Interaction between Electron Donor and Acceptor: MINDO/2 Calculations on the Ammonia-I_2, Benzene-I_2 and Benzene-TCNE Systems

Toshiaki OHTA, Takashi FUJIKAWA, and Haruo KURODA
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

(Received April 17, 1974)

The MINDO/2 method was applied to typical molecular complexes such as ammonia–I_2, benzene–I_2, and benzene–TCNE, these bimolecular systems being treated as single molecules. The intermolecular interaction energy was calculated as a function of intermolecular distance. Stable complex formation with a reasonable stabilization energy was predicted in the ammonia–I_2 system. It was predicted in the benzene–I_2 system for the axial model, but not for the resting model. However, the stabilization energy for the former was found to be too large. No stable conformation was found in the case of the benzene–TCNE system.

The concept of charge-transfer interaction between donor and acceptor in a molecular complex has been well established, but several problems concerning molecular complexes remain unclarified. The charge-transfer force has been considered to be of primary importance in stabilizing molecular complexes, and the conformations of complexes have often been discussed on the basis of the charge-transfer theory. However, several authors have pointed out the possibility that Coulomb and polarization forces play an important role in the complex formation.[1–4)]

The intermolecular interaction has been treated most frequently by means of perturbation theory. However, in order to give quantitative prediction, an approach based on the molecular orbital method seems to have several advantages for carrying out numerical calculations. On the π-π complexes which involve polycyclic aromatic hydrocarbons as donor and tetracyanoethylene (TCNE) as acceptor, we have shown that their electronic spectra can be predicted by semi-empirical SCF–MO–CI calculations within the framework of the π-electron approximation by treating the bimolecular system as a single molecule.[5)] However, in order to discuss the stabilization energy of a complex, this method seems inadequate since the contribution of σ- and/or n-electrons might not be negligible even in a typical π-π complex.

Wold[6)] carried out an extended Hückel calculation on the benzene–TCNE complex, but failed to find any stable conformation. In the CNDO/2 calculation of the same complex, Chesnut and Wormer[7)] predicted an extraordinarily deep potential minimum at an unreasonably short intermolecular distance.

As compared with the CNDO/2 method, the MINDO/2 method proposed by Bodor *et al.*[8)] often gives better predictions as regards the heat of formations and ionization energies, at least, for relatively small organic molecules. The present paper reports on the results of MINDO/2 calculations of the ammonia–I_2, benzene–I_2, and benzene–TCNE systems. The purpose of this study is to elucidate the applicability and limitation of this type of calculation for studying the interaction between donor and acceptor molecules.

Method of Calculation

The MINDO/2 calculation was performed on a bimolecular system by the treatment as a single molecule. All empirical parameters except those related to the iodine atom were taken as proposed by Dewar and his collaborators.[8,9)] For the iodine atom, we took only the 5s and 5p orbitals into account and determined the empirical parameters. For the CNDO/2 calculation, Whitehead[10)] gave the core energies of 5s and 5p orbitals, U_{ss} and U_{pp}, and the one center Coulomb integral, F^0 for the iodine atom. We adopted these values with a slight modification. The one center exchange integral and electron repulsion integral can be expressed in terms of the Slater-Condon parameters, F^2 and G^1. The values of the Slater-Condon parameters have been given by Pople *et al.*[11)] for the fluorine atom, but not for the iodine atom. The empirical values of F^2 and G^1 are usually estimated by means of spectroscopic data, but no such data were available for iodine. We therefore determined the empirical values of F^2 and G^1 of iodine in the following manner. F^2 and G^1 were first calculated non-empirically for the iodine and fluorine atoms by use of the Slater orbitals with the orbital exponents 1.90 and 2.60 for iodine and fluorine, respectively. The empirical values for iodine were then estimated so that their ratios to the non-empirical values are the same as the corresponding ratios in the fluorine atom. The ionization energy of the iodine 5s orbital was estimated by means of the equation given by Dewar *et al.*,[9)] while the observed first ionization energy of the iodine atom was taken to be the 5p ionization energy. The iodine parameters thus obtained are listed in Table 1.

TABLE 1. ATOMIC PARAMETERS OF IODINE

U_{ss}	-76.905(eV),	U_{pp}	-67.202(eV)
F^0	9.448(eV),	F^2	4.077(eV)
G^1	6.526(eV),		
I_s	-26.743(eV),	I_p	-10.454(eV)
neutral atom energy			-305.010(eV)
ΔH_f for free atom			33.412(kcal)
Slater exponent			1.90

In MINDO/2 calculations, the following relation is assumed for the resonance integral:

$$\beta_{ij} = B_{ij} \times (I_i+I_j) \times S_{ij}, \qquad (1)$$

where I_i and I_j are the ionization energies of the orbitals concerned, S_{ij} is the overlap integral, and B_{ij} is an empirical parameter. Ohno's approximation[12)] is used for the electron repulsion integral γ_{mn}, and the core-core repulsion integral CR_{mn} is estimated by means of the following equation,

$$CR_{mn} = \gamma_{mn} + (Z_m Z_n e^2/r_{mn} - \gamma_{mn})e^{-\alpha r_{mn}}, \qquad (2)$$

where Z_m and Z_n are the core charges, r_{mn} is the distance between atoms m and n, and α is an empirical parameter.[13] Parameters B_{ij} and α are both characteristic of the kinds of atoms concerned. Their values had to be estimated for cases which involve iodine. We determined them by using I_2, HI, CH_3I, and ICN as the reference molecules so that the calculated heat of formations, equilibrium bond lengths and dipole moments of these molecules are in good agreement with the experimental values. The values of B_{ij} and α thus determined are listed in Table 2.

TABLE 2. PARAMETERS α and B_{ij} FOR IODINE

	I–H	I–C	I–N	I–I
α	0.78	1.403	1.22	0.40
B	0.60	0.52	0.58	0.88

The calculations were carried out for the bimolecular systems and for each constituent molecule. The intermolecular interaction energy ΔE was estimated by taking the difference between the total energy of the bimolecular system and the sum of the total energies of the isolated molecules.

The calculations were performed with a HITAC 5020E computer at the Computer Centre, the University of Tokyo, with our program.

Results and Discussion

Ammonia–I_2 Complex (n-σ type). As a typical example of n-σ complexes, we examined in detail the ammonia–I_2 system. We assumed a model (Fig. 1) in which the iodine molecule lies on the three-fold axis of the ammonia molecule, taking only the I–I distance, l, and N···I distance, z, as the variables specifying the conformation of the system. The bond distances and bond angles within the NH_3 moiety were fixed to be the same as those in the free ammonia molecule.[14]

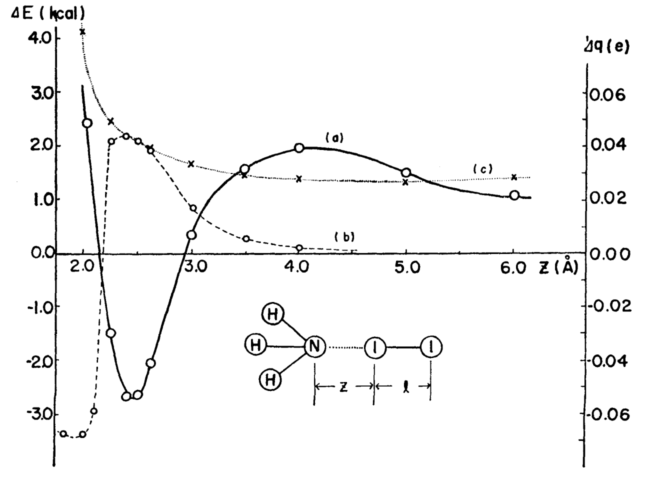


Fig. 1. Intermolecular interaction energy ΔE (a), net amount of charge transfer from NH_3 to I_2 Δq (b), and the decrease of the charge at N atom of ammonia, $-\Delta q_N$, (c) of the ammonia-iodine system as a function of the intermolecular separation, z(Å).

Although the actual structure of the ammonia–I_2 complex is not known, it should resemble the structure of the triethylamine–I_2 complex, where the I–I and N···I distances have been determined to be 2.83 and 2.27 Å respectively, from crystal structure data.[15] Thus we first carried out calculations for various z values assuming that l=2.8 Å. The results are shown in Fig. 1. On decreasing z from infinite, ΔE gradually increases and reaches a very broad maximum around 4 Å, and shows a well-defined minimum at z=2.5 Å with ΔE=−2.75 kcal/mol. Although the general shape of this energy curve is reasonable, the appearance of the repulsive region at z>3 Å is unexpected. A similar phenomenon appears also in other complexes. This seems to be a problem inherent to the present method of calculation.

Figure 1 also shows the net amount of charge transfer Δq, from ammonia to the iodine molecule, together with the decrease of the charge at N atom, $-\Delta q_N$, caused by the intermolecular interaction. While $-\Delta q_N$ is always positive and increases with decreasing N···I distance, the net amount of charge transfer shows a maximum at the distance corresponding to the minimum of the ΔE curve, and becomes negative in the region z<2.2 Å. This means that, at a short intermolecular distance, electron is transferred from iodine to ammonia, which results in the increase of the electron density at H atoms.

We next looked for the ΔE minimum by varying both l and z values. A minimum was found at z= 2.45 Å and l=2.67 Å, where ΔE was −7.5 kcal/mol. This seems to correspond to the stable conformation of the ammonia–I_2 complex. Figure 2 shows the dependence of ΔE and Δq on the I–I distance, for z= 2.45 Å. Since the lowest vacant orbital of the iodine molecule is an anitibonding σ-orbital, we can expect the I–I distance to increase with the amount of charge transfer. The relation between Δq and l shown in Fig. 2 is consistent with this expectation. The I–I distance in the free iodine molecule is 2.667 Å, while it is 2.83 Å in the triethylamin–I_2 complex, indicating

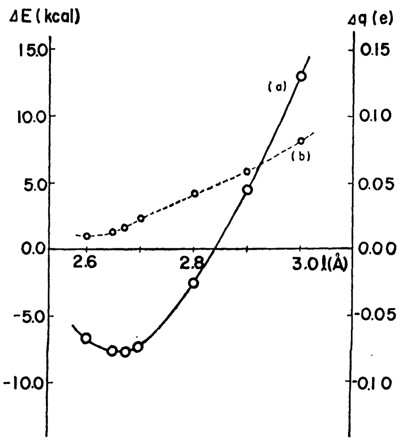


Fig. 2. Intermolecular interaction energy ΔE (a), and net amount of charge transfer Δq (b) of ammonia-iodine system as a function of the bond length of the iodine molecule, l(Å).

a relatively large charge transfer. As compared with the observed I–I distance in the triethylamine–I_2 complex, the l value 2.67 Å at the predicted ΔE minimum seems to be a little too small.

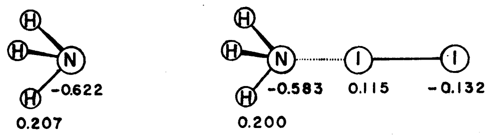
The heat of formation, dipole moment and other properties calculated for the predicted conformation of the ammonia–I_2 complex are summarized in Table 3 together with the corresponding experimental values. The calculated dipole moment is in reasonable agreement with the observed one. However, the amount of charge transfer, 1.8×10^{-2} electron, is quite small as compared with the ionic character of the complex estimated from the dipole moment by the conventional procedure without giving any allowance for the polarization effect.[16)]

Table 3. Comparison of the calculated and experimental values of NH_3–I_2 complex

	Calcd	Exptl
μ(Debye)	4.5	6.1∼6.7[a)]
$-\Delta E$(kcal/mol)	7.5	4.84[b)]
Δq(e)	0.018	
z(Å)	2.45	
l(Å)	2.67	

a) Ref. 16. b) Ref. 25.

The calculated charge density for the stable conformation of the complex as well as for the ammonia molecule is shown in Fig. 3. As compared with the results of the calculation on the free molecule, the electron density in the complex is smaller by 0.039 at N atom, but larger by 0.007 at each H atom. A significant change is found in the I_2 part, where the density at the I atom directly contacting the N atom of ammonia decreases by 0.115, on the other hand, the density at the other I atom increases by 0.132. This means that a considerably large dipole moment has been induced in the I_2 molecule, making a significant contribution to the dipole moment of the complex.



(a) free ammonia (b) ammonia-iodine complex

Fig. 3. Net charges of free ammonia (a) and the ammonia–iodine complex at the most stable configuration (b).

Several authors have recently pointed out the importance of the induced polarization in the observed dipole moments of molecular complexes.[1–3,17)] The results of our calculation support the view.

Since the amount of charge transfer was calculated to be quite small, it seems of interest to examine the contribution of charge transfer in the stabilization energy of the complex. We estimated the contributions of different types of interaction by means of the approximations described in the Appendix, and found that the attraction energy due to the charge-transfer force is of primary importance for stabilizing the complex. The orbital energies of the molecular orbitals of the ammonia and iodine molecules are given in Table 4, and the contributions of different charge-transfer configurations to the intermolecular attraction energy in Table 5. The charge transfer from the highest occupied orbital of ammonia to the lowest vacant orbital of iodine makes the largest contribution, but there is an almost comparable contribution of a charge transfer from a deeper occupied orbital of ammonia. It should be noted that the contributions of back charge transfer are also quite significant.

Table 4. Energies of molecular orbitals

orbital	energy(eV)	orbital	energy(eV)
NH_3		C_6H_6[a)]	
2e	4.91	$5e_2$	4.08
$3a_1$	3.21	$4e_1$	2.88
		4b(π)	2.66
$2a_1$	−10.45	4a	2.33
1e	−13.99	$4e_2$	2.19
$1a_1$	−35.58	3b	1.38
		$3e_2$(π)	0.42
I_2		$3e_1$(π)	−9.57
3a	0.26	$2e_2$	−10.01
		2b	−12.20
3s	−8.97	$2e_1$	−12.88
2a(π)	−12.1	3a(π)	−13.33
2s(π)	−15.4	1b	−14.82
1a	−25.6	2a	−17.61
1s	−36.8	$1e_2$	−20.67
		$1e_1$	−29.24
		1a	−38.53

a) Some higher orbitals less significant in the CT interaction have been omitted.

Table 5. Contribution of each component to the charge-transfer stabilization energy for NH_3–I_2 complex[a)]

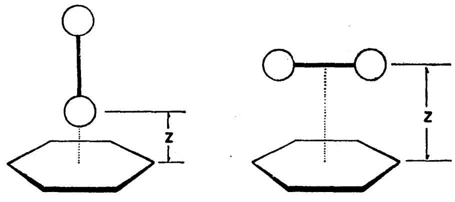
Donation			Back donation		
NH_3	I_2	energy(eV)	I_2	NH_3	energy(eV)
$2a_1$ →	3a	0.997	3s →	$3a_1$	0.425
1e →	3a	0.0	1a →	$3a_1$	0.098
$1a_1$ →	3a	0.601	1s →	$3a_1$	0.165
			2a(π) →	2e	0.010
			2s(π) →	2e	0.006

a) Only the important components are listed in this table.

From the results of energy analysis described above, we can conclude that the prime effect in the ammonia–I_2 complex, *viz.*, stabilization of the system, is the charge-transfer force, but the net amount of charge transfer is small because of the significant contribution of the charge transfer from occupied orbitals of iodine to vacant orbitals of ammonia.

Benzene–I_2 Complex (π-σ type). For the benzene–I_2 complex, Mulliken[18)] first proposed the resting model where the iodine molecule lies parallel to the benzene molecule. The model was considered doubtful from the analysis of infrared spectrum of the complex, which seemed to support the axial or oblique model.[19)] However, it was realized later that the infrared spectrum does not provide any definite conclusion as regards the conformation of the benzene–I_2 complex.[20–22] In the crystals of the benzene–halogen complexes, the halogen molecules are oriented perpendicular to the molecular plane of benzene,[23] but the conformation of an isolated complex is not necessarily the same as the one found in the crystal of the molecular complex. Thus the actual conformation of the benzene–I_2 complex still remains unclarified.

We examined two models, axial and resting, in the present calculation (Fig. 4). Assuming the geometries of the benzene and iodine molecules to be the same as those of the free molecules, we varied the intermolecular distance z which is defined in Fig. 4.



(a) (b)

Fig. 4. Two models for the benzene–iodine complex: (a) axial model, (b) resting model.

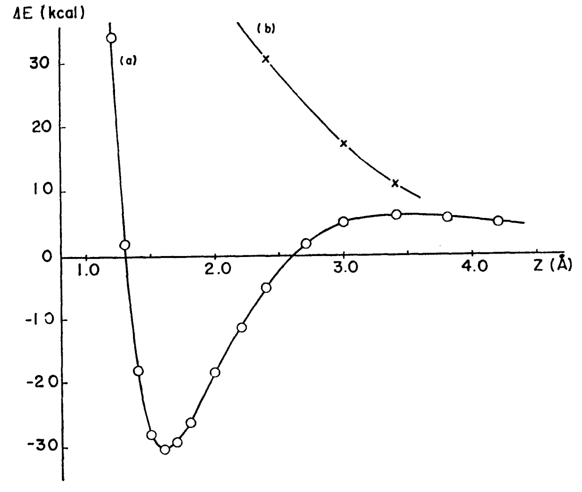


Fig. 5. Intermolecular interaction energy ΔE of the benzene-iodine system as a function of the intermolecular separation, z(Å).

The calculated ΔE is plotted against z in Fig. 5. The results indicate that the axial model is more stable than the resting model. It is also to be noted that a well-defined energy minimum is predicted in the former but not in the latter. The axial model is plausible for the benzene–I_2 complex. Quantitatively, however, our results confront serious problems. The z value at the energy minimum, 1.7 Å, is unreasonably short for the intermolecular separation between benzene and iodine, and the stabilization energy of the complex is predicted to be too large. The net amount of charge transfer from benzene to iodine is calculated to be -3.21×10^{-1} electron for the conformation corresponding to the energy minimum. This means that a considerable amount of charge is transferred from iodine to benzene and not from benzene to iodine, which is unreasonable. Thus it is hard to take the conformation at the ΔE minimum as the real structure of the benzene–I_2 complex.

The z-value dependence of the amount of charge transfer and dipole moment of the system is shown in Fig. 6. Δq is positive in the region $z>2.1$ Å, which first increases on decreasing z, reaches a maximum value, 3.72×10^{-2} electron, at $z=2.5$ Å, then steeply decreases to change its sign. The actual value of z for the axial model would be about 3.4 Å. Although the intermolecular interaction at this value is predicted to be repulsive, it seems worthwhile to examine the properties predicted for the conformation. The calculated dipole moment is 0.34 Debye, which is approximately one fifth of the observed value.[24] Even so, the ionic character of the complex corresponding to this calculated value of the dipole moment will be estimated as about 1.5%, if this dipole moment is attributed entirely to the charge transfer, but the amount of charge transfer actually obtained from the predicted electron densities is only 5.77×10^{-3} electron. The electron density is 6.994 at the iodine atom which is in direct contact with benzene, and 7.009 at the other iodine atom. This implies that a considerable polarization has been induced in the iodine molecule, which is of primary importance in the predicted dipole moment. The situation is more or less similar for other intermolecular distances.

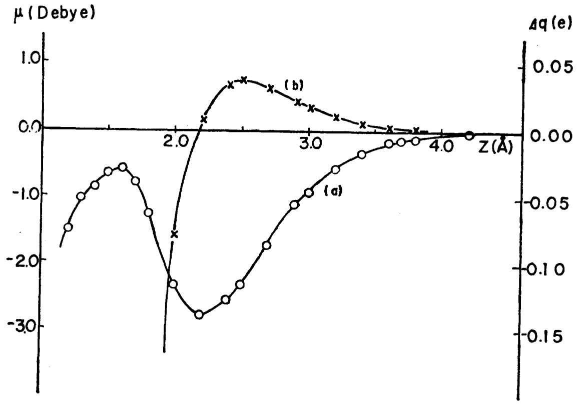


Fig. 6. Dipole moment μ (a) and net amount of charge transfer Δq from benzene to iodine (b) of the benzene-iodine complex as a function of z(Å).

The orbital energies of benzene and iodine are listed in Table 4. We estimated the contributions of various charge transfers for ΔE in the case of the conformation with $z=3.4$ Å. The results are shown in Table 6. One can see that the charge transfer from a lower π-orbital, $3a(\pi)$, of benzene to the lowest vacant orbital, $3a$, of iodine is of primary importance.

Benzene-TCNE Complex (π-π type). As an example of π-π complex we chosed the benzene–TCNE system. We assumed that the molecular planes of benzene and TCNE are parallel to each other, the center of the TCNE molecule being on the six-fold axis of benzene. The calculated interaction energy ΔE is plotted against the intermolecular distance z in Fig. 7.

Table 6. Contribution of each component to the charge-transfer stabilization energy for C_6H_6–I_2 complex[a)]

Donation			Back donation		
C_6H_6	I_2	energy(eV)	I_2	C_6H_6	energy(eV)
$3e_1(\pi)$ →	3a	0.0	3s	→ 4a	0.258
$3a(\pi)$ →	3a	4.193	1a	→ 4a	2.181
2a →	3a	0.355	1s	→ 4a	0.098
1a →	3a	0.765	$2a(\pi)$	→ $4e_1$	0.315
			$2s(\pi)$	→ $4e_1$	0.139
			$2a(\pi)$	→ $5e_2$	0.0
			$2s(\pi)$	→ $5e_2$	0.257

a) Only the important components are listed in this table.

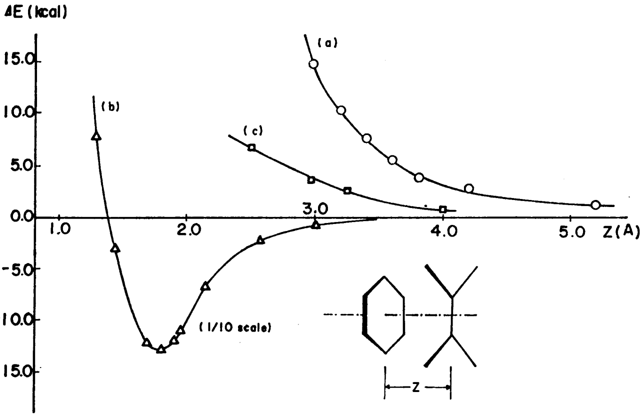


Fig. 7. Intermolecular interaction energy ΔE of the benzene–TCNE system from various methods. (a) MINDO/2 method in this work, (b) CNDO/2 method from Ref. 7, (c) extended Hückel method from Ref. 6.

The interaction between benzene and TCNE was predicted to be always repulsive. This result is quite different from that of the CNDO/2 calculation by Chesnut and Wormer,[7)] and resembles the result of the extended Hückel calculation by Wold.[6)]

We performed calculations on some other π-π complexes, but again failed to predict any stable conformation. Seemingly, the MINDO/2 calculation cannot give satisfactory results for a system consisting of weakly interacting π-donor and π-acceptor.

Conclusion

In the present study, we carried out MINDO/2 calculations on bimolecular systems composed of an electron donor and an electron acceptor. The calculation gave satisfactory results in the case of the ammonia–I_2 system, and succeeded in predicting the formation of a stable ammonia–I_2 complex. The dipole moment and other properties calculated for the predicted conformation of the complex were in reasonable agreement with the experimental results. The calculation was less successful for the benzene–I_2 system, where an unreasonably small intermolecular distance was predicted as the most stable conformation of the system. In the case of the benzene-TCNE system, the calculation completely failed to predict the formation of a stable complex.

Parametrization of MINDO/2 has been carried out for application on relatively small molecules. It gives good prediction as regards the heat of formation and ionization energy of various organic molecules, but it is not always suitable for calculations on a bimolecular system.

In MINDO/2 as well as in CNDO/2, the Slater atomic orbitals are used as the basis set with the Slater-Zener orbital exponents. This may be sufficient in calculations of small molecules, but not in those of bimolecular systems where the integrals between atoms with relatively large interatomic distance have significant contributions. This situation might not be so important for the ammonia–I_2 system, but seems to be of prime importance for the benzene–TCNE system.

While the MINDO/2 calculation fails to predict the stabilization of the benzene–TCNE complex, the CNDO/2 calculation gives an unreasonably large stabilization energy for the same complex. When we compare the two methods, the resonance integrals between the 2p orbitals of two carbon atoms are estimated to be more than twice as large in the CNDO/2 method as in the MINDO/2 method. As is known, the resonance integral between atoms with a large interatomic distance is usually markedly underestimated when the Slater AO's are used as the basis set. This can be improved by the use of the SCF-AO's. A possible way for the improvement of calculations on bimolecular systems, is to perform parametrization by use of the SCF-AO's as the basis set.

Appendix

In a molecular orbital approach on a bimolecular system, the physical nature of the intermolecular interaction cannot be understood straightfowardly. We will show an approximate way to separate the contributions of different types of interaction.

Let us express the Fock matrix of a bimolecular system composed of molecules A and B as follows.

$$\mathbf{F} = \begin{vmatrix} \mathbf{A}+\mathbf{A}' & \mathbf{C} \\ {}^t\mathbf{C} & \mathbf{B}+\mathbf{B}' \end{vmatrix} \tag{1}$$

where **A** and **B** are the SCF Fock matrices of the isolated molecules, **A′** and **B′** the perturbation matrices, **C** is the interaction matrix and ${}^t\mathbf{C}$ the transposed matrix of **C**. The molecular orbital approach on the bimolecular system is to solve

$$\mathbf{FX} = \varepsilon\mathbf{X} \tag{2}$$

Any eigenvector **X** can be expressed in terms of the eigenvectors of **A** and **B** matrices as follows.

$$\mathbf{X} = \sum_{i=1}^{n} a_i \begin{bmatrix} \mathbf{a}_i \\ \mathbf{O} \end{bmatrix} + \sum_{j=1}^{m} b_j \begin{bmatrix} \mathbf{O} \\ \mathbf{b}_j \end{bmatrix} \tag{3}$$

where $\mathbf{a}_i$ $(i=1, 2, \cdots, n)$ and $\mathbf{b}_j$ $(j=1, 2, \cdots, m)$ are the eigenvectors of **A** and **B** matrices, respectively, and **O** and **O′** zero vectors of m and n rows, respectively.

Substituting Eqs. (1) and (3) into Eq. (2), we obtain

$$\begin{bmatrix} (\mathbf{A}+\mathbf{A})\sum_i a_i\mathbf{a}_i + \mathbf{C}\sum_j b_j\mathbf{b}_j \\ {}^t\mathbf{C}\sum_i a_i\mathbf{a}_i + (\mathbf{B}+\mathbf{B}')\sum_j b_j\mathbf{b}_j \end{bmatrix} = \varepsilon \begin{bmatrix} \sum_i a_i\mathbf{a}_i \\ \sum_j b_j\mathbf{b}_j \end{bmatrix} \tag{4}$$

from which the following equation can be derived.

$$\sum_i(\alpha_i-\varepsilon+\mathbf{A}')a_i\mathbf{a}_i + \mathbf{C}\sum_j b_j\mathbf{b}_j = 0 \tag{5}$$

and

$$^t\mathbf{C}\sum_i a_i\mathbf{a}_i + \sum_j(\beta_j-\varepsilon+\mathbf{B}')b_j\mathbf{b}_j = 0 \tag{6}$$

where α_i's are the eigenvalues of **A** matrix, and β_i's those of **B** matrix. Premultiplying Eq. (5) by $\mathbf{a}_k$ and Eq. (6) by $\mathbf{b}_l$, we get the following equations.

$$(\alpha_k-\varepsilon)a_k + \sum_i a_i\langle\mathbf{a}_k|\mathbf{A}'|\mathbf{a}_i\rangle + \sum_j b_j\langle\mathbf{a}_k|\mathbf{C}|\mathbf{b}_j\rangle = 0 \tag{7}$$

and

$$\sum_i a_i\langle\mathbf{b}_l|\mathbf{C}|\mathbf{a}_i\rangle + (\beta_l-\varepsilon)b_l + \sum_j b_j\langle\mathbf{b}_l|\mathbf{B}'|\mathbf{b}_j\rangle = 0 \tag{8}$$

These equations are reduced to the secular equation given below.

$$\left|\begin{array}{cccc:cccc}
\alpha_1-\varepsilon+A'_{11} & A'_{12} & \cdots & A'_{1n} & C_{11} & C_{12} & \cdots & C_{1m} \\
A'_{21} & \alpha_2-\varepsilon+A'_{22} & & \vdots & \vdots & C_{22} & & \vdots \\
\vdots & \vdots & & & & & & \\
A_{n1} & \cdots & \cdots & \alpha_n-\varepsilon+A'_{nn} & C_{n1} & \cdots & \cdots & C_{nm} \\
\hdashline
C_{11} & C_{12} & \cdots & C_{1n} & \beta_1-\varepsilon+B'_{11} & \cdots & \cdots & B'_{1m} \\
\vdots & C_{22} & & \vdots & B'_{21} & & & \vdots \\
\vdots & \vdots & & & \vdots & & & \\
C_{m1} & \cdots & \cdots & C_{mn} & B'_{m1} & \cdots & \cdots & \beta_m-\varepsilon+B'_{mm}
\end{array}\right| = 0 \tag{9}$$

where $A'_{ik}=\langle\mathbf{a}_i|\mathbf{A}'|\mathbf{a}_k\rangle$, $B'_{il}=\langle\mathbf{b}_i|\mathbf{B}'|\mathbf{b}_l\rangle$, and $C_{ij}=\langle\mathbf{a}_j|\mathbf{C}|\mathbf{b}_j\rangle$. This is exactly the same as the secular equation which we have to solve in the molecular orbital calculation on the bimolecular system. When the interaction matrix **C** and the perturbation matrices **A**$'$ and **B**$'$ are sufficiently small, the solutions of Eq. (9) can be approximately given by the perturbation method as follows.

$$\varepsilon_i = \alpha_i + A'_{ii} + \sum_{k\neq i}\frac{A'^2_{ik}}{\alpha_i-\alpha_k} + \sum_j\frac{C_{ij}{}^2}{\alpha_i-\beta_j} + \cdots \tag{10}$$

and

$$\varepsilon_j = \beta_j + B'_{jj} + \sum_k\frac{C_{jk}{}^2}{\beta_j-\alpha_k} + \sum_{l\neq j}\frac{B'^2_{jl}}{\beta_j-\beta_l} + \cdots \tag{11}$$

where we have neglected higher order terms. The total energy of a closed-shell molecule is

$$E = 2\sum_i^{\text{occ}}\varepsilon_i - \sum_{i,j}^{\text{occ}}(2J_{ij}-K_{ij}) + \sum_{n,m}CR_{nm} \tag{12}$$

where J_{ij} is the Coulomb integral, K_{ij} the exchange integral, and $\sum_{n,m}CR_{nm}$ the sum of the core repulsion energy. Thus the intermolecular interaction energy $\varDelta E$, defined as the difference between the total energy of the bimolecular system and the sum of the total energies of the constituent molecules, can be expressed as follows.

$$\begin{aligned}\varDelta E = {} & [2\sum_{i(\mathrm{A})}^{\text{occ}}A'_{ii}+2\sum_{j(\mathrm{B})}^{\text{occ}}B'_{jj}-\sum_{i,j(\mathrm{A-B})}^{\text{occ}}(2J_{ij}-K_{ij}) \\
& +\sum_{i,i'(\mathrm{A})}^{\text{occ}}(2J_{ii'}-K_{ii'})+\sum_{l,l'(\mathrm{B})}^{\text{occ}}(2J_{ll'}-K_{ll'})+\sum_{n(\mathrm{A})}\sum_{m(\mathrm{B})}CR_{nm}] \\
& + 2\left[\sum_{i(\mathrm{A})}^{\text{occ}}\sum_{k(\mathrm{A})}^{\text{vac}}\frac{A'^2_{ik}}{\alpha_i-\alpha_k}+\sum_{j(\mathrm{B})}^{\text{occ}}\sum_{l(\mathrm{B})}^{\text{vac}}\frac{B'^2_{jl}}{\beta_j-\beta_l}\right] \\
& + 2\left[\sum_{i(\mathrm{A})}^{\text{occ}}\sum_{l(\mathrm{B})}^{\text{vac}}\frac{C_{il}{}^2}{\alpha_i-\beta_l}+\sum_{j(\mathrm{B})}^{\text{occ}}\sum_{k(\mathrm{A})}^{\text{vac}}\frac{C_{jk}{}^2}{\beta_j-\beta_k}\right]\end{aligned} \tag{13}$$

where $\sum_{i(\mathrm{A})}^{\text{occ}}$ stands for the summation over all occupied orbitals of the molecule A, and $\sum_{j(\mathrm{B})}^{\text{occ}}$ the corresponding summation for the molecule B. Roughly speaking, the terms in the first brackets give the contribution of the Coulomb and core repulsion energies, those in the second brackets give that of the induction energy and dispersion force, and those in the last brackets correspond to the charge transfer force. All of the integrals in Eq. (13) can be easily evaluated. As an example, C_{il} can be expressed as follows.

$$C_{il} = \sum_{r,s}a_{ir}b_{ls}F_{rs} \tag{14}$$

where a_{ir} is the coefficient of the atomic orbital r in the i-th molecular orbital of molecule A, b_{ls} the coefficient of the atomic orbital s in the l-th molecular orbital of molecule B, and F_{rs} is the element of the Fock matrix, which is given as follows in the MINDO/2 method.

$$F_{rs} = \beta_{rs} - \frac{1}{2}P_{rs}\gamma_{nm}$$

Thus, we can estimate the contribution of a charge-transfer configuration, CT($i\rightarrow l$),

$$\varDelta E_{\mathrm{CT}(i\rightarrow l)} = \frac{C_{il}{}^2}{\alpha_i-\beta_l}$$

by using the results of the molecular orbital calculations of the bimolecular system and those of the isolated molecules.

References

1) M. W. Hanna, *J. Amer. Chem. Soc.*, **90**, 285 (1968).

2) J. L. Lippert, M. W. Hanna, and P. J. Trotter, *ibid.*, **91**, 4035 (1969).

3) M. J. S. Dewar and C. C. Thompson Jr., *Tetrahedron, Suppl.*, **7**, 97 (1966).

4) W. C. Herndon and J. Feuer, *J. Amer. Chem. Soc.* **90**, 5914 (1968).

5) T. Ohta, H. Kuroda, and T. L. Kunii, *Theoret. Chim. Acta*, **19**, 167 (1970).

6) S. Wold, *Acta Chem. Scand.*, **20**, 2379 (1966).

7) D. B. Chesnut and P. E. Wormer, *Theoret. Chim. Acta*, **20**, 250 (1971).

8) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 3854 (1970).

9) N. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1269 (1969).

10) M. A. Whitehead, "Sigma Molecular Orbital Theory," ed. by O. Sinanoglu and K. B. Wiberg, Yale University Press, New Haven and London (1970), p. 50.

11) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

12) K. Ohno, Y. Tanabe, and F. Sasaki, *Theoret. Chim. Acta*, **1**, 378 (1963).

13) M. J. S. Dewar and G. Klopman, *J. Amer. Chem. Soc.*, **89**, 3089 (1967).

14) A. Almeningen and O. Bastiansen, *Acta Chem. Scand.*, **9**, 815 (1955).

15) O. K. Stroemme, *ibid.*, **15**, 407 (1961).

16) S. Kobinata and S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 3905 (1966).

17) M. Manitone, *Theoret. Chim. Acta*, **11**, 119 (1968).

18) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).

19) E. E. Ferguson, *J. Chem. Phys.*, **25**, 577 (1956), **26**, 1357 (1957), *Spectrochim. Acta*, **10**, 123 (1957).

20) J. Collin and L. D'or, *J. Chem. Phys.*, **23**, 397 (1955).

21) E. E. Ferguson and F. A. Matsen, *J. Amer. Chem. Soc.*, **82**, 29 (1960).

22) H. B. Friedrich and W. B. Person, *J. Chem. Phys.*, **44**, 2161 (1966).

23) O. Hassel and K. O. Stroemme, *Acta Chem. Scand.*, **12**, 1146 (1958), **13**, 1781 (1959).

24) G. Kortüm and H. Walz, *Z. Elektrochem.*, **57**, 73 (1953).

25) H. Yada, J. Tanaka, and S. Nagakura, This Bulletin, **33**, 1660 (1960).