Robust and Affordable Multicoefficient Methods for Thermochemistry and Thermochemical Kinetics: The MCCM/3 Suite and SAC/3

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Scaling all correlation (SAC) and multicoefficient correlation methods (MCCMs) have been shown to provide excellent ratios of accuracy to cost for the calculation of atomization energies. Inspired by this success, we have now fine-tuned the choices of correlation-energy levels and basis sets to determine the four most promising MCCMs and the most promising SAC method, and we optimized them against a larger and more diverse database than has previously been used for MCCM methods; the new database, called Database/3, consists of atomization energies, ionization potentials, electron affinities, and reaction barrier heights. The end results of this process are labeled as MCCM-version 3 (or MCCM/3) and SAC/3; the members of MCCM/3 are labeled MC-CO/3, MC-UT/3, MC-QCISD/3, and MCG3/3. The new methods are compared to other single-level ab initio methods, to hybrid density functional theory, and to the G3, G3S, and CBS-Q schemes. For neutral molecules, the mean unsigned error in atomization energies per bond using the SAC/3, MC-CO/3, MC-UT/3, MC-QCISD/3, and MCG3/3 methods are 1.4, 0.7, 0.5, 0.4, and 0.2 kcal/mol respectively, and these errors as well as the mean unsigned errors in ionization energies, electron affinities, and barrier heights compare very well with those in previous methods with higher costs.

1. Introduction

Multilevel calculations involve combining more than one level of electronic structure theory and/or different one-electron basis sets, usually with empirical parameters, to try to extrapolate to a more accurate result than the most accurate component calculation, and methods based on this approach have been developed into a very powerful alternative to ab initio methods for many types of calculations.[1−29] Multicoefficient correlation methods[14−17,21,23,26] (MCCMs) and scaling all correlation (SAC) methods[3,13,17] are classes of multilevel methods that have proven to be very successful at predicting accurate atomization energies,[3,13−17,23] reaction barrier heights,[28,30] ionization potentials,[21,26] and electron affinities.[21,26] The goal of this project is to develop improved SAC and multicoefficient methods that can be used to treat a broad range of systems in a cost-effective way.

Several methods such as Gaussian 2,[4,10,11] Gaussian 3[9,24] (G3), scaled G3[21,24,26] (G3S, which is a special case of MCCM), G3 methods with reduced-order Møller−Plesset perturbation theory[12,21,22,26] (G3(MP3), G3(MP2), G3S(MP3), and G3S-(MP2)), the complete basis set methods of Petersson and co-workers[1,5,8,10,24] (e.g., CBS-APNO, CBS-Q), and multicoefficient Gaussian 3[16,17] (MCG3) 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. In addition, these methods are very expensive (sometimes prohibitively so) when the desired calculation requires consistent gradients or Hessians. Ideally, we would have a suite of methods of varying accuracy and cost suitable for a variety of problems with different sizes of molecules and different accuracy requirements. The previously mentioned methods have a good performance-to-cost ratio for

energy calculations, but ideally, one would have at least one method with affordable analytic gradients and at least one method with affordable analytic Hessians available to avoid the cost of performing numerical derivatives. Some such less expensive methods are available, but there is room for improvement. We will therefore optimize several new methods to a set atomization energies, ionization potentials, electron affinities, and chemical reaction barrier heights. The training set is designed to yield parameters that are suitable for a broad range of applications. Based on our examination of a very large number of combinations of basis sets and correlation levels, we recommend a suite of five methods spanning a range of computational costs but all having especially good performance for a given cost.

Hybrid density functional theory[31−37] (HDFT), which is a hybrid of Hartree−Fock theory and gradient-corrected density functional theory, has proven to be a very cost-effective strategy when applied to many problems. We will therefore compare the cost and effectiveness of multilevel and HDFT calculations. The four HDFT methods used for such comparisons in the present paper are the three-parameter B3LYP[32,33] method and the one-parameter PBE1PBE,[35] mPW1PW91,[34] and MPW1K[36,37] methods. (PBE1PBE is sometimes called PBE0.)

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

2. Database

The training set used in the present paper consists of 109 atomization energies (AEs), 13 ionization potentials (IPs), 13 electron affinities (EAs), and 44 barrier heights (BHs). All 179 data are pure electronic energies, i.e., zero-point energies and thermal vibrational−rotational energies have been removed. The

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entire training set is in the Supporting Information and is referred to as Database/3. The 109 zero-point-exclusive atomization energies are identical to those used previously.[37] The 13 IPs and EAs are computed from a subset of the G2 data set[4] where both the EA and the IP were available for the same molecule or atom. These zero-point exclusive atomization energies are also identical to those published previously.[37] The best estimates for the 44 reaction barrier heights in Database/3 are identical to those previously reported[28] with the exception of the $CH_3 + H_2$ reaction where the forward and reverse barriers have been lowered by 0.7 kcal/mol based on a recent experimental/theoretical comparison.[38] The other 42 barriers were obtained, as explained elsewhere,[28,36,39] from a combination of experimental and theoretical reaction rates.

3. Theory and Parametrization

All electronic structure calculations were performed with the Gaussian 98[40] computer program. All calculations used the spin-restricted formalism for closed shells and the spin-unrestricted formalism (in which the HF wave function is a single Slater determinant with different orbitals for different spins) for open-shell systems.

The basis sets used include the 6-31G(d),[41] 6-31G†,[42] 6-31+G(d,p),[41] 6-31G(d(f),d,p),[43] 6-31G(2df,p),[41] cc-pVTZ,[44] aug-cc-pVTZ,[44] G3Large,[9] modified Gaussian 3[16] (MG3), and modified Gaussian 3 semidiffuse[37] (MG3S) basis set. We note that the MG3 basis[16] is also denoted G3LargeMP2.[12]

The levels of electron correlation used in the present paper include Møller−Plesset second, third, and fourth order perturbation theory (MP2,[45] MP3,[41] MP4[41]), Møller−Plesset fourth order perturbation theory without triples contributions[41] (MP4SDQ), quadratic configuration interaction with single and double excitations[46] (QCISD), QCISD with quasiperturbative connected triples[46] (QCISD(T)), and coupled cluster with single and double excitations and quasiperturbative connected triples[47] (CCSD-(T)). In general, core orbitals are doubly occupied in all configurations except for some MP2 calculations, and those are denoted MP2(full). We also studied the hybrid DFT methods mentioned in the Introduction.

The geometries of *all* neutral molecules, ions, and saddle points used in all calculations in the present paper were optimized at the QCISD level with the MG3 basis set. Although we make this choice for parametrization and testing in the present paper, it is not considered an intrinsic part of the methods. The methods may be used with any reasonable geometry or they may be used to optimize[48] geometries.

The multilevel methods described here use the "single pipe" and "double pipe" notation for the level (L) and basis set (B); this was introduced elsewhere[14] with the definitions being

$$\Delta E\,(L2|L1/B) \equiv E\,(L2/B) - E\,(L1/B) \quad (1)$$

$$\Delta E\,(L|B2/B1) \equiv E\,(L/B2) - E\,(L/B1) \quad (2)$$

$$\Delta E\,(L2|L1/B2|B1) \equiv$$
$$E\,(L2/B2) + E\,(L1/B1) - E\,(L1/B2) - E\,(L2/B1) \quad (3)$$

To specify the version of the method, we use a new notation. The MCG3, version 2s, method is now simply referred to as MCG3/2, and the MC-QCISD, version 2m, method is referred to as MC-QCISD/2m. Previously, 2s referred to version 2 with explicit spin−orbit coupling, but now we consider explicit spin−orbit coupling to be the default so we can abbreviate this as version 2. Furthermore, 2m refers to the minimal version 2. A minimal version is one that does not include spin−orbit
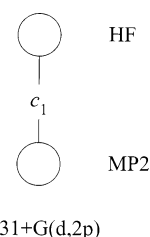

Figure 1. Coefficient tree for SAC/3.

explicitly, nor does it include core correlation or relativistic effects explicitly; instead, these effects are implicitly included in the parametrization. Similarly, the MCG3, version 3s, and MC-QCISD, version 3s, methods are simply referred to as MCG3/3 and MC-QCISD/3. MCG3/2 and MC-QCISD/2m energies are defined below in eqs 4 and 5 using the notation in eqs 1−3:

$$E(\text{MCG3/2}) = c_0 E(\text{HF/6-31G(d)}) +$$
$$c_1 \Delta E(\text{HF/MG3|6-31G(d)}) + c_2 \Delta E(\text{MP2|HF/6-31G(d)}) +$$
$$c_3 \Delta E(\text{MP2|HF/MG3|6-31G(d)}) +$$
$$c_4 \Delta E(\text{MP4SDQ|MP2/6-31G(d)}) +$$
$$c_5 \Delta E(\text{MP4SDQ|MP2/6-31G(2df,p)|6-31G(d)}) +$$
$$c_6 \Delta E(\text{MP4|MP4SDQ/6-31G(d)}) +$$
$$c_7 \Delta E(\text{QCISD(T)|MP4/6-31G(d)}) + E_{\text{SO}} \quad (4)$$

$$E(\text{MC-QCISD/2m}) = c_0 E(\text{HF/6-31G(d)}) +$$
$$c_1 \Delta E(\text{MP2|HF/6-31G(d)}) + c_2 \Delta E(\text{MP2/MG3|6-31G(d)}) +$$
$$c_3 \Delta E(\text{QCISD|MP2/6-31G(d)}) \quad (5)$$

where E_{SO} is the spin−orbit energy, which is taken from a compendium given elsewhere.[13] (We note that E_{SO} is zero by symmetry for closed-shell molecules, atoms in S states, linear molecules in Σ states, and singlet and doublet molecules in $\tilde{A}$ or $\tilde{B}$ states.) The coefficients c_i for the MCG3/2 and MC-QCISD/2m methods are illustrated in Figures 1 and 2. In the new version of MCG3, the MG3 basis set was replaced with MG3S because we checked that the diffuse function on hydrogen that is removed in forming MG3S from MG3 has negligible effect on the performance of the method for our test set, which does not include metal hydrides (the new methods in this paper are not designed for systems with significant negative polar character on H). Furthermore, in the new version of MCG3, the MP4 energy component is removed. This results in

$$E(\text{MCG3/3}) = c_0 E(\text{HF/6-31G(d)}) +$$
$$c_1 \Delta E(\text{HF/MG3S|6-31G(d)}) + c_2 \Delta E(\text{MP2|HF/6-31G(d)}) +$$
$$c_3 \Delta E(\text{MP2|HF/MG3S|6-31G(d)}) +$$
$$c_4 \Delta E(\text{MP4SDQ|MP2/6-31G(d)}) +$$
$$c_5 \Delta E(\text{MP4SDQ|MP2/6-31G(2df,p)|6-31G(d)}) +$$
$$c_6 \Delta E(\text{QCISD(T)|MP4SDQ/6-31G(d)}) + E_{\text{SO}} \quad (6)$$

The coefficient c_0, which scales the HF energy evaluated with the small basis set, is set to 1 for most MCCMs and all SAC methods. If the c_0 coefficient is not specified, it is equal to 1. The coefficient c_0 is set to 1 for the new versions of several MCCM methods.

In the new version of MC-QCISD, the coefficient c_0 is set to 1. Instead of scaling the Hartree−Fock energy, the difference between the Hartree−Fock energies obtained with the two basis
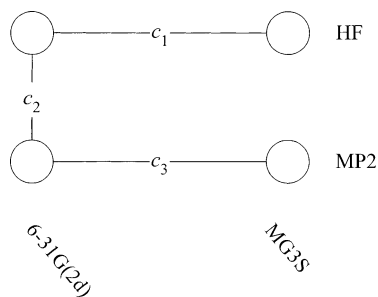
Figure 2. Coefficient tree for MC-CO/3.

sets is scaled:

$$E(\text{MC-QCISD/3}) = E(\text{HF/6-31G(d)}) +$$
$$c_1\Delta E(\text{HF/MG3S}|\text{6-31G(d)}) + c_2\Delta E(\text{MP2}|\text{HF/6-31G(d)}) +$$
$$c_3\Delta E(\text{MP2}|\text{HF/MG3S}|\text{6-31G(d)}) +$$
$$c_4\Delta E(\text{QCISD}|\text{MP2/6-31G(d)}) + E_{\text{SO}} \quad (7)$$

The third new method is called MC-UT/3. It requires an MP4-(SDQ) calculation with the 6-31G(d) basis set and an MP2 calculation with the MG3S basis:

$$E(\text{MC-UT/3}) = E(\text{HF/6-31G(d)}) +$$
$$c_1\Delta E(\text{HF/MG3S}|\text{6-31G(d)}) + c_2\Delta E(\text{MP2}|\text{HF/6-31G(d)}) +$$
$$c_3\Delta E(\text{MP2}|\text{HF/MG3S}|\text{6-31G(d)}) +$$
$$c_4\Delta E(\text{MP4SDQ}|\text{MP2/6-31G(d)}) + E_{\text{SO}} \quad (8)$$

We note that MC-QCISD/3 and MC-UT/3 are special cases of "Utah" methods, as described previously.[14]

The fourth new method is called MC-CO/3. It requires two calculations with MP2 theory with two different basis sets. The basis sets used are 6-31G(2d) and MG3S:

$$E(\text{MC-CO/3}) = E(\text{HF/6-31G(2d)}) +$$
$$c_1\Delta E(\text{HF/MG3S}|\text{6-31G(2d)}) +$$
$$c_2\Delta E(\text{MP2}|\text{HF/6-31G(2d)}) +$$
$$c_3\Delta E(\text{MP2}|\text{HF/MG3S}|\text{6-31G(2d)}) + E_{\text{SO}} \quad (9)$$

We note that MC-CO/3 is a special case of a "Colorado" method, as described previously.[14]

The fifth method is called SAC/3. In the more general notation explained previously,[14] it is simply SAC-MP2/6-31+G-(d,2p). It follows the general formula for a SAC energy as shown below, where $c_1 \equiv 1/F$:

$$E_{\text{SAC}} = E(\text{HF}) + \frac{E_{\text{correlation}}}{F} \quad (10)$$

Notice that this method has only a single coefficient, namely c_1, and therefore it is not an MCCM.

The coefficient trees for the five new methods appear in Figures 1−5. The coefficients for the five new methods were adjusted to minimize the error in the following function:

$$F = \sqrt{\frac{1}{2}[\text{RMSE(AE)}]^2 + \frac{1}{2}[\text{RMSE(OD)}]^2} \quad (11)$$

where the root-mean-squared errors (RMSE) in atomization
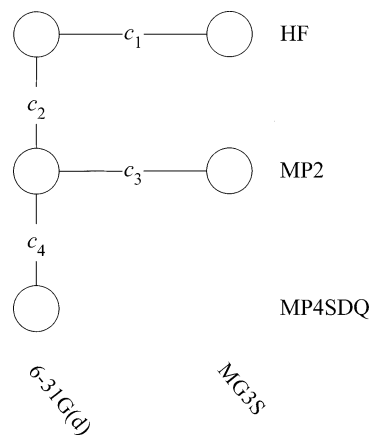
Figure 3. Coefficient tree for MC-UT/3.
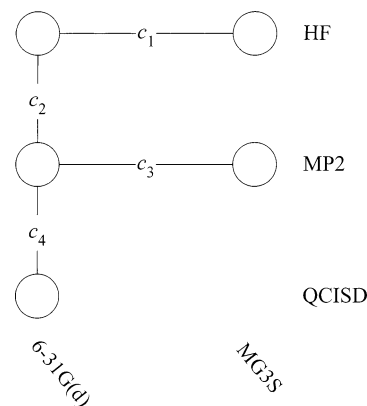
Figure 4. Coefficient tree for MC-QCISD/3.

energies (AE) and other data (OD) are defined below:

$$\text{RMSE(AE)} = \sqrt{\frac{1}{109}\sum_{i=1}^{109}(\text{AE}_i^{\text{calc}} - \text{AE}_i^{\text{exp}})^2} \quad (12)$$

$$\text{RMSE(OD)} =$$
$$\sqrt{\frac{1}{70}\left(\sum_{i=1}^{13}(\text{IP}_i^{\text{calc}} - \text{IP}_i^{\text{exp}})^2 + \sum_{i}^{13}(\text{EA}_i^{\text{calc}} - \text{EA}_i^{\text{exp}})^2 + \sum_{i=1}^{44}(\text{BH}_i^{\text{calc}} - \text{BH}_i^{\text{exp}})^2\right.}$$
(13)

where $\text{IP}_i^{\text{calc}}$ is the calculated ionization potential (IP), IP_i^{exp} is the experimental IP, $\text{EA}_i^{\text{calc}}$ is the calculated electron affinity (EA), $\text{EA}_i^{\text{calc}}$ is the calculated EA, $\text{BH}_i^{\text{calc}}$ is the calculated barrier height (BH), and $\text{BH}_i^{\text{calc}}$ is the experimental BH from the database.

The coefficients used in MCG3/3, MC-QCISD/3, MC-CO/3, SAC/3, CBS-Q/3, G3/3, and G3S/3 were all optimized with a slightly earlier version of the database before the barrier heights for the $CH_3 + H_2$ reaction and the atomization energy for H_2CCO[49] were updated. Nevertheless, all errors reported in this paper are based on the most current database described in section 2.

In the process of determining which basis sets and combinations of basis sets and levels have the best performance for a given cost, we optimized the coefficients for a large number of SAC and MCCM methods. The five most highly recommended methods comprise the MCCM/3 suite described above plus SAC/3. The scaling coefficients used in these five methods are listed in Table 11. The scaling coefficients determined in the present study for 33 other SAC methods and 36 other MCCM methods are given in Supporting Information.

TABLE 1: Mean Unsigned Errors (kcal/mol), Root-Mean-Square Errors, and Computer Times for N^7 Methods

quantity	item	CBS-Q//Q	G3//Q	G3S//Q	MCG3/2	CBS-Q/3	G3/3	G3S/3	MCG3/3
MUE	atomization energies (109)	1.42	1.21	1.29	1.13	1.36	0.90	0.94	1.04
	HCO compounds (54)	1.37	1.25	1.14	1.01	1.17	0.66	0.68	0.77
	containing second row (34)	1.50	1.11	1.48	1.16	1.61	1.19	1.26	1.33
	other (21)	1.42	1.27	1.38	1.40	1.43	1.04	1.11	1.28
	error per bond (109)	0.30	0.26	0.27	0.24	0.29	0.19	0.20	0.22
	HCO compounds (54)	0.22	0.20	0.18	0.16	0.19	0.11	0.11	0.12
	containing second row (34)	0.54	0.40	0.53	0.42	0.57	0.42	0.45	0.48
	other (21)	0.37	0.33	0.36	0.36	0.37	0.27	0.29	0.33
	barrier heights (44)	0.87	1.07	0.83	1.05	0.89	1.14	0.76	1.01
	electron affinities (13)	1.12	0.97	0.86	0.95	1.11	0.85	1.21	0.92
	ionization potentials (13)	1.26	0.92	1.15	0.98	1.25	0.67	1.02	0.95
	all data (179)[a]	1.25	1.14	1.14	1.10	1.22	0.94	0.92	1.01
RMSE	all data	1.75	1.47	1.49	1.49	1.71	1.25	1.26	1.38
cost	energy	110	240	240	100	110	240	240	88
	gradient	1500	6300	6400	940	1500	6300	6400	810
	Hessian	57 000	290 000	290 000	38 000	57 000	290 000	290 000	32 000

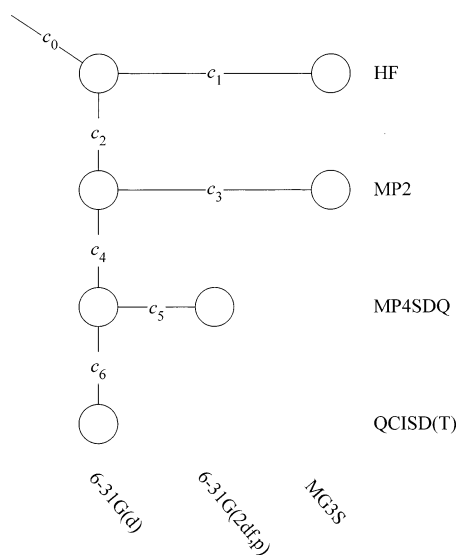[a] Based on rows 1, 9, 10, and 11.

Figure 5. Coefficient tree for MCG3/3.

4. Results and Discussion

We discuss the results in the next three sections, divided according to the scaling properties[50] of the various methods. We note that, for large numbers N of electrons, MCG3/3 scales as N^7, MC-QCISD/3 and MC-UT/3 scale as N^6, and MC-CO/3 and SAC/3 scale as N^5.

4.1. N^7 Methods. Table 1 gives the errors for the MCG3 methods and for G3,[9] G3S,[21] and CBS-Q.[8] The results presented in this paper *all* use the QCISD/MG3 geometries; to emphasize this, in tables, when we use QCISD/MG3 geometries for methods optimized by other groups with different geometries, we append //Q. The errors in all tables are calculated against the electronic-energy database described in section 2. Root-mean-square errors (RMSE) in the tables always give equal weight to all 179 data (as do mean unsigned and mean signed errors).

The cost function used in Table 1 and the rest of the paper, is the time to calculate an energy, gradient, or Hessian (as stated in each case) for phosphinomethanol with a single 500 MHz R14000 processor on a Silicon Graphics Origin 3800 with the *Gaussian 98*[40] electronic structure package normalized by dividing by the time for a HF/6-31G(d) energy calculation on the same molecule on the same computer.

TABLE 2: HLC Parameters (in millihartrees) for G3-Type Methods

	freq.	ref	*A*	*B*	*C*	*D*
G3//MP2(full)/6-31G(d)	a	b	6.386	2.977	6.219	1.185
G3//B3LYP/6-31G(d)	c	d	6.760	3.233	6.786	1.269
G3//B3LYP/6-31G(2df,p)	e	f	6.688	3.007	6.763	1.107
G3X//B3LYP/6-31G(2df,p)	e	f	6.783	3.083	6.877	1.152
G3/3	g	h	8.186	3.414	8.256	1.843

[a] Frequencies calculated with HF/6-31G(d) and scaled by 0.8929. [b] Reference 8. [c] Frequencies calculated with B3LYP/6-31G(d) and scaled by 0.9600. [d] Reference 19. [e] Frequencies calculated with B3LYP/6-31G(2df,p) and scaled by 0.9854. [f] Reference 27. [g] Optimized against the electronic-energy database of section 2. [h] Present work; optimized with QCISD/MG3 geometries but intended for use with any accurate geometries.

A standard G3 calculation includes a high-level correction (HLC), which is a function with four empirical parameters *A*, *B*, *C*, and *D*. We noticed that the G3 method performed significantly worse in calculating D_e for the 109 molecules in our database than in calculating ΔH_f^{298} for the same 109 molecules in the G2 data set. The MUE for D_e is 1.2 kcal/mol, whereas G3 predicts only a 0.9 kcal/mol MUE in ΔH_f^{298} over the same molecules in the G2 set. The cause of this is that the parameters for the high-level correction (HLC) in G3 were fitted to minimize the error over experimental heats of formation and other data when using HF/6-31G(d) frequencies scaled by 0.8929. The scaling factor of 0.8929 was obtained to reproduce experimental fundamental frequencies.[51] Similarly, another study[52] showed that the optimum scaling factor for fundamental frequencies to minimize the error over 122 molecules was determined to be 0.8953. Over the same 122 molecules, the optimum scale factor for obtaining accurate ZPEs with HF/6-31G(d) was determined[52] to be 0.9135. Although it is unclear why the scaling factor of 0.8929 was used instead of 0.9135 to calculate ZPE in G2 and G3, the HLC can easily make up for some of the systematic errors in the ZPE. Using our current database, we reoptimized the HLC parameters in G3, and we give the errors for this method, called G3/3, in Table 1. The G3 HLC parameters optimized in this and previous work are in Table 2.

G3S, like G3, has systematic deficiencies in calculating D_e, because, like G2, the errors in its treatment of vibration are needlessly large. The six empirical parameters in the G3S method were optimized[21] using the scale factor of 0.8929 for the HF/6-31G(d) frequencies. In Table 1, we list the errors for

TABLE 3: Scaling Factors (unitless) for G3S-Type Methods

	ref	S_{E234}	S_{QCI}	$S_{HF'}$	$S_{E2'}$	$S_{E3'}$	$S_{E4'}$
G3S	a	1.0596	1.1504	1.0868	1.1477	1.3780	0.9529
G3S/3	b	1.0489	1.2102	1.0886	1.2100	1.2768	0.8464

[a] Reference 21. [b] Present work; optimized with QCISD/MG3 geometries but intended for use with any accurate geometries.

G3S/3, where we optimized the six empirical coefficients in G3S to Database/3. The G3/3 and G3S/3 parameters should be preferred to the G3 and G3S ones if one is not using the original inaccurate treatment of vibration. The scaling parameters for G3S and G3S/3 are in Table 3.

CBS-Q has similar performance to G3 and MCG3. Like G3, CBS-Q was designed to give accurate results when using a particular way of calculating the geometry and frequencies. The CBS-Q empirical parameters were optimized using MP2/6-31G† geometries, with frequencies calculated using HF/6-31G† and scaled by 0.91844. To ensure a fair test of the CBS-Q method on this particular data set, we therefore optimized the empirical parameters in CBS-Q to Database/3, and we list this method as CBS-Q/3. As expected, the parameters and the error did not change significantly, because the frequency-scaling factor of 0.91844 used in the CBS-Q parametrization is very appropriate for obtaining accurate ZPE, and as a result, the original empirical parameters in CBS-Q already give accurate electronic energies that agree well with Database/3. Unlike G2 and G3, but like the new methods presented here, the CBS-Q energy calculated with any accurate combination of geometry and frequency calculations should yield similar results without changing any parameters.

MCG3/3 has an 8% lower MUE over Database/3 when compared to MCG3/2 while at the same time reducing the cost by 12−16%. MCG3/3 is the most accurate of the MCCM/3 methods, having a MUE 38% lower than MC-QCISD/3. Though MCG3/3 has a lower cost than G3 or CBS-Q, optimizations and frequency calculations at the MCG3/3 level are still limited to small systems.

4.2. N^6 Methods. The MC-QCISD/3 and MC-UT/3 methods scale as N^6. MC-UT has a cost between that of MC-CO/3 and MC-QCISD/3. Although it scales as N^6, the MC-UT method does not rely on a post-SCF iterative process (recall that Møller−Plesset perturbation theory is noniterative, whereas coupled cluster and quadratic configuration interaction methods involve nonlinear equations for the amplitudes of excitation operators, and these nonlinear equations must be solved iteratively). Avoiding iterations gives the MC-UT/3 method a lower cost than QCISD-based methods, and it avoids problems that sometimes occur when the QCI iterations are difficult to converge.

MC-QCISD/3 has a 27% lower MUE over Database/3 than MC-UT/3 and a 14% lower MUE than MC-QCISD/2m. On the basis of past experience,[28] we expect that MC-QCISD/3 will be very efficient for optimizations as well as energy calculations on a variety of systems.

4.3. N^5 Methods. Although MC-CO/3 scales as N^5, it has a MUE only 38% higher than MC-UT/3. SAC/3, which also scales as N^5 is the simplest of the MCCM/3 methods, and it also has the lowest cost. SAC/3 simply requires the scaling of the MP2/6-31+G(d,2p) correlation energy by a factor of 1.1512. After scaling, the errors in all twelve categories in Table 4 decrease as compared to those for MP2/6-31+G(d,2p). This extremely simple modification of MP2 theory reduces the MUE over the entire database by 61% (as compared to the unscaled ab initio result) at no additional cost.

As compared to SAC/3, MC-CO/3 has only half as large of an MUE over Database/3. Although it uses the larger MG3S basis set, MC-CO/3 still has the advantage of low-cost analytic Hessians, which are not available for any of the N^6 or N^7 methods.

4.4. Average Errors in Bond Energies. The 109 molecules in our atomization energy database have a total of 513 bonds (counting double and triple bonds as a single bond) or an average of 4.71 bonds per molecule. This yields 1.4, 0.7, 0.5, 0.4, and 0.2 kcal/mol mean error per bond for SAC/3, MC-CO/3, MC-UT/3, MC-QCISD/3, and MCG3/3, respectively, which qualifies at least the last four methods as having "chemical accuracy" (usually defined as 1 kcal/mol for the quantity of interest). Note that 1 kcal/mol for the total atomization energy would be a more stringent requirement, satisfied only by the MCG3/3 method.

4.5. Other Combinations. Many other basis set combinations were tried in the process of developing SAC/3, MC-CO/3, and MC-UT/3. The final decision of which basis sets to use in MC-UT/3, MC-CO/3, and SAC/3 was based on the performance-to-cost ratio. The balance of the basis set is very important in MCCM methods, especially for SAC methods. The single empirical parameter in a SAC method accounts for both the incomplete correlation treatment and the basis set deficiencies. The optimal basis set to use is not necessarily the one that

TABLE 4: Mean Unsigned Errors (kcal/mol), Root-Mean-Square Errors, and Times for N^6 and N^5 Methods

quantity	item	N^6 Methods			N^5 Methods	
		MC-QCISD/2	MC-QCISD/3	MC-UT/3	MC-CO/3	SAC/3
MUE	atomization energies (109)	1.96	1.73	2.12	3.23	6.48
	HCO compounds (54)	1.72	1.37	1.70	1.94	5.02
	containing 2nd row (34)	1.85	1.70	2.01	4.30	7.49
	other (21)	2.76	2.62	3.41	4.85	8.62
	error per bond (109)	0.42	0.37	0.45	0.69	1.38
	HCO compounds (54)	0.28	0.22	0.27	0.31	0.81
	containing second row (34)	0.66	0.66	0.72	1.54	2.68
	other (21)	0.72	0.64	0.88	1.26	2.23
	barrier heights (44)	1.76	1.33	2.67	3.23	3.64
	electron affinities (13)	1.97	1.38	1.27	2.11	7.82
	ionization potentials (13)	1.51	1.95	1.93	2.09	8.64
	all data (179)[a]	1.88	1.62	2.22	3.07	6.04
RMSE	all data	2.47	2.09	3.17	4.23	7.53
cost	energy	65	56	52	51	4.1
	gradient	170	180	170	160	13
	Hessian	2800	2800	2100	1800	160

[a] Based on rows 1, 9, 10, and 11.

TABLE 5: Mean Unsigned Errors, Root-Mean-Square Errors, and Times for Hybrid DFT/MG3S Methods[a]

quantity	item	B3LYP	PBE1PBE	mPW1PW91	MPW1K
MUE	atomization energies (109)	4.24	4.37	4.19	11.02
	HCO compounds (54)	3.20	4.02	3.20	9.66
	containing 2nd row (34)	6.51	5.09	5.56	10.58
	other (21)	3.25	4.09	4.50	15.24
	error per bond (109)	0.90	0.93	0.89	2.34
	HCO compounds (54)	0.51	0.64	0.51	1.55
	containing second row (34)	2.33	1.82	1.99	3.79
	other (21)	0.84	1.06	1.17	3.95
	barrier heights (44)	4.25	4.19	3.56	1.38
	electron affinities (13)	2.29	2.78	2.62	3.71
	ionization potentials (13)	4.72	3.24	3.72	3.53
	all data (179)[b]	4.13	4.12	3.88	7.58
RMSE	all data	5.73	5.40	4.91	10.30
cost	energy	48	48	48	48
	gradient	64	64	64	64
	Hessian	390	390	390	390

[a] Geometries used are QCISD/MG3. MG3S basis set used for all HDFT energies in this table. [b] Based on rows 1, 9, 10, and 11.

TABLE 6: Mean Unsigned Errors, Root-Mean-Square Errors, and Times for Hybrid DFT/6-31+G(d,p) Methods[a]

quantity	item	B3LYP	PBE1PBE	mPW1PW91	MPW1K
MUE	atomization energies (109)	8.04	6.34	7.51	14.94
	HCO compounds (54)	4.75	4.18	4.17	10.94
	containing 2nd row (34)	13.62	10.55	12.63	18.17
	other (21)	7.47	5.05	7.79	20.00
	error per bond (109)	1.71	1.35	1.60	3.17
	HCO compounds (54)	0.76	0.67	0.67	1.75
	containing second row (34)	4.87	3.78	4.52	6.50
	other (21)	1.94	1.31	2.02	5.19
	barrier heights (44)	4.68	4.40	3.76	1.41
	electron affinities (13)	3.24	2.96	2.83	4.11
	ionization potentials (13)	4.91	3.43	3.99	4.49
	all data (179)[b]	6.64	5.40	5.99	10.07
RMSE	all data	9.98	8.00	8.90	14.70
cost	energy	6.3	6.3	6.3	6.3
	gradient	8.6	8.6	8.6	8.6
	Hessian	55	55	55	55

[a] Geometries used are QCISD/MG3. 6-31+G(d,p) basis set used for HDFT energies in this table. [b] based on rows 1, 9, 10, and 11.

performs best on its own, but one that complements the systematic behavior of MP2 (or other level of theory used in a SAC method). As an example of this, SAC-MP2/G3Large offers little improvement over a MP2/G3Large calculation, and it performs worse on atomization energies and barrier heights than SAC/3, even though G3Large is a much more complete basis set than 6-31+G(d,2p).

Several other SAC, MCSAC, and MCCM methods were optimized to the new database. Most of the SAC combinations had not been tried previously, but the MCSAC and MCCM methods are new versions of MCCM methods developed in earlier work.[17] The errors and costs for these methods are in the Supporting Information, and they may occasionally be useful for one reason or another although generally we recommend that the methods in the MCCM/3 suite provide sufficient flexibility for most work.

4.6. Comparison to Hybrid DFT and ab Initio Methods. The hybrid DFT methods in Tables 5 and 6 are comparable in performance to the MC-CO/3 and SAC/3 methods, but hybrid DFT has the advantage of scaling as N^4 as opposed to the N^5 scaling of MC-CO/3 and SAC/3. The MPW1K method gives accurate barriers and reaction energies at a very affordable price. It will tend to work best when a single bond is broken and formed because of its systematic underestimate of bond strengths. Despite the small systematic errors in bond strength, MPW1K/6-31+G(d,p) has a 10% lower MUE over the database than CCSD(T)/cc-pVTZ in Table 7.

Tables 7−10 show the mean unsigned errors and cost for all ab initio methods which are components of multilevel methods recommended in this work, as well as for three more expensive (but very highly regarded) ab initio methods: QCISD(T)/6-31+G(2df,p), CCSD(T)/cc-pVTZ, and CCSD(T)/aug-cc-pVTZ. Like all other calculations discussed, the energies were evaluated at the QCISD/MG3 geometries. Because of the high cost, only the 36 least expensive barrier heights and the 67 least expensive atomization energies were calculated at the CCSD(T)/aug-cc-pVTZ level. The MUE for AEs was estimated as the MUE for this subset times the ratio of the average error for the full set by CCSD(T)/cc-pVTZ to the average error for this subset by CCSD(T)/cc-pVTZ. The MUE for BHs is calculated using the same procedure. Tables 7−10 show that ab initio methods are plagued with large errors and high costs.

The CCSD(T)/aug-cc-pVTZ method, which is sometimes called the "gold standard", gives especially disappointing results. Despite its enormous cost, it is outperformed by MC-UT, which has an 81% lower error for AEs, 1% lower error for IPs, 37% lower error for EAs, and an energy cost 99.4% lower than CCSD(T)/aug-cc-pVTZ. Though its systematic errors prevent it from performing well on total atomization energies, EAs, and IPs, the CCSD(T)/aug-cc-pVTZ method has an error for barrier heights similar to the best methods in Table 1. However, with an energy cost about 40 times larger than G3S/3, and about 100 times larger than MCG3/3, there are few affordable applications for the method.

TABLE 7: Mean Unsigned Errors (kcal/mol) and Cost of Single-Level ab Initio N^7 Methods

	AE	BH	IP	EA	all[a]	cost(E)	cost(G)	cost(H)
CCSD(T)/aug-cc-pVTZ	12.3[b]	0.82[c]	1.9	2.0	8.0[d]	9300	450000	2.1×10^7
CCSD(T)/cc-pVTZ	15.5	1.4	3.5	15.1	11.1	860	41000	2.0×10^6
QCISD(T)/6-31+G(2df,p)	18.6	2.3	3.9	6.1	12.6	230	11000	520000
MP4/6-31G(2df,p)	13.5	3.7	4.7	21.7	11.1	98	4800	230000
QCISD(T)/6-31+G†	50.7	4.9	11.1	11.4	33.7	23	1100	55000
MP4/6-31+G(d)	44.8	5.9	10.6	10.8	30.3	11	520	25000
QCISD(T)/6-31G(d)	46.2	5.1	11.7	28.9	32.3	10	500	24000
MP4/6-31G(d)	43.8	6.2	11.6	28.7	31.1	5.3	260	13000

[a] All 179 data; all results are //Q. [b] Estimated from 67 of the 109 atomization energies as explained in text. [c] Estimated from 36 of the 44 barriers. [d] Calculated from preceding four numbers in table.

TABLE 8: Mean Unsigned Errors (kcal/mol) and Cost of Single-Level ab Initio N^6 Methods

	AE	BH	IP	EA	all[a]	cost(E)	cost(G)	cost(H)
MP4SDQ/6-31G(2df,p)	22.6	4.8	4.7	22.2	16.9	28	130	5900
MP3/6-31G(2df,p)	20.9	5.3	3.9	21.5	15.8	20	85	4100
MP4SDQ/6-31+G(d(f),d,p)[b]	37.7	4.4	8.4	11.1	25.5	8.5	49	2300
QCISD/6-31G(d)	51.7	5.9	11.5	28.9	35.8	6.0	15	760
MP3/6-31+G(d)	52.1	7.5	9.8	11.9	35.1	2.6	11	470
MP4SDQ/6-31G(d)	50.6	6.9	11.2	28.7	35.4	2.3	7.1	340
MP3/6-31G(d)	50.5	7.5	10.4	28.3	35.4	2.1	6.1	290

[a] All 179 data; all results are //Q. [b] Reference 43.

TABLE 9: Mean Unsigned Errors (kcal/mol) and Cost of Single-Level ab Initio N^5 Methods

	AE	BH	IP	EA	all[a]	cost(E)	cost(G)	cost(H)
MP2(full)/G3Large	9.3	4.3	3.3	3.0	7.2	180	350	4700
MP2/6-311++G(3d2f,2df,2p)	9.8	4.3	3.6	3.0	7.5	59	160	2000
MP2/MG3	9.7	4.4	3.6	3.0	7.4	59	160	2000
MP2/MG3S	9.7	4.4	3.6	3.0	7.5	50	140	1800
MP2/6-31G(2df,p)	11.8	4.8	5.4	21.3	10.3	9.3	83	360
MP2/6-31+G(d,2p)	21.0	4.6	9.6	9.6	15.3	4.1	8.8	140
MP2/6-31+G(d,p)	24.5	5.8	9.9	10.0	17.8	2.2	6.7	81
MP2/6-31G(2d)	34.0	5.8	8.1	23.0	24.4	2.2	5.1	56
MP2/6-31+G(d)	38.9	7.0	10.1	10.2	26.9	1.8	4.7	39
MP2/6-31G(d)	38.1	6.8	11.0	27.5	27.7	1.3	3.6	23

[a] All 179 data; all results are //Q.

TABLE 10: Mean Unsigned Errors (kcal/mol) and Cost of Single-Level ab Initio N^4 Methods

	AE	BH	IP	EA	all[a]	cost(E)	cost(G)	cost(H)
HF/G3Large	145.0	13.2	18.0	27.0	94.7	92	120	600
HF/MG3	145.2	13.2	17.9	26.9	94.9	55	73	370
HF/MG3S	145.2	13.2	17.9	27.0	94.9	46	71	320
HF/6-31G(2df,p)	143.3	12.9	18.0	39.7	94.6	4.6	7.2	49
HF/6-31+G(d,2p)	148.7	13.0	17.8	25.7	96.9	2.4	4.3	20
HF/6-31+G(d,p)	148.9	13.2	17.8	25.7	97.0	1.9	3.7	12
HF/6-31G(2d)	150.5	12.8	18.1	39.2	98.9	1.4	2.6	9.3
HF/6-31+G(d)	152.4	13.6	17.8	25.8	99.3	1.3	2.3	7.0
HF/6-31G(d)	150.6	13.4	18.1	38.1	99.1	1.00[b]	1.8	4.7

[a] All 179 data; all results are //Q. [b] This calculation is the unit for all cost comparison.

TABLE 11: Coefficients (unitless) for MCCM/3 and SAC/3 Methods

method	c_0	c_1	c_2	c_3	c_4	c_5	c_6
MCG3/3	1.0067	1.1249	1.0585	1.2027	1.1369	0.5024	1.2666
MC-QCISD/3		1.0452	1.1305	1.2302	1.1673		
MC-UT/3		1.0038	1.1420	1.1773	1.3002		
MC-CO/3		0.9436	0.8677	1.8814			
SAC/3		1.1512					

4.7. Barrier Heights. A well-known problem with barrier height calculations is that ab initio methods tend to have a systematic error; the predicted barrier height is almost always too high. In contrast, DFT barrier heights are usually too low.[36] To systematically test the extent of these systematic errors for ab initio, SAC, MCCM, and HDFT methods, Table 12 gives mean signed errors for the barrier heights in this work. We see

TABLE 12: Mean Signed Error (kcal/mol) in 44 Reaction Barrier Heights[a]

method	MSE	method	MSE
B3LYP/6-31+G(d,p)	−4.64	MP3/6-31G(2df,p)	5.26
PBE1PBE/6-31+G(d,p)	−4.40	MP4SDQ/6-31G(d)	6.80
mPW1PW91/6-31+G(d,p)	−3.76	MP4SDQ/6-31+G(d(f),d,p)	4.41
MPW1K/6-31+G(d,p)	−0.83	MP4SDQ/6-31G(2df,p)	4.77
B3LYP/MG3S	−4.17	QCISD/6-31G(d)	5.56
PBE1PBE/MG3S	−4.19	MP4/6-31G(d)	5.93
mPW1PW91/MG3S	−3.55	MP4/6-31+G(d)	5.87
MPW1K/MG3S	−0.73	MP4/6-31G(2df,p)	3.58
HF/6-31G(d)	12.75	QCISD(T)/6-31G(d)	4.64
HF/6-31+G(d)	13.10	QCISD(T)/6-31+G†	4.51
HF/6-31+G(d,p)	12.84	QCISD(T)/6-31+G(2df,p)	2.28
HF/6-31+G(d,2p)	12.65	CCSD(T)/cc-pVTZ	0.91
HF/6-31G(2df,p)	12.47	CCSD(T)/aug-cc-pVTZ	0.24
HF/MG3S	12.92	CBS-Q//Q	−0.01
HF/MG3	12.90	CBS-Q/3	−0.06
HF/G3Large	12.89	G3//Q	0.89
MP2/6-31G(d)	6.78	G3S//Q	0.51
MP2/6-31+G(d)	6.89	G3/3	1.02
MP2/6-31+G(d,p)	5.59	G3S/3	0.34
MP2/6-31+G(d,2p)	4.18	SAC/3	2.90
MP2/6-31G(2df,p)	4.49	MC-CO/3	2.92
MP2/MG3S	4.01	MC-UT/3	2.67
MP2/MG3	3.97	MC-QCISD/2	1.76
MP2/6-311++G(3d2f,2df,2p)	3.91	MC-QCISD/3	1.33
MP2(full)/G3Large	3.90	MCG3/2	0.68
MP3/6-31G(d)	7.46	MCG3/3	0.68
MP3/6-31+G(d)	7.52		

[a] All results are for QCISD/MG3 geometries.

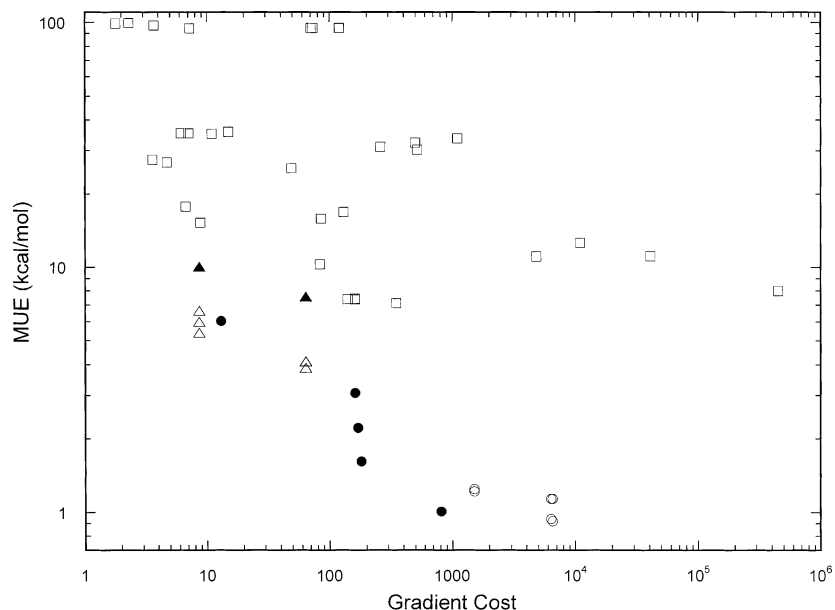that MCCM methods are very successful at reducing the systematic errors as are MPW1K, CBS-Q, G3, G3S, SAC,

The MCCM/3 Suite and SAC/3

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Figure 6. Mean unsigned error over Database/3 vs cost for ab initio (□), MCCM (●), G3 and CBS-Q (○), MPW1K (▲), and other HDFT (△) methods.
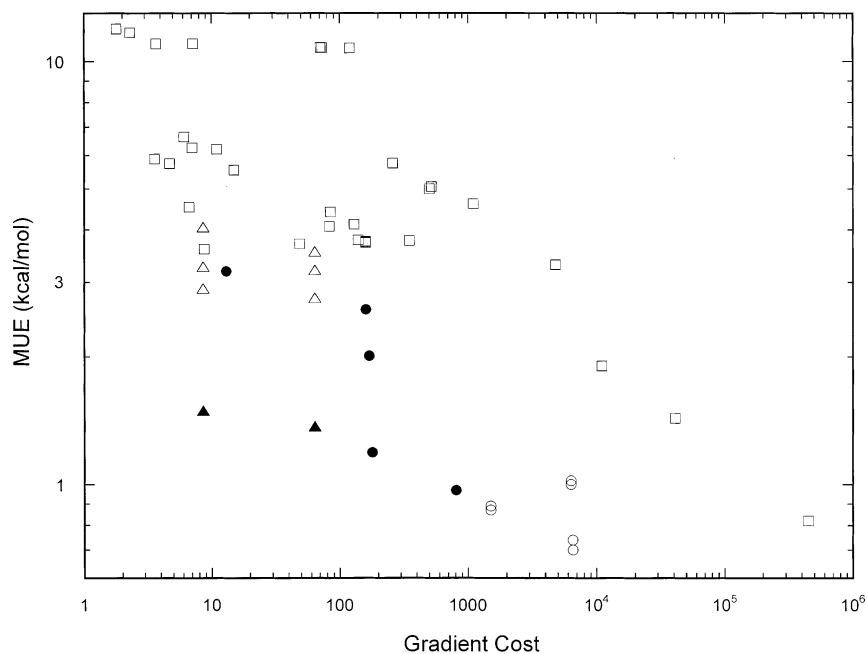

Figure 7. Mean unsigned error in reaction barrier heights and energies of reaction (66 data) vs cost for ab initio (□), MCCM (●), G3 and CBS-Q (○), MPW1K (▲), and other HDFT (△) methods.

CCSD(T), and QCISD(T). All other methods in Table 12 have systematic errors of at least 3 kcal/mol.

4.8. General Comparison. Figure 6 is a scatter plot of the MUE in Database/3 vs cost for all the ab initio, HDFT, and MCCM/3 methods discussed, except for the top three methods in Table 7, which would be off scale to the right. The figure includes the individual components of all the MCCM/3 methods. It illustrates the cost efficiency of MCCM/3 and HDFT methods compared to ab initio methods. Figure 7 is a scatter plot of the same methods for the MUE in 44 barrier heights and 22 energies of reaction for the 22 reactions in Database/3. Again the advantages of the semiempirical MCCM and HDFT methods over pure ab initio methods are clear.

5. Concluding Remarks

After optimizing coefficients for 74 combinations of the treatment of electron correlation energy, the one-electron basis set, and the spin−orbit energy, we have selected five particularly successful combinations that span a range of computational efforts to serve as the MCCM/3 suite of multicoefficient correlation methods. In particular, we introduce the SAC/3, MC-CO/3, MC-UT/3, MC-QCISD/3, and MCG3/3 methods for dynamics and thermodynamics calculations. MC-QCISD/3 and MCG3/3 are the most accurate and most expensive of these methods for predicting thermochemical properties and thermochemical kinetics properties at an affordable price. MC-UT/3

has the lowest mean unsigned error (MUE) in Database/3 for a method that does not require a post-SCF iterative process. MC-CO/3 and SAC/3 are the most affordable methods and provide very reasonable alternatives to hybrid DFT in cases where hybrid DFT may have questionable validity or where its validity has not been demonstrated. In comparison to the MCCM/3 suite, we find that the MPW1K hybrid DFT method is a very efficient method for predicting energies of reaction and barrier heights and is the only hybrid DFT method that has a similar cost-to-performance ratio as multilevel methods for these quantities.

In recent years, the aura of purely ab initio methods has faded. Hartree−Fock theory is seldom the final method of choice as compared with semiempirical molecular orbital theories such as AM1, PM3, B3LYP, etc. Furthermore, it seems foolhardy for all but the most fundamental studies to eschew the use of semiempirical parameters even with explicitly correlated wave functions. For example, faced with large systematic errors in single-level ab initio methods, and their slow rate of convergence with respect to increasing the basis set (as exemplified by CCSD(T)/aug-cc-pVTZ), it seems wasteful and foolhardy to use pure ab initio methods. The search for optimum strategies may never be completely over, but we believe that the MCCM/3 suite and SAC/3 represent a very good compromise of accuracy, cost, and ease of use for practical calculations of dissociation energies, ionization potentials, electron affinities, and barrier heights, and these methods, along with hybrid DFT and similar multilevel correlated-wave function methods developed in other groups, should probably replace pure ab initio methods for most calculations of this kind of property.

6. Software

MCCM/3 and SAC/3 energies, gradients, and Hessians can be calculated, and MCCM/3 and SAC/3 optimizations can be performed by using the program MULTILEVEL[53] in conjunction with *Gaussian 98*.[40]

Supporting Information Available: The entire Database/3 training set and the scaling coefficients determined in the present study for 33 other SAC methods and 36 other MCCM methods and the errors and costs for these methods (Tables S1−S10). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Nyden, M. R.; Petersson, G. A. *J. Chem. Phys.* **1981**, *75*, 1843.
(2) Brown, F. B.; Truhlar, D. G. *Chem. Phys. Lett.* **1985**, *117*, 307.
(3) Gordon, M. S.; Truhlar, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 5412.
(4) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.
(5) Montgomery, J. A., Jr.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900.
(6) Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788.
(7) Glukhovtsev, M. N.; Pross, A.; McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 1878.
(8) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598.
(9) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.
(10) Irikura, K. K., Frurip, D. J., Eds. *Computational Thermochemistry: Prediction and Estimation of Molecular Thermodynamics*; ACS Symp. Ser. 677; American Chemical Society: Washington, DC, 1998.
(11) Pople, J. A. *Rev. Mod. Phys.* **1999**, *77*, 1267.
(12) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.
(13) Fast, P. L.; Corchado, J.; Sanchez, M. L.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 3139.
(14) Fast, P. L.; Corchado, J. C.; Sanchez, M. L.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 5129.
(15) Fast, P. L.; Sanchez, M. L.; Corchado, J. C.; Truhlar, D. G. *J. Chem. Phys.* **1999**, *110*, 11679.
(16) Fast, P. L.; Sanchez, M. L.; Truhlar, D. G. *Chem. Phys. Lett.* **1999**, *306*, 407.
(17) Tratz, C. M.; Fast, P. L.; Truhlar, D. G. *PhysChemComm* **1999**, *2*, 14.
(18) Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843.
(19) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650.
(20) Vreven, T.; Morokuma, K. *J. Comput. Chem.* **2000**, *21*, 1419.
(21) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 1125.
(22) Redfern, P. C.; Zapol, P.; Curtiss, L. A.; Raghavachari, K. *J. Phys. Chem. A* **2000**, *104*, 5850.
(23) Fast, P. L.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 6111.
(24) *Quantum-Mechanical Prediction of Thermochemical Data*; Cioslowski, J., Ed.; Understanding Chemical Reactivity Series Vol. 22; Kluwer: Dordrecht, 2001.
(25) Li, Z. H.; Wong, M. W. *Chem. Phys. Lett.* **2001**, *337*, 209.
(26) Curtiss, L. A.; Redfern, P. C.; Rassolov, V.; Kedziora, G.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 9287.
(27) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 108.
(28) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2002**, *106*, 842.
(29) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *Chem. Phys. Lett.* **2002**, *359*, 390.
(30) Truong, T. N.; Truhlar, D. G. *J. Chem. Phys.* **1990**, *93*, 1761.
(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(32) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
(33) Stephens, P. J.; Devlin, F. J.; Ashvar, C. S.; Bak, K. L.; Taylor, P. R.; Frisch, M. J. *ACS Symp. Ser.* **1996**, *629*, 105.
(34) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.
(35) Adamo, C.; Cossi, M.; Barone, V. *THEOCHEM* **1999**, *493*, 145.
(36) Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811.
(37) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A*, in press.
(38) Pu, J.; Truhlar, D. G. *J. Chem. Phys.* **2002**, *116*, 1468.
(39) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936.
(40) 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.; 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.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98,*; Gaussian, Inc.: Pittsburgh, PA, 1998.
(41) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
(42) Petersson, G. A.; Tensfeldt, T. G.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1991**, *94*, 6091.
(43) This basis is used in ref 42 but not discussed. It is equivalent to 6-31+G(df, p) for P, S, and Cl and 6-31+G(d, p) for all other atoms.
(44) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
(45) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(46) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
(47) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
(48) Rodgers, J. M.; Fast, P. L.; Truhlar, D. G. *J. Chem. Phys.* **2000**, *112*, 3141.
(49) Ruscic, B.; Litorja, M.; Asher, R. L. *J. Phys. Chem. A* **1999**, *103*, 8625.
(50) Raghavachari, K.; Anderson, J. B. *J. Phys. Chem. A* **1996**, *100*, 12960.
(51) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; Defrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1981**, *15*, 269.
(52) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.
(53) Rodgers, J. M.; Lynch, B. J.; Fast, P. L.; Zhao, Y.; Pu, J.; Chuang, Y.-Y., Truhlar, D. G.; MULTILEVEL-version 3.0.1/G98; University of Minnesota, Minneapolis, 2002.