

Lynch, B. J.; Truhlar, D. G. In *Electron Correlation Methodology*; Wilson, A. K., Peterson, K. A., Eds.; ACS Symposium Series Vol. 958; American Chemical Society: Washington, 2007; pp. 153–167.

## Chapter 9

### **Multilevel Methods for Thermochemistry and Thermochemical Kinetics**

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This chapter presents an overview of the performance of current multilevel methods for computational thermochemistry and thermochemical kinetics. Multilevel methods extrapolate to the exact solution of the electronic Schrödinger equations by using calculations carried out with two or more levels, where a level is a combination of a specific form for the many-electron wave function and a specific one-electron basis set. This chapter compares the performance for thermochemistry and thermochemical kinetics of several multilevel methods, including scaling-all-correlation (SAC), complete basis set (CBS) methods, multi-coefficient correlation methods (MCCM), and Gaussian-3 extended (G3X) methods. It also compares these methods to hybrid density functional theory, and additional calculations are presented to test the importance of diffuse basis functions on hydrogen. In order of decreasing cost, the G3SX(MP3), MCG3/3, MC-QCISD/3, CBS-4, mPW1PW91/MG3S, and SAC/3 methods are shown to provide especially good performance-to-cost tradeoffs.

## Introduction

Computational thermochemistry and computational thermochemical kinetics are based on the Born-Oppenheimer approximation and the use of quantum-mechanical electronic structure theory to calculate potential energy surfaces. The electronic structure methods may be based on interacting-electron wave functions or on density functional theory. The present overview is primarily concerned with the former approach. The starting point is Hartree-Fock (HF) theory. In HF theory, the electrons occupy a set of molecular orbitals, which are an orthogonal set of one-electron functions typically constructed from linear combinations of atom-centered basis functions. In HF theory, each electron moves in the average field of the other electrons, and so the correlated motion of the electrons is ignored. This is sometimes called a single-configuration method, and explicitly correlated wave functions based on an HF starting point are called single-reference methods. The error in energy due to the HF approximation is called the correlation energy ( $T$ ). Neglect of the correlation energy leads to many systematic errors in the predicted thermochemical and dynamical properties at the HF level. The cost and poor performance of HF calculations have engendered the development of a variety of more cost-efficient semi-empirical methods. Two very popular semi-empirical methods related to HF theory are AM1 (2,3) and PM3 (4). These methods remove the most expensive parts of a minimum-basis-set HF calculation, and they introduce 15 empirical parameters for each element. The empirical parameters effectively estimate the parts of HF theory that are ignored, and they also implicitly account for effects due to extended basis sets and correlation energy. Methods like AM1 and PM3 tend to outperform minimum-basis-set HF for most problems of chemical interest.

Although semi-empirical methods like AM1 and PM3 are fairly accurate, especially considering their low cost, we need to pursue higher levels of theory to attain chemical accuracy ( $\sim 1$  kcal/mol) in calculating quantities such as bond strengths, electron affinities, ionization potentials, and reaction barrier heights. To achieve higher accuracy, we can use larger basis sets and explicitly account for electron correlation. Full configuration interaction (FCI) accounts for *all* electron correlation energy within the limitations of the one-electron basis set. This type of calculation is prohibitively expensive for all but the smallest of systems, and it is even more expensive to converge the calculation with respect to the size of the one-electron basis set. Therefore we introduce empirical parameters or we extrapolate, or both. For example, we can employ partial treatments of electron correlation, and then use empirical parameters to extrapolate from two or more incomplete levels of calculation to the exact solution. Such calculations, based on two or more levels, are called multilevel methods. All of the multilevel methods presented here include explicitly correlated, extended basis set, post-HF calculations, and so the empirical

parameters in these methods need only to account for high-level electron correlation and the remaining basis set effects. By using extended-basis-set post-HF calculations as our starting point, we can attain higher accuracy than is possible with AM1 and PM3 semi-empirical methods. A disadvantage though, is that the popular post-HF methods scale as  $N^5$ ,  $N^6$ , or  $N^7$  (for large  $N$ ) as the number of atoms  $N$  is increased (5), and the coefficient of  $N^a$  becomes larger as the number of basis functions on each atom is increased. (We will give the scaling exponent  $a$  for various methods in section 3.)

One of the first methods to take advantage of the systematic nature of the errors in explicitly correlated *ab initio* methods and extrapolate toward complete configuration interaction (CCI, which is the combination of FCI with a converged one-electron basis set) is the scaling external correlation (6) (SEC) method. This method scales the correlation energy calculated from a multi-reference wave function. Although it has been shown to be very accurate, the calculation of the correlation energy from a multi-reference wave function is computationally expensive and technically difficult. The scaling-all-correlation (7-11) (SAC) method was therefore developed as a simplified method that only requires the correlation energy to be calculated with a single-reference wave function. Though it is less accurate than SEC, SAC is much more cost-efficient.

MCCM methods (11-18) are the general class of methods that use a linear combination of explicitly correlated *ab initio* calculations with two or more basis sets and two or more levels of electron correlation. The linear combinations extrapolate the correlation energy and the basis set to the CCI limit. One example of an MCCM is MCG3/3 (18), which has been shown (18) to calculate bond energies with less than  $1/10^{\text{th}}$  the error of CCSD(T)/aug-cc-pVTZ (19,20) at less than  $1/100^{\text{th}}$  the cost. (All "costs" in this paper are based on gradient calculations as explained below.) This comparison is especially striking because the CCSD(T) method is sometimes called "the gold standard," due to its high accuracy. Furthermore, the accuracy of MCG3/3 in calculating reaction barrier heights is only achieved by *ab initio* methods that are about 100 times more expensive (18).

Increasing either the basis set or the explicit level of correlation greatly increases the cost of *ab initio* calculations. If high-level correlation effects could be accurately estimated with a small basis, and large-basis-set effects could be estimated with a low level of correlation, then a large-basis high-level-correlation calculation would be unnecessary. Methods such as Gaussian-2 (21-23) (G2), Gaussian-3 (24,25) (G3), and G3 extended (26) (G3X) use such an additive approximation to reduce the cost of explicitly correlated calculations. In particular, starting with a modest *ab initio* calculation, various high-level and larger-basis-set contributions are estimated separately and assumed additive. Furthermore, an empirical correction, called the high-level-correction (HLC), is added to account for missing higher-level effects and nonadditivity, which may also be considered a higher-level effect. As an example, consider the G3 and G3X methods. In these methods the 6-31 G(d) basis is used to calculate the

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energy with quadratic configuration interaction with double and single excitations and quasiperturbative connected triples (QCISD(T)) (27), and larger-basis-set effects are added on by calculations with lower levels of electron correlation. This effectively approximates a large-basis-set calculation at the QCISD(T) level of theory. Finally, a HLC that is a function of the number of valence electron pairs and unpaired electrons is added in an attempt to extrapolate to CCI. The G2, G3, and G3X methods all have the disadvantage of discontinuous potential energy surfaces because of the form of the HLC. In response to this problem, the MCCM-style methods G3S (15) and G3SX (26) were developed. These are similar to G3 and G3X, but they scale various energy components (as in SAC and MCG3) rather than assuming separability and correcting systematic errors with a HLC. The same group (26) has also developed less expensive methods in which MP3 or MP2 calculations are substituted for more expensive calculations in certain steps; we will consider two such methods, namely G3SX(MP3), and G3 SX(MP2).

The CBS methods of Petersson and coworkers (22,25,28-30) extrapolate the basis set and add empirical terms to extrapolate to experiment. Two especially powerful versions of the CBS approach are CBS-4 (30) and CBS-Q (30). For CBS-Q, the empirical terms are based on the overlap matrix and the spin contamination (which arises in some partial treatments of the electron correlation). CBS-4 also includes these terms plus a term based on the number of electrons in the system.

A qualitatively different approach to the problem of treating electron correlation is provided by the Kohn-Sham implementation of density functional theory (DFT) (31,32) and the empirically more successful hybrid DFT (32-34). Although this is not the primary focus of the current paper, hybrid DFT results will be presented for comparison to the multilevel methods. In hybrid DFT, the correlation energy and a portion of the exchange energy are accounted for by a density functional. Very useful hybrid DFT functionals include B3LYP (35,36), mPW1PW91 (37), MPW1K (38), and PBE1PBE (39,40) which are functionals based on the density and magnitude of the local gradient of the density. (We note that mPW1PW91, MPW1K, and PBE1PBE are sometimes called MPW25, MPW42.8, and PBEO, respectively.) Like other methods that do not explicitly account for electron interactions, hybrid DFT is not systematically improvable. Increasing the basis set can often improve the quality of the results (41,42); however, just as for *ab initio* methods, there is no guarantee that it will.

Section 2 describes the methods used and the experimental test data used for comparison. Section 3 presents results and discussion, and Section 4 gives conclusions.

## Methods and Test Data

All electronic structure calculations in this paper were performed with GAUSSIAN98 (43). All calculations use the spin-restricted formalism for closed

shells and the spin-unrestricted formalism for open-shell systems. The four basis sets explicitly discussed and used in calculations are 6-31G(d)(44), 6-31G(2df,p)(44), MG3 (14,45), and MG3S (42). We note that the MG3 basis is identical to 6-311++G(3d2f,2df,2p) (44,46) for atoms H through Si, but is an improved version of this basis for atoms P–Cl; it includes a diffuse s function on H and a diffuse sp shell on Li through Cl, and it is a modification (14) of the G3Large basis (24) of Curtiss et al. MG3S is the same except the diffuse functions on H atoms are deleted (42). Several other basis sets are used as part of the multilevel techniques, and they are as described in the original papers.

For all results in this paper, spin-orbit coupling corrections have been added to open-shell calculations from a compendium given elsewhere (10); we note that this consistent treatment sometimes differs from the original methods employed by other workers, e.g., standard G3 calculations include spin-orbit contributions only for atoms. In the SAC and MCCM calculations presented here, core correlation energy and relativistic effects are not explicitly included but are implicit in the parameters (i.e., we use parameters called versions 2s and 3s in the notation of previous papers (11,16,18)).

The hybrid DFT methods used here are B3LYP (35,36), PBE1PBE (39,40,47), mPW1PW91 (37), and MPW1K (38). The *ab initio* methods discussed in this article include HF, MP4SDQ (44), and QCISD(T) (27). We consider only one pure DFT method, namely BLYP (48,49).

The cost function used in all tables and figures is the sum of the time to calculate an energy, gradient, or Hessian (as stated in each case) for the two molecules, 1-phosphinopropane and 2,2-dichloro-1-ethanol, with a single 500MHz R14000 processor on a Silicon Graphics Origin 3800 with the GAUSSIAN98 (43) electronic structure package normalized by dividing by the sum of the times for MP2/6-31 G(2df,p) gradient calculations on the same two molecules with the same program on the same computer. The test molecules were chosen to give a balanced cost at a variety of levels and sizes of basis sets. The cost for calculations with basis sets such as aug-cc-pVTZ (20) will be dominated by the cost of 1-phosphinopropane, which has nine hydrogen atoms, because aug-cc-pVTZ includes a very large number (23) of basis functions for each hydrogen atom. The cost of calculations using the MG3 or MG3S basis set will tend to be dominated by the cost of 2,2-dichloro-1-ethanol, which has two second-row atoms, because these basis sets weigh more heavily on 2<sup>nd</sup> row atoms rather than hydrogen.

The test set used for most comparisons in the present paper is Database/3 (18), which was introduced elsewhere. It consists of 109 atomization energies (AEs), 44 forward and reverse reaction barrier heights (BHs) of 22 reactions, 13 electron affinities (EAs), and 13 ionization potentials (IPs). There are a total of 513 bonds among the 109 molecules used for AEs, where double or triple bonds are only counted as a single bond. Note that all ionization potentials and electron affinities are adiabatic (not vertical), i.e., the geometry is optimized for the ions

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as well as the neutrals. Our tests in the present paper will also include 2 data for LiH (see below) and 22 values  $\Delta E_{\text{reaction}}$ , which are the zero-point-exclusive energies of reaction for the 22 reactions in the database. All mean unsigned and root-mean-squared errors in the tables and text are unweighted averages over the specified data.

Database/3 and the other data used in this paper consist entirely of zero-point-exclusive data, which allows for direct comparisons with calculated Born-Oppenheimer potential energy surfaces, i.e., the sum of the electronic energies and nuclear repulsion. Although the G3X and CBS families of methods have standard geometry and frequency calculations associated with them, in this paper only the potential energy surfaces are required to compare with Database/3. The geometries used are optimized QCISD/MG3 geometries for all calculations in this paper.

One additional system, namely LiH, is discussed in this paper. The heat of formation and electron affinity of LiH are taken from the G3/99 (50) data set. The zero-point-exclusive atomization energy ( $D_0$ ) was obtained from the heat of formation using the method described elsewhere (10). The electron affinity is converted into a zero-point exclusive electron affinity by removing the neutral and anionic zero-point energies calculated at the mPW1PW91/MG3 level and scaled (18) by 0.9758.

## Discussion

Diffuse functions are often omitted on hydrogen because hydrogen has a lower electronegativity than many elements of general interest (C, N, O, F, S, Cl), and there is very little electron density around hydrogen. Hydrogen is the most numerous atom type in many systems of interest (e.g., amino acids and carbohydrates), and for methods to be cost-effective it is important not to use too many basis functions on such a common atom. The MCG3/3 and MC-QCISD/3 methods have no diffuse functions on hydrogen for any component of the calculation, and they perform very well compared to multilevel methods that use diffuse functions on hydrogen for one or more components (CBS-4, CBS-Q, G3X, G3SX, MCG3/2, MC-QCISD/2). It is desirable to test the limits of this observation, and the calculations presented next are designed to do this. If diffuse functions are required for systems where hydrogen is bonded to a less electronegative atom, then a metal hydride system, such as LiH (which is not in Database/3) may be poorly treated. Tables 1 and 2 test this hypothesis. Table 1 presents calculations of the electron affinity (EA) and atomization energy (AE) of LiH by methods that do not include diffuse functions on H, and Table 2 presents calculations of these same quantities by methods that do include diffuse functions on H. It can be seen in Table 1 that MCG3/3 and MC-QCISD/3 perform very well on the LiH AE and EA. On average they outperform MCG3/2



**Table 1. Atomization energies and electron affinities (kcal/mol) for LiH at QCISD/MG3 geometries for methods that do not involve diffuse functions on hydrogen.**

Method	AE <sup>a</sup>	EA <sup>b</sup>	MUE <sup>c</sup>
Experiment	57.4	7.9	...
QCISD(T)/MG3S	55.9	6.6	1.4
MCG3/3	58.0	7.9	0.3
MP4SDQ/MG3S	55.4	6.5	1.7
MC-QCISD/3	57.8	6.9	0.8
MC-UT/3	57.3	6.5	0.7
MC-CO/3	54.5	5.9	2.4
B3LYP/MG3S	58.3	9.7	1.4
PBE1PBE/MG3S	52.7	9.6	3.2
mPW1PW91/MG3S	53.2	9.7	3.0
MPW1K/MG3S	52.8	9.6	3.1
BLYP/MG3S	57.9	7.5	0.5
SAC/3	49.8	5.2	5.1
AM1	58.7	-15.1	12.1

<sup>a</sup> atomization energy

<sup>b</sup> electron affinity

<sup>c</sup> mean unsigned error in AE and EA

**Table 2. Atomization energies and electron affinities (kcal/mol) for LiH at QCISD/MG3 geometries for methods that involve diffuse functions on hydrogen.**

Method	AE <sup>a</sup>	EA <sup>b</sup>	MUE <sup>c</sup>
Experiment	57.4	7.9	...
QCISD(T)/MG3	55.9	6.8	1.3
G3SX	57.9	7.8	0.4
G3X	57.3	8.8	0.5
CBS-Q	57.6	6.8	0.7
G3SX(MP3)	58.0	7.8	0.3
G3SX(MP2)	57.6	7.2	0.5
G3X(MP3)	57.0	9.5	1.0
MCG3/2	58.1	9.0	0.9
MP4SDQ/MG3	55.4	6.7	1.6
CBS-4	55.3	9.5	1.8
MC-QCISD/2	57.5	8.6	0.4
B3LYP/MG3	58.3	9.8	1.4
mPW1PW91/MG3	53.1	9.8	3.1

<sup>a</sup> atomization energy

<sup>b</sup> electron affinity

<sup>c</sup> mean unsigned error in AE and EA

and MC-QCISD/2, both of which have a component calculation that involves diffuse functions on hydrogens (and therefore these methods are in Table 2). On the whole, the accurate multilevel methods in Table 1 (MCG3/3, MC-QCISD/3) and the hybrid DFT methods mPW1PW91 and B3LYP do not have systematically higher errors than the methods in Table 2. Therefore, since metal hydrides are seemingly a "worst case" for omitting diffuse functions on H, it appears to be confirmed that diffuse functions on hydrogen have little importance for most thermochemical calculations. Tables 3, 4, and 5, which are discussed next include errors on the two LiH test cases in the "All data" rows.

Table 3 shows the errors for the multilevel methods that scale (5) as  $N^7$ , where  $N$  is the number of atoms (in this table and in Table 4 the methods are arranged in order of decreasing cost for gradient calculations). Table 3 also shows one single-level method, namely QCISD(T)/MG3S. All of the multilevel methods in Table 3 have similar mean unsigned errors, in the range (all errors quoted in the text are mean unsigned errors for all data) of 0.84–1.20 kcal/mol. However they have gradient costs varying by over an order of magnitude, from 45 to 460. Thus they have a broad range of performance-to-cost ratios. G3SX is both the most expensive and the most accurate among these methods. However if gradient calculations are required, MCG3/3 and G3SX(MP3) are only about one tenth the cost of G3SX, and the increase in MUE is less than 15% as compared to G3SX. The MCG3/3 method not only has a relatively low cost for gradients, it also has a relatively low cost for energies. Furthermore, the single-level method in Table 3 is not competitive in terms of either cost or accuracy.

Table 4 gives the errors for the multilevel methods with much lower costs. These methods are ideal for geometry optimizations or frequency calculations on many systems and for energy calculations on very large systems. These methods are, however, still much more accurate than any *ab initio* method of similar cost. To illustrate this Table 4 also gives the results for a single-level  $N^6$  method for comparison. We also note that MC-QCISD/3 has an error only 27% larger than CBS-Q, but a gradient cost 14 times less. The CBS-4 method has an error 44% larger than MC-QCISD, but a gradient cost 2 times smaller. SAC/3 method has a mean unsigned error 2.5 times larger than CBS-4, but the cost is 9 times lower yet. If one considers larger systems, eventually the  $N^5$  methods become the winner because in the limit of large  $N$  their cost rise more slowly than the other methods in Tables 3 and 4.

Table 5 gives the errors for a DFT method, four hybrid DFT methods, and AM1. Although hybrid DFT is very affordable, it lacks the accuracy of multi-coefficient semi-empirical methods based on explicitly correlated wave functions. Nevertheless the mPW1PW91/MG3S and AM1 methods have performance/cost characteristics that put them near the envelope of best performance in Figure 1. AM1 is valuable for larger systems where the other methods in the figure are not affordable.

Figure 1 is a scatter plot of the MUE over Database/3 versus the cost of a gradient for all methods in tables 3–5. Notice that the abscissa spans seven decades of cost.



**Table 3. Mean Unsigned Errors (kcal/mol), Root-Mean-Square Errors, and Times at QCISD/MG3 Geometries for Methods with  $N^7$**

Quantity	Item	QCISD(T)/ MG3S	G3SX	G3X	CBS-Q	G3SX(MPS)	G3SX(MP2)	G3X(MP3)	MCG3/3	
MUE	Atomization energies (109)	15.06	0.87	0.86	1.42	0.95	1.23	1.02	1.04	
	Error per bond (513)	3.2	0.18	0.18	0.30	0.20	0.26	0.22	0.22	
	Barrier heights (44)	1.37	0.81	1.07	0.87	0.94	0.92	1.26	1.01	
	$\Delta E_{rxn}$ (22)	0.98	0.55	0.88	0.86	0.63	0.84	0.97	0.90	
	Electron affinities (13)	3.72	1.06	1.27	1.12	1.00	1.42	1.60	0.92	
	Ionization potentials (13)	2.78	1.07	1.81	1.26	1.34	1.54	2.11	0.95	
	All Database/3 data (179) <sup>a</sup>	9.98	0.88	1.01	1.25	0.98	1.19	1.20	1.01	
	All data (203) <sup>b</sup>	8.92	0.84	0.99	1.20	0.94	1.15	1.17	0.99	
	RMSE	All Database/3 data (179)	13.70	1.24	1.39	1.75	1.33	1.68	1.64	1.38
		All data (203)	12.87	1.20	1.37	1.70	1.29	1.63	1.61	1.33
Cost	Energy	50	13.5	13.5	3.8	8.1	5.3	7.9	3.3	
	Gradient	3100	460	450	79	66	56	54	45	
Hessian		200000	29000	29000	4600	3500	3200	2700	2600	

<sup>a</sup> based on rows 1, 3, 5, and 6.

<sup>b</sup> Database/3 plus 22 values of  $\Delta E$  and atomization energy and electron affinity of LiH

Table 4. Mean Unsigned Errors (kcal/mol), Root-Mean-Square Errors, and Times at QCISD/MG3 Geometries for Methods with  $N^6$  and  $N^6$  Scaling

Quantity	Item	MP4SDQ/ MG3S	MC-QCISD/3	MC-UT/3	MC-CO/3	CBS-4	SAC/3
MUE	Atomization energies (109)	21.91	1.73	2.17	3.23	2.78	6.48
	Error per bond (513)	4.66	0.37	0.46	0.69	0.59	1.38
	Barrier heights (44)	3.95	1.33	2.69	3.23	1.64	3.64
	$\Delta E_{RXN}$ (22)	1.28	0.90	0.69	1.38	0.64	2.30
	Electron affinities (13)	4.92	1.38	1.42	2.11	2.11	7.82
	Ionization potentials (13)	3.00	1.95	1.94	2.09	2.28	8.64
	All Database/3 data (179) <sup>a</sup>	14.89	1.62	2.22	3.07	2.41	6.04
All data (203) <sup>b</sup>	13.29	1.53	2.04	2.88	2.21	5.63	
RMSE	All Database/3 data (179)	19.68	2.09	3.17	4.23	3.27	7.53
	All data (203)	18.49	2.01	3.00	4.03	3.10	7.18
Cost scaling		6	6	6	5	6	5
Cost	Energy	4.9	1.9	1.7	1.7	1.0	0.078
	Gradient	27	5.5	5.0	4.9	2.7	0.31
	Hessian	1700	140	110	100	110	6.3

<sup>a</sup> based on rows 1, 3, 5, and 6

<sup>b</sup> Database/3 plus 22 values of  $\Delta E$  and atomization energy and electron affinity of LiH.

Table 5. Mean Unsigned Errors (kcal/mol), Root-Mean-Square Errors, and Times for hybrid DFT and DFT Methods and AMI at QCISD/MG3 Geometries

Quantity	Item	mPW1PW91/ MG3S	PBE1PBE/ MG3S	B3LYP/ MG3S	MPW1K/ MG3S	BLYP/ MG3S	AMI
MUE	Atomization energies (109)	3.56	4.36	4.23	11.02	7.05	26.70
	Error per bond (513)	0.89	0.93	0.90	2.34	1.50	5.67
	Barrier heights (44)	3.56	4.19	4.25	1.63	7.42	9.09
	$\Delta E_{\text{ex}}(22)$	1.15	1.26	2.16	1.31	2.60	9.53
	Electron affinities (13)	2.62	2.78	2.29	3.71	2.63	17.61
	Ionization potentials (13)	3.72	3.24	4.72	3.53	4.87	16.01
	All Database/3 data (179) <sup>a</sup>	3.88	4.12	4.13	7.64	6.66	20.93
	All data (203) <sup>b</sup>	3.58	3.80	3.89	6.86	6.16	19.61
RMSE	All Database/3 data (179)	4.91	5.40	5.73	10.32	8.57	28.98
	All data (203)	4.65	5.12	5.46	9.69	8.13	27.58
Cost scaling		4	4	4	4	4	3
Cost	Energy	1.2	1.2	1.2	1.2	1.2	$2 \times 10^{3c}$
	Gradient	1.7	1.7	1.7	1.7	1.7	$4 \times 10^{3c}$
	Hessian	12.7	12.7	12.7	12.7	12.7	$4 \times 10^{3c}$

<sup>a</sup> based on rows 1, 3, 5, and 6.

<sup>b</sup> Database/3 plus 22 values of  $\Delta E$  and atomization energy and electron affinity of LiH

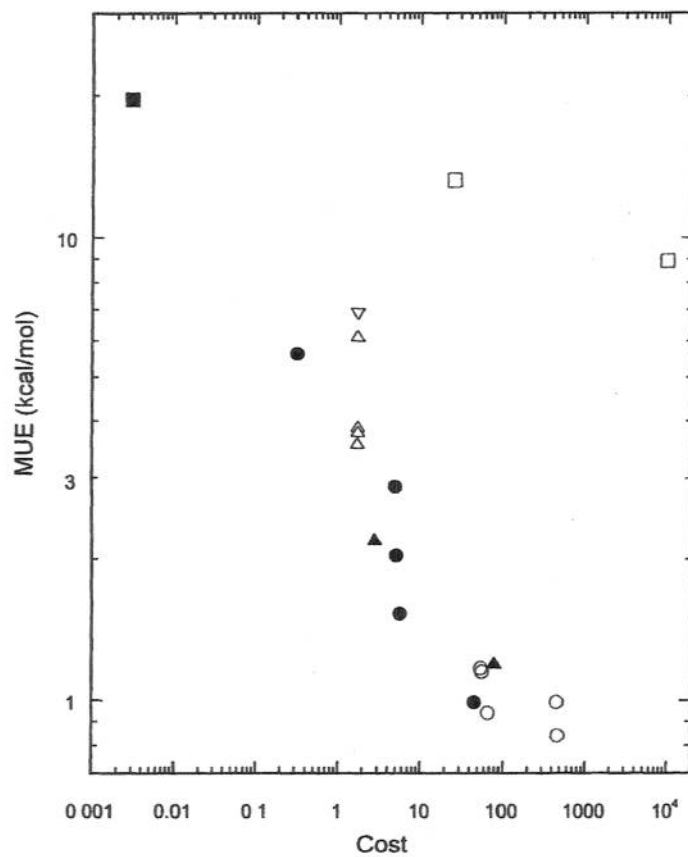


Figure 1. Mean unsigned error over all 203 data vs. gradient cost for AM1 (■), ab initio (□), CBS (▲), G3 (○), MCCM (●), DFT (▽), and hybrid DFT (△) methods. The figure includes all the methods that are included in Tables 3-5.

## Conclusions

The comparisons in this paper indicate that diffuse functions on hydrogen atoms have little effect on the performance of multilevel methods. Furthermore, tests against 209 data show that multilevel methods provide very attractive performance levels for a given cost for applications requiring thermochemical calculations. We also note that some multilevel methods have performance-to-cost ratios that rise above the rest of the crowd of even the very select group of highly efficient methods considered here. Among  $N^7$  methods, G3SX(MP3) and MCG3/3 methods have very favorable costs and only mild loss in accuracy as compared to the most accurate levels. MC-QCISD/3 has the best performance among  $N^6$  methods, with a MUE over all data of 1.5 kcal/mol. Another  $N^6$  method with notable performance is CBS-4, which has an error over all data of 2.2 kcal/mol.

## Acknowledgement

This work was supported in part by the U. S. Department of Energy, Office of Basic Energy Sciences.

## Literature Cited

1. Löwdin, P.-O. *Adv. Chem. Phys.* **1959**, *2*, 207.
  2. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
  3. Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 221.
  4. Stewart, J. J. P. *J. Comp. -Aided Molecular Design*, *4*, 1.
  5. Raghavachari, K.; Anderson, J. B. *J. Phys. Chem. A* **1996**, *100*, 12960.
  6. Brown, F. B.; Truhlar, D. G. *Chem. Phys. Lett.* **1985**, *117*, 307.
  7. Gordon, M. S.; Truhlar, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 5412.
  8. Rossi, I.; Truhlar, D. G. *Chem. Phys. Lett.* **1995**, *234*, 64.
  9. Corchado, J. C.; Truhlar, D. G. *ACS Symp. Ser.* **1998**, *712*, 106.
  10. Fast, P. L.; Corchado, J.; Sanchez, M. L.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 3139.
  11. Tratz, C. M.; Fast, P. L.; Truhlar, D. G. *Phys. Chem. Comm.* **1999**, *2*, 14.
  12. Fast, P. L.; Corchado, J. C.; Sanchez, M. L.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 5129.
  13. Fast, P. L.; Sanchez, M. L.; Corchado, J. C.; Truhlar, D. G. *J. Chem. Phys.* **1999**, *110*, 11679.
  14. Fast, P. L.; Sanchez, M. L.; Truhlar, D. G. *Chem. Phys. Lett.* **1999**, *306*, 407.
-

15. Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 1125.
16. Fast, P. L.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 6111.
17. Curtiss, L. A.; Redfern, P. C.; Rassolov, V.; Kedziora, G.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 9287.
18. Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A*, submitted.
19. Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
20. Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
21. Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.
22. Irikura, K. K., Frurip, David J., Eds. *Computational Thermochemistry: Prediction and Estimation of Molecular Thermodynamics*; ACS Symp. Ser., **1998**; 677, 1998, Washington.
23. Pople, J. A. *Rev. Mod. Phys.* **1999**, *77*, 1267.
24. Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.
25. *Quantum-Mechanical Prediction of Thermochemical Data*; Cioslowski, J., Ed.; Understanding Chemical Reactivity Series Vol. 22; Kluwer: Dordrecht, **2001**.
26. Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 108.
27. Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
28. Nyden, M. R.; Petersson, G. A. *J. Chem. Phys.* **1981**, *75*, 1843.
29. Montgomery, J. A., Jr.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900.
30. Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598.
31. Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.
32. Kohn, W.; Becke, A. D.; Parr, R. G. *J. Phys. Chem.* **1996**, *100*, 12974.
33. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
34. Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040.
35. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
36. Stephens, P. J.; Devlin, F. J.; Ashvar, C. S.; Bak, K. L.; Taylor, P. R.; Frisch, M. J. *ACS Symp. Ser.* **1996**, *629*, 105.
37. Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.
38. Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811.
39. Ernzerhof, M.; Scuseria, G. E. *J. Chem. Phys.* **1999**, *110*, 5029.
40. Adamo, C.; Cossi, M.; Barone, V. *Theochem* **1999**, *493*, 145.
41. Bauschlicher, C. W., Jr.; Partridge, H. *Chem. Phys. Lett.* **1995**, *240*, 533.



42. Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A*, in press.
  43. Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; 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, 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. GAUSSIAN98; Gaussian, Inc.: Pittsburgh, PA, 2001.
  44. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
  45. Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.
  46. McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.
  47. Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
  48. Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
  49. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
  50. Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 7374.
-