

ent of field. Perhaps more striking is an example such as methylammonium ion at low pH.<sup>16</sup> Here the methyl proton group is a quartet from interaction with the three protons, of the  $\text{NH}_3^+$  ion. The total quantum number for the  $\text{NH}_3^+$  group protons can be  $3/2$ ,  $1/2$ ,  $-1/2$  or  $-3/2$ , and the multiplicity would be  $2 \sum I + 1$ . The  $\text{NH}_3^+$  spectrum is a triplet arising from  $\text{N}^{14}$  with spin 1.

In the latter example especially, one observes that while the several portions of the molecule are undergoing relative reorientations there is nevertheless a mechanism whereby the effects of nuclear polarizations are communicated. This immediately excludes direct magnetic interaction. It is to be noted that whenever this type of multiplicity occurs, the bonds between the atoms affected are all covalent. On a naive picture, the spin orientation of the first nucleus shows some correlation with that of one of the bonding electrons. The orientation of the second electron of the bond is necessarily anti-parallel, and this electron may produce a correlation of the spin of the second nucleus. Transmission of polarization of protons may occur through at least three bonds *via* the s-electrons of

(16) E. Grunwald, A. Loewenstein and S. Meiboom, *J. Chem. Phys.*, **25**, 382 (1956).

the system. Thus nuclei which are remote from one another are indirectly coupled. When both s and p electrons are involved in a covalent bond, there will be an additional orbital interaction with the nuclei. For protons, McConnell has attempted to calculate proton bond orders.<sup>17</sup>

With very high resolution, one may detect more lines than the simple considerations outlined here would predict.<sup>18</sup> Anderson and Arnold found that such further multiplicity arises when second and third orders of perturbation of the chemically-shifted system are considered. In the simplest cases, these higher order effects serve to remove some of the energy level degeneracies which previously existed. McConnell<sup>19</sup> has observed a very large number of lines in fluorinated ethylenes and has shown how their multiplicity and intensity may be calculated by application of group theory.

In summary, nuclear spin resonance spectra may by their line position, shape or multiplicity reflect the subtle or gross interactions of atoms which chemists designate as bonds.

(17) H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

(18) W. A. Anderson and J. T. Arnold, *Disc. Faraday Soc.*, **19**, 226 (1955).

(19) H. M. McConnell, A. D. McLean and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

## PRESENT SITUATION OF QUANTUM CHEMISTRY

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It is pointed out that the nature of the covalent bond may be understood only by means of modern quantum mechanics. The introduction of Planck's quantum of action  $h$  leads to Heisenberg's uncertainty relation for a single particle which indicates that the idea of the existence of the classical orbits has to be abandoned. In a many-electron system there is then no longer any possibility for identifying the individual particles, and all chemically and physically measurable results must hence be independent of the labeling of the particles. It is shown that this symmetry law leads to a new form of energy, the "exchange energy," which among other things also explains the chemical bond according to Heitler and London. A brief survey is given of the development of quantum chemistry, and the main problems of actual interest in the valence bond method and in the molecular orbital theory are discussed. The simplification in the interpretations recently obtained by introducing density matrices and natural spin-orbitals is finally described.

In investigating the highly different phenomena in nature, scientists have always tried to find some principles which explain the variety out from a basic unity. They have found not only that all the various kinds of matter are built up from a rather limited number of atoms, but also that these atoms are constituted of a few elementary particles. From the point of view of ordinary chemistry, an atom may be considered as consisting of a positive point charge, the nucleus, surrounded by an electronic cloud which determines its chemical properties and, in principle, all chemical problems may therefore be reduced to problems concerning the interaction between the electronic clouds and the nuclei. The laws which regulate the behavior of the electrons are therefore of basic nature, and the discovery of modern quantum mechanics has thus been of greatest importance for our understanding of the properties of molecules and crystals, the latter being nothing but molecules of a tremendous size.

**Uncertainty Principle.**—Planck's discovery that in nature there exists the smallest quantum of

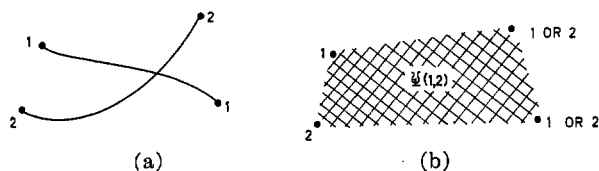
action,  $h = 6.626 \times 10^{-27}$  erg sec., has been of revolutionary importance for the development of modern science. In physics and chemistry, only those quantities in nature which are physically and chemically measurable are studied. However, every measurement implies an interaction between the object to be measured and the apparatus, and the smallest interaction possible is regulated by the above-mentioned quantum of action. This means that every measurement will disturb the object concerned and that this disturbance cannot be brought under a certain limit. It was found by Heisenberg that, if one tries to measure the position  $x$  and the momentum  $p$  of a particle simultaneously, the uncertainties in the measurements,  $\Delta x$  and  $\Delta p$ , respectively, must fulfil the famous relation  $\Delta x \cdot \Delta p \geq h/4\pi$ , which is now known as Heisenberg's uncertainty relation. The implication of this result is that, from the point of view of the measurements, an elementary particle cannot simultaneously have a fixed position and a fixed momentum, and consequently the idea of the existence of a

classical orbit for such a particle has to be abandoned.

In the discovery of modern quantum mechanics in 1925, it was found that, as a consequence of the existence of Planck's constant  $h$ , physical observables could no longer be considered as ordinary numbers, and that they instead should be described by mathematical quantities which do not fulfil the commutative law of multiplication. They may be represented by either matrices (Heisenberg), or by operators (Schrödinger), or simply by so called  $q$ -numbers (Dirac). The existence of the quantum of action led in this way to a quantization of the physical observables in the form of eigenvalue problems. However, from the chemical point of view, we are interested also in another consequence of a more indirect nature.

**Identity Principle—Exchange Energies.**—It was pointed out above that, because of the existence of the smallest quantum of action, an elementary particle cannot have a classical orbit. This implies that, if we consider a system of similar particles having the same charge and the same mass, it is impossible to distinguish the different particles individually, since one cannot follow them in any orbits. We have to observe that the individuality of a particle in the classical sense is intimately associated with the existence of its orbit. In a quantum-mechanical system, two particles may therefore exchange their places without any possibility to discover this phenomenon experimentally. This exchange phenomenon leads to a new form of energy, the "exchange energy" which is characteristic for modern quantum mechanics and which is of basic importance for the understanding of the nature of the electronic clouds within the atoms, the homopolar chemical bond, the ferromagnetism, the saturation of the nuclear forces, and many other phenomena.

In order to obtain a mathematical formulation of this "identity principle," let us consider any two particles 1 and 2 having the same mass and charge; see Fig. 1. If  $F(1,2)$  denotes any physically or



(a) Classical physics; identification of the particles possible in principle by following their respective orbits.

(b) Quantum mechanics; no classical orbits exist and no identification of the two particles is possible, which leads to the fundamental symmetry law  $F(2,1) = F(1,2)$  for any measurable quantity  $F$ .

Fig. 1.—Difference in behavior of two particles in classical physics and in quantum mechanics.

chemically measurable result, the outcome of the measurement must be independent of our attempt to label the two particles and thus we get the relation

$$F(2,1) = F(1,2) \quad (1)$$

which is the basic symmetry law characteristic for modern quantum mechanics.

The quantum-mechanical situation of a system of  $N$  particles is described in full detail by a wave

function  $\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ , where  $\mathbf{x}_i$  is a combination of the space and spin coordinates of the particle  $i$ . The physical meaning of this wave function is that  $|\Psi|^2$  gives the probability density for finding the particles in the point  $(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N)$  in configuration space. However, since all physical results must be independent of the individuality of the particles, this quantity  $|\Psi|^2$  must remain invariant when the coordinates of the particles change their places. If  $P$  is an arbitrary permutation of the coordinates, hence we have

$$P|\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 = |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 \quad (2)$$

This implies also that, under a permutation, the wave function itself may be changed only by a phase factor of the absolute value one, and, if we assume that this phase factor for a single exchange of the coordinates of two particles is a constant characteristic for the particles under consideration, the only possible values are  $+1$  and  $-1$ , corresponding to symmetric and antisymmetric wave functions, respectively. By using relativistic arguments, it may be shown that particles having half-integer spins are "antisymmetric," whereas those having integer spins are "symmetric." The electrons have therefore antisymmetric wave functions fulfilling the relation

$$P\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = (-1)^p \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \quad (3)$$

where  $p$  is the parity of the permutation  $P$ .

In  $\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N)$  each coordinate place corresponds to a particle state, and, if two such states are identical, the wave function should not change its value under a simple exchange of the coordinates in these places. This implies that an antisymmetric wave function having two particle states identical must vanish. An antisymmetric wave function is hence characteristic for a system of particles, where never more than one particle may be placed in every fully specified state. The electrons fulfil therefore automatically Pauli's famous exclusion principle, which leads to a certain saturation phenomenon in their symmetry property. It is this new property which is of such importance for the understanding of the behavior of the electronic structure of matter, and we emphasize again that this symmetry is only indirectly a consequence of the existence of Planck's quantum of action.

**Stationary States.**—The stationary states of a molecular system are characterized by the wave functions  $\Psi$  which are solutions to the Schrödinger equation

$$H_{op}\Psi = E\Psi \quad (4)$$

This equation has solutions, which are normalizable so that

$$\int |\Psi|^2(dx) = 1 \quad (5)$$

only for selected values of  $E$ , which are called the eigenvalues of the equation; the corresponding solutions are called the eigenfunctions. The eigenvalues form together the energy spectrum of the molecule under consideration, and they give the energies of the possible stationary states of the electronic structure. In addition to the discrete eigenvalues, there may also be a continuous spectrum corresponding to free particles within the molecular system; the corresponding wave func-

tions have a somewhat generalized normalizability condition. The operator  $H_{op}$  in the left-hand member is the quantum-mechanical Hamiltonian, which is obtained from the classical Hamiltonian for the molecular system

$$H_{op} = \frac{e^2}{2} \sum_{gh} \frac{Z_g Z_h}{r_{gh}} + \sum_i \frac{p_i^2}{2m} - e^2 \sum_g \frac{Z_g}{r_{ig}} + \frac{1}{2} \sum_{ij} \frac{e^2}{r_{ij}} \quad (6)$$

by replacing the classical momentum  $p_i$  by the operator

$$p_i = \frac{\hbar}{2\pi i} \left( \frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i} \right) \quad (7)$$

In the Hamiltonian the first term represents the electrostatic nuclear repulsion energy, the second term the kinetic energy of the electrons, the third term the attraction potential between the nuclei and the electrons, and the fourth term the electronic repulsion energy. In constructing this Hamiltonian, one has assumed that the nuclei have fixed positions and that relativistic effects may be neglected, which causes some approximations.

The Hamiltonian  $H_{op}$  is defined in a "configuration space" ( $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N$ ), where each particle  $i$  has its own space-spin coordinate  $\mathbf{x}_i$ . Mathematically Heisenberg's uncertainty relation

$$\Delta x \cdot \Delta p \geq \hbar/4\pi$$

follows now from the operator equation 7. We note further that the exchange phenomenon<sup>1</sup> and the basic symmetry law may be derived from (4) and the fact that the Hamiltonian is symmetric in the coordinates  $\mathbf{x}_i$ ; the eigenfunctions are either automatically symmetry functions or may (in degenerate cases) be chosen as symmetry functions, *i.e.*, as eigenfunctions also to the permutation operators  $P$ . The Schrödinger equation 4 forms therefore the basis for the entire molecular theory with an auxiliary condition entering in the form of the mathematical formulation (3) of the Pauli principle.

**Homopolar Chemical Bond.**—In chemistry, the electrostatic nature of the heteropolar bond was rather well explained by a series of authors from Berzelius to Kossel, but the inner nature of the homopolar bond was a real mystery. According to Lewis, each covalent bond was supposed to be connected with an electron pair, but it was first the establishment of modern quantum mechanics which could explain its real nature. In 1927, Heitler and London<sup>2</sup> discovered that the covalent bond in the hydrogen molecule was associated with a pair of electrons and that the binding essentially arose from the above-mentioned "exchange effect," which is associated with the impossibility of individually distinguishing the two particles. They found that, if  $a$  and  $b$  are the space wave functions for the two separated hydrogen atoms, a combined wave function of the type  $a(1)b(2)$  would not correspond to a chemical bond, whereas a symmetrized combination

$$\Psi(1,2) = a(1)b(2) + a(2)b(1) \quad (8)$$

(1) W. Heisenberg, *Z. Physik*, **38**, 411 (1926); **39**, 499 (1926); **41**, 239 (1927).

(2) W. Heitler and F. London, *ibid.*, **44**, 455 (1927).

would give a binding energy of the correct order of magnitude. The existence of the covalent chemical bond depends therefore on a typical quantum-mechanical phenomenon—the identity principle and the symmetry requirement—and, since there is no classical counterpart to this effect, it is certainly very difficult to give an elementary description of the nature of the covalent chemical bond. The saturation of the covalent bond is further explained by the Pauli principle.

Usually classical mechanics provides a first approximation to a quantum-mechanical system, but, as regards the symmetry properties, no such correspondence seems to exist. Heitler and London's discovery opened therefore an entirely new field, "Quantum Chemistry," which provides a natural link between the physics of the elementary particles and chemistry. Soon after the appearance of Heitler and London's work, Heisenberg recognized that the exchange phenomenon may be of fundamental importance also for the understanding of ferromagnetism. With the development of modern nuclear theory, it seems now as if the identity principle and the symmetry laws would be one of the most important consequences of the whole quantum theory.

**Development of Quantum Chemistry.**—Heitler and London's investigation of the hydrogen molecule gave a qualitative understanding of the homopolar chemical bond in general, and it started the development of modern quantum chemistry. There are several ways of constructing this link between chemistry and particle physics, and one of the most fruitful methods was explored by the chemists themselves by starting from the ordinary chemical terminology and translating and adapting it to the quantum-mechanical ideas. Of course, it is very hard to decide whether the electronic interpretations given in this way have a real background in nature or not, and the whole approach may hence be compared with building a tunnel in a certain direction under a mountain from one side without having yet reached the other side.

By unifying chemical and quantum-mechanical ideas, *semi-empirical theories* have been developed which are devices for correlating one set of experimental chemical data with another set. This approach has been particularly successful in organic chemistry in treating the conjugated systems. We will here only mention the explanation of the properties of the aromatic bond, the calculation of dipole moments, the directing power of substituents in aromatic systems, the color of organic molecules, the problem of addition to conjugated systems, the stability of free radicals, and so on. Important contributions have here been given by Hückel, Pauling, Wheland, Mulliken, Sklar, Coulson, Longuet-Higgins, Platt and others.

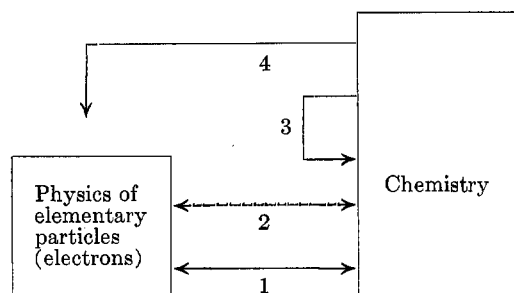
These semi-empirical theories have the advantage of being comparatively simple, and if their applications are not extended too far, the quantitative results are usually very good. They seem to be excellent devices for interpolation and extrapolation of chemical results. However, it has usually been found impossible to use the semi-empirical parameters determined for the ground state to describe also

the lower excited states, and the whole approach appears therefore to be oversimplified in many ways. Some of the parameters have also been determined purely theoretically, but the agreement with the semi-empirical values has usually not been as good as one would desire.

The other way of obtaining a connection between the theory of electrons and the ordinary chemistry is to start from the quantum-mechanical electron theory itself and try to derive solutions of the Schrödinger equation. The explanation of the homopolar covalent bond was found this way and, among other fundamental problems which have been at least approximately solved by this method, the derivation of the repulsive Born-Mayer forces within the ionic crystals, and the explanation of the Hume-Rothery-rules for alloys by Jones should be mentioned. The difficulty is here that the many-electron Schrödinger equation is very hard to solve even in an approximate form.

In distinguishing between "semi-empirical" and "pure" theories, one should always remember that all theories in physics and chemistry are basically semi-empirical in the sense that they correlate some experimental data with other experimental data—really pure theories belong to metaphysics and not to modern science. However, a theory is here called "pure" in a restrictive sense, if it derives for instance chemical data from the knowledge of only the physical values of the electronic mass and charge, Planck's constant, the atomic numbers, and the form of the Schrödinger equation, which itself represents the quintessence of a great deal of physical experience. A schematic survey of the various branches of quantum chemistry as a link between physics and chemistry is given in Fig. 2.

In this connection, it can also be discussed whether the Schrödinger equation itself forms a sufficient basis for our understanding of chemistry or not.



1. Theory of covalent bond ( $H_2$ ).
2. Theory of van der Waals forces, repulsive forces in ionic crystals, Hume-Rothery rules for alloys, etc.
3. Semi-empirical theories of dipole moments, spectra of molecules, conjugation and aromatic bond, directing power of substituents, stability of free radicals, etc.
4. Chemistry in quantum-mechanical language, theory of resonance, etc.

Fig. 2.—Quantum chemistry as a link between chemistry and the physics of the elementary particles.

**The Drastic Extrapolation.**—When Bohr in 1913 established his theory of the hydrogen atom, it was soon found out that it was impossible to generalize the theory from one electron to the case of two or more electrons. Bohr's theory gave there-

fore a description of the simplest atom but failed in giving a quantitative explanation of the remaining part of the periodic system. One of the most important points after the discovery of modern quantum mechanics in 1925 was therefore the question whether it would give a satisfactory treatment of the helium atom and the higher atoms in the periodic system. The helium atom represents a three-body problem, and, from the very beginning, it is obvious that it is impossible to solve it in a closed form. In an important series of papers, Hylleraas investigated carefully this problem and could show that it was possible to obtain the different energy levels of the atom with any accuracy desired by the spectroscopists. Even the problems concerning the relativistic effects and the Lamb-shift seem now to be rather satisfactorily solved.

Another two-electron problem of great interest was the hydrogen molecule. Heitler and London had here given only an approximate solution and, by using the same technique as was developed by Hylleraas for helium, James and Coolidge could derive the eigenfunction for the ground state of  $H_2$  and show that the quantum mechanical energy was in full agreement with the experimental value. The treatments of He and  $H_2$  both were based on Schrödinger's equation in configuration space for two-electrons, and from these successful results one has then drawn the conclusion that the same type of Schrödinger equation should be valid for a system containing an arbitrary number  $N$  of particles, *i.e.*, one has drastically extrapolated from  $N = 2$  to arbitrary values of  $N$ . The solutions of the Schrödinger equation for many-particle systems have not yet been determined with such an accuracy that one can decide whether this extrapolation is strictly valid or not, but so far there have been no objections in principle against this procedure. Dirac's general prediction in 1929 is famous in this connection:

"The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions. . . . The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. . . ."

**Solution of the Many-electron Schrödinger Equation.**—It is evident that it is mathematically impossible to solve the many-electron Schrödinger equation in a closed form, but this does not mean that one cannot obtain solutions with any accuracy desired, and the existence of the eigenfunctions has been discussed by, among others, Kato. In order to find approximate solutions, a number of schemes are now in use and a diagrammatic survey of them is given in Fig. 3.

The simplest approach is based on the one-electron model in which the total wave function is built

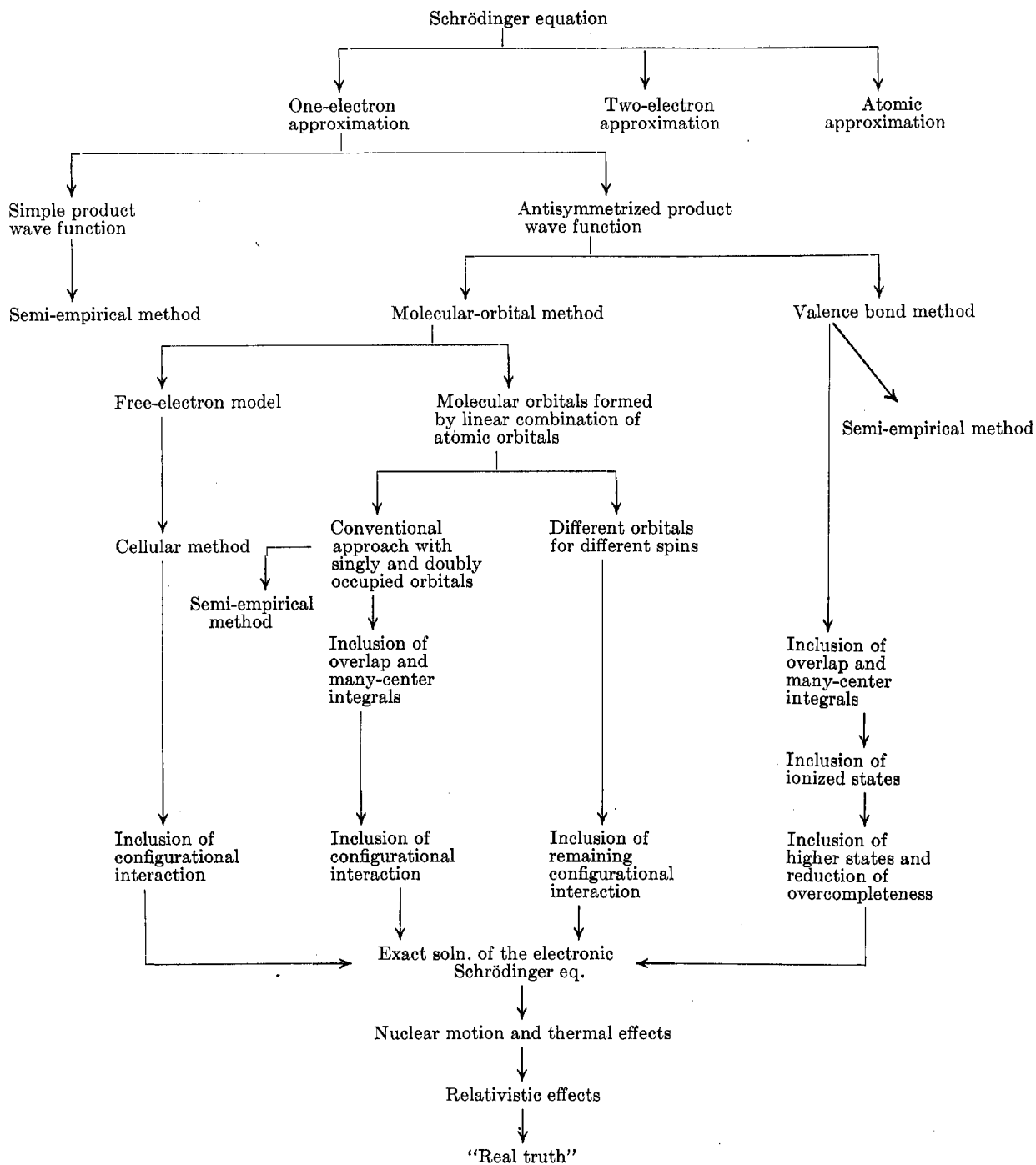


Fig. 3.—Quantum chemistry. Schematic survey of the various methods now used in molecular and solid-state theory for the solution of the Schrödinger equation.

up from one-electron functions or spin-orbitals. In a first crude approximation the total wave function for  $N$  electrons may be approximated by a product of  $N$  spin-orbitals containing each one electronic coordinate; since the total wave function is not antisymmetric, Pauli's exclusion principle has to be added as a supplementary condition. Many of the papers written on the theory of conjugated systems have been based on this approach, but it should be remembered that the accuracy in such a case cannot be too high, and usually the integrals involved have been estimated from empirical data.

If a product wave function is antisymmetrized, it is transformed to a determinant (Slater). The conventional methods have here been of two types, depending on the basic assumptions about the one-electron functions. If these one-electron functions have been taken from the atoms constituting the molecule, they have been called atomic spin-orbitals and the whole approach the valence bond method (Heitler-London, Slater, Pauling). On the other hand, if the electrons have been considered as belonging to the molecule as an entirety, the one-electron functions have been chosen as molec-

ular orbitals which are extended over the molecule as a whole (Lennard-Jones, Hund, Mulliken). Some details of the calculations according to the different schemes will be discussed below.

Originally Heitler and London developed also another variant of the valence bond method, in which the total molecular wave function was built up from the atomic wave functions of the constituents. A semi-empirical form of this atomic approximation recently has been presented<sup>3</sup> under the name of "atoms in molecules." Even a two-electron scheme has now been proposed.<sup>4</sup>

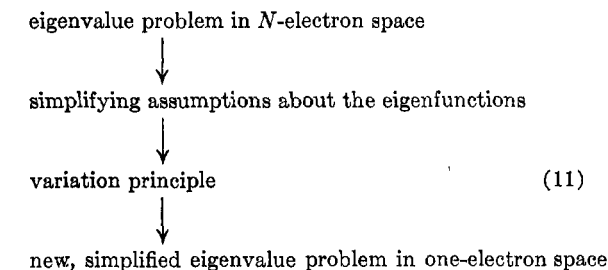
A few words should be said about the mathematics. The strongest tool up till now for deriving approximate solutions of an eigenvalue problem of the type of the many-electron Schrödinger equation is the variation principle which says that the best approximation makes the expectation value of the Hamiltonian operator, given by the mathematical expression

$$\langle H_{op} \rangle_{av} = \int \Psi^* H_{op} \Psi (dx) \quad (9)$$

an extreme value, *i.e.*

$$\delta \langle H_{op} \rangle_{av} = 0 \quad (10)$$

If this is true for all variations, then the wave function is an exact solution to the eigenvalue problem. Usually one assumes that the total wave function  $\Psi$  has a specific form containing a series of parameters, the best values of which are then determined by the condition (10). Since the original equation is an eigenvalue problem in configuration space, the variation principle is often applied in the following way



The simplified eigenvalue problem is often expressed in the form

$$H_{eff} \psi(x) = \epsilon \psi(x) \quad (12)$$

where the "effective Hamiltonian"  $H_{eff}$  is a one-particle operator which corresponds to the classical energy of a single particle (moving in the average field of all the other particles) modified to take also the quantum-mechanical symmetry effects and the Pauli principle into account. The eigenvalues  $\epsilon$  are called the orbital energies.

A standard method for solving an eigenvalue problem of this type is Ritz's method, in which the eigenfunction  $\Psi$  is expressed as a linear combination of a complete set  $\Psi_K$

$$\Psi = \sum_K \Psi_K C_K \quad (13)$$

The undetermined coefficients  $C_K$  are here obtained by the variation principle, which leads to a series of

linear equations containing the eigenvalue  $E$  as an unknown parameter

$$\sum_L (H_{KL} - E \delta_{KL}) C_L = 0 \quad (14)$$

$$H_{KL} = \int \Psi^* {}_K H_{op} \Psi_L (dx)$$

The eigenvalue is then determined by the condition that the determinant of the coefficients of this homogeneous system should vanish

$$\det \{ H_{KL} - E \delta_{KL} \} = 0 \quad (15)$$

The secular equation obtained in this way may be solved either by numerical computations or by expansions which correspond to the conventional perturbation method. Since Ritz's method may be applied either to the original eigenvalue problem (4) in  $N$ -electron space or to the simplified eigenvalue problem (12) in one-electron space, there are two types of secular equations of the same mathematical form but of essentially different physical meaning. The mathematics used is nowadays of a standard form, and a schematic survey of the various steps needed in solving the Schrödinger equation is given in Fig. 4.

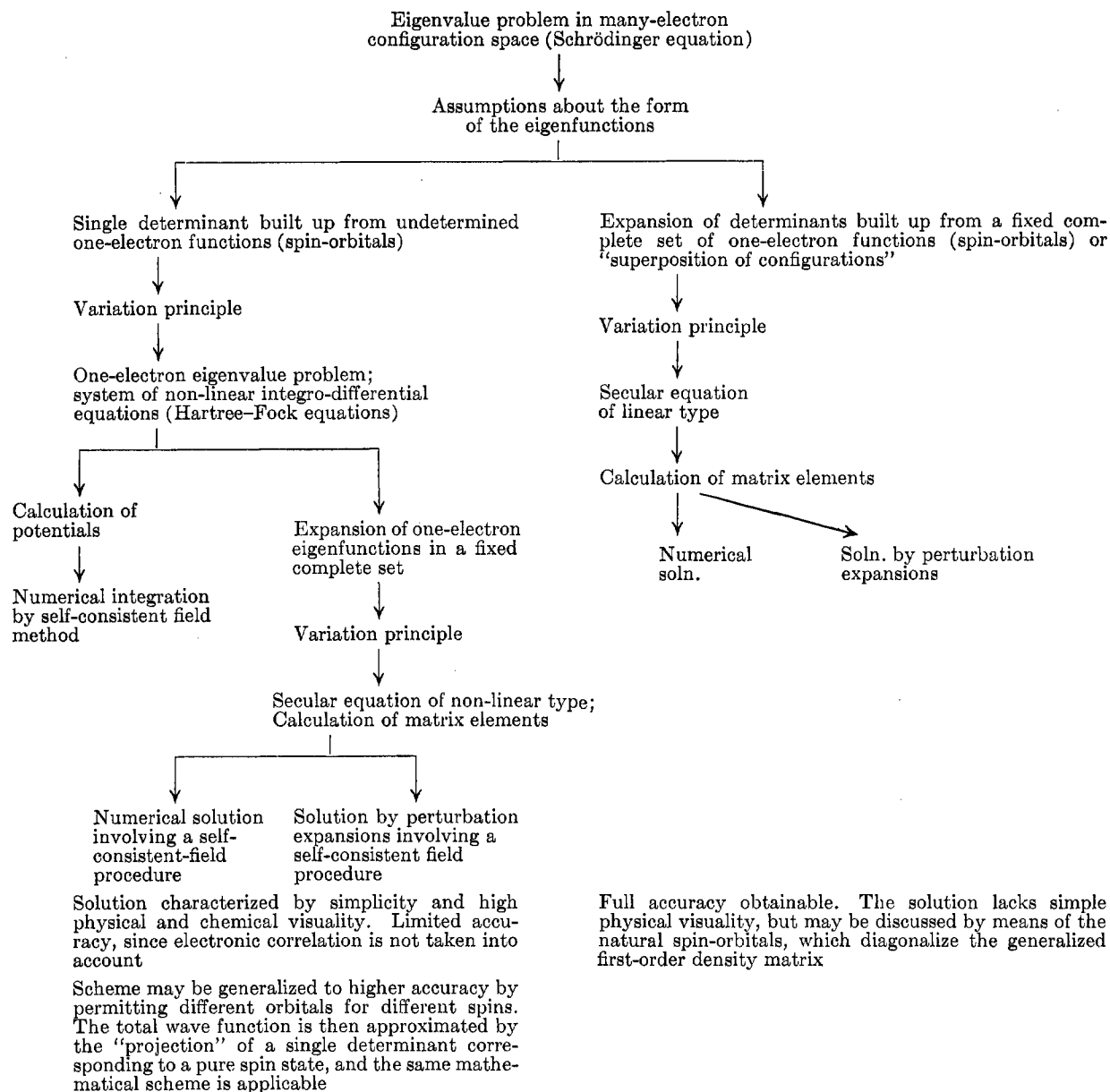
However, if the general scheme is almost the same for all the methods, the details are rather different, and we will now give some comments on the various approaches.

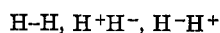
(a) **Valence Bond Method. The Theory of Chemical Resonance.**—The valence bond method developed by Heitler-London, Rumer, Slater, and Pauling is a direct generalization of the former's pioneer work on the hydrogen molecule. It was found in this simple case that, if the electrons are assigned to atomic orbitals belonging to the two hydrogen atoms involved, the bond itself corresponded formally to a total function which could be written as the difference between two determinants having the spin functions  $\alpha$  and  $\beta$  interchanged. The wave function for a molecule containing only a number  $r$  of single bonds is then built up analogously by forming the algebraic sum of the  $2^r$  determinants which are obtained from a given determinant by carrying out an  $\alpha$ - $\beta$  reversal including change of sign for every single bond occurring in the chemical structure formula and taking all possible combinations.<sup>5</sup> This method for constructing a singlet state of the total spin has its great advantage in the close parallelism between the quantum-mechanical wave function and the corresponding chemical formula for the compound. However, the method is connected with mathematical difficulties which are not yet solved and which depend on the fact that the atomic orbitals involved overlap mutually with the effect that the various determinants are not orthogonal.<sup>6</sup> The matrix elements of two non-orthogonal determinants are easily constructed, but, so far, it has not been possible to give a simple expression for the matrix elements of two general valence bond structures taking the non-orthogonality into full ac-

(5) See, *e.g.*, G. Rumer, "Göttinger Nachr.," 1932; L. Pauling, *J. Chem. Phys.*, **1**, 280 (1933).

(3) W. Moffitt, *Proc. Roy. Soc. (London)*, **A210**, 224, 245 (1951).  
 (4) Hurley, Lennard-Jones and Pople, *ibid.*, **A220**, 446 (1953);  
 L. A. Schmid, *Phys. Rev.*, **92**, 1373 (1953).

(6) The non-orthogonality problem was first emphasized by J. C. Slater, *Phys. Rev.*, **35**, 210 (1930).





which are in "chemical resonance" with each other.<sup>10</sup> In the case of the conjugated systems in organic chemistry, the positions of the double bonds are not entirely fixed in the conventional chemical formulas and, for instance in the benzene molecule, one has the following five "canonical" structures



consisting of two Kekulé structures and three Dewar structures. The total wave function is then a linear superposition of the valence bond functions corresponding to these structures. This "theory of resonance" seems first to have been suggested by Slater,<sup>11</sup> and it has then in the hands of Pauling<sup>12</sup> and others been successfully developed and applied to many fundamental chemical problems.

The resonance theory has a simplicity and chemical visuality which is striking, and it is therefore unfortunate that the basic overlap and non-orthogonality problem still appears to remain unsolved. We have previously pointed out that the non-orthogonality problem has not yet been solved for the case of a single general valence bond structure, and the problem is still worse for molecules containing resonating bonds. It is often emphasized that it is mainly the coefficients for the resonating structures in the total wave function which have the basic chemical importance, but, in this connection, it should be remembered that the structures themselves are not strictly orthogonal to each other, which means that the coefficients are not even uniquely determined. In many of the leading textbooks in quantum chemistry, the theory of resonance is usually developed in a form where all overlap integrals are neglected. This does not prevent the theory from being useful for certain purposes, for instance interpolation or extrapolation of chemical data, but one should always remember that an essential refinement of this theory is needed to bring it in full connection with quantum mechanics.

In addition to the non-orthogonality problem, there is another fundamental question in the valence bond method which has not yet been solved, namely the problem of the degree of linear dependence of a system of atomic orbitals associated with two or more nuclei. Usually one introduces just the atomic orbitals which are occupied in the conventional chemical formula for the compound, but, even if all ionized states involving these orbitals are included, the accuracy of the total wave functions cannot be brought beyond a certain limit. In order to obtain a complete accuracy, it is necessary to introduce also the excited atomic orbitals. However, if a complete system of atomic orbitals is introduced on every nucleus, the total system of basic one-electron functions will certainly be overcomplete, and essential difficulties will then occur in the theory, since the secular equation for solving the variation problem will be identically vanish-

ing, because of the existence of linear dependencies within the basic set. Even if only a limited number of atomic orbitals are introduced on every nucleus, there may exist approximate linear dependencies which are just as disastrous for the numerical solution of the secular equation as the overcompleteness.<sup>13</sup>

The problems of non-orthogonality and overcompleteness may both be solved by constructing an orthonormal set by linear combinations of the given atomic orbitals, for instance by a combination of the symmetric and successive orthonormalization procedures,<sup>14</sup> but this implies that one is losing the direct correspondence between the new valence bond method<sup>15</sup> and the simple chemical formulas and that the theory of resonance will then mainly be a mathematical scheme without direct chemical interpretation. For the moment, the whole valence bond method is therefore in a rather difficult dilemma.

(b) **The Molecular-Orbital Method.**—The valence bond method is partly based on the idea of the existence of individual atoms within the molecule. However, when the atoms are put together in a molecular system, the valence electrons may be considered as belonging to the molecule as a whole, and this point of view forms the basis for the molecular-orbital method (Lennard-Jones, Hund, Mulliken). This aspect has been particularly important for the understanding of the aromatic bond<sup>16</sup> and the general properties of the conjugated compounds. In this approach, the total wave function is approximated by a single determinant built up from the occupied spin-orbitals. In order to obtain the best approximation to a real eigenfunction, one may apply the variation principle, and this leads to certain equations for the orbitals involved which are usually called the Hartree-Fock equations and which have the form (12). These equations have been solved numerically for a whole series of atoms in the periodic system, but, only for a few molecules have they been investigated on a more exact basis. The Hartree-Fock equations are non-linear integro-differential equations of a rather complicated type, and they are usually solved by means of a self-consistent-field procedure.

For a system containing a large number of mobile electrons like the metals or the conjugated compounds, one may start from an approximate free-electron model, where the extension of the system gives the dimensions of the box within which the electrons are enclosed. For metals this model has been essentially refined in the cellular method, which is an attempt to solve the Hartree-Fock equations more accurately for a solid-state system having high symmetry.

For molecules, there is little hope that one will be able to apply the self-consistent-field method in the same way as in atoms and metals, and instead one may try to solve the basic equations by expanding

(13) R. H. Parmenter, *Phys. Rev.*, **86**, 552 (1952).

(14) P. O. Löwdin, *J. Chem. Phys.*, **18**, 385 (1950); *Adv. Phys.*, **5**, 1 (1956), Sec. 3.2.

(15) R. McWeeny, *Proc. Roy. Soc. (London)*, **A223**, 63, 306 (1954).

(16) E. Hückel, *Z. Physik*, **60**, 423 (1930); **70**, 204 (1931); **72**, 310 (1931).

(10) J. C. Slater, *Phys. Rev.*, **35**, 210 (1930).

(11) J. C. Slater, *ibid.*, **37**, 481 (1931), particularly p. 489.

(12) L. Pauling, *J. Chem. Phys.*, **1**, 280 (1933), and a series of papers in *J. Chem. Phys.* and *J. Am. Chem. Soc.*



the solutions in a fixed complete set.<sup>17</sup> This set may be chosen as consisting of the atomic orbitals of the molecule under consideration, and this leads to an approach usually denoted by the symbol MO-LCAO, which means that the molecular orbitals are formed by "linear combinations of atomic orbitals." When these orbitals are substituted in the total wave function, the matrix elements of the energy will contain integrals of the same type as in the valence bond method. In the molecular orbital method, there is no basic non-orthogonality problem of the same type as occurred in the valence bond method, but one must certainly take the overlap integrals into full account even in this approach. The calculation of the molecular integrals in general will be discussed below.

The molecular orbitals are of particular importance in the physical description of a molecule, since it may be shown that they may be used in constructing the wave functions for the ionized and excited states of the compound. The real and virtual solutions of the Hartree-Fock equations form further a complete system together, and this system may be used for describing the exact eigenfunctions to the total Hamiltonian. Each determinant built up from  $N$  spin-orbitals selected from a complete orthonormal system is called a "configuration"—a name which is borrowed from the theory of atomic spectra—and, since it may be shown that the exact wave function may be expanded in a sum of such determinants, the method is called "superposition of configurations" or sometimes "configurational interaction."

A determinant is invariant against unitary transformations of the orbitals under consideration. By carrying out a suitable transformation of this type, it has been shown that the molecule may be described by means of equivalent orbitals<sup>18</sup> which have the property that the corresponding exchange integrals are particularly small so that the chemical forces may be described as closely as possible by means of electrostatic forces of the "classical" type. The equivalent orbitals give hence a rather visual description of the electronic structure of the chemical bonds.

(c) **Calculation of Molecular Integrals.**—In both the valence bond method and the molecular orbital method, one has usually based the whole description of the system on a set of atomic orbitals, and the expectation values of physical and chemical quantities are then expressed as integrals containing these orbitals. In the energy calculations, the main problem is represented by the calculation of the electronic repulsion integrals, which may contain as many as four atomic orbitals, since each electron density is a product of two atomic orbitals. Such an electronic repulsion integral may therefore be associated with maximum four nuclei, but if two or more nuclei coincide, the integral will degenerate into a three-, two- or one-center integral. Some of the molecular integrals of atomic orbitals, which occurred in Heitler and London's the-

ory for the hydrogen molecule, were only estimated, and the first "exchange integral" was actually evaluated by Sugiura. Different types of molecular integrals were later calculated by various authors, but it was soon discovered that, if it should be possible to work out the detailed structure of all molecules of interest, it would be necessary to standardize the integrals, since it would be too laborious and tedious to evaluate the integrals for every special case. The first extensive tables were worked out by Kotani and his school in Japan immediately before the war.

After 1945, the problems of the calculation of the molecular integrals have been taken up at several places. In the United States Mulliken in Chicago, Slater at M.I.T., Eyring in Utah and others have been interested in various aspects of the problem, in England Coulson and Barnett have prepared auxiliary tables, and in Germany Kopineck has investigated two-center integrals—many other important projects not mentioned. In Uppsala we have specialized on evaluating molecular integrals for the atomic self-consistent field functions. Numerical tables are now partly available<sup>19</sup> or under publication, but it will probably take several years until the problem of the standard integrals has been concluded. The two-center integrals may be tabulated in a rather condensed form, but it is evident that, for the tabulation of the three- and four-center integrals, a rather large number of books would be needed, and instead one has tried to work out accurate formulas for converting these integrals into two-center integrals, particularly overlap and coulomb integrals. The standard integrals are now evaluated for mostly Slater exponentials, but the question remains whether one should use hydrogen-like functions including the continuum or an entirely discrete set.

(d) **Configurational Interaction.**—If one looks at the diagram in Fig. 3 over the conventional methods now used for solving the many-electron Schrödinger equation, one will find that the whole development of quantum chemistry is hindered by the large amount of numerical work involved. In the valence bond method as well as in the MO-LCAO method, the evaluation of the molecular two-center integrals has represented a major problem, and it is evident that the question of the inclusion of the many-center integrals will be much harder to solve. The question of the non-orthogonality and the inclusion of the overlap integrals represents a theoretical and numerical problem which has now been solved successfully, at least for the molecular-orbital method.

The calculation of the molecular integrals is not the only obstacle, however. Even if all these numerical difficulties have been overcome, one cannot expect a too high accuracy of the two standard methods applied in their simplest or naive forms, since the basic sets are far from being complete.

In order to improve the accuracy, it is necessary to extend the basic set from  $N$  to  $M$  functions,

(17) C. A. Coulson, *Proc. Camb.*, **33**, 104 (1937); C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951); P. O. Löwdin, *Phys. Rev.*, **97**, 1490 (1955).

(18) J. Lennard-Jones, *Proc. Roy. Soc. (London)*, **A198**, 1, 14 (1949), and a series of papers by him and his school in the same journal.

(19) A list of references may be found in A. Dalgarno, *Math. Tab. Aids. Comp.*, **8**, 203 (1954); see also Kotani, Amemiya, Ishiguro and Kimura, "Table of Molecular Integrals," Maruzen Co., Ltd., Tokyo, 1955, and H. Preuss, "Integraltafeln zur Quantenchemie," Springer, Berlin, 1956.

where  $M$  goes to infinity when the set tends to be complete. The total wave function may then be expanded in determinants over the configurations obtained by selecting  $N$  functions from the basic set, and, since the number of configurations is given by the binomial coefficient  $\binom{M}{N} = M!/N!(M-N)!$ , the secular equation will be of this order. Since the number  $\binom{M}{N}$  is quickly increasing with  $M$ , the order of the secular equation goes up so rapidly that it may be possible to solve this equation numerically, only if an electronic computer of sufficiently high capacity is available. The total wave function obtained in this way is complicated and difficult to interpret physically and chemically, but, by introducing the natural spin-orbitals<sup>20</sup> which diagonalize the generalized first-order density matrix, one obtains the configuration expansion of most rapid convergency, and the whole problem is then usually essentially simplified.

In this way it is possible to approach the exact solution with any accuracy desired, and it is evident that the final result will be independent of the starting point. The molecular orbital method including configurational interaction will therefore give the same result as the valence bond method including ionized and excited states—provided that, in the latter, one has taken the non-orthogonality into proper account and reduced away the linear dependencies caused by the overcompleteness. However, the numerical work involved in carrying out even a modest “configurational interaction” is of such an order of magnitude that one is eagerly looking for any possibilities of simplifying the procedure. In the molecular-orbital method, the main effect of the higher configurations is that they take the “electronic correlation” into account, and the question is whether this effect could be included in a simpler way.

(e) **Electronic Correlation.**—The molecular orbital method is based on the “independent-particle model” which assumes that, in a first approximation, one can neglect the mutual interaction between all the electrons or take it into account only by means of an “average” field. However, a repulsive potential, like the Coulomb potential  $e^2/r_{ij}$ , tries naturally to keep the particles  $i$  and  $j$  apart, and, since this “correlation” between the movements of the particles is entirely neglected in constructing a total wave function in the form of a simple product of the occupied spin-orbitals, the corresponding wave function and energy are affected by errors which are usually called “correlation errors.” The situation is somewhat changed by the antisymmetrization procedure, which has the direct consequence that the probability density for two particles with the same spin to be in the same place will be zero of at least the second order (the “Fermi hole”). The main problem in treating antisymmetrized functions is therefore to take the correlation between electrons having anti-parallel spins into proper account. This problem is of fundamental importance for the understanding of the

homopolar chemical bond, since this bond is associated with an electron pair having opposite spins. Extensive calculations have shown that each doubly filled orbital is associated with a correlation error which amounts to about 1 electron volt. The correlation energy is therefore a very important quantity in the theory of the chemical bond.

In the first successful treatments of the simplest two-electron systems, the He atom (Hylleraas) and the  $H_2$  molecule (James and Coolidge), the interelectronic distance  $r_{12}$  was explicitly introduced into the total wave function, which is then called a “correlated” wave function. However, there are essential difficulties in generalizing this procedure to many-electron systems and recently one has therefore tried another approach, which is based on the idea of the existence of a more “static” correlation. One has abandoned the idea of the doubly filled orbitals which occur in the original formulation of Pauli’s exclusion principle, and instead assumed that electrons having different spins may occupy different orbitals in space.<sup>21</sup> This means that the molecular orbitals have got a new degree of freedom and that the number of orbitals is twice as high as before. It is possible to extend the ordinary Hartree–Fock scheme to have different orbitals for different spins, and the main point is that even the generalized scheme preserves a great deal of the mathematical simplicity and physical visuality which is characteristic for the “independent-particle-model.” In applications to simple atoms and molecules, it has been shown that the main part of the correlation energy may be taken into account in this simple way without any further configurational interaction.

In a scheme where there are different orbitals for different spins, a single determinant  $D$  is a mixture between spin states of various multiplicities so that, for an even number of electrons, we have

$$D = \text{singlet} + \text{triplet} + \text{quintet} + \dots \quad (16)$$

However, one can always select any pure spin component desired by means of a “projection operator”  $O$  having the simple property  $O^2 = O$ . Measuring the spin in units of  $\hbar$ , we find for instance that the operator  ${}^1O$  for selecting the singlet component has the form

$${}^1O = \left(1 - \frac{S^2}{1.2}\right) \left(1 - \frac{S^2}{2.3}\right) \left(1 - \frac{S^2}{3.4}\right) \dots \quad (17)$$

In this operator the first factor will annihilate the triplet term in (16), the second factor the quintet term, etc., whereas the singlet term will survive the operation in an unchanged form. In the extended independent-particle model, the total wave function  $\Psi$  is therefore a projection of a single determinant,  $\Psi = OD$ , and this has the important mathematical consequence that the expectation value of any physical or chemical quantity is easily formally evaluated.

$$\begin{aligned} \int \Psi^* H_{op} \Psi(dx) &= \int (O^* D^*) H_{op} (OD)(dx) = \\ &= \int D^* O^* H_{op} OD(dx) = \int D^* H_{op} (OD)(dx) \end{aligned} \quad (18)$$

This is an essential difference against the valence bond method, where the problem of calculating

(20) P. O. Löwdin, *Phys. Rev.*, **97**, 1474 (1955); P. O. Löwdin and H. Shull, *ibid.*, **101**, 1730 (1956).

(21) P. O. Löwdin, *Rep. Nikko Symp. Mol. Phys.*, 113 (1954); *Phys. Rev.*, **97**, 1509 (1955).

the matrix elements has not yet been fully solved. There is consequently good hope that the correlation problem may be solved with a comparatively high accuracy ( $\approx 0.15$  e.v. per electron pair) without a more or less complete configurational interaction.

(f) **The United Atom-Model. A Simple Solution of the Many-Electron Problem in Principle.**—In the survey given above, it has been pointed out that large difficulties are involved in calculating for instance the two- and many-center integrals occurring in the standard treatments of the molecular problems. In this connection, it could be pointed out that the mathematical problem of the solution of the many-electron Schrödinger equation may be solved, at least in principle, in a very simple way. In order to describe the total wave function, one can select a basic set which is associated with a single center in space and forms a complete set. One set of this type is of the form

$$r^l L_{n+1}^{2l+2} (2\eta r) e^{-\eta r} Y_{lm}(\vartheta, \varphi)$$

where the radial functions are Laguerre polynomials (without principal quantum number in the variable),  $\eta$  is an adjustable effective charge, and the functions  $Y_{lm}$  are the ordinary spherical harmonics. The matrix elements of the Hamiltonian of an arbitrary molecular system with respect to this set are easily constructed and evaluated, and, since the total wave function may always be expanded in Slater determinants built up from configurations of the basic set, one may solve the Schrödinger equation by means of "superpositions of configurations." The main problem is apparently to solve the secular equation corresponding to this problem, and this is possible if an electronic computer having sufficiently large capacity is available. With the development of the mathematical machines, one can expect to get higher and higher accuracy in this process, and there are no limitations in principle as to the accuracy obtainable. The essential difference with respect to the conventional methods is that here no many-center integrals are involved and that the matrix elements are easily calculated. Since only a single center is used, the mathematical scheme corresponds to some extent to the "united atom model," which was frequently discussed in the early days of molecular theory. No problem of including the continuum occurs, since the basic set is entirely discrete. It is clear that this model may be successful for molecules having a small extension in space, but that it also may be rather cumbersome and require an enormous number of configurations for describing a large molecule. It may be anticipated that the model should be particularly good for describing the excited states of the Rydberg type.

The choice between the conventional methods using atomic orbitals associated with different nuclei and the one-center model is therefore essentially a choice between the solution of a secular equation of lower order with complicated matrix elements and a secular equation of very high order having simple matrix elements. It is true that, in the one-center model, the basic set has no natural association with the problem itself, but, after having ob-

tained the total wave function, one may transform the result to another basic set—the natural spin-orbitals—which is directly associated with the problem under consideration.

(g) **Recent Development of Valence Theory. Density Matrices.**—Some simplifications of the valence theory have recently been suggested. In quantum mechanics all physical and chemical quantities are represented by hermitean operators  $F_{op}$ , but we note that only the expectation values of these operators

$$\langle F_{op} \rangle_{av} = \int \Psi^* F_{op} \Psi (dx) \quad (19)$$

are really measurable. For a many-particle system, the operator  $F_{op}$  may be expressed in the form

$$F_{op} = F_{(0)} + \sum_i F_i + \frac{1}{2!} \sum_{ij}' F_{ij} + \frac{1}{3!} \sum_{ijk}' F_{ijk} + \dots \quad (20)$$

where  $F_{(0)}$  is a constant,  $F_i$  a one-particle operator,  $F_{ij}$  a two-particle interaction,  $F_{ijk}$  a three-particle interaction, etc. The operator  $F_{op}$  is said to be of the order  $p$ , if the highest interaction occurring is of this order. It has recently been emphasized<sup>22</sup> that, in order to find the value of (19), it is not necessary to know the wave function in detail but only a certain density matrix of order  $p$  of the form

$$\Gamma(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_p | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_p) = \binom{N}{p} \int \Psi^*(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_p \mathbf{x}_{p+1} \dots \mathbf{x}_N) \Psi(\mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_p \mathbf{x}_{p+1} \dots \mathbf{x}_N) d\mathbf{x}_{p+1} \dots d\mathbf{x}_N \quad (21)$$

This matrix is hermitean and antisymmetric in each set of its indices, and it satisfies further the normalization condition

$$\int \Gamma(\mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_p | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_p) d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_p = \binom{N}{p} \quad (22)$$

The expectation value of  $F_{op}$  is then given by the formula

$$\langle F_{op} \rangle_{av} = F_{(0)} + \int F_1 \Gamma(\mathbf{x}'_1 | \mathbf{x}_1) d\mathbf{x}_1 + \int F_{12} \Gamma(\mathbf{x}'_1 \mathbf{x}'_2 | \mathbf{x}_1 \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 + \int F_{123} \Gamma(\mathbf{x}'_1 \mathbf{x}'_2 \mathbf{x}'_3 | \mathbf{x}_1 \mathbf{x}_2 \mathbf{x}_3) d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_3 + \dots \quad (23)$$

where, in the integrals, we have introduced the additional convention that the operators  $F_1$ ,  $F_{12}$ ,  $F_{123}$ , . . . should work only on the unprimed coordinates and that, after the operations have been carried out, we put all  $\mathbf{x}'_i = \mathbf{x}_i$ . According to (9) and (22), the total energy of a molecular system is for instance given by the expression

$$\langle H_{op} \rangle_{av} = \frac{e^2}{2} \sum_{gh} \frac{Z_g Z_h}{r_{gh}} + \frac{1}{2m} \int \mathbf{p}_1^2 \Gamma(\mathbf{x}'_1 | \mathbf{x}_1) d\mathbf{x}_1 - e^2 \sum_g Z_g \int \frac{\Gamma(\mathbf{x}_1 | \mathbf{x}_1)}{r_{1g}} d\mathbf{x}_1 + e^2 \int \frac{\Gamma(\mathbf{x}_1 \mathbf{x}_2 | \mathbf{x}_1 \mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 \quad (24)$$

which implies that the energy and the valence properties are determined already by the density matrix  $\Gamma(\mathbf{x}'_1 \mathbf{x}'_2 | \mathbf{x}_1 \mathbf{x}_2)$  of the second order and that it is not necessary to know the total wave function  $\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N)$  of all  $N$  coordinates. The first term in (23) is the internuclear repulsion energy, the second is the kinetic energy of the electrons, the third

(22) P. O. Löwdin, *Phys. Rev.*, **97**, 1474 (1955); R. McWeeny, *Proc. Roy. Soc. (London)*, **A232**, 114 (1955).

represents the interaction energy between the electrons and the nuclei, whereas the last one is the interelectronic repulsion energy.

The density matrix of order  $p = N$  is defined by the relation

$$\Gamma(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_N | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N) = \Psi^*(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_N) \Psi(\mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N) \quad (25)$$

and the lower order density matrices may then be found successively by integration

$$\Gamma(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_{p-1} | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_{p-1}) = \frac{p}{N-p+1} \int \Gamma(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_{p-1} \mathbf{x}'_p | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_{p-1} \mathbf{x}_p) dx_p \quad (26)$$

It would also be of interest to investigate the *reverse* problem and to see how much the knowledge of a lower-order density matrix ( $p < N$ ) would determine the higher-order density matrices and the wave function. This problem is far from being solved and only a few special cases have been treated up till now.

It has been shown<sup>21</sup> that, in the Hartree-Fock scheme where the total wave function is approximated by a single Slater determinant, the first-order density matrix  $\Gamma(\mathbf{x}'_1 | \mathbf{x}_1)$  fulfills the two basic relations

$$\Gamma^2 = \Gamma, \text{ trace } \{\Gamma\} = N \quad (27)$$

and that it further determines also all the higher-order density matrices according to the formula

$$\Gamma(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_p | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_p) = \frac{1}{p!} \det \{\Gamma(\mathbf{x}'_i | \mathbf{x}_i)\} \quad (28)$$

where the determinant is of order  $p$ . This result implies that, in the molecular orbital treatment of for instance the ground state of a molecule, it would be possible to determine all chemical properties without the explicit knowledge of the individual molecular orbitals, since  $\Gamma(\mathbf{x}'_1 | \mathbf{x}_1)$  describes entirely the quantum-mechanical situation. A practical method for the direct calculation of the first-order density matrix has also been constructed.<sup>23</sup> It should be observed, however, that the simple relation (28) is not valid in higher approximations than the Hartree-Fock scheme.

It would certainly be worthwhile to investigate under which conditions the variation principle (10) may be formulated in terms of the second-order density matrix  $\Gamma(\mathbf{x}'_1 \mathbf{x}'_2 | \mathbf{x}_1 \mathbf{x}_2)$  instead of the wave function.<sup>24</sup> In this connection we note that not all hermitean matrices  $f(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_p | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_p)$  with the correct antisymmetry and normalization properties are necessarily density matrices and that, for instance for  $p = N$ , a necessary and sufficient condition for the existence of the product form (25) is expressed by the relation

$$\frac{\Gamma(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_N | \alpha_1 \alpha_2 \dots \alpha_N) \Gamma(\alpha_1 \alpha_2 \dots \alpha_N | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N)}{\Gamma(\alpha_1 \alpha_2 \dots \alpha_N | \alpha_1 \alpha_2 \dots \alpha_N)} = \Gamma(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_N | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N), \quad (29)$$

for arbitrary values of the parameters  $\alpha_1, \alpha_2, \dots, \alpha_N$ . In a two-electron system, the second-order density matrix must therefore be varied subject to the condition (29) for  $N = 2$ , which is a rather severe restriction. It remains to investigate the auxiliary

conditions which may exist for many-electron systems with  $N \geq 2$ .

There seems to be no question that the density matrix formalism renders a considerable simplification of the quantum theory of many-particle systems. It emphasizes such points as are of essential physical and chemical interests, and it avoids such concepts and ideas, which are of a more artificial or conventional type, as for instance different types of basic orbitals. However, the orbital idea itself is certainly useful, and we will now discuss how it may be preserved and utilized in connection with the density matrices.

(h) **Natural Spin-orbitals.**—The idea of the existence of certain spin-orbitals is of essential importance in describing atomic and molecular systems, since it gives a high degree of simplicity and visuality to the theoretical explanation of a great deal of physical and chemical experimental experience. The idea goes back to classical quantum mechanics, where it was assumed that each electron occupies its own fully specified quantum state, and we will now discuss whether it is possible to maintain this basic idea also in a more exact theory taking the interelectronic repulsion and correlation into full account.

Another reason for the introduction of spin-orbitals is of a more mathematical nature and depends on the fact that, if we introduce a complete orthonormal set of one-electron functions  $\psi_k(\mathbf{x})$ , it is possible to expand an arbitrary antisymmetric wave function  $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$  as an infinite sum of Slater determinants built up from this set

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \sum_K C_K \Psi_K(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad (30)$$

where the sum should be taken over all ordered configurations  $K$ , *i.e.*, over all selections of  $N$  indices  $k_1 < k_2 < \dots < k_N$ . The coefficients  $C_K$  for an eigenfunction may in principle be determined by the variation principle, which leads to the linear system (14) and the secular equation 15; this is the method we have previously mentioned under the name of "configurational interaction." In the different approaches to a molecular quantum theory, one has hoped to obtain good accuracy with only one or a few terms included in the expansion (30) and, for this purpose, one has chosen different basic sets of spin-orbitals: atomic orbitals, molecular orbitals and so on. A survey is given in Fig. 5, showing also the main advantages of the different descriptions.

If the basic set is not properly chosen, the series of determinants in (30) may be very slowly convergent with a corresponding difficulty in interpreting the results. In this connection, it seems therefore natural to ask whether there exists any basic set of spin-orbitals  $\chi_k(\mathbf{x})$  which leads to the most "rapid convergence" in the expansion of the wave function  $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$  for a specific state.<sup>25</sup> The answer may be found by a consideration<sup>26</sup> of the first-order density matrix defined by (21) for  $p = 1$

$$\Gamma(\mathbf{x}'_1 | \mathbf{x}_1) = N \int \Psi^*(\mathbf{x}'_1 \mathbf{x}_2 \dots \mathbf{x}_N) \Psi(\mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N) dx_2 \dots dx_N \quad (31)$$

(23) R. McWeeny, *Proc. Roy. Soc. (London)*, **A235**, 496 (1956).

(24) J. E. Mayer, *Phys. Rev.*, **100**, 1579 (1955).

(25) J. C. Slater, *ibid.*, **51**, 385 (1951).

(26) P. O. Löwdin, *ibid.*, **97**, 1474 (1955).

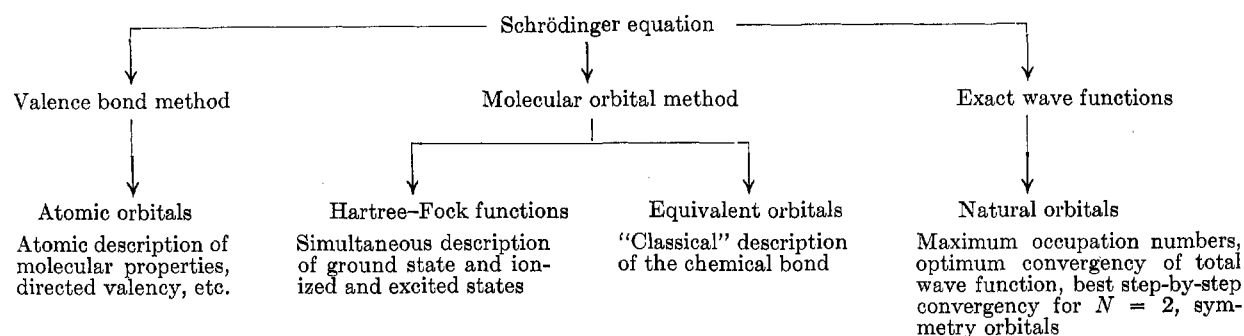


Fig. 5.—Development of the orbital idea in quantum chemistry.

By using the arbitrary complete orthonormal set  $\psi_k(\mathbf{x})$ , this matrix may be expressed in the form

$$\Gamma(\mathbf{x}'_1 | \mathbf{x}_1) = \sum_{kl} \psi_k^*(\mathbf{x}'_1) \psi_l(\mathbf{x}_1) \gamma_{lk} \quad (32)$$

where the coefficients  $\gamma_{lk}$  form an hermitean matrix, which may be found from the coefficients  $C_K$  by substituting (30) into (31). For the diagonal elements, we obtain the simple formula

$$\gamma_{kk} = \sum_K^{(k)} |C_K|^2 \quad (33)$$

where the summation should be carried out over all configurations  $K$  containing the specific index  $k$ . The element  $\gamma_{kk}$  may be interpreted as the *occupation number* for the spin-orbital  $\psi_k(\mathbf{x})$ , and we note that it depends only on the given state characterized by  $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$  and the orbital  $\psi_k(\mathbf{x})$  under consideration. By combining (31) and (32), we obtain the explicit formula

$$\begin{aligned} \gamma_{kk} &= \int \psi_k(\mathbf{x}'_1) \Gamma(\mathbf{x}'_1 | \mathbf{x}_1) \psi_k^*(\mathbf{x}_1) d\mathbf{x}'_1 d\mathbf{x}_1 = \\ &= N \int \psi_k(\mathbf{x}'_1) \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \psi_k^*(\mathbf{x}_1) \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ &\quad d\mathbf{x}'_1 d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \end{aligned} \quad (34)$$

The occupation numbers  $\gamma_{kk}$  have simple properties. The normalization condition (5) gives  $\sum_K |C_K|^2 = 1$ , and (33) leads then to the inequality

$$0 \leq \gamma_{kk} \leq 1 \quad (35)$$

showing that there is never more than one electron in any chosen spin-orbital. This theorem follows from the antisymmetry property and is an expression for Pauli's exclusion principle. In the naive formulation of this principle, each spin-orbital could be occupied by a full electron which then would exclude any other electron from entering the same orbital. This model has the advantage of a high degree of physical visuality, and, in order to approach it as much as possible, we will now introduce the basic orthonormal set  $\chi_1, \chi_2, \chi_3, \dots$  which has *maximum occupation numbers*.

Let  $\mathbf{U}$  be the unitary matrix which brings the hermitean matrix  $\gamma_{lk}$  to diagonal form

$$\mathbf{U}^+ \gamma \mathbf{U} = \mathbf{n} = \text{diagonal matrix} \quad (36)$$

Introducing the set  $\chi$  by the matrix formula  $\chi = \psi \mathbf{U}$  or

$$\chi_k = \sum_{\alpha} \psi_{\alpha} U_{\alpha k} \quad (37)$$

we obtain  $\gamma = \mathbf{U} \mathbf{n} \mathbf{U}^+$ ,  $\psi = \chi \mathbf{U}^+$ , and finally

$$\Gamma(\mathbf{x}'_1 | \mathbf{x}_1) = \sum_k \chi_k^*(\mathbf{x}'_1) \chi_k(\mathbf{x}_1) n_k \quad (38)$$

The basic set  $\chi$  defined by (37) has thus the occupa-

tion numbers  $n_k$ , and the extremum properties follow then immediately from the fact that  $n_1, n_2, n_3, \dots$  (with  $n_1 \geq n_2 \geq n_3 \dots$ ) are the *eigenvalues* of the matrix  $\gamma_{lk}$ .

The functions  $\chi_1, \chi_2, \chi_3, \dots$  will in the following be called the *natural spin-orbitals* associated with the state under consideration. The first function  $\chi_1$  is the spin-orbital which has the highest occupation number possible, the second function  $\chi_2$  has the same property within the class of orbitals orthogonal to  $\chi_1$ , the third function has the same property within the class of orbitals orthogonal to  $\chi_1$  and  $\chi_2$ , etc.

If the relation  $\psi = \chi \mathbf{U}^+$  is substituted into (30), we obtain an expansion of  $\Psi$  into configurations of the natural spin-orbitals

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = (N!)^{-1/2} \sum_K A_K \det \{ \chi_{k1}, \chi_{k2}, \dots, \chi_{kN} \} \quad (39)$$

which will be called the *natural expansion*. This series is characterized by a most "rapid convergence" in the following sense: according to an elementary theorem<sup>27</sup> for the eigenvalues of an hermitean matrix, the sum of the  $r$  highest eigenvalues is always larger than the sum of any  $r$  diagonal elements, which gives

$$\sum_{k=1}^r n_k \geq \sum_{k=(1)}^{(r)} \gamma_{kk} \quad (40)$$

By using (33) and (39), we then obtain

$$\sum_{k=1}^r \sum_K^{(k)} |A_K|^2 \geq \sum_{k=(1)}^{(r)} \sum_K |C_K|^2 \quad (41)$$

which expresses the optimum convergency property of the natural expansion.

The natural spin-orbitals are *symmetry orbitals*. This important property may be used for separating the  $\sigma$ - and  $\pi$ -electrons in an exact theory for the conjugated organic compounds, for an exact formulation of the band theory for crystals, etc.

The case of two electrons ( $N = 2$ ) is of particular importance for the understanding of the chemical bond and has been analyzed in greater detail.<sup>28</sup> It has been shown that, in this case, the natural expansion of the total wave function  $\Psi(\mathbf{x}_1, \mathbf{x}_2)$  has another important optimum convergency property in addition to (41). If the natural expansion is interrupted after  $r$  terms, the renormalized function

(27) This theorem is easily derived from the separation theorems given e.g., in J. K. L. MacDonald, *Phys. Rev.*, **48**, 830 (1933).

(28) P. O. Löwdin and H. Shull, *ibid.*, **101**, 1730 (1956).

$\Psi_r$  has the smallest total quadratic deviation from the exact solution.

$$\int |\Psi - \Psi_r|^2 dx_1 dx_2 \quad (42)$$

of all functions built up by configurations selected from a finite basic set  $\psi_1, \psi_2, \dots, \psi_r$  of order  $r$ . The result implies that  $\chi_1$  is closely related to but not identical with the corresponding Hartree-Fock function.

Detailed calculations on the ground state of the helium atom have given the following occupation numbers for the first three natural spin-orbitals

$$n_1 = 0.99562, n_2 = 0.00431, n_3 = 0.00007 \quad (43)$$

The result shows how the coulomb repulsion is breaking up the closed shell  $(1s)^2$ , since it is energetically cheaper to have a small fraction of the electron in  $\chi_1$  excited to the higher spin-orbitals  $\chi_2$  and  $\chi_3$ . Similar calculations for the ground state of the hydrogen molecule are now in progress, and we hope that they will lead to a simple but at the same time accurate treatment of the covalent bond.

The measurements in modern chemistry are now so refined that a very high degree of accuracy is needed in the corresponding theories. In quantum mechanics good methods have been worked out for determining eigenvalues, *i.e.*, total energies  $E$ , but unfortunately the chemists and physicists are usually measuring only energy differences  $\Delta E$  which are very small fractions of the total quantities. This implies that rough models are no longer sufficient and that, in many cases, not even the Hartree-Fock scheme has a high enough accuracy. The problem of the electronic correlation has thus become of great importance, but it seems as if the introduction of density matrices and natural spin-orbitals would prevent the theory from becoming too complicated in its mathematical form to be given a simple physical and chemical interpretation.

**Goal of Quantum Chemistry.**—It is sometimes said that a theoretician is a person who knows how to solve a problem, but who cannot do it. This remark is certainly true concerning the quantum chemists since it is pointed out above that we know several ways of solving the many-electron Schrödinger equation in principle, but that there are large difficulties in carrying out these solutions. The difficulties are therefore transformed from the purely mathematical plane to a plane where both mathematics and numerical technique are involved. Unfortunately this does not mean that the problem

has been solved or even essentially simplified, since numerical technique is a domain which requires just as much ingenuity as pure mathematics. The development of the modern electronic computers may here be of fundamental importance.

The problems involved in quantum chemistry are comparatively hard, and the scientists working within this field have therefore found it desirable to arrange a series of international conferences in order to get a common attack on all these problems (Shelter Island 1951, Nikko 1953, Stockholm-Uppsala 1955, Austin 1955). The arrangements of these symposia have greatly helped the development of molecular theory, but, since there is an extremely small number of quantum chemists in relation to the total number of chemists, it will probably take a considerable time before even the more fundamental problems of chemistry have been thoroughly treated by quantum mechanical methods. Today there is therefore no answer to the question whether the above-mentioned drastic extrapolation from  $N = 2$  to an arbitrary  $N$  is justified or not, but so far there have not been any essential objections to it, and we have thus good reasons for believing that the many-electron Schrödinger equation in configuration space is the correct basis for the description of molecular or solid-state systems.

There seems to be a rather long way to go before we reach the mathematical goal of quantum chemistry, which is to be able to predict accurately the properties of a hypothetical polyatomic molecule before it has been synthesized in the laboratories. The aim is also to obtain such knowledge of the electronic structure of matter that one can construct new substances having properties of particular value to mankind. To learn to think in terms of electrons and their quantum mechanical behavior is probably of greater technical importance than we can now anticipate. We have further shown that quantum mechanics is necessary to understand the covalent bond, and there is certainly no doubt that the tool of quantum mechanics will appear to be more and more fundamental for the discussion of chemical problems in general. It seems therefore urgent to incorporate the language and technique of quantum mechanics in the domain of chemistry, and particularly to find the correct electronic interpretations of the ordinary chemical phenomena. Many important qualitative and quantitative problems remain here to be solved.