

## Toward accurate thermochemical models for transition metals: G3Large basis sets for atoms Sc–Zn

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An augmented valence triple-zeta basis set, referred to as G3Large, is reported for the first-row transition metal elements Sc through Zn. The basis set is constructed in a manner similar to the G3Large basis set developed previously for other elements (H–Ar, K, Ca, Ga–Kr) and used as a key component in Gaussian-3 theory. It is based on a contraction of a set of  $15s13p5d$  Gaussian primitives to  $8s7p3d$ , and also includes sets of  $f$  and  $g$  polarization functions, diffuse  $spd$  functions, and core  $df$  polarization functions. The basis set is evaluated with triples-augmented coupled cluster [CCSD(T)] and Brueckner orbital [BD(T)] methods for a small test set involving energies of atoms, atomic ions, and diatomic hydrides. It performs well for the low-lying  $s \rightarrow d$  excitation energies of atoms, atomic ionization energies, and the dissociation energies of the diatomic hydrides. The Brueckner orbital-based BD(T) method performs substantially better than Hartree–Fock–based CCSD(T) for molecules such as NiH, where the starting unrestricted Hartree–Fock wavefunction suffers from a high degree of spin contamination. Comparison with available data for geometries of transition metal hydrides also shows good agreement. A smaller basis set without core polarization functions, G3MP2Large, is also defined. © 2008 American Institute of Physics.

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### I. INTRODUCTION

The last two decades have witnessed enormous progress in the development of composite theoretical techniques for the accurate prediction of the thermochemical properties of molecules. While direct application of an accurate theoretical method such as CCSD(T) can be carried out with progressively larger basis sets and extrapolated to attain convergence,<sup>1–8</sup> an alternative successful strategy that makes it possible to approach chemical accuracy for significantly larger molecules involves a composite multilevel approach typically combined with a small number of empirical parameters.<sup>9–15</sup> The Gaussian- $n$  series that we have developed<sup>16–19</sup> exploits this idea to predict thermochemical data for molecules containing first- and second-row elements and has subsequently been extended to include third-row nontransition metals (K, Ca, Ga–Kr).<sup>20</sup> In our approach, high level correlation calculations [e.g., QCISD(T), CCSD(T)] with moderate sized basis sets are combined with results from lower level calculations (e.g., MP4, MP2, or even HF) using larger basis sets to approximate the results of more expensive calculations. In addition, molecule-independent empirical parameters are used in these methods to estimate the remaining deficiencies in the calculations. This avoids the use of very large basis sets containing high angular mo-

mentum functions and such an approach using “higher level corrections” (additive parameters that depend on the number of paired and unpaired electrons in the system) has been quite successful and the latest versions, extended Gaussian-3 (G3X) (Ref. 21) and Gaussian-4 (G4) (Ref. 19) theories, achieve an overall accuracy of 1.0 kcal/mol or better for the large G3/05 test set containing 454 experimental energies.<sup>22</sup>

The development of similar computational models for molecules containing transition metal elements is, however, a very challenging problem.<sup>23,24</sup> Many groups are working to develop and apply both density functional theory (DFT) and wavefunction based methods for application to such systems.<sup>1,2,25–32</sup> In order to develop a Gn-type method for use in transition metal systems, many significant challenges must be overcome. The presence of low-lying electronic states in transition metals makes it difficult to provide an accurate description of electron correlation effects, particularly if it involves a change in the  $3d$  electron population.<sup>33–35</sup> This makes simple models of electron correlation such as MP2 or MP4 to be highly deficient. Relativistic effects have to be taken into account to provide an accurate description of chemical bonding in such systems.<sup>33,36</sup> The number of molecules where the experimental heats of formation are known to chemical accuracy is far fewer for transition metals. This limits the collection of test sets that are useful for a critical evaluation of the performance of theoretical models for these systems. Finally, systematic basis sets have not been developed to the same extent as for main group elements. For

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example, the equivalent basis sets comparable to G3Large (used in G3 theory) are not yet available for transition metal systems.

This is the first in a series of papers in which we plan to explore how to modify and extend accurate computational models such as G3 theory to the transition metals Sc–Zn. In this paper we present new basis sets for the elements Sc–Zn and then carry out calibration studies with this basis set on some simple, but challenging, systems. In particular, we investigate the excitation and ionization energies of transition metal atoms as well as the geometries and binding energies of the series of diatomic hydrides MH, M=Sc–Zn. In future papers, we plan to present new composite models for predictive thermochemistry in these systems.

## II. STANDARD BASIS SETS IN GAUSSIAN-*n* THEORIES

The reliability of both *ab initio* and density functional calculations of transition metal compounds is dependent on the availability of quality basis sets. In particular, the applicability of methods such as G3 requires *standard* basis sets for transition metals that are compatible with existing basis sets for the main group elements, such as 6-31G\*,<sup>37</sup> 6-311G\*,<sup>38</sup> and G3Large.<sup>18</sup> (In the notation used here, the “\*” denotes polarization functions on heavy atoms, which is a *d* function on Li–Ar, K, Ca, Ga–Kr, and an *f* function on Sc–Zn.) Unless the basis sets for elements in the different groups are balanced and compatible, the description of bonding involving transition metals and main group elements will be deficient. Thus, our initial goal in this study is to prepare standard basis sets for transition metals that are comparable in size and performance to the corresponding basis sets used for the main group elements.

Basis sets comparable to 6-31G\* are already available for the first-row transition metal elements. Rassolov *et al.*<sup>39,40</sup> published the 6-31G\* basis for the atoms K–Zn. This basis set was constructed similar to the 6-31G\* basis set for atoms through Ar and should be useful for the calculation of properties such as geometries and vibrational frequencies of molecules containing transition metal elements. However, several followup papers have suggested improvements to this 6-31G\* basis set. First, the lack of *d*-functions on K and Ca causes poor geometries in some molecules, and therefore a 3*d* shell was added to these elements.<sup>40</sup> Second, the 3*d*-shell of the 6-31G\* basis for Sc–Cu was found by Mitlin *et al.*<sup>41</sup> to lack a sufficiently diffuse exponent that is important for transition metals near the end of the series (Co, Ni, and Cu). They reoptimized the 3*d* shell exponents and found improved performance. This new basis set was referred to as m6-31G\*. In the Appendix, we present a m6-31G\* basis set for Zn that was not included in the paper by Mitlin *et al.*

It is well known that basis sets larger than 6-31G\* are important for energy evaluations. One of the widely used larger basis sets is the valence triple-zeta 6-311G\* basis set, which was initially developed for H–Ne. A similar type of basis set referred to as 6-311G\* is also available for the second-row elements (Na–Ar). Although this basis set is referred to as “6-311G,” it is actually constructed from the existing triple-zeta basis set (12*s*9*p* contracted to 6*s*5*p*) of

McLean and Chandler. Together, these 6-311G\* basis sets for the first two rows have been combined with supplemental functions for use in the calculation of single point energies in Gaussian-2 theory. In the development of G3 theory, it was noted that 6-311G had deficiencies for some second-row elements, and an improved version was optimized for Na–Ar for use in high level energy calculations. This basis set was then augmented with diffuse and polarization functions (diffuse *sp* functions, *df* valence polarization functions, and *pd* core polarization functions), and is referred to as “G3Large.” The G3Large basis set has also been defined for the first-row H–Ne by adding analogous diffuse and polarization functions to the existing 6-311G basis. In addition, a similar G3Large basis set has been developed for atoms Ga–Kr.<sup>20</sup> The G3Large basis set is used in Gaussian-3 theory for single point MP2 calculations, and the resulting accurate performance suggests that it is balanced for the different main group elements in the first three rows.

In this paper we report the development of a similar G3Large basis set for the first-row transition metal elements, Sc–Zn. This basis set is a contracted 8*s*7*p*3*d* set plus diffuse and polarization functions. It is constructed in a manner consistent with the G3Large basis set for the second- and third-row main group elements, and is intended to be used with them. The performance of the basis set is assessed on a small test set of atomic and diatomic species. In Sec. III, the G3Large basis set for the first-row transition metals is presented. In Sec. IV, the results are assessed for atomic excitation energies, atomic ionization energies, and the geometries and dissociation energies of diatomic hydrides. Conclusions are presented in Sec. V.

## III. DESCRIPTION OF G3LARGE BASIS SETS FOR Sc–Zn

The G3Large basis set for the third-row transition metal atoms is a contracted Gaussian set with diffuse and polarization functions. The contracted set was derived similar to the G3Large basis set for third-row nontransition metal elements in G3 theory.<sup>20</sup> This procedure involves a full optimization of the basis set on atomic restricted open shell Hartree–Fock (ROHF) wavefunctions in high spin, high orbital angular momentum states of Sc–Zn using a modified version of the ATOM-SCF program.<sup>42</sup> The atomic states used in the basis set optimization are Sc(2D), Ti(3F), V(4F), Cr(5D), Mn(6S), Fe(5D), Co(4F), Ni(3F), Cu(2D), and Zn(1S). The core *spd* contraction scheme is the same as for the main group third-row elements, which was chosen based on the error analysis of the thermochemical calculations in the G3 theory.<sup>20</sup> The resulting basis set is a contraction of a 15*s*13*p*5*d* primitive set to 8*s*7*p*3*d*. The *p* contraction is 6211111 and the *d* contraction is 311. The exponents and coefficients of the G3Large basis set are given in supplemental information<sup>43</sup> and are also available on the web.<sup>44</sup>

Diffuse and polarization functions were derived for the G3Large basis set. Diffuse functions (*spd*) were derived from optimization on metal chloride anions in singlet states, such as ScCl<sub>2</sub><sup>−</sup>, TiCl<sub>2</sub><sup>−</sup>, VCl<sub>2</sub><sup>−</sup>, etc. The geometries were optimized at the UHF/6-31G level, and then exponents of the

TABLE I. Atomic energies at the HF/G3Large and HF/G3MP2Large levels of theory.

Atom	Energies (Hartrees)	
	HF/G3MP2Large	HF/G3Large
Sc $^2D(d^1s^2)$	-759.731 404	-759.731 425
Ti $^3F(d^2s^2)$	-848.401 366	-848.401 399
V $^4F(d^3s^2)$	-942.876 376	-942.876 428
Cr $^7S(d^5s^1)$	-1043.335 694	-1043.335 711
Mn $^6S(d^5s^2)$	-1149.844 328	-1149.844 347
Fe $^5D(d^6s^2)$	-1262.421 753	-1262.422 372
Co $^4F(d^7s^2)$	-1381.384 871	-1381.386 322
Ni $^3F(d^8s^2)$	-1506.830 492	-1506.832 284
Cu $^2S(d^{10}s^1)$	-1638.905 190	-1638.905 277
Zn $^1S(d^{10}s^2)$	-1777.779 001	-1777.779 080

diffuse functions were optimized to minimize unrestricted Hartree–Fock (UHF) energies calculated with the  $8s7p3d$  contracted set. Diffuse  $d$  and  $sp$  functions were optimized separately. The ratio of outermost valence exponents to optimized diffuse exponents is found to be relatively constant for each angular momentum type, with average ratios of 2.5 for  $sp$  basis functions and 4.0 for  $d$  functions. We used these ratios to generate final values of diffuse exponents, shown in the Appendix. The  $f$  polarization functions were optimized at the UHF level on the transition metal molecules used for the 6-31G\* basis. The  $g$  polarization functions were optimized on this same set and included a  $2f$  polarization set on the basis set during optimization. The  $f$  and  $g$  polarization functions are listed in the Appendix. The core  $d$  and  $f$  polarization functions were optimized at the MP2(full) level on the atoms. These functions are also listed in the Appendix.

The G3MP2Large (G3MP2L) basis is obtained by not including the core polarization functions. The total energies for the G3Large and G3MP2Large basis sets for the atoms are given in Table I. The GAUSSIAN03 computer program was used in the energy calculations.<sup>45</sup>

## IV. RESULTS AND DISCUSSION

### A. Atomic excitation and ionization energies

It is well known that accurate calculation of the electronic excitation energies of transition metal atoms that differ

in the occupation of the  $3d$  and  $4s$  orbitals is a challenging problem.<sup>34,35</sup> Large basis sets as well as an accurate treatment of electron correlation are both important factors in this context. We have evaluated the performance of the G3Large basis set for the computation of low-lying electronic excitation energies obtained from  $d^n s^2 \rightarrow d^{n+1} s^1$  atomic transitions using the triples-augmented CCSD(T)/G3Large and BD(T)/G3Large methods. While the coupled cluster-based CCSD(T) method was chosen as the standard electron correlation technique, the Brueckner orbital-based BD(T) can be seen to offer significant advantages in spin contaminated cases such as NiH (*vide infra*). We have used both methods using nonrelativistic techniques as well as with scalar relativistic corrections. For the latter case, we used the second-order Douglas–Kroll–Hess scalar relativistic Hamiltonian,<sup>46–49</sup> denoting the relativistic calculations as DKH-CCSD(T) and DKH-BD(T). In all cases, the correct  $d$  orbital combinations that lead to the proper pure electronic state were occupied.

Table II lists the computed excitation energies and compares these to spin-orbit corrected (i.e.,  $J$ -averaged) experimental values. In previous work,<sup>35</sup> computed scalar relativistic corrections were used to correct the experimental values in order to evaluate the performance of nonrelativistic theoretical models. In the present study, we have opted to refrain from correcting the measured experimental values and to include the scalar relativistic corrections in the computed values. This enables us to compare calculated results directly to experiment, consistent with the general philosophy that we have followed in our  $G_n$  approach. The computed values in Table II correspond to the inclusion of all the electrons in the correlation treatment.

All the excitation energies represent  $s \rightarrow d$  transitions. As seen in previous studies,<sup>35</sup> the deviations of the relativistic calculations from experiment appear to be fairly systematic and of the same sign (computed excitation energies being larger than those from the experiment). The mean absolute deviation (MAD) from experiment for the nine DKH-CCSD(T) excitation energies is 0.17 eV, and errors larger than 0.2 eV occur for Mn, Fe, Co, and Ni. The MAD for the DKH-BD(T) excitation energies is slightly larger, 0.19 eV, and the errors larger than 0.2 eV occur for Cr, Mn, Fe, and

TABLE II. Deviations in the calculated excitation energies. DKH signifies the relativistic calculation. All electrons were correlated.

$d^n s^2 \rightarrow d^{n+1} s^1$	Excitation energies (eV)			Experiment( $J$ -averaged)-Theory			
	Transition	Experiment <sup>a</sup>	Exp( $J$ -averaged)	CCSD(T)/G3Large	DKH-CCSD(T)/G3Large	BD(T)/G3Large	DKH-BD(T)/G3Large
Sc	$d^1 s^2 \rightarrow d^2 s^1$	1.428	1.427	-0.030	-0.145	-0.032	-0.147
Ti	$d^2 s^2 \rightarrow d^3 s^1$	0.813	0.806	-0.001	-0.139	-0.003	-0.142
V	$d^3 s^2 \rightarrow d^4 s^1$	0.262	0.245	0.033	-0.131	0.029	-0.134
Cr	$d^4 s^2 \rightarrow d^5 s^1$	-0.961	-1.003	0.087	-0.111	-0.304	-0.277
Mn	$d^5 s^2 \rightarrow d^6 s^1$	2.114	2.145	-0.075	-0.264	-0.081	-0.270
Fe	$d^6 s^2 \rightarrow d^7 s^1$	0.859	0.875	0.006	-0.233	0.004	-0.235
Co	$d^7 s^2 \rightarrow d^8 s^1$	0.432	0.417	0.070	-0.212	0.073	-0.209
Ni	$d^8 s^2 \rightarrow d^9 s^1$	0.025	-0.030	0.129	-0.200	0.138	-0.190
Cu	$d^9 s^2 \rightarrow d^{10} s^1$	-1.389	-1.490	0.260	-0.129	0.278	-0.110
Max Dev				0.260	-0.260	-0.304	-0.277
MAD				0.077	0.174	0.105	0.191

<sup>a</sup>Reference 62.

TABLE III. Deviations in the calculated ionization energies. DKH signifies the relativistic calculation. All electrons were correlated.

M → M <sup>+</sup>	Transition	Ionization energies (eV)		Experiment( <i>J</i> -averaged)-Theory			
		Experiment <sup>a</sup>	Exp( <i>J</i> -averaged)	CCSD(T)/G3Large	DKH-CCSD(T)/G3Large	BD(T)/G3Large	DKH-BD(T)/G3Large
Sc	$d^1s^2 \rightarrow d^1s^1$	6.560	6.561	0.050	0.018	0.049	0.016
Ti	$d^2s^2 \rightarrow d^2s^1$	6.830	6.830	0.068	0.027	0.067	0.026
V	$d^3s^2 \rightarrow d^4s^0$	6.740	6.726	0.095	-0.168	0.093	-0.170
Cr	$d^5s^1 \rightarrow d^5s^0$	6.763	6.763	0.096	-0.023	0.096	-0.021
Mn	$d^5s^2 \rightarrow d^5s^1$	7.432	7.432	0.112	0.043	0.112	0.043
Fe	$d^6s^2 \rightarrow d^6s^1$	7.900	7.902	0.126	0.035	0.127	0.035
Co	$d^7s^2 \rightarrow d^8s^0$	7.860	7.848	0.209	-0.245	0.212	-0.242
Ni	$d^9s^1 \rightarrow d^9s^0$	7.633	7.617	0.181	-0.010	0.177	-0.014
Cu	$d^{10}s^1 \rightarrow d^{10}s^0$	7.724	7.724	0.202	-0.007	0.195	-0.014
Zn	$d^{10}s^2 \rightarrow d^{10}s^1$	9.391	9.391	0.216	0.030	0.216	0.029
Max Dev				0.216	-0.245	0.216	-0.242
MAD				0.145	0.065	0.144	0.066

<sup>a</sup>Reference 62.

Co. Note that the excitation results in a change of multiplicity for the early transition metals Sc–Cr, while for the later metals the multiplicity remains unchanged. The results do not show larger errors for the former cases (in fact, they are smaller on average), a clear indication that spin change is not the dominant factor. It will be interesting to see the implications for our *Gn*-type approaches that apply a correction factor based on the number of paired and unpaired electrons. Results using the QCISD(T) method (not listed) yield very similar errors, as seen in an earlier study<sup>35</sup> using somewhat different basis sets.

We have also evaluated the lowest ionization energies of the atoms using the same methods. Again, they are compared with *J*-averaged measured experimental values. Table III lists the deviations found with each of the theoretical methods using the G3Large basis set. The DKH-CCSD(T) and DKH-BD(T) methods demonstrate a better description of the ionization process than of the  $d \rightarrow s$  excitation process (a result of the unchanging *d* orbital population for most ionization transitions). Both methods perform equally well having MADs of only 0.07 eV. In fact, the errors are smaller than 0.05 eV in all cases except for V and Co where they are larger. A closer look at the electronic states provides a simple explanation. The ground states of the ions for all the elements except for V and Co are obtained by a removal of a 4*s* electron. The performance of DKH-CCSD(T) and DKH-BD(T) is excellent for all such cases. In the case of V and Cr, the ionization process is more complicated, involving a loss of a 4*s* electron (as for the other elements) along with a simultaneous  $s \rightarrow d$  promotion of a second electron. This yields additional contribution to the errors that result from the promotion energy (seen earlier). Overall, the performance of the G3Large basis set is very accurate.

Table IV lists the atomic excitation and ionization energies at the MP2, MP3, MP4, and CCSD levels of theory using the G3Large basis set. In all cases, relativistic effects were included and all electrons are correlated as in the case of the CCSD(T) results listed in Table II. The convergence of perturbation theory is good for the early elements, but deteriorates strongly for the later elements. As pointed out previously,<sup>34,35</sup> fairly strong oscillations between the differ-

ent perturbation orders are seen for Fe, Co, Ni, and Cu. The dramatic failure of perturbation theory is evident for Cu, where the errors in the excitation energies at second, third, and fourth orders are 1.30, -1.55, and 1.76 eV. The CCSD method (without the perturbative triples correction) behaves fairly well, though errors in computed excitation energies greater than 0.3 eV are seen for all of the later transition elements Mn–Cu. However, the behavior is more systematic with the computed  $s \rightarrow d$  excitation energies being larger than experiment in all cases. Another distinction between the MP*n* and CCSD methods arises in the differing capabilities of describing the two different excitation processes. For each order of perturbation, the ionization process is much better described than the  $s \rightarrow d$  excitation process (the MAD of excitation energies is roughly twice that of the ionization energies). However, CCSD exhibits similar performance for both excitation energies and ionization energies (MAD for both processes is about 0.2 eV). It is clear that an infinite order method is needed to get accurate results for transition metals. Again, it will be interesting to see the implications for *Gn*-type approaches that use results from low order perturbation theory assuming additivity of basis set and correlation effects.

We have investigated the effect of correlating different numbers of electrons in the calculations on the computed excitation and ionization energies. Table V compares CCSD(T) results correlating (a) all electrons (b)

TABLE IV. Deviations in the calculated excitation and ionization energies using perturbation theory and CCSD. All electrons were correlated. The mean absolute absolute deviation is followed by the maximum deviation in parentheses.

Level of theory	MAD (max) from experiment (eV)	
	Excitation energy $d^n s^2 \rightarrow d^{n+1} s^1$	Ionization energy M → M <sup>+</sup>
DKH-MP2/G3Large	0.475 (1.30)	0.217 (0.69)
DKH-MP3/G3Large	0.617(-1.55)	0.320(-0.65)
DKH-MP4/G3Large	0.465 (1.76)	0.205(-0.58)
DKH-CCSD/G3Large	0.241(-0.39)	0.155(-0.23)

TABLE V. Comparison of frozen-core calculations with all electron calculations. Shown is the mean average deviation from CCSD(T,Full)/G3Large.

MAD from all electron calculation (eV)		
Electrons correlated	Excitation energy $d^n s^2 \rightarrow d^{n+1} s^1$	Ionization energy $M \rightarrow M^{+1}$
Full	0	0
3s3p3d4s	0.004	0.002
3d4s	0.124	0.073

3s, 3p, 3d, 4s electrons, and (c) 3d, 4s electrons. Overall, the results including 3s, 3p, 3d, 4s correlation are very close to those correlating all electrons with a MAD of 0.004 eV for excitation energies and 0.002 eV for ionization energies. This is not surprising since the G3Large basis set does not include functions of high polarization needed for correlating the core orbitals accurately. The results including only 3d, 4s correlation show larger deviations up to 0.2 eV and a MAD of 0.124 eV for excitation energies and 0.073 eV for ionization energies. Clearly, inclusion of 3s, 3p correlation is needed to achieve quantitatively reliable results.

In recent work by Peterson and Balabanov,<sup>2</sup> excitation and ionization energies are calculated for the first-row transition elements using scalar relativistic CCSD(T) and extrapolating to the complete basis set limit. By comparing the CCSD(T) results obtained with the G3Large basis set to the corresponding core-valence corrected complete basis set results, we are able to estimate the completeness of the G3Large basis set. Table VI shows the difference between the CBS and G3Large atomic excitation and ionization energies. The mean absolute deviations between the G3Large results and the CBS results is 0.168 eV for excitation energies and 0.076 eV for ionization energies. In the case of the  $s \rightarrow d$  excitation energies, as pointed out earlier, the G3Large results for each atom favor the  $d^n s^2$  state relative to the  $d^{n+1} s^1$  state. Extrapolating to the CBS limit, the additional differential correlation effects stabilize the  $d^{n+1} s^1$  state, which greatly improves comparison to experiment. These factors have to be taken into account in designing modified  $G_n$  procedures for transition metals.

## B. Geometries and dissociation energies of diatomic hydrides

### 1. Geometries

Initially we determined the appropriate wave functions for several low-lying electronic states of the ten diatomic hydrides MH (Sc–Zn) at the Hartree–Fock level. In many cases, incorrect ground states are predicted at the Hartree–Fock level, but inclusion of electron correlation effects at the CCSD(T) level reverses the ordering and yields the correct known ground states. For each hydride, Table VII compares the optimized bond length to experiment<sup>50–59</sup> at both the CCSD(T)/G3Large and BD(T)/G3Large (both with and without the inclusion of scalar relativistic effects) levels of theory. The table also lists  $\langle S^2 \rangle$  values. For both levels of theory, the inclusion of relativistic effects improves the comparison to experiment. For DKH-CCSD(T)/G3Large and

TABLE VI. The difference, in eV, between the CBS and G3Large excitation and ionization energies.

Excitation energies (eV)		Complete basis set <sup>a</sup> —G3Large
$d^n s^2 \rightarrow d^{n+1} s^1$	Transition	DKH-CCSD(T, 3s3p3d4s)
Sc	$d^1 s^2 \rightarrow d^2 s^1$	–0.144
Ti	$d^2 s^2 \rightarrow d^3 s^1$	–0.134
V	$d^3 s^2 \rightarrow d^4 s^1$	–0.133
Cr	$d^4 s^2 \rightarrow d^5 s^1$	–0.123
Mn	$d^5 s^2 \rightarrow d^6 s^1$	–0.237
Fe	$d^6 s^2 \rightarrow d^7 s^1$	–0.215
Co	$d^7 s^2 \rightarrow d^8 s^1$	–0.199
Ni	$d^8 s^2 \rightarrow d^9 s^1$	–0.194
Cu	$d^9 s^2 \rightarrow d^{10} s^1$	–0.135
MAD		0.168

  

Ionization energies (eV)		
$M \rightarrow M^{+}$	Transition	DKH-CCSD(T, 3s3p3d4s)
Sc	$d^1 s^2 \rightarrow d^1 s^1$	0.000
Ti	$d^2 s^2 \rightarrow d^2 s^1$	0.006
V	$d^3 s^2 \rightarrow d^4 s^0$	–0.155
Cr	$d^5 s^1 \rightarrow d^5 s^0$	–0.007
Mn	$d^5 s^2 \rightarrow d^5 s^1$	0.035
Fe	$d^6 s^2 \rightarrow d^6 s^1$	0.029
Co	$d^7 s^2 \rightarrow d^8 s^0$	–0.204
Ni <sup>b</sup>	$d^8 s^2 \rightarrow d^9 s^0$	–0.193
Cu	$d^{10} s^1 \rightarrow d^{10} s^0$	0.007
Zn	$d^{10} s^2 \rightarrow d^{10} s^1$	0.049
MAD		0.076

<sup>a</sup>Reference 2.

<sup>b</sup>Referenced to the  $3d^8, 4s^2$  state.

DKH-BD(T)/G3Large we find respective MADs of 0.017 and 0.014 Å from experiment. For CCSD(T) [and DKH-CCSD(T)] the largest deviation occurs for NiH where the theoretically optimized bond length is 0.071 Å (0.061 Å) shorter than experiment. Closer inspection reveals that this unexpectedly large deviation is a result of a very highly contaminated starting UHF wavefunction. It is clear from Table VII that the calculated UHF  $\langle S^2 \rangle$  value of NiH (1.71) is dramatically deficient (ideal value is 0.75). Consequently, the resulting bond length is deficient and the corresponding bond energy is too low (*vide infra*). For NiH we see BD(T) performing substantially better. This is clearly due to the observation that orbitals which satisfy the Brueckner condition often do not suffer from significant spin contamination. Indeed, in the case of NiH, the  $\langle S^2 \rangle$  value of the Brueckner determinant is 0.78, close to the ideal value. Other molecules with significant spin contamination are FeH (computed  $\langle S^2 \rangle$  value of 4.75 instead of the ideal value of 3.75) and CoH (computed  $\langle S^2 \rangle$  value of 2.99 instead of the ideal value of 2.0). However, the resulting error in the bond length for FeH and CoH is much smaller than in NiH. If we exclude NiH from the results both methods perform similarly.

There are two other important points that should be noted for these systems.

- (1) In some of the hydrides (e.g., CoH and NiH), multiple solutions of the unrestricted HF wavefunctions were found, some with low spin contamination and some

TABLE VII. Optimized bond lengths ( $\text{\AA}$ ) and  $\langle S^2 \rangle$  values. For the orbital occupations of TiH and CoH, the  $\delta'$  illustrates that the second delta orbital is being occupied. Since the existence of two distinct electronic states for both TiH and CoH is a result of using only real orbitals, the experimental bond length shown corresponds to the true  $\Phi$  states. All electrons are correlated. When multiple experimental values are available the most recent is used to compare to theory.

Optimized bond lengths ( $\text{\AA}$ )				Experiment-Theory							
M-H	State	Occupation	Experiment	CCSD(T)/G3Large	$\langle S^2 \rangle$	DKH-CCSD(T)/G3Large	$\langle S^2 \rangle$	BD(T)/G3Large	$\langle S^2 \rangle$	DKH-BD(T)/G3Large	$\langle S^2 \rangle$
ScH	$^1\Sigma^+$	...	1.7754 <sup>a</sup>	0.008	0.00	0.008	0.00	0.008	0.00	0.009	0.00
TiH	$^4\Phi$	$\delta, \pi, \sigma$	1.761 <sup>b</sup>	-0.016	3.76	-0.017	3.76	-0.016	3.76	-0.017	3.76
	$^4\Phi$	$\delta', \pi, \sigma$	1.761 <sup>b</sup>	-0.023	3.75	-0.024	3.75	-0.022	3.75	-0.023	3.75
VH	$^5\Delta$	$\pi, \pi, \delta, \sigma$	...	...	6.01	...	6.01	...	6.01	...	6.01
CrH	$^6\Sigma^+$	$\pi, \pi, \delta, \delta, \sigma$	1.6554 <sup>c</sup>	0.013	8.78	0.019	8.77	-0.011	8.79	0.000	8.79
MnH	$^7\Sigma^+$	$\delta, \delta, \pi, \pi, \sigma, \sigma$	1.731 <sup>d</sup>	-0.008	12.00	-0.003	12.00	-0.008	12.00	-0.003	12.00
FeH	$^4\Delta$	$\pi, \pi, \delta$	1.6074 <sup>e</sup> (1.589) <sup>f</sup>	0.021	4.75	0.025	4.74	0.032	4.14	0.039	4.19
CoH	$^3\Phi$	$\delta, \pi$	1.5327 <sup>g</sup> (1.52) <sup>h</sup>	0.009	2.99	0.013	2.99	0.017	2.17	0.031	2.21
	$^3\Phi$	$\delta', \pi$	1.5327 <sup>h</sup> (1.52) <sup>h</sup>	0.052	2.98	0.039	2.98	0.003	2.06	0.022	2.09
NiH	$^2\Delta$	$\delta$	1.475 <sup>d</sup>	0.071	1.71	0.061	1.71	0.001	0.78	0.020	0.79
CuH	$^1\Sigma^+$	...	1.4625 <sup>i</sup>	-0.026	0.00	-0.003	0.00	-0.026	0.00	-0.004	0.00
ZnH	$^2\Sigma^+$	$\sigma$	1.5935 <sup>j</sup>	-0.010	0.76	0.001	0.77	-0.010	0.76	0.002	0.76
MAD				0.020		0.017		0.014		0.014	
MAD excluding NiH				0.014		0.011		0.016		0.013	

<sup>a</sup>Reference 56.

<sup>b</sup>Reference 53.

<sup>c</sup>Reference 52.

<sup>d</sup>Reference 59.

<sup>e</sup>Reference 54.

<sup>f</sup>Reference 51.

<sup>g</sup>Reference 55.

<sup>h</sup>Reference 50.

<sup>i</sup>Reference 57.

<sup>j</sup>Reference 58.

with high contamination. We have performed a stability analysis of the corresponding wavefunctions to determine the solution to be used for correlation studies. In general, when multiple solutions are obtained, the wavefunctions corresponding to low spin contamination are not stable. Such solutions appear to be basis set dependent and frequently collapse to lower energy (higher contaminated) solutions. The high spin contaminated states are stable solutions at the UHF level. They yield consistent results though they lead to significant deficiencies in the performance of some theoretical models (*vide supra*).

- (2) There are two molecules where the starting UHF (or UDFT) wave function is deficient. These are TiH and CoH where the ground states are known to be  $^4\Phi$  and  $^3\Phi$ , respectively. The correct orbital occupations are shown in Table VII. However, they cannot be represented as a single determinant with real coefficients, leading to broken symmetry solutions. In both cases, the problem arises from having unpaired electrons in both  $\pi$  and  $\delta$  orbitals. While complex molecular orbitals will yield proper  $\Phi$  states, the inclusion of electron correlation effects starting from complex orbitals is not incorporated in most quantum chemical programs. Using real orbitals, two different broken symmetry UHF (or UDFT) solutions have been found for both molecules, and we have included both solutions in Table VII. While they have significantly different energies at the UHF level, the energies of the two solutions are typically within 1–2 kcal/mol of each other at highly correlated levels such as CCSD(T) or BD(T).

## 2. Dissociation energies

Table VIII compares the calculated bond dissociation energies to experiment.<sup>24,53,55,60,61</sup> Zero-point energy corrections were calculated at each level of theory and included for comparison to experiment. The mean absolute deviations at the DKH-CCSD(T)/G3Large and DKH-BD(T)/G3Large levels of theory are 3.91 and 2.55 kcal/mol, respectively. After neglecting NiH the MAD of the DKH-CCSD(T)/G3Large level of theory decreases to 3.09 kcal/mol. For all cases where the BD(T) and CCSD(T) results are significantly different, the BD(T) yields higher bond dissociation energies. The most pronounced differences are for FeH, CoH, and NiH, which are the most spin contaminated hydrides. The differences in the computed bond energies between DKH-CCSD(T) and DKH-BD(T) are 2 kcal/mol (FeH), 5 kcal/mol (CoH), and 13 kcal/mol (NiH), while for most of the other hydrides they are within 1 kcal/mol. Recently, Balabanov and Peterson have investigated some of the transition metal hydrides with CCSD(T) based on a ROHF starting point and thus do not have issues related to spin contamination. It will be interesting to investigate potential Gn models based on restricted references.

Table IX compares the bond dissociation energies of TiH, MnH, and CuH calculated with the G3Large basis set with those extrapolated to the complete basis set.<sup>1</sup> The cc-pVTZ and CBS calculations enable us to estimate deficiencies in the G3Large basis set for the calculation of bond dissociation energies. The cc-pVTZ and G3Large basis sets perform similarly. This puts the G3Large basis set within about 2 kcal/mol of the CBS limit for the calculation of bond dissociation energies for these three molecules.

TABLE VIII. Comparison of calculated M–H bond dissociation energies with experiment. All calculations used the G3Large basis set. All electrons were correlated. Zero-point energy corrections, calculated at the listed level of theory, are included.

M–H	Bond dissociation energies ( $D_0$ ) (kcal/mol)		[Expt- $\Delta$ SO]—Theory			
	Expt <sup>a</sup>	$\Delta$ SO <sup>b</sup>	CCSD(T,Full)	DKH-CCSD(T,Full)	BD(T,Full)	DKH-BD(T,Full)
ScH	48.0 ± 2.1	-0.29	-2.35	-3.27	-2.37	-3.28
TiH	48.2 ± 2.3	-0.11 (-0.53) <sup>c</sup>	2.61	3.82	2.45	3.68
	48.2 ± 2.3	-0.11 (-0.53) <sup>c</sup>	1.91	3.03	1.73	2.89
VH	49.1 ± 2.3	-0.41 (-0.50) <sup>d</sup>	-4.46	-2.74	-4.88	-3.11
CrH	44.5 ± 1.6	0	-2.53	-3.86	-3.88	-5.29
MnH	31.6 ± 4.4	0	-4.30	-3.51	-4.28	-3.50
FeH	36.9 ± 1.8	-0.65 (-0.50) <sup>e</sup>	-0.80	1.17	-3.21	-0.71
CoH	45.7 ± 3.2	-0.77 (-1.51) <sup>f</sup>	5.96	8.32	-0.72	2.92
	45.7 ± 3.2	-0.77 (-1.51) <sup>f</sup>	7.60	9.17	-3.20	0.83
NiH	58.6 ± 3.7	-1.38 (-1.40) <sup>g</sup>	8.95	11.27	-6.15	-1.50
CuH	60.6 ± 4.2	0	1.55	-0.59	1.19	-1.03
ZnH	19.6 <sup>h</sup> ± 0.2	0	-0.67	0.55	-0.70	0.50
MAD			3.42	3.91	2.98	2.55
MAD (neglecting NiH)			2.80	3.09	2.63	2.67

<sup>a</sup>Reference 24.<sup>b</sup>Contribution of experimental spin-orbit corrections to the binding energies of the hydrides. Atomic spin-orbit values were taken from Ref. 62 in deriving these values. Values in parentheses denote the spin-orbit corrections for hydrides (references given below).<sup>c</sup>Reference 53.<sup>d</sup>Estimated value. No experimental data available.<sup>e</sup>The three lowest term values have been measured (Ref. 60). The highest one has not been measured. An estimate for  $\Delta$ (SO) was obtained from the three lowest ones and an estimate for the missing one.<sup>f</sup>The two lowest term values have been measured (Ref. 55). The highest one has not been measured. An estimate for  $\Delta$ (SO) was obtained from the two lowest ones and an estimate for the missing one.<sup>g</sup>Reference 61.<sup>h</sup>Reference 59.

The performance of the BD(T) merits further discussion. By rotating the UHF reference orbitals, BD(T) corrects substantially for spin contaminated reference functions, thereby yielding more correlation energy. Since significant spin contamination in our test molecules is seen only for the hydrides, one would expect an increase in bond dissociation energy on going from CCSD(T) to BD(T). This is indeed observed as pointed out earlier, and BDE's are mostly larger when calculated with BD(T) as opposed to CCSD(T), with the most notable increases occurring for the most highly spin contaminated systems (FeH, CoH, and NiH). It should be noted that the dissociation energies in Table VIII correspond to the ground electronic states of the atoms, viz.,  $d^n s^2$  except for CrH and CuH where the atomic ground state is  $d^{n+1} s^1$ . Interestingly, we note that CrH is the most overbound species (5.3 kcal/mol overbound), and the deficiency of the G3Large basis set noted previously for the  $d^{n+1} s^1$  state contributes partly to the overbinding.

It can be noted that many of the errors for the computed bond energies are quite significant even at the BD(T) level.

TABLE IX. Comparison of G3Large results with CBS results.

DKH-CCSD(T)	$D_0$ (kcal/mol)		
	TiH	MnH	CuH
G3Large	45.28	35.11	61.19
cc-pVTZ <sup>a</sup>	45.44	35.05	62.00
CBS <sup>a</sup>	47.37	35.90	61.78

<sup>a</sup>Reference 1.

However, the uncertainties in the experimental bond dissociation energies may make a critical comparison difficult. It is clear from the experimental values listed in Table VIII that quoted uncertainties of order of 4 kcal/mol are common even for these simple diatomic molecules. These factors also have to be taken into account when designing new procedures such as *Gn* and assessing their performance with respect to known experimental values.

### C. G3MP2Large basis set

Table X compares the G3Large basis set to the slightly smaller G3MP2Large basis set, which is obtained by neglecting the core polarization function that are included in G3Large. A comparison of the MADs from experiment for both of the basis sets [using the DKH-CCSD(T) model for correlation] shows that the  $s \rightarrow d$  excitation energies are more sensitive to changes in the core correlation than the ionization energies. This is to be expected since in Table V we see that the excitation energies are affected more than the ioniza-

TABLE X. Comparison of G3Large basis set with slightly smaller G3MP2Large basis set with all electron calculations. The mean absolute deviation from experiment is given.

Level of theory	MAD from experiment (eV)	
	Excitation energy $d^n s^2 \rightarrow d^{n+1} s^1$	Ionization energy $M \rightarrow M^+$
DKH-CCSD(T)/G3Large	0.174	0.060
DKH-CCSD(T)/G3MP2Large	0.190	0.066

tion energies when the size of the frozen core is increased. With deviations of 0.016 eV for excitation energies and 0.006 eV for ionization energies, the G3MP2Large basis set performs similarly to the full G3Large basis set but at a reduced cost. This basis set will be useful in future applications of *Gn*-type methods.

## V. CONCLUSIONS

The following conclusions can be drawn from this investigation of application of the G3Large basis set to transition metal atomic ionization potentials, excitation energies, and diatomic hydrides (M=Sc–Zn).

- (1) Overall, the new G3Large basis set for the transition metals performs adequately in calculations of the excitation and ionization energies of the transition metal atoms. The geometries and dissociation energies for diatomic hydrides are described quite well with the exception of NiH, which suffers from a highly spin contaminated wavefunction.
- (2) There are several hydrides (FeH, CoH, NiH) where the starting UHF wavefunction is significantly spin contaminated. While they are stable solutions, they provide

a poor starting point for correlation studies. This results in the bond length and the corresponding dissociation energy to be fairly poor. A much better starting point is provided by the corresponding Brueckner orbitals. The corresponding triples-augmented BD(T) method yields significantly higher binding energies than the conventional CCSD(T) in such cases. For the other hydrides with very little contamination, the performance of BD(T) and CCSD(T) is virtually identical.

- (3) These simple hydride and atomic systems are very challenging to describe accurately by these conventional *ab initio* methods. In the future we will continue this assessment on more complex systems involving transition metals that will be used to help develop an improved version of *Gn* theories.

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## APPENDIX: SUPPLEMENTARY FUNCTIONS FOR THE G3MP2LARGE AND G3LARGE BASIS SETS

Atom	Diffuse exponents			Polarization exponents		Core exponents	
	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>d</i>	<i>f</i>
Sc	0.020 03	0.015 69	0.040 52	0.4306	0.2616	18	20
Ti	0.021 87	0.017 6	0.052 67	0.4306	0.2616	20	22
V	0.023 62	0.019 1	0.063 07	0.4306	0.2616	23	23
Cr	0.025 33	0.020 57	0.073 15	0.4306	0.2616	25	6
Mn	0.015 46	0.020 41	0.084 18	0.4306	0.2616	27	6
Fe	0.016 53	0.022 49	0.091 12	0.4306	0.2616	30	6
Co	0.017 55	0.022 92	0.099 83	0.4306	0.2616	32	6
Ni	0.018 46	0.023 86	0.109 4	0.4306	0.2616	35	6
Cu	0.019 43	0.024 14	0.118 9	0.4306	0.2616	37	7
Zn	0.020 33	0.025 87	0.129 7	0.4306	0.2616	40	7

In the G3large and G3MP2large basis sets the 3d2f polarization set is obtained by splitting the *f* exponent into 4*f*, *f*, and 0.25*f* and the *g* exponent into 2*g*, 0.5*g*.

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