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The Intermolecular Potential of Hydrocarbon Dimers as Examined by the Perturbation Theory Including Exchange Energy in the PPP Approximation

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By using the perturbation method, including the exchange energy, the interaction potential curves for the intermolecular distances from 2.0 Å to 6.0 Å of the ethylene dimer, the butadiene dimer, the hexatriene dimer, and the benzene dimer were obtained. The matrix elements were evaluated in the Pariser-Parr-Pople approximation. Reasonable intermolecular potential curves were obtained for all the dimers studied. The analysis of the perturbation energy leads to the conclusion that the induction and dispersion energies and the exchange repulsion energy of the second order in the overlap integral give the potential minimum for the interaction of small molecules, such as ethylene or butadiene dimers, but for large molecules, such as benzene or hexatriene dimers, the exchange repulsion energy of the fourth order in the overlap integral should also be included in order to obtain the potential minimum. An important role of the charge transfer term was suggested for the chemical reaction; this was in agreement with the indications of previous researchers. The calculated depth of the potential minimum and the equilibrium molecular distance are in fairly good agreement with the experimental data.

The calculation of exact intermolecular potential curves for various large molecules is a very important but still unsolved problem. The relative geometries of charge-transfer complexes and the excimer or exciplex, the orientation of molecules in molecular crystals, and the conformation of such biopolymers as proteins and DNA are intimately related to the intermolecular potential energy between the corresponding molecules. Moreover, for the illustration of reaction mechanisms or the calculation of cross sections for the collisions of molecules, the intermolecular potential curves are indispensable.

The approaches to the evaluation of intermolecular force may mainly be classified into two types, according to whether the system is treated as one molecule or as a composite of two molecules. In the former type, variational methods, including configuration interactions or *ab initio* treatments, have been used. However, especially for large molecules, these methods are not reliable, since the contribution of ionic configurations is apt to be excessively included; hence, plausible intermolecular potential curves have been obtained for only small molecules or atoms.[1,2] In the latter, a difficult problem is the evaluation of the exchange repulsion energy, which heretofore has been treated only semi-empirically, when it has been taken into account at all.[3] One approach to this problem is the perturbation theories including exchange energy recently developed

1) G. Das and A. C. Wahl, *J. Chem. Phys.*, **47**, 2934 (1967).
2) G. H. F. Diercksen, *Chem. Phys. Lett.*, **4**, 373 (1969).
3) M. J. Huron and P. Claverie, *ibid.*, **4**, 429 (1969).

by many authors.[4-9] However, these theories have as yet been applied only to sets of small molecules or atoms.[10,11] On the other hand, for large molecules many phenomena have been studied, for example, the Diels-Alder reactions,[12,13] the excimer formations,[14-16] the spectra of the hydrocarbon dimers,[17] the charge-transfer complexes,[18,19] and the stacking energies of nucleic acid's bases.[20] However, in these calculations various types of approximations are employed, that is, the use of the iterative extended Hückel method, or the neglect of exchanges of electrons or a truncation of the expansion by excited levels.

In this paper, the intermolecular energies of the ethylene dimer, butadiene dimers, the hexatriene dimer, and the benzene dimer were calculated using the Pariser-Parr-Pople (PPP) approximation and by means of the perturbation method, including exchange energy, by Murrell *et al.*[4,5] The potential curves thus obtained are found to be reasonable, giving the potential minimum at an appropriate intermolecular distance. From the analysis of each term of the perturbation energy, it was found that the contribution of exchange energy due to the exchanges of two pairs of electrons, which corresponds to the fourth order term in the overlap integral, is very important for the interaction of large molecules.

Moreover, the contributions of the charge-transfer term is rather small for all the dimers studied except for the *trans*-butadiene-*cis*-butadiene dimer at short distances. The fact that this butadiene dimer has a remarkable contribution of the charge-transfer term is very interesting, since this dimer can be considered to become an activated complex of the Diels-Alder reaction. Those results correspond well with those obtained by Fukui and Fujimoto.[21] The comparison of the calculated intermolecular potential and the equilibrium intermolecular distance with those of the experimental data leads to the conclusion that the theoretical method in the present paper gives relatively reliable results.

Method

The perturbation theories recently developed[4-8] for intermolecular potentials including exchange integrals are multifarious in their formulas. This is because nonperturbed wave functions are not linearly independent of each other; hence, the expansion coefficients of these wave functions for an arbitrary function can not be uniquely determined, as has been pointed out by Lekkerkerker and Laidlaw.[9] However, the various formulas give almost the same results for the interaction energy between two atoms.[10,11] In the present paper, the formulas derived by Murrell and Shaw[4] were adopted for calculating all the intermolecular potential energies except for the charge-transfer term. For the charge-transfer term, the formula of Murrell, Randic, and Williams was employed.[5,22] The outline of the perturbation method will be given below.

The Shrödinger equations of the separated molecules, A and B, are:

$$H_A(i)A_r(i) = E_r{}^A A_r(i),$$
$$H_B(j)B_s(j) = E_s{}^B B_s(j). \quad (1)$$

Here, A_r and B_s are wave functions in ground or singly-excited configurations of the A and B molecules respectively.[23] Hereafter, the ground state will be denoted by the suffix '0', *i.e.*, A_0, B_0, *etc.* The Shrödinger equation of the total system is:

$$H\Psi = E\Psi, \quad (2)$$

where:

$$H = H_A(i) + H_B(j) + U,$$

and where U is the interaction potential:

$$U = \sum_s\sum_t e^2/r_{st} - \sum_a\sum_t Z_a{}^A e^2/r_{at} - \sum_b\sum_s Z_b{}^B e^2/r_{sb} + \sum_a\sum_b Z_a{}^A Z_b{}^B/r_{ab}. \quad (3)$$

Here s and t denote electrons in the A and B molecules respectively, and a and b, nuclei or cores in the A and B molecules. Z is the effective charge, and r represents the distance. The wave function of a configuration constituting the total wave function, Ψ, is constructed from the products of the wave functions of the separated molecules, allowing for exchanges of electrons; that is, for the ground state:

$$\Psi = \Psi_0 + \sum_{t\neq 0} b_t \Psi_t, \quad (4)$$

where:

$$\Psi_0 = \mathcal{A}A_0(i)B_0(j), \quad (5)$$
$$\Psi_t = \mathcal{A}A_r(i)B_s(j), \quad (6)$$

4) J. N. Murrell and G. Shaw, *J. Chem. Phys.*, **46**, 1768 (1967).
5) J. N. Murrell, M. Randic, and D. R. Williams, *Proc. Roy. Soc.*, **A284**, 566 (1965).
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7) J. O. Hirschfelder and R. Silbey, *J. Chem. Phys.*, **45**, 2188 (1966).
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15) R. Polak and J. Paldus, *Theoret. Chim. Acta*, **4**, 37 (1966).
16) B. N. Srinivasan, J. V. Russell, and S. P. McGlynn, *J. Chem. Phys.*, **48**, 1931 (1968).
17) A. K. Chandra, *Chem. Phys. Lett.*, **5**, 229 (1970).
18) W. C. Herndon and J. Feuer, *J. Amer. Chem. Soc.*, **90**, 5914 (1968).
19) S. Iwata, J. Tanaka, and S. Nagakura, *ibid.*, **89**, 2813 (1967).
20) R. Rein and M. Pollak, *J. Chem. Phys.*, **47**, 2039 (1967); R. Rein, N. S. Goel, N. Fukuda, M. Pollak, and P. Claverie, *Ann. N. Y. Academy Sci.*, **153**, 805 (1969).
21) K. Fukui and H. Fujimoto, This Bulletin, **41**, 1989 (1968); **42**, 3399 (1969).

22) The charge-transfer term can not be treated together with other locally-excited terms by the perturbation method since the perturbed Hamiltonian for locally-excited terms is different from that for charge-transfer terms. Accordingly, after perturbed wave functions have been obtained for ground and locally-excited configurations, the variational method in which the wave function is represented by a linear combination of charge-transfer and locally-excited configurations (perturbed wave function) should be used. This treatment will give the total wave function for two interacting molecules.

23) Doubly-excited configurations are disregarded since the matrix element between the ground and doubly-excited configurations vanishes.

or:

$$\Psi_t = \mathscr{A}A_k^+(i')B_l^-(j'), \tag{7}$$

where $A_k^+B_l^-$ represents a charge-transfer configuration and where $\mathscr{A}$ is the antisymmetrizing operator, which allows for exchanges of electrons between the i and j sets (or i' and j'); *i.e.*:

$$\mathscr{A} = \{(2n)!(2m)!/(2n+2m)!\}^{1/2}(1+P_{ij}^1+P_{ij}^2+\cdots), \tag{8}$$

where $2n$ and $2m$ are the number of electrons of the i and j sets, respectively. P_{ij}^1 is the operator which exchanges one pair of electrons, accompanied by a change in the sign, while P_{ij}^2 is the one which exchanges two pairs of electrons with no change of the sign, and so on. The total energy for the ground state can be calculated by means of the perturbation method; that is, the substitution of the total energy and the total wave function of Eq. (4) into Eq. (2) yields the following Eqs. (9)—(13):[4,5,9]

$$E^{10} = U_{00}^{10}, \tag{9}$$

$$E^{20} = \sum_{t(\neq 0)} (U_{t0}^{10})^2/(E_0-E_t), \tag{10}$$

$$E^{12} = U_{00}^{12} - S_{00}^{02}U_{00}^{10}, \tag{11}$$

$$E^{22} = \sum_{t(\neq 0)} U_{t0}^{10}(U_{t0}^{12}-S_{t0}^{02}U_{00}^{10})/(E_0-E_t) - S_{00}^{02}E^{20}, \tag{12}$$

$$E^{CT} = \sum_{t(\neq 0)} (U_{t0}^{11}-S_{t0}^{01}U_{00}^{10})^2/(E_0-E_t), \tag{13}$$

where, for convenience, the interaction energies are classified according to the powers of U (the first upper index) and S, *i.e.*, the overlap integral by the electron exchange (the second upper index). E^{10} represents the electrostatic interaction energy between two molecules, A and B; E^{20}, the dispersion and induction energies; E^{12}, the exchange energy of the second order in the overlap integral; E^{22}, the exchange polarization energy, and E^{CT}, the charge-transfer energy. E_0 and E_t are:

$$\begin{aligned} E_0 &= E_0^A + E_0^B \\ E_t &= E_r^A + E_s^B. \end{aligned} \tag{14}$$

The matrix elements are as follows:

$$\begin{aligned} U_{00}^{10} &= \langle A_0(i)B_0(j)\,|\,U\,|\,A_0(i)B_0(j)\rangle, \\ U_{t0}^{10} &= \langle A_r(i)B_s(j)\,|\,U\,|\,A_0(i)B_0(j)\rangle, \\ U_{00}^{12} &= \langle P_{ij}^1A_0(i)B_0(j)\,|\,U\,|\,A_0(i)B_0(j)\rangle, \\ U_{t0}^{12} &= \langle P_{ij}^1A_r(i)B_s(j)\,|\,U\,|\,A_0(i)B_0(j)\rangle, \\ U_{t0}^{11} &= ((2m+1)/2n)^{1/2}\langle A_k^+(i')B_l^-(j')\,|\,U\,|\,A_0(i)B_0(j)\rangle, \\ S_{00}^{02} &= \langle P_{ij}^1A_0(i)B_0(j)\,|\,A_0(i)B_0(j)\rangle, \\ S_{t0}^{02} &= \langle P_{ij}^1A_r(i)B_s(j)\,|\,A_0(i)B_0(j)\rangle, \\ S_{t0}^{01} &= ((2m+1)/2n)^{1/2}\langle A_k^+(i')B_l^-(j')\,|\,A_0(i)B_0(j)\rangle. \end{aligned} \tag{15}$$

As we will show in the latter section, for large molecules the exchange energy up to the second order in the overlap integral, E^{12}, has a negative value at short distances; hence, the potential minimum can not be found. Accordingly we introduce E^{14}, the exchange energy of the 4*th* order in the overlap integral corresponding to the exchanges of two pairs of electrons. According to Murrell and Shaw,[4] the first-order correction for the energy is:

$$E^{(1)} = \langle\psi_0\,|\,U\,|\,\Psi_0\rangle/\langle\psi_0\,|\,\Psi_0\rangle, \tag{16}$$

where Ψ_0 is as given in Eq. (5) and where ψ_0 is:

$$\psi_0 = A_0B_0.$$

The expansion of Eq. (16) up to the 4*th* order in the overlap integral leads to the following formula:

$$\begin{aligned} E^{(1)} &= (U_{00}^{10}+U_{00}^{12}+U_{00}^{14})/(1+S_{00}^{02}+S_{00}^{04}) \\ &= U_{00}^{10} + (U_{00}^{12}-U_{00}^{10}S_{00}^{02}) \\ &\quad + (U_{00}^{14}-U_{00}^{12}S_{00}^{02}-U_{00}^{10}S_{00}^{04}+U_{00}^{10}(S_{00}^{02})^2). \end{aligned}$$

The second term as the right side of the above equation corresponds to E^{12} in Eq. (11), while the last term corresponds to E^{14} *i.e.*, the 4*th*-order term in the overlap integral:

$$E^{14} = U_{00}^{14} - U_{00}^{12}S_{00}^{02} - U_{00}^{10}S_{00}^{04} + U_{00}^{10}(S_{00}^{02})^2), \tag{17}$$

which can be rewritten as Eq. (18) for non-polar molecules since the U_{00}^{10} vanishes:

$$E^{14} = U_{00}^{14} - U_{00}^{12}S_{00}^{02}. \tag{18}$$

The applicability of Eq. (18) to polar molecules was confirmed numerically in the range of the equilibrium distances.

The ground-state wave functions of the separated A and B molecules were assumed to be antisymmetrized molecular orbitals (ASMO's). The coefficients of the atomic orbitals were obtained using the Pariser-Parr-Pople (PPP) method[24] for the π electron system. They can also be obtained by means of other molecular orbital methods such as the CNDO/2 method or *ab initio* calculation. The results by the CNDO/2 method is given in this paper only for the ethylene dimer. The E_t values in Eq. (14) were evaluated as follows: for locally excited configurations,

$$\begin{aligned} E_t &= E_0^A + E_0^B + \varepsilon_k^A - \varepsilon_i^A - J_{ik}^A + 2K_{ik}^A \\ &\quad + \varepsilon_l^B - \varepsilon_j^B - J_{jl}^B + 2K_{jl}^B, \end{aligned} \tag{19}$$

where J and K denote the Coulomb and exchange integrals respectively, and ε, the molecular orbital energies. On the other hand, for charge-transfer configurations,

$$E_t = E_0^A + E_0^B + \varepsilon_l^B - \varepsilon_k^A. \tag{20}$$

Mulliken's approximation was used for the atomic integrals between the different molecules. The two-center electron repulsion integrals (γ) were evaluated using Mataga and Nishimoto's approximation and the nuclear-repulsion potential, $Z_a^AZ_b^B\gamma_{ab}$, in the PPP approximation. The other approximations and parameters used are the same as those in Ref. 25 for the PPP method or in Ref. 26 for the CNDO/2 method. The matrix elements in Eq. (15) are given in terms of molecular orbitals in the Appendix.

Results and Discussion

1. Contribution of Each Term to the Total Interaction Energy. The total intermolecular potential curves in the PPP approximation for the ethylene dimer, the *trans*-butadiene dimer, the *trans*-hexatriene dimer, and the benzene dimer are shown, along with the E^{12}, E^{14},

24) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

25) C. Nagata, A. Imamura, Y. Tagashira, and M. Kodama, This Bulletin, **38**, 1638 (1965).

26) J. A. Pople and G. A. Segal, *J. Chem. Phy .*, **44**, 3289 (1966).

and E^{20} values, in Figs. 1—4. In all these dimers, configurations of the sandwich type are assumed. In Tables 1—3, the values of all the terms are tabulated in more detail. The calculated intermolecular potential curves are reasonable, because the potential curves have a minimum point at an appropriate molecular distance and increase rapidly when two molecules come closer each other. However, the contributions of such terms as E^{10}, E^{20}, E^{12}, and E^{14} to the total energy differ from molecule to molecule. The electrostatic interaction (E^{10}) between two unsaturated hydrocarbons is very small or non-existent. The second-order term, E^{20}, contains the dispersion interaction energy, the dipole-induced dipole interaction energy, and so on. In the case of hydrocarbons, the former is dominant.

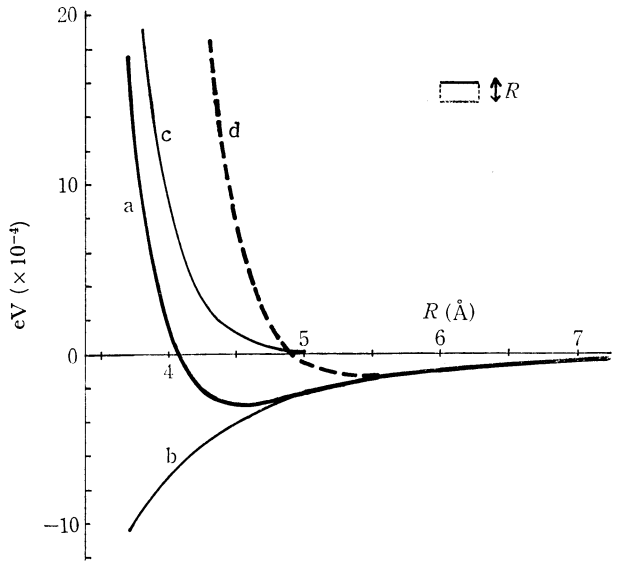

Fig. 1. The interaction energy of the ethylene dimer.
a, total; b, E^{20}; c, E^{12}; d, total in OMAO.

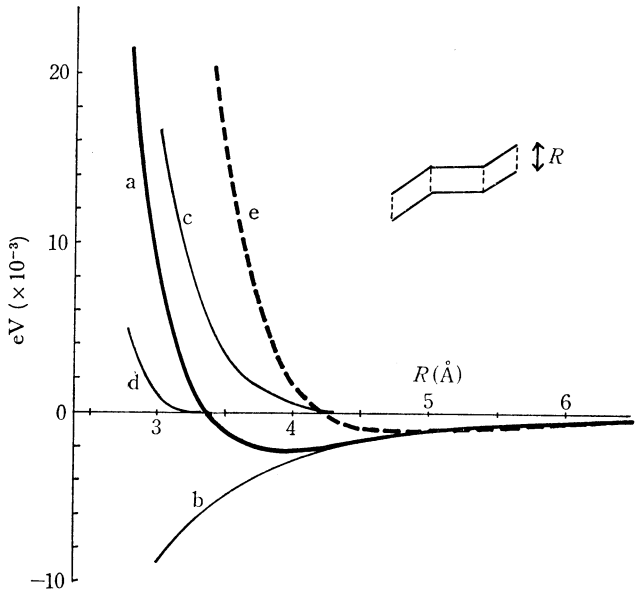

Fig. 2. The interaction energy of the *trans*-butadiene dimer type 1.
a, total; b, E^{20}; c, E^{12}; d, E^{14}; e, total in OMAO.

The magnitude of E^{20} depends upon the sizes of the interacting molecules; that is, this interaction energy is large in magnitude for the benzene dimer, small for the ethylene dimer, and intermediate for the butadiene dimer. The dependence of the magnitude of the dispersion force on the sizes of the molecules may easily be explained by the fact that large molecules have many energy levels. However, this interaction also depends upon the relative orientation between two interacting molecules (see Table 3 and Table 4). At any rate, the dispersion energies stabilize the interacting systems.

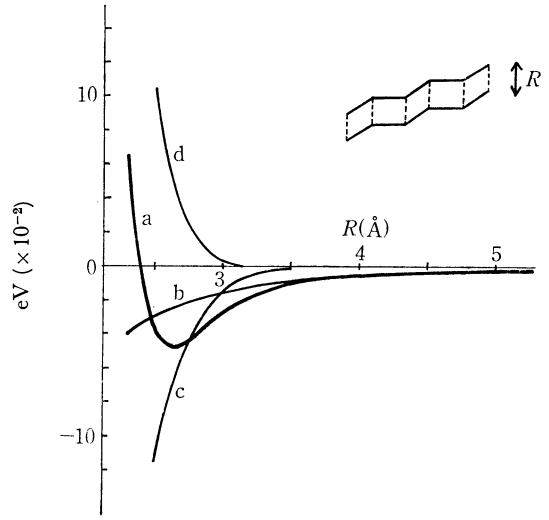

Fig. 3. The interaction energy of the *trans*-hexatriene dimer.
a, total; b, E^{20}; c, E^{12}; d, E^{14}.

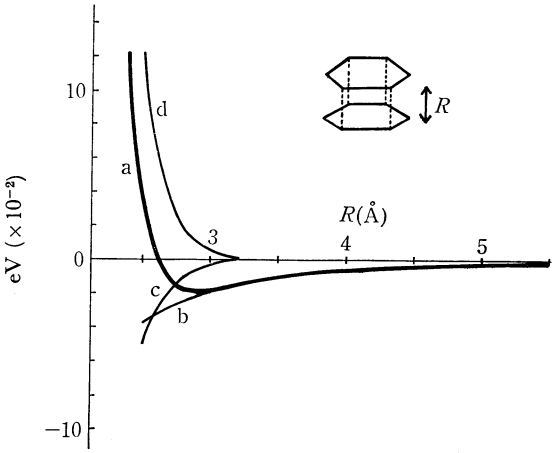

Fig. 4. The interaction energy of the benzene dimer.
a, total; b, E^{20}; c, E^{12}; d, E^{14}.

Table 1. The interaction energies of the ethylene dimer (in eV)

R(Å)	E^{10}	E^{20}	E^{12}	E^{14}	E^{22}	E^{CT}	Total
2.0	0.0	−0.0144	0.4465	0.0478	0.0	0.0	0.4799
3.0	0.0	−0.0027	0.0342	0.0002	0.0	0.0	0.0317
4.0	0.0	−0.0007	0.0009	0.0	0.0	0.0	0.0002
5.0	0.0	−0.0002	0.0	0.0	0.0	0.0	−0.0002
6.0	0.0	−0.0001	0.0	0.0	0.0	0.0	−0.0001

Table 2. The interaction energies of the *trans*-butadiene dimer type 1 (in eV)

R(Å)	E^{10}	E^{20}	E^{12}	E^{14}	E^{22}	E^{CT}	Total
2.0	0.0004	−0.0378	0.0502	0.4356	−0.0012	0.0	0.4472
2.5	0.0003	−0.0174	0.0506	0.0317	0.0	0.0	0.0652
3.0	0.0002	−0.0089	0.0167	0.0011	0.0	0.0	0.0091
4.0	0.0001	−0.0029	0.0006	0.0	0.0	0.0	−0.0022
5.0	0.0	−0.0011	0.0	0.0	0.0	0.0	−0.0011

Table 3. The interaction energies of the benzene dimer (in eV)

R(Å)	E^{10}	E^{20}	E^{12}	E^{14}	E^{22}	E^{CT}	Total
2.0	0.0	−0.0761	−0.3165	1.6435	−0.0092	−0.0	1.2416
2.5	0.0	−0.0377	−0.0503	0.1229	−0.0012	0.0	0.0336
3.0	0.0	−0.0199	−0.0027	0.0043	−0.0002	0.0	−0.0190
4.0	0.0	−0.0064	0.0002	0.0	0.0	0.0	−0.0061
5.0	0.0	−0.0024	0.0	0.0	0.0	0.0	−0.0024

Table 4. The interaction energies of the *trans*-butadiene dimer type 2 (in eV)

R(Å)	E^{10}	E^{20}	E^{12}	E^{14}	E^{22}	E^{CT}	Total
2.0	0.0001	−0.0048	0.0501	0.0619	0.0005	−0.0121	0.0957
3.0	0.0	−0.0014	0.0116	0.0002	0.0	−0.0006	0.0100
4.0	0.0	−0.0005	0.0004	0.0	0.0	−0.0	−0.0
5.0	0.0	−0.0002	0.0	0.0	0.0	0.0	−0.0002
6.0	0.0	−0.0001	0.0	0.0	0.0	0.0	−0.0001

Table 5. The interaction energies of the *trans*-butadiene-*cis*-butadiene dimer (in eV)

R(Å)	E^{10}	E^{20}	E^{12}	E^{14}	E^{22}	E^{CT}	Total
2.0	−0.0	−0.0120	0.0046	0.0097	0.0004	−0.0164	−0.0138
2.5	−0.0	−0.0063	0.0134	0.0013	0.0001	−0.0045	0.0040
3.0	0.0	−0.0035	0.0054	0.0001	0.0	−0.0009	0.0012
4.0	0.0	−0.0012	0.0003	0.0	0.0	−0.0	−0.0010
5.0	0.0	−0.0005	0.0	0.0	0.0	0.0	−0.0005

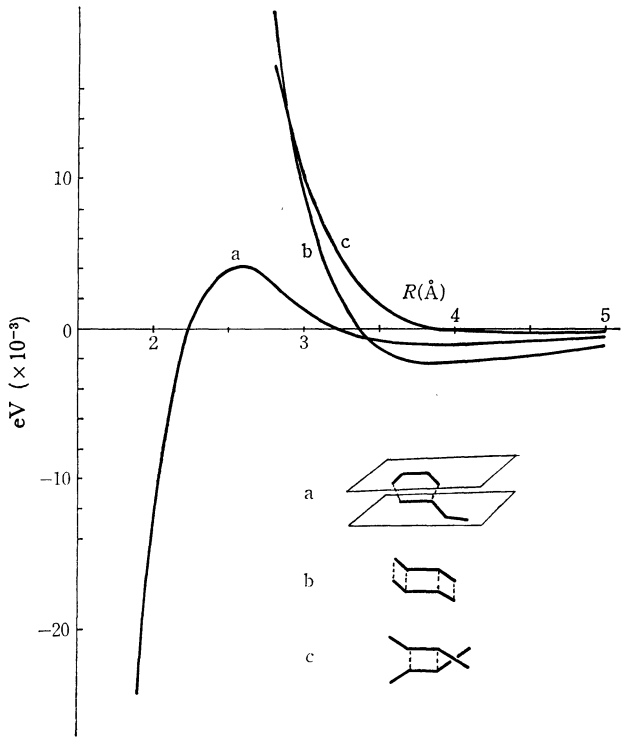

Fig. 5. The interaction energies of the *trans*-butadine-*cis*-butadine dimer (a), the *trans*-butadiene dimer type 1 (b), the *trans*-butadiene dimer type 2 (c).

The contribution of the charge-transfer interaction to the intermolecular potential is negligibly small for hydrocarbon dimers in sandwich-type configuration. On the other hand, the charge-transfer interactions of the *trans*-butadiene dimer in a type-2 configuration (Fig. 5 and Table 4) and of the *trans*-butadiene-*cis*-butadiene dimer (Table 5) are not negligible, especially at short distances. Moreover, among the three butadiene dimers in Fig. 5, only the *trans*-butadiene-*cis*-butadiene dimer has the potential maximum which comes from the remarkable increase in the stabilization energy caused by the charge-transfer interaction, while the other two dimers, the *trans*-butadiene dimer type 1 and type 2, give the increasing potential curves. Although these potential curves at short distances may not be reliable since the contribution of higher-order terms in the perturbation expansion and that of σ-electrons should be taken into account, these features of the potential curves can explain well the fact that the *trans*-butadiene-*cis*-butadiene dimer can bring about a Diels-Alder reaction, while the other two dimers can not. A similar approach to the chemical reaction by making use of the perturbation method has already been made by Fukui *et al.*,[21] emphasizing the importance of the charge-transfer interaction (delocalization interaction in Fukui's nomenclature). Our results are in complete agreement with theirs.

The other terms which depend upon the magnitude

of the overlap integral are the exchange interaction terms, E^{12}, E^{14}, and E^{22}. Among them, the exchange polarization term, E^{22}, is negligibly small for all the molecules studied. The most striking aspect of the results is the relative magnitude of the E^{12} and E^{14} terms at intermediate distances (~2.5 Å). That is, the absolute value of the term of E^{12} is much larger than that of E^{14} for the interaction between small molecules, such as ethylene and butadiene, while the reverse is true for the benzene dimer as well as for the hexatriene dimer. Moreover, E^{12} is negative and E^{14} is positive for large molecules, such as benzene and hexatriene. In other words, if the fourth-order term in the overlap integral is disregarded for the interaction of large molecules, the potential minimum can not be obtained and two molecules come closer to coalescing. Therefore, the inclusion of E^{14} term in the calculation of the intermolecular potential is indispensable for large molecules. However, the situation is different for small molecules; that is, here the potential minimim can be obtained without E^{14}. This characteristic behavior of the exchange interaction term can be ascribed to the fact that the overlap integral between molecular orbitals of the interacting molecules is quite large in magnitude for large molecules, but is relatively small for small

Table 6. The values of σ type overlap integral of two π orbitals of carbons

Distance (Å)			
2.0	2.5	3.0	4.0
−0.2389	−0.1258	−0.0556	−0.0080

Table 7. The values of molecular overlap integral (S^{02}_{00}) for the sandwich type dimers at R=2.5 Å

Dimers			
Ethylene	*trans*-Butadiene	*trans*-Hexatriene	Benzene
−0.0647	−0.1399	−0.2151	−0.2310

molecules, as is indicated in Table 7, although the value of the each atomic overlap integral is the same for all the dimers (Table 6). The signs of the terms of E^{12} and E^{14} are noteworthy since E^{12} is positive for the ethylene and butadiene dimers, except for very short distances, and negative for the hexatriene dimer, while E^{14} is positive for all the dimers. E^{12} is negative at short distances, but positive at the larger distances, for the benzene dimer (Table 3). The sign of E^{12} results from the nine terms with plus or minus signs in U^{12}_{00} given by Eq. (A-5); that is, the No. 1, 2, 3, 4, and 9 terms have negative signs, while the other terms, No. 5, 6, 7, and 8, positive signs. The values of each term for the ethylene and benzene dimers are listed in Tables 8(a) and 9(a) respectively. The dependence of each term on the size of the molecules is shown in Fig. 6. From this figure, it is apparent that the values of the terms, No. 4, 6, 8, and 9, increase rapidly with the increase in the size of the molecules, while the values of the other terms increase only slightly. This tendency can be explained by the number of sums

Table 8. E^{12} and E^{14}, and the values of each term in U^{12}_{00} and in U^{14}_{00} for the ethylene dimer at R=2.5 Å

(a). E^{12} (eV)			(b). E^{14} (eV)		
U^{12}_{00}	No. 1	−0.3864	U^{11}_{00}	No. 1	0.0
	2	−0.3864		2	0.0
	3	−0.3864		3	0.0
	4	−0.2356		4	0.0
	5	0.7727		5	0.0
	6	0.4712		6	0.0
	7	0.7727		7	0.0
	8	0.4712		8	0.0
	9	−0.9424		9	0.0
$-U^{10}_{00}\,S^{12}_{00}$		0.0	$-1/2\,U^{12}_{00}\,S^{02}_{00}$		0.0049
E^{12}		0.1508	E^{14}		0.0049

Table 9. E^{12} and E^{14}, and the values of each term in U^{12}_{00} and in U^{14}_{00} for the benzene dimer at R=2.5 Å

(a). E^{12} (eV)			(b). E^{14} (eV)		
U^{12}_{00}	No. 1	−1.3717	U^{14}_{00}	No. 1	0.0815
	2	−5.0488		2	0.2085
	3	−5.0488		3	0.2085
	4	−18.8695		4	0.4677
	5	6.0876		5	−0.4187
	6	22.6417		6	−0.9344
	7	6.0876		7	−0.4187
	8	22.6417		8	−0.9344
	9	−27.1700		9	1.8689
$-U^{10}_{00}\,S^{02}_{00}$		0.0	$-1/2\,U^{12}_{00}\,S^{02}_{00}$		−0.0058
E^{12}		−0.0503	E^{14}		0.1229

included in each term in U^{12}_{00} (Eq. (A-5)); that is, the former terms are calculated by a fourfold summation, while, on the other hand, the summations for the latter terms are double or triple. From this tendency, the appearance of the negative sign of E^{12} for large molecules can easily be understood. These situations are the same for the terms of U^{14}_{00} except that each term of U^{14}_{00} has a sign opposite to the corresponding one of U^{12}_{00} because of the exchanges of two pairs of electrons. The values of each term in U^{14}_{00} or the ethylene and benzene dimers are listed in Tables 8(b) and 9(b) respectively. As has been mentioned above, all the terms of U^{12}_{00} and U^{14}_{00} have different signs, hence cancel each other out to make the exchange energy positive, as a whole, leading to the appearance of the potential minimum.

The importance of the term of E^{14} for large molecules was pointed out in a previous paragraph. In connection with this, the contribution of the E^{16} term should be investigated since this term probably has a sign different from that of E^{14}. However, the comparison of the magnitude of each term of U^{12}_{00} with that of U^{14}_{00} for the benzene dimer (Tables 9(a) and 9(b)) lead to a finding that each term in the equation of U^{12}_{00} is much larger in absolute magnitude than that of U^{14}_{00}, although the value of E^{14} is, as a whole, larger than that of E^{12}. Accordingly, it can resonably be

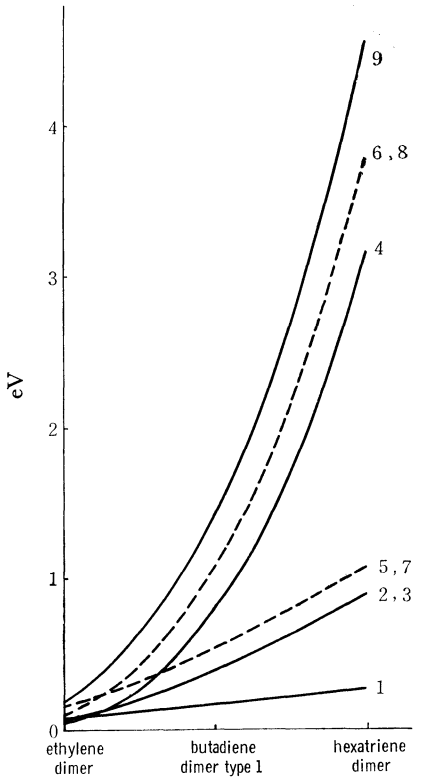

Fig. 6. The absolute value of the each term in U_{00}^{12} at R= 3.0 Å. The numbers represent the each term.———, negative value;--------- positive value.

expected that each term in U_{00}^{16} is too small in magnitude to contribute to the total intermolecular energy, even as a whole. In the present paper, other terms with a fourth order in overlap integrals such as E^{24} are completely neglected. This approximation is reasonable judging from the magnitude of E^{22}.

2. *Comparison of the Calculated Values with the Experimental Values.* It is very difficult to compare the calculated intermolecular potential and the equilibrium distance with those experimentally obtained, since the value obtained in the gas phase is an average of those of all possible geometries. The relative geometry of molecules in its molecular crystal gives some information, although the interactions between only two molecules are calculated in this paper.

The energy at the calculated potential minimum for both ethylene and butadiene dimers is much less than the thermal energy (0.026 eV at 300°K); hence these molecules have no ability to form stable dimers, a finding which is in accordance with the experimental results. Moreover, the calculated result that the ethylene dimer is more unstable than the butadiene dimer in a type-1 conformation is consistent with the relative stability of these molecules, which can be estimated from the boiling points if the entropic contribution is not serious. For benzene, the potential minimum becomes much deeper than the thermal energy. The experimental value derived from the viscosity (0.015 eV)[27] is very close to that obtained theoretically, although the experimental value corresponds to the average of various relative orientations. On the other hand, the intermolecular energy obtained from the heat of sublimation (0.40 eV) seems to be much larger. However, the difference between the experimental values from the heat of sublimation and the calculated value is not tremendous, since the heat of sublimation includes the interaction energies for all pairs of molecules in the crystal. As a whole, the calculated values of the intermolecular energies agree qualitatively fairly well with the experimental data, although the theoretical values should be calculated in more elaborate approximations in order to compare them with the experimental data quantitatively.

The calculated equilibrium molecular distances are noteworthy in connection with the geometry of the dimer of the molecular crystal. The equilibrium intermolecular distance for the ethylene dimer is located at about 4.5 Å (Fig. 1), which is comparable with the experimental values (4.2—4.8 Å) estimated from the value of viscosity or the second Virial coefficient.[27] On the other hand, the potential minimum for the benzene dimer in Fig. 4 is found at 2.9 Å, which seems to be slightly small in comparison with the value obtained for graphite (3.4 Å). This is because, for the ethylene dimer, the dispersion energy is reasonably balanced with the exchange energy, giving rise to a good agreement with the experimental results for the equilibrium intermolecular distance; on the other hand for the benzene dimer, the dispersion energy overcomes the exchange energy, leading to the slightly short intermolecular distance. From the results described above, we can conclude that the theoretical methods in the present paper are considerably reliable for the prediction of the intermolecular interaction energy and the intermolecular distance, though the quantitative agreement with the experimental data is not entirely satisfactory.

3. *Discussion of the Method.* In order to improve the present results, the use of a more exact atomic orbital and the explicit inclusion of σ electrons are important. As is well known, the SCF atomic orbitals for various atoms are considerably different form those of the usual Slater atomic orbitals, especially in the region distant from the atomic nucleus. Therefore, the improvement of the atomic orbital may be important for obtaining the exact intermolecular potential.[28] However, the use of the SCF atomic orbital, which is usually represented by the linear combination of several Slater-type atomic orbitals, is cumbersome in the expansion of the matrix elements into atomic orbitals. Instead of the SCF atomic orbital, the overlap matched atomic orbital (OMAO)[29] was employed in order to investigate the dependence of the result on the atomic orbitals used in the present paper. This orbital (OMAO) is a single Slater-type atomic orbital whose exponent was determined so as to reproduce overlap integrals calculated by SCF atomic orbitals. The value of the Slater exponent in OMAO[29] is 1.42, while the

27) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York (1954).

28) J. N. Murrell and G. Shaw, *Mol. Phys.*, **12**, 475 (1967).

29) L.C. Cusachs, B.L. Trus, D.G. Carroll, and P.S. McGlynn, *Int. J. Quant. Chem., Sympo.*, **1**, 423 (1967).

Slater rule gives 1.625 for the carbon atom. Obviously, OMAO has an overlap integral larger in magnitude. The intermolecular potential curves for the ethylene dimer and the butadiene dimer obtained by using OMAO are indicated in Figs. 1 and 2 in comparison with those obtained by the use of the Slater rule. The potential minimum obtained in OMAO is located at a distance longer by about 1 Å for both dimers, because of the increasing contribution of the exchange repulsion energy.

Table 10. The interaction energies in ONDO/2 approximation of the ethylene dimer (in eV)

R(Å)	E^{10}	E^{20}	E^{12}	Total
3.5	0.0051	−0.0150	0.0181	0.0081
4.0	0.0008	−0.0075	0.0030	−0.0037
4.5	0.0004	−0.0040	0.0004	−0.0032

Next, the explicit treatment of σ electrons was carried out in the framework of the CNDO/2 approximation for the ethylene dimer. In this calculation, however, the terms of E^{14}, E^{22}, and E^{CT} are neglected since these terms may not make large contributions to the equilibrium distance and since the calculation of these terms takes much computer time.[30] The results listed in Table 10 indicate that the inclusion of σ electrons increases the contribution of E^{20} because of the increase in the number of energy levels in the summation of Eq. (10). Since E^{20} is negative, the equilibrium distance obtained in the CNDO/2 approximation is shorter than that obtained in the PPP approximation. As a result of the above investigations, it can be concluded that the effects of the improvement of the atomic orbital and the explicit treatment of σ electrons cancel each other out to some extent, resulting in a relatively small correction for the equilibrium distance obtained in the PPP approximation using the usual simple Slater atomic orbitals. On the other hand, the magnitude of the interaction energy in the CNDO/2 approximation is much more than that in the PPP approximation because of the dominant increase in the contribution of E^{20}.

4. Comparison with Other Methods. The finding that the potential curves for the ground state have the minima shown in the present paper may be compared with the results by other authors. The results of the extended Hückel method show that, for example, for the ethylene dimer in Ref. 15 or the benzene dimer in Ref. 16, the potential minimum for the ground state does not appear, contrary to our calculations, while it does exist in the excited states, hence, they concluded that the excimer formations may be expected for these dimers. On the other hand, Chandra investigated the origin of the stability of aromatic hydrocarbon dimers using the Hückel-type π perturbation theory and showed that, in the ground state, the tilted configuration was stable, while the sandwich configuration was not.[17] However, our calculation for the benzene dimer in the sandwich configuration gives the potential minimum, although the magnitude is small because of the use of the π approximation. As was mentioned in the previous paragraph, the inclusion of σ electrons results in an increase in the interaction energy for the ethylene dimer; hence, it can probably be expected that, for the benzene dimer, the interaction energy involving the contribution of σ electrons is also larger by one order than that in the PPP approximation. Therefore, the intermolecular interaction energy obtained by the Hückel or the extended Hückel method, in which the electron-electron repulsion energies are not explicitly included, is substantially different from the results of the present paper with regard to the appearance of the potential minimum.

5. Summary. The method and the approximation used in the present paper give a satisfactory qualitative agreement with the experimental results for the intermolecular potential. In order to obtain a quantitative agreement, more elaborate and cumbersome approximations are required; that is, these must be an improvement in the atomic orbital and in the explicit treatment of σ electrons.

Appendix

The Matrix Elements. The matrix elements in PPP approximation are as followes.

(1)

$$U_{00}^{10} = \sum_a\sum_b Z_a^A Z_b^B \gamma_{ab}^{AB} - 2\sum_b Z_b^B \sum_i^{occ.} \langle \varphi_i^A(1) | e^2/r_{1b} | \varphi_i^A(1) \rangle$$
$$- 2\sum_a Z_a^A \sum_j^{occ.} \langle \varphi_j^B(1) | e^2/r_{1a} | \varphi_j^B(1) \rangle$$
$$+ 4\sum_i^{occ.}\sum_j^{occ.} \langle \varphi_i^A(1)\varphi_j^B(2) | e^2/r_{12} | \varphi_i^A(1)\varphi_j^B(2) \rangle$$
$$= \sum_a (Z_a^A - P_a^A) \sum_b (Z_b^B - P_b^B) \gamma_{ab}^{AB}, \quad \text{(A-1)}$$

where $P_a = 2\sum_i^{occ.} (C_{ai})^2$.

(2) In evaluating the matrix element U_{t0}^{10}, the following cases are separately treated according to the configuration of $A_r(i)B_s(j)$.

(i) When the configuration is A_rB_0, where r denotes the $i \rightarrow k$ singly excitation,

$$U_{t0}^{10} = 2\sqrt{2}\sum_j \langle \varphi_k^A(1)\varphi_j^B(2) | e^2/r_{12} | \varphi_i^A(1)\varphi_j^B(2) \rangle$$
$$- \sqrt{2}\sum_b Z_b^B \langle \varphi_k^A(1) | e^2/r_{1b} | \varphi_i^A(1) \rangle$$
$$= -\sqrt{2}\sum_a C_{ak}^A C_{ai}^A \sum_b (Z_b^B - P_b^B) \gamma_{ab}^{AB}. \quad \text{(A-2)}$$

(ii) When the configuration is A_0B_s, where s denotes the $j \rightarrow l$ singly excitation,

$$U_{t0}^{10} = -\sqrt{2}\sum_b C_{bj}^B C_{bl}^B \sum_a (Z_a^A - P_a^A) \gamma_{ab}^{AB}. \quad \text{(A-3)}$$

(iii) When the configuration is A_rB_s, *i.e.*, both molecules are in excited states, where r denotes the $i \rightarrow k$, singly excitation and s does the $j \rightarrow l$,

$$U_{t0}^{10} = 2\langle \varphi_k^A(1)\varphi_l^B(2) | e^2/r_{12} | \varphi_i^A(1)\varphi_j^B(2) \rangle$$
$$= 2\sum_a C_{ak}^A C_{ai}^A \sum_b C_{bl}^B C_{bj}^B \gamma_{ab}^{AB}. \quad \text{(A-4)}$$

(3)

$$U_{00}^{12} = -2\sum_i\sum_j \langle \varphi_i^A(2)\varphi_j^B(1) | e^2/r_{12} | \varphi_i^A(1)\varphi_j^B(2) \rangle \quad 1)$$
$$-4\sum_l\sum_i\sum_j \langle \varphi_j^B(1)\varphi_l^B(2) | e^2/r_{12} | \varphi_i^A(1)\varphi_l^B(2) \rangle$$
$$\times \langle \varphi_i^A(3) | \varphi_j^B(3) \rangle \quad 2)$$

30) The calculation of the intermolecular potential including these terms by using the CNDO/2 method is in progress; the results will be published in the future.

(when $l=j$, multiplied by 1/2)

$$-4\sum_{l}\sum_{i}\sum_{j}\langle\varphi_i^A(2)\varphi_l^A(1)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle \times\langle\varphi_j^B(3)\,|\,\varphi_i^A(3)\rangle \quad 3)$$

(when $l=i$, multiplied by 1/2)

$$-8\sum_{m}\sum_{l}\sum_{i}\sum_{j}\langle\varphi_i^A(1)\varphi_j^B(2)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle \times\{\langle\varphi_l^A(3)\,|\,\varphi_m^B(3)\rangle\}^2 \quad 4)$$

(when $j=m$ or $i=l$, multiplied by 1/2)

$$+2\sum_{a}\sum_{i}\sum_{j}\langle\varphi_i^A(1)\,|\,Z_a^A e^2/r_{a1}\,|\,\varphi_j^B(1)\rangle \times\langle\varphi_j^B(2)\,|\,\varphi_i^A(2)\rangle \quad 5)$$

$$+4\sum_{a}\sum_{i}\sum_{j}\sum_{l}\langle\varphi_j^B(1)\,|\,Z_a^A e^2/r_{a1}\,|\,\varphi_j^B(1)\rangle \times\{\langle\varphi_i^A(2)\,|\,\varphi_l^B(2)\rangle\}^2 \quad 6)$$

(when $j=l$, multiplied by 1/2)

$$+2\sum_{b}\sum_{i}\sum_{j}\langle\varphi_j^B(1)\,|\,Z_b^B e^2/r_{1b}\,|\,\varphi_i^A(1)\rangle \times\langle\varphi_i^A(2)\,|\,\varphi_j^B(2)\rangle \quad 7)$$

$$+4\sum_{b}\sum_{i}\sum_{j}\sum_{l}\langle\varphi_i^A(1)\,|\,Z_b^B e^2/r_{1b}\,|\,\varphi_i^A(1)\rangle \times\{\langle\varphi_j^B(2)\,|\,\varphi_i^A(2)\rangle\}^2 \quad 8)$$

(when $i=l$, multiplied by 1/2)

$$-2\sum_{a}\sum_{b}Z_a^A Z_b^B\gamma_{ab}^{AB}\sum_{i}\sum_{j}\{\langle\varphi_j^B(1)\,|\,\varphi_i^A(1)\rangle\}^2. \quad 9)$$

(A-5)

U_{00}^{12} is written down here only in terms of the molecular orbitals. In the calculation, if the value of overlap integral between a pair of atomic orbiatls is less than 10^{-4} in magnitude, the contributions of this term could be neglected. This cut off procedure was taken through the computation of any matrix elements including overlap integrals, *i.e.*, U_{00}^{14}, U_{10}^{12} *etc.*

(4)

$$S_{00}^{02} = -2\sum_{i}\sum_{j}\{\langle\varphi_i^A(1)\,|\,\varphi_j^B(1)\rangle\}^2 = -2\sum_{i}\sum_{j}(\sum_{a}\sum_{b}C_{ai}^A C_{bj}^B S_{ab}^{AB})^2. \quad \text{(A-6)}$$

(5) The each term of U_{00}^{14} can be obtained by allowing the exchange of one pair of electrons in the electronic configuration of each term in U_{00}^{12}.

If $D_{fg}=\{\langle\varphi_f^A|\varphi_g^B\rangle\}^2$,

$$U_{00}^{14} = 1/2U_{00}^{12}S_{00}^{02}$$

$$+2\sum_{i}\sum_{j}\langle\varphi_i^A(2)\varphi_j^B(1)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle \times\sum_{\substack{f\\(\neq i)}}\sum_{\substack{g\\(\neq j)}}D_{fg} \quad 1)$$

$$+4\sum_{l}\sum_{i}\sum_{j}\langle\varphi_j^B(1)\varphi_l^B(2)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_l^B(2)\rangle \times\langle\varphi_i^A(3)\,|\,\varphi_j^B(3)\rangle\sum_{\substack{f\\(\neq i)(\neq l,f)}}\sum_{g}D_{fg} \quad 2)$$

(when $l=j$, multiplied by 1/2)

$$+4\sum_{l}\sum_{i}\sum_{j}\langle\varphi_i^A(2)\varphi_l^A(1)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle \times\langle\varphi_j^B(3)\,|\,\varphi_i^A(3)\rangle\sum_{\substack{f\\(\neq i,l)(\neq j)}}\sum_{g}D_{fg} \quad 3)$$

(when $l=i$, multiplied by 1/2)

$$+8\sum_{m}\sum_{l}\sum_{i}\sum_{j}\langle\varphi_i^A(1)\varphi_j^B(2)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle \times\{\langle\varphi_l^A(3)\,|\,\varphi_m^B(3)\rangle\}^2\sum_{\substack{f\\(\neq i,l)(\neq j,m)}}\sum_{g}D_{fg} \quad 4)$$

(when $j=m$ or $i=l$, multiplied by 1/2)

$$-2\sum_{a}\sum_{i}\sum_{j}\langle\varphi_i^A(1)\,|\,Z_a^A e^2/r_{a1}\,|\,\varphi_j^B(1)\rangle \times\langle\varphi_j^B(2)\,|\,\varphi_i^A(2)\rangle\sum_{\substack{f\\(\neq i)}}\sum_{\substack{g\\(\neq j)}}D_{fg} \quad 5)$$

$$-4\sum_{a}\sum_{i}\sum_{j}\sum_{l}\langle\varphi_j^B(1)\,|\,Z_a^A e^2/r_{a1}\,|\,\varphi_j^B(1)\rangle \times\{\langle\varphi_i^A(2)\,|\,\varphi_l^B(2)\rangle\}^2\sum_{\substack{f\\(\neq i,l)(\neq j)}}\sum_{g}D_{fg} \quad 6)$$

(when $j=l$, multiplied by 1/2)

$$-2\sum_{b}\sum_{i}\sum_{j}\langle\varphi_j^B(1)\,|\,Z_b^B e^2/r_{1b}\,|\,\varphi_i^A(1)\rangle \times\langle\varphi_i^A(2)\,|\,\varphi_j^B(2)\rangle\sum_{\substack{f\\(\neq i)}}\sum_{\substack{g\\(\neq j)}}D_{fg} \quad 7)$$

$$-4\sum_{b}\sum_{i}\sum_{j}\sum_{l}\langle\varphi_i^A(1)\,|\,Z_b^B e^2/r_{1b}\,|\,\varphi_i^A(1)\rangle \times\{\langle\varphi_j^B(2)\,|\,\varphi_i^A(2)\rangle\}^2\sum_{\substack{f\\(\neq i,l)(\neq j)}}\sum_{g}D_{fg} \quad 8)$$

(when $i=l$, multiplied by 1/2)

$$+2\sum_{a}\sum_{b}Z_a^A Z_b^B\gamma_{ab}^{AB}\sum_{i}\sum_{j}\{\langle\varphi_j^B(1)\,|\,\varphi_i^A(1)\rangle\}^2 \times\sum_{\substack{f\\(\neq i)}}\sum_{\substack{g\\(\neq j)}}D_{fg}. \quad 9)$$

(A-7)

(6) U_{10}^{12} and S_{10}^{02} can be classified as follows.

(i) When the configuration is A_rB_0, where r represents the $i\rightarrow k$ singly excitation,

$$U_{10}^{12} = -\sqrt{2}\sum_{n}\langle\varphi_k^A(2)\varphi_n^B(1)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_n^B(2)\rangle -4\sqrt{2}\sum_{n}\sum_{m}\sum_{f}\langle\varphi_k^A(1)\varphi_n^B(2)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_n^B(2)\rangle \times\{\langle\varphi_f^A(3)\,|\,\varphi_m^B(3)\rangle\}^2$$

(when $m=n$ or $f=i$, multiplied by 1/2)

$$-4\sqrt{2}\sum_{f}\sum_{n}\sum_{m}\langle\varphi_f^A(1)\varphi_n^B(2)\,|\,e^2/r_{12}\,|\,\varphi_f^A(1)\varphi_n^B(2)\rangle \times\langle\varphi_k^A(4)\varphi_m^B(3)\,|\,\varphi_i^A(3)\varphi_m^B(4)\rangle$$

(when $m=n$ or $f=i$, multiplied by 1/2)

$$-2\sqrt{2}\sum_{m}\sum_{n}\langle\varphi_k^A(1)\varphi_n^A(2)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_m^B(2)\rangle \times\langle\varphi_m^B(3)\,|\,\varphi_n^A(3)\rangle$$

(when $n=i$, multiplied by 1/2)

$$-2\sqrt{2}\sum_{m}\sum_{n}\langle\varphi_n^B(2)\varphi_m^B(1)\,|\,e^2/r_{12}\,|\,\varphi_n^B(2)\varphi_i^A(1)\rangle \times\langle\varphi_k^A(3)\,|\,\varphi_m^B(3)\rangle$$

(when $n=m$, multiplied by 1/2)

$$-2\sqrt{2}\sum_{m}\sum_{n}\langle\varphi_n^A(1)\varphi_k^A(2)\,|\,e^2/r_{12}\,|\,\varphi_n^A(1)\varphi_m^B(2)\rangle \times\langle\varphi_m^B(3)\,|\,\varphi_i^A(3)\rangle$$

(when $n=i$, multiplied by 1/2)

$$+\sqrt{2}\sum_{a}\sum_{n}\langle\varphi_k^A(1)\,|\,Z_a^A e^2/r_{a1}\,|\,\varphi_n^B(1)\rangle \times\langle\varphi_n^B(2)\,|\,\varphi_i^A(2)\rangle$$

$$+2\sqrt{2}\sum_{m}\sum_{a}\sum_{n}\langle\varphi_m^B(1)\,|\,Z_a^A e^2/a_1\,|\,\varphi_m^B(1)\rangle \times\langle\varphi_k^A(2)\varphi_n^B(3)\,|\,\varphi_i^A(3)\varphi_n^B(2)\rangle$$

$$+\sqrt{2}\sum_{b}\sum_{n}\langle\varphi_n^B(1)\,|\,Z_b^B e^2/r_{1b}\,|\,\varphi_i^A(1)\rangle \times\langle\varphi_k^A(2)\,|\,\varphi_n^B(2)\rangle$$

$$+2\sqrt{2}\sum_{b}\sum_{n}\sum_{m}\langle\varphi_m^A(1)\,|\,Z_b^B e^2/r_{1b}\,|\,\varphi_m^A(1)\rangle \times\langle\varphi_n^B(2)\varphi_k^A(3)\,|\,\varphi_n^B(3)\varphi_i^A(2)\rangle$$

(when $m=i$, multiplied by 1/2)

$$+2\sqrt{2}\sum_{n}\sum_{m}\sum_{b}\langle\varphi_k^A(1)\,|\,Z_b^B e^2/r_{1b}\,|\,\varphi_i^A(1)\rangle \times\langle\varphi_m^A(3)\varphi_n^B(2)\,|\,\varphi_n^B(3)\varphi_m^A(2)\rangle$$

(when $m=i$, multiplied by 1/2)

$$-\sqrt{2}\sum_{n}\langle\varphi_k^A(2)\varphi_n^B(1)\,|\,\varphi_i^A(1)\varphi_n^B(2)\rangle \times\sum_{a}\sum_{b}Z_a^A Z_b^B\gamma_{ab}^{AB} \quad \text{(A-8)}$$

$$S_{10}^{02} = -2\sqrt{2}\sum_{j}\langle\varphi_k^A(2)\varphi_j^B(1)\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle. \quad \text{(A-9)}$$

(ii) When the configuration is A_0B_s, where s represents the $j\rightarrow l$ singly excitation, the matrix elements U_{i0}^{12} and S_{i0}^{02} in this case are obtained from (i) by exchanging upper indices A and B and substituting j and l for i and k, respectively.

(iii) When the configurations A_rB_s, *i.e.*, both molecules are in excited states, where r represents the $i\rightarrow k$ singly excitation and s represents the $j\rightarrow l$,

$$\begin{aligned}U_{i0}^{12} = & -\langle\varphi_k^A(2)\varphi_l^B(1)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle\\ & -4\sum_n\sum_m\langle\varphi_n^A(1)\varphi_m^B(2)\,|\,e^2/r_{12}\,|\,\varphi_n^A(1)\varphi_m^B(2)\rangle\\ & \times\langle\varphi_k^A(3)\varphi_l^B(4)\,|\,\varphi_i^A(4)\varphi_j^B(3)\rangle\end{aligned}$$

(when $n=i$ or $m=j$, multiplied by 1/2)

$$\begin{aligned}& -2\sum_n\langle\varphi_n^A(1)\varphi_k^A(2)\,|\,e^2/r_{12}\,|\,\varphi_n^A(1)\varphi_j^B(2)\rangle\\ & \times\langle\varphi_l^B(3)\,|\,\varphi_i^A(3)\rangle\end{aligned}$$

(when $n=i$, multiplied by 1/2)

$$\begin{aligned}& -2\sum_n\langle\varphi_k^A(1)\varphi_n^A(2)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle\\ & \times\langle\varphi_l^B(3)\,|\,\varphi_n^A(3)\rangle\end{aligned}$$

(when $n=i$, multiplied by 1/2)

$$\begin{aligned}& -2\sum_n\langle\varphi_n^B(2)\varphi_l^B(1)\,|\,e^2/r_{12}\,|\,\varphi_n^B(2)\varphi_i^A(1)\rangle\\ & \times\langle\varphi_k^A(3)\,|\,\varphi_j^B(3)\rangle\end{aligned}$$

(when $n=j$, multiplied by 1/2)

$$\begin{aligned}& -2\sum_n\langle\varphi_l^B(2)\varphi_n^B(1)\,|\,e^2/r_{12}\,|\,\varphi_j^B(2)\varphi_i^A(1)\rangle\\ & \times\langle\varphi_k^A(3)\,|\,\varphi_n^B(3)\rangle\end{aligned}$$

(when $n=j$, multiplied by 1/2)

$$\begin{aligned}& -4\sum_m\sum_n\langle\varphi_n^A(1)\varphi_l^B(2)\,|\,e^2/r_{12}\,|\,\varphi_n^A(1)\varphi_j^B(2)\rangle\\ & \times\langle\varphi_k^A(4)\varphi_m^B(3)\,|\,\varphi_i^A(3)\varphi_m^B(4)\rangle\end{aligned}$$

(when $m=j$ or $n=i$, multiplied by 1/2)

$$\begin{aligned}& -4\sum_m\sum_n\langle\varphi_k^A(1)\varphi_m^B(2)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_m^B(2)\rangle\\ & \times\langle\varphi_n^A(4)\varphi_l^B(3)\,|\,\varphi_j^B(4)\varphi_n^A(3)\rangle\end{aligned}$$

(when $m=j$ or $n=i$, multiplied by 1/2)

$$\begin{aligned}& -4\sum_m\sum_n\langle\varphi_k^A(1)\varphi_l^B(2)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle\\ & \times\langle\varphi_n^A(4)\varphi_m^B(3)\,|\,\varphi_m^B(4)\varphi_n^A(3)\rangle\end{aligned}$$

(when $m=j$ or $n=i$, multiplied by 1/2)

$$\begin{aligned}& +\sum_a\langle\varphi_k^A(1)\,|\,Z_a^Ae^2/r_{a1}\,|\,\varphi_j^B(1)\rangle\langle\varphi_l^B(2)\,|\,\varphi_i^A(2)\rangle\\ & +2\sum_a\sum_n\langle\varphi_n^B(1)\,|\,Z_a^Ae^2/r_{a1}\,|\,\varphi_n^B(1)\rangle\\ & \times\langle\varphi_l^B(2)\varphi_k^A(3)\,|\,\varphi_i^A(2)\varphi_j^B(3)\rangle\end{aligned}$$

(when $n=j$, multiplied by 1/2)

$$\begin{aligned}& +2\sum_a\sum_n\langle\varphi_l^B(1)\,|\,Z_a^Ae^2/r_{a1}\,|\,\varphi_j^B(1)\rangle\\ & \times\langle\varphi_n^B(3)\varphi_k^A(2)\,|\,\varphi_i^A(3)\varphi_n^B(2)\rangle\end{aligned}$$

(when $n=j$, multiplied by 1/2)

$$\begin{aligned}& +\sum_b\langle\varphi_l^B(1)\,|\,Z_b^Be^2/r_{1b}\,|\,\varphi_i^A(1)\rangle\langle\varphi_k^A(2)\,|\,\varphi_j^B(2)\rangle\\ & +2\sum_b\sum_n\langle\varphi_n^A(1)\,|\,Z_b^Be^2/r_{1b}\,|\,\varphi_n^A(1)\rangle\\ & \times\langle\varphi_k^A(2)\varphi_l^B(3)\,|\,\varphi_j^B(2)\varphi_i^A(3)\rangle\end{aligned}$$

(when $n=i$, multiplied by 1/2)

$$\begin{aligned}& +2\sum_b\sum_n\langle\varphi_k^A(1)\,|\,Z_b^Be^2/r_{1b}\,|\,\varphi_i^A(1)\rangle\\ & \times\langle\varphi_n^A(3)\varphi_l^B(2)\,|\,\varphi_j^B(3)\varphi_n^A(2)\rangle\end{aligned}$$

(when $n=i$, multiplied by 1/2)

$$-\langle\varphi_k^A(2)\varphi_l^B(1)\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle\sum_a\sum_b Z_a^AZ_b^Be^2/r_{ab} \tag{A-10}$$

$$S_{i0}^{02} = -2\langle\varphi_k^A(2)\varphi_l^B(1)\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle. \tag{A-11}$$

When $(U_{i0}^{10})^2/(E_0-E_t)$ is less than a critical value, the term including U_{i0}^{12} in E^{22}, *i.e.*, $U_{i0}^{10}U_{i0}^{12}/(E_0-E_t)$, can also be expected to be small in magnitude and hence the contribution of this term to E^{22} was neglected in order to save computation time. We found the critical value of 10^{-4} is sufficient for the result within the accuracy of 10^{-4} eV in total intermolecular potential.

(7)

$$\begin{aligned}U_{i0}^{11} = & 2\sqrt{2}\sum_j\langle\varphi_j^B(2)\varphi_l^B(1)\,|\,e^2/r_{12}\,|\,\varphi_k^A(1)\varphi_j^B(2)\rangle\\ & +4\sqrt{2}\sum_i\sum_j\langle\varphi_i^A(1)\varphi_j^B(2)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle\\ & \times\langle\varphi_l^B(3)\,|\,\varphi_k^A(3)\rangle\end{aligned}$$

(when $i=k$, multiplied by 1/2)

$$\begin{aligned}& -2\sqrt{2}\sum_i\sum_j\langle\varphi_i^A(1)\varphi_l^B(2)\,|\,e^2/r_{12}\,|\,\varphi_i^A(1)\varphi_j^B(2)\rangle\\ & \times\langle\varphi_j^B(3)\,|\,\varphi_k^A(3)\rangle\end{aligned}$$

(when $i=k$, multiplied by 1/2)

$$\begin{aligned}& -\sqrt{2}\sum_j\langle\varphi_j^B(1)\varphi_l^B(2)\,|\,e^2/r_{12}\,|\,\varphi_k^A(1)\varphi_j^B(2)\rangle\\ & -2\sqrt{2}\sum_a\sum_j\langle\varphi_j^B(1)\,|\,Z_a^Ae^2/r_{a1}\,|\,\varphi_j^B(1)\rangle\\ & \times\langle\varphi_l^B(2)\,|\,\varphi_k^A(2)\rangle\\ & +\sqrt{2}\sum_a\sum_j\langle\varphi_l^B(1)\,|\,Z_a^Ae^2/r_{a1}\,|\,\varphi_j^B(1)\rangle\\ & \times\langle\varphi_j^B(2)\,|\,\varphi_k^A(2)\rangle\\ & -\sqrt{2}\sum_b\langle\varphi_l^B(1)\,|\,Z_b^Be^2/r_{1b}\,|\,\varphi_k^A(1)\rangle\\ & -2\sqrt{2}\sum_b\sum_i\langle\varphi_i^A(1)\,|\,Z_b^Be^2/r_{1b}\,|\,\varphi_i^A(1)\rangle\\ & \times\langle\varphi_l^B(2)\,|\,\varphi_k^A(2)\rangle\end{aligned}$$

(when $i=k$, multiplied by 1/2)

$$+\sqrt{2}\sum_a\sum_b Z_a^AZ_b^Be^2/r_{ab}\langle\varphi_l^B(1)\,|\,\varphi_k^A(1)\rangle \tag{A-12}$$

$$S_{i0}^{01} = \sqrt{2}\langle\varphi_l^B(1)\,|\,\varphi_k^A(1)\rangle. \tag{A-13}$$

The matrix element of the charge transfer from B to A,

$$U_{i0}^{11} = (2n+1/2m)^{1/2}\langle A_l^-(i')B_k^+(j')\,|\,U\,|\,A_0(i)B_0(j)\rangle,$$

is obtained by exchanging upper indices A and B in Eq. (A-12).