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The DBH24/08 Database and Its Use to Assess Electronic Structure Model Chemistries for Chemical Reaction Barrier Heights

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Abstract: The diverse barrier height database DBH24 is updated by using W4 and W3.2 data (Karton, A.; Tarnopolsky, A.; Lamère, J.-F.; Schatz, G. C.; Martin, J. M. L. *J. Phys. Chem. A* **2008**, *112*, 12868) to replace previous W1 values; we call the new database DBH24/08. We used the new database to assess 348 model chemistries, each consisting of a combination of a wave function theory level or a density functional approximation with a one-electron basis set. All assessments are made by simultaneous consideration of accuracy and cost. The assessment includes several electronic structure methods and basis sets that have not previously been systematically tested for barrier heights. Some conclusions drawn in our previous work (Zheng, J.; Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2007**, *3*, 569) are still valid when using this improved database and including more model chemistries. For example, BMC-CCSD is again found to be the best method whose cost scales as N^6, and its cost is an order of magnitude smaller than the N^7 method with best performance-to-cost ratio, G3SX(MP3), although the mean unsigned error is only marginally higher, namely 0.70 kcal/mol vs 0.57 kcal/mol. Other conclusions are now broader in scope. For example, among single-reference N^6 methods (that is, excluding MRMP2), we now conclude not only that doubly hybrid density functionals and multicoefficient extrapolated density functional methods perform better than second-order Møller–Plesset-type perturbation theory (MP2) but also that they perform better than any correlation-energy-scaled MP2 method. The most recommended hybrid density functionals, if functionals are judged only on the basis of barrier heights, are M08-SO, M06-2X, M08-HX, BB1K, BMK, PWB6K, MPW1K, BHandHLYP, and TPSS25B95. MOHLYP and HCTH are found to be the best performing local density functionals for barrier heights. The basis set cc-pVTZ+ is more efficient than aug-cc-pVTZ with similar accuracy, especially for density functional theory. The basis sets cc-pVDZ+, 6−31+G(d,p), 6−31B(d,p), 6−31B(d), MIDIY+, MIDIX+, and MIDI! are recommended for double-ζ-quality density functional calculations on large systems for their good balance between accuracy and cost, and the basis sets cc-pVTZ+, MG3S, MG3SXP, and aug-cc-pVDZ are recommended for density functional calculations when larger basis sets are affordable. The best performance of any methods tested is attained by CCSD(T)(full)/aug-cc-pCV(T+d)Z with a mean unsigned error of 0.46 kcal/mol; however, this is several orders of magnitude more expensive than M08-SO/cc-pVTZ+, which has a mean unsigned error of only 0.90 kcal/mol.

1. Introduction

We recently developed a representative database for thermochemical kinetics, called DBH24,[1,2] based on the full

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database NHTBH38/04[3] and 44 hydrogen transfer reactions in Database/3.[4] The databases, NHTBH38/04 and Database/ 3, have 38 barrier heights for non-hydrogen-transfer reactions and 44 barrier heights for hydrogen-transfer reactions. The DBH24 database is a statistically representative subset of

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NHTBH38/04 and the hydrogen-transfer reactions in Database/3. It contains 6 barrier heights each for heavy-atom transfer, nucleophilic substitution, unimolecular and association reactions, and hydrogen-transfer reactions, respectively. This representative database can adequately reproduce the mean signed errors (MSEs), mean unsigned errors (MUEs), and root-mean-square errors (RMSEs) of the entire database. Because the representative database is much smaller than the entire databases, it significantly reduces the computational costs and makes testing of high-level model chemistries more affordable.

A single-level model chemistry is a combination of a level of electronic structure wave function theory or density functional approximation and a basis set; a multilevel model chemistry is a way to combine such combinations to extrapolate to a more accurate result. A model chemistry is also called a "method". In our previous work,[1] we assessed 205 model chemistries for chemical reaction barrier heights using the entire database or the representative DBH24 database. The model chemistries tested included various levels of single-level wave function theory, multicoefficient correlation methods, local and hybrid density functional approximations, and semiempirical molecular orbital methods. In the present article we retest these methods against an improved database, and we add 143 additional methods to the comparison.

The best estimates of barrier heights in the DBH24 database are from either high-level theoretical calculations, e.g., the Weizmann-1[5] (W1) or the multireference configuration interaction method[6] (MRCI), or they are values derived from experimental data. Recently, Karton et al.[7] carried out calculations with the Weizmann-4 (W4) and Weizmann-3.2 (W3.2) model chemistries[8] for these 24 barrier heights. These W4 and W3.2 calculations are more reliable than the W1 values[3] used in the original DBH24 database. This motivated us to update the DBH24 database, and in the present article we present the updated database called DBH24/08.

After the publication of our first comprehensive assessment of model chemistries for barrier heights in 2007,[1] a number of new density functionals, wave function methods, and basis sets became available, and it also became apparent that more of the previously available methods needed testing. Here we make our assessment more complete by adding additional model chemistries not covered in our previous papers[1,9] to our benchmark data set.

2. DBH24/08 Database

Table 1 lists the new best estimates of barrier height that constitute the DBH24/08 database. We updated 14 barrier heights calculated at W1 values in the original DBH24 database by the new[7] W4 or W3.2 values. Those values of barrier heights based on other theoretical calculations than W1 and values derived from experimental rate constants are still considered to be the best estimates for those cases. Below is a brief review of the methods used for the best estimates of barrier height in the DBH24/08 database that are not taken as W4 or W3.2 values.

Table 1. Best Estimates of Barrier Height (in kcal/mol) in the DBH24/08 Database

reactions	forward/reverse BH	method
Heavy-Atom Transfer		
$H + N_2O \leftrightarrow OH + N_2$	17.13/82.47	W4
$H + ClH \leftrightarrow HCl + H$	18.00/18.00	CAS+1+2+QC/CBS plus core-valence correlation
$CH_3 + FCl \leftrightarrow CH_3F + Cl$	6.75/60.00	W3.2
Nucleophilic Substitution		
$Cl^- \cdots CH_3Cl \leftrightarrow ClCH_3 \cdots Cl^-$	13.41/13.41	W3.2
$F^- \cdots CH_3Cl \leftrightarrow FCH_3 \cdots Cl^-$	3.44/29.42	W3.2
$OH^- + CH_3F \leftrightarrow HOCH_3 + F^-$	−2.44/17.66	W3.2
Unimolecular and Association		
$H + N_2 \leftrightarrow HN_2$	14.36/10.61	W4
$H + C_2H_4 \leftrightarrow CH_3CH_2$	1.72/41.75	VSEC
$HCN \leftrightarrow HNC$	48.07/32.82	W4
Hydrogen Transfer		
$OH + CH_4 \leftrightarrow CH_3 + H_2O$	6.7/19.6	experiment
$H + OH \leftrightarrow O + H_2$	10.7/13.1	CAS+1+2+QC/CBS plus core-valence correlation
$H + H_2S \leftrightarrow H_2 + HS$	3.6/17.3	experiment

Barrier heights for the reactions $H + ClH \leftrightarrow HCl + H$ and $H + OH \leftrightarrow O + H_2$ were calculated using the CAS+1+2+QC method at the complete basis set limit including core-valence correlation by Peterson and Dunning.[10] Here CAS+1+2 denotes MRCI with single and double excitations from a complete active space self-consistent field (CASSCF) reference, and +QC denotes a Davidson correction for higher excitations. The active space used in the CASSCF and MRCI calculations is the full valence space plus two additional orbitals of π_x and π_y symmetry. The best estimates of barrier heights of $H + C_2H_4 \leftrightarrow CH_3CH_2$ are based on the variable scaled external correlation (VSEC) method.[11] The VSEC method[12] adjusts the dynamical correlation energy along the reaction path to reproduce the high-pressure limit experimental rate constants for the addition and the unimolecular corrections[13] (VTST/MT). Therefore, this barrier height based on the VSEC method can be considered to have the quality of experimental data. The best estimated barrier heights for the $OH + CH_4 \leftrightarrow CH_3 + H_2O$ and $H + H_2S \leftrightarrow H_2 + HS$ reactions were made by comparing the best available theoretical calculation and best experiment for the reaction rate constants at 600 K.[14] For $OH + CH_4$ the theoretical rate constant[15] was calculated by using VTST/MT, and the experimental data were taken from ref 16. Peng et al. performed experiments and calculations using conventional TST and an Eckart correction for quantum mechanical tunneling for the rate constant of the $H + H_2S$ reaction.[17] Since we used rate constants at 600 K at which the tunneling contribution is moderate, the one-dimensional Eckart correction for tunneling is considered to be acceptable for this case. For these reactions, the best estimate of forward barrier height is determined by $V^{\ddagger}(\text{best estimate}) = V^{\ddagger}(\text{theory}) + \Delta V^{\ddagger}$. The adjustment to the barrier height is calculated using the equation $\Delta V^{\ddagger} = RT \ln (k_{\text{theory}}(T)/k_{\text{experiment}}(T))$, where k_{theory} and $k_{\text{experiment}}$ are respectively the theoretical and experimental reaction rate constants at 600 K, and R is the molar gas constant. The reverse barrier height is calculated by adding

the reaction exoergicity to the best estimate of the forward barrier height. The exoergicity is calculated from experimental total atomization energies.[18]

3. Computational Details

Details for the calculations not mentioned here can be found in the previous papers.[1,9,19]

3.1. Electronic Structure Levels. We carried out calculations employing a diverse array of density functionals, electronic structure wave function levels, basis sets, and multilevel methods for the 24 barrier heights, and we assessed their accuracy statistically against the DBH24/08 database. Some of the calculations were available from previous studies,[1,9,19] and others are new. The added multilevel methods are BMC-CCSD-C,[20] BMC-QCISD,[20] G2,[21] G3,[22] G3/3,[4] G3S,[23] G3S/3,[4] G3SX(MP2),[24] G4,[25] G4(MP2),[26] SCS-MP2,[27] and SOS-MP2.[28,29] We also added one single-level model chemistry based on the CEPA[30] version 1 approximation. We also added calculations with multireference perturbation theory, in particular MRMP2/nom-CPO/MG3S from ref 19. The added density functionals are B2-PLYP,[31] B2GP-PLYP,[7] B2K-PLYP,[32] B2T-PLYP,[32] mPW2-PLYP,[33] mPW2K-PLYP,[32] B3PW91,[34−36] B3P86,[34,35,37] M06,[38] M06-2X,[38] M08-HX,[39] M08-SO,[39] MOHLYP,[40] mPW1KK,[41] mPW25B95,[42] PBEsol,[43] SOGGA,[44] TPSS-20B95,[42] and TPSS25B95.[42] Note that some of the multilevel methods may also be considered to be single-level methods with adjusted coefficients, and other multilevel methods involving both wave function correlation and density functional correlation may be considered to be fifth rung density functional approximations. Calculations involving both Hartree−Fock exchange and density functional exchange (generalized Kohn-sham theory) are, as usual, considered to be a hybrid-type of density functional approximation. In single-level wave function methods, core electrons are uncorrelated except where indicated "(full)". In density functional calculations all electrons are explicit, and all are correlated.

3.2. Basis Sets. The additional basis sets used in this work are 3−21G,[45] 6−31B(d,p),[20] cc-pVDZ+,[46] cc-pVTZ+,[46] cc-pV(T+d)Z+,[46] G3LargeXP,[25] G3MP2LargeXP,[25] G45Z,[25] G4QZ,[25] G4MP2QZ,[26] G4MP2TZ,[26] MG3SXP,[39] MID-IX+,[47] MIDIY+,[47] STO-2G,[48] STO-3G,[48] and STO-3G+.[48,49] The MG3SXP (where XP denotes "extra polarization") basis differs from the MG3S[4] one in the same way that G3LargeXP[25] differs from G3Large,[22] in particular, the 2df polarization functions of G3Large on Li−Ne are replaced by a 3df set, and the 3d2f polarization functions on Al−Ar are replaced by 4d2f, where the polarization functions are those recommended by Curtiss et al.[25] The basis set cc-pVTZ+[46] is cc-pVTZ[50] for H and cc-pVTZ plus the Pople-style diffuse s and p functions[49] for non-hydrogenic atoms, while cc-pV(T+d)Z+ is the cc-pV(T+d)Z[51] basis set plus the same diffuse functions as in the cc-pVTZ+. The cc-pVDZ+ basis is constructed in the same way as the cc-pVTZ+ basis. The basis 6−31B(d,p) is 6−31+B(d,p)[20] without diffuse functions. MIDIX+ and MIDIY+ basis sets are obtained by adding diffuse function on all elements with nuclear charges of 3 or larger to MIDIX[52] (also called MIDI!)

and MIDIY[47] basis sets. The MIDIY basis set is the same as MIDIX (or MIDI!) but with a polarization function added to hydrogen. STO-3G+ is STO-3G plus the Pople-style diffuse s and p functions[49] for non-hydrogenic atoms.

3.3. Software. The additional calculations mentioned above were carried out using the *Gaussian 03* package[53] and *MN-GFM 4.1* module[54] except that CCSD(T)[55] and CEPA calculations were done by the *Molpro* program.[56]

3.4. Relativistic Effects. The effect of spin−orbit coupling was added to the energies of the Cl, O, OH, and HS radicals, which lower their energies by 0.84, 0.22, 0.20, and 0.54 kcal/mol, respectively.[57] Scalar relativistic effects[58] were neglected, which is not a serious approximation since the heaviest element involved in DBH24/08 is Cl.

3.5. Geometries. Most calculations in this work used structures optimized using the QCISD/MG3 method with the spin-restricted formalism for closed-shell and the spin-unrestricted formalism for open-shell systems. Note that we also use the QCISD/MG3 geometries for those multilevel methods, e.g., Gn (n = 2, 3, 4) and CBS, which were originally defined to use a lower-level geometry. The only exception is MRMP2, for which calculations were carried out at consistently optimized geometries. We also tested a few methods for fully optimized calculations.

3.6. Vibrational Contributions. The barrier heights calculated in this work are all zero-point exclusive. No vibrational, rotational, or translational contributions are included in DBH24/08 or in any of the calculations in this paper.

3.6. Timings. The computational "cost" of a given method is assessed as the single-processor CPU time for calculating an energy gradient of the molecule phosphinomethanol divided by the time for an MP2/6−31+G(d,p) energy gradient calculation with the same computer program on the same computer. We use gradient calculations to illustrate computational cost because gradients are important for geometry optimization and dynamics calculations. Analytic gradients were always used unless they are not available in the computer program that we used, in which case we used numerical gradients. In *Gaussian 03* a numerical gradient of phophinomethanol uses 49 single-point energies, whereas in *Molpro* it uses 19 single-point energies for phophinomethanol. For local DFT methods, we calculated two costs corresponding to carrying out the calculation with and without density fitting,[59] and the table gives the smaller of the two. The timings for CR-CC(2,3) were not run directly but were estimated as 1.5 times the cost of CCSD(T) with the same basis set.

In a few cases the timings were run more than once under different computer load conditions, and the results were averaged. The SOS-MP2 timings were run with the *Q-Chem* program, and all other timings were run using the software specified in Section 3.3 or refs 1, 9, and 19. Although some multilevel wave function methods, e.g., Gn (n = 2, 3, 4) and CBS, are usually defined to use a lower-level geometry and are not normally employed in gradient calculations, we include gradient timing for them here so that the reader can judge their approximate cost on the same grounds as the other methods.

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4. Results and Discussion

In the present article, we employed 348 model chemistries to calculate the 24 barrier heights in the DBH24/08 database. We selected the electronic structure methods that are often used in the literature or that are new but tend to give promising results. When we run a calculation with a multilevel method, we also can get the results for each single-level method in the multilevel components simultaneously. Therefore we also listed these single-level methods' results in Table 2, so that one can see how much the multilevel method improves the accuracy over each of its components. Most density functionals are run with MG3S basis sets at first. If a density functional gives good results, we also run this density functional with more basis sets so that we can assess the methods with a greater variety of performance-to-cost ratios.

All electronic structure methods will be assessed based on a combination of accuracy against DBH24/08, the scaling power σ, and the "cost". The scaling power is defined such that the number of arithmetic operations in the calculation increases as N^σ in the limit of large N, where N is the number of atoms, and the scaling refers to increasing N with a given number of basis functions on each atom. The scaling would be different if one increased the number of basis functions with N fixed.[60] Furthermore, one does not reach the large-N limit with respect to system size until very large systems (much larger than those considered here) are considered. So one must be cautious in using σ to categorize methods. One must be even more cautious in using the cost values. One cannot stress too much the somewhat arbitrary character of the timings. We tried to minimize this by computing every cost as the relative cost of two calculations with the same software on the same computer where the denominator is a method (MP2/6−31+G(d,p)) that is available in almost all software packages. Nevertheless the timings do depend on the software. Timing differences less than a factor of 2 are not meaningful except when one is comparing similar methods, and timings of inexpensive methods are inevitably contaminated by overhead. Thus all timings greater than 1.0 are rounded to two significant figures, and those less than 1.0 are rounded to one significant figure. Another disadvantage of using timings as costs is that the true cost also involves components of memory and disk usage, software cost, and human time.

An example showing the vagaries of timings is a comparison the timings for SOS-MP2/MG3S and SOS-MP2/cc-pVTZ. Our standard method of assessing cost gives 17 and 15, respectively (see Table 2). If the former calculation had the same number of iterations as the latter, the timing would be only 11. Such an effect is partly noise, but it may also be due in part to the fact that calculations involving diffuse functions often require more iterations. Furthermore, unlike cc-VTZ, the MG3S basis set has the same exponents for s and p functions; this gives a cost savings in *Gaussian* but not in most other computer programs.

Despite all these complex considerations, no evaluation of methods that does not consider cost can serve as a guide to practical work, so we must consider cost. Therefore, after consideration of various cost estimates, we selected the simple relative timings explained above, which has the advantage of being systematic, easy to understand, and easy for a reader to apply to new methods when he or she has a new method to assess in comparison to those considered here. To avoid tediousness, we will not repeat the cautionary notes about timings, but the reader should keep them in mind as we proceed with discussion.

4.1. Calculations at Standard Geometries. Table 2 lists, for calculations at geometries optimized with the QCISD/MG3 method (and for consistently optimized MRMP2/MG3S), the mean signed errors and mean unsigned errors for the DBH24/08 database as well as the errors for its components: heavy-atom transfer (HATBH6), nucleophilic substitution (NSBH6), unimolecular and association (UABH6), and hydrogen-transfer (HTBH6) reactions. All methods are listed in order of increasing MUE for the DBH24/08 database and are listed in separation sections for each scaling order σ. Table 2 also gives references[3,4,7,14,19,21−44,55,61−111] for the electronic structure methods, which should be useful since some of the acronyms are more familiar than others.

To systematically create a list of recommended methods, we started with the best N^7 method, (where "best" is defined as lowest MUE), then added the best N^7 method that has a lower cost, and then added the best N^7 method that has a lower cost than both of these, etc., until we got to the bottom of the N^7 list. Then we did the same for the N^6, N^5, N^4, and N^3 methods. When adding methods to the recommended list, we also checked the scaling. For example, if there is an N^4 method that has both lower cost and lower MUE than an N^5 method on the list, then that N^5 method is removed from the list. This created a list based on the performance for the overall DBH24/08 database. MUEs that remain on the list when the process is complete are in bold in Table 2. This process was then repeated for each of the four smaller databases. The MUEs of the five resulting lists are all in bold in Table 2. When searching for an affordable method for a specific application, the bold entries in Table 2 provide a short list of methods that should be considered. Any method that earned at least one bold MUE is also in bold with its timing in bold, in order to make the table easier to read.

The most accurate method overall is CCSD(T) with all electrons correlated and a triple-ζ core-valence correlated basis set, which can achieve accuracy better than 0.5 kcal/mol. But the cost of this accuracy is that this method is 2 orders of magnitude higher than for any other method listed in Table 2. G3SX(MP3) has the best cost-adjusted performance; it has the same accuracy as the CCSD(T)/aug-cc-pV(T+d)Z method, but it is about 18 times more efficient.

CCSD(T)-KS denotes a CCSD(T) calculation based on reference orbitals from a density functional calculation (using a spin-restricted calculation with the BLYP functional here); otherwise oribtals were obtained from a restricted Hartree−Fock calculation. Comparison of the results for CCSD(T)-KS/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ calculations shows that the choice of orbitals makes only a very small difference in the MUE for the representative barrier height calculations and using Kohn−Sham orbitals actually raises the MUE by 0.03 kcal/mol.

Table 2. Mean Signed Errors (MSEs) and Mean Unsigned Errors (MUEs) (in kcal/mol) for the DBH24/08 Database Calculated at QCISD/MG3 Geometries[a]

methods	type	theory ref	HATBH6 MSE	HATBH6 MUE	NSBH6 MSE	NSBH6 MUE	UABH6 MSE	UABH6 MUE	HTBH6 MSE	HTBH6 MUE	DBH24 MUE	cost
					N^7 Methods							
CCSD(T)(full)/aug-cc-pCV(T+d)Z	WFT	55	0.52	0.63	−0.34	0.36	0.14	0.28	0.08	0.58	**0.46**	**25000**
CCSD(T)(full)/aug-cc-pCVTZ	WFT	55	0.54	0.67	−0.37	0.38	0.14	0.28	0.08	0.58	0.47	32000
CCSD(T)(full)/aug-cc-pVTZ	WFT	55	−0.14	0.59	−0.63	0.63	0.31	0.33	−0.60	0.60	**0.54**	**14000**
CCSD(T)/aug-cc-pV(T+d)Z	WFT	55	0.45	**0.63**	−0.63	0.63	0.07	0.33	0.06	0.67	0.57	**2200**
G3SX(MP3)	ML	24	−0.34	**0.76**	−0.11	0.43	−0.02	0.41	0.57	0.68	**0.57**	**120**
G3SX	ML	24	−0.38	**0.74**	−0.64	0.64	0.08	0.31	0.39	0.60	0.57	**890**
G4	ML	25	0.34	0.81	−0.34	0.56	0.07	**0.24**	0.72	0.72	0.58	**7700**
G4(MP2)	ML	26	0.25	**0.33**	0.50	0.57	−0.26	0.44	1.04	1.04	0.59	**3100**
CR-CC(2,3)(full)A/aug-cc-pCVTZ	WFT	65	1.13	1.13	−0.06	0.17	0.37	0.45	0.27	0.66	0.60	48000
CR-CC(2,3)A/aug-cc-pV(T+d)Z	WFT	65	1.02	1.03	−0.34	0.34	0.30	0.45	0.26	0.73	0.64	3300
CR-CC(2,3)(full)D/aug-cc-pCVTZ	WFT	65	1.00	1.00	−0.32	0.42	0.36	0.48	0.24	0.68	0.64	48000
CR-CC(2,3)(full)C/aug-cc-pCVTZ	WFT	65	0.99	0.99	−0.32	0.43	0.36	0.48	0.24	0.68	0.64	48000
CR-CC(2,3)B/aug-cc-pV(T+d)Z	WFT	65	1.24	1.24	−0.16	**0.16**	0.33	0.49	0.33	0.76	0.66	**3300**
CR-CC(2,3)(full)B/aug-cc-pCVTZ	WFT	65	1.35	1.35	0.13	0.17	0.40	0.48	0.34	0.69	0.67	48000
CR-CC(2,3)C/aug-cc-pV(T+d)Z	WFT	65	0.87	0.87	−0.64	0.64	0.29	0.49	0.21	0.74	0.69	3300
MCG3-MPW	ML	64	−0.67	1.09	−0.61	0.61	−0.13	0.61	−0.07	**0.44**	0.69	**100**
CR-CC(2,3)D/aug-cc-pV(T+d)Z	WFT	65	0.88	0.88	−0.64	0.64	0.29	0.49	0.21	0.74	0.69	3300
CCSD(T)/aug-cc-pVTZ	WFT	55	0.59	0.95	−0.78	0.78	0.07	0.33	0.09	0.70	0.69	4700
CCSD(T)-KS/aug-cc-pVTZ	WFT	55	0.47	0.91	−0.92	0.92	0.06	0.31	0.03	0.76	0.72	3900
MCG3-MPWB	ML	64	−0.67	1.05	−0.36	0.62	−0.15	0.62	−0.31	0.59	0.72	100
G3	ML	22	0.62	0.75	−1.10	1.10	0.22	0.39	0.68	0.68	0.73	1500
G3S/3	ML	4	−0.86	1.08	−0.85	0.85	−0.09	0.42	0.25	0.58	0.73	1500
G3S	ML	23	−0.38	1.00	−0.93	0.93	0.09	0.35	0.42	0.69	0.74	1500
MCG3-TS	ML	64	−0.50	**0.86**	−1.09	1.09	0.11	0.53	−0.22	0.55	0.76	**100**
CR-CC(2,3)A/aug-cc-pVTZ	WFT	65	1.16	1.35	−0.49	0.49	0.30	0.45	0.28	0.75	0.76	7100
CR-CC(2,3)B/aug-cc-pVTZ	WFT	65	1.37	1.49	−0.31	0.31	0.33	0.49	0.35	0.78	0.77	7100
CR-CC(2,3)C/aug-cc-pVTZ	WFT	65	1.03	1.14	−0.81	0.81	0.29	0.49	0.23	0.77	0.80	7100
CR-CC(2,3)D/aug-cc-pVTZ	WFT	65	1.04	1.15	−0.81	0.81	0.29	0.49	0.23	0.76	0.80	7100
G3/3	ML	4	0.91	1.04	−0.98	0.98	0.26	0.40	0.87	0.87	0.82	1500
MCG3/3	ML	4	−0.52	1.25	−0.53	0.69	−0.30	0.58	−0.33	0.86	0.84	90
CCSD(T)/cc-pV(T+d)Z+	WFT	55	1.51	1.51	−0.18	0.75	0.34	0.55	0.72	0.97	0.94	540
CCSD(T)/cc-pVTZ+	WFT	55	1.65	1.65	−0.33	0.81	0.34	0.55	0.75	0.99	1.00	870
G2	ML	21	1.18	1.43	−0.48	0.75	0.41	0.53	1.33	1.33	1.01	2300
CCSD(T)(full)/MG3S	WFT	55	1.50	1.57	−0.11	0.91	0.83	0.83	1.06	1.16	1.12	1000
CR-CC(2,3)(full)C/MG3S	WFT	65	1.73	1.73	0.00	0.79	0.96	0.96	1.11	1.16	1.16	1500
CR-CC(2,3)(full)D/MG3S	WFT	65	1.74	1.74	0.00	0.80	0.95	0.95	1.11	1.16	1.16	1500
CCSD(T)/MG3S	WFT	55	1.63	1.71	−0.35	1.12	0.67	0.67	1.16	1.22	1.18	300
QCISD(T)/MG3S	WFT	66	1.58	1.65	−0.69	1.31	0.65	0.65	1.10	1.20	1.20	5100
CR-CC(2,3)C/MG3S	WFT	65	1.85	1.85	−0.28	1.00	0.79	0.79	1.21	1.22	1.22	450
CR-CC(2,3)D/MG3S	WFT	65	1.86	1.86	−0.28	1.00	0.79	0.79	1.21	1.22	1.22	450
CR-CC(2,3)(full)A/MG3S	WFT	65	2.07	2.07	0.17	0.82	1.06	1.06	1.25	1.27	1.31	1500
CR-CC(2,3)A/MG3S	WFT	65	2.20	2.20	−0.08	0.92	0.90	0.90	1.36	1.36	1.34	450
G3SX(MP2)	ML	24	0.44	1.69	−0.20	0.69	−0.52	1.06	1.87	1.90	1.34	150
CR-CC(2,3)(full)B/MG3S	WFT	65	2.29	2.29	0.36	0.82	1.10	1.10	1.32	1.32	1.38	1500
CR-CC(2,3)B/MG3S	WFT	65	2.42	2.42	0.12	0.85	0.93	0.93	1.42	1.42	1.41	450
CCSD(T)/aug-cc-pVDZ	WFT	55	1.00	2.27	−1.99	1.99	−0.33	0.68	0.03	0.76	1.42	140
CBS-QB3	ML	67,68	−0.62	1.68	−0.96	1.07	−2.07	2.42	−1.22	1.32	1.62	360
CBS-Q	ML	69	−1.88	1.91	−1.60	1.63	−2.47	2.53	−0.68	0.86	1.73	370
CEPA(1)/MG3S	WFT	30	−2.05	4.19	0.53	0.86	0.94	1.10	1.78	1.81	1.99	90
CCSD(T)/MG3SXP	WFT	55	3.09	4.13	1.03	2.01	0.31	0.86	1.12	1.18	2.04	280
CBS-Lq	ML	70	−1.31	2.31	0.06	1.52	−3.12	3.55	−0.80	1.20	2.14	180
CCSD(T)/cc-pV(T+d)Z	WFT	55	1.76	1.76	−3.01	5.10	0.32	0.47	0.87	1.38	2.18	670
CCSD(T)/cc-pVTZ	WFT	55	1.90	1.90	−3.15	5.27	0.32	0.47	0.89	1.41	2.26	630
CBS-4M	ML	68,69	1.14	3.51	2.50	2.98	−2.24	2.71	−0.20	0.55	2.44	170
CCSD(T)/6−311G(2df,2p)	WFT	55	1.88	2.20	−3.92	8.15	0.57	0.76	1.35	1.85	3.24	380
QCISD(T)/6−311G(2df,2p)	WFT	66	1.77	2.28	−4.23	8.37	0.56	0.75	1.16	1.62	3.25	2300
MP4/MG3S	WFT	62	7.81	7.81	−1.34	1.42	3.23	3.62	2.40	2.40	3.81	2900
QCISD(T)/6−31G(d)	WFT	66	4.25	4.93	−2.73	8.19	1.45	3.04	4.76	5.61	5.44	63
CCSD(T)/6−31G(d)	WFT	55	4.56	5.18	−2.53	8.15	1.53	3.09	4.80	5.62	5.51	8.1
MP4/6−311G(2df,2p)	WFT	62	8.00	8.00	−4.58	8.64	3.20	3.82	2.35	2.35	5.70	1600
MP4/6−31+G(d)	WFT	62	10.07	10.07	−0.47	2.28	3.97	4.88	5.64	5.64	5.72	82
MP4/6−311G(2d,p)	WFT	62	9.13	9.13	−5.00	8.88	3.08	4.02	2.98	3.36	6.35	460
MP4/6−31G(2df,p)	WFT	62	8.22	8.22	−4.34	9.31	4.22	4.48	4.09	4.26	6.57	610
MP4/6−31G(d)	WFT	62	10.73	10.73	−2.88	8.58	4.22	5.40	6.02	6.45	7.79	37
					N^6 Methods							
BMC-CCSD	ML	20	0.52	1.28	−0.02	0.54	−0.24	0.37	0.19	0.63	**0.70**	**17**
BMC-CCSD-C	ML	20	0.50	1.37	0.07	0.53	−0.37	0.37	0.26	0.64	0.73	17
BMC-QCISD	ML	20	1.35	1.50	0.08	0.56	0.10	**0.30**	0.55	0.77	0.78	**16**

DBH24/08 Database

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Table 2. Continued

methods	type	theory ref	HATBH6 MSE	HATBH6 MUE	NSBH6 MSE	NSBH6 MUE	UABH6 MSE	UABH6 MUE	HTBH6 MSE	HTBH6 MUE	DBH24 MUE	cost
MCQCISD-MPWB	ML	64	−0.49	**0.94**	−0.08	0.65	−0.09	0.89	−0.53	0.63	0.78	**29**
MCQCISD-MPW	ML	64	−0.72	1.19	−0.34	0.55	−0.14	0.94	−0.42	0.52	0.80	27
MC-QCISD/3	ML	4	1.48	1.53	−0.20	**0.21**	0.49	0.66	0.89	0.98	0.84	**16**
MCQCISD-TS	ML	64	−0.80	1.00	−1.12	1.12	0.06	0.69	−0.65	0.79	0.90	29
MCUT-MPWB	ML	64	1.53	1.53	−0.22	0.59	1.09	1.52	−0.52	0.56	1.05	28
MCUT-MPW	ML	64	1.38	1.81	−0.90	0.90	1.17	1.54	−0.54	0.54	1.20	26
MCUT-TS	ML	64	1.18	1.61	−1.56	1.56	1.27	1.32	−0.59	0.68	1.29	28
CCSD(full)/aug-cc-pVTZ	WFT	71	3.43	3.43	1.72	1.72	1.42	1.42	1.18	1.18	1.94	3200
CCSD/aug-cc-pVTZ	WFT	71	4.11	4.11	1.56	1.56	1.17	1.22	1.84	1.84	2.18	2400
CCSD/aug-cc-pV(T+d)Z	WFT	71	3.98	3.98	1.72	1.72	1.17	1.22	1.82	1.82	2.18	2500
CCSD(full)/aug-cc-pCVTZ	WFT	71	4.19	4.19	2.01	2.01	1.26	1.26	1.88	1.88	2.34	6800
QCISD/MG3S	WFT	66	4.41	4.41	1.18	1.28	1.30	1.30	2.37	2.37	2.34	150
CCSD(full)/aug-cc-pV(T+d)Z	WFT	71	4.18	4.18	2.04	2.04	1.26	1.26	1.89	1.89	2.34	3500
CCSD/cc-pVTZ+	WFT	71	5.00	5.00	1.95	1.95	1.42	1.47	2.39	2.39	2.70	320
CCSD/MG3S	WFT	71	5.00	5.00	1.92	1.92	1.72	1.72	2.75	2.75	2.85	240
CCSD(full)/MG3S	WFT	71	4.93	4.93	2.18	2.18	1.90	1.90	2.68	2.68	2.92	380
MC-UT/3	ML	4	7.02	7.02	0.25	**0.35**	3.12	3.12	2.33	2.33	3.21	**15**
CCSD/MG3SXP	WFT	71	6.09	6.31	2.96	3.04	1.41	1.60	2.63	2.63	3.40	350
CCSD/cc-pV(T+d)Z+	WFT	71	4.87	4.87	2.11	2.11	1.42	1.47	6.35	6.35	3.70	350
MP4SDQ/MG3S	WFT	62	8.95	8.95	1.40	1.42	3.38	3.38	3.56	3.56	4.33	95
QCISD/6−31B(d)	WFT	66	6.40	9.04	−0.72	**5.20**	2.26	**2.41**	4.86	5.06	5.43	**1.5**
CCSD/6−31B(d)	WFT	71	6.74	9.17	0.32	5.45	2.57	2.68	4.99	5.08	5.59	2.3
MP3/MG3S	WFT	62	10.70	10.70	3.33	3.33	4.44	4.44	4.29	4.29	5.69	71
QCISD/6−31G(d)	WFT	66	6.18	6.26	−1.75	8.09	1.98	2.71	5.44	5.89	5.74	19
CCSD/6−31G(d)	WFT	71	6.44	6.50	−1.04	7.95	2.19	2.83	5.56	5.91	5.80	2.4
MP4SDQ/6−31+G(d)	WFT	62	10.69	10.69	1.53	2.38	4.15	4.57	6.30	6.30	5.98	1.6
MP4SDQ/6−31G(2df,p)	WFT	62	9.05	9.05	−2.12	8.23	4.32	4.32	4.96	4.96	6.64	14
MP3/6−31+G(d)	WFT	62	12.36	12.36	3.65	3.65	5.22	5.22	7.13	7.13	7.09	1.4
MP3/6−31G(2df,p)	WFT	62	10.77	10.77	−0.39	7.57	5.38	5.38	5.54	5.54	7.32	2.8
MP4SDQ/6−31G(d)	WFT	62	11.17	11.17	−1.29	8.21	4.38	**5.06**	6.02	6.45	7.72	**0.9**
MP4DQ/6−31B(d)	WFT	62	12.84	12.84	1.85	**6.18**	5.62	5.62	6.90	6.90	7.89	**0.8**
MP3/6−31G(d)	WFT	62	12.85	12.85	0.51	**7.60**	5.43	5.64	7.34	7.34	8.36	**0.7**
					N^5 Methods								
MRMP2/nom-CPO/MG3S	WFT	19, 72	−1.38	1.88	0.84	0.89	−0.40	1.06	1.28	1.58	0.90	540
B2GP-PLYP/MG3S	DFT	7	0.42	1.37	−1.28	1.28	1.26	1.26	−0.34	0.55	1.12	21
mPW2K-PLYP/MG3S	DFT	32	1.80	1.80	−0.77	1.02	1.79	1.79	0.22	**0.32**	1.23	**21**
B2T-PLYP/MG3S	DFT	32	−0.58	1.27	−1.67	1.67	0.89	0.98	−0.87	1.04	1.24	21
MC3BB	ML	63	1.69	2.31	0.42	**0.60**	1.60	1.60	−0.43	0.63	1.28	**13**
B2K-PLYP/MG3S	DFT	32	2.12	2.12	−0.58	0.87	1.85	1.85	0.52	0.52	1.34	21
MC3MPWB	ML	64	1.78	2.46	0.14	**0.59**	1.71	1.71	−0.53	0.75	1.38	**14**
MCCO-MPWB	ML	64	1.10	1.65	0.98	1.38	1.11	1.27	−1.27	1.27	1.39	26
MC3MPW	ML	63	1.91	**2.49**	0.06	**0.72**	2.19	2.19	−0.46	**0.61**	1.50	**12**
MC3TS	ML	64	2.02	2.31	−0.90	0.90	2.28	2.28	−0.22	**0.52**	1.50	**14**
MCCO-TS	ML	64	1.16	2.10	−1.15	1.45	1.63	1.63	−0.92	0.92	1.53	27
mPW2-PLYP/MG3S	DFT	33	−1.81	1.87	−2.17	2.17	0.49	0.98	−1.75	1.75	1.69	21
MCCO-MPW	ML	64	2.16	2.64	0.28	1.54	1.90	1.90	−0.65	1.09	1.79	24
B2-PLYP/MG3S	DFT	31	−2.29	2.40	−2.52	2.52	0.33	**0.78**	−1.79	1.84	1.88	**21**
MC-CO/3	ML	4	9.44	9.44	−0.11	1.19	4.80	4.80	2.66	2.66	4.52	13
MP2/aug-cc-pVTZ	WFT	73	10.69	10.69	0.34	0.67	4.70	5.53	3.06	3.20	5.02	120
MP2/G3MP2LargeXP	WFT	73	11.18	11.18	0.99	1.28	4.99	5.84	3.94	3.94	5.49	31
MP2(full)/G3LargeXP	WFT	73	11.04	11.04	1.25	1.25	5.07	5.92	3.81	3.81	5.50	56
MP2/MG3	WFT	73	11.38	11.38	0.62	0.93	5.16	6.06	3.96	3.96	5.58	14
MP2/MG3S	WFT	73	10.70	10.70	3.33	3.33	4.44	4.44	3.99	3.99	5.62	14
SAC-MP2/6−31+G(d,2p)	ML	4	11.17	**11.17**	0.52	3.04	5.49	6.25	2.81	2.81	5.82	**1.5**
MP2/6−31+G(d,2p)	WFT	73	12.08	12.08	1.17	**2.46**	5.28	5.66	4.06	4.06	6.07	**1.5**
MP2/cc-pVTZ	WFT	73	11.74	11.74	−2.22	4.83	4.91	5.87	3.51	3.51	6.49	18
SAC-MP2/6−31+G(d,p)	ML	4	11.99	**11.99**	0.65	3.04	6.27	7.09	4.32	4.32	6.61	**1.0**
MP2/6−31++G(d,p)	WFT	73	12.51	12.51	1.36	2.48	5.67	6.32	5.50	5.50	6.70	1.1
MP2/6−31+G(d,p)	WFT	73	12.93	12.93	1.39	**2.48**	5.94	6.40	5.57	5.57	6.85	**1.0**
SCS-MP2/MG3S	ML	27	14.23	14.23	1.46	1.46	6.01	6.47	5.57	5.57	6.93	14
MP2/aug-cc-pV(D+d)Z	WFT	73	12.09	12.09	−2.42	7.64	4.57	6.01	3.76	3.76	7.37	4.3
SCS-MP2/cc-pVTZ	ML	27	14.36	14.36	−1.48	4.68	5.70	6.24	5.06	5.06	7.58	18
MP2/6−31+G(d)	WFT	73	13.34	13.34	1.38	**2.67**	6.01	7.45	6.71	6.71	7.54	**0.6**
MP2(full)/6−31G(2df,p)	WFT	73	11.30	11.30	−2.61	8.68	6.23	7.08	4.82	4.82	7.97	3.6
MP2/6−31B(d)	WFT	73	13.11	**13.11**	−1.04	5.22	6.33	7.50	6.22	6.22	**8.01**	**0.4**
MP2/6−31G(2df,p)	WFT	73	11.51	11.51	−2.88	8.60	6.04	6.90	5.06	5.06	8.02	3.0
MP2/6−31G(d)	WFT	73	13.86	13.86	−1.59	8.62	6.19	7.93	6.89	6.89	9.33	0.4
					N^4 Methods								
M08-SO/cc-pVTZ+	DFT	39	−0.42	0.95	0.41	**0.45**	0.14	1.32	−0.82	0.89	**0.90**	**21**

Table 2. Continued

methods	type	theory ref	HATBH6		NSBH6		UABH6		HTBH6		DBH24	cost
			MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MUE	
M06-2X/aug-cc-pVTZ	DFT	38	−0.27	**0.67**	0.54	0.66	0.06	1.10	−0.58	1.30	0.93	**60**
M06-2X/MG3S	DFT	38	−0.06	**0.73**	0.60	0.85	0.36	1.09	−0.50	1.25	**0.98**	**16**
M06-2X/cc-pVTZ+	DFT	38	−0.06	0.77	0.38	0.76	0.18	1.13	−0.50	1.30	0.99	22
M08-SO/MG3SXP	DFT	39	−0.43	1.06	0.41	**0.64**	0.09	1.39	−0.87	1.09	**1.04**	**15**
M06-2X/MG3SXP	DFT	38	−0.02	0.85	0.73	0.99	0.23	1.12	−0.49	1.28	1.06	20
M08-SO/MG3S	DFT	39	−0.53	1.09	0.19	**0.67**	0.23	1.43	−0.86	1.05	**1.06**	**14**
M08-HX/cc-pVTZ+	DFT	39	0.20	1.27	0.69	1.28	0.49	1.29	−0.48	**0.65**	1.12	**21**
M08-HX/MG3SXP	DFT	39	0.12	1.09	0.88	1.43	0.51	1.26	−0.45	0.71	1.12	15
M08-HX/MG3S	DFT	39	0.02	1.18	0.73	1.35	0.72	1.29	−0.50	**0.71**	1.14	**14**
BB1K/MG3S	DFT	34, 74, 75	0.04	1.07	0.96	1.10	0.55	1.56	−0.95	1.06	**1.20**	**11**
M06-2X/MG3	DFT	38	−0.52	0.81	0.57	0.88	0.66	1.93	−0.51	1.27	1.22	18
BMK/MG3S	DFT	76	−0.94	**0.94**	0.62	**0.77**	0.98	2.06	−1.12	1.12	1.22	**13**
MPWB1K//MG3S	DFT	75, 77, 78	−0.05	1.08	0.91	1.01	0.60	1.63	−1.24	1.24	1.24	12
BB1K/cc-pVTZ+	DFT	34, 74, 75	0.10	1.00	1.03	1.35	0.37	1.57	−0.98	1.08	1.25	19
BB1K/MG3SXP	DFT	34, 74, 75	0.06	1.15	1.09	1.23	0.43	1.57	−0.94	**1.04**	1.25	**13**
MPWB1K/cc-pVTZ+	DFT	75, 77, 78	0.03	1.00	0.99	1.18	0.41	1.64	−1.26	1.26	1.27	20
PWB6K/MG3S	DFT	79	0.58	1.33	0.85	0.94	0.85	1.59	−0.91	1.23	1.27	12
MPWB1K/MG3SXP	DFT	75, 77, 78	−0.02	1.16	1.03	1.13	0.47	1.63	−1.17	1.20	1.28	14
PWB6K/cc-pVTZ+	DFT	79	0.65	1.33	0.92	1.10	0.67	1.60	−0.93	1.08	1.28	20
M06-2X/aug-cc-pVDZ	DFT	38	−0.75	1.46	−0.01	1.25	−0.37	1.35	−1.27	1.27	**1.33**	**4.0**
MPWB1K/aug-pc2	DFT	75, 77, 78	−0.29	0.95	1.47	1.51	0.42	1.61	−1.29	1.40	1.37	58
M06-2X/6−31+G(d,p)	DFT	38	−0.86	**1.38**	0.51	1.36	0.44	1.52	−0.83	1.64	**1.48**	**3.0**
MPW1K/MG3S	DFT	14	−0.15	**1.07**	0.81	1.10	0.95	2.42	−1.06	1.34	1.48	**11**
M06-2X/cc-pVDZ+	DFT	38	−0.71	1.90	0.48	1.34	−0.31	1.24	−1.44	1.53	1.50	2.6
MPWB1K/MG3	DFT	75, 77, 78	−0.51	1.26	0.86	0.95	0.92	2.45	−1.26	1.37	1.51	13
MPW1K/MG3SXP	DFT	14	−0.13	1.21	0.93	1.14	0.82	2.46	−0.98	1.29	1.53	11
MPW1K/cc-pVTZ+	DFT	14	−0.06	1.07	0.89	1.42	0.76	2.47	−1.07	1.35	1.58	16
M08-SO/aug-cc-pVDZ	DFT	39	−1.69	1.69	−0.49	0.96	−0.35	1.99	−1.94	1.94	1.64	5.2
BB1K/6−31+G(d, p)	DFT	34, 74, 75	−0.31	1.62	0.81	**1.32**	0.84	2.19	−0.95	1.53	**1.66**	**2.0**
M08-SO/6−31+G(d,p)	DFT	39	−1.37	1.71	−0.01	**0.83**	0.57	2.51	−1.03	1.62	1.67	**2.1**
M08-HX/6−31+G(d,p)	DFT	39	−0.76	1.84	0.60	1.62	0.92	2.21	−0.79	**1.05**	1.68	**2.1**
MPWB1K/6−31+G(d,p)	DFT	75, 77, 78	−0.41	1.69	0.75	1.33	0.88	2.36	−1.25	1.45	1.71	2.0
M08-SO/cc-pVDZ+	DFT	39	−1.64	1.78	−0.03	1.13	−0.32	1.92	−2.11	2.11	1.74	2.2
M05-2X/MG3S	DFT	80	1.36	2.31	−1.05	1.65	1.38	1.76	−0.28	1.29	1.75	14
M05-2X/MG3	DFT	80	0.98	1.93	−1.07	1.67	1.64	2.24	−0.28	1.31	1.79	13
BB1K/cc-pVDZ+	DFT	34, 74, 75	−0.44	2.09	0.71	1.36	0.02	1.73	−2.01	2.01	1.79	23
PWB6K/6−31+G(d,p)	DFT	79	0.19	2.12	0.69	1.38	1.13	2.29	−0.94	1.40	**1.80**	**1.9**
B97-3/MG3S	DFT	81	−2.29	2.50	−0.49	0.98	0.71	1.63	−2.14	2.19	1.82	11
MPWB1K/aug-pc1	DFT	75, 77, 78	−0.63	2.30	0.26	1.37	−0.18	1.82	−2.09	2.09	1.90	4.0
MPW1K/6−31+G(d,p)	DFT	14	−0.50	**1.40**	0.50	**1.56**	1.29	3.21	−0.97	**1.42**	1.90	**1.4**
M05-2X/6−31+G(d,p)	DFT	80	0.72	2.56	−0.90	1.87	1.46	1.90	−0.56	1.49	1.95	2.1
MPW1K/cc-pVDZ+	DFT	14	−0.66	1.62	0.42	1.63	0.50	2.55	−1.96	2.04	**1.96**	**1.4**
BB1K/6−31+B(d,p)	DFT	34, 74, 75	−1.49	3.42	0.03	1.68	1.04	2.22	−1.21	1.21	2.13	2.3
MPWKCIS1K/MG3S	DFT	3, 75, 82	−1.29	1.90	1.38	1.38	0.95	3.35	−1.89	2.01	2.16	13
BHandHLYP/MG3S	DFT	34, 83, 84	1.70	2.87	0.71	1.45	1.02	2.37	0.18	2.09	2.19	10
M08-SO/MIDIY+	DFT	39	−1.57	3.07	−2.94	2.94	1.05	1.43	−1.41	1.41	2.21	1.7
BB1K/MIDIY+	DFT	34, 74, 75	−2.03	2.19	−2.55	2.55	1.69	2.35	−1.80	1.84	2.23	1.7
B1B95/MG3S	DFT	34, 75	−3.81	3.81	−1.23	1.23	−0.55	1.09	−3.06	3.06	2.30	11
M06/MG3S	DFT	38	−3.61	4.05	−1.62	1.65	0.54	1.91	−1.57	1.68	2.32	16
M06-2X/MIDIY+	DFT	38	−2.06	2.67	−2.91	2.91	1.30	1.70	−1.35	2.06	2.34	1.9
MPW1B95/MG3S	DFT	75, 77, 78	−3.73	3.73	−0.67	1.18	−0.44	1.23	−3.30	3.30	2.36	12
M05/MG3S	DFT	80	−3.25	4.79	0.02	0.94	1.00	2.48	−0.68	1.54	2.43	14
BHandHLYP/cc-pVDZ+	DFT	34, 83, 84	1.04	3.62	0.26	**1.82**	0.43	2.44	−0.92	2.09	**2.49**	**1.2**
M06-HF/MG3S	DFT	85	4.33	4.41	−0.89	1.86	1.11	1.80	1.49	2.03	2.53	16
M06-HF/6−31+G(d,p)	DFT	85	3.57	4.79	−0.20	1.54	1.39	1.66	0.90	2.42	2.60	3.0
MPW1K/MIDIY+	DFT	14	−2.32	2.32	−2.68	2.68	2.09	3.58	−1.85	2.03	2.65	1.2
M08-SO/MIDIX+	DFT	39	−2.66	3.60	−2.51	2.51	0.75	2.06	−2.39	2.48	2.66	1.6
BB1K/MIDIX+	DFT	34, 74, 75	−3.01	3.31	−2.30	2.30	1.41	2.20	−2.68	2.93	2.69	1.6
B97-2/MG3S	DFT	86	−3.04	4.16	−1.74	1.74	0.92	1.81	−2.80	3.11	2.71	11
PW6B95/MG3S	DFT	79	−4.28	4.28	−2.19	2.19	−0.54	1.17	−3.38	3.38	2.76	12
M05/6−31+G(d,p)	DFT	80	−3.73	4.95	−0.58	1.00	0.88	3.23	−0.82	1.98	2.79	2.1
M06-2X/MIDIX+	DFT	38	−2.88	3.40	−2.69	2.69	1.06	2.03	−2.21	3.08	2.80	1.9
M06-2X/6−31B(d,p)	DFT	38	−1.16	3.49	−2.11	5.18	0.79	1.26	−1.28	**1.33**	2.81	**1.8**
BHandHLYP/6−31+G(d,p)	DFT	34, 83, 84	1.17	3.46	0.37	**1.74**	1.23	3.20	0.05	2.97	2.84	**1.3**
TPSS25B95/MG3S	DFT	42	−4.39	4.39	−3.55	3.55	−0.47	**0.88**	−2.95	2.95	2.94	**7.8**
MPW1KK/MG3S	DFT	41	4.32	4.32	3.20	3.20	2.12	2.96	1.41	1.41	2.97	10
MPW1K/MIDIX+	DFT	14	−3.22	3.22	−2.40	2.40	1.85	3.15	−2.65	3.14	**2.98**	**1.0**
BB1K/6−31B(d,p)	DFT	34, 74, 75	−0.57	3.68	−1.95	4.97	1.13	2.31	−1.39	**1.44**	3.10	**1.3**
MPWB1K/MG3T	DFT	75, 77, 78	−0.88	1.39	−3.78	7.26	0.83	2.26	−1.56	1.68	3.15	8.8
BHandHLYP/MIDIX+	DFT	34, 83, 84	−1.55	2.52	−2.65	2.65	1.73	3.16	−1.73	4.32	**3.16**	0.9

DBH24/08 Database

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Table 2. Continued

methods	type	theory ref	HATBH6		NSBH6		UABH6		HTBH6		DBH24	cost
			MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MUE	
BHandHLYP/MIDIY+	DFT	34, 83, 84	−0.54	3.53	−3.00	3.00	2.08	3.56	−0.72	2.61	3.18	1.1
M06-2X/6−31B(d)	DFT	38	−0.75	4.81	−2.21	5.22	1.05	**1.05**	−0.70	1.84	3.23	**1.7**
mPW1PW/MG3S	DFT	36, 78	−5.09	5.09	−2.10	2.10	−0.39	1.93	−3.87	3.87	3.25	11
MPWB1K/6−31B(d,p)	DFT	75, 77, 78	−0.67	3.69	−1.96	5.22	1.19	2.48	−1.69	1.69	3.27	1.3
MPW25B95/MG3S	DFT	42	−5.51	5.51	−2.21	2.21	−0.94	1.17	−4.32	4.32	3.30	12
MPW1K/6−31B(d,p)	DFT	14	−0.75	3.32	−2.08	4.83	1.63	3.63	−1.48	**1.65**	3.36	**1.0**
M05-2X/6−31B(d,p)	DFT	80	0.53	4.91	−3.43	5.47	1.82	1.89	−0.91	**1.36**	3.41	**1.5**
PWB6K/6−31B(d,p)	DFT	79	−0.01	4.36	−1.94	5.32	1.44	2.50	−1.36	1.47	3.41	1.4
B98/MG3S	DFT	87	−4.75	4.75	−3.16	3.16	0.09	1.84	−3.92	3.92	3.42	11
B97−1/MG3S	DFT	86	−4.81	4.81	−3.31	3.31	0.19	1.67	−4.06	4.06	3.46	11
M08-SO/6−31B(d,p)	DFT	39	−1.92	4.36	−2.58	5.48	1.00	2.31	−1.61	1.68	3.46	2.0
M08-SO/6−31B(d)	DFT	39	−1.67	5.33	−2.63	5.47	1.12	1.90	−1.09	1.35	3.51	1.8
M05-2X/MG3T	DFT	80	0.64	1.87	−5.66	8.69	1.54	2.04	−0.46	1.49	3.52	11
PBE1PBE/MG3S	DFT	92, 111	−5.81	5.81	−2.09	2.09	−0.63	1.93	−4.54	4.54	3.59	10
BB1K/6−31B(d)	DFT	34, 74, 75	−0.27	5.23	−2.08	4.97	1.24	1.92	−0.83	2.27	3.60	1.3
mPW1PW/6−31+G(d,p)	DFT	36, 78	−5.56	5.56	−2.27	2.27	−0.17	2.76	−3.86	3.86	3.61	1.4
M08-HX/6−31B(d)	DFT	39	−0.81	5.61	−2.04	5.55	1.46	**1.69**	−1.09	1.69	3.64	**1.4**
MPW1K/6−31B(d)	DFT	14	−0.32	4.56	−2.22	4.83	1.77	3.24	−0.84	**2.07**	**3.67**	**0.8**
M08-HX/6−31+G(d,p)	DFT	39	−0.90	1.95	−3.83	9.51	1.01	1.85	−0.99	1.55	3.72	1.6
B3PW91/MG3S	DFT	34−36	−6.19	6.19	−2.60	2.60	−0.79	1.87	−4.34	4.34	3.75	9.1
TPSS20B95/MG3S	DFT	42	−5.80	5.80	−4.49	4.49	−0.86	1.05	−3.67	3.67	3.75	7.8
M06-2X/6−31G(d,p)	DFT	38	−1.12	1.58	−4.10	10.25	0.48	1.23	−1.00	2.06	3.78	1.8
B1LYP/6−31+G(d,p)	DFT	34, 83, 110	−5.64	5.64	−3.14	3.14	−0.78	2.48	−3.71	4.07	3.83	1.4
MPWB1K/6−31G(d,p)	DFT	75, 77, 78	−0.68	**1.98**	−3.74	9.52	0.84	2.12	−1.47	2.18	3.95	**1.3**
PBE1PBE/6−31+G(d,p)	DFT	92, 111	−6.26	6.26	−2.26	2.26	−0.39	2.75	−4.53	4.53	3.95	1.4
BHandH/MG3S	DFT	34, 83, 84	−4.82	5.16	−0.19	1.25	−0.51	3.32	−6.30	6.30	4.01	10
BHandHLYP/6−31B(d,p)	DFT	34, 83, 84	1.03	5.37	−2.08	4.81	1.55	3.75	−0.45	2.21	4.03	0.8
X3LYP/MG3S	DFT	34, 36, 83, 89	−6.72	6.72	−2.96	2.96	−1.20	1.75	−4.83	4.83	4.07	11
MPWB1K/cc-pVDZ	DFT	75, 77, 78	−1.29	3.01	−5.18	9.03	−0.17	**1.48**	−2.76	2.76	4.07	**1.6**
B3PW91/6−31+G(d,p)	DFT	34−36	−6.67	6.67	−2.76	2.76	−0.59	2.69	−4.36	4.36	4.12	1.5
B3LYP/MG3S	DFT	34, 35, 83	−6.74	6.74	−3.55	3.55	−1.21	1.69	−4.65	4.65	4.15	9.4
BHandHLYP/6−31B(d)	DFT	34, 83, 84	1.35	**5.31**	−2.20	4.81	1.66	3.34	0.03	**3.53**	**4.25**	**0.7**
M05-2X/6−31G(d,p)	DFT	80	0.43	2.34	−5.44	11.05	1.52	1.77	−0.70	1.98	4.28	1.5
MPW1K/6−31G(d)	DFT	14	−0.60	**2.04**	−3.65	9.28	1.64	**3.13**	−0.59	2.76	4.30	**0.8**
τ-HCTHh/MG3S	DFT	86, 90	−6.24	6.24	−4.69	4.69	0.05	1.84	−4.78	4.78	4.39	11
B3LYP*/6−31+G(d,p)	DFT	91	−5.88	5.88	−2.55	2.84	1.86	4.87	−3.73	4.11	4.42	1.3
PBE1KCIS/MG3S	DFT	82, 88, 92, 93	−7.57	7.57	−2.01	2.01	−0.87	2.80	−5.62	5.62	4.50	12
M06/6−31+G(d,p)	DFT	38	−4.02	4.40	−2.19	2.25	0.50	2.62	−8.51	9.22	4.62	3.0
M05-2X/6−31G(d)	DFT	80	0.62	2.86	−5.36	11.01	1.91	1.91	−0.20	2.75	4.63	1.5
M06/6−31B(d,p)	DFT	38	−4.97	7.10	−5.24	6.77	0.64	2.51	−2.27	2.27	4.66	1.8
B97-3/6−31G(d)	DFT	81	−2.89	4.13	−5.62	10.46	1.22	**1.92**	−2.14	2.19	4.67	**0.9**
M05/6−31B(d,p)	DFT	80	−3.96	8.01	−3.29	5.84	1.09	3.03	−1.26	1.91	4.70	1.5
O3LYP/MG3S	DFT	83, 94, 95	−7.34	7.34	3.31	5.02	−1.29	2.09	−4.37	4.37	4.70	11
B3LYP/6−31+G(d, p)	DFT	34, 35, 83	−7.44	7.44	−3.84	3.84	−1.17	2.59	−4.91	5.12	4.75	1.4
MPW3LYP/MG3S	DFT	77, 78, 83	−7.53	7.53	−4.66	4.66	−1.34	1.80	−5.19	5.19	4.80	11
mPW1PW/6−31B(d,p)	DFT	36, 78	−5.74	6.14	−5.24	6.04	0.11	2.87	−4.32	4.32	4.84	1.0
TPSS1KCIS/MG3S	DFT	64, 82, 96	−7.81	7.81	−5.06	5.06	−1.16	1.59	−4.91	4.91	4.84	13
B3P86/MG3S	DFT	34, 35, 37	−8.13	8.13	−3.28	3.28	−1.34	2.78	−5.95	5.95	5.04	9.1
PBE1PBE/6−31B(d,p)	DFT	92, 111	−6.33	6.59	−5.27	6.17	−0.10	2.73	−4.93	4.93	5.10	1.0
B3P86/6−31+G(d,p)	DFT	34, 35, 37	−8.63	8.63	−3.43	3.43	−1.17	3.58	−5.99	5.99	5.41	1.4
MPW1KCIS/MG3S	DFT	3, 75, 82	−8.81	8.81	−4.54	4.54	−1.24	2.61	−6.28	6.28	5.56	13
B97-2/6−31G(d)	DFT	86	−3.63	5.96	−6.81	11.19	1.39	2.07	−2.32	3.19	5.60	0.9
B3LYP/6−31B(d,p)	DFT	34, 35, 83	−7.52	7.52	−6.96	7.66	−0.97	2.71	−5.33	5.33	5.80	0.9
TPSSh/MG3S	DFT	96	−10.11	10.11	−5.92	5.92	−2.81	2.86	−6.64	6.64	6.38	13
HFLYP/MG3S	DFT	97	11.81	11.81	5.18	5.18	3.64	4.24	5.52	5.52	6.69	9.4
HFLYP/6−31+G(d,p)	DFT	97	11.66	11.66	4.52	4.52	4.11	5.17	5.66	5.67	6.76	1.4
HFTPSS/6−31+G(d,p)	DFT	96	10.34	10.34	6.73	6.73	3.12	6.33	4.40	5.32	7.18	2.0
BB1K/6−31B(d)	DFT	34, 74, 75	−0.27	5.23	−16.92	19.82	1.24	1.92	−0.83	2.27	7.31	1.2
SOS-MP2/MG3S	ML	28, 29	15.35	15.35	1.51	1.51	6.60	6.96	5.89	5.89	7.43	17
MPW1K/3−21G+	DFT	14	−4.57	6.90	−9.15	9.15	5.91	8.50	−3.42	6.11	7.67	0.8
M05-2X/MIDI!	DFT	80	−5.16	5.92	−12.44	18.31	1.40	2.75	−3.36	3.83	7.70	1.2
M06-2X/MIDI!	DFT	38	−6.63	6.82	−11.76	17.91	0.15	2.23	−3.52	4.24	7.80	1.5
BB1K/MIDI!	DFT	34, 74, 75	−6.71	7.21	−11.17	16.86	0.55	2.24	−3.99	5.01	7.83	1.2
BHandHLYP/MIDI!	DFT	34, 83, 84	−5.54	5.54	−10.85	17.01	0.70	**3.29**	−3.23	**5.64**	**7.87**	**0.6**
MPW1K/MIDI!	DFT	14	−6.80	6.99	−11.19	16.41	1.04	**3.25**	−3.84	4.96	**7.90**	**0.7**
M08-SO/MIDI!	DFT	39	−7.02	7.37	−11.47	18.00	−0.34	2.31	−4.07	4.74	8.11	1.2
SOS-MP2/cc-pVTZ	ML	28, 29	15.67	15.67	−1.11	4.60	6.09	6.43	5.83	5.83	8.13	15
HF/MIDIX+	WFT	98	15.61	15.61	3.03	**3.19**	4.59	5.32	10.54	10.54	**8.66**	**0.2**
HF/MIDI!	WFT	98	11.74	11.74	−2.25	**10.46**	3.53	**4.94**	8.98	9.65	**9.20**	**0.1**
HF/MIDIY+	WFT	98	16.78	16.78	2.45	3.26	5.07	5.07	11.87	11.87	9.24	0.3

Table 2. Continued

methods	type	theory ref	HATBH6 MSE	HATBH6 MUE	NSBH6 MSE	NSBH6 MUE	UABH6 MSE	UABH6 MUE	HTBH6 MSE	HTBH6 MUE	DBH24 MUE	cost
HF/6−31+G(d,2p)	WFT	98	18.10	18.10	5.47	5.56	3.83	4.02	12.29	12.29	9.99	1.0
HF/6−31+G(d,p)	WFT	98	18.14	18.14	5.52	5.63	4.10	4.10	12.50	12.50	10.09	0.7
HF/6−31+G(d)	WFT	98	18.01	18.01	5.49	5.60	4.39	4.39	12.47	12.47	10.12	0.3
HF/G4MP2TZ	WFT	98	18.01	18.01	6.65	6.65	3.35	3.53	12.29	12.29	10.12	5.1
HF/G3Large	WFT	98	18.14	18.14	6.31	6.31	3.61	3.68	12.41	12.41	10.14	13
HF/6−31G(d)	WFT	98	17.62	17.62	2.67	6.36	**4.31**	4.31	12.28	12.28	10.14	**0.2**
HF/MG3S	WFT	98	18.29	18.29	6.28	6.28	3.66	3.72	12.43	12.43	10.18	9.2
HF/G3MP2LargeXP	WFT	98	18.20	18.20	6.37	6.37	3.49	3.69	12.45	12.45	10.18	10
HF/G3LargeXP	WFT	98	18.21	18.21	6.40	6.40	3.49	3.69	12.45	12.45	10.19	17
HF/G4MP2QZ	WFT	98	18.07	18.07	6.69	6.69	3.42	3.63	12.46	12.46	10.21	47
HF/G3HFQZ	WFT	98	18.13	18.13	6.59	6.59	3.42	3.63	12.47	12.47	10.21	39
HF/G4HF5Z	WFT	98	18.08	18.08	6.74	6.74	3.41	3.64	12.50	12.50	10.24	350
MPW1K/STO-3G+	DFT	14	−7.80	11.57	1.23	**2.06**	4.05	15.15	−0.377	12.86	10.41	**0.4**
HF/6−31B(d,p)	WFT	98	18.27	18.67	3.81	6.81	4.64	4.64	11.95	11.95	10.51	0.2
HF/6−31B(d)	WFT	98	18.44	18.79	3.59	6.69	4.63	4.63	12.08	12.08	10.55	0.2
MPW1K/3−21G	DFT	14	−5.48	**5.48**	−15.96	23.87	6.16	9.16	−4.52	**7.71**	11.56	**0.5**
HF/STO-3G+	WFT	98	10.62	21.03	8.83	8.83	8.63	14.23	10.51	16.75	15.21	0.09
MPW1K/STO-3G	DFT	14	−6.11	**6.79**	−17.18	37..83	11.09	16.82	−7.11	16.77	19.55	**0.4**
HF/STO-3G	WFT	98	8.14	17.93	7.31	35.94	13.92	16.72	5.90	21.30	22.97	0.08
HF/STO-2G	WFT	98	6.68	15.50	6.96	46.63	14.73	17.61	6.21	19.09	24.71	0.06
					N^3 Methods							
MOHLYP/MG3SXP	DFT	40	−1.40	**2.94**	−0.70	2.92	−0.77	1.94	2.72	4.20	**3.00**	**4.2**
MOHLYP/MG3S	DFT	40	−1.45	**3.02**	−0.80	3.12	−0.64	1.83	2.68	4.21	**3.05**	**4.0**
MOHLYP/cc-pVTZ+	DFT	40	−1.33	**2.78**	−0.91	3.26	−0.92	2.04	2.65	4.18	3.07	**5.1**
MOHLYP/6−31+G(d,p)	DFT	40	−1.88	3.21	−1.34	3.21	−0.59	1.55	2.46	4.48	**3.11**	**1.4**
MOHLYP/cc-pVDZ+	DFT	40	−1.84	**4.10**	−1.16	**3.02**	−1.25	2.45	0.98	**2.99**	3.14	**1.3**
MOHLYP/aug-cc-pVTZ	DFT	40	−1.51	**2.65**	−0.02	3.78	−1.05	2.17	2.62	4.12	3.18	**7.6**
MOHLYP/MIDIY+	DFT	40	−4.01	**4.73**	−5.30	5.30	0.15	1.84	1.36	**3.87**	3.93	**1.2**
M06-L/aug-cc-pVTZ	DFT	99	−6.11	6.85	−3.18	3.18	0.27	1.57	−4.22	4.22	3.95	13
M06-L/MG3S	DFT	99	−6.08	6.91	−3.35	3.35	0.92	2.58	−2.92	3.05	3.98	5.7
M06-L/cc-pVTZ+	DFT	99	−6.10	6.99	−3.28	3.28	0.32	1.59	−4.27	4.27	4.03	7.5
M06-L/MG3SXP	DFT	99	−5.97	6.90	−3.29	3.29	0.37	1.77	−4.06	4.16	4.03	7.3
MOHLYP/6−31B(d,p)	DFT	40	−1.67	**5.97**	−5.01	5.39	−0.36	**1.17**	2.27	**4.24**	4.19	**0.9**
M06-L/6−31+G(d,p)	DFT	99	−6.26	7.19	−4.24	4.24	0.43	2.32	−4.01	4.01	4.44	2.1
VSXC/MG3S	DFT	100	−6.89	6.89	−5.01	5.01	−0.05	1.49	−4.90	4.90	4.57	5.2
HCTH/MG3S	DFT	86	−8.82	8.82	−2.88	**2.88**	−0.66	1.64	−5.17	5.17	4.63	**3.9**
VSXC/6−31+G(d,p)	DFT	100	−7.42	7.42	−4.63	4.63	0.01	2.16	−4.97	4.97	4.79	2.0
M06-L/cc-pVDZ+	DFT	99	−6.44	7.88	−4.41	4.41	−0.18	2.56	−4.89	4.89	4.94	2.4
MOHLYP/MIDIX+	DFT	40	−4.89	5.97	−5.06	5.97	−0.20	3.31	0.62	5.90	5.06	1.0
MOHLYP/6−31B(d)	DFT	40	−1.19	**7.45**	−5.03	5.47	−0.26	**1.49**	3.05	6.05	5.11	**0.8**
OLYP/MG3S	DFT	83, 94	−10.17	10.17	−3.20	3.20	−2.21	2.21	−5.80	5.80	5.34	3.7
M06-L/MIDIY+	DFT	99	−7.15	8.74	−6.74	6.74	1.44	2.83	−4.75	4.75	5.65	2.0
τ-HCTH/MG3S	DFT	90	−9.19	9.19	−6.12	6.12	−0.57	1.99	−6.13	6.13	5.86	5.4
M06-L/MIDIX+	DFT	99	−8.10	9.87	−6.21	6.21	1.26	2.79	−5.14	5.14	6.00	1.8
M06-L/6−31B(d,p)	DFT	99	−7.37	9.13	−7.31	7.78	0.68	2.37	−4.77	4.77	6.01	1.7
M06-L/6−31B(d)	DFT	99	−6.90	10.55	−7.18	7.71	0.76	1.95	−3.83	3.83	6.01	1.5
VSXC/6−31B(d,p)	DFT	100	−7.68	9.75	−7.79	8.30	0.22	2.18	−5.29	5.29	6.38	1.3
M06-L/6−31G(d)	DFT	99	−6.31	8.56	−8.52	12.01	0.71	1.79	−3.13	3.20	6.39	1.6
G96LYP/MG3S	DFT	83, 101	−10.93	10.93	−6.35	6.35	−2.75	2.75	−6.52	6.52	6.64	3.9
TPSSKCIS/MG3S	DFT	82, 96	−11.63	11.63	−7.67	7.67	−2.22	2.22	−7.00	7.00	7.13	5.7
mPWKCIS/MG3S	DFT	75, 82	−11.98	11.98	−6.80	6.80	−2.46	2.46	−7.48	7.48	7.18	6.1
BB95/MG3S	DFT	75	−12.57	12.57	−6.60	6.60	−3.06	3.06	−7.94	7.94	7.54	5.4
mPWPW91/MG3S	DFT	36, 78	−12.71	12.71	−7.42	7.42	−2.59	2.59	−8.39	8.39	7.78	3.8
BLYP/MG3S	DFT	34, 83	−12.37	12.37	−8.74	8.74	−3.06	3.06	−7.75	7.75	7.98	3.7
BLYP/6−31+G(d, p)	DFT	34, 83	−13.24	13.24	−7.64	7.64	−3.18	3.18	−8.18	8.18	8.06	1.3
TPSS/MG3S	DFT	96	−13.03	13.03	−7.53	7.53	−3.62	3.62	−8.22	8.22	8.10	5.5
PBE/MG3S	DFT	88	−13.61	13.61	−7.01	7.01	−2.88	2.88	−9.25	9.25	8.19	3.7
PBEsol/6−31+G(d,p)	DFT	43	−14.25	14.25	−7.06	7.06	−2.81	2.83	−9.41	9.41	8.39	1.4
mPWLYP/MG3S	DFT	78, 83	−13.45	13.45	−8.19	8.19	−3.24	3.24	−8.77	8.77	8.41	3.7
BP86/MG3S	DFT	34, 37	−14.00	14.00	−7.13	7.13	−3.40	3.40	−9.21	9.21	8.43	3.9
BLYP/6−31B(d,p)	DFT	34, 83	−13.26	13.26	−11.31	11.31	−3.08	3.08	−8.49	8.49	9.04	1.0
MOHLYP/MIDI!	DFT	40	−9.26	**9.96**	−16.57	19.50	−1.37	**3.99**	−1.11	6.84	**10.07**	**0.7**
M06-L/MIDI!	DFT	99	−11.24	12.77	−16.57	18.98	0.76	2.86	−6.12	6.12	10.18	1.4
SOGGA/MG3S	DFT	44	−17.46	17.46	−7.14	7.14	−3.93	3.93	−12.96	12.96	10.38	3.7
SOGGA/cc-pVTZ+	DFT	44	−17.34	17.34	−7.09	7.09	−4.13	4.13	−12.96	12.96	10.38	4.7
SOGGA/MG3SXP	DFT	44	−17.50	17.50	−7.03	7.03	−4.07	4.07	−12.95	12.95	10.39	4.1
SOGGA/6−31+G(d,p)	DFT	44	−17.98	17.98	−7.07	7.07	−3.76	3.79	−12.90	12.90	10.44	1.4
PM3	SEMO	102	−12.88	16.51	13.82	**14.56**	6.10	13.94	−3.44	5.64	**12.67**	5×10^{-5}
AM1	SEMO	103	−8.51	**11.82**	10.43	15.62	13.19	18.90	−0.02	**5.13**	12.87	5×10^{-5}
SPL/MG3S	DFT	104	−22.41	22.41	−8.44	8.44	−5.07	5.07	−17.67	17.67	13.40	2.5

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Table 2. Continued

methods	type	theory ref	HATBH6		NSBH6		UABH6		HTBH6		DBH24	cost
			MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MUE	
SPWL/MG3S	DFT	105	−22.52	22.52	−8.36	8.36	−5.21	5.21	−17.89	17.89	13.49	3.5
PM6	SEMO	106	−21.07	22.38	−0.90	**4.19**	14.10	22.07	−8.03	14.09	15.68	1×10^{-4}
RM1	SEMO	107	−19.47	20.59	0.17	15.41	10.61	19.86	−5.60	7.15	15.75	5×10^{-5}
PDDG/PM3	SEMO	108	−16.32	17.97	15.46	15.46	5.38	**13.57**	−8.91	17.55	16.14	5×10^{-5}
SCC-DFTB[b]	SEMO	109	9.69	**11.54**			1.10	**9.77**	−30.34	30.34	17.22	4×10^{-4}

[a] WFT denotes wave function theory; ML denotes multilevel method; DFT denotes density functional theory; SEMO denotes semiempirical molecular orbital method. [b] For this method, the value for the HAT category includes only the reaction $H + N_2O \rightarrow OH + N_2$ and its reverse.

In CCSD(T) calculations, using the cc-pVTZ+ basis set instead of the cc-pVTZ basis set improves the MUE from 2.26 to 1.00 kcal/mol, but it only increases the cost by 40%. For S_N2 reactions, cc-pVTZ+ has a significantly lower MUE (0.81 kcal/mol) than cc-pVTZ. Although the aug-cc-pVTZ basis set further improves the MUE to 0.69 kcal/mol, the cost of aug-cc-pVTZ is about 7.5 times larger than that of cc-pVTZ for CCSD(T) calculations. In DFT calculations, cc-pVTZ+ is almost as good as the aug-cc-pVTZ basis set. The latter has *s*, *p*, *d*, and *f* diffuse functions for all elements except H and has *s*, *p*, and *d* diffuse functions on H, whereas the only diffuse function in cc-pVTZ+ are diffuse *s* and *p* functions on non-hydrogenic atoms. As compared with the aug-cc-pVTZ and cc-pVTZ basis sets, the basis cc-pVTZ+ has a very good balance between computational cost and accuracy.

In the methods that scale as N^6, BMC-CCSD outperforms all the other methods. It even has almost the same accuracy as the CCSD(T)/aug-cc-pVTZ method, but it is about 280 time more efficient. The MUE is only 23% higher than that of G3SX(MP3), but the computational cost is about 6 times smaller than that of G3SX(MP3). Furthermore, BMC-CCSD scales as N^6, whereas G3SX(MP3) and CCSD(T) scale as N^7. The other variants, BMC-QCISD and BMC-CCSD-C, have similar performance to BMC-CCSD, but BMC-CCSD is the most recommended. All single-level coupled cluster calculations only with single and double excitations (CCSD) have MUEs of 1.94 kcal/mol or higher.

In the methods that scale as N^5, the MUEs for DBH24 have a large gap between 1.9 and 4.5 kcal/mol. The methods with MUEs smaller than 1.9 kcal/mol are doubly hybrid density functionals or MRMP2, while the methods with MUEs larger than 4.5 kcal/mol are MP2 or correlation-energy-scaled MP2 methods. Some of the doubly hybrid density functionals, MC3BB,[63] MC3MPW,[63] MC3MPWB,[64] MC3TS,[64] MCG3-MPW, -MPB, and -TS,[64] and MCCO-MPW, -MPWB and -TS,[64] are sometimes called multicoefficient extrapolated DFT methods. In these models, HF orbitals are used for the occupied and unoccupied orbitals to calculate the second-order Møller−Plesset-type perturbation theory correction, although in unpublished past original studies it was checked that similar results are obtained with Kohn−Sham orbitals. The B2P-LYP, B2GP-PLYP, B2K-PLYP, and mPW2-PLYP density functionals employ the Kohn−Sham occupied and unoccupied orbitals. Our calculations show that spin-component scaled (SCS) MP2 and scaled opposite-spin (SOS) MP2 methods (which scales as N^4) consistently overestimate the barrier heights and degrade

the MP2 accuracy for barrier height calculations, which was also pointed out by Jung et al. in a previous paper.[28] Methods that involve scaling all correlation (SAC) with MP2 have better performance than SCS-MP2 even with smaller basis sets. In unpublished work, we tried to reparameterize the scaling coefficients in SCS-MP2 using the DBH24/08 database and found that the accuracy cannot be improved significantly, with errors that are always larger than 5.0 kcal/mol. This study and the large gap in the N^5 methods shown in Table 2 imply that it is difficult to achieve accuracy better than 4.0 kcal/mol for calculating barrier height only by using the correlation energy or scaled correlation energy calculated by single-reference second-order perturbation theory. The accuracy for barrier height calculations can be improved dramatically by mixing density functional correlation energy and MP2 correlation energy.

As listed in bold in Table 2, the most recommended hybrid density functionals for barrier heights are M08-SO, M06-2X, M08-HX, BB1K, BMK, PWB6K, MPW1K, BHandH-LYP, and TPSS25B95. The newly developed M06-2X, M08-HX, and M08-SO density functional have the best performance among the fourth-rung hybrid density functionals (even including fifth-rung doubly hybrid density functionals), and they can achieve accuracy better than 1.2 kcal/mol with a reasonable triple-ζ basis set, e.g., cc-pVTZ+, MG3S, and MG3SXP. The density functionals M06-2X, BB1K, PWB6K, and MPW1K can achieve accuracy better than 2.0 kcal/mol with a double-ζ basis set, 6−31+G(d,p).

The recommended cost-effective basis sets as shown in Table 2 are MIDIX+, 6−31B(d), and MIDI!. The relative costs of these basis sets are below 1.0 when using the BHandHLYP and MPW1K density functionals. Actually, MIDIY+ has better performance than MIDIX+ and has similar or a little bit higher cost than MIDIX+ because MIDY+ has a *p* set of polarization functions on each hydrogen. The basis set 6−31B(d,p) was tested by using a number of density functionals; this basis set has the same size as the Pople's 6−31G(d,p), but it is more diffuse without using diffuse functions. A few density functional calculations, in particular, M06-2X, M05-2X, and MPWB1K, give smaller MUEs with 6−31B(d,p) than 6−31G(d,p) by 0.7−1.0 kcal/mol. Although 6−31B(d,p) rather than 6−31G(d,p) is more diffuse, it still cannot be as accurate as the 6−31+G(d,p) basis set. This shows the importance of diffuse functions to calculate barrier heights with density functional theory, as was already pointed out by Lynch et al.[112] The MG3SXP basis set includes more polarization functions than MG3S, but it dose not improve MG3S systematically for the tested

Table 3. Comparison of Mean Signed Errors (MSEs) and Mean Unsigned Errors (MUEs) (in kcal/mol) Calculated at Different Geometries

methods	HATBH6 MSE	HATBH6 MUE	NSBH6 MSE	NSBH6 MUE	UABH6 MSE	UABH6 MUE	HTBH6 MSE	HTBH6 MUE	DBH24 MUE
CCSD/MG3S//QCISD/MG3	5.00	5.00	1.92	1.92	1.72	1.72	2.75	2.75	2.85
CCSD/MG3S	4.70	4.70	1.92	1.92	1.50	1.50	2.58	2.58	2.67
MP2/MG3S//QCISD/MG3	11.59	11.59	0.69	0.86	5.25	6.10	0.14	2.88	5.63
MP2/MG3S	9.87	9.87	0.61	0.79	5.51	5.75	4.40	4.40	5.20
B3LYP/MG3S//QCISD/MG3	−6.74	6.74	−3.55	3.55	−1.21	1.69	−4.65	4.65	4.15
B3LYP/MG3S	−6.16	6.16	−3.64	3.64	−0.83	1.70	−4.34	4.36	3.97
M05-2X/MG3S//QCISD/MG3	1.36	2.31	−1.05	1.65	1.38	1.76	−0.28	1.29	1.75
M05-2X/MG3S	1.59	2.46	−1.02	1.65	1.64	1.99	0.03	1.36	1.87
M06-2X/MG3S//QCISD/MG3	−0.06	0.73	0.60	0.85	0.36	1.09	−0.50	1.25	0.98
M06-2X/MG3S	0.03	0.72	0.58	0.90	0.46	1.07	−0.36	1.19	0.97

density functionals (e.g., M06-2X, M08-HX, M08-SO, and SOGGA) and wave function methods (e.g., CCSD(T) and CCSD).

It is very interesting that MOHLYP and HCTH are the only local density functionals in the bold recommended combinations of local density functional and basis set on the cost-to-performance basis used to make entries bold in Table 2. The MOHLYP density functional was originally designed for inorganometallic and organometallic chemistry. It has MUEs for HAT reactions about 3.0 kcal/mol, while the other local density functionals have MUEs for HAT reactions around 7.0 kcal/mol or above. M06-L which has a better performance over broader test sets has a similar performance to MOHLYP for barrier heights of all types of reactions except HAT reactions.

A word of caution is in order in interpreting the bold entries in Table 2. In presenting these bold entries in Table 2 we considered only barrier heights. Even for thermochemical kinetics one wants a method that accounts for energies of reaction as well as barrier heights, and in other cases one might also want to consider other properties such as ionization potential, dipole moments, or noncovalent interactions in selecting a method for a given application. We know, for example, that MPW1K and MPWB1K are better overall methods than BHandHLYP, and M06-L is a better overall method than MOHLYP. Nevertheless the selection of bold entries in Table 2 emerges from a rigorous impartial screening, and the boldface methods deserve consideration whenever we consider barrier heights.

4.2. Effect of Consistent Geometry Optimization. Table 3 lists mean signed errors and mean unsigned errors for the CCSD, MP2, B3LYP, M05-2X, and M06-2X methods with the MG3S basis set calculated at QCISD/MG3 geometries and at the geometries optimized with the corresponding methods.[19] The deviations between the two sets of MUEs for DBH24/08 are around 0.4 kcal/mol or smaller for all the tested methods. M06-2X/MG3S gives the smallest deviation between the MUEs at QCISD/MG3 geometries and at the consistently optimized geometries; these deviations of MUEs for each type of reactions in the DBH24/08 database are smaller than 0.06 kcal/mol. We conclude that using either QCISD/MG3 geometries or consistently optimized geometries gives similar results for the more accurate methods listed in Table 2.

5. Conclusions

In this paper, we updated our DBH24 database by using W4 and W3.2 data to replace previous W1 values; we call the new database DBH24/08. We assessed 348 model chemistries, each containing of a combination of wave function theory level or density functional approximation with a one-electron basis set. There are too many methods in the table to comment explicitly on all the interesting pairwise comparisons, but a few key issues will be summarized here to conclude the paper. Some conclusions drawn in our previous work[1] are reconfirmed by using this improved database and including more methods. For example, BMC-CCSD is still the best model chemistry whose cost scales as N^6 and its cost is an order of magnitude smaller than the N^7 method with the best cost-adjusted performance, G3SX(MP3), although the mean unsigned error is only marginally higher, namely 0.70 kcal/mol vs 0.57 kcal/mol. Other conclusions are now broader in scope. For example, among the N^5 methods except MRMP2 we now conclude not only that doubly hybrid density functionals and multicoefficient extrapolated density functional methods perform better than MP2 but also that they perform better than any correlation-energy-scaled MP2 method. The most recommended hybrid density functionals, judged entirely on the basis of barrier height calculations, are M08-SO, M06-2X, M08-HX, BB1K, BMK, PWB6K, MPW1K, BHandHLYP, and TPSS25B95. MOHLYP, M06-L, VSXC, and HCTH are found to be the best performing local density functionals for barrier heights. The basis set MG3S and 6−31+G(d,p) are the most recommended triple-ζ and double-ζ basis sets for calculations using density functional theory according performance-for-cost considerations. The basis set cc-pVTZ+ is more efficient than aug-cc-pVTZ with similar accuracy, especially for density functional theory. The basis sets cc-pVDZ+, 6−31+G(d,p), 6−31B(d,p), 6−31B(d), MIDIY+, MIDIX+, and MIDI! are recommended for density functional calculations on large systems for their good balance between accuracy and cost, and the basis sets cc-pVTZ+, MG3S, MG3SXP, and aug-cc-pVDZ are recommended for density functional calculations when larger basis sets are affordable. The best performance of any methods tested is attained by CCSD(T)(full)/aug-cc-pCV(T+d)Z with a mean unsigned error of 0.46 kcal/mol; however, this is several orders of

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magnitude more expensive than M08-SO/cc-pVTZ+ with a mean unsigned error of 0.90 kcal/mol.

References

(1) Zheng, J.; Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2007**, *3*, 569.

(2) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 8996.

(3) Zhao, Y.; Gonzalez-Garcia, N.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 2012.

(4) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 3898.

(5) Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843.

(6) (a) Brown, F. B.; Shavitt, I.; Shepard, R. *Chem. Phys. Lett.* **1984**, *105*, 363. (b) Werner, H.-J. *Adv. Chem. Phys.* **1987**, *69*, 1.

(7) Karton, A.; Tarnopolsky, A.; Jean-François, L.; Schatz, G. C.; Martin, J. M. L. *J. Phys. Chem. A* **2008**, *112*, 12868.

(8) Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108.

(9) Zheng, J.; Gour, J. R.; Lutz, J. J.; Wloch, M.; Piecuch, P.; Truhlar, D. G. *J. Chem. Phys.* **2008**, *128*, 044108.

(10) Peterson, K. A.; Dunning, T. H. *J. Phys. Chem. A* **1997**, *101*, 6280.

(11) Villa, J.; Corchado, J. C.; Gonzalez-Lafont, A.; Lluch, J. M.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 5061.

(12) Villa, J.; Gonzalez-Lafont, A.; Lluch, J. M.; Truhlar, D. G. *J. Am. Chem. Soc.* **1998**, *120*, 5559. Brown, F. B.; Truhlar, D. G. *Chem. Phys. Lett.* **1985**, *117*, 307.

(13) Fernandez-Ramos, A.; Ellingson, B. A.; Garrett, B. C.; Truhlar, D. G. Variational Transition State Theory with Multidimensional Tunneling. In *Reviews in Computational Chemistry*; Cundari, T. R., Lipkowitz, K. B., Eds.; Wiley-VCH: Hoboken, NJ, 2007; Vol. 23, pp 125.

(14) Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811.

(15) Melissas, V. S.; Truhlar, D. G. *J. Chem. Phys.* **1993**, *99*, 3542.

(16) Atkins, R. *J. Phys. Chem. Ref. Data Monograph* **1989**, *1*, 18.

(17) Peng, J.; Hu, X.; Marshall, P. *J. Phys. Chem. A* **1999**, *103*, 5307.

(18) Tratz, C. M.; Fast, P. L.; Truhlar, D. G. *PhysChemComm* **1999**, *2*, 70.

(19) Tishchenko, O.; Zheng, J.; Truhlar, D. G. *J. Chem. Theory Comput.* **2008**, *4*, 1208.

(20) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 1643.

(21) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(22) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(23) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 1125.

(24) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 108.

(25) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **2007**, *126*, 084108.

(26) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **2007**, *127*, 124105.

(27) Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095. Grimme, S. *J. Comput. Chem.* **2003**, *24*, 1529.

(28) Jung, Y.; Lochan, R. C.; Dutoi, A. D.; Head-Gordon, M. *J. Chem. Phys.* **2004**, *121*, 9793.

(29) Jung, Y.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2831.

(30) Meyer, W. *J. Chem. Phys.* **1973**, *58*, 1017.

(31) Grimme, S. *J. Chem. Phys.* **2006**, *124*, 034108.

(32) Tarnopolsky, A.; Karton, A.; Sertchook, R.; Vuzman, D.; Martin, J. M. L. *J. Phys. Chem. A* **2008**, *112*, 3.

(33) Schwabe, T.; Grimme, S. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4398.

(34) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(35) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(36) Perdew, J. P. In *Electronic Structure of Solids'91*; Ziesche, P., Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991.

(37) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(38) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

(39) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2008**, *4*, 1849.

(40) Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 11127.

(41) Thompson, J. D.; Cramer, C. J.; Truhlar, D. G. *Theor. Chem. Acc.* **2005**, *113*, 107.

(42) Quintal, M. M.; Karton, A.; Iron, M. A.; Boese, A. D.; Martin, J. M. L. *J. Phys. Chem. A* **2006**, *110*, 709.

(43) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X.; Burke, K. *Phys. Rev. Lett.* **2008**, *100*, 136406.

(44) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2008**, *128*, 184109.

(45) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(46) Papajak, E.; Leverentz, H.; Zheng, J.; Truhlar, D. G. *J. Chem. Theory Comput.*, in press.

(47) Lynch, B. J.; Truhlar, D. G. *Theor. Chem. Acc.* **2004**, *111*, 335.

(48) Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 2769. Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(49) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. *J. Comput. Chem.* **1983**, *4*, 294.

(50) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007. Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.

(51) Dunning, T. H.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.

(52) Thompson, J. D.; Winget, P.; Truhlar, D. G. *PhysChem-Comm* **2001**, 6.

(53) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; 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. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian03; Revision E.01 ed.*; Gaussian, Inc.: Pittsburgh, PA, 2003.

(54) Zhao, Y.; Truhlar, D. G. *MN-GFM: Minnesota Gaussian Functional Module; version 4.1 ed.*; University of Minnesota: Minneapolis, 2009.

(55) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(56) Werner, H.-J.; Knowles, P. J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schtuz, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. *MOLPRO; 2006.1 ed.*; University of Birmingham: Birmingham, 2006.

(57) Moore, C. E. Atomic Energy Levels;Natl. Bur. Stand. (US) Circ. , 1949.

(58) Martin, J. M. L.; Sundermann, A.; Fast, P. L.; Truhlar, D. G. *J. Chem. Phys.* **2000**, *113*, 1348.

(59) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283. Dunlap, B. I. *J. Mol. Struct. (Theochem)* **2000**, 37.

(60) Raghavachari, K.; Anderson, J. B. *J. Phys. Chem.* **1996**, *100*, 12960.

(61) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.

(62) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(63) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 4786.

(64) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2005**, *7*, 43.

(65) Piecuch, P.; Wloch, M. *J. Chem. Phys.* **2005**, *123*, 224105. Piecuch, P.; Wloch, M.; Gour, J. R.; Kinal, A. *Chem. Phys. Lett.* **2006**, *418*, 467. Wloch, M.; Lodriguito, M. D.; Piecuch, P.; Gour, J. R. *Mol. Phys.* **2006**, *104*, 2149.

(66) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(67) Montgomery, J. J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822.

(68) Montgomery, J. J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532.

(69) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. J. A. *J. Chem. Phys.* **1996**, *104*, 2598.

(70) Petersson, G. A.; Tensfeldt, T. G.; Montgomery, J. J. A. *J. Chem. Phys.* **1991**, *94*, 6091.

(71) Purvis III, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(72) Hirao, K. Quantum Chem. *Int. J.* **1992**, 517. Hirao, K *Chem. Phys. Lett.* **1992**, *196*, 397.

(73) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(74) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 2715.

(75) Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040.

(76) Boese, A. D.; Martin, J. M. L. *J. Chem. Phys.* **2004**, *121*, 3405.

(77) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 6908.

(78) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.

(79) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 5656.

(80) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364.

(81) Keal, T. W.; Tozer, D. J. *J. Chem. Phys.* **2005**, *123*, 121103.

(82) Krieger, J. B.; Chen, J.; Iafrate, G. J.; Savin, A. *Electron Correlations and Materials Properties*; Gonis, A.; , Kioussis, N., Eds.; Plenum: New York, 1999; p 463. Rey, J.; Savin, A. *Int. J. Quantum Chem.* **1998**, *69*, 581. Toulouse, J.; Savin, A.; Adamo, C. *J. Chem. Phys.* **2002**, *117*, 10465.

(83) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(84) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(85) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2006**, *110*, 13126.

(86) Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *109*, 6264.

(87) Schmider, H. L.; Becke, A. D. *J. Chem. Phys.* **1998**, *108*, 9624.

(88) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(89) Xu, X.; Goddard, W. A. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 2673.

(90) Boese, A. D.; Handy, N. C. *J. Chem. Phys.* **2002**, *116*, 9559.

(91) Reiher, M.; Salomon, O.; Hess, B. A. *Theor. Chem. Acc.* **2001**, *107*, 48.

(92) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

(93) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2005**, *1*, 415.

(94) Handy, N. C.; Cohen, A. J. *Mol. Phys.* **2001**, *99*, 403.

(95) Hoe, W. M.; Cohen, A. J.; Handy, N. C. *Chem. Phys. Lett.* **2001**, *341*, 319.

(96) Staroverov, V. N.; Scuseria, G. E.; Tao, J. M.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119*, 12129. Tao, J. M.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(97) Di Valentin, C.; Pacchioni, G.; Bredow, T.; Dominguez-Ariza, D.; Illas, F. *J. Chem. Phys.* **2002**, *117*, 2299.

(98) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

(99) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101.

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J. Chem. Theory Comput., Vol. 5, No. 4, 2009 **821**

(100) Van Voorhis, T.; Scuseria, G. E. *J. Chem. Phys.* **1998**, *109*, 400.

(101) Gill, P. M. W. *Mol. Phys.* **1996**, *89*, 433.

(102) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

(103) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(104) Seidl, M.; Perdew, J. P.; Levy, M. *Phsy. Rev. A* **1999**, *59*, 51.

(105) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(106) Stewart, J. J. P. *J. Mol. Model.* **2007**, *13*, 1173.

(107) Rocha, G. B.; Freire, R. O.; Simas, A. M.; Stewart, J. J. P. *J. Comput. Chem.* **2006**, *27*, 1101.

(108) Jorgensen, W. L.; Tubert-Brohman, I.; Guimaraes, C. R. W. *Improved semiempirical MO methods: PDDG/PM3*; Abstracts of Papers of the American Chemical Society, 2004. Repasky, M. P.; Chandrasekhar, J.; Jorgensen, W. L. *J. Comput. Chem.* **2002**, *23*, 1601. Tubert-Brohman, I.; Guimaraes, C. R. W.; Jorgensen, W. L. *J. Chem. Theory Comput.* **2005**, *1*, 817. Tubert-Brohman, I.; Guimaraes, C. R. W.; Repasky, M. P.; Jorgensen, W. L. *J. Comput. Chem.* **2004**, *25*, 138.

(109) Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, T.; Suhai, S.; Seifert, G. *Phys. Rev. B* **1998**, *58*, 7260.

(110) Adamo, C.; Barone, V. *Chem. Phys. Lett.* **1997**, *274*, 242.

(111) Ernzerhof, M.; Scuseria, G. E. *J. Chem. Phys.* **1999**, *110*, 5029.

(112) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 1384.