# Contribution of Many-Body Terms to the Energy for Small Water Clusters: A Comparison of ab Initio Calculations and Accurate Model Potentials

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We have tested the ability of two new model potentials constructed using intermolecular perturbation theory methods to reproduce ab initio results at a comparable level of theory. Several configurations of water trimer, tetramer, and pentamer are studied, and in addition to the contributions to the interaction energy, the potential energy surfaces are compared by optimizing the model potential geometries to local stationary points within a rigid-body framework. In general the agreement between the two methods is good, validating the model potentials as suitable candidates for providing starting geometries for further ab initio calculations and for the simulation of larger systems.

## 1. Introduction

The ability of a model interaction potential to reproduce experimental results ranging from the dimer to the bulk should be considered an important goal. Available interaction potentials for water range from simplistic ones such as TIP4P[1] to more complicated ones that account for the intramolecular relaxation (RWK-2),[2] the induced polarization due to the environment (POL-1),[3,4] or even the dissociation of water into ions.[5]

The dimer structure has been determined experimentally,[6−8] and more recently, larger clusters from the trimer to the hexamer have been probed by far-infrared vibration−rotation tunnelling spectroscopy.[9−14] Such experiments have stimulated theoretical investigation of both the structure[15−17] and dynamics[18−21] of these clusters. Model potentials provide an efficient and increasingly accurate method for approaching dynamical techniques for which large numbers of energy (and gradient) calculations may be required.

Many existing potentials are designed for a particular application and cannot be applied elsewhere. For example the TIP4P model comprises a spherically symmetric dispersion−repulsion term and point charges, and the evaluation of the interaction energy between many monomers is therefore relatively cheap, so it is useful for simulation of water in the bulk. However TIP4P is not appropriate for the dimer because the dipole is enhanced to recover the bulk binding energy, accounting in an average way for the cooperative polarization.

Our two anisotropic site−site potentials, ASP-W2 and ASP-W4, on the other hand, are intended to be universal. They are constructed from ab initio data using intermolecular perturbation theory (IMPT) methods, with separate terms to describe the dispersion, repulsion, charge-transfer, induction, and electrostatic contributions. This approach means that for any configuration the total energy is calculated as a sum of distinct, physically meaningful terms, allowing considerable insight into the bonding. This has clear advantages over obtaining the total interaction energy from, for example, a supermolecule calculation. A less obvious advantage is that basis set superposition error (BSSE) is avoided. Details of the IMPT methods can be found

elsewhere;[22,23] see also Millot and Stone[24] for details of its application to the original ASP water potentials.

Both the first-order electrostatic and higher order induction terms are considered. In fact the only term in the energy that is not pairwise additive for this model is the induction. Of course some of the other terms should not be strictly pairwise additive: the repulsion between a pair of molecules is modified in the presence of a third, for example, and the Axilrod−Teller triple-dipole dispersion[25] is perhaps the most well-known of the many-body contributions. However, previous investigations[26] suggest that the induction energy is by far the biggest contribution to the many-body terms, so it is the only one included here. Optimized water cluster geometries from the dimer to the hexamer have previously been reported[16] and the many-body interactions studied.[27,28] In a similar study, Pedulla et al.[29] commented that correlated calculations are crucial for the two-body contributions to the energy, but that the many-body contributions are not significantly affected by correlation. This is true if, for example, Hartree−Fock (HF) and Møller−Plesset[30] (MP2) calculations are carried out at the same geometry, but if HF contributions are calculated at the HF optimized geometry, then all contributions will be underestimated.

For the trimer to pentamer, all our energy calculations are made at fully optimized MP2/aug-cc-pVDZ[31,32] geometries, with the same basis and level of theory. Although this is a reasonably large set and, for the larger clusters, the calculations represent a considerable computational effort, it is conceivable that the results might change with the use of an even larger basis set, especially the ones that are corrected for BSSE. Available results for the water dimer indicate that changes due to larger basis sets are likely to be larger than the corresponding ones due to inclusion of higher orders of electron correlation. This is perhaps more significant for the hexamer, for which several low-lying isomers have been found within a small energy range.[21,33]

## 2. Method

**2.1. The Model Potentials.** The two model potentials considered here, ASP-W2 and ASP-W4, represent refinements to the original Millot−Stone[24] potential. The multipoles have been updated using results from a multireference configuration interaction calculation, instead of the MP2 values used in the

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⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1997.

**TABLE 1: Properties of the Water Dimer Global Minimum (See also Figure 1). The ab Initio Structure Is the Result of a Full Optimization at the MP2/aug-cc-pVTZ Level Followed by Reoptimization of the O−O Separation at MP2/aug-cc-pV5Z**

| source | energy/kJ mol$^{-1}$ | $R$/Å | $\alpha$/deg | $\beta$/deg |
|--------|---------------------|-------|--------------|-------------|
| ASP-W2 | −21.08 | 2.957 | 64.2 | 6.2 |
| ASP-W4 | −20.88 | 2.970 | 57.0 | −2.1 |
| MP2[39,40] [a] | −20.65 | 2.913 | 56.8 | 5.6 |

[a] Additional parameters are necessary to describe this structure fully; see text.
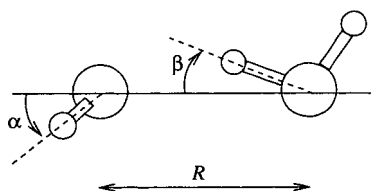


**Figure 1.** Water dimer minimum energy geometry, $C_s$ symmetry.



**Figure 2.** Optimized ab initio water cluster structures: (a−c) (H$_2$O)$_3$ geometries 1−3; (d−g) (H$_2$O)$_4$ geometries 1−4; (h) (H$_2$O)$_5$ geometry 1 (cyclic); (i) (H$_2$O)$_5$ geometry 2 (cage).

previous version. The induction energy is converged via an iterative process, instead of a single (first-order) calculation. Dispersion surfaces due to Rijks and Wormer[34,35] are still employed, and a charge-transfer term has been added using results from IMPT.[36] The major difference between these ASP potentials is the rank to which the multipoles are calculated, with ASP-W2 including moments up to quadrupole and ASP-W4 up to hexadecapole. Further details, including values of all the parameters, will be published elsewhere.[37] The calculations using these potentials were carried out using the Orient program.[38] Both the program and the data files describing the potentials are available on request from the authors.

Details of the $C_s$ minimum of the water dimer are given in Table 1; the coordinate system employed is shown in Figure 1. The ab initio geometry optimization was performed at the MP2/aug-cc-pVTZ[31,32] level with reoptimization of the O−O separation, keeping all other internal coordinates fixed, at MP2/aug-cc-pV5Z. The model potentials reproduce the ab initio binding energy accurately, but the O−O separation is too large by about 0.05 Å. The potential energy surface is extremely flat with respect to the angular coordinates, and ASP-W2 appears to perform better in this case. Note that for the ab initio geometry[39,40] both of the intramolecular bond angles and three bond lengths will differ from their monomer values. For this dimer geometry using the notation of ref 16, these parameters are $\Psi_{donor} = 104.5°$, $\Psi_{acceptor} = 104.5°$, $R_{acceptor} = 0.962$ Å, $(r_1)_{donor} = 0.969$ Å, and $(r_2)_{donor} = 0.960$ Å. The ASP monomers have the gas-phase geometry,[41] i.e. both values of $\Psi$ equal to 104.5° and all values of $R$ and $r$ equal to 0.9571 Å. The ab initio structures can be represented within the rigid-body framework to a good approximation because the relaxation of the monomers in terms of bond lengths and bond angles is in fact quite small. The approach we have taken is to define the monomer $C_2$ axis parallel to the sum of the two O−H vectors for each molecule. This is not the only possible choice, but because of the small distortion, other constraints would lead to very similar results. We can quantify this by calculating the rms deviation of the Cartesian coordinates from the rigid-body structures for each geometry. The maximum value of this quantity is 0.015, 0.020, and 0.021 Å for the trimer, tetramer, and pentamer structures, respectively.

**2.2. Decomposition of the Energy.** Recently, for a number of water clusters, the contribution to the binding energy from fragment relaxation, i.e. the energy required to distort each monomer from its equilibrium geometry to its complexed geometry, has been examined.[39] For the water dimer this is
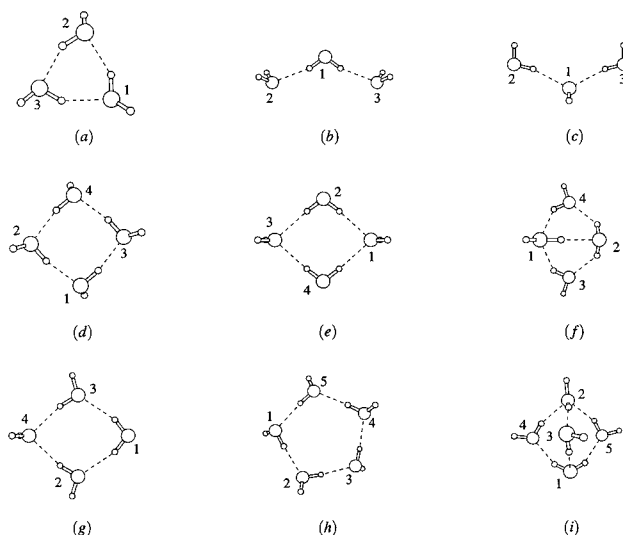
small ($\approx 0.4$ kJ mol$^{-1}$). As our model potentials treat the molecules as rigid bodies, we have no obvious way of estimating this contribution. We therefore make comparison with ab initio results for which it is not included. The structures we considered were optimized at the MP2 level of theory with the aug-cc-pVDZ basis sets.[31,32] The decomposition of the energy was performed by taking into account the correction for BSSE according to the scheme outlined in ref 27. The trimer, tetramer, and pentamer geometries are shown in Figure 2.

Using the same notation as ref 27, we write the total energy of the complex as a sum of one-, two-, ...$n$-body terms:

$$E = \sum_i E(i) + \sum_{j>i} \Delta^2 E(ij) + \sum_{k>j>i} \Delta^3 E(ijk) + \sum_{l>k>j>i} \Delta^4 E(ijkl) + ... \quad (1)$$

with, for example,

$$\Delta^2 E(12) = E(12) - E(1) - E(2) \quad (2)$$

$$\Delta^3 E(123) = E(123) - \sum_{i=1}^{3} E(i) - \Delta^2 E(12) - \Delta^2 E(13) - \Delta^2 E(23) \quad (3)$$

and so on. Now, for the supermolecule calculations, the two-body energies are calculated as the difference between the energy of the complex and the energies of the monomers at their complexed geometries. Because our model potentials give us the interaction energy directly, we can formalize this by taking $E(i) = 0$, so that $\Delta^2 E(ij) = E(ij)$.

Clearly this summation is truncated according to the number of molecules we are considering, so for the trimer we must consider three two-body and one three-body contributions. For the tetramer we must consider six two-body, four three-body, and one four-body contributions. As stated before this does not account for the energy associated with fragment relaxation, so we must compare with ab initio results for which this has not been included.

For comparison with previous work, this means simply subtracting the relaxation term from the total interaction energy expression (denoted $BE_n$). The relaxation energy is defined as $E_R = \sum_i E(i) - nE_w$, where $E_w$ is the energy of an optimized

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**TABLE 2: Decomposition of the Energies for the Water Trimer. The Model Potentials Approximate the MP2/aug-cc-pVDZ Geometries within a Rigid-Body Framework**

| terms | | | interaction energy (kJ mol$^{-1}$) | | |
|---|---|---|---|---|---|
| $i$ | $j$ | $k$ | MP2 | ASP-W2 | ASP-W4 |
| | | | Geometry 1 | | |
| 1 | 2 | | −17.02 | −19.08 | −18.01 |
| 1 | 3 | | −15.46 | −17.46 | −16.70 |
| 2 | 3 | | −16.90 | −19.12 | −18.18 |
| 1 | 2 | 3 | −10.24 | −10.69 | −8.78 |
| | total 2-body | | −49.38 | −55.66 | −52.70 |
| | total 3-body | | −10.24 | −10.69 | −8.97 |
| | total energy | | −59.63 | −66.35 | −61.67 |
| | | | Geometry 2 | | |
| 1 | 2 | | −18.60 | −20.99 | −20.15 |
| 1 | 3 | | −18.60 | −20.99 | −20.15 |
| 2 | 3 | | 2.20 | 2.38 | 2.36 |
| 1 | 2 | 3 | 1.93 | 1.95 | 1.63 |
| | total 2-body | | −35.00 | −39.60 | −37.94 |
| | total 3-body | | 1.93 | 1.95 | 1.63 |
| | total energy | | −33.08 | −37.66 | −36.31 |
| | | | Geometry 3 | | |
| 1 | 2 | | −18.70 | −21.03 | −20.27 |
| 1 | 3 | | −18.70 | −21.03 | −20.27 |
| 2 | 3 | | 2.98 | 3.01 | 3.07 |
| 1 | 2 | 3 | 1.28 | 0.86 | 0.77 |
| | total 2-body | | −34.43 | −39.06 | −37.48 |
| | total 3-body | | 1.28 | 0.86 | 0.77 |
| | total energy | | −33.15 | −38.19 | −36.71 |

**TABLE 3: Percentage Contribution of the *n*-Body Terms for MP2/aug-cc-pVDZ and Model Potential Results for the Water Trimer**

| | MP2 geometry[a] | | model geometry[b] | |
|---|---|---|---|---|
| | 2-body | 3-body | 2-body | 3-body |
| | Geometry 1 | | | |
| MP2 | 82.8 | 17.2 | | |
| ASP-W2 | 83.9 | 16.1 | 85.0 | 15.0 |
| ASP-W4 | 85.5 | 14.5 | 88.2 | 11.8 |
| | Geometry 2 | | | |
| MP2 | 105.8 | −5.8 | | |
| ASP-W2 | 105.2 | −5.2 | 104.4 | −4.4 |
| ASP-W4 | 104.5 | −4.5 | 103.7 | −3.7 |
| | Geometry 3 | | | |
| MP2 | 103.8 | −3.8 | | |
| ASP-W2 | 102.3 | −2.3 | 101.6 | −1.6 |
| ASP-W4 | 102.1 | −2.1 | 102.5 | −2.5 |

*[a] Geometry approximated by the rigid monomers. [b] Optimized to the closest stationary point.*

water monomer at the same level of theory, and $E(i)$ is the energy of molecule $i$ in its distorted geometry in the complex.

## 3. Results and Discussion

Figure 2 shows the optimized ab initio geometries, all of which represent stationary points on the MP2/aug-cc-pVDZ potential energy surfaces. For the model potentials, we consider both the rigid-body approximations of these structures and the clusters relaxed to the nearest local stationary points. Most of the structures converged within about six steps, preserving the symmetry, although some of the optimized structures did not have the same Hessian index. For both the ab initio and model potential geometries, we present the complete breakdown of the total energy into its *n*-body components. In addition we tabulate, for comparison, the total percentage contributions of each *n*-body term for these two cases and for the optimized model potential geometries.

**3.1. Trimer.** From Tables 2 and 3 we observe that geometry 1 is significantly stabilized by the three-body contribution,

**TABLE 4: Decomposition of the Energies for the Water Tetramer. The Model Potentials Approximate the MP2/aug-cc-pVDZ Geometries within a Rigid-Body Framework**

| terms | | | | interaction energy (kJ mol$^{-1}$) | | |
|---|---|---|---|---|---|---|
| $i$ | $j$ | $k$ | $l$ | MP2 | ASP-W2 | ASP-W4 |
| | | | | Geometry 1 | | |
| 1 | 2 | | | −16.07 | −17.20 | −16.35 |
| 1 | 3 | | | −16.07 | −17.20 | −16.35 |
| 1 | 4 | | | −6.68 | −7.03 | −6.92 |
| 2 | 3 | | | −6.68 | −7.03 | −6.92 |
| 2 | 4 | | | −16.07 | −17.20 | −16.35 |
| 3 | 4 | | | −16.07 | −17.20 | −16.35 |
| 1 | 2 | 3 | | −6.52 | −7.11 | −6.04 |
| 1 | 2 | 4 | | −6.52 | −7.11 | −6.04 |
| 1 | 3 | 4 | | −6.52 | −7.11 | −6.04 |
| 2 | 3 | 4 | | −6.52 | −7.11 | −6.04 |
| 1 | 2 | 3 | 4 | −2.27 | −4.17 | −3.29 |
| | total 2-body | | | −77.64 | −82.85 | −79.25 |
| | total 3-body | | | −26.07 | −28.42 | −24.17 |
| | total 4-body | | | −2.27 | −4.17 | −3.29 |
| | total energy | | | −105.98 | −115.44 | −106.71 |
| | | | | Geometry 2 | | |
| 1 | 2 | | | −18.33 | −20.03 | −20.18 |
| 1 | 3 | | | 3.64 | 3.94 | 3.99 |
| 1 | 4 | | | −18.33 | −20.03 | −20.18 |
| 2 | 3 | | | −18.33 | −20.03 | −20.18 |
| 2 | 4 | | | 6.61 | 6.05 | 6.32 |
| 3 | 4 | | | −18.33 | −20.03 | −20.18 |
| 1 | 2 | 3 | | 1.76 | 1.85 | 1.63 |
| 1 | 2 | 4 | | 1.01 | 0.33 | 0.34 |
| 1 | 3 | 4 | | 1.76 | 1.85 | 1.63 |
| 2 | 3 | 4 | | 1.01 | 0.33 | 0.34 |
| 1 | 2 | 3 | 4 | −0.41 | −0.40 | −0.34 |
| | total 2-body | | | −63.04 | −70.12 | −70.41 |
| | total 3-body | | | 5.54 | 4.35 | 3.92 |
| | total 4-body | | | −0.41 | −0.40 | −0.34 |
| | total energy | | | −57.90 | −66.16 | −66.83 |
| | | | | Geometry 3 | | |
| 1 | 2 | | | −13.98 | −13.94 | −12.12 |
| 1 | 3 | | | −16.10 | −17.59 | −16.98 |
| 1 | 4 | | | −16.10 | −17.59 | −16.98 |
| 2 | 3 | | | −14.93 | −17.50 | −17.23 |
| 2 | 4 | | | −14.93 | −17.50 | −17.23 |
| 3 | 4 | | | 4.76 | 4.78 | 4.69 |
| 1 | 2 | 3 | | −8.51 | −8.66 | −7.27 |
| 1 | 2 | 4 | | −8.51 | −8.66 | −7.27 |
| 1 | 3 | 4 | | 1.66 | 1.78 | 1.53 |
| 2 | 3 | 4 | | 1.91 | 1.91 | 1.75 |
| 1 | 2 | 3 | 4 | 0.48 | 0.69 | 0.58 |
| | total 2-body | | | −71.28 | −79.35 | −75.86 |
| | total 3-body | | | −13.45 | −13.64 | −11.27 |
| | total 4-body | | | 0.48 | 0.69 | 0.58 |
| | total energy | | | −84.25 | −92.30 | −86.55 |
| | | | | Geometry 4 | | |
| 1 | 2 | | | −13.60 | −14.15 | −14.44 |
| 1 | 3 | | | −13.60 | −14.15 | −14.44 |
| 1 | 4 | | | −4.67 | −4.90 | −4.95 |
| 2 | 3 | | | 5.59 | 5.59 | 5.47 |
| 2 | 4 | | | −16.01 | −16.65 | −16.66 |
| 3 | 4 | | | −16.01 | −16.65 | −16.66 |
| 1 | 2 | 3 | | 2.75 | 2.66 | 2.48 |
| 1 | 2 | 4 | | −1.50 | −1.80 | −1.57 |
| 1 | 3 | 4 | | −1.50 | −1.80 | −1.57 |
| 2 | 3 | 4 | | 2.68 | 2.28 | 2.10 |
| 1 | 2 | 3 | 4 | 0.65 | 0.75 | 0.66 |
| | total 2-body | | | −58.31 | −60.93 | −61.68 |
| | total 3-body | | | 2.44 | 1.33 | 1.44 |
| | total 4-body | | | 0.65 | 0.75 | 0.66 |
| | total energy | | | −55.22 | −58.85 | −59.58 |

whereas for geometries 2 and 3, this term is repulsive but small. Therefore geometries 2 and 3 not only have an unfavorable two-body interaction between the end fragments but lack any three-body stabilization. The two-body components are always larger for the model potentials than for ab initio values, which is not

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**TABLE 5: Percentage Contribution of the *n*-Body Terms for MP2/aug-cc-pVDZ and Model Potential Results for the Water Tetramer**

|  | MP2 geometry[a] | | | model geometry[b] | | |
|---|---|---|---|---|---|---|
|  | 2-body | 3-body | 4-body | 2-body | 3-body | 4-body |
| | | | Geometry 1 | | | |
| MP2 | 73.3 | 24.6 | 2.1 | | | |
| ASP-W2 | 71.8 | 24.6 | 3.6 | 75.1 | 21.9 | 3.1 |
| ASP-W4 | 74.3 | 22.6 | 3.1 | 80.3 | 17.5 | 2.2 |
| | | | Geometry 2 | | | |
| MP2 | 108.9 | −9.6 | 0.7 | | | |
| ASP-W2 | 106.0 | −6.6 | 0.6 | 105.7 | −6.4 | 0.7 |
| ASP-W4 | 105.4 | −5.9 | 0.5 | 105.1 | −5.7 | 0.6 |
| | | | Geometry 3 | | | |
| MP2 | 84.6 | 16.0 | −0.6 | | | |
| ASP-W2 | 86.0 | 14.8 | −0.8 | 86.6 | 13.9 | −0.5 |
| ASP-W4 | 87.7 | 13.0 | −0.7 | 90.0 | 10.5 | −0.5 |
| | | | Geometry 4 | | | |
| MP2 | 105.6 | −4.4 | −1.2 | | | |
| ASP-W2 | 103.5 | −2.3 | −1.3 | 102.9 | −1.9 | −1.0 |
| ASP-W4 | 103.5 | −2.4 | −1.1 | 102.8 | −1.9 | −0.9 |

*[a]* Geometry approximated by the rigid monomers. *[b]* Optimized to the closest stationary point.

surprising since this level of theory obtains a smaller binding energy for the dimer than ASP-W2 and ASP-W4 (see Table 1). The three-body term, mediated by the induction contribution to the energy, compares reasonably well with the ab initio calculation, but it is underestimated for geometry 3. Note that ASP-W2 is in closer agreement with the ab initio result than ASP-W4 for the three-body term, but the opposite is true of the two-body contributions; ASP-W4 dimer has a binding energy closer to the ab initio value.

When optimized to the nearest local stationary points, the model potentials find the $C_{2v}$ geometries (2 and 3) to be first-order saddle points. Relaxing these to the closest minima yields slightly distorted ($C_2$) arrangements with ASP-W2, and with ASP-W4 for geometry 3 only. There seems to be no $C_2$ minimum for ASP-W4 close to geometry 2, which collapses to the global minimum on optimization. Table 3 shows that the two-body and three-body contributions to the energy do not change much on optimization of the structures.

**3.2. Tetramer.** Tables 4 and 5 show that the model potentials agree well with the ab initio calculations on the degree to which the three- and four-body terms contribute to the total energy. Generally, the two-body contributions are too large (as for the trimer). For geometry 2, the ab initio values of E(124) and E(234) (which are equal by symmetry) are considerably larger than those obtained by the model potentials, but we emphasize that larger basis calculations may have a significant effect on the many-body contributions. Table 5 shows how the contributions to the energy vary on optimization, and we note that in general the two-body energy increases.

We find that the potential energy surface is less well reproduced than for the trimer. Both ASP potentials find, in agreement with ab initio calculation, that the $S_4$ symmetry geometry 1 is a minimum and the $C_{2v}$ geometry 4 is an index 3 stationary point. Both ab initio calculation and the ASP-W4 potential find geometry 2 ($D_{2h}$ symmetry) to be a minimum, but according to ASP-W2 it is an index 2 stationary point (with imaginary normal mode frequencies of 59.7i and 62.7i cm$^{-1}$). On optimization, this collapses to the global minimum. Geometry 3 ($C_s$ symmetry) is a true saddle point according to the ab initio calculation but an index 2 stationary point according to both ASP-W2 and ASP-W4. Optimizing to the nearest transition state yields a $C_1$ structure, similar to geometry 3, with the major difference being the position of just one of the protons.

**TABLE 6: Decomposition of the Energies for the Water Pentamer. The Model Potentials Approximate the MP2/aug-cc-pVDZ Geometries within a Rigid-Body Framework**

| terms | | | | | interaction energy (kJ mol$^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| *i* | *j* | *k* | *l* | *m* | MP2 | ASP-W2 | ASP-W4 |
| | | | | | Geometry 1 | | |
| 1 | 2 | | | | −15.15 | −15.26 | −14.71 |
| 1 | 3 | | | | −4.20 | −4.35 | −4.29 |
| 1 | 4 | | | | −4.38 | −4.53 | −4.49 |
| 1 | 5 | | | | −15.04 | −15.19 | −14.78 |
| 2 | 3 | | | | −15.29 | −15.55 | −15.00 |
| 2 | 4 | | | | −4.73 | −4.93 | −4.88 |
| 2 | 5 | | | | −4.34 | −4.52 | −4.46 |
| 3 | 4 | | | | −13.09 | −12.32 | −12.03 |
| 3 | 5 | | | | −4.54 | −4.75 | −4.69 |
| 4 | 5 | | | | −15.21 | −15.59 | −15.05 |
| 1 | 2 | 3 | | | −6.24 | −6.88 | −5.85 |
| 1 | 2 | 4 | | | −1.51 | −1.55 | −1.41 |
| 1 | 2 | 5 | | | −6.30 | −6.91 | −5.90 |
| 1 | 3 | 4 | | | −1.45 | −1.48 | −1.34 |
| 1 | 3 | 5 | | | −1.39 | −1.41 | −1.28 |
| 1 | 4 | 5 | | | −6.34 | −6.93 | −5.93 |
| 2 | 3 | 4 | | | −5.87 | −6.38 | −5.44 |
| 2 | 3 | 5 | | | −1.49 | −1.51 | −1.37 |
| 2 | 4 | 5 | | | −1.46 | −1.50 | −1.36 |
| 3 | 4 | 5 | | | −6.12 | −6.72 | −5.70 |
| 1 | 2 | 3 | 4 | | −0.95 | −1.46 | −1.19 |
| 1 | 2 | 3 | 5 | | −0.97 | −1.52 | −1.24 |
| 1 | 2 | 4 | 5 | | −1.00 | −1.56 | −1.28 |
| 1 | 3 | 4 | 5 | | −1.03 | −1.53 | −1.25 |
| 2 | 3 | 4 | 5 | | −1.01 | −1.50 | −1.23 |
| 1 | 2 | 3 | 4 | 5 | −0.35 | −0.96 | −0.74 |
| | total 2-body | | | | −95.96 | −96.97 | −94.38 |
| | total 3-body | | | | −38.19 | −41.26 | −35.59 |
| | total 4-body | | | | −4.96 | −7.58 | −6.20 |
| | total 5-body | | | | −0.35 | −0.96 | −0.74 |
| | total energy | | | | −139.46 | −146.76 | −136.91 |
| | | | | | Geometry 2 | | |
| 1 | 2 | | | | −9.04 | −9.87 | −9.75 |
| 1 | 3 | | | | −12.93 | −13.71 | −12.08 |
| 1 | 4 | | | | −13.66 | −17.57 | −17.22 |
| 1 | 5 | | | | −13.92 | −16.63 | −16.48 |
| 2 | 3 | | | | −13.23 | −12.45 | −11.32 |
| 2 | 4 | | | | −15.25 | −16.30 | −16.05 |
| 2 | 5 | | | | −15.71 | −15.88 | −15.69 |
| 3 | 4 | | | | −7.50 | −8.09 | −7.99 |
| 3 | 5 | | | | −6.32 | −6.90 | −6.77 |
| 4 | 5 | | | | 6.07 | 6.06 | 5.93 |
| 1 | 2 | 3 | | | −8.39 | −8.92 | −7.45 |
| 1 | 2 | 4 | | | −3.20 | −3.43 | −2.92 |
| 1 | 2 | 5 | | | −3.32 | −3.74 | −3.21 |
| 1 | 3 | 4 | | | −5.84 | −6.24 | −5.39 |
| 1 | 3 | 5 | | | −5.23 | −5.55 | −4.74 |
| 1 | 4 | 5 | | | 3.37 | 3.19 | 2.75 |
| 2 | 3 | 4 | | | −4.54 | −4.78 | −3.99 |
| 2 | 3 | 5 | | | −5.47 | −5.84 | −4.98 |
| 2 | 4 | 5 | | | 3.25 | 2.82 | 2.53 |
| 3 | 4 | 5 | | | 0.23 | 0.22 | 0.22 |
| 1 | 2 | 3 | 4 | | −1.33 | −2.31 | −1.82 |
| 1 | 2 | 3 | 5 | | −1.38 | −2.67 | −2.11 |
| 1 | 2 | 4 | 5 | | 0.79 | 1.03 | 0.86 |
| 1 | 3 | 4 | 5 | | 0.08 | 0.28 | 0.22 |
| 2 | 3 | 4 | 5 | | 0.26 | 0.17 | 0.15 |
| 1 | 2 | 3 | 4 | 5 | 0.14 | 0.18 | 0.14 |
| | total 2-body | | | | −101.48 | −111.33 | −107.40 |
| | total 3-body | | | | −29.14 | −32.28 | −27.20 |
| | total 4-body | | | | −1.59 | −3.50 | −2.70 |
| | total 5-body | | | | 0.14 | 0.18 | 0.14 |
| | total energy | | | | −132.07 | −146.93 | −137.15 |

**3.3. Pentamer.** A previous study of the water pentamer[19] has found that contrary to some HF, DFT, and MP2 calculations, the two ASP potentials do not support the cyclic structure as the global minimum. Here we study both the cyclic structure and a cage minimum. The latter is found to lie about 7 kJ mol$^{-1}$

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**TABLE 7: Percentage Contribution of the *n*-Body Terms for MP2/aug-cc-pVDZ and Model Potential Results for the Water Pentamer**

| | MP2 geometry[a] | | | | model geometry[b] | | | |
|---|---|---|---|---|---|---|---|---|
| | 2-body | 3-body | 4-body | 5-body | 2-body | 3-body | 4-body | 5-body |
| | | | | Geometry 1 | | | | |
| MP2 | 68.81 | 27.38 | 3.56 | 0.25 | | | | |
| ASP-W2 | 66.07 | 28.11 | 5.16 | 0.65 | 71.68 | 23.64 | 4.17 | 0.50 |
| ASP-W4 | 68.93 | 26.00 | 4.53 | 0.53 | 77.03 | 19.50 | 3.13 | 0.34 |
| | | | | Geometry 2 | | | | |
| MP2 | 76.84 | 22.07 | 1.20 | −0.11 | | | | |
| ASP-W2 | 75.77 | 21.97 | 2.38 | −0.12 | 78.50 | 19.76 | 1.85 | −0.12 |
| ASP-W4 | 78.31 | 19.83 | 1.97 | −0.10 | 83.56 | 15.32 | 1.19 | −0.08 |

[a] Geometry approximated by the rigid monomers. [b] Optimized to the closest stationary point.

**TABLE 8: Rms Deviation of the ASP Energies from MP2 (kJ mol$^{-1}$), Using the Model Potentials at MP2 Geometries**

| | ASP-W2 | ASP-W4 |
|---|---|---|
| 2-body | 1.37 | 1.17 |
| 3-body | 0.39 | 0.55 |
| 4-body | 0.74 | 0.39 |
| 5-body | 0.43 | 0.28 |

higher in energy by the ab initio calculations. For each model potential, the energies predicted for the two structures are very similar. After optimization, for ASP-W2 the ring is about 0.07 kJ mol$^{-1}$ lower in energy than the cage, and for ASP-W4 the ring is more stable by about 4 kJ mol$^{-1}$. As noted above, the ring structure is not the global minimum for either of these potentials, and lower energy cage structures have been found with slightly different orientations of the protons. From Table 6 we see that for geometry 1 (cyclic) there is generally good agreement between the two-body terms for the different methods. However, for geometry 2 (the cage) the agreement is less good (especially $E(14)$ and $E(15)$), and the total two-body energy is more negative than found from ab initio calculation by about 10 kJ mol$^{-1}$ for ASP-W2 and 6 kJ mol$^{-1}$ for ASP-W4. Therefore, it appears that the erroneous ordering of these two minima is primarily a consequence of the two-body contributions. From Table 7 we can deduce that the importance of the many-body terms diminishes quite quickly. For the cyclic structures, from ab initio calculation, the highest order term contributes 17.2, 2.1, and 0.25% for the trimer, tetramer, and pentamer, respectively (the model potential results yielding similar magnitudes).

We have collected the rms deviations of the ASP and MP2 energies in Table 8 to give a general indication of the differences yielded by the two methods. More detailed comparison is at present not helpful, as the errors in both the ab initio and model potential calculations are probably of a similar magnitude. As an example, the difference in energy between uncorrected and counterpoise-corrected calculations on the cyclic pentamer is 27.9 kJ mol$^{-1}$, and the deformation energy (not accounted for by our rigid-body potentials) for the same structure is 5.8 kJ mol$^{-1}$. For an indication of the quality of basis required to significantly reduce the effects of BSSE, we refer the reader to results for the water dimer in ref 39, the binding energy varying by several kJ mol$^{-1}$ for aug-cc-pVDZ through aug-cc-pV5Z. However, at present, MP2 calculations close to the basis set limit for these larger systems are not feasible.

## 4. Conclusions

In this study we have benchmarked the ability of two model interaction potentials for water to reproduce the many-body interaction energy terms for several isomers of water clusters up to the pentamer. In general, the agreement is quite satisfactory, the main limitation being the inability of the model potentials to obtain the correct global minimum for the water pentamer potential energy surface. However, both model potentials accurately reproduce, for the first time, the results of high-level ab initio calculations regarding the binding energy of the water dimer.[39,42] Considering that these model potentials were formulated for the water dimer including only one many-body term in the energy, the results are very encouraging. The performance of these potentials for bulk water simulations will be tested in future studies.

Advances have been made that will allow the improvement of model potentials using symmetry-adapted perturbation theory (SAPT): see the recent review of Jeziorski et al.[43] For example, the repulsion within the framework of our model potentials does not account for electron correlation, which could contribute significantly,[44,45] and it would be more satisfactory to include the dispersion energy calculated at an equivalent level of theory: we have not used the IMPT dispersion surface because the electron repulsion is not treated in a self-consistent manner. A future aim is the development of the next generation of ASP potentials within the SAPT framework, and this work is in progress.

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