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Investigation of Gaussian4 Theory for Transition Metal Thermochemistry

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An investigation of the performance of Gaussian-4 (G4) methods for the prediction of 3d transition metal thermochemistry is presented. Using the recently developed G3Large basis sets for atoms Sc−Zn, the G4 and G4(MP2) methods with scalar relativistic effects included are evaluated on a test set of 20 enthalpies of formation of transition metal-containing molecules. The G4(MP2) method is found to perform significantly better than the G4 method. The G4 method fails due to the poor convergence of the Møller−Plesset perturbation theory at fourth-order in one case. The overall error for G4(MP2) of 2.84 kcal/mol is significantly larger than its previously reported performance for molecules containing main-group elements in the G3/05 test set. However, considering the relatively large uncertainties in the experimental enthalpies, the G4(MP2) method performs reasonably well. The performance of other composite methods based on G3 theory [G3(CCSD)//B3LYP and G3(MP2,CCSD)//B3LYP], as well as several density functional methods, are also presented in this paper. The results presented here will assist future development of composite model techniques suitable for use in transition metal-containing systems.

I. Introduction

As developments in transition metal chemistry continue to find applications in a growing number of areas, the need for theoretical techniques capable of accurately describing such systems becomes increasingly urgent. Density functional theory[1] (DFT) has witnessed immense popularity over the past decade, with significant contributions to a broad range of transition metal applications.[2−6] However, due to difficulties in the systematic improvement of DFT methods, wave function-based theories are likely to see increased interest for such systems.[7−9] In a recent paper, DeYonker et al. collected a test set comprising 17 enthalpies of formation for transition metal compounds for testing their method referred to as the correlation consistent composite approach (ccCA).[10] On this test set of 17 enthalpies, their ccCA method has a mean absolute deviation (MAD) of 5.6 kcal/mol, which is just under twice the average experimental uncertainty of 3.1 for this set of molecules. On a smaller subset of eight molecules with the most reliable enthalpies of formation, they found a significantly better MAD from experiment of 3.4 kcal/mol.

We have recently presented an augmented triple-ζ basis set, denoted as “G3Large”, for the 3d (or first-row) transition metal atoms Sc−Zn.[11] In that paper, the bond dissociation energies of the diatomic transition metal hydrides were evaluated at the DKH-CCSD(T)/G3Large (perturbative triples-augmented coupled cluster theory,[12] including Douglas−Kroll−Hess second-order scalar relativistic corrections[13−16]) and DKH-BD(T)/G3Large (using Brueckner-doubles method[17] instead of coupled cluster theory) methods, with a mean absolute deviation from experiment of 3.91 and 2.55 kcal/mol, respectively. The 1.4 kcal/mol difference between the two methods arises from the poor performance of the unrestricted version of CCSD(T) for the highly spin-contaminated systems, NiH ($^2\Pi$) and CoH ($^3\Phi$).

We have also recently developed G4 theory,[18] the fourth in the series of Gaussian-*n* theories,[19−22] a composite technique based on ab initio molecular orbital theory. Versions of G4 theory with reduced orders of perturbation theory, G4(MP2) and G4(MP3), have also been developed.[23] G4 theory gives an average absolute deviation of 0.83 kcal/mol on the G3/05 experimental test set of energies, a considerable improvement over G3 theory (1.13 kcal/mol) and well within the target accuracy of 1 kcal/mol. The G4(MP2) method performs very well, with an average absolute deviation of 1.04 kcal/mol, which is actually better than G3 theory.[22]

It is of interest to investigate the performance of G4 theory on transition metals. This is possible now because of our development of the transition metal G3Large basis sets for the main group atoms. In this paper, we report on an investigation of the G4 methods, modified to include scalar relativistic effects, on a carefully selected set of 20 molecules containing the elements Sc−Zn, all of which have quoted uncertainties of *less than 3 kcal/mol.* Our goal is to eventually use these and other results to design new and more accurate models for theoretical thermochemistry involving transition metal compounds.

II. Computational Methods

The Gaussian-4 (G4) composite model[18] combines high-level correlation/moderate basis set calculations with lower level correlation/larger basis set calculations to approximate the results of a more expensive calculation. The composite energy is obtained from results using CCSD(T), MP4, MP2, and HF calculations with progressively larger basis sets, and including first-order spin−orbit corrections for atoms and molecules (SO), zero-point energy corrections (ZPE), and an empirical higher-level correction (HLC) that depends on the number of paired and unpaired electrons. The G4 model contains new features, including extrapolation to the HF limit, use of CCSD(T)

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TABLE 1: Optimized Higher Level Correction (HLC) Parameters (in mH) for G3 and G4 Methods, Including Scalar Relativistic Effects

	HLC, mhartrees			
parameter[a]	G3(CCSD,rel)[b]	G3(MP2, CCSD,rel)[b]	G4(rel)[c]	G4(MP2,rel)[c]
A	6.5546	9.3413	7.2787	9.9121
B	2.9451	4.5078	2.6558	3.1708
C	6.2963	9.3134	7.4585	10.1855
D	1.1872	1.9708	1.4985	2.2554
A′			7.4459	10.2230
E			2.6343	2.3608

[a] See references for definition of parameters for G4 theories[18,23] and for G3 theories.[32] [b] Optimized on the G2/97 test set.[33,34] Mean absolute deviation on G2/97 is 1.04 kcal/mol (G3(CCSD,rel) and 1.31 kcal/mol for G3(MP2,CCSD,rel). [c] Optimized on the G3/05 test set.[31] Mean absolute deviation on G3/05 is 0.87 kcal/mol for G4(rel) and 1.07 kcal/mol for G4(MP2,rel).

TABLE 2: Atomic Energies (in Hartrees)

species	E [G4(rel)]	E [G4(MP2,rel)]
Sc (^{2}D)	−763.346 378	−763.029 989
Ti (^{3}F)	−852.679 579	−852.357 434
V (^{4}F)	−947.910 247	−947.585 085
Cr (^{7}S)	−1049.224 546	−1048.892 476
Mn (^{6}S)	−1156.705 575	−1156.361 059
Fe (^{5}D)	−1270.410 047	−1270.046 634
Co (^{4}F)	−1390.625 088	−1390.241 490
Ni (^{3}F)	−1517.464 414	−1517.058 761
Cu (^{2}S)	−1651.156 839	−1650.710 506
Zn (^{1}S)	−1791.656 461	−1791.202 293

energies, use of density functional geometries, an extension of the G3Large basis set with additional polarization on the first two rows referred to as G3LargeXP, and a slightly modified higher level correction. Apart from G4 theory, an approximate version labeled G4(MP2), which avoids the expensive MP4 calculations with larger basis sets, is an attractive alternative.[23] Equations that define the two methods more explicitly are given in the Appendix. In this paper, the performance of the composite techniques G4 and G4(MP2) are evaluated for a test set of enthalpies of formation of 20 representative molecules containing first-row transition metal elements Sc−Zn. The main criteria for choosing these 20 molecules were that they have an experimental uncertainty of less than 3 kcal/mol and to have all the transition metal elements represented as evenly as possible. We have reviewed the literature to the best of our knowledge to ascertain the uncertainties. Eight of these molecules are also in the previously mentioned work of DeYonker et al., whose test set also included some molecules with larger uncertainties[10] They have discussed the problems in finding accurate data for transition metals and sources of uncertainties.

Because this is the first application of G4 (and variants) to transition metal containing systems, we note the following details.

(A) In accord with G4 theory, all single-point calculations were performed at B3LYP/6-31G(2df,p) geometries. For Sc−Zn, this is based on the modified 6-31G* basis set appropriate for 3d transition metals.[24,25] This was originally derived by Rassolov et al. and then modified by Mitin, Baker, and Pulay.[26] The basis set is referred to as m6-31G* and has been described elsewhere.[11] The 2df (2fg for transition metals) polarization functions are described below in the Appendix. Zero-point energy corrections were also calculated at the B3LYP/6-31G(2df,p) level with frequencies scaled by 0.9854, the same as in G4 theory.[18] This scale factor was derived in our paper on G3X theory[27] from fitting the set of experimental zero-point energies compiled by Scott and Radom[28] in their paper on zero-point energies for different density functional methods.

(B) As the starting point for the G4 single point energy calculations, we use the m6-31G* basis set for the transition metals and the 6-31G* basis set for the main group elements (in the rest of the paper, we use the notation m6-31G* to represent both). Additionally, the G4 calculations require the corresponding m6-31+G* and m6-31G(2df,p) basis sets (the latter basis set actually uses 2f,1g polarization functions for transition metals, although we use the main group notation for convenience) to be defined for each element. The diffuse (s, p, d) and polarization (2f, 1g) exponents corresponding to the m6-31+G* and m6-31G(2df,p) basis sets for 3d transition metal atoms are listed in the Appendix. The G3LargeXP and G3MP2LargeXP basis sets used in the MP2 calculations have already been defined for the first three rows of the main group elements.[18,23] For the 3d transition metal atoms, it is equivalent to G3Large as described in ref 11.

(C) The G4 and G4(MP2) methods employ an extrapolation procedure[18,23] using two large correlation-consistent basis sets to obtain the Hartree−Fock (HF) limit for the transition metal species in a manner that is similar to that proposed for the H−Ar, Ga−Kr for these methods.[18,23] The HF extrapolation for G4 theory[18] is based on quadruple- and quintuple-ζ basis sets, aug-cc-pVQZ and aug-cc-pV5Z. We have used the nonrelativistic (NR) version of these basis sets for Sc−Zn from Balabanov and Peterson.[29] The HF extrapolation for G4(MP2) theory[23] is based on triple- and quadruple-ζ basis sets, aug-cc-pVTZ and aug-cc-pVQZ, with a tight d-function added to the d polarization set, denoted as aug-cc-pV(T+d)Z and aug-cc-pV(Q+d)Z. For the transition metals, the tight d basis sets are not available, so we have used the aug-cc-pVTZ-NR and aug-cc-pVQZ-NR basis sets from ref 29. The neglect of the tight-d functions in the basis sets for the transition metals in G4(MP2) theory should be reasonable, since the small transition metal systems considered here do not have hypervalency issues, as in the case of some of the Al−Cl containing molecules. The transition metal basis sets for HF extrapolation include only the sp diffuse functions, as was done for G4 and G4(MP2) theories.[18,23] In addition, the same hydrogen basis set, which is reduced in size, is used. The basis sets are available on the web[30] and in the Supporting Information.

(D) Since scalar relativistic effects are expected to be important for transition metals, we have derived G4 and G4(MP2) methods with reoptimized higher-level correction parameters when these effects are included. The scalar relativistic corrections to the energies are obtained from DKH-CCSD(T)/m6-31G* single-point energy calculations using a second-order Douglas−Kroll−Hess (DKH) scalar relativistic Hamiltonian.[13−16] The HLC parameters were reoptimized for the whole G3/05 test set[31] and are given in Table 1. No improvement in the results for the G3/05 test set is found when scalar relativistic effects are included. These methods with corrections for scalar relativistic effects included are referred to as G4(rel) and G4(MP2, rel), respectively. In a similar manner, we have reoptimized the HLCs for the G3(CCSD) and G3(CCSD,MP2) models[32] with scalar relativistic effects included and give them in Table 1. The reoptimization for these two models was done on the G2/97 test set.[33,34] The atomic spin−orbit corrections for the transition metal atoms are given in the Appendix; the values for the other elements are given in ref 22.

(E)Unless otherwise denoted, the valence space of the transition metal systems is defined to include the 3s, 3p, 3d, and 4s electrons. Our approach is different from that of

TABLE 3: Comparison of G3 and G4 Methods for Calculation of ΔH_f (298 K) for a Test Set of 20 Molecules

	ΔH_f (298 K)	experiment − theory (kcal/mol)			
molecule, state[a]	experiment	G3(CCSD,rel)	G3(MP2,CCSD,rel)	G4(rel)	G4(MP2,rel)
ScO $^2\Sigma^+$	-13.0 ± 2.2[b]	−2.25	−2.40	−4.21	−4.49
$ScCl_3$ $^1A_1'$	-160.5 ± 2.1[b]	6.88	5.97	3.49	3.38
TiO $^3\Delta$	13.7 ± 2.2[b]	1.28	0.68	−1.03	−2.32
TiF_4 $^1A_1$	-370.8 ± 1[c]	9.74	5.48	1.94	−1.27
VO $^4\Sigma^-$	31.8 ± 2[d]	−0.42	−1.97	−0.65	−3.17
CrCl $^6\Sigma^+$	31.0 ± 0.6[e]	−2.24	1.13	−4.95	−4.01
CrO_3 $^1A'$	-77.3 ± 1[e]	26.92	9.12	21.31	4.31
MnCl $^7\Sigma^+$	15.8 ± 1.6[f]	8.13	9.37	4.87	2.99
MnS $^6\Sigma^+$	63.31 ± 2[f]	0.68	1.50	−1.83	−3.64
FeCl $^6\Delta$	49.5 ± 1.6[g]	8.39	8.95	5.26	3.53
$FeCl_2$ $^5\Delta_g$	-32.8 ± 1[g]	7.96	7.71	4.54	3.24
$FeCl_3$ $^6A_1'$	-60.5 ± 1.2[c]	6.56	9.43	1.93	3.54
$CoCl_2$ $^4\Delta$	-22.6 ± 1[g,h]	6.18	5.56	2.65	1.75
$CoCl_3$ $^5A_1'$	-39.1 ± 2.5[c]	0.27	2.94	−4.87	−2.49
$NiCl_2$ $^3\Sigma_g^-$	-17.4 ± 1[g]	7.16	5.35	3.81	2.45
NiF_2 $^3\Sigma_g^-$	-77.8 ± 1.1[b]	10.83	8.90	6.31	4.75
CuH $^1\Sigma^+$	65.9 ± 2[b]	0.58	−0.53	−1.75	−2.54
CuCl $^1\Sigma^+$	19.3 ± 2[b]	0.74	0.83	−2.64	−1.87
ZnH $^2\Sigma^+$	62.9 ± 0.5[b]	2.23	0.31	0.82	−0.65
$Zn(CH_3)_2$ ^1A	12.86 ± 2[b]	6.21	3.52	2.58	0.46
MAD		5.78	4.58	4.07	2.84

[a] All open shell states have little or no spin contamination. The largest spin contamination occurs for VO (expectation value for $S^2 = 3.79$ compared to 3.75 for pure spin state) and MnS (8.83 compared to 8.75 for pure spin state) [b] Ref 45. [c] Ref 44. [d] Ref 38. [e] Refs 39, 40. [f] Ref 42. [g] Ref 41. [h] Ref 43.

DeYonker et al., who define the 3d, 4s correlation as valence shell, and include the effects of 3s, 3p as part of core-valence correlation. Our definition is sometimes referred to as a "small core" approximation,[35] and we have used it for K, Ca, and Ga−Kr in the G3 methodology.[36]

All calculations have been performed using the Gaussian03 program.[37] The enthalpies of formation at 298 K were calculated using the procedure described in ref 33. The enthalpies of formation at 0 K for the gaseous atoms used for the transition metal elements are given in the Appendix. Also included in this Appendix are the ($H^{298}-H^0$) values for the elements in their standard states. The same quantities for the other elements are given in ref 33.

III. Results and Discussion

Table 2 contains the total energies of the atoms Sc−Zn from the G4(rel) and G4(MP2,rel) methods. Table 3 contains the deviations from experimental[38−45] enthalpies of formation for the G4(rel) and G4(MP2,rel) methods. The deviations for all 20 molecules are given in this table with the mean absolute deviation at the bottom of the table. All of the deviations are in kilocalories per mole and calculated as experiment minus theory. The MAD of G4(rel) is 4.10 kcal/mol with a maximum deviation of 21.3 kcal/mol compared to a MAD of 2.84 kcal/mol for G4(MP2,rel) with a maximum deviation of 4.75 kcal/mol. The reason that G4(MP2,rel) does better than G4(rel) is primarily because the perturbation theory-based additivity approximations of the larger basis set effects fail for some species. Most notable is the result for CrO_3, where G4(rel) differs by 21.3 kcal/mol from experiment while G4(MP2,rel) differs by only 4.3 kcal/mol. This illustrates how a poorly converging (or simply diverging) perturbative series can translate into large deviations for composite methods, which rely on a similar rate of convergence of different correlation methods with larger basis set extensions. If CrO_3 is excluded, the G4(rel) mean absolute deviation is about the same as for G4(MP2,rel). There may also be some other species for which these additivity approximations do poorly and affect the reliability of the G4(rel) method.

TABLE 4: Comparison of Selected Density Functional Methods on the 20-Molecule Test Set[a]

		experiment − theory, (kcal/mol)		
ΔH_f (298 K)	experiment	B3LYP	PW91PW91	PBEPBE
ScO $^2\Sigma^+$	-13.0 ± 2.2	−1.75	20.51	19.67
$ScCl_3$ $^1A_1'$	-160.5 ± 2.1	−3.53	18.50	17.01
TiO $^3\Delta$	13.7 ± 2.2	2.02	32.27	31.12
TiF_4 $^1A_1$	-370.8 ± 1	3.70	55.11	50.99
VO $^4\Sigma^-$	31.8 ± 2	2.50	33.89	33.10
CrCl $^6\Sigma^+$	31.0 ± 0.6	−4.72	−0.93	−1.56
CrO_3 $^1A'$	-77.3 ± 1	−30.96	45.11	43.38
MnCl $^7\Sigma^+$	15.8 ± 1.6	−0.99	13.40	12.43
MnS $^6\Sigma^+$	63.31 ± 2	2.21	28.07	26.75
FeCl $^6\Delta$	49.5 ± 1.6	2.51	8.06	7.77
$FeCl_2$ $^5\Delta_g$	-32.8 ± 1	−0.67	11.79	11.10
$FeCl_3$ $^6A_1'$	-60.5 ± 1.2	−5.70	22.04	21.55
$CoCl_2$ $^4\Delta$	-22.6 ± 1	−2.50	48.54	46.49
$CoCl_3$ $^5A_1'$	-39.1 ± 2.5	−4.18	65.68	63.49
$NiCl_2$ $^3\Sigma_g^-$	-17.4 ± 1	−1.26	8.97	7.67
NiF_2 $^3\Sigma_g^-$	-77.8 ± 1.1	3.88	14.02	11.62
CuH $^1\Sigma^+$	65.9 ± 2	−5.31	−3.29	−3.57
CuCl $^1\Sigma^+$	19.3 ± 2	−8.18	−1.64	−1.85
ZnH $^2\Sigma^+$	62.9 ± 0.5	1.79	1.88	1.49
$Zn(CH_3)_2$ ^1A	12.86 ± 2	−4.35	9.34	7.12
MAD		4.64	22.15	20.99

[a] Using the G3MP2Large basis set.

Table 3 contains results for the G3(CCSD,rel) and G3(MP2,CCSD,rel) methods. We chose to investigate the CCSD(T) version of these methods, since deficiencies involving QCISD(T) have been pointed out previously for molecules containing third-row and transition metal elements.[18,46−50] The G3(CCSD,rel) model has a MAD of 5.81 kcal/mol, whereas the G3(MP2,CCSD,rel) model has a mean absolute deviation of 4.58 kcal/mol. Both are significantly larger than the respective G4 values, for which the mean absolute deviations are about 1.7 kcal/mol smaller. We have investigated the contributions to the improvement and find that over 50% comes from the HF extrapolation, with the three other features (new HLC, new geometry, new basis set) contributing less than 0.2 kcal/mol each.

Overall, the performance of G4(MP2,rel) is the best of the various methods tested and is quite good considering the uncertainties in the experimental values. This is especially interesting when considering the relative costs of the G4(rel) and G4(MP2,rel) methods. For the closed shell CrO_3 molecule, the G4(MP2,rel) calculation took one-tenth of the CPU time required to perform the G4(rel) calculation. However, comparing to direct large basis set CCSD(T) calculation, both composite methods offer significant computational savings. For CrO_3, the DKH-CCSD(T)/G3LargeXP calculation is 17 times and 55 times more expensive than the correlated parts of the G4(rel) and G4(MP2,rel) calculations, respectively.

Although the G4(MP2,rel) MAD of 2.85 kcal/mol is much larger than for the main-group molecules in the G3/05 test set (0.87 kcal/mol), the uncertainties in the experimental values are much larger for the transition metal species. The average uncertainty for the 20 molecule transition metal set is 1.5 kcal/mol, so the MAD is less than twice the experimental uncertainty. In addition, some experimental atomic enthalpies of formation, such as for Ti, V, and Ni, have uncertainties of 2−4 kcal/mol (see Appendix). These are used in the calculation of the molecular enthalpies and may introduce uncertainties in the theoretical values. For the eight molecules in common with the test of DeYonkers et al. (VO, CrO_3, FeCl, $FeCl_2$, $FeCl_3$, $CoCl_3$, $NiCl_2$, $Zn(CH_3)_2$), the average absolute deviation is 2.88 kcal/mol, as compared to 2.82 kcal/mol (with a maximum error of 4.7 kcal/mol) for the ccCA method. Thus, these results provide evidence that the various approximations in G4 theory work reasonably well for transition metals. Though these results are encouraging, the test set is small, and further work is needed to assess the reliability of the G4 methods and make improvements in the model to improve the accuracy.

We have also examined three density functional methods for the 20-molecule set. These results are given in Table 4. The density functional methods tested include B3LYP,[51] PW91-PW91,[52,53] and PBEPBE.[54,55] These are among the functionals that are often used in calculations on transition metals. The results indicate that B3LYP performs the best with a MAD of 4.64 kcal/mol. The PBE and PW91 functionals perform much worse, with MADs of 20.99 and 22.15 kcal/mol, respectively.

IV. Conclusions

The recently developed G4 and G4(MP2) methods in combination with new basis sets for 3d transition metal atoms and inclusion of scalar relativistic effects have been used to calculate the enthalpies of formation for a test set of 20 molecules containing transition metals Sc−Zn. The following conclusions can be drawn from the results:

1. The G4(MP2,rel) method, which includes scalar relativistic effects, has a mean absolute deviation of 2.84 kcal/mol and a maximum deviation of 4.75 kcal/mol for the test set of 20 enthalpies. Since the 20 enthalpies have an average experimental uncertainty of 1.5 kcal/mol, these results indicate that the G4(MP2,rel) method performs quite well for transition metals. The G4(rel) method has a much larger mean absolute deviation of 4.10 kcal/mol due to a failure of the additivity approximation in the perturbation series, which is particularly large for one molecule, CrO_3.

2. Composite models, such as G3(CCSD,rel) or G3(CCSD, MP2,rel), perform much worse for the 20 enthalpies than the G4 methods with the MADs of 5.81 and 4.85 kcal/mol, respectively. Thus, they are much less reliable than the G4 methods and are not recommended for use on transition metal systems.

3. Of the density functional methods assessed B3LYP performs the best with a MAD of 4.64 kcal/mol. In many cases, it performs well, but occasionally, it has large errors. The other two methods examined, PBE and PW91, perform considerably worse than B3LYP, with MADs of more than 20 kcal/mol.

In future work, we will be developing a larger collection of test molecules for transition metal species with sufficiently accurate experimental data. This will be important for critical assessments of the performance of theoretical methods and to make improvements in the G4 methodology as well as other methodologies.

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Appendix

Appendix A: Supplementary Functions for the m6-31G* Basis Set

	diffuse exponents		polarization exponents[a]	
atom	sp	d	f	g
Sc	0.011 84	0.045 004	0.8	0.2616
Ti	0.012 81	0.058 507	0.8	0.2616
V	0.013 72	0.070 06	0.8	0.2616
Cr	0.014 58	0.061 015	0.8	0.2616
Mn	0.015 37	0.093 619	0.8	0.2616
Fe	0.016 46	0.101 301	0.8	0.2616
Co	0.017 21	0.111 015	0.8	0.2616
Ni	0.018 08	0.121 309	0.8	0.2616
Cu	0.018 93	0.107 85	0.8	0.2616
Zn	0.019 72	0.144 446	0.8	0.2616

[a] For 2f polarization (e.g. m6-31G(2df,p)), split the f exponent into 2f and 0.5f.

Appendix B: Spin−orbit Corrections for Atoms, Enthalpies of Formation at 0 K for Gaseous Atoms and ($H^{298}-H^0$) Values for Elements in Their Standard States from Experiment

species	Δ(SO),[a] mhartrees	$\Delta_f H^0$ (0 K),[b] kcal/mol	$H^{298}-H^0$,[b] 298 K, kcal/mol
Sc (^{2}D)	−0.46	90.17 ± 0.8[c]	1.24[c]
Ti (^{3}F)	−1.02	112.55 ± 4	1.15
V (^{4}F)	−1.46	122.4 ± 2	1.11
Cr (^{7}S)	0.0	94.5 ± 1	0.97
Mn (^{6}S)	0.0	67.4 ± 1	1.19
Fe (^{5}D)	−1.84	98.7 ± 0.3	1.08
Co (^{4}F)	−3.62	101.6 ± 0.5	1.14
Ni (^{3}F)	−4.43	102.3 ± 2	1.14
Cu (^{2}S)	0.0	80.4 ± 0.3	1.20
Zn (^{1}S)	0.0	31.04 ± 0.05	1.35

[a] Ref 56. [b] Ref 44. [c] Ref 45.

Appendix C: Equations for G4(rel) and G4(MP2,rel)

$$E_0[\mathrm{G4(rel)}] = E[\mathrm{MP4/6\text{-}31G(d)}] + \Delta E(+) + \Delta E(\mathrm{2df, p}) + \Delta E(\mathrm{G3LargeXP}) + \Delta E(\mathrm{CC}) + \Delta E(\mathrm{HF}) + \Delta E(\mathrm{rel}) + \Delta E(\mathrm{SO}) + E(\mathrm{ZPE}) + E(\mathrm{HLC})$$

where

$$\Delta E(+) = E[\mathrm{MP4/6\text{-}31{+}G(d)}] - E[\mathrm{MP4/6\text{-}31G(d)}]$$

$$\Delta E(\text{2df, p}) = E[\text{MP4/6-31G(2df,p)}] - E[\text{MP4/6-31G(d)}]$$

$$\Delta E(\text{CC}) = E[\text{CCSD(T)/6-31G(d)}] - E[\text{MP4/6-31G(d)}]$$

$$\Delta E(\text{rel}) = E[\text{DKH-CCSD(T)/6-31G(d)}] - E[\text{CCSD(T)/6-31G(d)}]$$

$$\Delta E(\text{G3LargeXP}) = E[\text{MP2(full)/G3LargeXP}] - E[\text{MP2/6-31G(2df,p)}] - E[\text{MP2/6-31 + G(d)}] + E[\text{MP2/6-31G(d)}]$$

$$\Delta E(\text{HF}) = E_{\text{HF/limit}}(4, 5) - \text{E[HF/G3LargeXP]}$$

where

$$\text{E}_{\text{HF/limit}}(4, 5) = (\text{E}_{\text{HF}/5} - \text{E}_{\text{HF}/4}\exp(-1.63))/(1 - \exp(-1.63))$$

ΔE (SO) and E(ZPE) are defined as for G4 theory (ref 18). E(HLC) is defined as for G4 theory [$-\text{A}n_\beta$ for closed shell molecules, $-\text{A}'\ n_\beta - \text{B}(n_\alpha - n_\beta)$ for open shell systems, $-\text{C}n_\beta - \text{D}(n_\alpha - n_\beta)$ for atoms including atomic ions, and E for systems with a single pair of 2s or 3s electrons] with optimized parameters in Table 1.

$$E_{\text{o}}[\text{G4(MP2, rel)}] = \text{CCSD(T)/6-31G(d)} + \Delta E(\text{MP2}) + \Delta E(\text{HF}) + \Delta E(\text{rel}) + \Delta E(\text{SO}) + E(\text{HLC}) + E(\text{ZPE})$$

where

$$\Delta E(\text{MP2}) = E[\text{MP2/G3MP2LargeXP}] - E[\text{MP2/6-31G(d)}]$$

$$\Delta E(\text{HF}) = E_{\text{HF/limit}}(3, 4) - E[\text{HF/G3LargeXP}]$$

where

$$E_{\text{HF/limit}}(3, 4) = (E_{\text{HF/4}} - E_{\text{HF/3}}\exp(-1.63))/(1 - \exp(-1.63))$$

$$\Delta E(\text{rel}) = E[\text{DKH-CCSD(T)/6-31G(d)}] - E[\text{CCSD(T)/6-31G(d)}]$$

ΔE(SO) and E(ZPE) are defined as for G4(MP2) theory (ref 23). E(HLC) is defined as for G4(MP2) theory (ref 23) with optimized parameters in Table 1.

Supporting Information Available: Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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