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Molecular Orbital Theory for Large Molecules. Approximation of the SCF LCAO Hamiltonian Matrix[1]

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Abstract: Model SCF MO calculations for small molecules have been employed to establish methods and parameters for obtaining Hamiltonian matrix elements of larger related molecules, with all electrons included. Overlap and kinetic energy elements are calculated exactly, while the SCF models yield values of diagonal Hamiltonian elements (α's), and parameters which are used in a modified Mulliken approximation to generate the off-diagonal potential-energy parts of the Hamiltonian matrix. A general discussion of the Mulliken approximation is given. SCF α's are found not to vary linearly with net atomic charge, nor are they adequately approximated by free-atom parameters. It is shown that the assumption that Hamiltonian elements are proportional to overlap integrals neglects elements several electron volts in magnitude. A new formula is presented for calculating these zero-overlap elements.

Molecular orbitals (MO), expressed as linear combinations of atomic orbitals (LCAO), are the basis of a large body of theoretical molecular structural discussion, including predictions, correlations, and interpretations. The LCAO MO self-consistent-field (SCF) method[3] is becoming increasingly more useful as multi-centered integrals become manageable upon large computers, but the present limits of exact applications of this method are molecules of about the size of ethane and diborane. It is therefore no wonder that chemists have turned to more approximate methods[4] for complex molecules. Many of these latter methods have failed to consider the explicit form of the one-electron Hamiltonian, and nearly all of them have required some evaluation of parameters from experiment. The extended Hückel theory,[5] which goes beyond π-orbital theory, has recently been applied to a large number of molecular properties. However, its method for choosing parameters is somewhat questionable,[6] if it is to be considered as an attempt to approximate Hartree–Fock[3] results. We feel that all MO methods should be viewed and judged as approximations within a definite theoretical framework, and we furthermore think that the appropriate framework is Roothaan's SCF theory.[3] In the latter formulation, the MO's are eigenfunctions of a one-electron operator (whose matrix elements we denote as the FMATRIX), representing the sum of the kinetic energy of an electron in an MO, and the potential energy of the electron due to the nuclei and the total electron density of the molecule. Since exchange between electrons of like spin is provided for by this operator, the potential energy defined above does not contain the self-repulsion energy of the electron. In subsequent discussion the matrix elements of the potential energy part of Roothaan's operator will be referred to as the UMATRIX.

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[1] Paper I in a series of four papers.

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[3] Current applications of Hartree–Fock theory use the LCAO formulation given by C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[4] (a) For a recent review of these methods, see "The Quantum Theory of Molecular Electronic Structure," R. G. Parr, Ed., W. A. Benjamin, Inc., New York, N. Y., 1963; (b) see also J. A. Pople and D. P. Santry, *Mol. Phys.*, **7**, 269 (1963–1964); **9**, 301, 311 (1965); and ref 5.

[5] (a) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397; **40**, 3247, 2474, 2480 (1964); (b) R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962).

[6] (a) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **52**, 890 (1964); (b) M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *ibid.*, **53**, 1089 (1965).

One might ask, "Why not assume an unspecified effective one-electron Hamiltonian, and then fit its matrix elements to experimental numbers?" An answer is that one would tend to obtain a different wave function for each property, and therefore could not claim to have approximated in any unique way the molecular wave function; but much more important is our feeling that, without a clear theoretical reference point, empirical parametrization may yield misleading and even spurious information in spite of a superficial correlation with experimental data. Another argument for viewing Roothaan's theory as the proper framework is brought out when one realizes that all approximate MO theories assume that the complete set of occupied MO's may be obtained from a single Hamiltonian matrix (FMATRIX). This is a unique property of the Roothaan theory. In general, one might expect to solve a different secular equation for each MO. Indeed this is the case for the Hartree method[7] and Mulliken's "ionic" Hamiltonian method.[8]

The present series of papers is thus a development of the objective of placing electronic theories of complex molecules on a sounder basis within the realm of the SCF LCAO MO method. In the present paper we utilize currently available, exact minimum basis SCF results to examine previous methods and develop a new method, which simulates SCF MO's for large molecules. We have previously referred to this method as a nonempirical method,[6] not in the sense in which an *ab initio* calculation is nonempirical, but merely to emphasize that the parameters of our method are not fitted to experimental numbers. We feel that before we build experimental information into our method, it is desirable to gain a detailed understanding of our ability to correlate experimental data with the method in a form free of parameters based on experiment. Hopefully we may be able in the future to improve our agreement with experiment by introducing small adjustments (perhaps based on empirical results or refinements of theory) without essentially altering our fundamental outlook. The development of π-electron methods has illustrated the utility of this approach: after experience had been gained with the nonempirical Goeppert-Mayer-Sklar (GMS) method,[4] the Pariser-Parr and the Pople methods yielded better correlation of spectra by assigning empirical values to certain integrals in the GMS formulation.[4]

We shall find here that atomic parameters (*e.g.*, VSIP's)[9] are inadequate for representing the diagonal elements of the FMATRIX. The Mulliken integral approximation (modified as discussed below) is found to be suitable only for the potential energy part (UMATRIX) of the FMATRIX; both of these points are, we feel, implicit in Mulliken's work of 1949,[8] but neither has been adequately explored previously. We shall then describe in detail a method in which the elements of the SCF FMATRICES of suitable small molecules are used for calculations of similar elements of larger, closely related compounds. With our method calibrated to reproduce model SCF calculations in as much detail as possible, we shall attempt in subsequent papers to calculate known properties (*e.g.*, dissociation energies, ionization potentials, and charge distributions) of large boron hydride[10a] and organic[10b] molecules. Our reasonable agreement with experimental results, our ability to make several predictions, and our close approximation of SCF models illustrate the utility of our essentially nonempirical approach as a quantitative bridge between empirical and *a priori* methods. Moreover, we stress that although our method includes all electrons and is applicable to arbitrary geometries, it is basically no more complex than present empirical or semiempirical theories.

I. Limitations

The limitations of our proposed method are clear. Our procedure of extrapolation from model SCF calculations yields only approximate values of the FMATRIX elements. Antisymmetrization is not directly employed, although a method which approximates the LCAO Hartree-Fock (HF) FMATRIX will obviously contain antisymmetrization implicitly, and will uniquely determine approximate HF eigenvalues and eigenvectors. A present, perhaps temporary, limitation is the limit on computer time and memory. This limitation for us is not nearly so great as for the exact SCF LCAO calculations, where the computation of approximately n^4 (for n basis functions) two-electron integrals occupied, for example, 95% of the 3 hr of IBM 7094 time required for a recent diborane calculation.[11] Nevertheless, calculation of integrals (overlap and kinetic) and manipulation of matrices (multiplication and diagonalization), operations proportional respectively to n^2 and n^3, impose a current practical limit of about 130 basis functions on our method. The use of an extended basis set would severely restrict the number of molecules within reach. Thus only minimum basis sets and first-row atoms of the periodic table (1s orbitals included) have been considered so far. However, chemical information has been steadily forthcoming from theories of complex molecules in which limited basis sets are used, and, while we await larger computers and more efficient programs, we explore the development of more rigorous methods within the present framework. Our method is easily extended to larger atoms, once decisions have been made about which inner electrons to include. The inner electrons have previously been shown[6a] to exert strong influence on MO's formed from valence electrons. Another limitation is that our method does not directly yield total molecular energies. Nevertheless, approximate relations in terms of eigenvalues will be used to calculate these energies.[6a] Since exact values of the total kinetic energy are also available, we are able for the first time in the realm of complex molecules to apply an approximate form of the virial theorem[12] as a criterion of the goodness of a wave func-

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(7) "Quantum Theory of Atomic Structure," Vol. I, J. C. Slater, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 222.

(8) R. S. Mulliken, *J. Chim. Phys.*, **46**, 497, 675 (1949). A version in English is available in Technical Reports from the Physics Department, Spectroscopy Laboratory, The University of Chicago, for the period from Sept 1, 1947, to May 31, 1949.

(9) VSIP = valence state ionization potential. Subsequent calculations of VSIP's will be based on the definition given by W. Moffitt, *Rept. Progr. Phys.*, 17, 173 (1954).

(10) (a) Paper II: F. P. Boer, M. D. Newton, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2361 (1966); (b) paper III: M. D. Newton, F. P. Boer, and W. N. Lipscomb, *ibid.*, **88**, 2367 (1966).

(11) Paper IV: W. E. Palke and W. N. Lipscomb, *ibid.*, **88**, 2384 (1966).

(12) The virial theorem equates kinetic energy (T) to the absolute

tion. At present our method applies only to closed-shell, neutral systems.

II. The Mulliken Approximation and Two-Center Matrix Elements

The major equation for many LCAO methods in which all integrals are not calculated explicitly is the Mulliken approximation.[8] We wish to give a brief discussion of this approximation and of some attempts to justify it. Mulliken originally postulated the following relation, "easily seen by inspection to be valid for any function f which occupies the region between and near the centers *a* and *b* and is symmetrical about the midpoint between *a* and *b*"

$$\int \mathrm{f}\, \chi_a\chi_b \mathrm{d}\tau \approx {}^1\!/_2 S_{ab} \left(\int \mathrm{f}\chi_a{}^2\mathrm{d}\tau + \int \mathrm{f}\chi_b{}^2\mathrm{d}\tau\right) \qquad (1)$$

where χ_a and χ_b are identical atomic basis functions[13] except for their different origins, and S_{ab} is the overlap integral between them. In extensions of this approximation, Mulliken applied it to situations where AO's χ_a and χ_b belonged to nonequivalent atoms, and also introduced the following expression[14]

$$(ab|cd) \approx {}^1\!/_4 S_{ab}S_{cd}[(aa|cc) + (aa|dd) + (bb|cc) + (bb|dd)] \qquad (2)$$

This follows from eq 1 if f is taken as the integral operator $\int \chi_c(1)\chi_d(1)/r_{12}\mathrm{d}\tau_1$, although such an f will not in general have the symmetry property stipulated above. Mulliken used eq 1 for f ≡ u, a potential energy term in the approximate LCAO Hartree–Fock one-electron Hamiltonian, emphasizing that eq 1 did not apply to the total Hamiltonian because of the kinetic energy. Rigorously speaking, the permutation operation in the exchange moiety of u would rule out the use of u in eq 1. Mulliken, however, was using approximate expressions for the potential function and thus bypassed this difficulty.

While Mulliken's approximations were stated in terms of integrals, subsequent discussion assumed that eq 1 and 2 depended on the following relation.[15]

$$\chi_a\chi_b \approx S_{ab}(\chi_a{}^2 + \chi_b{}^2)/2 \qquad (3)$$

Ruedenberg attempted to derive eq 3 by taking the identity

$$\chi_a\chi_b \equiv \left(\sum_{a'}^{\infty} S_{ba'}\chi_a\chi_{a'} + \sum_{b'}^{\infty} S_{ab'}\chi_b\chi_{b'}\right)/2 \qquad (4)$$

and showing that for like orbitals χ_a and χ_b, (4) approaches (3) as center *a* gets close to center *b*.[16] For typical distances of 1–2 A, however, it is not clear how good the convergence of (4) would be, and which terms would be most important. Furthermore, at the midpoint of the *a*–*b* bond, where $\chi_a\chi_b = (\chi_a{}^2 + \chi_b{}^2)/2$, we see that eq 3 greatly underestimates the value of $\chi_a\chi_b$ for typical values of S_{ab}. Calculations[17,18] where χ_a and χ_b are 1*S* basis functions in the H_2 molecule have indicated root-mean-square (rms) errors of at least 10% in eq 3. Additional insight into eq 3 is gained by noting that, when the simple two-center charge distribution ϕ^2 is formed from the MO $\phi = (\chi_a \pm \chi_b)/(2 \pm 2S)^{1/2}$ and eq 3 is used to express the term containing $\chi_a\chi_b$, we obtain $\phi^2 = (\chi_a{}^2 + \chi_b{}^2)/2$, which is nothing but the classical approximation, where atomic densities, and not atomic orbitals, are superposed. This paradoxical situation, where the approximation for $\chi_a\chi_b$ appears to be equivalent to the classical approximation in which no interference terms exist, seems to cast further doubt on the validity of eq 3. Mulliken noted[8] a similar situation for the integral $(\phi\phi|ab)$: identical results were obtained either by assuming the classical approximation for the density ϕ^2, or by assuming the expression $\phi = (\chi_a \pm \chi_b)/(2 \pm 2S)^{1/2}$ and using eq 2.

Although eq 1, 2, and 3 all seem to share the above classical feature, it is clear that appreciable rms errors in eq 3 would not preclude higher accuracy in eq 1 and 2 through a balance of errors. For instance when f in eq 1 is simply unity, the approximation becomes an identity: *i.e.*, the simple error in eq 3 averages to zero, no matter how large the rms error. This underlines the fact that eq 3, *per se*, is not necessarily relevant to the suitability of eq 1 for given operators f. We conclude that little is to be gained from *a priori* consideration of 1, 2, and 3, with the caution that only after extensive calculations can one judge the utility of eq 1 for a particular f.

Since we are trying to approximate the FMATRIX elements we have taken the FMATRIX and its various component terms (kinetic energy, nuclear attraction energy, etc.) for several exact minimum basis set calculations,[11] and have examined the values of K_{ij}, defined in eq 5

$$M_{ij} = K_{ij}S_{ij}(M_{ii} + M_{jj})/2 \qquad (5)$$

where *M* is the energy matrix of interest, and *i* and *j* refer to basis orbitals on different centers. In Table I we list the values of K_{ij} for the typical case of methane. Particularly striking is the failure, already noted by Mulliken,[8] of eq 1 for kinetic energy and hence also for the FMATRIX. The currently popular Wolfsberg–Helmholz approximation,[19] which originally used eq 5 (*M* = FMATRIX) for symmetry basis orbitals, allowing different values of *K* for σ–σ and π–π interactions, now has been extended to Slater-type basis functions, with a single value of *K* for all interactions.[20] Our previous results for diatomics[6a] and present studies of polyatomic molecules,[11] as typified by Table I, indicate that use of eq 5 with only one value of *K*, or even with a different $K_{\sigma\sigma}$ and $K_{\pi\pi}$, certainly cannot be expected to give a reliable approximation to the FMATRIX elements. Even if suitable values of $K_{\sigma\sigma}$ and $K_{\pi\pi}$ could be found for use with multi-center symmetry orbitals, one

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magnitude of the total energy (E_{tot}) only for equilibrium molecular geometry. Thus our comparisons of *T* and E_{tot} will constitute only an approximate criterion because of small correction terms required for slight deviations from equilibrium. See discussion by J. C. Slater, *J. Chem. Phys.*, **1**, 687 (1933), and J. O. Hirschfelder and J. F. Kinkaid, *Phys. Rev.*, **52**, 658 (1937).

(13) Throughout this series of papers, Slater-type basis functions will be used, with Slater exponents on all atoms except hydrogen, which is given an exponent of 1.2. See J. C. Slater, *ibid.*, **36**, 57 (1930). Although the choice of exponents is arbitrary, our main conclusions would be the same for any reasonable set of atomic exponents, *e.g.*, best-atom exponents: E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(14) $(ij\,|\,kl) \equiv \int \chi_i(1)\chi_j(1)(1/r_{12})\,\chi_k(2)\chi_l(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2$.

(15) See ref 4a, p 61.

(16) K. Ruedenberg, *J. Chem. Phys.*, **19**, 1433 (1951). $\chi_{a'}$ and $\chi_{b'}$ represent complete, orthogonal basis sets on centers *a* and *b*, respectively.

(17) A. L. Companion and R. G. Parr, *ibid.*, **35**, 2268 (1961).

(18) M. D. Newton, unpublished results.

(19) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

(20) See ref 5a. A similar single-*K* method, which uses a geometric rather than an arithmetic mean of M_{ii} and M_{jj}, has been employed by L. L. Lohr and W. N. Lipscomb, *J. Chem. Phys.*, **38**, 1607 (1963).

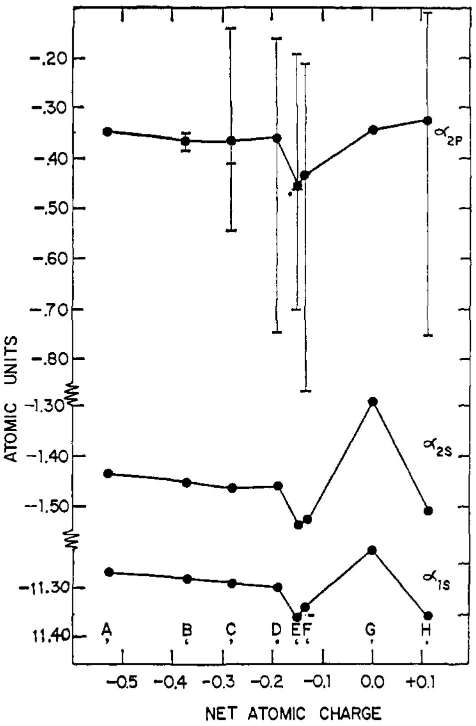

Figure 1. Plot of α's *vs.* net atomic charges for carbon atoms: A, CH_4; B, C_2H_6; C, C_2H_4; D, C_2H_2; E, H_2CO; F, HCN; G, C ($2s2p_x2p_y2p_z$ valence state); H, CO. The valence state atomic calculations are described in footnote *d* of Table IV. For 2p orbitals, the black circles denote the arithmetic mean of the three α values for each atom (except for BH_3, where only the two occupied 2p orbitals are considered), while the short horizontal bars indicate the individual α's. The BH wave function (B–H = 1.21 A) was calculated with the program referred to in footnote *e* of Table IV. See ref 31 for definition of net charges.

would only be "passing the buck," since the diagonal FMATRIX elements would then contain two-center FMATRIX elements over atomic basis functions. On the other hand, Table I reveals that eq 1 approximates the potential energy matrix (UMATRIX) elements reasonably well, all K_{ij} being within ±0.2 of unit. However, before exploring the possibility of obtaining the UMATRIX of large molecules from eq 1, or the generalized eq 5, we must discuss the problem of one-center FMATRIX elements. As a final comment we point out that in molecules of little or no symmetry, certain two-center FMATRIX elements may be expected to have nonzero values, in spite of corresponding overlap integrals which vanish. In paper III[166] we give some evidence that this basic deficiency in eq 5 leads to only small errors.

Table I. K_{ij} for Two-Center Matrix Elements of Methane[a]

	Total Hamiltonian	Kinetic energy	Potential energy	Nuclear attraction energy	2-Electron interaction energy
K_{1sH}	2.04	−0.01	0.83	0.92	1.14
K_{2sH}	1.46	0.37	1.05	1.00	0.98
K_{2pH}	2.10	0.54	1.00	0.93	0.91
K_{HH}	2.95	−0.04	1.19	1.09	1.05

[a] K_{ij}'s from eq 5 are listed, where *M* is taken as various terms in the one-electron FMATRIX.

III. One-Center FMATRIX Elements

The usefulness of eq 5 for obtaining UMATRIX elements obviously depends in part on the availability of values for the diagonal elements (U_{ii}). For convenience, we shall actually discuss here the diagonal FMATRIX elements (α's), from which the U_{ii} values are easily obtained by subtracting the appropriate kinetic energy integrals. Traditionally, values of α, when not obtained exactly according to the Roothaan method,[3] have either been left unspecified (certain approximate calculations of spectra and resonance energies were independent of α),[4] simply set equal to the negative of VSIP's,[5,19,20] or equated to the negative of VSIP's plus other terms.[4] In some cases α's based on neutral atoms have been allowed to vary linearly with the net charges which the atoms acquired in their molecular environments.[21] Mulliken made it clear that while net atomic charges would appreciably alter neutral-atom α's, much more substantial changes could be caused by the mere presence of neighboring atoms.[8] Thus for the π systems of C_2H_2, C_2H_4, and C_6H_6, where symmetry rules out charge transfer, Mulliken obtained $\alpha = -5.71$, -5.11, and -6.58 ev, respectively, as opposed to the VSIP of about 11 ev. Our study of exact minimum basis set FMATRICES[11] has confirmed this result for π systems[22] and has shown in general (Figures 1–3) that VSIP's are poor approximations for α's and that no linear (or any other simple) relationship appears to exist between α and the net charge. The two diborane hydrogen α's differ by 3 ev, although the corresponding charges are almost equal. Inductive effects due to neighboring atoms often appear to override shielding effects from net atomic charges. However, there seems to be no simple explanation (from shielding or electronegativity arguments) for the fact that the carbon 2p α's of H_2CO[23] are more negative than the corresponding oxygen 2p α's (not listed), the carbon and oxygen net charges being respectively −0.152 and −0.086. Furthermore, α's of orbitals which span an irreducible representation in a spherical environment (*e.g.*, $2p_x$, $2p_y$, and $2p_z$) are seen to have very different values in molecular environments of lower symmetry, a split of 16 ev occurring in C_2H_2. In section V a new method of choosing α's is proposed, which takes account of the above facts.

We now turn to a discussion of off-diagonal, one-center elements. The same reduction of symmetry which splits the 2p α's of certain atoms also causes the FMATRIX to have elements of appreciable magnitude between certain orthogonal orbitals on the same center. We shall be able to neglect[24] all such elements except the 2s–2p elements, for which we use eq 6 below. Attaining magnitudes of several electron volts (Table II), these hitherto unappreciated elements are shown in papers II[10a] and III[10b] to exert a strong influence on approximate wave functions and must be included in any attempt to simulate the FMATRIX accurately. As an initial approximation to these zero-overlap (ZO) elements, we offer the following intuitively

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(21) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949); A. Streitweiser, *J. Am. Chem. Soc.*, **82**, 4123 (1960).

(22) The SCF α's of ref 11 differ somewhat from Mulliken's values because the former calculation was more accurate and did not rely on an empirical value of the carbon $2p\pi$ VSIP.

(23) See footnote *c* of Table II.

(24) Partial justification for neglecting these elements is given in paper III (ref 10b).

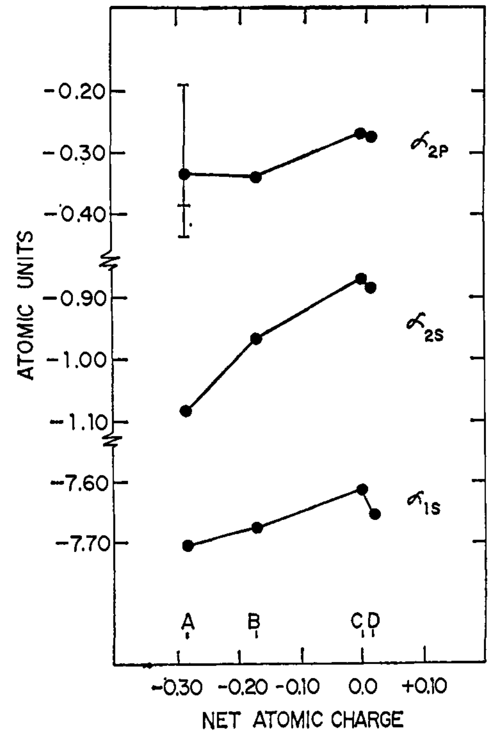

Figure 2. Plot of α's *vs.* net atomic charge for boron atoms: A, B_2H_6; B, BH_3; C, B ($2s2p_x2p_y$ valence state); D, BH. See also caption to Figure 1.

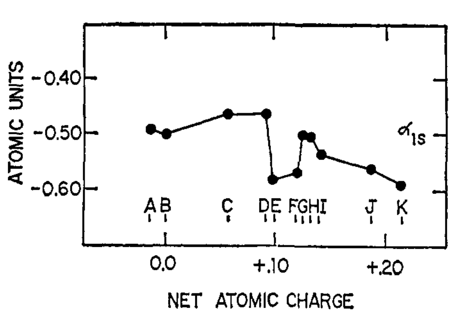

Figure 3. Plot of α's *vs.* net atomic charge for hydrogen atoms: A, BH; B, H (free atom); C, BH_3; D, B_2H_6 (terminal); E, B_2H_6 (bridge); F, H_2CO; G, C_2H_6; H, CH_4; I, C_2H_4; J, C_2H_2; K, HCN. See also caption to Figure 1.

reasonable formula, seen by inspection to satisfy symmetry requirements

$$F_{aa'} = K_{aa'}{}^{ZO}\sum_k S_{ak}S_{a'k}\bar{\alpha}_k \qquad (6)$$

where a and a′ are two orthogonal functions on center a, S_{ak} and $S_{a'k}$ are their respective overlap elements with all the basis functions, and $\bar{\alpha}_k$ is some linear function of the α's of the orbitals concerned. For the 2s–2p interactions required later, we have simply taken $\bar{\alpha}_k$ as α_k, with the values of $K_{2s2p}{}^{ZO}$ to be based on those listed in Table II for various minimum basis FMATRICES. In spite of their scatter, we see that a value of K^{ZO} close to 0.5 will generally give a reasonable approximation to F_{2s2p}. The only other one-center element remaining to be discussed, F_{1s2s}, will be found to be remarkably constant, and can be treated analogously to the two-center elements since it corresponds to a nonzero overlap integral.

Table II. One-Center 2s–2p FMATRIX Elements[a]

Molecule	Atom	$\lvert F_{2s2p}\rvert$, au	$K_{2s2p}{}^{ZO}$
B_2H_6[b]	B	0.104	0.33
C_2H_2[b]	C	0.185	0.48
C_2H_4[b]	C	0.106	0.40
C_2H_6[b]	C	0.029	0.22
H_2CO[c]	C	0.170	0.45
	O	0.190	0.64
NH_3[b]	N	0.119	0.86
N_2O[d]	N[e]	0.325	0.50
	N[f]	0.078	0.69
	O	0.213	0.49
HCN[b]	C	0.232	0.51
	N	0.279	0.58

[a] 2p refers to the 2p orbital lying along the principal rotation axis of the molecule, or in the case of B_2H_6 and C_2H_4, along the B–B and C–C bonds, respectively. Values of $K_{2s2p}{}^{ZO}$ were calculated using eq 6. Only the absolute value of F_{2s2p} is listed, since the sign depends on the relative orientations of the local coordinate systems. When the positive lobe of the axial 2p orbital is directed toward the center of the molecule, F_{2s2p} is negative. For N (internal) in N_2O, F_{2s2p} is positive when the positive lobe points toward the oxygen atom. [b] Reference 11. [c] J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 303 (1960). [d] M. D. Newton, unpublished, using method described in ref 11, with Slater basis set and N–N = 1.126 A, N–O = 1.186 (A E. Douglas and C. K. Moller, *J. Chem. Phys.*, **22**, 275 (1954). [e] Terminal nitrogen. [f] Internal nitrogen.

IV. Conditions for Rotational Invariance

Before eq 5 and 6 can be used to generate matrix elements for large molecules of arbitrary geometry, we must investigate the behavior of these equations under linear, nonsingular, transformations of the basis set. LCAO MO's should be invariant under any such transformations. Since eq 5 and 6 are intended for use with Slater-type atomic basis functions,[13] the only transformations of interest to us for first-row atoms are those which transform the 2p orbitals of a given atom among themselves or, equivalently, which rotate the local coordinate systems (CS) at the various atomic centers with respect to the fixed molecular CS, if the 2p-basis functions are always taken as $2p_x$, $2p_y$, and $2p_z$ in the local CS. Defining such a transformation by the matrix T, with $\chi_{i'} = \sum_j \chi_j T_{ji}$, we find that the overlap matrix and the energy matrix M of eq 5 become respectively $\tilde{T}ST$ and $\tilde{T}MT$.[25] It is apparent then from inspection that a sufficient, although not necessary, condition for the proper transformation of eq 5 is that all three 2p orbitals have the same diagonal matrix element (M_{ii}) and interact with other orbitals with the same value of K_{ij}. The rotational invariance of eq 6 is not so obvious. However, it is easily verified that the condition of a single value of α_{2p} and $K_{2s2p}{}^{ZO}$ for each atom guarantees proper behavior of eq 6.

One consequence of eq 5 is that each 2p–2p matrix element M_{ij} may be considered the sum of a σ–σ and a π–π interaction (with respect to the axis joining the two centers).[26a] As stated above, cross-terms are neglected by eq 5 because the corresponding overlap integrals are zero. We may thus rewrite eq 5 as

$$M_{ij} = (K^{\sigma}{}_{ij}S^{\sigma}{}_{ij} + K^{\pi}{}_{ij}S^{\pi}{}_{ij})(M_{ii} + M_{jj})/2 \qquad (7)$$

where $S^{\sigma}{}_{ij}$ and $S^{\pi}{}_{ij}$ are the overlap integrals due to the

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(25) $\tilde{T}_{ij} = T_{ji}$; T is a real matrix.

(26) (a) Similarly in interactions between s and p orbitals, only the σ component of the p orbital is used by eq 5. (b) One such formula ($F_{ij} = S_{ij}(2 - \lvert S_{ij}\rvert)(F_{ii} + F_{jj})/2$) has been introduced by L. C. Cusachs, *J. Chem. Phys.*, **43**, S157 (1965).

Table III. Coefficients for UMATRIX Elements[a]

	CH_4	C_2H_2	C_2H_4	C_2H_6	HCN	H_2CO	NH_3	BH_3[d]	B_2H_6
K_{1s2s}(one-center)	0.66	0.66	0.66	0.66	0.66	0.66	0.66	0.66	0.66
K_{1s2s}	...	0.82	0.81	0.80	0.81	0.81	...	...	0.81
K_{1s2p}	...	0.82	0.82	0.81	0.82	0.82	...	...	0.82
K_{2s2s}	...	1.08	1.02	0.94	1.07	1.00	...	...	1.05
K_{2s2p}	...	1.09	1.06	1.00	1.11	1.05	...	...	1.11
$K_{2p\sigma 2p\sigma}$	...	1.12	1.05	0.99	1.17	1.07	...	...	1.13
$K_{2p\pi 2p\pi}$[b]	...	1.07	1.10	...	1.05	1.05	...	...	...
$K_{2p\pi 2p\pi}$[c]	...	...	0.73	0.69	...	0.74	...	...	1.14[e]
K_{1sH}	0.83	0.83	0.83	0.83	0.83	0.83	0.84	0.81	0.81
K_{2sH}	1.05	1.07	1.05	1.04	1.07	1.04	1.06	1.05	1.04
K_{2pH}	1.00	0.95	0.98	0.99	0.92	0.94	1.02	1.02	1.05
K_{HH}	1.19	1.48	1.18	1.15	...	1.20	1.19	1.16	1.13

[a] The K's listed were obtained from eq 5 and averaged over certain similar interactions *via* eq 8. H denotes the hydrogen 1s orbital. All values are based on the same wave functions as were used in Table II. Except for the first entry, all K's refer to two-center interactions. [b] This row represents π–π interactions in the π MO's of C_2H_2, C_2H_4, HCN, and H_2CO. [c] This row contains K's for the in-plane π–π interactions in C_2H_4 and H_2CO, the C_2H_6 π–π interaction, and an average of the two K's for the B_2H_6 π–π interactions (see footnote *e*). [d] For BH_3, α_{2p} was taken as the α of one of the in-plane 2p orbitals, since the third 2p orbital is unoccupied. [e] Since the value of $K_{\pi\pi}$ for B_2H_6 is an average value (as required in paper II), it differs appreciably from other values in the same row.

components of 2p orbitals i and j respectively parallel and perpendicular to the axis joining the two centers. Since both S^{σ}_{ij} and S^{π}_{ij} transform individually in the same manner as the total overlap elements (proved in the Appendix), eq 7 is easily seen to transform correctly with different values for K^{σ}_{ij} and K^{π}_{ij}, provided that they both obey the restrictions imposed on the single K_{ij} of eq. 5.

Equations 5 and 7 transform correctly essentially because the M_{ij}'s are linear in the overlap integrals. Equation 6, although quadratic in overlap, nevertheless behaves properly because the summation is over the entire basis set. In general, however, nonlinear functions of overlap will not possess the requisite rotational invariance.[26b]

Since we plan to use (5) and (7) with M = UMATRIX, the condition that M_{ii} be constant for all 2p orbitals on an atom is in conflict with our finding (Figures 1–3) that the 2p α's (and hence also the diagonal UMATRIX elements) are often widely split. A partial resolution of this problem follows from the observation that although MO's should be invariant under arbitrary transformations of the basis set, in certain cases a unique basis set may be singled out. For example, in planar systems, where there is considerable anisotropy (Figure 1), we may rigorously separate σ and π basis functions. In such a situation it seems reasonable to assign different K_{ij}'s and α's to the σ and π 2p orbitals, while requiring invariance only with respect to rotation in the molecular plane. This procedure is followed in paper III. Hopefully, methods will be discovered for unambiguously introducing atomic anisotropies into more general systems.

V. Proposal of New Method

Utilizing all of the above discussion, we now outline a detailed procedure for applying known molecular SCF results to the calculation of wave functions for molecules not yet accessible to exact SCF methods. We shall then illustrate for the case of CH_4 the advantage of this procedure over other possible methods of choosing parameters.

Step 1. Choice of α's. In choosing α's for the atoms in a series of related, large molecules, one must find exact calculations for small molecules whose atoms see environments as similar as possible to those of the larger systems. The present body of SCF results[11,23] allows the following distinctions to be made: tetrahedral, trigonal, and digonal carbon atoms in pure hydrocarbons; trigonal carbon atoms bonded to oxygen and nitrogen;[27] the cyano carbon atom; tetrahedral, trigonal, and digonal nitrogen atoms; the carbonyl oxygen atom and hydrogen atoms bonded to all of the above carbon and nitrogen atoms (except digonal nitrogen). At present the only model SCF boron atoms available are those in BH_3 and B_2H_6. The latter calculation allows bridge and terminal hydrogen atoms to be distinguished. In accord with the discussion in the previous section, for atoms in a plane, $\alpha_{2p\pi}$ values can be taken directly, while a simple average of the other two α's is used for $\alpha_{2p\sigma}$. An average of all three α's will be taken for α_{2p} of atoms in nonplanar molecules.[28] Otherwise α's are to be transferred directly from the appropriate models.

Step 2. Overlap and kinetic energy integrals are calculated exactly.

Step 3. UMATRIX Elements. Diagonal elements of the UMATRIX, obtained by subtracting the diagonal kinetic energy integrals from the α's, are used with the overlap elements to generate two-center UMATRIX elements *via* eq 5. In assigning values of K to be used in eq 5, one must decide how many different types of two-center interactions it is feasible to distinguish. This decision will be based on the values of K listed in Table III for several molecules, including all those used as models in papers II and III. These K's were calculated according to eq 5, using values of diagonal UMATRIX elements obtained from ref 11 and 23. We then averaged over certain similar interactions according to eq 8, where the individual K_{ij}'s within our groupings are weighted by the absolute magnitude of the corresponding UMATRIX elements (U_{ij}).

$$K_{\mathrm{ab}} = (\sum_{ij} K_{ij}|U_{ij}|)/(\sum_{ij} |U_{ji}|) \qquad (8)$$

The subscripts a,b on K refer to those given in the first column of Table III. Since most of the K's in Table III are quite close to unity, one might initially

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(27) In paper III, parameters for this type of carbon atom are discussed.

(28) In paper III, distinct π-system parameters will be maintained for the unsaturated moieties of alkyl-substituted planar systems, even though the molecules are nonplanar.

Table IV. Methane Wave Functions[a]

	SCF	α's and K's SCF C_2H_6[b]	α's from SCF CH_4; 2-center K's = 1	α's from SCF valence-state carbon[c,d]	α's and K's from SCF CH[e,f]
$-\alpha_{1s}$	11.269	11.276	11.269	11.214	11.260
$-\alpha_{2s}$	1.432	1.449	1.432	1.292	1.295
$-\alpha_{2p}$	0.349	0.364	0.349	0.338	0.309
$-\alpha_H$	0.507	0.501	0.507	0.500	0.557
$-F_{1s2s}$	2.640	2.640	2.642	2.627	2.624
$-F_{1sH}$	0.787	0.787	0.949	0.947	0.785
$-F_{2sH}$	0.729	0.724	0.689	0.651	0.709
$-F_{2pH}$	0.253	0.250	0.254	0.251	0.280
$-F_{HH}$	0.274	0.263	0.230	0.229	0.239
$-\epsilon_1$	11.271	11.279	11.283	11.229	11.263
$-\epsilon_2$	0.932	0.932	0.864	0.751	0.860
$-\epsilon_3$	0.542	0.544	0.558	0.549	0.599
q_H	+0.133	+0.168	+0.188	+0.102	−0.061
OP_{CH}	+0.780	0.767	+0.693	0.772	0.793

[a] The symbols in column 1 refer to diagonal (α) and off-diagonal (F) FMATRIX elements, eigenvalues (ϵ), Mulliken (ref 31) charge on H (q_H), and C–H overlap population (OP_{CH}), where H denotes the hydrogen 1s orbital. All energies are in au. The CH_4 and C_2H_6 SCF parameters are from ref 11, the K's from Table III. For both $K = 1$ calculations, the correct one-center K_{1s2s} was maintained. [b] Best agreement with SCF CH_4. [c] Two-center K's = 1. [d] The wave function for the valence state (ref 9) of carbon ($2s2p_x2p_y2p_z$) was calculated with the "Atomic SCF Program No. 3," described by C. C. J. Roothaan and P. S. Bagus in "Methods in Computational Physics," Vol. II, Academic Press Inc., New York, N. Y., 1963, pp 47–94. The 1s α and 2s and 2p α's were taken respectively from the closed-shell and open-shell FMATRIX. α_H was taken as the energy of the hydrogen atom. [e] The CH ($^2\pi$) wave function, with methane C–H distance, was obtained from R. K. Nesbet's open-shell diatomic wave function program (*Rev. Mod. Phys.*, **35**, 552 (1963)), as modified by R. M. Stevens. [f] K_{HH} = 1.

attempt to use eq 5 for complex molecules with all K_{ab} set equal to unity (see Table IV). However, we notice that the value of K_{ab} for each chosen class of interactions is nearly constant, irrespective of the atom involved, except for hydrogen, which is treated separately, and the π–π interactions in B_2H_6 (see paper II). Remarkably, a K of 0.66 is seen to specify completely *all* one-center, 1s–2s UMATRIX elements in Table III. The anomalously large K_{HH} for C_2H_2 is insignificant, since it corresponds to a very small UMATRIX element. Even in the cases of greatest deviation from constancy, the spread in K's is only $\sim$0.1. This result suggests that it is reasonable to maintain the same degree of differentiation in applications to larger systems. Hence the K_{ab}'s for our subsequent calculations will be taken directly from Table III. As indicated in section IV we shall always be permitted to maintain distinct values of $K_{2p\sigma 2p\sigma}$ and $K_{2p\pi 2p\pi}$, and also an additional $K_{2p\pi 2p\pi}$ for the π systems of planar molecules.

Step 4. ZO Elements. The one-center, 2s–2p zero-overlap elements F_{2s2p} are obtained from eq 6 with a value of K^{ZO} based on Table II.

Step 5. The kinetic energy matrix and the UMATRIX are combined into the FMATRIX, and the secular equation is solved for eigenvalues and eigenvectors.

The first test of our proposed method is its ability to reproduce the model wave functions after the requisite averaging of parameters has been performed. In papers II and III we shall see that the eigenvalues are reproduced in the correct order[29] with accuracy usually better than ±0.05 au, while correspondingly reasonable agreement is obtained for charge distributions.

The transferability of parameters from one molecule to another is strikingly illustrated in Table IV, where SCF C_2H_6 parameters (α's and K's) accurately reproduce the CH_4 wave function. We note that the use of the correct CH_4 α's, but two-center K's = 1, leads to poor results, while equally bad agreement with column 2 is obtained from use of free-atom or diatomic (CH) parameters. The ability of C_2H_6 parameters to generate the CH_4 wave function gives us good reason to expect that the same parameters should also be a suitable basis for calculations on larger saturated hydrocarbons. We also feel that ethylene is a suitable model for large unsaturated hydrocarbons, while the SCF H_2CO, HCN, and NH_3 SCF calculations will allow heteroatoms and inductive effects to be included. These hypotheses are tested in paper III, while paper II examines the usefulness of BH_3 and B_2H_6 in obtaining wave functions for the larger boron hydrides. Clearly, as more exact SCF results become available, further refinements will become possible, allowing a finer differentiation among atoms and types of interactions. The transferability of SCF FMATRIX elements has previously been discussed in the more limited context of π systems by Orloff and Fitts.[30]

The regular relationships that we have described in previous sections between UMATRIX and SMATRIX (overlap) elements have proved very useful as a partial check on SCF LCAO calculations, and have enabled us to detect by inspection certain errors in our own and published SCF reports.

VI. Charge Distributions

We shall briefly discuss the charge distributions to be expected from our wave functions and consider the usefulness of Mulliken charges[8,31] in representing these distributions. First we must decide how important is our failure to allow fine adjustments in our α's by some self-consistent technique. We have already noted that Mulliken found slight differences in $\alpha_{2p\pi}$ for carbon atoms in different unsaturated nonpolar systems, although they were all within a range of less than 2 ev.

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(29) A slight exception occurs for B_2H_6 (ref 10a), where two near-degenerate levels are inverted.

(30) M. K. Orloff and D. D. Fitts, *J. Am. Chem. Soc.*, **85**, 3721 (1963).

(31) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2238, and 2343 (1955).

One might expect in general that the α's of a carbon atom in a hydrocarbon would depend on the number of carbon and hydrogen atoms to which it was bonded. We can only point to the remarkable similarity of the carbon α's for CH_4 and C_2H_6. With regard to the charge dependence of α's we emphasize that although Figure 1 does indicate some variation of α's with charge, no simple functional relationship is apparent. We believe that for cases of only moderate intramolecular transfer (relative to that in the model wave functions), our choice of α's is quite reasonable. For carbonyl molecules, a large portion of the charge transfer should be accounted for by use of H_2CO as a model. Some exaggeration of charge transfer may be expected when α's from nonpolar model compounds are used for larger polar molecules (*e.g.*, fulvene and azulene).

LCAO wave functions are generally accompanied by the easily calculated Mulliken point charges.[31] The question of how meaningful these charges are has received little attention. We decided that an appropriate criterion would be to calculate the dipole moments for all of our large-molecule calculations in terms of these point charges, and then compare these with the exact dipole moments. For this purpose we have written an IBM 7094 program which calculates the exact dipole moment for any LCAO wave function using a Slater-type basis set. We shall see[10] that in general the Mulliken charges yield surprisingly accurate dipole moments. Notable exceptions are some boron hydrides,[10a] and some nitrogen heterocycles[10b] in which a lone-pair sp^2 hybrid is generally assumed to exist. The large atomic dipoles associated with hybrid lone pairs disappear in the Mulliken approximation, being essentially replaced by the vanishing one-center overlap integrals between 2s and 2p orbitals. Hence the Mulliken charges should be used with caution.

VII. Relation to Other Methods

Although the relationship of our method to other approximate MO methods is implicit in the previous discussions, we briefly emphasize some important differences. As opposed to π-only methods,[30,32] we include all electrons, thus permitting an unbiased evaluation of the importance of polarization of the core electron density. We do not resort to the approximation of zero-differential-overlap[32] (ZDO) and empirical evaluation of integrals basic to the Pariser–Parr (P–P) method.[32] Although the latter approach has recently been applied to certain limited σ systems (a diatomic σ bond[33] and a hydrogen bond[34]), our investigation of multi-centered integrals indicates that the validity of extending the ZDO approximation to arbitrary molecular systems is still open to question, whereas our method is completely general. With regard to the extended Hückel method,[5] we have shown previously for CH_4[6b] that a fortuitous balance of errors results in excellent agreement with the SCF calculation. Inclusion of 1s electrons spoils this agreement. We conclude that methods which depend on VSIP's for α's, the Wolfsberg–Helmholz approximation, and valence electrons only cannot be considered valid approximation to the exact LCAO method, however useful and accurate their correlations of experimental data may be. The P–P MO method may possibly be viewed as an attempt to transcend the MO framework by empirically including correlation energy in its coulomb integrals. We feel that the importance of such extensions of MO theory will be more clearly understood when more attention has been paid to accurate approximations within the strict MO framework.

VIII. Summary

For clarity we summarize the steps in our method. After interatomic distances and orbital exponents have been chosen: (1) α's are selected from the FMATRIX of the model compounds; (2) kinetic energy and overlap integrals are calculated exactly; (3) using K's obtained from the UMATRIX of model compounds, UMATRIX elements are calculated according to eq 5 or 7; (4) one-center 2s–2p FMATRIX elements are calculated using eq 6; (5) the complete FMATRIX is assembled and the secular equation is solved.

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Appendix

We wish to prove that when the overlap matrix involving 2p–2p interactions is partitioned into a σ–σ and a π–π matrix ($S = S^\sigma + S^\pi$), each component matrix transforms in the same manner as S itself, when the transformation matrix T rotates local coordinate systems on the atomic centers which have 2p orbitals;[35] *i.e.*, $S' = \tilde{T}ST$ implies

$$(S^\sigma)' = \bar{T}S^\sigma T \qquad \text{(A1)}$$

and hence likewise for S^π. To verify eq A1, we note that T is simply a diagonal block matrix, with a 3×3 block T^a for each center, while S^σ is composed of 3×3 blocks $S^\sigma{}_{ab}$ for all pairs of centers a and b. For each pair of centers, the vector $\vec{R}_{ab}$ is defined to extend from a to b. The elements of $S^\sigma{}_{ab}$ may be written[36] as

$$S^\sigma{}_{i(a)j(b)} = K_{ab}x_{i(a)}x_{j(b)} \qquad \text{(A2)}$$

where $i(a)$, $j(b)$, and $x_{i(a)}$, $x_{j(b)}$ refer respectively to the x, y, and z 2p orbitals and to the x, y, and z components of $\vec{R}_{ab}$, based on the coordinate systems of a and b. K_{ab} is a constant for all a–b interactions. Since by definition of T

$$\chi_{i'(a)} = \sum_k^3 \chi_{k(a)}T^a{}_{ki}$$

we have

$$(S^\sigma{}_{ab})' = \bar{T}^a S_{ab} T^b \qquad \text{(A3)}$$

from which eq A1 follows.

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(32) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

(33) H. A. Pohl, R. Rein, and K. Appel, *ibid.*, **41**, 3385 (1964).

(34) R. Rein and F. Harris, *ibid.*, **41**, 3393 (1964).

(35) In this discussion S and T are the blocks of the total overlap and transformation matrices which involve only 2p orbitals.

(36) R. A. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).