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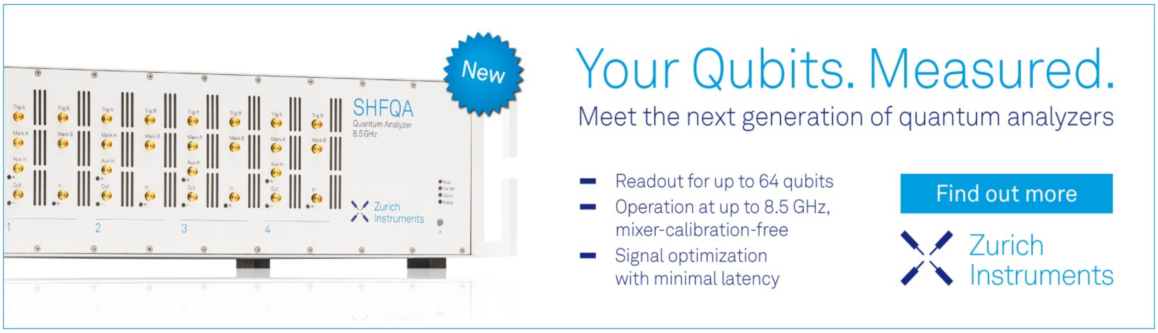

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effect: "We have decided that we might as well go along with the Senate and agree to your appointment as Rector, provided your will agree to the 17 points listed on this document." Hund said he would think it over and went to talk with a friend who was a lawyer. The friend said that he might as well agree to the 17 articles, that they were just formalities, so Hund agreed. But some time later he apparently did not do what was expected for a visiting Russian dignitary, and it was this which led to his retirement as Rector, though he remained as professor.

However, some time later, he had an offer of an appointment at Frankfort. At that time lecture visits of university people back and forth between East and West Germany, but not permanent transfers, were rather freely permitted. After some hesitation, Hund decided to accept the offer. He and each member of his family packed a suitcase. They all reached West Berlin, and went from there to Frankfort. But of course all their furniture was left behind. Nevertheless, quite astonishingly, the authorities, who apparently always felt Hund to be not a bad fellow, six months later sent everything after him to Frankfort. This was a sort of thing that did not normally happen to people who left East Germany in such an informal manner.

[*Note added in proof*: My wife and I and our younger daughter had a pleasant visit with Hund and his family in Göttingen in July 1965.]

I will conclude by wishing everyone a happy conference and good shelling on the beach. And I sincerely hope that during and after the conference all who are friends now will remain good friends, and that during the conference everyone will make many new friends.

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Molecular Orbital and Heitler–London Methods*

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The historical connection between the molecular orbital and Heitler–London treatments is traced, with particular attention to the contributions of Mulliken. Early discussions of the self-consistent-field problem, the relations of Heisenberg's work to the antisymmetry of the wavefunction, and configuration interactions in the two-electron problem, are reviewed, with references to the heteropolar as well as the homopolar cases. Early discussions of directed valence are mentioned. The Coulson–Fischer, Hurley–Lennard-Jones–Pople, and alternant molecular orbital approaches to bonding are discussed, with mention of recent work on correlation energy.

INTRODUCTION

In a symposium honoring Robert S. Mulliken, one can hardly do otherwise than trace the importance of the molecular orbital method of handling molecular structure, with which his name, together with that of Hund, is so closely associated. But at the same time one cannot avoid the other complementary method, originated by Heitler and London, considered in its earlier days to be a rival rather than an addition to the molecular orbital procedure. The older history of the relation of these two methods is well known. It is interesting, however, to trace the way in which the two approaches have had their effect on the present development of molecular theory. Some of these more recent advances may not be familiar to all the workers in chemical physics, many of whom may not have followed the current lines of development of the theory of the chemical bond.[1]

PREWAR PERIOD

The two methods under consideration had their start almost simultaneously, within a couple of years

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[1] The general point of view presented here is elaborated in the text by the present author, *Quantum Theory of Molecules and Solids. Electronic Structure of Molecules* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. 1, to which frequent reference is made in this paper.

after the development of Schrödinger's equation.[2] At first they were handled as different, almost rival methods. The molecular orbital method was based on the same idea as Hartree's self-consistent field, though Hund suggested the method for molecular problems independently of Hartree's work on atomic wavefunctions. This original suggestion came before the development of the determinantal wavefunction, and before the suggestion of varying the spin orbitals in such a determinantal function to render the energy stationary, which resulted in the Hartree–Fock method.[3] Consequently it is natural that the first papers treating the molecular orbital approach were descriptive and intuitive, rather than analytic. It is very simple, however, to describe the method for the two-electron problem, the helium atom or hydrogen molecule, in the elementary language first introduced by Heisenberg[4] in his treatment of the many-body problem and resonance in wave mechanics.

For a singlet state arising from a single determinantal function in which each electron is assigned to the same orbital function u, but with opposite spins, the wavefunction has an orbital part which is simply $u(1)u(2)$, 1 and 2 symbolizing the coordinates of the two electrons; this symmetric functon of the coordinates of the two electrons is multiplied for the singlet state by an antisymmetric function of the spins. In the ground state of the helium atom, the function u is the atomic $1s$ state of an electron in this atom. In the ground state of the hydrogen molecule, it is the lowest wavefunction in a two-center problem, and can be approximated by the LCAO, or linear combination of atomic orbitals, method as $a+b$, if a and b are atomic orbitals around the two nuclei. Hence the orbital part of the two-electron wavefunction is of the form

$$[a(1)+b(1)][a(2)+b(2)]=a(1)b(2)+b(1)a(2)+a(1)a(2)+b(1)b(2). \tag{1}$$

The Heitler–London method was an even more straightforward outgrowth of Heisenberg's work cited above. Heisenberg had shown that a more general expression for the orbital part of the wavefunction for a singlet state of a two-electron system is

$$u(1)v(2)+v(1)u(2), \tag{2}$$

where u and v are different orbital functions. The function of Eq. (2) cannot be derived from a single determinant, but instead must be written as a linear combination of two determinants, one of them describing the case where the electron in Orbital u has plus spin, that in Orbital v has minus spin, and the other with reversed spins, as became clear from the discussion given in Ref. 3. The requirement that the wavefunction describe a singlet is met merely by the condition that the function of Eq. (2) be symmetric in the coordinates of the two electrons. Heitler and London identified the function u with the atomic orbital a, the function v with the orbital b, and were able to give a physical meaning to the wavefunction of Eq. (2). The first term, $a(1)b(2)$, is large only if Electron 1 is located on Atom a, Electron 2 on Atom b, while the second term is large only if the electrons are interchanged. In no case is there a large possibility that both electrons be found on the same atom, so that the wavefunction is built up out of neutral atoms, rather than a positive and negative ion.

In contrast, we see that the wavefunction of Eq. (1), representing the molecular orbital method, contains not only the terms $a(1)b(2)+b(1)a(2)$, of the Heitler–London method, but also terms $a(1)a(2)+b(1)b(2)$, of which the first is large only when both electrons are on Atom a, so that it is a negative ion, Atom b being left as a positive ion, while the second represents the reversed ionic arrangement with Atom a positive, b negative. Surely this ionic contribution to the wavefunction should not be present in the molecular wavefunction in the limit of large internuclear distance, where the ionic state has a much higher energy than the state formed from neutral atoms, and consequently it is found that when the expectation value of the energy is calculated, the function (1) has a much higher energy, particularly at large internuclear distances, than the Heitler–London function, and consequently represents a poorer approximation to the true wavefunction.

As soon as these facts were clear, after the development of the determinantal method,[5] it was possible to trace the relationship between the two approaches. One could carry out what we now call a configuration interaction, between the configuration described by the determinantal function of Eq. (1), and another configuration in which both electrons are in the lowest molecular orbital antisymmetric in the nuclei, which can be approximated as $a-b$. This wavefunction is then of the form

$$[a(1)-b(1)][(a(2)-b(2)]=-[a(1)b(2)+b(1)a(2)]+a(1)a(2)+b(1)b(2). \tag{3}$$

It is obvious that an arbitrary linear combination of the functions (1) and (3) can equally well be written as an

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[2] For the molecular orbital method see, for instance, R. S. Mulliken, Phys. Rev. **32,** 186, 761 (1928); **33,** 730 (1929); **40,** 55 (1932); **41,** 49, 751 (1932); Chem. Rev. **9,** 347 (1931); and many other references given in the bibliography in Ref. 1. See also F. Hund, Z. Physik **40,** 742 (1927); **42,** 93 (1927); **51,** 759 (1928); and later papers; J. E. Lennard-Jones, Trans. Faraday Soc. **25,** 668 (1929), and later papers. For the Heitler–London method, W. Heitler and F. London, Z. Physik **44,** 455 (1927), and later papers. References to other workers are given in the papers and bibliography cited.

[3] J. C. Slater, Phys. Rev. **34,** 1293 (1929); **35,** 210 (1930); V. Fock, Z. Physik **61,** 126 (1930).

[4] W. Heisenberg, Z. Physik **38,** 411 (1926); **41,** 239 (1927).

[5] J. C. Slater, Phys. Rev. **35,** 509 (1930); **41,** 255 (1932).

arbitrary linear combination of the Heitler–London function $a(1)b(2)+b(1)a(2)$, and the ionic function $a(1)a(2)+b(1)b(2)$. One can set up a linear combination which will give just the Heitler–London function, but by allowing some of the ionic function to mix in, one can get a lower energy than by the Heitler–London function alone, thus securing a better approximation. This configuration interaction therefore not only modifies the molecular orbital method so as to bring it into agreement with the Heitler–London method, but allows one to make a significant improvement on that method.

Mulliken, in one of the papers in Ref. 2 [Phys. Rev. **41,** 49 (1932)], pointed out that the true situation of the hydrogen molecule, at its equilibrium distance of separation, is about halfway between the molecular orbital and Heitler–London solutions, if we take either one in its simple form, without configuration interaction (in the molecular orbital case) or admixture of ionic states (in the Heitler–London case). He and Lennard-Jones, in papers cited in Ref. 2, showed that the molecular orbital method furnished an adequate first approximation in many diatomic molecules more complicated than hydrogen, in particular leading at once to an explanation of the symmetry of the ground state of the O_2 molecule, which was already known to be $^3\Sigma_g^-$, a fact almost impossible to explain in any simple way on the basis of Heitler–London theory. This led to a decided preference for the molecular orbital method as a first approach to problems in molecular structure.

Mulliken, in the paper just referred to, mentioned one extension of this argument based on the hydrogen molecule, which is of great importance. In a heteronuclear diatomic molecule, there will, of course, be a dipole moment, one of the atoms tending to be more electropositive, the other more electronegative. If we consider two atomic orbitals forming a bond, as the a and b before, we no longer have symmetry between a and b, and the expression for the ground-state molecular orbital will be of the form $a+\lambda b$, where λ is no longer equal to unity. If λ is greater than unity, the electrons occupying this orbital will tend to be more on Atom b, while if λ is less than unity, they will be more on Atom a. Thus the molecular orbital method gives a simple picture of the way in which real bonds, in heteronuclear molecules, form a sort of compromise between the type of homopolar bond found in H_2, and in ionic bond between a positive and a negative ion. At first it was considered that the Heitler–London method was not competent to explain this situation, but as Mulliken showed, this is not in fact the case.

Mulliken's argument can be stated by setting up an antibonding molecular orbital, $a+\mu b$, where μ is not equal to -1, but where λ and μ would be related in such a way that the bonding and antibonding molecular orbitals would be orthogonal to each other. Then the wavefunction arising from the configuration where both electrons are in the bonding orbital, analogous to Eq. (1), is

$$[a(1)+\lambda b(1)][a(2)+\lambda b(2)] = \lambda[a(1)b(2)+b(1)a(2)] + a(1)a(2)+\lambda^2 b(1)b(2), \qquad (4)$$

and that where they are both in the antibonding orbital is

$$[a(1)+\mu b(1)][a(2)+\mu b(2)] = \mu[a(1)b(2)+b(1)a(2)] + a(1)a(2)+\mu^2 b(1)b(2). \qquad (5)$$

An arbitrary linear combination of these two functions, with Coefficients c_1 and c_2, respectively, will have coefficients for the Heitler–London function $a(1)b(2)+b(1)a(2)$, the ionic function $a(1)a(2)$ with both electrons on a, and the ionic function $b(1)b(2)$ with both electrons on b, which are, respectively, proportional to $c_1\lambda+c_2\mu$, c_1+c_2, and $c_1\lambda^2+c_2\mu^2$. In other words, by suitable choices of λ, μ, and the ratio c_2/c_1, these three coefficients can have any desired ratios to each other. The combination of the two configurations under the molecular orbital scheme has as much flexibility as an arbitrary combination of the covalent Heitler–London function, the ionic function with the atom a negative, and the ionic function with the atom a positive. It is obvious that this combination will allow one to describe a polar molecule perfectly adequately, by either method.

These considerations showed that when one was dealing with a bond formed from two electrons, either the molecular orbital or the Heitler–London method would allow one to treat both homonuclear and heteronuclear binding quite adequately, provided one made the mixtures of configurations which we have described. Without this mixing, the molecular orbital method gave somewhat more reasonable results than the Heitler–London method, both in the prediction of the correct ground state for the system, and in the facility with which a nonsymmetrical charge distribution with a resultant dipole moment could be described. To handle a problem adequately by either method, however, one would have to go beyond the first approximation. Mulliken, in the papers cited above, pointed out that it was rather an accident than otherwise that most chemical bonds are in fact formed from two electrons, and he cited the very simple example of the one-electron bond in H_2^+ as a case where the molecular orbital method is obviously correct, while the Heitler–London method was meaningless. This indicated that the success of the Heitler–London method would obviously be limited to that restricted set of cases in which the bonds were of the electron-pair type.

The situation was much more complicated as soon as one went to a polyatomic molecule, with more than one bond in the molecule. There is a good deal of chemical evidence that the bonds in such molecules in many cases appear to be rather independent of each other, and to be localized between pairs of atoms, making definite angles with each other. Pauling[6] and the present author[7] attempted to bring this experimental fact into the theory by setting up localized bonds between adjacent pairs of atoms, and building up a many-electron function from these, by analogy with the Heitler–London solution for the two-electron case. The localized functions had to show directional properties, similar to those found in actual bonds. The theory in this early form suffered from a severe difficulty, in that the atomic orbitals from which the bonds were formed were not orthogonal to each other; it was their overlapping which resulted in the overlap charge responsible for the binding, on either the Heitler–London or molecular orbital view. But it was extremely difficult to calculate the energy of a molecule if the overlapping and resulting nonorthogonality of the orbitals were taken into account. This difficulty was not really overcome until the postwar period, as we describe in the next section, with the result that this generalized Heitler–London method, though suggestive, could never be taken as rigorous in the prewar days.

There were some cases of polyatomic molecules in which a Heitler–London method definitely was not applicable. Mulliken pointed out that the molecular orbitals in general would extend over a number of atoms, so that the molecular orbital method did not suggest the localization of bonds which was proposed in the Heitler–London method. The most striking case in which the molecular orbital method was clearly superior to the Heitler–London procedure was in the benzene molecule, which Hückel[8] treated in an early application of the molecular orbital method. The so-called π bonds in the benzene molecule are not two-electron bonds: we have six bonds between nearest-neighboring atoms in the ring of six carbons, and only six electrons to form the bonds, so that each one can contain only one electron. The molecular orbital explanation, as Hückel showed, is very simple, whereas any method based on electron pairs is very artificial.

POSTWAR PERIOD

This sketch of some of the major steps in the prewar development of the theory of the chemical bond shows the two methods continuing to compete, in spite of the realization of most of the principal workers in the field that in the last analysis either one could be supplemented or refined to lead to equivalent and satisfactory results. Let us now come to postwar developments. Here one of the significant steps was the paper of Coulson and Fischer,[9] showing that the configuration interaction which we have described in the hydrogen molecule could be accomplished by using a single wavefunction of the type given in Eq. (2). Thus, in this function, let $u=a+\lambda b$, $v=b+\lambda a$. Then we have

$$\begin{aligned} u(1)v(2)+v(1)u(2) &= [a(1)+\lambda b(1)][\lambda a(2)+b(2)] \\ &\quad +[\lambda a(1)+b(1)][a(2)+\lambda b(2)] \\ &= (1+\lambda^2)[a(1)b(2)+b(1)a(2)] \\ &\quad +2\lambda[a(1)a(2)+b(1)b(2)]. \qquad (6) \end{aligned}$$

Thus, by suitable choice of λ one can adjust the ratio of the coefficients of the Heitler–London function $a(1)b(2)+b(1)a(2)$ and the ionic function $a(1)a(2)+b(1)b(2)$ at will, and hence reproduce the results of the configuration interaction. Coulson and Fischer regarded their procedure as one by which one could interpolate between the Heitler–London and molecular orbital methods, $\lambda=1$ corresponding to the molecular orbital method and $\lambda=0$ to the Heitler–London method, each without configuration interaction; but it is rather more informing to interpret it as a very condensed way of writing the result of the configuration interaction.

It is interesting to note that for a bond between unlike atoms, this method can also be used. In this case we may let $u=a+\lambda b$, $v=a+\mu b$, where λ and μ are not necessarily related. Then the function of Eq. (2) becomes

$$\begin{aligned} u(1)v(2)+v(1)u(2) &= [a(1)+\lambda b(1)][a(2)+\mu b(2)] \\ &\quad +[a(1)+\mu b(1)][a(2)+\lambda b(2)] \\ &= (\lambda+\mu)[a(1)b(2)+b(1)a(2)] \\ &\quad +2a(1)a(2)+2\lambda\mu b(1)b(2). \qquad (7) \end{aligned}$$

This function, in other words, allows the relative coefficients of the Heitler–London function $a(1)b(2)+b(1)a(2)$, and the two ionic functions $a(1)a(2)$ and $b(1)b(2)$, to be adjusted at will, as we assumed earlier in our disucssion of Eqs. (4) and (5). The author, in Ref. 1, Sec. 7-3, has described in detail how this method can be applied to the case of LiH.

A great advance in our understanding of molecular orbitals and polyatomic molecules was made in the series of papers by Lennard-Jones and his colleagues Hall, Hurley, and Pople, during the years 1949–1953,

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[6] L. Pauling, Proc. Natl. Acad. Sci. (U.S.) **14**, 359 (1928); Phys. Rev. **37**, 1185 (1931); J. Am. Chem. Soc. **53**, 1367, 3225 (1931); and later papers given in the bibliography of Ref. 1.

[7] J. C. Slater, Phys. Rev. **37**, 481 (1931); **38**, 325, 1109 (1931).

[8] E. Hückel, Z. Physik **60**, 423 (1930); **70**, 204 (1931); **72**, 310 (1931); and later papers.

[9] C. A. Coulson and I. Fischer, Phil. Mag. **40**, 386 (1949).

dealing with the molecular orbital theory of chemical valency. The first few papers of this series[10] introduced the concept of equivalent orbitals. These were much like the localized bonds suggested earlier by Pauling and Slater in Refs. 7 and 8. Lennard-Jones noted, as others had observed earlier, that in a single determinantal function one can replace the orbitals with new orbitals derived from the original ones by a unitary transformation, without changing the value of the determinant, and hence with no change in the energy. This fact had been used by Koopmans,[11] in a paper in which he suggested making such a unitary transformation that the energy matrix in the Hartree–Fock method was diagonalized, in which case the diagonal matrix elements form good approximations to the negatives of the various ionization energies in the system. This choice of orbitals results, however, in orbitals which tend to be diffuse, extending over the whole molecule or crystal. Lennard-Jones instead sought a unitary transformation which would localize the orbitals as much as possible. In the case of a ring of identical atoms, it was possible to find orbitals localized essentially on each atom, using a procedure which had been suggested before the war by Wannier[12] for the similar problem of making linear combinations of energy-band wavefunctions in crystals which were as localized as possible. The procedure of Wannier and Lennard-Jones results in localized orbitals, orthogonal to each other, which can be used instead of the molecular orbitals in constructing a determinantal wavefunction.

Lennard-Jones and his colleagues recognized that as long as one was working wholly within the framework of the molecular orbital method, without configuration interaction, nothing was gained by use of the equivalent orbitals, except an improvement in the possibility of visualizing the various bonds. For instance, in the methane molecule, one could set up four equivalent orbitals, more or less localized in the locations of the four tetrahedral bonds postulated by the chemist, and one could describe the molecule by placing two electrons in each of these orbitals, as well as having two electrons in the carbon $1s$ shell. This interpretation, in other words, was as good as the molecular orbital method without configuration interaction, but no better. To improve it, one would have to carry out a configuration interaction such as we have described in earlier paragraphs of this paper, removing two electrons from the equivalent orbital which serves as the bonding orbital for a given bond, and placing them in a corresponding antibonding orbital localized at the same bond. Here, unless one proceeds with care, one meets the same difficulty of nonorthogonality which had faced the similar attempt of Pauling and of Slater before the war, which we have commented on earlier.

In a later paper of the same series, Hurley, Lennard-Jones, and Pople[13] showed how this difficulty was to be removed. One must have both the bonding equivalent orbital, and the antibonding equivalent orbital, associated with a given bond, orthogonal to every other bonding or antibonding equivalent orbital encountered in the problem. In this case, as they showed, one can express the part of the wavefunction associated with a given bond in a form like that of Eq. (7), and the whole wavefunction is an antisymmetrized product of such wavefunctions of pairs of electrons. With the assumed properties of orthogonality, which are easy to secure if one sets the wavefunction up properly, the exact formula for the energy of the wavefunction becomes relatively simple, the troublesome orthogonality terms having largely disappeared. To a very large extent the energy of the molecular system can be written as the sum of terms arising from the various bonds, thereby verifying the empirical conclusions of the chemists regarding the independence of the various bonds in a molecule. This additivity of the energies of the bonds has been discussed further by Allen and Shull,[14] who have demonstrated this additivity quite directly by the use of the virial theorem, and the form of the kinetic energy in the energy expression of Hurley, Lennard-Jones, and Pople.

These developments have brought the extension of the Heitler–London method, in which configuration interaction is handled essentially by the method of Coulson and Fischer, into a rigorous form, applicable whenever the system really is held together by electron-pair bonds, which can be intermediate between covalent and ionic in their properties. For cases where this situation does not hold, such as the benzene π electrons, we have an alternative method of bringing a good deal of configuration interaction into the wavefunction in a relatively simple way. This is the method of alternant molecular orbitals, as treated by Löwdin, Pauncz, de Heer, and others.[15] This method, like that of Hurley, Lennard-Jones, and Pople, is based on the use of different orbitals u, v for electrons of different spins. The u and v are somewhat more spread out in space than in the method of equivalent orbitals. In the benzene case, for instance, u and v are similar to molec-

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[10] J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1, 14 (1949); G. G. Hall and J. E. Lennard-Jones, *ibid.* **A202**, 155 (1950); J. E. Lennard-Jones and J. A. Pople, *ibid.*, p. 166; J. A. Pople, *ibid.*, p. 323; G. G. Hall, *ibid.*, p. 336; G. G. Hall and J. E. Lennard-Jones, *ibid.* **A205**, 357 (1951). Further references are given in the bibliography in Ref. 1.

[11] T. Koopmans, Physica **1**, 104 (1933).

[12] G. Wannier, Phys. Rev. **52**, 191 (1937).

[13] A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, Proc. Roy. Soc. (London) **A220**, 446 (1953). See also Ref. 1, Appendix 14, for further discussion.

[14] T. L. Allen and H. Shull, J. Chem. Phys. **35**, 1644 (1961).

[15] P.-O. Löwdin, Symp. Mol. Phys., Nikko, Japan 1953, 599 (1954); Phys. Rev. **97**, 1509 (1955); T. Itoh and H. Yoshizumi, J. Phys. Soc. Japan **10**, 201 (1955); R. Pauncz, J. de Heer, and P.-O. Löwdin, J. Chem. Phys. **36**, 2247, 2257 (1962); R. Pauncz, *ibid.* **37**, 2739 (1962); J. de Heer, *ibid.*, p. 2080; **39**, 2314 (1963); J. Phys. Chem. **66**, 2288 (1962); Rev. Mod. Phys. **35**, 631 (1963).

ular orbitals for the π electrons, but one of them would put more charge on Atoms 1, 3, 5, and the other on Atoms 2, 4, 6, if we number the atoms as we go around the six-membered ring. By assuming that the u and v associated together are both orthogonal to all other orbitals concerned in the problem, the expression for the energy takes on as simple a form as that described in Ref. 13, though it assumes a different coupling scheme from those which we have described in this paper. This method of alternant orbitals seems to be as effective in such cases as benzene as is the method of Hurley, Lennard-Jones, and Pople for the cases to which it can be applied.

We have now sketched some of the main improvements which have been made in the theory of chemical bonds since the war. As we see, they are now sharing one feature in common: they start with the molecular orbital, or self-consistent-field, method, and then improve the accuracy of calculation of each of the bonds by a method which essentially is a configuration interaction. In this way it is assured that the methods will improve on the accuracy of the molecular orbital method, for making a linear combination of one wavefunction, the determinantal function of the molecular orbital method, with another, can only lower the energy and improve the wavefunction, as a result of the variational theorem. Let us now consider just what is being achieved by this modification of the wavefunction, changing it from the single determinant of the molecular orbital method.

A Hartree wavefunction, consisting of a product of orbitals, represents a situation where the electrons move independently of each other, with no correlation. If we use the determinantal function of the Hartree–Fock method, correlation is introduced between electrons of the same spin: the probability of finding two electrons of the same spin decreases as the positions of the electrons approach each other, and becomes zero when they coincide. However, no correlation is given in the wavefunction between electrons of opposite spin, as is seen for instance from Eq. (1), where the wavefunction for the singlet state is a product of functions of the two electrons. It is well known that the energy of an atomic or molecular system as calculated by the Hartree–Fock method is about a percent higher than the experimental energy (when due account is taken of the relativistic corrections, which are far from negligible), and the difference between these two energies, now defined as the correlation energy, represents the decrease of energy which arises when the wavefunction is modified to take account of electronic correlation, beyond what is implied by the antisymmetry of the wavefunction. Since the electrons do not approach as closely in the correct wavefunction as in the Hartree–Fock function, the repulsive Coulomb energy is decreased, accounting for the improvement in the energy as compared to the Hartree–Fock value.

These facts have been known for a long time. A comparison of the original Hartree–Fock self-consistent-field solution for the helium atom with Hylleraas's very accurate wavefunction, which includes correlation, had made the situation plain, and Mulliken, in the papers mentioned in Ref. 2, described this shortcoming of the molecular orbital method. The Heitler–London wavefunction, resulting in a tendency for one electron to be found on one atom when the other is on the other, represented the first successful effort to introduce correlation into a molecular wavefunction, and we see that this is the reason why it gives a lower, and better, energy than the molecular orbital calculation. The configuration interactions which we have been describing represent a somewhat more sophisticated attempt to describe this correlation. A particularly careful study of correlation effects was made at a conference on molecular quantum mechanics held at Shelter Island, New York, in 1951, and papers by Mulliken[16] and by Lennard-Jones and Pople,[17] resulting from that conference or reported at it, threw a great deal of light on the actual nature of correlation effects in atoms and molecules, and the modifications required in the wavefunctions to describe it.

Recent thinking on the correlation problem has tended to emphasize the point of view that the main part of the correlation effect is between pairs of electrons of opposite spin in the same localized orbital. This is the point of view which we have described in discussing the work of Hurley, Lennard-Jones, and Pople quoted in Ref. 13. The procedure adopted in that work, of building up the wavefunction out of an antisymmetrized product of functions of two electrons of opposite spin, each such function being adapted to describe fairly adequately the correlation effect between these two electrons, is finding a great deal of favor. Such a two-electron function has been called a geminal, following a suggestion by Shull,[18] the name coming from the Latin word for twins. The justification for this procedure comes from an increasing number of fairly accurate calculations, in which the correlation effects between two electrons in different bonds are found to be much less than those between two electrons in the same bond. As more calculations become available, it will be possible to check the adequacy of this assumption more completely.

This brings us to the question of calculations of molecular wavefunctions. Before the war, these calculations were so difficult that apart from the hydrogen molecule, very few cases had been worked out with any pretense of accuracy. Since the war, however, the existence of the digital computer has changed this situation completely. Here again Mulliken has led the way to a new period in molecular theory, by encouraging

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[16] R. S. Mulliken, Proc. Natl. Acad. Sci. (U.S.) **38,** 160 (1952).

[17] J. E. Lennard-Jones, J. Chem. Phys. **20,** 1024 (1952); J. E. Lennard-Jones and J. A. Pople, Phil. Mag. **43,** 581 (1952); J. E. Lennard-Jones, Proc. Natl. Acad. Sci. (U.S.) **38,** 496 (1952).

[18] H. Shull, J. Chem. Phys. **30,** 1405 (1959).

accurate calculations particularly of diatomic molecules.[19] His colleague Roothaan has developed the technique of expressing molecular orbitals as linear combinations of a large number of basis functions, and of solving the variation problem which is equivalent to the Hartree–Fock method, so as to obtain as good an approximation to the solution of the Hartree–Fock problem as can be achieved with the set of basis functions assumed. By the use of this technique, we now possess good self-consistent-field solutions for all the lighter atoms, and for many diatomic molecules formed from them, expressed in analytical form. It then becomes possible to calculate the total energy of the atom or molecule according to the Hartree–Fock method, and by comparison with the known experimental energy, as found by spectroscopic methods, to get accurate values for the correlation energy. Clementi,[20] formerly at Chicago but now at the IBM Corporation in San Jose, has been particularly active in this study, and it is through work of this type that conclusions are beginning to be drawn as to the possibility of treating the correlation energy as a sum of contributions of the various bonds.

These results will not really answer the main chemical problems, however, until analogous methods are applied to polyatomic molecules large enough so that the bonds in different parts of the molecule would be expected to be essentially independent of each other. The polyatomic problem is much more difficult, from the point of view of computation, than the diatomic, but techniques are now available by which it can be handled. We shall not go into these questions in the present paper, but it is appropriate to close by pointing out that the study of the chemical bond, though it has made great strides since the middle 1920's, is still far from completion and the next great step should be the application of already-existing techniques to an extensive study of the electronic structure of polyatomic molecules. Here, as in so many other aspects of molecular theory, Mulliken's work formed much of the earliest basis for understanding the problems, and here too we may expect him and his school to be in the forefront of future developments.

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[19] See for instance R. S. Mulliken and C. C. J. Roothaan, Proc. Natl. Acad. Sci. (U.S.) **45,** 394 (1959), as well as many other contributions from the group at the University of Chicago, some included in the bibliography in Ref. 1, but many too recent for that bibliography.

[20] See for example E. Clementi, J. Chem. Phys. **38,** 996, 2248, 2780 (1963); **39,** 175, 487 (1963); **41,** 295, 303 (1964); and numerous other papers, 1961–1964.

Discussion Following Slater's Paper

FRANK HARRIS: Dr. Slater pointed out that split-shell orbitals of the form

$$(a+\lambda b)(a+\mu b),$$

with λ and μ determined to minimize energy, yield a pair of distinct wavefunctions at large a–b distances, but identical MO's at sufficiently small internuclear separation. If, however, complex values of λ and μ are considered, at short distances the optimum orbitals are a complex conjugate pair which differ in phase rather than in displacement along the a–b line. This behavior is illustrated in recent work with Herbert Pohl[1] on hydrogen halides. We also find similar behavior when the Coulson–Fischer[2] work on H_2 is re-examined from this point of view. This suggests the importance of performing the numerical determination of orbital parameters like λ and μ by methods which consider complex values.

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[1] F. E. Harris and H. A. Pohl, J. Chem. Phys. **42,** 3648 (1965).

[2] C. A. Coulson and I. Fischer, Phil. Mag. **40,** 386 (1949).