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CNDO/2 Calculation of the Valence Electron Contribution to the Intermolecular Potential of Some Ground State Closed Shell Molecules

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The empirical or semiempirical theories of intermolecular forces seem to be able to yield satisfactory results for the problem of the stability of solids and for that of conformation of polymers, but in the quatitative calculation of the interaction energy they have more or less been clouded by ambiguous parameters or factors. This is also the result of the artificial distinction between a long- and a short-range force in the usual calculations of the interaction energy in the region of the van der Waals minimum. Thus, it is necessary now to seek a method by which these forces can be unified.

The possibility that a molecular orbital theory could yield an attractive interaction between two closed-shell atoms or molecules has often been discussed.[1] A careful CI calculation for He···He was done recently[2] using very elaborate multiconfigurational wavefunctions, and successful result was thus obtained. However, it is doubtful that this method can be practically applied to larger systems.

The energy of interaction, $U(M\cdots M)$, is generally defined as follows:

$$U(M\cdots M) = E(M\cdots M) - 2E(M) \quad (1)$$

where M is a molecule or an atom and where $M\cdots M$ is a dimer.

Assuming that intermolecular bonding is mainly brought about by an overlap between two molecular orbitals, we will calculate $U(M\cdots M)$ by means of the CNDO/2 SCF MO method[3] and will study the applicability of this method to the molecular-interaction problem by considering the contribution to the lattice energy of the molecular crystal.

The molecules treated in the present work are N_2, C_2H_2, and CO_2, which form crystals belonging to Pa3 space group, and C_2H_4, which forms a crystal belonging to the $P2_1/n$ space group.

Theoretical

Dimer Orbitals and Energies Obtained by the CNDO/2 Method. In this work, the dimer can be treated as one species, and there is essentially no difference between the intermolecular bond and the intramolecular bond so long as the LCAO MO approximation is used. The dimer orbitals and energies can, then, be obtained in the usual way, like the monomer orbital, from the following matrix elements:

$$F_{rr} = -\frac{1}{2}(I_r+A_r) + \left[(P_{AA}-Z_A)-\frac{1}{2}(P_{rr}-1)\right]\gamma_{AA} + \sum_{B(\neq A)}(P_{BB}-Z_B)\gamma_{AB} \quad \text{(orbital } r \text{ on atom } A) \quad (2)$$

$$F_{rs} = \frac{1}{2}S_{rs}(\beta_A+\beta_B) - \frac{1}{2}P_{rs}\gamma_{AB} \quad (r \text{ on } A,\ s \text{ on } B). \quad (3)$$

The total electronic energy of the dimer is expressed as follows:

$$E_{\text{elec}} = \frac{1}{2}\sum_{r,s} P_{rs}(H_{rs}+F_{rs}). \quad (4)$$

The Coulombic repulsion energy between cores is as follows:

$$E_{\text{core}} = \sum_{A\neq B} Z_A Z_B / R_{AB}. \quad (5)$$

The total dimer energy, $E(M\cdots M)$, is, therefore:

$$E_{\text{total}} = E_{\text{elec}} + E_{\text{core}}. \quad (6)$$

The intermolecular interaction energy is, then:

$$U(M\cdots M) = E_{\text{total}}(M\cdots M) - 2E_{\text{total}}(M). \quad (7)$$

The pair interaction energy (7) was summed over all the pairs in the crystal, assuming the pairwise additivity of the intermolecular forces. One half of the above sum was compared with the experimental heat of sublimation.

The assumption of the pairwise additivity is based upon the finding[4] that, in the system of He_3, the non-additive contribution in the neighbourhood of the van der Waals minimum is negligible.

Modification of Slater Atomic Functions at Larger Value. Simple Slater atomic orbitals are usually used for the calculation of the electronic states of molecules; they are expressed, for example, as follows:

$$\chi_{2p_z} = (\alpha^5/\pi)^{1/2}\exp(-\alpha r) r\cos\theta \quad (8)$$

χ in (8) gives a satisfactorily correct charge distribution when r is small, but it gives incorrect results when r becomes large.

One of the atomic functions accurate also in the region of large r values is the linear combination of (8) with different orbital exponent α's:

$$\chi'_{2p_z} = r\cos\theta\sum a_i(\alpha_i^5/\pi)^{1/2}\exp(-\alpha_i r) \quad (9)$$

The coefficients, a_i's, and orbital exponents, α_i's, have been determined by the Hartree–Fock–Roothan Method by Clementi.[5] In the present paper the above types of Clementi's atomic orbitals will be used as basic functions, unless otherwise stated.

The CNDO/2 parametrization was done as usual[3] except for the use of Slater's μ-values; the FORTRAN program for CNDO/2 written by Kikuchi[6] was modified so as to be applicable to Clementi's AO basis.

1) R. G. Gordon and Y. S. Kim, *J. Chem. Phys.*, **56**, 3122 (1972).
2) H. F. Schafer III, D. R. McLaughlin, F. E. Harris, and B. J. Alder, *Phys. Rev. Letts.*, **24**, 1469 (1970).
3) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill (1970).
4) O. A. Novaro and V. Beltran-Lopez, *J. Chem. Phys.*, **56**, 815 (1972).
5) E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965); *ibid., supplement*, "Tables of Atomic Functions".
6) O. Kikuchi, "Molecular Orbital Method—Practical Use by Computer", A Series of Monographs Modern Trends in Chemistry, No. 6, Kodansha, Tokyo (1971).

In the present work, μ-values appear, for example, as α_i in (9).

All the numerical calculations were done on a NEAC-2200 model 700 computer system at the Computer Center of Tohoku University.

Results and Discussion

Figures 1 and 2 indicate the dependency of the $U(M\cdots M)$ of C_2H_4 on the intermolecular distance, R, when the two molecules have a parallel and perpendicular configuration respectively.

The summation of (7) over all the pairs of molecules in the crystal was approximated by that over the nearest and the second-nearest neighbour molecules,

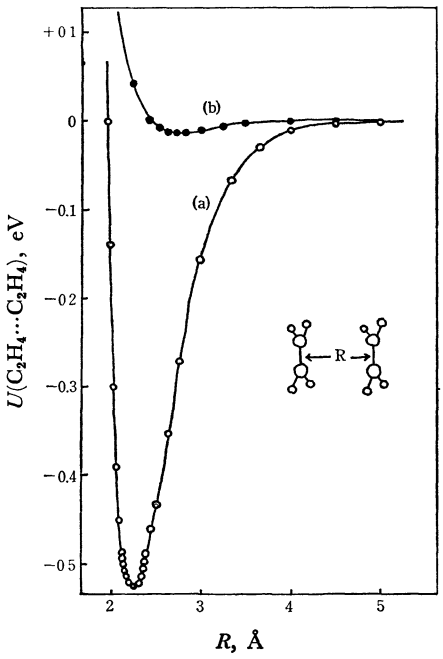

Fig. 1. The dependency of $U(M\cdots M)$ of C_2H_4 on intermolecular distance R when the two molecules have a parallel configuration.
(a) using Clementi's AO; (b) using simple Slater's AO.

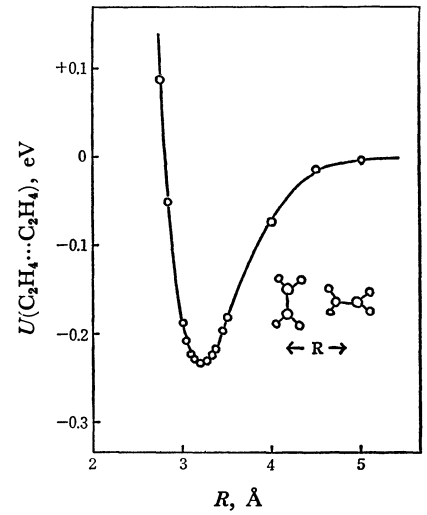

Fig. 2. The dependency of $U(M\cdots M)$ of C_2H_4 on intermolecular distance R when the two molecules have a perpendicular configuration (using Clementi's AO).

Table 1.[a)]

M	$1/2\sum U(M\cdots M)$	heat of Sublimation (obs.)
N_2	−0.06480	−0.07164[12)]
C_2H_2	−0.24834	−0.23851[13)]
C_2H_4	−0.11360	−0.18213[14)]
CO_2	−0.28465	−0.28621[15)]

a) In electron volt, error ±0.00025

since the third-nearest neighbour molecules in the crystal are from 11.1 to 19.4 Å away from the central molecule and in this region the $U(M\cdots M)$ might be negligible, as may be seen from Figs. 1(a) and 2. More or less similar situations are observed for the other crystals.

In Table 1, the experimental heat of sublimation, which does not include the zero-point energy, and a half of the calculated interaction energy summed over the nearest and the second-nerarest neighbour molecules in the crystals are compared. The consistency seems to be quite good.

In Fig. 1 the $U(M\cdots M)$ (a) calculated by using Clementi's AO is compared with that (b) calculated using the simple Slater AO.

The overlap integrals among the simple Slater AOs are very small and negligible in the region of the intermolecular distances. However they become effective if Clementi's AOs are used.

To show the partial reliability of the present work, we wish to cite two example: 1) Many authors have examined the refinement of Bunn's crystal structure for ethylene,[7)] and it is known today to have $P2_1/n$ space group.[8)] If the $\sum U(M\cdots M)$ of C_2H_4 is calculated for Bunn's structure, it becomes +3.37 eV and is strongly repulsive. This does not explain the formation of the stable crystal. 2) The lower-temperature form of the crystalline acetylene has already been suggested to be Cmca.[9,10)] The present calculation of $\sum U(M\cdots M)$ of C_2H_2 for the Cmca structure is −0.51456 eV, surely lower that of the high-temperature form, −0.49668 eV.

Furthermore, the *staggered* configuration of CH_3OH molecule was found to have an energy lower by 0.04486 eV or 1.03 kcal/mole than the *eclipsed* configuration. This is in good agreement with the experimental value of 1.07 kcal/mole.[11)]

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7) C. N. Bunn, *Trans. Faraday Soc.*, **40**, 23 (1944).
8) S. M. Blumenfeld, P. Reddy, and H. L. Welsh, *Can. J. Phys.*, **48**, 513 (1970).
9) M. Ito, T. Yokoyama, and M. Suzuki, *Spectrochim. Acta*, **26A**, 695 (1970).
10) M. Hashimoto M. Hashimoto, and T. Isobe, This Bulletin, **44**, 649 (1971).
11) C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, **31**, 841 (1959).
12) B. L. Kohin, *J. Chem. Phys.*, **33**. 882 (1960).
13) D. McIntosh, *J. Phys. Chem.*, **11**, 306 (1907).
14) C. J. Egan and J. D. Kemp, *J. Amer. Chem. Soc.*, **59**, 1264 (1937).
15) H. Sponer and M. Bruch-Willstatter, *J. Chem. Phys.*, **5**, 745 (1937).