# A New Energy Decomposition Scheme for Molecular Interactions within the Hartree-Fock Approximation

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## Abstracts

A new method is proposed for the analysis of components of molecular interaction energy within the Hartree-Fock approximation. The Hartree-Fock molecular orbitals of the isolated molecules are used as the basis for the construction of Fock matrix of the supermolecule. Then certain blocks of this matrix are set to zero subject to specify boundary conditions of the supermolecule molecular orbitals, and the resultant matrix is diagonalized iteratively to obtain the desired energy components. This method can be considered as an extension of our previous method, but has an advantage in the explicit definition of the charge transfer energy, placing it on an equal footing with the exchange and polarization terms. The new method is compared with existing perturbation methods, and is also applied to the energy and electron density decomposition of $(H_2O)_2$.

On propose une nouvelle méthode pour analyser les composantes de l'énergie d'interaction moléculaire dans le cadre de l'approximation Hartree-Fock. Les orbitales moléculaires des molécules isolées sont utilisées comme base pour construire la matrice de Fock de la supermolécule. Certains blocs de cette matrice sont mis egaux à zéro selon des conditions aux limites spécifiques et la matrice résultante est diagonalisée d'une façon itérative pour obtenir les composantes cherchées. Cette méthode-ci peut être considérée comme une extension de notre méthode antérieure mais elle a un avantage dans la définition explicite de l'énergie de transfert de charge, qui est mise ici au même rang que les termes d'échange et de polarisation. La nouvelle méthode est comparée aux méthodes de perturbation traditionelles. Elle a été appliquée à la décomposition de l'énergie et de la densité électronique de $(H_2O)_2$.

Es wird eine neue Methode für die Analyse der Komponenten der molekularen Wechselwirkungsenergie in der Hartree-Fock-Näherung vorgeschlagen. Die Hartree-Fock-Orbitale der freien Moleküle werden verwendet als Basis für die Konstruktion der Fock'schen Matrix des Supermoleküls. Gewisse Blöcke dieser Matrix werden nach spezifischen Grenzbedingungen gleich Null gesetzt, und die resultierende Matrix wird in einer iterativen Weise diagonalisiert um die gewünschten Energiekomponenten zu geben. Diese Methode kann als eine Ergäzung unserer früheren Methode betrachtet werden. Sie hat aber einen Vorteil in der expliziten Definition der Ladungsüberführungsenergie, die hier an denselben Niveau wie die Austausch- und Polarisationsglieder hingestellt wird. Die neue Methode wird mit existierenden Störungsmethoden verglichen. Sie wird auf die Zerlegung der Energie und der Elektronendichte von $(H_2O)_2$ angewandt.

## 1. Introduction

The most traditional way of calculating molecular interaction energies is through a perturbation expansion of each of the electrostatic, polarization, exchange, charge transfer, and dispersion energy terms [1, 2]. Their sum yields the total interaction energy. Alternatively, in recent *ab initio* calculations the interaction energy is defined as the difference between the Hartree-Fock energy of the entire system, complex, or supermolecule, and that of the isolated molecules [3, 4]. Furthermore, methods have been proposed which decompose the interaction energy into the above mentioned components within the Hartree-Fock approximation [5, 6]. (Within the Hartree-Fock approximation no dispersion energy can be obtained [7, 8]).

The energy decomposition scheme recently proposed by Morokuma [5] is the most extensive one within the Hartree-Fock approximation. The method has been successfully applied to ground and excited states of hydrogen-bonded complexes [3b, 5, 9], electron donor-acceptor complexes [10], and in an electron density decomposition [11]. In this scheme one defines the following four forms of the wave-function for the complex and calculates the energies of the respective components—electrostatic $E_{es}$, polarization $E_{pl}$, exchange repulsion $E_{ex}$, and charge transfer $E_{ct}$. The interaction energies are defined to be negative for destabilizing and positive for stabilizing.

(i) A Hartree product of isolated molecular wave-functions:

$$\psi_1 = A^0 \cdot B^0$$
$$E_1 = E_0 - E_{es} \tag{1}$$

(ii) A Hartree wave-function for the complex in which intermolecular electron exchange is not allowed:

$$\psi_2 = A \cdot B$$
$$E_2 = E_0 - (E_{es} + E_{pl}) \tag{2}$$

(iii) A Hartree-Fock product of isolated molecular wave-functions:

$$\psi_3 = \mathfrak{a}(A^0 \cdot B^0)$$
$$E_3 = E_0 - (E_{es} + E_{ex}) \tag{3}$$

(iv) A Hartree-Fock wave-function for the complex:

$$\psi_4 = \mathfrak{a}(A \cdot B)$$
$$E_4 = E_0 - \Delta E = E_0 - (E_{es} + E_{pl} + E_{ex} + E_{ct}) \tag{4}$$

where $A^0$ and $B^0$ are the Hartree-Fock wave-functions of the isolated molecules, the sum of their energies being $E_0$, and $\Delta E$ is the total stabilization energy. From

$E_i$, $i = 0$, 1, 2, 3, 4, one calculates the four energy components. A major drawback of this scheme lies in the definition of the charge transfer component $E_{ct}$. It can only be calculated as the difference between the total interaction energy $\Delta E$ and the sum of the remaining three terms. Hence, it includes all of the coupling terms between the components.

In the present paper we propose a new method of energy decomposition within the Hartree-Fock approximation. The Hartree-Fock molecular orbitals of the isolated molecules are used as the basis set for the construction of the Fock matrix of the complex. Then certain blocks of this matrix are set to zero, subject to specific boundary conditions of the supermolecule molecular orbitals. The resultant matrix is diagonalized iteratively to obtain the desired energy components. The primary advantage of this method over the existing ones is the explicit definition of the charge transfer interaction energy, placing it on an equal footing with the exchange and polarization terms.

## 2. A New Energy Decomposition Scheme

To simplify the discussion we assume that both A and B are closed-shell molecules in the ground state. The total Hamiltonian of the complex A $\cdot$ $\cdot$ $\cdot$ B is given as

$$H = H_A + H_B + H_{AB} \tag{5}$$

where $H_A$ and $H_B$ are the Hamiltonians for the isolated molecules and $H_{AB}$ is the interaction term. The total energy of the unperturbed state is the sum of the Hartree-Fock (HF) ground-state energies of $A$ and $B$

$$E^0 = \langle A^0|H_A|A^0\rangle + \langle B^0|H_B|B^0\rangle \tag{6}$$

where $A^0$ and $B^0$ are the HF wave-functions for the ground states of A and B, respectively. *The HF molecular orbitals (MO's of the isolated molecule A, $\phi_k$, and B, $\phi_\mu$, are used as a basis set for the MO's of the complex.*

$$\psi_i = \sum_k C_{ik}\phi_k^A + \sum_\mu C_{i\mu}\phi_\mu^B \tag{7}$$

The subscripts $k$, $l$, and $m$ are employed for the HFMO's of the isolated molecule $A$, while $\mu$, $\nu$, and $\gamma$ are used for $B$, and $i$ and $j$ for the complex. Superscripts $A$ and $B$ are redundant and used to emphasize the molecular origin of the particular orbitals. With this basis the HF equation for the complex is written as

$$(\mathbf{F} - \epsilon\mathbf{S})\mathbf{C} = 0 \tag{8}$$

where $\mathbf{F}$ is the Fock matrix, $\mathbf{S}$ is the overlap matrix, and $\mathbf{C}$ is the coefficient matrix whose $i$th column $\mathbf{C}_i$ is the eigenvector corresponding to the eigenvalue $\epsilon_i$. The

interaction energy $\Delta E$ (positive for stabilization) is given as

$$- \Delta E = \sum_i^{occ} \mathbf{C}_i^\dagger (\mathbf{F} + \mathbf{H}) \mathbf{C}_i - E^0 \qquad (9)$$

where $\mathbf{H}$ is the kinetic energy and nuclear attraction part of $\mathbf{F}$.

In order to clearly define the molecular interaction, we expand the quantity $(\mathbf{F} - \epsilon\mathbf{S})$ as follows:

$$(\mathbf{F} - \epsilon\mathbf{S}) = (\mathbf{F}^0 - \epsilon\mathbf{1}) + \mathbf{\Sigma} \qquad (10)$$

Here, $\mathbf{F}^0$ is the HF matrix at infinite separation, $\mathbf{1}$ is the unit matrix, and $\mathbf{\Sigma}$ is the molecular interaction matrix. The matrix elements are defined as

$$F_{k\,l}^0 = \epsilon_k^0 \delta_{kl}, \qquad F_{\mu\,\nu}^0 = \epsilon_\mu^0 \delta_{\mu\nu}, \qquad F_{k\,\nu}^0 = 0$$

$$\Sigma_{kl} = \langle k| V^B |l\rangle + \left\langle k \left| \sum_i^{occ} (2J_i - K_i) \right| l \right\rangle - \left\langle k \left| \sum_m^{occ} (2J_m^0 - K_m^0) \right| l \right\rangle \delta_{k1}$$

$$\Sigma_{\mu\nu} = \langle \mu| V^A |\nu\rangle + \left\langle \mu \left| \sum_i^{occ} (2J_i - K_i) \right| \nu \right\rangle - \left\langle \mu \left| \sum_\gamma^{occ} (2J_\gamma^0 - K_\gamma^0) \right| \nu \right\rangle \delta_{\mu\nu} \qquad (11)$$

$$\Sigma_{k\nu} = -\epsilon S_{k\nu} + \langle k| T + V^A + V^B |\nu\rangle + \left\langle k \left| \sum_i^{occ} (2J_i - K_i) \right| \nu \right\rangle$$

where $\epsilon_k^0$ and $\epsilon_\mu^0$ are the HFMO energies of $A$ and $B$, respectively; $V^A$ and $V^B$ are the nuclear attraction potentials of $A$ and $B$; $T$ is the kinetic energy operator; and $J_m^0$ and $K_m^0$ are the Coulomb and exchange operators, respectively, for orbital $\phi_m^A$ of the isolated molecule $A$ and $J_\gamma^0$ and $K_\gamma^0$ are for orbital $\phi_\gamma^B$. It should be noted that included in the interaction term is the off-diagonal part of the MO overlap matrix $\mathbf{S}$.

We now define the components of the interaction on the following principles which are based on traditional viewpoints and physical meanings (Fig. 1):

(i) Electrostatic: the classical electrostatic interaction between occupied MO's which does not cause any mixing of MO's.

(ii) Polarization: the interaction which causes the mixing between the occupied and vacant MO's within each molecule.

(iii) Exchange: the interaction between occupied MO's which causes electron exchange and delocalization between molecules.

(iv) Charge Transfer: the interaction which causes intermolecular delocalization by mixing the occupied MO's of one molecule with the vacant MO's of the other and vice versa.
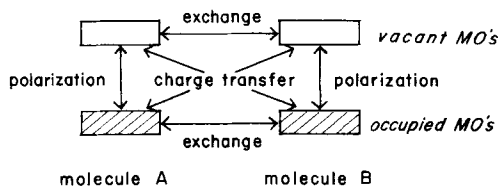
Figure 1. Interaction and mixing of mo's via various components of molecular interaction.

Based on these principles, the interaction matrix can be divided into the following blocks:

| | A,occ | A,vac | B,occ | B,vac |
|---|---|---|---|---|
| **A,occ** | $\Sigma_{oo}^{AA}$<br>ESX | $\Sigma_{ov}^{AA}$<br>PLX | $\Sigma_{oo}^{AB}$<br>E X' | $\Sigma_{ov}^{AB}$<br>C T |
| **A,vac** | $\Sigma_{vo}^{AA}$<br>PLX | $\Sigma_{vv}^{AA}$<br>ESX | $\Sigma_{vo}^{AB}$<br>C T | $\Sigma_{vv}^{AB}$<br>E X' |
| **B,occ** | $\Sigma_{oo}^{BA}$<br>E X' | $\Sigma_{ov}^{BA}$<br>C T | $\Sigma_{oo}^{BB}$<br>ESX | $\Sigma_{ov}^{BB}$<br>PLX |
| **B,vac** | $\Sigma_{vo}^{BA}$<br>C T | $\Sigma_{vv}^{BA}$<br>E X' | $\Sigma_{vo}^{BB}$<br>PLX | $\Sigma_{vv}^{BB}$<br>ESX |

Here $\Sigma_{ov}^{A,B}$, for instance, is the block of the interaction matrix between the occupied mo's of A and the vacant mo's of B. It can easily be seen from eq. (11) that the blocks designated as ESX include only the electrostatic interaction (intermolecular Coulomb integrals and one-electron integrals) and a part of the exchange interaction (intermolecular exchange integrals) that causes electron exchange, but not delocalization. The blocks between vacant mo's do not contribute directly to the total energy but should be included for consistency. The blocks designated as PLX include only the polarization interaction and a part of the exchange interaction (discussed as the exchange-polarization term in subsequent paragraphs). The EX' blocks comprise only the exchange interaction and the CT blocks contain only the charge transfer interaction.

Now that we have defined the component interaction matrices, one can consider the following model HF equations which contain only selected component interaction matrices with the rest of the matrix set to zero:

$$0 = (\mathbf{F}^x - \epsilon \mathbf{S}^x)\mathbf{C}^x \equiv (\mathbf{F}^0 - \epsilon \mathbf{1} + \mathbf{\Sigma}^x)\mathbf{C}^x \tag{12}$$

Using the one-electron operator $\mathbf{H}^x$ which is included in $\mathbf{F}^x$, the total energy of the

model system is given by the following expression:

$$E^x = \sum_i^{occ} \mathbf{C}_i^{x\dagger}(\mathbf{F}^x + \mathbf{H}^x)\mathbf{C}_i^x \qquad (13)$$

The stabilization energy $E_x$ due to the interaction $x$ is then given by

$$-E_x = E^x - E^0 \qquad (14)$$

Specifically, if $x = $ ESX, the solution of the model HF equation (12) mixes only the occupied MO's within each molecule. Therefore, one obtains the energy using the MO's of the isolated molecule (i.e., $\mathbf{C}^{ESX} = 1$), avoiding the explicit solution of eq. (12). If one neglects the intermolecular exchange operator in $\mathbf{\Sigma}^{ESX}$, one obtains the purely electrostatic energy $E_{ES}$ (i.e., $x = $ ES).

The remaining components are evaluated by choosing the appropriate contribution in $\Sigma$ along with ESX. For example, the charge transfer stabilization energy $E_{CT}$ is obtained by letting $x = $ ESX + CT. Thus both the ESX and the CT blocks are included in the model HF equation. (Since the ESX terms comprise the diagonal blocks in $\mathbf{\Sigma}$, inclusion of only the CT blocks without the ESX blocks is meaningless.) At this point the model $\Sigma$ matrix will have the following form:

| $\Sigma_{oo}^{AA}$ | O | O | $\Sigma_{ov}^{AB}$ |
|---|---|---|---|
| O | $\Sigma_{vv}^{AA}$ | $\Sigma_{vo}^{AB}$ | O |
| O | $\Sigma_{ov}^{BA}$ | $\Sigma_{oo}^{BB}$ | O |
| $\Sigma_{vo}^{BA}$ | O | O | $\Sigma_{vv}^{BB}$ |

The model HF equation is solved iteratively until self-consistency is achieved. The resulting MO's will satisfy the following restrictions:

$$\phi_i^{ESX+CT} = \sum_k^{occ} C_{ik}\phi_k^A + \sum_\nu^{vac} C_{i\nu}\phi_\nu^B$$

or

$$\phi_j^{ESX+CT} = \sum_\mu^{occ} C_{j\mu}\phi_\mu^B + \sum_l^{vac} C_{jl}\phi_l^A \qquad (15)$$

The entire MO space is divided into two subspaces—one defined by the set $\{\phi_i^{ESX+CT}\}$ and the other defined by the set $\{\phi_j^{ESX+CT}\}$ of eq. (15). The CT

stabilization energy $E_{CT}$ is then calculated by

$$- E_{CT} = E^{ESX+CT} - E^{ESX} \tag{16}$$

Essentially the same procedure applies for $x = ESX + PLX$ (or $ES + PL$ if the exchange operator is neglected) and $x = ESX + EX'$ to result in $- E_{PLX}$ and $- E_{EX'}$. An exception is the case where $x = ESX + EX'$. Solving the model HF equation once (equivalent to orthogonalizing the MO's) is sufficient to calculate the corresponding energy. The resulting MO's in each of the above cases again span two subspaces:

$$\phi_i^{ESX+PLX} = \sum_k^{occ} C_{ik}\phi_k^A + \sum_l^{vac} C_{il}\phi_l^A$$

or

$$\phi_j^{ESX+PLX} = \sum_\mu^{occ} C_{j\mu}\phi_\mu^B + \sum_\nu^{vac} C_{j\nu}\phi_\nu^B \tag{17}$$

$$\phi_i^{ESX+EX'} = \sum_k^{occ} C_{ik}\phi_k^A + \sum_\mu^{occ} C_{i\mu}\phi_\mu^B$$

or

$$\phi_j^{ESX+EX'} = \sum_l^{vac} C_{jl}\phi_l^A + \sum_\nu^{vac} C_{j\nu}\phi_\nu^B \tag{18}$$

Inclusion of all the contributions in $\Sigma$ is equivalent to the solution of eq. (8) for the total interaction energy $\Delta E$ of eq. (9). It has to be noted that in the present scheme one cannot include three components simultaneously. If only the EX' terms are omitted (i.e., $x = ESX + CT + PLX$), each MO spans the entire space, which is inconsistent with the removal of the EX' blocks in the interaction matrix. Upon completion of this process the separate energies $E_{ESX}$, $E_{ES}$, $E_{CT}$, $E_{PLX}$, $E_{PL}$, $E_{EX'}$, and $\Delta E$ become available, We define the following interaction energies:

$E_{ES}$    the electrostatic energy
$E_{PL}$    the polarization energy
$E_{EX}$    the exchange energy $= E_{EX'} + (E_{ESX} - E_{ES})$
$E_{CT}$    the charge transfer energy
$E_{EXPL}$ the exchange polarization energy $= E_{PLX} - E_{PL}$
$E_{MIX'}$ the coupling term $= \Delta E - (E_{ES} + E_{PL} + E_{EX} + E_{CT} + E_{EXPL})$    (19)

$E_{EX}$ is the sum of the exchange energy from the $EX'$ blocks and the exchange energy imbedded in the ESX blocks that is due to the exchange operator $K$ (see eq. (11)). $E_{EXPL}$ is the contribution of the exchange operator in the PLX blocks

which is neither pure polarization (without exchange) nor pure exchange (without intramolecular excitation) and should be called the exchange-polarization term as discussed later. $E_{MIX'}$ is the remaining contribution which contains coupling interactions between components.

We now compare the definitions of eq. (19) with our previous definitions given by eqs. (1)–(4). Since the Hartree product function of eq. (1) does not give rise to any intermolecular exchange operator, $E_{es}$ of eq. (1) is equal to the electrostatic energy $E_{ES}$ of eq. (19). The polarization energy $E_{pl}$ of eq. (2) does not include any exchange contribution, and therefore it should be identical to $E_{PL}$ of eq. (19). Since the exchange energy $E_{ex}$ of eq. (3) arises only from the MO overlap and exchange, it is equal to $E_{EX}$ of eq. (19). The 'charge transfer' term $E_{ct}$ of eq. (4) which includes all the remaining contributions is, in the present scheme, divided further into the true charge transfer term $E_{CT}$, the exchange polarization term $E_{EXPL}$, and the coupling term $E_{MIX}$. Since all the definitions of the present method are consistent with our previous definitions, one can consider the present method as an extension of our previous method. It should be emphasized that in the present scheme the charge transfer energy $E_{CT}$ is defined and calculated on the same footing as the polarization and exchange energies, which was not the case in our previous definition.

### 3. Comparison with Perturbation Methods

In order to compare the present method with perturbation expansion methods previously used [1, 2], we will show explicitly what kind of MO integrals are included in our various energy components. We solve the model Hartree-Fock equation for the first cycle (starting with HFMO's of isolated molecules) in the following way. If one defines one-electron Green's functions [12] $g$ and $g^0$ for the complex and the isolated systems, respectively, as

$$g = (F^x - \epsilon S^x)^{-1}$$
$$g^0 = (F^0 - \epsilon 1)^{-1} \tag{20}$$

then, from the definition of the model HF operator (12), one obtains

$$g = g^0 - g^0 \Sigma^x g \tag{21}$$

Using the fact that $g^0$ is diagonal in the isolated MO representation ($g_{kl}^0 = \delta_{kl}(\epsilon_k^0 - \epsilon)^{-1}$ where $\epsilon_k^0$ is the MO energy of the isolated systems), eq. (21) can be rewritten as

$$g_{kk} = g_{kk}^0 - g_{kk}^0 \Sigma_{kl}^x g_{lk}$$
$$g_{lk} = -g_{ll}^0 \Sigma_{lk}^x g_{kk} \qquad (l \neq k) \tag{22}$$

where the running index ($l$ in the first equation) is to be summed over all the basis

functions.* By solving eq. (22) explicitly for $(g_{kk})^{-1}$, one finds

$$(g_{kk})^{-1} = (g_{kk}^0)^{-1} - \Sigma_{kl}^x g_{ll}^0 \Sigma_{lk}^x \tag{23}$$

From the condition $(g_{kk})^{-1} = 0$, the orbital energy $\epsilon_k$ after the first cycle is obtained [12].

$$\epsilon_k = \epsilon_k^0 - \Sigma_{kl}^x g_{ll}^0 \Sigma_{lk}^x \tag{24}$$

Now using relationships (22)–(24) we analyze the energy components for appropriate choices of $x$.

### A. $x = $ ESX (or ES)

In this case one does not have to consider the coupling between MO's. Hence, the MO energies are written as follows:

$$g_{kk} = g_{kk}^0 - g_{kk}^0 \Sigma_{kk}^{ES(X)} g_{kk}$$

$$(g_{kk})^{-1} = (g_{kk}^0)^{-1} + \Sigma_{kk}^{ES(X)}$$

$$\epsilon_k^{ESX} = \epsilon_k^0 + \left\langle k \middle| V^B + \sum_\gamma^{occ} \left( 2J_\gamma^0 - K_\gamma^0 \right) \middle| k \right\rangle$$

$$\epsilon_\mu^{ESX} = \epsilon_\mu^0 + \left\langle \mu \middle| V^A + \sum_m^{occ} \left( 2J_m^0 - K_m^0 \right) \middle| \mu \right\rangle \tag{25}$$

If $K^0$ terms are neglected, one obtains the case of $x = $ ES. Summation of these MO energies over occupied MO's, while doubling the one-electron term to take $\mathbf{H}^x$ into account, gives the total energy $E^{ESX}$. The difference $E^0 - E^{ESX}$ is the ESX stabilization energy $E_{ESX}$.

$$\begin{aligned}
E_{ESX} = &-2 \sum_k^{occ} \left\{ \left\langle k \middle| V^B + \frac{1}{2} \sum_\gamma^{occ} \left( 2J_\gamma^0 - K_\gamma^0 \right) \middle| k \right\rangle \right\} \\
&-2 \sum_\mu^{occ} \left\{ \left\langle \mu \middle| V^A + \frac{1}{2} \sum_m^{occ} \left( 2J_m^0 - K_m^0 \right) \middle| \mu \right\rangle \right\} \\
= &- \left\{ 2 \sum_j^{occ} \langle k| V^B |k \rangle + 2 \sum_\mu^{occ} \langle \mu| V^A |\mu \rangle + 4 \sum_k^{occ} \sum_\mu^{occ} \langle kk| \mu\mu \rangle \right\} \\
&+ 2 \sum_k^{occ} \sum_\mu^{occ} \langle k\mu|k\mu \rangle \tag{26}
\end{aligned}$$

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*In general, terms including off-diagonal $g_{mk}$ appear on the left side of $g_{lk}$. But when only one energy component is considered in $\Sigma^x$, such terms disappear to give eq. (22).

The first term of eq. (26) is the electrostatic energy $E_{ES}$, and the second term, called $E_X$ and absent when $x = ES$, is a portion of the exchange energy EX as will be discussed later.

In the following calculations of MO energies for other choices of $x$, we use $\epsilon^{ESX}$ as the unperturbed orbital energy.

B. $x = ESX + PLX$ (or ES + PL)

From eq. (24) it can be shown that

$$\epsilon_k^{ESX+PLX} = \epsilon_k^{ESX} - \sum_l^{vac} \frac{|\langle k|V^B + \sum_\gamma^{occ}(2J_\gamma^0 - K_\gamma^0)|l\rangle|^2}{\epsilon_l^{ESX} - \epsilon_k^{ESX+PLX}} \tag{27}$$

$$\epsilon_\mu^{ESX+PLX} = \epsilon_\mu^{ESX} - \sum_\nu^{vac} \frac{|\langle \mu|V^A + \sum_m^{occ}(2J_m^0 - K_m^0)|\nu\rangle|^2}{\epsilon_\nu^{ESX} - \epsilon_\mu^{ESX+PLX}} \tag{28}$$

In the first cycle $\epsilon_k^{ESX+PLX}$ and $\epsilon_\mu^{ESX+PLX}$ on the right-hand side can be replaced by $\epsilon_k^{ESX}$ and $\epsilon_\mu^{ESX}$, respectively. The sum of MO energies over occupied MO's (with the one-electron terms multiplied by a factor of two) gives the total energy $E^{ESX+PLX}$. The difference $E^{ESX} - E^{ESX+PLX}$ gives the PLX stabilization energy $E_P^{(1)}{}_{LX}$ after the first cycle of SCF.

$$E_{PLX}^{(1)} \sim 2\sum_k^{occ}\sum_l^{vac} \frac{|\langle k|V^B + \sum_\gamma^{occ}(2J_\gamma^0 - K_\gamma^0)|l\rangle|^2}{\epsilon_l^{ESX} - \epsilon_k^{ESX}}$$

$$+ 2\sum_\mu^{occ}\sum_\nu^{vac} \frac{|\langle \mu|V^A + \sum_m^{occ}(2J_m^0 - K_m^0)|\nu\rangle|^2}{\epsilon_\nu^{ESX} - \epsilon_\mu^{ESX}} \tag{29}$$

$$= 2\left\{ \sum_k^{occ}\sum_l^{vac} \frac{|\langle k|V^B + \sum_\gamma^{occ}2J_\gamma^0|l\rangle|^2}{\epsilon_l^{ESX} - \epsilon_k^{ESX}} + \sum_\mu^{occ}\sum_\nu^{vac} \frac{|\langle \mu|V^A + \sum_m^{occ}2J_m^0|\nu\rangle|^2}{\epsilon_\nu^{ESX} - \epsilon_\mu^{ESX}} \right.$$

$$+ 2\left\{ \sum_k^{occ}\sum_l^{vac} \frac{-2\sum_\gamma^{occ}\langle k|K_\gamma^0|l\rangle\langle k|V^B + \sum_{\gamma'}^{occ}2J_{\gamma'}^0|l\rangle + \left|\sum_\gamma^{occ}\langle k|K_\gamma^0|l\rangle\right|^2}{\epsilon_l^{ESX} - \epsilon_k^{ESX}} \right.$$

$$+ \sum_\mu^{occ}\sum_\nu^{vac} \frac{-2\sum_m^{occ}\langle \mu|K_m^0|\nu\rangle\langle \mu|V^A + \sum_{m'}^{occ}2J_{m'}^0|\nu\rangle + \left|\sum_m^{occ}\langle \mu|K_m^0|\nu\rangle\right|^2}{\epsilon_\nu^{ESX} - \epsilon_\mu^{ESX}} \left. \right\} \tag{30}$$

The first term of eq. (30) is the polarization energy $E_{PL}$ and the second term is the exchange-polarization energy $E_{EXPL}$ arising from the polarization through exchange of electrons.

## C. $x = \text{ESX} + \text{EX}'$

With the same assumptions and same procedure as in B, one obtains the following:

$$\epsilon_k^{ESX + EX'} \sim \epsilon_k^{ESX}$$

$$- \sum_{\nu}^{occ} \frac{|- \epsilon_k^{ESX} S_{k\nu} + \langle k| T + V^A + V^B + \sum_m^{occ} (2J_m^0 - K_m^0) + \sum_{\gamma}^{occ} (2J_{\gamma}^0 - K_{\gamma}^0)|\nu\rangle|^2}{\epsilon_{\nu}^{ESX} - \epsilon_k^{ESX}}$$

$$\epsilon_{\mu}^{ESX + EX'} \sim \epsilon_{\mu}^{ESX}$$

$$- \sum_{l}^{occ} \frac{|- \epsilon_{\mu}^{ESX} S_{\mu l} + \langle \mu| T + V^A + V^B + \sum_m^{occ} (2J_m^0 - k_m^0) + \sum_{\gamma}^{occ} (2J_{\gamma}^0 - k_{\gamma}^0)|l\rangle|^2}{\epsilon_l^{ESX} - \epsilon_{\mu}^{ESX}}$$

$$E_{EX'}^{(1)} \sim -2 \sum_k^{occ} \sum_{\mu}^{occ} \frac{\left(- \epsilon_k^{ESX} S_{k\mu} + \epsilon_{\mu}^{ESX} S_{\mu k}\right)}{\epsilon_{\mu}^{ESX} - \epsilon_k^{ESX}}$$

$$\times \left\{ - \epsilon_k^{ESX} S_{k\mu} - \epsilon_{\mu}^{ESX} S_{\mu k} + \epsilon_k^0 S_{k\mu} + \langle k| V^B + \sum_{\gamma}^{occ} (2J_{\gamma}^0 - K_{\gamma}^0)| \mu\rangle \right.$$

$$\left. + \epsilon_{\mu}^0 S_{\mu k} + \langle \mu| V^A + \sum_m^{occ} (2J_m^0 - K_m^0)|k\rangle \right\}$$

$$= 2 \sum_k^{occ} \sum_{\mu}^{occ} \left[ S_{k\mu} \cdot \left\{ \langle k| V^B + \sum_{\gamma}^{occ} (2J_{\gamma}^0 - K_{\gamma}^0)| \mu\rangle \right. \right.$$

$$\left. + \langle \mu| V^A + \sum_m^{occ} (2J_m^0 - K_m^0)|k\rangle \right\}$$

$$\left. - S_{k\mu}^2 \left\{ \langle k| V^B + \sum_{\gamma}^{occ} (2J_{\gamma}^0 - K_{\gamma}^0)|k\rangle + \langle \mu| V^A + \sum_m^{occ} (2J_m^0 - K_m^0)| \mu\rangle \right\} \right]$$

$$(31)$$

The exchange energy $E_{EX}$ is the sum of $E_{EX'}$ (eq. (31)) and $E_X$, the second term of eq. (26).

## D. $x = \text{ESX} + \text{CT}$

$$\epsilon_k^{\text{ESX}+\text{CT}} \sim \epsilon_k^{\text{ESX}}$$

$$- \sum_{\nu}^{\text{vac}} \frac{|\langle k| V^B + \sum_{\gamma}^{\text{occ}} (2J_{\gamma}^0 - K_{\gamma}^0)|\nu\rangle - S_{k\nu}\left\{\langle k| V^B + \sum_{\gamma}^{\text{occ}} (2J_{\gamma}^0 - K_{\gamma}^0)|k\rangle\right\}|^2}{\epsilon_{\nu}^{\text{ESX}} - \epsilon_k^{\text{ESX}}}$$

$$\epsilon_{\mu}^{\text{ESX}+\text{CT}} \sim \epsilon_{\mu}^{\text{ESX}}$$

$$- \sum_{l}^{\text{vac}} \frac{|\langle \mu| V^A + \sum_{m}^{\text{occ}} (2J_{m}^0 - K_{m}^0)|l\rangle - S_{\mu l}\left\{\langle \mu| V^A + \sum_{m}^{\text{occ}} (2J_{m}^0 - K_{m}^0)|\mu\rangle\right\}|^2}{\epsilon_{l}^{\text{ESX}} - \epsilon_{\mu}^{\text{ESX}}}$$

$$E_{\text{CT}}^{(1)} \sim$$

$$2 \sum_{k}^{\text{occ}} \sum_{\nu}^{\text{vac}} \frac{|\langle k| V^B + \sum_{\gamma}^{\text{occ}} (2J_{\gamma}^0 - K_{\gamma}^0)|\nu\rangle - S_{k\nu}\left\{\langle k| V^B + \sum_{\gamma}^{\text{occ}} (2J_{\gamma}^0 - K_{\gamma}^0)|k\rangle\right\}|^2}{\epsilon_{\nu}^{\text{ESX}} - \epsilon_k^{\text{ESX}}}$$

$$+ 2 \sum_{\mu}^{\text{occ}} \sum_{l}^{\text{vac}} \frac{|\langle \mu| V^A + \sum_{m}^{\text{occ}} (2J_{m}^0 - K_{m}^0)|l\rangle - S_{\mu l}\left\{\langle \mu| V^A + \sum_{m}^{\text{occ}} (2J_{m}^0 - K_{m}^0)|\mu\rangle\right\}|^2}{\epsilon_{l}^{\text{ESX}} - \epsilon_{\mu}^{\text{ESX}}}$$

$$(32)$$

As is obvious from eqs. (26) and (31), the expressions for ES and EX interaction energies are completely identical to those of Murrel-Fueno et al. [1] and Fukui et al. [2]. The first term of eq. (30), the first-cycle polarization term $E_P^{(1)}{}_L$, is essentially equivalent to the polarization term of Murrel-Fueno and Fukui. The primary difference is that the denominator in their expression is the excitation energy from the ground state instead of the orbital energy differences, because they use CI wave-functions whereas we are within the HF framework. The second term of eq. (30) is a portion of Murrel's exchange polarization term. In the present method the rest of the exchange polarization term arises in calculations which include both EX' and PLX blocks and therefore forms a part of coupling terms. These two parts of the exchange polarization almost cancel each other, leaving a small net result [1]. In our definition, $E_{\text{EXPL}}$ and $E_{\text{MIX}'}$ are expected to be large and of opposite sign to each other at short distances. Fukui's CT term agrees with eq. (32) except for the denominator mentioned above, but the Murrel-Fueno expression lacks the exchange operators $K^0$.

The above comparison shows that our present definition of various terms is basically in agreement with definitions based on the CI perturbation expansion. It should be emphasized, however, that we actually never use the sum-of-MO-integral expressions of eqs. (25)–(32). Those expressions, as well as Murrel-Fueno and Fukui's perturbation expressions, require MO integrals which can be obtained only after expensive transformation (of the order $n^5$ operations, where $n$ is the size of basis set) of AO integrals. As will be shown in the next section, the present method, as well as our previous method [5], uses a modification of a standard HFSCF program and avoids the expensive transformation completely. Furthermore, being iterative, our methods can handle a rather strong interaction, whereas these perturbation methods require higher order corrections which are hard to evaluate.

## 4. Numerical Calculation and Results

Actual calculation of the new energy components can be accomplished economically by using a modification of any existing SCF program. The following steps were programmed for GAUSSIAN 70 *ab initio* package [13]:

1. Calculate MO's (MO$^0$) for isolated molecules.
2. Calculate F(AO) in the AO basis (in parenthesis) from AO integrals and AO density matrix D(AO).
3. Transform F(AO), H(AO), and S(AO) to the MO$^0$ basis and select blocks according to the choice of $x$ to obtain F$^x$(MO$^0$), H$^x$(MO$^0$) and S$^x$(MO$^0$).
4. Calculate the energy using eq. (13) in the MO$^0$ basis.
5. Diagonalize the matrix (F$^x$(MO$^0$) − S$^x$(MO$^0$)$\epsilon$) to obtain MO coefficients C$^x$(MO$^0$) in the MO$^0$ basis.
6. Construct the density matrix D$^x$(MO$^0$) in the MO$^0$ basis and transform it to AO basis D(AO). Go back to Step 2 if the convergence is not reached.
7. For calculation of ES and PL terms, neglect all AO integrals that include any intermolecular differential overlap.

As an example of the new analysis, calculated energy components for $(H_2O)_2$ are shown in Table I for three O · · · O distances including the experimental distance of 2.98Å. It is clear from the table that our previous "charge transfer energy" $E_{ct}$ is not very different from the true charge transfer energy $E_{CT}$ for all the distances studied. This supports our previous contention that the coupling term should be small, and our previous energy decomposition analyses [5, 8, 9] stand without reinterpretation. Though the sum, $E_{EXPL} + E_{MIX'}$ is small for all the distances, the individual terms, $E_{EXPL}$ and $E_{MIX'}$ are very sensitive to the distance. As was discussed in Section 3, since $E_{EXPL}$ is a part of exchange polarization and the rest is included in $E_{MIX'}$, the division is rather artificial and the sum $(E_{MIX} = E_{EXPL} + E_{MIX'})$ should be physically more meaningful and considered as the strength of coupled interactions.

The new decomposition method enables one to calculate directly the electron density change $\rho_{CT}$ (1|1) due to the charge transfer interaction

$$\rho_{CT}(1 \quad 1) = \rho^{ESX+CT}(1|1) - \rho^{ESX}(1|1) \tag{21}$$

TABLE I. Energy decomposition for $(H_2O)_2$ in kcal/mole. 4-31G basis set.[a]

| $R_{O \cdots O}$ | 2.78 | 2.98 | 3.18 |
|---|---|---|---|
| $E_{ES}$ | 12.91 | 8.98 | 6.62 |
| $E_{EX}$ | $-9.34$ | $-4.19$ | $-1.85$ |
| $E_{PL}$ | 0.73 | 0.47 | 0.32 |
| $E_{CT}$ | 2.78 | 2.11 | 1.74 |
| $E_{EXPL}$ | 2.95 | 0.40 | $-0.02$ |
| $E_{MIX'}$ | $-2.36$ | $-0.06$ | 0.18 |
| $(E_{ct})^b$ | (3.37) | (2.45) | (1.90) |
| $\Delta E$ | 7.67 | 7.72 | 6.99 |

[a]Experimental geometry (T. R. Dyke and J. S. Muenter, J. Chem. Phys. **60**, 2929 (1974)) was assumed except for the O $\cdots$ O distance, $R_{O \cdots O}$, which was changed around the experimental value, 2.98Å.

[b]$E_{ct}$, our previous "charge transfer" energy, is the sum of $E_{CT}$, $E_{EXPL}$, and $E_{MIX'}$.


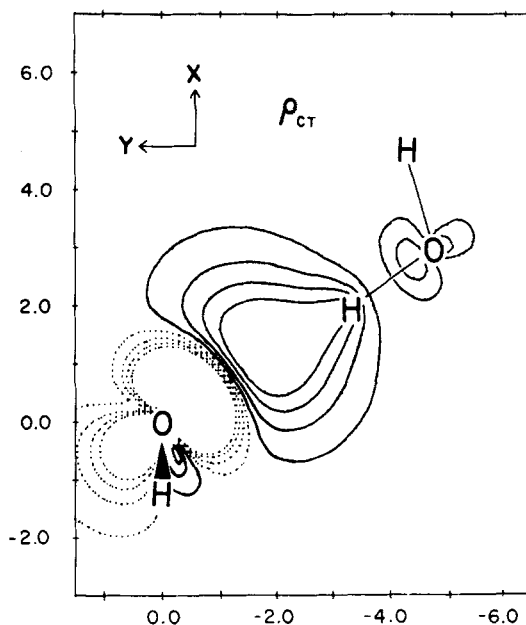
Figure 2. The electron density change $\rho_{CT}$ (1|1) due to the charge transfer interaction from the $(R_{O \cdots O} = 2.98A)$. Full lines indicate density increases and dotted lines indicate decreases. Values of these lines are, successively, $\pm 1.4$, $\pm 1.0$, $\pm 0.6$, and $\pm 0.2 \times 10^{-3}$ (Bohr$^{-3}$). The $x$ and $y$ coordinates are in Bohrs, relative to the oxygen atom of the proton acceptor.

where $\rho^x$ is the one-electron density matrix calculated with the wave-function from the model Fock operator $F^x$. Because the calculation with $x = $ ESX $+$ CT partitions the two subspaces, one corresponding to the charge transfer from A to B and the other from B to A, as was shown in eq. (15), $\rho_{CT}$ can be also evaluated in two parts. Figure 2 is the contour map of the electron density change $\rho_{CT}(1|1)$ due to the charge transfer from the proton acceptor (electron donor) to the proton donor (electron acceptor) for $(H_2O)_2$ at O $\cdots$ O $= 2.98\overset{\circ}{A}$ with the 4-31 G basis set. The contribution of the back donation (i.e., the charge transfer from the electron acceptor to the electron donor) is not shown here, but is extremely small and negligible in the present example. This system has been the subject of comprehensive study of electron density change by Yamabe and Morokuma [11] based on our previous decomposition scheme and the results will not be repeated here for other components. Figure 2 shows a substantial charge transfer from the electron donor to the O $\cdots$ H bonding region, corresponding to the intermolecular covalent bonding. This is compared with Yamabe-Morokuma's "charge transfer" change $\rho_{ct}$, which, in addition to the build-up in the O $\cdots$ H region, shows a substantial polarization of the electron acceptor molecule. The present analysis indicates the latter effect should be attributed to the coupling terms, $\rho_{EXPL+MIX'}$.

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