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Hydrogen Bonding in Water Clusters: Pair and Many-Body Interactions from Symmetry-Adapted Perturbation Theory

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This paper contains a study of the pair and many-body interactions in cyclic water clusters: trimer, tetramer, and pentamer. Symmetry-adapted perturbation theory (SAPT) is applied to compute the pair- and three-body interactions directly and to analyze the individual electrostatic, induction, dispersion, and exchange contributions. The total interaction energies are also obtained by supermolecule coupled-cluster calculations including single, double, and noniterative triple excitations, CCSD(T). The three-body interactions contribute up to 28% of the total interaction energy in these water clusters in their equilibrium geometries and up to 50% of the barriers for different tunneling processes investigated in the trimer. The main three-body contribution is due to second- and third-order induction effects, but also three-body exchange effects are substantial. Dispersion contributions are only significant in the pair energy. The four-body effects are relatively small, and the five-body effects were found to be negligible. Furthermore, we tested the quality of various density functional methods for describing these many-body interactions.

I. Introduction

Water is a universal solvent that influences many chemical and almost all biological processes. Much theoretical and experimental effort has been directed toward obtaining a quantitative description of hydrogen bonding by studying clusters of water molecules. Intermolecular pair potentials as well as pairwise nonadditive interactions have been subjects of numerous theoretical and experimental studies. Many empirical potentials (see, e.g., ref 1) have been devised for use in simulations of the liquid water properties. Generally, these are "effective pair potentials"; i.e., they employ simple pairwise additive forms that implicitly incorporate the nonadditive many-body effects in the parameters. None of these potentials can successfully account for more than a few properties of liquid water, so their reliability is limited.

Detailed information on the hydrogen bonding in aqueous systems can be obtained from high-resolution microwave and far-infrared spectra of water clusters.[2−15] The dimer has been studied extensively in the past,[2] but recently the center of attention has shifted to larger clusters.[3−15] In a series of papers Saykally and collaborators reported high-resolution far-infrared spectra of the water trimer,[3−5,15] tetramer,[9,10,13] pentamer,[11,14] and hexamer.[8,12] The rotational and distortion constants extracted from these spectra reflect the (vibrationally averaged) structures of the clusters and, hence, probe especially the regions around the global minima in their potential surfaces. The tunneling splittings observed in these spectra are explicit manifestations of the hydrogen bond network rearrangement (hydrogen bond breaking and formation). Since they depend strongly on the heights and shapes of the barriers in the potential surface, they form an extremely sensitive probe of the pair and nonadditive interactions in the trimer and larger clusters.

Small water clusters have also been the subject of a number of theoretical studies.[16−85] See ref 25 for a review of some older theoretical work on the dimer. Most of these investigations were restricted to the determination of the most stable structures and the corresponding binding energies and harmonic vibrational frequencies. While the availability of high-quality ab initio structural data is essential for the evaluation and improvements of the empirical potentials (see, for instance, ref 36), a theoretical characterization of the hydrogen-bonding and many-body cooperative effects in terms of physical contributions is also of interest. Surprisingly enough, despite the large body of theoretical studies of the water clusters, only a few of them[39,40,48,73] analyzed the physical origins of the bonding.

A question that was first addressed in a series of pioneering papers by Clementi and collaborators[16−21] is the importance of the nonadditive many-body interactions on the properties of liquid water. They included the three- and four-body contributions to the interaction potential that originate from the long-range induction energy, which they obtained from iterative calculations within the bond-polarization model. It was shown that the effect of these nonadditive interactions was essential to reproduce the correlation functions for the X-ray and neutron scattering intensities, as well as the enthalpy. These studies were limited to the Hartree−Fock level, however. Also, in more recent ab initio calculations,[42,43,64,65] which include electron correlation at the second- and fourth-order Møller−Plesset (MP2 and MP4) level, the nonadditive three-, four-, and five-body contributions to the interaction energy in water clusters were quantitatively

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analyzed. If the convergence of the many-body expansion of the interaction energy is sufficiently fast, various properties of large water clusters could be investigated using ab initio pair and three-body potentials. Pair potentials deduced from ab initio calculations are already available.[31,32] The nonadditive three-body part has been computed (implicitly) only along selected coordinates of the trimer,[56,57] but it will not take long before a full nonadditive potential for the water trimer is obtained by ab initio methods.

With the spectra for a number of small water clusters available now, a more detailed ab initio study of the origin of the nonadditive forces in these clusters seems timely, as the outcome of these computations can be used in calculations of the cluster dynamics[59,60,62,63,68] and confronted with experiment. Recent ab initio studies of the nonadditive interactions in the water trimer were limited to a few geometries not related to the spectroscopically important structures corresponding to the hydrogen bond breaking and formation.[39,40,42] The authors of ref 39 employed an approach[86] that combines the supermolecule third-order Møller−Plesset (MP3) theory with the simplest approximations to the induction and dispersion nonadditivities (see also ref 87 for a review). The supermolecule MP3 energy is decomposed into exchange, deformation, and dispersion contributions, the sum of the exchange and deformation (due to the induction interactions and their coupling with the exchange) components being defined as the difference between the supermolecule interaction energy and the corresponding dispersion energy. Xantheas[42] studied the pair-, three-body, and four-body interactions in the trimer and tetramer by means of MP2 and MP4 calculations and those in the pentamer and hexamer at the Hartree−Fock (HF) level. All of his results refer to the equilibrium geometries. Hodges et al.[43] made similar (MP2) calculations on the trimer, tetramer, and pentamer in their equilibrium geometries, as well as for a few other, rather arbitrary, geometries, to test their ASP-W2 and ASP-W4 model potentials. Since these were all supermolecule calculations, no decomposition into electrostatic, induction, dispersion, and exchange contributions was made. More simplistic approaches, based on the Kitaura−Morokuma decomposition of the Hartree−Fock interaction energy and some simple approximations to the dispersion energy, have been applied to characterize the hydrogen bonding in larger clusters.[48,73]

Recently, a symmetry-adapted perturbation theory (SAPT) of pair[88−96] and three-body[97,98] interactions has been developed (see refs 99 and 100 for recent reviews of the SAPT approach to pair and nonadditive interactions). In this method the pair and nonadditive interaction energies are represented as sums of physically meaningful contributions such as electrostatics, induction, dispersion, and exchange, with well-defined radial and angular dependencies. The pair potentials from SAPT calculations have been tested in dynamical calculations of the spectra and scattering cross sections of several van der Waals molecules. Comparison with the experimental data suggested that these potentials are very accurate in both the repulsive and well regions (see refs 101−103 for reviews of dynamical calculations). Less is known about the accuracy of the nonadditive SAPT potentials. The convergence of the SAPT expansion of the three-body energy was shown[104] to be satisfactory, and the first applications of this method to characterize nonadditive interactions in Ar_2 HF[105] and $OH^-(H_2O)_n$[106] clusters were successful.

In this paper we report an application of the symmetry-adapted perturbation theory to characterize the pair and nonadditive interactions in water clusters. We considered the structures corresponding to the global minima, those transition states of the trimer that govern the hydrogen bond rearrangement observed in the far-infrared spectra, as well as some other stationary points on the potential surfaces of the trimer and tetramer. The accuracy of the SAPT calculations will be checked by comparison with results from supermolecule coupled-cluster calculations including single, double, and noniterative triple excitations, CCSD(T).[107,108] The supermolecule results will also shed some light on the importance of the four-, and five-body contributions to the total interaction energy. Finally, the applicability of various density functional theories (DFT)[109−115] to nonadditive three-body interactions in the water trimer will be investigated. While the DFT methods were frequently applied to study the structure and harmonic vibration frequencies of small clusters (see, for instance, refs 44−46 and 81), very few studies were concerned with a DFT description of the many-body cooperative effects.[116,117] To our knowledge, the results of DFT calculations of the many-body contributions to the interaction energies were never compared with the results from highly correlated ab initio calculations. The plan of this paper is as follows. In section II we briefly introduce the theoretical methods used in our calculations. In section III we describe the computational details. Numerical results are presented and discussed in section IV. Finally, in section V we list our conclusions.

II. Methods of Calculation

In the present work both symmetry-adapted perturbation theory and the supermolecule approach have been used. In the SAPT calculations the interaction energy of the cluster is represented as

$$E_{\rm int}^{\rm SAPT} = E_{\rm int}^{\rm SAPT}(2,M) + E_{\rm int}^{\rm SAPT}(3,M) \qquad (1)$$

where $E_{\rm int}^{\rm SAPT}(N,M)$ denotes the N-body SAPT interaction energy for a cluster of M molecules. The pair interaction energy was computed from the following expression,

$$E_{\rm int}^{\rm SAPT}(2,M) = E_{\rm elst}^{(1)}(2,M) + E_{\rm ind}^{(2)}(2,M) + E_{\rm disp}^{(2)}(2,M) + E_{\rm exch}(2,M) \qquad (2)$$

where the consecutive terms on the right-hand side (rhs) of eq 2 denote the electrostatic, induction, dispersion, and exchange energies, respectively. The exchange contribution can further be decomposed as follows,

$$E_{\rm exch}(2,M) = E_{\rm exch}^{(1)}(2,M) + E_{\rm exch-ind}^{(2)}(2,M) + E_{\rm exch-def}^{(2)}(2,M) + E_{\rm exch-disp}^{(2)}(2,M) \qquad (3)$$

Here, $E_{\rm exch}^{(1)}(2,M)$ is the first-order exchange energy, while $E_{\rm exch-ind}^{(2)}(2,M)$, $E_{\rm exch-def}^{(2)}(2,M)$, and $E_{\rm exch-disp}^{(2)}(2,M)$ denote the exchange-induction, exchange-deformation, and exchange-dispersion terms. The contributions appearing on the (rhs) of eqs 2 and 3 have been evaluated using the many-body techniques developed in refs 89−96. The exchange-deformation energy was computed directly from the supermolecule Hartree−Fock interaction energy. The computational scheme for the pair interactions was the same as in our previous works (see, for instance, ref 118).

The three-body interaction energy in SAPT is represented by[97]

$$E_{\mathrm{int}}^{\mathrm{SAPT}}(3,M) = E_{\mathrm{ind}}^{(2)}(3,M) + E_{\mathrm{ind}}^{(3)}(3,M) + E_{\mathrm{ind-disp}}^{(3)}(3,M) + E_{\mathrm{disp}}^{(3)}(3,M) + E_{\mathrm{exch}}(3,M) \quad (4)$$

where the consecutive terms on the rhs of eq 4 denote the nonadditive second-, and third-order induction energies, the induction−dispersion and dispersion terms, and the exchange contribution, respectively. See ref 97 for precise definitions of these quantities and their physical interpretation. Similarly as in the two-body case, the exchange term collects several contributions,

$$E_{\mathrm{exch}}(3,M) = E_{\mathrm{HL}}^{(1)}(3,M) + E_{\mathrm{exch-ind}}^{(2)}(3,M) + E_{\mathrm{exch-ind}}^{(3)}(3,M) + \delta E_{\mathrm{int}}^{\mathrm{HF}}(3,M) + E_{\mathrm{exch-disp}}^{(2)}(3,M) + E_{\mathrm{exch}}^{\mathrm{MP2}}(3,M) \quad (5)$$

Here, $E_{\mathrm{HL}}^{(1)}(3,M)$ is the Heitler−London nonadditive energy, $E_{\mathrm{exch-ind}}^{(2)}(3,M)$ and $E_{\mathrm{exch-ind}}^{(3)}(3,M)$ denote the second-, and third-order exchange-induction terms, and $E_{\mathrm{exch-disp}}^{(2)}(3,M)$ is the exchange-dispersion nonadditivity. The two additional exchange contributions, $\delta E_{\mathrm{int}}^{\mathrm{HF}}(3,M)$ and $E_{\mathrm{exch}}^{\mathrm{MP2}}(3,M)$, approximate the nonadditive exchange-deformation effects [$\delta E_{\mathrm{int}}^{\mathrm{HF}}(3,M)$] and the sum of the first-order exchange-correlation and exchange-induction−dispersion terms [$E_{\mathrm{exch}}^{\mathrm{MP2}}(3,M)$]. See ref 105 for their precise definitions. In practice, the induction, induction−dispersion, and dispersion terms were evaluated within the random phase approximation,[97] while the exchange contributions were computed with the neglect of the intramolecular correlation effects.[97] The computational approach to nonadditive interactions in water clusters is the same as in our previous work on Ar_2-HF.[105]

The supermolecule interaction energies were represented by the following many-body expansion,

$$E_{\mathrm{int}}^{\mathrm{SM}} = \sum_{N=2}^{M} E_{\mathrm{int}}^{\mathrm{SM}}(N,M) \quad (6)$$

where $E_{\mathrm{int}}^{\mathrm{SM}}(N,M)$ denotes the N-body contribution to the supermolecule interaction energy for a cluster of M molecules and the superscript SM is the short-hand notation for the supermolecule method. The superscript CCSD(T) is used for the coupled-cluster single and double excitations calculations with a noniterative inclusion of the connected triple excitations. The usual symbols BP86, BLYP, and BPW91 will be used for the density functional approaches based on the exchange potential of Becke,[110] and the correlation potentials of Perdew,[111,112] Lee et al.,[113] and Perdew et al.[114,115] respectively. The hybrid approaches[109] utilizing a suitable combination of the Hartree−Fock-type and Becke's[110] exchange potentials, as well as the correlation potentials quoted above will be denoted by B3P86, B3LYP, and B3PW91, respectively. The pair and three-body interaction energies are given by the standard formulas

$$E_{\mathrm{int}}^{\mathrm{SM}}(2,M) = \frac{1}{2}\sum_{i\neq j=1}^{M} (E_{\mathrm{X}_i\mathrm{X}_j}^{\mathrm{SM}} - E_{\mathrm{X}_i}^{\mathrm{SM}} - E_{\mathrm{X}_j}^{\mathrm{SM}}) \quad (7)$$

$$E_{\mathrm{int}}^{\mathrm{SM}}(3,M) = \frac{1}{6}\sum_{i\neq j\neq k=1}^{M} (E_{\mathrm{X}_i\mathrm{X}_j\mathrm{X}_k}^{\mathrm{SM}} - E_{\mathrm{X}_i\mathrm{X}_j}^{\mathrm{SM}} - E_{\mathrm{X}_j\mathrm{X}_k}^{\mathrm{SM}} - E_{\mathrm{X}_k\mathrm{X}_i}^{\mathrm{SM}} + E_{\mathrm{X}_i}^{\mathrm{SM}} + E_{\mathrm{X}_j}^{\mathrm{SM}} + E_{\mathrm{X}_k}^{\mathrm{SM}}) \quad (8)$$

where $E_{\mathrm{X}_1 \ldots \mathrm{X}_m}^{\mathrm{SM}}$ denotes the total energy of a system composed of molecules X_1, ..., X_m. Similar definitions apply to four-body and higher-order terms in the many-body expansion (6). In all the supermolecular calculations the interaction energies were corrected for the basis set superposition error (BSSE) with the counterpoise method of Boys and Bernardi.[119] In accordance with the recommendations in some other studies of many-body forces,[42,120,121] we obtained the N-body interactions in an M-molecule cluster from calculations on all the N-body subclusters (for every $N \leq M$) in the full M-body basis. As discussed below, it turns out that the N-body interaction energies thus obtained—at the CCSD(T) level—are in good agreement with the results from our SAPT method, which computes these interaction energies directly and BSSE free.

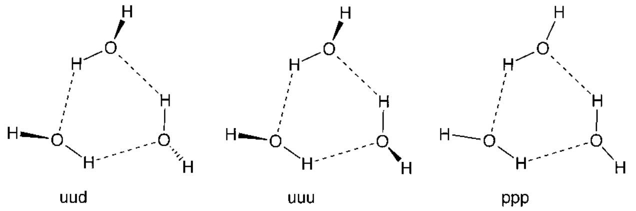

Figure 1. Geometry of the global (*uud*) and local (*uuu* and *ppp*) minima on the potential energy surface of the water trimer.

III. Computational Details

In the present paper we investigated the lowest energy structures of the water trimer, tetramer, and pentamer. For the trimer, we also considered the saddle points connecting various minima on the potential energy surface. The optimal geometries corresponding to these structures were obtained from analytic gradient calculations with the second-order Møller−Plesset theory. We performed full geometry optimizations; i.e., the geometrical parameters of the water monomers were relaxed, and not fixed at their experimental equilibrium values. In addition, harmonic frequency calculations at the same level of the theory were performed in order to check whether the stationary points obtained from the gradient calculations correspond to minima (all frequencies real) or saddle points (one imaginary frequency). The geometry optimizations and frequency calculations were made with the Gaussian 94 code.[122] In all calculations we used the aug-cc-pVDZ basis set[123] (41 Gaussian type orbitals per monomer). In the supermolecule CCSD(T) calculations we employed both the Gaussian 94 and the MOLPRO suite of codes[124] and kept the 1s orbitals frozen. SAPT calculations of the pair and nonadditive interaction energies were made with the programs SAPT[125] and SAPT3,[126] respectively. The SAPT pair energies were always computed with dimer basis sets, and the three-body interactions with the full trimer bases.

IV. Numerical Results and Discussion

A. Geometries of the Clusters. The global minima of all water clusters $(H_2O)_n$ with $n = 3-5$ correspond to cyclic hydrogen-bonded structures with each monomer acting simultaneously as proton donor and proton acceptor. The trimer has a triangular equilibrium structure with—because of geometry constraints—rather strongly bent hydrogen bonds, the tetramer has a square planar system of hydrogen bonds—with much less strain—and the pentamer has a strain free, slightly puckered, pentagonal hydrogen-bonded framework; see Figures 1−3. In all cases the external, non-hydrogen-bonded, protons lie above and below the planes of the hydrogen bonded "skeletons" (denoted "up" and "down", or *u* and *d*). The up−up−down and up−up−down−up−down equilibrium structures of $(H_2O)_3$ and $(H_2O)_5$ have no spatial symmetry, but there are six equivalent

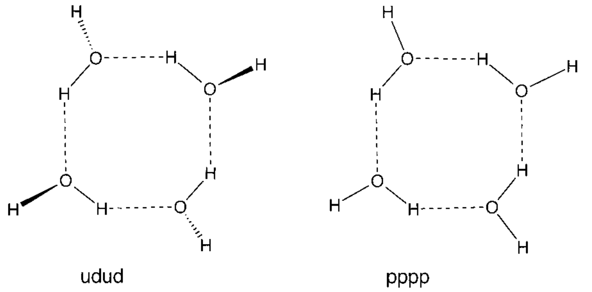

Figure 2. Geometry of the global (*udud*) and local (*pppp*) minima on the potential energy surface of the water tetramer.

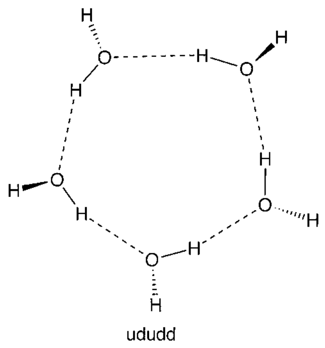

Figure 3. Geometry of the global (*ududd*) minimum on the potential energy surface of the water pentamer.

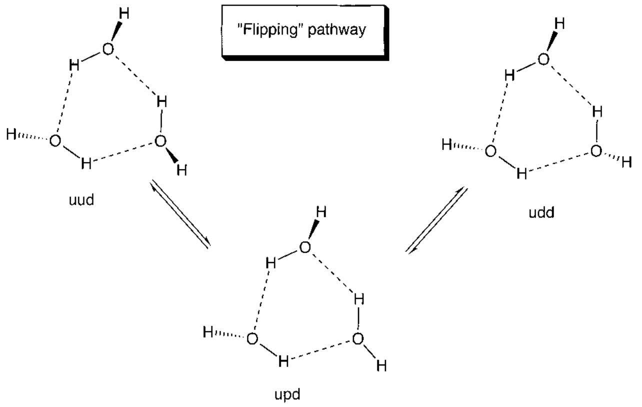

Figure 4. Geometry of the *upd* transition state on the potential energy surface of the water trimer and a schematic representation of the flipping pathway.

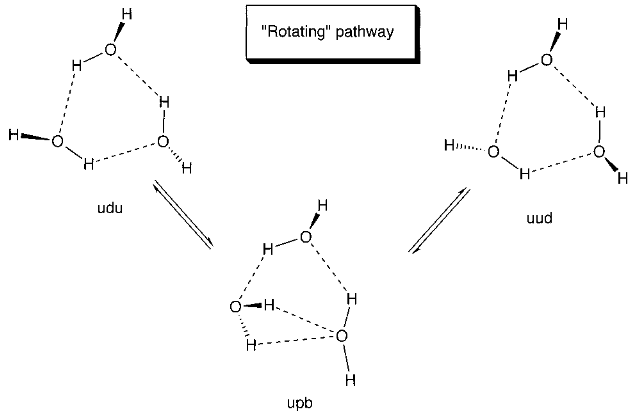

Figure 5. Geometry of the *upb* transition state on the potential energy surface of the water trimer and a schematic representation of the rotating pathway for bifurcation tunneling.

structures in the case of the trimer and 10 for the pentamer that are interconnected by up−down flipping motions of the out-of-plane protons, one at the time. For the pentamer this up−down flipping motion of one of the external protons is accompanied by a wagging motion of one of the flaps of the puckered hydrogen-bonded framework.[85] For $(H_2O)_4$ the symmetry of the up−down−up−down equilibrium structure is the point group S_4.

For the trimer we also considered a local minimum (the *uuu* structure with all three external protons lying above the plane of the hydrogen-bonded ring) and another stationary point on the potential surface (the planar *ppp* structure; cf. Figure 1). The symmetries corresponding to these structures are C_3 and C_{3h}, respectively. For the tetramer, the planar *pppp* structure was investigated (C_{4h} symmetry; cf. Figure 2).

In experimental studies of the low-frequency transitions in the far-infrared spectra of the water trimer,[3−5] it was conjectured that the observed splittings result from tunneling between the equivalent equilibrium structures via flipping and rotating pathways. Schematic representations of these two pathways are reported in Figures 4 and 5. The flipping motion is accomplished by rotating one water monomer about its donor hydrogen bond. It connects the global *uud* minimum with its enantiomeric *udd* form. The transition state corresponds to the *upd* structure with two free protons on the opposite sides of the hydrogen-bonded ring, and the third one in the plane of the ring; cf. Figure 4. The rotating pathway involves two monomers having their protons on the opposite sides of the hydrogen-bonded ring. The free donor proton replaces the hydrogen-bonded one, and the latter is moved to the other side of the ring. During this exchange a flipping of the free acceptor proton takes place. The transition state found in our calculations corresponds to a structure with the acceptor molecule in the plane of the ring and the donor molecule in the bifurcated hydrogen bond perpendicular to and bisected by this plane; cf. Figure 5.

The geometries corresponding to the stationary points on the potential energy surfaces of the water trimer, tetramer, and pentamer were considered previously by several authors. Here we compare our results with the most recent calculations,[41,54,56,70,85] since these employed similar methods and the same quality basis sets. The agreement with the geometries reported in the literature is very good. For the global and local minima our results agree with the previous calculations within 0.005 Å for the distances, 0.2° for the angles, and 2° for the dihedral angles (we give the largest deviation from the set of previous calculations cited above). The only exceptions are the dihedral angles in the pentamer, where the largest deviation is 7°.[127] For the transition states the agreement is within 0.06 Å for the distances and 5° for the angles.

B. Importance of the Many-Body Nonadditive Effects. The interaction energies and their decomposition into pair and many-body nonadditive contributions are reported in Tables 1−3 for various structures of the trimer, tetramer, and pentamer described above. An inspection of these tables shows that many-body cooperative effects are far from negligible. The pair interaction energy represents 83−86% of the total interaction energy of the trimer. For the tetramer the same percentage amounts to ≈75%, for the pentamer only to 68%. These percentages agree well with the MP2 and MP4 results of Xantheas[42] and with the MP2 results of Hodges et al.[43] for the equilibrium geometries of the trimer, tetramer, and pentamer. The results of Xantheas for the pentamer were only at the HF level, and the many-body contributions at this level are substantially smaller than in our SAPT and CCSD(T) results. The early estimate of Clementi et al.,[16] also at the Hartree−Fock level and too low as well, gave a three-body contribution for the trimer in its equilibrium geometry of about 10% of the total binding energy. They

TABLE 1: Components of the Pair and Three-Body Interaction Energies (kcal/mol) for Various Geometries of the Water Trimer[a]

	geometry				
	uud	*uuu*	*ppp*	*upb*	*upd*
$E^{(1)}_{\rm elst}(2,3)$	−26.645	−24.625	−20.781	−22.163	−25.380
$E^{(2)}_{\rm ind}(2,3)$	−12.252	−11.148	−8.481	−9.499	−11.407
$E^{(2)}_{\rm disp}(2,3)$	−9.121	−8.720	−7.832	−7.783	−8.843
$E_{\rm exch}(2,3)$	36.583	33.627	26.129	29.111	34.206
$E^{\rm SAPT}_{\rm int}(2,3)$	−11.435	−10.866	−10.965	−10.334	−11.424
$E^{\rm CCSD(T)}_{\rm int}(2,3)$	−11.624	−10.962	−10.690	−10.501	−11.502
$E^{(2)}_{\rm ind}(3,3)$	−1.351	−1.315	−1.124	−1.078	−1.283
$E^{(3)}_{\rm ind}(3,3)$	−0.688	−0.628	−0.359	−0.496	−0.590
$E^{(3)}_{\rm ind-disp}(3,3)$	−0.090	−0.068	0.013	−0.079	−0.061
$E^{(3)}_{\rm disp}(3,3)$	0.060	0.055	0.043	0.055	0.056
$E_{\rm exch}(3,3)$	−0.345	−0.350	−0.501	−0.117	−0.410
$E^{\rm SAPT}_{\rm int}(3,3)$	−2.414	−2.306	−1.928	−1.715	−2.288
$E^{\rm CCSD(T)}_{\rm int}(3,3)$	−2.371	−2.262	−1.893	−1.657	−2.238
$E^{\rm SAPT}_{\rm int}$	−13.849	−13.172	−12.893	−12.049	−13.712
$E^{\rm CCSD(T)}_{\rm int}$	−13.995	−13.224	−12.583	−12.158	−13.740
sum of monomer relaxation energies	0.336	0.331	0.321	0.335	0.347

[a] These interaction energies are defined with respect to the monomers in the same geometries as in the clusters. Binding energies with respect to the monomers in their own equilibrium structures can be obtained from the monomer relaxation energies listed at the bottom.

TABLE 2: Components of the Pair and Three-Body Interaction Energies (kcal/mol) for Two Geometries of the Water Tetramer[a]

	geometry	
	udud	*pppp*
$E^{(1)}_{\rm elst}(2,4)$	−48.963	−37.902
$E^{(2)}_{\rm ind}(2,4)$	−25.364	−18.069
$E^{(2)}_{\rm disp}(2,4)$	−16.088	−13.482
$E_{\rm exch}(2,4)$	72.445	52.847
$E^{\rm SAPT}_{\rm int}(2,4)$	−17.970	−16.606
$E^{\rm CCSD(T)}_{\rm int}(2,4)$	−18.111	−16.153
$E^{(2)}_{\rm ind}(3,4)$	−3.169	−2.742
$E^{(3)}_{\rm ind}(3,4)$	−1.165	−0.672
$E^{(3)}_{\rm ind-disp}(3,4)$	0.026	0.151
$E^{(3)}_{\rm disp}(3,4)$	0.077	0.046
$E_{\rm exch}(3,4)$	−1.958	−1.930
$E^{\rm SAPT}_{\rm int}(3,4)$	−6.189	−5.147
$E^{\rm CCSD(T)}_{\rm int}(3,4)$	−6.081	−5.064
$E^{\rm CCSD(T)}_{\rm int}(4,4)$	−0.562	−0.471
$E^{\rm SAPT}_{\rm int}$	−24.159	−21.753
$E^{\rm CCSD(T)}_{\rm int}$	−24.754	−21.689
sum of monomer relaxation energies	0.920	0.770

[a] Binding energies with respect to the monomers in their own equilibrium structures can be obtained from the monomer relaxation energies, listed at the bottom.

TABLE 3: Components of the Pair and Three-Body Interaction Energies (kcal/mol) for the Equilibrium Geometry of the Water Pentamer[a]

	ududd		*ududd*
$E^{(1)}_{\rm elst}(2,5)$	−64.090	$E^{(3)}_{\rm disp}(3,5)$	0.045
$E^{(2)}_{\rm ind}(2,5)$	−34.146	$E_{\rm exch}(3,5)$	3.558
$E^{(2)}_{\rm disp}(2,5)$	−20.932	$E^{\rm SAPT}_{\rm int}(3,5)$	−9.120
$E_{\rm exch}(2,5)$	96.634	$E^{\rm CCSD(T)}_{\rm int}(3,5)$	−8.978
$E^{\rm SAPT}_{\rm int}(2,5)$	−22.534	$E^{\rm CCSD(T)}_{\rm int}(4,5)$	−1.220
$E^{\rm CCSD(T)}_{\rm int}(2,5)$	−22.201	$E^{\rm CCSD(T)}_{\rm int}(5,5)$	−0.009
$E^{(2)}_{\rm ind}(3,5)$	−4.551	$E^{\rm SAPT}_{\rm int}$	−31.654
$E^{(3)}_{\rm ind}(3,5)$	−1.251	$E^{\rm CCSD(T)}_{\rm int}$	−32.481
$E^{(3)}_{\rm ind-disp}(3,5)$	0.195	sum of monomer relaxation energies	1.257

[a] The binding energy with respect to the monomers in their own equilibrium structures can be obtained from the monomer relaxation energy listed at the bottom.

estimated[21] the four-body energy in larger clusters to be about 20−30% of the three-body contribution.

Obviously, the structure and properties of these clusters cannot be described by assuming pairwise additivity of the interaction potential. Fortunately, the major part of the many-body cooperative effect is already accounted for by the three-body energies. Indeed, the four-body terms represent 2% of the total interaction energy of the tetramer, and less than 4% for the pentamer. The five-body contribution is negligible and represents only 0.03% of the total interaction energy of the pentamer. It is gratifying to observe a relatively fast convergence of the many-body expansion of the interaction energy, eq 6, since the calculations of the four-body terms are very computer time demanding, and their physical origins are not well understood. One may note here that the many-body effects are attractive for all the structures considered in the present work; i.e., they represent an additional stabilizing effect.

We may also look at the interaction energies per hydrogen bond, which show an interesting trend. Taking just the pair interaction energies (at the equilibrium geometries), we find 3.9 kcal/mol per bond for the trimer and 4.5 kcal/mol both for the tetramer and pentamer. This can be related to the hydrogen bond strain, as judged by the deviation of the actual hydrogen-bonding angle in each cluster from the ideal value found in the dimer. The trimer is highly strained, much less strain occurs in the tetramer, and strain is absent in the pentamer. The total interaction energy per hydrogen bond increases from 4.7 kcal/mol for the trimer, to 6.2 kcal/mol for the tetramer, to 6.5 kcal/mol for the pentamer, due to collective (many-body) effects.

Let us mention that we report in Tables 1−3 the interaction energies with respect to the monomers in the same geometries as they have in the clusters, not the binding energies with respect to the monomers in their own equilibrium structures. The latter can be obtained from the interaction energies by including the monomer relaxation energies. We also computed these monomer relaxation energies; they are explicitly listed in Tables 1−3. For the trimer in all geometries the total relaxation energy is about 0.33 kcal/mol, computed at the CCSD(T) level, i.e., about 2.5% of the total interaction energy. It increases with cluster size to about 4% of the total interaction energy for the pentamer, more or less in line with the interaction energy per hydrogen bond. The monomer geometry relaxation effects can only be obtained from (supermolecule) total energy calculations, not from SAPT, which computes purely the intermolecular interaction energy contributions. However, the SAPT method allows the computation of the interaction energy as a function of the monomer geometries, to which one may add the intramolecular force fields to obtain the monomer relaxation effects.

C. Nature of the Pair and Nonadditive Interactions in Water Clusters. In Tables 1−3 we report the decomposition of the SAPT pair and nonadditive energies into various physical contributions as defined by eqs 1−5. Before we look at the physical origins of the bonding in the water clusters, let us first discuss the accuracy of the SAPT results. An inspection of Tables 1−3 shows that the performance of the SAPT approach is excellent both for the pair and nonadditive interactions. Indeed, the comparison of the SAPT and CCSD(T) pair interaction energies shows that the deviations between the two sets of results are of the order of 1−2%, the largest being 2.8%. The same convergence pattern is observed for the three-body energies. Here the error of SAPT with respect to CCSD(T) oscillates between 1% and 2%, the largest being 3.5%. This level of agreement between the results from highly correlated supermolecule and perturbative calculations suggests that the SAPT method is a good tool to describe pair and three-body interactions in water clusters.

Let us discuss the most important contributions responsible for the bonding in the water clusters. As the results reported in Tables 1−3 show, the electrostatic energy is by far the largest contribution to the interaction energy for all clusters. This could be expected since the hydrogen bond is directional, and the structure of hydrogen-bonded complexes is largely determined by the electrostatic interactions. However, other contributions are far from negligible. For instance, the pair induction and dispersion energies are of the same order of magnitude as the total interaction energy, while the pairwise additive exchange term is more than twice the total interaction energy (in absolute value). Hence, the pairwise additive interaction energy is not dominated by a single component but rather results from a partial cancelation of large attractive and repulsive contributions. This conclusion is valid for all the geometries considered in Tables 1−3. In fact, a closer analysis of the results for the water trimer, Table 1, suggests that the global minimum corresponds to a structure with the largest attractive contributions and the highest exchange−repulsion term. The local minima and the transition states, in turn, show smaller attractive terms and lower repulsion (with respect to their values for the global minimum). The decrease of the exchange is always more important than the increase of the attractive terms, so these structures are mostly stabilized by the lowering of the exchange−repulsion energy. It is interesting to note that this lowering of the exchange term is more important for the local minima than for the saddle points.

The situation is quite different for the three-body interactions. Here, the induction terms are dominant. The second-order induction contribution is by far the largest. This could be expected since it describes the interactions of permanent moments of one molecule with the moments induced on the second molecule by the electrostatic field of the third one. However, higher induction terms are not negligible. The third-order induction represents 10−30% of the total three-body effect. Hence, if one wishes to include the induction effects by iteration[23,61,128] of the induced dipole moments and the corresponding electric fields, one should proceed with this iteration beyond the first step. The contribution of the third-order induction−dispersion energy is small and, even though the dispersion energy is an important component of the pair hydrogen-bonding energy, the Axilrod−Teller three-body dispersion energy is even smaller. The smallness of the induction−dispersion energy is quite unexpected. As shown in ref 97, this term describes the pair dispersion interaction between an unperturbed molecule A and a molecule B deformed (to the first order) by the electrostatic field of the molecule C. Given the relative importance of the pair dispersion interactions, and the large dipole moment of the water monomer, one would expect a large nonadditive induction−dispersion effect. By contrast the three-body exchange effects are substantial, so one cannot restrict the treatment of the nonadditive effects in water clusters to the classical induction terms only. One may note here that for all structures considered in the present paper the nonadditive exchange effect is always attractive, i.e., it reduces the large pair exchange−repulsion. All these observations concerning the different contributions to the three-body interaction energy apply equally to the trimer, tetramer, and pentamer.

TABLE 4: Decomposition of the Exchange Contributions to the Nonadditive Interaction Energy (kcal/mol) for Various Geometries of the Water Trimer[a]

	geometry				
	uud	*uuu*	*ppp*	*upb*	*upd*
$E_{\mathrm{HL}}^{(1)}(3,3)$	−0.254	−0.171	−0.228	−0.167	−0.233
$E_{\mathrm{exch-ind}}^{(2)}(3,3)$	−0.076	−0.141	−0.074	−0.019	−0.100
$E_{\mathrm{exch-ind}}^{(3)}(3,3)$	0.310	−0.013	0.251	0.258	−0.061
$\delta E_{\mathrm{int}}^{\mathrm{HF}}(3,3)$	−0.368	−0.186	−0.326	−0.228	−0.317
$E_{\mathrm{exch-disp}}^{(2)}(3,3)$	0.103	0.063	0.093	−0.019	0.094
$E_{\mathrm{exch}}^{\mathrm{MP2}}(3,3)$	−0.060	−0.174	−0.086	0.058	−0.105
$E_{\mathrm{exch}}(3,3)$	−0.345	−0.350	−0.501	−0.117	−0.410
$E_{\mathrm{ind}}^{(2)}(3,3)$	−1.351	−1.124	−1.315	−1.078	−1.283
$E_{\mathrm{ind}}^{(3)}(3,3)$	−0.688	−0.359	−0.628	−0.496	−0.590
$E_{\mathrm{ind-disp}}^{(3)}(3,3)$	−0.090	0.013	−0.068	−0.079	−0.061
$E_{\mathrm{disp}}^{(3)}(3,3)$	0.060	0.043	0.055	0.055	0.056
$E_{\mathrm{int}}^{\mathrm{SAPT}}(3,3)$	−2.414	−1.928	−2.306	−1.715	−2.288

[a] For completeness the polarization contributions are also included.

Since the nonadditive exchange effects play such an important role, it is interesting to analyze their decomposition into various contributions as defined by eq 5. The results reported in Table 4 show that $E_{\mathrm{exch}}(3,3)$ is not dominated by a single term. The Heitler−London nonadditivity is always the largest contribution. Depending on the geometry of the trimer, it represents between 45% and 143% of the total three-body exchange energy. The remaining parts result from the cancelations of various positive and negative contributions. Moreover, the importance of these contributions strongly varies from one geometry to another. Thus, we can conclude that in order to get an accurate description of the three-body exchange energy one has to consider all the terms appearing in eq 5.

We have also computed the effects of the pair and three-body interactions on the flipping and bifurcation tunneling barriers. From total energy calculations by the CCSD(T) method it follows that the total flipping barrier in the trimer, i.e., the difference between the *upd* and *uud* energies, is 0.27 kcal/mol. The bifurcation tunneling barrier, which is the energy difference between *upb* and *uud*, is 2.07 kcal/mol. These values agree well with the best results of Fowler and Schaefer (0.26 and 2.04 kcal/mol), who computed the two barriers at the CCSD level.[54] The corresponding values in Table 1, which are the barriers in the interaction energies with respect to the monomers as deformed in the trimer, are 0.26 kcal/mol for the flipping barrier and 1.84 kcal/mol for the bifurcation tunneling barrier. So, indeed, the effect of the geometry relaxation of the monomers is not very important. It follows from the analysis in Table 1 that the three-body contribution to these barriers, 52% of the flipping barrier height and 39% of the bifurcation barrier height (taking the numbers from the CCSD(T) calculations), is relatively stronger even than its contribution to the total interaction energy.

D. Applicability of DFT to Nonadditive Interactions in the Water Trimer. As discussed in the Introduction, the accuracy of various density functional theories to describe the many-body cooperative effects has not been tested by comparison with highly correlated results from ab initio calculations. This is the more relevant since the DFT methods are also implemented in the “ab initio molecular dynamics” approach of Car and Parrinello (see, for instance, ref 81), which is often used to describe dynamical phenomena in large clusters and in liquids. Here we report the comparison of DFT and CCSD(T) results for the minima and transition states of the water trimer. We restricted our work to the most popular (semi)local functionals available in Gaussian 94: BLYP, BP86, BPW91, and the hybrid functionals B3LYP, B3P86, and B3PW91.

TABLE 5: Comparison of the Three-Body and Total Interaction Energies (kcal/mol) Calculated by ab Initio and DFT Methods for Various Geometries of the Water Trimer

	geometry				
	uud	*uuu*	*ppp*	*upb*	*upd*
$E_{\text{int}}^{\text{SAPT}}(3,3)$	−2.41	−2.31	−1.93	−1.72	−2.29
$E_{\text{int}}^{\text{CCSD(T)}}(3,3)$	−2.37	−2.26	−1.89	−1.66	−2.24
$E_{\text{int}}^{\text{BLYP}}(3,3)$	−2.69	−2.18	−2.58	−1.87	−2.55
$E_{\text{int}}^{\text{BP86}}(3,3)$	−3.06	−2.52	−2.94	−2.22	−2.92
$E_{\text{int}}^{\text{BPW91}}(3,3)$	−3.15	−2.53	−3.01	−2.27	−2.99
$E_{\text{int}}^{\text{B3LYP}}(3,3)$	−2.53	−2.06	−2.43	−1.76	−2.40
$E_{\text{int}}^{\text{B3P86}}(3,3)$	−2.82	−2.32	−2.70	−2.02	−2.69
$E_{\text{int}}^{\text{B3PW91}}(3,3)$	−2.90	−2.34	−2.77	−2.08	−2.76
$E_{\text{int}}^{\text{SAPT}}$	−13.85	−13.17	−12.89	−12.05	−13.71
$E_{\text{int}}^{\text{CCSD(T)}}$	−14.00	−13.22	−12.58	−12.16	−13.74
$E_{\text{int}}^{\text{BLYP}}$	−12.73	−10.64	−11.86	−10.40	−12.29
$E_{\text{int}}^{\text{BP86}}$	−13.56	−10.83	−12.55	−10.95	−12.97
$E_{\text{int}}^{\text{BPW91}}$	−11.44	−8.79	−10.45	−9.01	−10.87
$E_{\text{int}}^{\text{B3LYP}}$	−14.30	−12.39	−13.42	−11.96	−13.92
$E_{\text{int}}^{\text{B3P86}}$	−15.26	−12.79	−14.24	−12.63	−14.75
$E_{\text{int}}^{\text{B3PW91}}$	−13.03	−10.70	−12.06	−10.62	−12.54

In Table 5 we report the nonadditive energies computed with these functionals for the minima and transition states of the water trimer. For completeness, the total interaction energies, and the CCSD(T) and SAPT results are also given. An inspection of this table shows that all currently available functionals fail to accurately reproduce the CCSD(T) results. The best performance is observed for the hybrid B3LYP functional, but even this method may be in error by as much as 29% (for the *ppp* structure; for other geometries the error oscillates between 6% and 9%). For other functionals the errors are even larger. Looking at the energy differences between the various higher stationary points and the global *uud* minimum, one finds that in all cases the DFT calculations strongly overestimate these differences. This holds, in particular, for the *upd* and *upb* barrier heights, relevant for the flipping and bifurcation tunneling processes. Also, all versions of DFT tend to strongly overemphasize the importance of the three-body contributions. It is interesting to note that the performance of DFT for the total interaction energies is somewhat better. This suggests that there is a compensation of errors even though the individual pair and three-body components are not correct. Again the B3LYP functional shows the best performance, the deviations from the CCSD(T) results being in the range 1−7%.

V. Conclusions

In this paper we reported the analysis of the nature and importance of the pair and many-body interactions in small water clusters. Our theoretical analysis was based on the SAPT decomposition, as well as on the results obtained from supermolecule coupled-cluster calculations. The results of this paper can be summarized as follows:

1. The assumption of pairwise additivity of the interaction in the water clusters is not correct. The nonadditive three-body contribution is very large, and represents as much as ≈17%, 25%, and 28% of the total interaction energy for the trimer, tetramer, and pentamer, respectively, for the equilibrium geometries. Its effect on the tunneling barriers investigated in the trimer is even larger: about 50% of the *upd* barrier height for the flipping process and nearly 40% of the *upb* barrier height for bifurcation tunneling. It is also noteworthy that the (both absolute and relative) contributions of the three-body interactions are always smaller in magnitude for the higher stationary points than for the global minima. The convergence of the many-body expansion of the interaction energy is satisfactory. The four-body effects are relatively small and represent 2% of the total interaction energy for the tetramer, and 4% for the pentamer. The five-body effects were found to be negligible.

2. The convergence of the symmetry-adapted perturbation expansion for the pair interactions (through second order in the intermolecular interaction) and the three-body interactions (through third order) in water clusters is very satisfactory. For both two- and three-body interaction energies the SAPT results reproduce the reference CCSD(T) values with a mean error of 2%. In all cases the largest deviation does not exceed 3.5%.

3. For all the geometries of the water clusters considered in the present paper the pair interaction potential results from a partial cancelation of large attractive electrostatic, induction, and dispersion contributions, and of a strongly repulsive exchange term.

4. The three-body potential for $(H_2O)_3$ is dominated by the second-order induction nonadditivity. However, the third-order induction represents 10−30% of the total three-body effect, so if one wishes to include the induction effects by iteration of the induced dipole moments and the corresponding electric fields, one should proceed with this iteration beyond the first step. The three-body exchange term was found to be a substantial stabilizing contribution to the total three-body potential. This information is important for the development of a realistic model of the three-body interactions that can be applied in simulations of liquid water.

5. All currently used density functional methods fail to correctly describe the three-body interactions in the water trimer. The best performance is observed for the hybrid B3LYP functional, which reproduces the reference CCSD(T) results with a mean error of ≈7% but still performs considerably worse for structures far from the equilibrium geometry (such as the *ppp* structure) and for the energy barriers.

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