

On the accuracy of density-functional theory exchange-correlation functionals for H bonds in small water clusters: Benchmarks approaching the complete basis set limit

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(Received 13 July 2007; accepted 4 September 2007; published online 9 November 2007)

The ability of several density-functional theory (DFT) exchange-correlation functionals to describe hydrogen bonds in small water clusters (dimer to pentamer) in their global minimum energy structures is evaluated with reference to second order Møller-Plesset perturbation theory (MP2). Errors from basis set incompleteness have been minimized in both the MP2 reference data and the DFT calculations, thus enabling a consistent systematic evaluation of the true performance of the tested functionals. Among all the functionals considered, the hybrid X3LYP and PBE0 functionals offer the best performance and among the nonhybrid generalized gradient approximation functionals, mPWLYP and PBE1W perform best. The popular BLYP and B3LYP functionals consistently underbind and PBE and PW91 display rather variable performance with cluster size. © 2007 American Institute of Physics. [DOI: 10.1063/1.2790009]

I. INTRODUCTION

Density-functional theory (DFT) is the most popular theoretical approach for determining the electronic structures of polyatomic systems. It has been extensively and successfully used to tackle all sorts of problems in materials science, condensed matter physics, molecular biology, and countless other areas. Many of these studies have involved the treatment of systems containing hydrogen bonds. Hydrogen bonds are weak (10–30 kJ/mol \approx 100–300 meV/H bond) bonds of immense widespread importance, being the intermolecular force responsible for holding water molecules together in the condensed phase, the two strands of DNA in the double helix, and the three dimensional structure of proteins.¹ A particularly important class of H-bonded systems is small water clusters. Small water clusters have been implicated in a wide range of phenomena (for example, environmental chemistry and ice nucleation^{2,3}) and, moreover, are thought to provide a clue as to the properties of liquid water. However, the ability of DFT to quantitatively describe H bonds between H₂O molecules in either small water clusters or the liquid state remains unclear. This is particularly true in light of recent experimental and theoretical studies, which have raised concerns over the ability of DFT to reliably describe the structure and properties of liquid water.^{4–10}

It is now well established that the simplest approximation to the electron exchange and correlation (XC) potential, the local-density approximation (LDA), is inappropriate for

treating H bonds. For example, the dissociation energies of small water clusters and the cohesive energy of ice are overestimated by $>50\%$ with the LDA.^{11–14} However, despite widespread practical application and several recent benchmark studies, it remains unclear precisely how well the many popular post-LDA functionals perform at describing H bonds between water clusters. Generalized gradient approximation (GGA) functionals such as PBE,¹⁵ PW91,¹⁶ and BLYP,^{17,18} for example, are widely used to examine liquid water,^{4–7,10} ice,^{14,19–21} and adsorbed water,^{19,22} yet ask three experts which one is “best” and one is likely to receive three different answers. Likewise, unanimity has not been reached on the performance of the many meta-GGA or hybrid functionals that are available, such as TPSS,²³ PBE0,²⁴ and B3LYP.^{18,25–27} Part of the reason for the lack of clarity, we believe, stems from the fact that in previous benchmark studies, insufficiently complete basis sets were employed and that comparisons were restricted to the simplest H-bonded systems involving H₂O, namely, the H₂O dimer and trimer. Basis set incompleteness effects can, of course, mask the true performance of a given functional and, as we will show below, the ability of a given functional to accurately predict the strength of the H bond in the dimer or even the trimer does not necessarily reveal how well that functional will perform even for the next largest clusters, tetramers, and pentamers.

In the following, we report a study in which the ability of several GGA, meta-GGA, and hybrid functionals to compute the energy and structure of H bonds between H₂O molecules is evaluated. So as to enable the use of large basis sets, which we demonstrate approach the complete basis set

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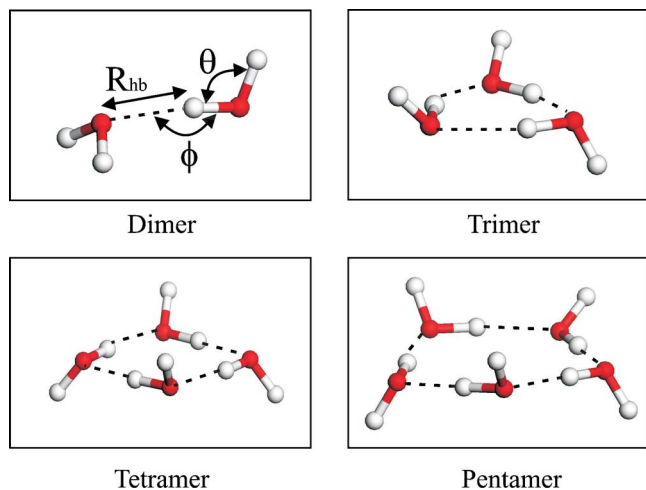


FIG. 1. (Color online) Structures of the four water clusters examined here in their global minimum energy configurations. The dashed lines indicate H bonds. Some of the structural parameters of the H bond are indicated alongside the dimer. We note that in the trimer, tetramer, and pentamer there is one H bond per water molecule.

(CBS) limit, in the generation of the benchmark data and the DFT data itself, this study is limited to the four smallest H_2O clusters (dimer, trimer, tetramer, and pentamer). In addition, this study is restricted to the established lowest energy conformer of each cluster,^{28–30} which, for orientation purposes, we show in Fig. 1. For this admittedly small structural data set, we find that, of the functionals tested, the hybrid X3LYP (Ref. 31) and PBE0 (Ref. 24) functionals offer the best performance. Among the regular (pure) GGAs, mPWLYP (Refs. 18 and 32) and PBE1W (Ref. 33) perform best. BLYP (Refs. 17 and 18) and B3LYP (Refs. 18 and 25–27) predict too weak H bonds and PBE (Ref. 15) and PW91 (Ref. 16) display rather variable performance with cluster size. Although MPWB1K,³⁴ PW6B95,³⁵ and B98 (Ref. 36) were previously shown to offer outstanding performance for water, this is not now the case when highly accurate basis sets are used.

II. REFERENCE DATA: MP2

For a systematic benchmark study such as this, reliable reference data are essential. Experiment is, in principle, one source of these data. However, experimental dissociation energies are simply not available or do not come with sufficiently small error bars for all the H_2O clusters we examine here. Further, with our aim to systematically evaluate the performance of many DFT XC functionals, it becomes impractical to compute all the small contributions to the experimental dissociation energy that come on top of the total electronic dissociation energy—an easily accessible total energy difference—such as zero point vibrations, relativistic contributions, etc. The obvious alternative source of reference data are the results obtained from correlated quantum chemistry methods such as second order Møller-Plesset perturbation theory³⁷ (MP2) or coupled-cluster theory.³⁸ Indeed, such methods have been widely applied to examine H-bonded systems.^{28,33,39–50} In particular, coupled cluster with single and double excitations plus a perturbative correction for con-

nected triples [CCSD(T)] produces essentially “exact” answers if sufficiently accurate basis sets are used. For example, the best CCSD(T) value for the binding energy of the water dimer is at 217.6 ± 2 meV (Ref. 51) in good agreement with the appropriate experimental number of 216.8 ± 30 meV.^{52,53} However, since the computational cost of CCSD(T) formally scales as N^7 , where N is the number of basis functions, the most extravagant use of computational power is required for CCSD(T) calculations with large basis sets. MP2, on the other hand, scales as N^5 and when compared to CCSD(T) for water dimers and trimers at the CBS limit yields binding energies that differ by no more than 2 meV/H bond.^{43,44} In addition, a recent study of water hexamers using CCSD(T) with an aug-cc-pVTZ basis set revealed that the MP2 and CCSD(T) dissociation energies of various hexamer structures differ by <3 meV/ H_2O .⁵⁴ Thus, MP2 is a suitable method for obtaining reference data with an accuracy to within a few meV/H bond. Such accuracy, which is well beyond the so-called chemical accuracy (1 kcal \approx 43 meV), is essential in studies of H-bonded systems. Since MP2 geometries are not available for all four clusters examined here, we have computed new MP2 structures for each one. All calculations have been performed with the GAUSSIAN03 (Ref. 55) and NWCHEM (Ref. 56) codes and all geometries were optimized with an aug-cc-pVTZ basis set within the “frozen core” approximation, i.e., correlations of the oxygen $1s$ orbital were not considered.⁵⁷ Although the aug-cc-pVTZ basis set is moderately large (92 basis functions/ H_2O), this finite basis set will introduce errors in our predicted MP2 structures. However, a test with the H_2O dimer reveals that the aug-cc-pVTZ and aug-cc-pVQZ MP2 structures differ by only 0.004 Å in the O–O bond length and 0.16° in the H bond angle (ϕ , Fig. 1). Likewise, Nielsen *et al.* have shown that the MP2 O–O distances in the cyclic trimer differ by 0.006 Å between the aug-cc-pVTZ and aug-cc-pVQZ basis sets with all other bonds differing by <0.003 Å.⁴⁹ For our present purposes, these basis set incompleteness errors on the structures are acceptable and it seems reasonable to assume that the aug-cc-pVTZ structures reported here come with error bars of ± 0.01 Å for bond lengths and $\pm 0.5^\circ$ for bond angles.

Total energies and dissociation energies are known to be more sensitive to basis set incompleteness effects than the geometries are. To obtain reliable MP2 total energies and dissociation energies, we employ the aug-cc-pVTZ, aug-cc-pVQZ (172 basis functions/ H_2O), and aug-cc-pV5Z (287 basis functions/ H_2O) basis sets in conjunction with the well-established methods for extrapolating to the CBS limit. Usually, the extrapolation schemes rely on extrapolating separately the Hartree-Fock (HF) and correlation contributions to the MP2 total energy. For extrapolation of the HF part, we use Feller’s exponential fit,⁵⁸

$$E_X^{\text{HF}} = E_{\text{CBS}}^{\text{HF}} + Ae^{-BX}, \quad (1)$$

where X is the cardinal number corresponding to the basis set ($X=3, 4,$ and 5 for the aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets, respectively). E_X^{HF} is the corresponding HF energy, $E_{\text{CBS}}^{\text{HF}}$ is the extrapolated HF energy at the CBS limit, and A and B are fitting parameters. For the correlation

part of the MP2 total energy, we follow an inverse power of highest angular momentum equation,^{59–61}

$$E_X^{\text{corr}} = E_{\text{CBS}}^{\text{corr}} + CX^{-3} + DX^{-5}, \quad (2)$$

where E_X^{corr} is the correlation energy corresponding to X , $E_{\text{CBS}}^{\text{corr}}$ is the extrapolated CBS correlation energy, and C and D are fitting parameters. We have tested various extrapolation schemes available in the literature^{58–64} and did not see a difference of more than 1.2 meV/H bond between all the predicted CBS values. We opted for the scheme provided by Eqs. (1) and (2) because we found that with the input from triple-, quadruple-, and pentuple- ζ basis sets, this method was best able to predict the total energy of a water monomer and dimer explicitly calculated with an aug-cc-pV6Z basis set (443 basis functions/H₂O). Having obtained MP2 CBS total energies for the H₂O monomer and each of the H₂O clusters, we thus arrive at the MP2 CBS electronic dissociation energies (D_e^n) per H bond which are given by

$$D_e^n = (E^{n\text{H}_2\text{O}} - nE^{\text{H}_2\text{O}})/n_{\text{H bond}}, \quad (3)$$

where $E^{n\text{H}_2\text{O}}$ is the total energy of each cluster with $n\text{H}_2\text{O}$ molecules, $E^{\text{H}_2\text{O}}$ is the total energy of a H₂O monomer, and $n_{\text{H bond}}$ is the number of H bonds in the cluster. Our CBS MP2 binding energies for the dimer, trimer, tetramer, and pentamer are 215.8, 228.5, 299.9, and 314.4 meV/H bond, respectively.⁶⁵ These values are all within 0.5 meV/H bond of the previous MP2 CBS dissociation energies reported by Xantheas *et al.*⁴⁰ We expect that the various errors accepted in producing these values [MP2 (valence only) treatment of correlation, aug-cc-pVTZ structures, extrapolation to reach the CBS, etc.] will lead to errors in our reference data from the exact electronic dissociation energies on the order of ± 5.0 meV/H bond at most. With our present aim to evaluate the performance of various DFT XC functionals, such errors are acceptable.

III. DFT

In a study such as this, there is an essentially endless list of functionals that we could consider evaluating. Here we have chosen to examine 16 different functionals, which are widely used or have been reported to perform particularly well for H-bonded systems in predicting dissociation energies and structures of the above-mentioned clusters. Specifically, we have chosen to optimize structures of each cluster with the following functionals: (I) PW91,¹⁶ an extremely popular nonempirical GGA widely used in calculations of bulk ice^{14,66,67} and other H-bonded systems.⁴⁶ (II) PBE,¹⁵ the twin of PW91 that has again been widely used and tested for H-bonded systems.^{33,42,45} (III) PBE1W, a parametrized empirical variant of PBE specifically designed to yield improved energetics of H bonds.³³ (IV) TPSS,²³ the meta-GGA variant of PBE, recently used in simulations of liquid water and evaluated for small water clusters.^{4,33,42,68} (V) PBE0,²⁴ a so-called parameter-free hybrid variant of PBE, also recently tested for water.^{4,42,48,69} (VI) BLYP (Becke88 (Ref. 17) exchange combined with LYP (Ref. 18) correlation), a popular functional for liquid water simulations.^{4–7,10} (VII) B3LYP,^{18,25–27} the extremely popular Becke three-parameter

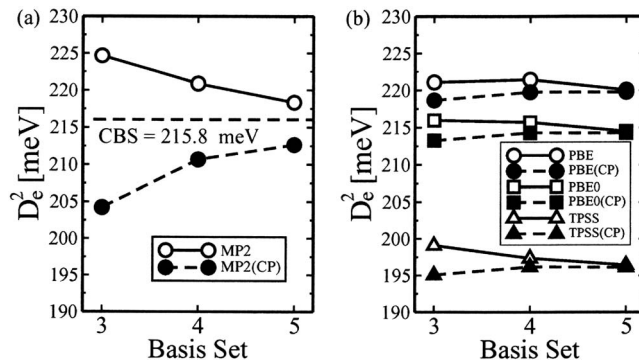


FIG. 2. (a) Variation in the MP2 dissociation energy for the H₂O dimer without a counterpoise correction for basis set superposition error (BSSE) (labeled MP2) and with a counterpoise correction for BSSE [labeled MP2(CP)] as a function of basis set size. The extrapolated complete basis set (CBS) dissociation energy for the H₂O dimer with MP2 is also indicated. (b) Variation in the dissociation energy for the H₂O dimer with and without a counterpoise BSSE correction as a function of basis set size for three different DFT functionals. The basis set labels on the X axis of (a) and (b) indicate aug-cc-pVXZ basis sets, where $X=3, 4,$ and 5 . Lines are drawn to guide the eyes only. All structures were optimized with an aug-cc-pVTZ basis set consistently with MP2 and with each DFT functional.

hybrid functional combined with LYP nonlocal correlation, which has, of course, been widely used to examine H-bonded systems.^{4,42,47,48} (VIII) mPWLYP, a combination of a modified PW91 exchange functional³² (mPW) with the LYP correlation functional, found to be the most accurate pure GGA for the energetics of H bonds in water dimers and trimers.³³ (IX) BP86, an empirical GGA combining Becke88 (Ref. 17) exchange and Perdew86 (Ref. 70) correlation that is well tested for hydrogen bonded systems.^{48,69} (X) X3LYP,³¹ another empirical hybrid functional designed to describe weak (noncovalent) interactions that is becoming a familiar name for calculations of water.^{4,42,50} (XI) XLYP,³¹ the nonhybrid GGA version of X3LYP, also tested for H-bonded systems.⁴² (XII) B98,³⁶ another hybrid functional, said to perform extremely well for water clusters.^{33,42} (XIII) MPWB1K,³⁴ a one parameter hybrid meta-GGA using mPW (Ref. 32) exchange and Becke95 (Ref. 71) correlation, said to be the joint best for H bonds between water molecules.^{33,42} (XIV) PW6B95,³⁵ another hybrid meta-GGA combining PW91 (Ref. 16) exchange and Becke95 (Ref. 71) correlation, found to be the other joint-best functional for the H bonds between water molecules.³³ (XV) B3P86 (Becke 3 parameter hybrid functional combined with Perdew86 nonlocal correlation), found to be the best functional for H-bonded systems in a recent benchmark study.⁴² (XVI) BH&HLYP,^{17,18,72} said to offer similar performance to B3P86 for H-bonded systems.⁴²

As with MP2, the question arises as to what basis sets to use in order to ensure that the DFT results reported here are not subject to significant basis set incompleteness errors, which would cloud our evaluations of the various functionals. There are no established extrapolation schemes for DFT. However, it is well known that DFT total energies are less sensitive to basis set size than explicitly correlated methods such as MP2.^{73–76} Indeed, from the plot in Fig. 2, it can be seen that the computed DFT dissociation energies converge much more rapidly with respect to basis set size than MP2 does [cf. Figs. 2(a) and 2(b)]. Specifically, we find that upon

TABLE I. Comparison of the MP2 complete basis set dissociation energies to those obtained with various DFT functionals computed with an aug-cc-pV5Z basis set for four different water clusters. DFT dissociation energies that come within ± 5.0 meV of the corresponding MP2 value are indicated in bold. The numbers in parentheses indicate the percentage cooperative enhancement in the H bond strength compared to the dissociation energy of the dimer. Averages of the signed and unsigned errors in the dissociation energies of all DFT functionals from the corresponding MP2 numbers over all four clusters are also provided as mean error (ME) and mean absolute error (MAE). The DFT functionals are ordered in terms of increasing MAE. All structures were optimized consistently with MP2 and with each DFT functional with an aug-cc-pVTZ basis set, and all values are in meV/H bond (1 kcal/mol=43.3641 meV).

| | Dimer | Trimer | Tetramer | Pentamer | ME | MAE |
|---------|--------------|--------------------|---------------------|---------------------|-------|------|
| MP2 | 215.8 | 228.5 (5.9) | 299.9 (38.9) | 314.4 (45.7) | ... | ... |
| X3LYP | 213.8 | 221.9 (3.8) | 298.3 (39.5) | 316.0 (47.8) | -2.2 | 2.9 |
| PBE0 | 214.5 | 224.6 (4.7) | 302.7 (41.1) | 320.9 (49.6) | 1.0 | 3.6 |
| mPWLYP | 218.5 | 226.0 (3.4) | 305.4 (39.8) | 323.7 (48.1) | 3.8 | 5.0 |
| B3P86 | 203.5 | 220.0 (8.1) | 299.4 (47.1) | 316.5 (55.5) | -4.8 | 5.9 |
| PBE1W | 207.9 | 216.6 (4.0) | 294.9 (41.8) | 312.7 (50.4) | -6.6 | 6.6 |
| BH&HLYP | 213.2 | 219.5 (2.9) | 291.3 (36.6) | 308.3 (44.6) | -6.6 | 6.6 |
| PBE | 220.1 | 233.5 (6.1) | 316.4 (43.8) | 334.8 (52.1) | 11.6 | 11.6 |
| B98 | 205.6 | 211.4 (2.8) | 285.9 (39.1) | 303.1 (47.4) | -13.2 | 13.2 |
| TPSS | 196.4 | 209.4 (6.6) | 288.8 (47.0) | 307.5 (56.6) | -14.1 | 14.1 |
| B3LYP | 197.4 | 206.3 (4.5) | 280.1 (41.9) | 297.2 (50.6) | -19.4 | 19.4 |
| PW6B95 | 200.9 | 210.5 (4.8) | 276.8 (37.8) | 292.7 (45.7) | -19.4 | 19.4 |
| MPWB1K | 199.1 | 210.6 (5.5) | 276.3 (38.8) | 292.3 (46.8) | -20.1 | 20.1 |
| BP86 | 184.4 | 205.7 (11.6) | 282.5 (53.2) | 300.8 (63.1) | -21.3 | 21.3 |
| PW91 | 232.5 | 244.9 (5.1) | 330.8 (42.3) | 350.5 (50.8) | 25.0 | 25.0 |
| XLYP | 191.4 | 198.6 (3.8) | 272.2 (42.2) | 288.9 (50.9) | -26.9 | 26.9 |
| BLYP | 180.7 | 191.7 (6.1) | 264.9 (46.6) | 281.2 (55.6) | -35.0 | 35.0 |

going from aug-cc-pVTZ to aug-cc-pV5Z, the dissociation energy of the H₂O dimer changes by only 1.0, 2.7, and 1.5 meV for the PBE, TPSS, and PBE0 functionals, respectively. Further, with the aug-cc-pV5Z basis set, we find that the counterpoise corrected and uncorrected dissociation energies essentially fall on top of each other, with the largest difference for the dimers and trimers being 0.45 meV/H bond with the TPSS functional. In addition, upon going beyond aug-cc-pV5Z to aug-cc-pV6Z, the dimer dissociation energies change by only 0.24, 0.11, 0.19, and 0.25 meV for the PBE, TPSS, PBE0, and BLYP functionals, respectively. Thus, the DFT dissociation energies we report in the following will all come from those obtained with the aug-cc-pV5Z basis set, which is sufficiently large to reflect the true performance of each functional at a level of accuracy that is reasonably expected to approach the basis set limit to within about 0.5 meV/H bond or better.

IV. RESULTS

A. Dissociation energy

In Table I the computed dissociation energies obtained with MP2 and with each of the DFT functionals are reported. To allow for a more convenient comparison of the performance of the various functionals, we plot in Fig. 3(a) the difference between the DFT and MP2 dissociation energies (ΔD_e^n) as a function of water cluster size. In this figure, positive values correspond to an overestimate of the dissociation energy by a given DFT functional compared to MP2. So, what do we learn from Table I and Fig. 3(a)? First, the functionals which offer the best performance for the clusters examined are the hybrid X3LYP and PBE0 functionals, coming

within 7 meV/H bond for all four clusters. Of the nonhybrid functionals, the pure GGAs mPWLYP and PBE1W perform best, coming within 12 meV/H bond for all four clusters. Second, the very popular BLYP and B3LYP functionals consistently underbind: B3LYP predicts H bonds that are ~ 20 meV too weak and BLYP predicts H bonds that are ~ 35 meV too weak. Third, PBE overestimates the binding in the dimer and trimer ever so slightly, coming within 5 meV/H bond, but for the tetramer and pentamer drifts away to yield errors of ~ 20 meV/H bond. Fourth, PBE and PW91 exhibit a non-negligible difference. Although it is often assumed that identical numerical results should be obtained from these two functionals, this is not the case here; PW91 is consistently 12–14 meV/H bond worse than PBE. Both functionals, however, exhibit a similar tendency toward increased overbinding as the cluster size grows. Indeed, it is clear from Fig. 3(a) that all PBE-related functionals (PBE, PW91, PBE1W, TPSS, and PBE0) show this trend, which in the case of TPSS means that it gets within ~ 7 meV/H bond for the pentamer starting from an error of ~ 20 meV/H bond for the dimer. Likewise, PBE1W gets closer to the reference value as the cluster size grows. Finally, despite previous suggestions to the contrary,^{33,42,69} none of the other functionals particularly stands out: B98 underbinds by just over 13 meV/H bond and BP86 exhibits a rather strong variation in performance with cluster size, ranging from 30 to 14 meV/H bond error. B3P86 shows similar behavior to BP86, although the magnitude of the error is much less and indeed for the tetramer and pentamer B3P86 gives values close (within 3 meV/H bond) to MP2. MPWB1K and PW6B95 both underbind by ≥ 20 meV/H bond.

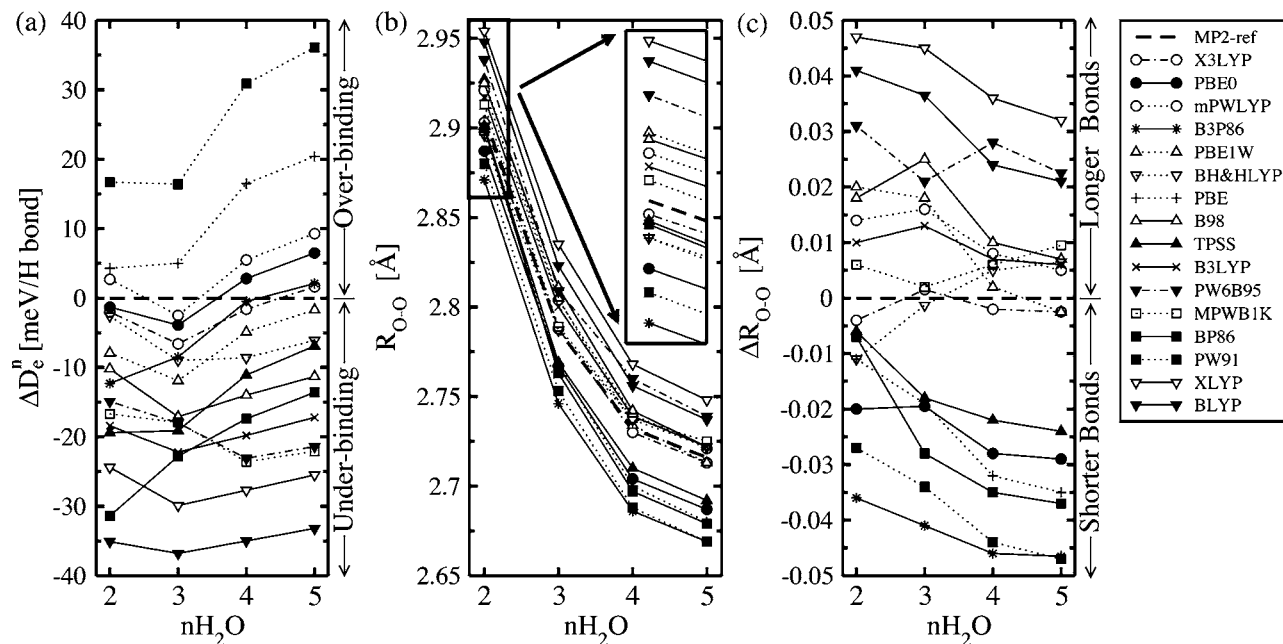


FIG. 3. (a) Difference in the dissociation energy (ΔD_e^n) in meV/H bond of the various DFT functionals compared to MP2, plotted as a function of cluster size. Positive values correspond to an overestimate of the dissociation energy by a given DFT functional. (b) Average value of the MP2 and DFT O–O distances (R_{O-O}) as a function of cluster size. The inset zooms in on the dimer region. (c) Difference in the average O–O distance (ΔR_{O-O}) between MP2 and DFT. Positive values correspond to an overestimate of the average O–O distances by a given DFT functional. [(a)–(c)] All DFT energies are calculated with an aug-cc-pV5Z basis set on geometries optimized consistently with each functional with an aug-cc-pVTZ basis set. Lines are drawn to guide the eyes only.

B. Cooperativity

An important aspect of the energetics of H bonds is that they tend to undergo cooperative enhancements, which for the present systems implies that the average strengths of the H bonds between the water molecules increase as the number of H bonds increase. The fact that the H bonds in water clusters undergo cooperative enhancements is now well established,^{1,2,77} as is the importance of cooperativity in many other types of H-bonded systems.^{1,22,78} Here we have evaluated the ability of each functional to correctly capture the computed MP2 cooperative enhancement, defined as the percentage increase in the average H bond strength compared to that in the H₂O dimer. These numbers are reported in the parentheses in Table I. We find that all functionals capture the correct trend, i.e., the average H bond strength increases upon going from dimer to pentamer. In addition, most functionals get the absolute percentage enhancement correct to within 5%. The notable exceptions are BP86, B3P86, and TPSS, which for the tetramer and pentamer predict cooperative enhancements that exceed the MP2 values by 10%–15%.

C. Geometry

Let us turn now to an assessment of the quality of the structural predictions made by each DFT functional. The five key structural parameters of the H₂O clusters that we evaluate are (i) the distance between adjacent oxygen atoms involved in a H bond, R_{O-O} ; (ii) the length of a H bond, given by the distance between the donor H and the acceptor O, $R_{O\cdots H} = R_{hb}$ (Fig. 1); (iii) the H bond angle, $\angle(O\cdots H-O) = \phi$ (Fig. 1); (iv) the internal O–H bond lengths of each

water, R_{O-H} ; and (v) the internal H–O–H angle of each water, $\angle(H-O-H) = \theta$ (Fig. 1). In Table II the mean absolute error (MAE) and mean error (ME) between the MP2 values and those obtained from each functional, averaged over all four clusters, are listed for each of the above parameters. This provides an immediate overview for how the functionals perform. Summarizing the results of this table, we find that X3LYP, BH&HLYP, B3LYP, and MPWB1K perform best for O–O distances. All those functionals yield results that are essentially identical to MP2, coming within our estimated MP2 bond distance error bar of 0.01 Å. B3P86 is the worst functional in terms of O–O distances, with a MAE of 0.04 Å. Largely, these conclusions hold for the related quantity, R_{hb} , although now B3P86, BP86, and PBE perform worst with MAE values of ~ 0.05 Å. In terms of the H bond angle ϕ , X3LYP, B3LYP, PW6B95, MPWB1K, and BH&HLYP are essentially identical to MP2 coming within our estimated MP2 error bar for angles of 0.5° and again PW91, PBE, and BP86 are the worst being $\sim 1.5^\circ$ away from MP2. For the internal O–H bond lengths, no functional is worse than ~ 0.015 Å and for the internal H–O–H angles θ , all functionals are within $\sim 1.5^\circ$ of MP2.

One specific aspect of the structures of the small cyclic water clusters examined here that is known from experiment and previous calculations^{2,79} is that the average O–O distances between the H₂O molecules in the clusters shorten as the cluster size increases. This trend is, of course, related to the cooperative enhancement in H bond strengths discussed already. As can be seen from the plot of computed O–O distances versus cluster size in Fig. 3(b), all functionals correctly capture this effect: the ~ 0.2 Å shortening in the O–O bond distances upon going from dimer to pentamer predicted by MP2 is also captured by every DFT functional. To look at

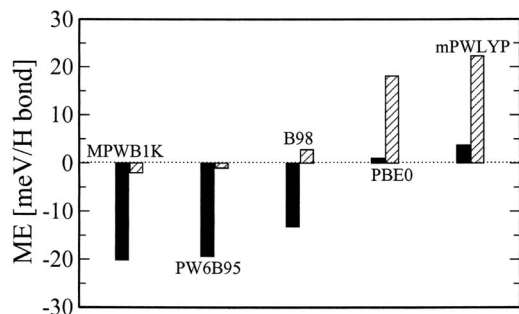


FIG. 4. Mean error (ME) in the dissociation energies obtained with aug-cc-pV5Z (solid bars) and MG3S (dashed bars) basis sets for five selected functionals for the four clusters examined here. Positive values correspond to an average overestimate of the dissociation energy compared to MP2 for the clusters. All errors are measured relative to our reference CBS MP2 values.

this issue more closely and specifically to examine how each functional varies with respect to MP2, we plot in Fig. 3(c) the difference between the MP2 and DFT O–O distances for the four clusters. Positive values in Fig. 3(c) indicate that the DFT O–O bonds are longer than the MP2 ones. We note that the average MP2 O–O distances for the dimer, trimer, tetramer, and pentamer are 2.907, 2.787, 2.732, and 2.716 Å, respectively. As indicated already in our previous discussion, X3LYP, B3LYP, BH&HLYP, and MPWB1K perform best at predicting the correct O–O bond length for each cluster, coming within 0.01 Å of the MP2 values on every occasion. Indeed, the consistent closeness of the X3LYP O–O distances to the MP2 ones is remarkable. PBE0 is a little worse than X3LYP for the O–O distances, predicting bonds which are consistently about 0.02–0.03 Å too short. Of the other functionals, B3P86 stands out as predicting the shortest O–O distances (always \sim 0.04 Å less than MP2) and XLYP and BLYP predict the longest O–O distances (always at least 0.02 Å longer than MP2).

V. DISCUSSION

Here we have shown that of the functionals tested, X3LYP and PBE0 offer exceptional performance for the H bonds in small water clusters in their global minimum energy structures. However, a previous benchmark study on the ability of most of the functionals considered here to describe the energetics of H bonds between water molecules has arrived at somewhat different conclusions.³³ Specifically, a MAE of 19.5 meV/H bond has been reported for PBE0, worse than the MAE of 3.6 meV/H bond obtained here. In addition, MAEs of 5–7 meV/H bond have been reported with the PW6B95, MPWB1K, and B98 functionals, suggesting improved performance for these functionals over what we find here. In that study the so-called MG3S basis set [identical to 6-311+G(2df,2p) for H₂O] was used. By comparing the performance of the above-mentioned functionals with the MG3S and the aug-cc-pV5Z basis sets for the four clusters under consideration here, it appears that the incompleteness of the MG3S basis set is the main reason for the small discrepancy. The results, illustrated in the histogram in Fig. 4, reveal that the dissociation energies obtained with the MG3S basis set are consistently \sim 18 meV (0.42 kcal/mol) per H bond larger than those obtained with the aug-cc-pV5Z basis set. Thus, although PW6B95, MPWB1K, and B98 perform well with the MG3S basis set (all within \pm 7 meV/H bond of MP2 for the clusters considered here), all exhibit a propensity to underbind when the more complete aug-cc-pV5Z basis set is used. Conversely, PBE0 and the other functional tested, mPWLYP, which predict too strong H bonds with the MG3S basis set (MAEs of 18.1 and 22.3 meV/H bond for the PBE0 and mPWLYP functionals, respectively, for the clusters examined here), actually perform very well with the more complete aug-cc-pV5Z basis set (MAEs of 3.6 and 5.0 meV/H bond for the PBE0 and mPWLYP functionals,

TABLE II. Mean absolute error (MAE) of various DFT functionals from MP2 for five different structural parameters, averaged over the four water clusters examined here. The numbers in bold all have MAE \leq 0.010 Å for bond lengths and \leq 0.50° for bond angles. Mean errors (MEs) are given in parentheses. All structures were optimized consistently with MP2 and with each DFT functional with an aug-cc-pVTZ basis set. The order of the functionals is the same as in Table I.

| | $\Delta R_{\text{O-O}}$ (Å) | ΔR_{hb} (Å) | $\Delta R_{\text{O-H}}$ (Å) | $\Delta \phi$ (°) | $\Delta \theta$ (°) |
|---------|-----------------------------|----------------------------|-----------------------------|--------------------|---------------------|
| X3LYP | 0.002 (–0.002) | 0.003 (–0.003) | 0.001 (0.000) | 0.21 (0.21) | 1.04 (1.04) |
| PBE0 | 0.024 (–0.024) | 0.023 (–0.023) | 0.002 (–0.001) | 0.77 (0.77) | 0.69 (0.69) |
| mPWLYP | 0.012 (0.012) | 0.008 (–0.004) | 0.012 (0.012) | 0.61 (0.47) | 0.51 (0.51) |
| B3P86 | 0.042 (–0.042) | 0.051 (–0.051) | 0.003 (0.001) | 1.00 (1.00) | 0.77 (0.77) |
| PBE1W | 0.011 (0.009) | 0.010 (–0.006) | 0.011 (0.011) | 1.13 (1.13) | 0.13 (0.13) |
| BH&HLYP | 0.006 (–0.003) | 0.015 (0.015) | 0.013 (–0.013) | 0.54 (–0.17) | 1.52 (1.52) |
| PBE | 0.024 (–0.024) | 0.046 (–0.046) | 0.012 (0.012) | 1.43 (1.21) | 0.13 (0.13) |
| B98 | 0.016 (0.016) | 0.015 (0.015) | 0.001 (–0.001) | 0.52 (0.52) | 0.66 (0.66) |
| TPSS | 0.018 (–0.018) | 0.037 (–0.037) | 0.010 (0.010) | 1.28 (1.25) | 0.22 (0.22) |
| B3LYP | 0.009 (0.009) | 0.007 (0.007) | 0.001 (0.001) | 0.31 (0.31) | 0.93 (0.93) |
| PW6B95 | 0.026 (0.026) | 0.029 (0.029) | 0.006 (–0.006) | 0.29 (0.24) | 0.81 (0.81) |
| MPWB1K | 0.006 (0.006) | 0.016 (0.016) | 0.012 (–0.012) | 0.38 (0.31) | 1.09 (1.09) |
| BP86 | 0.028 (–0.028) | 0.051 (–0.051) | 0.014 (0.014) | 1.58 (1.46) | 0.11 (0.11) |
| PW91 | 0.038 (–0.038) | 0.038 (–0.038) | 0.012 (0.012) | 1.44 (1.21) | 0.29 (0.29) |
| XLYP | 0.040 (0.040) | 0.028 (0.028) | 0.011 (0.011) | 0.53 (0.49) | 0.37 (0.37) |
| BLYP | 0.031 (0.031) | 0.015 (0.015) | 0.009 (0.009) | 0.69 (0.64) | 0.37 (0.37) |

respectively). The small and systematic overbinding due to the incompleteness of the MG3S basis set has also been pointed out by Csonka *et al.*⁶⁸

Another interesting aspect of the results of the present study is that the performance of some functionals differs appreciably from one cluster to another. For example, PBE is only $\sim 4\text{--}5$ meV/H bond away from MP2 for the dimer and trimer but >15 meV/H bond away from MP2 for the tetramer and pentamer. Conversely, TPSS is ~ 20 meV/H bond off MP2 for the dimer but within 7 meV/H bond of MP2 for the pentamer. Other functionals which show strong variation in performance with cluster size are PW91, BP86, and B3P86, and the functional in the admirable position of showing the least variation, consistently predicting H bonds that are ~ 35 meV too weak, is BLYP. The general conclusion of this analysis, however, is that it is not necessarily sufficient to use the performance of a given functional for a single system, such as, for example, the H₂O dimer, as a guide to how that functional will perform for H bonds between H₂O molecules in general. Indeed, the results reported here indicate that H bond test sets such as the “W7” test set³³ for water would benefit from the inclusion of structures other than dimers and trimers.

We now ask if the results and conclusions arrived at here are of general relevance to H₂O molecules in other environments and to other types of H-bonded systems. Some parallels with DFT simulations of liquid H₂O can be seen. It is generally found, for example, that (when everything else is equivalent) BLYP liquid H₂O is less structured [i.e., the first peak of the O–O radial distribution function (RDF) has a lower maximum] than PBE liquid H₂O,^{4–7,10} consistent with the weaker H bonds predicted by BLYP compared to PBE. Similarly, the first simulations of liquid H₂O with hybrid DFT functionals (B3LYP, X3LYP, and PBE0) have recently been reported⁴ and the trend in the position of the first peak in the O–O RDF can be interpreted as being consistent with the current observations. Specifically, it was found [although the error bars are large because the simulations were short (5 ps)] that the position of the first peak in the O–O RDF moves to shorter separation upon going from B3LYP to X3LYP to PBE0, which is consistent with the small decrease of the O–O distances [Fig. 3(b)] and increase in H bond strengths along this series (Table I). Looking at other H-bonded systems with slightly stronger (for example, NH₃···H₂O) or slightly weaker H bonds (for example, NH₃···NH₃) than those considered here, it is known, for example, that PBE generally overestimates these H bond strengths slightly: PBE overestimates NH₃···H₂O by ~ 30 meV and NH₃···NH₃ by 6 meV.⁴⁵ Likewise, BLYP and B3LYP have been shown to underestimate a range of H-bonded systems by 20–30 meV/H bond.⁴⁶ However, the general performance of X3LYP and PBE0 for other H-bonded systems has not been evaluated yet in any great detail with suitably large basis sets. In light of the present results, it will be interesting to see how well these functionals perform for other H-bonded systems. Likewise, mPWLYP and PBE1W are not widely used. Since they are pure GGAs (without any contribution from HF exchange), they will offer computational savings compared to X3LYP and

PBE0, particularly for condensed phase simulations, and would thus be interesting to explore further for other H-bonded systems.

Finally, we point out that an interesting conclusion of the present study is the non-negligible difference between the H bond energies predicted by PBE and PW91, with PW91 consistently being 12–14 meV/H bond worse than PBE. A similar discrepancy, although in a rather different area of application (surface and defect formation energies of metals), has been identified by Mattsson *et al.*⁸⁰ Specifically, they found that the PW91 and PBE monovacancy formation energies of Al differed by $\sim 30\text{--}40$ meV. As Mattsson *et al.* have done, we caution that it does not seem wise to expect identical numerical results from PBE and PW91.

VI. CONCLUSIONS

In summary, we have computed MP2 CBS values for the dissociation energies of small H₂O clusters (dimer to pentamer) in their global minimum energy structures. These data have been used to evaluate the performance of 16 DFT functionals. All DFT energies reported here have been obtained with an aug-cc-pV5Z basis set, which for DFT is sufficiently large to enable the true performance of each functional to be assessed, absent from significant basis set incompleteness errors. Among the functionals tested, we find that PBE0 and X3LYP perform best for the energetics of the H bonds considered here, always being within 10 meV/H bond of MP2. In terms of the structures, X3LYP offers outstanding performance, predicting structures essentially identical to MP2 for all four clusters. Of the pure GGAs considered, mPWLYP and PBE1W perform best. A small but non-negligible difference in the results obtained with PBE and PW91 has been identified, with PBE consistently being 12–14 meV/H bond closer to MP2 than PW91.

In closing, we note that, although X3LYP and PBE0 predict the most accurate H bond energies, it is important to remember that *all* functionals considered here do reasonably well. If, for example, one's definition of “good” is the so-called chemical accuracy (1 kcal/mol ≈ 43 meV/H bond) then it is clear from Fig. 3(a) that all functionals achieve chemical accuracy for all clusters. The problem is, of course, that for bonds as weak as H bonds, chemical accuracy is a rather loose criterion since it amounts to around 20%–30% of the total bond strength. Future work will involve the investigation of larger H₂O clusters in which the ability of DFT functionals to correctly describe the energetic ordering of low energy isomeric structures becomes crucial.

ACKNOWLEDGMENTS

This work is supported by the European Commission through the Early Stage Researcher Training Network MONET, MEST-CT-2005-020908 (see www.sljus.lu.se/monet). The work of A.M. is supported by a EURYI award (see www.esf.org/euryi). The authors are grateful to Martin Fuchs and Joel Ireta for helpful comments on an earlier version of this manuscript.

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difficult to describe exactly with finite Gaussian orbital basis sets [see Helgaker *et al.* for more details (Ref. 76)]. Since the importance of using large basis sets for MP2 is clear from Fig. 2, we caution that even the largest Pople-style basis set, 6-311+ +G(3df,3pd), yields a MP2 binding energy for the water dimer of 230 meV/H bond, which at ~ 15 meV from the MP2/CBS number is not necessarily of sufficient accuracy to serve as a reliable benchmark.

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