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Molecular Orbitals from Group Orbitals. 3. Quantitative Perturbational Molecular Orbital Analysis of ab Initio SCF-MO Wave Functions¹

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Abstract: The use of qualitative perturbational molecular orbital (PMO) methods to interpret or predict the results of ab initio SCF-MO calculations has become common. However, because quantitative definitions of fragment orbitals and a rigorous PMO formalism within the framework of SCF-MO theory have not existed, it has not been possible to analyze quantitatively the results of SCF-MO computations in terms of interactions between molecular fragments. In the present work, both the PMO formalism and a quantitative definition of fragment orbitals have been developed within the framework of SCF-MO theory. These developments permit a quantitative PMO analysis to be performed which is as rigorous as the SCF-MO calculation itself. Alternative methods also exist for the description of the interactions between molecular fragments. One of these, discussed in the present work, involves an energy partitioning and population analysis in terms of fragment orbitals. To illustrate these various procedures, computations are reported on two problems of current interest, viz., rotation in ethane and in propylene.

The capabilities of theoretical organic chemistry have expanded greatly in recent years. Two developments, especially, are responsible. The first is the discovery of the Woodward-Hoffmann rules,² which has focused attention upon the frontier³ and perturbational molecular orbital (PMO) methods⁴ for the analysis of chemical reactions. The second is the increasing accessibility of well documented computer programs⁵ and associated technology, which allow nonempirical SCF-MO computations to be performed on systems of reasonable size and chemical interest. It is now well established that ab initio calculations within the Hartree-Fock approximation reproduce faithfully the static and dynamic stereochemical properties of all classes of molecular systems.⁶

In its original formulation,⁴ the PMO method was founded upon the hypothesis that the reaction of a system A with another system B to form a new system AB can be rationalized in terms of the mutual perturbations of the molecular orbitals

of A and B. Subsequently,^{1,7} the method was extended to the treatment of conformational problems, the assumption being made that the stable structure of a molecule can be regarded as the result of a chemical reaction (or orbital interaction) between the different functional groups into which the molecule can be dissected conceptually. The advantage of such an approach is that the description of the total electronic structure of a molecule is simplified considerably if the molecule can be treated as two or more assemblies of atoms, i.e., functional groups, rather than individual atoms.⁸ The latter forms the basis of the LCAO-MO formalism. The approach has been justified by the observation that a molecular fragment is a near-transferable quantum mechanical entity.^{7a,9}

Although the PMO formalism requires a definition of the orbitals of the interacting moieties regardless of the nature of the problem, there are some fundamental differences between the analysis of a chemical reaction and the analysis of a con-

formational effect. In the PMO interpretation of a reaction, σ -type orbital interactions between the reactants are emphasized because these interactions lead to the bond that joins the reactants. However, in the PMO interpretation of a molecular conformation, the interacting moieties or "building blocks" are obtained by *dissection* of the bond joining them; and π -type orbital interactions between these fragments are subjected to analysis. It is assumed implicitly that the σ -bond orbital which represents the dissected bond is conformationally invariant so that, in terms of σ -type orbital interactions between them, the fragments are considered to remain united. The fragmentation of the molecule is thus a conceptual one, with the notion of building blocks having been introduced to simplify the description of the molecular electronic structure.

A second difference between PMO analyses of reactions and conformational effects becomes evident when an attempt is made to obtain the orbitals of a fragment. A real molecular system is characterized by its geometry and by the number of electrons it contains. These two quantities define an object for an SCF-MO calculation. Thus, an attempt to derive the orbitals of a fragment within the SCF-MO approximation requires specific choices for the geometry of this fragment and the number of electrons which it contains, i.e., whether the fragment should be treated as a radical, a cation, or an anion. To avoid the latter problem, one might provide⁷¹ PMO interpretations of the results of SCF-MO calculations in terms of fragments obtained by the Extended Hückel Molecular Orbital (EHMO) method.¹⁰ The orbitals and orbital energies generated by this procedure do not depend upon the number of electrons in the system, unlike those generated by SCF-MO methods. However, when the analysis of an SCF-MO result is performed in this way, using EHMO fragments, the interpretation would seem to be less rigorous than the calculation itself. If the objectives of theoretical conformational analysis include both the results of the computation *and* the interpretation of these results, it seems reasonable to expect that both should be obtained to the same degree of rigor.

The commonly employed PMO formalism has been derived within the framework of a one-electron Hamiltonian (e.g., the so-called "one-electron molecular orbital" procedure⁷³). In the usual application of such a PMO procedure, the interaction energy between two nondegenerate orbitals is given as directly proportional to the square of the overlap integral and inversely proportional to the orbital energy difference, the proportionality constant being unspecified.

The qualitative nodal properties of the orbitals of a large number of simple fragments are available from standard sources.^{7a} With these in hand, the conformational dependence of the overlap integrals associated with different conformational arrangements of two fragments can be estimated qualitatively. This is done by inspection of the bonding and antibonding relationships between the fragment orbitals in different conformations. The energy differences between the orbitals of different *fragments* are estimated from appropriate experimental and/or theoretical data on *molecules* that may contain the same or similar orbitals.⁷¹ When the estimation of overlap integrals is difficult, the conformational analysis has been restricted to effects of orbital energy differences only.^{7h}

These various assumptions allow *relative* stabilities of different conformations to be estimated qualitatively. A rigorous quantitative treatment is not possible because, even when overlap integrals and orbital energy differences between fragments *can* be evaluated, it is still necessary to provide a value for the proportionality constant. The PMO method therefore invariably leads to a qualitative rationalization of conformational effects based upon the consideration of certain specific orbital interactions in the system. The validity of such rationalizations is then tested by making predictions con-

cerning the behavior of the total molecular wave function and checking these predictions with explicit SCF-MO calculations.

The intent of the foregoing discussion is to establish a need for a PMO procedure based upon SCF-MO wave functions. Such a procedure would have two advantages over the present methods: the ambiguities inherent in the use of different levels of approximation for a computation and the interpretation of this computation would be removed; and the procedure would provide a *quantitative* mechanism for the analysis of SCF-MO results.

Theory

(A) Derivation of Orbital Interaction Energies. Let the set of n atomic orbitals χ_i be represented by the row vector χ , and the set of n molecular orbitals ϕ_i by the row vector ϕ . In the LCAO-MO representation, ϕ is given by

$$\phi = \chi C \quad (1)$$

where

$$\phi = (\phi_1 \phi_2 \dots \phi_n) \quad (2)$$

and

$$\chi = (\chi_1 \chi_2 \dots \chi_n) \quad (3)$$

and C is an $n \times n$ coefficient matrix. For a closed shell, C is a solution of the Fock equation

$$FC = SCe \quad (4)$$

We assume that eq 1 and 4 refer to the composite system AB which contains the closed shell constituents A and B . Without loss of generality, the row vector χ can be written as

$$\chi = (\chi_1 \chi_2 \dots \chi_m \chi_{m+1} \dots \chi_n) \quad (5)$$

in which $\chi_1, \chi_2, \dots, \chi_m \in A$, and $\chi_{m+1}, \chi_{m+2}, \dots, \chi_n \in B$. The Fock matrix F , one-electron Hamiltonian matrix H (i.e., the matrix representation of the kinetic and nuclear-electron attraction operators), and overlap matrix S of the composite system can be partitioned as follows:

$$F = \begin{bmatrix} F_A & F_{AB} \\ F_{AB}^\dagger & F_B \end{bmatrix} \quad (6a)$$

$$H = \begin{bmatrix} H_A & H_{AB} \\ H_{AB}^\dagger & H_B \end{bmatrix} \quad (6b)$$

$$S = \begin{bmatrix} S_A & S_{AB} \\ S_{AB}^\dagger & S_B \end{bmatrix} \quad (6c)$$

the elements of the matrices M_A , M_B , and M_{AB} ($M = F, H, S$) being defined by

$$\begin{aligned} (M_A)_{ij} &= \langle \chi_i | \hat{M} | \chi_j \rangle & \chi_i, \chi_j &\in A \\ (M_B)_{ij} &= \langle \chi_i | \hat{M} | \chi_j \rangle & \chi_i, \chi_j &\in B \\ (M_{AB})_{ij} &= \langle \chi_i | \hat{M} | \chi_j \rangle & \chi_i &\in A, \chi_j \in B \end{aligned} \quad (7)$$

with \hat{M} as the operator for M .

The molecular orbitals and Fock equations of A and B may be written as

$$\phi_A^0 = \chi_A C_A^0; \phi_B^0 = \chi_B C_B^0 \quad (8)$$

$$F_A^0 C_A^0 = S_A^0 C_A^0 e_A^0; F_B^0 C_B^0 = S_B^0 C_B^0 e_B^0 \quad (9)$$

The superscript zero is a reminder that eq 8 and 9 refer to isolated systems.

The molecular orbitals of an isolated system are orthonormal. Thus, for AB , we have

$$\begin{aligned} \langle \phi_i | \phi_j \rangle &= C_i^\dagger S C_j = \delta_{ij} \\ i, j &= 1, 2, \dots, n \end{aligned} \quad (10)$$

where C_i is the column vector of C ,

$$C_i = \begin{bmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{ni} \end{bmatrix} \quad (11)$$

Equation 10 is equivalent to eq 12

$$C^\dagger S C = 1 \quad (12)$$

The corresponding expressions for A and B are

$$(C_A^0)^\dagger S_A^0 C_A^0 = 1; (C_B^0)^\dagger S_B^0 C_B^0 = 1 \quad (13)$$

We can now examine exact and approximate relationships between the molecular orbitals and orbital energies of the composite system and the molecular orbitals and orbital energies of its constituents with the choice

$$\chi_A = (\chi_1 \chi_2 \dots \chi_m) \quad (14a)$$

and

$$\chi_B = (\chi_{m+1} \chi_{m+2} \dots \chi_n) \quad (14b)$$

(a) **Exact Relations.** The following matrices are introduced to simplify the notation:

$$F^0 = \begin{bmatrix} F_A^0 & 0 \\ 0 & F_B^0 \end{bmatrix} \quad (15a)$$

$$C^0 = \begin{bmatrix} C_A^0 & 0 \\ 0 & C_B^0 \end{bmatrix} \quad (15b)$$

$$H^0 = \begin{bmatrix} H_A^0 & 0 \\ 0 & H_B^0 \end{bmatrix} \quad (15c)$$

$$S^0 = \begin{bmatrix} S_A^0 & 0 \\ 0 & S_B^0 \end{bmatrix} \quad (15d)$$

$$e^0 = \begin{bmatrix} e_A^0 & 0 \\ 0 & e_B^0 \end{bmatrix} \quad (15e)$$

This simplifies eq 9 to

$$F^0 C^0 = S^0 C^0 e^0 \quad (16)$$

and eq 13 to

$$(C^0)^\dagger S^0 C^0 = 1 \quad (17)$$

Furthermore, the molecular orbitals ϕ_i^0 defined by eq 18

$$\phi_i^0 = \chi C_i^0 \quad (18)$$

correspond to the molecular orbitals of A if $i \in 1, 2, \dots, m$, and to those of B if $i \in m+1, m+2, \dots, n$.

The transformation of C^0 into C can be achieved by a matrix T , defined by

$$C = C^0 T \quad (19)$$

Here the physical meaning of the matrix T is that it expresses the molecular orbitals of AB in terms of linear combinations of the molecular orbitals of A and B .

By using eq 17 and 19, T can be expressed as

$$T = 1T = (C^0)^\dagger S^0 C^0 T = (C^0)^\dagger S^0 C \quad (20)$$

Let us decompose F as follows:

$$F = F^0 + \delta F^0 \quad (21)$$

where

$$\delta F^0 = \begin{bmatrix} F_A - F_A^0 & F_{AB} \\ F_{AB}^\dagger & F_B - F_B^0 \end{bmatrix} \quad (22)$$

Then, from eq 19 and 21, eq 4 can be rewritten as

$$(F^0 + \delta F^0) C^0 T = S C e \quad (23)$$

Premultiplying both sides of eq 23 by $T^\dagger (C^0)^\dagger$, i.e., C^\dagger , leads to

$$T^\dagger [(C^0)^\dagger F^0 C^0 + (C^0)^\dagger \delta F^0 C^0] T = C^\dagger S C e \quad (24)$$

From eq 12, 16, and 17, eq 24 can be rewritten as

$$T^\dagger (e^0 + \Delta) T = e \quad (25)$$

where

$$\Delta = (C^0)^\dagger \delta F^0 C^0 \quad (26)$$

Equations 19 and 25 provide exact relations between C and C^0 and between e and e^0 .

An alternative method for the determination of e can be derived by combining eq 19 and 23.

$$(F^0 + \delta F^0) C^0 T = S C^0 T e \quad (27)$$

Premultiplying both sides of eq 27 by $(C^0)^\dagger$ leads to

$$(e^0 + \Delta) T = \tilde{S} T e \quad (28)$$

where

$$\tilde{S} = (C^0)^\dagger S C^0 \quad (29)$$

Notice that S is the overlap matrix between the atomic orbitals χ_i , while \tilde{S} is the overlap matrix between the molecular orbitals ϕ_i^0 . For the i th orbital energy e_i , eq 28 becomes

$$[(e^0 + \Delta) - e_i \tilde{S}] T_i = 0 \quad (30)$$

(b) **Approximate Relations.** To simplify the discussion, we assume that

$$S_A^0 = S_A \text{ and } S_B^0 = S_B \quad (31)$$

That is, the geometries of the isolated species A and B do not change in the composite system AB . Consequently, if i and j are part of the same fragment (i.e., $i, j \in 1, 2, \dots, m$ refers to A and $i, j \in m+1, m+2, \dots, n$ refers to B), the block diagonal form of C^0 and eq 13 and 31 lead to

$$\tilde{S}_{ij} = (C_i^0)^\dagger S C_j^0 = \delta_{ij} \quad (32)$$

Approximate solutions of e_i and T_i may be obtained from eq 30 by using the perturbational formalism.^{4c,d} We introduce the following expansions:

$$e_i = e_i^{(0)} + e_i^{(1)} + e_i^{(2)} + \dots \quad (33a)$$

$$T_i = T_i^{(0)} + T_i^{(1)} + T_i^{(2)} + \dots \quad (33b)$$

$$\tilde{S} = \tilde{S}^{(0)} + \tilde{S}^{(1)} \quad (33c)$$

$$\begin{aligned} h &\equiv e^0 + \Delta \\ &= h^{(0)} + h^{(1)} \end{aligned} \quad (33d)$$

With eq 30 and 33 and the following choices

$$\tilde{S}^{(0)} = 1 \quad (34a)$$

$$\tilde{S}^{(1)} = \tilde{S} - 1 \quad (34b)$$

$$h^{(0)} = e^0 \quad (34c)$$

$$h^{(1)} = \Delta \quad (34d)$$

application of the perturbational formalism^{4c,d} leads to the following expressions for e_i and T_i to second order:

$$e_i = e_i^0 + \Delta_{ii} + \sum_{j \neq i} \frac{(\Delta_{ij} - e_i^0 \tilde{S}_{ij})^2}{e_i^0 - e_j^0} \quad (35)$$

$$\begin{aligned} T_{ii} = 1 - \sum_{j \neq i} \frac{\tilde{S}_{ij} (\Delta_{ij} - e_i^0 \tilde{S}_{ij})}{e_i^0 - e_j^0} \\ - \frac{1}{2} \sum_{j \neq i} \left[\frac{\Delta_{ij} - e_i^0 \tilde{S}_{ij}}{e_i^0 - e_j^0} \right]^2 \end{aligned} \quad (36a)$$

$$T_{ji} = \frac{\Delta_{ij} - e_i^0 \tilde{S}_{ij}}{e_i^0 - e_j^0} + \sum_{k \neq i} \frac{(\Delta_{ik} - e_i^0 \tilde{S}_{ik})(\Delta_{jk} - e_j^0 \tilde{S}_{jk})}{(e_i^0 - e_j^0)(e_i^0 - e_k^0)} \quad j \neq i \quad (36b)$$

In eq 35 and 36, it has been assumed that there is no degeneracy in $\{e_i^0\}$. In the derivation of eq 36a the orthonormality condition

$$C_i^\dagger S C_i = T_i^\dagger S T_i = 1 \quad (37)$$

has been used.

(c) **Orbital Interaction Energies.** The derivation presented above is based upon the SCF-MO formalism. We now consider how this can be reduced to the commonly employed PMO formalism. If it is assumed that the molecular orbitals of A and those of B have negligible overlap integrals, i.e.,

$$S \cong S^0 \quad (38)$$

then $\tilde{S}_{ij} \cong 0$, when i and j refer to different fragments (e.g., $i \in A$ and $j \in B$). Thus, eq 35 is simplified to

$$e_i = e_i^0 + \Delta_{ii} + \sum_{j \neq i} \frac{\Delta_{ij}^2}{e_i^0 - e_j^0} \quad (39)$$

If the Fock matrices that describe A , B , and AB are approximated by electron density independent matrix representatives such as those used in the simple and extended Hückel molecular orbital methods, we have

$$F_A = F_A^0 \text{ and } F_B = F_B^0 \quad (40)$$

under the condition of eq 32. Consequently

$$\Delta_{ii} = 0 \text{ for all } i \quad (41)$$

since $F_A - F_A^0 = 0$ and $F_B - F_B^0 = 0$. Frequently it is assumed that

$$\Delta_{ij} \cong k \tilde{S}_{ij} \quad (42)$$

with k a nonzero constant. This allows eq 39 to be rewritten as

$$e_i \cong e_i^0 + \sum_{j \neq i} \frac{(k \tilde{S}_{ij})^2}{e_i^0 - e_j^0} + \dots \quad (43)$$

Although eq 43 is a well-known PMO formula, it should be noted that the approximations made in eq 38 and 42 are actually incompatible. An alternative PMO expression might, therefore, be derived from eq 35 by making use of eq 41 and 42, i.e.,

$$e_i \cong e_i^0 + \sum_{j \neq i} \frac{[\tilde{S}_{ij}(k - e_i^0)]^2}{e_i^0 - e_j^0} + \dots \quad (44)$$

The term $(k \tilde{S}_{ij})^2/(e_i^0 - e_j^0)$ in eq 43 or $[\tilde{S}_{ij}(k - e_i^0)]^2/(e_i^0 - e_j^0)$ in eq 44 is said to be the orbital interaction energy between ϕ_i^0 and ϕ_j^0 . The effect of eq 33 and 42 is to cause this term to vanish when ϕ_i^0 and ϕ_j^0 refer to the same fragment.

On the basis of this analysis, it seems appropriate to designate the quantity

$$\frac{(\Delta_{ij} - e_i^0 \tilde{S}_{ij})^2}{e_i^0 - e_j^0} \quad (45)$$

which appears in eq 35, as the LCAO-SCF-MO orbital interaction energy between ϕ_i^0 and ϕ_j^0 .

(B) **A Quantitative Definition of Fragment Orbitals.** We consider the eigenvalue problem

$$\tilde{M}_A \tilde{C}_A = S_A \tilde{C}_A \tilde{e}_A \quad (46)$$

in which \tilde{M}_A is a matrix representative of a certain "model" energy operator associated with or related to a fragment A ,

whose orbitals $\tilde{\phi}_A (= \chi_A \tilde{C}_A)$ and orbital energies \tilde{e}_A can be defined. In a purely formal sense, \tilde{M}_A might correspond to H_A or F_A of eq 6. The matrix elements of H_A do not depend upon the molecular orbital coefficients C , and the choice of H_A will therefore produce unique $\tilde{\phi}_A$ and \tilde{e}_A so long as the geometry of A remains unchanged. This is not so in the case of F_A . However, because of the near-transferability of Fock matrix elements,^{9a-d} this is not a serious problem.

The PMO formalism derived in the previous sections remains the same when the matrices F_A^0 , C_A^0 , and e_A^0 are replaced by the corresponding model matrices \tilde{M}_A , \tilde{C}_A , and \tilde{e}_A , respectively. An important feature of the fragment orbitals defined by eq 46 is that the assignment of electron occupancies to such orbitals is not rigorous, because the matrix \tilde{M}_A used in eq 46 does not refer to an isolated species, in which the electron occupancies of the orbitals have been defined uniquely. Like bond functions and hybrid orbitals, fragment orbitals should be regarded as a set of *building blocks* which permit the molecular orbitals and energetics of a composite system to be analyzed conveniently.

(C) **Energy Partitioning and Population Analysis in Terms of Fragment Orbitals.** In the LCAO-SCF-MO theory, the sum of all the occupied orbital energies differs from the total energy and from the total electronic energy. In addition, eq 45, which defines an orbital interaction energy, is only an approximation. Consequently, the rationalization of the total energy behavior of a system in terms of orbital interaction energies *requires the singling out of certain specific orbital interactions and corresponds to an incomplete energy partitioning scheme*. Moreover, when the fragment orbitals of eq 46 are used for a PMO analysis, electron occupancies have to be provided to these fragments to permit the calculation of "two-electron stabilizing" or "four-electron destabilizing" interactions. To free our orbital interaction scheme from this arbitrariness, we consider a simple but complete energy partitioning scheme based upon fragment orbitals. In addition, a population analysis is also considered in terms of fragment orbital bases.

(a) **Energy Partitioning.** The total electronic energy E of the composite system AB , as obtained by direct SCF-MO calculation, is

$$E = \text{tr}[(H + F)D] \quad (47)$$

in which the density matrix D is given by

$$D = \sum_i^{\text{occ}} C_i C_i^\dagger \quad (48)$$

Because of eq 19, C_i becomes **Expansion into fragment orbitals**

$$C_i = \sum_{p=1}^n T_{pi} C_p^0 \quad (49)$$

so that D can be rewritten as

$$D = \sum_p \omega_{pp} C_p^0 (C_p^0)^\dagger + \sum_{p>q} \omega_{pq} [C_p^0 (C_q^0)^\dagger + C_q^0 (C_p^0)^\dagger] \quad (50)$$

where

$$\omega_{pq} = \sum_i^{\text{occ}} T_{pi} T_{qi} \quad (51)$$

Combination of eq 47 and 50 leads to the energy partitioning

$$E = \sum_p \omega_{pp} \text{tr}[(H + F)C_p^0 (C_p^0)^\dagger] + \sum_{p>q} \omega_{pq} \text{tr}\{(H + F)[C_p^0 (C_q^0)^\dagger + C_q^0 (C_p^0)^\dagger]\} \quad (52)$$

In the second term of eq 52, p and q may refer to the same

fragment or to different fragments. When p and q refer to the same fragment, e.g., A , we obtain for the second term

$$\omega_{pq} \text{tr}\{(\mathbf{H} + \mathbf{F})[\mathbf{C}_p^0(\mathbf{C}_q^0)^\dagger + \mathbf{C}_q^0(\mathbf{C}_p^0)^\dagger]\} = 2\omega_{pq} \text{tr}\{(\mathbf{H}_A + \mathbf{F}_A)(\mathbf{C}_A^0)_p(\mathbf{C}_A^0)_q^\dagger\} \quad (53)$$

where $(\mathbf{C}_A^0)_p$ is the p th column vector of \mathbf{C}_A^0 . If $p \in A$ and $q \in B$, the following expression is obtained

$$\omega_{pq} \text{tr}\{(\mathbf{H} + \mathbf{F})[\mathbf{C}_p^0(\mathbf{C}_q^0)^\dagger + \mathbf{C}_q^0(\mathbf{C}_p^0)^\dagger]\} = 2\omega_{pq} \text{tr}\{(\mathbf{H}_{AB} + \mathbf{F}_{AB})(\mathbf{C}_B^0)_{q-m}(\mathbf{C}_A^0)_p^\dagger\} \equiv \Delta E_{pq} \quad (54)$$

The energies given by eq 53 and 54 may be referred to as the intrafragment and interfragment interaction energy terms between ϕ_p^0 and ϕ_q^0 , respectively.

(b) **Population Analysis.** The population analysis¹¹ on AB is now considered in terms of the fragment orbital bases. From eq 1 and 19, ϕ_i becomes

$$\phi_i = \sum_p \phi_p^0 T_{pi} \quad (55)$$

Thus, the total number of electrons N of AB can be decomposed as

$$\begin{aligned} N &= 2 \sum_i^{\text{occ}} \langle \phi_i | \phi_i \rangle \\ &= \sum_p Q_{pp} + 2 \sum_{p>q} Q_{pq} \end{aligned} \quad (56)$$

where

$$\begin{aligned} Q_{pq} &= 2 \sum_i^{\text{occ}} \langle \phi_p^0 | \phi_q^0 \rangle T_{pi} T_{qi} \\ &= 2 \sum_i^{\text{occ}} \tilde{S}_{pq} T_{pi} T_{qi} \end{aligned} \quad (57)$$

Q_{pp} is the net population of ϕ_p^0 , and Q_{pq} is the overlap population between ϕ_p^0 and ϕ_q^0 . The gross population Q_p of ϕ_p^0 is defined by

Can we use this to define the population of ALMOs?

$$Q_p = Q_{pp} + \sum_{q \neq p} Q_{pq} \quad (58)$$

The energy partitioning just described contains no arbitrariness other than the definition of fragment orbitals itself. Likewise, the population analysis contains no further assumptions than those present in the population analysis of an atomic orbital basis. Therefore, these analyses are more complete than the PMO analysis.

(c) **Configuration Analysis.** The PMO, energy partitioning, and population analyses considered so far do not represent the only solutions to the description of the wave functions of composite systems. It is appropriate to draw attention to an alternative method, which is known as configuration analysis.¹² This method emphasizes the expansion of the total wave function Φ of AB in terms of the ground and excited configurations of A and B .

The Hartree-Fock wave function Φ of AB is given as a Slater determinant constructed from the molecular orbitals ϕ .

$$\Phi = \frac{1}{\sqrt{N!}} \det|\phi_1 \bar{\phi}_1 \dots \phi_{N/2} \bar{\phi}_{N/2}| \quad (59)$$

From eq 1, 18, and 19, we obtain

$$\phi = \phi^0 \mathbf{T} \quad (60)$$

Thus, Φ can be expanded as follows:

$$\begin{aligned} \Phi &= a_0 \Phi_0 + \sum a_i^k \Phi_i^k + \sum a_{ij}^{kl} \Phi_{ij}^{kl} + \dots \\ &\quad + \sum a_{ij}^{kl} \dots \Phi_{ij}^{kl} \dots + \dots \end{aligned} \quad (61)$$

where Φ_0 is the normalized Slater determinant constructed from the occupied molecular orbitals of A and B , and a_0 is its coefficient. $\Phi_{ij}^{kl} \dots$ results from Φ_0 when the occupied molecular orbitals $\phi_i^0, \phi_j^0, \dots$ are replaced by the unoccupied molecular orbitals of A and/or B ($\phi_k^0, \phi_l^0, \dots$, respectively, with $a_{ij}^{kl} \dots$ as its coefficient). The magnitude of the coefficient of each Slater determinant has been used as a weighting factor for the electronic configuration represented by the Slater determinant.¹² However, since the Slater determinants resulting from the expansion of Φ are not orthogonal in general due to the nonorthogonality between $\{\phi_A\}$ and $\{\phi_B\}$, their coefficients do not correspond rigorously to weighting factors.

Results

To exemplify the procedure developed herein, computations have been performed on two compounds whose conformations have been discussed previously using qualitative PMO arguments. These compounds are propylene^{7d-g} and ethane.^{1,7g} The problem is to analyze the interaction of a methyl rotor (fragment A) with a vinyl group (fragment B), in the case of propylene, or with another methyl group in the case of ethane. The computations on propylene were performed with the STO-3G basis set^{13a} of GAUSSIAN 70.^{5a} The calculations on ethane were performed using both the STO-3G and the 4-31G^{13b} basis sets.

The orbitals of the A and B fragments of the molecule AB were obtained with eq 46, taking \mathbf{F}_A and \mathbf{F}_B of AB as $\tilde{\mathbf{M}}_A$ and $\tilde{\mathbf{M}}_B$, respectively. The justification for this choice is the observation, already described,^{9a-d} that the Fock matrix elements of a molecular fragment are nearly transferable. As will be shown, this seems quite reasonable. With these choices, $\Delta_{ij} = 0$ and $\tilde{S}_{ij} = \delta_{ij}$, if i and j belong to the same fragment.

(a) **Two-Electron Stabilizing and Four-Electron Destabilizing Interactions.** To facilitate the discussion, one might wish to employ terminologies such as “two-electron stabilizing” and “four-electron destabilizing” interactions. For this purpose, electron occupancies have to be assigned to the fragment orbitals. Consideration of only the interaction between two fragment orbitals, ϕ_i^0 and ϕ_j^0 , leads to the expression

$$\begin{aligned} e_i + e_j &= (e_i^0 + e_j^0) \\ &\quad + \tilde{S}_{ij}[-2\Delta_{ij} + (e_i^0 + e_j^0)\tilde{S}_{ij}]/(1 - \tilde{S}_{ij}^2) \end{aligned} \quad (62)$$

from the corresponding secular determinant, eq 63.

$$\begin{vmatrix} e_i^0 - e & \Delta_{ij} - \tilde{S}_{ij}e \\ \Delta_{ij} - \tilde{S}_{ij}e & e_j^0 - e \end{vmatrix} = 0 \quad (63)$$

When it is assumed that both ϕ_i^0 and ϕ_j^0 are doubly occupied, the term

$$2\tilde{S}_{ij}[-2\Delta_{ij} + (e_i^0 + e_j^0)\tilde{S}_{ij}]/(1 - \tilde{S}_{ij}^2) \equiv \Delta e_{ij} \quad (64)$$

may be regarded as the four-electron destabilizing interaction energy between ϕ_i^0 and ϕ_j^0 . If it is assumed that only ϕ_i^0 is doubly occupied, the term

$$2(\Delta_{ij} - \tilde{S}_{ij}e_i^0)^2/(e_i^0 - e_j^0) \equiv \Delta e_{ij} \quad (65)$$

approximates the two-electron stabilizing interaction energy between ϕ_i^0 and ϕ_j^0 . In eq 64 and 65, the factor 2 enters because of the double occupancy of an orbital.

The mathematical form of eq 64 has an important consequence. In semiempirical SCF-MO methods such as CNDO¹⁴ and INDO,¹⁵ which invoke the zero differential overlap approximation, $\tilde{S}_{ij} = 0$ for $i \neq j$. Therefore, for wave functions generated by such methods, the four-electron destabilizing interaction energy between any pair of fragment orbitals is zero by definition. That is, when the two fragment orbitals interact, the destabilization of the higher lying orbital and the stabilization of the lower lying orbital are equal.^{4d} This is not the case in the extended Hückel and ab initio methods. It follows that

^a STO-3G calculations. ^b The following geometry was employed: $r_{\text{CH}} = 1.09 \text{ \AA}$, $r_{\text{C-C}} = 1.534 \text{ \AA}$, $r_{\text{C=C}} = 1.337 \text{ \AA}$. Valence angles associated with the C=C bond are 120° , and all other valence angles are 109.5° . ^c A positive or negative sign for an orbital coefficient means that, in the HOMO, the group orbital has, respectively, the same phase or the opposite phase of that shown in Figure 1.

From the T matrices of E and S, it is found that the HOMO's of these conformations can be written as linear combinations of π_{CC} , π^*_{CC} , π_{CH_3} , and $\pi^*_{CH_3}$, as shown in Table I.¹⁶ The HOMO's are dominated by an out-of-phase combination of π_{CC} and π_{CH_3} , the former being the major component. This indicates qualitatively that, in terms of the behavior of the HOMO, a destabilizing interaction associated with occupied fragment orbitals (cf. interaction 1 in Figure 1 of ref 7f) is the dominant factor in both conformations.

The data of Table II demonstrate that the gross populations of π_{CC} and π_{CH_3} are close to 2, and those of π^*_{CC} and $\pi^*_{CH_3}$ are small. The sum of the gross populations of the four group orbitals is 4, so that propylene is properly regarded as a 4 π -electron system. The sum of the gross populations of π_{CC} and $\pi^*_{CH_3}$ is 2. If it is supposed that the electron occupancies of π_{CC} and π_{CH_3} were 2 prior to the orbital interaction between the methyl and vinyl fragments, then the gross populations of π^*_{CC} and $\pi^*_{CH_3}$ can be said to reflect the amount of electron charge transfer from π_{CH_3} and π_{CC} , respectively, associated with the orbital interactions. It is within this context that the terms "four-electron destabilizing interaction between π_{CC} and π_{CH_3} " and "two-electron stabilizing interactions between π_{CH_3} and π^*_{CC} and between π_{CC} and $\pi^*_{CH_3}$ " have meaning.

As can be seen from the orbital energies, Table II also shows that the group orbitals of E are not exactly the same as those of S. However, the difference has no significant effect upon the PMO analysis, because the magnitudes of ($e^0_{\pi_{CC}} - e^0_{\pi_{CH_3}}$), ($e^0_{\pi^*_{CC}} - e^0_{\pi^*_{CH_3}}$), and ($e^0_{\pi_{CH_3}} - e^0_{\pi^*_{CH_3}}$) are virtually the same in both conformations.¹⁷

Table IV. The Computed^a Total Energy of Ethane, and the Orbital Energies (e_i^0) and Gross Populations (Q_i) of the π -Type Fragment Orbitals

Conformation	E_{tot} , au	ϕ_i^0	e_i^0 , au	Q_i
S(S) ^b	-78.306 14	π_{CH_3}	-0.5217	1.995
		$\pi^*_{\text{CH}_3}$	0.7060	0.005
E(S) ^b	-78.301 49	π_{CH_3}	-0.5213	1.996
		$\pi^*_{\text{CH}_3}$	0.7073	0.004
S(E) ^c	-78.305 78	π_{CH_3}	-0.5208	1.995
		$\pi^*_{\text{CH}_3}$	0.7062	0.005
E(E) ^c	-78.301 52	π_{CH_3}	-0.5205	1.996
		$\pi^*_{\text{CH}_3}$	0.7075	0.004

^a STO-3G basis set. ^b $r_{\text{CC}} = 1.5452 \text{ \AA}$; $r_{\text{CH}} = 1.0858 \text{ \AA}$; $\angle\text{CCH} = 110.66^\circ$. ^c $r_{\text{CC}} = 1.5587 \text{ \AA}$; $r_{\text{CH}} = 1.0849 \text{ \AA}$; $\angle\text{CCH} = 111.02^\circ$.

The orbital interaction energies Δe_{ij} are calculated from eq 64 and 65, using the orbital energies of Table II and the matrix elements Δ_{ij} and \tilde{S}_{ij} shown in Table III. The Δe_{ij} values reveal that each of the orbital interactions ($\pi_{\text{CC}} - \pi_{\text{CH}_3}$), ($\pi_{\text{CC}} - \pi^*_{\text{CH}_3}$), and ($\pi_{\text{CH}_3} - \pi^*_{\text{CC}}$) favors E over S by 0.97, 0.48, and 0.14 kcal/mol, respectively. The effect of these three orbital interactions, therefore, is to cause E to be more stable than S by 1.59 kcal/mol. This is very close to the 1.34 kcal/mol difference in the total energies of E and S that is obtained by the full SCF-MO calculations. We may conclude that the consideration of the π -type orbital interactions between methyl and vinyl fragments does indeed represent a useful basis for the quantitative analysis of the conformation of propylene. The largest contribution to the methyl rotational barrier in propylene is made by ($\pi_{\text{CC}} - \pi_{\text{CH}_3}$). This is the interaction emphasized in Lowe's analysis.^{7b} The fact that each of ($\pi_{\text{CC}} - \pi_{\text{CH}_3}$), ($\pi_{\text{CC}} - \pi^*_{\text{CH}_3}$), and ($\pi_{\text{CH}_3} - \pi^*_{\text{CC}}$) favors E over S has also been pointed out by Hehre et al.^{7f} from an inspection of the phase relationships between the interacting group orbitals.

The results of the energy partitioning for the ($\pi_{\text{CC}} - \pi_{\text{CH}_3}$), ($\pi_{\text{CC}} - \pi^*_{\text{CH}_3}$), and ($\pi_{\text{CH}_3} - \pi^*_{\text{CC}}$) pairs, denoted by ΔE_{ij} in Table III, reveal the same trends as found in Δe_{ij} . For example, a positive or negative overlap population Q_{ij} between two interacting fragment orbitals corresponds respectively to a stabilization or destabilization in both Δe_{ij} and ΔE_{ij} .

Ethane. The calculations just presented for propylene were performed within a rigid rotor model, using a minimal (STO-3G) basis set. However, this is not an obligatory procedure, because any internal mode of motion and any ab initio SCF-MO wave function can be subjected to the quantitative orbital interaction analysis. A standard computational approach, applicable to all problems, is not one of our objectives. For any specific problem the approach to be employed will depend, inter alia, upon the complexity of the system, the computational facilities that are available, and subjective considerations such as the level of computation deemed to be sufficient.

The consequences of the rigid rotor approximation and the use of a minimal basis set have been examined in the study of the ethane rotational barrier. Four geometries were computed at both the STO-3G and 4-31G levels; these geometries are designated S(S), E(S), S(E), and E(E), where S(S) refers to a fully optimized staggered conformation, and E(S) is the eclipsed conformation that results from a rigid rotation of S(S), etc.¹⁸ The results are summarized in Tables IV and V, for the STO-3G basis set, and in Tables VI and VII, for the 4-31G basis set.

As shown schematically in Figure 2, there is a degeneracy in the π -type orbitals of the methyl fragments. Only one of these two sets of orbitals is listed in Tables IV-VII. Table IV shows that the methyl fragments have virtually the same orbital energies in each of the four conformations. In addition, a comparison of the e_i^0 values of Tables II and IV indicates the degree of transferability of the methyl fragment orbitals in the two molecules propylene and ethane. We observe that the gross population of π_{CH_3} is almost 2 and that of $\pi^*_{\text{CH}_3}$ is small. It is therefore appropriate to consider a "four-electron destabilizing interaction energy" between the π_{CH_3} orbitals of two bonded methyl fragments, as well as the "two-electron stabilizing interaction energy" associated with the interaction between π_{CH_3} of one methyl fragment and $\pi^*_{\text{CH}_3}$ of the other. These are summarized in Table V.

If the only interactions considered are those associated with π_{CH_3} and $\pi^*_{\text{CH}_3}$, the total of these amounts to two of ($\pi_{\text{CH}_3} - \pi_{\text{CH}_3}$) and four of ($\pi_{\text{CH}_3} - \pi^*_{\text{CH}_3}$) for each conformation. This leads to total orbital interaction energies of 30.84, 28.82, 27.56, and 25.84 kcal/mol for E(S), E(E), S(S), and S(E), respectively. The methyl rotational barriers calculated from these interaction energies are 3.28 and 2.98 kcal/mol for the rigid rotation of S(S) and E(E), respectively. The corresponding barriers obtained from the total energies of the SCF-MO calculations are 2.92 and 2.67 kcal/mol, respectively. Thus, as in the case of propylene, the total energy behavior of the molecule is fairly well reproduced by the π -type orbital interactions calculated within a rigid rotor model with an STO-3G basis set.

However, the difference in the total interaction energies of S(S) and E(E) is only 1.26 kcal/mol. This is significantly smaller than the corresponding difference in the total energies of these conformations, 2.90 kcal/mol. The poorer quantitative agreement in this case can be traced to the different optimized geometries of the eclipsed and staggered conformations.^{18,19} The CC bond is longer and the CCH angles are larger in the eclipsed conformation. This decreases the interaction between the two methyl groups, and the magnitude of this effect can be seen in the Δe_{ij} values of Table V. It is clear that ($\pi_{\text{CH}_3} - \pi_{\text{CH}_3}$) is less destabilizing, and ($\pi_{\text{CH}_3} - \pi^*_{\text{CH}_3}$) is also less stabilizing when the eclipsed geometry is employed. The ΔE_{ij} and Δe_{ij} values of Table V show the same trends. The Q_{ij} values are also found to correlate with Δe_{ij} and ΔE_{ij} in the same way as observed for propylene.

Table V. The Matrix Elements, Interaction Energies, and Overlap Populations between the π -Type Fragment Orbitals in Ethane (STO-3G Basis Set)

$(\phi_i^0 - \phi_j^0)$	Conformation	Δ_{ij} , au	\tilde{S}_{ij}	Δe_{ij} , kcal/mol	ΔE_{ij} , au	Q_{ij}
$(\pi_{\text{CH}_3} - \pi_{\text{CH}_3})$	E(S)	-0.1182	0.1188	17.02	0.2537	-0.0283
	E(E)	-0.1143	0.1150	15.93	0.2202	-0.0265
	S(S)	-0.1136	0.1131	15.70	0.2141	-0.0254
	S(E)	-0.1099	0.1095	14.72	0.2002	-0.0238
	E(S)	-0.0615	0.0646	-0.80	-0.0298	0.0031
$(\pi_{\text{CH}_3} - \pi^*_{\text{CH}_3})$	E(E)	-0.0604	0.0638	-0.76	-0.0284	0.0030
	S(S)	-0.0703	0.0760	-0.96	-0.0366	0.0040
	S(E)	-0.0687	0.0746	-0.90	-0.0347	0.0038

Table VI. The Computed Total Energy of Ethane^a and the Orbital Energies and Gross Populations of the π -Type Fragment Orbitals (4-31G Basis Set)

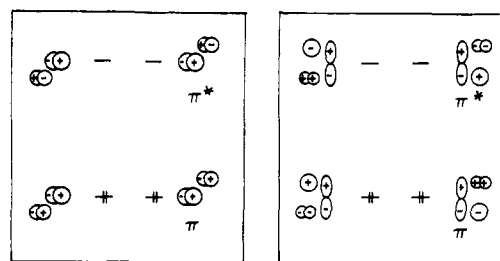
Conformation	$E_{\text{tot}}, \text{au}$	ϕ_i^0	e_i^0, au	Q_i^c
S(S) ^a	-79.115 93	π_{CH_3}	-0.5497	2.000
		$\pi^*_{\text{CH}_3}$	0.3018 ^d	0.011
E(S) ^a	-79.111 30	π_{CH_3}	-0.5492	2.004
		$\pi^*_{\text{CH}_3}$	0.3080	0.007
S(E) ^b	-79.115 72	π_{CH_3}	-0.5482	2.000
		$\pi^*_{\text{CH}_3}$	0.3027	0.011
E(E) ^b	-79.111 52	π_{CH_3}	-0.5477	2.004
		$\pi^*_{\text{CH}_3}$	0.3084	0.007

^a $r_{\text{CC}} = 1.5300 \text{ \AA}$; $r_{\text{CH}} = 1.0834 \text{ \AA}$; $\angle\text{CCH} = 111.07^\circ$. ^b $r_{\text{CC}} = 1.5412 \text{ \AA}$; $r_{\text{CH}} = 1.0828 \text{ \AA}$; $\angle\text{CCH} = 111.64^\circ$. ^c Besides π_{CH_3} and $\pi^*_{\text{CH}_3}$, the methyl fragment has two additional π -type fragment orbitals in the 4-31G basis set calculation. Each of these additional fragment orbitals is doubly degenerate and higher lying than $\pi^*_{\text{CH}_3}$. The 4-31G basis set represents a valence atomic orbital by two Gaussian type functions (GTF) with different exponents. The expansion coefficients of these GTF's of a valence atomic orbital have opposite signs in the additional fragment orbitals, in contrast to π_{CH_3} and $\pi^*_{\text{CH}_3}$. The sum of the gross populations of all π -type fragment orbitals having the same symmetry is exactly 2. To simplify the discussion and permit comparison with the results of the STO-3G calculations, only π_{CH_3} and $\pi^*_{\text{CH}_3}$ are listed in Tables VI and VII. ^d The orbital energy of $\pi^*_{\text{CH}_3}$ is approximately 0.7 au in the STO-3G basis set calculation (see Tables II and IV).

The essential features of the 4-31G calculations summarized in Tables VI and VII are exactly the same as those of the STO-3G calculations just discussed. From the Δe_{ij} values the methyl rotational barriers are 4.46, 2.78, and 1.75 kcal/mol for the processes S(S) \rightarrow E(S), S(E) \rightarrow E(E), and S(S) \rightarrow E(E), respectively. The corresponding barriers from the total energies of the SCF-MO calculations are 2.91, 2.64, and 2.77 kcal/mol, respectively.

In the STO-3G calculations, inspection of either Δe_{ij} or ΔE_{ij} reveals that the difference in the stabilities of the staggered and eclipsed conformations is dominated by the effect of the destabilizing interactions ($\pi_{\text{CH}_3} - \pi_{\text{CH}_3}$) when rigid rotation is considered. But in the case of relaxed rotation S(S) \rightarrow E(E), it is the change in the stabilizing interactions ($\pi_{\text{CH}_3} - \pi^*_{\text{CH}_3}$) which dominates. These findings parallel rather well the observation that the computed SCF-MO rotational barrier of ethane is "repulsive dominant" for rigid rotation and "attractive dominant" for relaxed rotation.²⁰

The 4-31G basis set calculations shown in Table VII do not display the same effects. When the Δe_{ij} values are considered, it is seen that the rotational barrier is dominated by the ($\pi_{\text{CH}_3} - \pi_{\text{CH}_3}$) interactions for rigid rotation as before, but in the relaxed rotation, the effects of the ($\pi_{\text{CH}_3} - \pi_{\text{CH}_3}$) and the ($\pi_{\text{CH}_3} - \pi^*_{\text{CH}_3}$) interactions are almost the same. On the other hand, the ΔE_{ij} values suggest that the ($\pi_{\text{CH}_3} - \pi_{\text{CH}_3}$) and

**Figure 2.** Schematic representation of the π -type fragment orbitals in ethane.

($\pi_{\text{CH}_3} - \pi^*_{\text{CH}_3}$) interactions contribute to the same extent to the energy difference between S(S) and E(S), but the ($\pi_{\text{CH}_3} - \pi^*_{\text{CH}_3}$) interaction is more important in the transformations S(E) \rightarrow E(E) and S(S) \rightarrow E(E).

Summary and Conclusions

The most advantageous feature of the PMO method is that it uniquely retains the chemically intuitive notion that the properties of a molecular system can be described in terms of interactions among its functional groups. In the present work, we have obtained the orbitals of a fragment within the framework of SCF-MO theory by solution of the formal eigenvalue problem defined in eq 46. The Fock matrix F_A of the molecule which contains fragment A has been set equal to \bar{M}_A . The computational tests reveal that the fragment orbitals thus determined are nearly transferable from conformation to conformation, and from molecule to molecule, and that, with these fragment orbitals, the PMO method can be employed to interpret *quantitatively* the result of an SCF-MO computation. With this development, we believe that PMO analysis can now complement rigorously other procedures currently in use for the interpretation of ab initio computations. These include energy component analysis,²¹ bond energy analysis,²² charge density analysis,²³ and localized molecular orbital analysis.²⁴

Finally, we wish to emphasize that we have purposely restricted the computational examples of the present work to ethane and propylene. A quantitative analysis of the torsional behavior of these two hydrocarbons seemed quite properly to represent the starting point for the presentation of a quantitative method for the analysis of conformational effects. In addition, the previous, qualitative, treatments of these same systems have been straightforward and noncontroversial, and there is a close correspondence between the language employed in the qualitative work and the interpretation given to the present quantitative results. Certain, relatively subtle, properties of the total energy can be reproduced by the quantitative PMO analysis. It remains to be determined whether there is some fundamental theoretical explanation for the finding that the total energy behavior of a molecular system can be reproduced so well by a quantitative consideration of π -type inter-

Table VII. The Matrix Elements, Interaction Energies, and Overlap Populations between the π -Type Fragment Orbitals in Ethane (4-31G Basis Set)

$(\phi_i^0 - \phi_j^0)$	Conformation	$\Delta e_{ij}, \text{au}$	\tilde{S}_{ij}	$\Delta e_{ij}, \text{kcal/mol}$	$\Delta E_{ij}, \text{au}$	Q_{ij}
$(\pi_{\text{CH}_3} - \pi_{\text{CH}_3})$	E(S)	-0.1470	0.1649	24.01	0.4329	-0.0542
	E(E)	-0.1425	0.1602	22.60	0.4072	-0.0511
	S(S)	-0.1410	0.1575	22.07	0.3866	-0.0482
	S(E)	-0.1390	0.1555	21.50	0.3764	-0.0470
$(\pi_{\text{CH}_3} - \pi^*_{\text{CH}_3})$	E(S)	-0.0946	0.1507	-0.21	-0.0536	0.0065
	E(E)	-0.0949	0.1521	-0.20	-0.0520	0.0063
	S(S)	-0.1163	0.1824	-0.38	-0.0762	0.0096
	S(E)	-0.1167	0.1841	-0.36	-0.0749	0.0095

actions alone. This finding is not restricted to the simple systems of the present work, but has also been observed in the quantitative PMO analysis of a large number of molecules containing multiple bonds and heteroatoms, which will form the subject of future papers. The qualitative analyses of some of these systems has led to controversy. This is not surprising, because the quantitative balance between attractive and repulsive effects is difficult to assess using qualitative arguments. The quantitative analysis, which is more objective, will hopefully permit a resolution of these controversies.

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