

What Are the Best Affordable Multi-Coefficient Strategies for Calculating Transition State Geometries and Barrier Heights?

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We compare hybrid density functional theory and multi-coefficient correlation methods for locating saddle point geometries and calculating barrier heights on a Born–Oppenheimer potential energy surface. We located reactant, product, and saddle point stationary points by the multi-coefficient Gaussian-3 (MCG3) method for 15 reactions, and by the multi-coefficient quadratic configuration interaction with single and double excitations (MC-QCISD) method for 22 reactions; and the resulting structures and energies are compared to those obtained by the Møller–Plesset second order perturbation theory (MP2), QCISD, and modified Perdew–Wang 1-parameter-for-kinetics (MPW1K) methods. We examined three single-level methods with two basis sets, 6-31+G(d,p) and MG3. By comparison to calculations on five systems where the saddle point has been optimized at a high level of theory, we conclude that the best saddle point geometries for the methods tested are those found at the MC-QCISD, MCG3, and MPW1K levels. MP2 was shown to have systematic deficiencies in predicting saddle point geometries. Our recommended most affordable methods are the MPW1K/6-31+G(d,p) and MC-QCISD methods for fully optimized calculations and the MCG3/MPW1K/6-31+G(d,p) method for single-point calculations with mean unsigned errors in calculating reaction energies and barrier heights of 1.6, 1.6, and 1.1 kcal/mol respectively.

1. Introduction

The ability of electronic structure theory to make reliable predictions of bond energies and enthalpies of formation has advanced extraordinarily rapidly in recent years. Computational thermochemistry now challenges experiment in accuracy, cost, and convenience for many kinds of molecules and even more so for reactive intermediates.¹ Both correlated-wave function theory, i.e., explicitly correlated methods (especially many-body perturbation theory and coupled cluster methods), and density functional theory (DFT) have contributed to the advances. There has also been progress in computational thermochemical kinetics and the calculation of potential energy surfaces, but such calculations are harder, and much more remains to be done. In the long-term, multireference explicitly correlated methods² and multireference DFT^{3,4} hold considerable promise for energies of transition states and arbitrary points on potential surfaces, but in the short term one would like to know the best strategy for using currently widely available methods. In fact, if one develops creative ways to use these tools, one may be able to attain higher accuracy even without solving some of the recalcitrant difficulties of multireference methods.

Reaction-path calculations and classical trajectory calculations (the latter are sometimes called molecular dynamics, but the implication that molecular dynamics calculations are always classical is becoming increasingly unsuitable as it becomes practical to employ a larger number of dynamics methods that incorporate quantum effects) require energy gradients as well as single-point energies (i.e., energy values for a fixed geometry), and the calculation of vibrational frequencies requires Hessians (second derivatives of the energy with respect to nuclear coordinates). Geometry optimization of minimum-energy structures and saddle points also requires gradients and

sometimes at least one Hessian. Characterization of stationary points as minima or saddle points also requires Hessians. Furthermore, both for fitting potential energy surfaces and for carrying out direct dynamics calculations, one requires a large number of energies and sometimes a large number of gradients and Hessians. A major consideration in selecting electronic structure methods and one-electron basis sets for dynamics applications is the performance-to-cost ratio for energies, gradients, and Hessians.

For some types of dynamics calculations, algorithms are available for calculating a transition state structure or a reaction path at one level and improving the energetic part of the calculation with single-point energies.⁵ The well-known “//” method⁶ (in which X//Y denotes a single-point energy calculation with level X at a geometry optimized by level Y) is the prime example, but this method is basically limited to conventional transition state theory and tunneling calculations that neglect reaction-path curvature and corner cutting. More general classical and semiclassical methods require consistent energies and gradients, though, and so there is great interest in learning the reliability of methods for which gradients are reasonably affordable.

One class of strategies for extracting the maximum performance from explicitly correlated methods involves extrapolating the one-electron basis (“infinite basis” methods⁷), scaling the correlation energy (SEC,⁸ SAC,^{9,10} and MCSAC methods¹¹), or both.^{11–16} A series of multi-coefficient correlation methods (MCCMs) has been developed for simultaneous extrapolation of the basis set and scaling of the correlation energy or its components; these methods include MCG3¹³ and MC-QCISD.¹⁶ A general name for all the methods in this paragraph is multi-level electronic structure methods because the final results are based on more than one of the conventional levels (where

“level” in general denotes both level of electron correlation and choice of one-electron basis set).

A strategy for improving the performance of DFT is to mix in some fraction of Hartree–Fock theory (as in mPW1PW91¹⁷) or to do this along with scaling one or more components of the exchange and correlation functionals (as in the popular B3PW91¹⁸ and B3LYP¹⁹ methods). Recently, we have optimized one such method for kinetics, resulting in a method called modified Perdew–Wang 1-parameter-method for kinetics²⁰ (MPW1K), and we have also tested this method for saddle point geometries. All such combinations of Hartree–Fock theory and DFT are called hybrid HF-DFT, or, more usually, hybrid DFT.

With either explicitly correlated methods or DFT (either pure or hybrid) one must choose not only the method to treat correlation but also the basis set. The performance and cost are both steep functions of basis set size (with cost typically increasing as the fourth power of the number of basis functions for a given system, which should not be confused with the even steeper scaling, up to the seventh power for popularly used methods, with system size if the number of basis functions per atom is fixed).²¹

The goal of the present paper is to study a variety of levels and combinations of levels, with and without “//” corrections, to learn more about which strategies lead to the best performance-to-cost ratios. The cost consideration is dependent on system size but for quantitative estimations we will use a cost measure based on primarily on a system with eleven atoms (2 carbons, 1 nitrogen, and 8 hydrogens). The conclusions clearly also depend on the test set; we will use a set of 22 reactions for which the true barrier heights have been estimated reasonably reliably by comparing experimental data to dynamics calculations in the literature. These reactions mainly involve making and breaking single bonds in neutral molecules, in most cases by the transfer of hydrogen.

Section 2 summarizes the test set. Section 3 summarizes all methods and basis sets to be tested. Section 4 presents results and discussion.

2. Databases

The energy test set we will use in our comparisons consists of the energy of reaction and forward and reverse barrier height for 22 reactions. We will call this the kinetics energy database. All energies reported in this paper will be molar energies in units of kcal. Table 1 lists our best estimate of the zero-point exclusive endoergicity ΔE and forward (f) and reverse (r) barrier height V_x^\ddagger , which are related by

$$V_f^\ddagger = V_r^\ddagger + \Delta E \quad (1)$$

Note that ΔE is also called the energy of reaction or classical endoergicity (it is negative for an exoergic reaction), and V_x^\ddagger is also called classical barrier height. The best estimates of the classical endoergicities were obtained from zero point-exclusive atomization energies which in turn were obtained by removing zero point energy contributions from experimental heats of formation at 0 K. An earlier version of the kinetics energy database was published elsewhere,²² but in the present paper we updated all energetic values to take account of more accurate experimental values for the heats of formation of CH₃,²³ H₂,²⁴ and OH.²⁵ Thus, the values of ΔE used in this paper were calculated from the zero-point exclusive atomization energies used previously¹³ with the exception of reactions involving CH₃, H₂, and OH. One of the barrier heights (either V_f^\ddagger or V_r^\ddagger) is estimated from the previously presented theoretical and experi-

TABLE 1: Best Estimates of Classical Barrier Heights and Classical Endoergicity

	reaction	ΔE	V_f^\ddagger	V_r^\ddagger
1.	H + HCl → Cl + H ₂	-3.0	5.7	8.7
2.	OH + H ₂ → H + H ₂ O	-16.1	5.7	21.8
3.	CH ₃ + H ₂ → H + CH ₄	-3.2	12.1	15.3
4.	CH ₃ + CH ₄ → CH ₃ + H ₂ O	-12.9	6.7	19.6
5.	H + CH ₃ OH → CH ₂ OH + H ₂	-6.0	7.3	13.3
6.	H + H ₂ → H ₂ + H	0.0	9.6	9.6
7.	OH + NH ₃ → H ₂ O + NH ₂	-9.5	3.2	12.7
8.	CH ₃ + HCl → CH ₄ + Cl	-6.2	1.7	7.9
9.	OH + C ₂ H ₆ → H ₂ O + C ₂ H ₅	-16.5	3.4	19.9
10.	F + H ₂ → H + HF	-31.6	1.8	33.4
11.	O + CH ₄ → OH + CH ₃	5.6	13.7	8.1
12.	H + PH ₃ → PH ₂ + H ₂	-20.1	3.1	23.2
13.	H + ClH' → HC1 + H'	0.0	18.0	18.0
14.	H + OH → O + H ₂	-2.4	10.7	13.1
15.	H + <i>trans</i> -N ₂ H ₂ → H ₂ + N ₂ H	-35.0	5.9	40.9
16.	H + H ₂ S → H ₂ + HS	-13.7	3.5	17.3
17.	O + HCl → OH + Cl	-0.6	9.8	10.4
18.	NH ₂ + CH ₃ → CH ₄ + NH	-14.4	8.0	22.4
19.	NH ₂ + C ₂ H ₅ → C ₂ H ₆ + NH	-10.8	7.5	18.3
20.	C ₂ H ₆ + NH ₂ → NH ₃ + C ₂ H ₅	-7.0	10.4	17.4
21.	NH ₂ + CH ₄ → CH ₃ + NH ₃	-3.3	14.5	17.8
22.	<i>s-trans cis</i> -C ₅ H ₈ → <i>s-trans cis</i> -C ₅ H ₈	0.0	38.4	38.4

mental kinetics data²⁰ using the method described in previous work.^{20,22} The other barrier height is then calculated from Equation 1 and the experimental endoergicity. As a result of using the new experimental endoergicities, the barrier height calculated from eq 1 changed for most of the reactions in the database (reactions 1–12, 14–18, and 21) by ~0.1–0.3 kcal/mol.

The database of saddle point geometries comes from our previous work.²² These are more difficult to determine, so our test set is smaller (reactions 1, 6, 10, 13, and 14), and it consists of reactions where very high-level calculations^{26–29} of saddle point geometries are available. The perpendicular looseness has been defined²² as the sum of the making and breaking bond distances; this is a measure of the looseness of the structure in the direction perpendicular to the reaction coordinate. For example, for the saddle point of reaction 14, the best estimate²⁹ of the making bond distance is 0.894 Å, and the perpendicular looseness is 2.109 Å.

3. Methods

The methods used to calculate endoergicities and barrier heights include both full optimization and single-point methods; in the latter, denoted X//Y, the energy is calculated at the higher level X at the geometry obtained by an optimization at the lower level Y. The methods used for geometry optimization include the hybrid density functional MPW1K method,²⁰ two ab initio methods: Møller–Plesset second-order perturbation theory³⁰ (MP2), quadratic configuration interaction with single and double excitations³¹ (QCISD), and two multi-coefficient correlation methods: multi-coefficient QCISD (MC-QCISD),¹⁶ and multi-coefficient Gaussian-3 (MCG3).¹³ MPW1K was selected because our previous studies^{20,22} showed that it is the most satisfactory hybrid DFT method for kinetics, the MC methods were chosen as candidates for best performance-to-cost ratio, MP2 was chosen for comparison because of its widespread use and relatively low cost, and QCISD was chosen for comparison because of its good performance²² for saddle point geometries and because it is a component of the MC-QCISD methods. The methods used for single-point calculations include some of those used in optimization as well as QCISD with quasiperturbative connected triples³¹ (QCISD(T)). All calculations are based on

TABLE 2: Mean Errors (Angstroms) in Saddle Point Internuclear Distances for Reactions 1, 6, 10, 13, and 14

method		bond distance			perpendicular looseness			cost
		MSE ^a	MUE ^b	RMSE ^c	MSE ^a	MUE ^b	RMSE ^c	
MPW1K/	6-31+G(d,p)	0.00	0.02	0.03	-0.01	0.02	0.02	2.5(2) ^d
MP2/	6-31+G(d,p)	-0.03	0.03	0.05	-0.05	0.05	0.07	2.6(2)
QCISD/	6-31+G(d,p)	-0.01	0.03	0.04	-0.02	0.03	0.04	1.9(4)
MPW1K/	MG3	-0.01	0.01	0.01	-0.01	0.02	0.02	1.6(3)
MP2/	MG3	-0.03	0.04	0.06	-0.07	0.07	0.08	3.3(3)
QCISD/	MG3	-0.01	0.02	0.03	-0.01	0.02	0.03	1.9(5)
MC-QCISD		-0.01	0.02	0.02	-0.01	0.01	0.02	5.4(3)
MCG3		0.00	0.01	0.01	0.00	0.01	0.02	7.8(4)

^a Mean signed error. ^b Mean unsigned error. ^c Root-mean-squared error. ^d Power of 10 in parentheses.

TABLE 3: Mean Errors (kcal/mol) for Consistently Optimized Calculations

method	MSE	MUE	RMSE	cost
66 data				
MPW1K/6-31+G(d,p)	1.6	2.3	2.5(2) ^a	
MP2/6-31+G(d,p)	4.4	5.3	2.6(2)	
QCISD/6-31+G(d,p)	3.8	4.4	1.9(4)	
MPW1K/MG3	1.6	2.0	1.6(3)	
MP2/MG3	3.6	4.4	3.3(3)	
QCISD/MG3	2.4	2.8	1.9(5)	
MC-QCISD	1.6	1.9	5.4(3)	
MCG3	1.2	1.7	7.8(4)	
44 barrier heights				
MPW1K/6-31+G(d,p)	-1.2	1.6	2.3	
MP2/6-31+G(d,p)	5.3	5.7	6.2	
QCISD/6-31+G(d,p)	4.0	4.3	4.8	
MPW1K/MG3	-1.2	1.7	2.2	
MP2/MG3	3.7	4.2	4.9	
QCISD/MG3	2.4	2.8	3.1	
MC-QCISD	1.1	1.7	2.1	
MCG3	0.4	1.2	1.8	
22 energies of reaction				
MPW1K/6-31+G(d,p)	1.6	2.2		
MP2/6-31+G(d,p)	1.9	2.8		
QCISD/6-31+G(d,p)	2.9	3.4		
MPW1K/MG3	1.3	1.6		
MP2/MG3	2.4	3.3		
QCISD/MG3	1.6	2.0		
MC-QCISD	1.3	1.6		
MCG3	1.1	1.6		

^a Power of 10 in parentheses.

the spin-unrestricted formalism, i.e., a single Slater determinant for the wave function or reference state with different orbitals for different spins and no spin projection operators. The basis sets employed for the ab initio and DFT methods are the 6-31+G(d,p) basis³² and the modified G3Large (MG3) basis,¹⁴ which is also called the G3LargeMP2 basis.³³

The most important relativistic effect for reaction dynamics with first and second row elements is spin-orbit coupling. The MC-QCISD calculations were performed with version 2m coefficients¹⁶ that implicitly account for spin-orbit coupling. In all other calculations presented in this paper, the spin-orbit stabilization energy was added to all atoms and to selected open-shell molecules, as described previously.¹⁰ Therefore, for MCG3 we used version 2s parameters.¹³

The single-level calculations presented were performed with the Gaussian98 program.³⁴ The MCCM calculations were performed with the aid of the program multilevel 2.0.³⁵ All saddle points were verified to be first order with a frequency calculation, with the exception of reactions 9, 19, 20, and 22 at the QCISD/MG3 level. For these 4 systems, the numerical Hessian would require an excessive amount of computing resources, but the structures are very similar to those confirmed at lower levels. The structures of all MCG3 and MC-QCISD

optimized saddle points are given in Supporting Information. Note that the multi-level optimization methods are sometimes called MCG3//ML and MC-QCISD//ML, but in the present paper we omit the “//ML” to simplify the notation.

The cost function we use is designed to be an estimate of the cost of a geometry optimization. The actual number of energies, gradients, and Hessians required for an optimization varies greatly depending on the system, initial geometry, coordinate system, and optimization algorithm. Therefore, for comparison purposes we defined a standard cost (C) by

$$C = 10(E + G) + H \quad (2)$$

where E is the CPU time to perform an energy calculation, G is the time to calculate a gradient, and H is the time to calculate a Hessian. All of the timed calculations were performed on a single 300 MHz R12000 processor on an Origin 2000 computer, and the value tabulated is the sum of the C functions for calculations on two of the saddle point structures, namely CIHCH₃ and H₂NHC₂H₅. For single point calculations, X//Y, where the geometry is optimized at level Y and a single point energy is calculated at level X, the standard cost function is defined as

$$C(X//Y) = C(Y) + E(X) \quad (3)$$

Note that, as expected, the cost function is dominated by the larger system.

4. Results and Discussion

4.1. Saddle Point Geometries. Table 2 summarizes the error in $R_{\text{making bond}}^{\ddagger}$ and $R_{\text{breaking bond}}^{\ddagger}$ and in perpendicular looseness for the five reactions in the saddle point geometry database. The errors in Table 2 were computed using the values in the reaction geometry database rounded to 0.001 Å along with the unrounded results of our calculations, but the mean errors are rounded to 0.01 Å to allow the significant trends to be seen more easily. The lowest RMS error in bond distances for each of the basis sets was achieved by MPW1K for both the 6-31+G(d,p) and MG3 basis sets. MCG3, which uses three basis sets, gives the smallest error. The methods MPW1K and MCG3 do not exhibit the systematic error in perpendicular looseness that is found in MP2. Geometries optimized with QCISD are well balanced with respect to perpendicular looseness; however, the method is prohibitively expensive for many systems. If one can afford the cost, MCG3 gives the lowest error in bond distances at the saddle point. MPW1K predicts saddle point geometries almost as well with only an augmented, polarized double- ζ basis and a much lower cost (the standard cost function is more than 300 times lower).

4.2. Energetics. Table 3 compares the mean signed error (MSE), mean unsigned error (MUE), and root-mean-squared

TABLE 4: Mean Errors (kcal/mol) for //MPW1K/6-31+G(d,p) Calculations

single-point energy	MSE	MUE	RMSE	cost
66 data				
QCISD(T)/MG3		1.3	1.6	1.9(3) ^a
MC-QCISD		1.5	1.9	3.2(2)
MCG3		1.1	1.6	3.6(2)
44 barrier heights				
QCISD(T)/MG3	0.9	1.4	1.7	
MC-QCISD	1.1	1.7	2.1	
MCG3	0.4	1.2	1.7	
22 energies of reaction				
QCISD(T)/MG3		1.0	1.3	
MC-QCISD		1.3	1.6	
MCG3		1.1	1.6	

^a Power of 10 in parentheses.

error (RMSE) for the barrier heights and reaction energies for the set of 22 reactions for the calculations in which the geometries are optimized at the same level that the energy is calculated. The first seven rows of Table 3 show the MSE, MUE, and RMSE over all 66 data (44 barrier heights and 22 energies of reaction). For MCG3, 15 of the structures were fully optimized, and for the remaining 7, the QCISD/MG3 geometry was used. Table 4 displays the same errors for single-point energy calculations on the structures optimized at the MPW1K/6-31+G(d,p) level. Table 5 shows the errors for seven other single-point-energy methods.

Among the fully optimized calculations, MCG3 outperforms all other methods in accuracy. MC-QCISD and MPW1K are similar in performance, although MPW1K is significantly lower in cost. As is well-known, the MP2 and QCISD methods both systematically overestimate the barrier height due to incomplete treatment of electron correlation energy.

Among the “//” methods, the methods using MCG3 energies have the lowest error. The MCG3//MPW1K/6-31+G(d,p) method has the lowest computational cost among the “MCG3//” methods.

In testing methods against experimental data, a universal problem that cannot be avoided is the diversity of the testing data. As one considers broader classes of reactions, it is always possible that one will find different levels of performance.

The costs in Table 3 are on the same scale as is used in Table 2 and in subsequent tables, as explained in section 3. Readers may of course convert these to relative costs or percentages. For example, the cost of MP2/6-31+G(d,p) is 8% of the cost of MP2/MG3.

5. Conclusions

This paper compares the cost and accuracy of a number of methods available for calculating saddle point geometries, reaction barrier heights, and reaction energies. It attempts to quantify the average error in the saddle point geometry predicted by several methods.

In previous work, we have proposed two quite different semiempirical approaches to calculating barrier heights for chemical reactions. The first, multi-coefficient correlation methods (MCCMs), builds on the success of earlier approaches such as SEC,⁸ SAC,^{9,10} Gaussian-*x* methods,^{14,33} extrapolating the one-electron basis,⁷ and MCSAC.¹¹ Two especially powerful MCCMs that emerged from this research are MC-QCISD¹⁶ and MCG3.^{13,15} The second semiempirical approach that we have advocated is hybrid DFT with one parameter for kinetics, in particular MPW1K,^{20,22} that builds on the success of earlier B3LYP¹⁹ and mPW1PW91¹⁷ methods. The present paper

TABLE 5: Mean Errors (kcal/mol) for Other // Methods

method	MSE	MUE	RMSE	cost
66 data				
QCISD(T)//QCISD/6-31+G(d,p)		3.0	3.6	2.0(4) ^a
MCG3//QCISD/6-31+G(d,p)		1.2	1.7	2.0(4)
QCISD(T)//QCISD/MG3		1.3	1.6	1.9(5)
MCG3//QCISD/MG3		1.2	1.7	1.9(5)
MC-QCISD//MPW1K/MG3		1.8	2.2	1.7(3)
MCG3//MPW1K/MG3		1.2	1.7	1.7(3)
MCG3//MC-QCISD		1.1	1.6	5.5(3)
44 barrier heights				
	2.9	3.2	3.8	
QCISD(T)//QCISD/6-31+G(d,p)	0.4	1.2	1.8	
MCG3//QCISD/6-31+G(d,p)	0.9	1.4	1.7	
QCISD(T)//QCISD/MG3	0.4	1.2	1.7	
MCG3//QCISD/MG3	1.4	1.9	2.4	
MC-QCISD//MPW1K/MG3	0.2	1.6	2.7	
MCG3//MPW1K/MG3	0.1	1.2	1.7	
MCG3//MC-QCISD	2.9	3.2	3.8	
22 energies of reaction				
QCISD(T)//QCISD/6-31+G(d,p)		2.6	3.1	
MCG3//QCISD/6-31+G(d,p)		1.1	1.8	
QCISD(T)//QCISD/MG3		0.9	1.3	
MCG3//QCISD/MG3		1.2	1.6	
MC-QCISD//MPW1K/MG3		1.4	1.8	
MCG3//MPW1K/MG3		1.3	1.6	
MCG3//MC-QCISD		1.1	1.5	

^a Power of 10 in parentheses.

presents a systematic comparison of these methods by applying them both to the same kinetics database of forward and reverse barrier heights and energies of reaction for 22 reactions and saddle point geometries for five reactions. For perspective, we also include three levels of ab initio theory, namely MP2,³⁰ QCISD,³¹ and QCISD(T).³¹ The MPW1K, MP2, and QCISD methods are each tested with two basis sets, whereas the MC-QCISD and MCG3 methods have built-in (intrinsic) basis set choices. We do not repeat comparisons in earlier papers of MPW1K to other hybrid DFT methods^{20,22} or of MC-QCISD to other MCCM and ab initio methods,¹⁶ but simply remind the reader that these methods emerged as having particularly attractive accuracy vs cost tradeoffs.

Our first test involved saddle point geometries. We will summarize these results in terms of the mean unsigned error in 5 saddle point interaction distances (making and breaking bond distances and perpendicular looseness for the 5 reactions). The second comparison involves barrier heights and energies of reaction, and we will summarize the results by focusing on the MUE in the 66 energy differences in our kinetics database. We list these two MUEs and the cost functions in Table 6, in this case listing all methods in order of increasing cost function. It is worthwhile to repeat the warning that the precise values of cost functions may depend strongly on how they are defined, but our conclusions on accuracy are independent of cost, and the actual cost function we use should be very reasonable for geometry optimization or a variety of dynamics applications. Because accurate saddle point geometries are usually required for calculating accurate barrier heights, our cost functions are also very appropriate for calculating barrier heights. Our cost function is dominated by a system with eleven atoms; as one proceeds to larger systems, the cost functions will increase in this order: MPW1K (most gradual increase), MP2, MC-QCISD, QCISD, MCG3, QCISD(T) (steepest increase).

Summarizing the data in this way makes the conclusions very apparent. Among the methods involving consistent geometry optimization (these are the methods that have a value in the geometries column in Table 6 and that are most useful for full dynamics calculations where one requires consistent energies

TABLE 6: Unsigned Error Summaries for All Methods in Order of Increasing Cost Function^a

method	MUE		
	saddle point geometries (A)	energies	cost/100
MPW1K/6	0.02	1.6	2.5
MP2/6	0.03	4.4	2.6
MC-QCISD//MPW1K/6		1.5	3.2
MCG3//MPW1K/6		1.1	3.6
MPW1K/M	0.01	1.6	16
MC-QCISD//MPW1K/M		1.6	17
MCG3//MPW1K/M		1.2	17
QCISD(T)/M//MPW1K/6		1.3	19
MP2/M	0.04	3.6	33
MC-QCISD	0.02	1.6	54
MCG3//MC-QCISD		1.1	55
QCISD/6	0.03	3.8	194
MCG3//QCISD/6		1.1	195
QCISD(T)/6//QCISD/6		3.0	195
MCG3	0.01	1.2	784
QCISD/M	0.02	2.4	1859
MCG3//QCISD/M		1.2	1860
QCISD(T)/M//QCISD/M		1.3	1875

^a In this table only, /6 denotes /6-31+G(d,p) and /M denotes /MG3.

and gradients), Table 6 shows that the MPW1K method is a clear winner for all but the highest-accuracy calculations. In particular it has better performance than MC-QCISD, QCISD, and MP2, but poorer performance than MCG3. The MCG3 method though, is relatively very expensive compared to MPW1K (although it is much faster than nonextrapolated methods such as QCISD(T) with a large basis set, which is too expensive to even include in Table 6). Although MC-QCISD is less accurate than MPW1K, it may still be very useful for reactions quite different from those in the database, at least until we get more definitive accuracy assessments for a broader range of reactions.

Among the double-slash methods, the winning strategy is clearly to use MPW1K with the smaller basis set, 6-31+G(d,p), to optimize geometries. When this is done, one can afford the MCG3 method as the high level, and this combination appears to be very accurate, a clear winner.

The answer to the question in the title to the paper is clearly MCG3//MPW1K. If one is considering a system for which hybrid DFT has not been validated, one might be more confident with a method that does not involve density functionals. In that case, MCG3//MC-QCISD is very accurate, with a moderate increase in cost.

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Supporting Information Available: Tables of gas-phase geometries for the reactants, products, and saddle points for the MC-QCISD//ML and MCG3//ML levels. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

(1) *Computational Thermochemistry*; Irikura, K. K., Frurip, D. J., Eds.; ACS Symposium Series 677; American Chemical Society: Washington, DC, 1998.

- (2) *Recent Advances in Multireference Methods*; Hirao, K., Ed.; World Scientific: Singapore, 1999.
- (3) Gräfenstein, J.; Cremer, D. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2091.
- (4) Sancho-García, J. C.; Pérez-Jiménez, A. J.; Moscardó, F. *Chem. Phys. Lett.* **2000**, *317*, 245.
- (5) Chuang, Y.-Y.; Corchado, J. C.; Truhlar, D. G. *J. Phys. Chem A* **1999**, *A103*, 1140, and references therein.
- (6) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.
- (7) (a) Peterson, K. A.; Dunning, T. H., Jr. *J. Phys. Chem.* **1995**, *99*, 3898. (b) Fast, P. L.; Sanchez, M. L. Truhlar, D. G.; *J. Chem. Phys.* **1999**, *111*, 2921.
- (8) (a) Brown, F. B.; Truhlar, D. G. *Chem. Phys. Lett.* **1985**, *117*, 307. (b) Varandas, A. J. C.; Brown, F. B.; Mead, C. A.; Truhlar, D. G.; Blais, N. C. *J. Chem. Phys.* **1987**, *86*, 6258.
- (9) Gordon, M. S.; Truhlar, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 5412.
- (10) Fast, P. L.; Corchado, J.; Sanchez, M. L.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 3139.
- (11) Fast, P. L.; Corchado, J. C.; Sánchez, M. L.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 5129.
- (12) Fast, P. L.; Sánchez, M. L.; Corchado, J. C.; Truhlar, D. G. *J. Chem. Phys.* **1999**, *110*, 11679.
- (13) Tratz, C. M.; Fast, P. L.; Truhlar, D. G. *PhysChemComm.* **1999**, *2/14*, 1.
- (14) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 1125.
- (15) Fast, P. L.; Sanchez, M. L.; Truhlar, D. G. *Chem. Phys. Lett.* **1999**, *306*, 407.
- (16) Fast, P. L.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 6111.
- (17) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.
- (18) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (19) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem. A* **1994**, *98*, 11 623.
- (20) Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 21.
- (21) Raghavachari, K.; Anderson, J. B.; *J. Phys. Chem. A* **1996**, *100*, 12 960.
- (22) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936.
- (23) Ruscic, B.; Litorja, M.; Asher, R. L. *J. Phys. Chem. A* **1999**, *103*, 8625.
- (24) Kolos, W.; Wolniewicz, L. *J. Chem. Phys.* **1965**, *43*, 2429.
- (25) Ruscic, B.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Harding, L. B.; Asher, R. L.; Wagner, A. F. *J. Phys. Chem. A* **2001**, *105*, 1.
- (26) Bian, W.; Werner, H.-J. *J. Chem. Phys.* **2000**, *112*, 220.
- (27) Diedrich, D. L.; Anderson, J. B. *J. Chem. Phys.* **1994**, *100*, 8089.
- (28) Stark, R.; Werner, H. J. *J. Chem. Phys.* **1996**, *104*, 6515.
- (29) Peterson, K. A.; Dunning, T. H. *J. Phys. Chem A* **1997**, *101*, 6280.
- (30) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
- (31) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
- (32) Francl, M. M.; Petro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
- (33) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.
- (34) Frisch, M. J.; Trucks, 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, 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. Gaussian98 (Revision A.7), Gaussian, Inc., Pittsburgh, 1998.
- (35) Multilevel-version 2.0/G98 by J. M. Rodgers, B. J. Lynch, P. L. Fast, Y.-Y. Chuang, and D. G. Truhlar, University of Minnesota, Minneapolis, 2000, based on Gaussian98 (ref 34).