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A study of hydrogen bond strengths of neutral water clusters $(H_2O)_n$ using modified MNDO

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Semi-empirical molecular orbital methods proposed up to now seriously fail to describe hydrogen bonded systems associated with $(H_2O)_n$. A new scheme of parametrization using a semi-empirical method is proposed. We tested hydrogen bonding associated with the water clusters $(H_2O)_n$. The results are found to be close to *ab initio* Hartree-Fock quality, indicating a good promise for studying hydrogen-bonding systems other than O—H···O moiety.

Key words: I-MNDO — MNDO — Hydrogen bond — Ionization potential — Water clusters — Water dimer — Electronic polarizability — Parametrization

1. Introduction

Semi-empirical self-consistent field HF (Hartree-Fock) LCAO (linear combination of atomic orbitals) MO (molecular orbitals) theories [1-4] are known to seriously fail to describe hydrogen bonded systems of water clusters [e.g., $(H_2O)_2$]. Among the semi-empirical theories (e.g. CNDO [5], INDO [5], MINDO [6, 7], and MNDO [8]), MNDO [modified NDDO (neglect of diatomic-differential overlap [5])] is the most advanced method in that only the overlap integrals involving atomic orbitals (μ_A and ν_B or λ_C and σ_D) between two different atoms (A and B or C and D) are neglected in the two-electron integrals that appear in the HF matrix elements; that is,

$$(\mu_A\nu_B|\lambda_C\sigma_D) = \delta_{AB}\delta_{CD}(\mu_A\nu_A|\lambda_C\sigma_C). \tag{1}$$

As a consequence, the treatment [8] of multipole-multipole interactions is more complete than in other semi-empirical methods mentioned above. For this reason, directional effects in bonding are more accurately taken care of. This, in turn, causes superior optimized geometries and heats of formation. However, we find that the MNDO method also seriously fails to predict acceptable geometry and binding energy of hydrogen-bonded water dimer. Further details will be discussed in the next section.

For conformational analysis, geometry optimization, and transition state search especially for large complex molecular systems, ab initio HF calculations require prohibitively large computational time. To avoid this difficulty, semi-empirical calculations are often desired. In this spirit, we present a new parametrization scheme to correct the difficult problem of hydrogen bonding unresolved by most semi-empirical methods.

A good semi-empirical MO should use parameters which produce a fit to a small number of selected (small-size if possible) molecules and demonstrate predictive power for other molecules, by showing results that agree with either the *ab initio* HF method or experiment. In view of presently available *ab initio* calculations for $(H_2O)_n$, our prime objective is to test the validity of this new parametrization scheme for reproducing the hydrogen-bond strengths and ionization potentials of the water clusters $(H_2O)_n$.

2. Parametrization for molecular clusters; hydrogen-bonded water clusters

To demonstrate the serious failures of various semi-empirical theories and the need for correction, a brief review of various semi-empirical MO results for the hydrogen bonded water dimer will be made. In addition, our calculated results using MNDO will be discussed here. Subsequently, improved (corrected) results for various water clusters will be presented based on a new scheme of parametrization.

Using CNDO/2, Thiel [1] found the most stable structure of the water dimer $(H_2O)_2$ to be C_{2h} symmetry with a partial O—O (oxygen-oxygen) bond, but with no hydrogen (O—H···O moiety) bond, in sharp contrast to the observed [9] translinear C_s symmetry dimer with an O—O distance of 2.98 Å. In addition, the stable C_{2h} dimer predicted by CNDO/2 has a strong binding energy of 14 kcal/mol rather than an expected repulsion energy. *Ab initio* [10] calculations by Clementi [11] and other researchers [12] have shown the most stable geometry to be the translinear dimer close to the observed geometric structure [9] and binding energy [13] shown in Table 1. Later, Zielenski et al. [3] and Klopman et al. [4] also found a serious failure with MINDO/3 in both the binding energy and equilibrium geometry for $(H_2O)_2$. They [4] found that the C_s water dimer at the equilibrium geometry of O—O distance, 2.98 Å has a repulsion energy of 7.5 kcal/mol. On the other hand, the INDO method [2] predicted −14.1 kcal/mol at this geometry. All of these results are unrealistic.

We computed the water dimer of the observed geometry of Dyke et al [9], using the MNDO method. Even with this advanced method, a repulsion energy of 7.3 kcal/mol similar to that of MINDO/3 was predicted at the same geometry used. This strongly indicates that improvement of the MNDO method over MINDO/3 [3], e.g. in directional effects or multipole-multipole interactions does

Table 1. Comparison of our fitted and predicted values with experiments and other theories for water dimers

Fitted value	I-MNDO[c]	AbHF[d]	EPEN[e]	Experiment
Binding energy (kcal/mole)	−5.6	−4.58	−5.44	−5.44[f]
Intermolecular equilibrium geometry[a]				
R_{O-O} (Å)	2.98	3.00	2.88	2.98[g]
θ_d (degree)	52.3	54.7	55.1	51.6[g]
θ_a (degree)	60.7	38.0	61.9	58.00[g]
Dipole moment (debye)	2.600	2.89	2.35	2.601[g]

Predicted N.V.F.[b] in cm^{-1}

Approximate characterization (symmetry)	I-MNDO[c]	AbHF[d]	EPEN[e]	Experiment
Out-of-plane H-bond shear (A_i'')	493	537	593	
In-plane H-bond shear (A_i')	360	319	496	
H-bond stretch (A_i')	190	161	168	150[g]
In-plane H-bond bend (A_i')	177	127	189	
Out-of-plane H-bond bend (A_i'')	144	116	161	
H-bond torsion (A_i'')	108	105	98	

[a] θ_d is the angle between the proton donating water axis and R_{O-O}, θ_a is the angle between the proton accepting water axis and R_{O-O} (see [9])

[b] N.V.F. stands for normal-mode vibrational frequency

[c] Our results based on the addition of intermolecular parametrization

[d] Ref. [12.i]

[e] Ref. [20]

[f] Ref. [13]

[g] Ref. [19]

not correct the difficulties with the hydrogen bonded molecular cluster, $(H_2O)_2$. This suggests that empirical parameters chosen in the usual semi-empirical MO methods [5–7] work best to fit physical and chemical properties associated with atoms separated by intramolecular but not intermolecular equilibrium distances, that is, associated only with the equilibrium geometry of the molecules. Thus the original MNDO parameters serve best for intramolecular, but not for intermolecular properties.

From geometry optimization using MNDO, we found the most stable geometry to be a bifurcated configuration with the O—O distance of 4.01 Å and the small binding energy of ~1 kcal/mol. Another failure of MNDO we found was a poor prediction of H_2O electronic polarizability, with calculated polarizabilities of $\alpha_{xx} = 0.47 \times 10^{-24}$ cm^3, $\alpha_{yy} = 0.04 \times 10^{-24}$ cm^3 and $\alpha_{zz} = 0.85 \times 10^{-24}$ cm^3 with the z-axis along the principal axis of H_2O. The mean polarizability $[\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})]$ is then 0.45×10^{-24} cm^3, compared to the observed value [14] of 1.44×10^{-24} cm^3. Both the induction and dispersion forces are important contributors to the hydrogen bond strength [14–16]. This is a partial cause of the

MNDO prediction of weaker intermolecular binding or weaker long-range attractive forces compared to *ab initio* [11, 12] and perturbation [15] results. Such deficiencies cannot be corrected by the present MNDO parameters, as they are intramolecular in nature.

From the discussions made above, we now clearly see why most of the semi-empirical methods including MNDO fail to reproduce the observed physical and chemical properties of molecular clusters (e.g. hydrogen-bonded water clusters). They are bound by long-range intermolecular attractive interaction forces. As mentioned above, the parameters of semi-empirical methods serve best for matching molecular properties particularly at equilibrium geometries wherein the interatomic distances are much shorter compared to intermolecular separations in molecular clusters. Indeed, this is the reason why all the semi-empirical methods illustrated above seriously failed to reproduce the observed properties of the hydrogen-bonded molecular cluster, $(H_2O)_2$. As we (S.H.S.S.) [17–19] found earlier with many other molecular systems, the success of MNDO in yielding good correlation with experiments suggests that the MNDO scheme of parametrization is, in general, operationally reliable. Thus we largely retain the original MNDO format of the parametrization procedure. However, we divide the parameters into two sets, one for intramolecular bonding and the other set for intermolecular bonding. The latter set is introduced to properly take into account the effects of the long-range intermolecular interactions between water molecules for the descriptions of hydrogen-bonded water clusters $[(H_2O)_n]$. Although some ambiguity may arise for ion clusters, e.g. $H_3O^+H_2O$, an intermolecular parametrization may be made for the hydronium ion H_3O^+ and H_2O as molecular units. Since the semi-empirical MO methods of parametrization are well documented elsewhere [7, 8], we avoid repetition here. The original MNDO parameter set, i.e. the intramolecular parameter set provided already good fits to the observed values of ionization potentials, dipole moments, binding energies, equilibrium geometries and intramolecular vibrational frequencies of H_2O, O_2, and H_2. However, parametrization for these molecules was repeated although it may not be necessary. In addition, for the sake of consistency, both the intramolecular (original MNDO) parameters and intermolecular parameters were chosen to fit the binding energy [13] and dipole moment [12] of the trans-linear water dimer at its equilibrium geometry, satisfying zero values of energy gradients and torque. Despite the new parametrization, the values of the freshly chosen intramolecular parameters were remarkably close to the original MNDO parameters. This is gratifying as it proves the soundness of our parametrization procedure, showing excellent consistency with the original MNDO parametrization scheme. The diagonal valence state energy, U_{pp} for O is -78.065 eV compared to the original MNDO value of -77.9975 eV, (U_{ss} for H is -13.0433 eV and U_{ss} for O, -103.2226 eV). The rest of the parameter values including intermolecular parameters are shown in Table 3. The intermolecular parameters were found to be markedly different from the intramolecular parameters as is expected. The details of the reparametrization will appear elsewhere.

Our fitted and predicted values (labeled as I-MNDO) of the C_S water dimer are shown in Table 1. Note that despite the parametrization without fitting the

Table 2. Vertical ionization potentials (I.P. in eV) and average hydrogen bond strengths (B_h in kcal/mole) of water clusters $(H_2O)_n$

n	Class[a]	*Ab initio*[b]		I-MNDO[c]		
		B_h	I.P.	B_h	ΔH^d	I.P.
1					−68.86	
2	II	7.72	11.88	5.59	−143.31	11.86
3	IIIa	6.54	11.93	5.49	−217.55	12.09
3	IIIb	6.54	10.45	5.36	−217.29	11.32
4	IVa	7.85	11.55	6.65	−295.39	11.72
4	IVb	6.42	10.62	6.10	−293.73	11.42
5	Va	8.50	11.31	7.52	−374.41	11.10
6	VIa	7.81	11.40	7.61	−451.19	11.22
7	VIb	7.72	9.87	7.88	−452.58	11.09
8	VIIIa	8.24	11.08	8.57	−621.87	10.89
9	IX			8.40	−695.37	10.69
10	X			8.41	−772.73	10.70
11	XI			8.84	−872.46	10.77
12	XII			8.88	−941.76	10.88

[a] Class here refers to the convention of different geometric configurations of $(H_2O)_n$ that were used in [21]

[b] *Ab initio* HF calculations from [21]

[c] Present results based on our I-MNDO optimized geometries

[d] Heat of formation (kcal/mole); ΔH for H_2O with the original MNDO is −60.9 kcal/mol

intermolecular vibrational frequencies of the dimer, their predicted values for the dimer are in excellent agreement with the *ab initio* HF results (labeled as AbHF) of Curtiss and Pople [12i] and the EPEN [20] study of Owicki et al. [20]. The latter used an analytic potential which fits the *ab initio* potential surface of Clementi and coworkers [11]. The largest discrepancy in frequency between ours and the *ab initio* HF values of Curtiss and Pople was found to be 50 cm^{-1}, corresponding to the normal mode of roughly the in-plane H-bond bend. In addition, ordering of normal mode vibrational frequencies is in precise agreement with the *ab initio* HF. The predicted values (based on the present combination

Table 3a. Intra- and intermolecular parameters

Parameter	$\beta_S(H)$	$\beta_S(O)$	$\beta_P(O)$	$\rho(H)$	$\rho(O)$	$\xi_S(H)$	$\xi_S(O)$	$\xi_P(O)$
Intramolecular	−4.8970	−32.6440	−25.5254	0.5603	0.4669	1.0958	2.3979	2.4031
Intermolecular	0.0	−1.3277	−41.4866	0.5611	0.4712	0.7776	0.4729	2.0559

Table 3b. α and γ parameters

Parameters	$\gamma(H—H)$	$\gamma(O—O)$	$\gamma(O—H)$	$\alpha(H—H)$	$\alpha(O—O)$	$\alpha(O—H)$
Values	11.9430	1.2841	0.8936	−6.3331	−2.6601	−2.1691

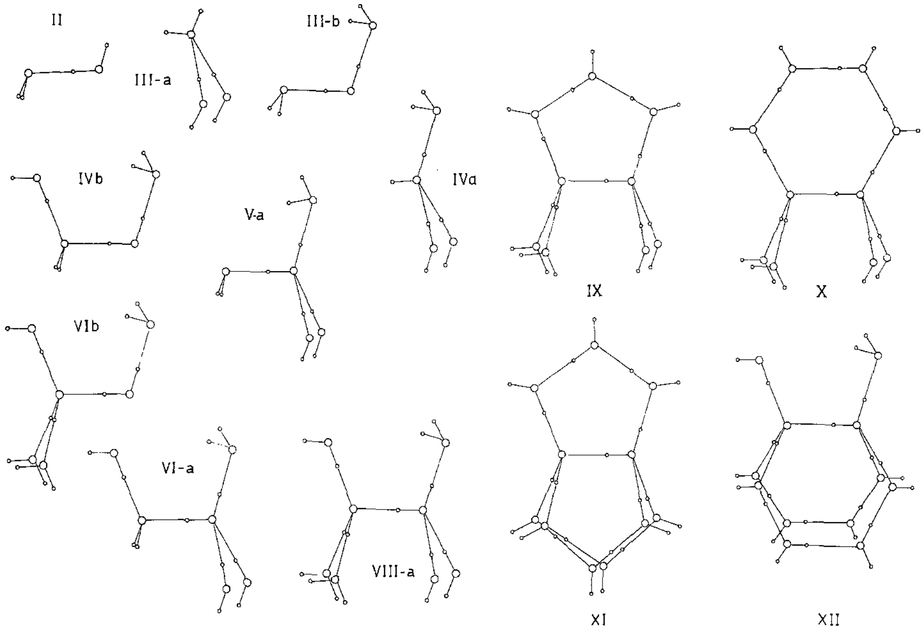

Fig. 1. Geometric configurations of $(H_2O)_n$ with $n = 2$ through 12

method of using both the intramolecular and intermolecular parameter sets) were shown to be close to *ab initio* quality. Encouraged by this, we further tested the hydrogen bond strengths per bond and ionization potentials of larger water clusters. Table 2 shows comparison between our results of I-MNDO (I-MNDO here refers to our addition of the intermolecular parameter set in MNDO parametrization procedure) and the *ab initio* HF calculations of Tomoda and Kimura [21] based on the geometric configurations of water clusters shown in Fig. 1. Comparison beyond $n = 8$ is not present as there exist no *ab initio* calculations reported thus far. Most recently, using the AM1 (Austin Model) Dewar et al. [22] have demonstrated the ability of reproducing hydrogen bonds. Their predicted heat of formation for the water dimer ($n = 2$) was −3.3 kcal/mol. Comparison beyond $n = 2$ is not feasible as there exists no further report. However for larger ($n > 2$) water clusters, the AM1 predictions are expected to be consistently smaller than our predicted values, considering their lower dimer value with $n = 2$. This I-MNDO method demonstrated the excellent predictive power (*ab initio* quality) in both the hydrogen bond strengths and ionization potentials for the larger water clusters examined.

3. Conclusion

Semi-empirical HF methods [1-4] perhaps with some exceptions [22, 23] are known to be undesirable for studying hydrogen-bonded systems, e.g. water clusters. We have shown that even the advanced MNDO method seriously failed to predict correct physical properties of water clusters. In view of increasing demands for understanding the large systems of molecular clusters and molecular crystals, a new development of semi-empirical procedure is necessary particularly for the inclusion of the effects of long-range intermolecular interactions as we demonstrated here. In general, parametrization in semi-empirical methods is done based on the properties of a variety of molecules. Due to the selection of intermolecular parameters to fit only the neutral water dimer $(H_2O)_2$, I-MNDO is expected to serve best for the neutral clusters of larger size $n > 2$ but not for other types of clusters such as $H_3O^+(H_2O)_n$ and $OH^-(H_2O)_n$.

By using the additional set of intermolecular parameters which fitted the binding energy and dipole moment of the water dimer, we observed *ab initio* quality in the results of a) the normal mode vibrational frequencies of the water dimer, b) the hydrogen bond strengths per bond, and c) ionization potentials of other larger neutral water clusters. Our present study of a new parametrization scheme is by no means sufficient to treat all types of hydrogen bonded molecular clusters. Rather this study should be regarded as only a beginning for study of difficult hydrogen-bond systems using semi-empirical molecular orbital methods. Judging from the present success of the hydrogen-bonded water clusters, the additional intermolecular parametrization scheme proposed here is expected to be highly successful not only for the hydrogen-bonded systems but also other types of bonding systems, e.g., Van der Waals adducts.

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Appendix 1: I-MNDO parametrization

Except for the modification of the core-core repulsion integral form, we retain the original MNDO parametric forms for intermolecular parametrization. Our newly chosen functional form for the core-core repulsion energy between atoms a and b is

$$E_{ab} = Z'_a Z'_b (S_a S_a | S_b S_b)[1 + \gamma_{ab} e^{-\alpha_{ab} R_{ab}}] \tag{1}$$

for all atom pairs, that is, O—O, H—H, and O—H. This differs from the core-core repulsion terms used by Dewar et al [22] and Burstein and Isaev [23].

The newly adjusted intramolecular and intermolecular parameters are shown in Table 3. Except for the parameters α and γ which appear in our new form of the core-core repulsion terms, the new intramolecular parameters are found to be close to the original MNDO parameters. This is encouraging. The one-electron one-center parameters $U_{\mu\mu}$, and α and γ in E^{core} are chosen to be the same between the intramolecular and intermolecular parameter sets.

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