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# Explicitly correlated composite thermochemistry of transition metal species

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Atomization energies were calculated using explicitly correlated coupled cluster methods with correlation consistent basis sets for a series of 19 small molecules containing 3d transition metal atoms. The atomization energies were calculated using a modified Feller-Peterson-Dixon approach in which CCSD(T) complete basis set (CBS) limits were obtained using extrapolations of aVTZ/aVQZ CCSD(T)-F12b correlation energies, and then a series of additive contributions for relativity, core correlation, higher order correlation, and zero-point vibrations were included. The frozen-core CBS limits calculated with F12 methods closely matched the more computational expensive conventional awCVQZ/awCV5Z CBS extrapolations, with a mean unsigned deviation of just 0.1 kcal/mol. In particular, the CCSD(T\*)-F12b/aVDZ and aVTZ atomization energies were more accurate on average than the conventional CCSD(T)/aVQZ and aV5Z results, respectively. In several cases the effects of higher order correlation beyond CCSD(T), as judged by CCSDT and CCSDT(Q)<sub>A</sub> calculations, were greater than 1 kcal/mol, reaching 4.5 kcal/mol for CrO<sub>3</sub>. For the 16 molecules of this study with experimental uncertainties of ~3.5 kcal/mol or less, the final composite heats of formation have a mean unsigned deviation (MUD) from experiment of just 1.3 kcal/mol, which is slightly smaller than the average of the experimental uncertainties, 1.8 kcal/mol. The root mean square deviation (RMS) is only slightly larger at 1.7 kcal/mol. Without the contributions due to higher order correlation effects, the MUD and RMS rise to 2.1 and 2.8 kcal/mol, respectively. To facilitate the F12 calculations, new (aug-)cc-pVnZ/MP2Fit ( $n = Q, 5$ ) and (aug-)cc-pwCVTZ/MP2Fit auxiliary basis sets were also developed for the transition metal atoms. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818725>]

## I. INTRODUCTION

Transition metal (TM) containing species have long held industrial and scientific importance as catalysts, materials, and synthetics. Quantitative energetics of these molecules can be used to elucidate mechanisms, detail intermediates, and predict ground states. Species containing TMs often present substantial experimental difficulties for determining quantitative thermochemical properties due to material instability, incomplete combustion, and non-stoichiometric oxide formation. Unfortunately high accuracy *ab initio* methods to determine chemically accurate ( $\pm 1$  kcal/mol) energetics for TM containing molecules have also proven much more difficult than for similar-sized main group molecules. These difficulties are largely due to the compact nature of the 3d shell, resulting in large electron correlation effects best treated by methods such as coupled cluster (CC) theory, as well as a high density of states which may require the use of multireference methods like multireference configuration interaction (MRCI). Both of these methods scale steeply with system size and the number of correlated electrons, which can severely limit the size of the systems that can be treated. Further limiting the size of treatable systems is that the energetics are often slow to converge with respect to the orbital basis set, requir-

ing large basis sets and basis set extrapolation to the complete basis set (CBS) limit to obtain accurate results.

Previous work on TM containing molecules with the goal of achieving chemical accuracy has been rather limited. A comprehensive review of composite thermochemistry schemes applicable to these species can be found in Peterson *et al.*,<sup>1</sup> as well as related work by Dixon and co-workers.<sup>2,3</sup> The correlation consistent composite approach (ccCA) of Wilson and co-workers,<sup>4,5</sup> the G4 method of Curtiss and co-workers,<sup>6</sup> and the composite thermochemistry approach of Feller, Peterson, and Dixon (FPD)<sup>7,8</sup> have all been applied to TM containing molecules to obtain results approaching chemical accuracy or at least “transition metal chemical accuracy” ( $\pm 3$  kcal/mol). All of these methods rely upon the use of large basis sets and basis set extrapolation to obtain accurate results. The use of CCSD(T) (coupled-cluster with singles, doubles, and perturbative triples) at the CBS limit, mostly within the FPD approach, has been used in a wide variety of transition metal containing molecules (see Refs. 9–11 and references therein). To avoid the computational expense present from using large basis sets with CCSD(T), the ccCA method uses a MP2 CBS extrapolation with a single triplet-zeta CCSD(T) correction to approximate CCSD(T) at the CBS limit. The G4 method similarly uses a composite scheme with MP4 and a correction for CCSD(T) with a smaller basis but also includes an empirical scaling factor. It should also be

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noted that the limited studies on the effects of higher order correlation beyond CCSD(T) have shown that CCSDT and CCSdT(Q) may be important to obtaining close to kcal/mol accuracy in molecules containing transition metals.<sup>12,13</sup> The goal of the present work is to develop a composite scheme that can obtain chemical accuracy for transition metals while using as small an orbital basis set as possible in a purely *ab initio* scheme with no empirical scaling.

Recent advances in methods that include terms which explicitly depend on the interelectronic distance, i.e., explicitly correlated methods, have demonstrated a dramatic improvement over conventional methods with respect to basis set convergence with a very similar computational cost. These techniques allow the use of much smaller basis sets to get results near the basis set limit. The CCSD(T)-F12x [x = a, b] methods in particular have been used with success for main group elements to achieve this accelerated convergence, often with near complete basis set limit results being obtained with triple-zeta correlation consistent basis sets.<sup>14</sup> Recent reviews of explicitly correlated methods are available.<sup>15–20</sup> In the present work these methods are applied to transition metal containing molecules to obtain both accurate frozen core CCSD(T) basis set limit results as well as converged CCSD(T) corrections accounting for core correlation (the 3d electrons of the metals are correlated). These are then combined into a FPD composite thermochemistry approach to give chemically accurate atomization energies and heats of formation. The number of molecules treated in this work, 19, is small by comparison to the extensive ccCA study of Jiang *et al.*,<sup>5</sup> but the results are expected to be indicative of the accuracies achievable with the current method.

## II. COMPUTATIONAL METHODOLOGY

### A. Basis sets and methods

Throughout this work both conventional and explicitly correlated coupled cluster calculations were carried out with single, double, and perturbative triple excitations, CCSD(T). The open-shell systems employed restricted open-shell Hartree-Fock (ROHF) orbitals but without spin restrictions in the CCSD equations.<sup>14,21,22</sup> Except for the cases when correlation methods beyond CCSD(T) were employed (see below), full symmetry equivalencing was imposed on the orbitals for the atomic calculations. The orbital basis sets corresponded to the standard diffuse-augmented correlation consistent basis sets, aug-cc-pVnZ ( $n = D-5$ ), with the second-row elements (i.e., Cl) including an additional tight *d* function, aug-cc-pV(n+d)Z.<sup>23–28</sup> When correlating the outer-core electrons ( $3s3p$  for the transition metals,  $1s$  for the 1st-row atoms, and  $2s2p$  for Cl), the aug-cc-pwCVnZ basis sets ( $n = T-5$ ) were used throughout.<sup>23,29</sup> These orbital sets will be denoted as aVnZ or awCVnZ ( $n = D-5$ ) throughout this work.

The explicitly correlated coupled cluster calculations utilized the F12x (x = a, b) methods of Werner and co-workers<sup>14,30</sup> with the fixed amplitude Ansatz 3C(FIX).<sup>31–33</sup> For the required auxiliary basis sets, density fitting (DF) of the Fock and exchange matrices used the def2-QZVPP/JKFIT

auxiliary basis sets (ABSs) of Weigend<sup>34</sup> for the transition metal elements and the cc-pVnZ/JKFIT sets of Weigend *et al.*<sup>35</sup> for the remainder (using  $n = T$  for both aVDZ and aVTZ orbital basis sets). For the non-transition metal elements, the DF of the remaining two-electron integrals used either the aug-cc-pVnZ/MP2FIT basis sets of Weigend *et al.*<sup>35</sup> (frozen-core calculations) or the aug-cc-pwCVnZ/MP2FIT sets of Hättig<sup>36</sup> (core correlation calculations), with  $n = T$  used for both double- and triple- $\zeta$  quality orbital basis sets in each case. The analogous DF sets for the transition metals used the aug-cc-pVTZ/MP2FIT basis sets of Hill and Platts<sup>37</sup> for the aVDZ and aVTZ orbital basis sets, while the aVQZ and awCVnZ calculations used new MP2FIT basis sets developed in this work (see below). The complementary auxiliary basis sets (CABS)<sup>38</sup> needed for the resolution of the identity (RI) utilized the aug-cc-pVnZ/OptRI sets of Yousaf and Peterson<sup>39</sup> for the light elements and the MP2FIT basis sets mentioned above for the transition metals. For the aug-cc-pwCVnZ orbital sets, the aug-cc-pwCVnZ/MP2FIT sets<sup>36</sup> were used as the CABS for the non-metal elements. The F12 calculations utilized the CABS singles correction<sup>30,40</sup> to the HF energies in all cases.

Since the F12 corrections are only applied to the CCSD energies, the basis set convergence of the (T) correction was often found to be a significant source of basis set incompleteness in the atomization energies. Hence use has also been made of the scaled triples correction of Knizia *et al.*,<sup>14</sup> denoted (T\*), where the scale factor is defined as  $E_{\text{corr}}^{\text{MP2-F12}}/E_{\text{corr}}^{\text{MP2}}$ . In order to retain size consistency in the calculations, the molecular scale factor was also used for its atoms in the calculation of each atomization energy.

The value of the geminal slater exponent,  $\gamma$ , was chosen to be 1.0 for all three basis sets aVDZ, aVTZ, and aVQZ. This contrasts previous work on the main group where values of 1.0, 1.2, and 1.4 were recommended for molecules containing just first- and second-row elements with these basis sets.<sup>41</sup> The rationale for the present choice is discussed below, but except for the case of aVDZ, the results were relatively insensitive to the choices of  $\gamma$ . When the awCVnZ sets were used,  $\gamma = 1.4$  was utilized throughout as has been previously recommended for core correlation.<sup>42</sup>

### B. Composite methodology

In the present work the FPD composite approach<sup>7</sup> has been used to determine atomization energies, which are utilized together with the known enthalpies of formation of the atoms to determine molecular enthalpies of formation. In the present case this is defined as

$$\begin{aligned} \Delta H_{\text{at}}(298 \text{ K}) = & \Delta E_{\text{at}}(\text{FC})/\text{CBS} + \Delta CV + \Delta DK + \Delta SO \\ & + \Delta HC + \Delta ZPE + \Delta H(298-0) \end{aligned} \quad (1)$$

The first two terms of Eq. (1) are of primary interest to the present work since they represent the frozen-core (FC) CCSD(T) atomization energy at the CBS limit and the contribution to the atomization enthalpy from core-valence (CV) electron correlation, respectively. As will be demonstrated in this work, the use of CCSD(T)-F12b is very advantageous for these contributions. The next term,  $\Delta DK$ , includes the effects

of scalar relativity through the use of the 2nd-order Douglas-Kroll-Hess (DKH) Hamiltonian,<sup>43–45</sup> while  $\Delta SO$  accounts for atomic spin-orbit coupling. The term  $\Delta HC$  extends the correlation treatment beyond the CCSD(T) level by including frozen-core CCSDT and CCSDT(Q)<sub>A</sub> calculations (see below for a description of the basis sets used for these contributions). Based on previous experience,<sup>46</sup> harmonic frequencies calculated at the CCSD(T)-F12a/aVDZ level of theory were utilized for the zero-point vibrational corrections,  $\Delta ZPE$ , and are expected to be within 0.1 kcal/mol of the CCSD(T) basis set limit. These are then combined with standard statistical mechanical expressions for the thermal corrections  $\Delta H(298-0)$ . All calculations were carried out with the MOLPRO suite of *ab initio* programs,<sup>47</sup> except for the higher order correlation work, which was performed with the MRCC program<sup>48</sup> as interfaced to MOLPRO.

### III. RESULTS

#### A. Development of new MP2FIT auxiliary basis sets for Sc–Zn

Auxiliary basis sets (ABSs) specifically matched to the cc-pVnZ ( $n = Q, 5$ ) and cc-pwCVTZ orbital basis sets (OBSs) for the 3d elements Sc–Zn<sup>23</sup> were designed and optimized by minimizing the quantity

$$\delta DF = \frac{1}{4} \sum_{aibj} \frac{[\langle ab||ij\rangle_{DF} - \langle ab||ij\rangle]^2}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j}, \quad (2)$$

where  $\langle ab||ij\rangle = (ai|bj) - (aj|bi)$ , with  $a$  and  $b$  denoting virtual orbitals,  $i$  and  $j$  occupied orbitals, and  $\varepsilon_x$  the Hartree-Fock orbital energies.<sup>49</sup> This optimization employed the analytical gradients available in the RICC2 module<sup>50,51</sup> of the TURBOMOLE package.<sup>52</sup>

The resulting ABSs, herein suffixed with /MP2FIT, were designed such that the total number of auxiliary basis functions in a given ABS was the same for all of the elements Sc–Zn. As transition elements are regularly found in multiple oxidation states, some exponents within a given basis were optimized for different cations of the element, giving an approximation of the more stable oxidation states. More specifically, the tightest exponents for Ti, Ni, Cu, and Zn were optimized for the 2<sup>+</sup> cations, and those for Sc on the 1<sup>+</sup> cation. The more diffuse functions were then optimized for the neutral atoms. For the remaining elements, tight functions were

typically optimized on the 3<sup>+</sup> cation (4<sup>+</sup> cation for Mn), a set of intermediate functions on the 2<sup>+</sup> cation, and the diffuse functions again optimized for the neutral atom. Further details of this procedure can be found in Ref. 37. For the cc-pVnZ sets the 1s–3p electrons were included in the frozen core approximation and excluded from the calculation of the  $\delta DF$  functional, while the 3s and 3p electrons were included in the correlation treatment and calculation of  $\delta DF$  for the cc-pwCVTZ sets.

The diffuse augmented correlation consistent basis sets, aug-cc-pVnZ and aug-cc-pwCVnZ,<sup>23</sup> for the 3d elements were originally obtained by the addition of a single extra function to each angular momentum symmetry present in the regular set in an even-tempered manner (for technical reasons this even-tempered extension was carried out using the exponents from the cc-pwCVnZ series of basis sets). In order to produce ABSs matched to these OBSs, two alternative strategies were pursued. First, a simple even-tempered extension of the cc-pVnZ/MP2FIT sets were constructed by adding an additional function for each angular momentum, and second, explicit optimization of an additional function for each angular momentum on the neutral atom was carried out. While the DF errors were similar in each case, the explicitly optimized values were generally more accurate and have been adopted throughout this work. While it is very unlikely that 3d elements will be found as anions even though their compounds often have large electron affinities, the resulting aug-cc-pVnZ/MP2FIT and aug-cc-pwCVTZ/MP2FIT ABSs have not been tested for Rydberg-type excited states and should be used with caution in such circumstances. Both of the strategies outlined above differ from that employed in the optimization of the aug-cc-pVTZ/MP2FIT ABSs, where the entire basis was reoptimized for the anions of the 3d elements.<sup>37</sup> It is assumed that the current strategies will produce ABSs that will be more balanced for the description of common oxidation states of 3d elements in molecules.

The composition of the cc-pVnZ/MP2FIT and cc-pwCVTZ/MP2FIT ABSs (along with their diffuse augmented counterparts) are detailed in Table I, along with the composition of the respective orbital basis set. For completeness, the previously published cc-pVTZ/MP2FIT sets are also included.<sup>37</sup> The ratio of functions in the ABSs compared to the OBSs are calculated assuming spherical angular momenta and it should be noted that the original ratios for the cc-pVTZ sets in Ref. 37 simply compared the number of exponents

TABLE I. Composition of the MP2FIT auxiliary basis sets compared to the orbital sets for the 3d transition metals. The ratio of functions assumes spherical angular momenta.

	OBS	ABS	Ratio of functions
cc-pVTZ	[7s6p4d2f1g]	(13s11p9d7f5g3h2i) <sup>a</sup>	3.6
cc-pwCVTZ	[7s6p4d3f2g]	(14s13p11d10f8g5h3i)	4.1
cc-pVQZ	[8s7p5d3f2g1h]	(13s12p10d9f7g5h4i2k)	3.5
cc-pV5Z	[9s8p6d4f3g2h1i]	(13s12p11d10f9g6h5i4k2l)	3.1
aug-cc-pVTZ	[8s7p5d3f2g]	(14s12p10d8f6g4h3i) <sup>a</sup>	3.2
aug-cc-pwCVTZ	[8s7p5d4f3g]	(15s14p12d11f9g6h4i)	3.6
aug-cc-pVQZ	[9s8p6d4f3g2h]	(14s13p11d10f8g6h5i3k)	3.0
aug-cc-pV5Z	[10s9p7d5f4g3h2i]	(14s13p12d11f10g7h6i5k3l)	2.8

<sup>a</sup>ABS described in Ref. 37, included for completion.

rather than the resulting number of auxiliary basis functions. As may be expected, to reach the desired accuracy it was necessary to include functions with an angular momentum of  $\ell_{\text{occ}} + \ell_{\text{bas}}$ ,<sup>36,49</sup> the highest occupied angular momentum symmetry for the ground state of the neutral atom and the largest angular momentum included in the OBS, respectively. A ratio of functions less than 4.0 is in-keeping with MP2FIT ABSs for lighter elements,<sup>49</sup> although a slightly higher ratio of 4.1 was required to accurately fit the cc-pwCVTZ orbital basis with the 3s and 3p electrons correlated. Table I shows that the QZ and 5Z ABSs have the same number of s and p functions. Several attempts were made to add additional, tighter functions to the 5Z set but the resulting exponents were poorly defined with no resulting gradient of the  $\delta$ DF functional. These exponents also had an entirely negligible effect on both the optimal value of the functional and the difference in correlation energy between conventional and density fitted MP2, thus they can be safely omitted.

The ABSs developed as part of the current investigation were validated by calculations on a test set of small to medium sized complexes containing the 3d elements: ScCl<sub>3</sub>, ScF<sub>3</sub>, ScH<sub>3</sub>, ScO, TiCl<sub>4</sub>, TiF<sub>3</sub>, TiF<sub>4</sub>, TiH<sub>4</sub>, TiO, TiO<sub>2</sub>, TiS<sub>2</sub>, VH<sub>5</sub>, VO, VOF<sub>3</sub>, CrCl<sub>3</sub>, CrF<sub>3</sub>, CrO<sub>3</sub>, MnF<sub>2</sub>, MnO, MnO<sub>3</sub>F, MnO<sub>4</sub><sup>-</sup>, MnS, FeF<sub>2</sub>, FeF<sub>3</sub>, FeO, CoCl<sub>3</sub>, CoF<sub>2</sub>, CoF<sub>3</sub>, NiCl<sub>2</sub>, NiF<sub>2</sub>, NiF<sub>3</sub>, NiO, NiS, Cu<sub>2</sub>, Cu<sub>2</sub>O, Cu<sub>2</sub>S, CuCN, CuCl, CuF, CuH, ZnCl<sub>2</sub>, ZnF<sub>2</sub>, ZnH<sub>2</sub>, and ZnMe<sub>2</sub>. The geometries of these complexes were taken from a previous study.<sup>34</sup> The basis set incompleteness error (BSIE) in the orbital basis sets was first assessed at the MP2 level of theory, before comparison with the density fitting error (defined as the difference between conventional and density fitted MP2 correlation energies). For non-3d elements the cc-pVnZ and aug-cc-pVnZ AO and auxiliary basis sets were used (see above). For the purposes of this investigation, BSIE for a given basis is defined as the difference between the conventional MP2 correlation energy and an estimate of the CBS limit produced via the extrapolation formula:<sup>53,54</sup>

$$E_n^{\text{corr}} = E_{\text{CBS}}^{\text{corr}} + \frac{A}{\ell_{\text{max}}^3}, \quad (3)$$

with the aug-cc-pVQZ and aug-cc-pV5Z AO basis sets for the (aug-)cc-pVnZ sets, and an estimate extrapolated from the aug-cc-pwCVTZ and aug-cc-pwCVQZ basis sets for the (aug-)cc-pwCVTZ sets. All correlation consistent basis sets for transition metals have  $\ell_{\text{max}} = n + 1$ , where  $n$  is the cardinal number of the basis set, and this has been used throughout, even though the test set contains many elements that are not transition metals. While basis set extrapolation formulas have not been extensively tested for transition metal elements, the above procedure should be sufficient for the purpose of comparison with the DF error (see also below).

The BSIEs for the test set of molecules are presented in Table S1 of the supplementary material<sup>55</sup> as the mean, standard deviation, and maximum error. Table II displays analogous statistics for the density fitting error associated with each ABS, with the mean unsigned error substituted for the mean error. Table S1 of the supplementary material<sup>55</sup> and Table II show that the DF error is entirely negligible when compared with the BSIE, being, in general, around three to four orders

TABLE II. Density fitting errors, per molecule, in the MP2 correlation energy for a test set of small to medium sized molecules. Statistics of the error are the mean unsigned ( $|\bar{\Delta}^{\text{DF}}|$ ), standard deviation ( $\Delta_{\text{std}}^{\text{DF}}$ ), and maximum ( $\Delta_{\text{max}}^{\text{DF}}$ ) error in  $mE_h$ . The molecule producing the largest density fitting error is noted in parentheses.

TM basis set	$ \bar{\Delta}^{\text{DF}} $	$\Delta_{\text{std}}^{\text{DF}}$	$\Delta_{\text{max}}^{\text{DF}}$
cc-pwCVTZ <sup>a</sup>	0.011	0.011	0.060 (ZnMe <sub>2</sub> )
cc-pVQZ	0.006	0.006	0.033 (ZnMe <sub>2</sub> )
cc-pV5Z	0.004	0.004	0.019 (ZnMe <sub>2</sub> )
aug-cc-pwCVTZ <sup>a</sup>	0.012	0.010	0.041 (ZnMe <sub>2</sub> )
aug-cc-pVQZ	0.008	0.006	0.024 (ZnMe <sub>2</sub> )
aug-cc-pV5Z	0.006	0.005	0.022 (TiCl <sub>4</sub> )

<sup>a</sup>The outer-core 3s3p electrons were correlated together with the valence 3d4s in these cases.

of magnitude smaller. The DF error for each molecule is plotted in Fig. S1 of the supplementary material<sup>55</sup> for the cc-pVnZ sets and it can be seen that the error is relatively constant across the 3d elements, although it may be marginally higher for Sc and Ti. Augmenting the basis sets with additional diffuse functions increases the mean unsigned value of the DF error by around 2  $\mu E_h$  compared to the standard basis sets, indicating that while the augmented MP2FIT sets may benefit from a more extensive reoptimization, simply adding a single additional exponent to each angular momentum level appears to be sufficient for practical purposes.

All of the QZ and 5Z ABSs developed during the current investigation include at least  $k$ -type functions, which are not supported in a number of available quantum chemistry packages. While it has been shown that the absolute errors in density fitting become large if ABSs are truncated to the largest available angular momentum symmetry,<sup>56</sup> it has also been demonstrated that the effect on relative energies and properties is small when there is no change in the oxidation state of the transition metal element.<sup>57</sup> Recently this was also tested for the atomization energy of the CuF<sub>2</sub> molecule,<sup>57</sup> where the DF error amounted to 0.09 kcal/mol for aVQZ and 0.14 kcal/mol for aV5Z. Where necessary within the current investigation, ABSs are truncated to  $i$  functions, the largest currently supported in MOLPRO.

As noted above, these MP2FIT sets were also used as RI sets in the F12 calculations. The effect of using these sets as the RI for the transition metals was tested by comparison to results using large reference RI sets.<sup>55</sup> These two sets were found to yield very similar CCSD(T)-F12b atomization energies, with differences being generally less than 0.1 kcal/mol. The results for a cross-section of the molecules included in this work can be found in the supplementary material<sup>55</sup> (Tables S2 and S3).

## B. Frozen core CCSD(T) basis set convergence of atomization energies

### 1. Reference CBS values

One of the main goals of this work is to determine the effectiveness of the CCSD(T)-F12b method in predicting the frozen-core CBS limits for transition-metal-containing molecules using standard aug-cc-pVnZ basis sets. This first requires obtaining reference CBS limits both at the HF and

TABLE III. Reference CCSD(T) CBS limits (kcal/mol) for atomization energies obtained by extrapolation of conventional, non-relativistic CCSD(T) correlation energies with awCVQZ and awCV5Z basis sets.

Molecule	HF/awCV5Z	Valence electrons correlated (FC)		$\Delta CV^a$	
		CCSD <sup>b</sup>	(T)	CCSD	(T)
CoCl <sub>2</sub>	147.2	181.4	6.2	-1.7	0.3
CoCl <sub>3</sub>	151.1	213.9	16.4	-2.2	1.4
CrO <sub>3</sub>	-57.7	262.9	70.2	-4.6	2.8
CuF	58.6	95.7	3.5	-0.4	-0.2
CuF <sub>2</sub>	154.2	182.1	0.9	-2.4	0.1
CuH	32.2	60.1	2.2	-0.4	0.2
FeCl	81.2	83.9	1.7	-0.7	-0.2
FeCl <sub>2</sub>	161.4	191.8	5.1	-0.9	0.2
FeCl <sub>3</sub>	196.0	240.1	11.8	-3.7	1.2
Fe(CO) <sub>5</sub>	793.3 <sup>c</sup>	1355.8 <sup>d</sup>	84.8	2.8 <sup>e</sup>	5.2 <sup>e</sup>
MnCl	79.3	83.3	1.6	-0.1	-0.4
NiCl <sub>2</sub>	137.0	177.1	7.8	-1.6	0.2
Ni(CO) <sub>4</sub>	662.1 <sup>c</sup>	1108.8 <sup>d</sup>	74.1	1.1 <sup>e</sup>	2.1 <sup>e</sup>
TiF	101.1	127.9	3.9	-0.3	-0.4
TiF <sub>2</sub>	208.6	274.8	8.3	0.8	0.3
TiF <sub>3</sub>	314.3	417.8	13.4	-0.2	1.4
VO	39.0	130.7	19.6	1.7	1.4
VO <sub>2</sub>	62.0	241.8	39.1	0.2	2.3
ZnH	18.7	24.1	-0.8	-0.2	-0.1

<sup>a</sup>The contributions to the atomization energies from the correlation of outer-core electrons. See the text.

<sup>b</sup>Includes contributions from HF.

<sup>c</sup>Obtained at the HF/aVQZ + CABS singles level of theory.

<sup>d</sup>These values were obtained by extrapolation of CCSD(T)-F12b correlation energies using aug-cc-pVTZ and aug-cc-pVQZ basis sets. See the text.

<sup>e</sup>Obtained at the CCSD(T)-F12b/awCVTZ level of theory.

CCSD(T) levels of theory. In the latter case this must be separated into CCSD and (T) contributions since explicit correlation in the CCSD(T)-F12b method is only included at the CCSD level. Table III displays reference atomization energies for HF, CCSD, and (T) contributions within the frozen-core approximation, as well as the effects of core-valence correlation ( $\Delta CV$ , which is the difference between valence + 3s3p and just valence electrons correlated) for both CCSD and (T). For all molecules except the two metal carbonyls, the HF/CBS limits are estimated by the awCV5Z basis set results. For Fe(CO)<sub>5</sub> and Ni(CO)<sub>4</sub> the HF/CBS limit is estimated by the HF/aVQZ result with the addition of the CABS singles correction. Table S4 of the supplementary material<sup>55</sup> demonstrates that the latter agrees with the conventional awCV5Z results to within 0.1 kcal/mol for all the non-carbonyl molecules. The reference CBS limits for the correlation energies were obtained via extrapolation of conventional CCSD(T)/awCVQZ and awCV5Z results using<sup>58</sup>

$$E_n^{corr} = E_{CBS}^{corr} + \frac{A}{(\ell_{max} + \frac{1}{2})^4}, \quad (4)$$

where as noted above,  $\ell_{max} = n + 1$  for the transition metals and this has been used directly on the atomization energies of this work. In the two cases where the awCV5Z basis set was too large for our resources, Fe(CO)<sub>5</sub> and Ni(CO)<sub>4</sub>, the frozen-core CBS limits for the CCSD correlation energy and the (T) contribution were obtained by extrapolating CCSD(T)-F12b/awCVTZ and awVQZ results as described by Hill *et al.*,<sup>41</sup>

$$E_{CBS}^{corr} = (E_{aVQZ}^{corr} - E_{aVTZ}^{corr})F^c + E_{aVTZ}^{corr}, \quad (5)$$

where  $F^c = 1.416422$  for CCSD-F12b and 1.663388 for (T). While these coefficients were obtained by calibration only against 1st and 2nd row main group molecules, the resulting CBS limits are not expected to be particularly sensitive due to the relative proximity of the aVQZ result to the CBS limit (which is certainly not the case in conventional calculations). Overall the majority of the values in Table III are expected to be accurate to about 0.2 kcal/mol, however those for the metal carbonyls are assigned conservative uncertainties of 0.4 kcal/mol due to the smaller basis sets used in those cases. The geometries employed in the calculations of these CBS limits corresponded to optimal FC-CCSD(T)-F12b/aVQZ ones, except for the CCSD(T)-F12b/awCVTZ calculations required for Fe(CO)<sub>5</sub> and Ni(CO)<sub>4</sub>, where F12b/awCVTZ optimal geometries were utilized. These can be found in the supplementary material.<sup>55</sup>

The justifications for using Eqs. (4) and (5) to obtain reference CBS limits are given in Table S5 of the supplementary material<sup>55</sup> where results using these extrapolation formulas are compared to results from using other common variants, including Eq. (3). The CBS limits obtained via Eq. (4) were deemed most reliable based on two observations, (i) the very similar CBS limits obtained with [TQ] and [Q5] with Eq. (4) and (ii) the excellent agreement between the CBS[Q5] value from Eq. (4) and the F12b/[TQ] results from Eq. (5). With the [Q5] basis set combination the ubiquitous  $n^{-3}$  extrapolation formula yielded nearly identical results on average as Eq. (4), but performed relatively poorly with the smaller basis set combination, [TQ]. The importance of having a reliable extrapolation scheme for the [TQ] basis set combination cannot be understated due to the prohibitively large

TABLE IV. Basis set incompleteness errors (BSIE) of the frozen-core CCSD(T) atomization energies (kcal/mol).<sup>a</sup>

Molecule	Conventional CCSD(T)					CCSD(T*)-F12b			
	aVTZ	aVQZ	aV5Z	CBS[TQ] <sup>b</sup>	CBS[Q5] <sup>b</sup>	aVDZ	aVTZ	aVQZ	CBS[TQ] <sup>c</sup>
CoCl <sub>2</sub>	-7.4	-2.9	-1.5	0.5	-0.1	-0.5	-0.8	-0.1	0.1
CoCl <sub>3</sub>	-8.9	-3.4	-1.7	0.6	0.0	10.3	2.5	0.9	-0.1
CrO <sub>3</sub>	-12.5	-5.6	-3.0	-0.4	-0.4	4.9	0.5	0.9	0.3
CuF	-2.2	-0.8	-0.5	0.3	-0.1	-1.3	-0.2	0.0	0.0
CuF <sub>2</sub>	-3.2	-1.2	-0.7	0.4	-0.2	0.0	-0.1	0.0	0.0
CuH	-0.5	-0.2	-0.1	0.0	-0.1	-0.2	0.1	0.0	-0.1
FeCl	-3.9	-1.5	-0.7	0.3	0.0	0.0	-0.4	0.0	0.2
FeCl <sub>2</sub>	-8.3	-3.6	-2.0	0.1	-0.4	-0.2	-0.8	-0.1	0.1
FeCl <sub>3</sub>	-8.8	-3.3	-1.6	0.8	0.0	8.8	2.0	0.8	0.1
Fe(CO) <sub>5</sub>	-40.3	-16.5	...	-0.4	...	-8.2	-3.9	-0.4	0.0
MnCl	-3.7	-1.5	-0.7	0.3	0.0	-0.4	-0.5	0.0	0.2
NiCl <sub>2</sub>	-7.6	-3.0	-1.4	0.4	0.1	0.2	-0.6	-0.1	0.0
Ni(CO) <sub>4</sub>	-31.6	-12.0	...	1.3	...	-2.6	-1.3	0.3	0.0
TiF	-2.8	-1.0	-0.6	0.3	-0.1	0.4	0.0	0.2	0.1
TiF <sub>2</sub>	-4.7	-1.7	-1.0	0.5	-0.2	0.6	0.2	0.3	0.2
TiF <sub>3</sub>	-7.0	-2.6	-1.4	0.7	-0.2	0.9	0.5	0.5	0.2
VO	-4.8	-2.1	-1.1	0.0	-0.1	2.5	0.5	0.3	-0.1
VO <sub>2</sub>	-9.1	-4.0	-2.1	-0.1	-0.2	4.7	1.1	0.8	0.0
ZnH	-0.5	-0.1	0.0	0.2	0.0	-0.4	0.0	0.0	0.0
MUD	8.8	3.5	1.2	0.4	0.1	2.5	0.9	0.3	0.1
Max	40.3	16.5	3.0	1.3	0.4	10.3	3.9	0.9	0.3

<sup>a</sup>The BSIE values are relative to the reference CBS limits of Table I.<sup>b</sup>Using Eq. (4).<sup>c</sup>CCSD(T)-F12b/CBS[TQ] with aug-cc-pVTZ and aug-cc-pVQZ using Eq. (5).

computational expense of using 5Z basis sets for molecules such as Fe(CO)<sub>5</sub>.

## 2. Approaching the CBS limit with CCSD(T) and CCSD(T)-F12b

In regards to calculating the atomization energies with CCSD(T)-F12b, it was not surprising that the results showed some sensitivity to the choice of the geminal exponent  $\gamma$ , particularly for the smallest basis set, aVDZ. The results of varying  $\gamma$  with the aVDZ basis are shown in Table S6 of the supplementary material.<sup>55</sup> Using  $\gamma = 1.0$  yielded a mean unsigned deviation (MUD) between the reference CCSD(T)/CBS limit and CCSD(T)-F12b/aVDZ of 4.4 kcal/mol while  $\gamma = 1.4$  yielded 3.6 kcal/mol. The molecule with the largest BSIE, Fe(CO)<sub>5</sub>, also had its BSIE decrease from 24.8 kcal/mol with  $\gamma = 1.0$  to 20.0 kcal/mol with  $\gamma = 1.4$ . A CCSD(T)-F12b/CBS[DT] extrapolation was also carried out using Eq. (5) with  $F^c = 1.575845$  for CCSD and 1.476233 for (T).<sup>41</sup> Neither  $\gamma = 1.0$  nor  $\gamma = 1.4$  in the extrapolation gave a MUD that was less than the raw CCSD(T)-F12b/aVTZ value, although the maximum error for the latter was 10.5 kcal/mol compared to 6.6 kcal/mol obtained in the extrapolation with  $\gamma = 1.0$ . The lack of definitive improvement seems to be a clear indication that for quantitative extrapolation of transition metal CCSD(T)-F12b correlation energies using small basis sets, new correlation consistent basis sets designed for explicitly correlated calculations should be explored as has been done for the main group elements. Use of multiple geminals with different exponents<sup>59</sup> or an

Ansatz which employs some optimization of the amplitudes could also perhaps mitigate some of this sensitivity to the choice of  $\gamma$  for this small basis set, but these were not investigated here. For completeness, the sensitivity of CCSD(T)-F12b/aVTZ and aVQZ results to the choice of  $\gamma$  are shown for four molecules in Table S7 of the supplementary material.<sup>55</sup> Not unexpectedly the BSIE is much less sensitive for these basis sets and  $\gamma = 1.0$  is a convenient and accurate compromise.

Table IV summarizes the convergence of the frozen-core atomization energies calculated with conventional CCSD(T) and CCSD(T\*)-F12b relative to the reference CBS limits of Table III. A breakdown of the CCSD(T\*)-F12b results into separate BSIE values for CCSD-F12b, (T), and (T\*) are also summarized in Figure 1, with all values given explicitly in Table S8 of the supplementary material.<sup>55</sup> It should be noted at this point that the geometries used in the F12 calculations corresponded to those optimized with each respective basis set. For the conventional CCSD(T) calculations, the atomization energies were derived from DK-CCSD(T) results at the optimal aVTZ-DK geometries by subtracting the  $\Delta$ DK correction as described below in order to obtain the non-relativistic CCSD(T) values shown in Table IV. The effect on the BSIE values, however, due to the differences in geometries and the use of the  $\Delta$ DK correction is not expected to exceed 0.2 kcal/mol and does not impact the comparisons made here to any substantial degree.

As shown in Table IV the conventional CCSD(T) atomization energies converge relatively slowly with basis set, particularly for the two carbonyls where the BSIE values are greater than 30 kcal/mol for the aVTZ basis set and still

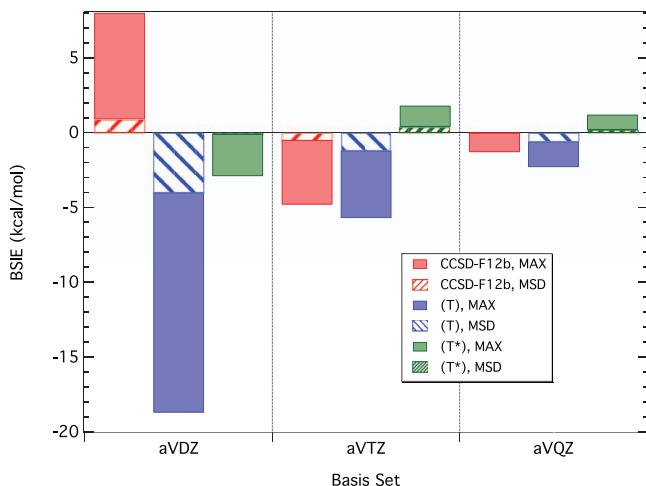


FIG. 1. Basis set incompleteness errors (kcal/mol), maximum (MAX), and mean signed deviations (MSD), for the frozen-core atomization energies of this work.

greater than 12 kcal/mol for the aVQZ set. On the other hand the CCSD(T\*)-F12b results exhibit much lower BSIE values, e.g., already with the aVDZ basis set the F12b BSIE values are actually smaller on average than the conventional results with the large aVQZ basis. These errors decrease by about a factor of two with the use of the aVTZ set, where the MUD is then just below 1 kcal/mol. The maximum BSIE is still just under 5 kcal/mol however due to  $\text{Fe}(\text{CO})_5$ . Curiously it can be noticed that in several cases there is not a significant improvement between aVDZ and aVTZ in the F12b cases, particularly for the carbonyls. The reason for this is clearly seen in Figure 1 (and also Table S8 of the supplementary material<sup>55</sup>), whereby the BSIE in the CCSD-F12b atomization energies with the aVDZ basis set are generally opposite in sign to both the (T) and (T\*) contributions. As shown in Table S8 of the supplementary material,<sup>55</sup> use of the F12a approximation with the aVDZ basis set would on average lead to even better fortuitous error cancellations since it leads to larger atomization energies than F12b in all cases. While not investigated here, this error cancellation may persist for F12a even with the aVTZ basis set. As the basis set is increased beyond aVDZ for F12b, such fortuitous error cancellations do not in general occur. Note that in the conventional CCSD calculations, the BSIE is always negative (the CCSD atomization energies converge to the CBS limits from below), hence the decrease in the BSIE with basis set is always strongly monotonic in those cases. It is also clear from Table IV that there is little advantage to using the large aV5Z basis set in conventional CCSD(T) calculations since the [TQ] extrapolation with Eq. (4) is so effective, at least for the molecules of this study. In fact the conventional CBS[TQ] results are comparable in accuracy to the CCSD(T\*)-F12b/aVQZ values, which are within 1 kcal/mol of the reference CBS limits in all cases. However, the F12b/CBS[TQ] basis set incompleteness errors are nearly a factor of 3 smaller than the conventional CBS[TQ] BSIE values and essentially identical to the reference values as discussed above (for essentially the same computational cost as a conventional aVQZ calculation).

What is also clear from Figure 1 and Table S8 of the supplementary material<sup>55</sup> is that in the F12 calculations the BSIE in the (T) contributions are generally much larger than the CCSD-F12b values and hence dominates the total BSIE at the CCSD(T)-F12b level of theory. In the conventional CCSD(T) calculations, the same BSIE in the (T) contribution accounts for nearly half of the large CCSD(T)/aVTZ BSIE in the cases of the slowly convergent carbonyls. Particularly for the smaller basis sets, the (T\*) incompleteness errors are significantly smaller and hence its use is strongly recommended.

### C. Recovery of core-valence correlation effects

Table V summarizes the convergence with basis set of the core ( $3s3p$ ) correlation contributions to the atomization energies, both by conventional CCSD(T) and CCSD(T)-F12b, as compared to the reference CBS limits given in Table III. The BSIE values are decomposed into CCSD and (T) contributions in Table S9 of the supplementary material.<sup>55</sup> In all cases the geometries used in these calculations corresponded to the frozen-core CCSD(T)-F12b/aVQZ equilibrium geometries. As shown in Table V, the  $\Delta\text{CV}$  contributions calculated at the CCSD(T)/awCVTZ level of theory, which is a typical level for composite thermochemistry approaches, are not highly accurate in the present cases with mean unsigned and maximum deviations of 0.5 and 1.5 kcal/mol, respectively. This is consistent with what has previously been shown for molecules containing post-3d main group elements.<sup>60</sup> The use of CCSD(T)-F12b with the awCVTZ basis set, however, does lead to accurate results with analogous errors smaller by about a factor of two and comparable on average to the conventional results with the large awCVQZ basis set. As shown in Table S9 of the supplementary material,<sup>55</sup> the average and maximum BSIE values at the CCSD-F12b/awCVTZ level for  $\Delta\text{CV}$  are identical to those obtained with CCSD/awCV5Z. It should also be noted (see Table S9 of the supplementary material<sup>55</sup>) that the convergence of the (T) contribution with basis set is relatively rapid for  $\Delta\text{CV}$  and in particular there is no advantage to using a scaled triples correction for this contribution. In fact it is not recommended in general since it strongly overshoots the (T) contribution in a few cases. However, as shown in Table V, in the few cases where the larger awCVQZ basis set was used in F12 calculations,  $\text{CoCl}_3$ ,  $\text{CrO}_3$ , and  $\text{FeCl}_3$ , there is little or no improvement over the F12b/awCVTZ values. As seen in Table S9 of the supplementary material,<sup>55</sup> this is due to a fortuitous cancellation of BSIE at the awCVTZ level between the CCSD-F12b and (T) contributions to  $\Delta\text{CV}$ .

### D. Higher order electron correlation beyond CCSD(T)

The effects of higher order electron correlation have previously been found to be important in composite thermochemistry schemes when sub-kcal/mol accuracy for main group molecules is desired. These contributions have also been found necessary to even attempt kcal/mol accuracy in some transition metal containing molecules,<sup>7,12,13</sup> as well as for molecules containing post-3d main group elements.<sup>60</sup> In

TABLE V. Basis set incompleteness errors (BSIE) in the core-valence correlation corrections<sup>a</sup> to the CCSD(T) atomization energies (kcal/mol).

Molecule	Conventional CCSD(T)				CCSD(T)-F12b	
	awCVTZ	awCVQZ	awCV5Z	CBS[TQ]	awCVTZ	awCVQZ
CoCl <sub>2</sub>	-0.2	-0.1	-0.1	0.0	-0.3	
CoCl <sub>3</sub>	0.2	0.1	0.0	0.0	-0.2	-0.3
CrO <sub>3</sub>	1.5	0.7	0.3	0.0	-0.6	-0.6
CuF	-0.1	0.0	0.0	0.0	-0.1	
CuF <sub>2</sub>	0.8	0.5	0.3	0.3	-0.2	-0.1
CuH	0.1	0.1	0.0	0.1	0.0	
FeCl	-0.2	-0.1	-0.1	0.0	-0.1	
FeCl <sub>2</sub>	-0.4	-0.2	-0.1	-0.1	-0.2	
FeCl <sub>3</sub>	0.4	0.2	0.1	0.1	-0.1	-0.2
Fe(CO) <sub>5</sub>	-0.3				0.0 <sup>b</sup>	
MnCl	-0.1	-0.1	0.0	0.0	-0.1	
NiCl <sub>2</sub>	-0.2	-0.2	-0.1	-0.1	-0.2	
Ni(CO) <sub>4</sub>	-1.3				0.0 <sup>b</sup>	
TiF	-0.6	-0.3	-0.1	0.0	-0.2	
TiF <sub>2</sub>	-0.5	-0.3	-0.1	-0.1	-0.3	
TiF <sub>3</sub>	-0.5	-0.3	-0.2	-0.1	-0.5	
VO	-1.1	-0.6	-0.3	-0.2	-0.4	
VO <sub>2</sub>	-0.9	-0.5	-0.3	-0.2	-0.4	
ZnH	0.0	0.0	0.0	0.0	0.0	
MUD	0.5	0.2	0.1	0.1	0.2	
Max	1.5	0.7	0.3	0.3	0.6	

<sup>a</sup>The core correlation calculations only included contributions from the 3s3p electrons of the metals, i.e., the 1s of O and F and the 1s2s2p of Cl were always frozen.<sup>b</sup>By definition.

this study the effects of correlation beyond CCSD(T) were investigated at the frozen-core level by CCSDT<sup>61–63</sup> in order to test the accuracy of the perturbative triples contribution, as well as the effects of quadruples via CCSDTQ<sup>64–67</sup> and the perturbative estimates CCSDT(Q) and CCSDT(Q)<sub>A</sub>.<sup>68–71</sup> The  $\Delta T = \text{CCSDT} - \text{CCSD(T)}$  contribution is shown in Table VI with both the aVDZ and VTZ basis sets. As has been noted before (see, for instance, Ref. 7), this difference can be rather sensitive to basis set incompleteness. As shown in Table VI, the CoCl<sub>2</sub>, CrO<sub>3</sub>, and VO<sub>2</sub> molecules are excellent examples of how using just aVDZ basis sets can greatly underestimate this contribution.

As was also previously studied by Chan *et al.* in the case of CrO<sub>3</sub>,<sup>12</sup> the CCSDTQ correction was investigated using multiple approximations to full iterative quadruples, as for most of these molecules CCSDTQ calculations could not be carried out using available computational resources. For the diatomic molecules in the study, as well as VO<sub>2</sub>, the CCSDTQ-CCSDT contributions were calculated using the VDZ basis set and these results are also shown in Table VI. Interestingly using a UHF reference versus a ROHF one for the CCSDTQ calculation yields results which differ by over half a kcal/mol for VO and VO<sub>2</sub>. While a ROHF reference would be preferable in this work to remain consistent with the present CCSD(T) calculation, unfortunately the CCSDT(Q) and CCSDT(Q)<sub>A</sub> methods are only implemented using a UHF reference in the MRCC program. As shown in Table S10 of the supplementary material,<sup>55</sup> the CCSDT(Q)<sub>A</sub> method does a somewhat better job reproducing ROHF-CCSDTQ than

CCSDT(Q), by an average of almost half a kcal/mol. A large difference between CCSDT(Q) and CCSDT(Q)<sub>A</sub> seems to be indicative of a molecule where neither method approximates ROHF-CCSDTQ particularly well. The better performance of CCSDT(Q)<sub>A</sub>, however, is exemplified by the VO molecule where CCSDT(Q)<sub>A</sub> differs from the CCSDTQ result by just -0.5 kcal/mol while CCSDT(Q) strongly overestimates this contribution by 1.9 kcal/mol. The basis set convergence of the quadruples correction was also investigated in two cases (CuH and VO, see Table S10 of the supplementary material<sup>55</sup>), and even for the case of VO the CCSDTQ -CCSDT difference only increased by about 0.3 kcal/mol between aVDZ and aVTZ. It should be noted that sometimes the quadruples correction is opposite in sign to  $\Delta T$ , which is often the case in main group molecules and leads to the often fortuitous high accuracy of the CCSD(T) method, but in many cases the contributions here have the same sign such that they do not effectively cancel. The NiCl<sub>2</sub> molecule appears to be a difficult case for this reason.

Finally to investigate the effects of pentuple excitations, CCSDTQP atomization energy calculations were carried out for the VO molecule with the VDZ basis set and a ROHF reference. The difference between this result and CCSDTQ was calculated to be -0.6 kcal/mol. This indicates that for the molecules with larger multireference effects, the higher order correlation effects beyond quadruple excitations could perhaps total more than one kcal/mol. It should also be noted that Table VI contains the  $T_1$  diagnostic<sup>72</sup> for all the molecules where the  $\Delta HC$  contribution was included. Disappointingly,

TABLE VI. Summary of higher order correlation corrections to the FC-CCSD(T) atomization energies (kcal/mol).

Molecule	$\Delta T^a$		$\Delta Q^b$	$\Delta(Q)^c$	$\Delta(Q)_\Lambda^d$	$T_1$ diagnostic <sup>e</sup>
	aVDZ	VTZ	VDZ	VDZ	VDZ	
CoCl <sub>2</sub>	0.5	1.4		0.7	0.5	$3.1 \times 10^{-2}$
CoCl <sub>3</sub>	1.3	1.4		4.0	0.2	$6.7 \times 10^{-2}$
CrO <sub>3</sub>	-0.9	-2.6 <sup>f</sup>		5.3	7.1	$5.8 \times 10^{-2}$
CuF	0.7	0.3	0.2	0.6	0.2	$3.4 \times 10^{-2}$
CuF <sub>2</sub>	0.9	0.8		0.8	0.4	$2.7 \times 10^{-2}$
CuH	0.2	0.0	0.1	0.2	0.0	$3.9 \times 10^{-2}$
FeCl	0.0	0.0	0.1	0.2	0.2	$2.4 \times 10^{-2}$
FeCl <sub>2</sub>	0.1	0.0		0.5	0.3	$2.6 \times 10^{-2}$
FeCl <sub>3</sub>	1.1	1.0		1.9	0.2	$5.1 \times 10^{-2}$
MnCl	-0.1	-0.2	0.1	0.2	0.1	$1.9 \times 10^{-2}$
NiCl <sub>2</sub>	1.3	1.4		1.2	0.7	$4.0 \times 10^{-2}$
TiF	0.7	0.2	0.5	0.5	0.3	$2.9 \times 10^{-2}$
TiF <sub>2</sub>	0.0	-0.3		0.7	0.5	$2.1 \times 10^{-2}$
TiF <sub>3</sub>	0.2	-0.3		1.2	0.8	$2.3 \times 10^{-2}$
VO	-0.5	-1.0	1.3	3.2	0.9	$5.7 \times 10^{-2}$
VO <sub>2</sub>	-0.5	-1.5	3.6	4.7	2.0	$6.4 \times 10^{-2}$
ZnH	0.2	0.2	0.0	0.0	0.0	$2.9 \times 10^{-2}$

<sup>a</sup>CCSDT – CCSD(T) with the indicated basis sets.<sup>b</sup>CCSDTQ – CCSDT in the cc-pVDZ basis set.<sup>c</sup>CCSDT(Q) – CCSDT in the cc-pVDZ basis set.<sup>d</sup>CCSDT(Q)<sub>Λ</sub> – CCSDT in the cc-pVDZ basis set.<sup>e</sup>From the CCSD-F12a/aVDZ calculations.<sup>f</sup>Taken from Ref. 12.

there is not a strong correlation between a large value of  $T_1$  and the magnitude of  $\Delta H_C$ . This is also consistent with the recent study by Jiang *et al.*<sup>73</sup>

### E. Relativistic contributions

The contributions to the atomization energies due to scalar relativistic effects ( $\Delta DK$ ) are shown in Table VII. These were calculated as the differences between DKH-CCSD(T) and non-relativistic CCSD(T) calculations, generally with the aVTZ basis sets (contracted for DKH2 in the former case). In order to reuse some of the results from Ref. 4, the geometries corresponded to the optimal DKH-CCSD(T)/aVTZ ones. The  $\Delta DK$  correction contributes about 2 kcal/mol to the atomization energies on average and reached a maximum of 8.5 kcal/mol for CrO<sub>3</sub>. For a selected number of molecules where the correction was somewhat large (CoCl<sub>2</sub>, CrO<sub>3</sub>, CuF<sub>2</sub>, NiCl<sub>2</sub>, FeCl<sub>2</sub>, MnCl, TiF, and TiF<sub>3</sub>), the basis set convergence of the  $\Delta DK$  correction was tested by computing the contributions with the aVQZ basis set. The MUD between these results and those obtained with the aVTZ basis set was just 0.05 kcal/mol, with the only value above 0.07 kcal/mol occurring for CrO<sub>3</sub> (0.18 kcal/mol). The values in Table VII reflect the aVQZ results where available.

Also shown in Table VII are the contributions to the atomization energies due to atomic spin-orbit coupling. These were calculated as a *J*-average from the experimental energy levels,<sup>74</sup> see, e.g., Ref. 1. In nearly all cases these contributions are far from being negligible, reaching 4–5 kcal/mol for molecules containing Ni and Co. Molecular spin-orbit has been neglected, but it is expected to be relatively small for the molecules of this work based on the expected small zero-field

splittings of their electronic ground states (only  $\Sigma$ ,  $\Delta$ , and  $\Phi$  states).

## IV. DISCUSSION

A summary of all the contributions to the final atomization energies and resulting heats of formation is given in Table VII. The latter are obtained through use of the experimental formation enthalpies of the gaseous atoms. As also noted by Jiang *et al.* (see Table III of Ref. 5), these latter quantities can carry significant uncertainties, e.g.,  $\pm 4$  kcal/mol for Ti,  $\pm 2$  kcal/mol for V, and  $\pm 2$  kcal/mol for Ni. In regards to the composite *ab initio* atomization energies of Table VII, these are expected to be accurate to within 1–2 kcal/mol in the cases where higher order correlation corrections have been applied. For the molecules that have stated experimental uncertainties of less than 2.5 kcal/mol, the agreement with theory is generally excellent, with nearly all values falling within or only slightly outside the experimental uncertainties. CrO<sub>3</sub> is a notable exception, but the value obtained from the present approach (-67.6 kcal/mol) agrees well with the similarly obtained composite R-CM result of Chan *et al.*, -68.5 kcal/mol. This good agreement can be a bit misleading however. The FC-CCSD(T)/CBS limits differ by just over 2 kcal/mol (the present value is larger) while the core correlation contribution of Chan *et al.* is less negative by 0.8 kcal/mol. These differences somewhat offset, yielding the good agreement noted. In any event, both of these latter high level *ab initio* results agree much better with the adopted JANAF value,  $-70 \pm 10$  kcal/mol, which carries much larger error bars. Another outlier is the CuF molecule, where the current value, 1.3 kcal/mol, is well outside the error bars of the experimental

TABLE VII. Summary of contributions to the final atomization energies and enthalpies of formation (kcal/mol).

Molecule	CCSD(T)-F12b/ CBS[TQ]	$\Delta CV$	$\Delta T$	$\Delta Q$	$\Delta DK$	$\Delta SO$	ZPE	$\Delta H_{atom}$ (0K)	$\Delta H_{atom}$ (298K)	$\Delta H_f$ (298K)	$\Delta H_f$ (298K) Expt.
$\text{CoCl}_2$ $^4\Delta_g$	187.7	-1.4	1.4	0.5 <sup>a</sup>	-1.9	-3.9	-1.5	180.8	182.0	-22.0	-22.6 $\pm$ 1.6 <sup>b</sup>
$\text{CoCl}_3$ $^5A_1$	230.2	-0.9	1.4	0.2 <sup>a</sup>	-0.3	-4.8	-2.2	223.6	225.3	-36.3	-39.1 $\pm$ 2.5 <sup>c</sup>
$\text{CrO}_3$ $^1A_1$	333.4	-1.8	-2.6 <sup>d</sup>	7.1 <sup>d</sup>	8.5	-0.7	-5.7	338.1	341.2	-67.6	-77.3 $\pm$ 1 <sup>e</sup> -70 $\pm$ 10 <sup>e</sup>
$\text{CuF}$ $^1\Sigma^+$	99.2	-0.7	0.3	0.2 <sup>f</sup>	-0.4 <sup>g</sup>	-0.4	-0.9	97.5	98.4	1.3	-3.0 $\pm$ 1 <sup>h</sup> 1.1 $\pm$ 3 <sup>i</sup>
$\text{CuF}_2$ $^2\Sigma_g^+$	183.1	-2.3	0.8	0.4 <sup>a</sup>	3.8	-0.8	-2.5	182.5	184.2	-65.5	-63.8 $\pm$ 1.3 <sup>i</sup>
$\text{CuH}$ $^1\Sigma^+$	62.2	-0.3	0.0	0.1 <sup>f</sup>	2.6	0.0	-2.7	62.0	62.9	69.9	68.9 $\pm$ 1.4 <sup>j</sup>
$\text{FeCl}$ $^6\Delta$	85.8	-1.0	0.0	0.1 <sup>f</sup>	-2.1	-2.0	-0.6	80.2	81.1	47.2	49.5 $\pm$ 1.6 <sup>b</sup>
$\text{FeCl}_2$ $^5\Delta$	197.0	-0.8	0.0	0.3 <sup>a</sup>	-3.1	-2.8	-1.5	189.2	190.4	-33.1	-32.8 $\pm$ 1.6 <sup>b</sup>
$\text{FeCl}_3$ $^6A_1$	252.0	-2.5	1.0	0.2 <sup>a</sup>	0.2	-3.7	-2.4	244.9	246.7	-60.5	-60.5 $\pm$ 1.2 <sup>c</sup>
$\text{Fe}(\text{CO})_5$ $^1A'_1$	1440.7	8.0			1.8	-2.7	-26.8	1421.0	1430.8	-177.3	-174.0 $\pm$ 1.7 <sup>c</sup>
$\text{MnCl}$ $^7\Sigma^+$	85.1	-0.5	-0.2	0.1 <sup>f</sup>	-1.6	-0.8	-0.5	81.5	82.2	14.5	15.8 $\pm$ 1.6 <sup>b</sup>
$\text{NiCl}_2$ $^3\Sigma_g^-$	184.8	-1.4	1.4	0.7 <sup>a</sup>	-3.0	-4.5	-1.5	176.6	177.8	-17.0	-17.4 $\pm$ 1.6 <sup>b</sup>
$\text{Ni}(\text{CO})_4$ $^1A'_1$	1183.0	3.1			-1.7	-4.0	-19.7	1160.7	1167.9	-141.7	-143.8 $\pm$ 2.5 <sup>c</sup>
$\text{TiF}$ $^4\Phi$	131.9	-0.7	0.2	0.5 <sup>f</sup>	-1.3	-1.0	-0.9	128.8	130.0	2.2	-3.8 $\pm$ 8.0 <sup>k</sup>
$\text{TiF}_2$ $^3\Delta_g$	283.3	1.1	-0.3	0.5 <sup>a</sup>	0.6 <sup>g</sup>	-1.4	-1.9	281.9	283.5	-132.3	-146 $\pm$ 8 <sup>k</sup>
$\text{TiF}_3$ $^2A'_1$	431.4	1.2	-0.3	0.8 <sup>a</sup>	1.4	-1.8	-3.7	429.1	431.7	-261.6	-280.4 $\pm$ 5.0 <sup>k</sup>
$\text{VO}$ $^4\Sigma^-$	150.2	3.1	-1.0	1.6 <sup>f,l</sup>	-0.6 <sup>g</sup>	-1.1	-1.4	150.1	151.5	31.3	32.3 $\pm$ 2.4 <sup>m</sup>
$\text{VO}_2$ $^2A_1$	280.8	2.5	-1.5	3.6 <sup>f</sup>	1.1 <sup>g</sup>	-1.4	-3.1	282.1	284.5	-42.2	-44.2 $\pm$ 3.6 <sup>m</sup>
$\text{ZnH}$ $^2\Sigma^+$	23.3	-0.4	0.2	0.0 <sup>a</sup>	-1.3	0.0	-2.3	19.5	20.4	62.9	62.9 $\pm$ 0.5 <sup>n</sup>

<sup>a</sup>CCSDT(Q)<sub>A</sub>-CCSDT with a VDZ basis set.<sup>b</sup>Reference 78.<sup>c</sup>Reference 79.<sup>d</sup>Reference 12.<sup>e</sup>Reference 80.<sup>f</sup>CCSDTQ-CCSDT with a VDZ basis (VO and CuH use a VTZ basis).<sup>g</sup>Reference 4.<sup>h</sup>Reference 75.<sup>i</sup>Reference 76.<sup>j</sup>Reference 81, which used the D<sub>0</sub> of Ref. 82.<sup>k</sup>Reference 85.<sup>l</sup>Includes a -0.6 kcal/mol correction for CCDSTQ5 – CCSDTQ using the VDZ basis set.<sup>m</sup>Reference 83.<sup>n</sup>Reference 84.

result of Hildenbrand,<sup>75</sup>  $-3.0 \pm 1$  kcal/mol, but in good agreement with the older value of Ehlert and Wang,  $1.1 \pm 3$  kcal/mol.<sup>76</sup> It is worth noting that the higher order correlation contributions to the atomization energy of CuF (Table VII) are also calculated to be small in magnitude. For the molecules with larger experimental uncertainties, i.e., all of the TiF<sub>n</sub> species, the present *ab initio* results for their atomization energies are expected to be the most accurate values available for these species. The mean unsigned deviation between theory and experiment for all molecules except the three TiF<sub>n</sub> species (using the JANAF value for CrO<sub>3</sub> and Ehlert and Wang for CuF) is just 1.3 kcal/mol, which is actually smaller than the mean of the experimental uncertainties, 1.8 kcal/mol (the latter does not include the uncertainties for CrO<sub>3</sub> or CuF). The root mean square (RMS) deviation for the composite heats of formation is just 1.7 kcal/mol. If the  $\Delta HC$  correction is ignored, the former increases to 2.8 kcal/mol, but most of this arises from the large  $\Delta HC$  contribution for the CrO<sub>3</sub> molecule—the RMS without  $\Delta HC$  is only 2.2 kcal/mol when not including CrO<sub>3</sub>. Overall this is very encouraging and suggests that the normal definition of “chemical accuracy,” i.e., 1 kcal/mol, may not need to be redefined for the transition metals as has been pre-

viously proposed.<sup>4</sup> Unfortunately the current experimental data on gas phase 3d-transition metal thermochemistry are not sufficiently accurate to determine if true chemical accuracy (within 1 kcal/mol) is routinely possible with the current composite methodology, either with or without the expensive  $\Delta HC$  contributions.

All of the molecules of the current study have also been treated previously by the ccCA-TM composite methodology.<sup>5,77</sup> In principle, ccCA-TM is an approximation to the present approach without a  $\Delta HC$  contribution and involves CBS extrapolations at the MP2 level of theory with CCSD(T) finite basis set corrections. For the 16 molecules of this work that do not involve the TiF<sub>n</sub> species, ccCA-TM yields a MUD of 1.9 kcal/mol and a RMS of 2.5 kcal/mol. Surprisingly this is even better than the present treatment when  $\Delta HC$  is not included. This improved agreement must arise from fortuitous error cancellation in ccCA-TM. The mean unsigned deviation between ccCA-TM and the present approach without  $\Delta HC$  is 1.4 kcal/mol with a maximum deviation of 6.2 kcal/mol. Several molecules show deviations of 2–4 kcal/mol. One such example is the CrO<sub>3</sub> molecule, where ccCA-TM yields<sup>5</sup> a 298 K heat of formation of -69.3 kcal/mol, which can be compared to the present,

non- $\Delta$ HC corrected value of  $-63.1$  kcal/mol and a previous FPD result (also no  $\Delta$ HC) of Li *et al.*<sup>8</sup> of  $-62.3$  kcal/mol. The heats of formation for 11 of the molecules of this study have also been investigated using the G4(MP2,Rel) methodology,<sup>6</sup> which includes an empirical “higher level correction.” For these molecules, G4(MP2,Rel) has a MUD with respect to experiment of  $3.2$  kcal/mol with a maximum deviation of  $11.6$  kcal/mol (using the JANAF value for CrO<sub>3</sub>).

## V. CONCLUSIONS

In the present study explicitly correlated coupled cluster methods are incorporated into a composite thermochemistry scheme including higher order correlation contributions up to CCSDT(Q)<sub>A</sub> to yield accurate heats of formation for 3d-transition-metal-containing molecules. For the cases where the experimental uncertainties were on the order of  $3$  kcal/mol or less, the average deviation of the *ab initio* composite results,  $1.3$  kcal/mol, was slightly less than the average of the experimental uncertainties,  $1.8$  kcal/mol. Even without the inclusion of the expensive higher order correlation contributions, the mean unsigned deviation increased to just  $2.1$  kcal/mol. The key to these levels of accuracy lies in the accurate CBS limits obtained for both the frozen-core and  $\Delta$ CV contributions to the atomization energies, which were efficiently attained with the CCSD(T)-F12b method with basis sets only as large as aVQZ and awCVTZ, respectively.

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