Small Representative Benchmarks for Thermochemical Calculations

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We propose a small set of atomization energies and a small set of barrier heights as benchmarks for comparing and developing theoretical methods. We chose the data sets to be subsets of the Database/3 collection of atomization energies and barrier heights. We show that these data sets, consisting of six barriers and six atomization energies, are very representative of all the atomization energies and barrier heights in Database/3, and we call them the AE6 and BH6 benchmarks, respectively. Benchmark values are tabulated for 80 standard methods, including Hartree−Fock, Møller−Plesset perturbation theory, quadratic configuration interaction, coupled cluster theory, hybrid density functional theory, and multicoefficient correlation methods.

1. Introduction

Broad data sets of experimental data such as Database/3,[1] G2/97,[2−4] and G3/99[3−5] are useful tools for assessing the performance of new theoretical methods. A hindrance to using these data sets for such purposes is that comparing to these data sets requires calculations on hundreds of structures. This can be both computationally expensive and technically cumbersome, and as a result few methods have been tested using the full data sets. The testing of most methods is done using smaller sets of data. Unfortunately, reported mean errors in predicting heats of formation or total atomization energies using different data sets cannot be directly compared because they are very dependent on the average size of molecules in the test set used as well as the diversity of the bond types represented.

A smaller set of data might prove useful as a standard benchmark if it is computationally inexpensive and yet representative of larger data sets. A small data set would be very useful not only for *testing* but also to help in *developing* new theoretical methods. Using a small, yet diverse test set could allow one to gain a basic understanding of a method's strengths and weaknesses without the time and expense of performing more thorough tests.

Database/3 contains 109 atomization energies and 44 barrier heights,[1] as well as 13 ionization potentials and 13 electron affinities. Although it provides good diversity without being as large as G2/97 or G3/99, it can still be prohibitively expensive for some methods. An interesting question is whether representative subsets of the atomization energies and barrier heights could be chosen to closely reproduce the same errors as exhibited by the entire set. We can compare the mean signed error (MSE), mean unsigned error (MUE), and root-mean-square errors (RMSE) of different subsets of data to the same errors using a full set. The most representative subset for a fixed cost is the subset whose MSEs, MUEs, and RMSEs for a large number of methods show the smallest deviation from the same error measures calculated using the entire Database/3. The present paper will answer the following questions: How rapidly do these deviations decrease with the size of the data set? Do economical but representative data sets exist? Can we recommend a standard small but representative data set?

Section 2 describes the methods used. Section 3 gives the results, section 4 gives some discussion, and section 5 gives our conclusions.

2. Methods

The first step in developing the new test sets was to calculate the atomization energies (AEs) and barrier heights (BHs) in Database/3[1] using 80 methods (where a method is a combination of theory level and basis set). We then compare the errors calculated using small subsets of data to the errors calculated using the entire Database/3 for 80 methods. The 80 methods consist of a wide variety of types of methods, in particular pure DFT (mPWPW91[6]), hybrid DFT (B3LYP,[7,8] mPW1PW91,[6] MPW1K,[9] PBE1PBE[10,11]), Hartree−Fock (HF), Møller−Plesset second-, third-, and fourth-order perturbation theory (MP2,[12] MP3,[13] MP4[13]), Møller−Plesset fourth-order perturbation theory without triples contributions[13] (MP4SDQ), coupled cluster theory (CCD[14] and CCSD(T)[15]), and quadratic configuration interaction (QCISD[16] and QCISD(T)[16]), using one or more of 12 basis sets: 6-31G,[13] 6-31G(d),[13] 6-31G†,[17] 6-31G(d,p),[13] 6-31+G(d),[13] 6-31+G†,[17] 6-31+G(d,p),[13] 6-31G(2df,p),[13] 6-31+G(2df,p),[13] 6-311+G(3df,2p),[13] cc-pVDZ,[18] cc-pVTZ,[19] G3Large,[20] MG3,[21,22] MG3S,[23] and MG3T.[23] The methods also include four multicoefficient correlation methods,[21,24−29] in particular MC-QCISD/3,[1] MCG3/3,[1] G3S,[27,29,30] and G3S/3,[1] and the multilevel method CBS-Q.[31] We note that PBE1PBE is also known as PBE0,[11] and MG3 is also known as G3LargeMP2;[22] furthermore, for H through Si, MG3, MG3S, and MG3T are the same as 6-311++G(3d2f,2df,2p), 6-311+G-(3d2f,2df,2p), and 6-311G(3d2f,2df,2p), respectively. The complete list of 80 methods is provided later in the article.

All electronic structure calculations in the present work were performed using the *Gaussian 98*[32] software package, except that the error in the mPW functional was corrected.[23]

All calculations in the present work use QCISD/MG3 optimized structures. All calculations used the spin-restricted formalism for closed shells and the spin-unrestricted formalism for open-shell systems. The atomization energies and barrier heights in Database/3 are all zero-point-exclusive and can therefore be directly compared to the differences in electronic

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energies. The effect of spin−orbit coupling is added to open-shell systems from a compendium given elsewhere.[33]

To determine the most representative set of data, we find a subset that minimizes the root-mean-square deviation (RMSD) between the three standard error measures (MSE, MUE, and RMSE) calculated using Database/3 and the same error measures calculated using the subset, e.g., the deviation between the MSE using Database/3 (*MSE*(*DB3*)) and the MSE using the small subset (*MSE*(*SS*)). The RMSD is calculated using eq 1, where the deviations are summed over all 80 methods considered.

$$\mathrm{RMSD} = \left[\frac{1}{240}\sum_{i=1}^{80}[(MSE_i(DB3) - MSE_i(SS))^2 + (MUE_i(DB3) - MUE_i(SS))^2 + (RMSE_i(DB3) - RMSE_i(SS))^2]\right]^{1/2} \quad (1)$$

The mean error (ME) is calculated using eq 2.

$$\mathrm{ME} = \frac{1}{240}\sum_{i=1}^{80}(|MSE_i(DB3)| + MUE_i(DB3) + RMSE_i(DB3)) \quad (2)$$

Finally, we calculate the percent error in representation (PEIR) using eq 3.

$$\mathrm{PEIR} = 100\% \times \frac{\mathrm{RMSD}}{\mathrm{ME}} \quad (3)$$

The values of RMSD, ME, and PEIR are calculated separately for atomization energies and for barrier heights. The value of ME is 44.5 kcal/mol for atomization energies and 5.98 kcal/mol for barrier heights.

One of the primary motivations for developing representative subsets is cost. The cost indicator we use is based on the computer time to calculate the single-point energy of a molecule or single-point energy of a transition state using the mPW1PW91/MG3 method on a 500 MHz R14000 processor on an Origin 3800 computer. In particular, the cost for a given subset of AEs is the sum of the costs for all the molecules in the subset. For barrier heights one must calculate the energies of the reagents as well as the transition states, but for bimolecular reactions the cost is usually dominated by the transition state. Therefore, for barrier heights the cost indicator is taken as the sum of the costs to calculate the transition state energies for all reactions in the subset. Costs are quoted as unitless values by dividing all costs by 4.0 s.

3. Results

The cost of calculating all 109 atomization energies in Database/3 is 6000. We initially chose to look for the most representative subset of atomization energies that has a cost less than 300 (5% of 6000), where the criterion for most representative is smallest PEIR. The PEIRs for the best AE subsets meeting the cost cap are plotted in Figure 1 as a function of subset size. The figure shows the PEIR is already under 4% with the three most representative atomization energies, and it is under 3% with the four most representative. However, to increase diversity, we elected to include six atomization energies, which yields a PEIR of 1.9%. This set of six atomization energies is the best subset with cost under 300 and is listed in Table 1. Note that because of our 5% cost criterion, the curve in Figure 1 does not decrease to zero as more data are added. Instead, using more data with a given cost cap forces one to select smaller molecules that are less representative. We also tried adjusting the cost cap to other values; however we found that, compared to the increase in cost, there was not a worthwhile reduction in the error when using larger, more expensive subsets.

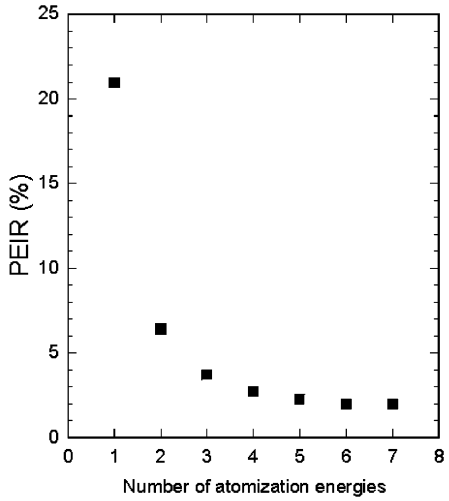

Figure 1. Percentage error in representation vs size of atomization energy subset for a 5% cost limitation.

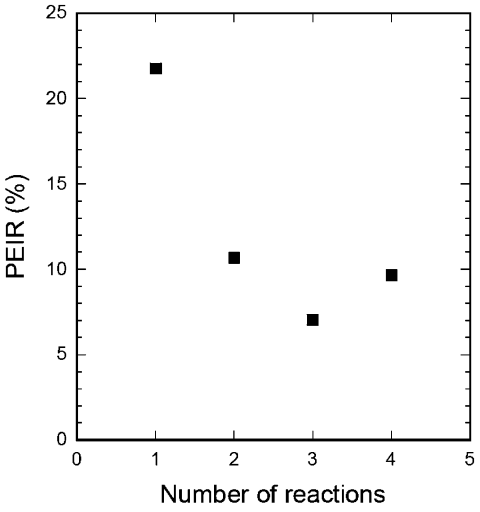

Figure 2. Percentage error in representation vs number of reactions in barrier height subset for a 5% cost limitation.

TABLE 1: Accurate Values (kcal/mol) for Atomization Energies

molecule	D_e
SiH_4	322.40
SiO	192.08
S_2	101.67
propyne (C_3H_4)	704.79
glyoxal ($C_2H_2O_2$)	633.35
cyclobutane (C_4H_8)	1149.01

TABLE 2: Accurate Values (kcal/mol) for Forward (f) and Reverse (r) Barrier Heights

reaction	$V_f^{\ddagger}$	$V_r^{\ddagger}$
$OH + CH_4 \rightarrow CH_3 + H_2O$	6.7	20.2
$H + OH \rightarrow O + H_2$	10.1	13.1
$H + H_2S \rightarrow H_2 + HS$	3.6	17.4

The cost to calculate all 44 barrier heights in Database/3 is 3000. Again we looked for the best subset (smallest RMSD) with a cost less than 5% of the entire set (150). The PEIRs for the best BH subsets are plotted in Figure 2. The PEIR for a set

TABLE 3: Deviation, Percentage Error in Representation, and Cost of the Representative Sets from Database/3

data set	RMSD (kcal/mol)	PEIR (%)	cost[a]
AE6	0.88	1.9	201
BH6	0.42	7.0	131

[a] Units of 4 s on R14000 processor as explained in section 2.

of four reactions is higher than for three reactions, due to the decrease in possible subsets that meet the 5% cost cap. The subset with the lowest RMSD is listed in Table 2. The lowest PEIR for a subset that meets this cap is 7.05%; it is interesting to mention that the best set of three reactions without any cost restriction has a PEIR of 6.95% and a cost of 438 (a 334% increase in cost and a 1% decrease in RMSD). Again the improvement obtained by increasing the cost cap does not seem to be worthwhile.

The two new data sets will be called AE6 and BH6. The RMSD, PEIR, and cost for each of the final small test sets that we selected by the above criteria are shown in Table 3.

TABLE 4: Example of Errors Calculated Using AEs and BHs from Database/3 and the AE6 and BH6 Benchmark Data Sets[a]

		HF/6-31G(d)	MP2/MG3S	QCISD/6-31G(d)	PBE1PBE/6-31+G(d,p)	MCG3/3
			Atomization Energies			
Database/3 (109)	MSE	−150.6	−5.2	−51.7	−3.1	−0.1
	MUE	150.6	9.7	51.7	6.3	1.0
	RMSE	171.8	11.9	58.9	9.6	1.4
AE6 (6)	MSE	−151.0	−5.4	−52.3	−3.9	0.0
	MUE	151.0	9.2	52.3	7.1	0.8
	RMSE	171.5	11.1	58.5	8.8	1.1
			Barrier Heights			
Database/3 (44)	MSE	12.8	4.0	5.6	−4.7	0.7
	MUE	13.4	4.4	5.9	4.7	1.0
	RMSE	14.9	5.1	6.6	5.1	1.3
BH6 (6)	MSE	12.2	3.9	5.4	−4.6	0.6
	MUE	12.2	3.9	5.8	4.6	0.8
	RMSE	14.2	4.5	6.4	4.8	0.9

[a] Number of data in parentheses.

TABLE 5: AE6 and BH6 Benchmark Values (MUE in units of kcal/mol) Using QCISD/MG3 Optimized Geometries

method	AE6	BH6	method	AE6	BH6
HF/6-31G	190.2	11.7	CCSD(T)/cc-pVTZ	15.3	1.3
HF/6-31G†	152.2	12.1	QCISD/6-31G(d)	52.3	5.8
HF/6-31G(d)	151.0	12.2	QCISD/6-31+G(d)	53.7	4.8
HF/6-31+G†	153.4	12.3	QCISD/6-31+G(d,p)	38.6	3.9
HF/6-31G(d,p)	148.0	12.2	QCISD/MG3	23.3	2.3
HF/6-31G+(d,p)	149.5	12.4	QCISD(T)/6-31G(d)	46.5	5.5
HF/6-31G(2df,p)	143.7	12.3	QCISD(T)/6-31+G†	50.0	5.0
HF/6-31+G(2df,p)	144.9	12.6	QCISD(T)/6-31G(d,p)	30.7	4.2
HF/cc-pVDZ	157.1	11.2	QCISD(T)/6-31+G(d,p)	32.3	3.1
HF/cc-pVTZ	147.2	12.2	QCISD(T)/6-31+G(2df,p)	18.5	2.3
HF/MG3	145.3	12.3	B3LYP/6-31+G(d,p)	7.3	5.0
HF/MG3S	145.3	12.3	B3LYP/6-311+G(3df,2p)	2.9	4.8
HF/G3Large	145.0	12.3	B3LYP/MG3S	3.2	4.7
MP2/6-31G†	39.8	7.1	MPW1K/6-31G(d)	15.0	2.7
MP2/6-31G(d)	38.4	6.8	MPW1K/6-31+G(d)	17.3	2.0
MP2/6-31+G†	40.5	7.0	MPW1K/6-31G(d,p)	13.5	2.0
MP2/6-31G(d,p)	23.4	5.7	MPW1K/6-31+G(d,p)	14.9	1.4
MP2/6-31+G(d,p)	24.4	5.5	MPW1K/MG3T	10.3	1.7
MP2/6-31G(2df,p)	9.1	5.0	MPW1K/MG3S	10.9	1.4
MP2/6-31+G(2df,p)	10.8	4.8	MPW1K/MG3	11.0	1.4
MP2/6-31+G(2df,2p)	9.2	4.0	mPW1PW91/6-31G(d)	8.0	3.5
MP2/cc-pVDZ	33.9	3.7	mPW1PW91/6-31+G(d)	10.0	3.4
MP2/MG3	9.2	3.9	mPW1PW91/6-31G(d,p)	7.8	4.1
MP2/MG3S	9.2	3.9	mPW1PW91/6-31+G(d,p)	8.0	3.9
MP2(full)/G3Large	8.4	3.8	mPW1PW91/MG3T	3.9	4.2
MP3/6-31G(d)	51.1	7.3	mPW1PW91/MG3S	4.6	3.9
MP3/6-31+G(d)	52.5	7.0	mPW1PW91/MG3	4.8	4.0
MP3/6-31+G(d,p)	36.7	5.9	mPWPW91/6-31+G(d,p)	7.4	8.6
MP3/6-31G(2df,p)	21.0	5.5	mPWPW91/MG3S	9.8	8.5
MP4SDQ/6-31G(d)	50.7	6.6	mPWPW91/MG3	9.6	8.5
MP4SDQ/6-31+G(d)	51.9	6.2	PBE1PBE/6-31G(d)	7.2	4.2
MP4SDQ/6-31G(d,p)	35.1	5.5	PBE1PBE/6-31+G(d)	7.3	4.1
MP4SDQ/6-31+G(d,p)	36.6	5.1	PBE1PBE/6-31+G(d,p)	7.1	4.6
MP4SDQ/6-31G(2df,p)	22.5	4.9	PBE1PBE/MG3S	5.3	4.6
MP4SDQ/6-31+G(2df,p)	24.0	4.6	PBE1PBE/MG3	5.3	4.6
MP4/6-31G(d)	43.2	6.4	CBS-Q	1.3	0.8
MP4/6-31+G(d)	44.3	5.6	MC-QCISD/3	1.1	0.9
MP4/6-31G(2df,p)	12.7	4.2	MCG3/3	0.8	0.8
CCD/6-31G(d)	54.8	7.3	G3S	1.2	0.6
CCD/6-31+G(d)	56.2	7.1	G3S/3	0.8	0.5

4. Discussion

The AE6 set of atomization energies consists of SiH_4, S_2, SiO, C_3H_4 (propyne), $C_2H_2O_2$ (glyoxal), and C_4H_8 (cyclobutane). This set of atomization energies is very diverse considering its size. It has of a total of 18 hydrogens, 12 first-row atoms, and four second-row atoms. Five systems are ground-state singlets (no unpaired electrons), and one is a ground-state triplet (two unpaired electrons). The set contains single bonds to first-row atoms, double bonds to first-row atoms (glyoxal), triple bonds to first-row atoms (propyne), single bonds to second-row atoms (SiH_4), double bonds to second-row atoms (S_2), and a triple bond to a second-row atom (SiO). Also, it contains a compound with a strained ring (cyclobutane). The errors calculated using this subset have only a 1.9% deviation from the same errors using the 109 atomization energies in Database/3.

The average number of bonds in the 109 molecules in Database/3 atomization energy test set is 4.71, and the average number of bonds in AE6 is 4.83. Thus the RMSD of 0.88 kcal/mol corresponds to only 0.18 kcal/mol per bond, whereas the average bond energy in AE6 is 112.3 kcal/mol. Note that in these comparisons we count all bonds (bond order 1, 2, or 3) as one bond.

The BH6 data set of barrier heights consists of the forward and reverse barrier heights for three reactions: $OH + CH_4 \rightarrow CH_3 + H_2O$, $OH + H \rightarrow O(^3P) + H_2$, and $H + H_2S \rightarrow HS + H_2$. Two of these reaction systems are doublets, and one is a triplet. Two of the reactions involve only first-row atoms, and one involves a second-row atom. The errors calculated using this subset have a 7.0% deviation from the errors calculated using all 44 barrier heights.

Overall, the subsets of atomization energies and barrier heights yield errors that are very representative of their respective errors using Database/3. Table 4 gives five examples of the errors calculated using the subset of six atomization energies and the entire set of 109 and the subset of six barrier heights and the entire set of 44. Table 5 lists the MUE of 80 methods using the representative subset of atomization energies and using the representative set of barrier heights.

It should be pointed out that the AE6 and BH6 benchmarks are by no means a comprehensive measure of the overall performance of a theoretical method. The AE6 and BH6 benchmarks are not necessarily predictive of other properties such as electron affinity, ionization potential, or energy of reaction. For example, it can be seen in Table 5 that mPW1PW91 using the 6-31G(d,p) and 6-31+G(d,p) basis sets has AE6 and BH6 benchmarks that differ by only 3−5%; however, a previous study showed[34] that mPW1PW91/6-31G(d,p) gives a MUE 5.2 times larger than mPW1PW91/6-31+G(d,p) for electron affinities and 1.3 times larger for calculating energies of reaction (for 328 isogyric reactions). Adding diffuse functions to the basis set also was shown[34] to greatly improve the accuracy of relative conformational energies.

5. Conclusions

We were able to determine a small test set of six atomization energies as representative of the 109 atomization energies in Database/3 within 1.9% and a small set of six barrier heights (based on three transition states) that is representative of the 44 barrier heights in Database/3 within 7.0%. The costs of testing electronic structure methods against the AE6 and BH6 benchmarks are 3% and 4%, respectively, of running the large test set.

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Supporting Information Available: The MSEs, MUEs, and RMSEs for all 80 methods for the Database/3, AE6, and BH6 test suites. This material is available free of charge via the Internet at http://pubs.acs.org.

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