Super ccCA (s-ccCA): An Approach for Accurate Transition Metal Thermochemistry

Bradley K. Welch[a], Nuno M. S. Almeida[a], and Angela K. Wilson[a*]

[a]*Department of Chemistry, Michigan State University, East Lansing, USA;*

*akwilson@msu.edu

Abstract

Computational chemistry provides a powerful route to determine thermochemical properties. For transition metal thermochemistry, typically high-level quantum methodologies are required. *Ab initio* composite methods - which aim to replicate the predictions possible from a high level method and basis set pairing by combining a series of lower level and basis set pairings, while reducing computational cost – have proven to be effective for transition metal species, with better than chemical accuracy for transition metal energetics (<12 kJ mol^{-1}), on average. While useful, to provide a more robust computational approach, Super ccCA (s-ccCA) is introduced herein, and varies from its predecessor, ccCA, by utilizing higher-level coupled cluster corrections along with a spin-orbit contribution from a Breit-Pauli Hamiltonian. In this work, s-ccCA has been utilized for the prediction of dissociation energies for a set of 3d and 4d molecules. A set of borides, sulfides and carbides in conjunction with three early first-row transition metals (Sc, Ti, V) and three second-row transition metals (Y, Zr, Nb) were studied with this new composite method. The energies calculated herein were compared with experiment and shown to be in excellent agreement. The energetic predictions show that for cases where a balance of static and dynamic correlation is of paramount important, s-ccCA offers an effective approach.

Keywords: electronic structure; transition metal thermochemistry; multireference; ab initio composite; ccCA

Introduction

Fundamental understanding at a molecular level of transition metal compounds is important for multiple technologies and industries which include: catalytic conversion [1–3], magnets [4–6], and optical devices [7]. The key to understanding the relevant processes that underlie such applications are thermodynamic properties. Computational chemistry can provide an effective route for the prediction of thermochemical properties. However, the multireference character of many of the transition metals (TMs), close-lying excited states, and a variety of possible spin states can substantially complicate TM calculations [8,9]. In fact, the prediction of thermodynamic properties for TMs can require robust computational methods that not only recover the static, but also the dynamic correlation of the system.

For diatomic transition metal oxides, the bond length/bond strength can be utilized as a descriptor of chemical activity providing insight towards molecular design [10–13]. In addition, the bond strength, which is directly associated with the bond length and is measured by the bond dissociation energy (BDE) is widely used towards understanding reactivity. Accurate theoretical determination is especially important for hard to measure bond dissociation energies (BDEs) where experiments have not been feasible, or the experimental uncertainties are large.

Accurate determination is also important to kinetics and chemical equilibrium. Kinetic rate constants can deviate by several orders of magnitude from experiment, if the underlying thermodynamic computations are incorrect. This can lead to an incorrect assignment of the mechanism, wrongly predicting the fundamental steps of a chemical reaction. Chemical equilibrium can shift 1 pKa unit every 4 kJ mol^{-1}. Thermochemical methods that do not meet this metric will be unable to achieve accurate equilibrium constants.

Computational chemistry approaches have been widely used to calculate thermochemical properties. For the first and second rows of the periodic table, effective routes are well-demonstrated, with some methods aiming towards chemical accuracy – energetic predictions within 1 kcal mol^{-1} (4.184 kJ mol^{-1}) of reliable, well-established experimental determinations – and others striving towards spectroscopic accuracy – energetic predictions (i.e., dissociation energies, enthalpies of formation, ionization energies, electron affinities) within 1 kJ mol^{-1} of experiment. Approaches such as Active Thermochemical Tables (ATcT) have reduced the uncertainty of enthalpies of formation of many fundamental key organic compounds to well below 1 kJ mol^{-1} [14,15]. High-end thermochemical *ab initio* composite schemes such as HEAT(High Accuracy Extrapolated ab initio Thermochemistry) [16–19], W4(Weizmann 4) [20], and the FPD (Feller-Peterson-Dixon) scheme [21–23] have allowed for spectroscopic accuracy to be achieved for small early main group molecules. These schemes rely upon a layer of post-CCSD(T) computations to obtain this level of accuracy. While the accuracy of these schemes is excellent, the schemes are computationally expensive, with steps involving scaling as high as N^{12}, where N is the number of basis functions, limiting the highest accuracy versions of these composites to the smallest of molecules. Even the truncated versions of these schemes, where basis set size and higher order coupled cluster terms are reduced, are limited to at most ten main-group (non-hydrogen) atoms in symmetrical systems. More economical composite schemes are available such as the well-known

Gaussian-n approaches [24–26], and the correlation consistent Composite Approaches (ccCA) [27–29].

In brief, the main group application of ccCA relies upon a complete basis set (CBS) extrapolated MP2 energy improved with contributions from core-core, core-valence, and relativistic effects. ccCA is advantageous, as it does not rely upon parameterization, in comparison to methods such as the Gaussian-n approaches, and can obtain ~4 kJ mol^{-1} accuracies, on average [28,29]. When evaluated in comparison with the W4-17 set, a large diverse set of 200 first and second-row atomization energies, ccCA obtained a mean absolute deviation (MAD) of 2.64 kJ mol^{-1} for the 183 molecules of the non-multireference subset of W4-17 [30]. For the multireference subset of 17 molecules, the MAD was 4.10 kJ mol^{-1}. For each of these subsets, ccCA obtained better error statistics compared to many other "economical" composite schemes and was competitive with the more costly CCSD(T) based W1 and W2 composite schemes. ccCA can be applied to much larger systems in comparison to the composite methods that strive towards spectroscopic accuracy, particularly when paired with reduced scaling methods such as DLPNO (i.e., DLPNO-ccCA[31]), where systems as large as the coronene dimer were considered. Furthermore, modified versions of the ccCA composite scheme have incorporated modifications beyond single reference theories to make it applicable to systems with significant multireference character or reactions via the MR-ccCA and ccCA-CC(2,3) schemes[32–34].

In comparison to the main group, there are more challenges for computational transition metal thermochemistry. There is a greater chance of closely lying excited states to the ground state. This can make describing the ground state with a single reference wavefunction difficult. Relativistic effects are larger for the transition metals, requiring treatment by approaches such as effective core potentials (ECPs), scalar relativistic Hamiltonians, or Dirac-Hartree-Coulomb approaches [35,36]. Despite these challenges, computational thermochemistry centred around single reference methods, has been effective overall. In terms of composite methods for transition metal species, the HEAT approach has been applied to a small set of transition metals, and been used to re-evaluate hydride dissociation energies [37]. FPD has also been used for transition metal species, demonstrating the suitability of coupled cluster-based composite methods for transition metals [36,38,39]. More economical composite schemes have been developed by the Wilson group for 3d, 4d, and, most recently, 5d transition metal containing molecules; these schemes have been applied to hundreds of transition metal species [40–42]. The transition metal version of ccCA (ccCA-TM) has a number of key differences from the main group formulation of ccCA. For ccCA-TM, the core-valence term is based upon a coupled cluster calculation rather than MP2. Relativistic effects are treated in each step of the composite rather than with a separate relativistic computation. Finally, molecular spin-orbit is treated when linear molecules have angular momentum greater than zero, such as molecules with a $\pi(1)$ or $\Delta(2)$ term symbol. For the 4d molecules, ECPs are used for the MP2, CCSD(T), and core-valence contributions which capture the important relativistic effects of these molecules throughout the steps of the composite scheme, which reduces computational cost relative to the use of all-electron basis sets. In the 3d work, the term 'transition metal thermochemical accuracy' of 3 kcal mol^{-1} or ~12 kJ mol^{-1} was introduced [40], and was extended to 4d containing molecules as well [42]. The value was based upon the average experimental uncertainties of ~200 3d enthalpies of formation in the ccCA-TM/11all molecule set, representing the 3d metals. The increase in the "chemical accuracy" target from 1 to 3 kcal mol^{-1} from main group to transition metals reflects a challenge of transition metal thermochemistry - the comparative limited number of quality reference thermochemical values. While the early main group species are well-represented with over a thousand energies with experimental enthalpies of < 1 kcal mol^{-1}, there have been only just over thirty 3d species with enthalpies of formation that have such small experimental uncertainties in the ccCA-TM/11all test set [40].

Many of the energies from experiment used as references for transition metal thermochemical schemes have error bars that are tens of kcal mol^{-1} (see supporting information of ref [40]). These large error bars can cause great difficulty in determining if a computation is in agreement with experiment, or if the agreement is simply attributed to being an artifact of the large experimental uncertainty. Atomization energies are particularly challenging due to multiple homolytic bond breakages for the reactant, and the different spins and electronic states of the product atoms. Generally, for polyatomic species a reaction scheme (isodesmic and homodesmotic for example) is preferred due to the error cancellation possible with such approaches [43,44]. For diatomic species the only possible route to the dissociation energy and enthalpies is an atomization reaction. Energies from experiment with small uncertainties have been instrumental in gauging theoretical methods essentially from the start of computational chemistry as a field. For the transition metals, the limited amount of data has resulted in reduced ability to broadly define the best computational methodologies for these species and gauge the accuracy. For the 4d species, there is a slight increase in what would be considered the transition metal chemical accuracy (though it is maintained at 3 kcal mol^{-1} for the sake of comparison), and the number of species for which there is any experimental enthalpies of formation is substantially fewer than for the 3d metals.

Recently, experimental approaches have evolved substantially. Predissociation [45–47], pulsed field ionization [48–50], and velocity map imaging [51–53] have greatly reduced the uncertainty of fundamental diatomic thermochemistry. Two-Photon Predissociation Ionization measurements such by the Morse group have led to experimental uncertainties far below 1 kJ mol^{-1}. A few systems examined include silicides [47,54] and sulfides [55]. This new thermochemical data provides a useful gauge of methodologies, and helps to determine whether single reference methods such as coupled cluster based thermochemical schemes are suitable.

Here, to target the accuracy by this new generation of experimental data, the super ccCA (s-ccCA) composite scheme has been designed. While the goal for ccCA is to achieve transition metal accuracy, s-ccCA is intended to far surpass this, towards spectroscopic accuracy. In principal, such a scheme can help to provide reliable energetic data, especially in the absence of experimental data. Another important aspect of the s-ccCA composite is to obtain a clearer understanding of the necessity of higher order coupled cluster in 3d and 4d transition metal thermochemistry, in achieving accuracy beyond transition metal thermochemical accuracy, especially in light of the often significant multireference character of transition metals. Although a single reference determinant may qualitatively describe the ground state of main group species, for transition metals a poor one-electron description by Hartree-Fock molecular orbitals can sometimes be problematic. However, it is also necessary to distinguish between true multireference character (static correlation, i.e, more than one determinant needed to describe the ground state) and orbital relaxation effects (dynamic correlation, i.e, contributions from excited states due to instantaneous movement of electrons). If the guess Hartree-Fock orbitals (starting orbitals of single reference based methods such as coupled cluster or MP2) are quite different than the natural orbitals (e.g., CASSCF,) this can create difficulties in calculating accurate properties such as dissociation energies or excitation energies [56]. An example which demonstrates the importance of orbital relaxation effects in describing the ground state is MnO_4^- [56]. Even though, the ground state is a closed shell singlet, the canonical Hartree-Fock orbitals provide a very poor description of the ground state. With the restricted active space SCF (RASSCF) method, the dominant configuration (Hartree-Fock determinant) only accounts for 73% of the ground state, and the orbital relaxation via T_1 amplitudes (generated from the T_1 operator) is so large, that methods which do not include at least the full $\hat{T}_2$ terms within coupled cluster generate unreasonable electronic excitation energies [56]. It has also been shown previously that higher order coupled cluster approaches have already been useful for addressing main group molecules with significant multireference character[20,57,58], and even quintuple excitations in CCSDTQP can play an important role in the correct description of the dissociation energy. For CCSDTQP, in addition to the full $\hat{T}_2$ terms, $\hat{T}_3$, $\hat{T}_4$ and $\hat{T}_5$ which include triple, quadruple and quintuple excitations, respectively, are also included. To provide an example of the impact of these higher-level excitations, for ozone, the total contribution to the atomization energy from CCSDTQ+CCSDTQP is 4.22 kJ mol^{-1}, with CCSDTQP contributing 0.41 kJ mol^{-1} [20,30]. The combined total of this contribution is greater than main-group targeted chemical accuracy of 4.184 kJ mol^{-1}. Even a seemingly well-behaved molecule such as benzene was shown by Stanton *et. al.* to require a -4.4 kJ mol^{-1} higher order coupled cluster contribution from CCSDT and CCSDTQ to improve agreement between theory and experiment [59]. The inclusion of full connected terms such as singles, doubles, triples, quadruples (S,D,T,Q,P, etc) can recover the necessary dynamic/weak correlation which is fundamental to spectroscopic/thermodynamic properties of transition metals. The computational cost becomes prohibitively expensive as the size of the molecule increases, though for small transition metal complexes, such as diatomics, higher order coupled-cluster methods can be employed successfully. Such treatment has not been incorporated in the HEAT extension to transition metals. FPD has multiple implementations for transition metals [36,38,60,61], and does not have widespread implementations of a version with higher order correlation. Thus, here, s-ccCA is introduced.

In prior work, a prototype of s-ccCA was used to consider three vanadium diatomics, all with substantial multireference character, achieving excellent agreement with experimental dissociation energies. The calculated dissociation energies resulted in a 1.7 kJ mol^{-1} mean unsigned error (MUE) deviation, on average, in comparison to experiment [62]. Here, s-ccCA is more broadly introduced, targeting a number of 3d and 4d transition metal diatomic species, and comparing to available experimental data. Herein borides, carbides, and sulfides of the three first row transition metals (Sc, Ti, V) and three second-row transition metals (Y, Zr, Nb), which have recently determined experimental dissociation energies, were studied [54,55,63–65].

2. Computational Details

Structures were optimized with CCSD(T) paired with the cc-pVQZ basis sets for the 3d transition metals [66] and first row elements [67], with the revised and recommended correlation consistent basis sets, cc-pV(Q+d)Z, utilized for second-row elements [68,69]. For simplicity, the notations cc-pVXZ and aug-cc-pVXZ (X=D,T,Q,P) are used throughout, where the tight-d correlation consistent basis sets are implied for second-row atoms. This was followed by a frequency computation to confirm the structure was a minimum, and to enable the conversion of D_e to D_0. Each of the steps for the *ab initio* composite calculation was performed as a single point calculation at the optimized geometry.

To obtain the composite energy, a number of components are included as shown in Equation 1:

$$E(\text{s-ccCA})=E_0(\text{s-ccCA})+\Delta E(\text{Rel})+\Delta E(\text{HOC})+\Delta E(\text{CV})+\Delta E(\text{SO})+\Delta E(\text{ZPVE}) \quad (1)$$

E_0(s-ccCA) is the reference CCSD(T) energy, ΔE(Rel) is a contribution to account for relativistic effects, ΔE(HOC) corresponds to higher orders of correlation, which includes coupled cluster terms beyond CCSD(T) to address correlation shortcomings at the CCSD(T) level. ΔE(CV) represents the higher order correlation contribution to account for core-valence, ΔE(SO) is the spin-orbit contribution, and ΔE(ZPVE) includes the zero point energy. The atomic energies to obtain D_0 are computed in the same way, except the spin-orbit for these is obtained from experimental data.

Initially the reference energy, E_0(s-ccCA), was obtained using CCSD(T)/ aug-cc-pwCVXZ(X=T,Q,5) [66,70] including correlated core electrons, and extrapolating the resulting energies with the ℓ^{-3} formula of Helgaker [71] to the complete basis set (CBS) limit. The included core orbitals for the metal are the 3s and 3p orbitals. For the first-row elements the 1s orbital was correlated. For the second-row elements the 2s and 2p orbitals were correlated.

Contributions to relativistic effects, ΔE(Rel), were determined as the difference between second order Douglas-Kroll-Hess (DKH) CCSD(T) [72] and the aug-cc-pVQZ-DK basis set [66,73] and a standard valence CCSD(T) computation with aug-cc-pVQZ basis set [66–68] as shown in equation (2).

$$\Delta E(\text{Rel})=E[\text{CCSD(T)/aug-cc-pVQZ-DK}]-E[\text{CCSD(T)/aug-cc-pVQZ}] \quad (2)$$

ΔE(HOC), the higher order correlation is obtained via coupled cluster excitations beyond CCSD(T), and is summarized in equation 3. Equations (4-6) show further details of the HOC contributions.

$$\Delta E(\text{HOC})= \Delta E(\text{CCSDT/CBS}) + \Delta E(\text{CCSDTQ/PVTZ}) + \Delta E\text{CCSDTQP/PVDZ} \quad (3)$$

ΔE(CCSDT/CBS) was determined the following way: The contribution from CCSDT ($\hat{T}_3$) was found as the difference between CCSDT and CCSD(T), and extrapolated to the complete basis set limit with the cc-pVTZ and cc-pVQZ (PVQZ) basis sets [66–69], extrapolated with the two point Helgaker ℓ^{-3} formula to CBS limit.

$$\Delta E(\text{CCSDT/CBS})= E[\text{CCSDT/CBS}] - E[\text{CCSD(T)/CBS}] \quad (4)$$

The CCSDTQ contribution ($\hat{T}_4$) was determined as the difference between CCSDTQ and CCSDT with the cc-pVTZ (PVTZ) basis set.

$$\Delta E(\text{CCSDTQ/PVTZ})= E[\text{CCSDTQ/cc-pVTZ}] - E[\text{CCSDT/cc-pVTZ}] \quad (5)$$

The contribution from CCSDTQP ($\hat{T}_5$) was found as the difference between CCSDTQP and CCSDTQ with the cc-pVDZ (PVDZ) basis set [66–69]. cc-pVDZ was chosen due to the steep N^{12} scaling of CCSDTQP.

ΔE(CCSDTQP/PVDZ)= E[CCSDTQP/cc-pVDZ] – E[CCSDTQ/cc-pVDZ] (6)

For the core-valence (CV) contribution from CCSDT, ΔE(CV), was calculated as the difference between CCSDT/CV and CCSD(T)/CV and CCSDT/VAL, VAL=valence, and CCSD(T)/VAL with the cc-pwCVTZ (PWCVTZ) basis set, as shown in equation (7).

ΔE(CV)= E[CCSDT/CORE/cc-pwCVTZ]-E[CCSD(T)/CORE/cc-pwCVTZ]-

E[CCSDT/VAL/cc-pwCVTZ]-E[CCSD(T)/VAL/cc-pwCVTZ] (7)

For species that do not have lambda (Λ)=0 electronic states i.e π (Λ=1) and Δ (Λ=2) electronic states the spin-orbit splitting, ΔE(SO), was found as the difference between the lowest spin-orbit state and the state averaged energy (equation 8). This was determined with a state averaged CASSCF [74,75] wavefunction with the state interacting Breit-Pauli operator [76] with CASSCF/aug-cc-pVTZ. The spin-orbit contribution was calculated as follows:

ΔE(SO)=E[CASSCF/Spin-orbit] – E[CASSCF/State averaged] (8)

For the atomic species the spin-orbit was derived from experimental levels by j-averaging the levels [77]. The active electrons for molecules with $\Lambda>0$ consisted of the valence electrons of the metal plus the valence electrons of the ligand. The active space was made from the total number of valence orbitals of the metal and total number of valence orbitals of the ligand.

To directly compare with experiment, the dissociation energy was computed as follows:

D_0=E(A) + E(B) – E(AB) (9)

where A, and B are the atoms of the diatomic AB, and E is the energy obtained by s-ccCA. Due to the inclusion of ZPVE for molecules in equation (1), a direct comparison with experiment is possible.

For the 4d transition metal species a few small, but key differences are present. For the 4d metal a pseudopotential with its developed basis set (aug-cc-pVxZ-PP, x=D,T,Q,P) is used rather than an all electron basis set [78]. For the core correlation the 4s and 4p orbitals are correlated on the transition metal. Secondly to determine the relativistic correction the difference between a CCSD(T)/aug-cc-pVTZ-DK [78] and CCSD(T)/aug-cc-pVTZ-PP computation was utilized. A pseudopotential captures a large portion of the relativistic effects of the transition metal, and so this contribution is useful to account for relativistic effects, without the cost of all-electron basis set calculations.

All CCSD(T) computations [79] were performed with MOLPRO 2015.1 [80]. MRCC was used for all computations beyond CCSD(T), i.e CCSDT, CCSDTQ, and CCSDTQP [81]. MOLPRO 2015.1 was used to generate orbitals for MRCC and used as a front end to prepare the necessary input for MRCC [82]. Spin-orbit computations for molecular species with CASSCF was performed with MOLPRO 2015.1 [80].

3.Results

3.1 3d Transition Metal Results

Table 1 presents the results for all of the 3d transition metal species. [Table 1 near here] Table 2 shows the breakdown of the higher order coupled cluster terms. Error statistics are also provided and compared. The MAD is 2.35 kJ mol^{-1} for the 3d transition metal dissociation energies when compared to experiment. Unlike previous experiments with rather large error bars, Resonant 2 Photon Ionization (R2PI) results have rather small experimental uncertainties; often they are well below 1 kJ mol^{-1}. And, even with this much smaller experimental uncertainty, the MAD obtained here are substantially smaller than the "transition metal accuracy" of ~12 kJ mol^{-1}. The BDEs for every 3d transition metal molecule considered other than VC are within 2-3 kJ mol^{-1} of experiment. Without VC, the MAD drops to 1.93 kJ mol^{-1}. VC deviates the most from experiment at 5.66 kJ mol^{-1}.

To obtain such a small MAD, the s-ccCA composite scheme requires higher order corrections such as quadruple (CCSDTQ) and quintuple excitations (CCSDTQP), the later scales as N^{12}. These are resource intensive computations even with cc-pVDZ basis sets. [Table 2 near here] In light of the computational cost, the impact of each term in the composite has been considered. [Table 3 near here] Table 3 provides the MAD and the Mean Signed Error (MSE) resulting from the removal of each contribution from the composite scheme). The removal of the CCSDTQP (contribution from the quintuple excitations) from s-ccCA increases the MAD to 3.17 kJ mol^{-1}. Subsequent removal of terms increases the MAD, as well as the MSE. If the MSE is negative the dissociation energies are more negative compared to the reference value. Removing CCSDT/PWCVTZ, the treatment of core-valence electrons with CCSDT, increases the MAD to 4.27 kJ mol^{-1}. Stopping at CCSDTQ computed with a double-ζ basis set already results in a MAD at 4.97 kJ mol^{-1}. While the MAD is still below ~12 kJ mol^{-1} this shows the necessity of higher order coupled cluster terms, including a higher order coupled cluster contribution for core electrons, to lower the MAD to below 4 kJ mol^{-1} for 3d transition metal containing systems.

The MAD for removing CCSDTQ is higher than the MAD when all HOC is removed from s-ccCA. CCSDT is known to give poorer results compared to CCSD(T), and it has been observed that CCSDT needs to be paired with CCSDTQ or CCSDT(Q) in composite schemes [16]. Table 3 shows that the treatment of CCSDT and CCSDTQ is necessary to achieve better than 'transition metal chemical accuracy' for 3d containing molecules.

3.2 3d Transition Metal Multireference Diagnostics

Multireference character is usually associated with static correlation, especially in open-shell systems. Not properly accounting for multireference character can lead to substantial errors in the prediction of chemical properties. While many of the species considered here only deviate from experiment by 2-3 kJ mol^{-1}, VC does deviate by a larger amount (5.66 kJ mol^{-1}). One of the most common reasons for this issue is the ground state of a molecule not being well defined by a single determinant. To evaluate the multireference character of these species, there are a number of routes that can be utilized. A popular route is to consider the percentage of (T) to the total atomization energy (TAE),i.e, %TAE[(T)] as suggested by Martin, *et al.* [20,83]. This percentage provides a rough estimate of the likely importance of post-CCSD(T) contributions; it is easily obtained from CCSD(T) calculations, requiring no additional calculations. For %TAE[(T)] values of 5-10%, CCSD(T) should be used with caution. For values exceeding 10%, this typically suggests (at least for main group species), that CCSD(T) should generally not be used. Other types of diagnostic are T_1, the Frobenius norm of the t_1 vector [84,85] and D_1, the measure of the largest single excitation amplitude [86]. These terms provide some insight about the importance of singlet excited determinants. Another route is $|T_{2max}|$, the absolute value of the largest doubles amplitude. Values above 0.10 for the T_2 amplitudes suggests that excited state determinants play an important role in an electronic state [37].

[Table 4 near here]Table 4 provides an evaluation of the multireference character for the 3d transition metal molecules. In the present work, the %TAE[(T)] was taken from a CCSD(T)/aug-cc-pWCV5Z computation. For many of the species considered here the percent of (T) to the TAE is substantial (> 20%). However, as noted in prior studies, for 3d transition metal molecules there are some potential challenges associated with this diagnostic [87]. For weakly bound transition metal dimers where the %TAE[(T)] can be negative, using this criteria alone is not reliable. However, in prior work, for 59 transition metal species, this diagnostic was found to be useful, and, when partnered with the T_1 and D_1 diagnostics – *revised for transition metal species* – can be useful [87]. $T_1>0.05$, $D_1>0.15$, and %TAE[(T)] >10% are diagnostic criteria for substantial static correlation for 3d transition metal species.

Seven of the species have $T_1>0.05$, $D_1>0.15$, and %TAE[(T)] >10%, suggesting multireference character. TiC, TiS, have %TAE[(T)]>10%, but $T_1<0.05$, and $D_1<0.15$, indicating that they are less likely to have significant multireference character. None of the species had large $|T_{2max}|$ (above 0.10), which indicates that none of the species have excited determinants that have a large contribution to the ground state. Interestingly, despite the significant indicators of multireference character, predictions for the BDEs within "transition metal accuracy" are obtained when compared to experiment. Even the largest discrepancy for any of the species is only 5.66 kJ mol^{-1} from experiment, as noted earlier.

For these species, though a single-particle picture describes the nature of the ground state, the amount of mixing configurations from the dynamic correlation can be inaccurate if higher excitations are not included. This directly implies that the orbital relaxation achieved by considering $\hat{T}_2$, $\hat{T}_3$, $\hat{T}_4$ and $\hat{T}_5$ in the coupled cluster connected terms is fundamental to achieve better accuracy for 3d transition metal thermodynamic predictions. In addition, for many of these species, more than 1% of the dissociation energy comes from the $\hat{T}_4 + \hat{T}_5$ contributions; for VC, this contributes ~16 kJ mol^{-1}! Neglecting such contributions would result in a substantial error in comparison to experiment.

In considering the diagnostics in Table 4, a large %TAE[(T)] suggests a non-negligible $\hat{T}_4$+$\hat{T}_5$ contribution. From Table 3, even when the $\hat{T}_3$ term is opposite in sign of $\hat{T}_4$+$\hat{T}_5$, it does not cancel the effect of $\hat{T}_4$+$\hat{T}_5$ and contributes multiple kJ mol^{-1} to the dissociation energies. Moreover, it is interesting to note that the $\hat{T}_4$ contributions have a larger absolute contribution to the final dissociation energy predictions than $\hat{T}_3$. The percentage of TAE from $\hat{T}_4$+$\hat{T}_5$ mirrors what molecules have potential issues when considering multireference diagnostics. Even in the case of TiC which has $T_1<0.05$ and $D_1<0.15$ the percentage of TAE from $\hat{T}_4 + \hat{T}_5$ is 3.28%.

3.3 4d Transition Metal Results

Table 5 provides the dissociation energies for the 4d transition metal species. [Table 5 near here]Table 6 presents the breakdown of the higher order coupled cluster terms. The MAD for the 4d transition metal molecules is 2.44 kJ mol^{-1}. NbB is the largest outlier at 9.30 kJ mol^{-1}. ZrS deviates from experiment by 3.69 kJ mol^{-1}. All other species are within ~2 kJ mol^{-1}. If NbB is removed from consideration the MAD is reduced to 1.65 kJ mol^{-1}. It was found that 'transition metal chemical accuracy' for 4d transition metal systems is ~12 kJ mol^{-1} and this scheme falls well within that rule of thumb. The mean signed error (MSE) was found to be 1.19 kJ mol^{-1} suggesting that the scheme overestimates the calculated BDEs compared to experiment. On the other hand, for the 3d transition metal results in section 3.1, the MSE shows a slight underestimation.

[Table 6 near here]The MAD for the 4d transition metal species compared to the 3d transition metal species does not increase as much when higher orders of correlation (quadruple and quintuple excitations) are removed (see Table 7).[Table 7 near here] The smaller contributions from higher order excited states, and the decreased size (double-ζ) of the basis set for CCSDTQ have a reduced effect on the MAD, when compared to the 3d transition metal systems. In addition, the average deviation from experiment is also smaller (4.97 vs. 4.37 kJ mol^{-1}). Compared to the 3d set, removing the CCSDTQP term from the composite scheme increases the MAD by a mere ~0.20 kJ mol^{-1}. Further removing the core-valence CCSDT/PWCVTZ term only increases the MAD to 3.43 kJ mol^{-1}. The removal of the core-valence CCSDT term has a larger impact on the MAD compared to CCSDTQP.

In order to obtain a MAD above 4 kJ mol^{-1} removing CCSDTQP/PVDZ and CCSDT/PWCVTZ from the s-ccCA scheme and reducing the basis set for CCSDTQ from cc-pVTZ to cc-pVDZ is required. Even then, the MAD is just 4.30 kJ mol^{-1}. Finally, removing the CCSDTQ and CCSDT terms shows the importance of including both terms, should terms beyond CCSD(T) be included in a composite scheme. The MAD increases when only the CCSDTQ term is removed and decreases when CCSDT is additionally removed. Overall, considering the smaller effect that higher order correlation has on 4d transition metal species, it does demonstrate how previous work obtained good agreement with experiment with rp-ccCA for a molybdenum hexa-substitute reaction (39.9 kcal mol^{-1} versus 40.5 kcal mol^{-1}) [42]. While the set of molecules studied in the rp-ccCA 4d set had four outliers out of thirty molecules, many of the results were in the range ~3 kcal mol^{-1}, or 12 kJ mol^{-1}. Nonetheless, improving transition metal thermochemical predictions which are better than 'transition metal chemical accuracy' of ~12 kJ mol^{-1}, using basis sets beyond triple- and double-ζ quality to calculate CCSDTQ and CCSDTQP, respectively, may be important, though still computationally prohibitive.

3.4 4d Multireference Diagnostics

[Table 8 near here]Table 8 shows an analysis of the %TAE[(T)] and percentage of $\hat{T}_4$ and $\hat{T}_5$ for the 4d transition metal species. The %TAE[(T)] is generally less than for the 3d transition metal species. In contrast to the 3d species, the relaxation via T_2, T_3, T_4 and T_5 amplitudes is smaller for 4d transition metals. However, as for the 3d transition metals, the $\hat{T}_4$ has a larger contribution to the TAE than $\hat{T}_3$ for 4d species. The main difference for the second-row transition metals comes from $\hat{T}_4$+$\hat{T}_5$. The %TAE[(T)] from the CCSD(T)/aug-cc-pWCV5Z is smaller when comparing 4d transition state diatomics versus 3d transition state diatomics. NbC has the highest %TAE[(T)], 13.67%, compared to VC at 24.81%.

Previous work on a set of 4d transition metal molecules also showed that %TAE[(T)] >10%, T_1>0.045, and D_1>0.120 suggest multireference character [88]. None of the species considered meet all of the criteria as developed in ref [88]. None of them have a large $|T_{2max}|$>0.10; this suggests the dominance of their ground state, which can be described by a single determinant. Similar as for 3d transition metals, a single reference ground state is able to describe the ground state of the system, although the dynamic correlation of the system still needs to be corrected by intensive coupled-cluster calculations including at least T_3/T_4 amplitudes. Moreover, for second row transition metals, overall, the $\hat{T}_4$+$\hat{T}_5$ terms are compensated by the $\hat{T}_3$ contribution. However, the carbides ZrC and NbC have $\hat{T}_4$+$\hat{T}_5$ contributions greater than 1%. Overall even considering the carbides, the multireference character is lower for the 4d transition metal species. The contribution for core-valence CCSDT is comparatively smaller for 4d transition metal species than for 3d transition metals. Generally the core-valence CCSDT term in the composite increases the TAE for the 4d species. The one species not following this trend is NbB, i.e, it has a small, negative contribution from CCSDT/PWCVTZ.

4. Conclusions

The Super ccCA (s-ccCA) composite was introduced and was used to determine accurate dissociation energies when compared to experiment. The 3d transition metal results showed the necessity of higher order coupled cluster to improve comparison with state-of-the-art experimental determination. Comparatively the 4d transition metal results were less sensitive to contributions from higher order coupled cluster, and even a highly truncated s-ccCA scheme with all higher order coupled cluster terms removed obtained good error statistics when compared to experimental values. Overall, for both the 3d and 4d transition metal sets, a higher order coupled cluster centric composite scheme including CCSDTQP can obtain excellent results with minor changes going from 3d to 4d transition metals. It is important to note that even for systems that are notoriously troubling for single reference methods, an accurate treatment of dynamic correlation can provide accurate results for bond dissociation energies for 3d and 4d transition metal diatomics.

s-ccCA is shown to be effective for transition metal species. The MAD for both the 3d and 4d transition metal species was well below the ‘transition metal chemical accuracy’ (<12 kJ mol^{-1}). The method provides a robust computational approach utilizing higher order theories, recovering most of the necessary correlation from the system at double-ζ (quintuple excitations) and triple-ζ levels (quadruple excitations). Improving the scheme would rely upon increasing basis set size for given terms or consider improving the scheme with terms beyond what is currently implemented in the algorithm, which would become new variants of the s-ccCA algorithm. Presently, the computational power necessary for this improvement is extremely high.

The work herein shows the impact of the new s-ccCA composite method and how it can be used in future calculations that target transition metal accuracy. S-ccCA offers a new composite scheme that is capable of very accurate BDE predications, which can aid not only theoretical chemists but also experimentalists.

Acknowledgements

This material is based upon work supported by the National Science Foundation under Grant No. CHE-1900086. This work utilized computational facilities at the Institute for Cyber-Enabled Research (ICER) at Michigan State University. We acknowledge the tremendous influence that John Stanton has had upon the field, particularly upon spectroscopy and thermochemistry.

References

[1] K.M. Dawood and K. Nomura, Adv. Synth. Catal. **363**, 1970 (2021).
[2] J.A. Song, G.I. Peterson, K.T. Bang, T.S. Ahmed, J.C. Sung, R.H. Grubbs, and T.L. Choi, J. Am. Chem. Soc. **142**, 10438 (2020).
[3] X. Hou and K. Nomura, J. Am. Chem. Soc. **137**, 4662 (2015).
[4] G.K. Gransbury, B.N. Livesay, J.T. Janetzki, M.A. Hay, R.W. Gable, M.P. Shores, A. Starikova, and C. Boskovic, J. Am. Chem. Soc. **142**, 10692 (2020).
[5] E. Haviv, B. Chen, R. Carmieli, L. Houben, H. Cohen, G. Leitus, L. Avram, and R. Neumann, J. Am. Chem. Soc. **142**, 14504 (2020).
[6] M. Atzori, F. Santanni, I. Breslavetz, K. Paillot, A. Caneschi, G.L.J.A. Rikken, R. Sessoli, and C. Train, J. Am. Chem. Soc. **142**, 13908 (2020).
[7] K. Thakar and S. Lodha, Mater. Res. Express **7**, 014002 (2019).
[8] M. Roemelt and D.A. Pantazis, Adv. Theory Simulations **2**, 1800201 (2019).
[9] D. Süß, S.E. Huber, and A. Mauracher, J. Chem. Phys. **152**, 114104 (2020).
[10] N.M.S. Almeida, I.R. Ariyarathna, and E. Miliordos, J. Phys. Chem. A **123**, 9336 (2019).
[11] L. Li and D.S. Sholl, ACS Catal. **5**, 5174 (2015).
[12] S. Pellizzeri, M. Barona, V. Bernales, P. Miró, P. Liao, L. Gagliardi, R.Q. Snurr, and R.B. Getman, Catal. Today **312**, 149 (2018).
[13] D.J. Durand and N. Fey, Chem. Rev. **119**, 6561 (2019).
[14] B. Ruscic, R.E. Pinzon, M.L. Morton, G. Von Laszevski, S.J. Bittner, S.G. Nijsure, K.A. Amin, M. Minkoff, and A.F. Wagner, J. Phys. Chem. A **108**, 9979 (2004).
[15] B. Ruscic, J. Phys. Chem. A **119**, 7810 (2015).
[16] A. Tajti, P.G. Szalay, A.G. Császár, M. Kállay, J. Gauss, E.F. Valeev, B.A. Flowers, J. Vázquez, and J.F. Stanton, J. Chem. Phys. **121**, 11599 (2004).
[17] Y.J. Bomble, J. Vázquez, M. Kállay, C. Michauk, P.G. Szalay, A.G. Császár, J. Gauss, and J.F. Stanton, J. Chem. Phys. **125**, 064108 (2006).
[18] M.E. Harding, J. Vázquez, B. Ruscic, A.K. Wilson, J. Gauss, and J.F. Stanton, J. Chem. Phys. **128**, 114111 (2008).
[19] J.H. Thorpe, C.A. Lopez, T.L. Nguyen, J.H. Baraban, D.H. Bross, B. Ruscic, and J.F. Stanton, J. Chem. Phys. **150**, 224102 (2019).
[20] A. Karton, E. Rabinovich, J.M.L. Martin, and B. Ruscic, J. Chem. Phys. **125**, 144108 (2006).
[21] D. Feller, J. Chem. Phys. **147**, 034103 (2017).
[22] D. Feller, J. Chem. Phys. **138**, (2013).
[23] D. Feller, K.A. Peterson, and B. Ruscic, Theor. Chem. Acc. **133**, 1 (2014).
[24] L.A. Curtiss, K. Raghavach Ari, P.C. Redfern, V. Rassolov, and J.A. Pople, J. Chem. Phys. **109**, 7764 (1998).
[25] L.A. Curtiss, P.C. Redfern, and K. Raghavachari, J. Chem. Phys. **126**, 084108 (2007).
[26] L.A. Curtiss, K. Raghavachari, P.C. Redfern, and J.A. Pople, J. Chem. Phys. **106**, 1063 (1997).

[27] N.J. DeYonker, T.R. Cundari, and A.K. Wilson, J. Chem. Phys. **124**, 114104 (2006).
[28] N.J. DeYonker, T. Grimes, S. Yockel, A. Dinescu, B. Mintz, T.R. Cundari, and A.K. Wilson, J. Chem. Phys. **125**, 104111 (2006).
[29] N.J. DeYonker, D.S. Ho, A.K. Wilson, and T.R. Cundari, J. Phys. Chem. A **111**, 10776 (2007).
[30] A. Karton, N. Sylvetsky, and J.M.L. Martin, J. Comput. Chem. **38**, 2063 (2017).
[31] P. Patel and A.K. Wilson, J. Comput. Chem. **41**, 800 (2020).
[32] G.A. Oyedepo and A.K. Wilson, J. Phys. Chem. A **114**, 8806 (2010).
[33] B. Mintz, T.G. Williams, L. Howard, and A.K. Wilson, J. Chem. Phys. **130**, 214103 (2009).
[34] S.A. Nedd, N.J. DeYonker, A.K. Wilson, P. Piecuch, and M.S. Gordon, J. Chem. Phys. **136**, 144109 (2012).
[35] Q. Lu and K.A. Peterson, J. Chem. Phys. **145**, 054111 (2016).
[36] K.S. Thanthiriwatte, M. Vasiliu, S.R. Battey, Q. Lu, K.A. Peterson, L. Andrews, and D.A. Dixon, J. Phys. Chem. A **119**, 5790 (2015).
[37] L. Cheng, J. Gauss, B. Ruscic, P.B. Armentrout, and J.F. Stanton, J. Chem. Theory Comput. **13**, 1044 (2017).
[38] Z. Fang, M. Vasiliu, K.A. Peterson, and D.A. Dixon, J. Chem. Theory Comput. **13**, 1057 (2017).
[39] M. Vasiliu, K.A. Peterson, and D.A. Dixon, J. Phys. Chem. A **124**, 6913 (2020).
[40] W. Jiang, N.J. Deyonker, J.J. Determan, and A.K. Wilson, J. Phys. Chem. A **116**, 870 (2012).
[41] N.J. DeYonker, K.A. Peterson, G. Steyl, A.K. Wilson, and T.R. Cundari, J. Phys. Chem. A **111**, 11269 (2007).
[42] M.L. Laury, N.J. Deyonker, W. Jiang, and A.K. Wilson, J. Chem. Phys. **135**, 214103 (2011).
[43] S.E. Wheeler, K.N. Houk, P.V.R. Schleyer, and W.D. Allen, J. Am. Chem. Soc. **131**, 2547 (2009).
[44] F.J. Guzman and J. Bozzelli, J. Phys. Chem. A **123**, 4452 (2019).
[45] M.D. Morse, Acc. Chem. Res. **52**, 119 (2019).
[46] B. Simard, M.A. Lebeault-Dorget, A. Marijnissen, and J.J. Ter Meulen, J. Chem. Phys. **108**, 9668 (1998).
[47] A. Sevy, J.J. Sorensen, T.D. Persinger, J.A. Franchina, E.L. Johnson, and M.D. Morse, J. Chem. Phys. **147**, 084301 (2017).
[48] C.S. Lam, K.C. Lau, and C.Y. Ng, J. Phys. Chem. A **123**, 7454 (2019).
[49] H. Huang, Z. Luo, Y.C. Chang, K. Lau, and C.Y. Ng, Chinese J. Chem. Phys. **26**, 669 (2014).
[50] P.B. Armentrout, Y.C. Chang, and C.Y. Ng, J. Phys. Chem. A **124**, 5306 (2020).
[51] A.S. Gentleman, A. Iskra, H. Köckert, and S.R. MacKenzie, Phys. Chem. Chem. Phys. **21**, 15560 (2019).
[52] W.S. Hopkins, S.M. Hamilton, P.D. McNaughter, and S.R. Mackenzie, Chem. Phys. Lett. **483**, 10 (2009).
[53] G.A. Cooper, A.S. Gentleman, A. Iskra, and S.R. Mackenzie, J. Chem. Phys. **147**, 013921 (2017).
[54] A. Sevy, D.M. Merriles, R.S. Wentz, and M.D. Morse, J. Chem. Phys. **151**, 24302 (2019).
[55] J.J. Sorensen, E. Tieu, C. Nielson, A. Sevy, K.H. Tomchak, and M.D. Morse, J. Chem. Phys. **152**, 194307 (2020).
[56] N.M.S. Almeida, R.G. McKinlay, and M.J. Paterson, Chem. Phys. **446**, 86 (2015).
[57] A. Karton, J. Chem. Phys. **149**, 034102 (2018).

[58] A. Karton, Chem. Phys. Lett. **737**, 136810 (2019).

[59] M.E. Harding, J. Vázquez, J. Gauss, J.F. Stanton, and M. Kállay, J. Chem. Phys. **135**, 044513 (2011).

[60] S. Li, J.M. Hennigan, D.A. Dixon, and K.A. Peterson, J. Phys. Chem. A **113**, 7861 (2009).

[61] R. Feng, M. Vasiliu, K.A. Peterson, and D.A. Dixon, J. Phys. Chem. A **121**, 1041 (2017).

[62] J.L. Bao, B.K. Welch, I.S. Ulusoy, X. Zhang, X. Xu, A.K. Wilson, and D.G. Truhlar, J. Phys. Chem. A **124**, 9757 (2020).

[63] D.M. Merriles, C. Nielson, E. Tieu, and M.D. Morse, J. Phys. Chem. A (2021).

[64] E.L. Johnson, Q.C. Davis, and M.D. Morse, J. Chem. Phys. **144**, 234306 (2016).

[65] A. Sevy, D.J. Matthew, and M.D. Morse, J. Chem. Phys. **149**, 44306 (2018).

[66] N.B. Balabanov and K.A. Peterson, J. Chem. Phys. **123**, 064107 (2005).

[67] T.H. Dunning, J. Chem. Phys. **90**, 1007 (1989).

[68] J. Dunning, K.A. Peterson, and A.K. Wilson, J. Chem. Phys. **114**, 9244 (2001).

[69] D.E. Woon and T.H. Dunning, J. Chem. Phys. **98**, 1358 (1993).

[70] K.A. Peterson and T.H. Dunning, J. Chem. Phys. **117**, 10548 (2002).

[71] T. Helgaker, W. Klopper, H. Koch, and J. Noga, J. Chem. Phys. **106**, 9639 (1997).

[72] G. Jansen and B.A. Hess, Phys. Rev. A **39**, 6016 (1989).

[73] W.A. De Jong, R.J. Harrison, and D.A. Dixon, J. Chem. Phys. **114**, 48 (2001).

[74] P.J. Knowles and H.J. Werner, Chem. Phys. Lett. **115**, 259 (1985).

[75] H.J. Werner and P.J. Knowles, J. Chem. Phys. **82**, 5053 (1985).

[76] A. Berning, M. Schweizer, H. Werner, P.J. Knowles, and P. Palmieri, Mol. Phys. **98**, 1823 (2000).

[77] C.E.Moore, Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand. (1971).

[78] K.A. Peterson, D. Figgen, M. Dolg, and H. Stoll, J. Chem. Phys. **126**, 124101 (2007).

[79] P.J. Knowles, C. Hampel, and H.J. Werner, J. Chem. Phys. **99**, 5219 (1993).

[80] H.-J. Werner, (2015).

[81] M. Kállay and P.R. Surján, J. Chem. Phys. **115**, 2945 (2001).

[82] M. Kállay, P.R. Nagy, D. Mester, Z. Rolik, G. Samu, J. Csontos, J. Csóka, P.B. Szabó, L. Gyevi-Nagy, B. Hégely, I. Ladjánszki, L. Szegedy, B. Ladóczki, K. Petrov, M. Farkas, P.D. Mezei, and Á. Ganyecz, J. Chem. Phys. **152**, 074107 (2020).

[83] A. Karton, S. Daon, and J.M.L. Martin, Chem. Phys. Lett. **510**, 165 (2011).

[84] T.J. Lee and P.R. Taylor, Int. J. Quantum Chem. **36**, 199 (1989).

[85] T.J. Lee, J.E. Rice, G.E. Scuseria, and H.F. Schaefer, Theor. Chim. Acta **75**, 81 (1989).

[86] C.L. Janssen and I.M.B. Nielsen, Chem. Phys. Lett. **290**, 423 (1998).

[87] W. Jiang, N.J. Deyonker, and A.K. Wilson, J. Chem. Theory Comput. **8**, 460 (2012).

[88] J. Wang, S. Manivasagam, and A.K. Wilson, J. Chem. Theory Comput. **11**, 5865 (2015).

Table 1. s-ccCA dissociation energies for 3d transition metal species determined from CCSD(T)/CBS and s-ccCA, and compared with experiment. Contributions to the s-ccCA energy including the relativistic contribution (spin-orbit plus DKH) and the higher-order correction (HOC=CCSDT/CBS+CCSDTQ/PVTZ+CCSDTQP/PVDZ+CCSDT(CV)) are also provided. All energies and energy contributions are provided in kJ mol^{-1}. The references for the experimental values are included in brackets.

Molecule	CCSD(T)/CBS	Relativistic	HOC	ZPVE	s-ccCA D_0	Exp.
ScB	168.86	-3.71	4.45	-5.30	164.30	165.95[63]
TiB	190.65	-6.82	7.99	-4.31	187.50	188.73[63]
VB	214.12	-12.73	8.09	-3.59	205.89	207.44[63]
ScC	294.63	-3.98	5.91	-4.33	292.23	293.18[54]
TiC	372.18	-5.11	8.39	-5.79	369.68	372.14[65]
VC	402.62	-17.35	10.58	-5.06	390.79	396.42[64]
ScS	472.67	-3.94	6.39	-3.38	471.73	468.15[55]
TiS	454.73	-5.40	8.16	-3.46	454.03	452.52[55]
VS	439.79	-12.25	10.67	-3.19	435.02	437.56[64]

Table 2: Higher order coupled cluster contributions for the 3d transition metal diatomics. Results are in kJ mol^{-1}.

Molecule	CCSDT/CBS	CCSDTQ/PVTZ	CCSDTQP/PVDZ	CCSDT/PWCVTZ
ScB	1.17	3.19	0.08	0.01
TiB	2.36	4.41	0.45	0.77
VB	1.76	3.18	0.30	2.85
ScC	-0.40	3.96	-0.12	2.47
TiC	-6.48	9.51	2.64	2.73
VC	-9.37	12.44	3.57	3.94
ScS	-2.76	6.14	-0.99	4.00
TiS	1.79	5.73	-1.98	2.62
VS	4.69	4.69	-2.46	3.76

Table 3: The impact of each contribution of s-ccCA on the MAD and MSE for 3d transition metal molecules. Results are in kJ mol^{-1}.

Term Removed	MAD	MSE
Minus CCSDTQP	3.17	-1.38
Minus CCSDT/PWCVTZ	4.27	-3.95
CCSDTQ/PVDZ	4.97	-4.85
Minus CCSDTQ	9.87	-9.87
Minus CCSDT	9.06	-9.06

Table 4: Multireference considerations for the 3d transition metal species. (T)% is percentage of TAE from the (T) contribution to a CCSD(T)/aug-cc-pWCV5Z. $\hat{T}_4+\hat{T}_5$ are from the s-ccCA TAE in kJ mol^{-1}. T_1 and D_1 are common diagnostics. $T_{2\text{max}}$ is the absolute value of the largest T_2 amplitude.

Molecule	%TAE[(T)]	$\hat{T}_4+\hat{T}_5$%	T_1	D_1	$\lvert T_{2\text{max}}\rvert$
ScB	19.81	1.99	0.06	0.16	0.04
TiB	20.67	2.65	0.06	0.22	0.07
VB	22.53	1.66	0.05	0.15	0.09
ScC	15.56	1.31	0.05	0.16	0.07
TiC	22.59	3.28	0.04	0.11	0.04
VC	24.81	4.03	0.09	0.25	0.05
ScS	11.33	1.09	0.05	0.19	0.03
TiS	12.57	0.83	0.04	0.12	0.03
VS	13.89	0.56	0.07	0.18	0.02

Table 5: Dissociation energies for 4d transition metal species determined from CCSD(T)/CBS and s-ccCA, and compared with experiment. Contributions to the s-ccCA energy including the relativistic contribution (spin-orbit plus DKH) and the higher-order correction (HOC=CCSDT/CBS+CCSDTQ/PVTZ+CCSDTQP/PVDZ+CCSDT(CV)) are also provided. All energies and energy contributions are in kJ mol^{-1}. The references for the experimental values are included in brackets.

Molecule	**CCSD(T)/CBS**	**Relativistic**	**HOC**	**ZPVE**	**s-ccCA D_0**	**Exp.**
YB	204.86	-3.28	2.59	-3.45	200.72	198.47[63]
ZrB	255.00	-5.03	2.03	-3.64	248.35	248.26[63]
NbB	284.97	-5.64	3.36	-3.59	279.09	288.39[63]
YC	333.76	-2.39	1.76	-4.10	329.03	329.98[54]
ZrC	482.10	-6.40	0.63	-5.31	471.01	472.01[65]
NbC	538.24	3.40	4.31	-6.06	539.90	537.58[65]
YS	529.53	-5.79	0.18	-2.88	521.04	520.15[55]
ZrS	552.83	-9.17	2.03	-3.27	542.42	546.11[55]
NbS	542.79	-6.21	2.22	-3.23	535.57	537.62[55]

Table 6: Higher order coupled cluster contributions for the 4d transition metal diatomics. Results are in kJ mol^{-1}.

Molecule	**CCSDT/CBS**	**CCSDTQ/PVTZ**	**CSDTQP/PVDZ**	**CCSDT/PWCVTZ**
YB	0.00	1.75	0.02	0.81
ZrB	-0.61	1.78	0.12	0.74
NbB	0.83	2.72	0.24	-0.43
YC	-1.07	1.37	0.01	1.45
ZrC	-6.27	5.00	0.84	1.06
NbC	-6.31	8.61	1.53	0.48
YS	-4.04	3.00	-0.39	1.61
ZrS	-5.83	4.63	-0.85	4.08
NbS	-2.19	3.91	-0.91	1.41

Table 7: The impact of each contribution of s-ccCA on the MAD and MSE for 4d transition metal molecules. Results are in kJ mol^{-1}.

Term Removed	**MAD**	**MSE**
Minus CCSDTQP	2.65	-1.87
Minus PWCVTZ	3.43	-3.11
CCSDTQ/PVDZ	4.39	-3.96
Minus CCSDTQ	6.06	-5.69
Minus CCSDT	4.08	-3.92

Table 8: Multireference considerations for the 3d transition metal species. (T)% is percentage of TAE from the (T) contribution to a CCSD(T)/aug-cc-pWCV5Z. $\hat{T}_4 + \hat{T}_5$ are from the s-ccCA TAE in kJ mol^{-1}. T_1 and D_1 are common diagnostics. T_{2max} is the absolute value of the largest T_2 amplitude.

Molecule	%TAE[(T)]	$\hat{T}_4 + \hat{T}_5$%	T_1	D_1	$\lvert T_{2max} \rvert$
YB	8.21	0.89	0.05	0.17	0.03
ZrB	7.76	0.77	0.04	0.10	0.04
NbB	11.35	1.06	0.03	0.08	0.05
YC	8.04	0.42	0.04	0.13	0.07
ZrC	10.82	1.24	0.03	0.11	0.05
NbC	13.67	1.88	0.03	0.07	0.05
YS	5.95	0.50	0.03	0.12	0.03
ZrS	10.77	0.70	0.03	0.09	0.06
NbS	10.91	0.56	0.03	0.10	0.04