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Doubly Hybrid Meta DFT: New Multi-Coefficient Correlation and Density Functional Methods for Thermochemistry and Thermochemical Kinetics

Yan Zhao, Benjamin J. Lynch, and Donald G. Truhlar
Department of Chemistry and Supercomputing Institute,
University of Minnesota, 207 Pleasant Street S.E.,
Minneapolis, MN 55455-0431

***Abstract*.**

This paper presents two new multi-coefficient correlation and density functional methods based on mixing scaling-all-correlation (SAC) theory and hybrid density functional theory (HDFT) with empirical parameters. Both methods were optimized against a database of 109 atomization energies and 42 barrier heights. The resulting methods, called MC3BB and MC3MPW, were tested against a database of saddle point geometries, and scaling factors were optimized for calculating vibrational frequencies. The two new methods were compared to the methods that we have previously determined to be most efficient for thermochemistry and thermochemical kinetics, where the criterion is the average of the mean unsigned errors for bond energies and barrier heights. These comparisons show that MC3BB is more accurate than any other method that has comparable cost. Both new methods are well suited for direct dynamics calculations that require Hessians. The new approach is called doubly hybrid density functional theory (DHDFT).

1. Introduction

Multi-coefficient correlation methods[1-8] (MCCMs) use empirical parameters to combine a set of low-cost single-level electronic structure calculations. The multi-level energy obtained by a linear combination of single-level calculations corresponds to extrapolating to a complete one-electron basis and an infinite-order treatment of electron correlation.[1] The final prediction is much less expensive than comparably accurate single-level calculations, which are often not affordable. For example, the coupled cluster method with single and double excitations and quasiperturbative connected triples[9] (CCSD(T)) and an augmented correlation-consistent polarized triple zeta basis set is eight times less accurate for bond energies than multi-coefficient Gaussian-3 (MCG3) but about two orders of magnitude more expensive.[8] MCCMs have been shown to be affordable and robust for predicting accurate atomization energies,[1-6,8] reaction barrier heights,[7,8] potential energy surfaces,[10-13] ionization potentials,[8,14,15] electron affinities,[8,14,15] proton affinities,[16] and vibrational frequencies[17]

Several MCCMs such as scaled Gaussian-3 (G3S and G3SX),[14,15,18] scaled G3 methods with reduced-order Møller-Plesset perturbation theory[14,15,18] (G3S(MP3), G3S(MP2), G3SX(MP3) and G3SX(MP2)), and multi-coefficient Gaussian-3 (MCG3)[4,8] have proven to be very accurate for predicting thermochemical properties. Unfortunately, the computational costs of these methods formally scale as N^7, where N is the number of atoms. If one wants to calculate consistent gradients or Hessians (for example, in dynamics calculations or geometry optimizations), these methods are very expensive, and sometimes prohibitively so. In a previous paper,[8] our group developed a suite of MCCMs of varying accuracy and cost, namely the MCCM/3 suite, that is suitable for a variety of problems with different sizes of molecules and different accuracy requirements. The recommended methods in the MCCM/3 suite are MC-CO/3, MC-UT/3, MC-QCISD/3, and MCG3/3. These methods are constructed by taking linear combinations of wave-function-based single-level methods such as Hartree-Fock (HF) theory, Møller-Plesset perturbation theory (MP2,[19] MP4SDQ,[20] and MP4[20]), quadratic configuration interaction with single and double excitations (QCISD),[9] and QCISD with quasiperturbative connected triples[9] (QCISD(T)). A particularly powerful version of the MC method is the MC-QCISD method,[6,8] which scales as N^6. In the limit of only a single coefficient, the MCCM methods reduce to the older scaling-all-correlation (SAC) method.[21] When we say SAC without any further explanation, it means SAC based on MP2 theory, also called SAC-MP2, which scales as N^5.

Hybrid density functional theory[22-30] (HDFT), which involves taking a linear combination of HF theory and density functional theory (DFT) at the Fock-Kohn-Sham operator level, has been widely applied to many problems due to its excellent cost-to-performance ratio. Its computational cost scales as N^4. Recently we optimized a Becke88–Becke95 1-parameter model for kinetics;[30] the method was called BB1K. BB1K and the previously optimized MPW1K model[27] give very good performance for kinetics as measured against a database of barrier heights.[30,31] MPW1K is an example of HDFT, and BB1K is an example of hybrid meta DFT (HMDFT), where meta denotes that kinetic energy density is included in the functional. Both HDFT and HMDFT include gradient corrections in the density functionals.

The goal of the project reported here was to generalize the multi-coefficient methods to allow mixing of the wave-function-based methods with hybrid density functional methods. In particular, we use a multi-coefficient approach to mix the SAC method[1,5,8,21,32] with HDFT or HMDFT. The new resulting methods are called the multi-coefficient three-parameter Becke88-Becke95 (MC3BB) method and multi-coefficient three-parameter modified Perdew-Wang (MC3MPW) method (both methods are further discussed in Section 3). We optimize both methods against a set of atomization energies and chemical reaction barrier heights. The training set is designed to yield parameters that are suitable for thermochemistry and thermochemical kinetics.

Section 2 presents our training and test sets. Section 3 discusses the theory and parametrization of the new methods. Section 4 presents results and discussion.

2. Databases

2.1. Training Set. The training set used in the present paper consists of 109 atomization energies (AEs) and 42 barrier heights (BHs). The AE training set contains a diverse set of molecules including organic and inorganic molecules and radicals, but there are very few metallic species. The barrier height set consists primarily of open-shell reactions (as opposed to, say, closed-shell S_N2 reactions or closed-shell proton transfer reactions), and there are no metallic species involved in the 21 reactions that define the 42 barrier heights.

All 151 data are pure electronic energies, i.e, zero-point energies and thermal vibrational-rotational energies have been removed. The 109 zero-point-exclusive atomization energies are part of Database/3 and are identical to those used previously;[8,29] for convenience they are listed in the supporting information. This database will be called AE109/3. The barrier height database has also been published previously,[30] and it comprises what is called the BH42/03 database. The best estimates for the barrier heights were obtained, as explained elsewhere,[7,8,27,30,33] from a combination of experimental and theoretical kinetics data, and for completeness they are listed in the supporting information as well.

2.2. Saddle Point Geometries. After optimization against atomization energies and barrier heights, we test the MC3BB and MC3MPW methods against a database of saddle point geometries. The database of saddle point geometries comes from previous work.[7,33] The test set consists of five reactions where very high-level calculations[34-37] of saddle point geometries are available. These data for saddle point geometries are listed in supporting information, and this data set is called the SPG15/01 database. In testing various methods against saddle point geometries, we compare calculated values of these quantities to results from the accurate calculations; these three quantities are the length of the forming bond, the length of the breaking bond, and the perpendicular looseness. The perpendicular looseness has been defined[7,30,33] as the sum of the forming and breaking bond distances; this is a measure of the looseness of the saddle point structure in the direction perpendicular to the reaction coordinate.

2.3. Vibrational Zero Point Energies Database. A database of thirteen anharmonic vibrational zero point energies (ZPEs) has been presented in a previous paper;[1] it is based on the work of Martin.[38] This is called the ZPE13/99 database. We will employ this vibrational ZPE database to develop scale factors for vibrational frequencies calculated both by MC3BB and MC3MPW. The scale factors are optimized to minimize the root-mean-square errors in the calculated ZPEs for these 13 molecules.

2.4. Geometries and Spin-Orbit Energy. All calculations of the 42 barrier heights and 109 atomization energies in section 2.1 are single-point calculations at QCISD/MG3 geometries, where MG3 is the modified[4,39] G3Large[40] basis set. The MG3 basis set,[4] also called G3LargeMP2,[39] is the same as 6-311++G(3d2f, 2df, 2p)[41] for H-Si, but improved[40] for P-Ar. The QCISD/MG3 geometries needed to calculate the 109 atomization energies and 42 barrier heights can be obtained from the Truhlar group database website.[42]

The calculations in sections 2.2 and 2.3 involve geometry optimization with each level of theory tested.

In all of the calculations presented in this paper, the spin-orbit stabilization energy was added to all atoms and to selected open-shell molecules, as described previously.[4] All calculations were performed with the GAUSSIAN03[43] and MULTILEVEL 3.1[44] programs.

3. Theory and Parametrization

3.1. SAC. SAC[1,5,8,21,32] is a very simple approach for extrapolating correlated electronic structure calculations to the limit of full dynamical correlation of the valence electrons and a complete one-electron basis set for the valence electrons. In particular, Gordon and Truhlar[21] defined the SAC energy by:

$$E_{SAC} = E_{HF} + \frac{E_{AC}}{F_{SAC}} \tag{1}$$

where E_{AC} is the calculated valence correlation energy, E_{HF} is the Hartree-Fock (HF) energy, and F_{SAC} is a parameter for scaling correlation energy.

The methods described here use the "pipe" notation for the level (L) and basis set (B); this was introduced elsewhere[2] with the definition needed here being:

$$\Delta E(\mathrm{L2}|\mathrm{L1/B}) \equiv E(\mathrm{L2/B}) - E(\mathrm{L1/B}) \tag{2}$$

Using this notation, SAC /6-31+G(d,p) can be expressed as:

$$\mathrm{E(SAC/DIDZ)} = E(\mathrm{HF/DIDZ}) + c_1\Delta E(\mathrm{MP2}|\mathrm{HF/DIDZ}) \tag{3}$$

where DIDZ is a shorthand (used in equations) for the 6-31+G(d,p) basis set, and $c_1 = 1/ F_{SAC}$ may be parametrized by using experimental data. Note that the extrapolation to full CI is explicit in equation (1), whereas the extrapolation to a complete one-electron basis set is implicit. Nevertheless, because c_1 is determined from experiment, both extrapolations are included.

3.2. HDFT and HMDFT. The one-parameter hybrid Fock-Kohn-Sham operator can be written as follows:[24,27]

$$F = F^{\mathrm{H}} + (X/100)\, F^{\mathrm{HFE}} + [1 - (X/100)]\, (F^{\mathrm{SE}} + F^{\mathrm{GCE}}) + F^{\mathrm{C}} \tag{4}$$

where F^{H} is the Hartree operator (i.e., the nonexchange part of the Hartree-Fock operator), F^{HFE} is the Hartree-Fock exchange operator, X is the percentage of Hartree-Fock exchange, F^{SE} is the Dirac-Slater local density functional for exchange,[45,46] F^{GCE} is the gradient correction for the exchange functional, and F^{C} is the total correlation functional including both local and gradient-corrected parts. In the BB1K model, we used the Becke88[47] functional for F^{GCE} and the Becke95[24] functional for F^{C}, and we set $X = 42$,[30] whereas in the original B1B95 method, $X = 28$. In the MPW1K model, Adamo and Barone's modified Perdew-Wang 1991 exchange functional[25,48] (MPW) is used for F^{GCE}, Perdew and Wang's 1991 correlation functional[48] (PW91) is used for F^{C}, and $X = 42.8$.

3.3. Parametrization of MC3BB and MC3MPW. Because SAC calculations scale as N^5, while HDFT methods scale as N^4, in order to lower the cost of the new methods we use a smaller basis set for the SAC part than for the HDFT part. In particular we use a recommended[29,33] augmented polarized valence double zeta set, 6-31+G(d,p),[20,49] for the SAC method, and a recommended augmented polarized triple zeta set, MG3S, for the HDFT methods. The MG3S basis set[29] is the same as MG3 (explained above) except that it omits diffuse functions on hydrogens.

We use a multi-coefficient approach to combine the SAC and HMDFT and HDFT methods. The MC3BB method is defined in eq. (5):

$$E(\text{MC3BB}) = c_2\,[E(\text{HF/DIDZ}) + c_1 \Delta E(\text{ MP2|HF/DIDZ})] + (1-c_2)\,E(\text{BBX/MG3S}) \tag{5}$$

where BBX is same as BB1K except that the percentage, *X*, of HF exchange will be determined by parametrization.

The MC3MPW method is defined in eq. (6):

$$E(\text{MC3MPW}) = c_2\,[E(\text{HF/DIDZ}) + c_1 \Delta E(\text{ MP2|HF/DIDZ})] + (1-c_2)\,E(\text{MPWX/MG3S}) \tag{6}$$

where MPWX is same as MPW1K except that the percentage, *X*, of HF exchange will be determined by parametrization.

The three parameters in eq. (5) and eq. (6), namely, c_1, c_2, and *X*, were adjusted to minimize the average mean unsigned error defined by:

$$AMUE = 0.5[MUEPB(\text{AE109/3}) + MUE(\text{BH42/03})] \tag{7}$$

where MUEPB denotes the mean unsigned error (MUE, also called mean absolute error) per bond. MUEPB is equal to MUE(AE109/3)/4.71, where 4.71 is the average number of bonds for the 109 species in the atomization energy database. Therefore the first term in eq. (7), MUEPB(AE109/3), is a measure of the mean error on a per bond basis, and it is a measurement of the performance for calculating bond energies. Equation (7) equally weights the errors in bond energies and in barrier heights (BH). The motivation for this target function is that we want the optimized methods to give good results for both bond energies (thermochemistry) and barrier heights (kinetics).

The optimized parameters c_1, c_2, and X for MC3BB and MC3MPW are listed in Table 1. If we were to rewrite c_1 as $1/F_{SAC}$, as in eq. (1), we would obtain $F_{SAC} \approx 0.75$ for both methods, which is quite reasonable for a basis the size of DIDZ. Furthermore the values of c_2 and X are both in the reasonable range we have come to expect based on past experience (0.2 – 0.5 for c_2 and 20 – 50 for X).

4. Results and Discussion

4.1. Bond Energies. Table 2 gives the errors for MC3BB and MC3MPW as well as for some other methods. Note that the error in atomization energy is given on a per bond basis, which means that the errors for atomization energy are divided by 4.71, the average number of bonds for the 109 species in the atomization energy database. In all tables in this paper, MSE denotes mean signed error, and RMSE denotes root mean square error.

The cost function used in Table 2 is the same as the one described in a previous paper.[8] The cost function used here is the cost to calculate a single energy, gradient, or Hessian (as stated in the column heading) for phosphinomethanol divided by the computer time for an HF/6-31G(d) energy calculation on the same molecule with the same computer program and same computer. Most of the costs are taken from a previous paper[8] except that the costs of BB1K and MC3BB are determined by using GAUSSIAN03 program with a single 1.7 GHz Power4 processor on a IBM p690 (Regatta) supercomputer. The effects of the difference in software and platform are estimate so that the costs tabulated for BB1K and MC3BB are on the scale used in Ref. 8.

From the mean errors in Table 2 we can see that the new MC3BB method reduces MUEPB(AE) and RMSEPB(AE) by ~45% and ~50%, respectively, as compared to BB1K/MG3S, although the Hessian cost of MC3BB is only ~20% higher than BB1K. The other new method, MC3MPW, reduces MUEPB(AE) and RMSEPB(AE) by ~65% and ~60%, respectively, as compared to MPW1K/MG3S, and the Hessian cost of MC3MPW is only ~25% higher than MPW1K.

The mean unsigned errors per bond in the atomization energies for MC3BB and MC3MPW are 0.6 and 0.8 kcal/mol, respectively, which qualifies both methods as having "chemical accuracy" (usually defined as 1 kcal/mol for a bond energy).

4.2. Barrier Heights. Table 2 shows that MC3BB reduces MUE(BH) and RMSE(BH) by ~35% and ~40%, respectively, as compared to BB1K/MG3S. MC3MPW reduces MUE(BH) and RMSE(BH) by ~40%, as compared to MPW1K/MG3S.

4.3. Average Mean Unsigned Errors. If we examine the value of the error function AMUE defined in eq. (7), we see that MC3BB reduces AMUE by 46% as compared to BB1K/MG3S, and MC3MPW reduces AMUE by 56% as compared to MPW1K/MG3S.

Although the MUEPB(AE)s of MC3BB and MC3MPW are greater than MC-QCISD, CBS-Q, G3S, and MCG3, both new MCCMs exceed or rival the expensive methods in terms of MUE(BH) or RMSE(BH). Note (see Table 2) that MC-QCISD, CBS-Q, G3S and MCG3 have much more expensive Hessian calculations as compared to MC3BB and MC3MPW.

If we use the AMUE criterion to classify the methods listed in Table 2, we conclude that CBS-Q, G3S, and MCG3 are the most accurate methods. The AMUEs are ~0.5 kcal/mol for these three methods, but they are very expensive. The AMUEs for MC-QCISD, MC3BB, and MC3MPW are ~0.7-0.8 kcal/mol. These three MCCMs have very good cost-to-performance ratios. BB1K and MPW1K are the most efficient single-level methods for thermochemical kinetics, and AMUE is 1.25 kcal/mol for BB1K and 1.84 kcal/mol for MPW1K. B1B95 is a new-generation HDFT method, and it outperforms B3LYP for both atomization energy calculations and barrier height calculations. As shown by its low MUEPB(AE), B1B95 is the most accurate single-level method for thermochemistry, but it has unsatisfactory performance on barrier height calculations as compared to BB1K and MPW1K, and AMUE is 1.68 kcal/mol for B1B95.

From Table 2, we also can see that the expensive *ab initio* method CCSD(T)/cc-pVTZ gives disappointing results for atomization energy calculations, and the most popular HDFT method B3LYP suffers from a large error for barrier height calculations.

4.4. Saddle Point Geometries. We tested our new methods for the prediction of transition state geometries and compared both methods with some other methods. The bond lengths and angles calculated by MC3BB, and MC3MPW are listed in the supporting information. Table 3 summarizes the error in $R^{\neq}_{\text{forming bond}}$ and $R^{\neq}_{\text{breaking bond}}$ and in perpendicular looseness for the five reactions (four for B3LYP, B1B95) in Table 3. The fifth reaction $F + H_2 \rightarrow HF + H$ was left out for B3LYP and B1B95 because B3LYP and B1B95 predict that there is a monotonically downhill reaction path for this reaction; thus they predict that the highest-energy point on the reaction path is at reactants where the forming bond length is ∞. Table 3 shows that MC3BB outperforms MC-QCISD and MCG3, and it gives the best results for calculating the bond length and perpendicular looseness for the five saddle points. The performance of MC3MPW is comparable to MC-QCISD and MCG3. Table 3 also shows that B3LYP has high RMS errors, and it predict looser saddle points in the perpendicular direction (i.e., B3LYP tends to overestimate the sum of the bond lengths of the forming bonds and breaking bonds at the saddle point). The performance of QCISD is slightly worse than MC3BB and MC3MPW, although it is a much more expensive method.

Although the saddle point geometry database consists of only five transition state structures, and all of them are for hydrogen transfer reactions, the conclusions we drew in this section are consistent with the results for energetics in Table 2. Table 2 shows that B3LYP and B1B95 systematically underestimate the barrier heights as indicated by their high negative MSE. As a consequence one expect that the barrier are too early for exothermic reactions, and this is consistent with their positive MSE for the perpendicular looseness. Testing DFT methods for more general classes of reactions is an ongoing research project in our group.

4.5. Vibrational Frequencies Scale Factor. We employed the database[1,38] of thirteen anharmonic vibrational zero point energies to determine the vibrational frequency scale factor for MC3BB and MC3MPW. These scale factors are listed with scale factors for MC-QCISD and some other methods in Table 4. Use of the scale factor reduces the RMS error calculated by MCSABB from 0.46 kcal/mol to 0.07 kcal/mol, and the scale factor reduces RMS error calculated by MC3MPW from 0.45 kcal/mol to 0.07 kcal/mol. Table 4 also shows that the scale factor for the new method is not too far from unity, which is a serious problem for Hartree-Fock theory. Using MP2 instead of HF to mix with DFT leads to scale factors closer to unity (compare, for example, MC3BB to BB1K/MG3S).

The scale factors will be useful for applying the MC3BB and MC3MPW methods to theoretical kinetics calculations.

4.6. AE6 and BH6 Benchmarks. Table 5 summarizes the mean errors for the benchmark AE6 and BH6 representative databases[50] for the MC3BB and MC3MPW methods. 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 a representative subset of the 109 atomization energies training set, and it was developed[50] such that performance on this database is indicative of performance on the much larger 109 atomization energies database. Note that the MSEs and MUEs for AE6 are given on a per bond basis as described in our previous paper.[30,31] The BH6 set consists of the forward and reverse barrier heights of the three reactions, namely, $OH + CH_4 \rightarrow CH_3 + H_2O$, $H + OH \rightarrow O + H_2$, and $H + H_2S \rightarrow HS + H_2$. The BH6 database is a representative subset of the 42 barrier heights training set, and was developed[50] such that performance on this database is indicative of performance on the 42 barrier heights database. Recently we have developed the BB1K[30] model by using the BH6 representative database.

If we compare the MSEs per bond and MUEs per bond of MC3BB and MC3MPW in Table 5 to these errors for the entire 109 atomization energies and 42 barrier heights in Table 2, we see that the errors for AE6 and BH6 correlate fairly well with the errors for the much larger databases. This is important because the mean error with respect to the small AE6 and BH6 database have been calculated for a large number of methods than for the large database (see

Ref. 42), and it is encouraging that tests like this confirm the representative character of the small database.

5. Concluding Remarks

This paper developed two new MCCMs by mixing the SAC method with HMDFT AND HDFT methods by using empirical parameters. The resulting methods, MC3BB and MC3MPW, were assessed against databases of atomization energies, barrier heights, saddle point geometries, and zero point energies. In addition, scaling factors were determined for calculating improved vibrational frequencies with the new methods.

Although we motivated the methods as an extension of the successful multi-coefficient correlation methods to including hybrid DFT or hybrid meta DFT, the methods may also be considered from another point of view, namely as a generalization of hybrid DFT. Although hybrid DFT has been much more successful than pure DFT, it suffers from the deficiencies of HF theory because 20 – 50% of the Fock-Kohn-Sham operator is based on HF theory, which has no electron correlation. One is therefore motivated to replace the HF part by MP2, or – even better – by SAC theory. Such a replacement yields the present multi-coefficient three-parameter HDFT methods, which may more simply be called doubly hybrid DFT (DHDFT) because the new methods are a "hybrid" of the SAC method and hybrid DFT methods. Similarly, we obtain DHMDFT by combining SAC and HMDFT.

Conventional HDFT has a well defined theoretical basis, namely the adiabatic connection theory,[51] and hence they are sometimes called adiabatic connection methods. The theoretical foundation of MC3BB and MC3MPW is the empirical multi-coefficient correlation approach. It was pointed out in a previous paper[8] that "it seems foolhardy for all but the most fundamental studies to eschew the use of semiempirical parameters even with explicitly correlated wave functions". The DHDFT methods developed in the present paper are an empirical "hybrid" of the SAC method and HDFT. We believe that the MC3BB and

MC3MPW methods represent a very good compromise of accuracy, cost, and ease of use for practical calculations.

The key results in this paper are the average mean unsigned errors (AMUEs) in Table 2. These results and the other results in the present paper demonstrate that the multi-coefficient procedure used in doubly hybrid DFT is a successful way to combine wave-function-based methods with HDFT and HMDFT methods. The three parameters (c_1, c_2, and X) in the new methods turn out to have quite reasonable values, and they effectively provide basis set extrapolation and scaling of correlation energies. We believe that the multi-coefficient approach to improving HDFT provide a robust way to improve the accuracy of currently available density functional methods methods.

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Supporting Information Available: The AE109/3, BH42/03 and SPG15 database and the calculated saddle point geometric parameters are given in the supporting information. This material is available free of charge via the internet at http://pubs.acs.org.

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Table 1. Parameters for MC3BB and MC3MPW

Methods	c_1	c_2	X
MC3BB	1.332	0.205	39
MC3MPW	1.339	0.266	38

Table 2. Mean Errors (kcal/mol for Barriers and kcal/mol per Bond for Atomization Energies) and Costs [a]

Methods	AE (per bond)			BH			AMUE	Costs[b]		
	MSEPB	MUEPB	RMSEPB	MSE	MUE	RMSE		Energy	Gradient	Hessian
MC3MPW	-0.40	0.83	1.08	-0.28	0.78	0.98	0.80	50	74	483
MC3BB	-0.14	0.62	0.80	-0.21	0.75	0.92	0.68	59	84	592
MP2/DIDZ	-5.20	5.20	5.89	5.42	5.66	6.07	5.43	2.2	6.7	81
SAC-MP2/DIDZ[c]	-0.69	1.85	2.21	4.16	4.76	5.52	3.30	2.2	8.5	91
B3LYP/MG3S	-0.68	0.89	1.32	-4.40	4.31	4.89	2.60	48	64	390
MPW1K/MG3S	-2.33	2.34	2.75	-0.69	1.34	1.66	1.84	48	64	390
BB1K/MG3S	-1.32	1.34	1.61	-0.61	1.16	1.52	1.25	56	74	501
B1B95/MG3S	-0.23	0.56	0.74	-2.80	2.80	3.12	1.68	56	74	501
MC-QCISD/3	0.00	0.37	0.48	1.05	1.24	1.43	0.80	56	180	2800
MCG3/3	-0.02	0.22	0.30	0.58	0.92	1.16	0.57	88	810	32000
CBS-Q	-0.01	0.30	0.43	-0.11	0.78	1.05	0.54	110	1500	57000
G3S	-0.15	0.27	0.35	0.41	0.75	0.91	0.51	240	6400	290000
CCSD(T)/cc-pVTZ	-3.30	3.30	3.73	0.85	1.32	1.53	2.31	860	41000	2.0×10^6

[a] QCISD/MG3 geometries are used. AMUE is defined by eq. (7). MUEPB denotes mean unsigned error (MUE) per bond. MSE denotes mean signed error. RMSE denotes root mean square error.

[b] The cost function is the same as described in a previous paper.[8] It is the time to calculate an energy, gradient, or Hessian for phosphinomethanol normalized by the time for a HF/6-31G(d) energy calculation. Costs are either determined on a Silicon Graphics Origin 3800 computer directly or determined on an IBM Power4 supercomputer and corrected to the original scale.

[c] DIDZ denotes 6-31+G(d,p) basis. The SAC parameter, c_1 = 1.1707, is taken from Ref. 8.

Table 3. Mean errors (angstroms) in Internuclear Distances at Saddle Point of the Five Reactions in the Saddle Point Geometry Database. [a]

	bond distance			perpendicular looseness			
Method	MSE	MUE	RMSE	MSE	MUE	RMSE	Ref.
MC3MPW	-0.01	0.01	0.01	-0.02	0.02	0.02	This work
MC3BB	-0.00	0.01	0.01	-0.01	0.01	0.01	This work
MP2/DIDZ	-0.03	0.03	0.05	-0.05	0.05	0.07	33
SAC/DIDZ	-0.02	0.03	0.04	-0.05	0.05	0.06	This work
MC-QCISD/3	-0.00	0.01	0.02	-0.00	0.01	0.02	This work
MCG3/3	0.00	0.01	0.02	0.00	0.02	0.02	This work
B3LYP/MG3[b]	0.01	0.05	0.09	0.03	0.06	0.09	33
BB1K/MG3S	0.00	0.02	0.02	0.00	0.01	0.01	30
B1B95/MG3S	0.01	0.03	0.04	0.01	0.02	0.03	30
MPW1K/MG3S	-0.01	0.01	0.02	-0.02	0.02	0.02	30
QCISD/MG3	-0.01	0.02	0.03	-0.01	0.02	0.03	33
MC-QCISD/2	-0.01	0.02	0.02	-0.01	0.01	0.02	7
MCG3/2	0.00	0.01	0.01	0.00	0.01	0.02	7

[a] The methods are listed in the same order as in Table 2. MUE denotes mean unsigned error. MSE denotes mean signed error. RMSE denotes root mean square error.

[b] The results for B3LYP and B1B95 are calculated only for four reactions, because B3LYP and B1B95 do not yield a finite-distance saddle point for $F + H_2 \rightarrow HF + H$.

Table 4. Root-Mean-Square Error and Scale Factor for Calculating Zero Point Energies

	RMS error in ZPE(kcal/mol)			
Method	unscaled	scaled	scale factor	Ref.
MC3MPW	0.45	0.07	0.9675	This work
MC3BB	0.46	0.07	0.9669	This work
MC-QCISD	0.10	0.03	0.9940	This work
MP2/DIDZ	0.50	0.30	0.9700	This work
HF/DIDZ	1.21	0.25	0.9173	30
MPW1K/MG3S	0.60	0.18	0.9581	30
BB1K/MG3S	0.59	0.18	0.9590	30
B1B95/MG3S [a]	0.35	0.14	0.9758	28

[a] Note that GAUSSIAN03 has a bug for B1B95; it used 25% Hartree-Fock exchange. The results presented in the present paper were calculated with the correct value[24] of 28% Hartree-Fock exchange.

Table 5. Mean Errors (kcal/mol for Barriers and kcal/mol per Bond for Atomization Energies) for BH6 and AE6 Benchmarks

	AE6			BH6		
Method	MSEPB	MUEPB	RMSEPB	MSE	MUE	RMSE
MC3MPW	-0.39	0.71	0.91	-0.53	0.72	0.81
MC3BB	-0.02	0.47	0.53	-0.51	0.72	0.87

[a] MUEPB denotes mean unsigned error (MUE) per bond. MSE denotes mean signed error. RMSE denotes root mean square error.