

# Application of the dispersion energy correction to the third order single excitation perturbation theory based on the locally projected molecular orbitals: weak electron-donor-acceptor complexes and water clusters

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The third order single excitation perturbation theory corrected with the dispersion energy based on the locally projected molecular orbital was applied to study the weak electron-donor-acceptor (charge-transfer) complexes and the hydrogen bonds in the water clusters. In the weak electron-donor-acceptor complexes, the dispersion energy is larger than the charge-transfer energy in absolute value. The dispersion energy is as large as the charge-transfer energy in the hydrogen bond. The cage form of (H<sub>2</sub>O)<sub>6</sub> is the most stable among eight isomers examined, because the dispersion energy is the largest among them.

## Introduction

The molecular orbitals (MO) in quantum chemistry are expanded in terms of the one-electron basis functions centered on each nucleus in a molecule. Historically the basis functions are the atomic orbitals, so that a linear combination of atomic orbital (LCAO) has been a synonym of MO. The Hartree-Fock-Roothaan (HFR) equation is the equation to variationally determine the MO coefficients of the basis functions which are placed at least on every atom. The solution is the canonical MOs, and they are delocalized all over the molecule. The correct form of the HFR equation under the strict local condition on the basis functions was first derived by Stoll et al.<sup>1</sup> The occupied MOs are expanded within a set of restricted basis sets, not using all of the basis sets in the molecules; the local condition is imposed, dependent on the nature of the MO to be determined. The equation does not require the orthogonal condition of the MOs. Later, Italian quantum chemists developed two sets of local MOs, by utilizing the local expansion of the molecular orbitals. One is the SCF-MI (self-consistent field method for molecular interaction) by Gianinetti et al.<sup>2-4</sup> and the other is ELMO (Extremely Localized MO) by Sironi et al.<sup>5-7</sup> The SCF-MI, as the name implies, is the method developed for studying the molecular interaction. The basis sets used are constrained to those on each molecule. Because of this constraint, the SCF energy is free of basis set superposition error (BSSE). The ELMO is more general, and can be applied to the covalent bonded system, allowing the overlap of the basis sets.

We were stimulated by SCF-MI, and re-formulated the equations using the projection operator. Because SCF-MI is a too general name, we started to call it locally projected (LP)

MO.<sup>8</sup> We proved the inherent deficiency in the method that no charge-transfer is allowed between the molecules in the LP MO wave function and that the binding energy is always underestimated. Khaliullin et al also used the same equation to obtain the absolutely local molecular orbital (ALMO), first to evaluate the efficient procedure to reach the SCF convergence,<sup>9</sup> and then applied it to analyze the molecular interaction.<sup>10</sup>

The other related works are by Surjan<sup>11</sup>, and the embedded molecular cluster by Shidlovskaya,<sup>12</sup>

The fragment molecular orbital (FMO), proposed by Kitaura and later extended by several groups in Japan, also uses the local basis sets.<sup>13</sup> The molecule (or molecular assemble) is fragmented, and the quantum chemical calculations are performed for the dimer of the fragments. Thus, the MOs are confined at most in the dimer.

The divide-and-conquer (DC) approaches, proposed by Yang and Lee<sup>14</sup> and extensively implemented by Kobayashi, Nakai and their collaborators<sup>15</sup>, can be regarded as a generalized form of the local basis sets. By introducing the buffer atoms, or the common basis sets, connecting the fragments and the partition matrix to define the density matrix, they can determine the electron density of the full system, by only solving the HF (or Kohn-Sham) equation for each fragment. Fermi function which defines the partial occupation numbers of the orbitals plays a crucial role in evaluating the density matrix.

Realizing the serious deficiency of LP MO (SCF-MI), we developed the perturbation theory based on LP MO.<sup>16,17</sup> The target of the project is to find a practical and reliable way to study the molecular clusters, consisting of many molecular units with the effects of BSSE as small as possible. As was emphasized by Liu and McLean,<sup>18</sup> there are two kinds of inconsistency between the monomer and the complex, which cause the BSSE; one results from the orbital basis inconsistency (OBI), and the other is the configuration basis inconsistency (CBI). Knowing two distinct causes of the BSSE, we

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where  $W_{(Z,W),(X,Y)}$  is the matrix of  $\langle \Phi_0 | (t_Z^\dagger c_Z) (u_W^\dagger d_W) | \hat{H}_0 - E_0^0 | (s_X^\dagger b_X) (r_Y^\dagger a_Y) \Phi_0 \rangle$ . The matrix elements can be expanded in terms of the intermolecular MO overlap integrals. It can be proved that the matrix elements  $W_{(X,Y),(X,Y)}$  is the zero order of the intermolecular MO overlap integrals; the leading terms result from the non-canonical nature of LP MO. Symbolically it can be expressed as  $S_{inter-M}^0$ . Similarly  $W_{(X,Z),(X,Y)}$  with  $(Z \neq Y)$  is the order of  $S_{inter-M}^1$ , and  $W_{(Z,W),(X,Y)}$  with  $(Z \neq X, Y \text{ and } W \neq X, Y)$  is the order of  $S_{inter-M}^2$ .

The linear equation (2) is pre-conditioned using the diagonal matrix  $\Xi$  as

$$\left[ 1 + \Xi^{-1/2} W \Xi^{-1/2} \right] \Xi^{1/2} \underline{w} = -\Xi^{-1/2} \underline{v} \quad (4)$$

$$\left[ 1 + \underline{W} \right] \underline{w} = -\underline{v} \quad (5)$$

The matrix  $\underline{W}$  and the solution  $\underline{w}$  are expanded in terms of  $S_{inter-M}^\mu$  as

$$\underline{W} \equiv \mu^0 \underline{W}^{(0)} + \mu \underline{W}^{(1)} + \mu^2 \underline{W}^{(2)} \quad (6)$$

$$\underline{w} = \mu^0 \underline{w}^{(0)} + \mu^1 \underline{w}^{(1)} + \mu^2 \underline{w}^{(2)} + \mu^3 \underline{w}^{(3)} + \dots \quad (7)$$

and the equation becomes

$$\left[ 1 + \mu^0 \underline{W}^{(0)} + \mu \underline{W}^{(1)} + \mu^2 \underline{W}^{(2)} \right] \times \left( \mu^0 \underline{w}^{(0)} + \mu^1 \underline{w}^{(1)} + \mu^2 \underline{w}^{(2)} + \mu^3 \underline{w}^{(3)} + \dots \right) = -\underline{v} \quad (8)$$

and is solved perturbatively as

$$\left( 1 + \underline{W}^{(0)} \right) \underline{w}^{(0)} = -\underline{v} \quad (9)$$

$$\left( 1 + \underline{W}^{(0)} \right) \underline{w}^{(1)} = -\underline{W}_1 \underline{w}^{(0)} \quad (10)$$

$$\begin{aligned} \left( 1 + \underline{W}^{(0)} \right) \underline{w}^{(\kappa)} &= -\underline{W}^{(2)} \underline{w}^{(\kappa-2)} - \underline{W}^{(1)} \underline{w}^{(\kappa-1)} \\ &\equiv -\underline{v}^{(\kappa)} \text{ for } \kappa \geq 2 \end{aligned} \quad (11)$$

Because  $\underline{W}^{(0)}$  is block-diagonal, the linear equations to be solved is

$$\left( 1 + \underline{W}_{(X,Y),(X,Y)}^{(0)} \right) \underline{w}_{(X,Y)}^{(\kappa)} = -\underline{v}_{(X,Y)}^{(\kappa)} \quad (12)$$

Thus, the dimension of the linear equations is shrunk to  $M_X^{occ} M_X^{ex} M_Y^{occ} M_Y^{ex}$  from  $\sum_{X<Y} (M_X^{occ} M_X^{ex} M_Y^{occ} M_Y^{ex})$  when only the dispersion type excitations are taken into account.

The correction energy  $\Delta E^{[2]}$  is

$$\begin{aligned} \Delta E^{[2]} &= -\tilde{v} \underline{w} = -\tilde{v} \Xi^{-1/2} \Xi^{1/2} \underline{w} \\ &= -\tilde{v} \underline{w} \simeq -\tilde{v} \underline{w}^{(0)} - \tilde{v} \underline{w}^{(1)} - \tilde{v} \underline{w}^{(2)} \dots \end{aligned} \quad (13)$$

A new code was developed, based on equation (12), and several test calculations were carried out to compare them with those calculated with the previous version which uses equation (2). They demonstrated that the dispersion energy evaluated by taking into account only  $S_{inter-M}^0$  terms agrees with that of the previous version within  $1 kJ mol^{-1}$  for a pair of molecules in the cluster.

## Analysis of the interaction energy

In the empirical model theory such as Mulliken originally developed for the charge-transfer complexes, the molecular interaction energy could be expressed by a sum of various terms. But with the ab initio calculations, the analysis is not unique. From the pioneer work by Morokuma<sup>23</sup>, numerous procedures and definitions are proposed. With the supermolecule approach for the molecular interaction, the decomposition of the interaction energy is not unique. Even when the molecular orbitals are localized in each component molecule, the definition of the energy components is not straightforward. The energy evaluated with the SAPT calculations is given as a sum of the components, but the charge-transfer (electron delocalization) component cannot be easily extracted from the polarization terms. Khaliullin et al used the absolutely local molecular orbital (ALMO), whose occupied MOs are equivalent to LP MO, for the energy decomposition analysis.<sup>10,24</sup> Their definition for the charge-transfer energy

$$\Delta E \equiv E_{HF}(\Psi_{supermol}) + \Delta E_{BSSE} - E_{HF}(\Psi_{LPMO}) \quad (14)$$

This definition is based on a theorem that the electron delocalization between molecules is forbidden in LP MO, proved by us.<sup>8</sup> This definition requires the full supermolecule calculation, and can be applied only for the dimer. Recently Stone and Misquitta<sup>25</sup> defined the CT energy within symmetry-adaptive perturbation theory (SAPT), in which the CT contribution is a part of the induction energy. To evaluate it, they have to perform the calculations with the monomer basis sets and with the dimer basis sets. The evaluation is possible also only for the dimer.

We proposed an alternative definition<sup>19</sup> using the first order wave function  $\Psi^{(1)SPT}$  of the single excitation perturbation theory. The second order correction  $E^{2SPT} = \langle \Phi_0 | \hat{V} | \Psi^{(1)SPT} \rangle$  is a sum of the contributions from the local excitations (LE)  $\langle \Phi_0 | \hat{V} | (r_X^\dagger a_X) \Phi_0 \rangle$  of molecule X and from the charge-transfer (CT) excitations  $\langle \Phi_0 | \hat{V} | (r_X^\dagger a_Y) \Phi_0 \rangle$  between molecules X and Y. The sums are quickly evaluated once the first order wave function  $\Psi_{LPMO}^{1SPT}$  is solved. The third order correction  $E^{3SPT} = \langle \Psi^{(1)SPT} | \hat{V} | \Psi^{(1)SPT} \rangle$ , which is essential to obtain the approximately BSSE-free binding energy, consists of the coupled terms of LE and CT excitations, which can be grouped to the contributions from LE of molecule X and CT between molecules X and Y (see eq.20 of reference<sup>19</sup>). The advantage of this definition is that it can be applied to any size of clusters and that the charge-transfer contributions of X→Y and Y→X are separately calculated. Besides, no extra calculations are required. Below, the analysis is applied to isomers of (H<sub>2</sub>O)<sub>8</sub> and (H<sub>2</sub>O)<sub>10</sub>.

The binding energy evaluated by the 3rd order SPT and the

2nd order dispersion-type DPT can be written as

$$E_{BindE}^{3SPT+disp} \equiv \left( E_{HF}(\Psi_{LPMO}) - \sum_X E_{HF}^X \right) \quad (15)$$

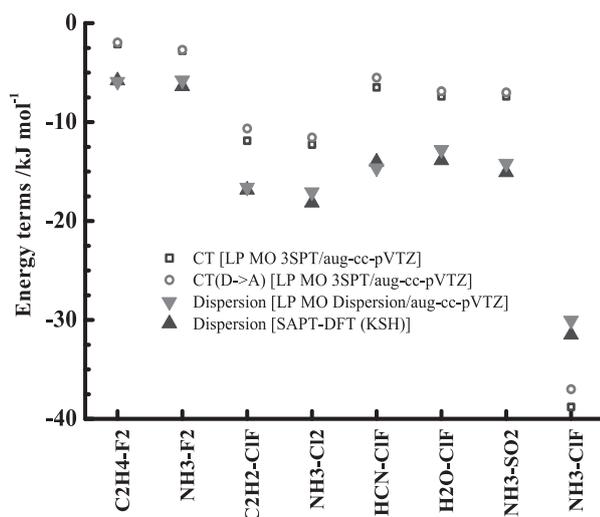
$$+ (E^{2SPT} + E^{3SPT}) + E^{2DPTdisp} \quad (16)$$

$$\equiv E_{BindE}^{3SPT} + E^{2DPTdisp}$$

The first parenthesis of the first line contains the electrostatic, exchange-repulsion and induction terms. It is because the LP MO wave function is symmetry-adaptive and properly normalized, and because the Fock matrix is that of the supermolecule. The parenthesis of the second line is nearly equal to the sum of the charge-transfer terms defined above, because the contribution from the LE is very small. As the previous papers shows,  $E_{BindE}^{3SPT}$  is nearly equal to the counterpoise corrected HF bind energy  $E_{CPcorr}^{HF}$  if the basis set used is as large as aug-cc-pVTZ.

## Results and Discussion

### Weak Electron-Donor-Acceptor Complexes



**Fig. 1** Dispersion and charge-transfer energies in the weak electron-donor-acceptor complexes

When Mulliken first presented the theory of interaction of electron donors and acceptors, it is based on the valence bond type wave functions of the empirical model hamiltonian.<sup>26,27</sup> The theory was successful in understanding the physical and chemical properties of the electron-donor-acceptor (EDA), or charge-transfer (CT), complexes. In particular, the appearance of the new electronic transitions at the UV, visible and near-infrared regions could be analyzed only in terms of the charge-transfer theory of Mulliken. On the other hand, there were some skeptics on the contribution of the charge-transfer terms to the binding energy of the weak complexes. The importance of the electrostatic interaction was often mentioned.

As early as in 1968<sup>28,29</sup>, Hanna estimated the quadrupole - induced dipole interaction energy between benzene and halogen molecule, and concluded that it is more important in the complex formation than the charge-transfer interaction. Recently Karthikeyan, Sedlak and Hobza<sup>30</sup> examined the nature of the stability in charge-transfer complexes using CCSD(T)/CBS and DFT-SAPT (with the PBE0 functional). One of the important findings is the importance of the dispersion force in forming the stable weak complexes. The dispersion energy was evaluated by DFT-SAPT of Hesselmann and Jansen,<sup>31</sup> although it was not mentioned in their paper. There is another version for DFT-SAPT by Misquitta et al.<sup>32</sup> In both versions, the dispersion energy is evaluated with the Casimir-Polder form, which requires to solve the time-dependent coupled-perturbed DFT (TDDFT) to obtain the frequency dependent polarizability. The intermolecular Coulomb exchange is not in their dispersion energies. This paper demonstrated that the binding energies evaluated with SAPT-DFT/CBS are comparable with those of CCSD(T)/CBS even for the strong EDA complexes. It is claimed that the charge-transfer energy is contained in their  $\delta(HF)$ .

As described above, the present LP MO based perturbation theory clearly defines the charge-transfer contribution to the binding energy within the Hartree-Fock level of theory. Table 1 compares the binding energies of the present calculations with those of Karthikeyan et al.<sup>30</sup> Except for NH<sub>3</sub>-SO<sub>2</sub>,  $E_{BindE}^{3SPT+disp}$  agrees with those of MP2/aug-cc-pVTZ and CCSD(T)/CBS within 1kcal mol<sup>-1</sup>(=4.184kJ mol<sup>-1</sup>). The sixth column is  $E_{BindE}^{3SPT}/aug-cc-pVTZ$ , which is nearly equal to the BSSE-free HF binding energy, and contains the charge-transfer (electron delocalization) term. It is clearly seen that for weak complexes without the dispersion term the complexes are not formed. Figure 1 shows the dispersion and CT contributions of these complexes. The dispersion energies evaluated by the present method are in good agreement with those of DFT-SAPT. The absolute values are larger than the CT terms except for the strongest complex examined (NH<sub>3</sub>-ClF). The sixth column of Table 1 and Figure 1 indicate for these weak halogen complexes that the dispersion term is dominant and the CT term plays a secondary role in the binding energy, and that the classical electrostatic interaction and static polarization (induction) do not contribute to the binding energy. This is contrary to Hanna's empirical estimation for the benzene - halogen complex.

The last column of Table 1 is the energy destabilized by the geometric changes resulting from the complex formation. They are positive as they should be, except for (NH<sub>3</sub> - SO<sub>2</sub>). The molecule in the complex is deformed by accepting or donating an electron; the complex is formed by "sacrificing the intramolecule bonds" in the wording of Mulliken. A negative value for (NH<sub>3</sub> - SO<sub>2</sub>) implies that the input geometric parameters for the complex, which was kindly sent to the author by Sedlak,<sup>30</sup> was not a correct one. For ClF as an electron acceptor, four electron donors are examined. The difference of the geometric destabilization energy is that of the electron donor.

**Table 1** Comparison of the binding energy for the electron - donor - acceptor complexes

Compl	DFT-SAPT <sup>a</sup>	CCSD(T) <sup>a</sup>	MP2 <sup>a</sup>	3SPT+Disp	3SPT	Geom. Destb <sup>b</sup>
	CBS <sup>c</sup>	CBS	apVTZ <sup>d</sup>	apVTZ	apVTZ	apVTZ
C <sub>2</sub> H <sub>4</sub> -F <sub>2</sub>	-4.35	-3.97	-5.19	-3.01	2.90	2.23
NH <sub>3</sub> -F <sub>2</sub>	-5.31	-6.57	-7.24	-5.09	0.68	3.57
C <sub>2</sub> H <sub>2</sub> -ClF	-17.11	-15.98	-18.07	-17.08	-0.47	3.16
NH <sub>3</sub> -Cl <sub>2</sub>	-19.04	-18.74	-21.21	-19.09	-2.02	1.65
HCN-ClF	-17.99	-19.16	-21.63	-23.54	-8.89	1.49
H <sub>2</sub> O-ClF	-19.50	-20.33	-21.42	-24.52	-11.74	2.42
NH <sub>3</sub> -SO <sub>2</sub>	-25.06	-23.10	-21.55	-33.21	-19.02	-0.23
NH <sub>3</sub> -ClF	-42.47	-44.73	-48.58	-47.29	-17.24	11.78

a) Refer. [30] b) Destabilization energy by geometric change included. c) "Complete Basis Set Limit". d) aug-cc-pVTZ

Table 1 and Figure 1 show that the geometric destabilization energies of these four complexes are correlated with the CT and dispersion energies, but not with the total binding energy.

**Table 2** The binding energy corrected with the geometric change, and dispersion and CT contributions for weak EDA complexes

Complexes <sup>a)</sup>	basis <sup>b)</sup>	3SPT+D	Disp	CT
C <sub>2</sub> H <sub>2</sub> -ClF	D	-9.24	-16.70	-18.17
C <sub>2</sub> H <sub>2</sub> -ClF	T	-10.45	-21.18	-18.50
HC <sub>2</sub> CH <sub>3</sub> -ClF	D	-12.14	-23.47	-28.21
HC <sub>2</sub> CH <sub>3</sub> -ClF	T	-13.05	-29.70	-27.41
C <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> -ClF	D	-11.87	-31.65	-42.24
C <sub>2</sub> H <sub>2</sub> -Cl <sub>2</sub>	D	-7.07	-12.14	-7.11
C <sub>2</sub> H <sub>2</sub> -Cl <sub>2</sub>	T	-7.31	-14.70	-6.91
HC <sub>2</sub> CH <sub>3</sub> -Cl <sub>2</sub>	D	-10.42	-17.52	-10.77
HC <sub>2</sub> CH <sub>3</sub> -Cl <sub>2</sub>	T	-10.46	-21.13	-10.29
C <sub>2</sub> H <sub>2</sub> -Cl <sub>2</sub> -C <sub>2</sub> H <sub>2</sub>	D	-11.92	-24.54	-13.41
Cl <sub>2</sub> -C <sub>2</sub> H <sub>2</sub> -Cl <sub>2</sub>	D	-14.33	-24.36	-14.13

a) Optimized with MP2/aug-cc-pVTZ b) D: aug-cc-pVDZ, T: aug-cc-pVTZ

Table 2 examines a series of complexes of ClF and Cl<sub>2</sub> with acetylene and methyl substituted acetylenes. The geometry of the complexes and monomers are optimized with MP2/aug-cc-pVTZ without the counterpoise correction. The binding energies in Table 2 are relative to the energy of the optimized monomer. The dispersion and CT energies for C<sub>2</sub>H<sub>2</sub>, HCC(CH<sub>3</sub>) and (CH<sub>3</sub>)CC(CH<sub>3</sub>) complexes with ClF and Cl<sub>2</sub> increase as the number of methyl groups increases; that is, the ionization energy decreases. But the total binding energy of HCC(CH<sub>3</sub>) - ClF is larger than that of (CH<sub>3</sub>)CC(CH<sub>3</sub>) - ClF by 0.27 kJ mol<sup>-1</sup>, though the CT term of the latter (-42.24 kJ mol<sup>-1</sup>) is larger than that of the former (-27.41 kJ mol<sup>-1</sup>); it might be the repulsive part that changes the ordering of the total binding energy.

To examine the additivity of the dispersion and CT energies, the binding energies for the D-A-D and A-D-A complexes are compared with the D-A complexes for D=C<sub>2</sub>H<sub>2</sub> and A=Cl<sub>2</sub>. The conformation is fixed to that of the D-A complex. The dispersion term is nearly additive for both complexes, but the non-additivity is found for the D-A-D complex significantly in the total binding energy and slightly in the CT

term. Because C<sub>2</sub>H<sub>2</sub> has no bulky group, the cause of the non-additivity of the total energy is of electronic nature. Interestingly, the smaller binding energy for the D-A-D might be consistent with the assumption by Hanna that the interaction between the induced dipole moment of a halogen molecule and the quadrupole moment of a conjugated hydrocarbon contributes to the binding energy, because the induced dipole of Cl in D-A-D is smaller than that in D-A.

Another finding in Table 2 is that the CT energy is less basis-set dependent than the dispersion energy.

## Water Clusters

Recently Shanker and Bandyopadhyay found many isomers of (H<sub>2</sub>O)<sub>20</sub> and (H<sub>2</sub>O)<sub>25</sub> using their new efficient and fast method, Monte Carlo Temperature Basin Paving method, finding low energy structures.<sup>33</sup> They used the effective fragment potential (EFP1)<sup>34</sup> for evaluating the interaction energy. In these isomers there are various types of pair of hydrogen bonded water molecules and of hydrogen bonded networks. The analysis will be separately published.<sup>35</sup> The EFP1 parameters are determined to fitting the HF binding energy and does not contain the dispersion term, while the new EFP2 includes the dispersion contribution to the hydrogen bond. The LP MO 3SPT calculations can be used to confirm the relative binding energies for various isomers of (H<sub>2</sub>O)<sub>25</sub> evaluated with EFP1. The single point calculation for (H<sub>2</sub>O)<sub>25</sub> with LP MO 3SPT/aug-cc-pVDZ requires about 350min on Xenon Core2 Duo Quad (2.93GHz). The number of basis sets is 1075. Figure 2 shows the comparison of the relative isomer energies of LP MO 3SPT  $E_{BindE}^{3SPT}$ , EFP1 and EFP2. The relative EFP1 energy agrees with  $E_{BindE}^{3SPT}/aug-cc-pVDZ$ , which is nearly equal to the counterpoise corrected HF binding energy, as shown in the previous papers.<sup>19</sup> The EFP1 mimics the relative HF binding energy quite well even for large water clusters having various types of the conformation of the hydrogen bonding. Figure 2 exhibits that the large difference between the relative energies of EFP1 and EFP2 for less stable isomers. It implies that the dispersion term is required to obtain accurate relative energies among the water clusters.

The dispersion terms  $E_{BindE}^{3SPT+disp}$  for smaller water clusters are evaluated and analyzed, because with the present version

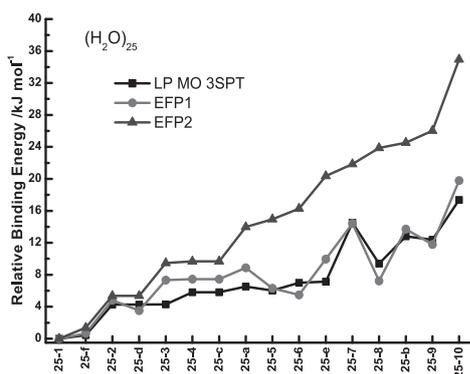


Fig. 2 Comparison of relative binding energy of water clusters  $(\text{H}_2\text{O})_{25}$

of codes, the calculations for  $(\text{H}_2\text{O})_{25}$  are not feasible. Figure 3 compares the relative binding energies of  $(\text{H}_2\text{O})_6$ , the geometries of which were determined by Ohno et al with B3LYP/6-311+(d,p).<sup>36</sup> The most stable isomer among eight isomers is KO-1 of cage form, which is consistent with more accurate computations by Xantheas et al.<sup>37</sup> In their calculations, the cage and prism forms of the isomers are close in the binding energy and the most stable. The plots of  $E_{\text{Bind}E}^{3\text{SPT}+\text{disp}}/\text{aug-cc-pVDZ}$  and  $E_{\text{Bind}E}^{\text{uncorrMP2}}/\text{aug-cc-pVTZ}$ , both containing the dispersion terms, are in good agreement with the relative EFP1 energies for these clusters, although EFP1 has no dispersion term. It seems that the parameters of EFP1 are well fitted to the correct binding energy of small water clusters. On the other hand, the plots of  $E_{\text{Bind}E}^{3\text{SPT}}/\text{aug-cc-pVDZ}$  behave very differently; that is, the HF binding energy for these isomers cannot predict the correct ordering of the isomer stability. Without the dispersion term, isomer KO-4 of cyclic chair form is the most stable among eight isomers. Isomer KO-4 becomes more stable than KO-1, because of the larger CT term;  $(E^{2\text{SPT}} + E^{3\text{SPT}})$  of equation (15) is  $-63.4$  ( $-57.9$ )  $\text{kJ mol}^{-1}$  for KO-4 and is  $-56.6$  ( $-49.7$ )  $\text{kJ mol}^{-1}$  for KO-1 with aug-cc-pVDZ (aug-cc-pVTZ). The large CT term for KO-4 results from the linear conformation of the hydrogen bond. It is the dispersion term that makes Isomer KO-1 the most stable.

Figure 4 plots the cumulative dispersion energies, where the pairs of the hydrogen bonded waters are aligned in the order of the hydrogen bond strength. In the cyclic chair form (KO-4), all of the neighboring pair of water molecules are nearly equivalent to each other, and the dispersion energy is  $-10.0$   $\text{kJ mol}^{-1}$ , while the dispersion energy between the non-neighboring water molecules is very small ( $-0.3$   $\text{kJ mol}^{-1}$  for the next neighboring pair). The charge-transfer energies for these pair are  $-9.9$   $\text{kJ mol}^{-1}$  for the hydrogen acceptor to hydrogen donor and  $-0.4$   $\text{kJ mol}^{-1}$  for the hydrogen donor to the hydrogen acceptor. Below, for simplicity, the components of the interaction energy for a pair of hydrogen bond are written as  $[E^{\text{disp}}; E^{\text{CT}-\text{AtoD}}, E^{\text{CT}-\text{DtoA}}]_{\text{D-A}}$ . For example, the interaction energy of the neighboring pair is  $[-10.0; -9.9, -0.4]_{\text{W1-W6}}$ .

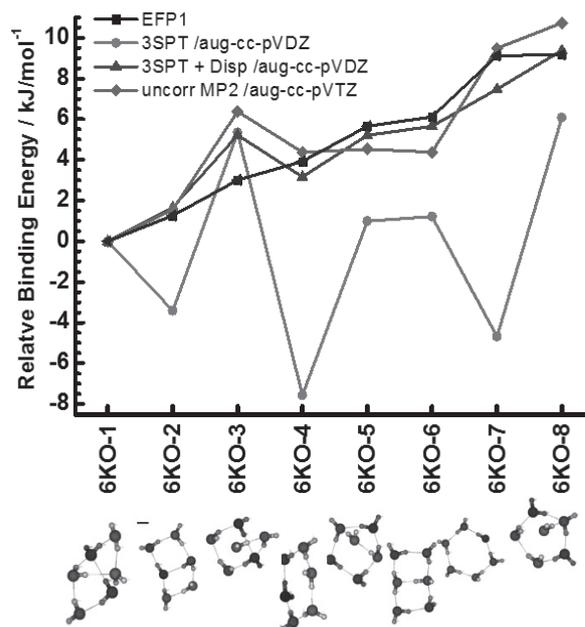


Fig. 3 Comparison of relative binding energy of water clusters  $(\text{H}_2\text{O})_6$

The interaction energy of the next neighboring waters in KO-4 is  $[-0.3; -0.2, -0.0]_{\text{W1-W5}}$ . In the cage form (KO-1) the hydrogen bonds are not uniform. There are eight hydrogen bonds. The strongest hydrogen bond is between W2 and W3; the energy components are  $[-11.1; -12.7, -0.4]_{\text{W3-W2}}$ . Water W2 has two hydrogen-donor bonds and one hydrogen-acceptor bond (denoted as 2D1A) and water W3 is 1D2A. The next and third strongest bonds are between W1[1D2A] and W5[1D1A]  $[-9.5; -8.7, -0.4]_{\text{W1-W5}}$  and between W4[2D1A] and W6[1D1A]  $[-9.0; -8.0, -0.3]_{\text{W6-W4}}$ . The weakest hydrogen bond is between W3[1D2A] and W4[2D1A]  $[-5.4; -2.7, -0.3]_{\text{W4-W3}}$ . Besides, the substantial dispersion energies are noted between the non-hydrogen bonded pairs, such as between W2 and W4  $[-1.8; -0.2, -0.2]_{\text{W4-W2}}$  and between W1 and W3  $[-1.1; -0.1, -0.1]_{\text{W3-W1}}$ . Note that because both W2 and W4 are 2D1A type, no more hydrogen bonds can not be formed between W2 and W4. So the reason why cage isomer KO-1 is more stable than cyclic KO-4 becomes clear. Because of the compact structure of a cage form, there are more pairs of water molecules interacting through the dispersion force than in the flat cyclic KO-4. Thus, the dispersion terms is expected to play a key role in determining the relative stability of the large water clusters.

The interaction energy of pairs of hydrogen bonds in larger water clusters,  $(\text{H}_2\text{O})_8$  and  $(\text{H}_2\text{O})_{10}$ , is shown in Figure 5. Both geometries are given by Xantheas.<sup>38</sup> In  $(\text{H}_2\text{O})_8$ , waters W1, W2, W3 and W4 are type of [1D2A], and the others are [2D1A]. For a [1D2A] water as hydrogen donor and a [2D1A] water as hydrogen acceptor, the energy component is  $[-11.3; -12.8, -0.4]_{\text{[1D2A]-[2D1A]}}$ . On the other hand, for the

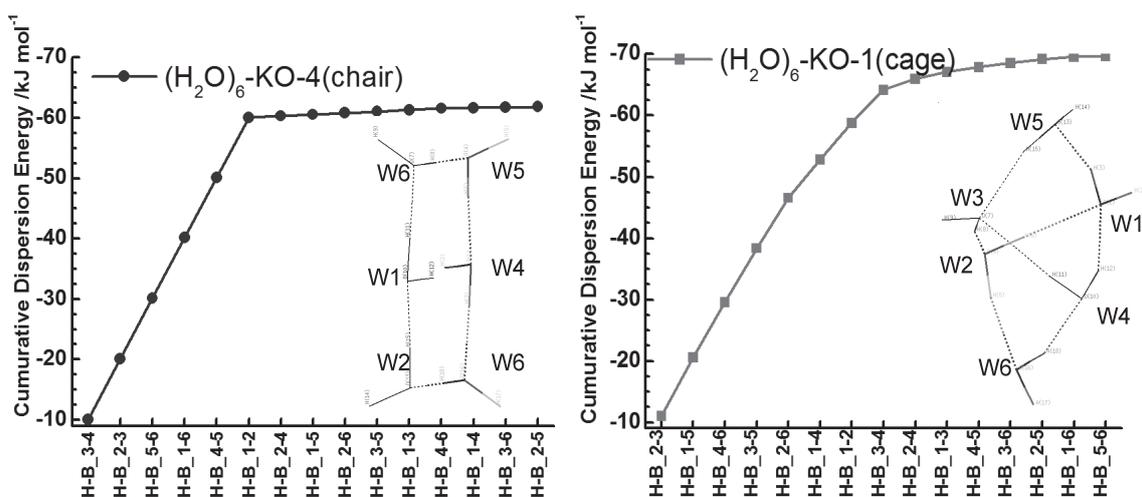


Fig. 4 Cumulative dispersion energy of cage and chair water clusters  $(\text{H}_2\text{O})_6$

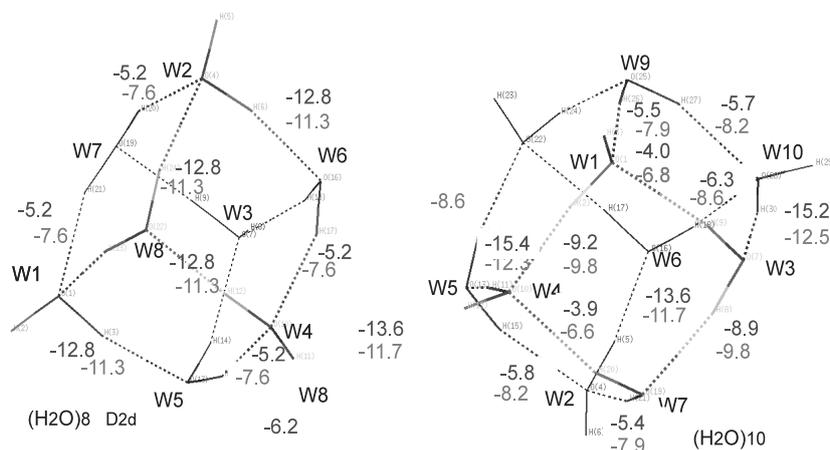


Fig. 5 Charge-transfer and dispersion energies in isomers of  $(\text{H}_2\text{O})_8$  and  $(\text{H}_2\text{O})_{10}$ . For each hydrogen bond, the upper number is the CT term of the hydrogen acceptor to donor, and the lower number is the dispersion term.

hydrogen bond having [2D1A] as hydrogen donor and [1D1A] as hydrogen acceptor, it is  $[-7.6; -5.2, -0.4]_{[2D1A]-[1D2A]}$ . Previously the calculated harmonic frequencies are used for the measure of the strength of the hydrogen bond. The present method clearly shows the difference of the hydrogen bonds, dependent on the type of waters involved.

Because of the low symmetry,  $(\text{H}_2\text{O})_{10}$  contains various strengths of the hydrogen bonds. The [1D2A] type of water molecules are W1, W2, W4, W8, and W10. The others are [2D1A] also in  $(\text{H}_2\text{O})_{10}$ . There are four hydrogen bonds which have [1D2A] as hydrogen donor and [2D1A] as hydrogen acceptor. The energy components are  $[-12.5; -15.2, -0.5]_{W10-W3}$ ,  $[-12.3; -15.4, -0.5]_{W4-W5}$ ,  $[-11.7; -13.7, -0.4]_{W8-W9}$ , and  $[-9.8; -9.2, -0.4]_{W1-W4}$ . The other hydrogen bonds have [2D1A] as hydrogen donor and [1D2A] as hydrogen acceptor, except for the pair, W3-

W7, in which both molecules are of [2D1A] and the energy component is  $[-9.8; -8.9, -0.4]_{W3-W7}$ . For the pairs of [2D1A] as hydrogen donor and [1D2A] as hydrogen acceptor, the dispersion energies range from -8.6 to -6.6, and the charge-transfer energies ranges from -6.3 to -4.0. They vary, dependent on the constraint forms of the hydrogen bond networks. There are stronger hydrogen bonds in  $(\text{H}_2\text{O})_{10}$  than in  $D_{2d}(\text{H}_2\text{O})_8$ , in which the networks are strictly constraint.

More systematic analysis for many isomers of larger water clusters using the energy components of the hydrogen bonding pairs may reveal the determining factors of the stable hydrogen bond networks and clusters. The work is under way.

## Concluding Remark

The method used in this paper has sever restrictions because of the lack of the intramolecular correlation effects on the molecular interaction. The electronic correlation changes the electron distribution of the monomer, and it does effect on the electrostatic interaction between molecules. Besides, the occupied MOs of the monomer are changed (polarized) by the other molecules, and the intramolecular correlation is changed. This effect becomes important in the strong molecular complexes. With these restrictions in mind, the present work has demonstrated that the third order single excitation perturbation theory with the dispersion correction (LP MO 3SPT + Disp ) can be utilized in studying the molecular clusters consisting of many closed shell molecules. The method is now at the stage of the practical calculations. Because the energy-gradient technique is not ready yet, the combination with the Monte Carlo simulation might be an appropriate technique to study the molecular clusters. The collaborative work using the replica switching method is under way.

The computations consist of three steps; 1) obtaining the LP MO, 2) solving the first order wave function  $\Psi^{(1)SPT}$  for calculating  $E_{Bind}^{3SPT}$ , and 3) solving Eq. (12) for the first order wave function  $\Psi^{(1)DPT-Disp}$ . The parallel implementation for all steps is possible. In particular, the parallelization of the most time-consuming part, the evaluation of the dispersion energy, enhances the applicability of the method. The present code occasionally encounters some difficulty in solving the LP MO equation. Because of this convergence problem, the  $\pi$  stacking complexes have to be avoided in the study. These are only a part of a 'to do' list. There are many technical tasks to enhance the applicability of the method as well as theoretical problems to improve the accuracy of the theory. Because the LP MO based many-electron functions are fully antisymmetric (symmetry-adaptive), the systematic improvement is expected by the better quality of the basis sets and by the higher level of electron-correlation theories. The author sincerely welcomes the other research groups to overtake his works on this project.

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