Matrix and Wave Mechanics.

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IN an article on spinning electrons (NATURE, Jan. 15, p. 90) it was stated that recent progress in atomic physics is mainly due to two primary ideas: the use of a better model of the electron and of a better formal mechanics more suited than classical mechanics to the description of atomic phenomena. The changes and successes consequent on the adoption of this new model of the electron have already been described. We shall try here to give some sort of description of the ideas of the new mechanics and some of the successes to which they have led. We shall try at the same time to exhibit the two independent lines of thought which have led separately to the same new system of mechanics, but by such widely divergent paths that they have justifiably received the different names of *matrix mechanics* and *wave mechanics*. The equivalence of these two systems is perhaps the most striking and satisfactory feature of the present development.

The really fundamental features of atomic systems, as analysed with the help of the older quantum theory, are described in Bohr's first two postulates—the existence of stationary states and the frequency relation $E_1 - E_2 = h\nu_{12}$. Of these, the first is perhaps the most fundamental characteristic of all, for it is this characteristic, properly viewed, which imposes on us the particular change of the laws of mechanics which has had to be made. To describe an atom and its interaction with radiation we may agree (apart almost from all theory) that we must have (1) a set of stationary states, (2) a set of interconnexions between the stationary states which we may call transition probabilities. Collision interactions have proved harder to analyse with certainty than radiative, but we all agree that they fit perfectly into the same scheme. Our requirements, therefore, are very different from anything that can be satisfied by a system of particles obeying classical dynamics. Such systems do not have discrete stationary states. This difficulty was provisionally turned by Bohr by his third postulate ($J_u = n_u h$) which, of course, had striking successes. But these were only partial, for though the postulate gives us stationary states it cannot give us transition probabilities, except on occasions by temporary devices of interpretation based on the correspondence principle. Transition probabilities are essentially connexions between two states, whereas all the characteristics of a classical motion are functions of the one state alone. In short, a classical system in any (multiply periodic) state can be fully described by Fourier series, the coefficients and fundamental frequencies of which are functions of the parameters defining the state. An atom cannot be so described. Its coefficients must always be functions of two states, not one. Now that we know the answer it seems (as it should) very obvious—it is not a Fourier series or one-dimensional array of periodic terms with constant coefficients, but a matrix or two-dimensional array of such terms which is required to describe the atom. Any term of such an array depends on two integers m and n, defining the two states of the atom which the term connects or to which it belongs.

It may be helpful to interpolate here a few remarks on matrices. Matrices were introduced into algebra by Cayley, and form a branch of that subject interesting in itself, but hitherto not very familiar to physicists. The matrices with which the physicist is now concerned are, like determinants, square arrays of symbols, but, unlike the determinants, the matrix is not multiplied out. Instead, each symbol or term is regarded as a constituent member of the whole matrix. Thus, if we say that two matrixes are equal, we mean that each term of the first is equal to the corresponding term of the second. Matrices can be handled by a set of algebraic rules rather like the rules of the algebra of ordinary numbers. Many results go over into the new calculus unaffected, but there is one striking difference. The law of multiplication, which, loosely speaking, is that by which two determinants are multiplied together, is non-commutative—when matrix x is multiplied by matrix y the result, xy, is a matrix of which the terms are *not* the same as those of yx. The difference between these products provides exactly the necessary gap in the algebra into which the quantum theory can insert itself.

The question then arises, can one formulate a dynamics of matrices which is a natural generalisation of classical dynamics with classical dynamics as its limit, and yields rules for calculating the terms of any relevant matrix just like the classical rules for calculating any term of a Fourier series? Something, of course, must be given besides the laws of dynamics—that something is classically the potential energy function of the system, giving the field of force in which the particles of the system move, and we may demand that the same data shall suffice in the new form. This is equivalent to asking that everything shall be derived by direct unambiguous calculation from the Hamiltonian equation of the system, using generalisations of the classical laws. The quantum conditions of the older theory disappear and the essential h now enters the equations via the new non-commutative multiplication of conjugate canonical variables p and q, in the form

$$pq - qp = \frac{h}{2\pi i} \quad (i = \sqrt{-1}).$$

The answer to the opening question of the paragraph is, yes! Everything seems to work out as it should, as the work of Heisenberg, Born, Jordan, Dirac, and Pauli has abundantly shown.

The need for the matrix mechanics can nowadays perhaps be put forward as convincingly as possible in the manner adopted above, which shows that its constructs have direct physical counterparts. Every term in a matrix represents something ideally observable. Heisenberg was originally led to formulate the matrix mechanics by a deliberate development of a demand for ideal

observability of the counterpart of every construct, a demand which we have just seen to be satisfied by the matrix mechanics. He pointed out that the selected mechanical orbits of the older theory cannot satisfy this demand, because they cannot even ideally be directly presented to us for measurement. On the other hand, the frequencies and intensities of the light emitted, scattered, or absorbed by an atom, are observable in just this way. The older theory tried with partial success to derive the observed frequencies and amplitudes from the abstract theoretical ones. Heisenberg's new method was to do away entirely with every theoretical construct which could not be directly related to an observable property of the atom. Perhaps the distinction set up cannot always be rigidly maintained. It served at least to suggest to Heisenberg that we should stop trying to *interpret the results* of classical calculations and instead should *re-formulate the equations* of the motion, and re-formulate in such a way that every symbol has a physical meaning, just as in an astronomical problem in the classical mechanics. Physical meaning is no longer to be confined to interpretations of the final result. Since the matrix is the mathematical construct with the properties of any natural atomic co-ordinate, Heisenberg's idea led at once to the formulation of the matrix mechanics.

An entirely different point of view has been developed by Schrödinger. Following up the speculations of L. de Broglie, in which he drew an illuminating analogy between the free motion of particles such as electrons and groups of plane waves of a special type, Schrödinger came to examine more closely than before the analogy between mechanics and optics which formed in fact the basis of Hamilton's whole treatment of mechanics. The analogy due to Hamilton is that between the dynamics of particles and geometrical optics, let us say between the paths of particles and of light *rays*. We all know, however, that the propagation of light can only be adequately discussed by the optics of rays so long as the wave length of the light is very small compared with the dimensions of every obstacle encountered. Once this condition is broken diffraction effects occur, and we need the *wave* theory of physical optics with which to describe the phenomena. To this breakdown of the *ray* theory of light there has been hitherto no Hamiltonian analogy. In setting out to find such an analogy Schrödinger has formulated what we now call the wave mechanics. We shall not attempt here to describe his arguments but only the results. Instead of thinking of an atom as a set of particles, we retain from the particle picture only the potential energy V, and the masses of the particles, m. The atomic motion can be derived from a wave equation of the usual type

$$\text{Div. grad. } \psi + \frac{4\pi^2\nu^2}{u^2}\psi = 0.$$

In this equation u is the phase-velocity of waves of frequency ν, and ψ and its operators must probably be taken to refer to the configuration-space of the whole system, of dimensions equal to the number of freedoms. The Hamiltonian analogy demands, moreover, that u, E, the energy, and ν shall be connected by the relations

$$\nu = \frac{E}{h}, \quad \frac{1}{u^2} = \frac{2(E-V)}{E^2}.$$

A universal constant of action h enters naturally into the analogy; that it has exactly Planck's value is of course only fixed at a later stage. The resulting partial differential equation,

$$\text{Div. grad. } \psi + \frac{8\pi^2}{h^2}(E-V)\psi = 0, \quad . \quad . \quad (1)$$

must be conformed to by all wave forms which correspond to states of the atomic system with energy E. The wave function ψ must naturally be subjected to continuity and boundary conditions. To represent a possible stable state of the atom it is natural to suppose that ψ must satisfy (1) and besides be one-valued, bounded, twice differentiable over the whole configuration-space, and vanish at infinity. So far there has been no mention of discrete states. Any value of E would be admissible for which a suitable ψ exists. But we come now to the most beautiful point of Schrödinger's theory, for it appears in general that suitable ψ's only exist for a set of discrete values E_n of E, perhaps together with continuous ranges of values as well. The E_n are the energies of the various stationary states and the corresponding ψ_n the wave functions of these stationary states which specify what the atom is then doing.

For the simplest example let us take the linear harmonic oscillator. The wave equation then becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - 2\pi^2\nu_o^2 x^2)\psi = 0,$$

where ν_o would be the classical frequency of the oscillator. The smallest value of E for which a satisfactory ψ exists is $E_o = \frac{1}{2}h\nu_o$, and then

$$\psi_o = e^{-2\pi^2 m\nu_o x^2/h}.$$

We observe that ψ_o never vanishes, so that the corresponding wave is of infinite length and has no finite nodes. The next solution is $E_1 = \frac{3}{2}h\nu_o$, and then

$$\psi_o = 4\pi\left(\frac{m\nu_o}{h}\right)^{\frac{1}{2}} x e^{-2\pi^2 m\nu_o x^2/h}.$$

The wave has now one finite node at $x = 0$. The following values of E are $E_n = (n + \frac{1}{2})h\nu_o$, and the corresponding ψ_n have each one more finite node, so that the wave-length of the atomic oscillation gets shorter as n increases, and tends to zero as n tends to infinity.

For the earlier values of the set E_n it is impossible to speak of orbits and point electrons. For the later values the behaviour of the simple example above is general. The wave mechanics then degenerates, so that from a group of waves of various frequencies and directions we can build up a small bundle of waves, in phase only in the immediate neighbourhood of one point. This point of coincidence in phase will move with the group-velocity of the group of waves, and actually in the limit propagates itself along an orbit obeying the

laws of classical mechanics. In this limit orbits and point electrons again have a meaning.

Two constructs more different in conception than the matrix mechanics and the wave mechanics can scarcely be imagined, except that they are both generalisations of classical mechanics, retaining classical mechanics as a common limit. Schrödinger has suggested a physical analogy which perhaps shows their connexion. Suppose we have a stretched string of variable density. Then the wave mechanics finds the various ways in which the string can vibrate, and determines, *inter alia*, the nodes of the possible vibrations. These nodes are what we want, and the matrix mechanics is a calculus which determines them directly. It is perhaps not surprising that the ignoration of the rest of the string should lead to an unfamiliar procedure. Both schemes appear to make just those changes in the energy values of the stationary states which the facts were known to require. But the connexion between them is very deep and amounts almost, if not quite, to complete equivalence. To illustrate the connexion we must temporarily become technical. The change made in the wave mechanics is equivalent to deriving from the ordinary Hamiltonian equation of the system

$$H(q, p) - E = 0,$$

where (p, q) are canonical variables, the wave equation

$$\left[H\left(q, \frac{h}{2\pi i}\frac{\partial}{\partial q}\right) - E\right]\psi = 0 \qquad (2)$$

for the wave function ψ, instead of deriving the Hamilton-Jacobi equation

$$H\left(q, \frac{\partial S}{\partial q}\right) - E = 0$$

for the 'principal function' S. Equations (1) and (2) are different versions of the same equation. The p thus become differential operators. The close connexion between the operator algebra required in the wave mechanics and the matrix algebra of the matrix mechanics can be seen by a simple example. The commutative rule of the matrix mechanics already given becomes in the operator calculus, with $\frac{h}{2\pi i}\frac{\partial}{\partial q}$ for p,

$$\frac{\partial}{\partial q}(q\psi) - q\frac{\partial \psi}{\partial q} = \psi,$$

which is obviously satisfied. This example may perhaps remove the element of surprise at finding that Schrödinger has shown how to derive from the complete set of wave functions ψ_n for any atom a definite corresponding set of matrices which solve the problem of the same atom in the matrix mechanics. Whether the converse is true and the equivalence complete is less certain. At the moment it seems that matrix solutions may be possible which are not represented in the wave mechanics. The case in doubt is the rigid symmetrical top, for which in the matrix mechanics solutions appear to be possible both with whole and half quantum numbers, while only the former are allowable in the wave mechanics.[1]

It is probably futile at this stage to attempt to decide which of the new forms is the more fundamental. It will of course be found by the majority of workers that the wave mechanics, owing to the greater familiarity and convenience of its algebra, is the more powerful tool for solving any particular problem.

Let us now take a last glance at what the new mechanics in either form has done for us. In every case yet worked out completely, it has given us just exactly those changes of quantum numbers from the older theory, which had been forced on us already by the facts. Thus with the spinning electron the general theory of spectra is now an orderly whole. Weights, magnetic displacements, structure rules and intensity rules for multiplets and the complete form of the spectrum of the hydrogen atom are now at last correctly predicted by the theory. (It must be recorded that this requires us to assume that the spinning electron can be likened to a top with half quantum numbers. This assumption may require a trivial alteration of the wave mechanics in view of the wave theory of the top.) But the wave mechanics has done more than this. It has already led us successfully to the attack of problems in which the results of the older theory could not be described as qualitatively correct. Such problems are, for example, the calculation of the exact values of the higher terms of the spectrum of neutral helium and the calculation of the terms of the positive molecular ion of hydrogen. Of the latter it is too early to speak with certainty. The successful calculation of the higher terms of ortho- and par-helium by Heisenberg marks outstanding progress. In the course of this work he has been led to study with success the phenomena of resonance between similar atoms or between the necessarily similar electrons in one atom. These phenomena promise to be of outstanding importance in the further development of the theory, and have already thrown much light on Pauli's important empiral principle that no two electrons in an atom can have the same quantum numbers, and on the problems of statistical mechanics. Nor is this all. A successful attack has at last been opened on the quantum theory of collisions and on non-periodic orbits, largely by Born and Oppenheimer.

However abstract the new mechanics may yet seem to us, however incomplete our grasp of its fundamental principles, it is impossible to overestimate its value to theoretical physics. We have, at least in the simpler problems, ceased to grope, and fudge our results until they are useable. We have at last a general dynamical method to apply to any atom, which is capable of yielding us by direct calculation any result for which we may ask. We cannot yet expect all such results to be right, but we are confident that only minor modifications and generalisations will be required.

[1] For the matrix form, Dennison, *Phys. Rev.*, **28**, 318 (1926); the wave form, Reiche, *Zeit. f. Phys.*, **39**, 444 (1926). An interesting survey of wave mechanics is given by L. de Broglie, *J. de Phys. et le Radium*, **7**, 321 (1926). I have not attempted to enumerate the primary references, which will be familiar to students of the quantum theory.