

Proper Gaussian Basis Sets for Density Functional Studies of Water Dimers and Trimers

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Received: September 25, 2005; In Final Form: October 17, 2005

The accuracy of the Perdew–Burke–Ernzerhof and Tao–Perdew–Staroverov–Scuseria density functionals for describing noncovalent interaction energies in small water clusters is studied by testing 11 basis sets on a reduced test set proposed by Dahlke and Truhlar (*J. Phys. Chem. B* **2005**, *109*, 15677). We have also tested variants of the Perdew–Burke–Ernzerhof functional and the Becke98 hybrid functional. While moderate basis sets give converged density functional theory results for covalent dissociation energies, this is not true for noncovalent interaction energies. Our results show that density functionals give converged interaction energies with aug-cc-pVTZ and aug-cc-pVQZ basis sets. Gradual simplification of the basis set introduces an increasing overbinding effect. The best agreement with the high-level result was obtained by the Perdew–Burke–Ernzerhof functional at the basis set limit. The converged Tao–Perdew–Staroverov–Scuseria interaction energies show a systematic underbinding effect that can be compensated by a somewhat systematic overbinding basis set effect of smaller basis sets such as 6-31+G(d,2p). The inclusion of the diffuse functions in the oxygen basis set is very important, while the inclusion of the f functions practically does not influence the results. Improvement can be obtained by adding more hydrogen p functions to the 6-31+G basis set.

1. Introduction

The correct description of water clusters is one of the important tests of theoretical methods in chemistry. The use of molecular dynamics and Monte Carlo methods to study bulk water^{1,2} requires an accurate density functional model. Non-hybrid (no Hartree–Fock exchange) density functionals are advantageous for the simulations that use plane waves.³ The nonhybrid density functional theory (DFT) functionals also perform considerably better for metal–water interfaces^{4,5} and for systems containing transition metals.^{6–8} Hall et al.⁹ observed that most density functionals underestimate the binding energy of the water dimer. Recent results show that hybrid meta-generalized gradient approximation (GGA) functionals can be used to describe noncovalent interactions such as hydrogen bonding, π – π stacking, and dipole and charge transfer interactions.^{10,11} In these calculations, hybrid functionals perform considerably better for nonbonded interactions than the non-hybrid GGA or meta-GGA functionals.

Recently, we have tested the Perdew–Burke–Ernzerhof (PBE)¹² and Tao–Perdew–Staroverov–Scuseria (TPSS)¹³ functionals and their hybrids on nonbonded weak interactions of noble gas dimers and the Be dimer.¹⁴ Our results have shown that the van der Waals (vdW) bond of a diatomic system can be dominated by the short-range part of the vdW interaction and is thus amenable to description by a GGA or meta-GGA. While some empirical GGAs such as BLYP fail to bind the rare-gas diatomics,^{15–17} the nonempirical PBE GGA and TPSS

meta-GGA describe the short-range part of the vdW interaction sufficiently well to bind them.^{15,18,19} Nonempirical GGAs and meta-GGAs tend to overbind those van der Waals-bound diatomics that have valence s electrons (like He₂ and Be₂) and to underbind those that have valence p electrons (like Ne₂ and Ar₂).¹⁴ GGAs and meta-GGAs fail to reproduce the long-range part of the vdW interaction, which tends to $-C_6/R^6$ as $R \rightarrow \infty$. While it is proper for GGAs and meta-GGAs to describe the short-range part of the vdW interaction, a consistent description of the vdW attraction requires a different treatment of the long-range part.^{20–23} The TPSS binding energy curves in Ne₂ and Ar₂ are somewhat too repulsive at small internuclear distances, R , and this accounts for the tendency of TPSS to bind less strongly than PBE.¹⁴ This could be favorable for the addition of a damped attractive long-range correction.^{20–22} However, the TPSS overbinding in Be₂ is not favorable for such a correction.¹⁴ Small basis sets without diffuse functions can produce severe overbinding of weakly bound systems,^{14,24,25} but the addition of diffuse basis functions fixes much of this error.¹⁴

In water clusters beside a sizable electrostatic contribution to binding, the dispersion contribution becomes less significant, and despite the problems above, a reasonable picture of such species can be constructed at moderate computational cost. Considering these observations, we determine the basis set dependence of the accuracy of PBE and TPSS functionals against a database of water dimer and trimer data.

2. Methods

Dahlke and Truhlar²⁶ proposed a set of 28 water dimers and 8 water trimers whose structures were taken from the literature

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TABLE 1: Accurate Reference and DFT Binding Energies, E_{bind} , and Statistics for the W6 Water Data Set^a

structure	E_{bind} (kcal/mol)					
	reference	PBE ^b	PBE1W ^c	PBE1W ^b	TPSS ^d	TPSS ^b
nonplanar open Cs dimer	4.99	5.04	5.21	4.77	5.37	4.55
Cyclic C2h dimer	4.00	3.35	3.42	3.14	3.43	2.71
C3 local min trimer	14.99	15.01	14.98	14.00	15.37	13.53
Ice VIII 50GPa dimer	-1.30	-0.71	-1.20	-1.59	-0.79	-1.53
NVT dimer	4.60	4.71	4.76	4.33	4.91	4.17
NVT trimer	7.05	6.79	6.84	6.17	6.67	5.62
statistics						
mean error		0.02	0.05	0.58	-0.10	0.88
standard deviation		0.41	0.30	0.36	0.46	0.57
root-mean-square error		0.38	0.28	0.67	0.43	1.02
mean absolute error		0.28	0.21	0.58	0.42	0.88
maximum error		0.65	0.58	0.99	0.57	1.46
minimum error		-0.59	-0.22	0.22	-0.51	0.23

^a The clusters, the notation for the elements, and the reference energies of the W6 water data set were taken from ref 26. The basis set limit and the best performer basis sets are shown. The PBE functional performs best at the basis set limit. ^b The applied basis set is aug-cc-pVTZ or QZ. It was observed that these basis sets give converged results for water cluster binding energies. ^c The applied basis set is 6-311+G(2d,2p). ^d The applied basis set is 6-31+G(d,2p).

and from simulation. This test set was used for testing the performance of 25 density functionals. On the basis of these test results, a representative test set, called W7, was constructed.²⁶ The W7 set contains two literature dimers (“nonplanar open Cs” and “Cyclic C2h”), one liquid-phase dimer and one vapor-phase dimer from simulations (“NVT dimer” and “vapor.523K”, respectively), one high-pressure dimer from simulation (“Ice VIII 50GPa”), and one trimer taken from the literature and simulation (“C3 local min” and “NVT trimer”, respectively; more information can be found in the Supporting Information of ref 26). We have selected the representative W7 test set for testing various model chemistries in this letter.

The binding energy of a dimer is defined as

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

The binding energy of a trimer is defined similarly. For literature clusters, the monomer is a relaxed gas-phase water molecule ($E_A = E_B$). For clusters taken from simulations, we use the unrelaxed monomers of each cluster, as was proposed in ref 26.

We test PBE and TPSS functionals with 6-31+G(d,p), 6-31+G(d,2p), 6-31+G(d,3p), 6-311+G(d,p), 6-311+G(d,2p), 6-311+G(2d,2p), 6-311+G(2df,2p), cc-pVTZ, and aug-cc-pVNZ with N = D, T, Q basis sets using the Gaussian 03 program.²⁷ We also test the PBE1W²⁶ variant of the PBE functional parametrized empirically for the larger water dimer and trimer test set of Dahlke and Truhlar. The PBE1W functional applies a scaling factor that scales down the GGA correlation part of the PBE functional by 0.74 (the keyword required to carry out a PBE1W calculation in Gaussian 03 is IOP (3/78 = 0740010000)). This and other functionals perform very similarly on the smaller W7 test set compared to the full test, so using the small W7 set for our purposes is justified. All calculations were performed with tight self-consistent field convergence criteria (the keyword required in Gaussian 03: SCF = TIGHT).

Finally, we add a note on the counterpoise correction (CP). For small basis sets, CPs are usually in the correct direction but do not yield an agreement with the larger basis set results.¹⁰ For moderate or large basis sets, other sources of errors might be comparable to or larger than the basis set superposition error (BSSE) and CPs do not always improve the results, and such a posteriori corrections are still contaminated by BSSE artifacts (overcorrection).²⁸ Zhao and Truhlar have published a large

number of CP and no-CP binding energies of weakly bound dimers calculated with 6-31+G(d,p), 6-311+G(2df,2p), and aug-cc-pVTZ basis sets.¹⁰ We noticed that CP of the PBE/aug-cc-pVTZ binding energies in the HB6/04 test set changes the mean absolute error (MAE) by 0.01 kcal/mol;¹⁰ thus, the CPs are negligible beside other errors. More importantly, for trimers and N-body clusters, the CPs become ambiguous.²⁹ We decided to present the computational models with their functional and basis set error (cf. the no-CP optimization procedure applied in ref 26).

3. Results and Discussion

3.a. The W6 Test Set. As discussed earlier, the representative W7 test set was constructed from a larger test set of water clusters.²⁶ The magnitudes of the binding energies are in the range -1.30 to 14.99 kcal/mol (cf. Table 1). The average binding energy is 4.92 kcal/mol. This test set contains a so-called vapor.523K dimer that was taken from the vapor box of the 523 K Monte Carlo simulations.²⁶ This dimer is characterized by a large, 7.32 Å, O···O distance and a very small binding energy, 0.11 kcal/mol. It is expected that even a relatively large 0.02 kcal/mol (20%) error would be negligible beside the much larger binding energy errors of the other elements of the W7 test set. We have calculated the binding energies for the vapor.523K dimer with several methods and found a small (≤ 0.01 kcal/mol) error, independent of functional and basis set. Due to this insensitivity of the errors on the basis sets and DFT functional, we omitted this structure, and we use the smaller W6 water data set shown in Table 1 in the remaining part of this letter. The average binding energy of the W6 test set is 5.72 kcal/mol. The mean absolute errors of the W6 test set are about one-sixth larger than that of the W7 test set. Consequently, the W6 test set is slightly more sensitive to the computational model errors than the large test set of Dahlke and Truhlar.²⁶ The mean absolute errors obtained with W6 are no longer truly representative of the large data set. The mean error (ME) is not affected.

3.b. Performance of the PBE Functional on the W6 Test Set. The results in Table 1 show that the PBE functional (that is already used in many molecular dynamics and Monte Carlo codes) gives good results with the aug-cc-pVTZ basis set. This result is consistent with the results of Ireta et al.³⁰ They have found that the PBE functional gives very good accuracy for the energetics of several hydrogen bonded dimers using ab initio

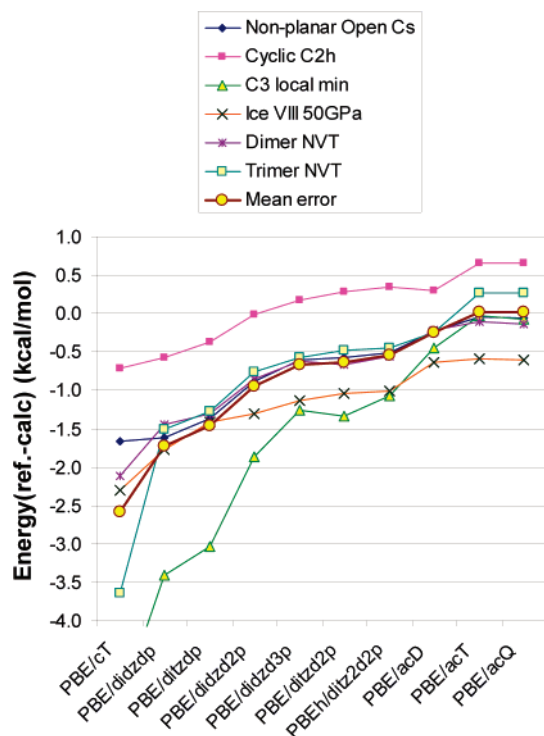


Figure 1. Basis set dependence of the binding energy errors (reference – calculated) of the PBE¹² functional for the elements of the W6 water data set. The notation of the water cluster elements and the reference energies are shown in Table 1. The shorthand notation for basis sets in the figure is the following: cT, didz, ditz, dp, d2p, d3p, 2d2p, acD, acT, and acQ denote cc-pVTZ, 6-31+G, 6-311+G, (d,p), (d,2p), (d,3p), (2d,2p), aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets, respectively.

pseudopotentials, a plane wave basis set, and periodic boundary conditions to integrate the Kohn–Sham equations. Plane waves are inherently free of the BSSE. The basis set dependence of the dissociation energies of the individual elements of the W6 test set is shown in Figure 1. The best PBE results can be obtained with the aug-cc-pVTZ basis set. This result is consistent with the results of Zhao and Truhlar for the HB6/04 test set.¹⁰ Further increase of the basis set to aug-cc-pVQZ does not improve the results (cf. Figure 1). Gradual simplification of the basis set introduces an increasing overbinding effect, as observed in ref 14. Figure 1 shows that the large cc-pVTZ basis set gives very poor results, and smaller basis sets supplemented with diffuse functions give considerably better results. This shows the importance of the diffuse functions in DFT calculations for hydrogen bonds in accordance with earlier observations.^{31,32} The improved performance of the PBE/6-31+G(d,2p) model compared to the PBE/6-31+G(d,p) model shows that adding more p orbitals to the hydrogen basis set helps the DFT functionals to give improved results with a small basis set at relatively low cost.

The two most problematic clusters for the PBE functional are the Cyclic C2h dimer (systematic relative underbinding) and the compressed Ice VIII 50GPa dimer (systematic relative overbinding). It can also be observed in Figure 1 that the binding energy error for the C3 local min trimer is strongly dependent upon basis set quality. (This is not surprising because this trimer has the largest absolute value of binding energy in the data set; cf. Table 1.)

3.c. Performance of the PBE1W Functional on the W6 Test Set. Inspection of Table 1 and Figure 2 shows that the PBE1W²⁶ functional has its optimum performance at smaller basis sets, while at the basis set limit it does not deliver

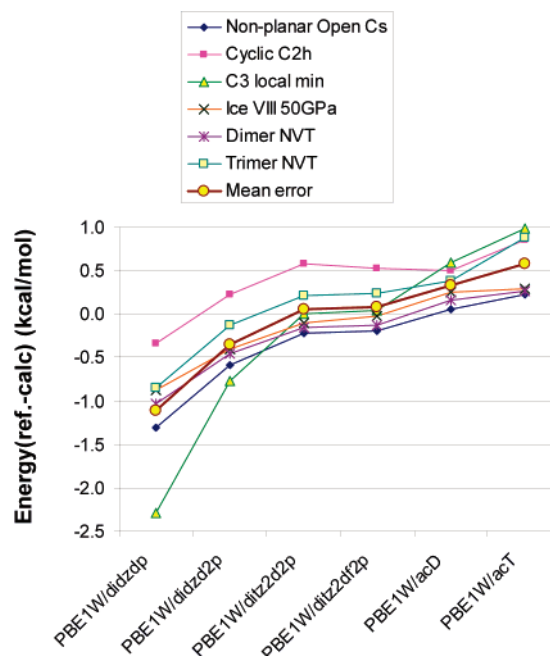


Figure 2. Basis set dependence of the binding energy errors (reference – calculated) of the PBE1W functional²⁶ for the elements of the W6 water data set. The notation of the water cluster elements and the reference energies are shown in Table 1. The shorthand notation for basis sets in the figure is the following: didz, ditz, dp, d2p, 2d2p, 2df2p, acD, and acT denote 6-31+G, 6-311+G, (d,p), (d,2p), (2d,2p), (2df,2p), aug-cc-pVDZ, and aug-cc-pVTZ basis sets, respectively.

improvements compared to the original PBE functional for the W6 test set. We note that the PBE1W functional was optimized for the full data set of 28 water dimers and 8 water trimers using the 6-311+G(2df,2p) basis set. (This basis set is quite good for strong bonds; however, it introduces a slight overbinding effect for the PBE and TPSS functionals for the Ne₂, Ar₂, and Be₂ dimers.¹⁴) Figure 2 shows that the considerably cheaper 6-311+G(2d,2p) basis set gives very similar and in effect slightly better results. Thus, applying f functions in the water basis set is not necessary for DFT, in agreement with ref 33. The results in Table 1 also show that the PBE1W/6-311+G(2d,2p) model gives very good results for water trimers. We suspect that this is because the optimization procedure was dominated by the relatively large binding energies of the trimers (average 12.93 kcal/mol) in the database (the average dimer binding energies are 2.47 kcal/mol). Dahlke and Truhlar observed that the PBE1W/6-311+G(2df,2p) model gives a mean absolute error for the dimers and trimers of 0.10 and 0.20 kcal/mol, respectively.²⁶ These errors represent 4.0 and 1.5% of the average binding energies. It is possible that the PBE1W functional is optimized for the binding energies of those trimers. This is one possibility to check in the future; however, the lack of precise tetramer and pentamer reference data makes further decisive tests currently impossible. Figure 2 also shows that the relative over- and underbinding error of the PBE functional for Cyclic C2 and Ice VIII 50GPa is eliminated by the PBE1W functional. It can be observed that at the basis set limit for PBE1W two groups are formed: The two trimers and Cyclic C2h show considerable underbinding (0.9 kcal/mol), and the other three dimers show excellent agreement with the reference data (only 0.2 kcal/mol underbinding). The gap between the two groups is about 0.5 kcal/mol. Comparison of the results in Table 1 with the results in ref 26 shows that our W6 test set gives slightly worse statistical parameters than the W7 test set. The origin of this deviation is well understood, as noted earlier.

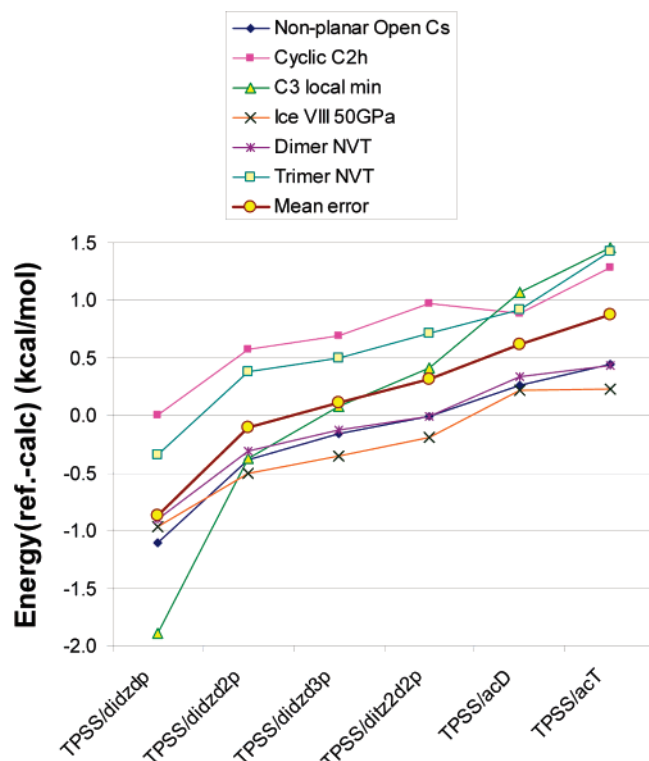


Figure 3. Basis set dependence of the binding energy errors (reference – calculated) of the TPSS functional for the elements of the W6 water data set. The notation of the water cluster elements and the reference energies are shown in Table 1. The shorthand notation for basis sets in the figure is the following: didz, ditz, dp, d2p, d3p, 2d2p, acD, and acT denote 6-31+G, 6-311+G, (d,p), (d,2p), (d,3p), (2d,2p), aug-cc-pVDZ, and aug-cc-pVTZ basis sets, respectively.

We note that scaling the gradient-dependent term of PBE correlation violates two exact constraints: (a) the second-order gradient expansion for the correlation energy, where the exact gradient coefficient is known in the high-density limit, and (b) scaling of the correlation energy to a constant under Levy uniform density scaling. The local term has a singularity in this limit, which in the PBE functional is canceled by a singularity in the gradient-dependent term.¹²

3.d. Performance of the TPSS Functional on the W6 Test Set. Comparison of Figures 2 and 3 shows that the TPSS and PBE1W functionals give similar results. The main difference is the larger deviations of the TPSS results and the stronger underbinding tendency. Due to the stronger underbinding, the TPSS functional gives better results with smaller basis sets that show a stronger overbinding tendency. The optimal basis set is the relatively small 6-31+G(d,2p) basis set, as shown in Figure 3 and Table 1. This shows that probably the TPSS functional can be used with relatively small basis sets for weakly bound systems. The same grouping of the results can be observed as previously for the PBE1W functional; at the basis set limit, two groups are formed: The two trimers and Cyclic C2h show similar underbinding (about 1.4 kcal/mol), and the other three dimers show better agreement with the reference data (about 0.4 kcal/mol underbinding only). The gap between the two groups is about 0.7 kcal/mol.

3.e. Performance of the Other Functionals. We have measured the performance of the PBE hybrid¹² and the Becke 98³⁴ (B98) functionals on the W6 test set. Our results agree with the tendencies found by Dahlke and Truhlar for the large test set and various models.²⁶ The good performance of the B98/6-311+G(2d,2p) model is reproduced (ME = 0.00 kcal/mol, MAE = 0.23 kcal/mol), and the PBE hybrid model shows a

similar performance to the nonhybrid PBE models. We note that all of the five functionals in this study show the same type of basis set dependence for the binding energies. The 6-31+G(d,p) basis set systematically overbinds compared to the basis set limit results on average by 1.5 kcal/mol. Increasing the basis set size, by adding d and p functions, decreases the overbinding effect on average to 0.5 kcal/mol. Consequently, a functional that underbinds on average by 0.5 kcal/mol produces better agreement with the reference energies than it does with the larger aug-cc-pVTZ basis set. Larger systematic underbinding can be compensated with a smaller basis set. A very good performance of the aug-cc-pVDZ basis set was observed: this basis set produces the smallest standard deviations for any functional and shows a relatively small (≈ 0.25 kcal/mol) overbinding effect compared to the aug-cc-pVTZ basis set. The detailed results are available from the web site of the authors (<http://web.in.bme.hu/csonka>).

4. Conclusion

The most important results of this letter can be summarized as follows:

(1) The W7 test set proposed by Dahlke and Truhlar contains one dimer (vapor.523k) that should be excluded from the test set. The O...O distance is too large, and consequently, the interaction energy (0.11 kcal/mol) is insensitive to the variation of the methods and basis sets. All methods and basis sets studied in this paper gave a 0.01 kcal/mol error for this interaction energy. We propose to exclude the vapor.523k dimer from the test set and use the reduced W6 test set for water cluster studies. The W6 test set is more sensitive to basis set and method errors than the W7 test set (the errors obtained with W6 overestimate the errors of the large data set).

(2) The basis set limit PBE results give the best agreement (ME = 0.02 kcal/mol, MAE = 0.28 kcal/mol) with the reference results taken from very expensive extrapolated wave function results. Applying smaller basis sets results in an overbinding effect, thus worsening the results. The PBE functional systematically underbinds the Cyclic C2h dimer ($\Delta E = 0.65$ kcal/mol) and systematically overbinds the Ice VIII 50GPa dimer ($\Delta E = -0.59$ kcal/mol). The other four interaction energies show very good agreement with the high-level reference results.

(3) It was observed that the empirically fitted PBE1W functional gives the best agreement with reference results with the 6-311+G(2d,2p) basis set (ME = 0.05 kcal/mol, MAE = 0.21 kcal/mol). The addition of the f function to the oxygen basis set does not improve the agreement with the reference interaction energies. The best results were obtained for trimers. It can be noticed that the PBE1W functional effectively remedies the underbinding (C2h dimer) and the overbinding (Ice VIII 50GPa) errors of PBE, thus leading to improved results. At the basis set limit, the PBE1W results show a considerable underbinding tendency (ME = 0.58 kcal/mol, MAE = 0.58 kcal/mol). This shows that the modification introduced in the PBE1W functional versus the PBE functional is mostly compensating the basis set imperfections. The PBE1W functional violates two exact constraints.

(4) The TPSS functional has a known slight underbinding effect for weak interactions. This effect is compensated by the 6-31+G(d,2p) basis set, and thus, the TPSS/6-31+G(d,2p) model shows the best agreement with the high-level results among TPSS models (ME = -0.10 kcal/mol, MAE = 0.42 kcal/mol). It can be observed that three dimers are quite correctly bound at the basis set limit, and the trimers and the cyclic C2h dimer are underbound by the TPSS model. There is a 0.7 kcal/mol gap between the two groups.

(5) The 6-31+G(d,p) basis set systematically overbinds the investigated functionals, on average, by 1.5 kcal/mol. An increase of the basis set size, by adding d and p functions, decreases the overbinding effect on average to 0.5 kcal/mol. The inclusion of the f functions in the oxygen basis set does not improve the results. The aug-cc-pVDZ basis set performs very well (small standard deviation and 0.25 kcal/mol average overbinding), and the basis set limit is practically reached with the aug-cc-pVTZ basis set.

Acknowledgment. G.I.C. acknowledges the support of OTKA under grant T034764 (Hungary), A.R. acknowledges fellowship support from the Pro Progressio Foundation and OTKA under grant PD050014, and J.P.P. acknowledges the support of the U.S. National Science Foundation under grant DMR-05-01588.

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