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Water 26-mers Drawn from Bulk Simulations: Benchmark Binding Energies for Unprecedentedly Large Water Clusters and Assessment of the Electrostatically Embedded Three-Body and Pairwise Additive Approximations

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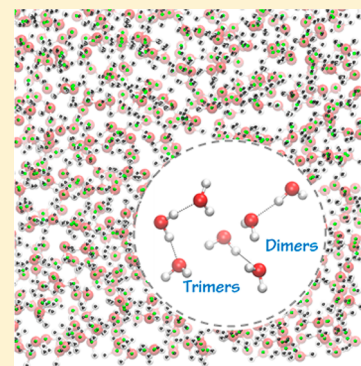
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S Supporting Information

ABSTRACT: It is important to test methods for simulating water, but small water clusters for which benchmarks are available are not very representative of the bulk. Here we present benchmark calculations, in particular CCSD(T) calculations at the complete basis set limit, for water 26-mers drawn from Monte Carlo simulations of bulk water. These clusters are large enough that each water molecule participates in 2.5 hydrogen bonds on average. The electrostatically embedded three-body approximation with CCSD(T) embedded dimers and trimers reproduces the relative binding energies of eight clusters with a mean unsigned error (MUE, kcal per mole of water molecules) of only 0.009 and 0.015 kcal for relative and absolute binding energies, respectively. Using only embedded dimers (electrostatically embedded pairwise approximation) raises these MUEs to 0.038 and 0.070 kcal, and computing the energies with the M11 exchange-correlation functional, which is very economical, yields errors of only 0.029 and 0.042 kcal.



SECTION: Liquids; Chemical and Dynamical Processes in Solution

Quantum mechanical electronic structure calculations are now being applied to calculate energies and forces for larger and more complex problems. However, the cost of accurate calculations on large systems increases as a high power of system size, for example, as the seventh power for calculations on large systems by the widely used and generally highly accurate CCSD(T) method (this acronym denotes coupled cluster theory with single and double excitations and a quasiperturbative treatment of connected triple excitations¹). One way to circumvent the cost is to use fragment methods, where one breaks up the system into monomers, out of which one forms fragments (e.g., dimers, trimers, ...), and the energy and forces of the entire system are approximated by a series of calculations on the fragments.

Fragment methods hold great promise for extending accurate quantum mechanical calculations to larger systems because, for large enough systems, the cost scales as a low power of the number of monomers rather than with the intrinsic scaling power of the quantum mechanical method. By omitting interactions between distant monomers, one can make the number of fragments to be considered and hence the amount of computational work to be done on large systems scale only linearly ($N \ln N$) with system size. For systems of moderate

size, where the saving from neglecting long-range interactions is not fully realized, the scaling power is higher, for example, quadratic scaling for pairwise additive methods or cubic scaling for methods including all trimers.

Fragment methods are so appealing that a large number of different fragment methods have been proposed.^{2–15} It is important to test them to learn which methods give the highest accuracy for a given cost and to validate the more accurate methods so that one has an idea about how reliable applications employing them may be. However, here we run into a difficulty. The natural domain of application of fragment methods is very large systems, but accurate results are usually not available for validation on large systems; however, validation on small systems might be unrepresentative of performance in applications to large and complex systems. Consider, for example, fragment methods designed for studying processes in aqueous solution. Fragment methods were tested against CCSD(T) calculations on hexamers,¹³ which have interesting

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hydrogen bond structures, but every water molecule in a hexamer is on the surface and is unrepresentative of the bulk.

Coupled cluster calculations were not affordable for larger clusters, but more approximate calculations were used for testing by asking whether a fragment method with a given electronic structure method reproduces a calculation on the entire system with the same method. In this way, we made tests using Møller–Plesset second order perturbation theory (MP2) on clusters as large as $(\text{H}_2\text{O})_{20}$ ¹⁴ and especially on optimized $(\text{H}_2\text{O})_{16}$ and $(\text{H}_2\text{O})_{17}$ clusters,¹⁵ which are just at the border of the size where one begins to find tetra-coordinated water molecules. These tests are valuable but have three characteristics upon which one would like to improve: (i) the water clusters are still not large enough to contain several tetra-coordinated water molecules; (ii) optimized clusters are less representative of the structures found in the bulk than are clusters sampled from a molecular dynamics or Monte Carlo simulation of a thermal ensemble of the bulk liquid, and (iii) it is less reliable to make tests with a method like MP2 than to test against the more accurate standard of CCSD(T) with a complete basis set (CBS). In the present paper we circumvent all three drawbacks. In particular, we report calculations on larger clusters, $(\text{H}_2\text{O})_{26}$, that are drawn from bulk simulations, and we test against CCSD(T)/CBS calculations. These dramatically improved tests are made possible by recent advances in electronic structure calculations that allow CCSD(T)/CBS calculations for much larger systems than previously possible. In particular, we present CCSD(T)/CBS results obtained by a fully automated implementation¹⁶ of the incremental scheme proposed by Stoll.¹⁷

There are two ways to test fragment methods. (1) One is to see if the fragment method can reproduce a full calculation at the same level of theory. (2) The other is to compare fragment calculations that are inexpensive enough to be affordable for lengthy simulations to accurate results obtained by any method (experiment or benchmark-quality theory). In the past, we and others have presented both kinds of comparisons, and both are valuable. The present paper emphasizes type-2 comparisons. The reason that type-2 comparisons are especially interesting at the present time is that the CCSD(T)/CBS benchmarks we present are for an unprecedentedly large water cluster, so that this paper pushes the boundary of available type-2 validations.

Test Systems. We consider clusters selected from a snapshot of an equilibrated simulation ($T = 298$ K and $p = 1$ atm) with 1024 rigid water molecules (bond length 0.9572 Å, bond angle 104.52 deg), using the TIP4P force field¹⁸ with periodic boundary conditions and Ewald summation. Eight $(\text{H}_2\text{O})_{26}$ clusters were carved from this snapshot. Each cluster contains the 26 water molecules whose centers of mass were closest to the center of each of the eight octants of the simulation cell.

Results and Discussion. The binding energy of each cluster was calculated by the incremental CCSD(T)(F12*)/IMP2-F12 method¹⁹ with the cc-pVTZ-F12²⁰ basis set. This method essentially yields the complete basis set limit of CCSD(T), and so we denote it as CCSD(T)/CBS.

We define the binding energy as cluster electronic energy (including nuclear repulsion) relative to the energy of separated monomers. With this definition, the clusters studied here have binding energies of -111.3 to -151.8 kcal/mol (i.e., per mole of $(\text{H}_2\text{O})_{26}$). The average binding energy is -130.6 kcal/mol with a standard deviation of 13.9 kcal/mol. To facilitate comparison with bulk water and other clusters, all energies in the rest of this Letter will be stated per mole of water

molecules. Making this conversion yields an average binding energy of -5.02 kcal/mol with a standard deviation of 0.54 kcal/mol.

The first thing we notice about the values in the preceding paragraph is that clusters drawn from simulations have much less negative binding energies than optimized clusters of the kind usually used for testing theory, and they are much more diverse. Consider, for example, the five optimized $(\text{H}_2\text{O})_{16}$ clusters of our previous cluster study.¹⁵ Those clusters have an average binding energy of -10.67 kcal/mol with a standard deviation of 0.014 kcal/mol. Thus even though the present clusters have a much higher fraction of interior monomers, their condition of not being optimized means that they are much more weakly bound.

To further characterize the $(\text{H}_2\text{O})_{26}$ clusters, we counted the hydrogen bonds. Using the definition of a hydrogen bond suggested by Wernet et al.²¹ we found 33–37 such hydrogen bonds per cluster, corresponding to an average of 1.35 hydrogen bonds per monomer with a standard deviation of 0.065. Since each hydrogen bond involves two monomers, this implies that each monomer participates on average in 2.7 hydrogen bonds, somewhat smaller than the value of 3.3 of bulk liquid water because the clusters contain a significant fraction of exterior molecules. We also counted the number of water monomers in these clusters with various numbers of hydrogen bonds and found, on average, 7%, 15%, 31%, 34%, and 13% are involved in five, four, three, two, and one hydrogen bond.

In the present Letter we use the benchmark results to test the standard many-body expansion, which can be truncated at the two-body level (called pairwise additive or PA approximation) or the three-body level (called the three-body or 3B approximation) and also to test electrostatically embedded (EE) PA and 3B approximations.^{3–5} In EE-PA and EE-3B calculations, each monomer and dimer is calculated in a background of point charges at the nuclei of the other monomers, and in the latter the trimers are also embedded. The background charges for these calculations are taken from CHelpG analysis²² of rigid monomer calculations carried out with Kohn–Sham density functional theory²³ (KS theory) using the M06-2X exchange-correlation functional²⁴ and the 6-311+G(2df,2p) basis set;²⁵ this yields $q_{\text{H}} = 0.361158$ for the charge on H and $-2q_{\text{H}}$ for the charge on O. (For H and O, the 6-311+G(2df,2p) basis set is the same as the MG3S basis set,²⁶ and henceforth we will use the shorter name.)

In testing the approximate methods, we consider both relative binding energies and absolute binding energies. With eight clusters, we have $8 \times 7/2 = 28$ pairs of structures and hence 28 relative binding energies, and we compute the mean unsigned error (MUE) by averaging the absolute deviation from the benchmark results over all of them. For absolute binding energies, we compute both the MUE and the mean signed error (MSE).

Table 1 shows the errors for electrostatically embedded many-body calculations where the fragments are calculated by coupled cluster theory, either CCSD(T)-F12b²⁷ or CCSD-F12b,²⁸ both with a cc-pVDZ-F12 basis set. The MUEs of the relative binding energies are pleasingly small, ranging from 0.009 kcal/mol for CCSD(T)-F12b:EE-3B calculations to 0.054 kcal/mol for CCSD-F12b:EE-PA calculations. These mean errors are 72 to 12 times smaller than the mean relative binding energy and 44 to 7 times smaller than the standard deviation of the relative binding energies. In the classical rigid-molecule approximation, a free water molecule would have 3RT

Table 1. Mean Errors (kcal per Mole of Water Molecules) for Electrostatically Embedded Many-Body Approximations

method	EE-3B	EE-PA
Mean Unsigned Error in 28 Relative Binding Energies (Average: 0.651; Standard Deviation: 0.395)		
CCSD(T)-F12b/cc-pVDZ-F12	0.009	0.038
CCSD-F12b/cc-pVDZ-F12	0.031	0.054
Mean Signed Error in 8 Absolute Binding Energies ^a (Average: -5.02; Standard Deviation: 0.54)		
CCSD(T)-F12b/cc-pVDZ-F12	-0.015	-0.070
CCSD-F12b/cc-pVDZ-F12	0.47	0.39

^aThe table gives the MSE, but for all cases the MUE is the absolute value of the mean signed error. The absolute binding energy is negative, and a negative (positive) signed error corresponds to overbinding (underbinding).

of thermal energy, and 0.009 kcal/mol is only 0.5% of 3RT at 298 K. Clearly the electrostatically embedded many-body theory is a success, and this is the best evidence yet that EE-PA and EE-3B should provide useful results for calculations on bulk water.

Table 1 shows that CCSD(T)-F12b:EE-3B errors in absolute binding energies are only slightly larger than those in the relative binding energies. The difference is larger for CCSD(T)-F12b:EE-PA and large for CCSD-F12b-based calculations. However, since the absolute binding energies are an order of magnitude larger than the relative binding energies, the errors are still encouragingly small, especially for CCSD(T)-F12b, where they are 335 (EE-3B) or 72 (EE-PA) times smaller than the average binding energy.

Table 2 shows relative computer times for applying these methods to an (H₂O)₂₆ cluster. (Computer times, even relative

Table 2. Relative Computer Times^a for a Calculation on (H₂O)₂₆

method	EE-3B	EE-PA	3B	PA ^a
CCSD(T)-F12b/cc-pVDZ-F12	1500	15		
CCSD-F12b/cc-pVDZ	440	6		
M11/maug-cc-pVTZ	50	4	50	4
M11/MG3S	50	5	50	5
M06-2X/MG3S	50	1	50	1

^aRounded to the nearest integer if less than 10 or to the nearest round number otherwise.

ones, depend significantly on the size of the system, the basis set, the software, the machine and its load, and the compiler and operating system; thus one should not draw conclusions based on small differences, but when used with caution, they provide perspective in evaluating the potential usefulness of various methods.) For CCSD(T)-F12b fragments, EE-3B is 2 orders of magnitude more demanding in computer time than is EE-PA. The table also shows timings for KS theory with three different methods, where a KS method is a combination of basis set (MG3S or maug-cc-pVTZ²⁹) and exchange-correlation functional (M06-2X or M11³⁰). KS theory reduces the cost ratio of EE-3B to EE-PA from 2 orders of magnitude to 1. Thus it is useful to also consider employing KS theory for the fragments.

The timings show the negligible cost of the EE operation. Although the number of point charges grows with the size of the system, the cost of the EE operations remains negligible

because it simply involves adding inexpensive analytic one-electron integrals into the energy calculations.

Before considering the KS theory results, we summarize the nature of the exchange-correlation functionals considered here. M06-2X and M11 are hybrid meta-GGAs. M06-2X has 54% Hartree–Fock exchange (HFE) as a global constant. M11 has range-separated exchange with 42.8% HFE at small interelectronic separations and 100% HFE at long interelectronic separations. Both functionals have good accuracy on broad databases of chemical properties.³¹ Hybrid functionals are orders of magnitude more expensive than less accurate local functionals for periodic calculations, but the cost difference is much smaller for the fragments of the present calculations.

For KS theory, we consider both straight many-body calculations and electrostatically embedded ones. The mean errors are in Table 3. For KS fragments, we see no advantage in

Table 3. Mean Errors (kcal per Mole of Water Molecules) for Many-Body and Electrostatically Embedded Many-Body Approximations

method	EE-3B	EE-PA	3B	PA
Mean Unsigned Error in 28 Relative Binding Energies (Average: 0.651; Standard Deviation: 0.395)				
M11/maug-cc-pVTZ	0.064	0.032	0.058	0.27
M11/MG3S	0.063	0.029	0.056	0.24
M06-2X/MG3S	0.046	0.061	0.050	0.23
Mean Signed Error in 8 Absolute Binding Energies ^a (Average: -5.02; Standard Deviation: 0.54)				
M11/maug-cc-pVTZ	0.39	0.55	0.34	0.89
M11/MG3S	-0.092	0.042	-0.12	0.30
				(0.31)
M06-2X/MG3S	-0.37	-0.73	-0.36	-0.48

^aThe MUE in the absolute binding energy is given in parentheses when it differs from the MSE. The absolute binding energy is negative, and a negative (positive) signed error corresponds to overbinding (underbinding). For the EE calculations, for each method we calculated a new set of embedding charges with the method under consideration but the differences are small (values are given in the Supporting Information).

going to EE-3B; one can always obtain better answers with either EE-PA or 3B, sometimes with both. Averaging over the three methods, over EE-PA and EE-3B, and over relative and absolute binding energies, the KS fragment calculations have roughly the same accuracy as the CCSD ones, but at much lower cost for EE-3B, and (H₂O)₂₆ is already large enough the cost is also significantly lower for EE-PA. The newer M11 functional is more accurate than M06-2X for this application; the results with M11/MG3S are uniformly excellent for both the 3B and EE-PA approximations (and also for the more expensive EE-3B approximation) for both relative and absolute binding energies. The less costly EE-PA approximation is more accurate than the 3B approximation.

Possible Improvements. We also examined some possible improvements on the EE-PA method, in particular, EE-PA for the correlation energy,^{13,14} EE-PA for the nonlocal energy,¹⁵ and EE-PA for a higher-level energy,¹⁵ but the errors did not go down enough for the present application to merit the additional complications. We also found that the jun-cc-pVTZ basis³² did not offer significant improvement over maug-cc-pVTZ. Full results are in Supporting Information.

In conclusion, the CCSD(T)-F12b:EE-3B approximation reproduces the CCSD(T)/CBS results for (H₂O)₂₆ with a

mean unsigned error of only 0.009 kcal (per mole of water molecules) for relative energies and 0.015 kcal/mol for absolute binding energies. The EE-PA approximation has MUEs of respectively 0.038 and 0.070 kcal/mol for these quantities. Using KS theory with M11/MG3S for the EE-PA dimers lowers the cost for $(\text{H}_2\text{O})_{26}$ by a factor of 300 with respect to CCSD(T)-F12b:EE-3B and a factor of 3 with respect to CCSD(T)-F12b:EE-PA (the factors would be larger for bigger clusters), but the errors remain encouragingly small at 0.029 and 0.042 kcal/mol for relative and absolute binding energies, respectively.

■ ASSOCIATED CONTENT

Supporting Information

Computational details for CCSD(T) calculations by incremental scheme, embedding charges, more hydrogen bond counts, coordinates of the eight structures, and full tables of raw data. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

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