with a quadrupole on group A. The leading term will again vary as $1/R^4$; furthermore, if one always chooses the positive direction of z_{B2} to point away from group A this dipole quadrupole interaction may be replaced by an equivalent monopole-octapole interaction between a positive charge on B with the same form of octapole distribution on A as above.

The magnitude of this equivalent positive charge will be seen from Eq. (24) to be $(a/b)\alpha_2$. This provides the physical basis for the many-electron model of Jones and Eyring.[10] One cannot make the same correspondence for the interaction of two electric dipole transitions, since a different distance and angular dependence is inherently involved, as may be seen from the integral in the sixth term of Eq. (2),

$$\iint \frac{Z_{A1} Z_{B2} e^{-kr_{A1}-k'r_{B2}}}{r_{12}} d\tau_1 d\tau_2 .$$

This gives the energy of interaction between two dipoles of charge and will lead to a $1/R^3$ dependence.

The helical pattern is once again formed by two separate electrons. The linear motion of a transition of group B becomes a circular motion as viewed from group A with A as center. Then one observes a linear motion of its own electron and a circular motion of the electron on B giving rise to a helical drift of charge. If one attempts to make the centers coincide, as was done in the previous discussion, the net motion of charge is linear and the effect vanishes.

It is accordingly best to visualize the effect of two electric dipole transitions in this way with the transitions remaining on different groups. The models of Kirkwood[3] and Kuhn[11] are particularly instructive. Although it is possible to set up equivalent monopole-quadrupole interactions, no simple correspondence with the static-charge, one-electron effect is feasible. It is observed that a right-handed screw pattern of polarizability does not always give dextro rotation, for the sign also depends on the angles which the symmetry axes make with the line of centers.

Preliminary calculations indicate that the exponential terms will be negative corrections involving 10–20% of the total rotation. Calculations with the Kirkwood polarizability formula[3] on hydrocarbons indicate that the coupled oscillator effect may account for less than one-half of the total rotation.

In the case of two methyl groups forming a screw pattern, it will be worthwhile to take into consideration the destruction of cylindrical symmetry of the groups by adjacent bonds. This will split the degeneracy for orbitals directed along radial directions enabling magnetic dipole transitions to occur with axial components of magnetic moment parallel to the electric dipole transitions known to occur. The method for doing this has been outlined by Condon, Altar and Eyring[7] in conjunction with the multipole expansion, which gives the net charge effect. For aliphatic carbon–carbon bonding the net charges will be nearly zero and the incomplete screening effect will predominate.

ACKNOWLEDGMENT

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[10] L. L. Jones and H. Eyring, Tetrahedron **13**, 235 (1961).

[11] W. Kuhn, Z. Phys. Chem. **B4**, 14 (1929).

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Quantum Theory of Conjugated Systems

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1. INTRODUCTION

As the previous papers have indicated, it is still an extremely difficult matter to treat even simple atoms and molecules by quantum-mechanical methods. The most useful treatments at present available can give binding energies with an accuracy little better than one percent. We are now going to consider the application of quantum-mechanical methods to complex organic molecules containing perhaps fifty or one hundred atoms, and we are also going to consider chemical problems in which an error of 0.1 eV would be intolerable. Stated in this way the problem seems quite hopeless. Even if the more refined "Group

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One" methods could be applied to molecules of this size, which at present is out of the question, they would not begin to give results with the required accuracy. Thus the resonance energy of benzene, a very large quantity in the chemical sense, is only a few tenths of a percent of the total binding energy.

Nevertheless, a great deal of effort has been put into solving this apparently hopeless problem, because the answers are badly needed by organic chemists—and, surprisingly enough, much progress has been made. The trick has been to use simplified methods which in principle are much less accurate than the Group One Methods used for small molecules, but which in practice work well, because they contain adjustable parameters. Any theoretical treatment always benefits greatly, in terms of practical success, for a parameter of two; the same is true in the case of the "Group Two" or parametric methods for conjugated systems.

2. BASIC METHOD

Let us first consider how we would treat our problem in a Group One manner. The only possible approach would be an SCF MO procedure, with the further approximation of writing the molecular orbitals Ψ_m as linear combinations of atomic orbitals φ_i;

$$\Psi_m = \sum_i a_{mi}\varphi_i . \tag{1}$$

The coefficients a_{mi} and the corresponding orbital energies could be found by the general method first suggested by Roothaan,[1] being given by a set of simultaneous equations that can be solved by an iterative procedure. The coefficients in these equations can be expressed in terms of certain integrals over the set of AO's φ_i used as a basis. These AO's should in principle be SCF AO's for the component atoms; however technical difficulties in evaluating the integrals make it necessary to use AO's that can be expressed in analytical form. Nearly all work in this field has made use of Slater AO's as the basis functions.

Even with these assumptions and approximations, the calculations remain exceedingly difficult, mainly because of the difficulty of evaluating three- and four-center electron-repulsion integrals. The full Roothaan treatment has been applied only to a few simple molecules, and its extension to molecules of the type we are considering would require much larger computers than any available. Calculations of this kind would, in any case, be of doubtful value to chemists, since we know from work on simple molecules that the method is not accurate enough for chemical purposes. Our problem is first to simplify the treatment to a point at which calculations can be carried out quickly for large molecules and, secondly, to patch up the weak points in it with parameters so as to improve the over-all accuracy. In this endeavor, we will, of course, be guided more by practical expediency than by mathematical theorizing, for our object is the purely practical one of getting results that will be useful to chemists, rather than of constructing an elegant mathematical edifice.

The first simplification rests on the use of the localized bond model of molecules. We know empirically that many molecules can be represented well, for most chemical purposes, in terms of localized bonds. Thus the heats of formation of saturated molecules can be represented as additive functions of bond energies and their dipole moments as vector sums of bond moments. This situation breaks down in the case of conjugated molecules, where a set of adjacent atoms are linked by π bonds; here the properties of the molecule can no longer be represented as additive functions of the bonds in it. Thirty years ago Hückel suggested that the π electrons could be treated independently of the rest of the molecule. We suppose each π electron to move in the field of a "core," composed of a framework of atoms linked by localized two-center bonds whose energies are additive, and we then calculate separately the nonadditive contribution to the total energy due to the π electrons moving in the field of the core. Virtually all calculations for conjugated systems have been based on this Hückel approximation, which of course represents a very great simplification. Thus, the simplest conjugated hydrocarbon, 1,3-butadiene, contains thirty-two electrons; the Hückel approximation reduces this to a four-electron problem.

Even with this simplification, the Roothaan treatment still remains too difficult. The trouble lies in the terms involving three- and four-center integrals. The number of terms involving these integrals is formidable, and the integrals are also very difficult to evaluate. Pople[2] met this situation in an Alexandrian manner by simply ignoring the integrals altogether. This approximation is usually described as "neglecting differential overlap," i.e., the assumption that in any small volume $\alpha\tau$ of space

$$\varphi_i\varphi_j d\tau = 0 \quad (i \neq j) . \tag{2}$$

However, in practice this assumption is applied only to the electron-repulsion integrals and to the overlap integrals between pairs of AO's. The one-electron ex-

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[1] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).

[2] J. A. Pople, J. Phys. Chem. **61**, 6 (1957).

change or resonance integrals β_{ij},

$$\beta_{ij} = \int \varphi_i H \varphi_j d\tau \,, \tag{3}$$

are assumed to have finite (and often quite large) values. Various attempts have been made to justify these approximations theoretically, but the only question that really matters for our purpose is whether the resulting treatment works. Present evidence suggests that it does—and, indeed, in at least one connection the simplified treatment seems to work better than the "correct" approach where all integrals are included.

With these assumptions, the Roothaan equations for a closed-shell molecule (i.e., one in which all electrons are paired) can be written in a very simple form.[2] We first define two quantities, the π-electron charge density q_i at atom i, and the bond order p_{ij} of the bond between atoms i, j;

$$q_{ij} = \sum\nolimits_m n_m a_{mi}^2 \,, \tag{4}$$

$$p_{ij} = \sum\nolimits_m n_m a_{mi} a_{mj} \,, \tag{5}$$

where n_m is the number of electrons occupying the MO Ψ_m. If Eq. (2) held, q_i would be the expectation value for the number of electrons occupying the region of space defined by the AO φ_i. The coefficients a_{mi} of the AO's [Eq. (1)], and the corresponding Hartree–Fock orbital energies E_m, are then given by the eigenvectors and eigenvalues of the F matrix, whose elements are

$$F_{ii} = \alpha_i + \tfrac{1}{2}\, q_i(ii,ii) + \sum\nolimits_j q_j(ii,jj) \tag{6}$$

$$F_{ij}(i \neq j) = \beta_{ij} - \tfrac{1}{2}\, p_{ij}(ii,jj) \,. \tag{7}$$

Here, the Coulomb integrals α_i and the resonance integral β_{ij} are defined by

$$\alpha_i = \int \varphi_i \mathbf{H}_\mathrm{C} \varphi_i d\tau ; \beta_{ij} = \int \varphi_i \mathbf{H}_\mathrm{C} \varphi_j d\tau \,, \tag{8}$$

where $\mathbf{H}_\mathrm{C}$ is the core Hamiltonian,

$$\mathbf{H}_\mathrm{C} = \sum_i \left[-\frac{h^2}{2m} \nabla_i^2 - \sum_u \frac{Z_u e^2}{r_{iu}} \right] , \tag{9}$$

r_{iu} being the distance of the ith electron from the uth nucleus, and Z_u the effective nuclear charge of nucleus u. The electron-repulsion integral (ii,jj) is defined by

$$(ii,jj) = \sum \sum \varphi_i^2(1) \frac{e^2}{r_{12}} \varphi_j^2(2) d\tau_1 d\tau_2 \,. \tag{10}$$

(We assume that the functions φ_i are real; this involves no loss of generality.)

Since the F matrix contains the quantities q_i and p_{ij}, which are defined in terms of the coefficients a_{mi}, an iterative procedure has to be used to determine the coefficients and orbital energies. The a_{mi}'s found in one cycle are used to compute the F matrix for the next. It is, however, a very simple matter to program computers to carry out the necessary calculations automatically, and suitable programs are now available at many centers. The integrals (ii,jj) can either be calculated by direct quadrature or approximated by simple classical models.[3]

The Coulomb integrals α_i can be calculated using a Goeppert–Mayer–Sklar potential:

$$\alpha_i = (W_{2p})_i + \sum_{j \neq i} [(ii,j) - (ii,jj)] \,. \tag{11}$$

If penetration integrals can be neglected, Eq. (6) becomes

$$F_{ii} = (W_{2p})_i + \tfrac{1}{2}\, q_i(ii,ii) + \sum_{j \neq i} (q_j - 1)(ii,jj) \,. \tag{12}$$

The one-electron resonance integrals β_{ij} can be calculated, but they are usually treated as parameters. If differential overlap were neglected in a consistent way [Eq. (2)], these integrals would presumably vanish; nevertheless in practice a finite value has to be ascribed to them. It is usual, however, to assume that β_{ij} vanishes, unless atoms i, j are directly linked to one another.

Calculations carried out in this way do not lead to very satisfactory results, even though the treatment does contain adjustable parameters (the β_{ij}). This failure could be attributed to several factors.

(1) The whole treatment may be inadequate; this could well be the case, in view of the gross approximations involved. However, to admit this would be an admission of defeat.

(2) The integrals (ii,jj) should in principle be calculated using SCF AO's; it is, however, very difficult to do this. Most published calculations have used integrals based on Slater AO's; these must differ considerably from the SCF values, the SCF AO's being much more diffuse. Thus, the overlap integral between $2p$-AO's on adjacent carbon atoms 1.4 Å apart is calculated to be 0.25 using Slater AO's, but 0.33 using SCF AO's.[4] One would expect the values for the electron-repulsion integrals to be less, using SCF AO's; and one would expect the difference to be greatest for the one-center integrals (ii,ii), and to decrease, in the case of two-center integrals (ii,jj), with increasing separation of the centers i, j.

(3) The treatment does not allow adequately for

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[3] R. Pariser and R. Parr, J. Chem. Phys. **21**, 466, 767 (1953).

[4] R. S. Mulliken, J. Am. Chem. Soc. **72**, 4493 (1950).

the effects of electron correlation. Two types of correlation can be distinguished[5]: *vertical correlation,* which controls the interchange of electrons between the two halves or lobes of a p or π orbital, and *horizontal correlation,* which controls the motions of electrons along a given π lobe. The usual SCF treatment ignores vertical correlation completely, and allows for horizontal correlation only by using antisymmetric wave functions.

Pariser and Parr[2] and Moffitt[6] have pointed out that the repulsion integrals calculated from Slater orbitals do not give a good account of atomic-energy states.

Moffitt[6] suggested a procedure in which experimental values are taken for the energies of the component atoms of a molecule, and where the relatively small difference in energy between the atoms and the molecule (the chemical heat of formation) is calculated directly by a perturbation method. This seems a very logical procedure; it has not been much used, mainly because machine programs for it are not readily available. Calculations by this AIM (atoms-in-molecules) method have been reported only for a few molecules and the results have not always been too good. However, Slater values for the electron-repulsion integrals were used in these calculations; the arguments given below suggest that an analogous parametric treatment might be very successful indeed.

Pariser and Parr[2] followed a different approach. They proposed that the electron-repulsion integrals be treated as parameters. They chose the one-center integrals (ii,ii) to give correct values for the atomic-valence states, and adjusted the remaining integrals so that: (a) the plot of integral vs $i - j$ separation was a smooth line; and (b) the values of (ii,jj) approximate to the "normal" Slater values for large internuclear distances. If these modified integrals are used in the Pople treatment, the results are greatly improved.

The argument used by Pariser and Parr was based on the energy change in the reaction:

$$\mathrm{C}\cdot + \mathrm{C}\cdot \rightarrow \mathrm{C}^{+} + \mathrm{C}^{-} . \tag{13}$$

Assuming that the cores of the carbon atom remain unchanged, and that the transfer involves a $2p$-electron, this reaction should be endothermic by the value of the (ii,ii) integral for a carbon $2p$ AO. The value estimated empirically in this way (11 eV) is much less than that calculated using Slater AO's (17 eV). The difference could be due either to the inadequacy of Slater AO's [cf. (2) above], or to electron correlation (which must reduce the interelectronic repulsion in the ion C$^-$). Pariser and Parr assumed that both these possibilities could be covered by using a reduced value for the (ii,ii) integral, and similar arguments suggested that the other repulsion integrals should also be modified.

The correlation involved in this case is what we have described as vertical correlation. Dewar and Wulfman[5] suggested that one might allow for this by using an extreme model in which the pair of electrons occupying a given p or π orbital are never allowed to occupy the same lobe simultaneously. This idea has been pursued[7-9] by the author in collaboration with Mrs. Sabelli (formerly Miss Hojvat). We suggested that the two-electron function Ψ for the pair of electrons occupying a given p orbital φ might be written in the form

$$\Psi = (\xi^1\eta^2 + \xi^2\eta^1)(\alpha^1\beta^2 - \alpha^1\beta^2) , \tag{14}$$

where ξ, η are the two lobes or *split p orbitals* of the p orbital

$$\varphi = (1/\sqrt{2})(\xi + \eta) . \tag{15}$$

Likewise, the electrons in a π MO would be represented as occupying one or other of two split π orbitals, Ξ, H

$$\Xi_m = \textstyle\sum_i a_{mi}\xi_i ; H_m = \sum_i a_{mi}\eta_i . \tag{16}$$

Preliminary applications[7-9] of this split p-orbital (SPO) treatment to simple π-electron systems seem promising.

There are, however, difficulties in the way of this formalism. Many of the objections that were raised at first are groundless,[8,9] but one very serious difficulty remains. Functions of the type indicated in Eq. (14) are not orthogonal to the inner core orbitals ($1s$ and $2s$ in the case of carbon). If then the π electrons are regarded as occupying SΠO's instead of normal π-MO's, the Hückel approximation is no longer justifiable. This objection would certainly invalidate the use of the SPO method in Group One calculations.

The same difficulties inevitably arise, although in a less aggressive form, in any attempts to write correlated wave functions for π electrons. One obvious procedure for doing this would be to use functions of

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[5] M. J. S. Dewar and C. E. Wulfman, J. Chem. Phys. **29**, 158 (1958); M. J. S. Dewar and H. N. Schmeising, Tetrahedron **5**, 166 (1959).

[6] W. Moffitt, Proc. Roy. Soc. (London) **A210**, 245 (1951).

[7] M. J. S. Dewar and N. L. Hojvat, J. Chem. Phys. **34**, 1232 (1961).

[8] M. J. S. Dewar and N. L. Hojvat, Proc. Roy. Soc. (London) **A264**, 431 (1961).

[9] M. J. S. Dewar and N. L. Sabelli, J. Phys. Chem. **66**, 2310 (1962).

Hylleraas type, containing the interelectronic distance explicitly. Procedures of this kind have been used by Kolos[10] and by Julg and his collaborators.[11] However, as soon as we multiply the π-electron function by factors involving interelectronic distances, we destroy its orthogonality to the core. In order to include correlation, we must either abandon the Hückel approximation (which is out of the question) or we must use correlated functions that *are* orthogonal to the core. No one has yet found a satisfactory way of doing this. The problem of orthogonality escaped notice in the earlier treatments because they followed accepted paths; the SPO treatment drew attention to the problem by stating it in an extreme and unorthodox form.

If we are to allow for correlation, we must then do it empirically within the framework of the Pople treatment, by empirical adjustment of parameters. The main achievement of the SPO method has been the insight it has given into the way this should be done. A detailed study[9] has shown that the SPO treatment, in spite of its apparent waywardness, in fact leads to a set of equations for the orbital coefficients a_{mi} [in Eq. (16)] very similar to the usual Pople equations. The corresponding F-matrix elements are given [with the assumptions inherent in Eq. (12)] by

$$F_{ii} = (W_{2p})_i + \tfrac{1}{2}\, q_i(\bar{\imath}\bar{\imath},ii) + \underset{j\neq i}{E}\ (q_i - 1)(ii,jj)\,, \quad (17)$$

$$F_{ij} = (i \neq j) = \beta_{ij} - \tfrac{1}{2}\, p_{ij}(\bar{\imath}\bar{\imath},\bar{\jmath}\bar{\jmath})\,. \quad (18)$$

Here, $(\bar{\imath}\bar{\imath},jj)$ implies a repulsion integral between an electron occupying the upper lobe of the AO φ_i, and one occupying the lower lobe of the AO φ_j, i.e., an integral we describe as an "upper–lower" integral; while $(\bar{\imath}\bar{\imath},\bar{\jmath}\bar{\jmath})$ implies a similar repulsion integral between electrons on the same side of the nodal plane of the π system (i.e., an "upper–upper" integral). Although the theoretical basis of the SPO method may be suspect, these results draw attention to a physical interpretation of the integrals appearing in the Pople treatment that enables one to see very clearly the way in which the integrals must be changed to allow for vertical correlation.

Consider the diagonal element F_{ii} in the F matrix. This is defined by

$$F_{ii} = \int \varphi_i(\mathbf{H}_1)\varphi_i d\tau\,, \quad (19)$$

where $\mathbf{H}_i$ is the one-electron Hamiltonian representing the motion of a given electron in the field of the nuclei and a statistical distribution of negative charge corresponding to all the other electrons. On this basis, we can interpret the terms in Eq. (12) very simply.

The first term, $(W_{2p})_i$, represents the sum of the kinetic energy of an electron adjacent to nucleus i, and of its potential energy due to the attraction of that nucleus. It is, in fact, equal to the binding energy of a $2p$-electron at a trigonal carbon atom. The terms $\sum_{j=i}(-(ii,jj))$ represent the attraction of all the other nuclei, using a Goeppert–Mayer–Sklar potential and ignoring penetration integrals. The repulsion by an electron occupying the AO φ_j would produce a potential (ii,jj); since there are q_j electrons in the orbital φ_j, the terms $\sum_{j\neq i} q_j(ii,jj)$ represent the total repulsion of all the other electrons in the system, other than those in the AO φ_i. In a closed-shell problem, half the electrons at any point have α spin, half β spin; if the electron we are considering has α spin, there will be $\frac{1}{2}\, q_i$ electrons at atom i with β spin. The repulsion due to these is covered by the term $\frac{1}{2}\, q_i(ii,ii)$.

What will happen now if we allow for the effects of vertical correlation? Vertical correlation tends[5,9] to segregate the electrons by spin on opposite sides of the π-nodal plane. It does not effect the total electron density at a given atom, but it makes the distribution of α- and β-spin electrons in the two lobes of the relevant $2p$ AO uneven. Correlation of this kind does not therefore affect the terms $q_i(ii,jj)$ in Eq. (12), since each of these represents the total repulsion between our electron in the AO φ_i and *all* the electrons (of either α or β spin) in the orbital φ_j. However it reduces the term $\frac{1}{2}\, q_i(ii,ii)$; for this represents the repulsion between two electrons occupying the *same* AO φ_i—and vertical correlation keeps these apart and so reduces their mutual repulsion.

Let us now consider the off-diagonal terms of the F matrix. First, the one-electron terms β_{ij}. These can be interpreted in the following way (cf. Ruedenberg[12]). Consider a simple diatomic molecule in which electrons occupy a MO Ψ given by

$$\Psi = a_1\varphi_1 + a_2\varphi_2\,, \quad (20)$$

where φ_1, φ_2 are AO's of the two atoms. The total electron density function, Ψ^2, is given by

$$\Psi^2 = a_1^2\varphi_1^2 + a_2^2\varphi_2^2 + 2a_1a_2\varphi_1\varphi_2\,. \quad (21)$$

This differs from the sum $(a_1^2\varphi_1^2 + a_2^2\varphi_2^2)$ of the two individual density functions $(a_1\varphi_1)^2$, $(a_2\varphi_2)^2$, by the

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[10] W. Kolos, J. Chem. Phys. **27**, 592 (1957).

[11] A. Julg, J. Chim. Phys. **57**, 19 (1960); A. Julg and P. François, *ibid.* **57**, 63, 490 (1960); A. Julg and M. Bonnet, *ibid.* **57**, 434 (1960).

[12] K. Ruedenberg, Rev. Mod. Phys. **34**, 326 (1962).

term $2a_1a_2\varphi_1\varphi_2$. This term represents an additional density in the region, where the AO's φ_1,φ_2 overlap, due to the nonclassical phenomenon of interference between wave functions. Consequently an electron occupying the MO Ψ will be more tightly held than one would expect from the binding energies of the component AO's φ_1, φ_2. This extra binding energy appears in the off-diagonal elements of the F matrix as the one-electron resonance integral β_{ij}.

The two-electron exchange terms $-\frac{1}{2}\, p_{ij}(ii,jj)$ can also be given a simple physical meaning. Consider two electrons occupying orbitals Ψ_1, Ψ_2. If the electrons behaved classically, the average Coulombic repulsion between them would be given by

$$\iint \Psi_1^2(1)\,\frac{e^2}{r_{12}}\,\Psi_2^2(2)d\tau_1d\tau_2\,. \qquad (22)$$

This result holds also in quantum theory, if the electrons have opposite spins. However, if the electrons have like spins, the Pauli principle forbids them to occupy the same point in space at any instant. This has qualitatively the same effect on the mutual Coulombic repulsion energy as would a restriction imposing a minimum value $(r_{12})_0$ on the interelectronic distance—as would be the case, for example, if electrons of like spin behaved like spheres of finite size. One can see that the correction to the Coulombic energy depends on the extent to which the electron distribution represented by the wave function Ψ_1, Ψ_2 overlap in space; the more they overlap, the more likely it is that the electrons try to occupy the same point in space and the larger is the corresponding correction to the repulsion energy. It is not surprising to find that the correction amounts to

$$\iint \Psi_1(1)\Psi_2(1)\,\frac{e^2}{r_{12}}\,\Psi_1(2)\Psi_2 d\tau_1d\tau_2\,. \qquad (23)$$

This expression leads to the correction terms $-\frac{1}{2}$ $p_{ij}(ii,jj)$ in Eq. (7). Here the bond order p_{ij} is a measure of the extent of overlap of the electron occupying the AO φ_i with electrons in the AO φ_j; and the factor $\frac{1}{2}$ appears because only half the electrons in the AO φ_i have the same spin as our first electron in the orbital φ_i.

With this analysis to guide us, we can see at once the effect of correlation on the off-diagonal elements of the F matrix. Correlation does not affect the resonance integrals β_{ij}, since these depend only on the behavior of single electrons and are unaffected by electron correlation. However, correlation tends to *increase* the two-electron terms, and hence to increase the integrals (ii,jj) occurring in them, since such an increase reduces the total mutual Coulombic repulsion of the π electrons and so reduces the total energy.

The SPO Eqs. (17) and (18) appear as estimates of the extreme variations that must be made in the repulsion integrals to allow for almost complete vertical correlation.

We can now arrive at a general scheme for parametric variation of the repulsion integrals:

(1) The integrals (ii,jj) must approximate to the "normal" values at large internuclear distances, since the corresponding charge distributions do not then overlap, and the repulsions between them are independent of their exact shapes;

(2) The use of Slater AO's in calculating repulsion integrals is likely to give values that are too large, particularly for small internuclear separations;

(3) Vertical correlation can be allowed for by *increasing* the repulsion integrals that arise from the molecular exchange integrals K_{mn}; these correspond to the off-diagonal two-electron exchange terms $-\frac{1}{2}$ $p_{ij}(ii,jj)$ in the F matrix. The term $\frac{1}{2}$ $q_i(ii,ii)$ is also affected, for this arises as a difference between a term $q_i(ii,ii)$ coming from expansion of Coulomb integrals J_{mn}, and a term $\frac{1}{2}$ $p_{ij}(ii,ii)$ coming from the exchange integrals K_{mn}; of course p_{ii} and q_i are identical, by definition. Increasing the integral (ii,ii) in the K term therefore has the effect of reducing the integral (ii,ii) in the over-all term $\frac{1}{2}$ $q_i(ii,ii)$.

3. HORIZONTAL CORRELATION

We are still left with the problem of horizontal correlation. This, as Löwdin[13] has pointed out, tends to make the densities of α-spin and β-spin electrons alternate at any instant along a π-electron chain. Löwdin has suggested a way of taking this into account by using different orbitals for α-spin and β-spin electrons, chosen so that the total α-spin and β-spin densities alternate along a conjugated system. There are, however, technical difficulties in the way of this treatment, and calculations have so far been made only for simple molecules. One difficulty is that of choosing over all functions that are eigenfunctions of the total spin operator S^2, a point which is discussed in more detail below.

There seems to be a simpler alternative to this. Consider the effect that correlation has on the total energy of a molecule. Correlation cannot effect the one-electron terms α_i and β_{ij} in Eqs. (6) and (7); it acts only by reducing the interelectronic repulsions by ensuring that the electrons synchronize their motions so as to keep apart. Now it is difficult to allow

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[13] P. O. Löwdin, in Proceedings of the Symposium on Molecular Physics, Nikko, Japan, 1953 (unpublished).

for this in a standard LCAO MO wave function because each AO occupies the whole of space. When we expand such a MO in terms of the AO's, each term in the expansion is a function covering all space. It is impossible to write satisfactory correlated wave functions in terms of orbitals of this type. The difficulty would be avoided if we could use as a basis a set of AO's that do not overlap; in this case the three- and four-center integrals between them would vanish. The success of the apparently illogical Pople approximation, where these two-electron integrals are neglected and yet the one-electron integrals β_{ij} are retained, may be due to this; it may in effect be adjusting the repulsion integrals in just the right way to allow for horizontal correlation.

Correlation, however, has another effect. By reducing the probability that two electrons occupy the same point in space, it reduces the correction terms ("exchange energy") of Eq. (23). This could be allowed for by reducing the two-electron exchange terms, $-\frac{1}{2}\, p_{ij}(ii,jj)$, in Eq. (7). The correction should presumably be greater, the further apart the AO's φ_i, φ_j. Combined with the argument given above, this suggests that one could take both vertical and horizontal correlations into account by increasing the terms $-\frac{1}{2}\, p_{ij}(ii,jj)$ for neighboring atoms, but making them decrease rapidly with increasing interatomic distance for nonneighboring atoms, and of course correspondingly decreasing the terms $\frac{1}{2}\, q_i(ii,ii)$ in the diagonal matrix elements [Eq. (12)].

4. CONFIGURATION INTERACTION

The use of configuration interaction in LCAO MO calculations was introduced some time ago by Craig.[14] Although the SCF ground-state configuration does not mix with singly excited configurations, it can mix with more highly excited ones, and of course the single excited configurations can mix with one another. The possibility that configuration interaction may be important is one of the ugly spectres of MO theory; for the number of possible configurations is so large, even in molecules of quite moderate size, that it is out of the question to take them all into account. If this were found to be necessary, it would invalidate the entire MO approach. One could of course try to limit the damage by including only a limited number of arbitrarily chosen configurations; but this would introduce a most undesirable intuitive element into the treatment—and would at the same time complicate it greatly. A further objection is the difficulty of picturing the results of configuration interaction in chemical terms; this would limit the chemical utility of any treatment based on it. For these reasons it seems an admission of defeat to introduce configuration interaction into our treatment of complex molecules; our treatment if it is to be of any practical value must rest on the use of single-determinant wave functions.

We can make one exception to this stricture. As Moffitt[15] has pointed out, configuration interaction is much more important in cases where the interacting configurations are degenerate; here, indeed, it is essential to take the interactions into account. The inclusion of this first-order configuration interaction presents no difficulty or ambiguity, however, since the number of interacting configurations is clearly defined and small. We must on the other hand try to avoid including the smaller and very numerous second order interactions between nondegenerate configurations.

Similar difficulties arise in the valence bond and Pariser–Parr methods, where the philosophy is to use configurations built up from simple basic orbitals and to compensate for the inadequacy of the individual configurations by introducing configuration interaction. These methods seem to have fallen out of favor in recent years. A further objection to the Pariser–Parr method is that it predicts far more excited states of low energy than are observed; thus pentacene is predicted[16] to have twenty-one states of energy less than 7 eV above the ground state, whereas the ultraviolet spectrum gives evidence only for four. It is true that the transitions to most of the states are predicted to be forbidden, but this restriction would probably be removed if allowance were made for the effects of molecular vibrations (cf. the "forbidden" band of benzene at 208 $m\mu$ which has an extinction coefficient of 10^4). Moreover, the calculations covered only singly excited configurations; inclusion of more highly excited configurations would presumably have still further increased the number of states predicted to have energies below 7 eV.

5. ALTERNANT HYDROCARBONS

An alternant[17] conjugated system is one in which the π-bonded atoms can be divided into two sets, no two atoms of the same set being directly linked. This is always possible in molecules where there are no odd-numbered rings. The MO treatment for an alternant hydrocarbon with an even number of con-

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[14] D. P. Craig, Proc. Roy. Soc. (London) **A200**, 474 (1950).

[15] W. E. Moffitt, J. Chem. Phys. **22**, 320, 1820 (1954).

[16] R. Pariser, J. Chem. Phys. **24**, 250 (1956).

[17] See C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) **A192**, 16 (1947).

jugated atoms (even AH) assumes a particularly simple form, first deduced for the Hückel treatment and later shown[18] to hold also in the Pople approximation. The essential features can be summed up as follows:

(1) $q_i = 1$ for each atom; (2) $p_{ij} = 0$ if atoms i, j, belong to the same set; (3) To each occupied MO Ψ_m^+ there corresponds an empty or virtual MO Ψ_m^- related by

$$\Psi_m^+ = \sum^{*} a_{mi}\varphi_i + \sum^{0} a_{mj}\varphi_j \ , \tag{24}$$

$$\Psi_m^- = \sum^{*} a_{mi}\varphi_i - \sum^{0} a_{mj}\varphi_j \ , \tag{25}$$

where each summation is over atoms belonging to the same set; (4) Singly excited configurations arising from transitions between pairs of related orbitals Ψ_m^+, Ψ_m^-, are unique, but the remaining transitions appear in degenerate pairs.

Several phenomena can be explained very simply in these terms:

(a) AH's are nonpolar, whereas nonalternant hydrocarbons (e.g., azulene, fulvene) have significant dipole moments.

(b) Inductive substituents have little effect on the energy of the lowest π–π^* transition; this would be expected[19] since the transition is between orbitals where the orbital densities a_{mi}^2 of the various atoms are the same. There is, therefore, no change in the π-electron distribution in passing from the ground state to the excited state. This is not the case for nonalternant hydrocarbons; here, inductive substituents produce quite large shifts in the absorption bands, the shifts depending in a predictable way on the position of the substituent.[19,20]

(c) The first four absorption bands correspond to transitions between the two highest occupied MO's Ψ_{m-1}^+, Ψ_m^+, and the two lowest unoccupied MO's Ψ_m^-, $\bar{\Psi}_{m-1}$. Two of these are unique, but the other two, $(\Psi_m^+ \longrightarrow \Psi_{m-1}^-)$ and $(\Psi_{m-1}^+ \longrightarrow \Psi_m^-)$ are degenerate. A detailed analysis[21] shows that first-order configuration interaction between them leads to a splitting into two states, and that the transition to the lower of these should be forbidden or partially forbidden, the transition to the other being correspondingly more intense. Clar[22] has indeed found that aromatic hydrocarbons commonly show four distinct bands in the uv-visible region, two strong (p,β'), one very strong (β), and one weak (α). Moreover, the α and β bands seem to be related since the ratio of their frequencies is always about 1:1.3. This pattern corresponds very nicely to that predicted for an AH using the Pople approximation.

One interesting point is that the regularities indicated above hold *only* in the Pople approximation. They disappear in a full SCF treatment where three- and four-center and overlap integrals are included. The weakness of the α bands, for example, could then be explained only by introducing very extensive configuration interaction. This supports the suggestion made earlier, that the Pople approximation may actually give a better representation of molecular structure in terms of single determinants than can a full SCF LCAO MO treatment based on Slater AO's.

6. HÜCKEL APPROXIMATION

The elements of the Pople F matrix for an even AH assume a particularly simple form:

$$F_{ii} = (W_{2p})_i + \tfrac{1}{2}\,(ii,ii) \ , \tag{26}$$

$$F_{ij}(i \neq j) = \beta_{ij} - \tfrac{1}{2}\,p_{ij}(ii,jj) \ . \tag{27}$$

Equation (26) is derived by setting the q_i's in Eq. (12) equal to unity. All the diagonal elements have the same value, and this value (α) is the same in all AH's. The term $\frac{1}{2}\,p_{ij}(ii,jj)$ vanishes as atoms i, j are separated by an even number of bonds, since atoms i, j then belong to the same set so that p_{ij} vanishes. If then we neglect β_{ij} for nonbonded atoms, and neglect $\frac{1}{2}\,p_{ij}(ii,jj)$, if the atoms i, j are separated by three or more bonds (which seems reasonable), then F_{ij} vanishes unless atoms i, j are directly linked. The bond lengths and bond orders in aromatic hydrocarbons vary little; one may then as a first approximation replace β_{ij}, p_{ij}, and (ii,jj) in Eq. (27) by mean values. The off-diagonal elements F_{ij} then vanish for nonbonded atoms i, j and have a common value (β) for bonded ones. Thus,

$$F_{ii} = \alpha \ , \tag{28}$$

$$F_{ij} = \beta \ (\text{atoms } i, j \text{ bonded}) \ , \tag{29}$$

$$F_{ij} = 0 \ (\text{atoms } i, j \text{ not bonded}) \ . \tag{30}$$

The resulting treatment is very simple since the elements of the F matrix have fixed values. The orbital coefficients and energies can be found directly without any need for an iterative procedure. This treatment is the so-called Hückel method which remained for a long time the only feasible method for treating

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[18] J. A. Pople, Proc. Phys. Soc. (London) **68**, 81 (1955).

[19] H. C. Longuet-Higgins and R. G. Sowden, J. Chem. Soc. **1952**, 1404.

[20] E. Heilbronner, in *Non-Benzenoid Aromatic Compounds*, edited by D. Ginsberg (Interscience Publishers Inc., New York, 1959), p. 171.

[21] M. J. S. Dewar and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) **A67**, 795 (1954).

[22] A. Clar, *Aromatische Kohlenwasserstoffe* (Julius Springer-Verlag, Berlin, 1941).

conjugated systems. It has proved remarkably successful in the interpretation of chemical and physical properties of alternant aromatic hydrocarbons, and it still remains an important tool in chemistry. It has, indeed, been so successful, that attempts have been made to extend it to molecules of other types; applications of this kind are suspect, however, for the following reasons:

(a) Application to molecules where the bond orders alternate significantly (e.g., polyenes) is unsatisfactory, since it is no longer justifiable to use a fixed value β for the off-diagonal elements F_{ij}. The two-electron exchange term $\frac{1}{2}$ $p_{ij}(ii,jj)$ in Eq. (27) introduces a kind of positive feedback that increases the alternation between strong and weak bonds. The Hückel method therefore underestimates bond alternation. It predicts, for example, much too high an order (0.45) for the central bond in butadiene. The Pople approximation predicts orders ranging from 0.12–0.25, depending on the values used for the electron-repulsion integrals.

(b) Application to nonalternant hydrocarbons is unsatisfactory since the π-electron densities q_i are no longer equal to unity. The diagonal elements in the F matrix can then no longer be given the constant value α. The same difficulty arises in applying the method to closed-shell ions, where there are an even number of electrons but an odd number of conjugated atoms (e.g., $CH_2=CH-CH_2^+$, $PhCH_2^+$). Wheland and Mann[23] suggested that allowance could be made for this by writing the diagonal elements F_{ii} as

$$F_{ii} = \alpha + (1 - q_i)\omega \, . \qquad (31)$$

This certainly allows for variations in the term $\frac{1}{2}$ $q_i(ii,ii)$ in Eq. (12), but it does not allow for the effects of nonneutrality (i.e., $q_j \neq 1$) in more distant atoms. This treatment, which Streitwieser[24] has termed the ω technique, seems therefore to be of doubtful value. If one is going to make allowance for the terms in F_{ii} involving the charge densities q_i, one might as well do the thing properly and use the full Pople expression.

(c) Similar difficulties arise in application of the Hückel method to conjugated systems containing heteroatoms. The standard procedure has been to write the diagonal elements F_{ii} in the form

$$F_{ii} = \alpha + [\,(W_{2p})_i - (W_{2p})_c\,] \, , \qquad (32)$$

where $(W_{2p})_c$ is the ionization potential of the $2p$-electron in a trigonal carbon atom, and $(W_{2p})_i$ that in atom i. Unfortunately, the condition $q_i = 1$ fails in compounds containing heteroatoms, and attempts to allow for this by using the ω technique are unsatisfactory for the reasons indicated above. Our calculations[25] for boron-containing aromatic compounds indicate that the ω technique does not give a satisfactory explanation for the observed chemical properties, even when allowance is made for differences in the one-electron resonance integrals β_{ij} between bonds formed by different types of atom.

For these reasons one must regard Hückel-type calculations for molecules other than aromatic hydrocarbons with some reserve. It would seem wiser to use the Pople method in such cases; this involves no more difficulty if the calculations are carried out with a computer.

7. CHEMICAL APPLICATIONS

The introduction of MO theory has completely revolutionized organic chemistry, and it is impossible to do more here than comment on one or two salient aspects.

First, the MO treatment is, as we have seen, most easily applied in the case of aromatic hydrocarbons. If we wish to use MO theory as a guide in studying the mechanism of a given chemical reaction, we should try if possible to collect experimental data for cases where the reactants are alternant hydrocarbons.

We have used this technique in a number of connections. Thus, a study of relative reactivities of aromatic hydrocarbons in nitration provides[26] a new and useful approach to the mechanism of electrophilic substitution. A similar study[27] of the solvolysis of chloromethyl derivatives of such hydrocarbons threw a new light on the relation between the two extreme mechanisms (S_N1, S_N2) for nucleophilic substitution on saturated carbon. Recently a study[28] of the charge-transfer spectra of π complexes formed by aromatic hydrocarbons with suitable acceptors has been used as evidence for the structure of such complexes.

An interesting development[29] has been the use of perturbation methods in discussing chemical prob-

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[23] G. W. Wheland and D. E. Mann, J. Chem. Phys. **17**, 264 (1949).

[24] See A. Streitwieser, *Molecular Orbital Theory for Organic Chemists* (John Wiley & Sons, Inc., New York, 1961), p. 115.

[25] M. J. S. Dewar and W. H. Poesche (unpublished work).

[26] M. J. S. Dewar, T. Mole, and E. W. T. Warford, J. Chem. Soc. **1956**, 3581.

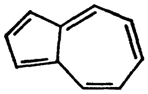
[27] M. J. S. Dewar and R. J. Sampson, J. Chem. Soc. **1956**, 2789; **1957**, 2946.

[28] M. J. S. Dewar and A. R. Lepley, J. Am. Chem. Soc. **83**, 4560 (1961); M. J. S. Dewar and H. Rogers, *ibid.* **84**, 395 (1962).

[29] M. J. S. Dewar, J. Am. Chem. Soc. **74**, 3341, 3345, 3350, 3353, 3355, 3357 (1952).

lems. Most chemical problems involve calculations of small differences in energy between closely related structures; thus the rate of a chemical reaction depends on the difference in energy between the reactants, and a transition state which differs from the reactants only by one or two bonds. Such energy differences can be calculated very simply by applying perturbation theory to the Hückel approximation. This approach has provided a new and much superior alternative to the resonance theory as a general basis for organic chemistry. It not only avoids the vague and intuitive nature of arguments based on resonance theory, but it also gives predictions of reactivity, etc., in a quantitative form.

The success of these simple methods is gratifying, but not unexpected. It must always be better to calculate a small difference between two large energies by a direct perturbation method than to calculate the two large energies separately and then subtract one from the other. In certain cases the PMO (perturbational MO) method has correctly made predictions that follow from no other theoretical approach. Thus it gives[29] an immediate and simple derivation of the Hückel rule for aromaticity, and it predicts[29] that azulene (I) should be aromatic, unlike pentalene (II) or heptalene (III); none of the more elaborate MO methods has been satisfactory in these connections.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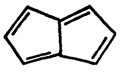
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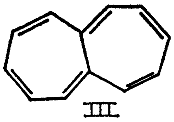
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These perturbation methods are reliable only for alternant systems since they derive from the Hückel method; they can, however, be applied in some cases to nonalternant molecules if these can be derived from alternants by a perturbation (as is the case for I, II, III above). Perturbation methods can also be used for systems containing heteroatoms by treating them as perturbed forms of the corresponding or isoconjugate hydrocarbons. All these calculations have the advantage of "pencil and paper" simplicity —a point of obvious importance to practical chemists.

The success of these methods suggests that more refined perturbation methods might be even more successful. Pople[30] has developed methods of this kind based on his simplified SCF treatment, and of course Moffitt's AIM method[6] is based entirely on a perturbational approach. A parametric form of the AIM method might turn out to be ideal for chemical problems in general and conjugated systems in particular.

8. RADICALS

So far we have considered only closed-shell molecules where all the MO's are either full or empty. This cannot be the case for a radical where one electron remains unpaired. Conjugated radicals (e.g., $CH_2=CH-CH_2\cdot$, $PhCH_2\cdot$) must therefore contain singly occupied π-MO's.

The simplest way to deal with such a compound is to suppose that the electrons occupy a single set of MO's; these can be found by applying the usual closed-shell SCF treatment either to the positive ion formed by loss of one electron from the radical, or to the negative ion formed by addition of one electron to it. In this picture all the electrons but one remain paired; there is then an unpaired spin density at each atom proportional to a_{0i}^2 where a_{0i} is the coefficient of the AO φ_i in the singly occupied MO. The distribution of unpaired spin can be estimated experimentally by standard ESR techniques and the values compared with those calculated.

Comparisons of this kind show a serious discrepancy between theory and experiment. The theoretical treatment indicates that the unpaired spin at each position can be due only to the unpaired electron; if this has α spin, the interactions with nuclei must correspond to interactions with an α-spin electron. However, in certain positions, one finds evidence for an excess of unpaired electrons of opposite spin to that of the odd electron. Thus, in the allyl radical $CH_2=CH-CH_2\cdot$, theory predicts that the unpaired electron (of, say, α spin) should be confined to the end atoms; ESR studies show that there is indeed a high density of unpaired α spin at these positions, but there is also a significant density of excess β spin at the central atom. Many other analogous cases of "negative spin densities" in radicals are now known.

The reason for this discrepancy is easily seen. Consider a radical with n α-spin electrons and $(n-1)$ β-spin electrons. The interpretation of F-matrix elements given above showed how the total energy could be divided into a classical part (corresponding to the diagonal elements F_{ii}) and a nonclassical part (corresponding to the off-diagonal elements F_{ij}). The latter contains corrections to the interelectronic repulsions, due to the effect of the Pauli principle. Now in the case of our radical the corrections will not be symmetrical. The potential of an α-spin electron needs correction for interactions with the $(n-1)$

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[30] J. A. Pople, Proc. Roy. Soc. (London) **A233**, 233 (1955); J. A. Pople and P. Schofield, *ibid.* **A233**, 241 (1955).

other α-spin electrons, but that of a β-spin electron needs correction for interactions with only $(n-2)$ other electrons. If we are going to represent the radical by a single determinant, we must then use different orbitals for electrons of α and β spin. If we introduce appropriate charge densities q_i^α, q_i^β, and bond orders p_{ij}^α, p_{ij}^β for the two kinds of electrons defined by

$$q_i^\alpha = \sum_m n_m^\alpha a_{mi}^\alpha ; \; p_{ij}^\alpha = \sum_m n_m^\alpha a_{mi}^\alpha a_{mj}^\alpha \qquad (33)$$

with analogous expressions for q_i^β and p_{ij}^β, we can see that the orbital coefficients a_{mi}^α for the α-spin electrons will be the eigenvectors of one F matrix. The corresponding coefficients a_{mi}^β for the β-spin electrons will be eigenvectors of a different F matrix, the matrix elements for the F^α matrix being

$$F_{ii}^\alpha = (W_{2p})_i + q_i^\beta(ii,ii) + \sum_{j\neq i} (q_i^\alpha + q_i^\beta - 1)(ii,jj) , \qquad (34)$$

$$F_{ij}^\alpha = \beta_{ij} = p_{ij}^\alpha(ii,jj) . \qquad (35)$$

The matrix elements of the F^β matrix are derived from these by interchanging α and β. The eigenvalues and eigenvectors of the two F matrices are found in the usual way by an iterative procedure, leading to two sets of MO's, one for the α-spin electrons and one for the β-spin electrons.

This treatment gives a qualitatively correct picture of radicals in which negative spin densities duly appear. The reason for this is easily seen. Suppose that in the simple MO treatment (with a single set of MO's for all electrons) the unpaired α-spin electron has a larger density at position i. Consider the two electrons occupying some other orbital Ψ_m. The repulsion between the α-spin member of the pairs and the α-spin electron on atom i will be less than that between the β-spin member and the unpaired electron; the densities of the two electrons at atom i are, therefore, not the same. This unpairing of the electrons has the effect of concentrating more of the α-spin electron at position i and so squeezing out an excess of β-spin electrons onto the rest of the conjugated system. In allyl, where the unpaired electron is concentrated on the end atoms, the effect is to produce a surplus of β spin at the central position.

This difficulty can be met in the simple MO treatment by introducing configuration interaction, but this is a desperate expedient to be avoided at all costs. The open-shell MO treatment avoids this difficulty at the expense of another; it is easily shown that although the one-configuration open-shell wave function is an eigenfunction of the spin operator $\mathbf{S}_z$, it is not an eigenfunction of $\mathbf{S}^2$. This difficulty in turn can be met by what is in effect another kind of configuration interaction treatment;[31] this is certainly less objectionable than the one indicated above, in that the number of configurations is less and in that their coefficients can be found by using projection operators. However, the whole procedure is offensively cumbersome in the case of large radicals.

Even though the open-shell single-determinant wave functions are not eigenfunctions of $\mathbf{S}^2$, it seems quite likely that they may in practice give good accounts of the properties of radicals provided that the repulsion integrals occurring in the F matrix are adjusted as indicated earlier. Calculations carried out[32] in this way for the allyl radical have given good agreement with experiment, and with the results of more rigorous calculations by McConnell.[33]

Similar difficulties arise in the treatment of excited states of molecules, where there are two unpaired electrons; structures of this kind are becoming increasingly important in organic photochemistry, where excited triplet states play a dominant role. Most calculations for triplet states have so far used the simple model in which the same set of MO's is used for electrons of either spin; however, it may well prove better to use the open-shell treatment, particularly for triplet states where the number of α- and β-spin electrons differ.

9. BOND FIXATION AND THE VALIDITY OF THE HÜCKEL APPROXIMATION

One basic assumption made throughout has been the Hückel approximation; this in turn is tied up with the idea that bonds other than those involved in conjugated systems can be represented in terms of sharing of localized pairs of electrons between pairs of atoms. The following argument[34] throws light on this problem.

Consider a molecule containing two bonds of given type (e.g., C–C single bonds). In a localized bond picture, these correspond to interactions of pairs of AO's on the bonded atoms to form pairs of MO's, the lower of which in each case is occupied by a pair of electrons (Fig. 1).

Let us now consider the effects of interactions between the bonds. There will be first-order interactions between the degenerate pair of filled orbitals, and between the degenerate pair of empty orbitals [Fig. 1(b)]; these interactions delocalize the electrons over both bonds and greatly alter the orbital en-

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[31] P. O. Löwdin, Phys. Rev. **97**, 1509 (1955).

[32] M. J. S. Dewar and N. L. Sabelli (unpublished work).

[33] H. M. McConnell, J. Chem. Phys. **29**, 244 (1958).

[34] M. J. S. Dewar, *Hyperconjugation* (Ronald Press, New York, 1962); Tetrahedron (to be published).

ergies; they do not, however, alter the total energy or total spatial distribution of the electrons. Secondly, there will be a much smaller second-order interaction between the filled and empty orbitals, depressing the former and raising the latter [Fig. 1(c)]. This will alter the total energy and the total electron distribution.

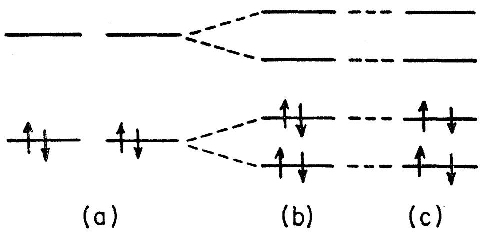

FIG. 1. Interactions between a pair of similar bonds: (a) unperturbed system; (b) effect of first-order perturbation; (c) effect of second-order perturbation.

What then do we mean when we ask if the localized bond model is valid? If we are interested in some *one-electron property* of the molecule, i.e., a property that depends on the individual MO's, such as the ionization potential or nuclear spin coupling of the unpaired electron in a radical, then the first-order interactions will be important, and we will not expect to get any kind of agreement with experiment unless we take them into account. If, however, we are interested in some property that depends collectively on all the electrons taken together, e.g., the total binding energy or dipole moment of a molecule, then we may get a good estimate from the localized bond model—for the deviations from this in the case of such *collective properties* are due only to the small second-order interactions which may well be unimportant. The difference is analogous to that between first-order configuration interaction in conjugated systems—which *must* be taken into account—and higher order configuration interaction—which we devoutly hope need not be. Much confusion has been caused by failure to realize this distinction. The localized bond model is *never* a correct description, but many molecules behave *as if* the electrons in them were delocalized, insofar as their collective properties are concerned. The localized bond model must not, however, be used in discussing one-electron properties, especially in cases where there are two or more bonds of the same kind between which large first-order interactions can occur.

Similar difficulties may arise in the case of conjugated systems with reference to the Hückel approximation. Things are made better here by the fact that the π-MO's are orthogonal to σ bonds formed by the conjugated atoms, and by the fact that π-MO's and σ-MO's probably have very different energies. Nevertheless, it may prove necessary to allow for interactions between π-MO's and σ-MO's in discussing one-electron properties of conjugated molecules. Hyperconjugation constitutes the most crucial case of this kind; the importance of this type of σ–π interaction is still a matter of controversy.[33]

10. BOND LOCALIZATION IN CONJUGATED SYSTEMS; EQUIVALENT ORBITAL PRINCIPLE

The arguments of the previous section link up well with the equivalent orbital method of Lennard-Jones.[35] One can state, on this basis, a principle that might be termed the *equivalent orbital principle.*

If the basic orbitals for a molecule can be put in such a form that they overlap efficiently only in pairs or small groups, then the collective properties of the molecule can be well represented in terms of corresponding localized bonds.

The usefulness of this principle can be illustrated by two simple examples:

(*a*) *Classical conjugated molecules.* Certain conjugated molecules (e.g., butadiene, $CH_2=CH-CH=CH_2$) behave[6,34] in many respects (i.e., those corresponding to collective properties) as though the bonds in them were simple single or double bonds. This is true of *classical* conjugated molecules, i.e., ones for which only single classical resonance structures can be written. As we have seen, the bond orders in molecules of this kind alternate strongly; the interaction terms F_{ij} [Eq. (7)] for the weak "single" bonds will be small. If we apply perturbation theory to a classical model with alternating single and double bonds, the interactions between the two-center π bonds will be correspondingly small. The arguments given above suggest then that the collective properties should be little changed by the interaction, so that the classical model should be a good "as if" description. The situation is indeed even more favorable, for one may absorb an averaged allowance for the interactions into the empirical bond properties we attribute to "pure" single and double bonds. The collective properties of such molecules can therefore be interpreted in terms of a localized bond model, although of course there is no question that the π-electrons are in fact delocalized.

(*b*) *π-Bonding involving d orbitals.* Just as σ bonds can be treated in terms of a localized overlap of directed hybrid orbitals of the component atoms, so

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[35] J. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1, 14 (1949).

also can be the π bonds formed by $d\pi:p\pi$ overlap. A good example is provided by the phosphonitrile chlorides. Craig[36] thought these to be aromatic compounds of novel type, but Dewar, Lucken, and Whitehead[37] have pointed out that one can write a localized bond model in which each nitrogen is π bonded to its adjacent phosphorus atoms by three-center π bonds, the successive three-center π-MO's not interacting significantly with each other. This is illustrated schematically in Fig. 2, the dotted lines implying $d\pi:p\pi:d\pi$ three-center π-MO's seen from above.

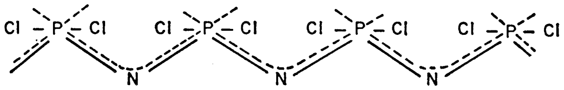
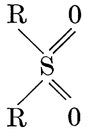


FIG. 2. Schematic representation of $d\pi:p\pi:d\pi$ three-center π-MO's is a phosphonitrile chloride.

According to this representation, each three-center unit should be independent of its neighbors. Molecules of this kind should be quite flexible, unlike aromatic systems where a set of p-AO's fuse into extended π-MO's, and their heats of formation per $PNCl_2$ unit should be the same, regardless of the degree of polymerization. These conclusions agree very well with the experimental facts, suggesting that this "as-if" description in terms of segmented three-center π bonds is a very good one.

A similar situation must arise in other molecules where π bonds are formed by mutual overlapping of p and d orbitals. Thus in sulphones (I)



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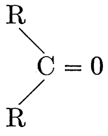

II

the two $S = 0$ π bonds can be regarded as being essentially independent of one another, and there will be no conjugation (in the chemical sense) between unsaturated groups R and $S = 0$ π bonds. The situation is therefore entirely different from that in a corresponding ketone (II); here the $C = 0$ π bond is a $p\pi:p\pi$ bond and the p orbital of the carbon atom will overlap and interact with p or π orbitals on the adjacent groups R.

The distinction between $p\pi:d\pi$ and $p\pi:p\pi$ bonds is of course obscured in ordinary chemical symbolism by the use of single lines to denote bonds of all kind; this has caused considerable confusion in organic chemistry, where no clear distinction has been drawn between the two kinds of unsaturation. Another immediate consequence is that $d\pi:p\pi$ bonding cannot lead to aromaticity, since bonds of this kind do not lend themselves to extensive conjugation.

11. SUMMARY

The purpose of this paper is primarily to arouse discussion; nevertheless, certain conclusions seem to follow from the arguments presented in it:

(1) The only reason for trying to treat complex organic molecules in general, and conjugated systems in particular, by quantum mechanical methods lies in the chemical value of such calculations. The main criterion used to judge them must therefore be pragmatic and we must be prepared to make any approximations, however outrageous, if they lead to useful results.

(2) For the same reason it seems a waste of time to attempt Group One calculations for molecules of this kind; simple molecules still present problems of quite sufficient complexity.

(3) On the other hand, parametric treatments of Group Two type have been both successful and useful; the evidence suggests that they may be made even more so by a more judicious choice of the parameters occurring in them.

(4) Conversely, there has been too much tendency to rely on treatments which are unjustified either by theory or by experiment, simply on the grounds that similar methods have worked well in certain cases and regardless of the fact that those cases may have been very special ones.

(5) The most promising lines seem to be the use of simple perturbation methods where these are applicable, and the use of the Pople method with suitable adjustment of the electron repulsion integrals.

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