Intermolecular Interaction in Water Hexamer

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The origin of the intermolecular interaction, especially the many-body interaction, in eight low-lying water hexamer structures (prism, cage, book-1, book-2, cyclic-chair, bag, cyclic-boat-1, and cyclic-boat-2) is unraveled using the localized molecular orbital energy decomposition analysis (LMO-EDA) method at the second-order Møller−Plesset perturbation (MP2) level of theory with a large basis set. It is found that the relative stabilities of these hexamer structures are determined by delicate balances between different types of interaction. According to LMO-EDA, electrostatic and exchange interactions are strictly pairwise additive. Dispersion interaction in these water hexamer structures is almost pairwise additive, with many-body effects varying from −0.13 to +0.05 kcal/mol. Repulsion interaction is roughly pairwise additive, with many-body effects varying from −0.84 to −0.62 kcal/mol. Polarization interaction is not pairwise additive, with many-body effects varying from −13.10 to −8.85 kcal/mol.

1. Introduction

Considerable experimental and theoretical efforts have been paid to understanding the structures of water clusters. For relatively small water clusters, very accurate ab initio results have been obtained and used together with experiments to characterize some equilibrium structures of water trimer, tetramer, pentamer, and hexamer.[1] For simulations of bulk water and solution, however, only force field methods and some density functional theory methods[2] are practical. A good understanding of the intermolecular interaction, especially the many-body interaction, is key to the development of accurate force field and density functional theory methods.

In this work, the localized molecular orbital energy decomposition analysis method (LMO-EDA)[3] recently implemented by Su and Li was employed to unravel the origin of the intermolecular interaction, especially the many-body interaction, in eight low-lying water hexamer structures (Figure 1). These structures have been identified for a long time,[4−7] and were recently studied by the groups of Truhlar, Gordon, and Tschumper using the very accurate coupled cluster singles, doubles, and noniterative triples [CCSD(T)] method.[8−10] Following the literature, these structures are named as prism, cage, bag, cyclic-chair, book-1, book-2, cyclic-boat-1, and cyclic-boat-2. Recently, Wang et al. used the LMO-EDA method to assess the performance of popular density functional theory methods in describing the interaction energies of four water hexamer structures.[11]

2. Computational Method

All calculations were performed with the quantum chemistry program package GAMESS.[12,13] The geometries of the hexamer structures and a single, isolated water molecule were optimized with the second-order Møller−Plesset perturbation theory method (MP2)[14] and the aug-cc-pVTZ basis set (aTZ).[15] Although the cyclic-chair, cyclic-boat-1, and cyclic-boat-2 structures should have C_i, C_2, and C_2 symmetry, respectively, no symmetry was imposed in any of the geometry optimization processes.

The MP2/aTZ-optimized geometries then were used to perform the LMO-EDA calculation with the MP2 method and the aug-cc-pV5Z basis set,[15] in which the h-type functions were deleted because currently GAMESS cannot use h-type Gaussian basis functions. This basis set is denoted as a5Z-h. In later discussion, the aug-cc-pVQZ basis set[15] is denoted as aQZ. In all the calculations, only the pure spherical harmonic components in the d-, f-, and g-type functions were used. In all of the MP2 calculations, the 1s core orbitals of the oxygen atoms were frozen.

The total interaction energy ΔE in each hexamer is defined as the difference between the energy of the hexamer and the energy of six isolated water molecules (zero-point energy and thermal energy are not considered). Due to intermolecular interaction, water molecules in a cluster have geometries slightly different from that of a single, isolated water molecule, resulting in some deformation energies (ΔE_{def}). In this work, the total interaction energy ΔE is decomposed into two parts, the deformation energy ΔE_{def} and the interaction energy between the water molecules in their hexamer geometries, which is denoted as ΔE_{MP2} because it will be further decomposed with the LMO-EDA method at the MP2/a5Z-h level of theory:

$$\Delta E = \Delta E_{MP2} + \Delta E_{def} \qquad (1)$$

The ΔE_{def} was calculated with the MP2/a5Z-h method for each water molecule (using its own basis set) in two geometries, one as in the hexamer structure optimized with MP2/aTZ (hexamer basis set) and one as a single, isolated water molecule optimized with MP2/aTZ (monomer basis set). Such a definition of deformation energy is exactly the same as the "fragment relaxation energy" defined by Xantheas.[16] The ΔE_{def} for each hexamer structure is the sum of the individual ΔE_{def} of the six monomers in it.

The ΔE_{MP2} between the six water molecules in each hexamer structure was obtained by subtracting the MP2/a5Z-h energies of individual water molecules (as in their hexamer geometries, but with either monomer's own basis set or the hexamer basis set) from the MP2/a5Z-h energy of the hexamer.

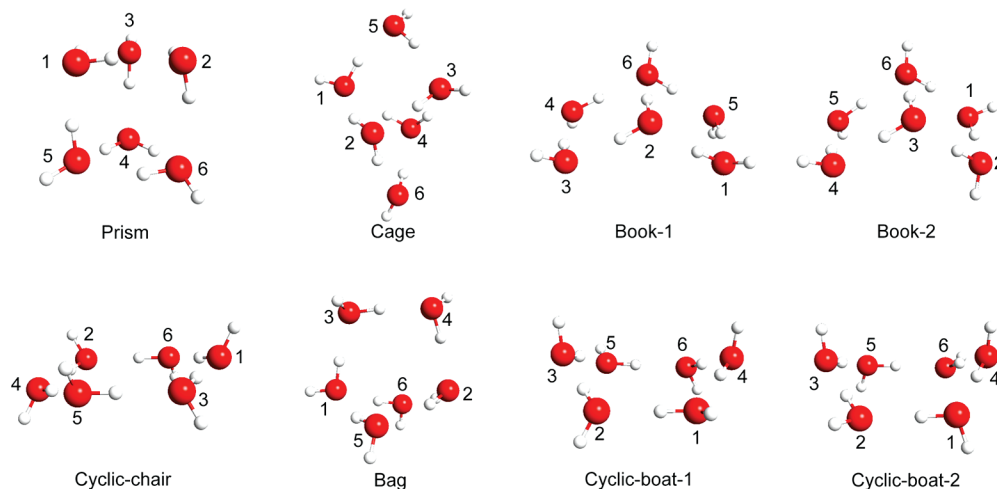* To whom correspondence should be addressed. E-mail: hli4@unl.edu.

Figure 1. Eight low-lying water hexamer structures optimized with the frozen core MP2/aTZ method.

TABLE 1: Absolute and Relative Electronic Energies of Eight Low-Lying Water Hexamer Structures

	absolute (hartree)		relative (kcal/mol)		
	MP2/aTZ	MP2/a5Z-h[a]	MP2/a5Z-h[a]	MP2/CBS[b]	CCSD(T)/CBS[b]
prism	−458.050 365 12	−458.217 189 51	0.00	0.00	0.00
cage	−458.050 243 79	−458.217 126 26	0.04	0.06	0.25
book-1	−458.049 602 60	−458.216 698 88	0.31	0.33	0.72
book-2	−458.049 158 44	−458.216 187 89	0.63	0.64	1.02
cyclic-chair	−458.047 850 84	−458.215 367 36	1.14	1.21	1.80
bag	−458.048 261 88	−458.215 265 67	1.21	1.23	1.62
cyclic-boat-1	−458.046 302 52	−458.213 791 83	2.13	2.20	2.79
cyclic-boat-2	−458.046 148 27	−458.213 654 16	2.22	2.28	2.85

[a] Current work using MP2/a5Z-h//MP2/aTZ. [b] Bates and Tschumper's results in ref 10.

In LMO-EDA, ΔE_{MP2} is decomposed into five terms: electrostatic (ΔE_{ele}), exchange (ΔE_{ex}), repulsion (ΔE_{rep}), polarization (ΔE_{pol}), and dispersion (ΔE_{disp}):

$$\Delta E_{MP2} = \Delta E_{ele} + \Delta E_{ex} + \Delta E_{rep} + \Delta E_{pol} + \Delta E_{disp} \tag{2}$$

The details of the LMO-EDA method can be found in our previous paper.[3] Here we emphasize that the dispersion term in LMO-EDA is actually the MP2 correction to Hartree−Fock interaction energy, which contains mainly dispersion, but includes higher-order corrections to the electrostatic, exchange, repulsion, and polarization energies. In quantum chemical intermolecular interaction calculation, basis set superposition error (BSSE) must be considered. Here the ΔE_{MP2} and all the interaction terms in eq 2 were calculated using two basis sets for the monomers in hexamer geometries: one is the monomer basis set and the results are called BSSE uncorrected results, and one is the hexamer basis set (i.e., the counterpoise method originally proposed by Boys and Bernadi[17]) and the results are called BSSE corrected results. Such a definition of BSSE correction is exactly the same as the posteriori BSSE correction defined by Xantheas.[16] At the complete basis set (CBS) limit, the BSSE will converge to zero.

Because ΔE_{MP2} can be obtained with and without BSSE correction, the total interaction energy ΔE also has BSSE-corrected and uncorrected values.

3. Results and Discussion

3.1. Geometry and Deformation Energy. The MP2/aTZ-optimized hexamer structures (Figure 1; Cartesian coordinates

are available as Supporting Information) are very similar to those reported in recent literature,[8−10] especially those obtained by Bates and Tschumper using a different basis set.[10] As shown in Table 1, the optimized MP2/aTZ energies of the prism, book-1, and cyclic-chair structures are −458.050 365 12, −458.049 602 60, and −458.047 850 84 hartree, respectively, almost identical to those (−458.050 358 04, −458.049 601 43, and −458.047 853 03 hartree) obtained by Xantheas et al.[7] using the same frozen core MP2/aTZ method. In principle, these structures should be identical to each other if numerical errors could be avoided. The cage structure in the current work ($E_{MP2/aTZ}$ = −458.050 243 79 hartree) is different from the cage structure ($E_{MP2/aTZ}$ = −458.050 171 38 hartree) in the paper of Xantheas et al.,[7] due to a different orientation of an H atom (atom 15 in Table S4, Supporting Information). The relative electronic energies computed with the MP2/a5Z-h//MP2/aTZ method in the current work are very close to the MP2/CBS//MP2/haTZ (CBS = complete basis set, haTZ is a mixed basis set with aTZ for O and cc-pVTZ for H) results reported by Bates and Tschumper.[10] The largest deviation is 0.07 kcal/mol. Bates and Tschumper's CCSD(T)/CBS//MP2/haTZ results are also shown in Table 1 for comparison. In general, CCSD(T) predicts slightly larger electronic energy separation for these hexamer structures. Since the current work focuses on interaction analysis, extrapolation, CCSD(T) correction, zero-point energy, and thermal energy are not considered.

The values of the deformation energy ΔE_{def} are +2.36, +2.35, +2.42, +2.46, +2.33, +2.58, +2.34, and +2.30 kcal/mol, respectively, for the prism, cage, book-1, book-2, cyclic-chair, bag, cyclic-boat-1, and cyclic-boat-2 structures (Table 2). Using the prism structure as the reference, the values of the relative ΔE_{def} are 0.00, −0.01, +0.06, +0.10, −0.03, +0.22, −0.02,

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TABLE 2: MP2/a5Z-h//MP2/aTZ Deformation Energy ΔE_{def} (kcal/mol) of Each Water Molecule in Eight Water Hexamer Structures

	1	2	3	4	5	6	total	relative total
prism	0.43	0.15	0.41	0.20	0.90	0.27	2.36	0.00
cage	0.43	0.27	0.85	0.17	0.29	0.35	2.35	−0.01
book-1	0.56	0.27	0.25	0.24	0.52	0.60	2.42	+0.06
book-2	0.53	0.56	0.26	0.27	0.23	0.60	2.46	+0.10
cyclic-chair	0.39	0.39	0.39	0.39	0.39	0.39	2.33	−0.03
bag	0.79	0.26	0.55	0.61	0.17	0.20	2.58	+0.22
cyclic-boat-1	0.41	0.38	0.38	0.38	0.41	0.38	2.34	−0.02
cyclic-boat-2	0.36	0.39	0.40	0.40	0.36	0.39	2.30	−0.06

and −0.06 kcal/mol, respectively. Obviously, the difference in the deformation energy is not the main factor determining the relative stabilities of these low-lying hexamer structures, because the maximum difference is 0.28 kcal/mol. The average ΔE_{def} for all these 48 water molecules is 0.40 kcal/mol. The fifth water molecule in the prism structure has the largest individual ΔE_{def}, which is 0.90 kcal/mol, more than twice of the average. Three water molecules (number 1, 3, and 4, Table 2) in the bag structure show ΔE_{def} that are well above the average. This can explain why the bag structure has the largest ΔE_{def} among the six hexamer structures.

3.2. Interaction Energy. The relative stabilities of the eight low-lying hexamer structures can be understood from the intermolecular interactions (Table 3). With no BSSE correction, the MP2/a5Z-h interaction energy ΔE_{MP2} values are −48.45, −48.40, −48.21, −47.92, −47.28, −47.47, −46.30, and −46.17 kcal/mol, respectively, for the prism, cage, book-1, book-2, cyclic-chair, bag, cyclic-boat-1, and cyclic-boat-2 structures. Including ΔE_{def}, the relative total interaction energies ΔE are 0.00, +0.04, +0.31, + 0.63, +1.14, +1.21, +2.13, and +2.22 kcal/mol, respectively (Table 3). These are exactly the relative stabilities listed in Table 1. The BSSE-corrected MP2/a5Z-h interaction energies are −47.41, −47.33, −47.15, −46.87, −46.27, −46.41, −45.29, and −45.17 kcal/mol, respectively. Including ΔE_{def}, the relative total interaction energies ΔE are 0.00, +0.07, +0.32, + 0.64, +1.11, +1.22, +2.10, and +2.18 kcal/mol (Table 3). The BSSE-uncorrected interaction is ~1 kcal/mol larger in magnitude than the corresponding counterpoise corrected values. The MP2/CBS interaction energies lie almost for sure between the BSSE-uncorrected and -corrected

values.[7] It is worth noting that when the relatively large a5Z-h basis set is used, the BSSE in the Hartree−Fock interaction energies are only ~0.03 kcal/mol (Table 3). Therefore, almost all of the ~1 kcal/mol BSSE arise from MP2 electron correlation energy. This is due to the well-known fact that MP2 electron correlation energy shows a slow basis set convergence, as discussed, for example, by Kutzelnigg and Morgan.[18]

Here the BSSE-corrected results in Table 3 are discussed. The electrostatic energies ΔE_{ele} vary from −79.64 to −83.38 kcal/mol. The prism structure, which shows the strongest ΔE_{MP2}, does not show the strongest ΔE_{ele}. The book-1 structure, which is the third most stable one, shows the strongest ΔE_{ele}. The cyclic-boat-2 structure, which shows the weakest ΔE_{MP2}, indeed shows the weakest ΔE_{ele}. The exchange energies ΔE_{ex} vary from −103.09 to −107.29 kcal/mol. The prism structure (most stable) and the cyclic-boat-2 structure (least stable) both show the weakest ΔE_{ex}. The bag structure (3rd least stable) shows the strongest ΔE_{ex}. The repulsion energies ΔE_{rep} vary from 187.66 to 197.70 kcal/mol. The prism structure shows the smallest ΔE_{rep}. The book-2 structure (3rd most stable) shows the strongest ΔE_{rep}. For simple atomic or molecular clusters, repulsion energy is usually proportional to exchange energy: the larger the exchange energy, the larger the repulsion energy. However, this is not always true. For example, the prism structure shows a ΔE_{ex} similar to those in cyclic-boat-1 and cyclic-boat-2 (all around −103 kcal/mol), but has a significantly smaller ΔE_{rep} (+187.66 versus +192.30 and +191.02 kcal/mol). The polarization energies ΔE_{pol} vary from −34.69 to −43.03 kcal/mol. The prism structure (most stable) shows the smallest ΔE_{pol}, −34.69 kcal/mol. The cyclic-chair structure shows the largest ΔE_{pol}, −43.03 kcal/mol.

The sum of the electrostatic, exchange, repulsion, and polarization interactions is the Hartree−Fock interaction energy ΔE_{HF} (Table 3). The cyclic-chair structure shows the strongest ΔE_{HF}, −34.40 kcal/mol. The prism and cage structures, which are the two most stable ones, actually show the weakest ΔE_{HF}, −32.16 and −32.05 kcal/mol, respectively. The dispersion energies vary from −11.84 to −15.28 kcal/mol. The prism and cage structures, which are the most stable ones, indeed show the strongest dispersion interactions. The cyclic-chair, cyclic-boat-1, and cyclic-boat-2 structures show the weakest dispersion energies.

TABLE 3: MP2/a5Z-h//MP2/aTZ Interaction Energies (kcal/mol) in Eight Water Hexamer Structures

	ΔE_{ele}	ΔE_{ex}	ΔE_{rep}	ΔE_{pol}	ΔE_{HF}	ΔE_{disp}	ΔE_{MP2}	ΔE^a	relative ΔE
				BSSE Uncorrected					
prism	−82.03	−103.30	+187.94	−34.79	−32.17	−16.28	−48.45	−46.09	0.00
cage	−82.71	−105.44	+192.75	−36.68	−32.08	−16.32	−48.40	−46.05	0.04
book-1	−83.40	−107.33	+197.89	−40.49	−33.34	−14.87	−48.21	−45.79	0.31
book-2	−83.15	−106.90	+197.00	−39.92	−32.97	−14.95	−47.92	−45.46	0.63
cyclic-chair	−81.85	−105.87	+196.43	−43.12	−34.42	−12.86	−47.28	−44.95	1.14
bag	−82.38	−107.40	+197.82	−40.37	−32.33	−15.14	−47.47	−44.89	1.21
cyclic-boat-1	−80.03	−103.80	+192.40	−41.91	−33.34	−12.96	−46.30	−43.96	2.13
cyclic-boat-2	−79.63	−103.14	+191.12	−41.71	−33.35	−12.82	−46.17	−43.87	2.22
				BSSE Corrected (counterpoise method)					
prism	−81.98	−103.15	+187.66	−34.69	−32.16	−15.26	−47.41	−45.05	0.00
cage	−82.67	−105.31	+192.51	−36.58	−32.05	−15.28	−47.33	−44.98	0.07
book-1	−83.38	−107.24	+197.70	−40.39	−33.31	−13.84	−47.15	−44.73	0.32
book-2	−83.14	−106.79	+196.80	−39.81	−32.94	−13.92	−46.87	−44.41	0.64
cyclic-chair	−81.87	−105.83	+196.33	−43.03	−34.40	−11.87	−46.27	−43.94	1.11
bag	−82.36	−107.29	+197.61	−40.27	−32.31	−14.10	−46.41	−43.83	1.22
cyclic-boat-1	−80.04	−103.75	+192.30	−41.82	−33.31	−11.98	−45.29	−42.95	2.10
cyclic-boat-2	−79.64	−103.09	+191.02	−41.62	−33.33	−11.84	−45.17	−42.87	2.18

[a] The same ΔE_{def} in Table 2 are used for BSSE-uncorrected and -corrected cases.
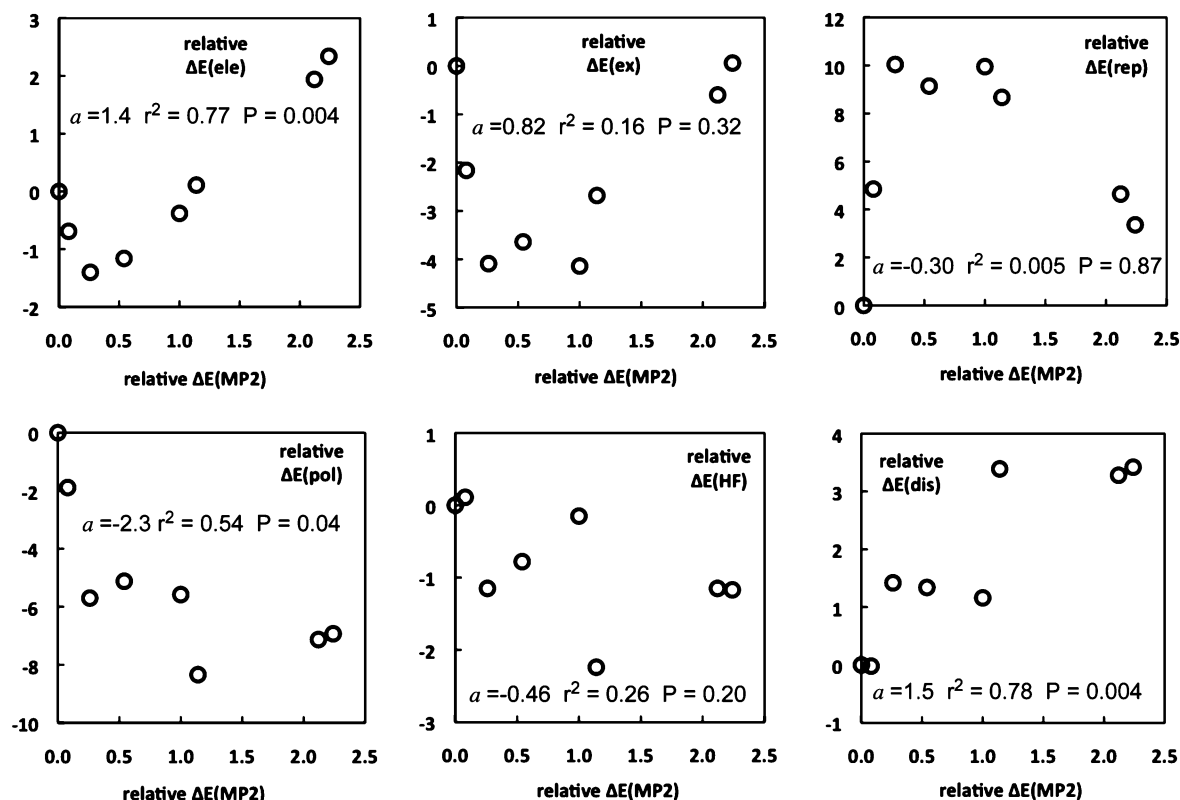
Figure 2. Comparisons between the relative ΔE_{ele}, ΔE_{ex}, ΔE_{rep}, ΔE_{pol}, ΔE_{HF}, and ΔE_{disp} interaction energies and the relative MP2 interaction energies (ΔE_{MP2}). Plots are made using the BSSE-corrected data (in kcal/mol) in Table 3.

In Figure 2, the relative ΔE_{ele}, ΔE_{ex}, ΔE_{rep}, ΔE_{pol}, ΔE_{HF}, and ΔE_{disp} interaction energies are plotted versus the relative ΔE_{MP2} for the eight hexamer structures (using the BSSE-corrected data in Table 3). The prism structure is used as the reference so all of its values are zero. Least-squares linear regression analysis ($y = ax + b$) gives slopes a of 1.4, 0.82, −0.30, −2.3, −0.46, and 1.5, and statistic r^2 values of 0.77, 0.16, 0.005, 0.54, 0.26, and 0.78, respectively, for the six terms; the "F-test" gives P values of 0.004, 0.32, 0.87, 0.04, 0.20, and 0.004. Clearly, there are some correlations among ΔE_{ele}, ΔE_{pol}, ΔE_{disp}, and ΔE_{MP2}.

In Figure 3 the relative ΔE_{ele}, ΔE_{ex}, ΔE_{rep}, ΔE_{pol}, ΔE_{HF}, and ΔE_{disp} interaction energies are plotted versus the sum of the 15 pairs of O−O distances in each hexamer (using the BSSE-corrected data in Table 3). Such sums are 49.332, 50.915, 55.404, 54.395, 60.409, 51.811, 59.314, and 59.064 Å, respectively, for the prism, cage, book-1, book-2, cyclic-chair, bag, cyclic-boat-1, and cyclic-boat-2 structures (Tables S1−S16, Supporting Information). Least-squares linear regression analysis gives slopes a of 0.18, 0.058, 0.19, −0.60, −0.17, and 0.33, and r^2 values of 0.31, 0.02, 0.05, 0.82, 0.84, and 0.95, respectively, for the six terms; the "F-test" gives P values of 0.15, 0.75, 0.61, 0.002, 0.001, and 0.00005. The small P values suggest that there are strong correlations between ΔE_{pol}, ΔE_{HF}, and ΔE_{disp} and the sum of the O−O distances. There is also a correlation between ΔE_{MP2} and the sum of O−O distances, with $a = 0.16$, $r^2 = 0.61$, and $P = 0.023$.

3.3. Pair Interaction and Many-Body Effects. Pair interactions were calculated for the 15 pairs of dimers in every hexamer structure with the MP2/a5Z-h method (with no BSSE correction), and the results are listed in supplementary Tables S1−S16 (Supporting Information). As is well-known, the most stable water dimer has C_s symmetry and a nearly linear hydrogen bond. Optimized with the frozen core MP2/aQZ method, the O−O distance (R_{OO}) in the linear water dimer is 2.904 Å.[3] A

subsequent interaction analysis performed at the frozen core MP2/a5Z-h level of theory (no BSSE correction) revealed that the ΔE_{ele}, ΔE_{ex}, ΔE_{rep}, ΔE_{pol}, and ΔE_{disp} are −8.40, −8.83, +15.99, −2.38, and −1.38 kcal/mol, respectively, with ΔE_{MP2} = −5.01 kcal/mol.[3] Due to geometric distortions, all the pair interactions in the eight hexamer structures are weakened. The strongest pair interactions occur between monomers 3 and 4 in the book-1 structure (R_{OO} = 2.768 Å, ΔE_{MP2} = −4.86 kcal/mol, with ΔE_{ele} = −10.89, ΔE_{ex} = −13.87, ΔE_{rep} = +25.55, ΔE_{pol} = −3.79, ΔE_{disp} = −1.87, all in kcal/mol, Table S5, Supporting Information) and between monomers 4 and 5 in the book-2 structure (R_{OO} = 2.760 Å, ΔE_{MP2} = −4.85 kcal/mol, with ΔE_{ele} = −11.16, ΔE_{ex} = −14.40, ΔE_{rep} = +26.57, ΔE_{pol} = −3.94, ΔE_{disp} = −1.91, all in kcal/mol, Table S7, Supporting Information). The strongest pair interaction in the prism structure occurs between monomers 2 and 6 (R_{OO} = 2.907 Å, ΔE_{MP2} = −4.75 kcal/mol, with ΔE_{ele} = −8.06, ΔE_{ex} = −8.57, ΔE_{rep} = +15.43, ΔE_{pol} = −2.19, ΔE_{disp} = −1.36, all in kcal/mol, Table S1, Supporting Information). The strongest pair interaction in the cage structure occurs between monomers 4 and 6 (R_{OO} = 2.755 Å, ΔE_{MP2} = −4.59 kcal/mol, with ΔE_{ele} = −11.27, ΔE_{ex} = −14.95, ΔE_{rep} = +27.60, ΔE_{pol} = −3.93, ΔE_{disp} = −2.04, all in kcal/mol, Table S3, Supporting Information). The pair interactions depend on the R_{OO} distances and the relative orientations of the O−H bonds. Among all the hexamer structures, the shortest R_{OO} distance, 2.651 Å, occurs between monomers 1 and 5 in the prism structure (Table S1, Supporting Information). Due to the close contact and more orbital overlap (penetration), all the five interaction terms in this pair have very large magnitudes: the ΔE_{ele}, ΔE_{ex}, ΔE_{rep}, ΔE_{pol}, and ΔE_{disp} are −15.05, −22.77, +42.83, −6.51, and −2.58 kcal/mol, respectively, with ΔE_{MP2} = −4.09 kcal/mol. Similarly short R_{OO} distances such as 2.655, 2.661, and 2.679 Å, are found in other structures. According to the LMO-EDA scheme, the significant
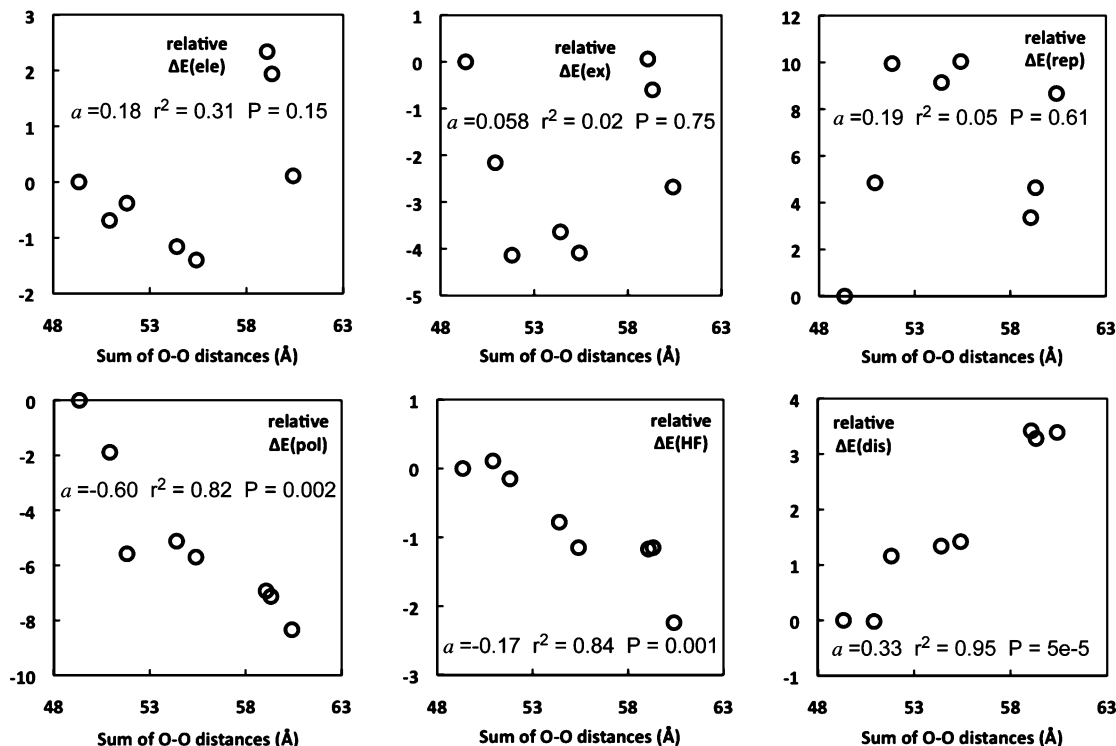
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Figure 3. Comparisons between the relative ΔE_{ele}, ΔE_{ex}, ΔE_{rep}, ΔE_{pol}, ΔE_{HF}, and ΔE_{disp} interaction energies and the sum of the O−O distances. Plots are made using the BSSE-corrected data (in kcal/mol) in Table 3.

TABLE 4: MP2/a5Z-h//MP2/aTZ Pair Interaction Energies and Many-Body Effects in Eight Hexamer Structures (kcal/mol)[a]

isomer		ΔE_{ele}	ΔE_{ex}	ΔE_{rep}	ΔE_{pol}	ΔE_{HF}	ΔE_{disp}	ΔE_{MP2}
prism	pair sum	−82.03	−103.30	+188.74	−25.94	−22.52	−16.31	−38.84
	hexamer	−82.03	−103.30	+187.94	−34.79	−32.17	−16.28	−48.45
	MBE	0.00	0.00	−0.80	−8.85	−9.65	+0.03	−9.62
cage	pair sum	−82.71	−105.44	+193.53	−27.64	−22.27	−16.37	−38.64
	hexamer	−82.71	−105.44	+192.75	−36.68	−32.08	−16.32	−48.40
	MBE	0.00	0.00	−0.78	−9.03	−9.81	+0.05	−9.76
book-1	pair sum	−83.39	−107.33	+198.54	−29.56	−21.75	−14.79	−36.54
	hexamer	−83.39	−107.33	+197.88	−40.49	−33.34	−14.87	−48.21
	MBE	0.00	0.00	−0.65	−10.93	−11.58	−0.08	−11.66
book-2	pair sum	−83.15	−106.90	+197.65	−29.35	−21.75	−14.85	−36.61
	hexamer	−83.15	−106.90	+197.00	−39.92	−32.97	−14.95	−47.92
	MBE	0.00	0.00	−0.65	−10.57	−11.21	−0.10	−11.31
cyclic-chair	pair sum	−81.86	−105.87	+197.05	−30.02	−20.70	−12.75	−33.44
	hexamer	−81.85	−105.87	+196.43	−43.12	−34.42	−12.86	−47.28
	MBE	0.00	0.00	−0.62	−13.10	−13.72	−0.11	−13.84
bag	pair sum	−82.38	−107.40	+198.65	−29.54	−20.65	−15.10	−35.76
	hexamer	−82.38	−107.40	+197.82	−40.37	−32.33	−15.14	−47.47
	MBE	0.00	0.00	−0.84	−10.84	−11.68	−0.04	−11.71
cyclic-boat-1	pair sum	−80.03	−103.80	+193.04	−29.40	−20.19	−12.83	−33.02
	hexamer	−80.03	−103.80	+192.40	−41.91	−33.34	−12.96	−46.30
	MBE	0.00	0.00	−0.64	−12.51	−13.15	−0.13	−13.28
cyclic-boat-2	pair sum	−79.63	−103.14	+191.76	−29.20	−20.21	−12.72	−32.93
	hexamer	−79.63	−103.14	+191.12	−41.71	−33.35	−12.82	−46.17
	MBE	0.00	0.00	−0.63	−12.51	−13.15	−0.09	−13.24

[a] BSSE are not corrected. More data are in Tables S1−S16 (Supporting Information).

increase in ΔE_{ele} at short distances is mainly due to orbital overlap or charge penetration, which increases exponentially as the intermolecular distance shortens. The increases in ΔE_{ex} and ΔE_{rep} are also due to orbital overlap: the exchange integral would be zero if there is no overlap between the occupied orbitals of two molecules, and an additional orthonormalization procedure (which is enforced in the LMO-EDA scheme) has no effect (thus no repulsion).

Many-body effect (MBE) in intermolecular interaction in water clusters was first studied by Hankins et al.[19] and followed by many other researchers.[20−26] However, most of these previous studies have not studied the MBE in different interaction components or have not been performed using a sufficiently large basis set to minimize BSSE. In the current work, the MBE in the intermolecular interactions in the water hexamer structures is defined as the difference between the *sum of the pair interactions* and the *hexamer interaction* (Table 4; more data are in Tables S1−S16, Supporting Information). According to the LMO-EDA scheme employed here, the electrostatic and exchange energies are strictly pairwise additive if the BSSE is

not considered. The BSSE uncorrected results in Table 4 and Tables S1–S16 (Supporting Information) show that the MBE in the dispersion energy varies from -0.13 to $+0.05$ kcal/mol, the MBE in the repulsion energy varies from -0.84 to -0.62 kcal/mol, and the MBE in the polarization energy varies from -13.10 to -8.85 kcal/mol. So, dispersion interaction is almost pairwise additive in water hexamer structures. Repulsion interaction is not pairwise additive, but the MBE is relatively small and differs by at most 0.22 kcal/mol in different hexamer structures. The polarization energy is not additive, and the MBE differs by up to 4.25 kcal/mol in different hexamer structures. In a previous work, we performed LMO-EDA calculations at the MP2/a5Z-h//MP2/aQZ level of theory for a cyclic water trimer (up–up–down) and a cyclic tetramer (up–down–up–down).[3] With no BSSE correction, the trimer shows a ΔE_{MP2} of -16.23 kcal/mol, with $\Delta E_{ele} = -28.37$, $\Delta E_{ex} = -34.43$, $\Delta E_{rep} = +62.71$, $\Delta E_{pol} = -10.72$, $\Delta E_{disp} = -5.42$ kcal/mol; the tetramer shows a ΔE_{MP2} of -28.85 kcal/mol, with $\Delta E_{ele} = -52.01$, $\Delta E_{ex} = -67.07$, $\Delta E_{rep} = +124.05$, $\Delta E_{pol} = -25.03$, and $\Delta E_{disp} = -8.79$ kcal/mol. In addition, the BSSE-uncorrected MBE in dispersion, repulsion, and polarization energies are -0.04, -0.42, and -6.64 kcal/mol, respectively, in the water tetramer. In this work, we calculated MBE in the trimer for comparison: the BSSE-uncorrected MBE in dispersion, repulsion, and polarization energies are $+0.02$, -0.28, and -2.32 kcal/mol, respectively. Therefore, the total MBE increases from -2.57 to -7.10 and -13.84 kcal/mol ongoing from the cyclic trimer to the cyclic tetramer and the cyclic-chair hexamer. In all of these trimer, tetramer, and hexamer structures, the MBE in ΔE_{disp} is almost additive, the same as reported earlier by Pedulla et al.[21]

3.4. Comparison with Other Methods. Various other interaction analysis methods are available.[27–33] For closed shell molecules, the LMO-EDA scheme is a simplified version of the Kitaura–Morokuma (KM) scheme[27] and the reduced variational space (RVS) scheme.[28] The ΔE_{ele}, ΔE_{ex}, and ΔE_{rep} are identical in these three methods. The main difference is that KM and RVS schemes further decompose the HF polarization energy ΔE_{pol} into two basis set dependent terms (called polarization and charge transfer) and an inseparable mixing term. Using a large basis set such as a5Z-h, the charge transfer term should be very small. Therefore, the LMO-EDA results can be considered as the basis set converged KM and RVS results, and comparisons between them are unnecessary. Similar to LMO-EDA, KM and RVS schemes can be used to study many-body systems, as shown by Chen and Gordon.[25] In various recent works, we have compared LMO-EDA results to available SAPT[34,35] results (for dimer interactions). It is well-known that most interaction analysis methods share two common terms: electrostatic and exchange-repulsion. Given the same molecular geometry and basis set, the SAPT term $E_{elst}^{(1)}$ should be identical to the LMO-EDA term ΔE_{ele}, and the SAPT term $E_{exch}^{(1)}$ should be identical to the combined LMO-EDA term $\Delta E_{ex} + \Delta E_{rep}$. Other terms are not directly comparable, however. Since the current work focuses on water hexamer, we did not use SAPT because it can only be used for dimers and at most for trimers.[24]

4. Conclusion

In conclusion, the relative stabilities of water hexamer structures are determined by the balances between different types of interaction. The dispersion interaction in water hexamer is almost pairwise additive, and can be correlated to the O–O

distances in the hexamer structures. According to the LMO-EDA calculation, the many-body effect in water hexamer structures is mainly due to polarization energy. This lends credibility to the approach adopted by most polarizable water models, which account for the many-body effects via an induction scheme such as induced dipoles. In future studies, we will explore various force field functions to reproduce the accurate ab initio results for water clusters.

Supporting Information Available: Tables S1–S16. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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