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An Energy Decomposition Scheme Applicable to Strongly Interacting Systems

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An energy decomposition scheme useful for the analysis of the coupled types of interactions in strongly interacting systems is developed within the Hartree-Fock approximation. A dominant characteristic of the scheme is that it involves the interactions between vacant orbitals of component molecules, as can be justified from the third-order perturbation theory. On the basis of *ab initio* molecular orbital calculations, the utility of the scheme is illustrated for the BH_3–NH_3 complexation and the S_N2 reaction of CH_4 with H^-. It is found that the charge transfer from electron donor (i.e. NH_3 or H^-) to acceptor (i.e. BH_3 or CH_4) is strongly coupled with the polarization of the acceptor, to contribute appreciably to the stabilization of the entire system. A specific role of this coupling mode in the progress of reactions is discussed.

Key words: Energy decomposition – Strong interaction – Coupled interactions

1. Introduction

The nature of intermolecular interactions as involved in molecular complexations and chemical reactions has been of prime interest to both theoretical and experimental chemists. Theoretical investigations based on the molecular orbital (MO) method have been made extensively on a variety of interacting systems such as the hydrogen-bonded [1] and chemically reacting [2] systems. The most typical way of dealing with such a system is to regard the entire system as a "supermolecule" rather than as a molecular aggregate and to calculate the interaction energy merely as the difference in total energy between the supermolecule and the isolated components. However, the results often obscure a body of chemically appealing information. To cope with the situation, alternative methods such as the intermolecular configuration analysis [3–6] and the interaction-energy decomposition

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analysis [7–9] have been proposed. These latter methods share one important common feature that the electronic structure of a given supermolecule is projected on the eigenfunctions of its component molecules, thus permitting a visual interpretation of the interaction in terms of the electronic properties of the isolated components.

Recently, Kitaura and Morokuma [10] have put forth a refined energy-decomposition scheme based on the Fock matrix fragmentation technique. Thus, certain blocks of the Fock matrix for a supermolecule which has been constructed of the Hartree-Fock MO's for component molecules are intentionally set to zero, and the resultant Fock equation is solved iteratively. In accordance with the types of the matrix blocks used, four interaction terms – the electrostatic (E_{ES}), exchange-repulsion (E_{EX}), polarization (E_{PL}), and charge-transfer (E_{CT}) energies – have been defined. The total intermolecular interaction energy (ΔE_{int}) is a sum of these four energy components *plus* an unspecified energy term of the mixed type (E_{MIX}):

$$\Delta E_{\mathrm{int}} = E_{\mathrm{ES}} + E_{\mathrm{EX}} + E_{\mathrm{PL}} + E_{\mathrm{CT}} + E_{\mathrm{MIX}}. \tag{1}$$

As far as weak interactions like hydrogen bondings are concerned, the contribution of E_{MIX} is actually small enough to be ignored [10]. In the case of strong interactions, however, it can be considerably large in magnitude and may even be the most dominant contribution. In the BH_3–CO complex, for instance, $-E_{\mathrm{MIX}}$ was calculated to be as large as 172.4 kcal/mole at an intermolecular B–C distance of 1.57 Å while ΔE_{int} was only -5.3 kcal/mole [11]. Obviously, the energy decomposition into the afore-mentioned four terms alone lacks adequacy in the strong interaction region.

The purpose of the present paper is to propose a general method by which one can evaluate E_{MIX} directly and thereby analyze the modes of coupled interactions involved. Adequacy of the method will be demonstrated by *ab initio* calculations for a typical charge-transfer complex BH_3–NH_3 and an S_N2 reaction system $CH_4 \cdots H^-$. A specific role of the coupling between charge transfer and local polarization in strong interaction will be clarified.

2. Method of Calculation

2.1. Specification of the Interaction Energies

Before considering the interaction energy of the mixed type E_{MIX}, we will briefly outline how the total intermolecular interaction energy ΔE_{int} can be decomposed into various specific energy terms. For simplicity, we assume that both molecules A and B are in the closed-shell ground state. A key point is that the Hartree-Fock (HF) MO's of A and B, which may well be deformed from their original equilibrium geometries, are used as a basis set for the MO's of the supermolecule AB. With this basis set the HF equation for AB is constructed:

$$(\boldsymbol{F} - \varepsilon \boldsymbol{S})\boldsymbol{C} = \boldsymbol{0}, \tag{2}$$

where $\boldsymbol{F}$ is the Fock matrix, $\boldsymbol{S}$ is the overlap matrix, and $\boldsymbol{C}$ is the LCMO coefficient matrix whose i'th column C_i is the eigenvector corresponding to the eigenvalue ε_i. By using the Hartree-Fock matrix F^0 at infinite separation, one can conveniently define the interaction matrix

$$\Sigma=(F-\varepsilon S)-(F^0-\varepsilon I), \tag{3}$$

where I is the unit matrix. Explicit MO expressions for the elements of Σ have been given elsewhere [10].

In conformity to the types of its elements, Σ can be decomposed into the following six component matrices:

$$\Sigma=\Sigma^{\mathrm{ESX}}+\Sigma^{\mathrm{EX}'}+\Sigma^{\mathrm{PLX(A)}}+\Sigma^{\mathrm{PLX(B)}}+\Sigma^{\mathrm{CT(A\rightarrow B)}}+\Sigma^{\mathrm{CT(B\rightarrow A)}}. \tag{4}$$

These six components correspond respectively to the block representations as shown in Fig. 1. The matrix $\Sigma^{\mathrm{CT(A\rightarrow B)}}$, for instance, is represented by the matrix blocks comprising the interactions between the occupied MO's (A_o) of A and the vacant MO's (B_v) of B. It in effect brings about the charge transfer from A to B by the mixing of A_o with B_v.

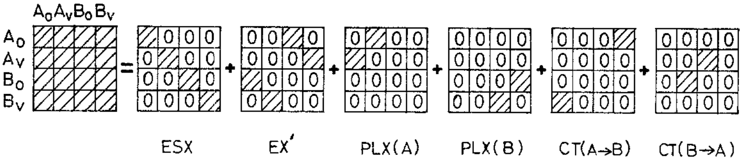


Fig. 1. Interaction blocks

For the electrostatic (ES) interaction, the following pseudo HF equation is solved:

$$\{(F^0-\varepsilon I)+\Sigma^{\mathrm{ES}}\}C^{\mathrm{ES}}=\mathbf{0}, \tag{5}$$

where Σ^{ES} is an interaction matrix which is given by dropping the intermolecular exchange operator from Σ^{ESX}. The resulting solutions, when combined with the nuclear repulsion energy, give a pseudo total energy E^{ES}. The electrostatic interaction energy E_{ES} is obtained as

$$E_{\mathrm{ES}}=E^{\mathrm{ES}}-E^0 \tag{6}$$

where E^0 is the total energy of isolated (but deformed) molecules A and B.

For the interactions other than ES, the following pseudo HF equation is set up with the diagonal matrix Σ^{ESX} included:

$$\{(F^0-\varepsilon I)+\Sigma^{\mathrm{ESX}}+\Sigma^{y}\}C^{\mathrm{ESX}+y}=\mathbf{0},$$
$$y=\mathrm{EX}', \mathrm{PLX(A)}, \mathrm{PLX(B)}, \mathrm{CT(A\rightarrow B)}, \text{ or } \mathrm{CT(B\rightarrow A)}. \tag{7}$$

The diagonal blocks are always needed in order to assure the SCF condition of the pseudo HF equation. Eq. (7) is solved iteratively, to give a pseudo total energy $E^{\mathrm{ESX}+y}$. The exchange-repulsion energy E_{EX} is given by

$$E_{\mathrm{EX}}=E^{\mathrm{ESX}+\mathrm{EX}'}-E^{\mathrm{ES}}. \tag{8}$$

The remaining four interaction energies are obtained from

$$E_y = E^{\mathrm{ESX}+y} - E^{\mathrm{ESX}}, \tag{9}$$

where E^{ESX} is the energy obtained by letting $\boldsymbol{\Sigma}^y = \mathbf{0}$ in Eq. (7). The polarization energy E_{PLX} (with the exchange-polarization included) and the charge-transfer energy E_{CT} are expressed as

$$E_{\mathrm{PLX}} = E_{\mathrm{PLX(A)}} + E_{\mathrm{PLX(B)}}, \tag{10}$$

and

$$E_{\mathrm{CT}} = E_{\mathrm{CT(A \to B)}} + E_{\mathrm{CT(B \to A)}}, \tag{11}$$

respectively. (Note, however, that the equalities (10) and (11) may not always hold; there may well be a coupling between the component interactions in each case.) The modes of orbital interactions involved in the ES, EX, PLX, and CT energies are diagrammatically illustrated in Fig. 2.

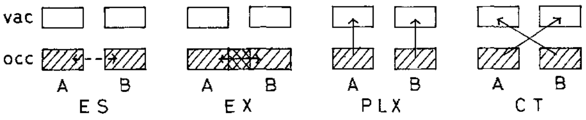


Fig.2. Modes of orbital interactions as involved in the energies, E_{ES}, E_{EX}, E_{PLX}, and E_{CT}

2.2. *The Interaction Energy of the Mixed Type* E_{MIX}

We are now in the position to consider the mixing term E_{MIX}, which is a principal object of this work. Naively, one may expect that E_{MIX} will result simply from simultaneous use of some of the component matrices appearing in Eq. (4). The expectation is correct in principle, but in practice extra care must be taken for proper choice of the interaction blocks. For the case of a coupling between CT(A → B) and PLX(A), for example, simple use of the interaction blocks $\boldsymbol{\Sigma}^y = \boldsymbol{\Sigma}^{\mathrm{CT(A \to B)+PLX(A)}}$ as shown in Fig. 3(a) gives rise to an SCF divergence, which is physically of no significance. Theoretically, this failure in the SCF convergence stems from the absence of interaction between A_v and B_v. That is, an entire space to be spanned by the eigenfunctions of the pseudo HF equation cannot be described completely without including mutual interactions between the subspaces of A_v and B_v. That these specific types of orbital interactions are indispensable for our purpose, can readily be demonstrated by the third-order perturbation theory (Appendix A).

The correct form of $\boldsymbol{\Sigma}^y$ to be used for the coupling between CT(A → B) and PLX(A) should be such as is shown in Fig. 3(b). Phenomenologically, the new interaction block due to the A_v–B_v combination prevents charge density from invading the intermolecular space unlimitedly during the SCF procedure. The interaction energy E_{I} of the mixed type which is ascribable to the block pattern as

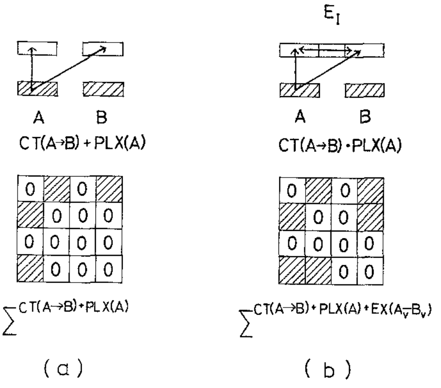


Fig. 3. Interaction blocks and the modes of orbital interactions for $E_{\rm I}$. (a) Without EX(A_v–B_v). (b) With EX(A_v–B_v)

shown in Fig. 3(b) is calculated as

$$E_{\rm I}=(E^{\rm I}-E^{\rm ESX})-(E_{\rm CT(A\to B)}+E_{\rm PLX(A)}). \tag{12}$$

Here, $E^{\rm I}$ is the total energy obtained by solving Eq. (7) with $\Sigma^y=\Sigma^{\rm CT(A\to B)+PLX(A)+EX(\mathit{A}_v-\mathit{B}_v)}$.

The significance of the Σ^y adopted can readily be understood (Appendix B).

Shown in Fig. 4 are all the remaining forms of Σ^y to be considered for the CT–PLX coupling. Note that in every case the arrows which have been drawn to indicate the directions of electron migration form a closed diagram, a triangle. The corresponding interaction energies, $E_{\rm II}$, $E_{\rm III}$, and $E_{\rm IV}$, are calculated respectively by

$$E_{\rm II}=(E^{\rm II}-E^{\rm ESX+EX'})-(E_{\rm CT(A\to B)}+E_{\rm PLX(B)}), \tag{13}$$

$$E_{\rm III}=(E^{\rm III}-E^{\rm ESX+EX'})-(E_{\rm CT(B\to A)}+E_{\rm PLX(A)}), \tag{14}$$

$$E_{\rm IV}=(E^{\rm IV}-E^{\rm ESX})-(E_{\rm CT(B\to A)}+E_{\rm PLX(B)}), \tag{15}$$

where $E^{\rm ESX+EX'}$ is obtainable by letting $\Sigma^y=\Sigma^{\rm EX'}$ in Eq. (7).

We regard all these energies $E_{\rm I}$ through $E_{\rm IV}$ as being due to the coupling interactions between CT and PLX, even though EX(A_o–B_o) or EX(A_v–B_v) has been involved. As will be shown later, these coupling interactions are not necessarily stabilizing

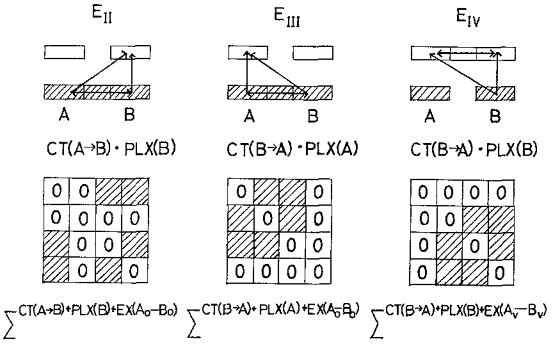


Fig. 4. Interaction blocks and the modes of orbital interactions for $E_{\rm II}$, $E_{\rm III}$, and $E_{\rm IV}$

contributions to ΔE_{int}; they may tend to destabilize the system as well. Either way, if E_{I}–E_{IV} constitute the bulk of E_{MIX}, then we may write

$$E_{\text{MIX}} = E_{\text{I}} + E_{\text{II}} + E_{\text{III}} + E_{\text{IV}} + E_{\text{Res}}, \tag{16}$$

where E_{Res} is a small residue whose nature still remains to be unraveled. Adequacy of Eqs. (12)–(16) should be judged from the magnitude of E_{Res}. Should E_{Res} prove to be still as large in magnitude as E_{MIX}, the present attempt would have to be regarded as entirely fruitless.

All computations reported herewith were carried out with the minimal STO-3G [12] and split-valence 4-31G [13] basis sets, employing a modified version of the GAUSSIAN 70 programming system [14].

3. Illustrative Calculations

The absolute values of the calculated energy components are generally highly sensitive to the basis sets used as well as the molecular geometries assumed. Hence, the results of calculations to be presented below should be taken as only semi-quantitative. Our primary concern is rather with the relative importances of the various energy components, especially of the coupling terms.

3.1. BH_3–NH_3 CT Complex

Borazane (ammonia–boron hydride) is a typical donor-acceptor CT complex caused by an effective overlapping between the σ lone-pair orbital of nitrogen and the vacant p_σ orbital of boron. It already received a good deal of theoretical interest [15–17] in the past.

We have calculated the energy components of the complex at an optimized geometry [17], by use of the STO-3G basis set. The results are given in Table 1, where a negative (positive) value corresponds to stabilization (destabilization) of the complex. As has been pointed out previously [11], E_{ES} (−24.71 kcal/mole) and E_{CT} (−26.68 kcal/mole) constitute the largest stabilizing contributions. The stabilization of the complex brought about by these two energies outweighs the opposing destabilization due to E_{EX} (34.24 kcal/mole). As compared with these three energies, E_{PLX} is small (−1.67 kcal/mole). The separation of E_{PLX} into

Table 1. Interaction energies in the BH_3–NH_3 complex[a, b]

E_{ES}	E_{EX}	E_{PLX}	E_{CT}	E_{MIX}	ΔE_{int}
−24.71	34.24	−1.67 (−1.42[c]) (−0.31[d])	−26.68 (−0.56[e]) (−25.99[f])	−7.62	−26.44

[a] Values given in kcal/mole.
[b] Molecular geometry taken from Ref. [17].
[c] PLX(BH_3).
[d] PLX(NH_3).
[e] CT($BH_3 \rightarrow NH_3$).
[f] CT($NH_3 \rightarrow BH_3$).

$E_{PLX(BH_3)}$ and $E_{PLX(NH_3)}$ reveals that the polarization of the electron acceptor, BH_3, is more marked than that of the donor, NH_3. As for E_{CT}, the electron transfer from NH_3 to BH_3 is seen to be much preponderant over the backward transfer, as is intuitively obvious. More importantly, E_{MIX} is calculated to be -7.62 kcal/mole, a value which is by no means negligibly small in magnitude. It is this last point that concerns directly with the most important facet of the present computational work.

Table 2 shows the results of the component analysis of E_{MIX}. E_{Res} is found to be considerably smaller than E_{MIX}, a result which suggests that our analysis is indeed of practical significance. Of the four CT-PLX coupling terms, the most dominant are E_{III} (-5.43 kcal/mole) and E_{IV} (-1.58 kcal/mole) for both of which the charge transfer from donor to acceptor is responsible. The relative dominance of the former energy over the latter is no doubt related to the greater polarization tendency of BH_3 as compared to NH_3 (Table 1). By contrast, the energy terms E_I and E_{II}, both involving the backward charge transfer from BH_3 to NH_3, take on small positive values, indicative of a destabilization effect. Seemingly, the magnitudes of the coupling terms are strongly dependent on the direction of charge transfer involved as well as on the ease of polarization of the constituent molecules.

Table 2. Further decomposition of E_{MIX} for the BH_3–NH_3 complex

Component	Mixed interaction type	Value[a, b]
E_I	$CT(BH_3 \rightarrow NH_3) \cdot PLX(BH_3)$	0.02
E_{II}	$CT(BH_3 \rightarrow NH_3) \cdot PLX(NH_3)$	0.34
E_{III}	$CT(NH_3 \rightarrow BH_3) \cdot PLX(BH_3)$	−5.43
E_{IV}	$CT(NH_3 \rightarrow BH_3) \cdot PLX(NH_3)$	−1.58
E_{Res}		−0.97

[a] Given in kcal/mole. [b] The total sum is $E_{MIX} = -7.62$ kcal/mole.

3.2. $(CH_4 + H^-)$ S_N2 Reaction

It is widely recognized that S_N2 reactions proceed by a back-side displacement, resulting in an inversion of configuration about the atom on which the displacement takes place. The potential energy surface of the $CH_4 \cdots H^-$ system has been investigated by several groups of workers [18–22].

We have undertaken the energy component analysis of the $(CH_4 + H^-)$ reaction, assuming that the reaction proceeds along the path as reported by Dedieu and Veillard [19]. Preliminary calculations showed that the 4-31G basis set can better reproduce the overall potential energy profile of Dedieu and Veillard than can the STO-3G set, so we decided to use the former set for the present purpose.

Figure 5 shows the calculated energy components, E_{ES}, E_{EX}, E_{PLX}, E_{CT}, and E_{MIX}, and their total sum ΔE_{int} as the functions of the intermolecular distance R. We will not go into detailed discussion of the variations in these energy terms with R. It should be noted, however, that as R is decreased the methane molecule suffers an increasing deformation from its original tetrahedral geometry. The energy increment ΔE_{def} due to this intramolecular deformation should be added up to ΔE_{int} to give the overall potential energy (ΔE) profile.

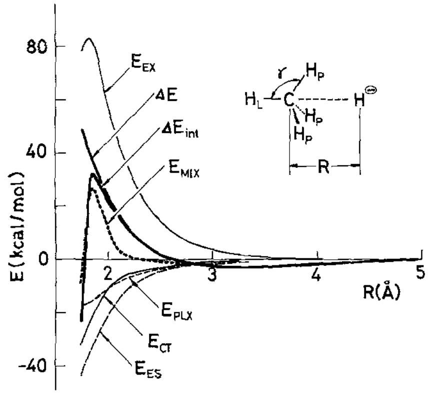


Fig. 5. Variations in the energy components (E_{ES}, E_{EX}, E_{PLX}, E_{CT}, and E_{MIX}) with the intermolecular distance R for the reaction $CH_4 + H^- \rightarrow H^- + CH_4$.

$\Delta E_{int} = E_{ES} + E_{EX} + E_{PLX} + E_{CT} + E_{MIX}$.

$\Delta E = \Delta E_{int} + \Delta E_{def}$

The results of energy decomposition analysis at a path point $R = 2.646$ Å (where $R_{C\text{-}H_L} = 1.103$ Å, $R_{C\text{-}H_P} = 1.079$ Å, and $\gamma = 111.3°$) are given in Table 3. The large destabilization due to E_{EX} is not entirely canceled out by the stabilizing energies E_{ES}, E_{PLX}, and E_{CT} altogether. E_{MIX} joins as a stabilizing contribution to render ΔE_{int} negative at this path point. It should be noted that E_{MIX} is as large in magnitude as each of the stabilizing energies E_{ES}, E_{PLX}, and E_{CT} there. Incidentally, E_{PLX} arises exclusively from the polarization of CH_4. Also, E_{CT} is due primarily to the charge transfer from H^- to CH_4, reflecting the nucleophilicity of H^-.

The results of further decomposition of E_{MIX} are given in Table 4. Here also, E_{Res} is seen to be sufficiently smaller in magnitude than E_{MIX} to warrant the adequacy of our energy decomposition procedure. The most dominant contribution to E_{MIX} is again E_{III}, in harmony with the large polarization of CH_4 and the efficient charge transfer from H^- to CH_4.

In order to gain further insight into the effects of various types of interactions on the progress of reaction, the changes in the Mulliken population [23] effected by individual interactions have been calculated at $R = 2.646$ Å. The results obtained are illustrated in Fig. 6.

Table 3. Interaction energies in the S_N2 reaction of CH_4 with H^- [a, b]

E_{ES}	E_{EX}	E_{PLX}	E_{CT}	E_{MIX}	ΔE_{int}
−2.09	8.60	−2.51 (−2.38[c]) (−0.01[d])	−2.73 (−0.24[e]) (−2.50[f])	−1.84	−0.57

[a] At an intermolecular distance $R = 2.646$ Å.
[b] Values given in kcal/mole. [c] PLX(CH_4). [d] PLX(H^-).
[e] CT($CH_4 \rightarrow H^-$). [f] CT($H^- \rightarrow CH_4$).

Table 4. Further decomposition of E_{MIX} for the $CH_4 \cdots H^-$ system[a]

Component	Mixed interaction type	Value[b, c]
E_I	$CT(CH_4 \rightarrow H^-) \cdot PLX(CH_4)$	0.06
E_{II}	$CT(CH_4 \rightarrow H^-) \cdot PLX(H^-)$	0.16
E_{III}	$CT(H^- \rightarrow CH_4) \cdot PLX(CH_4)$	−2.02
E_{IV}	$CT(H^- \rightarrow CH_4) \cdot PLX(H^-)$	0.11
E_{Res}		−0.16

[a] At an intermolecular distance $R = 2.646$ Å.
[b] Values given in kcal/mole.
[c] The total sum is $E_{MIX} = -1.84$ kcal/mole.

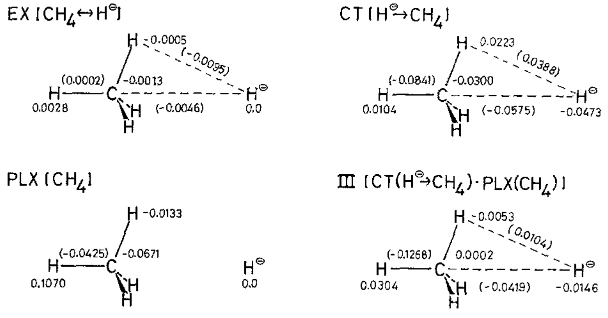


Fig. 6. Changes in atomic electron density and bond population (in parentheses) caused in the $CH_4 \cdots H^-$ system by various types of interactions at $R = 2.646$ Å

Through the exchange interaction (EX), the electronic charge on CH_4 is shifted as a whole toward the terminal leaving hydrogen (H_L), with the electron population in the intermolecular region somewhat reduced. The EX interaction appears to act as though it assisted in unfolding the umbrella which is composed of the central carbon atom and the three pyramidal hydrogen atoms (H_P's). The polarization interaction (PLX) produces a large excess of electron density on H_L while weakening the C–H_L bond appreciably. The charge-transfer interaction (CT) allows electronic charge to flow from H^- into CH_4, thereby weakening the C–H_L bond to a considerable extent. It is interesting to note that the $C \cdots H^-$ bond population is reduced (by 0.0575) whereas the $H_P \cdots H^-$ bond population is increased (by 0.0388). This is because at $R = 2.646$ Å the central carbon atom is still too distant from H^- to accept electrons in the σ^* MO of CH_4. The H_P atoms instead are good targets at this separation to accept electrons in the lowest unoccupied MO of CH_4.

The coupled interaction III appears to behave like an average of the above three interactions, aside from its effect on the C–H_L bond population. It appears as if the excessive electron density which the CT interaction has brought on H_P were forcibly redistributed toward C and H_L by virtue of this coupling interaction. Interestingly enough, the weakening of the C–H_L bond is brought about most effectively by this particular type of interaction. It is thus expected that the CT · PLX interaction may exert a profound influence on the decision of the most favorable reaction path over the potential energy surface.

4. Concluding Remarks

It has been ascertained that the interaction energy of the mixed type E_{MIX} is ascribable chiefly to the couplings between the charge-transfer (CT) and locally-excited (PLX) configurations. Among various modes of such couplings, the combination of CT from donor to acceptor and PLX of the acceptor is found to be distinctively important. The importance of the role of this particular coupling mode is also manifest in molecular deformation which should develop progressively as the interaction becomes strong.

The electronic excitation of a molecule is usually accompanied by its geometrical deformation. As calculations show, the PLX configuration plays an even more important role in interaction when coupled with CT than when it acts alone. In the strong-interaction region, PLX cooperates significantly with CT. In other words, the third-order perturbation is no longer negligible there for discussing a smooth deformation of interacting molecules.

A major merit of the present energy decomposition procedure lies in the technical ease with which we can treat the perturbational problems of third and higher orders. The illustrative calculations presented here seem to clearly demonstrate versatile utility of the method for studies of strong intermolecular interactions.

Appendix A

For understanding the mode of orbital interactions, it is expedient to expand the wavefunction Ψ of a supermolecule AB over various electronic configurations of constituent molecules A and B. Thus, we can write

$$\begin{aligned}\Psi = \Phi_0 + C_{i\to l}\Phi_{i\to l}^{\mathrm{CT(A\to B)}} + C_{i\to j}\Phi_{i\to j}^{\mathrm{PLX(A)}} \\ + (\text{a number of similar terms}),\end{aligned} \tag{a}$$

where Φ_0 is the lowest-energy configuration, $\Phi_{i\to l}$ stands for the charge transfer from the occupied MO i of A to the vacant MO l of B, and $\Phi_{i\to j}$ corresponds to the local excitation from MO i to j within A (Fig. 7).

To simplify the discussion, we will consider only the first three configurations explicitly. According to the Brillouin-Wigner expansion, the coupling energy E_{I} of $\Phi_{i\to l}$ and $\Phi_{i\to j}$ is obtained as the third-order correction $E^{(3)}$. With an operator $V = H - H_{00}S$, $E_{\mathrm{I}}^{(3)}$ is written as

$$E_{\mathrm{I}}^{(3)} = \frac{\langle\Phi_0|V|\Phi_{i\to l}\rangle\langle\Phi_{i\to l}|V|\Phi_{i\to j}\rangle\langle\Phi_{i\to j}|V|\Phi_0\rangle}{(H_{00} - \langle\Phi_{i\to l}|H|\Phi_{i\to l}\rangle)(H_{00} - \langle\Phi_{i\to j}|H|\Phi_{i\to j}\rangle)}. \tag{b}$$

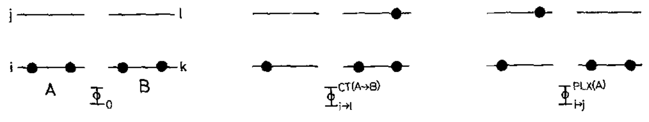


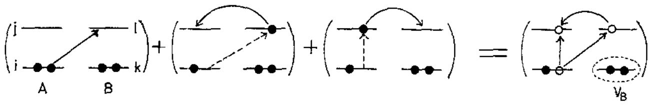
Fig. 7. Various electronic configurations which are assumed to mix as molecule A interacts with molecule B

Noting that i and j (and l) are the HF MO's of molecule A (and B), we can rewrite the numerator of Eq. (b) at the orbital level as

$$\begin{aligned}\text{Numerator} &= 2\Sigma_{il}^{(1)}\Sigma_{lj}^{(1)}\Sigma_{ij}^{(1)}+\cdots\\ &= 2\langle i|v_{\mathrm{B}}|l\rangle\langle l|v_{\mathrm{B}}|j\rangle\langle i|v_{\mathrm{B}}|j\rangle+\mathcal{O}(s_{ab}^{4}).\end{aligned} \tag{c}$$

Here, $\Sigma_{mn}^{(1)}$ is the matrix element of Eq. (4) for the first SCF cycle, and v_{B} is the potential field of B.

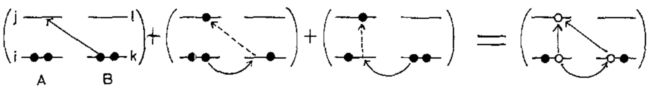
As is apparent from Eq. (c), the interaction between vacant MO's j and l plays an essential role while the coupling energy is caused by the mixing of i with both l and j. The orbital interactions involved can be represented schematically as follows:



It is worth noting that the configuration $\Phi_{i\to l}$ (or $\Phi_{i\to j}$) can be produced not only from Φ_0 but from $\Phi_{i\to j}$ (or $\Phi_{i\to l}$) as well. When we use the first-order corrections of the expansion coefficients $C_{i\to l}^{(1)}$ and $C_{i\to j}^{(1)}$, Eq. (b) is expressed approximately as

$$E_{\mathrm{I}}^{(3)} \simeq C_{i\to l}^{(1)}\langle l|v_{\mathrm{B}}|j\rangle C_{i\to j}^{(1)}. \tag{d}$$

In the case of the coupling between $\Phi_{k\to j}^{\mathrm{CT(B\to A)}}$ and $\Phi_{i\to j}^{\mathrm{PLX(A)}}$, the mode of orbital interactions is represented in the following manner:



In this case the interaction between occupied MO's i and k plays an essential role. The third-order energy is written as

$$E_{\mathrm{III}}^{(3)} \simeq -C_{k\to j}^{(1)}\langle i|v_{\mathrm{A}}^{*}|k\rangle C_{i\to j}^{(1)}, \tag{e}$$

where v_{A}^{*} is the potential field of molecule A which is excited locally by the one-electron transition from i to j.

Appendix B

The interaction blocks in $\Sigma^{\mathrm{CT(A\to B)+PLX(A)+EX}(A_v-B_v)}$ bring forth the mixings of A_o with B_v and A_v, keeping B_o unchanged. In a simple case as shown in Fig. 7, we have two occupied MO's, $i+al+bj$ and k (instead of just i and k) after the self-consistency has been attained. With these new MO's the wavefunction of AB is written as

$$\begin{aligned}\Psi &= \left|(i+al+bj)\overline{(i+al+bj)}k\bar{k}\right| \\ &= \Phi_0 \\ &\quad + (a\Phi_{i\to l} + a^2\Phi_{i\to l,\, i\to l}) && \mathrm{CT(A \to B)} \\ &\quad + (b\Phi_{i\to j} + b^2\Phi_{i\to j,\, i\to j}) && \mathrm{PLX(A)} \\ &\quad + ab\Phi_{i\to l,\, i\to j} && \mathrm{CT(A \to B)\cdot PLX(A)}\end{aligned}$$

Thus, the wavefunction obtained by solving the pseudo HF equation should include all possible charge transfers from A to B and polarization of A.

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