The INDO and CNDO/2 SCF LCAO MO Calculation of Intermolecular Forces and Their Pairwise Additivity

Masao HASHIMOTO and Taro ISOBE
The Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Sendai 980

(Received June 28, 1973)

The assumption of pairwise additivity of the intermolecular forces was examined within a CNDO/2-Clementi approximation. It was found that the deviation from the pairwise additivity, defined as the difference between the three-body interaction and the sum of the two-body interaction energies in the system of three neighboring molecules in a crystal, was small enough to be neglected as compared with the lattice energy. The CNDO/2-Clementi method, in which the overlap integrals are calculated by using the Clementi AO's, was found to be more useful than the usual CNDO/2 method, in which the overlap integrals are calculated by means of Slater AO's. The discrepancy in the calculated interaction energies from the experimental ones in the form of the heat of sublimation was found to be quite large for CO. This discrepancy becomes small, though, if the centers of the molecules are displaced away from the origin and along the nonintersecting threefold axes of the unit cell; the crystal structure belongs not to the Pa3 space group, but to the $P2_13$ space group. From a comparison of the CNDO/2-Clementi results and the results of the exp-6 potential superimposed on the quadrupole-quadrupole interaction potential, it was found that the former is superior to the latter in anticipating the conformation of the $(CO_2)_2$ dimer.

In a previous paper1) (designated **I** henceforth), we calculated the intermolecular forces between closed-shell molecules in the ground-state, treating the dimer system as if it were one molecule and using the difference between the total energy of this system and that of the monomeric molecules. The total energies were calculated with the CNDO/2 SCF LCAO MO (completely neglecting the differential overlaps in self-consistent field molecular orbital approximated by a linear combination of atomic orbitals) method by using the Clementi AO's (we will designate this by "CNDO/2-Clementi method" henceforth).

In **I**, the calculated interaction energy was compared with the experimental one in the form of the lattice energy by assuming a pairwise additivity of the intermolecular forces. This assumption is justified if the deviation from the pairwise additivity is relatively small. However, no examination for the pairwise additivity was made in **I**.

In the present paper, we will calculate the interaction energy among three molecules treating them as if they were one molecule. The deviation from the pairwise additivity will, then, be obtained as the difference between the three-body interaction energy and the sum of the two-body interaction energies. We will compare the interaction energy obtained by using the Slater AO's and that obtained by using Clementi AO's. This comparison was made in **I** only for ethylene. Furthermore, the INDO (with an intermediate neglect of the differential overlaps) and CNDO/2 results will be compared.

TABLE 1. CRYSTAL STRUCTURAL DATA

Crystal	Space group	Lattice onstant	Literature
α-N_2	T_h^6–Pa3	$a=5.667$	2)
CO_2	T_h^6–Pa3	$a=5.883$	3)
High temperature form C_2H_2	T_h^6–Pa3	$a=6.14$	4)
α-N_2O	T_h^6–Pa3	$a=5.72$	5)
α-CO	T_h^6–Pa3	$a=5.63$	6)
Low temperature form HCN	C_{2v}^{20}–Imm2	$a=4.13$ $b=4.85$ $c=4.34$	7)
C_2H_4	C_{2h}^{5}–$P2_1/n$	$a=4.87$ $b=6.46$ $c=4.14$ $\beta=90.0°$	8)
α-F_2	C_{2h}^{3}–C2/m	$a=5.50$ $b=3.28$ $c=10.01$ $\beta=134.66°$	31)

The substances treated in this paper and their crystal data are summarized in Table 1.

Theoretical

In this section, we will supplement the theoretical part of **I**.

INDO Parametrization. The F matrix in INDO is as follows:

$$F_{rr} = U_{rr} + \frac{1}{2}P_{rr}\gamma_{AA} + \sum_{s(\neq r)}^{(A)} P_{ss}\left[(rr/ss) - \frac{1}{2}(rs/rs)\right] + \sum_{B(\neq A)} (P_{BB} - Z_B)\gamma_{AB} \qquad (r,\ s \in A) \tag{1}$$

$$F_{rs} = P_{rs}\left[(3/2)(rs/rs) - \frac{1}{2}(rr/ss)\right] \qquad (r \neq s,\ r,\ s \in A)$$

$$F_{rs} = \frac{1}{2}S_{rs}(\beta_A + \beta_B) - \frac{1}{2}P_{rs}\gamma_{AB} \qquad (r \neq s,\ r \in A,\ s \in B)$$

The integrals appearing in (1) are expressed as follows:

$$\begin{aligned} (ss/ss) &= (ss/xx) = F^\circ = \gamma_{AA} \\ (xx/xx) &= F^\circ + (4/25)F^2 \\ (xx/yy) &= F^\circ - (2/25)F^2 \\ (xs/xs) &= (1/3)G^1 \\ (xy/xy) &= (3/25)F^2,\ etc., \end{aligned} \tag{2}$$

where s, x, y, *etc.* are 2s, $2p_x$, $2p_y$, and so on; F^2 and G^1 are semiempirical parameters given by Pople *et al.*9) F^0 is calculated theoretically by using the Slater AO's.10) The bonding parameters β's, were parametrized as usual.9)

The overlap integrals, S_{rs}, were calculated by using both Slater AO's and Clementi AO's (see **I**); they are compared in part in Tables 2 and 3.

Table 2. Comparison of overlap integrals calculated by using Clementi AO's and Slater AO's (1s and 2s)

Å	S_{rs}	
r(C···H)	Slater AO	Clementi AO
1.0500	0.5414	0.5277
1.0631	0.5340	0.5210
1.0800	0.5245	0.5123
2.0998	0.1301	0.1387
2.2500	0.1019	0.1105
3.2760	0.0165	0.0205
3.3700	0.0138	0.0174
3.4568	0.0117	0.0150
4.7506	0.0009	0.0015
4.9623	0.0006	0.0010
5.3803	0.0002	0.0005
5.6882	0.0001	0.0003
6.7276	0.0	0.0

Table 3. Comparison of overlap integrals calculated by using Clementi AO's and Slater AO's (2s and 2s)

Å	S_{rs}	
r(C···C)	Slater AO	Clementi AO
1.2000	0.5114	0.5250
1.3400	0.4368	0.4511
3.8523	0.0051	0.0084
3.9248	0.0043	0.0073
4.1274	0.0028	0.0051
4.3391	0.0017	0.0034
4.6301	0.0014	0.0020
4.8471	0.0005	0.0013
5.6300	0.0001	0.0003
6.1400	0.0000	0.0001
6.8196	—	0.0000

In this series of papers, one- and two-center electron repulsion integrals, γ_{AA} and γ_{AB}, are always calculated by using the Slater AO's. There is no clear *rationale* for this. However, the final results using the γ_{AA} and γ_{AB}, which were calculated with the Clementi AO's, did not seem to be superior to those calculated with the Slater AO's.

Deviation from Pairwise Additivity. In the previous paper, we calculated the lattice energy taking the summation of the pair interaction energies over the 1st and the 2nd neighboring pairs in a crystal, and assuming the pairwise additivity of the intermolecular forces. This assumption is, however, not strictly justified. Several authors[11-15] have approached the problem of the non-additive part of molecular interactions in $(He)_3$ using an SCF LCAO MO approximation. Novaro and Beltran-Lopez[15] have indicated that the three-body effect, which is considered to be the main part of the deviation from the pairwise additivity in many particle systems, can be quite large at smaller distances, but wanes quickly when approaching the region of the $(He)_2$ van der Waals well.

The three-body effects, or the deviation from the pairwise additivity, is defined as follows:

$$D = U_{abc} - (U_{ab} + U_{bc} + U_{ca}) \tag{3}$$

where:

$$U_{abc} = E(M_a, M_b, M_c) - [E(M_a) + E(M_b) + E(M_c)] \tag{4}$$

and

$$U_{ab} = E(M_a, M_b) - [E(M_a) + E(M_b)], \textit{ etc.} \tag{5}$$

In Eqs. (4) and (5), the E's are the sums of the total electronic and Coulombic repulsion energies between the cores (see **I**).

Results and Discussion

In Figs. 1 and 2, D, the deviation from the pairwise additivity, is plotted against the intermolecular distances, R, keeping the relative orientations of the molecules fixed to those in real crystals. These figures show that, D at R_0, which is the intermolecular distance in a real crystal, can be neglected in comparison with the lattice energy (see Table 4). The assumption of the pairwise additivity in **I** is thus satisfied approximately.

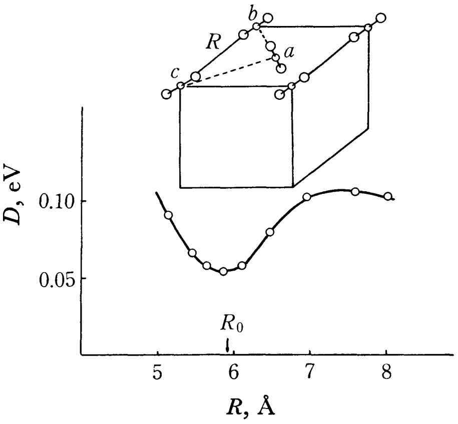

Fig. 1. Deviation from the pairwise additivity of intermolecular force of CO_2 by CNDO/2-Clementi method.

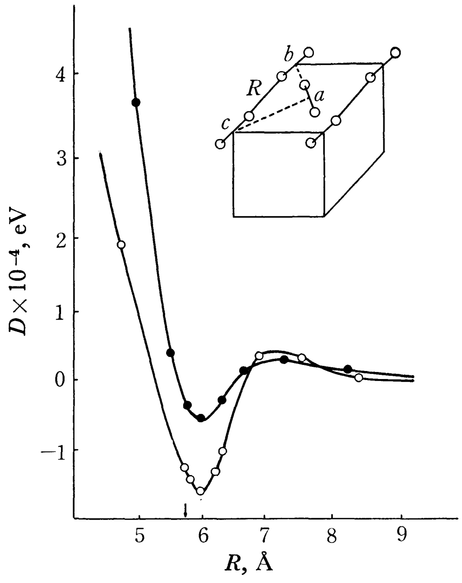

Fig. 2. Deviation from the pairwise additivity of intermolecular force of N_2 by CNDO/2-Clementi method. (●) with the space group Pa3, (○) $P2_13$.

Table 4. Calculated and experimental heat of sublimation of crystals, in electron volts, error ± 0.00025

	$1/2\sum U_{ab}$				
	CNDO/2		INDO		Obsd
	Slater	Clementi	Slater	Clementi	
HCN	−0.09612	−0.51174	−0.10355	−0.59502	−0.39727[24]
CO	−0.02808	−0.55290	+0.00750	−0.71835	−0.08617[25]
N_2O	−0.09502	−0.17718	−0.16406	—	−0.25153[26]
CO_2	−0.04971	−0.28465	−0.08034	−0.38247	−0.28621[27]
N_2	−0.00105	−0.06480	−0.00246	−0.08205	−0.07164[28]
C_2H_2	−0.01584	−0.24834	−0.01992	−0.16101	−0.23851[29]
C_2H_4	−0.01715	−0.11360	−0.01697	−0.13868	−0.18213[30]
F_2	−0.00088	−0.07882	−0.00099	−0.09134	−0.08066[32]

In Table 4, the calculated heats of sublimation (a half of the lattice energy) are compared with the experimental ones. These calculated values were obtained by taking the summation of (5) over the nearest and the 2nd-nearest neighbor molecules in the crystals. The contribution of the higher neighbors is small enough to be neglected (see **I**). The 3rd column of Table 4 shows the CNDO/2-Clementi results obtained by using the Clementi AO's to calculate the overlap integrals. The 5th column shows the corresponding INDO-Clementi resulst. The 2nd and 4th columns show those for usual CNDO/2 and INDO calculations. From this Table we can see that the best agreement between the calculated and the observed interaction energies is obtained when the calculation is done by using the Clementi AO's. We can also see that the INDO results are not so superior to the CNDO/2 results as is generally expected.

The deviation of the calculated heat of sublimation from the experimental one in CO becomes small if we assume that the molecules in the crystal are displaced from the approximate centers of inversion and, hence, if we assume that the resultant space group is not Pa3, but $P2_13$. Defining the displacement from the centrosymmetric positions by δ, as is shown in Fig. 3, we calculated the δ-dependency of the heat of the sublimation of α-CO crystals. $\delta=0.0$ Å corresponds to the Pa3 space group. The results are shown in Table 5. We can see that the Pa3 space group is not preferable in explaining the heat of the sublimation of the α-CO crystal. Thus, the crystal structure of α-CO may belong to the $P2_13$ space group. This situation is somewhat analogous to that with the α-N_2 crystal, for which the space group might be $P2_13$, according to recent far-IR absorption spectral data.[16] In order to check this, we calculated the δ-dependency of the α-N_2 crystal (see Table 5). It may be seen that the agreement with the experimental heat of sublimation is best when $\delta=-0.1$ Å. X-Ray diffraction study of α-N_2 by Lipscomb *et al.*[17] has given this δ-value as from −0.1 to −0.2 Å. By the way, the deviation from the pairwise additivity of α-N_2 is small, even with the $P2_13$ space group, compared with the heat of sublimation, as may be seen from Curve (b) of Fig. 2 ($\delta=-0.1$ Å). Thus, evidence has been reported both for [16–18] and against [19] the $P2_13$ space group for α-N_2 in experiments; our calculations support $P2_13$.

Table 5. Dependency of heat of sublimation upon the deviation from Pa3 structure

δ deviation from Pa3, Å	$1/2\sum U_{ab}$ by CNDO/2-Clementi, eV	
	CO	N_2
−0.25	−0.11669	—
−0.20	−0.13428	—
−0.17	—	−0.06336
−0.15	−0.15246	−0.06624
−0.10	−0.50166	−0.07386
−0.05	−0.19380	−0.05904
0.0	−0.55290	−0.06480
+0.05	−0.24258	−0.09162
+0.10	−0.26946	−0.10056
+0.15	−0.64942	−0.10998
+0.20	−0.34674	−0.09900

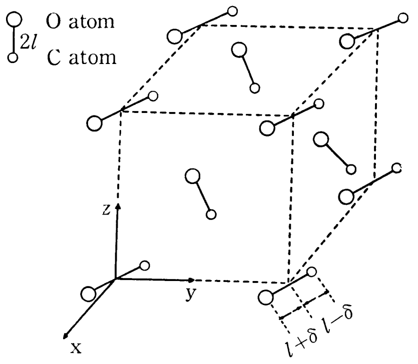

Fig. 3. Definition of displacement δ from centrosymmetric positions of the structure with space group Pa3.

Thus, the CNDO/2-Clementi method for the calculation of the intermolecular forces is quite useful, as may be seen from Table 4, if we use the Clementi AO's to calculate the overlap integrals. Moreover, this method is more rigorous from the theoretical point of view than is the usual method,[20] in which intermolecular forces are divided into three parts (exchange repulsion, dispersion, and electrostatic interaction forces) and calculated separately in terms of each different method. The CNDO/2-Clementi method unifies these forces and reduces the unknown errors due to the above

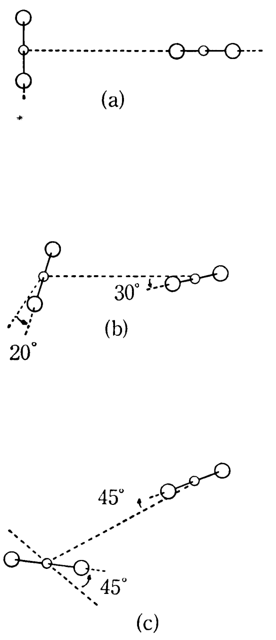

Fig. 4. Typical configurations of two CO_2 molecules separated by distance 4.1 Å.

division of intermolecular forces.

Now let us examine the reliability of the present method. This has been discussed partially in **I**; we would now like to add the following facts.

Figure 4 shows three typical configurations of two CO_2 molecules, separated by an R_0 distance of 4.1 Å. The interaction energies calculated by the present method are −0.17135, −0.08876, and −0.06419 eV for Configurations (a), (b), and (c) respectively. We can see that the (a) configuration, that is, the T-configuration, is the most stable one; this corresponds to the experimental results of Welsh *et al.*[21] They found that the two components of the (ν_1, $2\nu_2$) Fermi doublet of gaseous CO_2 show a complex structure in a long-absorption pathlength at a low temperature. They analyzed this absorption and interpreted it in terms of the rotation and vibration of $(CO_2)_2$ dimers held in a locked T-position at an intermolecular distance of 4.1 Å.

For comparison, we have done this configuration calculation by using the non-bonded-atom-atom pair interaction potential superimposed on the quadrupole-quadrupole interaction potential. This is shown by the following equation:

$$V(R,\theta,\theta',\phi,\phi') = V_{\text{exp-6}} + V_{Q\text{-}Q} \tag{6}$$

$$V_{\text{exp-6}} = \sum_j [a_j \exp(-b_j r_j)/r_j^{d_j} - c_j/r_j^6] \tag{7}$$

$$\begin{aligned} V_{Q\text{-}Q} = {} & 3Q^2\{1-5(\sin^2\phi\sin^2\theta+\sin^2\phi'\sin^2\theta') \\ & -15\sin^2\phi\sin^2\theta\sin^2\phi'\sin^2\theta' \\ & +2[4\sin\phi\sin\theta\sin\phi'\sin\theta' \\ & -(1-\sin^2\phi\sin^2\theta)^{1/2}(1-\sin^2\phi'\sin^2\theta')^{1/2} \\ & \times\cos(\theta-\theta')]^2\}/4R^5 \end{aligned} \tag{8}$$

TABLE 6. PARAMETERS IN Eq. (7), IN kcal/mol AND Å UNITS

j	$a_j\times 10^5$	b_j	c_j	d_j
C···C	3.012	0.0	327.0	12.0
C···O	1.785	2.304	202.2	6.0
O···O	1.057	4.608	125.10	0.0

In Eq. (7), the summation over j is taken over all the pairs of atoms between two molecules. The four parameters, a_j, b_j, c_j, and d_j, were derived from the Table of Liquori *et al.*[22] (Table 6). In Eq. (8), Q is a molecular quadrupole moment and is 4.3×10^{-26} cm² esu for CO_2 molecule;[23] the relative orientation $(\theta,\theta',\phi,\phi')$ of the two molecules is defined as is shown in Fig. 5.

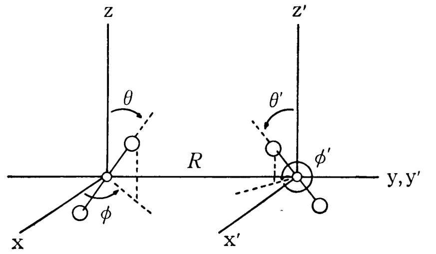

Fig. 5. Geometrical representation of two CO_2 molecules in interaction.

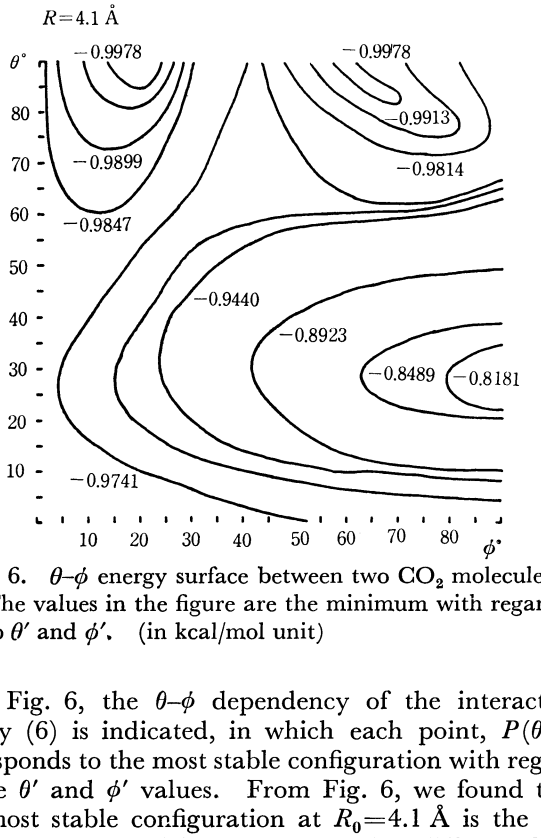

Fig. 6. θ–ϕ energy surface between two CO_2 molecules. The values in the figure are the minimum with regard to θ' and ϕ'. (in kcal/mol unit)

In Fig. 6, the θ–ϕ dependency of the interaction energy (6) is indicated, in which each point, $P(\theta,\phi)$, corresponds to the most stable configuration with regard to the θ' and ϕ' values. From Fig. 6, we found that the most stable configuration at R_0=4.1 Å is the one indicated in Fig. 4(b); this is somewhat different from the experimental findings.

Thus, the present CNDO/2 method is superior to a method using such a potential as (6).

In conclusion, the CNDO/2-Clementi method is useful in calculating the interaction energy between such molecules, as is indicated in Table 1.

We are now proceeding to calculate the interaction energy of more complex molecules by the same method. The results will be reported elsewhere.

All the computing in the present paper was done at the Computer Center of Tohoku University using the NEAC-2200 model 700 and its TSS.

References

1) M. Hashimoto and T. Isobe, This Bulletin, **46**, 2581 (1973).

2) B. C. Kohin, *J. Chem. Phys.*, **33**, 883 (1960).

3) T. Kihara, *Adv. Chem. Phys.*, **5**, 147 (1963).

4) T. Sugawara and E. Kanda, *Sci. Rept. Res. Inst., Tohoku Univ. Ser.*, **A4**, 607 (1952).

5) W. C. Hamilton and M. Petrie, *J. Phys. Chem.*, **65**, 1453 (1961).

6) L. Jansen, A. Michels, and J. M. Lupton, *Physica*, **20**, 1235 (1954).

7) A. I. M. Rae, *Mol. Phys.*, **16**, 257 (1969).

8) S. M. Blumenfeld, S. P. Reddy, and H. L. Welsh, *Canad. J. Phys.*, **48**, 513 (1970).

9) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill (1970).

10) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

11) P. Rosen, *ibid.*, **21**, 1007 (1953).

12) A. Shostak, *ibid.*, **23**, 1808 (1955).

13) R. Block, R. Roel, and G. T. Maten, *Chem. Phys. Lett.*, **11**, 425 (1971).

14) R. F. W. Bader, O. A. Navaro, and V. Beltran-Lopez, *ibid.*, **8**, 568 (1971).

15) O. A. Navaro and V. Beltran-Lopez, *J. Chem. Phys.*, **56**, 815 (1972).

16) E. J. Wachtel, *ibid.*, **57**, 5620 (1972).

17) T. H. Jordan, H. W. Smith, W. E. Streib, and W. N. Lipscomb, *ibid.*, **41**, 756 (1964).

18) J. R. Brookman, M. M. McEnaan, and J. A. Scott, *Phys. Rev.*, **B4**, 3661 (1971).

19) A. F. Schuch and R. L. Mills, *J. Chem. Phys.*, **52**, 6000 (1970).

20) See for example, M. Hashimoto, M. Hashimoto, and T. Isobe, This Bulletin, **44**, 649 (1971).

21) L. Mannik, J. S. Stryland, and H. L. Welsh, *Can. J. Phys.*, **49**, 3056 (1971).

22) P. de Santis, E. Giglio, A. M. Liquori, and A. Ripamonti, *J. Polym. Sci.*, **A1**, 1383 (1963).

23) A. D. King, *J. Chem. Phys.*, **51**, 1262 (1969).

24) W. F. Giauque and R. A. Ruehrwein, *J. Amer. Chem. Soc.*, **61**, 2626 (1939); see also literature (7).

25) J. O. Clayton and W. F. Giauque, *ibid.*, **54**, 2610 (1932); see also literature (6).

26) R. W. Blue and W. F. Giauque, *ibid.*, **57**, 991 (1935).

27) W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

28) See literature (2).

29) D. McIntosh, *J. Phys. Chem.*, **11**, 306 (1907).

30) C. J. Egan and J. D. Kemp, *J. Amer. Chem. Soc.*, **59**, 1264 (1937).

31) L. Meyer, C. S. Barret, and S. C. Greer, *J. Chem. Phys.*, **49**, 1902 (1968).

32) J. H. Hu, D. White, and H. L. Johnston, *J. Amer. Chem. Soc.*, **75**, 5642 (1953).