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Original investigations

A new method for partition of interaction energy. Relation between stabilization energy and orbital mixing

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A new method for partition of interaction energy is proposed. The scheme given here easily connects the calculated stabilization energy with the orbital mixing in analyzing orbital interactions of molecules. The method can reveal the relation between the change of electron distribution and stabilization energy. As an example, orbital interaction energies are estimated for diazocompounds, diazomethane and diazirine.

Key words: method for partition of interaction energy—stabilization energy and orbital mixing

Introduction

The intra- or inter-molecular interaction is one of the most interesting problems in theoretical chemistry. Therefore, there are many methods for dealing with the nature of interactions. The frontier orbital theory developed by Fukui [1] is the most convenient tool in order to describe the qualitative orbital interactions. The orbital mixing rule and configuration analysis [2] are also used to analyze complicated systems. On the other hand, it is necessary to calculate interaction energies in order to clarify the bonding nature in more detail. The configuration analysis also gives this quantitative information in weak interacting systems [3]. However, the method is not suitable for discussing the bonding nature in strong interacting systems such as a metal-ligand bond in transition metal complexes. In order to overcome such a difficulty, other types of energy decomposition

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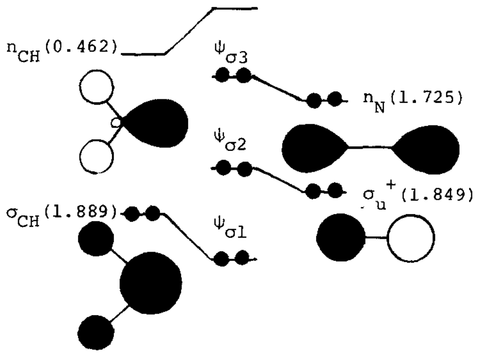
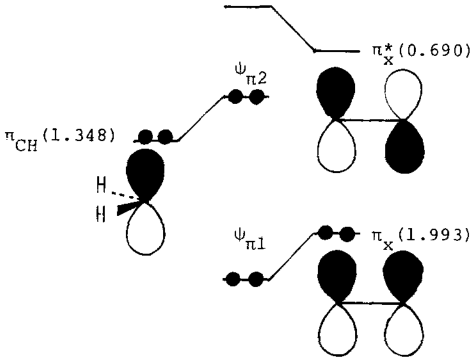
schemes have been developed by several authors [4]. A method proposed by Morokuma [5] was often applied to calculate interaction energies in weak interacting systems. Moreover, the method has been improved by Kitaura and Morokuma [6] for analyzing the relatively strong interactions and was applied to some transition metal complexes with CO_2, C_2H_4 as ligands [7]. In this method, the interaction energy is divided into energy contributions such as electrostatic (ES), charge transfer (CT), polarization (PL), and exchange (EX) interactions. However, calculated energies cannot be directly connected with the orbital mixing rule.

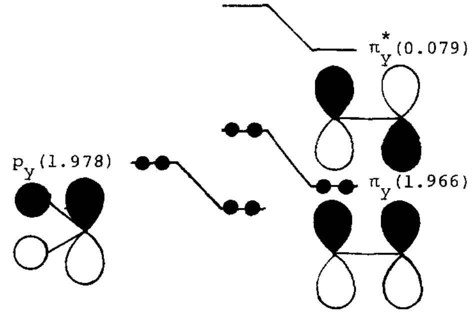
On the other hand, the stabilization due to the orbital mixing is brought from mixture of all interactions. The π back-donation of diazomethane shown in Fig. 1 is adopted as an example in order to explain this effect. MO's in Fig. 1b all have the b_1 symmetry. In general, three types of interactions are considered except for the electrostatic interaction. The first is the charge transfer (CT) which is caused by an electron density transfer from occupied MO's of the one fragment (A) to unoccupied MO's of the another fragment (B) and vice versa. The second is the polarization (PL) from occupied MO's to unoccupied MO's within the same fragment. In this case, they correspond to $\pi_{CH} - \pi_x^*$ and $\pi_x - \pi_x^*$ interactions,



(a) σ donation



(b) π back-donation



(c) b_2 interaction

Fig. 1a–c. Schematic representation of orbital interactions in diazomethane. (**a**), (**b**), and (**c**) represent σ donation, π back-donation and b_2 interaction, respectively

respectively. The last is the exchange repulsion (EX) between occupied MO's of both fragments, for example, that between π_{CH} and π_x. Therefore, the orbital interaction includes all of these interactions. On the other hand, the interaction does not include the electron repulsion between π_x or π_{CH} and other occupied MO's such as n_{N} or p_y. It is because the former MO's do not overlap with the latter ones. Therefore, the orbital interaction energy includes CT, PL and EX interactions and excludes the electron repulsion between MO's without overlapping. It is very interesting to understand the bonding natures by calculating the energies which can be defined as the stabilization energies originating from orbital mixing.

In this paper, a new method for analyzing stabilization energies is developed and applied to compounds, diazomethane and diazirine.

2. Method of calculations

2.1 Energy partition scheme

In elucidating orbital interactions in a molecule (a combined system), it is often divided into two parts which are called isolated systems. The total stabilization energy, ΔE_{stab}, is defined as the difference between the total energy of the combined system. E_t, and sum of those calculated for isolated submolecules, E_0,

$$\Delta E_{\mathrm{stab}} = E_t - E_0, \tag{1a}$$

where

$$E_t = \sum_i 2H_i + \sum_{ij} (2J_{ij} - K_{ij}), \tag{1b}$$

$$E_0 = E_A + E_B$$

$$= \sum^{A+B} \left[\sum_r 2H_r + \sum_{rs} (2J_{rs} - K_{rs}) \right]. \tag{1c}$$

Here, i, j and r, s denote indexes of combined and isolated MO's respectively. Moreover, E_A and E_B denote total energies of isolated submolecules, A and B. In order to relate stabilization energies to the orbital mixing, it is necessary to express E_t using isolated MO's. MO's of combined system, $\{\psi_i\}$, are expressed using the linear combination of isolated MO's $\{\phi_r\}$ such as

$$\psi_i = \sum_r \phi_r C_{ri} \tag{2}$$

where $\{C_{ri}\}$ is the set of expansion coefficients. Substituting Eq. (2) into (1), we obtain

$$E_t = \sum_{rs} P_{rs} H_{rs} + \tfrac{1}{2} \sum_{rs} \sum_{tu} P_{rs} P_{tu} \{(rs|tu) - 1/2(rt|su)\}, \tag{3a}$$

where

$$P_{rs} = \sum_i^{\mathrm{occ}} 2C_{ri} C_{si}. \tag{3b}$$

The classical coulombic stabilization energy, ΔE_{es}, is the energy difference between E_0 and the energy evaluated by use of a Hartee product of isolated MO's,

$$\begin{aligned}\Delta E_{es} &= E_0 - E_{hp}\\ &= -4\sum_r{}^A \sum_s{}^B (rr|ss)\\ &= -\tfrac{1}{2}\sum_r\sum_s Q^A_{rr}Q^B_{ss}(rr|ss),\end{aligned} \tag{4}$$

where $Q_{rr}=2$ if r is an occupied MO in isolated molecules and, in other cases, they are always equal to zero. A or B denote that ϕ_r is the MO of the isolated submolecules A or B. However, the ES interaction does not directly concern with the orbital mixing. Therefore, the energy difference between E_t and E_{hp} can be defined as the interaction energy, ΔE_{int}, caused by all types of orbital interactions,

$$\Delta E_{\text{int}} = E_t - E_{hp}. \tag{5}$$

If a combined system has a symmetry, occupied MO's can be divided into several groups according to the symmetry or the type of the orbital interaction. As there are no overlaps between MO's with different symmetries, the density matrix using isolated MO's have the form represented in Fig. 2. E_t and E_{hp} are expressed by use of this density matrix and Q_{rs},

$$\begin{aligned}E_t = \sum_{\Gamma a}\Bigg[&\sum_{rs\subset\Gamma a} P_{rs}H_{rs} + \tfrac{1}{2}\sum\sum_{rstu\subset\Gamma a} P_{rs}P_{tu}\{(rs|tu)-\tfrac{1}{2}(rt|su)\}\Bigg]\\ &+\tfrac{1}{2}\sum_{\Gamma a}\sum_{\Gamma b}\sum_{rs\subset\Gamma a}\sum_{tu\subset\Gamma b} P_{rs}P_{tu}\{(rs|tu)-\tfrac{1}{2}(rt|su)\},\end{aligned} \tag{6a}$$

$$\begin{aligned}\mathrm{E}_{\mathrm{hp}} = \sum_{\Gamma a}\Bigg[&\sum_{r\subset\Gamma a} Q_{rr}H_{rr} + \tfrac{1}{2}\sum_{rs\subset\Gamma a}\delta_{AB}Q_{rr}Q_{ss}\{(rr|ss)-\tfrac{1}{2}(rs|rs)\}\\ &+\tfrac{1}{2}\sum_{rs\subset\Gamma a} Q^A_{rr}Q^B_{ss}(rr|ss)\Bigg]\\ &+\tfrac{1}{2}\sum_{\Gamma a}\sum_{\Gamma b}\sum_{r\subset\Gamma a}\sum_{s\subset\Gamma b}\delta_{AB}Q_{rr}Q_{ss}\{(rr|ss)-\tfrac{1}{2}(rs|rs)\}\\ &+\tfrac{1}{2}\sum_{\Gamma a}\sum_{\Gamma b}\sum_{r\subset\Gamma a}\sum_{s\subset\Gamma b} Q^A_{rr}Q^B_{ss}(rr|ss),\end{aligned} \tag{6b}$$

where P_{rs} $(rs\subset\Gamma a)$ is an element of the density matrix with the symmetry Γa. In this equation, δ_{AB} is equal to 1 when both ϕ_r and ϕ_s are MO's of the same submolecule, A or B, and otherwise equal to 0. Substituting Eqs. (6) into (5),

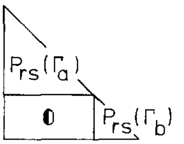


Fig. 2. Form of density matrix when molecule symmetry has two elements, Γa and Γb

then we have,

$$\Delta E_{\text{int}} = \sum_{\Gamma a} \Delta E(\Gamma a) + \Delta E_{er} \tag{7a}$$

where

$$\begin{aligned}\Delta E(\Gamma a) = &\sum_{rs} (P_{rs} - Q_{rs}) H_{rs} + \tfrac{1}{2} \sum_{rs} \sum_{tu} P_{rs} P_{tu} \{(rs|tu) - \tfrac{1}{2}(rt|su)\} \\ &- \tfrac{1}{2} \sum_{rs} \delta_{AB} Q_{rr} Q_{ss} \{(rr|ss) \\ &- \tfrac{1}{2}(rs|rs)\} - \tfrac{1}{2} \sum_{rs} Q^A_{rr} Q^B_{ss} (rr|ss) \quad (rs \subset \Gamma a),\end{aligned} \tag{7b}$$

$$\begin{aligned}\Delta E_{er} = \sum_{\Gamma a} \sum_{\Gamma b} \Bigg[&\tfrac{1}{2} \sum_{rs \subset \Gamma a} \sum_{tu \subset \Gamma b} P_{rs} P_{tu} \{(rs|tu) - \tfrac{1}{2}(rt|su)\} \\ &- \tfrac{1}{2} \sum_{r \subset \Gamma a} \sum_{s \subset \Gamma b} \delta_{AB} Q_{rr} Q_{ss} \{(rr|ss) \\ &- \tfrac{1}{2}(rs|rs)\} - \tfrac{1}{2} \sum_{r \subset \Gamma a} \sum_{s \subset \Gamma b} Q^A_{rr} Q^B_{ss} (rr|ss) \Bigg].\end{aligned} \tag{7c}$$

Therefore, the interaction energy can be divided into energies which contribute to the bond formation owing to the orbital mixing. Terms in Eq. (7) are classified into two categories. One is the energy which is represented only by the density matrix of a symmetry, (7b), and the other needs those of the different symmetries, (7c). Hereafter, they are called the orbital interaction energy, $\Delta E(x)$ (x indicates the type of an interaction) and the electron repulsion energy, ΔE_{er}. The orbital interaction energies can be analyzed in more detail as follows;

$$\begin{aligned}\Delta E(x) &= \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 \\ &\cong \Delta E_1 + \Delta E_2 + \Delta E_3,\end{aligned} \tag{8a}$$

where

$$\Delta E_1 = \sum_{rs} (P_{rs} - Q_{rs}) H_{rs} \tag{8b}$$

$$\begin{aligned}\Delta E_2 = &\tfrac{1}{4} \sum_{rs} [P^2_{rs} \{3(rs|rs) - (rr|ss)\} + P_{rr} P_{ss} (2(rr|ss) - (rs|rs)\}] \\ &- \tfrac{1}{2} \sum_{rs} \delta_{AB} Q_{rr} Q_{ss} \{(rr|ss) - \tfrac{1}{2}(rs|rs)\} + \tfrac{1}{2} \sum_{r \neq s} P_{rr} P_{rs} (rr|rs) \\ &- \tfrac{1}{2} \sum_{r} \sum_{s} Q^A_{rr} Q^B_{ss} (rr|ss),\end{aligned} \tag{8c}$$

$$\Delta E_3 = \tfrac{1}{2} \sum_{\substack{r \neq s, r \neq t \\ s \neq t}} [(2 P_{rr} P_{st} - P_{rs} P_{rt})(rr|st) + (3 P_{rs} P_{rt} - P_{rr} P_{st})(rs|rt)]. \tag{8d}$$

All suffixes have the same symmetry. Negative and positive values indicate the stabilization and destabilization, respectively. ΔE_1 and ΔE_2 contain only one and two center integrals. ΔE_3 which is sum of the three center integrals does not appear in calculation of E_{hp}. It is not necessary to estimate the remaining four center terms, ΔE_4, because they do not make a serious contribution to the orbital interaction energy [8]. $\Delta E_1 \sim \Delta E_3$ show the change of one and two electron energies brought by the rearrangement of electron distribution due to orbital mixing.

It is considered that the main part of the interaction energy of a system originates from the rearrangement of the electron density in valence MO's. That is, core MO's scarcely change before and after formation of the combined system. While the orbital interaction energy of core MO's is probably negligible, the electron repulsion energy between core and valence MO's, ΔE (core-x), should be taken into account because the change of valence MO's is drastic. Therefore, this term is also added to the orbital interaction energy,

$$\Delta E(x) = \Delta E(\text{core-}x) + \Delta E_x, \tag{9}$$

where ΔE_x is the contribution from the valence MO parts. However, the partition of core orbitals is not always possible. It is necessary to use large basis sets in order to represent the correct electronic structures of molecules with heavy atoms such as transition metal complexes. Not only compact but diffuse orbitals, i.e., various orbital functions with different exponents through a wide range, are necessary to describe core orbitals precisely. On the other hand, these basis functions are also important for valence MO's. Therefore, both orbitals have relatively large overlaps with valence or core MO's of the other fragment. Orbital interactions in these molecules cannot be divided into the contribution from core or valence MO parts.

Eqs. (7-8) are expressed using MO indexes. However, it is possible to calculate these energies without transforming atomic orbital (AO) integrals into MO integrals. They are easily obtained by the following process.

(1) Divide occupied MO's of combined and isolated systems into several groups according to types of symmetries.

(2) Make density matrices of both systems, $P_{\mu\nu}(\Gamma a)$, and $P^{es}_{\mu\nu}(\Gamma a)$, respectively, using partitioned MO's.

(3) Calculate electron energies of each interaction. A general *ab initio* SCF program automatically calculates these energies in terms of the density matrixes previously mentioned. In this step, therefore, it is no use changing a program or getting self-consistent field (SCF) convergence. However, it is necessary to modify two electron atomic integrals in order to evaluate ΔE_{es} [5]. The orbital interaction energy of the Γa symmetry, $\Delta E(\Gamma a)$ is given by,

$$\Delta E(\Gamma a) = E(\Gamma a) - E_{es}(\Gamma a), \tag{10a}$$

where

$$E(\Gamma a) = \sum_{\mu\nu} P_{\mu\nu}(\Gamma a) H_{\mu\nu} + \tfrac{1}{2} \sum_{\mu\nu} \sum_{\kappa\lambda} P_{\mu\nu}(\Gamma a) P_{\kappa\lambda}(\Gamma a) \times \{(\mu\nu|\kappa\lambda) - \tfrac{1}{2}(\mu\kappa|\nu\lambda)\}, \tag{10b}$$

Here, μ, ν, etc. denote indexes of atomic orbitals. $E_{es}(\Gamma a)$ is calculated by substituting $P_{\mu\nu}$ for $P^{es}_{\mu\nu}$ and using modified atomic integrals.

On the other hand, the electron repulsion energy, ΔE_{er} is estimated by difference between ΔE_{int} and sum of $\Delta E(\Gamma a)$,

$$\Delta E_{er} = \Delta E_{\text{int}} - \sum \Delta E(\Gamma a). \tag{10c}$$

In the case that more detailed analysis is required, orbital interaction energies must be estimated and discussed by use of Eqs. (8).

(4) The interaction energy due to orbital mixing is the sum of $\Delta E(x)$ and ΔE_{er}.

The change of electron distribution due to orbital mixing can also be analyzed. A difference density between combined and isolated systems is calculated in terms of interactive orbitals for each type of interactions as follows

$$\Delta\rho(\Gamma a) = \sum_i |\psi_i(\Gamma a)|^2 - \sum_r |\phi_r(\Gamma a)|^2, \tag{11}$$

where ψ_i and ϕ_r indicate MO's of combined and isolated systems, respectively.

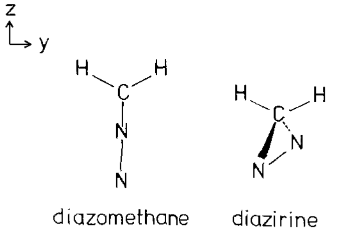
2.2 MO calculation

LCAO-MO-SCF calculations are carried out with GAUSSIAN-80 program [9] and IMSPAK one [10]. 3-21G basis sets internal to the program are used and geometries of small molecules are optimized by the energy gradient method, assuming a C_{2v} symmetry for both compounds. Results of vibration analysis show that they have the symmetry at their most stable structures. N-N bond lengths optimized for N_2, diazomethane, and diazirine are 1.083, 1.131, and 1.217 Å, respectively. C-H, C-N lengths and HCH angle in diazomethane are 1.065, 1.275 Å and 114.4°, respectively. Those in diazirine are 1.064, 1.552 Å and 121.4°, respectively.

3. Results and discussions

3.1 Orbital interaction energies

As an example of a new method, diazomethane and diazirine are employed. These small molecules are considered model compounds of dinitrogen complexes and have already been investigated [11]. The CH_2 planes of these molecules are located on the *yz*-plane as shown in **1**.



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The symmetries of MO's are assigned on this condition. Therefore, MO's related to σ donation and π back-donation have a_1 and b_1 symmetries, respectively, in both these diazo-compounds. In diazirine, we had better designate the π donation rather than the σ donation because a donating orbital is not n_N but π_z of the dinitrogen ligand. However, n_{CH} accepts the density in both cases. Therefore, all the electron donation to n_{CH} is designated as the σ donation. There is another interaction with the b_2 symmetry different from the two interactions and is called the b_2 interaction. This interaction causes the redistribution of the electron density which is transferred by the former two interactions.

Results of the energy partition scheme are summarized in Table 1. Orbital interaction energies of diazomethane are 0.26801, −0.49320, and −0.23372 a.u. for σ donation, π back-donation, and b_2 interactions, respectively. ΔE_{er} is 0.49642 a.u. and the total stabilization energy is −0.15780 a.u.

The π back-donation leads to the formation of the C-N bond because the stabilization energy is negative. The b_2 interaction also gives stabilization. However, the σ donation does not lead to the formation of the C-N bond. As mentioned above, $\Delta E(\sigma \text{ donation})$ is the sum of two contributions, $\Delta E(\text{core-}\sigma)$ and ΔE_σ. They are calculated to be −0.30789 and 0.57590 a.u., respectively. The negative value of the former indicates decrease of an electron repulsion energy between core and σ valence MO's. On the other hand, the change of ΔE_σ indicates destabilization. In discussing orbital mixing in diazomethane, four orbitals are taken into account as is shown in Fig. 1a [12]. Since σ_{CH} and n_{CH} of the CH_2 moiety overlap with n_N and σ_u^+ in a dinitrogen ligand, they also relate to σ donation. The orbital mixing rule says that $\sigma_{CH}-\sigma_u^+$ and $\sigma_{CH}-n_N$ in ϕ_{σ_2} and ϕ_{σ_3} overlap in an out-of-phase fashion. In fact, $\Delta E_1(\sigma_{CH}-\sigma_u^+)$ and $\Delta E_1(\sigma_{CH}-n_N)$ are 1.531 and 1.554 a.u., respectively. This shows that these types of orbital mixing do not give a stabilization energy. On the other hand, $n_{CH}-n_N$ and $n_{CH}-\sigma_u^+$ in ϕ_{σ_2} and ϕ_{σ_3} interact in an inphase manner and this interaction leads to stabilization (ΔE_1 between these orbitals are −0.808, −2.621 a.u., respectively). On the other hand, due to CT from n_N and σ_u^+ to n_{CH}, the absolute value of one electron terms decreases by 3.583, 1.168 a.u. for the two former ones and increases by 1.713 au for the last orbital. The destabilization due to orbital mixing of σ_{CH} override the stabilization brought by CT from n_N and σ_u^+ to n_{CH} and PL from σ_{CH} to n_{CH}.

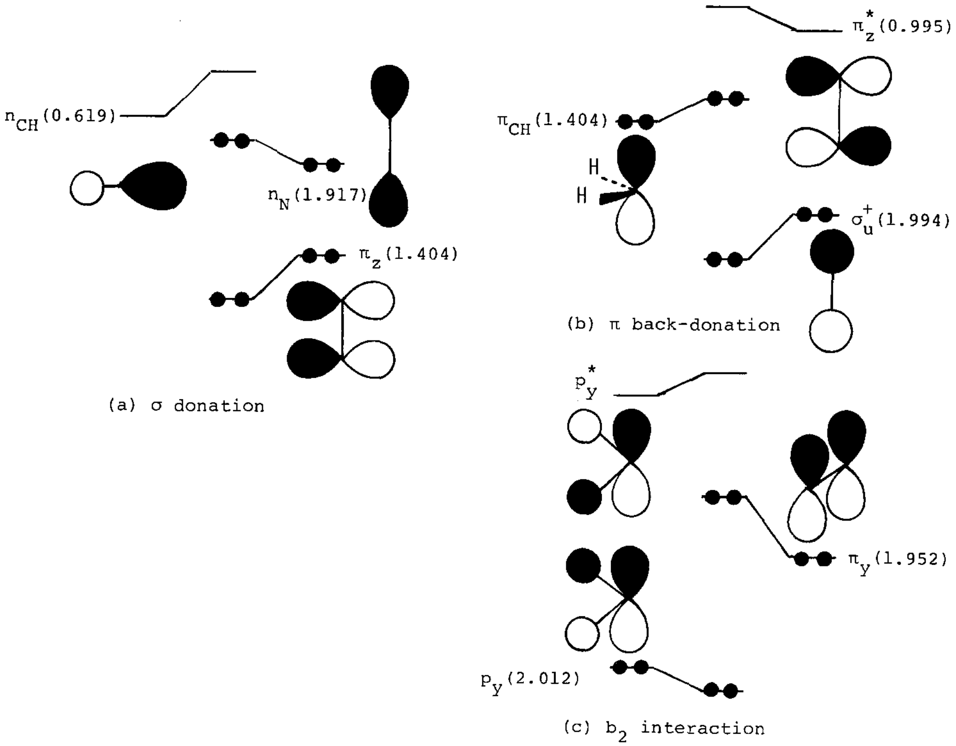
Table 1. Orbital interaction energies calculated for diazomethane and diazirine

	Diazomethane	Diazirine
ΔE (es)	−0.19312	−0.15936
ΔE (core)	−0.00231	−0.00496
ΔE (σ donation)	0.26801	−0.24634
ΔE (π back-donation)	−0.49320	−0.63720
ΔE ($b2$)	−0.23372	0.46691
ΔE_{er}	0.49642	0.43336
Total	−0.15780	−0.14762

The sum of the four terms and electrostatic energies is −0.65434 a.u. ΔE_{er} is the sum of changes in $\Delta E(\sigma-\pi)_{er}$ (0.32821 a.u.), $\Delta E(\sigma-b2)_{er}$ (0.11029 a.u.), $\Delta E(\pi-b2)_{er}$ (0.05743 a.u.) and other small terms, where σ, π and b_2 correspond to one of Γa, Γb in Eq. (7c). The stabilization energy of all the interactions considered in the calculations is −0.15780 a.u. Therefore, the contribution of other higher term (a mixed term of all interactions) is only −0.00012 a.u.

The difference density maps of the σ donation and π back-donation are shown in Fig. 4. The σ donation causes both the decrease of the electron density in n_N and σ_u^+ and the increase in n_{CH} as easily understood from Fig. 4a. On the other hand, Fig. 4b shows the π back-donation, which includes CT and PL interactions. While the former interaction has changed the density around a carbon atom and a dinitrogen ligand, the latter decreases the π density between two nitrogen atoms.

The energy contributions of σ donation, π back-donation and b_2 interactions in diazirine are −0.24634, −0.63720, and 0.46691 a.u., respectively. The electron repulsion energy calculated for the molecule is −0.43336 a.u., so that the higher term (0.00003 a.u.) is small in comparison with other components. The change of electron density due to these interactions is well described by the difference



(a) σ donation

(b) π back-donation

(c) b_2 interaction

Fig. 3a–c. Schematic representation of orbital interactions in diazirine. (**a**), (**b**) and (**c**) correspond to σ donation, π back-donation and b_2 interaction, respectively

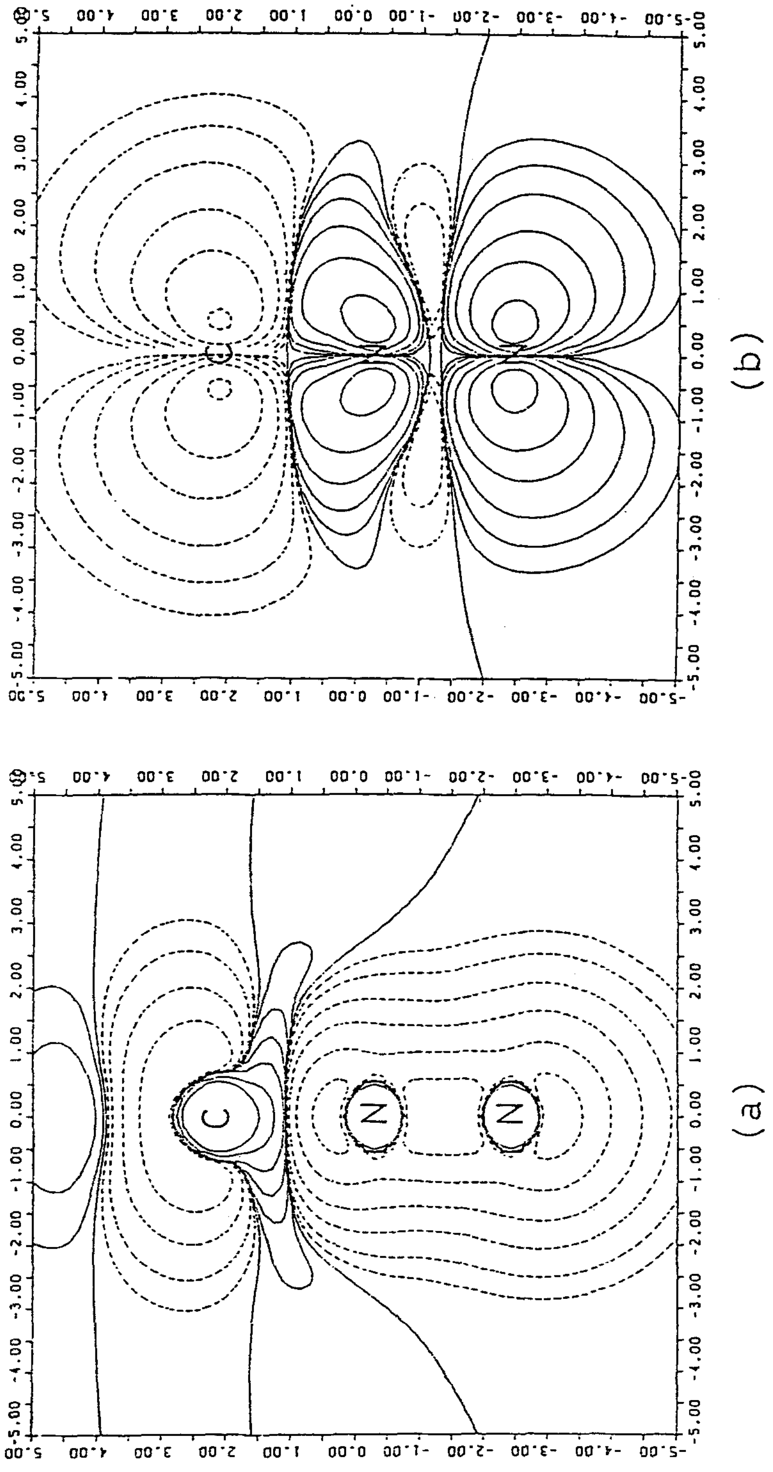


Fig. 4. Difference density maps of (**a**) σ donation and (**b**) π back-donation calculated for diazomethane

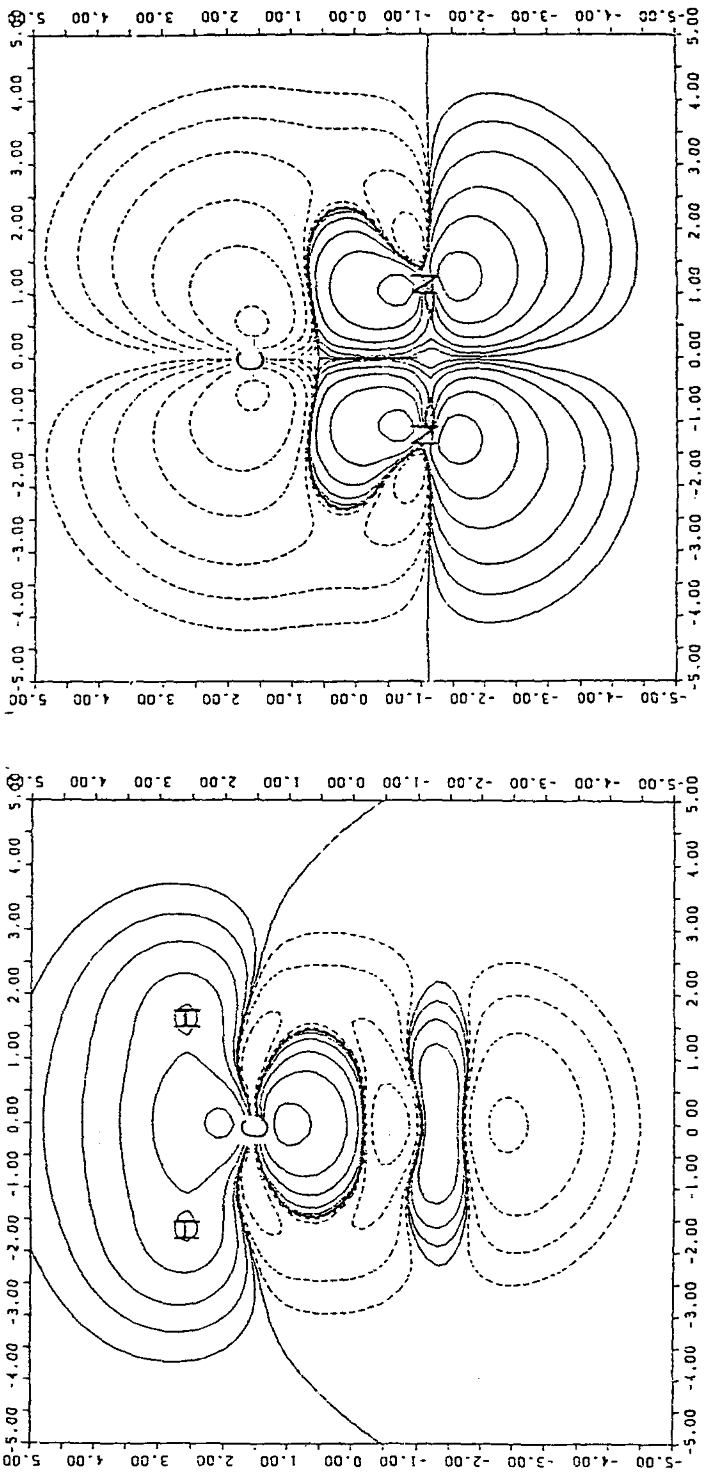


Fig. 5. Difference density maps of (**a**) σ donation and (**b**) π back-donation calculated for diazirine

density map as shown in Fig. 5. The increase and decrease between C and N atoms in Fig. 5a show the σ donation from π_z and n_N to n_{CH}. On the other hand, the π back-donation from π_{CH} to π_z^* in Fig. 5b causes the increase and decrease of the density around N_2 and CH_2 moieties, respectively. Occupation numbers of these orbitals change as shown in Figs. 1 and 3.

Total energies of diazomethane and diazirine, −146.99578 and −146.94779 a.u., respectively, indicate that the former is more stable than the latter. However, ΔE_{stab} of these molecules are calculated to be −0.15780 and −0.14762 a.u., respectively. Therefore, the magnitude of the interactions between carbene and nitrogen molecule does not decide the relative stability of the two compounds. While total energies of the CH_2 fragments for these isomers are close to each other (−38.54407 and −38.54157 a.u. for moieties of diazomethane and diazirine, respectively), the deformation energy [13] of the N_2 fragment in forming the C-N bond are 0.00734 and 0.04235 a.u., respectively. The difference of the energy determines the stable structure between the two isomers. The larger deformation energy is attributed to the fact that the decrement of π_z electron and the increment of the π_z^* density are larger in diazirine than those in diazomethane.

3.2 Comparison of the new method with the KM method

In order to compare the present method with the KM one, interaction energies, ΔE_{EX}, ΔE_{FCTPLX}, and ΔE_{BCTPLX} of diazo-compounds are calculated and results are listed in Table 2. Some differences are seen between the two methods. The most characteristic dissimilarity exists in the contribution of the σ donation. The stabilization energies of the interaction is 0.26801 ($\Delta E(\sigma$ donation)) and −0.17462 (ΔE_{FCTPLX}) a.u. for the present and KM methods, respectively. Several reasons are considered for this discrepancy between the two methods. The first one is about the standard energy in calculating stabilization energies. FCTPLX of the KM method is defined as the difference between the energy using Hartree–Fock product (E_{hfp}) and that obtained by solving FCTPLX Fock-equation. On the other hand, our method adopts the orbital interaction energy as the difference between E_t and E_{hp}. When E_{hp} is used as the standard energy in the KM method, this interaction as well as the BCTPLX gives positive stabilization energies (destabilization) as listed in parentheses of Table 2. These results are attributed

Table 2. Results of energy decomposition by use of the *KM* method for diazomethane and diazirine

	Diazomethane	Diazirine
ΔE_{es}	−0.19312	−0.15936
ΔE_{EX}	0.40517	0.29599
ΔE_{FCTPLX}	−0.17462 (0.01850)	−0.15055 (0.00882)
ΔE_{BCTPLX}	−0.18725 (0.00587)	−0.20724 (−0.04787)
R	−0.00889	0.07355
Total	−0.15780	−0.14762

to the fact that our method includes all the interactions while the KM method is estimated by use of the energy of the specific interactions. For example, in calculating an FCTPLX energy, CT from N_2 to CH_2 and PL in a CH_2 moiety are only allowed. However, a $n_N - \sigma^*$ type polarization in N_2 also facilitates the CT interaction because the orbital balloons up at the N atom adjacent to CH_2 as is shown in **2**.

2

Moreover, the number of MO's in estimating the stabilization energy is different each other. Other trends are similar in these two methods. For example, the π back-donation is more effective than the σ donation in the two isomers though the absolute values are not consistent with each other.

4. Concluding remarks

The new method represented here can divide the energy which is defined as the difference of E_t and E_{hp} to orbital interaction energies. It has several features and convenience. The first is that the energy are obtained without SCF calculation. A method including iteration process must make Fock-matrix and diagonalyze it repeatedly until the convergence would be achieved. The step is the most time consuming one in large molecules, for example, transition metal complexes. Moreover, such a method cannot afford detailed informations in SCF convergence failure. Moreover, subroutines for a special Fock matrix must be added to a usual *ab initio* program. The present method does not have such a proposal. It is only making density matrixes that need to estimate orbital interaction energies.

The second is that the energies explicitly concern with orbital mixing rule because they are calculated by use of only MO's with overlapping. Therefore, origin of the stabilization energy can be easily analyzed. The method also shows the relation between the density distribution and the energy contribution.

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