On how good DFT exchange-correlation functionals are for H bonds in small water clusters: Benchmarks approaching the complete basis set limit

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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 Möller 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 non-hybrid GGA functionals mPWLYP and PBE1W perform the best. The popular BLYP and B3LYP functionals consistently underbind and PBE and PW91 display rather variable performance with cluster size.

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 ≈ 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 are 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 is evaluated. So as to enable the use of large basis sets, which we demonstrate approach the complete basis set (CBS) limit, in the generation of the benchmark data and the DFT data itself, this study is 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 (CBS) limit, in the generation of the benchmark data and the DFT data itself, this study is limited to the four smallest H₂O clusters (dimer, trimer, tetramer, and pentamer). In addition, this study is restricted to the established lowest energy conformer of each cluster [28, 29, 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 [31] and PBE0 [24] functionals offer the best performance. Among the regular (pure) GGAs

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various hexamer structures differ by
that the MP2 and CCSD(T) dissociation energies of
using CCSD(T) with an aug-cc-pVTZ basis set revealed
[43, 44]. In addition, a recent study of water hexamers
energies that differ by no more than 2 meV/H bond
dimers and trimers at the CBS limit, yields binding
scales as
visions with large basis sets. MP2, on the other hand,
computational power is required for CCSD(T) calcula-
tions with large basis functions, the most extravagant use of
basis set is moderately large (92 basis functions/H
water molecule.

II. Reference data - MP2

For a systematic benchmark study such as this, reliable reference data is essential. Experiment is, in
principle, one source of this data. However, experimental dissociation energies are simply not available
or do not come with sufficiently small error bars for all the H2O clusters we examine here. Further, with
our aim to systematically evaluate the performance of many DFT XC functionals it becomes impractical to
calculate 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 theory (MP2) [37]
or coupled-cluster theory [88]. Indeed such methods have been widely applied to examine H-bonded systems
[28, 33, 34, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50]. In particular coupled-cluster with single and double
excitations plus a perturbative correction for connected 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 [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 N³, 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 N⁵ 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/H2O [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 so-called chemical accuracy (1 kcal ≈ 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 [55] and NWChem
[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/H2O), this finite basis set will introduce errors in our predicted
MP2 structures. However, a test with the H2O 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 and co-workers 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
±0.5° 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/H2O) and aug-cc-pV5Z (287 basis functions/H2O) basis sets in conjunc-
tion 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]:

\[ E_X^{HF} = E_{CBS}^{HF} + A e^{-B_X} \]

where X is the cardinal number corresponding to the

\[ \varepsilon = A (R_b - R_a) \]
where $E$ is the dissociation energy (by , $^2$ and dimer explicitly calculated with an aug-cc-pV6Z basis set, quadruple-, and pentuple-eqns. (1-2) because we found that with input from triple-[58, 59, 60, 61, 62, 63, 64] and did not see a difference
various extrapolation schemes available in the literature
where the corresponding HF energy , energy we follow an inverse power of highest angular momentum equation

$$E_{X}^{Corr} = E_{CBS}^{Corr} + CX^{-3} + DX^{-5},$$  \hspace{0.2cm}

(2)

where $E_{X}^{Corr}$ is the correlation energy corresponding to $X$, $E_{CBS}^{Corr}$ is the extrapolated CBS correlation energy, and $C$ and $D$ are fitting parameters. For the correlation part of the MP2 total energy we follow an inverse power of highest angular momentum equation \[53, 60, 61\].

$$E^{X} = E^{CBS} + CX^{-3} + DX^{-5},$$

(2)

for $X=3$, 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, $E^{X}_{CBS}$ 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 \[53, 60, 61\].

$E^{X}_{CBS}$ is the extrapolated CBS correlation energy, and $C$ and $D$ are fitting parameters. We have tested various extrapolation schemes available in the literature \[58, 59, 60, 61, 62, 63, 64\] 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 eqns. \[112\] because we found that with input from triple-, quadruple-, and pentuple-$\zeta$ 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/H$_2$O). Having obtained MP2 CBS total energies for the H$_2$O monomer and each of the H$_2$O clusters, we thus arrive at the MP2 CBS electronic dissociation energies ($D^e$) per H bond which are given by,

$$D^e = (E^{nH_2O} - nE^{H_2O})/n_{H_{-bond}} ,$$

(3)

where $E^{nH_2O}$ is the total energy of each cluster with $n$ H$_2$O molecules, $E^{H_2O}$ is the total energy of a H$_2$O monomer, and $n_{H_{-bond}}$ 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 $\pm$0.5 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 non-empirical 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 parameterized empirical variant of PBE specifically designed to yield improved energies 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 \[4, 43, 33, 42, 68\]; (V) BLYP - Becke88 exchange combined with LYP correlation, a popular functional for liquid water simulations \[4, 33, 34, 46\]; (VI) BLYP - Becke88 exchange combined with LYP correlation, a popular functional for liquid water simulations \[4, 33, 34, 46\]; (VII) B3LYP - a one-parameter free hybrid functional with BLYP correlation, which has, of course, been widely used to examine H-bonded systems \[4, 42, 43, 48\]; (VIII) mPW-LYP - a combination of a modified PW91 exchange functional (mPW) \[32\] 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 exchange and Perdew86 correlation that is well-tested for hydrogen bonded systems \[48, 69\]; (X) X3LYP \[31\] - an empirical hybrid functional designed to describe weak (non-covalent) interactions that is becoming a familiar name for calculations of water \[4, 42, 50\]; (XI) XLYP \[31\] - the non-hybrid 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 \[41\] - a one parameter hybrid meta-GGA using mPW exchange and Becke95 correlation, said to be the joint-best
for H bonds between water molecules [33, 42]; (XIV) PW6B95 - another hybrid meta-GGA combining PW91 exchange and Becke95 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 best functional for H-bonded systems in a recent benchmark study [42]; and (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, 74, 75, 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 (c.f. Figs. 2(a) and (b)). Specifically we find that upon going from aug-cc-pVTZ to aug-cc-pV5Z the dissociation energy of the H$_2$O 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, 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 ($\Delta D_n$) 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 1 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 non-hybrid functionals the pure GGAs mPWLPY 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 $\sim 20$ meV too weak; and BLYP predicts H bonds that are $\sim 35$ 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 $\sim 20$ 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 towards increased overbinding as the cluster size grows. Indeed it is clear from Fig. 4(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 $\sim 7$ meV/H bond for the pentamer starting from an error of $\sim 20$ 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, 09], none of the other functionals particularly stand out: B98 underbinds by just over 13 meV/H bond, and BP86 exhibits a rather strong variation in performance with cluster size, ranging from a 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 $\geq 20$ meV/H bond.

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 increases as the number of H bonds increases. 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 H$_2$O dimer. These numbers are reported in parenthesis 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.
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 parenthesis 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 ME (mean error) and MAE (mean absolute error). 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 (1Kcal/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  |

FIG. 3: (a) Difference in the dissociation energy ($\Delta D_n^e$) 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 ($\Delta R_{O-O}$) 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 eye only.
The five key structural parameters of the H$_2$O 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$_{O-H}$ = R$_{hb}$ (Fig. 1); (iii) The H bond angle, $\angle$(O···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 the 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 0.02 Å. The other functionals B3P86, BP86, and PBE perform worst with MAE values of ~0.05 Å. In terms of the H bond angle, $\phi$, 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 ~1.5° away from MP2. For the internal O-H bond lengths no functional is worse than ~0.01 Å and for the internal H-O-H angles, $\theta$, all functionals are within ~1.5° of MP2.

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$0.01 Å for bond lengths and $\leq$0.5° for bond angles. Mean errors (ME) are given in parenthesis. 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.

| Functional | $\Delta$R$_{O-O}$ (Å) | $\Delta$R$_{hb}$ (Å) | $\Delta$R$_{O-H}$ (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       | 0.021 (-0.021)       | 0.023 (-0.023)       | 0.002 (-0.002)       | 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&HLYYP   | 0.006 (-0.003)       | 0.015 (0.015)        | 0.013 (-0.013)       | 0.48 (-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)      |

One specific aspect of the structures of the small cyclic water clusters examined here, that is known from experiment and previous calculations [2, 72] is that the average O-O distances between the H$_2$O 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 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 the 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 ~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. 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 performance for these functionals over what we find here. 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 ~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 ±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 one 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, respectively). The small and systematic overbinding due to the incompleteness of the MG3S basis set has also been pointed out by Csonka et al. 33.

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 ~4-5 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 set 33 for water would benefit from the inclusion of structures other than dimers and trimers.

FIG. 4: Mean error (ME) in the dissociation energies obtained with aug-cc-pV5Z (solid bars) and MG3S (hashed 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.

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, 5, 6, 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 reported 4 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. 4(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 15. 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 and co-workers [80]. Specifically they found that the PW91 and PBE monovacancy formation energies of Al differed by ~30-40 meV. As Mattsson and co-workers have done, we caution that it does now 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 H$_2$O clusters (dimer to pentamer) in their global minimum energy structures. This data has 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 mPWL YP 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 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 H$_2$O clusters in which the ability of DFT functionals to correctly describe the ordering of low energy isomeric structures becomes crucial.

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Auxiliary Materials

See EPAPS document No. —- for a database of the coordinates of the structures (optimized consistently with MP2 and 16 DFT functionals with an aug-cc-pVTZ basis set) of all the cluster studied here in xyz format. The total energies of each clusters obtained from MP2 and the 16 DFT functionals are also provided. This document can be reached through —–.

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