

Efficient Diffuse Basis Sets for Density Functional Theory

Ewa Papajak and Donald G. Truhlar*

Department of Chemistry and Supercomputing Institute,
University of Minnesota, 207 Pleasant Street S.E.,
Minneapolis, Minnesota 55455-0431

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Abstract: Eliminating all but the *s* and *p* diffuse functions on the non-hydrogenic atoms and all diffuse functions on the hydrogen atoms from the aug-cc-pV(*x*+*d*)Z basis sets of Dunning and co-workers, where *x* = D, T, Q, ..., yields the previously proposed “minimally augmented” basis sets, called maug-cc-pV(*x*+*d*)Z. Here, we present extensive and systematic tests of these basis sets for density functional calculations of chemical reaction barrier heights, hydrogen bond energies, electron affinities, ionization potentials, and atomization energies. The tests show that the maug-cc-pV(*x*+*d*)Z basis sets are as accurate as the aug-cc-pV(*x*+*d*)Z ones for density functional calculations, but the computational cost savings are a factor of about two to seven.

1. Introduction

For many quantum mechanical electronic structure calculations on molecules and chemical reactions, the results are sensitive to the inclusion of diffuse basis functions. Diffuse basis functions are spherical harmonics (or powers of Cartesian coordinates) times Gaussian functions with small exponents. These functions have long tails that allow the electrons to be farther from the nuclei. This is especially important for calculations on systems that require a good description of electrons in weakly bound orbitals or the outer parts of orbitals, such as many anions, transition states, and noncovalently bound systems.

Two systematic approaches to adding diffuse functions have emerged. The first is to add standard diffuse *s* and *p* functions (4 functions altogether) to nonhydrogenic atoms—this is called a “plus” or “+” basis set—or to add diffuse *s* and *p* basis functions to nonhydrogenic atoms and diffuse *s* basis functions to H and He—is called a “double +” or “++” basis set.¹ The second approach is to add a diffuse function to every atom for every symmetry already present in the original basis; this is

called the augmented (“aug”) approach.² For example, if a given basis set for sulfur atom has *s*, *p*, *d*, and *f* basis functions, one adds *s*, *p*, *d*, and *f* diffuse functions to that atom (a total of 16 functions, where all basis functions in this article use the spherical harmonic option—not the Cartesian one). Thus, as the underlying basis set becomes more complete, the number of diffuse functions increases. This makes the aug basis sets both larger and more rapidly convergent than the plus basis sets as the highest angular momentum of nondiffuse basis functions increases. However, in our previous paper,³ we have shown that, in density functional calculations, the more expensive aug approach is not necessary; that is, the fixed number of diffuse functions of the plus sets is sufficient for results of double-, triple-, and quadruple- ζ quality. In particular, we showed that augmentation of the cc-pV*x*Z (where *x* = D, T, Q, ...) basis sets with the diffuse functions from the basis sets of Pople and co-workers, which yields cc-pV*x*Z+ basis sets, accounts for most of the effect that the full, much more expensive aug basis set provides. We also mentioned that the aug-cc-pV*x*Z basis sets can be truncated to contain only *s* and *p* diffuse functions on the non-hydrogenic atoms. We called this series of basis sets minimally augmented and abbreviated them as maug-cc-pV*x*Z, and we presented some calculations with this kind of basis set; however, the primary focus of the previous paper was on the plus strategy.

We have now carried out systematic tests of the performance of the maug-cc-pV*x*Z basis sets (where *x* stands for (D+d), (T+d), or (Q+d)) for density functional calculations, using both the popular B3LYP^{4–7} density functional and also the recent, highly accurate M06-2X⁸ density functional. We present the results of these tests here as a letter. Our tests involve computation of several commonly calculated and challenging molecular energetic properties. Barrier heights are the most important reaction parameters used for mechanism evaluation and kinetics calculations. Moreover, they are a good challenge for our purposes, since the accuracy of the description of transition states sometimes depends strongly on the presence and quality of the diffuse functions in a basis set. Since diffuse functions are often crucial in the description of noncovalent interactions such as hydrogen bonding, we also present tests on hydrogen bonding. Perhaps the most difficult test of the adequacy of the diffuse part of the basis set is the prediction of electron affinity values, because it involves anion calculations. Ionization potentials and atomization energy are also considered, because they are key thermochemical quantities.

In order to more specifically investigate the need for the diffuse basis functions on hydrogen atoms, we calculated electron affinity values for metal hydride.

* Corresponding author e-mail: truhlar@umn.edu.

Table 1. Definitions of the Diffuse Spaces in the Various Basis Sets, Numbers of Basis Functions in the Databases, Normalized and Relative Numbers of Basis Functions Raised to the Fourth Power, and the Normalized and Relative Computational Time of a Single-Point Energy Calculation on C₄H₁₀S₂ Using M06-2X

basis set	Li–Ar	H–He	<i>N</i>	(<i>N</i> ⁴) _{Nor}	(<i>N</i> ⁴) _{Rel}	(C ₄ H ₁₀ S ₂) _{Nor}	(C ₄ H ₁₀ S ₂) _{Rel}
aug-cc-pV(Q+d)Z	<i>spdfg</i>	<i>spdf</i>	17597	934	1.00	411	1.00
maug-cc-pV(Q+d)Z	<i>sp</i>		12665	251	0.27	74	0.18
cc-pV(Q+d)Z			12073	207	0.22	53	0.13
aug-cc-pV(T+d)Z	<i>spdf</i>	<i>spd</i>	10035	99	1.00	36	1.00
maug-cc-pV(T+d)Z	<i>sp</i>		7209	26	0.27	11.5	0.32
cc-pV(T+d)Z			6609	19	0.19	8.6	0.24
aug-cc-pV(D+d)Z	<i>spd</i>	<i>sp</i>	4989	6	1.00	4.5	1.00
maug-cc-pV(D+d)Z	<i>sp</i>		3783	2	0.33	1.5	0.32
cc-pV(D+d)Z			3183	1	0.17	1.0	0.22

To warn readers that all conclusions about the need for diffuse functions in density functional theory (DFT) calculations cannot be extended with equal success to wave function theory (WFT) calculations, we also present results of the electron affinity calculations at the second-order perturbation theory (MP2)⁹ level.

Similar truncations as in maug-cc-pV(*x*+d)Z basis sets were performed for the maug-cc-pV_{*x*}Z basis sets. The conclusions about the diffuse functions are the same as for the (*x*+d) series, which contains tight *d* functions on the elements in the 3p block of the periodic table. However, the use of (*x*+d) basis sets is recommended as they provide better quality results, especially at the DZ level and for hypervalent molecules. The results for aug-cc-pV_{*x*}Z, maug-cc-pV_{*x*}Z, and cc-pV_{*x*}Z basis sets are available in the Supporting Information, and the main body of this letter will discuss only aug-cc-pV(*x*+d)Z, maug-cc-pV(*x*+d)Z, and cc-pV(*x*+d)Z basis sets.

2. Methods and Databases

The databases employed for the present study are for barrier heights, hydrogen-bond interaction energies, electron affinities, ionization potentials, and bond energies. All energetic results presented in this communication were obtained using the *Gaussian 03*¹⁰ program and the MN-GFM¹¹ functional module. The cost estimates listed in Table 1 were calculated using the *Gaussian 09* program. All results are based on single-point calculations run at geometries¹² optimized with the QCISD/MG3 method (for the BH24, EA13/3, IP13/3, and AE6 databases) and the MC-QCISD/3¹³ method (for the HB6 database), and vibrational contributions are excluded (that is, we are testing the methods for Born–Oppenheimer electronic energies (including nuclear repulsion), not for enthalpies). QCISD denotes quadratic configuration interaction with single and double excitations.¹⁴ The geometries for all the species in the five databases considered are available in the databases' respective references given below.

The results provided by the two density functionals B3LYP and M06-2X with the fully augmented aug-cc-pV(*x*+d)Z basis sets, minimally augmented maug-cc-pV(*x*+d)Z basis sets, and unaugmented cc-pV(*x*+d)Z basis sets containing no diffuse functions were compared to the best estimates in the following databases:

- DBH24/08^{15,16} database of diverse barrier heights, consisting of the best estimates for 24 barrier heights for the heavy-atom transfer reaction, nucleophilic substitution, hydrogen transfer, and unimolecular and association reactions
- HB6¹⁷ database, consisting of hydrogen bond energies for (NH₃)₂, (HF)₂, (H₂O)₂, NH₃(H₂O), (HCONH₂)₂, and (HCOOH)₂

- EA13/3^{18,19} database, consisting of electron affinities for C, S, O, Si, P, Cl, OH, PH, SH, PH₂, O₂, S₂, and Cl₂
- IP13/3^{18,19} database, consisting of ionization potentials for the same 13 species as in the EA13/3 database
- AE6²⁰ representative atomization energy database, consisting of atomization energies of SiH₄, SiO, S₂, propyne, glyoxal, and cyclobutane.

Since the computed values are compared here with experimental or well converged theoretical values in the databases, all the computed energetic data had the spin–orbit contributions added on for F, C, O, Cl, Si, S, OH, and HS,²¹ and the experimental data had the zero-point contributions subtracted from them.

In Table 1, we define the diffuse space in the fully augmented, minimally augmented, and unaugmented basis sets. In order to compare the approximate cost of the calculations involving the basis sets used in the tests, we report the sum *N* of the number of basis functions used in the calculations, summed over all the test cases in all five databases used, and the sum raised to the fourth power (*N*⁴), which is how the cost of the hybrid DFT calculations in popular computer programs scale in the limit of large systems, when linear-scaling algorithms are not used. For clarity, the *N*⁴ values were normalized (denoted by subscript Nor) to the *N*⁴ value for the least expensive basis set cc-pV(D+d)Z. In order to quantify the cost savings for a given *x* (*x* = D, T, Q) achieved by using maug basis sets instead of aug ones, we show in the (*N*⁴)_{Rel} column values normalized to the aug-cc-pV(*x*+d)Z *N*⁴ values for each *x*. Since the limit of asymptotic scaling is never fully reached in practice, we also illustrate the timings with a real example; in particular, we list timings of single-point energy calculations on the medium-size molecule 1,4-butanedithiol (C₄H₁₀S₂).

3. Results

Tables 2–7 provide the mean signed errors (MSEs) and the mean unsigned errors (MUEs, which can also be called mean absolute errors) for a given level of theory in the calculations involving species in a given database. We define MSE and MUE as follows:

$$\text{MSE} = \frac{1}{n} \sum_{i=1}^n e_i \quad (1)$$

$$\text{MUE} = \frac{1}{n} \sum_{i=1}^n |e_i| \quad (2)$$

In eqs 1 and 2, *e_i* is an error in a single property value (for example, an ionization potential value for one molecule) in the database, which contains a total of *n* such values for different

Table 2. Errors in Predictions of the Barrier Heights (kcal/mol) in the BH24/08 Database

basis set	B3LYP		M06-2X	
	MSE	MUE	MSE	MUE
aug-cc-pV(Q+d)Z	-3.99	4.06	0.03	0.93
maug-cc-pV(Q+d)Z	-3.97	4.06	0.09	0.92
cc-pV(Q+d)Z	-4.79	4.85	-0.50	1.38
aug-cc-pV(T+d)Z	-4.08	4.14	-0.06	0.88
maug-cc-pV(T+d)Z	-4.02	4.10	0.08	0.91
cc-pV(T+d)Z	-5.26	5.42	-0.87	2.06
aug-cc-pV(D+d)Z	-4.83	4.90	-0.60	1.20
maug-cc-pV(D+d)Z	-4.69	4.72	-0.39	1.33
cc-pV(D+d)Z	-7.01	7.54	-2.32	3.75

Table 3. Errors in Predictions of the Hydrogen Bonding Energies (kcal/mol) in the HB6 Database

basis set	B3LYP		M06-2X	
	MSE	MUE	MSE	MUE
aug-cc-pV(Q+d)Z	-0.76	0.76	0.11	0.29
maug-cc-pV(Q+d)Z	-0.73	0.73	0.10	0.28
cc-pV(Q+d)Z	-0.23	0.55	0.42	0.46
aug-cc-pV(T+d)Z	-0.73	0.73	0.17	0.31
maug-cc-pV(T+d)Z	-0.67	0.67	0.17	0.34
cc-pV(T+d)Z	0.51	0.74	1.02	1.02
aug-cc-pV(D+d)Z	-0.39	0.40	0.37	0.37
maug-cc-pV(D+d)Z	-0.27	0.64	0.43	0.61
cc-pV(D+d)Z	2.97	2.97	2.91	2.91

Table 4. Errors in Predictions of the Electron Affinities (kcal/mol) in the EA13/3 Database

basis set	B3LYP		M06-2X	
	MSE	MUE	MSE	MUE
aug-cc-pV(Q+d)Z	-1.99	2.33	0.78	1.47
maug-cc-pV(Q+d)Z	-1.96	2.31	0.82	1.49
cc-pV(Q+d)Z	4.35	5.30	5.30	5.30
aug-cc-pV(T+d)Z	-2.07	2.37	0.67	1.46
maug-cc-pV(T+d)Z	-2.04	2.36	0.70	1.49
cc-pV(T+d)Z	9.49	10.13	9.99	9.99
aug-cc-pV(D+d)Z	-2.45	2.75	0.87	2.21
maug-cc-pV(D+d)Z	-2.53	2.92	0.71	2.28
cc-pV(D+d)Z	20.59	20.85	20.37	20.37

Table 5. Errors in Predictions of the Ionization Potentials (kcal/mol) in the IP13/3 Database

basis set	B3LYP		M06-2X	
	MSE	MUE	MSE	MUE
aug-cc-pV(Q+d)Z	3.42	4.62	0.66	2.26
maug-cc-pV(Q+d)Z	3.41	4.61	0.64	2.25
cc-pV(Q+d)Z	3.19	4.42	0.51	2.14
aug-cc-pV(T+d)Z	3.54	4.65	0.99	2.63
maug-cc-pV(T+d)Z	3.53	4.63	0.96	2.62
cc-pV(T+d)Z	2.94	4.14	0.57	2.31
aug-cc-pV(D+d)Z	4.01	4.72	1.08	2.81
maug-cc-pV(D+d)Z	4.14	4.67	1.26	2.99
cc-pV(D+d)Z	1.67	3.15	-0.67	2.84

species. The mean error values for the atomization energies of the molecules in AE6 are divided by 4.83, which is the average number of bonds per molecule in this database, so that the results may be interpreted on a per bond basis.

It may be useful to comment on the meaning of the electron affinities. It is well known that density functional calculations with certain kinds of approximate density functionals predict

Table 6. Errors in Predictions of the Atomization Energies (kcal/mol per bond) in the AE6 Database

basis set	B3LYP		M06-2X	
	MSE	MUE	MSE	MUE
aug-cc-pV(Q+d)Z	-0.42	0.59	0.01	0.22
maug-cc-pV(Q+d)Z	-0.43	0.61	0.01	0.22
cc-pV(Q+d)Z	-0.38	0.56	0.03	0.22
aug-cc-pV(T+d)Z	-0.68	0.76	-0.19	0.33
maug-cc-pV(T+d)Z	-0.70	0.79	-0.23	0.36
cc-pV(T+d)Z	-0.59	0.69	-0.16	0.29
aug-cc-pV(D+d)Z	-2.31	2.31	-1.65	1.73
maug-cc-pV(D+d)Z	-2.67	2.67	-1.94	1.94
cc-pV(D+d)Z	-2.29	2.29	-1.59	1.65

Table 7. Electron Affinity (kcal/mol) of Lithium Hydride LiH

basis set	B3LYP	M06-2X
aug-cc-pV(Q+d)Z	10.12	6.55
jul-cc-pV(Q+d)Z	10.14	6.52
maug-cc-pV(Q+d)Z	10.05	6.42
cc-pV(Q+d)Z	7.82	3.71
aug-cc-pV(T+d)Z	9.97	6.28
jul-cc-pV(T+d)Z	9.96	6.20
maug-cc-pV(T+d)Z	9.84	6.09
cc-pV(T+d)Z	6.24	1.96
aug-cc-pV(D+d)Z	10.33	6.51
jul-cc-pV(D+d)Z	10.20	6.18
maug-cc-pV(D+d)Z	10.05	6.18
cc-pV(D+d)Z	5.75	1.15

unbound negative results in the limit of a large basis set.²² Nevertheless, calculations with standard basis sets have been shown to often give stable and useful results.^{23,24} The results presented here are a test of the stability of such standard calculations to the size of the diffuse subspace of the basis set.

4. Discussion

The tables show that there is essentially complete agreement between predictions of the fully (aug) and minimally (maug) augmented basis sets for density functional calculations in the triple- ζ and quadruple- ζ cases. For quadruple- ζ , the MUE of the maug results is actually lower than the MUE of the aug results in six of the ten cases, and in the other four cases, the maug MUE is never higher than the aug MUE by more than 3%. And yet, the diffuse functions have a very important effect. For example, in Table 4 for electron affinities, the MUE for the unaugmented quadruple- ζ basis is a factor of 2 or 4 times higher than the error in the maug basis, but no significant increase in accuracy is attained by proceeding from the maug basis to the fully augmented basis. At the triple- ζ level, the effects of diffuse functions are larger, for example, decreasing the MUE by factors of 4 and 7 for the electron affinities, but again the maug MUE is almost the same as the aug MUE. For triple- ζ , maug has a lower MUE for five of the ten cases and never has a MUE higher than the aug one by more than 9%.

The effect of diffuse functions is largest for double- ζ basis sets, with the MUE for electron affinities in unaugmented calculations being 7 or 9 times larger than that for the maug basis. We believe it is due to the fact that the unaugmented cc-pVDZ basis set is the least diffuse basis set considered in the present article. Therefore, the effect of pruning of some of the diffuse functions on the quality of the results is the most significant at the double- ζ level. On average though, the ratio

Table 8. Errors in Predictions of the Electron Affinity (kcal/mol) in the EA13/3 Database in MP2 Calculations

basis set	MSE	MUE
aug-cc-pV(T+d)Z	1.44	2.26
maug-cc-pV(T+d)Z	4.01	4.31
cc-pV(T+d)Z	14.36	14.36

of the maug MUE to the aug one is greater than unity by only 13%, and it is only 2% greater than unity if we omit hydrogen bonding. The full aug set of the diffuse functions decreases the double- ζ MUE for hydrogen bonding by a factor of 7–8, whereas the maug diffuse functions decrease it by only a factor of 5.

The cost savings that come from using the maug series of basis sets instead of aug are very large. Using the N^4 asymptotic scaling factors of Table 1 shows that the minimally augmented diffuse basis sets maug-cc-pV(x +d)Z offer the same quality results as their aug analogs at a cost reduced by 73%, 73%, and 67% for $x = Q, T$, and D , respectively. Alternatively if we use actual costs for specific calculations on 1,4-butanedithiol, the time savings using maug vs aug basis sets are 82%, 68%, and 68% for quadruple, triple, and double- ζ basis sets, respectively, and for the B3LYP functional (these timings not shown in the table), they are 86%, 76%, and 52%.

One caveat on the conclusions drawn here is that the databases used for the tests presented here include no metal atoms, so the conclusions have been established only for nonmetals, although it would not be surprising if they were also found to hold for compounds containing metal atoms.

Another noteworthy point is that maug triple- ζ is usually very close to the basis set limit for DFT, at least for the nonmetal systems in the present study.

To show that the diffuse functions on hydrogen are practically redundant, we present the dependence on the electron affinity of lithium hydride (LiH) in Table 7. A metal hydride would be the case where H would be most likely to need diffuse functions, and electron affinities provide the toughest test of the need for diffuse functions, so the particular choice of an electron affinity of a metal hydride is a serious challenge. Deleting the diffuse functions on hydrogenic atoms from an “aug-” basis set yields what we call a “jul-” basis set. From the data shown in Table 7, one can see that even for the electron affinity of metal hydride the diffuse functions on hydrogen are unnecessary for DFT calculations of energetic molecular properties. In particular, the difference in performance of aug and jul basis sets is practically nonexistent. Results for two other metal hydrides (BeH and MgH) are available in the Supporting Information; the error encountered by using jul instead of aug varies from 0.2% to 3.2% and from 1.4% to 9.4% for MgH and BeH, respectively, and so the results for these systems confirm the unimportance of diffuse functions on hydrides. For completeness, we note that the monatomic hydrogen anion is an exception; for this one-center, two-electron system, it is essential to include diffuse functions for an accurate description (however, since the energy of this system has already been calculated accurately to several significant figures with explicitly correlated basis functions, its basis set requirements are a not a major concern here).

Table 8 shows that WFT is more slowly convergent than DFT with respect to the number of the diffuse functions on heavy

atoms in the basis set used. However, the effect of diffuse functions on H has previously been shown to be negligible for energetic calculations even in WFT. In particular, an extensive study of basis set effects on the calculated bond energy and electron affinity of LiH showed that “diffuse functions on hydrogen have little importance for thermochemical calculations.”²⁵

The present study adds to previous work showing that conclusions about basis sets derived from many years of experience with WFT calculations do not necessarily hold for DFT.^{18,26–31}

Although it is not the main point of this paper, we note that Tables 2–6 contain 45 direct comparisons of mean unsigned errors for B3LYP to those for M06-2X for a given basis set and database. In one case, the mean unsigned errors are the same, and in all other cases, M06-2X has the better performance.

5. Conclusions

The only case in Tables 2–6 where the augmentation of the cc-pV(x +d)Z basis sets with the full aug set of the diffuse functions performs significantly better in the density functional theory calculations than the maug basis set is for two studied cases of hydrogen bonding at the double- ζ level. In the other 28 cases considered here, the maug basis actually has a lower mean unsigned error (MUE) than the aug one in 12 of the cases, and the average ratio of the maug MUE to the aug one is only 1% greater than unity.

The present tests have been restricted to the main group. We recommend that, for energetic molecular properties, including barrier heights, the aug basis sets be truncated to the maug level for density functional calculations on systems composed of main-group atoms.

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Supporting Information Available: Additional tables showing root-mean-square errors and results for basis sets without tight d functions plus calculations on MgH and BeH. This information is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. *R. J. Comput. Chem.* **1983**, *4*, 294.
- (2) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
- (3) Papajak, E.; Leverentz, H. R.; Zheng, J.; Truhlar, D. G. *J. Chem. Theory Comput.* **2009**, *5*, 1197. Erratum and addendum: Papajak, E.; Leverentz, H. R.; Zheng, J.; Truhlar, D. G. *J. Chem. Theory Comput.* **2009**, *5*, 3330.
- (4) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (5) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (6) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5848.
- (7) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
- (8) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215. Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.
- (9) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

- (10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (11) Zhao, Y.; Truhlar, D. G. *MN-GFM: Minnesota Gaussian Functional Module*, version 3.0; University of Minnesota: Minneapolis, MN, 2007.
- (12) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 1384.
- (13) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 3898.
- (14) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
- (15) Zheng, J.; Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2007**, *3*, 569.
- (16) Zheng, J.; Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2009**, *5*, 808.
- (17) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2005**, *1*, 415.
- (18) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 1384.
- (19) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 3898.
- (20) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *107*, 8996. Erratum: *J. Phys. Chem. A* **2004**, *108*, 1460.
- (21) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 1643.
- (22) Jarecki, A. A.; Davidson, E. R. *Chem. Phys. Lett.* **1999**, *300*, 44.
- (23) Galbraith, J. M.; Schaefer, H. F., III. *J. Chem. Phys.* **1996**, *105*, 862.
- (24) Horny, L.; Petraco, N. D. K.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **2002**, *124*, 14716.
- (25) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *ACS Symp. Ser.* **2007**, *958*, 153.
- (26) Jensen, F. *J. Chem. Phys.* **2002**, *116*, 7372. Jensen, F. *J. Chem. Phys.* **2002**, *117*, 9234.
- (27) Prascher, B. P.; Wilson, A. K. *Mol. Phys.* **2007**, *105*, 2899.
- (28) Schneider, A. C.; Andzelm, J. W. *J. Comput. Chem.* **1997**, *18*, 775.
- (29) Halls, M. D.; Schlegel, H. B., *J. Chem. Phys.* **1998**, *109*, 10587.
- (30) Florian, J.; Johnson, B. G. *J. Phys. Chem.* **1995**, *99*, 5899.
- (31) Bauschlicher, C. W.; Partridge, H., Jr. *Chem. Phys. Lett.* **1995**, *240*, 533.

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