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, which has focused attention upon the frontier orbital and perturbational molecular orbital (PMO) methods for the analysis of chemical reactions. The second is the increasing accessibility of well documented computer programs 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.

In its original formulation, 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, 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 as the result of a chemical reaction (or orbital interaction) has not existed, it has not been possible to analyze quantitatively the results of SCF–MO calculations 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.

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

Myung-Hwan Whangbo, H. Bernhard Schlegel, and Saul Wolfe*

Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6. Received June 7, 1976

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.
formational effect. In the PMO interpretation of a reaction, $\sigma$-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 $\pi$-type orbital interactions between these fragments are subjected to analysis. It is assumed implicitly that the $\sigma$-bond orbital which represents the dissected bond is conformationally invariant so that, in terms of $\sigma$-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 provide PMO interpretations of the results of SCF-MO calculations in terms of fragments obtained by the Extended Hückel Molecular Orbital (EHMO) method. The orbitals and orbital energies generated by this procedure do not depend on 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” procedure). 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. 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 anti-bonding 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. When the estimation of overlap integrals is difficult, the conformational analysis has been restricted to effects of orbital energy differences only.

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 concerning 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 $\chi_i$ be represented by the row vector $\chi$ and the set of $m$ molecular orbitals $\phi_j$ by the row vector $\phi$. In the LCAO–MO representation, $\phi$ is given by

$$\phi = \chi C$$

where

$$\phi = (\phi_1, \phi_2, \ldots, \phi_n)$$

and

$$\chi = (\chi_1, \chi_2, \ldots, \chi_n)$$

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

$$FC = SC$$

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 $\chi$ can be written as

$$\chi = (\chi_1, \chi_2, \ldots, \chi_m, \chi_{m+1}, \ldots, \chi_n)$$

in which $\chi_1, \chi_2, \ldots, \chi_m \in A$, and $\chi_{m+1}, \chi_{m+2}, \ldots, \chi_n \in B$. 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:

$$F = \begin{bmatrix} F_{AA} & F_{AB} \\ F_{AB}^\dagger & F_{BB} \end{bmatrix}$$

$$H = \begin{bmatrix} H_{AA} & H_{AB} \\ H_{AB}^\dagger & H_{BB} \end{bmatrix}$$

$$S = \begin{bmatrix} S_{AA} & S_{AB} \\ S_{AB}^\dagger & S_{BB} \end{bmatrix}$$

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

$$M_{ij} = \langle \chi_i | \hat{M} | \chi_j \rangle$$

where

$$\begin{align*}
(M_{AA})_{ij} &= \langle \chi_i | \hat{M} | \chi_j \rangle, \quad \chi_i, \chi_j \in A \\
(M_{BB})_{ij} &= \langle \chi_i | \hat{M} | \chi_j \rangle, \quad \chi_i, \chi_j \in B \\
(M_{AB})_{ij} &= \langle \chi_i | \hat{M} | \chi_j \rangle, \quad \chi_i \in A, \chi_j \in B
\end{align*}$$

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

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

$$\phi_A^0 = \chi_A C_A^0; \phi_B^0 = \chi_B C_B^0$$

$$F_A^0 C_A^0 = S_A^0 C_A^0 \phi_A^0; F_B^0 C_B^0 = S_B^0 C_B^0 \phi_B^0$$

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

$$\langle \phi_i | \phi_j \rangle = C_i^\dagger C_j = \delta_{ij}$$

$$i, j = 1, 2, \ldots, n$$
where \( C_i \) is the column vector of \( C \),

\[
C_i = \begin{bmatrix} C_{i1} \\ C_{i2} \\ \vdots \\ C_{in} \end{bmatrix}
\]  

Equation 10 is equivalent to eq 12

\[
C^T SC = 1
\]  

The corresponding expressions for \( A \) and \( B \) are

\[
(C_A^0)^T S_A^0 C_A^0 = 1; \quad (C_B^0)^T S_B^0 C_B^0 = 1
\]  

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

\[
\chi_A = (X_1 X_2 \cdots X_m)
\]  

and

\[
\chi_B = (X_{m+1} \cdots X_n)
\]  

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

\[
F^0 = \begin{bmatrix} F_A^0 & 0 \\ 0 & F_B^0 \end{bmatrix}
\]  

\[
C^0 = \begin{bmatrix} C_A^0 & 0 \\ 0 & C_B^0 \end{bmatrix}
\]  

\[
H^0 = \begin{bmatrix} H_A^0 & 0 \\ 0 & H_B^0 \end{bmatrix}
\]  

\[
S^0 = \begin{bmatrix} S_A^0 & 0 \\ 0 & S_B^0 \end{bmatrix}
\]  

\[
e^0 = \begin{bmatrix} e_A^0 \\ e_B^0 \end{bmatrix}
\]  

This simplifies eq 9 to

\[
F^0 C^0 = S^0 C^0 e^0
\]  

and eq 13 to

\[
(C^0)^T S^0 C^0 = 1
\]  

Furthermore, the molecular orbitals \( \phi_i^0 \) defined by eq 18

\[
\phi_i^0 = X_i C_i^0
\]  

correspond to the molecular orbitals of \( A \) if \( i \in 1, 2, \ldots, m \), and to those of \( B \) if \( i \in m + 1, m + 2, \ldots, n \). The transformation of \( C^0 \) into \( C \) can be achieved by a matrix \( T \), defined by

\[
C = C^0 T
\]  

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

\[
S_A^0 = S_A \quad \text{and} \quad S_B^0 = S_B
\]  

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., \( i, j \in 1, 2, \ldots, m \) refers to \( A \) and \( i, j \in m + 1, m + 2, \ldots, n \) refers to \( B \)), the block diagonal form of \( C^0 \) and eq 13 and 31 lead to

\[
\tilde{S}_{ij} = \langle C_i^0 \rangle^T S^0 C_j^0 = \delta_{ij}
\]  

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

\[
e_i = e_i^{(0)} + e_i^{(1)} + e_i^{(2)} + \ldots
\]  

\[
T_i = T_i^{(0)} + T_i^{(1)} + T_i^{(2)} + \ldots
\]  

\[
\tilde{S}^{(0)} = \tilde{S}^{(1)}
\]  

\[
h_i = e_i + \Delta
\]  

With eq 30 and 33 and the following choices

\[
\tilde{S}^{(1)} = 1
\]  

\[
h^{(0)} = e^0
\]  

\[
h^{(1)} = \Delta
\]  

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

\[
e_i = e_i^{(0)} + \Delta_i + \sum_{f \neq i} \frac{(\Delta_{ij} - e_i^{(0)} \tilde{S}_{ij})^2}{e_i^{(0)} - e_f^{(0)}}
\]  

\[
T_{ii} = 1 - \sum_{f \neq i} \tilde{S}_{ij} (\Delta_{ij} - e_i^{(0)} \tilde{S}_{ij})^2 e_i^{(0)} - e_f^{(0)}
\]  

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

\[
T^T[(C^0)^* F^0 C^0 + (C^0)^* \delta F^0 C^0] T = C^* S C e
\]  

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

\[
T^T(e_0 + \Delta) T = e
\]  

where

\[
\Delta = (C^0)^* \delta F^0 C^0
\]  

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.

\[
(F^0 + \delta F^0) C^0 T = S^0 C e
\]  

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

\[
(e_0 + \Delta) T = \tilde{S} e
\]  

Journal of the American Chemical Society / 99:5 / March 2, 1977
\[ T_{ij} = \frac{\Delta_{ij} - \varepsilon_i \varepsilon_j}{\varepsilon_i^0 - \varepsilon_j^0} \]

\[ + \sum_{k \neq i} \left( \frac{\Delta_{ik} - \varepsilon_i \varepsilon_k}{\varepsilon_i^0 - \varepsilon_k^0} \right) \left( \frac{\Delta_{jk} - \varepsilon_j \varepsilon_k}{\varepsilon_j^0 - \varepsilon_k^0} \right), \quad j \neq i \] (36b)

In eq 35 and 36, it has been assumed that there is no degeneracy in \( |e_i^0\rangle \). In the derivation of eq 36a the orthonormality condition

\[ C^\dagger S C = T^\dagger S T = 1 \] (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.,

\[ S \approx S^0 \] (38)

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

\[ \varepsilon_i = \varepsilon_i^0 + \Delta_{i0} + \sum_{j \neq i} \frac{\Delta_{ij}^2}{\varepsilon_i^0 - \varepsilon_j^0} \] (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

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

under the condition of eq 32. Consequently

\[ \Delta_{i0} = 0 \quad \text{for all} \quad i \] (41)

since \( F_A - F_A^0 = 0 \) and \( F_B - F_B^0 = 0 \). Frequently it is assumed that

\[ \Delta_{ij} \approx k \tilde{S}_{ij} \] (42)

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

\[ \varepsilon_i \approx \varepsilon_i^0 + \sum_{j \neq i} \frac{(k \tilde{S}_{ij})^2}{\varepsilon_i^0 - \varepsilon_j^0} + \ldots \] (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.,

\[ \varepsilon_i \approx \varepsilon_i^0 + \sum_{j \neq i} \frac{(\tilde{S}_{ij}(k - \varepsilon_i)^0)^2}{\varepsilon_i^0 - \varepsilon_j^0} + \ldots \] (44)

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

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

\[ \frac{(\Delta_{ij} - \varepsilon_i \varepsilon_j)^2}{\varepsilon_i^0 - \varepsilon_j^0} \] (45)

which appears in eq 35, as the LCAO-SCF-MO orbital interaction energy between \( \phi_i^0 \) and \( \phi_j^0 \).

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

\[ \mathbf{M}_A \tilde{C}_A = S_A \tilde{C}_A \tilde{e}_A \] (46)

in which \( \mathbf{M}_A \) 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 \( \tilde{\varepsilon}_A \) can be defined. In a purely formal sense, \( \mathbf{M}_A \) might correspond to \( \mathbf{H}_A \) or \( \mathbf{F}_A \) of eq 6. The matrix elements of \( \mathbf{H}_A \) do not depend upon the molecular orbital coefficients \( \mathbf{C} \), and the choice of \( \mathbf{H}_A \) will therefore produce unique \( \tilde{\phi}_A \) and \( \tilde{\varepsilon}_A \) so long as the geometry of \( A \) remains unchanged. This is not so in the case of \( \mathbf{F}_A \).

However, because of the near-transferability of Fock matrix elements, this is not a serious problem.

The PMO formalism derived in the previous sections remains the same when the matrices \( \mathbf{F}_A^0 \), \( \mathbf{C}_A^0 \), and \( \varepsilon_i^0 \) are replaced by the corresponding model matrices \( \mathbf{M}_A \), \( \tilde{C}_A \), and \( \varepsilon_i \), 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 \( \mathbf{M}_A \) 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

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

in which the density matrix \( \mathbf{D} \) is given by

\[ \mathbf{D} = \sum_i \chi_i^0 \tilde{C}_i \tilde{C}_i^\dagger \] (48)

Because of eq 19, \( \tilde{C}_i \) becomes

\[ \tilde{C}_i = \sum_{p=1}^P T_{pi} C_p^0 \] (49)

so that \( \mathbf{D} \) can be rewritten as

\[ \mathbf{D} = \sum_p \omega_{pp} C_p^0 (C_p^0)^\dagger \]

\[ + \sum_{p > q} \omega_{pq} [C_p^0 (C_q^0)^\dagger + C_q^0 (C_p^0)^\dagger] \] (50)

where

\[ \omega_{pq} = \sum_i \mathbf{T}_{pi} \mathbf{T}_{qj} \] (51)

Combination of eq 47 and 50 leads to the energy partitioning

\[ E = \sum_p \omega_{pp} \text{tr}[(\mathbf{H} + \mathbf{F}) C_p^0 (C_p^0)^\dagger] \]

\[ + \sum_{p > q} \omega_{pq} \text{tr}[(\mathbf{H} + \mathbf{F}) (C_p^0 (C_q^0)^\dagger + C_q^0 (C_p^0)^\dagger)] \] (52)

In the second term of eq 52, \( p \) and \( q \) may refer to the same fragment.
Thus, the total number of electrons \( N \) of \( AB \) can be decomposed as

\[
N = 2 \sum_{i} \langle \phi_{i} | \phi_{i} \rangle
\]

where

\[
Q_{pq} = 2 \sum_{i} \langle \phi_{p,i} | \phi_{q,i} \rangle T_{pi} T_{qi}
\]

\[
Q_{pp} = 2 \sum_{i} \langle \phi_{p,i} | \phi_{p,i} \rangle T_{pi} T_{qi}
\]

\[
Q_{qp} = 2 \sum_{i} \langle \phi_{q,i} | \phi_{p,i} \rangle T_{pi} T_{qi}
\]

where \( Q_{pp} \) is the net population of \( \phi_{p,0} \), \( Q_{qp} \) is the overlap population between \( \phi_{p,0} \) and \( \phi_{q,0} \), and \( Q_{qp} \) is defined by

\[
Q_{qp} = Q_{pp} + \sum_{q \neq p} Q_{pq}
\]

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 the interfragment and intrafragment interaction energy terms between \( \phi_{p,0} \) and \( \phi_{q,0} \), respectively.

\[
\Phi = \frac{1}{\sqrt{N!}} \det \left| \phi_{0}^{\prime} \phi_{1}^{\prime} \ldots \phi_{N/2}^{\prime} \phi_{N/2} \right|
\]

From eq 1, 18, and 19, we obtain

\[
\phi = \phi^{T} \Phi
\]

Thus, \( \Phi \) can be expanded as follows:

\[
\Phi = a_{0} \Phi_{0} + \sum a_{1}^{i} \Phi_{1}^{i} + \sum a_{2}^{ij} \Phi_{2}^{ij} + \ldots
+ \sum a_{h}^{ijk} \Phi_{h}^{ijk} + \ldots
\]

where \( \Phi_{0} \) is the normalized Slater determinant constructed from the occupied molecular orbitals of \( A \) and \( B \), and \( a_{0} \) is its coefficient. \( \Phi_{i}^{k} \ldots \) results from \( \Phi_{0} \) when the occupied molecular orbitals \( \phi_{i,0}^{k} \), \( \phi_{j,0}^{k} \), \ldots are replaced by the unoccupied molecular orbitals of \( A \) and/or \( B \) \( \phi_{i,0}^{k} \), \( \phi_{j,0}^{k} \), \ldots respectively, with \( a_{i}^{k} \) 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.\(^{15}\) However, since the Slater determinants resulting from the expansion of \( \Phi \) are not orthogonal in general due to the nonorthogonality between \( \phi_{i,0}^{k} \) and \( \phi_{j,0}^{k} \), 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\(^{16} \) and ethane.\(^{14} \) 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 calculations on propylene were performed with the STO-3G basis set\(^{1} \) of GAUSSIAN 70.\(^{7} \) The calculations on ethane were performed using both the STO-3G and the 4-31G\(^{18} \) basis sets.

The orbitals of the \( A \) and \( B \) fragments of the molecule \( AB \) were obtained with eq 46, taking \( F_{A} \) and \( F_{B} \) of \( AB \) as \( M_{A} \) and \( M_{B} \), respectively. The justification for this choice is the observation, already described,\(^{11} \) that the Fock matrix elements of a molecular fragment are nearly transferable. As will be shown, this seems quite reasonable. With these choices, \( \Delta_{i,j} = 0 \) and \( S_{ij} = \delta_{ij} \) 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, \( \phi_{0}^{k} \) and \( \phi_{0}^{k} \), leads to the expression

\[
e_{i} + e_{j} = (e_{i}^{0} + e_{j}^{0}) + S_{ij}[-2\Delta_{ij} + (e_{i}^{0} + e_{j}^{0})S_{ij}]/(1 - S_{ij})^{2}
\]

from the corresponding secular determinant, eq 63.

\[
\begin{align*}
|e_{i}^{0} - e_{j}^{0} - S_{ij}|e_{i}^{0} - e_{j}^{0} & \left| S_{ij}\right|e_{i}^{0} - e_{j}^{0} = 0
\end{align*}
\]

When it is assumed that both \( \phi_{0}^{k} \) and \( \phi_{0}^{k} \) are double occupied, the term

\[
2S_{ij}[-2\Delta_{ij} + (e_{i}^{0} + e_{j}^{0})S_{ij}]/(1 - S_{ij})^{2} = \Delta e_{ij}
\]

may be regarded as the four-electron destabilizing interaction energy between \( \phi_{0}^{k} \) and \( \phi_{0}^{k} \). If it is assumed that only \( \phi_{0}^{k} \) is doubly occupied, the term

\[
2(\Delta_{ij} - S_{ij})^{2}/(e_{i}^{0} - e_{j}^{0}) = \Delta e_{ij}
\]

approximates the two-electron stabilizing interaction energy between \( \phi_{0}^{k} \) and \( \phi_{0}^{k} \). 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 CNDO\(^{14} \) and INDO,\(^{15} \) which invoke the zero differential overlap approximation, \( S_{ij} = 0 \) 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.\(^{14} \) This is not the case in the extended Hückel and ab initio methods. It follows that
any attempt to produce a nonzero four-electron destabilizing interaction energy by these semiempirical SCF-MO methods is inappropriate, because it introduces a logical inconsistency.

(b) Computational Examples. Propylene. The calculations on the staggered (S) and eclipsed (E) conformations of propylene are summarized in Tables I-III. For these conformations, the qualitative analyses have focused upon the interactions between \( \pi \) and \( \pi^* \) methyl group orbitals and the \( \pi \) and \( \pi^* \) orbitals of the double bond. These are illustrated schematically for the E conformation in Figure 1. Our present objectives are as follows: (i) to determine the quantitative nature of the various \( \pi \)-type two-electron and four-electron interactions among the fragment orbitals; (ii) to assess quantitatively the degree to which a consideration of these interactions alone simulates the total energy behavior of the molecule.

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 \( \pi_{\text{CC}}, \pi^*_{\text{CC}}, \pi_{\text{CH}_3}, \) and \( \pi^*_{\text{CH}_3} \), as shown in Table I. The HOMO's are dominated by an out-of-phase combination of \( \pi_{\text{CC}} \) and \( \pi_{\text{CH}_3} \), 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.

![Figure 1. Schematic representation of the \( \pi \)-type fragment orbitals in propylene.](image)

The data of Table II demonstrate that the gross populations of \( \pi_{\text{CC}} \) and \( \pi_{\text{CH}_3} \) are close to 2, and those of \( \pi^*_{\text{CC}} \) and \( \pi^*_{\text{CH}_3} \) are small. The sum of the gross populations of the four group orbitals is 4, so that propylene is properly regarded as a 4\( \pi \)-electron system. The sum of the gross populations of \( \pi_{\text{CC}} \) and \( \pi^*_{\text{CH}_3} \) is 2. If it is supposed that the electron occupancies of \( \pi_{\text{CC}} \) and \( \pi_{\text{CH}_3} \) were 2 prior to the orbital interaction between the methyl and vinyl fragments, then the gross populations of \( \pi^*_{\text{CC}} \) and \( \pi^*_{\text{CH}_3} \) can be said to reflect the amount of electron charge transfer from \( \pi_{\text{CH}_3} \) and \( \pi_{\text{CC}} \), respectively, associated with the orbital interactions. It is within this context that the terms "four-electron destabilizing interaction between \( \pi_{\text{CC}} \) and \( \pi_{\text{CH}_3} \)" and "two-electron stabilizing interactions between \( \pi_{\text{CH}_3} \) and \( \pi^*_{\text{CC}} \) and between \( \pi_{\text{CC}} \) and \( \pi^*_{\text{CH}_3} \)" 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 (\( e_{\text{CC}} - e_{\text{CH}_3} \)), (\( e_{\text{CC}} - e_{\text{CH}_3} \)), and (\( e_{\text{CC}} - e_{\text{CH}_3} \)) are virtually the same in both conformations.17

### Table I. The Computed Total Energy of the Eclipsed (E) and Staggered (S) Conformations of Propylene, and the Orbital Energy and Nodal Property of the HOMO

<table>
<thead>
<tr>
<th>Conformation</th>
<th>( E_{\text{tot}}, \text{au} )</th>
<th>( \epsilon_{\text{HOMO}}, \text{au} )</th>
<th>( \phi_{\text{HOMO}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>-115.665 70</td>
<td>0.3050</td>
<td>0.980( \pi_{\text{CC}} - 0.296\pi_{\text{CH}<em>3} - 0.034\pi^*</em>{\text{CC}} + 0.040\pi^*_{\text{CH}_3} )</td>
</tr>
<tr>
<td>S</td>
<td>-115.654 57</td>
<td>0.3033</td>
<td>0.981( \pi_{\text{CC}} - 0.302\pi_{\text{CH}<em>3} - 0.030\pi^*</em>{\text{CC}} + 0.035\pi^*_{\text{CH}_3} )</td>
</tr>
</tbody>
</table>

### Table II. The Orbital Energies (\( \epsilon_0 \)) and Gross Populations (\( Q_i \)) of the \( \pi \)-Type Fragment Orbitals of Propylene

<table>
<thead>
<tr>
<th>( \phi_i^0 )</th>
<th>Eclipsed</th>
<th>Staggered</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \pi_{\text{CH}_3} )</td>
<td>-0.5268</td>
<td>-0.5219</td>
</tr>
<tr>
<td>( \pi_{\text{CC}} )</td>
<td>-0.3242</td>
<td>-0.3240</td>
</tr>
<tr>
<td>( \pi^*_{\text{CC}} )</td>
<td>0.3115</td>
<td>0.3214</td>
</tr>
<tr>
<td>( \pi^*_{\text{CH}_3} )</td>
<td>0.6992</td>
<td>0.7002</td>
</tr>
</tbody>
</table>

### Table III. The Matrix Elements (\( \Delta_{ij}, S_{ij} \)), Interaction Energies (\( \Delta e_{ij}, \Delta E_{ij} \)), and Overlap Populations (\( Q_{ij} \)) between the \( \pi \)-Type Fragment Orbitals in Propylene

<table>
<thead>
<tr>
<th>( \phi_i^0 - \phi_j^0 )</th>
<th>Conformation</th>
<th>( \Delta_{ij}, \text{au} )</th>
<th>( S_{ij} )</th>
<th>( \Delta e_{ij}, \text{kcal/mol} )</th>
<th>( \Delta E_{ij}, \text{au} )</th>
<th>( Q_{ij} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \pi_{\text{CH}<em>3} - \pi</em>{\text{CC}} )</td>
<td>Eclipsed</td>
<td>-0.0995</td>
<td>0.0998</td>
<td>14.44</td>
<td>0.1902</td>
<td>-0.0192</td>
</tr>
<tr>
<td></td>
<td>Staggered</td>
<td>-0.1026</td>
<td>0.1041</td>
<td>15.41</td>
<td>0.2085</td>
<td>-0.0210</td>
</tr>
<tr>
<td>( \pi_{\text{CH}<em>3} - \pi^*</em>{\text{CC}} )</td>
<td>Eclipsed</td>
<td>-0.0949</td>
<td>0.0988</td>
<td>-2.68</td>
<td>-0.1045</td>
<td>0.0106</td>
</tr>
<tr>
<td></td>
<td>Staggered</td>
<td>-0.0904</td>
<td>0.0933</td>
<td>-2.54</td>
<td>-0.0967</td>
<td>0.0097</td>
</tr>
<tr>
<td>( \pi_{\text{CC}} - \pi^*_{\text{CH}_3} )</td>
<td>Eclipsed</td>
<td>-0.0627</td>
<td>0.0694</td>
<td>-1.98</td>
<td>-0.0601</td>
<td>0.0056</td>
</tr>
<tr>
<td></td>
<td>Staggered</td>
<td>-0.0546</td>
<td>0.0606</td>
<td>-1.50</td>
<td>-0.0462</td>
<td>0.0043</td>
</tr>
</tbody>
</table>
Table IV. The Computed Total Energy of Ethane, and the Orbital Energies ($\epsilon_i^0$) and Gross Populations ($Q_i$) of the $\pi$-Type Fragment Orbitals

<table>
<thead>
<tr>
<th>Conformation</th>
<th>$E_{\text{tot}}, \text{au}$</th>
<th>$\phi_i^0$</th>
<th>$\epsilon_i^0, \text{au}$</th>
<th>$Q_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(S)$^b$</td>
<td>-78.306 14</td>
<td>$\pi_{\text{CH}_3}$</td>
<td>-0.5217</td>
<td>1.995</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pi^*_{\text{CH}_3}$</td>
<td>0.7060</td>
<td>0.005</td>
</tr>
<tr>
<td>E(S)$^b$</td>
<td>-78.301 49</td>
<td>$\pi_{\text{CH}_3}$</td>
<td>-0.5213</td>
<td>1.996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pi^*_{\text{CH}_3}$</td>
<td>0.7073</td>
<td>0.004</td>
</tr>
<tr>
<td>S(E)$^c$</td>
<td>-78.305 78</td>
<td>$\pi_{\text{CH}_3}$</td>
<td>-0.5208</td>
<td>1.995</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pi^*_{\text{CH}_3}$</td>
<td>0.7062</td>
<td>0.005</td>
</tr>
<tr>
<td>E(E)$^c$</td>
<td>-78.301 52</td>
<td>$\pi_{\text{CH}_3}$</td>
<td>-0.5205</td>
<td>1.996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pi^*_{\text{CH}_3}$</td>
<td>0.7075</td>
<td>0.004</td>
</tr>
</tbody>
</table>

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

The orbital interaction energies $\Delta \epsilon_{ij}$ are calculated from eq 64 and 65, using the orbital energies of Table II and the matrix elements $\Delta \epsilon_i$ and $S_{ij}$ shown in Table III. The $\Delta \epsilon_{ij}$ 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 $\pi$-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. 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. 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 $\Delta \epsilon_{ij}$ in Table III, reveal the same trends as found in $\Delta \epsilon_{ij}$. For example, a positive or negative overlap population $Q_{ij}$ between two interacting fragment orbitals corresponds respectively to a stabilization or destabilization in both $\Delta \epsilon_{ij}$ and $\Delta \epsilon_{ij}$. 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.

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

<table>
<thead>
<tr>
<th>($\phi_{i}^0 - \phi_{j}^0$)</th>
<th>Conformation</th>
<th>$\Delta \epsilon_{ij}$, au</th>
<th>$S_{ij}$, kcal/mol</th>
<th>$\Delta \epsilon_{ij}$, kcal/mol</th>
<th>$Q_{ij}$, au</th>
</tr>
</thead>
<tbody>
<tr>
<td>($\pi_{\text{CH}<em>3} - \pi</em>{\text{CH}_3}$)</td>
<td>E(S)</td>
<td>-0.1182</td>
<td>0.1188</td>
<td>17.02</td>
<td>0.2537</td>
</tr>
<tr>
<td></td>
<td>E(E)</td>
<td>-0.1143</td>
<td>0.1150</td>
<td>15.93</td>
<td>0.2202</td>
</tr>
<tr>
<td></td>
<td>S(S)</td>
<td>-0.1136</td>
<td>0.1131</td>
<td>15.70</td>
<td>0.2141</td>
</tr>
<tr>
<td></td>
<td>S(E)</td>
<td>-0.1099</td>
<td>0.1095</td>
<td>14.72</td>
<td>0.2002</td>
</tr>
<tr>
<td></td>
<td>E(S)</td>
<td>-0.0615</td>
<td>0.0646</td>
<td>-0.80</td>
<td>-0.0298</td>
</tr>
<tr>
<td></td>
<td>E(E)</td>
<td>-0.0604</td>
<td>0.0638</td>
<td>-0.76</td>
<td>-0.0284</td>
</tr>
<tr>
<td></td>
<td>S(S)</td>
<td>-0.0703</td>
<td>0.0760</td>
<td>-0.96</td>
<td>-0.0366</td>
</tr>
<tr>
<td></td>
<td>S(E)</td>
<td>-0.0687</td>
<td>0.0746</td>
<td>-0.90</td>
<td>-0.0347</td>
</tr>
</tbody>
</table>

*Journal of the American Chemical Society* / 99:5 / March 2, 1977
Table VI. The Computed Total Energy of Ethane as and the Orbital Energies and Gross Populations of the \( \pi \)-Type Fragment Orbitals (4-31G Basis Set)

<table>
<thead>
<tr>
<th>Conformation</th>
<th>( E_{\text{tot}} ), au</th>
<th>( \phi_{i}^{0} )</th>
<th>( e_{i}^{0} ), au</th>
<th>( S_{ij} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(S)(^{a})</td>
<td>-79.115 93</td>
<td>( \pi^{*}_{\text{CH}_3} )</td>
<td>-0.5497</td>
<td>2.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \pi^{*}_{\text{CH}_2} )</td>
<td>0.3018</td>
<td>0.011</td>
</tr>
<tr>
<td>E(S)(^{a})</td>
<td>-79.111 30</td>
<td>( \pi^{*}_{\text{CH}_3} )</td>
<td>-0.5492</td>
<td>2.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \pi^{*}_{\text{CH}_2} )</td>
<td>0.3080</td>
<td>0.007</td>
</tr>
<tr>
<td>S(E)(^{a})</td>
<td>-79.115 72</td>
<td>( \pi^{*}_{\text{CH}_3} )</td>
<td>-0.5482</td>
<td>2.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \pi^{*}_{\text{CH}_2} )</td>
<td>0.3027</td>
<td>0.011</td>
</tr>
<tr>
<td>E(E)(^{a})</td>
<td>-79.111 52</td>
<td>( \pi^{*}_{\text{CH}_3} )</td>
<td>-0.5477</td>
<td>2.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \pi^{*}_{\text{CH}_2} )</td>
<td>0.3084</td>
<td>0.007</td>
</tr>
</tbody>
</table>

\(^{a}\) \( r_{\text{CC}} = 1.5300 \text{ Å}; r_{\text{CH}} = 1.0834 \text{ Å}; \angle \text{CCH} = 111.07^\circ. \)
\(^{b}\) \( r_{\text{CC}} = 1.5412 \text{ Å}; r_{\text{CH}} = 1.0828 \text{ Å}; \angle \text{CCH} = 111.64^\circ. \)

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

<table>
<thead>
<tr>
<th>((\phi_{i}^{0} - \phi_{j}^{0}))</th>
<th>Conformation</th>
<th>( \Delta_{ij} ), au</th>
<th>( \tilde{S}_{ij} )</th>
<th>( \Delta E_{ij} ), kcal/mol</th>
<th>( \Delta E_{ij} ), au</th>
<th>( Q_{ij} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \pi^{<em>}_{\text{CH}_3} - \pi^{</em>}_{\text{CH}_3} )</td>
<td>E(S)</td>
<td>-0.1470</td>
<td>0.1649</td>
<td>24.01</td>
<td>0.4329</td>
<td>-0.0542</td>
</tr>
<tr>
<td></td>
<td>E(E)</td>
<td>-0.1425</td>
<td>0.1602</td>
<td>22.60</td>
<td>0.4072</td>
<td>-0.0511</td>
</tr>
<tr>
<td></td>
<td>S(S)</td>
<td>-0.1410</td>
<td>0.1575</td>
<td>22.07</td>
<td>0.3866</td>
<td>-0.0482</td>
</tr>
<tr>
<td></td>
<td>S(E)</td>
<td>-0.1390</td>
<td>0.1555</td>
<td>21.50</td>
<td>0.3764</td>
<td>-0.0470</td>
</tr>
<tr>
<td>( \pi^{<em>}_{\text{CH}_3} - \pi^{</em>}_{\text{CH}_2} )</td>
<td>E(S)</td>
<td>-0.0946</td>
<td>0.1307</td>
<td>-0.21</td>
<td>-0.0536</td>
<td>0.0065</td>
</tr>
<tr>
<td></td>
<td>E(E)</td>
<td>-0.0949</td>
<td>0.1321</td>
<td>-0.20</td>
<td>-0.0520</td>
<td>0.0063</td>
</tr>
<tr>
<td></td>
<td>S(S)</td>
<td>-0.1163</td>
<td>0.1824</td>
<td>-0.38</td>
<td>-0.0762</td>
<td>0.0096</td>
</tr>
<tr>
<td></td>
<td>S(E)</td>
<td>-0.1167</td>
<td>0.1841</td>
<td>-0.36</td>
<td>-0.0749</td>
<td>0.0095</td>
</tr>
</tbody>
</table>

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 \( \Delta e_{ij} \) 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 \( \Delta e_{ij} \) or \( \Delta E_{ij} \) 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 \( \pi^{*}_{\text{CH}_3} - \pi^{*}_{\text{CH}_2} \) 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.

The 4-31G basis set calculations shown in Table VII do not display the same effects. When the \( \Delta e_{ij} \) values are considered, it is seen that the rotational barrier is dominated by the \( \pi^{*}_{\text{CH}_3} - \pi^{*}_{\text{CH}_2} \) 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 \( \pi^{*}_{\text{CH}_2} - \pi^{*}_{\text{CH}_2} \) interactions are almost the same. On the other hand, the \( \Delta E_{ij} \) values suggest that the \( \pi^{*}_{\text{CH}_3} - \pi^{*}_{\text{CH}_3} \) and

\[(\pi^{*}_{\text{CH}_3} - \pi^{*}_{\text{CH}_2})\] interactions contribute to the same extent to the energy difference between S(S) and E(S), but the \( \pi^{*}_{\text{CH}_3} - \pi^{*}_{\text{CH}_2} \) interaction is more important in the transformations E(S) \( \rightarrow \) 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 chemical 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 \( F_{ij} \) of the molecule which contains fragment \( A \) has been set equal to \( M_{ij} \). 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 \( \pi \)-type inter-
Acknowledgments. We thank Dr. P. W. Payne and Professor L. C. Allen for a detailed exchange of views concerning quantitative perturbational molecular orbital analysis and for providing the details of their independently derived approach to the problem. We also acknowledge discussions with Professor F. Bernardi during the initial stages of our own work. Professor I. G. Csizmadia generously read the theoretical development and made numerous helpful suggestions concerning the clarification of the formalism. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada for financial support. One of us (H.B.S.) thanks NRCC for the award of a 1967 Science Scholarship.

References and Notes

(3) E. Clementi and L. A. Curtiss, Rev. Mod. Phys., 35, 147 (1963); (b) T. Morino, Compt. Rend., 255, 3446 (1962); (c) E. Clementi, IBM Research Notes, 44, 2202 (1967).

Journal of the American Chemical Society / 99:5 / March 2, 1977