Cooperative Roles of the Charge-Transfer and Dispersion Terms in Hydrogen Bonds of Water Clusters

Iwata, Suehiro
岩田末廣

Toyota Physical and Chemical Research Institute¹
Department of Chemistry, Faculty of Science and Technology, Keio University²
Institute for Molecular Science and Graduate University of Advanced Studies³

iwatasuehiro@gmail.com

1) Fellow: 2008-2012, 2) Visiting Professor: 2012-2014
3) Emeritus Professor: 2000 -

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Suehiro Iwata

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Abstract

Hydrogen bonds between water molecules play an essential role in the structures, dynamics and thermochemical properties of liquid water and ices. So it is important to qualitatively and quantitatively characterize the hydrogen bonds between water molecules. In the talk, the recent computational analyses of the hydrogen bonds in water clusters (H₂O)ₙ up to n=25 are discussed. Our perturbation theory based on the locally projected molecular orbital (LP MO) allows us to evaluate the charge-transfer and dispersion contribution to the hydrogen bond energy for every pair of water molecules in the clusters. The two terms are strongly correlated to each other for the hydrogen-bonded pair, though the dispersion term is still substantial even for non hydrogen-bonded pairs. Every water molecule is given index DₙAₘ, where n is the number of donating hydrogen atoms (0~2), and m is the number of accepting hydrogen atoms (0~2, occasionally 3). The strength of the hydrogen bonds is dependent on the types of pair DₙAₘ←Dₙ′Aₘ′. The strong pair is found for the pairs D2A1←D1A2. This is previously known by the low-shifted calculated harmonic frequencies of OH stretching modes. The geometric distortion of a water molecule by the hydrogen bonding formation also depends on DₙAₘ. A short summary of the theory, which is approximately free of basis set superposition error (BSSE), is also given.

Contents

1. A short summary of the present theory
2. A few examples of weak molecular interaction
3. Water clusters (H₂O)ᵣ, n=2~25, and characteristics of the hydrogen bonds between water molecules
Targets of the theoretical methods

Molecular clusters consisting of many molecular units. The interaction energy per a pair of molecules is less than $\sim 30 \text{kJ/mol} (\sim 7 \text{kcal/mol})$.

Why is it difficult to evaluate the molecular interaction energy?

We have to evaluate a tiny difference of two large quantities, using an approximate method. For instance, the total Hartree-Fock electronic energy of $\text{(H}_2\text{O})_6$ is about $-456 \text{Hartree}$ ($1 \text{Hartree}=2625 \text{kJ mol}^{-1}$) and the total binding energy is $-189 \text{kJ mol}^{-1}$. 
We have to evaluate a tiny difference of two large quantities, using an approximate method.

For instance,

\[ 10^6 \text{ gram} \quad \text{A} \quad \text{1 gram} \quad 10^7 \text{ gram} \quad \text{B} \]

The key is a well-balanced approximation in calculating the energies (measuring the weights) of A, B and AB.

Our scale is the electronic structure theory of quantum chemistry. The electronic structure theory is an approximation method.

Two levels of approximations

- One-electron functions (Orbital)
- Many-electron functions (Electron Configuration)
The error is caused by the unbalanced approximation: Basis Set Superposition Error (BSSE)

Two causes of BSSE in evaluating the molecular interaction:

1. The errors are caused by the inconsistency in the one-electron basis sets (Orbital Basis Inconsistency, **OBI**). The counterpoise (**CP**) procedure works well and also the use of large basis sets avoids this error.

2. The errors are also caused by the inconsistency (unbalance) in the many-electron wave functions (Configuration Basis Inconsistency, **CBI**)

We need to differentiate two causes of the errors in evaluating the interaction energy.
Application of our new theory: "LP MO perturbation expansion theory" with Dispersion correction

Present status of our theory

<table>
<thead>
<tr>
<th>isomer</th>
<th>MP2/CBS</th>
<th>CCSD(T)/aug-cc-pVDZ</th>
<th>present method/aug-cc-pVDZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>prism</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>cage</td>
<td>0.3</td>
<td>1.9</td>
<td>0.9</td>
</tr>
<tr>
<td>book</td>
<td>1.0</td>
<td>4.8</td>
<td>1.9</td>
</tr>
<tr>
<td>cyclic</td>
<td>4.2</td>
<td>11.3</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Relative Energy (/kJ mol\(^{-1}\)) of Isomers of (H\(_2\)O\(_6\)) \(1\)Hartree=2625.5kJ mol\(^{-1}\)

CBS stands for the extrapolation to the basis set limit
Locally Projected Molecular Orbitals (LP MO) and the many-electron wave function for a cluster

\[ \Psi^{\text{LP MO}}_{\text{PT}} = \Phi^{\text{LP MO}} + \sum_{x} \sum_{a \in X} |a_x \rightarrow r_x \rangle A_{a_x r_x} + \sum_{y} \sum_{b \in Y} |b_x \rightarrow s_y \rangle A_{b_x s_y} \]

\[ + \sum_{x} \sum_{a \in X} \sum_{b \in Y} \sum_{y} |a_x b_y \rightarrow r_x s_y \rangle A_{a_x r_x b_y s_y} + \sum_{x} \sum_{a \in X} \sum_{b \in Y} |a_x b_x \rightarrow r_x s_x \rangle A_{a_x r_x b_x s_x} \]

The MO coefficient matrix is block-diagonal as

\( (\phi_D, \phi_c, \phi_B, \phi_A) = (\chi_D, \chi_C, \chi_B, \chi_A) \)T

\[ T = \begin{bmatrix} T_D & 0 & 0 & 0 \\ 0 & T_c & 0 & 0 \\ 0 & 0 & T_b & 0 \\ 0 & 0 & 0 & T_A \end{bmatrix} \]

The coefficient matrix is determined variationally under the absolute locality constraint.

The excited MOs can be determined under the locality condition using a proper projection operator.

This wave function avoids the basis set superposition error (BSSE) without the counterpoise procedure.

Binding Energy in LP MO 2nd & 3rd order Single Excitation + Dispersion correction

Binding energy

\[
E_{\text{BindE}}^{SPT+Disp} \equiv \left[ E_{\text{BindE}}^{\text{LP MO}} + E_{\text{LP MO}_2\&3\text{SPT}} \right] + E^{\text{Disp}}
\]

\[
E_{\text{BindE}}^{\text{LP MO}} \equiv E\left(\Phi_{\text{LP MO}}\right) - \sum_x E_x^{\text{HF}} \quad \text{electrostatic + induction + exch. repulsion}
\]

\[
E_{\text{BindE}}^{\text{LP MO}_2\&3\text{SPT}} \approx E_{\text{CP corrected HF}}
\]

if the augment functions are used

\[
E_{\text{BindE}}^{\text{LP MO}_2\&3\text{SPT}} \equiv E^{\text{CT}}
\]
Test calculations of the 2nd, 3rd & 4th SPT

\[(\text{H}_2\text{O})_2\]

The 3rd SPT agrees with the CP corrected energy!

\[E_{\text{BindD}} + E^{\text{SPT}}\]

\[E_{\text{BindD}} + E^{\text{LP MO}}\]

\[E_{\text{BindD}}\]

\[E^{\text{LP MO}}\]

2nd SPT

3rd & 4th SPT

only absolute local excited MO

all of excited MO

\[\text{JPC 112(2008) 16104}\]
Single Excitation 3rd order Perturbation Theory with Locally Projected MOs (LP MO 3SPT) for various water clusters

Keiichi Ohno’s isomers

LP MO 3SPT can be used in place of Counterpoise (CP) corrected HF

average error = 0.31kJ mol⁻¹
standard deviation = 0.14kJ mol⁻¹

average error = 0.40kJ mol⁻¹
standard deviation = 0.19kJ mol⁻¹ for linear and cyclic (HF)ₙ, n=2~8
Comparison of *halogen bonds* with those of Riley & Hobza \(^a\)

(/kJ mol\(^{-1}\))

<table>
<thead>
<tr>
<th></th>
<th>(\text{H}_3\text{CCl}--\text{OCH}_3)</th>
<th>(\text{F}_3\text{CCl}--\text{OCH}_3)</th>
<th>(\text{H}_3\text{CBr}--\text{OCH}_3)</th>
<th>(\text{F}_3\text{CBr}--\text{OCH}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{aug-cc-pVxZ})</td>
<td>(x=D)</td>
<td>(x=T)</td>
<td>(x=D)</td>
<td>(x=T)</td>
</tr>
<tr>
<td>(\text{SAPT}^a)</td>
<td>-3.14</td>
<td>-4.10</td>
<td>-8.20</td>
<td>-6.23</td>
</tr>
<tr>
<td>(\text{CCSD(T)}^a)</td>
<td>-3.26</td>
<td>-4.39</td>
<td>-7.70</td>
<td>-5.19</td>
</tr>
<tr>
<td>(\text{3SPT+D})</td>
<td>-3.82</td>
<td>-4.55</td>
<td>-8.62</td>
<td>-8.84</td>
</tr>
<tr>
<td>(\text{SAPT Dispersion})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{LP MO Dispersion})</td>
<td>-6.62</td>
<td>-7.35</td>
<td>-6.02</td>
<td>-7.01</td>
</tr>
<tr>
<td>(\text{3SPT})</td>
<td>+2.40</td>
<td>+2.80</td>
<td>-2.60</td>
<td>-1.83</td>
</tr>
<tr>
<td>(\text{CP corr HF})</td>
<td>+2.69</td>
<td>+2.79</td>
<td>-2.01</td>
<td>-1.86</td>
</tr>
</tbody>
</table>

1) The “3SPT+D” binding energies agree with the SAPT & CCSD(T) energy in less than 0.5kJ mol\(^{-1}\).
2) The “D” evaluated by LP MO 2nd PT agrees with the SAPT dispersion in less than 0.25kJ mol\(^{-1}\).
3) The “3SPT” energy agrees with the CP corrected HF energy in less than 0.60kJ mol\(^{-1}\) for aug-cc-pVDZ and 0.05kJ mol\(^{-1}\) for aug-cc-pVTZ.
4) The CT does contribute to the halogen bond, but it is much smaller than the dispersion energy.

Electron Donor-Acceptor Complex

$\sim$ CP HF

Dispersion energy

Binding Energy / kJ/mol

DFT-SAPT/CBS(KSH)
CCSD(T)/CBS(KSH)
MP2/aug-cc-pVTZ(KSH)
3SPT+D/aug-cc-pVTZ
3SPT/aug-cc-pVTZ

Comparison between the CT and dispersion terms in the binding energy of EDA complexes

The dispersion term is larger than the CT term, but they are the EDA complexes.

Two methods give almost equal dispersion correction.

CT+LE/aug-cc-pVTZ
CT(D->A)/aug-cc-pVTZ
Dispersion/SAPT-DFT (KSH)
Dispersion/aug-cc-pVTZ

Energy terms /kJ mol$^{-1}$

C2H4-F2    NH3-F2    C2H2-CIF    NH3-C12    HCN-CIF    H2O-CIF    NH3-SO2    NH3-CIF
Relative Energy (/kJ mol\(^{-1}\)) of Isomers of (H\(_2\)O\(_6\), (H\(_2\)O\(_{16}\) and (H\(_2\)O\(_{20}\)

<table>
<thead>
<tr>
<th>isomer</th>
<th>MP2</th>
<th>CCSD(T)</th>
<th>present method</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H(_2)O(_6)</td>
<td>E(<em>{\text{total}}) = -456 Hartree E(</em>{\text{bind}}) = -189 kJ mol(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>prism</td>
<td>CBS</td>
<td>aug-cc-pVDZ</td>
<td>aug-cc-pVDZ</td>
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<tr>
<td>cage</td>
<td>0.0</td>
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<tr>
<td>book</td>
<td>0.3</td>
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<tr>
<td>cyclic</td>
<td>1.0</td>
<td>4.8</td>
<td>1.9</td>
</tr>
<tr>
<td>(H(<em>2)O(</em>{16})</td>
<td>E(<em>{\text{total}}) = -1216 Hartree E(</em>{\text{bind}}) = -664 kJ mol(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4444-a</td>
<td>aug-cc-pVTZ</td>
<td>aug-cc-pVTZ</td>
<td>aug-cc-pVDZ</td>
</tr>
<tr>
<td>boat-a</td>
<td>-1.6</td>
<td>1.1</td>
<td>2.3</td>
</tr>
<tr>
<td>boat-b</td>
<td>-0.9</td>
<td>1.8</td>
<td>2.6</td>
</tr>
<tr>
<td>antiboat</td>
<td>-0.2</td>
<td>2.1</td>
<td>1.5</td>
</tr>
<tr>
<td>4444-b</td>
<td>1.9</td>
<td>2.3</td>
<td>2.8</td>
</tr>
<tr>
<td>(H(<em>2)O(</em>{20})</td>
<td>E(<em>{\text{total}}) = -1521 Hartree E(</em>{\text{bind}}) = -853 kJ mol(^{-1})</td>
<td></td>
<td></td>
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<tr>
<td>edge-sharing</td>
<td>MP2/aug-cc-pVDZ</td>
<td>MP2/aug-cc-pVTZ</td>
<td>aug-cc-pVDZ</td>
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<tr>
<td>fused cubes</td>
<td>7.4</td>
<td>10.5</td>
<td>6.2</td>
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<tr>
<td>face-sharing</td>
<td>4.9</td>
<td>7.9</td>
<td>6.5</td>
</tr>
<tr>
<td>dodecahedron</td>
<td>52.3</td>
<td>46.7</td>
<td>47.6</td>
</tr>
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</table>
In our theory, the binding energy is a sum of

\[ E_{\text{BindE}}^{\text{LPDO}} : \text{Electrostatic} + \text{Exchange Repulsion} + \text{Induction} \]

\[ E_{\text{CT}} \equiv E^{2\&3\text{SPT}} : \text{Charge-Transfer} \]

\[ E_{\text{Disp}} : \text{Dispersion} \]

\[ E_{\text{apprBSSEfreeHF}}^{\text{BindE}} = E_{\text{BindE}}^{\text{LPDO}} + E^{2\&3\text{SPT}}(E_{\text{CT}}) \]

\[ E_{\text{CT}} + E_{\text{Disp}} \]

Dispersion : prism > cyclic, Electrostatic : cyclic > prism
$E_{\text{prism}}^{\text{Disp}} > E_{\text{Cyclic}}^{\text{Disp}}$

**Importance of the structures in the isomer dependence of dispersion terms**

**Prism**

Dispersion terms even between non-hydrogen bonded pairs

**Cyclic**

No dispersion terms between non-hydrogen bonded pairs

LP MO Disp/ aug-cc-pVDZ
1. Dodecahedron isomer is unique; Large CT term, but small dispersion term. Also, the sum of electrostatic, exchange repulsion and induction terms is much smaller than the corresponding sums of the isomer.

2. Among the other three isomers, edge-sharing isomer is the most stable; Its CT term is larger than that of the other two.
## Relative Binding Energy \((\text{H}_2\text{O})_{25}\) /kJ mol\(^{-1}\)

| isomers\(^{a)}\) | \(\text{MP2/}
\text{apvdlz} \text{ b)}\) | \(\text{MTA-
\text{MP2(CBS)} \text{ a)}\) | \(\text{MTA-MP2/}
\text{apvtz} \text{ a)}\) | \(\text{MTA-MP2/}
\text{apvdz} \text{ a)}\) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>G25A</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>G25B</td>
<td>-3.1</td>
<td>3.0</td>
<td>0.8</td>
<td>2.1</td>
</tr>
<tr>
<td>G25C</td>
<td>1.9</td>
<td>4.1</td>
<td>1.3</td>
<td>2.5</td>
</tr>
<tr>
<td>G25D</td>
<td>-8.7</td>
<td>4.5</td>
<td>2.1</td>
<td>2.9</td>
</tr>
<tr>
<td>G25E</td>
<td>-2.2</td>
<td>3.7</td>
<td>2.9</td>
<td>3.4</td>
</tr>
<tr>
<td>G25F</td>
<td>-0.5</td>
<td>9.4</td>
<td>6.3</td>
<td>7.5</td>
</tr>
</tbody>
</table>

\(^{a)}\text{Furtado, Rahalkar, Shanker, Bandyopadhyay, Gadre, J. Phys. Chem. Lett. 3 (2012) 2253: Starting from the isomers found by the temperature basin paving method, the structures are optimized the molecular tailor approach (MTA) with MP2/aug-cc-pVDZ (=apvdz).}
\[
\begin{align*}
([n_{HB}, n_{D2A1} \rightarrow D1A2, n_{D1A2} \rightarrow D2A1, n_{D2A2} \rightarrow D2A2] \\
\{n_{m4}, n_{m5}, n_{m6}, n_{m7}\}
\end{align*}
\]
A Quiz:
How many five- and six-membered rings are found in isomer G25C?
Examples of the detailed analysis

X434

\[\{6, 2\}\]

\[n_{HB}, n_{D2A1}\rightarrow D1A2, n_{D1A2}\rightarrow D2A1, n_{D2A2}\rightarrow D2A2\]

\[[17, 4, 8, 0]\]

w8(O22) is D1A3

A water molecule in the cluster is classified by \textit{DnAm}.
The correlation of the O--O distance with the CT and dispersion energies

Strong correlation between $E_{\text{pair}}^{\text{CT}}$ and $E_{\text{pair}}^{\text{Dispersion}}$

In isomers of $(\text{H}_2\text{O})_n$, $n=2\sim10$

$E_{\text{pair}}^{\text{CT}}$, defined by LP MO 2&3SPT, is a good measure for the measure of the hydrogen bond strength.
CT and Dispersion Terms are pair-wise.

$(\text{H}_2\text{O})_n$, $n=17\sim21$

Xantheas

A water molecule in the cluster is classified by $DnAm$, where $n$ is the number of donating hydrogens, and $m$ is the number of accepting hydrogens in the molecule.
Dependence of CT energy and the lengthening of OH bonds on hydrogen bond length $R(O--O)$

$(H_2O)_n$, $n=17\sim21$

Xantheas
The terms for 4444-a and 4444-b are almost equal except for $E_{\text{BindE}}^{\text{LPMO}}$. The electrostatic, induction and exchange-repulsion determine the relative stability.
1. Almost no difference in $E_{CT}$ and $E_{Disp}$ for two isomers
2. The relative direction of the hydrogen bonded networks differs.
3. Probably, anti-clock, clock, anti-clock, and clock isomer is the most stable.
The dangling (non-hydrogen bonded) OH of D1A2 is ~0.962.

The lengthening of OH bonds and the CT energy

\[(H_2O)_n, \quad n=17\sim21\]

Xantheas

The lengthening of hydrogen bonded OH of D1A2 is strongly correlate with the CT energy.
Summary of water clusters

- Charge-Transfer energy of a hydrogen bonded water molecules is well-correlated with the dispersion energy of the pair, and it is a good measure of the strength of the hydrogen bonds.
- Hydrogen bond of a D1A2 type water as a hydrogen donor and a D2A1 type water as a hydrogen acceptor is stronger than that of the other types.
- More systematic studies of larger hydrogen-bonded clusters of more complex networks are required. The present theoretical technique makes it possible with the parallel implementation.
- The effect of the intramolecular correlation on the hydrogen bond has to be examined, and the efficient way should be developed without the configuration basis inconsistency (CBI).
## Summary of LP MO 3rdSPT+Dispersion correction

1. The Locally Projected MO based 3rd order Single excitation Perturbation Theory (LP SPT) can avoid both OBI and CBI at the single determinant Hartree-Fock level of the approximation. With the aug-cc-pVxZ type of basis sets, the binding energy evaluated by LPMO 3rdSPT approximates that of the counterpoise (CP) corrected HF binding energy even for large clusters. When a small size of basis set is used, the BSSE and charge-transfer (CT) contribution to the binding energy are never separable.

2. The counterpoise (CP) procedure for the many-determinant wave functions has to be used with care. In most cases, the convergence on the size of basis sets is slower for the CP corrected binding energy than for the uncorrected binding energy. In particular, with the cc-pVDZ and aug-cc-pVDZ basis sets, the CP procedure extremely underestimates the binding energy.

3. By simply adding the dispersion type (Disp) excitations in the double excitation perturbation (DPT) to the 3rd order SPT, the binding energies and potential energy curves with most of the basis sets used are consistently close to the more accurate (or expensive) levels of the correlated theories with the corresponding basis set.

4. The above approximation assumes that the change of the intramolecular correlation is cancel out when the binding energy is evaluated. This is a brave approximation.