

Improved Density Functionals for Water

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The accuracy of existing density functional methods for describing the noncovalent interaction energies in small water clusters is investigated by testing 25 density functionals against a data set of 28 water dimers and 8 water trimers whose structures are taken from the literature and from simulations. The most accurate functionals are found to be PW6B95 with a mean unsigned error of 0.13 kcal/mol and MPWB1K and B98 with mean unsigned errors of 0.15 kcal/mol; the best functional with no Hartree–Fock exchange is *m*PWLYP, which is a GGA with a mean unsigned error of 0.28 kcal/mol. In comparison, the most popular GGA functionals, PBE and BLYP, have mean unsigned errors of 0.52 and 1.03 kcal/mol, respectively. Since GGAs are very cost efficient for both condensed-phase simulations and electronic structure calculations on large systems, we optimized four new GGAs for water. The best of these, PBE1W and MPWLYP1W, have mean unsigned errors of 0.12 and 0.17 kcal/mol, respectively. These new functionals are well suited for use in condensed-phase simulations of water and ice.

1. Introduction

There has been a great deal of theoretical work focused on describing the energetics of small to moderately sized water clusters using both high-level quantum mechanical methods and density functional theory (DFT).^{1–14} The DFT methods are more economical, and the use of molecular dynamics and Monte Carlo methods to study bulk water^{15–23} has placed an increased importance on finding a density functional method that can accurately describe these systems. While a recent advance²⁵ has allowed for the inclusion of Hartree–Fock exchange into the plane wave code VASP,²⁶ many of the simulation methods that employ plane waves¹⁵ require the use of a density functional method that does not contain any Hartree–Fock exchange, that is, a nonhybrid method. (A hybrid functional contains Hartree–Fock exchange, hybrid meta functionals contain Hartree–Fock exchange and kinetic energy density, and generalized gradient approximations (GGAs) and local spin density approximations (LSDAs) contain neither.) Additionally, since calculation of the exchange terms is the bottleneck in hybrid DFT methods,^{25,27–29} if one is interested in studying large clusters, a nonhybrid method will be more efficient. Moreover, if one is interested in a broad range of aqueous chemistry, such as processes at water–metal interfaces,^{30,31} it may be desirable to use a nonhybrid method, as functionals with no Hartree–Fock exchange perform better than hybrid methods for many systems containing transition metals.^{32–35}

Several years ago, Hall et al.³⁶ pointed out that most density functionals underestimate the binding energy of the water dimer. Recent assessments of density functional methods for noncovalently bonded complexes,^{37,38} including complexes formed by hydrogen bonding, show that hybrid meta functionals can be used to accurately describe noncovalent interactions such as hydrogen bonding, π – π stacking, and dipole and charge transfer interactions. Furthermore, they show that both hybrid and hybrid

meta functionals perform substantially better for nonbonded interactions than generalized gradient approximations (GGAs) or meta functionals. (A meta functional is one that contains kinetic energy density. GGAs and meta functionals depend on the density gradient as well as the density; LSDAs do not.) With this in mind, we set out to determine the accuracy of a variety of density functional methods against a database of water dimer and trimer data and to investigate the usefulness of GGAs and meta functionals for studying water interactions.

2. Database

To create a database against which to test existing DFT methods, we selected a set of water dimers and trimers both from structures found in the literature and from simulations of liquid water and ice. The literature clusters consist of a collection of 10 water dimers and 6 water trimers representing stationary points on their respective potential energy surfaces, as taken from the work of Tschumper et al.^{39,40} The accurate binding energies for these clusters were reported in refs 39 and 40 on the basis of calculations using the focal point method. Additionally, a collection of 10 water dimers from molecular dynamics simulations of ice as well as 8 water dimers and 2 water trimers from Monte Carlo simulations of liquid water were included in the data set. Accurate binding energies for all clusters taken from simulations were computed, relative to the unrelaxed monomers, at the Weizmann-1^{41,42} level of theory using the MOLPRO⁴³ quantum chemistry package.

The dimers from the molecular dynamics simulations of ice consist of two structures taken from simulations⁴⁴ of ice XI as well as eight structures taken from simulations⁴⁴ of ice VIII at pressures ranging from 0 to 70 GPa in increments of 10 GPa (one dimer from each simulation). The eight dimers and two trimers from Monte Carlo simulations were taken from three different ensembles at seven different temperatures. One dimer

TABLE 1: Mean Errors (kcal/mol) for Previously Developed Functionals^a

	references	X	Y	MSE			MUE			RMSE		
				dimers	trimers	all	dimers	trimers	all	dimers	trimers	all
LSDA												
SVWN5	49, 50	0	0	3.98	9.67	5.24	3.98	9.67	5.24	4.45	9.86	6.08
GGA												
<i>m</i> PWLYP	51, 52	0	100	0.16	0.60	0.26	0.18	0.60	0.28	0.22	0.68	0.38
PBE	53	0	100	0.41	0.81	0.50	0.43	0.81	0.52	0.53	0.91	0.63
BLYP	52, 54	0	100	-0.82	-1.77	-1.03	0.82	1.77	1.03	0.87	1.79	1.14
PBELYP	52, 53	0	100	0.80	2.35	1.14	0.80	2.35	1.14	0.82	2.39	1.34
HCTH	55	0	100	-0.81	-3.06	-1.31	0.84	3.06	1.33	0.91	3.21	1.71
OLYP	52, 56, 57	0	100	-2.41	-6.98	-3.42	2.41	6.98	3.42	2.52	7.10	4.02
meta												
TPSS	58, 59	0	100	-0.15	-0.64	-0.26	0.20	0.64	0.30	0.30	0.76	0.44
TPSSLYP	52, 58, 59	0	100	0.43	1.31	0.62	0.43	1.31	0.62	0.47	1.38	0.77
BB95	54, 60	0	100	-1.31	-3.05	-1.69	1.31	3.05	1.69	1.36	3.07	1.88
hybrid GGA												
B98	61	21.98	100	0.03	-0.33	-0.05	0.10	0.33	0.15	0.14	0.39	0.22
B97-1	55	21	100	0.19	0.19	0.19	0.20	0.26	0.22	0.22	0.27	0.23
X3LYP	51, 52, 54, 62	21.8	87.1	0.18	0.31	0.20	0.19	0.33	0.22	0.22	0.37	0.26
B3LYP	52, 54, 63	20	81	-0.25	-0.75	-0.36	0.25	0.75	0.36	0.28	0.77	0.44
MPW1K	51, 64, 65	42.8	100	0.19	-0.49	0.04	0.32	0.50	0.36	0.47	0.55	0.49
<i>m</i> PW1PW91	51, 64	25	100	-0.01	-0.73	-0.17	0.27	0.73	0.37	0.35	0.78	0.48
PBE1PBE	53	25	100	0.43	0.46	0.43	0.44	0.47	0.45	0.58	0.52	0.57
MPW3LYP	51, 52, 66	20	81	0.46	0.98	0.57	0.46	0.98	0.57	0.49	1.01	0.64
B97-2	55	21	100	-0.67	-2.48	-1.07	0.67	2.48	1.07	0.71	2.54	1.35
hybrid meta												
PW6B95	38, 51, 60	28	100	0.02	-0.17	-0.02	0.11	0.19	0.13	0.14	0.24	0.17
MPWB1K	51, 60, 66	44	100	0.11	-0.21	0.04	0.13	0.23	0.15	0.18	0.27	0.20
MPW1B95	51, 60, 66	31	100	-0.05	-0.43	-0.13	0.09	0.43	0.16	0.11	0.47	0.24
PBE1KCIS	37, 53, 67-69	22	100	0.27	-0.11	0.19	0.30	0.15	0.27	0.74	0.21	0.66
PWB6K	38, 51, 60	46	100	0.54	0.82	0.60	0.54	0.82	0.60	0.56	0.83	0.63
B1B95	54, 60	25	100	-0.86	-2.32	-1.18	0.86	2.32	1.18	0.89	2.34	1.35

^a All results in this table were obtained using the MG3S basis set.

was taken from the liquid box of a Gibbs ensemble simulation²² at each of the following temperatures: 323, 373, 423, 473, and 523 K. Additionally, one trimer from the liquid box of the 323 K simulation and one dimer from the vapor box of the 523 K simulation were used. The remaining dimers and trimer were taken from the *NpT* and *NVT* ensembles, with one dimer from an *NpT* ensemble simulation²³ carried out at 298 K and 1 atm of pressure and one dimer and one trimer taken from an *NVT* ensemble simulation²⁴ run at 315 K.

We define the binding energy of a dimer and trimer, respectively, as

$$E_{\text{bind}} = E_A + E_B - E_{AB}$$

$$E_{\text{bind}} = E_A + E_B + E_C - E_{ABC}$$

For the literature clusters, the monomer is a relaxed gas-phase water molecule ($A = B = C$). For the clusters taken from simulations, we chose to use the unrelaxed monomers from each cluster. The molecular dynamics simulations from which some of the dimers were taken use rigid water molecules, making the two monomers within a given dimer equivalent. The structures from the Monte Carlo simulations, however, do not use rigid monomers, making the monomers for a given dimer or trimer different. The intramolecular O-H bond lengths in these structures vary from 0.92 to 1.05 Å, with a H-O-H angle in the range from 93.7 to 116.7°.

3. Tests of Previously Developed Methods

To assess the accuracy of existing DFT methods for describing small water clusters, 25 DFT methods were chosen to test against the data set described in the previous section. The

methods chosen include 22 standard functionals that were developed for broad applicability plus three unconventional combinations of standard exchange and correlation functionals (*m*PWLYP, PBELYP, and TPSSLYP). The methods tested were chosen on the basis of recent studies evaluating the performance of DFT methods for nonbonded interactions,^{37,38} including hydrogen bonding, and they also include those methods commonly used in the literature for the simulation of bulk water and ice. All DFT calculations were carried out using the Gaussian 03⁴⁵ software package, utilizing the MG3S⁴⁶ basis set. For water, the MG3S basis set is identical to 6-311+G(2df,2p).^{47,48}

Table 1 gives, for each DFT method tested, the mean signed error (MSE), mean unsigned error (MUE), and root-mean-square error (RMSE) averaged over the dimers, over the trimers, and over the total data set. We note that most of the hybrid and hybrid meta methods give substantially better performance than even the best GGA method. The most accurate hybrid method is B98, with a MUE of 0.15 kcal/mol, and the best hybrid meta method is PW6B95, with a MUE of 0.13 kcal/mol. Of the nonhybrid methods, *m*PWLYP and TPSS give the best results, with MUEs of 0.28 and 0.30 kcal/mol. These errors may be compared to the mean binding energy of the 36 structures, which is 4.80 kcal/mol.

4. Parametrization of New Method

The exchange-correlation energy can be written as

$$E_{\text{xc}} = \left(1 - \frac{X}{100}\right)(E_x^{\text{S}} + \Delta E_x^{\text{GCE}}) +$$

$$\frac{X}{100}E_x^{\text{HF}} + E_c^{\text{LSDA}} + \frac{Y}{100}\Delta E_c^{\text{GCC}}$$

where E_x^{S} is the local spin density approximation to the

TABLE 2: Mean Errors (kcal/mol) for DFT Functionals Newly Optimized in This Letter^a

	X	Y	MSE			MUE			RMSE		
			dimers	trimers	all	dimers	trimers	all	dimers	trimers	all
PBE1W	0	74	-0.01	-0.12	-0.03	0.10	0.20	0.12	0.15	0.35	0.21
MPWLYP1W	0	88	-0.08	-0.01	-0.06	0.15	0.20	0.17	0.21	0.27	0.22
TPSSLYP1W	0	74	-0.09	-0.02	-0.07	0.19	0.20	0.19	0.28	0.28	0.28
PBELYP1W	0	54	-0.11	0.00	-0.09	0.26	0.15	0.24	0.37	0.20	0.34

^a All results in this letter were obtained using the MG3S basis set.

exchange energy, E_x^{GCE} is the gradient correction to the exchange energy, E_x^{HF} is the Hartree–Fock exchange energy, E_c^{LSDA} is the local spin density approximation to the correlation energy, ΔE_c^{GCC} is the gradient correction to the correlation energy, and X and Y are parameters determining, respectively, the percentage of Hartree–Fock exchange and the percentage of gradient correction to the correlation energy that are included in a given functional. For a nonhybrid method (e.g., *m*PWLYP or TPSS), X is set equal to zero.

In general, Y is as an optimizable parameter. Although Y has been adjusted in some DFT functionals, including the popular B3LYP⁶³ where it has a value of 81, it has often been found that density functionals are more sensitive to X than to Y , and much recent work has focused on one-parameter methods in which X is varied.^{37,53,64–66,70} However, the sensitivity to Y is sometimes greater than is generally appreciated, and when one is interested in finding the best functional with $X = 0$ for other reasons (see the Introduction), it is worthwhile to re-examine the dependence of the results on Y . Since the current prescriptions for gradient corrections to correlation functionals are inexact, it seems unlikely that $Y = 100$ is optimum. With these considerations in mind, we set out to determine if the accuracy of GGAs and meta functionals could be improved by varying this single parameter to make them competitive with the hybrid and hybrid meta functionals.

For simplicity, we chose to investigate the effect of varying the Y values of the two most popular correlation functionals used in simulations, PBE and LYP. The *m*PW, PBE, and TPSS exchange functionals were chosen, as they were found to be components of the best GGA and meta functionals in the tests in Table 1. The optimal value of Y for each of four methods was found by iteratively adjusting the Y values to the nearest integer, such that the mean unsigned error (MUE) of the 36 water clusters in the database was minimized. The optimized methods found with this approach are referred to as MPWLYP1W ($Y = 88$), PBE1W ($Y = 74$), PBELYP1W ($Y = 54$), and TPSSLYP1W ($Y = 74$), where 1W denotes a one-parameter method optimized for water.

The keywords required to carry out an MPWLYP1W calculation in Gaussian 03 are

```
#MPWV5LYP
IOp(3/78=0880010000)
```

The keywords required to carry out a PBE1W calculation in Gaussian 03 are

```
#PBEPBE
IOp(3/78=0740010000)
```

The keywords required to carry out a PBELYP1W calculation in Gaussian 03 are

```
#PBEV5LYP
IOp(3/78=0540010000)
```

The keywords required to carry out a TPSSLYP1W calculation in Gaussian 03 are

```
#TPSSV5LYP
IOp(3/78=0740010000)
```

Since PBE is already used in many molecular dynamics and Monte Carlo codes and since PBE1W involves only scaling the gradient correction to the correlation energy, implementation of PBE1W should be especially straightforward, and it involves changing only a single number or line of code in many programs.

5. Results and Discussion

Table 2 shows the mean errors for the four methods parametrized in this work. The results show a substantial improvement for all of the optimized methods over their unoptimized counterparts. Additionally, the best optimized method, PBE1W, has mean unsigned errors that are comparable to those of PW6B95 and better than those of B98. This new method gives a mean unsigned error for the dimers, trimers, and total data set of 0.10, 0.20, and 0.12 kcal/mol, respectively. Given that the average binding energies for these three data sets are 2.47, 12.93, and 4.80 kcal/mol, respectively, these errors represent only 4.0, 1.5, and 2.5% of the average binding energies.

One way to put the results in the present letter into perspective is to compare the methods to X3LYP as a standard. The X3LYP functional was specifically designed to yield improved descriptions of hydrogen bonded and van der Waals systems,⁶² and it was found, along with PBE1PBE and *m*PW1PW91, to be particularly accurate for the water dimer.⁷¹ Indeed, for the present water data set, the mean unsigned errors for X3LYP, PBE1PBE, and *m*PW1PW91 are 0.22, 0.45, and 0.37 kcal/mol, respectively. In another study¹¹ devoted entirely to water, the authors tested X3LYP against the most accurate data available for $(\text{H}_2\text{O})_n$, with $n = 2-6, 8$, and concluded that X3LYP is “the most practical ab initio method today for calculating accurate water cluster structures and energies”. It is not clear what the authors mean by ab initio, since X3LYP has parameters, but the message is clear that X3LYP is quite competitive for water. Therefore, it is very significant to compare other functionals to X3LYP.

The present tests compare X3LYP to even more accurate data (although we are limited to smaller clusters), and as stated above, we confirm its accuracy. It is therefore interesting to note that seven of the density functionals studied here have mean unsigned errors in kilocalories per mole smaller than the 0.22 value of X3LYP, in particular, PBE1W (0.12), PW6B95 (0.13), B98 (0.15), MPWB1K (0.15), MPW1B95 (0.16), *m*PWLYP1W (0.17), and TPSSLYP1W (0.19). The mean unsigned error in X3LYP is 69% larger than that for PW6B95 (a general-purpose functional parametrized before the water test set was created) and 83% larger than that for PBE1W (a functional parametrized specifically for noncovalent interactions between water mol-

TABLE 3: Comparison of Mean Errors (kcal/mol) for the AE6 and BH6 Databases^a

	X	Y	AE6 ^b			BH6		
			MSE	MUE	RMSE	MSE	MUE	RMSE
<i>m</i> PWLYP	0	100	0.56	1.33	1.55	−8.85	8.85	9.32
PBE	0	100	2.39	3.04	3.47	−9.33	9.33	9.87
B98	21.98	100	−0.41	0.63	0.74	−4.00	4.00	4.49
B97-1	1	100	−0.34	0.91	0.96	−4.14	4.14	4.86
X3LYP	21.8	87.1	−0.51	0.56	0.72	−4.91	4.91	5.20
B3LYP	20	81	−0.60	0.66	0.85	−4.73	4.73	5.07
PW6B95	28	100	0.08	0.39	0.55	−3.46	3.46	3.71
MPWB1K	44	100	−0.69	0.98	1.31	−1.32	1.32	1.73
MPW1B95	31	100	0.35	0.78	0.86	−3.38	3.38	3.61
PBE1W	0	74	1.95	2.30	2.69	−8.50	8.50	8.93
MPWLYP1W	0	88	0.65	1.23	1.47	−8.47	8.47	8.96
TPSSLYP1W	0	74	−1.36	2.07	2.70	−5.95	6.35	7.06
PBELYP1W	0	54	1.92	1.92	2.28	−8.13	8.13	8.69

^a The functionals are listed in the same order as in Tables 1 and 2. All results in this table were obtained using the MG3S basis set. ^b For AE6, the mean errors are expressed on a per bond basis.

TABLE 4: Mean Errors (in kcal/mol) for Different Basis Sets

	DIDZ			aug-cc-pVDZ			aug-cc-pVTZ			MG3S			all ^a
	MSE	MUE	RMSE	MSE	MUE	RMSE	MSE	MUE	RMSE	MSE	MUE	RMSE	MUE
<i>m</i> PWLYP	1.27	1.27	1.63	0.03	0.16	0.22	−0.21	0.23	0.32	0.24	0.29	0.41	0.46
PBE	1.54	1.54	1.90	0.25	0.34	0.42	0.01	0.27	0.36	0.46	0.54	0.65	0.61
PBELYP	2.19	2.19	2.68	0.96	0.96	1.21	0.68	0.68	0.89	1.10	1.10	1.37	1.12
TPSSLYP	1.67	1.67	2.08	0.42	0.43	0.60	0.15	0.25	0.35	0.59	0.59	0.79	0.67
B98	0.98	0.98	1.19	−0.26	0.26	0.33	−0.47	0.47	0.61	−0.08	0.20	0.24	0.46
PW6B95	1.00	1.00	1.19	−0.19	0.21	0.27	−0.48	0.48	0.59	−0.03	0.10	0.12	0.44
MPWB1K	1.06	1.06	1.23	−0.15	0.16	0.26	−0.43	0.43	0.60	0.02	0.15	0.19	0.44
PBE1W	1.02	1.02	1.30	−0.24	0.24	0.29	−0.48	0.48	0.58	−0.05	0.17	0.24	0.46
MPWLYP1W	0.96	0.96	1.28	−0.28	0.28	0.35	−0.51	0.51	0.61	−0.07	0.24	0.27	0.47
TPSSLYP1W	0.99	0.99	1.31	−0.24	0.26	0.35	−0.50	0.50	0.61	−0.08	0.26	0.31	0.47
PBELYP1W	0.98	0.98	1.31	−0.22	0.25	0.38	−0.47	0.47	0.59	−0.08	0.24	0.34	0.46

^a Average over four basis sets.

ecules but having the distinct advantage of no Hartree–Fock exchange and no dependence on kinetic energy density).

One question that arises is whether changing the value of *Y* will greatly affect the performance of the new methods when tested against other properties such as atomization energies or barrier heights. The AE6 database⁷² is a representative set of data for organic atomization energies, and the BH6 database⁷² is a representative set of data for chemical reaction barrier heights. Table 3 contains the results of testing these new methods against the AE6 and BH6 databases, and it compares the results to those for the other methods that are found in this study to do well for the water and to those for the popular B3LYP and PBE functionals. We see that for all of the newly parametrized methods the mean errors per bond for AE6 are a factor of 2–3 higher than those for the hybrid and hybrid meta methods, while the errors in BH6 are higher by a factor of 1.3–1.8. However, a comparison of PBE1W and MPWLYP1W to their unoptimized functionals show that the new methods have smaller errors for both AE6 and BH6. Because the *m*PWLYP functional already performs quite well with *Y* = 100, its optimum value is close to 100, and therefore, its performance is not significantly degraded by optimizing one parameter for water.

Up to this point, all reported results are for the MG3S basis set. Another issue of concern is the performance of the newly parametrized functionals with basis sets other than MG3S or when used in conjunction with pseudopotentials, which are often used in simulations. To address these issues, a representative set of water dimers and trimers was taken from the complete set of 36 structures, following the procedure of Lynch et al.⁷² This representative set, called W7, contains two literature dimers, one liquid- and one vapor-phase dimer from simulations, one high-pressure dimer from simulation, and one trimer taken

from the literature and simulation (additional information about W7 can be found in the Supporting Information). Table 4 shows the results of using this representative set in testing the four new functionals against their unoptimized counterparts and the three best methods in Table 1 (PW6B95, B98, and MPWB1K) using the DIDZ⁷³ (also known as 6-31*G(d,p)) basis set and the aug-cc-pVDZ⁷⁴ and aug-cc-pVTZ⁷⁴ basis sets. For comparison, the MG3S values for W7 are also reported.

From the data in Table 4, we calculate the mean unsigned error, averaged over four basis sets, of the four new functionals (last four rows) to be 0.47 kcal/mol, whereas the mean unsigned error of the four functionals from the literature that do not contain Hartree–Fock exchange (first four rows) is 0.72 kcal/mol. If we limit the averages to the three larger basis sets, the MUE for the four new functionals is 0.32 kcal/mol, and that for the four older functionals without Hartree–Fock exchange is 0.49 kcal/mol. Thus, the mean unsigned errors are reduced by 30–36%. The details in the numbers that contribute to these averages are also of interest. For example, we see that the performance of various functionals with the DIDZ basis set follows the same trend as the MG3S basis set: all four of the newly optimized functionals do better than the unoptimized functionals, and PBE1W has errors similar to those of B98, MPWB1K, and PW6B95. For the Dunning basis sets, however, the trends are quite different. With the aug-cc-pVDZ basis set, PBE1W still has errors similar to those of B98, MPWB1K, and PW6B95; however, we find that *m*PWLYP becomes the best method and that MPWLYP1W and TPSSLYP1W do not do better than *m*PWLYP and TPSSLYP. When using the aug-cc-pVTZ basis, *m*PWLYP, PBE, and PBELYP outperform all of the other functionals (including the hybrid and hybrid meta functionals) by ~0.2 kcal/mol. Of the newly optimized func-

TABLE 5: Mean Errors (in kcal/mol) for Different Basis Sets, Including Counterpoise Corrections

	DIDZ			aug-cc-pVDZ			aug-cc-pVTZ			MG3S		
	MSE	MUE	RMSE	MSE	MUE	RMSE	MSE	MUE	RMSE	MSE	MUE	RMSE
<i>m</i> PWLYP	0.26	0.52	0.69	-0.42	0.42	0.52	-0.29	0.29	0.39	-0.34	0.34	0.46
PBE	0.53	0.53	0.81	-0.07	0.24	0.35	-0.07	0.24	0.35	-0.12	0.15	0.25
PBELYP	1.18	1.18	1.58	0.49	0.53	0.73	0.62	0.62	0.82	0.55	0.59	0.78
TPSSLYP	0.67	0.73	1.05	-0.03	0.26	0.31	0.05	0.24	0.30	0.01	0.24	0.32
B98	0.04	0.34	0.40	-0.67	0.67	0.81	-0.55	0.55	0.70	-0.62	0.62	0.76
PW6B95	0.07	0.39	0.45	-0.60	0.60	0.73	-0.57	0.57	0.70	-0.56	0.56	0.70
MPWB1K	0.16	0.36	0.40	-0.54	0.54	0.69	-0.52	0.52	0.70	-0.51	0.51	0.67
PBE1W	0.02	0.37	0.47	-0.67	0.67	0.78	-0.55	0.55	0.66	-0.61	0.61	0.72
MPWLYP1W	-0.05	0.44	0.59	-0.73	0.73	0.85	-0.60	0.60	0.70	-0.64	0.64	0.78
TPSSLYP1W	0.00	0.47	0.61	-0.70	0.70	0.83	-0.60	0.60	0.72	-0.65	0.65	0.80
PBELYP1W	0.00	0.49	0.64	-0.68	0.68	0.83	-0.54	0.54	0.67	-0.62	0.62	0.80

tionals, only TPSSLYP1W shows improved results. We do, however, find that the optimized functionals have errors similar to those of B98, MPWB1K, and PW6B95.

One possible explanation for these differences is basis set superposition error. Table 5 shows the results of computing errors after applying counterpoise corrections,⁷⁵ again for the W7 data set for the same four basis sets. We see that the general trends and magnitude of the errors for the aug-cc-pVDZ and MG3S basis sets are similar to those for the aug-cc-pVTZ basis set, which changed very little after inclusion of counterpoise correction. Additionally, we see that the trends for the DIDZ basis set are quite different from the other three, and they still show that the newly optimized methods have errors similar to those of B98, PW6B95, and MPWB1K and are better than the unoptimized functionals. Both of the Dunning basis sets and the MG3S basis sets have reduced errors after counterpoise correction and now predict that the *m*PWLYP, PBE, and TPSSLYP functionals outperform all of the other functionals by approximately 0.3 kcal/mol. Additionally, the PBE functional is shown to be the best method for all three basis sets.

Given the different results obtained when counterpoise correction is included, one may wonder if inclusion of counterpoise correction during the optimizations of the new functionals would be advantageous. However, the inclusion of counterpoise corrections is problematic. It has been argued⁷⁶ that counterpoise corrections are an overestimate because they involve all of the orbitals of the interactive partner, whereas only the unoccupied space is actually available. Nevertheless, for minimal basis sets, counterpoise corrections are usually appreciable and in the correct direction. For moderate and large basis sets, other sources of error may be comparable to or larger than the basis set superposition error and counterpoise corrections do not always improve the results. (This is consistent with previous findings.⁷⁷) However, there are other, even more serious issues. For example, counterpoise corrections on charge transfer processes, barrier heights, and bond energies are not negligible but are invariably neglected. Thus, workers who are interested in complex potential energy surfaces almost always omit counterpoise corrections, while workers entirely focused on dimer interaction energies often include them. When one considers trimers, though, counterpoise corrections become ambiguous,⁷⁸ and for larger oligomers or condensed-phase systems, they are essentially impossible to carry out, except by removing clusters from the liquid ensemble (generated without such corrections) for isolated analysis.⁷⁹ For these reasons, we chose to optimize our new functionals without counterpoise correction. One might then worry about canceling a systematic basis set superposition error with a systematic error in the density functionals. This is a possibility, but we consider it to be just one of the many sources of error that affect practical calculations. We do point out though that counterpoise corrections on

TABLE 6: Mean Errors (in kcal/mol) with and without Counterpoise Correction for the W7 Database Using the MG3S Basis Set with the CEP Effective Core Potential on Oxygen

	MSE		MUE		RMSE	
	no-cp ^a	cp	no-cp	cp	no-cp	cp
<i>m</i> PWLYP	0.56	-0.24	0.56	0.29	0.74	0.43
PBE	0.96	0.12	0.96	0.25	1.21	0.29
PBELYP	1.46	0.69	1.46	0.71	1.78	0.94
TPSSLYP	1.02	0.18	1.02	0.33	1.29	0.47
B98	0.15	-0.68	0.51	0.68	0.71	0.84
PW6B95	0.64	-0.21	0.80	0.26	0.93	0.35
MPWB1K	0.26	-0.13	0.29	0.20	0.40	0.27
PBE1W	0.42	-0.39	0.48	0.40	0.58	0.49
MPWLYP1W	0.25	-0.54	0.29	0.55	0.43	0.70
TPSSLYP1W	0.36	-0.49	0.40	0.49	0.56	0.67
PBELYP1W	0.28	-0.48	0.37	0.48	0.48	0.69

^a no-cp denotes no counterpoise correction, and cp denotes counterpoise correction.

noncovalent interactions tend to be smaller with DFT than with wave function theory (WFT), so those workers who have more experience with WFT than DFT sometimes overestimate the magnitude of the problem.

We have also considered the effect of adding an effective core potential⁸⁰ to represent the core of the oxygen atoms. Table 6 shows the results of using the CEP effective core potential,⁸¹ as implemented in Gaussian 03, with the MG3S all electron basis set, with and without counterpoise corrections. The results of adding the effective core potential without using counterpoise corrections show that the mean errors increase by ~ 0.3 kcal/mol for almost all of the methods. The two notable exceptions to this are the PW6B95 and MPWLYP1W functionals, which have increases in their mean unsigned errors by 0.7 and 0.05 kcal/mol, respectively. The effect of adding counterpoise corrections lowers the errors for all seven functionals taken from the literature, except for B98, and raises the errors for all of the newly parametrized methods, except for PBE1W, which improves by ~ 0.1 kcal/mol. Practitioners who employ effective core potentials must exercise due diligence to be sure that this does not increase the errors, especially if they also reduce the basis set.

Finally, one may want to consider whether results obtained using an atom-centered Gaussian basis set are relevant to those interested in using plane wave basis sets. A recent study²⁵ compared the atomization energies for the G2-1 test set computed with the PBE and PBE1PBE (PBE0) density functionals using an atom-centered basis set in Gaussian 03 and with a plane wave basis set in the VASP code. The authors found that the results obtained using the aug-cc-pV5Z basis set versus a plane wave basis set with an energy cutoff of 1000 eV (73.5 Ry) showed good agreement. Furthermore, Ireta et al.⁸² used

the PBE functional and plane wave basis set, with a 70 Ry energy cutoff, to determine the binding energies for a set of representative hydrogen bonded dimers. The binding energies obtained were in excellent agreement with a separate study³⁷ that calculated the binding energies for the same dimers using the PBE functional and the MG3S basis set. With these results in mind, we feel confident that the results obtained from this study are relevant to those using plane wave basis sets.

6. Concluding Remarks

In this letter, we have evaluated the performance of 25 previously developed and broadly parametrized density functionals against a database containing 28 water dimers and 8 water trimers. Among these existing methods, we have found the best GGA, meta GGA, hybrid GGA, and hybrid meta GGA to be *m*PWLYP, TPSS, B98, and PW6B95, respectively. As far as we know, *m*PWLYP, B98, and PW6B95 have never been used for a condensed-phase simulation of any system, although TPSS has been used for water. Furthermore, we propose a new GGA functional involving a single parameter, PBE1W, that gives mean errors smaller than the best hybrid method, B98, and comparable to the best hybrid meta method, PW6B95.

We have gone on to examine the performance of PBE1W when computing atomization energies and barrier heights as well as when used with several different basis sets and with a pseudopotential, and we have found that in the absence of counterpoise corrections it consistently outperforms PBE, which is one of the most commonly used density functionals in plane wave calculations. As there are differences in the accuracy of all of the density functionals when used with different basis sets, careful consideration should be given as to which basis set to use before calculations on water clusters are undertaken with any of the density functionals used in this study. Since the new PBE1W method should be easy to implement in most programs (it requires changing one parameter in the widely available PBE functional), its use for condensed-phase simulations of water would seem to be a promising avenue of research.

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Supporting Information Available: Tables showing the accurate binding energies and geometries for all dimers and trimers in the water database and a list of the dimers and trimers in the W7 database. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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