THE NEW QUANTUM MECHANICS

J. H. VAN VLECK

Department of Physics, University of Minnesota, Minneapolis[1]

I. INTRODUCTION

The quantum theory has been revolutionized within the past three years by the development of a new quantum mechanics which is a far more comprehensive and satisfying theory than the original form developed by Bohr, Sommerfeld and others in 1913 and subsequent years. This remarkable new mechanics cannot be regarded as the product of any one man, but instead must be considered the result of the reaction of mind on mind among European talent in theoretical physics. This new quantum dynamics has, in fact, been developed in a great diversity of mathematical forms, which present a rather confusing array to the student beginning the subject. However, it must be emphasized that these various formulations, though different in mathematical structure, are in harmony with each other, and yield substantially equivalent results when applied to physical or chemical problems. The three main mathematical forms are the following: (1) the matrix theory of Born, Heisenberg, and Jordan, (2) Schroedinger's wave mechanics, (3) the so-called "transformation theory," based on kinematical indeterminism, developed by Dirac and Jordan, and interpreted by Heisenberg. Of these three formulations, the third is the most comprehensive, and includes the other two as special cases. In this paper I shall not endeavor to give the mathematical foundations of the quantum mechanics, as that would be too long a task. Instead I shall begin by explaining some of the philosophy and logic underlying the new theory and shall later survey some of its accomplishments. The philosophy may be summarized in the

---

[1] Present Address: Department of Physics, University of Wisconsin, Madison.

statement that at atomic distances our concepts of space and time must be revamped. In fact Heisenberg's epoch-making development of the matrix theory was spurred by Born's repeated emphasis to his colleagues at Göttingen that the reason the old quantum theory was then (1925) failing was that we were all too anxious to use the same concepts of space and time within the atom as in ordinary measurable large-scale events. Einstein and the relativists made us rescrutinize the space-time correlation at cosmic distances, and now the quantum theories bid us do this at the other extreme of size. Now, after all, the concepts of distance and time have a meaning only when we tell how they can be measured. This is very nicely emphasized in Bridgman's recent book, "The Logic of Modern Physics." At ordinary distances we determine lengths by means of measuring rods and time intervals by clocks. However, one cannot use a meter stick to measure the diameter of an atom, or an alarm clock to record when an electron is at the perihelion of its orbit. Consequently we must not be surprised if within the atom the correlation of space and time is something which cannot be visualized, and that models cannot be constructed with the same kind of mechanics as Henry Ford uses in designing an automobile. After all, within the atom there may be no geometry in the ordinary sense.

The goal of theoretical physics and chemistry must ever be to explain observable rather than unobservable phenomena. The presence in a theory of unobservable quantities or concepts, such as the "phase" or instantaneous position of the electron in its orbit in the old quantum theory, must be regarded as an element of weakness rather than strength in the theory. What the physicist observes about an atom is primarily its radiations, while the chemist measures its heats of combination, affinities, etc. We may say that we have a sound atomic theory when we have a set of a small number of mathematical postulates from which these observed things can be calculated correctly, even though it forces us to discard the usual space-time models. The new quantum mechanics is often characterized as a matrix theory. Why is this possible? Because what is measured about the radiations of atoms may be tabulated in the form of a matrix. The term "matrix" may sound rather formidable to those not mathematically trained, but I think I can intimate some of the uses of matrices if I point out their rough similarity to something with which most readers are doubtless more familiar; namely, a baseball schedule. In a baseball schedule the entry in row 3 and column 2 gives the date when team 3 plays team 2. Now a typical quantum theory matrix is an expression of the form

$$\left|\begin{array}{llll} A(11) & A(12)e^{2\pi i\nu(12)t} & A(13)e^{2\pi i\nu(13)t} & \ldots\ldots\ldots\ldots \\ A(21)e^{2\pi i\nu(21)t} & A(22) & A(23)e^{2\pi i\nu(23)t} & \ldots\ldots\ldots\ldots \\ A(31)e^{2\pi i\nu(31)t} & A(32)e^{2\pi i\nu(32)t} & A(33) & \ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots & \ldots\ldots\ldots & \ldots\ldots\ldots & \ldots\ldots\ldots\ldots \end{array}\right|$$

Here the entry in row 3 and column 2, for instance, gives information about a transition between a 3 and 2 quantum state, just as the analogous baseball entry does about the meetings between teams 3 and 2. Each entry or "element" in the above matrix contains two factors; viz., an amplitude factor such as $A(32)$ and a frequency factor such as $e^{2\pi i\nu(32)t}$. The frequency factor determines the frequency $\nu(32)$ of the spectral line corresponding to the transition between the 3 and 2 quantum states. The amplitude factor determines whether such a line is intense, i.e., whether the transition probability is large or small. The intensity is, of course, proportional to the square of the amplitude; the exact formula for Einstein's transition probability coefficient $a_{n\to m}$ is $a_{n\to m} = 64\pi^4 e^2\nu(nm)^3|A(nm)|^2/3hc^3$. The diagonal elements, such as $A(11)$, $A(22)$, etc., give the properties which are associated with one stationary state rather than with the transitions between two states, and represent average values since the periodic exponential factors are absent. In the new quantum mechanics the Bohr frequency condition is still valid, so that we may still set $h\nu(nm) = W_n - W_m$. The conservation of energy means that the energy W is a "diagonal matrix" in which the periodic, or off-diagonal elements are all zero.

The above matrix scheme may be regarded as simply a method of recording laboratory observations regarding the intensity and frequency of spectral lines, for when we measure intensity we determine the amplitude A and when we measure the frequency we determine ν. However, the crux of the theory is that the matrices can be calculated mathematically as well as measured experimentally, and wherever the difficulties of computation in the mathematics or of technique in the laboratory can be overcome there is excellent, in fact astounding, agreement between the theoretical and experimental matrices.

I shall not enter upon the matrix algebra and calculus with which it is possible to calculate the intensity-frequency matrices from the equations of motion, formulated of course in the matrix language. I shall simply mention that this matrix algebra is a non-commutative one, or in other words $px \neq xp$. Instead it is assumed that we have the quantum condition $px - xp = h/2\pi i$, where i denotes $\sqrt{-1}$, and h is Planck's constant, which thus enters as a measure of the "irrationality" of the theory, or peculiar non-commutativeness of the algebra. Here x is a coördinate of position, and p is its corresponding momentum. In the case of ordinary Cartesian coördinates, p is, of course, the product mv of mass and velocity. If we have such an extraordinary state of affairs as $xp = px$, then surely x and p cannot both be ordinary numerical quantities, for any ordinary numbers a and b of course possess the property that $ab = ba$. Instead p and x must be interpreted as matrices. From this Heisenberg and others conclude that *when dealing with amounts of action comparable with Planck's h, one cannot assign accurate numerical values simultaneously to a coördinate and its corresponding momentum. Thus within the atom it is meaningless to talk of a simultaneous position and velocity of the electron.* It is, of course, possible to attach a meaning to a simultaneous position and velocity of a large body, such as an automobile or even a dust particle, because in such we have an enormous number of quanta. Within the atom this is no longer the case. Experiments may be devised which will determine either x or p accurately, but not both x and p simultaneously. Instead if Δx be the error in specifying the position x, and Δp that in specifying the monentum p, then the product $\Delta x \Delta p$ of the two errors is always of the order of magnitude of Planck's constant, so that

$$\Delta x \Delta p \backsim h \tag{1}$$

This is the so-called *Heisenberg indeterminism principle,* and, like the second law of thermodynamics, is very useful in predicting what experiments are possible, and what are inherently impossible. Thus high precision in position implies low precision in velocity, and vice versa, for the error Δv is of the order $h/m\Delta x$ and therefore increases as we decrease Δx. We may illustrate this in a crude arithmetical way by considering the motion of an electron. If we specify that this electron is exactly at a given position, say the origin, at a given instant $t = 0$, then the error Δx is zero, and consequently the error Δv is infinite; this means that the velocity is inherently undetermined and so can range anywhere from $-\infty$ to $+\infty$; so that at any subsequent instant of time, say one second, there is an overwhelming chance that the electron be an infinite distance away. Suppose, however, that instead of aiming to specify accurately the position of the electron at $t = 0$, we merely say that then it is somewhere between $x = -\frac{1}{2}$ and $x = +\frac{1}{2}$; then $\Delta x = 1$, and Δv is of the order h/m; now $h = 6.55 \times 10^{-27}$, while for an electron $m = 0.9 \times 10^{-27}$ hence the error Δv in velocity is 6.55/0.9, or about 7 centimeters a second. One could then not give accurately a numerical velocity, say 300 cm./sec., but one could say that the velocity lay somewhere between about 296½ and 303½ cm./sec., so that after 1 second the electron would be between about $x = 296$ and $x = 304$. (This is only a very crude calculation; a more accurate study leads to a Gaussian error curve.)

Another, and better illustration of the Heisenberg indeterminism principle is furnished by an attempt to measure simultaneously both the position and frequency of a packet or wave train of light energy. A prism will record a train of waves as being strictly monochromatic only if the train is infinitely long; the termination of the optical disturbance after a finite time interval will cause an interruption in periodicity and make the light in the prism appear diffuse. If the train contains n waves, it can be shown that the diffuseness in its spectrum will be of the order $1/n$, or in other words the fractional error $\Delta\nu/\nu$ in determining the frequency is comparable with $1/n$. If, following the light quant theory, we assign a packet or "quant" of light a momentum

$p = h\nu/c$, then Δp is of the order $h\nu/cn$. On the other hand the length of the wave train is $n\lambda$, where λ is the wave length, and consequently the position of the light is indefinite to an extent $\Delta x = n\lambda$. As $\nu = c/\lambda$, the product $\Delta x \Delta p$ of the two errors is of the order of Planck's h.

Because of the ambiguity resulting from the Heisenberg indeterminism principle, the future of a dynamical system can never be predicted with certainty. Instead only the *probability* that an electron be in a given configuration can be determined, and the future is only statistically determined. This is in sharp contrast to the "causality principle" of classical dynamics, whereby the subsequent history of a dynamical system is determined if we know its initial coördinates and velocities. The uncertainty as to subsequent motion in quantum mechanics is however, perhaps not due so much to failure of the ordinary cause and effect relation as to the inevitably indeterminate character of the initial conditions, as by the Heisenberg indeterminism principle one cannot give both the initial position and velocity accurately. This contrast between classical determinism and quantum indeterminism should interest the philosopher as well as the chemist or physicist, and is indicated graphically in table 1. Thus quantum mechanics is essentially a means of calculating the probabilities of events. In a labora-

TABLE 1

CLASSICAL DETERMINISM	QUANTUM INDETERMINISM
Given initially x, y, z, v_x, v_y, v_z	Given v_x, v_y, v_z accurately; then x, y, z are undetermined (i.e., all values of x, y, z are equally probable), or vice versa x, y, z given and v_x, v_y, v_z undetermined
↓ (Arrow indicates calculation by classical dynamics)	↓ (Arrow indicates calculation by quantum dynamics)
Accurate determination of x, y, z, v_x, v_y, v_z at all subsequent times	Only statistical determination of x, y, z, v_x, v_y, v_z at subsequent times

tory experiment one performs certain operations and observes certain consequences. The goal of a theory must ever be to explain "what goes out" in terms of "what is put in." At first thought it may appear as if the purely statistical correlation between cause and effect demanded by quantum mechanics is contradictory to the precision with which experiments can be performed. Experiments with large scale quantities, however, involve so many quanta that the Heisenberg indeterminism is obscured, and so there is only apparently a "sharp" correlation. On the other hand, our ordinary atomic or molecular experiments are in most cases fundamentally statistical in character, as what is measured is not particular values of the dynamical variables, but rather *average values* of certain functions of these variables, or else *distributions* telling how they are scattered over a wide range of values. Such statistical quantities have a meaning in and can be calculated with quantum mechanics, and so there is no contradiction of Heisenberg's principle. This idea is il-

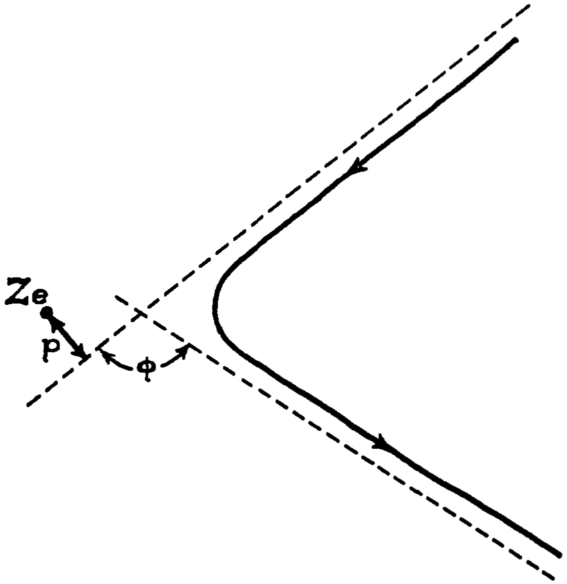

FIG. 1

lustrated in the next paragraph by a discussion of Rutherford's familiar experiment on the scattering of alpha particles by thin foils.

According to the classical theory of Rutherford's experiment, an alpha particle is deflected through a large angle in going through the gold foil if it happens to pass close to one of the gold atoms, and so is subject to large forces to bend it out of its course. On the basis of classical mechanics and the inverse square law it can be shown that the angle of deflection ϕ shown in figure 1 is connected with the closest distance of approach p which would result were the alpha particle to continue undisturbed in a straight line, by means of the relation

$$\cot \tfrac{1}{2}\phi = \frac{p\,Mv^2}{2Ze^2} \tag{2}$$

Now assuming that all distances of approach are equally probable, or, more precisely, that the probability of the alpha particle approaching between distances p and dp is proportional to the area $2\pi p dp$ of an angular ring of inner and outer radii p and $p + dp$ respectively, it is often shown that the number dN of alpha particles scattered between angles ϕ and $\phi + d\phi$ is

$$dN = \tfrac{1}{4}\pi\, Nnt \left(\frac{4Ze^2}{Mv^2}\right)^2 \operatorname{cosec}^2 \tfrac{1}{2}\phi \cot \tfrac{1}{2}\phi \, d\phi \tag{3}$$

where N is the number of alpha particles passing through the foil, t is the thickness of the latter, and Z is the atomic number of the atoms of the foil. n is the number of gold atoms per unit volume of foil, while M and v are the mass and velocity of an alpha particle. Formula (3) *which does not involve* p gives the so-called "distribution in angle" of the scattered alpha particles, and that is what is observed experimentally by counting scintillations on a fluorescent screen set at various angles of recoil.

Let us now turn to the quantum interpretation of the Rutherford scattering. Let us assume the initial beam of alpha particles is perpendicular to the foil, and that these particles have a common velocity. Then $v_x = v_y = 0$, while v_z equals v, supposing for simplicity that the face of the foil is the x-y plane. What does this mean?—that we are specifying all the velocity components of the alpha particles, and consequently by the Heisenberg indeterminism principle we cannot specify simultaneously the position coördinates x, y, z. Instead in a beam with definite velocity and direction the positions of the individual alpha particles within the beam must be regarded as entirely undetermined and it is hence meaningless to say whether an individual particle passes close to or far away from a scattering center (gold nucleus) of the foil. However, we have seen that the quantum mechanics determines the future motion of a particle in a statistical way. In the present problem this means that one can compute from quantum principles the probability that an alpha particle will recoil at a given angle. The "distribution in angle" of the scattered beam is thus determined, even though the concept of closest distance of approach p to the scattering center loses its meaning. This is in accord with experiment, for what is observed in the scintillation-counting is the relative abundance of different angles of recoil ϕ (cf. fig. 1), whereas there is no way of really measuring the quantity p.

The classical treatment of atomic problems introduces many concepts, such as the distance of approach p in the Rutherford experiment, which are not observed and hence not needed, whereas the quantum viewpoint usually divests the analysis of these superfluous quantities. This may be illustrated by the following rather foolish story. One time there was an Arabian chieftain who bequeathed to his oldest son one-half his camels, to his next oldest one-fourth of his camels, and to the third or youngest son one-sixth of them. There was great consternation in the tribe, because it was discovered at his death that he left only eleven camels, and fractional numbers of camels such as 11/2, 11/4 and 11/6 were of no particular value. The matter was finally referred to an old sage of the tribe, who said, "I have only one camel, but am growing old, and have little more use for camels. I will therefore contribute my camel to the total if this will facilitate the apportionment." This simplified things tremendously, for the fractions 12/2, 12/4, 12/6 were all integers.

To the oldest son, for instance, the sage said, "Half of twelve camels is six. Take these six and be happy, for thou hast more than thy share." Similarly the two other sons were apportioned 3 and 2 camels, or more than their quota. But, behold, the beauty of the whole procedure is that $12/2 + 12/4 + 12/6 = 6 + 3 + 2 = 11$, so that the old sage received his camel back. Now the classical treatment of atomic problems revels in superfluous or non-observable variables which like the twelfth camel in this story are put into the analysis and then taken out again. The distance of approach, p, in the classical theory of the Rutherford scattering experiment is such an auxiliary camel, for although it is a variable put in the original equation (2), it is soon taken out of the analysis by assuming that all positions of approach are equally probable, and then integrating over all values of p from zero to infinity. This assumption is a statistical one which is not implied by the classical mechanics without supplementary hypotheses concerning probability, but is necessary to get the final distribution formula (3), which is what is actually verified in the laboratory. The quantum mechanics, on the other hand, has the advantage that it is fundamentally statistical in nature, and need not be supplemented by further assumptions concerning the probabilities of different values of quantities which cannot be observed. Instead the quantum treatment yields the final formula (3) without the intermediary of the microscopic, non-observable distance p.

Twentieth century developments, especially relativity and quantum mechanics, have forced the physicist to rescrutinize the real meaning of the variables entering in his equations and in so doing he has discovered that many customary concepts (e.g., absolute time, in cosmogony and instantaneous position of the electron in atomistics) which are as superfluous as the twelfth camel in the preceding story, and which have sprung up because one is too prone to visualize either cosmic or atomic space and time in terms of the same picture as for ordinary measurable distances. I wonder whether the chemist has not also suffered from the same kind of prejudices and likewise introduced concepts which prove to be hallucinations when put to close scrutiny.

The chemist has often thought that he has found strong evidence on the instantaneous positions of electrons, and first and last there has been considerable controversy as to whether the facts of organic chemistry can be explained as well by assuming that the electrons are moving, as the physicist would like, as by supposing that they are standing still. However, is it really necessary to suppose that the structural bonds of the organic chemists represent instantaneous positions of the electrons, or would it not do just as well to suppose that they represent average positions, for the mathematics indicates that it is the average rather than instantaneous positions of the electrons which determine whether the nuclei are in equilibrium? Or going a step further from a picture, would it not perhaps do to suppose that these structural diagrams are simply a way of indicating diagrammatically some of the symmetry properties of the solutions of Schroedinger's wave equation, to be discussed later? Recent work of London and Heitler seems to indicate that the systematization of chemical compounds is closely related to the group theory of mathematicians. However, one must not necessarily infer from this that the group characteristics are the geometrical characteristics. There is, of course, much evidence for tetrahedral models of the carbon atom, but does this necessarily mean that the instantaneous positions of the electrons project out in four directions; could not this evidence mean that this symmetry is only true of average positions of the electrons, or even that there is some dynamical function, important for the mechanics of chemical combination, but without any immediate geometrical significance, which is symmetrical mathematically in the variables representing the coördinates of the four electrons?

According to the theoretical physicist, one has no right to speak of the *instantaneous* position of the electron in its path within the atom, for if one knew where the electron were located each successive instant of time, one would know both the position and velocity of the electron, which we have seen is contrary to the Heisenberg indeterminism principle. It can, however, be shown that it is legitimate to introduce the concept of the *average* position of the electron; such averages are, in fact, given by the diagonal elements of properly chosen Heisenberg matrices. It is these average positions, and not the instantaneous ones, which are revealed by experiments on the scattering of x-rays of the type which Professor Jauncey has so interestingly discussed in another paper of this symposium. Clearly the time of scattering of an x-ray quantum cannot be measured with any accuracy compared to the average time required for the electron to move from one side of the atom to the other. Chemists have often asked me this question, "Where are the electrons located in, say, the bond between two hydrogen atoms to form a hydrogen molecule. Does each electron remain with its own nucleus, or

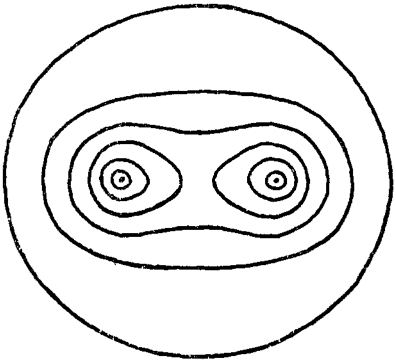

FIG. 2. ATTRACTION

are the two electrons shared 50–50 by both nuclei." According to the quantum mechanics, the latter alternative comes the closer to the true state of affairs, for in the hydrogen molecule the average electronic charge distribution is symmetrical with respect to the two nuclei, and the two electrons are continually exchanging places, so that it is impossible to say which electron belongs with which nucleus. When the hydrogen atoms are too far apart to form a molecule, say at a distance 3×10^{-7} cm. comparable with the distances of approach between molecules in the kinetic theory of gases, the exchange of places is very infrequent, only about once in 10^{30} years on the average, whereas when the atoms are so closely knit together as to form a molecule, the exchange transpires on the average about 10^{10} times per second! The statistical or average charge distribution in the hydrogen molecule can be calculated directly from the quantum postulates, and is shown in figure 2, taken from a paper by London. The contour lines in these figures represent the statistical charge density. Thus this density is large where the lines are close together, and small where they are far apart. The densest region is, of course, in general near the two nuclei. The mathematical analysis shows that there are two solutions of the Schroedinger wave equation corresponding to the interaction between two hydrogen atoms. In one of them, shown in figure 3, the forces exerted on the nuclei are entirely of a repulsive nature. The meaning of this is that two hydrogen atoms may be brought into contact without necessarily forming a molecule.

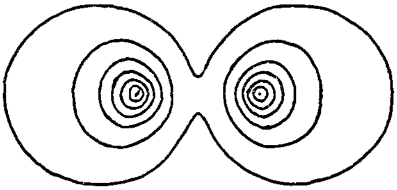

FIG. 3. REPULSION

In the other solution, figure 2, there is attraction as well as repulsion, and this is what makes possible the formation of a stable molecule. It is seen from figure 2 that in this other solution the negative electronic charge tends to pile up between the two nuclei, and it is the attraction of this negative charge which tends to bring the nuclei together and offsets the purely repulsive forces which exist between two positive charges by themselves. In the solution shown in figure 2, the nuclei are in positions of equilibrium, whereas in figure 3 they will fly apart.

The concept of a statistical or average charge density, such as is shown in figures 2 and 3, can perhaps be rendered more graphic by the following comparison. Supposing one were to photograph a swarm of fireflies at night by means of an exceedingly sensitive camera. If one were to take an instantaneous photograph or "snap-shot," each firefly would appear as a bright point on the photographic plate. If we took snap-shots at frequent intervals we could then trace the motion of each of the flies. Suppose, however, that instead we were to take a time exposure extending over a long period. Then the luminous points would be blurred out into a cloud of light upon the plate. The cloud would be brightest where the fireflies are most apt to congregate. Now the information which it is possible to obtain about the motion of the electron within the atom in quantum mechanics is analogous to that given by the time exposure in the firefly illustration. The statistical charge density corresponds to the density of the luminous cloud. Efforts have sometimes been made to interpret the electron in quantum mechanics as itself a sort of nebulous body spread over the entire atom, but that is no more correct than to say that a firefly is a bright cloud extending over a large distance. In either case it is only the time average of position that has the cloud or fluid-like appearance. The essence of the Heisenberg indeterminism principle is that a "snap-shot" of the electronic motion is inherently impossible, for position cannot be instantaneously specified if the energy has a definite value corresponding to a stationary state of the atom. It appears almost paradoxical that although one can never say *when* an electron is in a given position within the atom, one can nevertheless talk of the fraction of the time that it is in this position, for clearly the places of large average charge density are those where the electron spends a large fraction of its time.

II. THE WAVE VERSION

The new quantum mechanics is often spoken of as a "wave mechanics." Now the concept of waves has certainly not appeared in any of the material which I have presented so far, and so one may be wondering where this quantum theory acquires an undulatory nature. In order to introduce the wave idea it is necessary to probe a little further into the mathematical formulation of the theory. In this there is involved a function $\psi\,(x, y, z)$ which has the property that $|\psi(x, y, z)|^2\,dxdydz$ measures the probability that the electron be in a small element of volume

$dxdydz$. Thus the square of the magnitude of this function ψ may be regarded as proportional to the statistical charge density which we have already discussed at length. The places where the electron is likely to be located are those where ψ is large, while those where ψ is numerically small are seldom visited. The function ψ is determined by solving the differential equation

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(W-V)\psi=0 \qquad (4)$$

Here M is the mass of the particle, $V(x, y, z)$ is its potential energy in a field of force, and W is its total energy, a constant quantity. This is the Schroedinger wave equation, which although only two years old, is one of the most celebrated equations of mathematical physics. Its solution $\psi(x, y, z)$ which determines the statistical charge density, is called the "Schroedinger wave function." The term "wave" is used, because in many problems it is found that ψ exhibits wave-like recrudescences of maxima and minima. I shall not attempt to give the mathematics which Schroedinger used in getting this equation. Following a cue given by suggestive work of de Broglie, he found that this equation could be obtained by assuming that the modifications which it is necessary to introduce into the equations of classical mechanics to get those of quantum mechanics are very similar to those which it is necessary to introduce in the theory of geometrical optics to get that of physical optics. Now geometrical optics does not reveal the undulatory nature of light, but can usefully be employed as long as the optical objects are large compared to the wave-length, and we do not probe into the interference and diffraction phenomena in which the wave effects appear. Thus x-rays have such short wave-lengths that most experiments on their propagation can be described by geometrical optics, as it is a sensitive and difficult experiment to show the diffraction of x-rays. Now Schroedinger held that ultimately mechanics, like optics, has a wave-like structure, and that the reason ordinary large-scale experiments can be described by classical mechanics is because all the objects are large compared to the wave-length. On the other hand, in atomic phenomena the diameter of atoms is comparable with the quantum wave-length, and so it is necessary to use a new quantum mechanics which is the analog of physical rather than geometrical optics. This optical analog is exceedingly alluring, and it is dramatic to say that "Schroedinger has done for mechanics what Fresnel has for optics." However, it must be mentioned that it is possible to derive the equation (4) from the matrix theory without any appeal to the optical analog or the wave idea. The correlation with the matrix theory is, in fact, perhaps the most rigorous way of deriving (4). At first it seems like a far cry from the wave viewpoint to the Heisenberg matrices which we introduced near the beginning of our discussion. However, it can be shown that all the matrix elements can be determined by evaluating certain integrals involving the wave function ψ. In particular, if $x(nm)$ be the matrix elements of a coördinate of position x, it can be shown that

$$x(nm) = \int\int\int \psi_n^* \, x \, \psi_m \, dxdydz, \tag{5}$$

where the integration extends throughout all space, while ψ_n and ψ_m are respectively the wave functions belonging to the stationary states n and m. ψ^* means the complex conjugate of ψ. One way of interpreting the wave function ψ is that it is simply a mathematical tool for calculating the matrix elements by means of equation (5). This formal mathematical interpretation of ψ, however, does not give ψ the physical significance which it deserves. At the same time it must be mentioned that while Schroedinger has at various times expressed the hope that his wave mechanics would remove the "irrational" or discrete characteristics of our atomic dynamics and make it possible to construct an essentially classical model of the atom without the rather forced introduction of sudden quantum jumps, the consensus of opinion of theoretical physicists today seems to be that we cannot keep our classical pictures in dealing with small scale phenomena, and that instead the language of probabilities must be used with all the indeterminism involved in Heisenberg's principle.

Now phenomena described by means of differential equations in general exhibit a continuous rather than discrete character, for all of nineteenth century mathematical physics, with its continuous media, etc., was constructed primarily on differential equations. Consequently one may at first wonder how quantum discreteness can come out of formulation of atomic dynamics by means of differential equations. The answer is that we must admit only solutions of (4) which are of what I may dub of a "civilized character," and such solutions in many instances form a discrete succession even though in general a differential equation admits a continuous infinitude of solutions. By a "civilized solution" I mean one in which the wave function ψ is continuous, single-valued, and finite throughout all space. Most solutions do not possess this property. Very often, for instance, ψ increases without limit as we go out to infinity, and such a solution is worthless, as it would mean that the statistical charge density is greatest at infinity, and that the electron is infinitely far away most of the time. Instead it can be shown that there will be a civilized solution only if certain particular values be assigned to the constant W appearing in equation (4). Such values are called "Eigenwerte" or "characteristic values" by mathematicians, and the corresponding solutions ψ are the "Eigenfunktionen" or "characteristic functions." Schroedinger's papers bear the title "Quantisierung als Eigenwertproblem." These "Eigenwerte" are the values of the W's to be used in the Bohr frequency condition $h\nu = W_1 - W_2$, and thus *the quantized values of the energy are those which make Schroedinger's wave equation have a civilized solution.* Sometimes these allowed values of W form a continuous rather than discrete succession, and the quantum mechanics is thus able to explain very elegantly, directly from the fundamental postulates, the existence of both continuous and line spectra. When, for instance, the electron is completely liberated from a hydrogen atom, it can be shown that the "Eigenwerte" are continuous, and this means that when a free electron is captured by a hydrogen nucleus a continuous spectrum is emitted, whereas a line spectrum is emitted when there is a transition of a bound electron between two stationary states. This is in accord with the fact that beyond the "convergence frequency" of spectral series, corresponding to ionization of an atom, a continuous spectrum is observed experimentally.

How the requirement of a civilized solution ψ quantizes the energy may be illustrated by considering a particularly simplified dynamical system; viz., a dipole of moment of inertia I constrained to rotate in a plane. If φ denote the angle through which the dipole rotates, it can be shown that here the wave equation reduces to

$$\frac{\partial^2\psi}{\partial\varphi^2} + \frac{8\pi^2 I}{h^2} W\psi = 0$$

This is a differential equation of the same type form as that of simple harmonic motion, and has the solution

$$\psi = A \cos\left[(8\pi^2 IW/h^2)^{\frac{1}{2}} \varphi - \epsilon\right]$$

where A and ϵ are constants of integration. Now to be "civilized," the function ψ must be single-valued, and this means that ψ must revert to its original value when we go once around a circle and return to the starting point. Hence we must have $\psi(\varphi + 2\pi) = \psi(\varphi)$. Now a function of the form $f(\varphi) = A \cos (k\varphi - \epsilon)$ possesses the property that $f(\varphi + 2\pi) = f(\varphi)$ only if k is an integer n, as the cosine reverts to its original value when its argument increases by an integral multiple of 2π. Hence, as in our problem $k = (8\pi^2 IW/h^2)^{\frac{1}{2}}$, we must have $W = n^2h^2/8\pi^2 I$, where n is an integer. This is nothing other than the familiar so-called Deslandres formula for the energy of a rotating dipole in the quantum theory,—a formula which is constantly being used for describing rotational energy levels in molecular spectra. It should be mentioned that as we have derived the formula, the quantum number n is a whole integer, whereas to secure accord with experiment it is necessary for n to be a "half quantum number." However, when the rotating dipole is treated as a three- rather than two-dimensional problem, as of course it must be, the formula with half quantum numbers comes correctly out of the new mechanics, whereas it did not in the old quantum theory.

The mathematics which is used in solving Schroedinger's equation shows a rather striking similarity to that used in solving many problems in what I may term "nineteenth century mathematical physics"—problems in elasticity, vibrations of ropes and membranes, and the like. In fact many of the equations have already been solved before advent of the quantum theory by workers in elasticity, etc., and a very nice resumé of such classical "Eigenwertprobleme" is given in Courant and Hilbert's "Methoden der Mathematischen Physik," a book which is constantly being quoted in papers on the new quantum theory. For this reason, the wave formulation of the new mechanics is apt to appeal most strongly to mathematical physicists who have been trained primarily along the line of classical nineteenth century mathematical physics, whereas the matrix formulation appeals more strongly to those who have been trained in the mathematics of the old quantum theory, especially the correspondence principle. In classical vibration problems the solutions of the differential equations must fulfill certain so-called "boundary conditions"—the displacement, for instance, must vanish at the ends of a rope if it is fastened at either end. The differential equation for a uniform rope is

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2}$$

where v is a constant. If now we assume a periodic solution $y(x, t) = u(x) \cos (2\pi\nu t - \epsilon)$, then

$$d^2u/dx^2 = -4\pi^2\nu^2 v^{-2} u$$

The solution of this equation is

$$u = A \cos (2\pi\nu x/v) + B \sin (2\pi\nu x/v)$$

Let l be the length of the rope. Since the rope is fastened at either end, the displacement y must vanish at $x = 0$ and also at $x = l$. The first of these two conditions shows immediately that A equals zero, as the cosine does not vanish at $x = 0$. The vanishing of y at $x = l$ shows that $\sin (2\pi\nu l/v) = 0$ and hence $2\pi\nu l/v = n\pi$, where n is an integer. Thus the possible vibration frequencies of the rope are $\nu = nv/2l$ $(n = 1, 2, \ldots .)$, and form a definite discrete succession (fundamental, first harmonic, second harmonic, etc.). These are the "normal modes of vibration," and the general motion is the superposition of all of them. The important thing to be noted in this classical rope problem is that the boundary condition that the displacement vanish at the two ends restricts the vibration frequencies to certain particular values. Now in much the same way in quantum mechanics the energy and hence the spectroscopic frequencies given by the Bohr frequency condition are restricted to certain particular values by the requirement that ψ be a civilized function throughout all space. The latter requirement can be regarded as a boundary condition, for mathematicians show that at singular points of a differential equation, where the general solution ceases to be analytic, the requirement that ψ be merely finite, without specifying its numerical value, is as much of a restriction as can be imposed at these points, and so can be regarded as a boundary condition at such points. Thus it is in a sense the boundary conditions which limit the number of appropriate solutions of Schroedinger's equation and restrict the energy to certain particular quantized values. Hence quantization is formally similar to a classical boundary value problem. It is tempting to say that the characteristic or Schroedinger wave functions represent the normal modes of vibration of the atom, just as do the various harmonics in the rope problem, but this is a bit misleading, as the spectroscopic frequencies are proportional to the difference of two energy values, and so always involve a pair rather than just one stationary state or wave function.

A particularly simple case of the Schroedinger wave equation is that which corresponds to an electron moving in a straight line, say the x-axis, in the absence of any external field of force. If we set the potential energy V equal to zero, and assume that ψ is a function only of x, the wave equation (4) reduces to

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 mW}{h^2}\psi = 0$$

The solution of this is

$$\psi = A \cos\left[(8\pi^2 mW/h^2)^{\frac{1}{2}} x - \epsilon\right]$$

or if we set $W = \frac{1}{2}mv^2$, we can write this as $\psi = A \cos [2\pi mvx/h - \epsilon]$. Now the expression for a standing[2] wave of wave-length λ is $A \cos [2\pi x/\lambda - \epsilon]$. Hence the solution of the wave equation can be regarded as a plane wave of wave-length

$$\lambda = h/mv \tag{6}$$

That an electron beam has a wave-length of the value (6) is shown very nicely in the already celebrated recent experiments of Davisson and Germer. They show that when an electron beam is scattered by reflection from a single crystal of nickel, the spatial distribution of the scattered electrons is the same as that of the scattered x-rays in Laue's or Bragg's experiments on the scattering or reflection of x-rays from a crystal, provided the wave-length of the x-rays is assumed to have the value given by (6). Thus the electron scattering resembles optical scattering for a wave-length $\lambda = h/mv$. In general the quantum mathematics of scattering of an electron beam by impact with atoms is very similar to a classical diffraction problem in optics. Hence there is a good deal of talk at present about "waves of matter," and it is even said that the electron is a wave. This, however, is not quite right. It is much better to say that instead we have waves of probability which govern the motion of the electron, for we have seen that the Schroedinger wave function determines a statistical charge density, and the directions in which the scattered or diffracted wave has a large amplitude are those in which the electron is likely to be scattered. The diffracted wave, like a ripple, extends out in all directions, whereas an

---

[2] The Schroedinger waves appear here to be of the standing rather than moving type, because we have not used a rather more general form of his equation which allows for explicit appearance of the time, and in which ψ is a function of x, y, z, t, rather than just x, y, z. The dependence on the time in a conservative system proves to be of through a purely exponential "time factor," $e^{2\pi iWt/h}$ and makes the waves moving rather than stationary. The absolute value of the time factor is unity, and so does not affect the value of the statistical charge density.

individual electron can, of course, recoil in only one direction. The wave amplitudes simply determine the angles in which it is likely to go.

The Davisson-Germer experiments and the theory of quantum mechanics show that the motion of matter has undulatory as well as corpuscular aspects. Conversely the Compton effect shows that in some respects radiation exhibits a corpuscular nature rather than the exclusively undulatory nature presupposed in the wave theory of light. Thus matter and radiation both exhibit at the same time the traits of corpuscles and of waves. It has often appeared as if there were a flat contradiction between the corpuscular and wave viewpoints, especially in the case of radiation. However, the statistical interpretation of motions demanded by quantum mechanics at last removes this dilemma, and to a large extent the motions of particles, either of matter or of radiation, can be regarded as guided by waves of probability. This situation is reminiscent of the old theory of Bohr, Kramers, and Slater, but with the difference that the laws of conservation of energy and momentum now hold accurately, a possibility later suggested by Slater himself. The work of Dirac, in particular, is very important in showing how the properties of the electromagnetic field can be derived from quantum mechanics and statistics.

If the motion of *matter* is attended by wave-like maxima and minima, it seems at first a little surprising that this fact was not unearthed experimentally before the recent experiments of Davisson and Germer, whereas the wave nature of *light* has been known for over a century. Why should not, for instance, the quantum wave length h/mv appear in the classical experiments of Rutherford on the scattering of alpha particles? The explanation is that since the wave-length is inversely proportional to the mass, it is about 8000 times smaller in the scattering of alpha particles than in that of electrons. Hence in Rutherford's experiment the wave maxima and minima lie too close together to have been detected, and so it is possible to describe the experiment by a mechanics analogous to geometrical optics, in other words classical mechanics. Because of the short wave length the classical result has had the good fortune to agree with the quantum one, and so could explain Rutherford's experimental results, whereas in the Davisson-Germer experiment this agreement disappears and the classical theory breaks down.

III. WHAT THE QUANTUM MECHANICS HAS ACCOMPLISHED FOR THE PHYSICIST

I shall now turn abruptly from this rather sketchy discussion of some of the underlying ideas of the new quantum theory to a recital of some of the things which it has accomplished in the way of applications. As this new dynamics has been developed primarily by physicists rather than chemists, most of the applications are naturally to physical rather than chemical problems. Considering that the new quantum mechanics is only celebrating its third birthday, the success which it has had in "clearing up" problems that baffled the old quantum theory is little short of miraculous. One reason for this triumph is, of course, the large number of physicists that have been engaged in working over well-known material with the aid of the new theory. Ten of the items which the new quantum mechanics has to its credit are the following:

1. *Everything that the old quantum theory did correctly.* Although the old quantum theory had many inadequacies, it did nevertheless furnish a clue to the interpretation of an enormous mass of material, especially spectroscopic. The old theory was noted, perhaps more than for any one thing, for quantitative explanation of the spectra of hydrogen and ionized helium. Exactly the same numerical formulas, notably the Balmer formula for spectral series, Sommerfeld's fine-structure formula and the Epstein-Schwarzschild expression for the Stark effect, are obtained with the new theory as with the old. In non-hydrogenic atoms the presence of a large number of electrons usually makes it impossible to calculate quantitatively the position of spectral lines. But we all know that in the old quantum theory the concepts of stationary states, and of the Bohr frequency condition with its attendant Ritz combination principle, were exceedingly fruitful in explaining qualitatively the facts of non-

hydrogenic spectra, and in unravelling a maze of spectroscopic data which it would have been hopeless to correlate otherwise. All this can be done equally well with the new mechanics. Although we cannot attach as much reality and vividness to electron orbits in stationary states as previously, nevertheless the new theory has the vital feature of a discrete succession of energy levels, with spectroscopic frequencies proportional to their differences. Thus we can still keep our beloved energy level diagrams, selection principles, and the like. In particular, the fundamental relation $Ve = h\nu$ correlating critical potentials V with spectroscopic frequencies ν still remains valid.

2. Fine details of the hydrogen and ionized helium spectrum not explained previously. Although the old quantum theory gave in the main a very successful explanation of the hydrogen spectrum, it became increasingly obvious that in certain minor respects the old Bohr theory was in pretty flat contradiction with experiment. Among these may be mentioned the observation of a so-called "Paschen-Back" effect, or merging of the fine-structure in an extremely intense magnetic field, and the detection of certain fine-structure components which violated the selection principle. Also in some cases, especially in the Stark effect, the old theory gave more rather than fewer lines than were necessary to explain the experimental results, and to get rid of superfluous components it was necessary to rule out rather arbitrarily certain states on the ground that in them the electron would collide with the nucleus. All these difficulties disappear with the advent of the new quantum mechanics.

3. The spectrum of neutral helium. Although the old quantum theory dealt with ionized helium pretty successfully except for the items (2), the neutral helium atom, on the other hand, was a hopeless stumbling block to it. Dozens of models were proposed for the arrangement of the electron orbits in neutral helium, but none agreed with the observed critical potentials and optical frequencies. All this is now changed, for Heisenberg has calculated the term values of the excited states of helium with the new mechanics, while Slater, Kellner, and Sugiura have all independently computed the energy of the normal state. The agreement which they find with experiment is gratifying when it is considered that the calculations can only be made approximately because in neutral helium we have all the mathematical difficulties of the celebrated three-body problem.

4. A theory of intensities as well as frequencies. The old quantum theory was one-sided. It gave a perfectly definite scheme for calculating the frequencies of spectral lines, but it furnished no means of determining quantitatively their intensities, although actually the two things must be connected. In the old theory we could guage qualitatively the intensity of spectral lines by appealing to the correspondence principle, but this borrowing of the results of classical theory lacked adequate logic, and never gave unambiguous numerical results except in the particular case that it showed certain lines should be of zero intensity, or in other words that certain transitions should not occur. These exclusions of certain transitions gave selection principles of great usefulness, and the crude theory was adequate to predict zero intensities even though in general it might be in error by several hundred per cent, because fortunately any percentage of zero is still zero. The new mechanics not only gives the selection principles without artificial appeal to the correspondence principle, but also permits a "refined" or accurate calculation of the brightness of lines whose intensities are different from zero. In the mathematics of the matrix theory the intensities and frequencies are beautifully woven together. We have, in fact, mentioned near the beginning of the paper how the Heisenberg matrices contain both amplitude and frequency factors.

5. The anomalous Zeeman effect. It is found experimentally that in a magnetic field H the "Zeeman" displacements of spectral lines are usually equal to fractional multiples of the normal Lorentz unit $He/4\pi mc$, rather than to this unit itself. This is the phenomenon of the "anomalous Zeeman effect." Any ordinary theory would give only the normal effect, and the old quantum theory could explain the anomalous effect only in semiempirical fashion and with the aid of many contortions. In the new theory, of course, the anomalous effect comes out naturally. If I had been giving this paper just two or three months ago I would have said that the new quantum mechanics could explain the anomalous Zeeman effect only with the aid of the *spin electron.* By the term spin electron is meant the idea that the electron behaves like a spinning top, and so has an internal or rotational degree of freedom besides its three translational degrees of freedom. Such a fourth degree of freedom and hence fourth quantum number appears definitely to be demanded by the Smith-Stoner-Pauli classification of the periodic table. The suggestion that the electron have a magnetic moment due to internal motion is by no means a new one, and has been made by Parson, Compton, Kennard, and others but its incorporation in the spectroscopic work of quantum theory is due primarily to Uhlenbeck and Goudsmit. For a long time it appeared as though the internal spin was a hypothesis entirely supplementary to the quantum mechanics. However, within the past month or two, brilliant work by Dirac has shown that the requirement that the Schroedinger wave equation be orthogonal and compatible with relativity (which apparently demands several simultaneous wave equations) is alone sufficient to yield the dynamical terms ordinarily attributed to electronic spins. Thus in a certain sense the spin electron is the child of the new quantum mechanics rather than a supplementary assumption, but it is a bit doubtful if it would ever have been discovered if approached originally from the abstract mathematical rather than empirical spectroscopic viewpoint. The inclusion of the spinning motion of the electron is very vital in the theory of any magnetic effect, such as the Zeeman effect, or magnetic susceptibilities (item 7 below), as the internal motion gives the electron a magnetic moment even when its center of gravity is at rest. The spin is even necessary in interpreting the hydrogen fine-structure with the new mechanics. It also underlies the so-called "gyromagnetic anomaly;" viz., that the experiments of Barnett, de Haas and others on rotation by magnetization, or the converse, reveal a ratio of magnetic moment to angular momentum of twice the classical value. This is intimately connected with the fact that the ratio of the internal magnetic moment to internal angular momentum of the electron is $-e/mc$, or twice the value for ordinary orbital motions. This factor two is what makes all the anomalies in the Zeeman effect, gyromagnetic effect, etc.

Both in x-rays and in visible spectral regions there are certain doublet lines whose origin was previously shrouded in mystery. The doublet intervals obeyed numerically Sommerfeld's relativity formula, but nevertheless the doubling could not be due to relativity corrections. They are now interpreted as "spin doublets" due to two different orientations of the spin axis relative to the rest of the atom.

6. *Half quantum numbers no longer a bugaboo.* To secure agreement with experiment in the old quantum theory it was necessary to give certain quantum numbers half integral values 1/2, 3/2,.... rather than the integral values 0, 1, 2. Such a procedure was most disconcerting, as the rigorous old theory demanded only whole integers. The new mechanics, however, very obligingly gives unambiguously half quantum numbers where they are needed and whole quanta where the latter are required.

7. *Improvement in the theory of dielectric constants and magnetic susceptibilities.* The preceding items have been primarily spectroscopic in nature, and often deal with excited rather than normal states. The chemist is apt to conceive of the physicist as some one who is so entranced in spectral lines that he closes his eyes to other phenomena. However, it must be mentioned that a theory of spectral lines is also one of critical potentials. Also in the theory of dielectric constants and magnetic susceptibilities we have another quite different field in which we can test the quantum mechanics, and which involves only the normal, in distinction from excited, states of molecules. In this field the new quantum theory is far more successful than the old one. One reason for this is that the new mechanics gives results in much closer accord with the classical theory than did the old quantum theory. In the latter there was a conflict with classical theory even at high temperatures, and Pauling even showed that an innocent little magnetic field of 100 Gauss or so would have a prodigious effect on the dielectric constant, quite contrary

to experiment. In the new mechanics or in the pure classical theory this prodigious effect disappears. The new theory restores the factor 1/3 very generally in the Langevin-Debye formula. Because of the changes in the constant in this formula with the gradual development of quantum theory, there have been corresponding alterations in the electrical moments deduced from experimental data on dielectric constants. The electrical moment of the HCl molecule, for instance, has had quite a history, as indicated in table 2. The first column gives the value of the constant C in the Langevin-Debye formula:

$$(\epsilon - 1)/4\pi = N\alpha + (NC\mu^2/3kT)$$

Thus fortunately the electrical moment of the HCl molecule reverts to its classical 1912 value. The quantum theory of susceptibilities, however, does more than merely agree with classical theory regarding the factor 1/3. Since magnetic moments are quantized, it permits the calculation of the absolute value of the magnetic susceptibilities whenever the spectroscopic term values are known. The only common paramagnetic gases are NO and O_2, and the numerical magnitudes of their calculated susceptibilities agree with experiment to within 1.5 per cent.

TABLE 2

VALUE OF CONSTANT C	FORM AND YEAR OF THEORY	CORRESPONDING VALUE OF ELECTRICAL MOMENT μ OF HCl MOLECULE
$\frac{1}{3}$	Classical, 1912	1.034×10^{-18} e.s.u.
1.54	Whole quanta, 1921	0.492×10^{-18}
4.57	Half quanta, 1925	0.322×10^{-18}
$\frac{1}{3}$	New mechanics, 1926	1.034×10^{-18}

All the preceding results can usually be obtained with the ordinary matrix or wave formulations of the quantum mechanics. The remaining three items, however, mostly require the use of the more general "transformation theory" of Dirac and Jordan, or its equivalent.

8. Dispersion and the emission and absorption of radiation. Dispersion was particularly bothersome in the old quantum theory, which could never explain why the resonance frequencies in dispersion were experimentally the spectroscopic frequencies given by the Bohr frequency condition rather than the altogether different frequencies of motion in the orbits constituting the stationary states. The new mechanics, however, yields the Kramers dispersion formula, previously derived semi-empirically from the correspondence principle. In the new theory the dielectric constant equals the extrapolation of the square of the index of refraction to infinite wave lengths, as it should, whereas the validity of this relation was doubtful if the Kramers formula was forced into the old theory. As the result of masterful treatment by Dirac, a mechanism has at last to a certain extent been found for the previously so mysterious quantum jumps between stationary states. Dirac finds it is possible to treat radiation as a dynamical system obeying the Einstein-Bose statistics, and starting from such a postulate he is able to derive Einstein's values for the "A" and "B" transition probability coefficients. Dirac's work brings out nicely the parallelism between matter and radiation, and their corpuscular and wave aspects, which are complementary rather than contradictory.

9. Collisions of electrons with atoms. The old quantum theory furnished no real mechanics governing electron impact phenomena although a rather blind conservation of energy argument furnished the fundamental relation $Ve = h\nu$ between critical potentials and frequencies. The theory of collision phenomena has been developed with the new mechanics by Born and others. As already mentioned, there is a good deal of similarity to a diffraction problem in optics, and the square of the amplitude of the diffracted wave measures the probability that an electron will be scattered at a given angle. The requirement that the solutions be "civilized" yields nicely the proper discrete values for the critical potentials. In the case of collisions with hydrogen atoms, Born is able to compute numerically the excitation and ionization efficiencies, the angular distribution of scattered electrons, etc. The wave-like maxima and minima in the latter are confirmed at least qualitatively in the experiments of Dymond on the scattering of electrons in helium. A closely allied question is the polarization of radiation excited by electron impact, and the theory of this has been developed by Oppenheimer. A most peculiar phenomenon is the so-called "Ramsauer effect," whereby slow-speed electrons are able to go right through inert gas atoms with very little scattering. The theory of this has at last made its debut. We have already mentioned the theory of the Davisson-Germer effect and the scattering of alpha particles, both of which properly come under the present item (9).

10. New light on statistical mechanics. Because of the fact that the new mechanics is to such a large extent fundamentally statistical in nature, the supplementary assumptions which it is necessary to make to get the fundamental distribution formulas of statistical mechanics are much less violent than in the classical theory. The quantum statistics, of course, merge into those of classical theory at high temperatures, but differ from the latter at low temperatures. The proper quantum statistics to be used in treating radiation are those of the so-called Einstein-Bose type, as this furnishes the Einstein radiation law. On the other hand in dealing with matter it appears necessary to use the Fermi statistics, founded on the Pauli exclusion principle to be discussed later. A particularly significant application is that to electron conduction in solids. If there are about as many conduction electrons as atoms, as seem to be demanded by the optical properties of metals, the classical theory of equipartition would demand that the conduction electrons make an appreciable contribution to the specific heat. The latter would, in fact, be 9 rather than 6 calories per gram atom, contrary to Dulong and Petit's law. In the new quantum statistics, on the other hand, we can suppose that there are as many conduction electrons as atoms without contradicting specific heat data. The reason is that the conduction electrons in solids are relatively close together as compared to molecules in gases, and furthermore the electronic mass is very small in comparison to that of molecules. This means that even at ordinary temperatures the "electron gas" in the solid shows a characteristic quantum "gas degeneration," whereby the specific heat sinks to zero. In a real molecular gas, on the other hand, the degeneration effects would be important only very near the absolute zero, and even then only at extremely high pressures. Thus the conduction electrons test an aspect of the statistics which it would be difficult to verify otherwise. Pauli shows that the degeneration effects make the magnetism of solid alkalis very small, in agreement with experiment, even though the internal spin makes each electron a tiny magnet and so would give strong paramagnetism with classical theory. Extending Pauli's ideas, Sommerfeld and others have shown that the formulas of thermionic emission, the Wiedemann-Franz ratio, Hall effect, and other properties of conduction electrons are obtainable with the new Fermi statistics. The new vista into electron conduction is, in fact, one of the most pleasing recent developments in quantum mechanics.

IV. WHAT THE QUANTUM MECHANICS PROMISES TO DO FOR THE CHEMIST

Before passing to the chemical applications we must first describe one aspect of the quantum mechanics which seems to be of particular importance for chemistry. This is the so-called *Pauli exclusion principle*, which states that *no two electrons can have simultaneously all four quantum numbers the same.* The reason that there are four quantum numbers per electron is that the electron seems to be a spinning body having a fourth or internal degree of freedom in addition to the three translational degrees of freedom. Just what we take as the four quantum numbers depends somewhat on the type of quantization, which itself varies with the relative magnitude of the various atomic forces. The simplest thing is to suppose that the magnetic field is so powerful that it completely overpowers the inter-electronic forces, so that the orbital and spin angular momentum vectors of each electron are quantized separately relative to the axis of the field. Actually no ordinary magnetic field is powerful enough to do this, but our supposition nevertheless involves no loss of generality because the exclusion principle is a purely formal rule for eliminating certain combinations of quantum numbers, and in any field strength the states will be excluded which pass gradually ("adiabatically") over into states not allowed in extremely strong fields. In a strong field the four quantum numbers of each electron are the principal quantum number, n, the azimuthal quantum number, k, and the two "magnetic" or "equatorial" quantum numbers, m_k and m_s, quantizing the components of orbital and spin angular momentum in the direction of the applied field. The range of values for the quantum numbers k, m_k, m_s are

$$\begin{aligned} k &= 0, \ldots\ldots, n-1 \\ m_k &= -k, -(k-1), \ldots\ldots, 0, \ldots\ldots, k-1, k \qquad (7) \\ m_s &= -\tfrac{1}{2}, +\tfrac{1}{2}. \end{aligned}$$

It is to be noted that the azimuthal quantum number is usually numbered one unit lower in the new than in the old quantum theory, as formerly we had $k = 1, 2, \ldots, n$. We now have $k = 0, 1, 2, 3$ for optical s, p, d, f terms respectively instead of 1, 2, 3, 4. (This is purely a formal difference in notation and to emphasize the distinction the notation l instead of k is sometimes used in the new theory). The range of values for m_k is $-k$ to $+k$ because m_k being a component of k, cannot exceed k in absolute magnitude. The quantum number m_s has onlv the two values $-\frac{1}{2}$ and $+\frac{1}{2}$, because according to the hypothesis of Uhlenbeck and Goudsmit, the internal spin of the electron is associated with a half quantum of angular momentum. Now for given k, equation (7) shows that m_k has $2k + 1$ possible values, while m_s has just two possibilities. There are thus $2(2k + 1)$ different pairs of values for m_k and m_s. Hence one way of stating the exclusion principle is that *in any atom there are at most $2(2k + 1)$ electrons having the same values of n and k.*

Pauli advanced his exclusion principle on more or less empirical grounds before advent of the new mechanics, but the latter has placed this principle on a better and more general basis, as it amounts to using only solutions of Schroedinger's wave equation which are of a certain peculiar type of symmetry (viz., the so-called antisymmetric solutions which change sign when electrons are interchanged). We will not try to enter into the details of the mathematical description of what this type of symmetry is.

The only point that need be emphasized is that *because of Pauli's principle we must not only limit ourselves to "civilized" solutions of Schroedinger's equation, but also in particular only those which are of the "antisymmetric variety."*

Pauli's principle should appeal particularly to chemists, because it yields immediately the well-known interpretation of the Mendeléeff periodic table proposed by Smith and Stoner. These two men showed independently that by making certain apparently rather arbitrary assumptions about the assignment of quantum numbers to electrons of the various groups, one could account very nicely for the structure of the periodic table of the elements —why, for instance, there are 2 elements in the first period, 8 in each of the two next, 18 in the fourth and fifth, but 32 in the sixth. Also within the period many of the chemical properties of the elements, the existence of sub-periods, rare earths, etc., come out nicely. Now Pauli's principle gives automatically the Smith-Stoner assignment of quantum numbers. We will illustrate this, for simplicity, only for the first two periods, i.e., for the K and L shells. In the K shell the principal quantum number n has the value 1, and hence by (7) the azimuthal number k can only have the value zero. On the other hand in the L shell the principal quantum number n equals 2, and by (7) there are the two possibilities $k = 0$ and $k = 1$. The various possibilities for the four electronic quantum numbers are then by (7) those indicated in table 3. The essence of Pauli's principle is that no two columns can have four identical entries. As each column corresponds to a different electron, there are indeed two electrons in the K-shell and eight in the L.

TABLE 3

	K-SHELL ($n = 1$)		L-SHELL ($n = 2$)							
n	1	1	2	2	2	2	2	2	2	2
k	0	0	0	0	1	1	1	1	1	1
m_k	0	0	0	0	-1	-1	0	0	1	1
m_s	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$

The quantum mechanics should go further than furnish a model of the periodic table. It should tell us what atoms can combine and what do not. There is no essential difference between the mathematical procedure in the quantum mechanics of calculating a heat of dissociation and of calculating a spectroscopic frequency or critical potential. This fact does not seem quite as universally recognized as it should be. In either case what is required is a knowledge of the magnitude of the various allowed energy levels. The only distinction is that chemical problems involve more than one nucleus, and this considerably increases the labor of calculation. For the latter reason it may well be a long time before the quantum mechanics achieves as many quantitative results for the chemist as for the physicist, but from a standpoint of pure logic there seems to be no apparent reason why the quantum postulates as they now stand should not be adequate to explain the phenomena of chemical reactions. A dynamics which works for the physicist must also work for the chemist and vice versa. It seems scarcely conceivable that a theory which has been so successful in explaining atomic energy levels should fail in the closely related realm of molecular energies. *The mathematical problem of a chemical reaction seems to be this: to investigate whether there are stable solutions of the Schroedinger wave equation corresponding to the interaction between two (or more) atoms, using only the wave functions which have the type of symmetry compatible with Pauli's exclusion principle.*

A beginning in this program of investigating chemical reactions by means of quantum mechanics and Pauli's exclusion principle has been made within the past few months in important papers by London and by Heitler. Although this work is very new, it is already yielding one of the best and most promising theories of valency. The general trend of the work seems to be that because of the critical examination of symmetry properties required by the Pauli exclusion principle, the theory of the classification of valences in complicated organic compounds, etc., must be closely related to the group theory of the mathematicians. Some of the specific results which have already been obtained in the papers of London and Heitler are the following:

1. Two hydrogen atoms can combine to form a hydrogen molecule.
2. Two helium atoms cannot combine, unless excited, without

violating Pauli's exclusion principle. This, of course, agrees with the monatomic property of helium gas. Spectroscopists, to be sure, have observed the spectra due to helium molecules, but such molecules are transient, unstable creatures in which the electrons are in excited rather than normal states.

3. Inert gases cannot exhibit valences.
4. Halides may have the valences 1, 3, 5, 7 except that the valence of fluorine may only have the value 1.
5. S, Se, T may have valences 0, 2, 4, 6 but oxygen only the values 0, 2.
6. P, As, Sb, Bi may have 1, 3, 5 but N only 1, 3.
7. C, Si, Ge, etc., may have 0, 2, 4.

Chemists will immediately recognize that these predicted possible valences are in the main in excellent accord with experiment. Oxygen, for instance, is found to be pronouncedly only divalent, whereas S, Se, etc., have sometimes higher valences. Thus only OCl_2 is observed, whereas on the other hand one finds compounds such as SCl_4, SF_6, $SeCl_4$, SeF_6, etc. Similarly it is well known that Cl and I can exhibit higher valences than the unit valence characteristic of F. Some of the valences listed above are not realized experimentally. A notable example is that the valence of nitrogen is never unity, even though according to item 6 the values 1 and 3 are both possible. However, this state of affairs is not a serious difficulty, for I have attempted to list the valences which are possible from the standpoint of elementary symmetry considerations[3] rather than those which

---

[3] *Note added in proof.* It is perhaps a bit misleading to state that all of London's results follow unambiguously from symmetry considerations. In order for his definition of valence to be a useful one, it is necessary to suppose a bit empirically that the stable state of a molecule is in most cases one in which the electron spins have zero resultant. The fact that most molecules are diamagnetic shows that this supposition is usually true, but the paramagnetism of the oxygen molecule despite an even number of electrons shows that it does not have universal validity. Calculations with normal hydrogen and helium support London's supposition, but the writer is informed by Prof. Kemble that computations show that in excited states of the hydrogen molecule there is sometimes greater stability with the electron spins uncompensated than with them mutually compensated. Hence London's assumption concerning the predominance of closed spin configurations might well have more justification of a purely theoretical rather

actually exist. I have been very careful to say in every case "may have" according to the theory, rather than "should have." The different valences correspond to different apportionments of various values of the quantum numbers k, m_k among the electrons, and the relative prevalence of the different valences depends upon the relative prevalence of the states corresponding to different values of the quantum numbers k, m_k but given n. Some of these states may have such high energies that they are occupied only very infrequently, and so the corresponding valences may not exist. In other words the preceding inventory indicates only how valency is restricted by the Pauli exclusion principle, and energy considerations may give further limitations. Definite predictions in this respect should be possible if there were available complete spectroscopic evidence on the atomic stationary states corresponding to all assignments of quantum numbers. London's work, in fact, seems to show that there is a very intimate connection between valences and the spectroscopists' classification of spectral terms. Thus he finds that valences 1, 3, 5 in the nitrogen group are associated respectively with doublet, quartet, and sextet structures in the spectroscopists' "multiplets." The spectroscopists find experimentally that the normal state of the nitrogen atom is a quartet rather than doublet spectral term, and this is in agreement with the fact that the normal valence of N is 3. Complete absence of univalence in nitrogen must mean that the lowest doublet terms have considerably greater energy than the lowest quartet terms. Similarly the spectroscopists' observation that the normal spectral term of the O atom is of the triplet rather than singlet type means that normally oxygen is divalent rather than non-valent. This, of course, accords with the fact oxygen gas is diatomic rather than monatomic. Apparently the spectroscopists classifications into multiplets is going to be useful in correlating the relative prevalence of different possible valences.

---

than semi-empirical nature. It may be noted that Pauling shows (Proc. Nat. Acad. Sci. **14**, 359, 1928) that in simple cases London's theory gives results similar to those of Lewis's shared electron pair.

It must also be mentioned that sometimes valences are observed which are not allowed according to the above scheme. Thus nitrogen is sometimes observed to be quintavalent. Such exceptions London explains on the ground that his theory is only one of what he calls "homopolar valences," in which the molecule dissociates into neutral atoms rather than into ions. The valence 5 for nitrogen he claims belongs to the "polar" catagory in which the molecule breaks up into ions, in which case the symmetry arguments may lead to quite different results. It must be mentioned that London's use of the terms "homopolar" and "polar" may prove a bit confusing, as it has nothing whatsoever to do with the presence of an electric moment, but rather refers to the mode of dissociation. As mentioned in Dr. Darrow's paper in this symposium, recent experimental work shows that molecules are much more apt than has been previously supposed to dissociate into neutral atoms rather than ions. Thus optical dissociation of HBr furnishes H and Br rather than H^+ and Br^-. Hence London would presumably classify the formation of HBr as a homopolar bond despite the electric polarity of the HBr molecule. He is forced to admit that there is no hard and fast distinction between the two terms homopolar and polar as he uses them, since some molecules may dissociate in either of two ways. According to London a valence is of his polar type only if the electron affinity of one atom is greater than the ionization potential of the other.

A point which is particularly to be emphasized is that according to London the reason certain valences or bonds do not occur (e.g., compounds involving inert gases) is not that such bonds lead to molecules which are energetically unstable, but that the bonds, when stable, correspond to solutions of the Schroedinger wave equation which are of a type of symmetry contrary to Pauli's exclusion principle. Thus considerations of symmetry (group theory) are often quite as vital as those of energetics. The failure of a chemist to find a compound does not necessarily mean that the corresponding molecule is energetically unstable, but may mean rather that it would demand electronic groupings contrary to the exclusion principle. As an example consider the question of whether two normal helium atoms can combine to form a helium molecule. Here the mathematical analysis of Heitler and London shows that there are energetically stable solutions of the wave equation corresponding to the interaction of two helium atoms, as well as also energetically unstable ones. In the stable solutions the statistical charge distribution is roughly of the general type shown in figure 2, whereas in the unstable ones it is more of the type illustrated in figure 3. Hence helium gas might be diatomic, were it not for the fact that the stable solutions are all contrary to Pauli's exclusion principle, leaving only some of the unstable solutions corresponding to repulsion of the atoms rather than chemical affinity. On the other hand in the case of the hydrogen molecule the stable solution satisfies Pauli's principle.

In the application of the exclusion principle to chemical reactions, the existence of an electron spin is of vital consequence. Without the internal spin, for instance, it would be impossible to construct a stable molecule of the hydrogen molecule without violating Pauli's principle. Incidently, in the hydrogen molecule, the spin axes of the two electrons set themselves antiparallel, so that their magnetic moments compensate each other and make hydrogen gas diamagnetic. Thus indirectly the internal spin of the electron and its attendant magnetic moment is of considerable importance in chemistry. However, one must be very careful not to form the impression that the magnetic forces due to the internal spins are of any magnitude appreciable enough to affect the energy of a chemical bond in the slightest degree. Instead the magnetic forces are entirely negligible in comparison to the electrostatic ones. In the hydrogen molecule, for instance, the magnetic forces are less than 0.1 per cent of the electrostatic. Hence chemical bonds are fundamentally electrical in nature. In this respect the modern Uhlenbeck-Goudsmit spin electron is to be contrasted with the old Parson magneton which pictured the electrons as magnets exerting strong magnetic forces on each other. Instead the internal spin and magnetic moment are important only indirectly in altering the symmetry so that solutions are compatible with Pauli's principle which would not be otherwise. In other words with an extra degree of freedom and quantum number there are more different ways in which electrons can be arranged without making all quantum numbers the same. It must be confessed that Pauli's dogmatic exclusion principle implying a restriction to antisymmetric wave functions appears decidedly artificial, but is nevertheless the best that can be done in reducing observed spectroscopic and chemical phenomena to a minimum number of postulates, and any ultimate comprehensive theory of matter must presumably include the exclusion principle as one of its consequences.

The London and Heitler theory of valences is primarily based on symmetry properties of the wave functions and does not aim to say anything about the stability or heats of reaction of the various compounds, as this would require a detailed dynamical investigation. There is, however, one chemical reaction in which it has already proved possible to carry through a real mathematical analysis of the dynamical problem on the basis of quantum mechanics. This reaction is the combination of two hydrogen atoms to form a hydrogen molecule. Here only four bodies are involved (two electrons and two protons) so that the equations may really be integrated by rather laborious methods of successive approximations. This has been done indepedently by Condon, Sugiura, and Wang. The calculated value of the heat of dissociation is 87,000 calories per molecule, whereas the experimental value is 100,100 (spectroscopic) or 97,000 (calorimetric). At first sight this may appear like mediocre agreement, but it must be remembered that the mathematics can be handled only by successive approximations, and a heat of dissociation is a differential effect, viz., the difference in energy between a hydrogen molecule and that of two free hydrogen atoms. These two quantities are nearly equal, so that it is necessary to calculate the energy of the hydrogen molecule very accurately to get the heat of dissociation at all. It is perhaps more expressive of what the calculations have achieved to state the results in terms of the number of volts of energy required to completely disrupt the hydrogen molecule into four separate bodies; namely, two free electrons and two free protons. The calculated value is 30.9

volts and the experimental one is 31.5. The difference of less than a volt is within the error of the calculation. We have here an example of the computation of a chemical affinity by unambiguous methods directly from the quantum postulates, without any undetermined constants or other arbitrary features. Is it too optimistic to hazard the opinion that this is perhaps the beginnings of a science of "mathematical chemistry" in which chemical heats of reaction are calculated by quantum mechanics just as are the spectroscopic frequencies of the physicist? Of course the mathematics will be laborious and involved, and the results always successive approximations. The theoretical computer of molecular energy levels must have a technique comparable with that of a mathematical astronomer. The quantum mechanics is still very young, and surely it will ultimately be applied further than the hydrogen molecule.

SELECTED REFERENCES

General

Schroedinger, Physical Review, **28**, 1049–1070 (1926). A very ably written summary by Schroedinger himself of his original German papers.

Born, "Problems of Atomic Dynamics," Chaps. X–XX (Massachusetts Institute of Technology, 1926). Written in the early days of the quantum mechanics, but still one of the best accounts of the matrix formulation of the theory, exclusive of its correlation with the Schroedinger wave function. More detail is given in the original German articles, Zeitschrift für Physik, **34**, 858 and **35**, 557 (1925–6).

Haas, "Materiewellen und Quantenmechanik," (Akademische Verlaggesellschaft, Leipzig, 1928).

Birtwistle, "The New Quantum Mechanics" (Cambridge University Press, 1928).

Biggs, "Wave Mechanics," (Oxford University Press, 1927).

Jordan, die Naturwissenschaften, **15**, 614 and 636 (1927). An excellent survey of the different formulations of the theory.

Dirac's monumental, but highly mathematical, papers are found in Proceedings of the Royal Society, vol. **109**–date.

Heisenberg's Indeterminism Principle

Heisenberg, Zeitschrift für Physik., **43**, 172 (1927).

Bohr, Nature, **121**, 580–590 (1928).

The Wave Mechanics

Schroedinger, "Abhandlungen zur Wellenmechanik" (Barth, Leipzig, 1927). Reprint of papers originally in the Annalen der Physik and die Naturwissen-

schaften. An English translation has just been published (Blackie and Son, London).

Darrow, Bell System Technical Journal, **6**, 653 (1927). An elementary summary, especially good on the analog to classical vibration problems.

Application to Physical Problems

A bibliography on this would be too extensive to be feasible. The reader is referred to two reports by the writer in Journal of the Optical Society of America, **14**, 108–112 (1927) and **16**, 301–306 (1928). These are portions of the report of the progress committee of the Optical Society and are only brief summaries of the main physical applications during the preceding year. They are, however, documented fairly completely with the appropriate references to the literature.

Chemical Application

Pauli's original paper on his exclusion principle is Zeitschrift für Physik, **31**, 765 (1925). Summary in Hund, "Linienspektren," pp. 114–118.

Heitler and London, Zeitschrift für Physik, **44**, 455 (1927). Impossibility of forming normal helium molecule, etc.

London, Zeitschrift für Physik, **46**, 455; **50**, 24 (1928). Valency rules.

Heitler, Zeitschrift für Physik, **47**, 835 (1928). Group theory in relation to chemical bonds.

Wang, Physical Review, **31**, 579 (1928) and references to earlier work by Condon and Sugiura. Heat of dissociation and other properties of the hydrogen molecule.

During the printing of this paper, an excellent summary of the application of the quantum mechanics to the hydrogen molecule, molecule-ion and related problems has been given by L. Pauling, Chemical Reviews, **5**, 173 (1928).