

Multireference Character for 3d Transition-Metal-Containing Molecules

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 Supporting Information

ABSTRACT: Coupled cluster and configuration interaction diagnostics have been examined in order to assess the reliability of single reference quantum methods for a series of 3d transition metal species including hydrides, nitrides, chalcogenides, halides, small clusters, coordination complexes, and metal dimers. Several means of diagnostics have been considered including T_1 and D_1 diagnostics (the Frobenius norm and matrix 2-norm of coupled cluster amplitudes for single excitations, respectively), C_0^2 (the weight of leading configuration of a complete active space wave function), and %TAE (percent total atomization energy). T_1 and D_1 diagnostics are strongly correlated for certain metal–ligand bonding types. The use of T_1 and D_1 together with %TAE can provide more reliable assessment of the severity of nondynamical correlation than a single indicator can provide. New criteria, namely $T_1 > 0.05$, $D_1 > 0.15$, and $|\%TAE| > 10$, are suggested to identify inorganic species with substantial nondynamical correlation. For these systems, energies and spectroscopic properties computed using single reference electronic correlation methods may suffer from large errors and unpredictable behavior. Conversely, a computation where a molecule is below one or more of these thresholds does not always imply domination by a single reference. Some historically pathological molecules such as Mn_2 and Cr_2 show $T_1 < 0.05$ and $D_1 < 0.15$. Current implementations of coupled cluster diagnostics may still be insufficient for categorization of molecules that have pronounced nondynamical correlation.

1. INTRODUCTION

Ab initio quantum mechanical methods, particularly those based on a determinantal wave function description of the interaction of electrons, have been widely used to obtain accurate and reliable predictions of molecular properties. As approximations to an exact full configuration interaction (CI) expansion of determinants, theoretical methods can be divided into two categories: single reference (SR) and multireference (MR). Even with truncation of excitations at the double or triple level, single reference methods [e.g., MP2,¹ CCSD,² and CCSD(T)^{3,4}] can recover a large portion of dynamic correlation energy [related to excitations to virtual orbitals from the reference Hartree–Fock (HF) determinant] but may fail badly when the molecular system contains a significant amount of static (or nondynamical) correlation energy (related to strongly correlated valence and low-lying virtual orbitals). In contrast, multiconfiguration or multireference methods (e.g., MCSCF,⁵ CASPT2,^{6,7} MRCI,⁸ MRACPF,⁹ and MRAQCC¹⁰) are suitable for degenerate and quasidegenerate states, bond breaking processes, and excited states, but current available MR methods are usually more complicated in implementation and much less user-friendly than SR methods. The applications of these MR methods are mostly limited to molecules of small size because of the factorial scaling of a complete active space (CAS) including all valence orbitals and valence electrons. Unfortunately, even the use of a default full valence CAS does not guarantee results with desirable accuracy. Such failure was exemplified in the CASSCF calculation of the ground state of BO^+ , where the highest a_1 active orbital

predominantly consists of oxygen 3s character instead of the oxygen 2p_z orbital.¹¹ While a practical MRCCSD(T)^{12–14} method is not readily available, the CASPT2, MRCI, MRACPF, or MRAQCC methods recover both dynamical and nondynamical correlation energy. In many cases, however, these methods are not sufficiently accurate for atomization energies, possibly due to current standard implementations that are mostly limited to singles and doubles, and the lack of rigorous size consistency and size extensivity^{15,16} that single reference coupled cluster (CC) theory provides. We note that the explicit considerations of triple and quadruple excitations in the framework of MRCI or MRPT have not been fully developed or broadly used, although some progress with the nR-MRCISD(TQ) method,¹⁷ for example, has been achieved. The unavailability of MRCI, MRACPF, and MRAQCC implementations with explicit triple excitations and beyond remains an open challenge for molecular systems, such as FeCN/FeNC,^{18–21} that require simultaneous consideration of nondynamical correlation and high level dynamical correlation. As a result, single reference approaches have been used far more often to compute thermochemical properties rather than MR analogues.

Another route to the prediction of thermochemical properties over approximately two decades has been via composite methods, which can achieve the accuracy of a high level theory such as CCSD(T) with a relatively large basis set or the extrapolated

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complete basis set limit, but at a computational cost only fractional of the latter. Great successes, especially in terms of accuracy and efficiency, have been achieved with many SR composite approaches (for example, Gn ,^{22,23} Wn ,^{24–26} and $ccCA$,^{27–31} to name only a few) targeted for thermochemical properties and even spectroscopic constants (see examples in refs 32 and 33). To note, multireference analogues of composite approaches, e.g., MR- $ccCA$,^{34–37} also have been proposed, and despite many achievements, their applications are still restricted due to the shortcomings of their constituent MR methods (*vide supra*). A recent review of the performance of various SR composite approaches compared to the extremely high accurate W4 method was given in a study by Martin and co-workers.²⁶ The quality of all SR composite methods considered in their study degrades for molecular systems with salient multireference character. Such deficiency in the constituent SR theories cannot be effectively alleviated in a composite approach. Thus, it has become important to *a priori* analyze the multireference character of molecular systems in order to examine the appropriateness and reliability of both SR theories and the overall SR composite approaches.

Many diagnostics have been suggested to examine the SR/MR character for molecular systems. One earlier diagnostic is the coefficient C_0 , or the weight (C_0^2), of the reference HF configuration in a CISD wave function. The molecular system is regarded to possess significant multireference character if the coefficient C_0 is smaller than 0.95, or the weight C_0^2 is smaller than 0.90. This diagnostic has proven to be very useful and has been utilized for quantitative improvement of CISD energies as exemplified by Davidson's correction,³⁸ a commonly known *a posteriori* size consistency correction to the CISD energy. However, this diagnostic is based on canonical HF orbitals, which might be biased for the HF determinant of a pathological system, resulting in a misleadingly large coefficient for the HF determinant.³⁹ Alternatively, the weight (C_0^2) of the leading configuration or configuration state function (CSF) in a CASSCF wave function can be used to determine multireference character.^{40,41} This diagnostic is based on balanced CASSCF natural orbitals. However, it may not well represent the possibly strong correlation between valence and low-lying virtual orbitals since the latter may not be included in the CASSCF wave function. The MR analogue of Davidson's correction using the CASSCF and MRCISD coefficients of reference CSFs is readily available in common quantum chemical programs (e.g., the MRCI+Q in MOLPRO⁴²) and has been widely used. However, this MR analogue of the C_0^2 diagnostic is not amenable for relatively large molecular systems due to the prohibitive computational cost of CASSCF and MRCISD calculations and the practical limitations of available methods; e.g., the internally contracted MRCI and CASPT2 in MOLPRO⁴² can consider only up to 32 active orbitals. A full valence CASSCF for simple inorganic systems such as VBr_4 or $Cr(CO)_6$ can already breach this limit. However, very recent progress has been made to alleviate this technological hurdle.⁴³

It would be beneficial to use diagnostics based on the coupled cluster (CC) wave function in order to avoid arbitrarily constructed CAS or MRCI calculations to test the validity of single reference CC methods. Lee et al.^{39,44} suggested the use of the Frobenius norm of the t_1 vector of the closed shell CCSD wave function starting from a restricted HF (RHF) reference wave function. The obtained norm is further normalized by the number of correlated electrons to satisfy the condition of size consistency. The resulting so-called T_1 diagnostic has proven to

be superior to the analysis of C_0^2 in a CISD wave function. Any T_1 diagnostic larger than 0.02, as suggested by Lee and Taylor,³⁹ implies that single reference methods may not give reliable predictions. However, the T_1 diagnostic is an averaged value and does not reflect the nonhomogeneity of the t_1 vector or possible singular t_2 amplitudes. The maximal t_1 and t_2 amplitudes higher than a criterion such as 0.05 can be used together with the T_1 diagnostic for a thorough analysis of multireference character. The T_1 diagnostic was extended to open shell coupled cluster theory in a manner consistent with the original definition for closed shell CCSD.⁴⁵ Similar to the T_1 diagnostic, a diagnostic S_2 has also been proposed for perturbation theory, which requires substantially more computational cost than the MP2 energy evaluation but becomes free if the analytic gradient is computed.⁴⁶ The D_1 diagnostic, an alternative formulation of T_1 and S_2 , has been formulated for CCSD and MP2, respectively, by Janssen and Nielsen.⁴⁷ Unlike T_1 and S_2 diagnostics, which include the sum of contributions from all single excitation amplitudes, the D_1 diagnostic is more closely related to the value of the largest single excitation amplitude. Similar to D_1 , the D_2 diagnostic based on double excitation amplitudes was suggested.⁴⁸ The D_1 diagnostic was also extended to the open shell CCSD wave function initially by Leininger et al.⁴⁹ and then revised by Lee.⁵⁰ The T_1 and D_1 diagnostics are arguably the most widely used diagnostics for single reference coupled cluster calculations.

The T_1 and D_1 diagnostics, despite being useful for qualitative analysis, are difficult to interpret quantitatively. Criteria have been suggested for possible significant MR character, but no quantitative relationships have been established between the diagnostics and the error of theoretical predictions relative to experimental data or highly accurate theoretical benchmarks. During the development of W4 theory,^{24,26} Martin and co-workers found that the percentage of the (T) contribution to total atomization energy (%TAE_c[(T)]) correlated with the percentage of higher order coupled cluster [$T_4 + T_5$] contribution to the atomization energy (%TAE_c [$T_4 + T_5$]). On the basis of the W4 set of molecules, it was found, overall, that %TAE_c [$T_4 + T_5$] \approx 0.126 %TAE_c[(T)]. This quantitative relationship between CCSD(T) and CCSDT/CCSDTQ/CCSDTQP atomization energies implies a viable correction to the insufficiency of SR CCSD(T) for MR molecular systems. While the original definition of %TAE_c[(T)] is only possible with the W4 energies (including the extremely expensive CCSDT, CCSDTQ, and CCSDTQP calculations), an *a priori* metric %TAE_c[(T)] based on CCSD(T) energies was also proposed [eq 1 of ref 26].

However, these diagnostics have thus far been tested primarily on small and well-behaved organic molecules (see refs 51 and 52 for examples). The applicability of these diagnostics to inorganic and transition metal (TM)-containing molecules has only been discussed as a noteworthy aside within specific applications of *ab initio* theory, such as FeCN/FeNC,¹⁹ metal-salen complexes,^{40,41,53,54} metal oxides,⁵⁵ and chalcogenides of group 12 metals.⁵⁶ Compared to the main group species, accurate computation of energies and spectroscopic properties of species containing TM atoms is generally more challenging for SR methods since nondynamical electron correlation effects are more severe. This is particularly true for 3d metals due to the small atomic energy gap of 3d and 4s orbitals. The generally agreed upon criteria for organics has historically been $C_0^2 > 0.90$, $T_1 < 0.02$, $D_1 < 0.05$, and %TAE < 10. It is important to note that the criteria $T_1 < 0.02$ and $D_1 < 0.05$ were proposed for CCSD calculations while the attainable accuracy has been greatly

improved by the now common utilization of CCSD(T). However, the calibration of ccCA (which includes CCSD(T) within the approach) for the computation of inorganic energetic properties provides evidence that these criteria are rarely satisfied for many small closed-shell transition metal-containing species.³⁰ In an earlier study,⁵⁷ the diagnostics T_1 and D_1 were discussed in the context of assessing the reliability of ccCA-TM. However, as noted in this earlier work, comparisons to experimental data may not reflect the accuracy of the theoretical methods due to the many significant sources of error (both theoretical and experimental) for TM species. In spite of this, the single reference ccCA-TM methodology has been shown to provide high-quality results:^{30,31,57} on average, ccCA-TM is within 2.9 kcal mol⁻¹ of the experimental gas phase enthalpies of formation for a test set of 70 molecules with reported experimental error bars of ± 2.0 kcal mol⁻¹ or lower. It is quite surprising that ccCA, based on MP2 energies and containing no parametrization, provides quantitatively useful results for energies of molecules that do contain substantial multireference character. For example, ccCA-TM predicts the enthalpies of formation (ΔH_f) for 15 MR molecules ($C_0^2 < 0.90$, $T_1 > 0.05$, or $D_1 > 0.10$) with a mean absolute deviation (MAD) of 2.4 kcal mol⁻¹ from experimental data.⁵⁷ Mounting evidence suggests that the robustness of the d block correlation consistent basis sets (developed by Peterson and Balabanov⁵⁸ and employed in ccCA-TM) can be credited with improving the understanding between dynamical and nondynamical correlation in *ab initio* studies of transition metal-containing molecules.

It is known that many factors obfuscate the accurate experimental determination of gas phase thermochemical constants for transition-metal-containing species. This impairs the ability to create high-quality sets of data to calibrate new or modified *ab initio* techniques, as is possible with main group species via the JANAF Tables,⁵⁹ NIST WebBook,⁶⁰ or the database compiled by Goos et al.⁶¹ However, if an energetic property computed using a single reference-based model chemistry deviates substantially from an experimental value, but the amplitudes and diagnostics show no catastrophic multireference character within the system, this could indicate that the theoretical value is reliable. Indeed, ccCA, in tandem with CI coefficients and coupled cluster amplitudes/diagnostics, has been utilized to confidently assess experimental uncertainties and to encourage experimental and theoretical reinvestigation of outlying data points.^{57,62} Ideally, the preferred method of assessing the quality of experimental data would be to compare against post-CCSD(T) model chemistries such as HEAT⁶³ and Wn.^{24–26} However, significant technological issues must be overcome to be able to use these highly accurate quantum chemical approaches to compute properties of large classical inorganic or organometallic complexes.

The aim of this study is to analyze several diagnostics, including the %TAE_e[(T)] diagnostic, for different bonding types of 3d TM molecules. Given the omnipresence of MR character in TM species, such analysis will be helpful for the utilization of diagnostics to examine the quality of more approximate and efficient SR composite methods such as ccCA. With sufficient calibration and empirical understanding of nondynamical correlation, improved criteria could be proposed to determine the wave function behavior of novel molecular systems. Since post-CCSD(T) methods are likely more resilient to MR character, our proposed criteria are less useful for higher order coupled cluster methods. However, low-level calculations could be performed *a priori* to assess not only if SR methods can appropriately

describe degenerate or near-degenerate configuration effects but also if MR methods beyond double excitations are necessary to appropriately describe long-range (i.e., dynamical) correlation effects.

2. COMPUTATIONAL METHODS

In this study, all CASSCF and CCSD calculations for transition-metal-containing molecules were performed with the cc-pVTZ-DK basis set⁵⁸ using the one-particle Douglas–Kroll–Hess Hamiltonian for scalar relativistic effects.^{47,64} For the main group G2/97 set,^{65,66} nonrelativistic CCSD calculations were performed using the cc-pVTZ basis set. C_0^2 is the weight of the leading configuration or CSF of the CASSCF wave function based on natural orbitals. The T_1 , D_1 , $|t_{1\max}|$, $|t_{2\max}|$, and spin contamination are extracted from CCSD calculations based on the restricted open shell HF (ROHF) reference wave function. For open shell systems, the spin contamination is eliminated in the ROHF reference wave function but may reappear in R/UCCSD^{67,68} calculations as a result of unrestricted spin at the CCSD level. All calculations were done using MOLPRO.⁴²

In the following sections, the terms “[(T)]” for the (T) contribution to TAE, and “e” for equilibrium geometry are dropped for clarity from %TAE_e[(T)]. The formulation is the same as eq 1 of ref 26 but based on the CCSD(T)/cc-pVTZ-DK or CCSD(T)/cc-pVTZ results:

$$\begin{aligned} \%TAE = 100 \times (TAE_e[CCSD(T)] \\ - TAE_e[CCSD]) / TAE_e[CCSD(T)] \end{aligned} \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. Diagnostics for the G2/97 Set. Although the diagnostics T_1 , D_1 , $|t_{1\max}|$ (when > 0.05), and $|t_{2\max}|$ (when > 0.05) have been widely used to *a priori* examine the MR character of molecular systems, systematic analysis is generally missing for a large set of diverse main group molecules. The initial studies are limited and small in size; e.g., 23 species including atoms and small clusters were considered for closed shell T_1 diagnostic by Lee and Taylor,³⁹ 29 main group molecules for closed shell T_1 and D_1 diagnostics by Janssen and Nielsen,⁴⁷ and 10 diatomics and cations for open shell T_1 and D_1 diagnostics by Lee.⁵⁰ Martin and co-workers have reported the T_1 and D_1 diagnostics for the W4-11 data set of 140 species, but their discussion emphasized the various %TAE_e values.^{26,33} Before applying the diagnostics to transition metal species, we investigated the G2/97 set of 148 main group species used to test enthalpies of formation (ΔH_f) (see Table S1 of the Supporting Information).

In the smallest molecular systems such as H₂, Li₂, Na₂, LiH, and BeH, where there is only one active orbital (or two for BeH), $\sqrt{2}T_1 = D_1$ ($\sqrt{2}T_1 \approx D_1$ for BeH). For the 148 main group molecules, the T_1 diagnostic correlates with D_1 with an R^2 of 0.85, which is less than 0.94 for the 29 closed-shell molecules of an earlier study⁵⁰ but still demonstrates moderate correlation. For the 15 molecules found with significant $|t_{1\max}| > 0.05$, D_1 diagnostics correlate with $|t_{1\max}|$ with an R^2 of 0.91, while T_1 diagnostics versus $|t_{1\max}|$ gives an R^2 of 0.85. As pointed out earlier,⁵⁰ the ratio T_1/D_1 can be used to examine the homogeneity of the electronic structure. For the 148 molecules, the ratio T_1/D_1 spans from 0.252 to $1/\sqrt{2}$ (0.707) with a mean value of 0.431. It has been demonstrated that as the size of molecules increases, the T_1 diagnostic may decrease, and so does the ratio

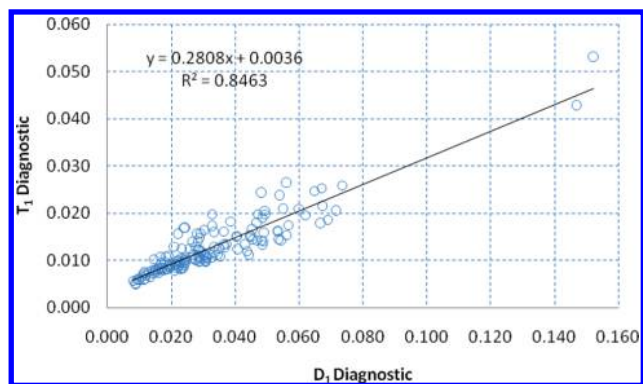


Figure 1. The scattering plot of T_1 and D_1 diagnostics for the G2/97 set of 148 molecules.

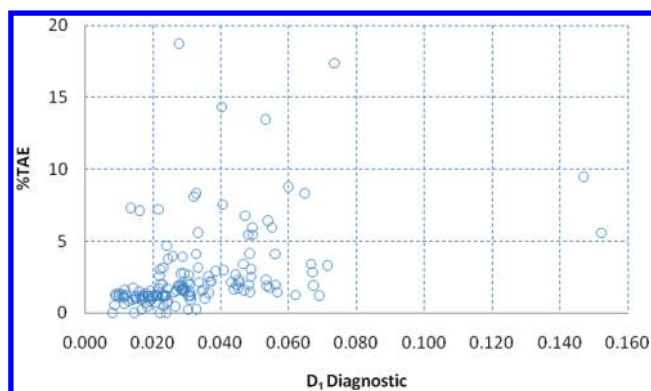


Figure 2. The scattering plot of %TAE against D_1 diagnostics for the G2/97 set of 148 molecules.

T_1/D_1 .⁴⁷ The slope of the trendline of T_1 against D_1 is 0.28 with an intercept of +0.0036 (Figure 1). Since the G2/97 set is predominantly comprised of systems dominated by a single reference, $D_1 < 0.06$ is thus suggested to replace $D_1 < 0.05$ as a criterion consistent with $T_1 < 0.02$ for reliable SR prediction of thermochemical properties.

No obvious correlation can be established between CC amplitude diagnostics and %TAE for the G2/97 set (see Figure 2 for a scatter plot of %TAE versus D_1 diagnostics). Both types of diagnostics confirm that ClO and O₃ are systems that require MR methods or consideration of post-CCSD(T) single reference methods. However, a few molecules, CN, HCO, ClNO, CH₃O-NO, CH₃CO, CH₃O, and NO₂, predicted with $T_1 \geq 0.02$ and $D_1 \geq 0.06$ were found with moderate %TAE. These are examples where CC energies may fortuitously attain good accuracy despite the poor quality of wave functions. Three molecules, F₂, OF₂, and ClF₃, were found with %TAE ≥ 10 (one criterion for severe nondynamical correlation²⁶), but the T_1 and D_1 diagnostics suggest that the CCSD wave function is of good quality: F₂ ($T_1 = 0.010$ and $D_1 = 0.028$), OF₂ ($T_1 = 0.015$ and $D_1 = 0.040$), and ClF₃ ($T_1 = 0.016$ and $D_1 = 0.053$). The large value of $|t_{2\max}|$ (=0.162) for F₂ suggests possible nondynamical correlation by double excitations. It is noteworthy that the relatively small CCSD(T) TAEs (38.3 kcal mol⁻¹ for F₂, 92.7 kcal mol⁻¹ for OF₂, 127.0 kcal mol⁻¹ for ClF₃) and large numbers of valence electrons (7, 20, and 28 for F₂, OF₂, and ClF₃, respectively) may cause overestimation of the nondynamical correlation by %TAE.

3.2. Transition Metal Species. The diagnostics T_1 , D_1 , $|t_{1\max}|$, $|t_{2\max}|$, spin contamination, and %TAE were calculated for the ccCA-TM/11all set of 225 TM molecules. For a detailed discussion of ground state geometries, point group symmetries, and electronic structure used, see ref 57. The TM-containing molecules are separated into various subcategories with representative bonding types, i.e., hydrides, chalcogenides, halides, metal dimers, clusters, and coordination complexes, in the subsequent analysis. Such discussion provides informative guidance for the assessment of nondynamical correlation for inorganic ligand bonding types.

3.2.1. Hydrides. Although values of $T_1 = 0.023$ and $D_1 = 0.044$ suggest that ScH is not a MR system, the computed value of C_0^2 (=0.876) implies otherwise (Table S2, Supporting Information). Further examination of the CASSCF wave function of ScH reveals three important doubly excited CSFs. Since the T_1 and D_1 diagnostics are based on single excitations, it is possible that T_1 or D_1 could not reflect strong correlation by double excitations. The importance of a few doubly excited CSFs is also confirmed by $|t_{2\max}|$, which is 0.115. However, the %TAE of 1.3 suggests that the nondynamical correlation may not cause a significant degradation of the CCSD(T) energies. T_1 and D_1 diagnostics of all other metal hydrides except MnH suggest the presence of severe nondynamical correlation. %TAE varies significantly across the monohydrides but is close to or more than 10 only for FeH, CoH, and NiH. Negative %TAEs are found for MnH and ZnH (−1.6 and −1.7, respectively), which implies that CCSD may overestimate the binding energy of these two hydrides.

3.2.2. Oxides and Heavier Chalcogenides. For the monochalcogenides of early transition metals Sc, Ti, V, and Cr, the C_0^2 value decreases, and all other diagnostics increase monotonically from oxides to selenides for each of the four metals with few exceptions (Table S2, Supporting Information), showing that the nondynamical correlation is increasingly important for heavier chalcogenides. Additionally, the nondynamical correlation may become increasingly severe from Sc to Cr. For the monochalcogenides of middle and late transition metals Mn, Fe, Ni, Cu, and Zn, diagnostics generally show that the nondynamical correlation becomes less important for heavier chalcogenides, the opposite of the trend that occurs for early metal monochalcogenides. %TAE is equal to or greater than 10 except for copper chalcogenides and ScO. The diagnostics ($T_1 > 0.04$, $D_1 \geq 0.10$, and %TAE > 10) of three dioxides, TiO₂, VO₂, and CrO₂, and one trioxide, CrO₃, show possible severe nondynamical correlation.

3.2.3. Halides. All diagnostics consistently show that the ground states of manganese, iron, and zinc monohalides (MnF, MnCl, MnBr, FeF, FeCl, FeBr, ZnCl, and ZnBr) are dominated by dynamical correlation effects. Other monohalides listed in Table S2 are subject to mild or severe nondynamical correlation. Three molecules (VF, CoF, and CuF) have a C_0^2 less than 0.90. Large D_1 diagnostics (>0.20) are predicted for CoCl, NiF, and the three chromium halides CrF, CrCl, and CrBr. The %TAE is largest for CoCl (9.1) but is less than 4 for all other halides. Similar to the trends found with metal chalcogenides, from fluoride to bromide, the T_1 and D_1 diagnostics increase for Ti, V, and Cr; remains the same for Mn and Fe; and decreases for Ni and Cu.

The C_0^2 values lie in a range of 0.89–0.92 for nickel dihalides and is greater than 0.96 for all other metal dihalides. Overall, the T_1 diagnostic is less than 0.04 and %TAE is less than 4.0. On the basis of the diagnostics C_0^2 , T_1 , and %TAE, it can be inferred that

Table 1. Listing of Metal Dimers with Diagnostics Calculated by CCSD with the cc-pVTZ-DK Basis Set

molecule	C_0^2	T_1	D_1	$ t_{1\max} $	$ t_{2\max} $	$\langle S^2 - S_z^2 - S_z \rangle$	TAE _e CCSD	TAE _e CCSD(T)	exptl. D_0^a	%TAE
Sc ₂ ($^5\Sigma_g^-$)	0.500	0.119	0.186	0.229	0.122	0.036	−10.0	−0.2	38.0	2331.4
Ti ₂ ($^1\Delta_g$)	0.793	0.068	0.121	0.098	0.072	0.004	−26.2	0.7	35.5	1502.1
V ₂ ($^3\Sigma_g^-$)	0.706	0.097	0.262	0.370	0.155	0.010	−33.7	10.7	63.5	354.1
Cr ₂ ($^1\Sigma_g^+$)	0.614	0.047	0.078	0.062	0.156		−74.8	−3.1	33.2	−2297.6
Mn ₂ ($^{11}\Pi_u$)	0.881	0.072	0.242	0.603	0.078	0.906	−35.0	−28.4	18.4	−23.0
Fe ₂ ($^7\Delta_u$)	0.482	0.045	0.105	0.148	0.233	0.056	−94.1	−43.1	26.5	−121.6
Co ₂ ($^5\Delta_g$)	0.513	0.037	0.083	0.095	0.131	0.024	−63.7	−12.0	39.0	−688.2
Ni ₂ ($^3\Sigma_g^-$)	0.518	0.041	0.111	0.108	0.251	0.035	−13.3	18.2	47.7	132.4
Cu ₂ ($^1\Sigma_g^+$)	0.969	0.027	0.069	0.054	0.070		39.1	44.1	46.4	11.4
Zn ₂ ($^1\Sigma_g^+$)		0.018	0.056		0.055		−0.3	0.0	1.3	750.3
CrCu ($^6\Sigma^+$)	0.968	0.036	0.081	0.107	0.060	0.080	27.4	32.4	37.7	15.5
CoCu ($^3\Delta$)	0.459	0.032	0.071	0.059	0.065	0.025	11.4	19.8	31.0	38.1
NiCu ($^2\Delta$)	0.672	0.034	0.104	0.106	0.061	0.012	27.1	36.4	47.2	24.8

^a Experimental D_0 from ref 72.

dynamical correlation is dominant and nondynamical correlation is mild for these dihalides. However, relatively large D_1 diagnostics for CrBr₂, NiCl₂, NiBr₂, CuF₂, and CuCl₂ suggest that nondynamical correlation resulting from single excitations or orbital relaxations may be critical. The (T) contribution to TAE is small (%TAE = 0.5) for CuF₂ and near zero for CuCl₂ despite the relatively large D_1 diagnostics (0.100 and 0.143 respectively).

Determination of the C_0^2 diagnostic is not tractable due to the prohibitively large full valence CASSCF for most trihalides, tetrahalides, and pentahalides. VBr₃, CrCl₃, FeBr₃, and CoCl₃ may have moderate nondynamical correlation since the diagnostic %TAE > 5.0. The T_1 and D_1 diagnostics are also relatively larger ($T_1 > 0.40$ and $D_1 > 0.10$) for these molecules. While %TAE increases from fluoride to bromide for Sc and Ti, the diagnostics T_1 and D_1 do not display a similar trend. All diagnostics (T_1 , D_1 , and %TAE) consistently show the increasing prominence of nondynamical correlation from fluoride to bromide for the iron trihalides. The T_1 diagnostic is between 0.02 and 0.04 for all tetrahalides considered in this study, as well as for VF₅. However, the D_1 diagnostic is between 0.06 and 0.12 for these 14 molecules. On the other hand, %TAEs are greater than 5.0 for VF₅ and all tetrahalides except TiF₄. Severe nondynamical correlation may exist for VBr₄ and CrCl₄ with %TAE > 10.

3.2.4. Classical Coordination Complexes. Complexes of transition metals with ligands such as CO, PF₃, C₅H₅, etc. are fascinating molecules with versatile coordinating bonds and labile reactivity. For the 30 larger complexes considered (Table S2), the T_1 diagnostic is less than or nearly 0.05. The D_1 diagnostic is relatively larger than expected, and there are only three species with $D_1 < 0.07$ ($0.05 \times \sqrt{2}$). Spin contamination is more critical for FeCO (0.287) than for other open shell carbonyls (<0.1) considered in this study. Single reference CCSD(T) energetics were found in good agreement with experimental results for FeCO,⁶⁹ Ni(CO)₄, and Fe(CO)₅,⁷⁰ and have been used to calibrate experimental ΔH_f° s for Fe(CO)₄.⁷¹ Except for the D_1 diagnostic of iron carbonyls, when the number of CO ligands increases, the T_1 , D_1 , $|t_{1\max}|$, and %TAE decrease for Cr, Fe, and Ni carbonyls, implying that nondynamical correlation becomes less important for larger polycarbonyls.

Based on the diagnostics, the electronic structure of Sc(C₅H₅)₃, Ti(C₅H₅)Cl₃, and Fe(C₅H₅)₃ can be described as SR with predominantly dynamical correlation. The T_1 (0.047) and D_1

(0.188) diagnostics for Fe(C₅H₅)₂ suggest severe nondynamical correlation while the diagnostic %TAE of 2.8 implies that reliable CC energies can be achieved. For the other molecules, %TAE is 4.0–7.6, except NiCO with a very large %TAE of 11.3.

3.2.5. Clusters. The clusters considered in this study include dimers and trimers of metal halides and oxides V₄O₁₀ and (CrO₃)₃. The diagnostics for the clusters (ScCl₃)₂, (MnCl₂)₂, (MnBr₂)₂, (ZnCl₂)₂, and (ZnBr₂)₂ meet the criteria $T_1 < 0.02$ and $D_1 < 0.06$ for SR systems, and the small %TAEs (2.1–2.5) are also consistent with the T_1 and D_1 results. Among the halide clusters, (FeCl₂)₂ and (FeBr₂)₂ have the largest diagnostics followed by (CoCl₂)₂ and (CoBr₂)₂. The oxides V₄O₁₀ and (CrO₃)₃ may have significant MR character with %TAE > 10.

3.2.6. Metal Dimers. Most 3d metal homo- and hetero-dimers are known to have pathological multireference character and are often considered “torture tests” for single and multireference methods.^{72–77} The C_0^2 reveals highly MR character of most dimers but is greater than 0.90 for Cu₂ and CrCu (Table 1). Except for Cu₂ and Zn₂, T_1 and D_1 diagnostics are greater than 0.03 and 0.07, respectively. Unlike covalent and coordination compounds discussed in previous sections, the metal dimers are observed with unusual %TAE values, which are either negative or much greater than 10. Further investigation of the CCSD and CCSD(T) TAEs ($=D_e$ for diatomics, see Table 1) shows that CCSD energies cannot be used to obtain qualitatively correct bonding energies of dimers Sc₂–Ni₂ and Zn₂ (see experimental D_0 's given in Table 1).⁷² Even CCSD(T) predicts dissociative Sc₂, Cr₂, Mn₂, Fe₂, Co₂, and Zn₂. Due to the small magnitude of the dissociation energy of Zn₂, with an experimental D_0 of 1.3 kcal/mol, the %TAE becomes very sensitive to minor changes in TAE_e[CCSD(T)] and/or TAE_e[CCSD], and thus it is not recommended to use %TAE as a diagnostic for systems when the TAE is small.

3.3. Discussion. The CC amplitude diagnostics demonstrate the great diversity in bonding and electronic structure of the ccCA-TM/11all set of molecules. The T_1 versus D_1 diagnostics for all TM species show a moderate correlation with an R^2 of 0.73 (Figure 3) but better correlation between T_1 and D_1 can be found within subcategories of bonding types. For example, comparison of T_1 and D_1 for hydrides, monohalides, and trihalides were well correlated with R^2 values of 0.95, 0.98, and 0.93, respectively. (Table 2) We note that for the 203 molecules

in the ccCA-TM/11all set with $|t_{1\max}| > 0.05$, the D_1 and $|t_{1\max}|$ values are correlated with an R^2 of 0.74 (Figure 4), confirming a relationship between the D_1 diagnostic and the largest absolute t_1 amplitude over a diverse set of molecules.

Despite the drastically varying electronic structure across the metals and ligands, general criteria for reliable (e.g., chemically accurate) TM thermochemistry are still useful. The averaged diagnostics $T_1 = 0.044$ and $D_1 = 0.127$ over the entire ccCA-TM/11all set indicates that the historical criteria $T_1 < 0.02$ and $D_1 < 0.05$ (or the suggested criterion $D_1 < 0.06$ in this study) for molecules containing only main group atoms are no longer practical for TM-containing species. On the basis of our data set, $T_1 < 0.05$ is suggested as the cutoff for reliable SR calculations for transition metal species. Accordingly, the $D_1 < 0.15$ is recommended on the basis of the linear fitting of T_1 and D_1 diagnostics for the ccCA-TM/11all set of 225 molecules. Excluding the metal dimer outliers Sc_2 – Ni_2 , 53 species have $T_1 \geq 0.05$ and $D_1 \geq 0.15$ and can be regarded as having salient MR behavior.

The averaged %TAE is 7.5 for the overall set excluding metal dimer outliers (Sc_2 – Ni_2 and Zn_2). Only two molecules other than the homonuclear metal dimers obtained negative %TAE: MnH (−1.6) and ZnH (−1.7). Consequently, %TAE > 10 recommended by Martin and co-workers²⁴ for main group atoms can also be a cutoff for reliable SR calculations on inorganic molecules. The %TAE is less than 10 for all halides and classical coordination complexes except VBr_4 , CrCl_4 and CrBr_4 , and NiCO . Excluding the metal dimers, 59 species were predicted with %TAE ≥ 10 . However, the reliability of the %TAE diagnostic could be undermined when the TAE[CCSD(T)] value was small in magnitude. It has also been found that SR

methods such as large basis set CCSD(T) computations and ccCA can still predict energetics in good agreement with experimental results despite the presence of large T_1 or D_1 diagnostics. By combining the criteria of CC amplitude diagnostics and %TAE, pathological systems can be identified more readily than via any single diagnostic. Combining all three criteria, 28 TM species were found with $T_1 \geq 0.05$, $D_1 \geq 0.15$, and %TAE ≥ 10 (Table 3). These 28 molecules, along with most of the hetero- and homonuclear dimers listed in Table 1 are determined as systems with severe nondynamical correlation. Accurate energetics of these molecules may require CC including excitations higher than perturbative triples and/or MRCI calculations. With accompanying reliable experimental data, these molecules may represent a stringent benchmark set for new highly accurate *ab initio* methodologies, either based on a single or multiple configuration reference. One could consider such a test set the antithesis of “mindless” thermochemical calibration.^{78,79} On the other hand, 107 species in the ccCA-TM/11all set have been found with all three diagnostics thresholds met, i.e., $T_1 < 0.05$,

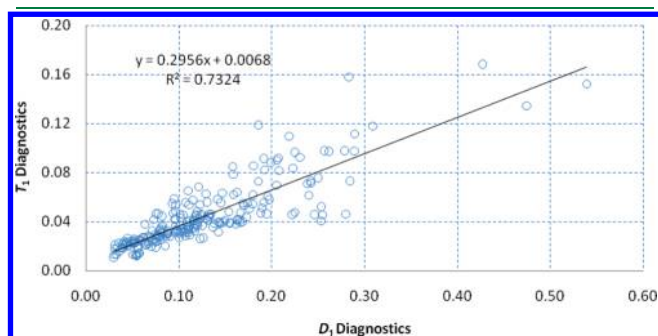


Figure 3. The scattering plot of T_1 and D_1 diagnostics for the ccCA-TM/11all set of 225 transition metal molecules.

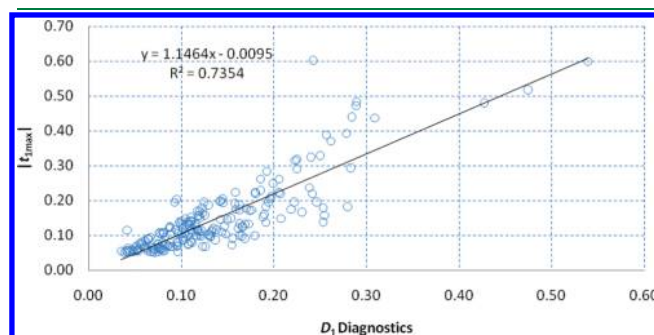


Figure 4. The scattering plot of D_1 diagnostic against $|t_{1\max}|$ for 203 transition metal molecules with $|t_{1\max}| > 0.05$.

Table 3. A List of 28 Transition-Metal-Containing Molecules That May Contain Severe Nondynamical Correlation

ScB_2 (2A_1)	CrN ($^4\Sigma^-$)	FeO ($^5\Delta$)	CoSi ($^2\Sigma^-$)
TiSe ($^3\Delta$)	CrO ($^5\Pi$)	FeS ($^5\Delta$)	CoGe ($^2\Sigma^-$)
TiB ($^6\Sigma^+$)	CrS ($^5\Pi$)	$(\text{FeCl}_2)_2$ (9B_2)	NiH ($^2\Delta$)
VS ($^4\Sigma^-$)	CrO_3 (1A_1)	$(\text{FeBr}_2)_2$ (9B_2)	NiSi ($^1\Sigma^+$)
VSe ($^4\Sigma^-$)	CrO_2Cl ($^2A'$)	CoH ($^3\Phi$)	NiGe ($^1\Sigma^+$)
VC ($^2\Delta$)	MnO ($^6\Sigma^+$)	CoO ($^4\Delta$)	NiO ($^3\Sigma^-$)
VO_2 (2A_1)	FeH ($^4\Delta$)	$(\text{CoCl}_2)_2$ (7A_u)	NiS ($^3\Sigma^-$)

Table 2. Statistics of Diagnostics

	T_1			D_1			R^{2a}	T_1/D_1			%TAE		
	mean	min	max	mean	min	max		mean	min	max	mean	min	max
hydrides (10)	0.065	0.023	0.168	0.172	0.044	0.427	0.952	0.40	0.31	0.54	3.8	−1.7	12.3
oxides (25)	0.063	0.022	0.118	0.147	0.064	0.309	0.721	0.45	0.29	0.62	14.5	6.4	34.6
monohalides (25)	0.046	0.018	0.152	0.147	0.031	0.539	0.979	0.38	0.25	0.68	3.2	1.4	8.9
dihalides (27)	0.026	0.014	0.038	0.075	0.042	0.145	0.608	0.37	0.22	0.50	2.5	0.0	3.9
trihalides (15)	0.033	0.013	0.062	0.089	0.030	0.180	0.926	0.39	0.27	0.47	4.3	2.2	6.9
tetrahalides (13)	0.031	0.023	0.041	0.092	0.063	0.125	0.838	0.34	0.29	0.37	7.7	3.8	10.9
coordination complexes (29)	0.039	0.011	0.056	0.150	0.030	0.280	0.584	0.28	0.16	0.38	5.5	2.0	11.3
small clusters (18) ^b	0.030	0.013	0.047	0.113	0.033	0.246	0.748	0.30	0.19	0.48	8.8	2.1	27.1
overall (225) ^b	0.044	0.011	0.168	0.127	0.030	0.539	0.732	0.37	0.16	0.68	7.5	−1.7	38.1

^a Correlation coefficients for T_1 and D_1 diagnostics. ^b $(\text{CrO}_3)_3$ is excluded for the T_1 and D_1 diagnostics.

$D_1 < 0.15$, and %TAE < 10. These species are most likely well described by SR methods. Figures 5 and 6 show scattering plots of %TAE.

However, it is difficult to evaluate the severity of systems for species where $T_1 < 0.05$ and $D_1 < 0.15$ but %TAE (or its absolute value) is greater than 10. In fact, many of the historically “pathological” homonuclear dimers belong in this category. In such cases, additional metrics such as $|t_{2\max}|$, C_0^2 , and spin contamination can be sought to determine the multireference character in the borderline molecular systems. As previously mentioned, many of the homonuclear dimers have atypically large absolute values of %TAE (the Cr_2 %TAE = −2297.6, for example) or extremely large values of $|t_{1\max}|$ and $|t_{2\max}|$, such as Mn_2 where $|t_{1\max}| = 0.603$. The chalcogenides of zinc, for example, may be deceptively difficult challenges for SR methods. ZnO , ZnS , and ZnSe have $T_1 < 0.05$ and $D_1 < 0.15$ but %TAE values greater than 20. It should again be noted that $|t_{1\max}|$ delivers the same information as D_1 and was superseded by the latter due to a lack of orbital invariance. However, $|t_{2\max}|$, despite its orbital variance, is the only double-substituted-based diagnostic available in current programs. The relatively larger $|t_{2\max}|$ in ZnO , ZnS , and ZnSe as compared to other metal chalcogenides may indicate important doubly excited configurations. Currently, MOLPRO and other programs that print coupled cluster amplitudes and diagnostics do not compute double substituted-based diagnostics, such as D_2 previously derived in

ref 48 and T_2 defined similarly to T_1 . Comparison and correlation of T_1 and D_1 to T_2 and D_2 diagnostics may be useful in allowing a more rigorous categorizing of molecules based on dynamical versus nondynamical electron correlation.

The weight C_0^2 of the leading configuration, or CSF, in the CASSCF wave function directly shows whether or not there are strongly correlated CSFs within the CAS. One example in this study is the C_0^2 of ScH , which shows possible important nondynamical correlation effects that do not appear in any of the other diagnostics based on single excitations or total energies. However, reliable and straightforward computation of C_0^2 is only possible for diatomics and a few triatomics due to the unfavorable cost of CASSCF calculations.

In the calculation of open shell species, the ROHF reference wave function is spin pure. The R/UCCSD implementation^{67,68} in MOLPRO typically provides accurate energetic (see an example in ref 80) and improved energies over a U/UCCSD wave function for both main group and TM-containing molecules.^{57,81} However, the utilization of UCCSD may result in the admixture of higher spin states in the excited configurations. When the weight of the reference configuration is predominant, the spin contamination is trivial, as found for most open shell species in this study where the expectation value of $\langle S^2 - S_z^2 - S_z \rangle$ is much less than 0.1. However, in a MR system, significant spin contamination may be introduced by strongly correlated excited configuration(s) that contribute significantly to nondynamical correlation. As can be seen in Table S2, large spin contamination is usually associated with small C_0^2 . For example, $C_0^2 = 0.571$ and $\langle S^2 - S_z^2 - S_z \rangle = 0.776$ for FeH ; $C_0^2 = 0.308$ and $\langle S^2 - S_z^2 - S_z \rangle = 0.622$ for CrS ; and $C_0^2 = 0.511$ and $\langle S^2 - S_z^2 - S_z \rangle = 0.587$ for CoCl . Consequently, spin contamination with $\langle S^2 - S_z^2 - S_z \rangle$ greater than 0.1 in an R/UCCSD wave function can be viewed as a strong indication of nondynamical correlation in an open shell system. Among the 162 open shell TM species considered in this study, 17 molecules were predicted with $\langle S^2 - S_z^2 - S_z \rangle$ greater than 0.1.

In our earlier study,^{30,57} the diagnostics T_1 and D_1 were discussed in the assessment of the reliability of the ccCA prediction for atomization energies. However, as pointed out earlier, comparisons to experimental data (enthalpies of formation) may not reflect the accuracy of the theoretical methods due to the many significant sources of error (both theoretical and experimental) for TM species. Although the ccCA-TM MAD for a subset of molecules with $T_1 < 0.05$, $D_1 < 0.10$, and $C_0^2 > 0.90$

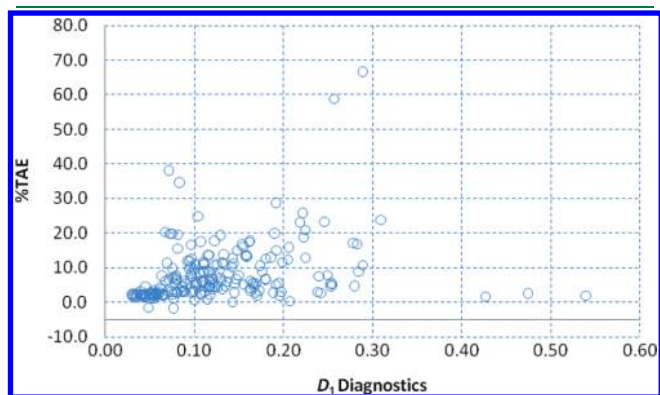


Figure 5. The scattering plot of %TAE and D_1 diagnostics for the ccCA-TM/11all set of transition metal molecules excluding metal dimers Sc_2 – Ni_2 and Zn_2 .

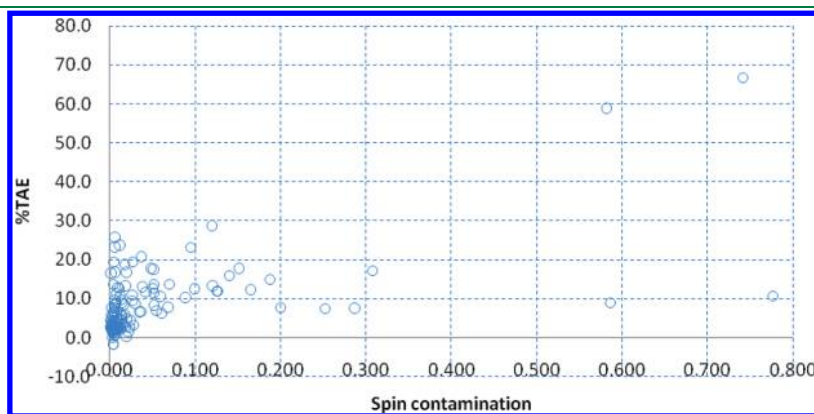


Figure 6. The scattering plot of %TAE and spin contamination for open shell transition-metal-containing molecules excluding homonuclear metal dimers.

was smaller than the overall MAD,⁵⁷ no clear linear correlation was found between the diagnostics and the accuracy of atomization energy predictions by single reference methods such as ccCA-TM. The diagnostics, as demonstrated in our earlier study,⁵⁷ were found important in identifying experimental values that may need to be revisited.

4. CONCLUSIONS

Various diagnostics of MR character for 3d TM species have been analyzed for metal hydrides, oxides and heavier chalcogenides, halides, coordination complexes, small clusters, and metal dimers. The weight of the leading configuration, C_0^2 , in a CASSCF wave function is useful only when a CASSCF calculation is feasible and the active space includes all critical molecular orbitals. Spin contamination can be a good indicator of non-dynamical correlation when the strongly correlated excited configuration(s) are severely admixed with high spin states. The T_1 and D_1 diagnostics reveal insights about the electronic structure of CCSD wave functions. However, the historical criteria $T_1 < 0.02$ and $D_1 < 0.05$ for organic computational chemistry is no longer valid or practical for TM-containing species. It is concluded that the additional diagnostic %TAE is extremely beneficial as %TAE is a direct indicator of the quality of CCSD and CCSD(T) energies. %TAE has a simple form as compared to T_1 or D_1 and also requires essentially no additional computational cost when CCSD(T) calculations are performed. However, %TAE as a sole diagnostic is not reliable for weakly bonded systems with moderate MR character such as Zn_2 . No linear correlation has been established between the diagnostics and the accuracy of single reference methods such as ccCA-TM compared to experiments. Nonetheless, based on the statistical analysis of the ccCA-TM/11all set of 225 species, $T_1 < 0.05$ and $D_1 < 0.15$ and $|\%TAE| < 10$ are proposed as amplitude/diagnostic criteria for the computation of reliable d-block energetic and spectroscopic properties using single reference-based model chemistries. When all three criteria are not met, C_0^2 , $|t_{2max}|$, and spin contamination can be used complementarily to determine the relative importance of SR/MR character. We recommend implementation of T_2 and D_2 diagnostics in production-level *ab initio* where coupled cluster energy computations are available.

■ ASSOCIATED CONTENT

S Supporting Information. The diagnostics for the G2/97 set of 148 molecules calculated by CCSD/cc-pVTZ and all diagnostics calculated by CCSD(T) or CASSCF with the cc-pVTZ-DK basis set. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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