

A Novel Development for the Simulator of Intermolecular Potentials

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A novel treatment for the estimation of intermolecular interactions is proposed, incorporating intermolecular parameters into the semiempirical MNDO MO method. These parameters vary depending on the atomic species, but are constants to be reduced to the original MNDO formalism when the atomic pair belongs to a same molecule. The core-core repulsion and the two electron integral terms were modified using these parameters. The parameters introduced have been determined so as to reproduce well the interaction energies of the different model systems of molecular interaction. The resulting parameters permit calculations of large systems with sufficient accuracy within reasonably short CPU time.

Intermolecular interactions play an important role in various fields of chemistry such as solution chemistry,¹⁾ quantum pharmacology,²⁾ and organic chemistry.³⁾ Although recently quantum-mechanical treatment has become accurate to be comparable to the experimental value in different systems, CPU time is still a limiting factor for the calculation of especially interaction energies in many-body systems. Semiempirical MO methods are expected to benefit short CPU time with reasonable accuracy of calculation. To this purpose, several investigators have made calculations.⁴⁾

A total reparameterization of a semiempirical MO method would be necessary including the intermolecular potentials besides the molecular properties such as heat of formation which are reproduced in the MNDO⁵⁾ and MINDO/3⁶⁾ MO methods. But such reparameterization is likely to disturb the results hitherto attained satisfactorily. Quite recently, Dewar et al.⁷⁾ proposed a new semiempirical MO formula, AM1, which is the improved version of the MNDO MO method. This method is reported to have better reproducibilities in single molecular property as well as in energies of intermolecular interactions, whose results are compared with our calculations below.

Another method may be pointed out for the treatment of intermolecular potentials. That is, a partial reparameterization of a semiempirical MO formalism. Burstein and Isaev⁸⁾ proposed the MNDO/H method using a new function for the core-core repulsion term, while Mohammad and Hopfinger⁹⁾ proposed the CNDO/2H and the MINDO/3H methods using new treatments of the resonance integral and the core-core repulsion terms. These methods enabled us to calculate the hydrogen bonding systems of the intermolecular as well as intramolecular origin. However, there are some shortcomings of them. The user has to determine in advance which atoms are hydrogen-bonded or not, and the applications are limited to those systems where intermolecular forces other than the hydrogen bond of interest are exactly calculable by the semiempirical MO methods.

We propose here a new method of treating intermolecular potentials, i.e., introduction of new parameters, intermolecular parameters, which contribute only to the intermolecular potentials.

Calculation

We selected the MNDO MO formalism for the basis of new method which can be used to study with a number of properties of molecular systems large enough to be interesting to the organic chemists and biochemists. The CNDO/2 MO formalism¹⁰⁾ might also be useful for the basis. In fact, CNDO/2H method is reported to be more reliable than MINDO/3H method.⁹⁾ However, the CNDO/2 MO method sometimes fails to predict correctly the heat of formation, molecular geometries, etc., and hence it is not adopted in the present paper.

A QCPE¹¹⁾ program was improved in great deal¹²⁾ and modified to include corrections stated below and the program NICER¹³⁾ was used as a diagonalization routine. The program SIMPLX¹⁴⁾ was used to optimize the intermolecular parameters. Ab initio MO calculations were carried out according to the IMSPAK program system¹⁵⁾ and its Osaka University version.¹⁶⁾ The 4-31G basis set¹⁷⁾ was adopted throughout. All molecular geometries were optimized using MNDO MO method. Numerical calculations were performed on an NEAC S1000 computer plus HFP system at the Computer Center, Osaka University and HITAC M-200H computer at the Computer Center, Institute for Molecular Science.

Formalism

There are some papers¹⁸⁾ which indicate that the MNDO MO method underestimates energies of intermolecular interactions, especially for hydrogen bonding systems. Energy decomposition analyses proposed by Kitaura and Morokuma¹⁹⁾ show that the unstabilization of the ES (electrostatic) term at longer distances is responsible for this underestimation (Fig. 1). Since the EX (exchange repulsion) term always

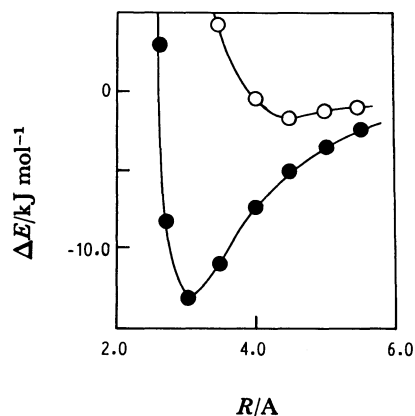


Fig. 1. Distance dependencies of the ES plus EX term for the $(\text{H}_2\text{O})_2$ system. MNDO (●); ab initio (○).

vanishes in MNDO approximation, ES term in MNDO MO method is thought to correspond to the ES+EX term in ab initio MO method. The simplest way to correct for the ES term is to modify the core-core repulsion term. We tried to correct this as follows:

$$E_{ij}^{\text{core}}(\text{SIMP}) = E_{ij}^{\text{core}}(\text{MNDO}) - (A_i + A_j) \{ \exp\{-B_i(R_{ij} + \alpha)\} + \exp\{-B_j(R_{ij} + \alpha)\} \}. \quad (1)$$

For atomic pairs of N-H and O-H a slightly different expression is used basing on the MNDO approximation:

$$E_{ij}^{\text{core}}(\text{SIMP}) = E_{ij}^{\text{core}}(\text{MNDO}) - (A_i + A_j)(R_{ij} + \alpha) \{ \exp\{-B_i(R_{ij} + \alpha)\} + \exp\{-B_j(R_{ij} + \alpha)\} \}, \quad (2)$$

where A_i , B_i , and α are intermolecular parameters. A 's and B 's vary depending on the atomic species, but A_i plus A_j is set to zero when i and j belong to a same molecule. A 's and B 's are determined empirically to fit to 110% of the most stable intermolecular distances and to 70% of the ES+EX calculated from 4-31G basis set. α is equal to 1.20 Å in all cases. Although it would be better to fit to the experimental data, our attempt was interrupted by the insufficient data of intermolecular interactions in gas phase. The percentages, 110 and 70%, were taken by considering the characteristics of the relevant basis set, that is, the overestimation of electrostatic interaction energies and the underestimation of intermolecular distances.²⁰ The fifteen different systems which are illustrated in Fig. 2 were used for this parameterization. By these modifications, interaction energies from MNDO method were found to be improved in great deal except for the strongly hydrogen bonding systems. To take into account the latter systems, correction was made with the two

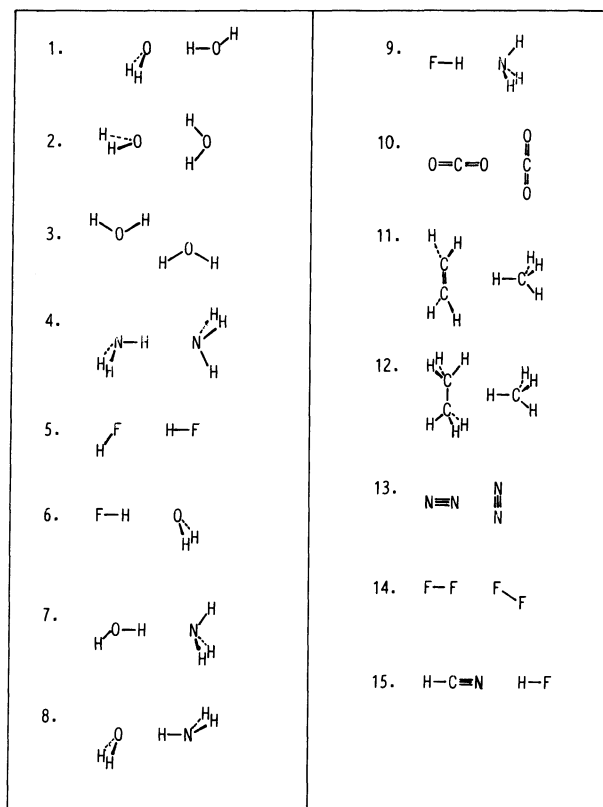


Fig. 2. Standard systems adopted for the SIMP parameterization.

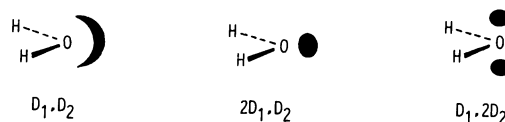


Fig. 3. Changes of the minimum point in molecular electrostatic potentials as a function of D_1 and D_2 .

center repulsion integrals.

The two-center repulsion integrals are expanded in terms of multipole-multipole interactions $[M_{lm}^A, M_{km}^B]$ in MNDO approximations. The formula for the integrals is expressed as follows:

$$\langle rs | tu \rangle = \sum_l \sum_k \sum_{m=-l}^{l \min} (e^2/2)^{l+k} \sum_{i=1}^{2^l} \sum_{j=1}^{2^k} [R_{ij}^2 + (\rho_i^A + \rho_i^B)^2]^{-1/2}, \quad (3)$$

where R_{ij} is the distance between the point charges i and j in the interacting configurations at atom A and B. For example, $\langle ss | sp_z \rangle$ is given by:

$$\langle ss | sp_z \rangle = [q^A, \mu_z^B] = -(e^2/2) \{ (R_{AB} - D_1^B)^2 + (\rho_0^A + \rho_1^B)^2 \}^{-1/2}, \quad (4)$$

where D_1 and D_2 are the charge separations of the

multipole moments. Since D_1 and D_2 have been determined in MNDO approximation so as to reproduce well the molecular constants of each isolated molecule, it may be changed slightly in the interacting systems. In fact, the minimum point of molecular electrostatic potentials around H_2O molecule using MNDO formula²⁰ varies with the values of D_1 and D_2 (Fig. 3), and the molecular electrostatic potential map is different from the one using ab initio MO formula²² when original values of D_1 and D_2 are used. This indicates that the changes in D_1 and D_2 may result in the correct map and the correct direction of the intermolecular interactions. Therefore, D_1 and D_2 are modified as follows:

$$D_l^{\text{SIMP}} = f_l D_l \quad (l=1 \text{ or } 2). \quad (5)$$

f_l is the intermolecular parameters and set equal to 1.0 when atoms A and B belong to a same molecule but not when they belong to different molecules. Such definition of f_l , together with that of A_i in Eqs. 1 and 2, makes SIMP equivalent to MNDO for an isolated molecule. Equation 5 is applied only to the case of linear quadrupole, Q_{aa} and between hydrogen and heavy atoms when $l=2$. These parameters have been determined so as to reproduce well the interaction energies calculated from ab initio MO method for the different systems of molecular interaction illustrated in Fig. 2.

Results and Discussion

Table 1 lists the optimized values of the SIMP parameters for elements of H, C, N, O, and F. f_l values are approximately equal in the three atoms of N, O, and F, which indicates that the original MNDO MO method has made a similar error in the directions of the lone pairs of these atoms.

Tables 2 and 3 list the interaction energies and the most stable intermolecular distances calculated by SIMP, MNDO MO, AM1 MO, and ab initio (4-31G) MO method. It is clear that the results of SIMP reproduce well the one of ab initio MO method considering the aforementioned characteristics of 4-31G basis set. The regression analyses according to a relation $y=ax$ resulted in:

Table 1. Optimized SIMP Parameters

	A	B	f_1	f_2
H	4.281	1.7120	—	—
C	0.00211	2.8058	1.0	1.0
N	40.0	2.4059	1.402	2.658
O	54.0	2.8079	1.560	2.616
F	50.6	2.2920	1.497	2.147

$$\Delta E(\text{SIMP}) = 0.713\Delta E(4-31\text{G}), \quad (6)$$

$$n = 15, R = 0.938, s = 4.85 \text{ kJ mol}^{-1},$$

$$Re(\text{SIMP}) = 1.033Re(4-31\text{G}), \quad (7)$$

$$n = 15, R = 0.822, s = 0.37 \text{ \AA}.$$

Table 2. Comparison of Interaction Energies^{a)} Calculated by Various Procedures

No. ^{b)}	SIMP	MNDO	AM1 ^{c)}	4-31G
1	-24.2	-2.5	-13.8	-32.6
2	-30.4	-4.1	—	-27.0
3	-21.6	-1.6	—	-25.5
4	-19.6	-1.3	—	-17.2
5	-22.2	-3.1	—	-31.8
6	-31.0	-5.8	—	-56.1
7	-27.9	-2.7	-11.3	-37.7
8	-17.2	-1.8	—	-17.2
9	-45.7	-6.4	—	-68.2
10	-1.8	-1.7	0.0	-7.8
11	-0.9	0.0	—	-2.7
12	-3.4	0.0	—	-0.2
13	-0.4	-0.4	—	-1.1
14	-0.3	0.0	—	-0.7
15	-28.4	-6.2	—	-36.2

a) Values in kJ mol^{-1} . b) See Fig. 2. c) Taken from Ref. 5.

Table 3. Comparison of Most Stable Intermolecular Distances^{a)} Calculated by Different Procedures

No. ^{b)}	SIMP	MNDO	4-31G
1	3.05	4.30	2.88
2	2.80	3.90	2.90
3	3.08	4.51	2.85
4	3.15	4.67	3.30
5	2.86	3.14	2.71
6	2.98	3.96	2.62
7	3.06	4.32	2.93
8	3.20	4.54	3.22
9	2.99	3.95	2.68
10	4.95	4.96	4.10
11	4.50	7.70	4.40
12	4.27	8.16	5.00
13	3.61	4.10	3.60
14	3.35	4.94	2.70
15	3.16	3.98	2.99

a) Values in \AA. b) See Fig. 2.

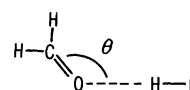


Fig. 4. Molecular configuration for the H_2CO plus HF system.

Table 4. Comparison of Interaction Energies and Optimized Intermolecular Distances Calculated from SIMP and ab initio (4-31G^d) MO Methods^b

H donor	H acceptor	Re/A	$\Delta E/\text{kJ mol}^{-1}$
HCN	NH ₃	3.18(3.15)	-32.4(-40.6 ^e)
CF ₃ H	CHONH ₂	3.24(3.11)	-18.9(-32.0 ^d)
CH ₄	NH ₃	3.33(4.02)	-8.0(-4.6 ^e)
HF	H ₂ CO	3.10(2.73)	-24.8(-41.9 ^e)
H ₂ O	CO ₂	3.34(3.10)	-10.6(-12.7 ^e)
NH ₄ ⁺	H ₂ O	2.56(2.68)	-91.7(-114.3 ^e)
H ₂ O	F ⁻	2.50(2.30)	-99.2(-101.6 ^e)

a) Except for H₂O plus F⁻ system. b) In parentheses listed are the results of ab initio MO method. c) Taken from Ref. 23. d) Taken from Ref. 24. e) Taken from Ref. 25. f) Near HF calculation. Taken from Ref. 26.

The regression coefficients are consistent with the initial purpose of fitting the results of the SIMP method to 110% of the *Re* values and to 70% of the ΔE values calculated from 4-31G basis set. The correlation coefficient is somewhat low in Eq. 7, but this is due to a small change in *Re* values.

We tested the SIMP method in the different 7 systems which were not used for the parametrization (Table 4). The reproducibility is satisfactory, considering the relations in Eqs. 6 and 7. SIMP also gives the correct molecular configurations in interacting systems. For example, although MNDO MO method gives 180 degree for the most stable values of θ in H₂CO plus HF system (Fig. 4), it gives 131 degree, which are approximately equal to that calculated from ab initio MO method.²²

We expect that the SIMP method can be applied to various fields of chemistry-solvent effects on molecular structure, charge distribution, orbital energies, etc. These applications are currently under way in our laboratories.

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