

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

Linus Pauling

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena

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

quantum in the treatment of the photoelectric effect, gave at once an explanation of the existence of a short-wavelength limit of light producing a chemical reaction, and of the amount of reaction produced by a given amount of light absorbed. The quantum theory has been fundamentally involved in all further developments of photochemistry—the development of the theory of molecular spectra and molecular structure, the Franck-Condon principle, the theory of photochemical chain reactions, and the special mechanisms involved in such important photochemical reactions as the photochemical fixation of carbon from carbon dioxide by chlorophyll.

Quantum theory has had great significance for practical chemical thermodynamics. The discovery of the ways of calculating the entropies of gases from spectroscopic and molecular structural data and of the residual entropy in some crystals, carbon monoxide, nitrous oxide, hydrogen, ice, etc., at very low temperatures has led to significant progress, and at the present time the best available free-energy data for many substances are those obtained by use of quantum mechanical calculations, rather than solely by direct experiment. Sackur and Tetrode, Eucken, F. Simon, Clausius, and especially Giauque have been great contributors in this work.

The most important periods in the development of chemical theory were the few years after the formulation of the Bohr theory of the atom, in 1913, and the few years after the discovery of quantum mechanics, in 1924. After Bohr and Sommerfeld had devised the methods of discussing the motion of electrons in atoms, with use of the old quantum theory, it became possible to interpret the greatest of all chemical generalizations, the periodic table of the elements, in terms of electronic structure. This step was taken by Bohr himself; a small refinement was introduced, largely on the basis of chemical data, by Main-Smith. Elementary electronic interpretations of chemical valence were formulated by Kossel and G. N. Lewis, in 1916. Kossel laid especial emphasis on the transfer of electrons from electropositive to electronegative atoms, with the resultant formation of ions, and quantitative calculations of predicted properties of ionic crystals were carried out by Madelung, Born, and Haber, with use of the concepts of ionization potentials, electron affinities, and the balancing of electrostatic attractive forces by characteristic repulsive forces between atoms. These calculations represented the first moderately successful effort to predict the properties of substances (enthalpy, entropy) from knowledge of their structure. G. N. Lewis was especially interested in the far greater class of non-ionic substances. In 1916 he introduced the concept of the chemical bond as a pair of electrons held jointly by two atoms, and he and Irving Langmuir showed that this postulate provided a satisfying basis for the systematization of a great amount of chemical knowledge.

During the period since 1913 powerful methods of

determining the structure of molecules and crystals have been developed. The first of these was the method of determining the structure of crystals by the diffraction of x-rays, which was originated in 1912 and 1913 by M. von Laue and W. H. and W. L. Bragg, and which, through application by a great many investigators, permitted during the following years the acquisition of a very great amount of structural information. This has assisted in the clarification of the structural chemistry of simple inorganic substances, inorganic complexes, organic substances, the silicate minerals, and metals and intermetallic compounds. The development of molecular spectroscopy, especially during the period 1918–1925, has also led to the acquisition of much structural information. Perhaps the most important experimental technique for the investigation of the molecular structure of organic substances has been the electron diffraction technique, developed in 1929 by H. Mark and R. Wierl, which has been used in the determination of interatomic distances and bond angles for many hundreds of organic gas molecules. The study of the electric and magnetic properties of substances has also been of value in the development of modern structural chemistry, and in recent years the methods of microwave spectroscopy have provided precise structural information for many rather simple molecules.

I myself remember well the exciting second period of progress in quantum theory, which occurred during the twenties. One after another, experimental facts were found to show a small or large incompatibility with the old quantum theory; in many cases a patched-up reconciliation was brought about by means of *ad hoc* changes, such as the use of half-integral quantum numbers; and finally the great clarification was achieved, through quantum mechanics and the spinning electron. The observed small difference in vapor pressure of isotopes in condensed isotope mixtures was recognized by O. Stern in 1919 as requiring zero-point oscillational energy, and this conclusion was soon verified by the isotope effect in the vibrational spectra of diatomic molecules. The pure rotation spectra of the hydrogen halides were found to require a change in the representation of quantized energy levels. Millikan and Bowen emphasized the anomaly in the explanation of two kinds of x-ray and optical doublets in terms of the same differences in the ellipticity of the Bohr-Sommerfeld orbits. The magnetic and electrical properties of dipolar gases were found to differ from those predicted by the old quantum theory. And no postulates about half-integral or otherwise abnormal quantum numbers could be devised that would permit the old quantum theory to be brought into quantitative accord with the known energies of formation of the helium atom and the hydrogen molecule-ion (a structure containing the simplest of chemical bonds). The old quantum theory, with its suggestion of two types of electronic orbitals, including either one or two atomic nuclei, seemed not to be compatible with the chemical evidence for a con-

tinuous sequence of chemical bonds, from the ionic extreme to the covalent extreme; and, indeed, the differences between the chemists' atom and the physicists' atom seemed to be so great as to make their synthesis inconceivable. Then the new quantum mechanics was discovered, and within a few years all of these problems were solved.

The discovery of the wave character of electrons by L. de Broglie, Davisson and Germer, and G. P. Thomson, and the development of quantum mechanics by Heisenberg, Schroedinger, and Dirac, initiated the second period of rapid progress in the process of conversion of theoretical chemistry into its present state. The Pauli exclusion principle, with its quantum mechanical explanation in terms of antisymmetric wave functions and the spinning electron, completed the fundamental theory of the periodic system of the elements in terms of electronic structure. The shared-electron-pair chemical bond postulated by G. N. Lewis was found to have a sound basis in quantum theory; B rrau, Heitler and London, Slater, Mulliken, Hund, H ckel, and many other people contributed to this development. In the period of a few years beginning in 1930 other aspects of the general theory of the electronic structure of substances were formulated, including the hybridization of bond orbitals and the resonance of molecules among two or more structures of the valence-bond type. The theory of the rates and mechanisms of chemical reactions was also brought into its present state. After early work had been done by R. C. Tolman, O. K. Rice, L. S. Kassel, H. Ramsperger, G. N. Lewis, and other workers (with the closely related problem of radioactive decomposition of nuclei treated by Condon and Shortley, Gamow, Born, and others), the theory was brought into its present form by F. London, Polanyi, Eyring, and Hinshelwood, and, in its application to organic reactions especially, by Ingold and F. O. Rice.

Another outstanding step in the development of an understanding of nature was the discovery of the explanation of van der Waals forces of attraction, by F. London, in 1929, as resulting from the mutual polarization of atoms through synchronization of their electronic motions. Important also was the formulation

of the electronic theory of metals by Pauli, in his treatment of the weak temperature-independent paramagnetism of the alkali metals in 1926, and its extension by Sommerfeld, Eckart, Houston, Mott, and many other workers. Although the part played by the quantum theory in their discovery is an indirect one, the many new elements that have been manufactured in recent years must also be mentioned in a review of chemistry during the twentieth century; it cannot be denied that the neutron and the transuranium elements are to be considered as a part of quantum chemistry, rather than of classical chemistry.

Thus we have reached the fiftieth anniversary of the discovery of the quantum of action, with the science of chemistry largely clarified as a result of this discovery. There are still problems to be solved, and some of them are great problems—an example is the problem of the detailed nature of catalytic activity. We can feel sure, however, that this problem will in the course of time be solved in terms of quantum theory as it now exists: there seems to be little reason to believe that some fundamental new principle remains to be discovered in order that catalysis be explained.

We may now ask about the puzzling problems in the other dimensional regions, in relation to quantum theory. It is clear that in the field of the elementary particles, their interaction with radiation, and their aggregation into nuclei—that is, in the dimensional region around 10^{-12} cm—significant changes in the present quantum theory remain to be made. On the other hand, I believe that in the region of the gene, the dimensional region around 10^{-6} cm, there are comprised only structures and reactions that can be interpreted in terms of the present system of chemical and physical theory, and that no fundamental new principles need to be applied. The problem of the gene and of biological phenomena in general will be solved, I believe, when more structural information about biological systems has been gathered. As to the dimensional region of universes, 10^{24} cm, I do not know: I do not know whether or not we have reason to anticipate the discovery of a megascopic quantum theory of the universe, but such a possibility should not be ruled out of consideration.

