

G4-SP, G4(MP2)-SP, G4-sc, and G4(MP2)-sc: Modifications to G4 and G4(MP2) for the Treatment of Medium-Sized Radicals

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Abstract: The G4-SP and G4(MP2)-SP procedures are introduced, as alternatives to G4 and G4(MP2), to overcome shortcomings associated with the treatment of spin polarization (SP) in large open-shell systems. The new methods employ a converging SP term, to replace the diverging A' treatment used in the G4 and G4(MP2) formulations. The G4-SP and G4(MP2)-SP procedures have mean absolute deviations (MADs) from experimental energies of 3.49 and 4.37 kJ mol⁻¹, respectively, for the G3/05 test set, which are comparable to the MAD values for G4 and G4(MP2) but eliminate the problem of a diverging A' term. For energies involving larger radicals, G4(MP2)-SP performs better than standard G4(MP2). Alternative methods, including G4-5H, G4(MP2)-5H, G4-sc, and G4(MP2)-sc, are also introduced to avoid the problem of an indefinitely increasing SP correction in standard G4 or G4(MP2) for reactions involving larger open-shell systems.

1. Introduction

The Gaussian series (G_n) of composite quantum chemistry methods were formulated by Curtiss, Raghavachari, and Pople et al. for the accurate evaluation of thermochemical properties using a series of relatively inexpensive component calculations.¹ The latest among the G_n series, namely G4,^{1d} has achieved impressive accuracy, with a mean absolute deviation (MAD) from experimental values of 3.48 kJ mol⁻¹ (0.83 kcal mol⁻¹) for the G3/05 test set² of 456 energies. More economical versions of G_n , termed $G_n(\text{MP2})$,³ have also been developed, that have a slightly lower accuracy. For instance, G4(MP2)^{3c} produces an MAD of 4.36 kJ mol⁻¹ (1.04 kcal mol⁻¹) for the G3/05 test set.

An empirical correction term called the “higher level correction” (HLC) is an integral part of the G_n and $G_n(\text{MP2})$

methods and was introduced to compensate for any residual deficiencies of the methods. For G3^{1c} and G3(MP2),^{3b} the HLC for molecular species takes the form $-An_\beta - B(n_\alpha - n_\beta)$, where A and B are parameters derived from empirical fitting to reliable experimental thermochemical data and n_α and n_β are the number of valence α and β electrons. As n_α and n_β are equal for closed-shell species, the HLC is simplified to $-An_\beta$ for such molecules. For G4 and G4(MP2), this component of the HLC for closed-shell species has the same form as that for G3, i.e., $-An_\beta$. For open-shell molecular species, however, a slightly different HLC has been introduced, which takes the form $-A'n_\beta - B(n_\alpha - n_\beta)$. The additional A' parameter was introduced in order to account for deficiencies in the treatment of open-shell systems.

It has recently been pointed out⁴ that the new form of HLC in G4 and G4(MP2) introduces a correction term for many radical reactions, such as radical additions and hydrogen abstractions, which was not present in earlier G_n procedures such as G3. For example, it is easy to show that for a generic radical-addition reaction:

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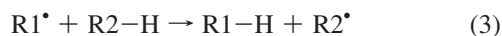
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the HLC correction with G4 or G4(MP2) is

$$(A - A')n_{\beta}(X) \quad (2)$$

Similarly, for a hydrogen-abstraction reaction:



the HLC contribution to the reaction is

$$(A - A')[n_{\beta}(R2^{\bullet}) - n_{\beta}(R1^{\bullet})] \quad (4)$$

Equation 2 indicates that for an addition reaction, the G4 HLC contribution is directly proportional to the size of X, the molecule to which R^{\bullet} is to be added. For a hydrogen-abstraction reaction, eq 4 indicates that the correction is proportional to the difference in the size of R1 and R2. Thus, as the size of the species in a radical reaction increases, the standard G4 HLC correction to the reaction energy may grow to a very large number.

This growth in the correction term seems somewhat counterintuitive. For example, in the stabilization energy reaction,



we might expect a substantial cancellation of errors in the calculation of the reaction energy using methods such as CCSD(T) with a large basis set, giving good results without the need for an empirical correction. However, standard G4 would lead to an HLC correction for reaction 5 of $-(18 + 9n)(A - A')$, which increases rapidly with n . For example, for $n = 10$, the HLC correction amounts to $-51.3 \text{ kJ mol}^{-1}$.

In the present study, we attempt to address this issue by examining three ways of reducing or eliminating the dependence of the HLC on the size of the system. First, we examine the effect of not having a separate A' parameter (i.e., as is the case in G3), thus reducing the number of empirical parameters to 5. This gives rise to G4-5H and G4(MP2)-5H (5H for 5 HLC parameters). Second, we examine whether the type of spin-contamination correction (sc) successfully used for open-shell systems by Petersson et al. in the CBS-QB3⁵ and W1Usc⁶ procedures would compensate for the removal of the A' parameter. This gives rise to G4-sc and G4(MP2)-sc (sc for spin contamination). Finally, we explore whether the use of damping in conjunction with the A' correction can alleviate the problems associated with a spin-polarization correction that increases indefinitely. This gives rise to G4-SP (SP for spin polarization) and G4(MP2)-SP.

2. Computational Details

Standard ab initio molecular orbital theory and density-functional theory (DFT) calculations⁷ were carried out with the Gaussian 09 program.⁸ Geometries were optimized at the B3-LYP/6-31G(2df,p) level. Zero-point vibrational energies (ZPVEs) and thermal corrections to enthalpy (ΔH) at 298 K, derived from scaled (0.9854) B3-LYP/6-31G(2df,p) frequencies, were incorporated into the total energy where

appropriate. W1⁹ single-point energies were obtained using B3-LYP/6-31G(2df,p) geometries and include ZPVEs and, for the calculation of heats of formation, thermal corrections, obtained with scaled B3-LYP/6-31G(2df,p) frequencies, i.e., W1//B3-LYP/6-31G(2df,p). Unless otherwise noted, empirical parameters are optimized by minimizing the MAD for the G3/05 test set.² The HLC parameters are listed in mhartree, while relative energies are reported in kJ mol^{-1} . All reported deviations are obtained as $E(\text{calculated}) - E(\text{reference})$.

3. Results and Discussion

3.1. G4-5H and G4(MP2)-5H Procedures. The dilemma of an indefinitely increasing HLC contribution arises from the use of different parameters, A and A' , for the number of β electrons in closed- and open-shell species, respectively. The most straightforward means to correct this problem is to eliminate A' and use a single parameter A for both closed- and open-shell species. This reduces the number of empirical HLC parameters to five. Using the G3/05 test set, we have reoptimized these five parameters (namely A , B , C , D , and E) of G4 and G4(MP2), and we term the modified procedures G4-5H and G4(MP2)-5H. We have also applied these new methods to the set of 49 radical reactions of Coote (referred to as the RR49 set).⁴ The RR49 set comprises 21 radical-addition reactions and 28 hydrogen-abstraction reactions, in which W1 values are used as benchmarks. The optimized parameters and indicators of the performance of the various G4-type procedures are shown in Table 1, which also includes corresponding data for the G4-sc and G4(MP2)-sc procedures, to be discussed in Section 3.2, as well as those for G4-SP and G4(MP2)-SP to be discussed in Section 3.3.

It is apparent that the exclusion of the A' parameter from G4 leads to slightly less good agreement with the G3/05 set of experimental data, as reflected in the slightly larger value of the MAD for G4-5H compared with G4 (though the largest deviation (LD) is smaller). On the other hand, the performance for the RR49 set is improved. However, this overall improvement is not uniform across the two types of reaction. Thus, omission of A' leads to a larger MAD for addition reactions but a smaller MAD for hydrogen abstraction. This is consistent with the previous observation,⁴ that the exclusion of the HLC from G4 makes the performance worse for radical additions but leads to an improvement for hydrogen abstraction. A comparison between G4(MP2) and G4(MP2)-5H results in the same observations. Why does omission of the A' parameter lead to the deterioration for radical-addition reactions? Why does it lead to an improvement for hydrogen abstraction? To address these questions, we compare the heats of formation (ΔH_f , 298 K) calculated for the component closed-shell molecules and radicals in the RR49 set with the W1 values (Table 2).

We can see that G4 and G4-5H perform comparably for the closed-shell species. However, the exclusion of A' from G4 leads to a somewhat poorer description by G4-5H for the radicals. Both G4 and G4-5H give larger deviations from the W1 results for the reactants in the hydrogen-abstraction reactions (mainly saturated species) than for the reactants in

Table 1. HLC Parameters A, A', B, C, D, E, s, and a (mhartree) and r for Various G4-Type Procedures and Indicators of Their Performance for the Various Test Sets (kJ mol⁻¹)

	G4	G4-5H	G4-sc	G4-SP	G4(MP2)	G4(MP2)-5H	G4(MP2)-sc	G4(MP2)-SP
A	6.947	6.727	6.741	6.946	9.472	9.570	9.914	9.477
A'	7.128				9.769			
B	2.441	3.101	2.890	2.426	3.102	4.686	4.434	3.103
C	7.116	6.897	6.911	7.115	9.741	9.838	10.166	9.741
D	1.414	1.304	1.300	1.414	2.115	2.162	2.312	2.121
E	2.745	2.725	1.642	1.816	2.379	2.810	2.962	2.769
s			3.914				9.799	
a				0.202				0.329
r				0.962				0.962
G3/05 ^a								
MD ^b	-0.21	-0.17	-0.32	-0.22	-0.80	-0.69	-0.67	-0.74
MAD ^c	3.48	3.58	3.51	3.49	4.36	4.60	4.47	4.37
LD ^d	-37.30	-32.01	-31.46	-36.09	-41.61	-33.04	-31.58	-39.62
STD ^e	4.96	4.98	4.94	4.96	6.22	6.37	6.23	6.21
NO ^f	36	39	40	38	69	80	73	67
RR49 ^g								
MD	1.79	0.97	1.02	1.68	2.44	1.10	1.22	2.26
MAD	2.75	2.21	2.09	2.27	4.44	2.96	2.67	3.46
LD	5.55	8.25	8.14	4.46	8.81	8.07	7.80	6.97
STD	2.56	2.79	2.63	1.94	4.48	3.48	3.12	3.26
NO	0	0	0	0	3	0	0	0
ADD ^h								
MD	-0.39	3.69	3.51	0.34	-1.99	4.70	4.25	-0.76
MAD	1.87	3.74	3.56	1.70	2.68	4.70	4.25	2.02
LD	-4.49	8.25	8.14	4.14	-7.42	8.07	7.80	-5.58
STD	2.27	2.11	2.06	2.12	2.72	1.96	2.00	2.38
NO	0	0	0	0	0	0	0	0
ABS ⁱ								
MD	3.42	-1.07	-0.85	2.69	5.75	-1.60	-1.05	4.53
MAD	3.42	1.07	0.99	2.69	5.75	1.65	1.48	4.53
LD	5.55	-3.42	-3.32	4.46	8.81	-4.51	-4.25	6.97
STD	1.17	0.71	0.86	0.95	1.88	1.03	1.37	1.48
NO	0	0	0	0	3	0	0	0
MSM11 ^j								
MD					-11.46	11.01	8.08	-1.07
MAD					9.00	8.94	6.43	3.63
LD					-23.58	22.39	11.97	-11.48
STD					8.23	6.46	3.93	5.72
NO					6	8	7	1

^a The G3/05 test set of ref 2. ^b Mean deviation. ^c Mean absolute deviation. ^d Largest deviation. ^e Standard deviation. ^f Number of outliers (absolute deviation > 8.4 kJ mol⁻¹ (~2 kcal mol⁻¹)). ^g The radical reaction test set of ref 4. ^h Radical-addition subset of RR49. ⁱ Hydrogen-abstraction subset of RR49. ^j Experimental IE values taken from the NIST Chemistry Webbook¹⁰ and ref 11.

the radical-addition reactions (unsaturated species). A detailed analysis of individual deviations for the radical-addition reactions (see Supporting Information, Table S2) shows that the poorer performance of G4-5H can be attributed mainly to the larger deviations for radicals. The apparent improved accuracy for hydrogen abstraction is also primarily due to the inferior description of radicals, which leads to a fortuitous cancellation of errors with those for the closed-shell reactants. We again find that the differences between G4(MP2) and G4(MP2)-5H are similar to those observed between G4 and G4-5H.

3.2. Spin-Corrected G4 and G4(MP2) Procedures.

With the benefit of knowing how the additional parameter A' affects the accuracy of G4 for different types of species, can we formulate an alternative form of parametrization, that retains the accuracy of G4 on radical species, but without the feature of a diverging HLC? One approach that has been used by Petersson et al. to account for deficiencies in the theoretical descriptions of radicals is to introduce a spin-correction (sc) term, such as the one employed in the CBS-

QB3⁵ and the W1Usc⁶ procedures. The spin-correction term (ΔE_{sc}) is given by the general formula:

$$\Delta E_{sc} = -s\Delta\langle S^2 \rangle \quad (6)$$

where s is a fitted parameter and $\Delta\langle S^2 \rangle$ is the deviation of the UHF spin-squared expectation value $\Delta\langle S^2 \rangle$ from the ideal value.

We have introduced this simple expression for the spin correction (ΔE_{sc}) in G4-5H and G4(MP2)-5H. The value of $\Delta\langle S^2 \rangle$ is evaluated with $\langle S^2 \rangle$ obtained from the UHF/aug-cc-pV5Z and UHF/aug-cc-pV(Q+d)Z calculations, for G4 and G4(MP2), respectively. The five HLC parameters A–E, as well as s , are optimized using the G3/05 set. The new procedures are termed G4-sc and G4(MP2)-sc, and have six HLC parameters.

For the G3/05 set, we see (Table 1) that the inclusion of ΔE_{sc} leads to a slightly smaller MAD than G4-5H. In a similar vein, G4(MP2)-sc also performs slightly better than G4(MP2)-5H. For the RR49 set, we again see a slightly lower

Table 2. Performance of G4-Type Procedures Compared With W1 for the Heats of Formation for Species Involved in the RR49 Set of Reactions (kJ mol⁻¹)^a

	G4	G4-5H	G4-sc	G4-SP	G4 (MP2)	G4 (MP2)-5H	G4 (MP2)-sc	G4 (MP2)-SP
Closed-Shell Reactants (X) in Radical-Addition Reactions (15)								
MD	1.54	1.53	1.58	1.55	0.55	0.50	0.52	0.59
MAD	3.01	3.01	3.01	3.01	3.61	3.59	3.54	3.62
LD	5.39	5.39	5.49	5.40	-8.82	-8.85	-8.72	-8.81
STD	3.02	3.02	3.00	3.02	4.33	4.32	4.26	4.33
NO	0	0	0	0	0	0	0	0
Closed-Shell Reactants (R2-H) in Hydrogen-Abstraction Reactions (22)								
MD ^b	4.78	4.77	4.79	4.79	5.08	5.01	4.93	5.14
MAD ^c	4.98	4.97	4.96	4.99	5.92	5.86	5.75	5.98
LD ^d	8.24	8.22	8.21	8.25	9.74	9.66	9.47	9.74
STD ^e	2.61	2.61	2.56	2.61	4.21	4.20	4.10	4.23
NO ^f	0	0	0	0	3	3	3	3
Radicals in Radical-Addition and Hydrogen-Abstraction Reactions (29)								
MD	0.30	4.02	4.30	0.95	-1.30	4.04	4.29	-0.22
MAD	1.62	4.34	4.54	1.86	2.54	4.96	5.06	2.41
LD	-7.17	7.37	7.77	-6.60	-15.77	-10.50	-9.54	-14.95
STD	2.21	2.44	2.59	2.18	3.73	3.81	3.97	3.65
NO	0	0	0	0	0	0	1	0
All Species in Radical-Addition and Hydrogen-Abstraction Reactions (66)								
MD	2.24	4.35	4.51	2.61	1.45	4.46	4.57	2.09
MAD	3.07	4.61	4.72	3.21	4.00	5.35	5.35	3.95
LD	8.24	8.22	8.21	8.25	-15.77	-10.50	-9.54	-14.95
STD	3.26	2.52	2.56	3.04	5.04	3.97	4.00	4.71
NO	0	0	0	0	3	3	4	3

^a From test set of ref 4. ^b Mean deviation. ^c Mean absolute deviation. ^d Largest deviation. ^e Standard deviation. ^f Number of outliers (absolute deviation > 8.4 kJ mol⁻¹ (~2 kcal mol⁻¹)).

MAD for G4-sc compared with G4-5H, for both the radical-addition reactions and hydrogen abstraction. There is also a more pronounced improvement for G4(MP2)-sc over G4(MP2)-5H. Thus, inclusion of the ΔE_{sc} term leads to a consistent improvement for both G4-5H and G4(MP2)-5H.

Despite this improvement, we find that G4-sc and G4-(MP2)-sc still perform slightly less well than standard G4 and G4(MP2) for the G3/05 test set. On the other hand, the sc variants show significantly improved overall performance for the RR49 set compared with G4 and G4(MP2). When we inspect the component species in the RR49 reactions (Table 2), we see that, like G4-5H and G4(MP2)-5H, the improvement in the reaction energies is partly the result of a fortuitous cancellation of errors, rather than a broad improvement for all species. Thus, while G4-sc performs comparably to G4 for closed-shell molecules, it deviates more substantially from W1 than does G4 for radicals. Similar features are observed for G4(MP2)-sc versus G4(MP2).

3.3. Formulation of the G4-SP and G4(MP2)-SP Procedures. We have seen in the last section that the “sc” procedures provide an alternative to G4 and G4(MP2), with an accuracy that approaches that of the original methods but without the shortcoming of a divergent A' correction term. In this section, we derive a second type of alternative, represented by G4-SP and G4(MP2)-SP. We aim to further close the gap in performance with G4 and G4(MP2), in addition to eliminating the drawback of a diverging HLC.

In the original G4 procedure,^{1d} the A' parameter was introduced to account for the effect of spin polarization by the radical center to the rest of the molecule. As such, one may consider A' as a perturbed version of the parameter A :

$$A' = A + x \quad (7)$$

Thus, the HLC for radicals can be written as:

$$-(A + x)n_{\beta} - B(n_{\alpha} - n_{\beta}) \quad (8)$$

The problem that exists with G4 is that the correction term increases linearly with n_{β} , i.e., each of the β electrons has the same individual effect in a large radical as they do in a small radical, and so, the total effect for n_{β} electrons, i.e., $-xn_{\beta}$ or $-(A' - A)n_{\beta}$, is likely to be overestimated. A more reasonable physical picture comes about by allowing the effect of successive electrons to be damped. This can be accomplished using a geometric series with ratio $r < 1$ and leads to contributions to xn_{β} of the individual n_{β} electrons in the HLC (eq 8) being of the form:

$$ar^{m-1} \quad (m = 1, \dots, n_{\beta}) \quad (9)$$

Standard G4 corresponds to $a = A' - A$ and $r = 1$, with each of the n_{β} electrons making an equal contribution of $A - A'$.

The sum for n_{β} electrons (for $r \neq 1$) is then:

$$xn_{\beta} = \sum_{m=1}^{n_{\beta}} ar^{m-1} = \frac{a(1 - r^{n_{\beta}})}{1 - r} \quad (10)$$

In this formulation, if $r < 1$, then as n_{β} becomes large the individual contributions of the β electrons (eq 9) approach zero and the sum (eq 10) approaches the limiting value:

$$\frac{a}{1 - r} \quad (11)$$

For radicals with no β electrons, i.e., $n_{\beta} = 0$, there is no correction for spin polarization, as should be the case. The

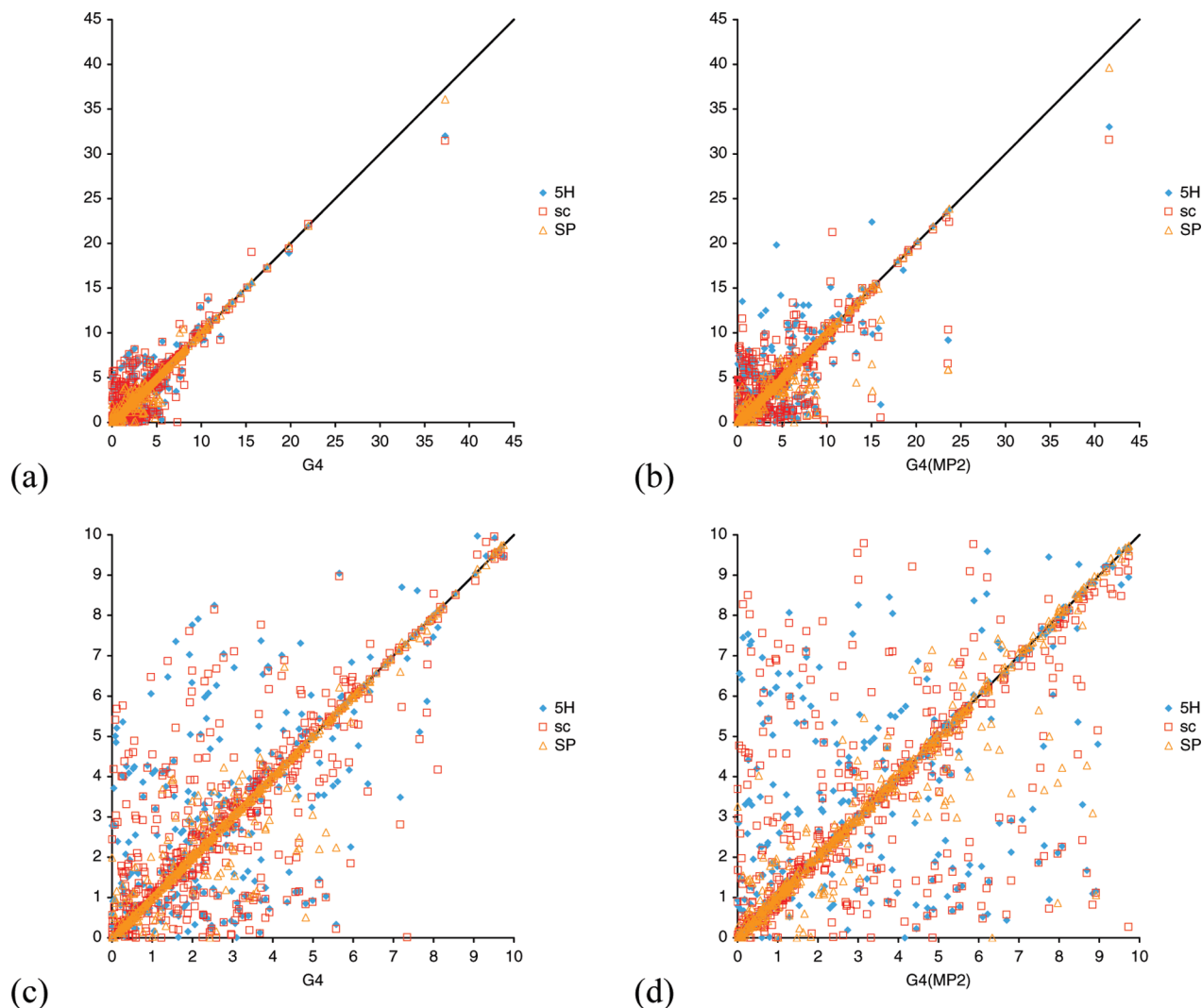


Figure 1. Absolute deviations (kJ mol^{-1}) for the modified versus the original procedures for G4 (G3/05 and RR49 sets) and G4(MP2) (G3/05, RR49, and MSM11 sets). The full set of results are presented in (a) (G4) and (b) (G4(MP2)), while expanded displays of the region up to 10 kJ mol^{-1} are presented in (c) (G4) and (d) (G4(MP2)).

term a represents the correction for the most proximate electron, while the parameter r governs the rate of decay for such a correction. Together, they determine the maximum correction for spin polarization in a radical. The total number of HLC parameters for G4-SP and G4(MP2)-SP is then seven.

In order to obtain appropriate optimum values for a and r , we need to include thermochemical data for larger molecules to allow for a representation of the converging behavior of spin polarization. To this end, we have added ionization energy (IE) data for a total of 11 larger molecules to the G3/05 set. These species include four polycyclic aromatic hydrocarbons (PAH): naphthalene (C_{10}H_8), anthracene ($\text{C}_{14}\text{H}_{10}$), pyrene ($\text{C}_{16}\text{H}_{10}$), and coronene ($\text{C}_{24}\text{H}_{12}$); three diamondoids: adamantane ($\text{C}_{10}\text{H}_{16}$), diadamantane ($\text{C}_{14}\text{H}_{20}$), and triadamantane ($\text{C}_{18}\text{H}_{24}$); two perfluorocarbons (PFC): perfluorobenzene (C_6F_6) and perfluoronaphthalene (C_{10}F_8); and finally CCl_4 and SF_6 . We term this collection of IEs the medium-sized-molecule (MSM11) set and the enlarged G3/05 set G3/05+. Optimization for G4(MP2) over this larger set yields $r = 0.962$.

Whereas all the parameters for G4(MP2)-SP are optimized using the full G3/05+ set, single-point G4 calculations for several of the MSM11 molecules are not computationally tractable for us at the present time. Consequently, to obtain the parameters for G4-SP, we assume that the value for r in G4-SP is the same as that in G4(MP2)-SP, i.e., 0.962. The HLC parameters A–E and a are then optimized using G3/05.

Having obtained the optimized parameters, we can describe the protocol for G4-SP and G4(MP2)-SP as follows: (1) Geometry optimization and harmonic frequency calculations are performed at the B3-LYP/6-31G(2df,p) level. ZPVEs and thermal corrections are obtained using frequencies scaled by 0.9854. (2) A series of single-point energies are obtained to approximate the CCSD(T)/CBS energy using composite schemes detailed in the G4^{1d} and G4(MP2)^{3c} papers. (3) An empirical higher-level correction (HLC) is added to the total energy. This takes the same form as detailed in G4 and G4(MP2), with the exception of open-shell molecular species, for which the (n_α, n_β) component of the HLC term is obtained as $-An_\beta - B(n_\alpha - n_\beta)$. The new

values for these parameters are included in Table 1. (4) In addition, for open-shell molecular species, a spin-polarization (SP) correction term is added to the total energy. This takes the form $a(1 - r^{n_\beta})/(1 - r)$, where n_β is the number of β electrons, $a = 0.202$ and 0.329 hartrees for G4-SP and G4(MP2)-SP, respectively, and $r = 0.962$ for both procedures.

3.4. Performance of G4-SP and G4(MP2)-SP. How do the “SP” procedures compare with the “sc” procedures? We can see from Table 1 that the SP procedures give slightly lower MAD values for the G3/05 set, with statistical indicators very similar to the original G4 and G4(MP2). For the RR49 set and its subsets, G4-SP appears to be superior to G4, and G4(MP2)-SP also compares favorably to G4(MP2). G4-sc and G4(MP2)-sc perform even better for the overall RR49 set, due to a smaller MAD for the abstraction reactions. However, it is evident from Table 2 that this is mainly due to the poorer description of the radicals, rather than to an improved performance for the closed-shell species. Comparison of the various G4(MP2) procedures for the IEs of the larger molecules (Table 1) shows quite striking results. We find that G4(MP2)-sc performs somewhat better than G4(MP2) and G4(MP2)-5H, while a more pronounced improvement can be seen for the G4(MP2)-SP procedure.

Figure 1 displays plots of the absolute deviations (from experiment or W1) of the various modified procedures against results for standard G4 and G4(MP2). It is apparent that, for most of the data, the “SP” procedures perform very similarly to G4 and G4(MP2), while they show improvement in a number of cases. Overall, the “5H” and “sc” procedures do not perform quite as well. There are somewhat more cases where these two types of modification lead to larger deviations than G4 and G4(MP2), i.e., they lie above the line, than cases where smaller deviations are achieved. Thus, we recommend the general use of G4-SP and G4(MP2)-SP as alternatives to G4 and G4(MP2). Nonetheless, the use of the “sc” methods may be beneficial for specific applications in which cancellation of errors may lead to closer agreement with experiment.

4. Concluding Remarks

In the standard G4 and G4(MP2) procedures, the difference in the treatment of closed-shell and open-shell species, by the use of different values for the HLC parameters for A (closed-shell) and A' (open-shell), can lead to shortcomings in the description of radical reactions. This pitfall is most evident when large radicals are involved and arises because of an indefinitely increasing HLC contribution to the reaction energy with increasing size of radical.

We have formulated a number of minor modifications to these procedures to overcome such a deficiency. One approach is simply to remove the A' parameter, i.e., make $A' = A$. These methods are termed G4-5H and G4(MP2)-5H and include five HLC parameters. Overall, they perform slightly worse than G4 and G4(MP2) but without the A' problem for large radicals.

A second approach is to remove the A' parameter but to include a spin-correction term instead. These methods are termed G4-sc and G4(MP2)-sc and include six HLC parameters. They again perform only slightly worse than G4 and

G4(MP2) overall but without the A' problem for large radicals. They are slightly better than G4-5H and G4(MP2)-5H. The use of G4-sc and G4(MP2)-sc may be beneficial for specific applications in which cancellation of errors may lead to closer agreement with the experiment.

A third type of alternative method, represented by G4-SP and G4(MP2)-SP, also equates A and A'. In this case, the spin-polarization effect, that is originally treated by having different A and A' values, is handled by a new damped SP term. This term is derived from a geometric series and converges to a predefined maximum. Hence, it does not have the dilemma of significant overestimation of spin polarization for large radicals. We have demonstrated that the “SP” formulation, which includes seven HLC parameters, performs somewhat better than the “sc” procedures. The SP procedures work as well as G4 and G4(MP2) for small molecules, while appearing to be somewhat more accurate for medium-sized systems.

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Supporting Information Available: Zero-point vibrational energies and thermal corrections from scaled B3-LYP/6-31G(2df,p) frequencies and G4-5H, G4-sc, G4-SP, G4(MP2)-5H, G4(MP2)-sc, and G4(MP2)-SP total electronic energies (Table S1) and deviations from experimental and W1 energies (Table S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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