinguishable. What will happen when a photon reaches the analyzer? If its polarization is parallel to the plane of transmission it certainly will be transmitted. If its polarization is perpendicular to that plane, it certainly will not be transmitted. But classical theory says, and experiment confirms, that on incidence of a photon whose polarization vector makes an angle of 45° with the plane of transmission only one-half the intensity will be transmitted. Since this is clearly impossible for a single photon, we must conclude that when many photons are incident, half of them are transmitted. But then, unless we wish to relinquish the classical idea of causality, we must attribute some difference in "internal parameters" to the photons, an assumption which directly contradicts our presupposition that the frequency, position, velocity and plane of polarization of a photon completely determine its properties. There seems to be no alternative but to give a single photon the *probability* one-half of passing through.

There are, however, some difficulties in the general application of such an idea in a consistent way, which will now be considered. One attempt to illuminate the situation was carried out by Bohr, Kramers and Slater[12] with a view to removing certain difficulties connected with the theory of emission and absorption of radiation. These investigators went so far as to permit violations of the principles of conservation of energy and of momentum, maintaining their

[12] Zeits. f. Physik 24, 69 (1924).

validity only in the average. They supposed that each atom is associated with a virtual radiation field consisting of simple harmonic oscillators having the frequencies of the possible transitions of the atom. The occurrence of transitions in an atom is then the result of interaction of the atom with its own virtual radiation field and with those of other atoms. A transition of atom A due to the virtual radiation field of atom B has a certain probability of occurring regardless of the activities of B. Thus energy and momentum are not conserved in individual processes, but only on the average. Conservation in the average comes about as the result of the fact that an atom which has been illuminated is assumed to send out waves of a secondary virtual radiation field which so interfere with the existing ones that conservation of energy and momentum is maintained in the large; for example, it becomes more probable that if atom A has emitted, atom B will absorb.

This theory was able to give a satisfactory qualitative account of the interaction between radiation and matter. But when quantitative calculations were made it predicted serious departures from observations. For example, the experiments of Geiger and Bothe[13] showed that the number of electrons scattered in hydrogen was far too small to be accounted for by the theory of Bohr, Kramers and Slater.

Born[14] was the first to suggest the statistical interpretation of wave mechanics held at present. In studying the application of the Schrödinger theory to the scattering of particles he noted that $|\psi|^2 d\Omega$ gave correctly the relative probability that a particle should be scattered into the element of solid angle $d\Omega$. He was thus led to the general conclusion: $|\psi|^2 dxdydz$ is the probability that the particle is in the element of volume $dxdydz$. This immediately makes plausible the normalization procedure chosen for the ψ function, for if $\int |\psi|^2 d\tau$ is not finite then the probability that a particle is *anywhere* in configuration space is not finite. Further, the semiclassical interpretation of $e\int q|\psi|^2 d\tau$ as the electric dipole moment of the atom is vaguely justified since $e|\psi|^2$, which was regarded by Schrödinger as an electron-cloud density, is now a probability density multiplied by a charge. Lastly, wave mechanics is then in complete accord with the matrix theory in its predictions. This enables one to deal more effectively with some of the difficulties previously noted, for example, the question concerning the photon's choice of transmission or absorption by the analyzer. For, according to the foregoing interpretation, classical wave laws are to be regarded as probability laws for photons or particles.

This completes the historical account of the development of ideas of the quantum theory. In presenting it, we have abstained from using the unifying bond of logical synthesis which is now available in the general operator theory of Dirac and Von Neumann, for its introduction *ab initio* would have done violence to history. The logical development, together with further refinements, will be reserved for the next article.

[*This is the first of three articles on atomic and molecular theory since Bohr.*]

[13] Zeits. f. Physik **26**, 44 (1924); **32**, 639 (1925).
[14] Zeits. f. Physik **38**, 803 (1926).

THE fact cannot be disputed that great discoveries regarding the behavior of the external world have been made by workers whose investigations in their field of research were not related in their own minds to any interest or belief outside it. But the effect of such segregated thinking has been to make science a departmental affair, having no influence on life and thought except indirectly through its applications. At the present time there is a movement in scientific circles aiming at securing for science a greater influence on human affairs, and even calling for a refounding of civilization on a scientific basis; but its advocates do not always understand that, as a necessary condition for the possibility of such a reform, science must be reintegrated into a unity with philosophy and religion.—E. T. WHITTAKER, presidential address, Royal Society of Edinburgh, 1942; *Science* **98**, 270 (1943).