

# Rapid Evaluation of Individual Hydrogen Bonding Energies in Linear Water Chains

HAO Jiaojiao, LI Shushi, JIANG Xiaonan, HUANG Cuiying and WANG Changsheng\*

*School of Chemistry and Chemical Engineering, Liaoning Normal University,  
Dalian 116029, P. R. China*

**Abstract** A model is proposed to rapidly evaluate the individual hydrogen bonding energies in linear water chains. We regarded the two O—H bonds of a water molecule as two dipoles. The magnitude of the O—H bond dipole moment can be varied due to the other water molecules' presence. An analytic potential energy function, which explicitly contains the permanent dipole-dipole interactions, the polarization interactions, the van der Waals interactions and the covalent interactions, was therefore established. The individual hydrogen bonding energies in a series of linear water chains were evaluated *via* the analytic potential energy function and compared with those obtained from the CP-corrected MP2/aug-cc-pVTZ calculations. The results show that the analytic potential energy function not only can produce the individual hydrogen bonding energies as accurately as the CP-corrected MP2/aug-cc-pVTZ method, but is very efficient as well, demonstrating the model proposed is reasonable and useful. Based on the individual hydrogen bonding energies obtained, the hydrogen bonding cooperativity in the linear water chains was explored and the natures of the hydrogen bonding in these water chains were discussed.

**Keywords** Hydrogen bond; Dipole-dipole interaction; Polarization; Covalency; Water chain; Cooperativity

## 1 Introduction

Water is the most common solvent in chemistry. The properties of water are truly remarkable and of the utmost importance in a host of chemical and biological processes<sup>[1,2]</sup>. The unique behavior of water may be attributed to its ability to establish a dynamic hydrogen bond network in which both the number and the strength of the hydrogen bonds continually fluctuate. Since hydrogen bond governs the characteristic nature of water, the studies on the hydrogen bonding in various water systems are intensive<sup>[3–12]</sup>.

High quality *ab initio* computations have led to significant progress in understanding the structural and energetic properties of simple hydrogen-bonding systems. High quality *ab initio* methods, such as the Møller-Plesset perturbation theory and coupled cluster technique, have become standard now in calculations of small intermolecular complexes. Parthasarathi *et al.*<sup>[6]</sup> used MP2 and density functional theory(DFT) method to study the structure, stability, and hydrogen-bonding interaction of hydrogen-bonded water clusters (H<sub>2</sub>O)<sub>n</sub>(*n*=2—4). Day *et al.*<sup>[7]</sup> used HF and MP2 method to perform a comprehensive search of water clusters (H<sub>2</sub>O)<sub>n</sub>(*n*=3—5). Bates and Tschumper<sup>[8]</sup> explored CCSD(T) complete basis set limit relative energies for low-lying water cluster (H<sub>2</sub>O)<sub>6</sub>. Sadlej *et al.*<sup>[9]</sup> used MP2 method to study the structure and spectra of cage water clusters (H<sub>2</sub>O)<sub>n</sub>(*n*=7—10). Neela *et al.*<sup>[10]</sup> used HF, MP2 and DFT

methods to study the four distinct hydrogen-bonded arrangements of water clusters and found that the caged water clusters are more stable. Yoo *et al.*<sup>[11]</sup> found the lowest-energy structures of water clusters (H<sub>2</sub>O)<sub>16</sub> and (H<sub>2</sub>O)<sub>17</sub> at the MP2 and CCSD(T) levels of theory. Although high level *ab initio* methods can produce accurate hydrogen bonding interaction energies for hydrogen-bonded complexes, they are limited when applied to large systems.

Recent studies have reported the presence of infinite linear chains of water molecules in nanoporous channels of organic hexahosts trichlorophloroglucinol and tribromophloroglucinol<sup>[13]</sup>. Linear water chains have also been observed in the X-ray diffraction studies of crystals of organic and inorganic molecules<sup>[14]</sup>. The prevalence and importance of linear water chains in protein structures has been demonstrated in numerous studies<sup>[15–19]</sup>.

We proposed a scheme to the rapid evaluation of the individual hydrogen bonding energies in linear water chains. Based on the results obtained, the hydrogen bonding cooperativity in the linear water chains was explored and the natures of the hydrogen bonding in these water chains are discussed.

## 2 Computation Details

We have proposed Eq.(1) as an analytic potential energy function to predict hydrogen bonding energy(*E*<sub>HB</sub>)<sup>[20–25]</sup>.

\*Corresponding author. E-mail: chwangcs@lnnu.edu.cn

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$$E_{\text{HB}} = \frac{\mu\mu'}{r^3}(2\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\zeta) + E_{\text{vdW}} \quad (1)$$

If two molecules are bonded together by more than one hydrogen bond, the binding energy ( $E_b$ ) of a hydrogen-bonded complex may be expressed as Eq.(2).

$$E_b = \sum \frac{\mu\mu'}{r^3}(2\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\zeta) + E_{\text{vdW}} \quad (2)$$

Eq.(1) or (2) has been successfully applied to evaluating hydrogen bond strength for hydrogen-bonded dimers containing peptide amides and nucleic acid bases<sup>[20–25]</sup>.

In this work we further developed Eq.(2) with polarization and covalent contributions taken into account explicitly. We regarded each O—H bond of a water molecule as a dipole. The magnitude of the O—H bond dipole moment in an isolated water molecule is different from that of the corresponding one in a water cluster. If we set the O—H bond dipole moment of an isolated water as  $\mu_0$ , the corresponding O—H bond dipole moment  $\mu$  in a water cluster may be expressed as  $\mu = \mu_0 + \Delta\mu$ , where  $\Delta\mu$  is the dipole moment increment induced by the environment. Here  $\Delta\mu$  is referred to the induced dipole moment. The first term of Eq.(2) can then be rewritten as Eq. (3).

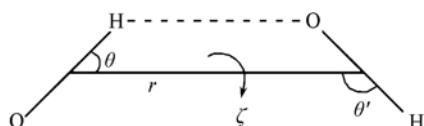
$$\begin{aligned} & \sum \frac{\mu\mu'}{r^3}(2\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\zeta) \\ &= \sum \frac{(\mu_0 + \Delta\mu)(\mu'_0 + \Delta\mu')}{r^3}(2\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\zeta) \\ &= \left[ \sum \frac{\mu_0\mu'_0}{r^3} + \sum \frac{(\mu_0\Delta\mu' + \mu'_0\Delta\mu + \Delta\mu\Delta\mu')}{r^3} \right] \\ & \quad (2\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\zeta) \\ &= E_{\text{dd}} + E_{\text{pol}} \end{aligned} \quad (3)$$

in which

$$E_{\text{dd}} = \sum \frac{\mu_0\mu'_0}{r^3}(2\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\zeta) \quad (4)$$

$$E_{\text{pol}} = \sum \frac{(\mu_0\Delta\mu' + \mu'_0\Delta\mu + \Delta\mu\Delta\mu')}{r^3} (2\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\zeta) \quad (5)$$

$E_{\text{dd}}$  is the summation of the interaction energies between dipoles  $\mu_0$  and  $\mu'_0$ , in which  $\mu_0$  belongs to one water molecule while  $\mu'_0$  belongs to another. Here the O—H bond dipole moment  $\mu_0$  of an isolated water is referred to the permanent dipole moment and  $E_{\text{dd}}$  is referred to the permanent dipole-dipole interaction or, briefly, the dipole-dipole interaction. For a water molecule dimer,  $E_{\text{dd}}$  contains four pairs of the permanent dipole-dipole interactions. As shown in Fig.1, the parameters  $r$ ,  $\theta$ ,  $\theta'$ , and  $\zeta$  can be calculated easily from the relative orientation of the two dipoles. And in this work, the magnitude of  $\mu_0$  is optimized to be  $5.84 \times 10^{-30}$  C·m. Therefore, the magnitude of  $E_{\text{dd}}$  can be evaluated easily.



**Fig.1 Relative orientation of two O—H dipoles**

$r$  is the distance joining the two dipoles' centers;  $\zeta$  is the angle between the OHO and HOH planes.

$E_{\text{pol}}$  is the summation of the interaction energies between two induced dipoles  $\Delta\mu$  and  $\Delta\mu'$  and between one induced dipole  $\Delta\mu$ (or  $\Delta\mu'$ ) and one permanent dipole  $\mu'_0$ (or  $\mu_0$ ).  $E_{\text{pol}}$  is referred to the polarization interaction because the magnitude of the induced dipole  $\Delta\mu$ (or  $\Delta\mu'$ ) depends on the polarization effect of the environment on the O—H bond dipole.  $E_{\text{pol}}$  can be easily estimated if  $\Delta\mu$  is known.

In this work,  $\Delta\mu$  is calculated via  $\Delta\mu = \Delta q_{\text{pol}} \cdot d$ , where  $\Delta q_{\text{pol}}$  is the charge difference between the hydrogen atomic partial charge of the isolated water molecule and the corresponding one in a water cluster, and  $d$  is the O—H bond length. Here  $\Delta q_{\text{pol}}$  is estimated with B3LYP/6-31G(d) method to calculate the Mulliken atomic partial charge for the hydrogen atom in an isolated water molecule and in a water chain.

Lennard-Jones 6-12 was used in this work to calculate all the van der Waals interactions  $E_{\text{vdW}}$  between atoms in different molecules.

$$E_{\text{vdW}} = \sum_{i < j} \left( \frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} \right) \quad (6)$$

The combining rules are  $A_{ij} = \varepsilon_{ij} (R_{ij}^*)^{12}$ ,  $B_{ij} = 2 \cdot \varepsilon_{ij} (R_{ij}^*)^6$ ,  $R_{ij}^* = R_i^* + R_j^*$ ,  $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$ , in which  $R^*$  is van der Waals radius and  $\varepsilon$  is van der Waals well depth. In this work  $R^*$  and  $\varepsilon$  were optimized to be 0.1721 nm and 0.8795 kJ/mol for the oxygen atom of water molecule and 0.0060 nm and 0.0656 kJ/mol for the hydrogen atom of water molecule.

It has been believed that the hydrogen bond is a complex interaction that has at least four chemical characteristics: electrostatic interaction, polarization, van der Waals(dispersion/repulsion) interaction, and covalency(charge transfer)<sup>[26,27]</sup>. Therefore, the covalent contribution should be considered properly for strong hydrogen bonds. In this work, we chose Eq. (7) to estimate the covalent contribution to a hydrogen bond.

$$E_{\text{orb}} = \sum D \exp \left[ \alpha (R - R_0)^\beta \right] \quad (7)$$

In Eq.(7),  $R$  is the hydrogen bond distance  $R(\text{O} \cdots \text{H})$ ;  $D$ ,  $\alpha$ ,  $\beta$  and  $R_0$  are parameters needed to be parameterized. The linear water chains containing from five to seven monomeric units were chosen as training systems to determine these parameters. The individual hydrogen bonding energies of these training systems were first calculated at the CP-corrected MP2/aug-cc-pVTZ level. The parameters of  $D$ ,  $\alpha$ ,  $\beta$  and  $R_0$  were then optimized to be  $-27.2$  kJ/mol,  $-11.544$ ,  $0.94$ ,  $0.170$  nm, respectively.

The total  $E_b$  for a hydrogen-bonded complex is therefore expressed as Eq.(8).

$$\begin{aligned} E_b &= E_{\text{dd}} + E_{\text{pol}} + E_{\text{vdW}} + E_{\text{orb}} \\ &= \sum \frac{\mu_0\mu'_0}{r^3}(2\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\zeta) + \\ & \quad \sum \frac{(\mu_0\Delta\mu' + \mu'_0\Delta\mu + \Delta\mu\Delta\mu')}{r^3} (2\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\zeta) + \\ & \quad \sum_{i < j} \left( \frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} \right) + \sum D \exp \left[ \alpha (R - R_0)^\beta \right] \end{aligned} \quad (8)$$

Eq.(8) was then used to calculate the individual hydrogen

bonding energies for water chains  $(\text{H}_2\text{O})_n (n=5-20)^{[14]}$ . The individual hydrogen bonding energies for the relative small linear water chains  $(\text{H}_2\text{O})_n (n=5-15)$  were also calculated by the CP-corrected MP2/aug-cc-pVTZ method and the three well-known force fields AMBER99<sup>[28,29]</sup>, CHARMM19<sup>[30,31]</sup> and OPLSAA/L<sup>[32,33]</sup>. All *ab initio* calculations were carried out with the help of the Gaussian 03 program package<sup>[34]</sup>.

### 3 Results and Discussion

The individual hydrogen bonding energies in the linear water chains[Fig.2(A)], calculated *via* Eq.(8), the CP-corrected

MP2/aug-cc-pVTZ, AMBER99, CHARMM19 and OPLSAA/L, are listed in Table 1. In Table 1 and Fig.2,  $n$  is the chain length,  $k$  is the hydrogen bond type. The first( $k=1$ ) type of hydrogen bonds exist in all water chains starting with the dimer. The second( $k=2$ ) type of hydrogen bonds occur in water chains containing four or more monomers. The third( $k=3$ ) type of hydrogen bonds occur in the chains of six or more water molecules, etc. For example, two types of hydrogen bonds( $k=1$  and 2) exist in the  $(\text{H}_2\text{O})_5$  chain[Fig.2(B)]; three kinds of hydrogen bonds( $k=1, 2$  and 3) exist in the  $(\text{H}_2\text{O})_6$  chain [Fig.2(C)]. In Table 1,  $E_{\text{HIB}}$  is the individual hydrogen bonding energy.  $E$  is

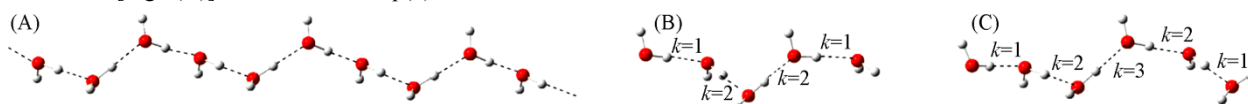


Fig.2 Illustration of the linear water chains(A), the hydrogen bond types in the  $(\text{H}_2\text{O})_5$ (B) and  $(\text{H}_2\text{O})_6$  chains(C)

Table 1 Individual hydrogen bonding energies  $E_{\text{HIB}}$ (kJ/mol) obtained by the CP-corrected MP2/aug-cc-pVTZ, Eq. (8), AMBER99, CHARMM19 and OPLSAA/L force fields for the water chains  $(\text{H}_2\text{O})_n (n=5-20)$

$k$	$n$	MP2		Eq. (8)		AMBER99			CHARMM19			OPLSAA/L		
		$E_{\text{HIB}}$	$E_{\text{HIB}}$	$E$	$\delta(\%)$	$E_{\text{HIB}}$	$E$	$\delta(\%)$	$E_{\text{HIB}}$	$E$	$\delta(\%)$	$E_{\text{HIB}}$	$E$	$\delta(\%)$
1	5	-29.8	-30.1	-0.3	0.7	-31.0	-1.2	3.9	-30.9	-1.1	3.6	-29.3	0.5	1.7
	6	-31.0	-30.7	0.3	0.9	-31.6	-0.6	1.9	-31.4	-0.4	1.5	-29.9	1.1	3.5
	7	-30.8	-30.8	0.0	0.2	-31.6	-0.8	2.9	-31.5	-0.7	2.3	-30.0	0.8	2.6
	8	-31.1	-31.1	0.0	0.2	-31.8	-0.7	2.3	-31.6	-0.5	1.6	-30.2	0.9	3.0
	9	-31.1	-31.2	-0.1	0.6	-31.9	-0.8	2.8	-31.8	-0.7	2.3	-30.3	0.8	2.6
	10	-31.2	-31.4	-0.2	0.5	-32.0	-0.8	2.7	-31.8	-0.6	2.0	-30.3	0.9	2.8
	11	-31.3	-31.3	0.0	0.2	-32.0	-0.7	2.4	-31.9	-0.6	1.9	-30.3	1.0	2.9
	12	-31.3	-31.6	-0.3	1.2	-32.2	-0.9	3.1	-32.0	-0.7	2.3	-30.5	0.8	2.4
	13	-31.3	-31.5	-0.2	0.7	-32.2	-0.9	2.9	-32.0	-0.7	2.3	-30.5	0.8	2.5
	14	-31.4	-31.5	-0.1	0.3	-32.1	-0.7	2.5	-31.9	-0.5	1.9	-30.5	0.9	2.8
	15	-31.4	-31.5	-0.1	0.3	-32.1	-0.7	2.5	-31.9	-0.5	1.9	-30.5	0.9	2.8
	16		-31.5											
	17		-31.5											
	18		-31.5											
	19		-31.6											
	20		-31.7											
2	5	-39.0	-39.4	-0.4	1.1	-35.4	3.6	9.1	-33.2	5.8	14.8	-33.4	5.6	14.4
	6	-40.9	-41.3	-0.4	1.0	-36.6	4.3	10.5	-34.0	6.9	16.8	-34.4	6.5	15.8
	7	-41.6	-41.9	-0.3	0.7	-37.0	4.6	11.0	-34.3	7.3	17.5	-34.9	6.7	16.2
	8	-42.2	-42.3	-0.1	0.4	-37.2	5.0	11.7	-34.4	7.8	18.3	-35.1	7.1	16.9
	9	-42.4	-42.6	-0.2	0.3	-37.5	4.9	11.6	-34.7	7.7	18.2	-35.3	7.1	16.8
	10	-42.8	-42.9	-0.1	0.4	-37.7	5.1	11.8	-34.9	7.9	18.5	-35.5	7.3	16.9
	11	-42.9	-43.1	-0.2	0.3	-37.7	5.2	12.1	-34.8	8.1	18.9	-35.5	7.4	17.2
	12	-43.0	-43.3	-0.3	0.7	-38.0	5.0	11.8	-35.0	8.0	18.7	-35.7	7.3	16.9
	13	-43.1	-43.3	-0.2	0.4	-38.0	5.1	11.8	-35.2	7.9	18.4	-35.8	7.3	16.9
	14	-43.2	-43.3	-0.1	0.3	-38.0	5.2	12.2	-35.0	8.2	19.0	-35.8	7.4	17.2
	15	-43.3	-43.3	0.0	0.2	-38.0	5.3	12.3	-35.0	8.2	19.0	-35.7	7.6	17.4
	16		-43.4											
	17		-43.4											
	18		-43.5											
	19		-43.5											
	20		-43.5											
3	6	-41.3	-41.9	-0.6	1.4	-36.3	5.0	12.1	-33.5	7.8	18.9	-34.2	7.1	17.3
	7	-43.9	-44.1	-0.2	0.5	-38.7	5.2	12.0	-34.5	9.4	21.5	-35.5	8.4	19.2
	8	-45.0	-45.1	-0.1	0.3	-38.3	6.7	14.9	-34.9	10.1	22.5	-36.0	9.0	19.9
	9	-46.0	-45.9	0.1	0.1	-38.7	7.3	15.9	-35.0	11.0	23.8	-36.4	9.6	20.9
	10	-46.4	-46.4	0.0	0.1	-39.0	7.4	15.9	-35.4	11.0	23.8	-36.7	9.7	20.9
	11	-46.7	-46.5	0.2	0.5	-39.1	7.6	16.3	-35.4	11.3	24.2	-36.8	9.9	21.3
	12	-47.3	-47.2	0.1	0.2	-39.4	7.9	16.7	-35.5	11.8	24.9	-37.0	10.3	21.7

To be continued on the next page.

$k$	$n$	MP2	Eq. (8)			AMBER99			CHARMM19			OPLSAA/L		
		$E_{\text{IHB}}$	$E_{\text{IHB}}$	$E$	$\delta(\%)$	$E_{\text{IHB}}$	$E$	$\delta(\%)$	$E_{\text{IHB}}$	$E$	$\delta(\%)$	$E_{\text{IHB}}$	$E$	$\delta(\%)$
3	13	-47.3	-47.2	0.1	0.4	-39.5	7.8	16.5	-35.7	11.6	24.5	-37.2	10.1	21.5
	14	-47.4	-47.1	0.3	0.6	-39.5	7.9	16.8	-35.7	11.7	24.8	-37.1	10.3	21.7
	15	-47.6	-47.3	0.3	0.6	-39.5	8.1	17.0	-35.8	11.8	24.8	-37.2	10.4	21.7
	16		-47.4											
	17		-47.4											
	18		-47.4											
	19		-47.5											
	20		-47.8											
4	8	-46.6	-46.4	0.2	0.3	-38.9	7.7	16.5	-35.2	11.4	24.5	-36.6	10.0	21.5
	9	-48.0	-47.9	0.1	0.3	-39.6	8.4	17.6	-35.6	12.4	25.9	-37.2	10.8	22.5
	10	-48.8	-48.6	0.2	0.5	-40.0	8.8	18.2	-35.8	13.0	26.7	-37.6	11.2	23.0
	11	-49.4	-48.9	0.5	1.0	-40.2	9.2	18.6	-36.0	13.4	27.2	-37.8	11.6	23.4
	12	-50.0	-49.7	0.3	0.6	-40.5	9.5	18.9	-36.1	13.9	27.7	-38.1	11.9	23.8
	13	-50.2	-49.7	0.5	0.9	-40.6	9.6	19.0	-36.3	13.9	27.7	-38.2	12.0	23.8
	14	-50.4	-49.8	0.4	1.1	-40.7	9.7	19.2	-36.3	14.1	27.9	-38.3	12.0	24.0
	15	-50.5	-50.0	0.5	1.0	-40.9	9.6	19.0	-36.5	14.0	27.7	-38.5	12.1	23.9
	16		-50.2											
	17		-50.2											
	18		-50.3											
	19		-50.4											
	20		-50.7											
5	10	-49.6	-49.6	0.0	0.1	-40.3	9.3	18.6	-36.0	13.6	27.4	-38.0	11.6	23.4
	11	-50.5	-50.3	0.2	0.5	-40.7	9.8	19.4	-36.2	14.3	28.4	-38.3	12.2	24.2
	12	-51.1	-50.8	0.3	0.6	-41.1	10.0	19.6	-36.5	14.6	28.6	-38.6	12.5	24.5
	13	-51.7	-51.3	0.4	0.6	-41.3	10.4	20.2	-36.6	15.1	29.2	-38.8	12.9	24.9
	14	-52.0	-51.5	0.5	0.9	-41.4	10.6	20.4	-36.6	15.4	29.6	-38.9	13.1	25.2
	15	-52.2	-51.7	0.5	0.9	-41.5	10.7	20.4	-36.8	15.4	29.5	-39.1	13.1	25.1
	16		-52.0											
	17		-52.0											
	18		-52.1											
	19		-52.2											
	20		-52.4											
	6	12	-51.4	-51.2	0.2	0.4	-41.2	10.2	19.9	-36.5	14.9	28.9	-38.7	12.7
13		-52.0	-51.8	0.2	0.5	-41.5	10.5	20.2	-36.8	15.5	29.3	-39.0	13.0	25.0
14		-52.5	-52.2	0.3	0.7	-41.8	10.7	20.5	-37.0	15.5	29.7	-39.3	13.2	25.3
15		-52.9	-52.6	0.3	0.7	-42.0	10.9	20.7	-37.1	15.8	29.9	-39.5	13.4	25.4
16			-52.8											
17			-52.8											
18			-52.9											
19			-53.0											
20			-53.3											
7	14	-52.9	-52.3	0.6	1.0	-41.8	11.1	21.0	-37.0	15.9	30.1	-39.3	13.6	25.7
	15	-53.4	-52.9	0.5	1.0	-42.1	11.3	21.1	-37.2	16.2	30.3	-39.6	13.8	25.8
	16		-53.1											
	17		-53.3											
	18		-53.6											
	19		-53.6											
	20		-53.7											
8	16		-53.5											
	17		-53.7											
	18		-53.8											
	19		-54.3											
9	20		-54.4											
	18		-54.2											
	19		-54.3											
	20		-54.6											
10	20		-54.6											
Mean unsigned error				0.3		6.4			9.4			8.2		
Root mean squared error(RMSE)				0.3		7.3			10.7			9.3		
Mean relative error(MRE)					0.6			13.4			19.6			17.4

the absolute error from MP2 result.  $\delta$  is the relative error from MP2 result.

As shown in Table 1, the individual hydrogen bonding energies  $E_{\text{IHB}}$  obtained *via* Eq.(8) are in good agreement with those obtained *via* the CP-corrected MP2/aug-cc-pVTZ calculations. For instance, the individual hydrogen bonding energies for six types of hydrogen bonds in the  $(\text{H}_2\text{O})_{13}$  chain were calculated to be -31.5, -43.3, -47.2, -49.7, -51.3 and -51.8 kJ/mol *via* Eq.(8) and -31.3, -43.1, -47.3, -50.2, -51.7 and -52.0 kJ/mol *via* MP2 method, the differences between the results obtained by means of Eq.(8) and MP2 are only -0.2, -0.2, 0.1, 0.5, 0.4 and 0.2 kJ/mol, the relative errors compared with MP2 results are only 0.7%, 0.4%, 0.4%, 0.9%, 0.6%, and 0.5%, respectively. For all 52 hydrogen bonds compared in this paper, Eq.(8) predicts the individual hydrogen bonding energies of water molecule clusters by the CP-corrected MP2/aug-cc-pVTZ to be within an error limit of 0.6 kJ/mol. Compared with the MP2 predicting individual hydrogen bonding energies, Eq.(8) exhibits a root mean square error(RMSE) of only 0.3 kJ/mol and a mean relative error(MRE) of only 0.6%. All these results suggest that Eq.(8) can reproduce the CP-corrected MP2/aug-cc-pVTZ predicted individual hydrogen bonding energies satisfactorily.

The data in Table 1 indicate that for most of the first( $k=1$ ) type of hydrogen bonds, the hydrogen bonding energies obtained from the three force fields are also in agreement with those obtained from MP2 calculations. For instance, for the first( $k=1$ ) type of hydrogen bonds in the  $(\text{H}_2\text{O})_{13}$  chain, the individual hydrogen bonding energies were calculated to be -31.3 kJ/mol from MP2 calculations, -32.2 kJ/mol from AMBER99, -32.0 kJ/mol from CHARMM19 and -30.5 kJ/mol from OPLSAA/L; the deviations from MP2 results are only -0.9, -0.7 and 0.8 kJ/mol; the relative deviations are only 2.9%, 2.3% and 2.5%, seemingly suggesting that the three well-known force fields can describe hydrogen bonding satisfactorily. However, it has been found that as the hydrogen bonds are close to the center of the chain, the differences between the individual hydrogen bonding energies obtained from the force fields and from MP2 calculations become large. For instance, for the second( $k=2$ ) type of hydrogen bonds in the  $(\text{H}_2\text{O})_{13}$  chain, the individual hydrogen bonding energies were calculated to be -43.1 kJ/mol from MP2 calculations, -38.0 kJ/mol from AMBER99, -35.2 kJ/mol from CHARMM19 and -35.8 kJ/mol from OPLSAA/L; the deviations of them from the MP2 results are 5.1, 7.9 and 7.3 kJ/mol respectively; the relative errors are 11.8%, 18.4% and 16.9% respectively. For the most central( $k=6$ ) hydrogen bonds in the  $(\text{H}_2\text{O})_{13}$  chain, the individual hydrogen bonding energies were calculated to be -52.0 kJ/mol from MP2 calculations, -41.5 kJ/mol from AMBER99, -36.8 kJ/mol from CHARMM19 and -39.0 kJ/mol from OPLSAA/L; the deviations of them from the MP2 results are as large as 10.5, 15.2 and 13.0 kJ/mol, respectively; the relative deviations are as large as 20.2%, 29.2% and 25.0%, respectively. These results indicate that the three force fields cannot correctly describe the hydrogen bonding interactions for water chains.

The cooperative effect of cumulative hydrogen bonds is

evident from Table 1. The data in Table 1 show that the hydrogen bond gradually gets stronger with the growth of the water molecule chain for the same hydrogen bond type. For example, for the first( $k=1$ ) type of hydrogen bonds, the hydrogen bonding energy is -31.7 kJ/mol in  $(\text{H}_2\text{O})_{20}$ , -31.5 kJ/mol in  $(\text{H}_2\text{O})_{15}$ , and -30.1 kJ/mol in  $(\text{H}_2\text{O})_5$ . About 5% increment of the first type hydrogen bond strength is achieved from  $(\text{H}_2\text{O})_5$  to  $(\text{H}_2\text{O})_{20}$ . For the third( $k=3$ ) type of hydrogen bonds, the hydrogen bonding energy is -47.8 kJ/mol in  $(\text{H}_2\text{O})_{20}$ , -47.3 kJ/mol in  $(\text{H}_2\text{O})_{15}$  and -41.9 kJ/mol in  $(\text{H}_2\text{O})_6$ . About 14% increment of the third type hydrogen bond strength is achieved from  $(\text{H}_2\text{O})_6$  to  $(\text{H}_2\text{O})_{20}$ .

Table 1 further shows that the central hydrogen bond gradually gets stronger with the growth of the water chain. For example, the central( $k=10$ ) hydrogen bonding energy in the  $(\text{H}_2\text{O})_{20}$  chain is -54.6 kJ/mol, the central( $k=7$ ) hydrogen bonding energy in the  $(\text{H}_2\text{O})_{15}$  chain is -52.9 kJ/mol, the central( $k=5$ ) hydrogen bonding energy in the  $(\text{H}_2\text{O})_{10}$  chain is -49.6 kJ/mol and the central( $k=2$ ) hydrogen bonding energy in the  $(\text{H}_2\text{O})_5$  chain is -39.4 kJ/mol. About 39% increment of the most central hydrogen bond strength is achieved from  $(\text{H}_2\text{O})_5$  to  $(\text{H}_2\text{O})_{20}$ .

The data in Table 1 also show that the hydrogen bonds located in the center of the chain are stronger than those located at the ends and that the strongest hydrogen bond is the central one in  $(\text{H}_2\text{O})_{20}$  (-54.6 kJ/mol) and the weakest hydrogen bond is the first type of hydrogen bond in  $(\text{H}_2\text{O})_5$  (-30.1 kJ/mol). The central hydrogen bond in  $(\text{H}_2\text{O})_{20}$  is about 1.8 times stronger than the first type of hydrogen bond in  $(\text{H}_2\text{O})_5$ .

In Table 2 are listed the individual hydrogen bonding energy components: the permanent dipole-dipole interactions  $E_{\text{dd}}$ , the polarization interactions  $E_{\text{pol}}$ , the van der Waals interactions  $E_{\text{vdw}}$  and the orbital interactions  $E_{\text{orb}}$ . The data in Table 2 clearly indicate that the permanent dipole-dipole interaction is the largest component of the hydrogen bonding energy and that the polarization interaction and the van der Waals interaction almost cancel with each other for all situations. For example, for the first type of hydrogen bonds in  $(\text{H}_2\text{O})_{13}$  chain, the permanent dipole-dipole interaction  $E_{\text{dd}}$  is -27.6 kJ/mol, contributing about 88% to the overall stabilization, whereas the attractive polarization interaction  $E_{\text{pol}}$  is -4.8 kJ/mol almost cancelled by the repulsive van der Waals interaction  $E_{\text{vdw}}$  (4.7 kJ/mol). In addition, the covalency  $E_{\text{orb}}$  (-3.8 kJ/mol) contributes only 12% to the overall stabilization. For the central( $k=10$ ) hydrogen bond in the  $(\text{H}_2\text{O})_{20}$  chain, the permanent dipole-dipole interaction  $E_{\text{dd}}$  is -38.1 kJ/mol, contributing about 70% to the overall stabilization, the attractive polarization interaction  $E_{\text{pol}}$  is -11.7 kJ/mol almost cancelled by the repulsive van der Waals interaction  $E_{\text{vdw}}$  (11.9 kJ/mol), and the covalency  $E_{\text{orb}}$  (16.7 kJ/mol) contributes as large as 30% to the overall stabilization. These results indicate that the permanent dipole-dipole interactions play the most important role in hydrogen bonding interaction of the water chains and the covalent contributions are also necessary for correctly describing the hydrogen bonding cooperativity of the water chains.

**Table 2** Individual hydrogen bonding energy components obtained from Eq.(8) for the water chains (H<sub>2</sub>O)<sub>n</sub>(*n*=5—20)

<i>k</i>	<i>n</i>	<i>R</i> (O···H)/nm	<i>E</i> <sub>dd</sub> /(kJ·mol <sup>-1</sup> )	<i>E</i> <sub>pol</sub> /(kJ·mol <sup>-1</sup> )	<i>E</i> <sub>vdW</sub> /(kJ·mol <sup>-1</sup> )	<i>E</i> <sub>orb</sub> /(kJ·mol <sup>-1</sup> )	<i>E</i> <sub>IHB</sub> /(kJ·mol <sup>-1</sup> )
1	5	1.860	-26.7	-4.3	4.4	-3.5	-30.1
	6	1.856	-27.2	-4.3	4.6	-3.7	-30.6
	7	1.857	-27.2	-4.6	4.6	-3.6	-30.8
	8	1.854	-27.4	-4.6	4.6	-3.8	-31.2
	9	1.854	-27.5	-4.7	4.7	-3.7	-31.2
	10	1.853	-27.5	-4.7	4.7	-3.8	-31.3
	11	1.854	-27.5	-4.7	4.7	-3.8	-31.3
	12	1.850	-27.8	-4.8	4.9	-3.9	-31.6
	13	1.854	-27.6	-4.8	4.7	-3.8	-31.5
	14	1.853	-27.6	-4.8	4.7	-3.8	-31.5
	15	1.853	-27.6	-4.8	4.7	-3.8	-31.5
	16	1.853	-27.7	-4.8	4.8	-3.8	-31.5
	17	1.853	-27.7	-4.8	4.8	-3.8	-31.5
	18	1.853	-27.7	-4.8	4.8	-3.8	-31.5
	19	1.853	-27.7	-4.8	4.8	-3.8	-31.5
	20	1.853	-27.8	-4.9	4.8	-3.8	-31.7
2	5	1.788	-31.2	-7.5	7.8	-8.4	-39.3
	6	1.779	-32.4	-7.8	8.4	-9.5	-41.3
	7	1.777	-32.7	-8.0	8.5	-9.7	-41.9
	8	1.775	-32.9	-8.2	8.7	-10	-42.4
	9	1.775	-33.1	-8.2	8.7	-9.9	-42.5
	10	1.773	-33.3	-8.3	8.9	-10.2	-42.9
	11	1.773	-33.4	-8.3	8.9	-10.2	-43.0
	12	1.772	-33.5	-8.4	8.9	-10.4	-43.4
	13	1.774	-33.5	-8.4	8.8	-10.1	-43.2
	14	1.772	-33.5	-8.4	8.9	-10.3	-43.3
	15	1.772	-33.5	-8.4	8.9	-10.3	-43.3
	16	1.773	-33.6	-8.5	8.9	-10.2	-43.4
	17	1.772	-33.6	-8.4	8.9	-10.3	-43.4
	18	1.772	-33.6	-8.5	8.9	-10.3	-43.5
	19	1.772	-33.6	-8.5	8.9	-10.3	-43.5
	20	1.773	-33.7	-8.5	8.9	-10.2	-43.5
3	6	1.776	-32.0	-8.7	8.7	-9.9	-41.9
	7	1.767	-33.3	-9.1	9.3	-11.0	-44.1
	8	1.763	-33.8	-9.3	9.6	-11.6	-45.1
	9	1.760	-34.2	-9.4	9.8	-12.0	-45.8
	10	1.759	-34.5	-9.6	9.9	-12.2	-46.4
	11	1.758	-34.6	-9.6	9.9	-12.3	-46.6
	12	1.755	-34.8	-9.7	10.2	-12.7	-47.0
	13	1.757	-34.9	-9.8	10.1	-12.5	-47.1
	14	1.757	-34.9	-9.7	10.1	-12.6	-47.1
	15	1.756	-35.0	-9.8	10.1	-12.7	-47.4
	16	1.756	-35.0	-9.8	10.2	-12.7	-47.3
	17	1.756	-35.0	-9.8	10.2	-12.7	-47.3
	18	1.756	-35.0	-9.8	10.1	-12.7	-47.4
	19	1.755	-35.1	-9.8	10.2	-12.8	-47.5
	20	1.755	-35.3	-9.9	10.2	-12.8	-47.8
4	8	1.758	-34.4	-9.6	9.9	-12.4	-46.5
	9	1.753	-35.1	-9.9	10.3	-13.2	-47.9
	10	1.751	-35.4	-10.1	10.5	-13.6	-48.6
	11	1.750	-35.7	-10.1	10.6	-13.8	-49.0
	12	1.747	-35.9	-10.3	10.8	-14.2	-49.6
	13	1.748	-36.0	-10.4	10.8	-14.1	-49.7
	14	1.747	-36.1	-10.3	10.8	-14.2	-49.8
	15	1.747	-36.2	-10.4	10.8	-14.2	-50.0
	16	1.746	-36.3	-10.5	10.9	-14.4	-50.3
	17	1.746	-36.3	-10.4	10.9	-14.4	-50.2
	18	1.746	-36.3	-10.5	10.9	-14.4	-50.3

To be continued on the next page.

<i>k</i>	<i>n</i>	<i>R</i> (O···H)/nm	<i>E<sub>dd</sub></i> /(kJ·mol <sup>-1</sup> )	<i>E<sub>pol</sub></i> /(kJ·mol <sup>-1</sup> )	<i>E<sub>vdW</sub></i> /(kJ·mol <sup>-1</sup> )	<i>E<sub>orb</sub></i> /(kJ·mol <sup>-1</sup> )	<i>E<sub>IHB</sub></i> /(kJ·mol <sup>-1</sup> )
4	19	1.746	-36.4	-10.5	11.0	-14.4	-50.3
	20	1.745	-36.5	-10.5	11.0	-14.6	-50.6
5	10	1.747	-35.8	-10.5	10.8	-14.2	-49.7
	11	1.745	-36.1	-10.5	11.0	-14.6	-50.2
	12	1.744	-36.4	-10.7	11.1	-14.8	-50.8
	13	1.743	-36.6	-10.8	11.2	-15.1	-51.3
	14	1.742	-36.7	-10.8	11.2	-15.3	-51.6
	15	1.742	-36.9	-10.9	11.3	-15.3	-51.8
	16	1.741	-37.0	-11.0	11.3	-15.4	-52.1
	17	1.741	-37.0	-10.9	11.3	-15.4	-52.0
	18	1.741	-37.1	-11.0	11.4	-15.4	-52.1
	19	1.741	-37.2	-11.0	11.4	-15.4	-52.2
6	20	1.740	-37.2	-11.0	11.4	-15.6	-52.4
	12	1.743	-36.5	-10.9	11.2	-15.0	-51.2
	13	1.742	-36.8	-11.0	11.3	-15.3	-51.8
	14	1.741	-37.0	-11.0	11.4	-15.5	-52.1
	15	1.740	-37.2	-11.2	11.5	-15.7	-52.6
	16	1.739	-37.3	-11.3	11.5	-15.7	-52.8
	17	1.739	-37.4	-11.2	11.5	-15.8	-52.9
	18	1.739	-37.5	-11.2	11.5	-15.8	-53.0
	19	1.739	-37.5	-11.3	11.6	-15.8	-53.0
	20	1.738	-37.6	-11.3	11.6	-16.0	-53.3
7	14	1.740	-37.1	-11.0	11.4	-15.6	-52.3
	15	1.739	-37.4	-11.2	11.5	-15.8	-52.9
	16	1.738	-37.4	-11.3	11.6	-16.0	-53.1
	17	1.738	-37.6	-11.2	11.6	-16.1	-53.3
	18	1.737	-37.7	-11.3	11.7	-16.2	-53.5
	19	1.737	-37.7	-11.3	11.7	-16.2	-53.5
	20	1.737	-37.8	-11.4	11.7	-16.2	-53.7
8	16	1.737	-37.6	-11.4	11.7	-16.2	-53.5
	17	1.736	-37.7	-11.3	11.7	-16.4	-53.7
	18	1.736	-37.8	-11.4	11.8	-16.4	-53.8
	19	1.735	-38.0	-11.5	11.8	-16.7	-54.4
	20	1.735	-38.0	-11.6	11.9	-16.7	-54.4
9	18	1.736	-38.0	-11.6	11.8	-16.4	-54.2
	19	1.736	-38.1	-11.6	11.8	-16.4	-54.3
	20	1.735	-38.1	-11.7	11.9	-16.7	-54.6
10	20	1.735	-38.1	-11.7	11.9	-16.7	-54.6

We here like to point out that our model not only can produce the individual hydrogen bonding energies of linear water chains as accurate as the high quality CP-corrected MP2/aug-cc-pVTZ method can, but is much more efficient as well. For example, it takes about a CPU time of 42 h 30 min to carry out a CP-corrected MP2/aug-cc-pVTZ single-point calculation for the first(*k*=1) type of hydrogen bonds in the water chain (H<sub>2</sub>O)<sub>15</sub> on the DELL server with 16 Intel Xeon CPUs, 96 GB memory, and a 4.0 TB hard disk. However, it takes a CPU time of only 40 s to obtain the individual hydrogen bonding energy for the first(*k*=1) type of hydrogen bonds in the water chain (H<sub>2</sub>O)<sub>15</sub> by our model. And among the 40 s of CPU time, 36 s of it is spent on calculating the Mulliken atomic charges of (H<sub>2</sub>O)<sub>15</sub> water chain and of the monomer with B3LYP/6-31G(*d*) method. These comparisons further demonstrate that our model is useful.

## 4 Conclusions

A model was proposed to evaluate the individual hydrogen bonding energies and explore the cooperativity in linear

water chains. The calculation results show that the individual hydrogen bonding energies obtained by our model are in good agreement with those obtained from the high quality CP-corrected MP2/aug-cc-pVTZ calculations, demonstrating our model is reasonable. Calculation results show that the hydrogen bond gradually gets stronger with the growth of the water chain for the same type of hydrogen bonds and that the hydrogen bonds located in the center of the chain are stronger than those located at the ends. The strongest hydrogen bond is the central one in (H<sub>2</sub>O)<sub>20</sub> and the weakest hydrogen bond is the first type of hydrogen bonds in (H<sub>2</sub>O)<sub>5</sub>. The central hydrogen bond in (H<sub>2</sub>O)<sub>20</sub> is about 1.8 times stronger than the first type of drogen bonds in (H<sub>2</sub>O)<sub>5</sub>. Calculation results further show that the permanent dipole-dipole interaction is the most important part in hydrogen bonding interaction and that the covalent interactions are absolutely necessary for correctly describing the hydrogen bonding cooperativity of the water chains.

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