

Fifty Years of Quantum Theory¹

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THE LIFE OF MAX PLANCK and his great discovery have been treated in a separate essay, and we shall limit the present discussion to the consequences of his discovery—consequences which, one may say without exaggeration, have formed the principal subject of the experimental and theoretical research of the past fifty years.

We believe that we should consider in detail the developments in the first twenty-five years, which have already faded from the memory of our contemporaries, who are under the influence of the fundamentally more important results of the past twenty-five years. Since it has proved impossible to present a complete bibliography, only occasional references to literature will appear in the text.

Part A. THE FIRST TWENTY-FIVE YEARS

Planck himself originally believed that the quantum hypothesis of radiation should be limited to the statistics of radiation exchange. Even in 1910 he mentioned that its application to the theory of the specific heat of matter seemed problematical to him. Not so to Einstein, who postulated in 1905 that a quantum $h\nu$ was involved in the case of the individual processes of photo-effect and fluorescence. He soon extended this postulate by assigning to the photon not only the energy $h\nu$, but also the momentum $h\nu/c$. In 1912 he formulated the law of photochemical equivalence from which originated what may be called a new discipline—quantum-photo-chemistry.

Einstein's theory of specific heat is based on the formula of Planck's resonator, assuming that the single molecules of the solid body oscillate independently of each other. At high temperatures this theory leads correctly to Dulong-Petit's law, as well as to the known exception for hard substances such as diamond. However, at low temperatures the theory predicts a decrease toward zero that is much faster than the measurements of Nernst and his collaborators indicated.

In 1912 P. Debye distributed the energy quanta $h\nu$, not over individual molecules, but over the independent normal oscillations of the solid, again according to the temperature dependence of a Planck resonator, whereas the solid body itself was treated as a classical continuum. Atomism, in this case, is established only in an ingenious prescription for a cutoff: the classical spectrum of elastic "eigenvibrations" of the solid body is cut off where $\nu = \nu_{\max}$ in such a way

that the number of proper frequencies becomes equal to the number of degrees of freedom of the molecular structure of the solid. The resulting T^3 law of specific heats and the characteristic temperature, $\theta = h\nu_{\max}/k$, are quantitatively in agreement with the experiment.

Debye, as early as 1910, had derived Planck's law of black-body radiation by means of a similar procedure. Again he distributed the energy quanta $h\nu$, according to statistical laws, over the electromagnetic "eigenvibrations of the Rayleigh-Jeans cube" and thus arrived at the spectrum of black radiation—this time without cutoff, because the number of degrees of freedom in this instance is unlimited.

A particularly impressive proof for the reality of energy quanta was given in 1913 by the experiment of James Franck and Gustav Hertz: electrons of precisely known energy passed through mercury vapor at low pressure. At an accelerating voltage of 4.9 the Hg-resonance line, $\lambda = 2537 \text{ \AA}$, appeared for the first time; with increasing voltage the remaining Hg-lines were excited. The excitation energy of the resonance line is thus 4.9 eV, which agrees exactly with the $h\nu$ of the excited wavelength $\lambda = 2537 \text{ \AA}$. Later the same behavior in other atoms was confirmed in innumerable cases (first tabulated by Foote and Mohler, *Origin of Spectra*, in 1922).

Through the cooperation of spectroscopists of all nations there was available an enormous amount of information on measurement of wavelengths, the most intimate manifestations of atoms. A first attempt at order² was the separation of the wave numbers into two terms by J. R. Rydberg. W. Ritz, through his combination principle, showed that each term had a physical reality of its own: the difference of any two terms of an atom gives in turn another line of the atom (actual or observed only under certain conditions). This principle was first proved by Paschen in the infrared series of hydrogen. No expert could doubt that the problem of the atom would be solved if one should learn to understand "the language of spectra."

We read in the beautiful biography of Carl Runge, the eminent spectroscopist and highly gifted mathematician, that he took every opportunity to learn the opinion of leading physicists regarding the possible interpretation of the curious series law which he had studied with H. Kayser. Thus he once called on Helmholtz and presented him with the manuscript of a treatise in this field. Helmholtz sat quietly in thought and then said, as if to himself: "Yes, the planets! How would that be? The planets . . . but no, it won't

¹ Translated from the German by members of the Department of Physics, Purdue University.

² The simplest example is the well-known Balmer series.

do!" Runge continues his description of this visit: "I could not imagine then in what manner the planets were connected with the matter. But later I realized that he had obviously thought of the orbits of electrons around the nucleus."

We do not wish to be as imaginative as Runge and ascribe to Helmholtz the prediction of E. Rutherford's atom nucleus and N. Bohr's nonradiating orbits. However, let us consider the last part: "It won't do." This indeed was the point of view generally taken by physicists confronted with the unbelievable riddle posed by the spectroscopy for classical physics: the convergence of series lines in a limit, the relation of the series among themselves, their transition to the continuous spectra, etc.

It took many new ideas to solve the mystery: Planck's discovery of h , the ingenious visualization of the atomic nucleus by Rutherford, as well as the daring postulates of young Niels Bohr on the stability of the atom; the nonradiating quantized electron orbits, the interpretation of series terms as energy levels (after multiplication by h), and their differences as energy of the emitted light quanta. When F. Paschen presented Bohr's first paper (*Phil. Mag.*, 26, 1913) in his laboratory in Tuebingen, he said: "This may be the most important paper in physics for the next decades."

For the H-atom it was sufficient to introduce one quantum number, the azimuthal quantum number. As J. Nicholson had done before Bohr, one sets the angular momentum " p " of the electron equal to a multiple of $h/2\pi$. This follows as a special case from the general quantization of the phase integrals $\oint p dq = nh$ derived in 1915 by W. Wilson from the theory of heat radiation and applied almost simultaneously by him and A. Sommerfeld to the hydrogen spectrum. Besides the azimuthal number one must consider a "radial quantum number."³ Whenever a direction in space is distinguished—e.g., by a magnetic field—a third number is added, the magnetic quantum number, which in 1916 led to a provisional understanding of the normal Zeeman effect. Simultaneously K. Schwarzschild and P. S. Epstein treated the Stark-effect of hydrogen by introducing parabolic coordinates and two parabolic quantum numbers, besides an azimuthal quantum number. By doing so they arrived at a complete reproduction of the experimental findings in regard to number and position of the components.

The quantum theory even threw light on that greatest of mysteries of chemistry, the periodic system of elements. Bohr conceived the electrons as being successively "caught" with increasing nuclear charge. Thus he was able to explain the shell structure of

the atoms and, with the help of spectroscopic and x-ray-spectroscopic data, the correct sequence of atoms within the periodic system, such as the order of K, Ca, up to the closure of the M -shell. The shell structure is defined by the principal quantum number n (the sum of the three quantum numbers mentioned previously). In 1925 E. C. Stoner divided the shells correctly into subdivisions, and the shell closure was definitely determined by the Pauli exclusion principle. However, for this a fourth quantum number was needed, $m_s = \pm \frac{1}{2}$, now called the spin quantum number. The period numbers 2×1^2 , 2×2^2 , 2×3^2 , 2×4^2 , . . . predicted somewhat alchemistically by Rydberg were thus explained through Pauli's postulate that each electron state (completely defined by the four quantum numbers mentioned) can appear only once in an atom. The same rule also holds for electrons in molecules, crystals, conduction electrons, etc.

We return now to the systematics of "hydrogenlike" spectra. The fundamental experiment by O. Stern and W. Gerlach (1921) demonstrates a clearly recognizable consequence of the spin quantum number m_s , the spatial orientation of the magnetic moment connected with the spin. An atomic beam of vaporized Ag (or gaseous H, etc.), appropriately collimated, is deflected in an inhomogeneous magnetic field. This experiment shows that the atomic unit of magnetic moment is Bohr's magneton, predicted quantum-theoretically, and not the "Weiss magneton," expected and one fifth as large. The Stern-Gerlach-effect has the basic advantage of being related to one state of the atom, the ground state, and not to a combination of both states, as is the Zeeman effect. The magnetic field in the Zeeman effect influences both states. Only by using the combination principle (T. van Lohuizen, 1919; A. Sommerfeld, 1920) is it possible to draw conclusions regarding the magnetic behavior of the initial and final state of the atom.

In 1916, application of relativistic mechanics showed that the Balmer terms, single according to ordinary mechanics, are relativistically separated into groups of neighboring components, and that the spacings between them are determined by the fine structure constant: $\alpha = e^2/\hbar c \sim \frac{1}{137}$. Spectrograms of ionized helium taken at this time by Paschen showed more than qualitative agreement with the theory. The relativistic fine structure in H finds its counterpart in non-hydrogenlike spectra in the separation into principal and subordinate series. It is to be hoped that once the connection between e and h , established through the value α , is theoretically clarified, it will lead to a more thorough understanding of the relations that seem to exist between the quantum of charge (e) and the quantum of action (h).

In order to disentangle the spectra, not only must the term values be known, but also their possible combinations. These are governed by certain selection rules, which take into consideration only the possibility or impossibility of combination. The "transition-

³ Calculation by means of the phase integral assumes, however, that the momentum p for each coordinate q be a pure function of q (case of separability). Thus the phase integral is a special case of the finiteness of the phase element: $\iint dp dq = h$ introduced earlier by Planck as a criterion of statistically indistinguishable cases, and nowadays basic for every statistics (e.g., the Sackur-Tetrode formula).

probabilities" calculated later by wave mechanics accomplished more. The value 0 indicates that a combination is forbidden; a value > 0 indicates that a combination is allowed and gives the expected intensity of emission.

If we confine ourselves to a one-electron system (e.g., alkali atom), the selection rules are: the azimuthal quantum number—called in wave mechanics l —can change only by $\Delta l = \pm 1$. There are no restrictions for the radial quantum number. For the "inner quantum number" the selection rule is: $\Delta j = \pm 1$ or 0. Let us discuss briefly the origin and meaning of quantum number j . This number (*Ann. Physik.* 63, 221, [1920]) originated from the structure of the so-called "complete doublet and triplet" analyzed by Rydberg. This consists in the doublet system of three, and in the triplet system of six components (principal lines and satellites.) The choice of the name "inner quantum number" is not a happy one, since it seems to point to a hidden characteristic of the atomic nucleus. Actually j represents the total resultant angular momentum of the atom. In the single electron case it is the resultant of the orbital angular momentum l and the spin momentum $m_s = \pm \frac{1}{2}$, and is $j = l \pm \frac{1}{2}$. Hence it follows necessarily from the conservation of areas, but is by no means a concealed constant of motion. The generalization of this definition for many-electron systems will be discussed later.

As can be seen from the preceding discussion, the selection rules had to be conjectured from spectroscopical data, and then adequately generalized. This was made possible only by the extraordinary precision of spectroscopical data. An approach that proved theoretically more satisfactory was found in Bohr's correspondence principle. This follows from considering radiation with large quantum-numbers (Fourier representation applied to the angle-coordinates first introduced by K. Schwarzschild) and uses the possibilities of combination found there in the case of small quantum numbers. The uncertainty of conjecture is thereby substantially reduced. H. A. Kramers, especially, has shown the value of this method.

In the many-electron system the salient point is the coupling of the individual l and m_s . (This concerns only outer valence-electrons; the inner electrons form closed shells with momentum zero, according to the Pauli principle.) The spin vectors m_s add algebraically to a resulting spin S , an integer or half-integer, depending on whether the number of electrons is even or odd. The orbital moments l add vectorially to form a resulting total moment L , an integer. L and S combine vectorially to form the resultant total angular momentum J . This is the normal or Russell-Saunders coupling. J , like S , is integral or half-integral, and thus follows the alternation or displacement law, which is valid throughout the periodic system: the spectra are, with regard to the quantum number J , integral or half-integral, depending on

whether the number of electrons in the atom is even or odd. The doublet system of the alkalis is followed by the singlet- and triplet-system of the alkaline earths, the doublet- and quartet-system of the elements in the third column of the periodic table, the singlet-triplet- and quintet-system in the fourth column, etc. This is valid all through to the very beginning of the periodic system. Hydrogen has a (relativistic) doublet spectrum. The helium spectrum consists of triplet lines (orthohelium) and singlet lines (parhelium). The selection rules for L and J are similar to those for l and j . In 1922, when Sommerfeld was lecturing at Harvard University on the selection rules, F. A. Saunders, who was present, confirmed, with satisfaction, that certain combinations of singlet and triplet terms for which he had looked in vain in the Ca spectrum were impossible because of these selection rules. The term notation now generally⁴ adopted fits the Russell-Saunders coupling. According to the value of L the terms are called $S, P, D, F, G, H, (L = 0, 1, 2, \dots)$ The superscript on the left indicates the multiplicity of the term ($r = 1$, singlet; $r = 2$, doublet, etc.), whereas the subscript on the right refers to the quantum number J of the level in question. For instance, the ground term of the iron spectrum is a quintet D -term 5D_J , where J can have the values 4, 3, 2, 1, 0, and where $J = 4$ represents the lowest term.

The complex line groups resulting from the combination of multiplet terms (a generalization of Rydberg's complete doublets and triplets) were known first through M. A. Catalan, who called them multiplets, and were found in the London laboratories by A. Fowler in an investigation of the Mn-spectrum. Following this study a rich multiplet literature developed. The disentanglement of the iron spectrum by O. Laporte (Diss., Munich [1924]) and F. M. Walters (*J. Optical Soc. Am.* [1924]) is a masterpiece in this field. Laporte's work was considerably aided by the results on the Zeeman effects of the iron lines of the solar spectrum, made available by H. D. Babcock, Sr., of the Mount Wilson Observatory. The iron spectrum consists of combinations and intercombinations of the quintet-septet-triplet-systems. The spectra of the rare earths, already analyzed in part, are still more complicated than the iron spectrum.

Another achievement of brilliant and bold induction was Lande's g -factor (1923), which regulates the anomalous Zeeman effects of any given multiplicity and any given quantum number L . This finding was prepared experimentally by the masterly magneto-optical measurements of E. Back.

Besides the energy levels of multiplets, it was also possible to predict theoretically their relative intensities. This was partially accomplished with the aid of the correspondence principle, and partially through the knowledge of the sum rules which the Utrecht

⁴ Compare in particular the atomic energy levels of the Bureau of Standards by Charlotte E. Moore and W. F. Meggers (1949).

laboratory (L. S. Ornstein, H. C. Burger, H. B. Dorgelo) investigated systematically. These efforts were crowned by the establishment of general intensity formulas, valid for any given multiplets, and found simultaneously and independently in three different places: H. N. Russell (*Nature*), R. de L. Kronig (*Z. Physik*), A. Sommerfeld and Hönig (*Preuss. Acad.*). The most significant application of these formulas was made by Russell, who determined the abundance of various elements in the sun from the intensity of their multiplets. More recent calculations by Unsöld could not substantially improve Russell's results.

F. Hund presented a complete system of these complex spectra. He and R. S. Mulliken applied similar principles to the band spectra of molecules. Other couplings besides that of Russell-Saunders are feasible: the (*jj*)-coupling seems especially important for the structure of nuclei.

The scheme sketched here seems to satisfy the practical needs of spectroscopy. Although there still exist some inconsistencies (concerning even the simple atoms H and He), and although a number of questions (such as the mutual disturbance of neighboring multiplets) remains to be discussed, the enormous body of material on wavelength measurements is now organized systematically with the help of integral and half-integral quantum numbers. The rules and designations described here will remain useful for practical applications. Even though the early naïve ideas had to yield to more abstract concepts, the conclusions drawn from them were confirmed to a large extent by developments during the next twenty-five years and have been but slightly changed.

Similar to the situation in the optical field is the situation in the field of x-rays. After the discovery of crystal analysis in 1912, the problem of the series connected with *K*, *L*, *M*-radiation was quickly solved. The experimental material was firmly anchored under the guidance of M. Siegbahn, was organized by means of the combination principle (W. Kossel), and applied to the periodic system (H. G. J. Moseley). Again, the relativistic doublet formula proved itself correct on a considerably enlarged scale because of the nuclear charge. These results must be considered as lasting and can hardly be changed by any possible refinements of quantum mechanics.

The establishment of a short-wave limit of the continuous x-ray spectrum by Duane-Hunt and D. L. Webster in 1915 was especially significant because it pointed directly to Einstein's light quanta. This was demonstrated still more convincingly by A. H. Compton's great discovery (1923), which left no possible doubt regarding the reality of wave and particle.

Part B. THE PAST TWENTY-FIVE YEARS

Today's quantum theory originated from the discussion of two questions, leading by two different paths to the same goal. One approach is characterized by the names of L. de Broglie, E. Schroedinger and C. J.

Davisson, and L. H. Germer; the other has been developed by W. Heisenberg, M. Born and P. Jordan, and last, but not least, by N. Bohr and W. Pauli. Both paths meet again in the work of P. A. M. Dirac.

In interpreting the Compton effect as a collision between a light quantum (considered as a particle) and an electron, an old question again became urgent: How can one understand light interference produced by a diffraction grating according to quantum theory? W. Duane pointed out in 1923 that a diffraction grating, considered as a periodic mechanical system and quantized according to Bohr-Sommerfeld, can only absorb discrete recoil momenta which, by the law of conservation of momentum, lead to specific deflections that correspond to the directions of constructive interference.

If the quantum conditions for the grating lead to interference, it must be irrelevant whether quanta or particles are diffracted by the grating. One can easily verify that thus any particles scattered by the grating behave like waves with a wavelength $\lambda = \frac{h}{p}$ (p = momentum).

This is exactly the relation which de Broglie postulated in 1924 as a relativistic corollary to Planck-Einstein's equation $E = h\nu$.

True, the objective of de Broglie is the opposite of that of Duane. De Broglie wanted to understand the quantum conditions as a consequence of interference phenomena; and he could show that the latter can be derived from the postulate that the wave train associated with a particle must include a whole number of wavelengths in a closed orbit.

As early as 1925, W. Elsasser drew attention to investigations of the Ramsauer-effect (scattering of slow electrons by atoms) and to experiments by C. J. Davisson and C. H. Kunsman (1923) on the reflection of electron beams from single crystals, as indications of particle interference. But only in 1927, about one year later than Schroedinger's first paper, the improved measurements by C. J. Davisson and L. W. Germer brought the definitive experimental proof of the reality of de Broglie's waves. Shortly afterward, G. P. Thomson and A. Reid obtained the first Debye-Scherrer pictures with electron beams. The wave properties of protons and atoms were demonstrated in 1928 in studies by Th. H. Johnson, F. Knauer, and O. Stern, and by I. Estermann and O. Stern.

As mentioned earlier, Schroedinger formulated de Broglie's hypothesis mathematically with unsurpassed skill, prior to the experimental verification of matter waves. The basis of Schroedinger's investigation is the understanding that, besides the de Broglie relation between wavelength and momentum, the classical equations of motion for massive particles must follow from the proposed wave theory of electrons as an approximation that corresponds to geometrical optics. Indeed, if one accepts the additional hypothesis that matter waves (as contrasted to electromagnetic waves) are represented by one single scalar wave function ψ , Schroedinger's nonrelativistic wave equation

tion for an electron in a potential field is uniquely determined as

$$\Delta \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0.$$

In spite of the fact that this hypothesis must be corrected later on, Schroedinger's method worked very well, especially for the derivation of Bohr's equation for energy levels in the hydrogen atom:

$$E = \frac{h \cdot c \cdot Ry}{n^2}.^5 \text{ The exclusion of the quantum number}$$

$n=0$ follows automatically, whereas it was obtained only empirically in the old quantum theory. Deviating from the older quantum theory, the energy terms for the oscillator and rotator have become

$$E = \hbar \omega \cdot (n + 1/2) \text{ and } E = \frac{\hbar^2}{2\theta} l(l+1).^6 \text{ The new formu-}$$

las agree with experimental fact and are identical with the results of matrix mechanics. The modified rotator equation had been deduced earlier, empirically, from band spectra.

The frequencies of the eigenvibrations of the electron waves in the atom are determined by the energy terms. However, the nature of the wave function ψ —(just what is oscillating?)—is unknown at first. It had been known, of course, that the phase S , of the generally complex wave function $\psi = \psi/e^{iS/\hbar}$ is closely connected with the action function of particle mechanics. What is, then, the quantity ψ ? From the time independence of the integral $\int \psi^* \psi d\tau$ (taken over all space) it follows that this same integral represents a quantity which is conserved in the course of motion just like the charge of the electron. This quantity will have to be related to the charge. Schroedinger assumed at first that $\psi^* \psi$ is the density of the continuously spread-out charge of the electron. This concept had to be rejected, because the charge density of a free particle would soon diffuse. For later discussions it should be kept in mind that the space integral over the density, $\int \psi_m^* \psi_n$, obtained from two solutions of Schroedinger's equation, is constant.

Further progress in wave mechanics came about only in connection with Heisenberg's matrix mechanics, already formulated in 1925 before Schroedinger's discovery. The sum rules (*Part A*), the derivation of the selection rule from the correspondence principle, as well as the estimation of intensities of spectral lines, had shown that the formulas of classical electrodynamics, for the intensity of radiation of revolving or oscillating charges, must also find their place in quantum mechanics. Heisenberg recognized the possibility of retaining those formulas and saw that the question to be asked was: which quantities must be substituted for frequency and amplitude of oscillation

under the changed condition of quantum mechanics? According to Bohr's theory, it was to be expected from the very beginning that these quantities could not be related directly to electron orbits, but to transitions between two stationary states (of Bohr's atom), and that the frequency ω_{nm} of the emitted quantum must be substituted for the orbital frequencies. Thus the "transition amplitudes" X_{mn} could be determined empirically. Heisenberg was able to derive the laws for X_{mn} from Thomas-Kuhn's sum rule and from considerations following from the correspondence principle. The formulation of these laws is particularly simple, if one writes the amplitudes for all transitions as matrices. First, because in this case the ordinary equations of motion hold for the matrices if one substitutes matrices for the coordinates, and if multiplication means matrix multiplication. Second, between the amplitudes x and the transition momentum $p = m\dot{x}$,

$$\text{commutation relations hold: } px - xp = \frac{\hbar}{i} I \text{ (} I = \text{unit}$$

matrix) which are integrals of the equation of motion and follow directly from the Thomas-Kuhn sum rule.

Next to Heisenberg, science is indebted to M. Born and P. Jordan (1926) for the development of the formalism of matrix mechanics. Born went further and found the bridge leading to wave mechanics. He interprets $\psi^* \psi$ (unlike Schroedinger) as probability density, so that diffusion of density means that the designation of the position of a free particle in the course of time becomes less and less determinate. Correspondingly, the transition density $\psi_m^* \psi_n$, mentioned above, characterizes the transition between two quantum states and permits the calculation of Heisenberg's matrix elements. Thus, for wave mechanics the calculation of intensities became possible. The atom had now become accessible to the elegant methods of analysis. Despite his dislike of the statistical reinterpretation of his beautiful wave picture, Schroedinger himself, as well as C. Eckart, soon proved the mathematical equivalence of wave mechanics and matrix mechanics.

Before proceeding to the numerous problems that could now be solved one after another, we must dwell on some attempts to interpret quantum mechanics, which are so profound that, to use Heisenberg's expression, it is no longer merely a matter of understanding physics, but a matter of "philosophical position."

First to be considered are the discussions in Copenhagen between Bohr and Heisenberg, which resulted in Heisenberg's formulation of the uncertainty principle and Bohr's concept of complementarity. Considered in this way the ideas of waves and particles are basic concepts that complement each other. Both describe a piece of reality in the same way as does the projection of a three-dimensional object on two planes, where alternately one or the other projection may give a better picture, but never a complete picture of reality. Their limitation is determined by the uncertainty principle, according to which it is not

⁵ E , the energy; h , Planck's quantum; c , the light velocity; Ry , the Rydberg constant; n , the principal quantum number.
⁶ These expressions approach, for large quantum numbers, n and l , Bohr's formulas (correspondence principle).

possible to determine accurately and simultaneously both position and momentum.

During the Solvay Congress of 1927 an even more profound question was discussed by Einstein and Bohr. This can be described with the help of the previous analogy of double projection as follows: Is it possible to unite the pictures obtained on the projection planes into one concept or image embracing both? Although such a union is possible, mathematically, without contradiction by quantum mechanics, no answer could be found that would satisfy all physicists. Lately, those discussions have been revived in articles of Bohr and Einstein in the publication honoring Einstein's seventieth birthday.⁷ Bohr was able to refute Einstein's objections, which were presented in the form of hypothetical experiments; Einstein apparently did not succeed in completely presenting the central points of his criticism in the form of these hypothetical experiments. These differences in comprehension cannot be disposed of lightly in the manner of the wise resignation that Planck expressed in his autobiographical annotations (*Naturwissenschaften*, 1947); namely, by pointing to a "difference in generation."

An essential contribution to the interpretation of quantum mechanics, preceding the Copenhagen discussions, is the statistical transformation theory which originated with Dirac and Jordan. Every complete set of quantities simultaneously and exactly observable forms a possible basis for the transformation theory—e.g., the position coordinates in the simple Schroedinger equation. At a given moment these quantities are statistically described by the wave function, in this connection called "probability amplitude." A wave function of this kind changes in the course of time within a free physical system, or during measurements, because of the interaction with the measuring instrument. The change, mathematically, is a transformation of the wave function, which is uniquely defined because of the process or because of the experimental arrangement, and which becomes an objective expression of the nature of the system or of the interference in the act of measuring, independent of any philosophical point of view.

J. v. Neumann, in 1927, was able to derive yet another important conclusion from the statistical transformation theory. Purely descriptively the motion of an electron resembles the Brownian movement of a colloidal particle in a gas. Therefore consideration has been given to interpreting the statistical character of quantum mechanics as a result of the coupling of atomic particles with a statistical system, unknown, but corresponding to the gas in question. J. v. Neumann has shown that any assumption of this kind leads to fluctuations other than those predicted by quantum mechanics.

Fundamental to quantum mechanics is the discussion of electron spin. With the help of Sommerfeld's

inner quantum numbers (1920–21), it was possible to understand the multiplet structure of spectral lines. Pauli had insisted quite early that this must be the manifestation of an electron property which, in turn, led S. Goudsmit and G. E. Uhlenbeck in 1925 to the hypothesis that the electron must have its own spin momentum of the magnitude $\frac{h}{2}$ and a magnetic moment

(Bohr's magneton) $\frac{e\hbar}{2mc}$. Pauli, in 1927, opened the

way to successful wave mechanical treatment of the spin by the assumption of two wave functions. Thus, one must abandon Schroedinger's hypothesis that the wave function has only one scalar component. The other two fundamentals of the wave equation—the de Broglie-relation and the identity between the approximation of geometrical optics and classical mechanics—remained unimpaired. Thus the spin becomes an essential quantum mechanical characteristic with nothing comparable in the classical approach.⁸

The entire development was completed in 1928 in a perfect manner by Dirac's relativistic wave equation of the electron. This wave equation combined four components of the wave function by a system of four linear partial differential equations of first order. The effect of Dirac's equation on spectroscopy is to surpass Pauli's equation in the confirmation and refinement of Sommerfeld's formula for the hydrogen fine structure. Its significance, however, reaches farther, since in later years there has been the undersanding that different particles correspond to different wave equations. The wave equations of the meson by A. Proca, H. Yukawa, and N. Kemmer can serve as examples.

Heisenberg's work on He (1926) is, next to the calculation* of intensities, one of the first applications of quantum mechanics. Here it became evident that the new theory was adapted to the quantitative treatment of many-body problems. This first, simple example led to the central concept of "exchange force," which has to do with the fact that the average energy of both electrons in the atom depends on the probability with which the electrons can approach each other (correlation). Whereas the analogous question concerning phase relations between two rotating electrons could not be solved with the older quantum theory, wave mechanics offered certain correlations, that is, the symmetry or antisymmetry in the position coordinates of the wave functions. The two types of solution led to the empirical term systems of ortho- and parahelium.

The hydrogen molecule can be handled in a similar manner, assuming the heavy hydrogen nuclei to be at rest, since in this case, one must deal with two electrons in a fixed potential field. Here again one arrives at two-term systems, the energy values of which depend, furthermore, on the distance between protons.

⁸ Lately, the possibility of correcting this viewpoint by means of the theory of elementary particles has slightly increased.

⁷ Albert Einstein: *Philosopher-Scientist*. The Library of Living Philosophers, Vol. VII (1949).

In 1927 F. London and W. Heitler were able to show that the energy of the lowest state becomes smaller at first as the protons approach each other, and only at very small distances does it increase rapidly. The resulting attraction explains the homopolar chemical bond. This created the basis for quantum chemistry, which was developed further by J. C. Slater and L. Pauling, and in particular by E. Hückel, who was able to explain the conjugated double bond (benzene ring). It also established a basis for the theory of molecular spectra (F. Hund, R. S. Mulliken, E. Wigner, *et al.*). In these investigations methods of group theory were useful. Heisenberg was able to show in 1928 that the Weiss force in ferromagnets is due to an exchange force between electrons; and F. Bloch in 1930 successfully applied the method of Heitler-London to electrons in ferromagnetics.

All these investigations are based on the Pauli principle (*Part A*). This means, expressed in terms of wave mechanics, that the total wave functions, depending on position and spin coordinates, must necessarily be antisymmetric. In quantum mechanics it appears as an empirical law that is consistent with the fundamental requirements. It could only be proved, by Pauli, in quantum theory of wave fields (*Revs. Modern Phys.* [1941]). A direct experimental confirmation is given by collision experiments with like particles (N. F. Mott's collision formula).

As in classical mechanics, the three- and many-body problem in quantum mechanics can be attacked only by means of approximation methods. In wave mechanics, such methods were developed by L. H. Thomas and E. Fermi (1928), and by D. R. Hartree and V. Fock (1928), and used for the calculation of atomic states. The first one is particularly convenient for many problems; it has been used for studies on heavy nuclei (Heisenberg, Solvay Congress, 1934), especially for investigating the saturation of nuclear forces.

The Fermi-Dirac statistics, already known in older quantum theory, is also based on the Pauli principle. Its application to conduction electrons in metals, which, in a first approximation, are treated as free particles, led Sommerfeld (1927-28) to a successful revival of P. Drude's theory of conductivity, as well as to an explanation of the Wiedemann-Franz law. The behavior of electrons in a lattice has been particularly studied by R. Peierls and F. Bloch (1930). Its most important result is the band structure of energy terms and the resulting classification of conductors, semiconductors, and insulators. Apparently the electrical resistance depends on the interactions between electrons and the irregular fluctuations of the potential in the lattice caused by thermal motion, impurities, and lattice defects (residual resistance at low temperatures). Lately, interest has been directed toward phosphors and semiconductors, which are important for technical applications. The problems of superconductivity and superfluidity have not yet been solved completely.

As early as 1927 Hund pointed to the predissocia-

tion of molecules in an electrical field as an example of the penetrability of the potential barrier by electrons, the energy of which is insufficient to surmount the barrier (tunnel effect). G. Gamow's theory of the α -decay of radioactive atoms (1928) is another example. Here, for the first time, quantum mechanics is being applied to problems of nuclear physics. Only after the discovery of the neutron (1932) was it possible to deal systematically with nuclei and to consider both the neutron and the proton as elementary nucleons. On the basis of Heisenberg's hypothesis (1933), the force between them could be considered as the result of an exchange of charge, whereby the particles constantly interchange roles. The fundamental problem of nuclear physics, to derive the elementary forces between nucleons from the behavior of atomic nuclei, has not yet been solved completely, in spite of many successful solutions of special problems (H. A. Bethe, *Revs. Modern Phys.* [1937-38]; L. Rosenfeld, *Nuclear Forces*, New York [1948]). According to general opinion, the difficulties are closely connected with problems of the theory of elementary particles. For this reason, the explanation of the "Magic Numbers" by Mrs. M. Goeppert-Mayer in America and by O. Haxel, H. E. Suess, and J. H. D. Jensen in Germany (1949) is especially gratifying. According to this, the nucleons in the densely packed nucleus can be considered as independent particles, moving in an average potential field.

Up to now, Bohr's frequency condition and the formula for the emitted intensity have not yet been made an integral part of quantum mechanics, although Jordan showed, in 1925, that this could be achieved by the application of quantum mechanics to the proper frequencies of the radiation field. This idea took hold only after Dirac's comprehensive work on radiation theory in 1927. It also laid the foundation for the general theory of wave fields. It seems particularly remarkable that light quanta become countable, though not individually distinguishable carriers of radiation without the help of a new hypothesis (Bose-Einstein statistics). Essential are operators describing the emission and absorption of light quanta.

If one attempts, on this basis, to take up the entire problem of "electron and radiation" (Jordan-Wigner, Jordan-Pauli, Pauli-Heisenberg, around 1930), one soon is confronted with grave difficulties, which arise from the fact that it is not permissible to talk of point charge in the immediate vicinity of the electron. Especially must it be kept in mind that particles and quanta are constantly produced and annihilated, some virtually and temporarily, others in reality, as in the case of pair production discovered in 1932 by C. D. Anderson (predicted four years earlier by Dirac).

In spite of successes, even the recent ones of R. P. Feynman, S. Tomonaga, J. Schwinger, and F. J. Dyson, and in spite of the certainty that quantum electrodynamics is on the right road, a rigorous solution of the present basic questions leads to divergencies. In order to remove these divergencies, methods of

renormalization have been proposed which appear to be concealed changes of the basic equations not yet analyzed in detail.

It has been mentioned that the discovery of new elementary particles has led to new equations (Kemmer), similar to the Dirac equation, but with a different spin. Investigation of these shows that the general quantum theory of wave fields is still more problematical than quantum electrodynamics. This is partly due to the fact that the coupling between fields cannot be considered as small, so that the first approximation, the

only convergent one, does not yield a good representation of reality, even in accessible energy ranges.

Here we close this chronicle. Questions concerning "a possible smallest length," the relation between elementary particles, and Born's "Apeiron"—an all-encompassing concept of the laws of all elementary particles—do not yet belong to history but represent subjects of contemporary work which, it is to be hoped, will be as successful as that of the period we have discussed. May our times favor this pursuit of pure knowledge!



Quantum Theory and Chemistry

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THE DEVELOPMENT OF THE SCIENCE OF CHEMISTRY during the first half of the twentieth century has been in great measure the result of the application of quantum theory to chemical problems. The history of quantum theory in chemistry during this period comprises nearly the whole of the recent history of the science in its theoretical aspects.

In 1900 chemistry was well developed as an art and as an empirical science, but it was replete with puzzles. Any chemist could ask hundreds of questions that no one could answer—questions as to the nature of matter and of chemical change, the structure of elements and compounds in the gaseous, liquid, and crystalline states, the mechanism of chemical reaction. The electron had been discovered, but it was not yet known that an atom contained, in addition to one or more electrons, a very small, heavy nucleus. Chemical valence was simply a part of the empirical structure of chemistry, with hardly more than a glimmering of structural interpretation, in terms of the transfer of electric charge that had been introduced by Berzelius a century before. The valence bond, fifty years after it had been brought into the chemical system by Cowper and Kekulé, remained just a line drawn between the symbols of two elements in a structural formula, or a coupled pair of hooks. Now, in 1951, nearly the whole of chemical science has been given an explanation, an interpretation, in terms of simple particles—electrons, nuclei, and light quanta—and simple, fundamental processes. The puzzling questions as to the nature of chemical substances and chemical reactions have been answered. There are still problems—many problems—in chemistry, but, with rare exceptions, they are problems rather than puzzles. We now understand the dimensional region of chemistry, the region involving lengths 10^{-8} to 10^{-7} cm. The great puzzles that nature now presents to us are

in the nuclear region, around 10^{-12} cm, in the region of the gene, around 10^{-6} cm, and in the region of universes, around 10^{24} cm.

The first significant application of quantum theory to chemistry was made by Einstein, in his explanation, in 1907, of the decrease in heat capacity of substances at low temperature. In the formulation of the third law of thermodynamics by Nernst it was necessary to assume that the reactants and the products in a chemical reaction should, at very low temperatures, have no difference in heat capacity. It was found by experiment, by Nernst and Eucken, that indeed the heat capacity of solids decreases, apparently asymptotically toward zero, at very low temperatures, and Einstein pointed out that the statistical mechanical treatment of a quantized oscillator leads to a heat capacity curve which falls off toward zero, as observed. Greatly improved quantitative agreement with experiment was obtained by Debye, through the discussion of the spectrum of vibrational frequencies of the solid substance, and the theory was further refined by Born and Kármán. During the next fifteen years the statistical mechanical interpretation of the whole of thermodynamics was achieved, through the application of quantum statistical mechanics. One of the most recalcitrant problems, that of the heat capacity of gaseous hydrogen, was finally solved in 1926, by D. M. Dennison, through the introduction of the postulate of a frozen equilibrium between two kinds of molecular hydrogen, ortho hydrogen and para hydrogen.

Einstein was also responsible for the next application of quantum theory to chemistry, the formulation of the law of photochemical equivalence, the role of the light quantum in chemical reactions. This contribution, made by Einstein in 1912, with the stimulus of early efforts by Warburg (1907, 1909), which in turn were based on Einstein's introduction of the light