

The MC-DFT Approach Including the SCS-MP2 Energies to the New Minnesota-Type Functionals

Po-Chun Liu and Wei-Ping Hu*

We have applied the multicoefficient density functional theory (MC-DFT) to four recent Minnesota functionals, including M06-2X, M08-HX, M11, and MN12-SX on the performance of thermochemical kinetics. The results indicated that the accuracy can be improved significantly using more than one basis set. We further included the SCS-MP2 energies into MC-DFT, and the resulting mean unsigned errors (MUEs) decreased by approximately 0.3 kcal/mol for the most accurate basis set

combinations. The M06-2X functional with the simple [6-311+G(d,p)/6-311+G(2d,2p)] combination gave the best performance/cost ratios for the MC-DFT and MC-SCS-MP2|MC-DFT methods with MUE of 1.58 and 1.22 kcal/mol, respectively. © 2014 Wiley Periodicals, Inc.

DOI: 10.1002/jcc.23656

Introduction

In the past two decades, density functional theory (DFT)^[1] has been the most popular theoretical method in the fields of chemistry, physics, and material sciences. On some systems, recently developed DFT methods can achieve accuracies that traditionally could only be obtained by much more expensive, wavefunction-based methods.^[2,3] The basis-set effects in conventional DFT were known to be smaller than the wavefunction-based methods that include high-level electron correlation. However, for many hybrid DFT, the sizes of the basis sets did affect the accuracy considerably.^[4,5] A few years ago, we developed the multicoefficient density functional theory (MC-DFT) approach^[6,7] as a convenient way to extrapolate the basis set to an optimal size in a DFT calculation. In the MC-DFT approach, the calculation was performed with two or three basis sets of different sizes. The differences in the calculated energies were scaled by coefficients which were determined to minimize the mean unsigned errors (MUEs) with respect to a set of accurate database values. We found that the MC-DFT methods can in most cases lead to better performance than using a single large basis set.^[6,7] The philosophy behind the approach was similar to many other multilevel or multicoefficient methods that this type of semiempirical parameterization of the scaling coefficients for electron correlation or basis set extrapolation is the most efficient way to achieve higher accuracy.^[8–14] In previous studies,^[6,7] we have tested the MC-DFT approach on several functionals, including B3LYP,^[15] B2K-PLYP,^[16] B2T-PLYP,^[16] and M06-2X.^[17] In this study, we applied the MC-DFT approach to the more recently developed Minnesota functionals, M08-HX,^[18] M11,^[19] and MN12-SX,^[20] and we compared their performance with that of M06-2X and B3LYP. Following the success of the M06 series of functionals,^[17–19] Zhao and Truhlar developed two new more accurate functionals, M08-HX and M08-SO.^[18] In 2011, Peverati and Truhlar developed a new density functional, called M11 using range-separated Hartree–Fock exchange^[19] which contained 100% of Hartree–Fock exchange at long range and an

optimum 42.8% at short range. More recently, they proposed a new density functional N12^[21] with a nonseparable gradient approximation. The N12 functional depends only on the spin-labeled electron densities and their reduced gradients. It was the first density functional that provided good accuracy for both molecular energetics and solid-state lattice constants. They then added a kinetic energy density term to N12 to obtain a more accurate functional MN12-L.^[22] Furthermore, they added a screened Hartree–Fock exchange term to the N12 and MN12-L and yielded two new functionals, N12-SX^[20] and MN12-SX. These two new functionals provided very accurate performance for both chemistry and solid-state physics.^[20] In addition to test the MC-DFT approach on the new Minnesota functionals, in the current study, we further added the MP2 and SCS-MP2 correction energies into our MC-DFT methods. The spin-component-scaling MP2 (SCS-MP2) was first proposed by Grimme,^[23] where the parallel (same)- and antiparallel (opposite)-spin correlation energies were separately scaled. The SCS-MP2 method provided a new way to increase the accuracy of the MP2 theory^[23] without additional cost. The idea of combining DFT and MP2 energies was first proposed by Truhlar and coworkers,^[13] and their “doubly hybrid” MC3BB and MC3MPW methods gave excellent performance/cost ratios as compared to wavefunction-based and several accurate hybrid DFT.^[13,14] In principle, the doubly hybrid approach can be applied directly to any functionals. Another similar approach called “double-hybrid DFT” was later developed by Grimme and coworkers.^[24–26] In this approach, the MP2 correction energies were obtained from the converged Kahn–Sham orbitals, and no additional wavefunction-based calculation was

P.-C. Liu, W.-P. Hu

Department of Chemistry and Biochemistry, National Chung Cheng University, Chia-Yi, Taiwan 621, Republic of China
E-mail: chewph@ccu.edu.tw

Contract grant sponsor: National Science Council of Taiwan; Contract grant number: NSC-100-2113-M-194-007.

© 2014 Wiley Periodicals, Inc.

needed. This could be both an advantage and a disadvantage. The double-hybrid approach can only be directly applied to those functionals with separable exchange and correlation parts, such as the Becke's exchange functional^[27] and the LYP correlation functionals.^[28] The double-hybrid approach, however, cannot be easily applied to the newer functionals such as B98,^[29] Boese-Martin functional for kinetics (BMK),^[30] M06,^[17] and so forth. The double-hybrid DFT showed significant performance improvement on predicting thermochemical kinetics.^[16,24,25,31] Very recently, Kozuch and Martin proposed a series of more accurate double-hybrid functional called dispersion corrected, spin-component scaled double hybrid DFT (DSD-DFT) which included the SCS-MP2 energies and empirical dispersion corrections.^[32] The DSD-PBEhB95 and DSD-PBEP86 functionals gave the overall best results. The MC-DFT tests on the DSD-DFT will be described in a forthcoming article.

As a further note to the current approach, the empirical basis set extrapolation in the MC-DFT method focused entirely on the electronic energies, which was also true in other basis set extrapolation methods^[33,34] and in various composite or multi-coefficient methods such as Gaussian-n,^[9,35] G3S,^[8] complete basis set (CBS),^[36,37] Wn,^[38,39] ccCA,^[40,41] HEAT,^[42,43] MCG3-DFT,^[14] and multi-level with scaled energy-DFT (MLSE-DFT).^[10] Extrapolation of the basis set effects has been known to be most crucial and most successful for predicting accurate bond energies, and, thus, it was applied primarily on the study of thermochemistry and chemical kinetics. While many recently developed all-purpose density functionals^{[17–22,24,26],[30–32,44]} have been benchmarked for a varieties of other properties such as weak interactions, molecular geometries, vibrational frequencies, and excitation energies, the prediction of these properties and the corresponding computational efficiency is not expected to be significantly improved by the current MC-DFT approach in its current form. This study thus focused on applying the MC-DFT approach to the recently developed Minnesota functionals and on the inclusion of SCS-MP2 energies for performance improvement on thermochemical kinetics.

Method

The density functionals tested included the M06-2X, M08-HX, M11, MN12-SX, and the popular B3LYP functionals. Four Dunning-type basis sets: cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ,^[45,46] five Pople-type basis sets: 6–311+G(d,p), 6–311+G(2d,2p), 6–311+(2df,2pd), 6–311+G(3df,2pd),^[47] and the MG3S basis set (G3large basis set without core polarization functions and without diffuse functions on hydrogens) were used.^[11,48,49] The following abbreviations for basis sets were used in this article:

pdz	cc-pVDZ
apdz	aug-cc-pVDZ
ptz	cc-pVTZ
aptz	aug-cc-pVTZ
Pop-dp	6–311+G(d,p)
Pop-2d2p	6–311+G(2d,2p)
Pop-2df2pd	6–311+G(2df,2pd)
Pop-3df2pd	6–311+G(3df,2pd)

The MC-DFT energy using the [B1/B2/B3] basis set combination was defined as:

$$E_{3B}(\text{MC-DFT}) = E(\text{DFT/B1}) + c_1[E(\text{DFT/B2}) - E(\text{DFT/B1})] + c_2[E(\text{DFT/B3}) - E(\text{DFT/B1})] \quad (1)$$

where "DFT" was any of the functionals listed above, and B2 and B3 were basis sets larger in size than that of B1, and c_1 and c_2 were scaling coefficients. In cases where only two basis sets were used the last term in eq. (1) was omitted. We further included the SCS-MP2 energies into the MC-DFT methods. For example, if apdz was used for the SCS-MP2 calculation and B1 was used for the DFT calculation, the combined SCS-MP2|DFT energy was

$$E_{1B}(\text{SCS-MP2|DFT}) = c_1(\text{HF/apdz} + c_o E_{E_2}^o / \text{apdz} + c_s E_{E_2}^s / \text{apdz}) + (1 - c_1)E(\text{DFT/B1}) \quad (2)$$

where $E_{E_2}^o$ and $E_{E_2}^s$ were the opposite- and same-spin correlation energies with scaling coefficients c_o and c_s , respectively. Accordingly, the SCS-MP2|MC-DFT energy calculated using three basis sets for DFT calculation was:

$$E_{3B}(\text{SCS-MP2|MC-DFT}) = c_1(\text{HF/apdz} + c_o E_{E_2}^o / \text{apdz} + c_s E_{E_2}^s / \text{apdz}) + (1 - c_1) \{E(\text{DFT/B1}) + c_2[E(\text{DFT/B2}) - E(\text{DFT/B1})] + c_3[E(\text{DFT/B3}) - E(\text{DFT/B1})]\} \quad (3)$$

In cases where only two basis sets were used for DFT calculation, the last term in eq. (3) was omitted. Similar to the MC-DFT approach, the MP2 energies can also be calculated using a basis set combination, which is called the MC-MP2 approach. If the basis set combination [pdz/apdz/ptz] was used then

$$E(\text{MC-MP2}) = \text{HF/pdz} + c_1 E_{E_2} / \text{pdz} + c_2(\text{HF/apdz} - \text{HF/pdz}) + c_3(\text{HF/ptz} - \text{HF/pdz}) + c_4[E_{E_2} / \text{apdz} - E_{E_2} / \text{pdz}] + c_5[E_{E_2} / \text{ptz} - E_{E_2} / \text{pdz}] \quad (4)$$

where E_{E_2} were the total second-order perturbation energies. We can also combined the SCS-MP2 method and the MC-MP2 approach to create the MC-SCS-MP2 method. If the combination of [pdz/apdz/ptz] was used then

$$E(\text{MC-SCS-MP2}) = \text{HF/pdz} + c_o E_{E_2}^o / \text{pdz} + c_s E_{E_2}^s / \text{pdz} + c_1(\text{HF/apdz} - \text{HF/pdz}) + c_2(\text{HF/ptz} - \text{HF/pdz}) + c_3[(c_o E_{E_2}^o / \text{apdz} + c_s E_{E_2}^s / \text{apdz}) - (c_o E_{E_2}^o / \text{pdz} + c_s E_{E_2}^s / \text{pdz})] + c_4[(c_o E_{E_2}^o / \text{ptz} + c_s E_{E_2}^s / \text{ptz}) - (c_o E_{E_2}^o / \text{pdz} + c_s E_{E_2}^s / \text{pdz})] \quad (5)$$

Note that the same c_o and c_s were used for different basis sets. It was also possible to combine the MC-DFT and MC-SCS-MP2 approaches in the following ways. If only one basis set (B1) was used for the DFT and the combination [pdz/apdz/ptz]

Table 1. Mean unsigned errors (kcal/mol) of the DFT and MC-DFT methods.

Basis set combination	B3LYP	M06-2X	M08-HX	M11	MN12-SX
pdz	11.46	8.37	8.00	8.87	6.87
apdz	9.22	6.03	6.11	6.63	6.00
ptz	5.50	2.92	3.17	2.92	3.71
pdz/ptz	4.22	2.22	1.85	2.37	2.91
pdz/apdz/ptz	3.96	1.54	1.81	2.13	2.86
aptz	4.83	1.99	2.57	2.11	3.06
pdz/ptz/aptz	3.88	1.55	1.70	1.99	2.67
MG3S	4.33	1.76	1.66	1.94	1.96
pdz/MG3S	3.87	1.53	1.59	1.94	1.95
Pop-dp	7.36	4.84	4.91	5.02	4.23
Pop-2d2p	5.45	2.66	2.48	2.43	2.39
Pop-dp/Pop-2d2p	3.78	1.58	1.66	2.04	2.23
Pop-2df2pd	4.40	1.85	1.75	2.04	2.12
Pop-dp/Pop-2df2pd	3.59	1.75	1.56	2.04	2.12
Pop-2d2p/Pop-2df2pd	3.62	1.81	1.66	2.03	2.12
Pop-dp/Pop-2d2p/ Pop-2df2pd	3.59	1.58	1.53	2.01	2.12
Pop-3df2pd	4.02	1.83	1.68	2.23	2.20
Pop-dp/Pop-3df2pd	3.58	1.82	1.68	2.10	2.16
Pop-2df2pd/Pop-3df2pd	3.70	1.81	1.64	2.04	2.10
Pop-dp/Pop-2d2p/ Pop-3df2pd	3.57	1.57	1.54	2.01	2.15

was used for the SCS-MP2 calculation, the MC-SCS-MP2|DFT energy can be written as:

$$E_{1B}(\text{MC-SCS-MP2|DFT}) = c_1 \{ \text{HF}/\text{pdz} + c_0 E_{E_2}^0/\text{pdz} + c_5 E_{E_2}^5/\text{pdz} + c_2 (\text{HF}/\text{apdz} - \text{HF}/\text{pdz}) + c_3 (\text{HF}/\text{ptz} - \text{HF}/\text{pdz}) + c_4 [(c_0 E_{E_2}^0/\text{apdz} + c_5 E_{E_2}^5/\text{apdz}) - (c_0 E_{E_2}^0/\text{pdz} + c_5 E_{E_2}^5/\text{pdz})] + c_5 [(c_0 E_{E_2}^0/\text{ptz} + c_5 E_{E_2}^5/\text{ptz}) - (c_0 E_{E_2}^0/\text{pdz} + c_5 E_{E_2}^5/\text{pdz})] \} + (1 - c_1) E(\text{DFT}/\text{B1}) \quad (6)$$

If three basis sets, for example the combination [pdz/apdz/ptz], were used for both the DFT and MP2 calculation, then the MC-SCS-MP2|MC-DFT energy was obtained by:

$$E_{3B}(\text{MC-SCS-MP2|MC-DFT}) = c_1 \{ \text{HF}/\text{pdz} + c_0 E_{E_2}^0/\text{pdz} + c_5 E_{E_2}^5/\text{pdz} + c_2 (\text{HF}/\text{apdz} - \text{HF}/\text{pdz}) + c_3 (\text{HF}/\text{ptz} - \text{HF}/\text{pdz}) + c_4 [(c_0 E_{E_2}^0/\text{apdz} + c_5 E_{E_2}^5/\text{apdz}) - (c_0 E_{E_2}^0/\text{pdz} + c_5 E_{E_2}^5/\text{pdz})] + c_5 [(c_0 E_{E_2}^0/\text{ptz} + c_5 E_{E_2}^5/\text{ptz}) - (c_0 E_{E_2}^0/\text{pdz} + c_5 E_{E_2}^5/\text{pdz})] \} + (1 - c_1) \{ E(\text{DFT}/\text{pdz}) + c_6 [E(\text{DFT}/\text{apdz}) - E(\text{DFT}/\text{pdz})] + c_7 [E(\text{DFT}/\text{ptz}) - E(\text{DFT}/\text{pdz})] \} \quad (7)$$

The coefficients in eqs. (1)–(7) above were determined by minimizing the MUE to the 211 accurate thermochemical kinetics data compiled by Truhlar and coworkers.^[50–52] The

database included 109 atomization energies from the MGAE109/11 database,^[50] 38 hydrogen transfer and 38 nonhydrogen transfer barrier heights from the HTBH38/08 and NHTBH38/08 databases,^[51] and 13 ionization potentials and 13 electron affinities from the IP13/3 and EA13/3 databases.^[52] All the electronic structure calculations, except for the M08-HX calculations, were performed using the Gaussian 09 program.^[53] The M08-HX energies were obtained using the Molpro program.^[54] The computational cost was evaluated from the sum of the CPU time required for calculating the energies of eight molecules including C₅H₅N, C₂Cl₄, C₄H₄O, C₄H₄S, C₄H₅N, CF₃CN, and SiCl₄.

Results and Discussion

Performance of the MC-DFT methods

B3LYP Functional. Table 1 showed the performance of the MC-DFT on the tested functionals. For the popular B3LYP functional, the large single basis sets aptz, MG3S, Pop-2df2pd, and Pop-3df2pd gave MUEs of 4.83, 4.33, 4.40, and 4.02 kcal/mol, respectively, which were notably smaller than those obtained using single smaller basis sets. The combinations that included these large basis sets [pdz/ptz/aptz], [pdz/MG3S], [Pop-dp/Pop-2df2pd], and [Pop-dp/Pop-2d2p/Pop-3df2pd] gave MUEs of 3.88, 3.87, 3.59, and 3.57 kcal/mol, respectively. For the Pople-type basis sets, it seemed that the combinations of two basis sets that included Pop-2df2pd were sufficient. The B3LYP functional did not perform satisfactorily for thermochemical kinetics, but the MC-DFT approach did improve the accuracy as compared to the single-basis-set results. For example, the combination [pdz/apdz/ptz] gave a significantly smaller (by ~1.5 kcal/mol) MUE than using only ptz. Similarly, the combination [Pop-dp/Pop-2df2pd] gave a smaller (by ~0.8 kcal/mol) MUE than using only Pop-2df2pd. Both the combinations gave results more accurate than the largest basis sets aptz and Pop-3df2pd. This illustrated the most essential advantage of the MC-DFT approach that the basis set combinations using smaller basis sets can often produce equally accurate or better results at less computational cost.

M06-2X Functional. The aptz, MG3S, and Pop-3df2pd basis sets gave MUEs of 1.99, 1.76, and 1.83 kcal/mol, respectively, which were significantly smaller than the B3LYP functional. The combinations [pdz/apdz/ptz], [pdz/MG3S], and [Pop-dp/Pop-2d2p/Pop-2df2pd] gave impressively small MUEs of 1.55, 1.53, and 1.58 kcal/mol, respectively. Notably, the [pdz/apdz/ptz] combination gave an MUE of 1.54 kcal/mol which was significantly better than that using aptz alone and was equally accurate to the more expensive combination [pdz/ptz/aptz]. The [pdz/MG3S] combination improved the already very accurate M06-2X/MG3S method by 0.2 kcal/mol. The very economical [Pop-dp/Pop-2d2p] combination gave results as accurate as the more expensive combination [Pop-dp/Pop-2d2p/Pop-3df2pd].

M08-HX Functional. The single large basis sets MG3S, Pop-2df2pd, and Pop-3df2pd gave slightly more accurate results than the M06-2X functional. The best basis set combination

Table 2. Mean unsigned errors (kcal/mol) of the SCS-MP2|DFT and SCS-MP2|MC-DFT method (MP2 basis set: apdz).

Basis set combination	B3LYP	M06-2X	M08-HX	M11	MN12-SX
pdz	4.68	4.48	4.35	4.53	4.01
apdz	4.13	2.86	3.11	3.49	2.87
ptz	3.66	2.51	2.24	2.63	2.71
pdz/ptz	2.58	1.71	1.71	1.92	2.43
pdz/apdz/ptz	2.54	1.51	1.64	1.92	2.09
aptz	3.23	1.68	1.71	2.03	1.98
pdz/ptz/aptz	2.57	1.43	1.49	1.81	1.96
MG3S	3.00	1.56	1.54	1.91	1.80
pdz/MG3S	2.88	1.41	1.53	1.91	1.78
Pop-dp	3.76	2.69	2.72	3.06	2.44
Pop-2d2p	3.29	1.93	1.88	2.16	2.10
Pop-dp/Pop-2d2p	2.76	1.32	1.44	1.77	2.07
Pop-2df2pd	3.09	1.70	1.66	1.95	1.94
Pop-dp/Pop-2df2pd	2.71	1.51	1.51	1.83	1.93
Pop-2d2p/Pop-2df2pd	2.78	1.64	1.62	1.92	1.92
Pop-dp/Pop-2d2p/ Pop-2df2pd	2.71	1.32	1.40	1.75	1.92
Pop-3df2pd	3.05	1.68	1.63	2.00	2.01
Pop-dp/Pop-3df2pd	2.81	1.61	1.59	1.98	2.00
Pop-2df2pd/Pop-3df2pd	3.03	1.68	1.62	1.95	1.91
Pop-dp/Pop-2d2p/ Pop-3df2pd	2.76	1.32	1.40	1.77	2.00

was found to be [Pop-dp/Pop-2d2p/Pop-2df2pd] which yielded an MUE of 1.53 kcal/mol. The MC-DFT approach also significantly lowered the MUEs than using only a single basis set. In this test, the MC-M08-HX results were very similar to those of the MC-M06-2X, and both functionals performed significantly better than B3LYP.

M11 and MN12-SX Functionals. These more recent functionals were optimized to much broader types of energies,^[19,20] they gave much more balanced performance for a wider range of interactions. As a result, their performance on main-group thermochemical kinetics was not expected to be as impressive as M06-2X or M08-HX. For the M11 and MN12-SX functional, the best single basis set MG3S yielded MUEs of 1.94 and 1.96 kcal/mol, respectively. Apparently, the increase of accuracy by the MC-DFT approach for M11 and MN12-SX was less significant than the other three functionals. As seen in Table 1, the performance of M11 and MN12-SX was quite similar, with MUEs approximately 0.3–0.4 kcal/mol higher than M06-2X and M08-HX but was nonetheless ~1 kcal/mol more accurate than B3LYP.

Performance of SCS-MP2|MC-DFT methods

Table 2 showed that performance of the SCS-MP2|MC-DFT methods. The idea of combining DFT functional and MP2 theory was similar to the N_5 multicoefficient methods developed by Truhlar and coworkers.^[13] However, the MC-DFT approach was used here for the DFT part, and the SCS-MP2 energies using the apdz basis set were used for the MP2 part. The reduction on the MUEs (relative to MC-DFT) for the best combinations was 1.5 kcal/mol for the B3LYP functional and 0.2–0.3 kcal/mol for other functionals. For B3LYP, the best combination [pdz/apdz/ptz] yielded an MUE of only 2.54 kcal/mol with the

SCS-MP2 energies, which was compared to the MUEs of 5.50 kcal/mol for the B3LYP/ptz method and 3.96 kcal/mol using the same combination but without the SCS-MP2 energies. The MUEs of other basis set combinations for the B3LYP functional were also significantly reduced. For the M06-2X functional, the combination [Pop-dp/Pop-2d2p] with SCS-MP2 energies yielded an MUE of 1.32 kcal/mol which was 0.26 kcal/mol smaller than that from the corresponding MC-DFT. For the M08-HX functional, the basis sets combination [Pop-dp/Pop-2d2p/Pop-2df2pd] yielded an MUE of 1.40 kcal/mol while the more cost effective [Pop-dp/Pop-2d2p] combination gave a similar MUE of 1.44 kcal/mol which was 0.22 kcal/mol lower than the MC-DFT results. For the M11 functional, the best combinations were [Pop-dp/Pop-2d2p] and [Pop-dp/Pop-2d2p/Pop-2df2pd] with MUEs of 1.77 and 1.75 kcal/mol, respectively. The MN12-SX functional yielded the lowest MUE of 1.78 kcal/mol with the [pdz/MG3S] combination. For the best basis set combinations, the SCS-MP2 lowered the MUEs of M11 and MN12-SX by ~0.2 kcal/mol. By including the SCS-MP2 energies, the differences in accuracy between the B3LYP and the Minnesota functionals were significantly reduced. The current results can also be compared to the similarly formulated N^5 multicoefficient methods such as MC3BB, MC3TS and MC3MPW.^[14] For the MGAE109 database, these N^5 methods gave MUEs of 2.87, 3.25, and 3.89 kcal/mol, respectively.^[14] In our test, the M06-2X and M08-HX functionals with the [Pop-dp/Pop-2d2p] combination and SCS-MP2 energies yielded the much smaller MUEs of 1.15 and 1.67 kcal/mol, respectively.

Performance of MC-SCS-MP2 and MC-SCS-MP2|MC-DFT methods

Since the MC-type approach was a very general way to extrapolate the basis set effects, it was expected that the MC-MP2 method would also improve the performance of the MP2 method. The test results by the MC-MP2 and MC-SCS-MP2 methods were included in the supporting information. As shown in Supporting Information Table S1, for every basis set combination the MP2 method was less accurate than all the functionals tested, which was expected from previous studies.^[2,3,51] The MC-MP2 approach did improve the performance of MP2 method. For example from ptz to the [pdz/apdz/ptz] combination, the MUE was reduced by 1.5 kcal/mol which paralleled the MC-DFT trends of B3LYP, M06-2X, and M08-HX. The accuracy limit of MC-MP2 seemed to be slightly over 5 kcal/mol. Supporting Information Table S1 also showed that there was a dramatic error reduction going from MC-MP2 to MC-SCS-MP2. The reduction was in most cases more than 1.5 kcal/mol. The MC-SCS-MP2 accuracy limit seemed to be slightly below 4 kcal/mol and was found to be as accurate as the MC-B3LYP methods. The [pdz/apdz/ptz] and [Pop-dp/Pop-2df2pd] seemed to be the most cost-effective combinations for the MC-SCS-MP2 methods, and thus we used the [pdz/apdz/ptz] combination for the MC-SCS-MP2 energies in subsequent MC-SCS-MP2|MC-DFT tests. Table 3 showed the performance of the MC-SCS-MP2|MC-DFT approach. We noticed that very significant improvement has been achieved as compared to the

Table 3. Mean unsigned errors (kcal/mol) of the MC-SCS-MP2|DFT and MC-SCS-MP2|MC-DFT methods (MP2 basis set: pdz/apdz/ptz).

Basis set combination	B3LYP	M06-2X	M08-HX	M11	MN12-SX
pdz	2.35	2.06	2.21	2.77	2.13
apdz	1.97	1.77	1.82	2.30	1.93
ptz	2.18	1.69	1.70	2.14	1.98
pdz/ptz	2.10	1.59	1.63	1.82	1.98
pdz/apdz/ptz	1.78	1.41	1.58	1.75	1.89
aptz	1.90	1.51	1.43	1.73	1.78
pdz/ptz/aptz	1.71	1.37	1.33	1.49	1.75
MG3S	1.81	1.39	1.35	1.76	1.72
pdz/MG3S	1.66	1.26	1.27	1.49	1.71
Pop-dp	1.94	1.75	1.49	2.03	1.86
Pop-2d2p	1.83	1.37	1.25	1.74	1.87
Pop-dp/Pop-2d2p	1.79	1.22	1.24	1.67	1.85
Pop-2df2pd	1.81	1.42	1.37	1.76	1.83
Pop-dp/Pop-2df2pd	1.77	1.41	1.35	1.75	1.82
Pop-2d2p/Pop-2df2pd	1.81	1.37	1.23	1.75	1.82
Pop-dp/Pop-2d2p/ Pop-2df2pd	1.77	1.21	1.23	1.69	1.82
Pop-3df2pd	1.81	1.51	1.49	1.81	1.89
Pop-dp/Pop-3df2pd	1.79	1.50	1.42	1.81	1.85
Pop-2df2pd/Pop-3df2pd	1.81	1.21	1.32	1.74	1.80
Pop-dp/Pop-2d2p/ Pop-3df2pd	1.77	1.20	1.20	1.66	1.84

MC-DFT and SCS-MP2|MC-DFT methods. For example, the MUEs for the B3LYP functional were lowered by approximately 1 kcal/mol as compared to the SCS-MP2|MC-DFT results. The best basis set combination, [pdz/MG3S] yielded an MUE of 1.66 kcal/mol which was 2.2 and 1.2 kcal/mol lower than the corresponding MC-B3LYP and SCS-MP2|MC-B3LYP values. The MUEs were also lowered by 0.1–0.2 kcal/mol for the most accurate basis set combinations for M06-2X and M08-HX, as compared to the SCS-MP2|MC-DFT methods. The combination [Pop-dp/Pop-2d2p] gave low MUEs of 1.22 and 1.24 kcal/mol for M06-2X and M08-HX, respectively. For the M11 functional,

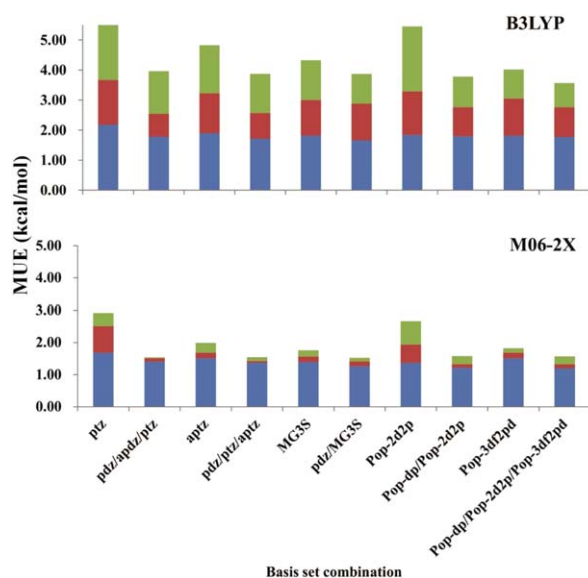


Figure 1. MUEs of the B3LYP and M06-2X functionals using various basis set combinations. The tops of the green, red, and blue bars were the results by the MC-DFT, SCS-MP2|MC-DFT, and MC-SCS-MP2|MC-DFT approaches, respectively.

Table 4. Relative computational cost^[a] and P/C ratios using the B3LYP functional.

Basis set combination	MC-B3LYP	MP2 MC-B3LYP	MC-MP2 MC-B3LYP
ptz	11% (0.29) ^[b]	20% (0.37)	46% (0.46)
pdz/apdz/ptz	20% (0.33)	28% (0.55)	54% (0.59)
aptz	91% (0.05)	99% (0.10)	125% (0.22)
pdz/ptz/aptz	105% (0.06)	113% (0.13)	139% (0.25)
MG3S	16% (0.34)	24% (0.46)	50% (0.61)
pdz/MG3S	18% (0.36)	27% (0.45)	52% (0.69)
Pop-2d2p	7% (0.50)	15% (0.60)	41% (0.73)
Pop-dp/Pop-2d2p	11% (0.64)	19% (0.67)	45% (0.69)
Pop-2df2pd	15% (0.34)	24% (0.44)	49% (0.62)
Pop-dp/Pop-2df2pd	19% (0.41)	28% (0.49)	53% (0.60)
Pop-dp/Pop-2d2p/ Pop-2df2pd	26% (0.30)	35% (0.39)	60% (0.53)
Pop-3df2pd	24% (0.25)	33% (0.33)	58% (0.52)
Pop-dp/Pop-3df2pd	29% (0.27)	37% (0.34)	63% (0.50)
Pop-dp/Pop-2d2p/ Pop-3df2pd	35% (0.22)	44% (0.30)	69% (0.46)

[a] Relative to the M06-2X/aptz calculation. [b] Numbers in parentheses refer to the performance/cost (P/C) ratios which were defined as 1/(relative cost × MUE²).

the MUEs of most combinations were lowered by 0.1–0.4 kcal/mol as compared to SCS-MP2|MC-M11 with the lowest MUE of 1.49 kcal/mol from the [pdz/ptz/aptz] and [pdz/MG3S] combinations. Although the MC-SCS-MP2|MC-M11 method was still less accurate than the MC-SCS-MP2|MC-M06-2X, they were as accurate as the MC-M06-2X methods. While the performance of the MN12-SX functional was the least affected by the MC approach, the MC-SCS-MP2 still lowered the MUEs by 0.1–0.2 kcal/mol as compared to the SCS-MP2|MC-MN12-SX results with the lowest MUE of 1.71 kcal/mol by the [pdz/MG3S] combination. Comparing the MUEs obtained using ptz and the [pdz/apdz/ptz] combination in DFT, the differences in MC-M06-2X, SCS-MP2|MC-M06-2X, and MC-SCS-MP2|MC-M06-2X methods

Table 5. Relative computational cost^[a] and P/C ratios using the M06-2X functional.

Basis set combination	MC-M06-2X	MP2 MC-M06-2X	MC-MP2 MC-M06-2X
ptz	13% (0.89) ^[b]	22% (0.73)	47% (0.74)
pdz/apdz/ptz	23% (1.81)	32% (1.38)	57% (0.88)
aptz	100% (0.25)	109% (0.33)	134% (0.33)
pdz/ptz/aptz	117% (0.36)	125% (0.39)	151% (0.35)
MG3S	26% (1.23)	35% (1.18)	60% (0.86)
pdz/MG3S	30% (1.45)	38% (1.32)	64% (0.99)
Pop-2d2p	8% (1.76)	17% (1.62)	42% (1.26)
Pop-dp/Pop-2d2p	13% (3.01)	22% (2.62)	48% (1.41)
Pop-2df2pd	17% (1.70)	26% (1.35)	51% (0.97)
Pop-dp/Pop-2df2pd	23% (1.45)	31% (1.42)	57% (0.89)
Pop-dp/Pop-2d2p/ Pop-2df2pd	30% (1.31)	39% (1.46)	65% (1.06)
Pop-3df2pd	27% (1.10)	36% (0.99)	61% (0.72)
Pop-dp/Pop-3df2pd	32% (0.93)	41% (0.94)	67% (0.67)
Pop-dp/Pop-2d2p/ Pop-3df2pd	41% (1.00)	49% (1.17)	75% (0.93)

[a] Relative to the M06-2X/aptz calculation. [b] Numbers in parentheses refer to the performance/cost (P/C) ratios which were defined as 1/(relative cost × MUE²).

Table 6. Relative computational cost^[a] and P/C ratios using the M11 functional.

Basis set combination	MC-M11	MP2 MC-M11	MC-MP2 MC-M11
ptz	16% (0.76) ^[b]	24% (0.60)	50% (0.44)
pdz/apdz/ptz	28% (0.78)	37% (0.74)	62% (0.52)
aptz	152% (0.15)	161% (0.15)	187% (0.18)
pdz/ptz/aptz	172% (0.15)	180% (0.17)	206% (0.22)
MG3S	46% (0.58)	54% (0.50)	80% (0.40)
pdz/MG3S	50% (0.54)	58% (0.47)	84% (0.54)
Pop-2d2p	11% (1.54)	20% (1.10)	45% (0.73)
Pop-dp/Pop-2d2p	18% (1.35)	26% (1.21)	52% (0.69)
Pop-2df2pd	31% (0.77)	40% (0.66)	65% (0.49)
Pop-dp/Pop-2df2pd	38% (0.64)	46% (0.64)	72% (0.45)
Pop-dp/Pop-2d2p/ Pop-2df2pd	49% (0.51)	57% (0.57)	83% (0.42)
Pop-3df2pd	61% (0.33)	69% (0.36)	95% (0.32)
Pop-dp/Pop-3df2pd	67% (0.34)	76% (0.34)	102% (0.32)
Pop-dp/Pop-2d2p/ Pop-3df2pd	78% (0.32)	87% (0.37)	113% (0.32)

[a] Relative to the M06-2X/aptz calculation. [b] Numbers in parentheses refer to the performance/cost (P/C) ratios which were defined as $1/(\text{relative cost} \times \text{MUE}^2)$.

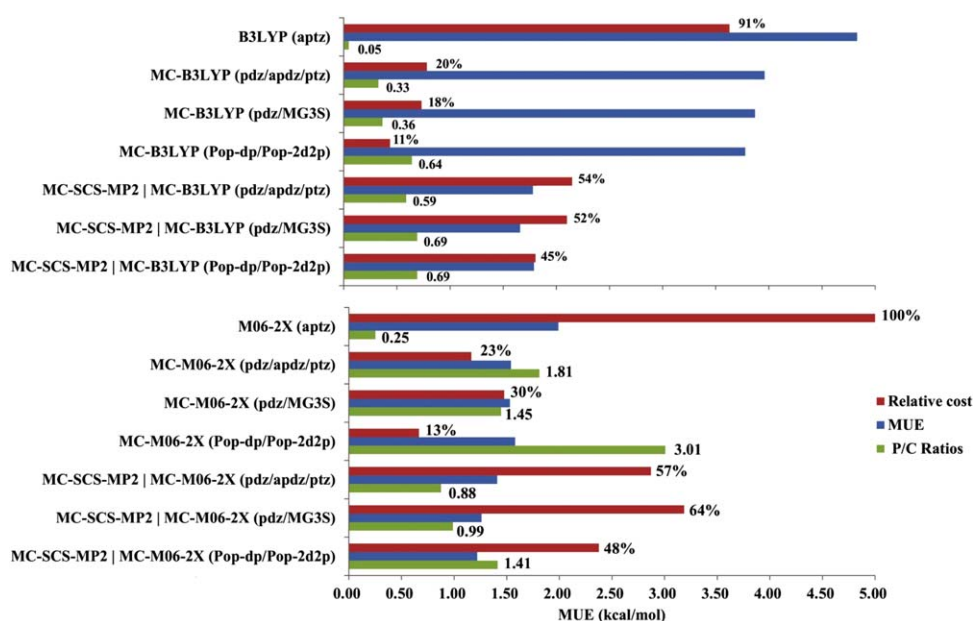
were found to be 1.4, 1.0, and 0.3 kcal/mol. Similarly, the differences in using Pop-2d2p and the [Pop-dp/Pop-2d2p] combination in the three methods were 1.1, 0.6, and 0.2 kcal/mol, respectively. This suggested that by including the MC-SCS-MP2 energies, the basis set combinations in the DFT calculation was not as crucial as in the MC-DFT methods. Conversely, the high accuracy of the MC-SCS-MP2|MC-DFT methods was not due entirely to the MC-SCS-MP2, since its accuracy limit was around 4 kcal/mol while the MC-SCS-MP2|MC-M08-HX could achieve accuracy of 1.2 kcal/mol.

Figure 1 showed the MUEs obtained by the B3LYP and M06-2X using various basis set combinations. The green bars indicated the MUE reduction from the MC-DFT to SCS-MP2|MC-

DFT, and the red bars indicated the reduction from SCS-MP2|MC-DFT to MC-SCS-MP2|MC-DFT. The MUE reduction from a single basis set to a basis set combination can be seen by comparing the neighboring bars. The corresponding figures for other functionals were included in the supporting information. In most cases, the SCS-MP2 energies reduced the MUE significantly for DFT calculation with single basis set. For the MC-DFT methods, the reduction of MUEs by the SCS-MP2 energies was also significant for the B3LYP functional, and to lesser extents for other functionals. Even the most accurate functionals, M06-2X and M08-HX, can benefit from the MC-DFT approach and the inclusion of the SCS-MP2 energies. Their MUEs were reduced from the best single basis set results of 1.8 kcal/mol to the best MC-SCS-MP2|MC-DFT results of 1.2 kcal/mol.

Computational cost and the performance/cost ratios

Tables 4–6 showed the relative computational cost of the B3LYP, M06-2X, and M11 using various basis set combinations. (The corresponding tables for M08-HX, MN12-SX, and SCS-MP2 were included in the supporting information.) Figure 2 showed the cost and accuracy graphically for several methods. The performance/cost (P/C) ratios which were defined as $1/(\text{relative cost} \times \text{MUE}^2)$ were also listed. The square to the MUE was designed to emphasize more on the accuracy. For B3LYP, the MC-DFT approach not only decreased the MUEs but also increased the P/C ratios. For example, the B3LYP/aptz had a P/C ratio of 0.05 while the MC-B3LYP with the [pdz/apdz/ptz] and [Pop-dp/Pop-2d2p] combinations gave the P/C ratios of 0.33 and 0.64, respectively. For the MC-SCS-MP2|MC-B3LYP methods, the Pop-2d2p basis set and the [pdz/apdz/ptz], [pdz/MG3S], [Pop-dp/Pop-2d2p] combinations gave both good accuracy (MUEs = 1.7–1.8 kcal/mol) with relatively higher P/C ratios of 0.6–0.7. The M06-2X/aptz method gave a P/C ratio of

**Figure 2.** MUEs, relative cost, and P/C ratios of several methods using the B3LYP and M06-2X functionals.

0.25, five times the value of B3LYP/aptz. The MC-M06-2X with the [pdz/apdz/ptz] and [Pop-dp/Pop-2d2p] combinations gave high P/C ratios of 1.81 and 3.01, respectively. For the MC-SCS-MP2|MC-M06-2X methods, the [pdz/apdz/ptz], [pdz/MG3S], and [Pop-dp/Pop-2d2p] combinations gave both very good accuracy (MUEs = 1.2–1.3 kcal/mol) and relatively high P/C ratios of 0.9–1.4. The cost and P/C ratios of M08-HX were similar to those of M06-2X. The computational cost of the M11 functional using larger basis sets was somewhat higher than that of B3LYP and M06-2X. This was possibly due to the more sophisticated range-separated exchange functional. Nevertheless, the M11 functional gave reasonably good accuracy (MUE ~2 kcal/mol), and the MC-M11 P/C ratios were higher than those of MC-B3LYP. The P/C ratios of MC-SCS-MP2|MC-M11, however, were lower than those of the MC-SCS-MP2|MC-B3LYP methods. This was because the SCS-MP2 energies lowered the MUEs of the MC-B3LYP methods much more significantly. The cost and P/C ratios of MN12-SX were similar to those of M11.

We noted that while most of the computational cost was obtained using the Gaussian 09 program, the required calculation can certainly be performed using many other modern quantum chemical packages as long as the density functionals of interest are included in the programs. Due to the different ways of implementing the SCF and MP2 methods and their relative efficiencies, the quantitative values of the relative cost and P/C ratios shown above would certainly be different using other programs or hardware architectures. However, the qualitative picture and the general trends are expected to be similar regardless of the computational platforms used.

Summary


In this study, the MC-DFT approach was applied to four recently developed Minnesota density functionals and the popular B3LYP functional. Using the MC-DFT approach, all four Minnesota functionals reached good accuracy for thermochemical kinetics with MUE equal to or less than 2 kcal/mol. We also found that the accuracy of MC-DFT methods can be significantly improved by adding the SCS-MP2 correction energies. We showed that the MC-DFT and MC-SCS-MP2|MC-DFT methods can achieve much higher accuracy at similar or less computational cost than using a single large basis set in the DFT and MP2 parts of calculation. The M06-2X and M08-HX were found to be the most accurate functionals, and the most accurate MC-DFT and MC-SCS-MP2|MC-DFT methods gave MUEs of 1.5 and 1.2 kcal/mol, respectively. The basis set combination [Pop-dp/Pop-2d2p] stood out in the current study to have the highest performance/cost ratios in most of the methods tested. The combinations [pdz/apdz/ptz] and [pdz/MG3S] were also good choices for the MC-DFT and MC-SCS-MP2|MC-DFT methods.

Acknowledgments

The authors are grateful to the National Center for High-Performance Computing (NCHC) for providing part of the computational resource. The authors are also grateful to the helpful discussion with Dr. Jien-Lian Chen and Mr. Chia-Yu Peng.

Keywords: Minnesota functionals • multicoefficient DFT • SCS-MP2 • doubly hybrid DFT • thermochemical kinetics • basis set combinations

How to cite this article: P.-C. Liu, W.-P. Hu, *J. Comput. Chem.* **2014**, *35*, 1560–1567. DOI: 10.1002/jcc.23656

 Additional Supporting Information may be found in the online version of this article.

- [1] W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, *140*, A1133.
- [2] Y. Zhao, B. J. Lynch, D. G. Truhlar, *J. Phys. Chem. A* **2004**, *108*, 2715.
- [3] Y. Zhao, N. González-García, D. G. Truhlar, *J. Phys. Chem. A* **2005**, *109*, 2012.
- [4] A. D. Boese, J. M. L. Martin, N. C. Handy, *J. Chem. Phys.* **2003**, *119*, 3005.
- [5] L. A. Curtiss, P. C. Redfern, K. Raghavachari, *J. Chem. Phys.* **2005**, *123*, 124107.
- [6] J.-L. Chen, Y.-L. Sun, K.-J. Wu, W.-P. Hu, *J. Phys. Chem. A* **2008**, *112*, 1064.
- [7] J.-L. Chen, J.-T. Hong, K.-J. Wu, W.-P. Hu, *Chem. Phys. Lett.* **2009**, *468*, 307.
- [8] L. A. Curtiss, K. Raghavachari, P. C. Redfern, J. A. Pople, *J. Chem. Phys.* **2000**, *112*, 1125.
- [9] L. A. Curtiss, P. C. Redfern, K. Raghavachari, *J. Chem. Phys.* **2007**, *126*, 084108.
- [10] Y.-L. Sun, T.-H. Li, J.-L. Chen, W.-P. Hu, *Chem. Phys. Lett.* **2009**, *475*, 141.
- [11] P. L. Fast, M. L. Sanchez, D. G. Truhlar, *Chem. Phys. Lett.* **1999**, *306*, 407.
- [12] B. J. Lynch, D. G. Truhlar, *J. Phys. Chem. A* **2003**, *107*, 3898.
- [13] Y. Zhao, B. J. Lynch, D. G. Truhlar, *J. Phys. Chem. A* **2004**, *108*, 4786.
- [14] Y. Zhao, B. J. Lynch, D. G. Truhlar, *Phys. Chem. Chem. Phys.* **2005**, *7*, 43.
- [15] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.
- [16] A. Tarnopolsky, A. Karton, R. Sertchook, D. Vuzman, J. M. L. Martin, *J. Phys. Chem. A* **2008**, *112*, 3.
- [17] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
- [18] Y. Zhao, D. G. Truhlar, *J. Chem. Theory Comput.* **2008**, *4*, 1849.
- [19] R. Peverati, D. G. Truhlar, *J. Phys. Chem. Lett.* **2011**, *2*, 2810.
- [20] R. Peverati, D. G. Truhlar, *Phys. Chem. Chem. Phys.* **2012**, *14*, 16187.
- [21] R. Peverati, D. G. Truhlar, *J. Chem. Theory Comput.* **2012**, *8*, 2310.
- [22] R. Peverati, D. G. Truhlar, *Phys. Chem. Chem. Phys.* **2012**, *14*, 13171.
- [23] S. Grimme, *J. Chem. Phys.* **2003**, *118*, 9095.
- [24] S. Grimme, *J. Chem. Phys.* **2006**, *124*, 034108.
- [25] T. Schwabe, S. Grimme, *Phys. Chem. Chem. Phys.* **2006**, *8*, 4398.
- [26] L. Goerigk, S. Grimme, *J. Chem. Theory Comput.* **2011**, *7*, 291.
- [27] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
- [28] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
- [29] H. L. Schmider, A. D. Becke, *J. Chem. Phys.* **1998**, *108*, 9624.
- [30] A. D. Boese, J. M. L. Martin, *J. Chem. Phys.* **2004**, *121*, 3405.
- [31] A. Karton, A. Tarnopolsky, J.-F. Lame're, G. C. Schatz, J. M. L. Martin, *J. Phys. Chem. A* **2008**, *112*, 12868.
- [32] S. Kozuch, J. M. L. Martin, *J. Comput. Chem.* **2013**, *34*, 2327.
- [33] K. A. Petersson, D. E. Wood, T. H. Dunning, Jr., *J. Chem. Phys.* **1994**, *100*, 7410.
- [34] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, J. Olsen, *Chem. Phys. Lett.* **1999**, *302*, 437.
- [35] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, J. A. Pople, *J. Chem. Phys.* **1998**, *109*, 7764.
- [36] J. W. Ochterski, G. A. Petersson, J. A. Montgomery, Jr., *J. Chem. Phys.* **1996**, *104*, 2598.
- [37] J. A. Montgomery, M. J. Frisch, J. W. Ochterski, G. A. Petersson, *J. Chem. Phys.* **1999**, *110*, 2822.
- [38] A. Karton, E. Rabinovich, J. M. L. Martin, *J. Chem. Phys.* **2006**, *125*, 144108.
- [39] A. Karton, S. Daon, J. M. L. Martin, *Chem. Phys. Lett.* **2011**, *510*, 165.
- [40] N. J. DeYonker, T. R. Cundari, A. K. Wilson, *J. Chem. Phys.* **2006**, *104*, 114104.
- [41] A. Mahler, A. K. Wilson, *J. Chem. Theory Comput.* **2013**, *9*, 1402.

- [42] A. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, J. F. Stanton, *J. Chem. Phys.* **2004**, *121*, 11599.
- [43] M. E. Harding, J. Vázquez, B. Ruscic, A. K. Wilson, J. Gauss, J. F. Stanton, *J. Chem. Phys.* **2008**, *128*, 114111.
- [44] S. Kozuch, D. Gruzman, J. M. L. Martin, *J. Phys. Chem. C* **2010**, *114*, 20801.
- [45] R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796.
- [46] D. E. Woon, T. H. Dunning, Jr., *J. Chem. Phys.* **1993**, *98*, 1358.
- [47] W. J. Hehre, L. Radom, P. V. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*; Wiley-VCH: New York, **1986**.
- [48] L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, J. A. Pople, *J. Chem. Phys.* **1999**, *110*, 4703.
- [49] B. J. Lynch, Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2003**, *107*, 1384.
- [50] R. Peverati, D. G. Truhlar, *J. Chem. Phys.* **2011**, *135*, 191102.
- [51] J. Zheng, Y. Zhao, D. G. Truhlar, *J. Chem. Theory Comput.* **2009**, *5*, 808.
- [52] Y. Zhao, N. E. Schultz, D. G. Truhlar, *J. Chem. Theory Comput.* **2006**, *2*, 364.
- [53] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, **2013**.
- [54] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, MOLPRO, version 2012.1, **2012**. A Package of Ab Initio Programs.

Received: 19 March 2014
Revised: 15 May 2014
Accepted: 28 May 2014
Published online on 13 June 2014