# Multireference Character for 4d Transition Metal-Containing Molecules

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S _Supporting Information_

ABSTRACT: Four diagnostic criteria have been examined to identify the suitability of single-reference wave function-based quantum chemistry methods for a set of 118 4d transition metal species. These diagnostics include the weight of the leading configuration of the CASSCF wave function, C_0^2; the Frobenius norm of the coupled cluster amplitude vector related to single excitations, T_1; the matrix 2-norm of the coupled cluster T_1 amplitude vector arising from coupled cluster calculations, D_1; and the percent total atomization energy, %TAE, corresponding to a relationship between energies determined with CCSD and CCSD(T) calculations. New criteria, namely, $T_1 \geq 0.045$, $D_1 \geq 0.120$, and %TAE $\geq$ 10%, are herein proposed as a gauge for 4d transition metal-containing molecules to predict the possible need to employ multireference (MR) wave function-based methods to describe energetic and spectroscopic properties.
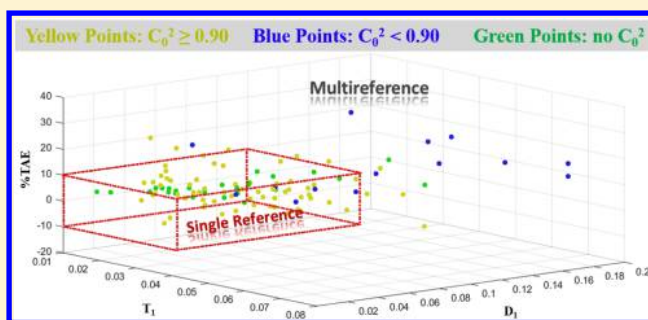
1. INTRODUCTION

Ab initio electron correlation methods are used to describe the interactions of electrons resulting from electronic interactions beyond the mean-field approximation of Hartree−Fock (HF) for atoms and molecules.[1] Electron correlation is commonly classified as two types: (a) dynamic correlation, which is related to the movements of electrons with respect to one another, and (b) nondynamic (or static) correlation, which arises from near degeneracies of occupied and virtual orbitals. Single-reference (SR) methods, such as truncated configuration interaction (CI), coupled cluster (CC), and many-body perturbation theory, are able to account for a large portion of the dynamic correlation energy, but they may not accurately describe molecular species with significant nondynamic correlation. For instance, coupled cluster with single, double, and perturbative triple excitations, CCSD(T),[2,3] with extrapolation of energetic properties to the complete basis set (CBS) limit (CCSD(T)/CBS)[4−7] can result in energetic properties within chemical accuracy (1 kcal mol^{-1} from experiment), on average, for small, main group molecules that are dominated by dynamic correlation.[8−15] However, for systems with significant non-dynamic correlation, SR methods can result in significant errors. For example, the enthalpy of formation determined using CCSD(T)/CBS for O_3 results in a deviation of ∼3.0 kcal mol^{-1} in comparison to experiment (34.10 ± 0.4 kcal mol^{-1}),[16,17] as a single-reference Hartree−Fock wave function reference, on which CCSD(T) is built, provides an inadequate description of the molecular ground state. Multiconfiguration or multireference (MR) methods, such as MCSCF,[18,19]

MRCI,[20−22] and CASPT2,[23] are better suited than SR methods to describe degenerate and quasi-degenerate states.

MR methods, however, are generally unable to address molecules as large as those that can be addressed by SR methods, since MR methods can quickly become computationally intractable due to the inclusion of all chemically relevant electrons and orbitals within an active space. In fact, an active space with ∼32 active orbitals is near the present limit for most computer architectures and _ab initio_ software packages, meaning that molecules such as VBr_4 or $Cr(CO)_6$ with a full-valence CASSCF have reached the number of active orbitals that can be correlated utilizing internally contracted CASPT2.[24,25] An additional challenge in terms of MR methods is that their application, through the utilization of a restricted active space (i.e., restricted active space (RAS), generalized active space (GAS), occupation restricted multiple active space (ORMAS)) typically requires much more chemical intuition[26] than is required for SR methods since user's selection of active space for MR methods can significantly affect the predicted properties (e.g., refs 27−29).

Before engaging in potentially complicated MR calculations, multireference diagnostic criteria can be used for _a priori_ analysis of the SR or MR character for molecular systems. These diagnostics can help to gauge suitable approaches (i.e., single or multireference wave function) to be used in calculations.

Several diagnostic criteria that can be used to assess the quality of the reference wave function have been developed to aid in determining the SR/MR character of molecules. One common diagnostic is the square of the CI coefficient, C_0, the leading configuration in CISD or CASSCF calculations.[30−33] Considering this diagnostic, molecules with significant MR character typically are indicated by a $C_0 \leq 0.95$ ($C_0^2 \leq 0.90$).[30] However, the determination of C_0^2 is not practical for large molecules due to the computational cost of large full-valence CASSCF calculations required. For 3d TM-containing systems considered in a study by Jiang et al.,[25] C_0^2 was not used for molecules of more than a few atoms due to the computational impracticality of using large full-valence CASSCF to establish the criteria.

As an alternative, the T_1 and D_1 diagnostics from CCSD calculations are widely used.[31,34−38] The T_1 diagnostic is defined as the Frobenius norm of the single substitution amplitudes vector (t_1) of the closed-shell CCSD wave function (utilizing restricted HF orbitals) divided by the square root of the number of correlated electrons to address size consistency concerns (eq 1).

$$T_1 = \| t_1 \| / \sqrt{N} \tag{1}$$

SR methods typically perform well for molecules with a T_1 diagnostic smaller than 0.02, as suggested by Lee and Taylor in a study of 23 main group species.[31,34] The D_1 diagnostic (eq 2) by Janssen and Nielsen[36]

$$D_1 = \| t_1 \|_2 \tag{2}$$

is based on the matrix 2-norm of t_1 from single excitations of the closed-shell CCSD wave function and is closely related to the value of the largest single excitation amplitude. Molecules are commonly dominated by dynamic correlation if the D_1 diagnostic is smaller than 0.05.[41] Both T_1 and D_1 diagnostics have been extended to open-shell CCSD wave functions.[37,38]

Lee performed a correlation analysis of T_1 and D_1 diagnostics and determined a squared correlation coefficient (R^2) of 0.96 based upon 10 open-shell main group species and of 0.90 based on 29 closed-shell main group molecules.[38] Although this high degree of correlation between the T_1 and D_1 diagnostics shows that the diagnostics may provide similar predictions of the SR/MR character (as both diagnostics are related by the t_1 amplitudes), the T_1 diagnostic is an average value for the whole molecule and may fail to indicate problems for small regions of a molecule that can be indicated by a large D_1 diagnostic. For instance, *para*-benzyne has a T_1 of 0.0189, which means that the majority of the molecule can be described successfully with SR methods. However, D_1 (0.0646) of *para*-benzyne is greater than 0.05, which means that SR methods may fail to describe the electronic structure of a small part of this molecule properly.[36] Therefore, these two diagnostics were suggested to be used together as a diagnostic.[38]

In the development of W4 theory, Martin et al.[39,40] proposed an energy-based diagnostic, $\%TAE_e[(T_4 + T_5)]$, which is the percentage of the coupled cluster CCSDTQ5 total energy that arises from connected quadruple and quintuple excitations. Although $\%TAE_e[(T_4 + T_5)]$ provides a useful indicator of nondynamic correlation effects, it is not a practical diagnostic due to its immense computational cost. Instead, the diagnostic $\%TAE_e[(T)]$, the percentage of the CCSD(T) TAE resulting from triple excitations, has been utilized (eq 3).[40]

$$\%TAE_e[(T)] = 100 \times (TAE_e[CCSD(T)] \\ - TEA_e[CCSD])/TAE_e[CCSD(T)] \tag{3}$$

$\%TAE_e[(T)]$ has been shown to provide a prediction that strongly correlates with the $\%TAE[(T_4 + T_5)]$ diagnostic (e.g., R^2 of 0.941 between $\%TAE_e[(T)]$ and $\%TAE[(T_4 + T_5)]$) for 20 mostly main group diatomic molecules).[39] Additionally, $\%TAE_e[(T)]$ is a much less expensive diagnostic than $\%TAE_e[(T_4 + T_5)]$. Martin and co-workers suggested $\%TAE_e[(T)] \leq 2\%$ as the cutoff for reliable SR calculations, $\%TAE_e[(T)]$ between 2 and 5% for mild nondynamic correlation, $\%TAE_e[(T)]$ between 5 and 10% for moderate nondynamic correlation, and $\%TAE_e[(T)] \geq 10\%$ for significant nondynamic correlation, as determined in a study of the W4 set of molecules (main group molecules).[40]

The historical interpretation of the T_1, D_1, and $\%TAE_e[(T)]$ diagnostics was developed based on small, well-behaved main group species. Due to partially filled d orbitals and the similar spatial extent and energy of the $(n + 1)$ s and n d orbitals, many transition metal (TM)-containing species are open-shell systems that may have degenerate or low-lying nearly degenerate electronic states that may necessitate a multi-reference wave function-based approach to properly describe the near degeneracies.[41−43] As such, the computational study of TM-containing species can become quite challenging due to the need to address these nondynamical electron correlation effects.[44−49] Since TM species tend to have more degenerate states and a smaller atomic energy gap between n d and $(n + 1)$ s orbitals than main group species and may have greater MR character as a result, the historical diagnostic criteria ($T_1 \leq 0.02$, $D_1 \leq 0.05$, and $\%TAE \leq 10\%$) may be not appropriate for TM-containing molecules.

As the proper methodology choice (e.g., single or multi-reference wave function-based approach) is imperative in the description of molecules and because diagnostics can serve as an important aid in this choice, investigations of suitable diagnostic criteria for TM-containing molecules are needed. A study by Jiang et al. focused on the analysis of several diagnostics (T_1, D_1, $\%TAE$, and spin contamination) for the ccCA-TM/11all set of 225 3d TM-containing species. Jiang showed that 3d TM-containing species do need different diagnostic criteria than the diagnostic criteria, $T_1 \leq 0.02$, $D_1 \leq 0.05$, developed for main group species and proposed $T_1 \leq 0.05$ and $D_1 \leq 0.15$ as diagnostic criteria for SR methods for 3d TM-containing species. Jiang also found a moderate correlation between T_1 and D_1 diagnostics with a R^2 of 0.73, which is much smaller than the R^2 of 0.96 and 0.90, mentioned earlier, for small main group species.[25] Therefore, T_1 and D_1 yield less similar information about properties of the electronic structure for 3d TM-containing species than for main group species, which reaffirms that using T_1 and D_1 together rather than using a single diagnostic may provide a more reliable prediction of multireference character as molecules increase in size.[38]

Although various diagnostics for 3d TM-containing molecules have been analyzed in Jiang's previous study, analysis of diagnostics on the basis of 4d TM-containing molecules is needed to provide more comprehensive insight into the MR character of d-block molecules. Since 4d TMs have different atomic energy gaps between the 4d and 5s orbitals than the 3d TMs have between the 3d and 4s orbitals,[50] 4d TM-containing species may exhibit a different degree of nondynamic correlation than 3d TM-containing species. Therefore, the

diagnostic criteria for indicating MR character in 3d TM-containing species may not be ideal for 4d TM-containing species. Thus, in this study, the T_1, D_1, and $\%TAE_e[(T)]$ diagnostic criteria are re-examined for 118 4d TM-containing species. These molecules investigated are from the 4dHf-210 data set,[51] a set of molecules that includes a variety of binding types including hydrides, chalcogenides, halides, metal dimers, and coordination complexes.

2. COMPUTATIONAL METHODS

In this study, four diagnostics, C_0^2, T_1, D_1, and $\%TAE_e[(T)]$, were applied for 4d TM-containing species. (Hereafter, for simplicity, %TAE will be used to represent $\%TAE_e[(T)]$, where e represents the equilibrium geometry.)

The optimized geometries for the 118 structures were determined in earlier work,[51] using B3LYP[52−54] in combination with cc-pVTZ basis sets and small core pseudopotentials, which were utilized for elements gallium through krypton and 4d TMs.[55−60] CASSCF, CCSD, and CCSD(T) single-point calculations with cc-pVTZ-DK basis sets[55,59−61] (tight-d correlation consistent basis sets were used for second-row elements Si, S, and Cl)[62] based on a restricted open-shell HF (ROHF) reference wave function were performed. Scalar relativistic effects were included using the second-order one-particle Douglas−Kroll−Hess Hamiltonian.[63,64] The C_0^2 diagnostic was obtained by employing a CASSCF calculation with a full-valence active space. All calculations were carried out using MOLPRO.[65]

3. RESULTS AND DISCCUSION

3.1. 4d Transition Metal Species. The four diagnostics considered (C_0^2, T_1, D_1, and %TAE) were examined for a set of 118 4d TM-containing molecules, including hydrides, chalcogenides, halides, and metal dimers. The square of the leading coefficient, C_0^2, in the full-valence CASSCF wave function directly shows the extent to which the configuration state functions (CSFs) correlate within the CAS. For molecules with C_0^2 greater than 0.9, nondynamic correlation (MR character) is significant. Calculations for C_0^2 are considered only for molecules with three or fewer main group elements (83 molecules) due to the unfavorable cost of large full-valence CASSCF calculations. The predictions from the C_0^2 coefficient for these small molecules can be used to calibrate the T_1, D_1, and %TAE diagnostics.

3.1.1. Hydrides. The T_1, D_1, C_0^2, and %TAE diagnostics are presented for hydride systems in Table 1. The values of C_0^2 (greater than 0.9) for all hydrides except RuH (0.483) suggest that these hydrides do not have significant MR character. The

Table 1. Diagnostics for Metal Hydrides Calculated by CCSD, CCSD(T), or CASSCF with the cc-pVTZ-DK Basis Set

molecule	T_1	D_1	C_0	C_0^2	%TAE
YH	0.018	0.032	0.950	0.903	−0.2
ZrH	0.042	0.079	0.991	0.983	−1.2
NbH	0.048	0.095	0.990	0.980	−0.3
MoH	0.028	0.061	0.997	0.994	−5.0
TcH	0.032	0.083	0.998	0.995	−2.5
RuH	0.037	0.100	0.695	0.483	4.0
RhH	0.020	0.046	0.983	0.967	−7.6
PdH	0.025	0.057	0.987	0.974	−2.1

corresponding T_1 and D_1 values of ZrH, MoH, TcH, RuH, and PdH are less than 0.045 and 0.120, respectively. The values of %TAE for all of the hydrides are less than 10%. The %TAE is positive only for RuH. The negative values of %TAE for all other hydrides imply that the binding energies of these hydrides may be overestimated by the CCSD method.

3.1.2. Chalcogenides. The T_1, D_1, C_0^2, and %TAE diagnostics are presented for chalcogenides in Table 2. All

Table 2. Diagnostics for Metal Chalcogenides Calculated by CCSD, CCSD(T), or CASSCF with the cc-pVTZ-DK Basis Set

molecule	T_1	D_1	C_0	C_0^2	%TAE
YO	0.035	0.079	0.967	0.936	5.4
YS	0.035	0.068	0.964	0.928	5.2
YSe	0.039	0.076	0.964	0.929	5.6
ZrO	0.034	0.060	0.964	0.929	6.5
ZrS	0.039	0.068	0.965	0.930	7.4
ZrSe	0.044	0.079	0.977	0.954	8.4
NbO	0.035	0.065	0.962	0.926	0.3
NbS	0.039	0.069	0.972	0.945	0.2
NbSe	0.043	0.075	0.972	0.944	0.1
MoO	0.040	0.068	0.955	0.912	9.8
TcO	0.039	0.073	0.960	0.922	17.7
TcS	0.044	0.110	0.967	0.935	9.2
TcSe	0.054	0.131	0.968	0.938	−7.9
RuO	0.056	0.144	0.948	0.898	26.0
RuS	0.064	0.160	0.946	0.896	17.2
RhO	0.072	0.182	0.679	0.461	17.3
PdO	0.026	0.054	0.983	0.967	−2.2
PdS	0.018	0.047	0.979	0.959	−10.3
ZrO$_2$	0.035	0.079	0.941	0.886	6.0
NbO$_2$	0.039	0.083	0.926	0.858	1.1
MoO$_2$	0.045	0.121	0.923	0.852	10.6

values for C_0^2 are greater than 0.9 for the monochalcogenides of all early TMs (Y, Zr, Nb, and Mo), which indicates that nondynamic correlation may not play an important role for these early TM molecules. The values of T_1, D_1, and %TAE for these early transition metal monochalcogenides species are less than 0.045, 0.120, and 10%, respectively. For late monochalcogenides, values of C_0^2 are less than 0.9 for RuO, RuS, and RhO, which suggests that these three molecules have significant nondynamic correlation. These three molecules also have large values of T_1, D_1, and %TAE (greater than 0.045, 0.120, and 10%, respectively). Other late monochalcogenides (Tc and Pd species), predicted to be dominated by dynamic correlation based on C_0^2 diagnostics (C_0^2 greater than 0.9), have T_1 less than 0.045, D_1 less than 0.120, and %TAE less than 10%, with the exception of TcO (%TAE = 17.7%) and TcSe (T_1 = 0.056 and D_1 = 0.131). For the three dioxides (ZrO$_2$, NbO$_2$, and MoO$_2$), the values of C_0^2 were less than 0.9, which suggests possible nondynamic correlation. The corresponding T_1, D_1, and %TAE of MoO$_2$ are greater than 0.045, 0.120, and 10%, respectively.

3.1.3. Halides. The T_1, D_1, C_0^2, and %TAE diagnostics are presented for halides in Table 3. The C_0^2 values were calculated only for mono- and dihalides because of the large full-valence CASSCF active space requirements for larger molecules. The values of C_0^2 are greater than 0.9 for all monohalides, which implies that dynamic correlation is the dominant effect in the monohalides. The T_1 diagnostics for all of the monohalides are

Table 3. Diagnostics for Metal Halides Calculated by CCSD, CCSD(T), or CASSCF in Combination with the cc-pVTZ-DK Basis Set

molecule	T_1	D_1	C_0	C_0^2	%TAE	molecule	T_1	D_1	C_0	C_0^2	%TAE
YF	0.020	0.035	0.983	0.966	2.2	$RuCl_2$	0.044	0.115	0.991	0.983	3.2
ZrF	0.022	0.038	0.985	0.971	14.0	$RuBr_2$	0.041	0.100	0.991	0.983	0.0
ZrCl	0.022	0.054	0.985	0.970	5.1	RhF_2	0.035	0.104	0.990	0.981	4.8
ZrBr	0.024	0.059	0.985	0.971	4.0	$RhCl_2$	0.037	0.109	0.990	0.980	13.9
NbF	0.027	0.058	0.992	0.984	−0.1	$RhBr_2$	0.022	0.070	0.990	0.979	12.1
NbCl	0.031	0.088	0.992	0.983	−0.2	PdF_2	0.023	0.056	0.996	0.991	7.3
NbBr	0.035	0.102	0.992	0.984	−0.2	$PdCl_2$	0.015	0.062	0.995	0.990	16.6
MoF	0.022	0.035	0.999	0.999	6.5	$PdBr_2$	0.029	0.107	0.970	0.942	13.9
MoCl	0.020	0.035	0.996	0.991	7.3	YF_3	0.035	0.059			1.8
MoBr	0.022	0.039	0.997	0.995	9.0	YCl_3	0.010	0.022			1.6
TcF	0.025	0.044	0.998	0.995	1.8	YBr_3	0.012	0.026			1.8
TcCl	0.024	0.046	0.998	0.995	1.2	ZrF_3	0.021	0.047			2.2
TcBr	0.027	0.051	0.998	0.995	1.1	$ZrCl_3$	0.017	0.040			2.2
RuF	0.031	0.060	0.999	0.997	3.0	$ZrBr_3$	0.020	0.045			2.5
RuCl	0.035	0.071	0.999	0.997	2.9	$NbCl_3$	0.022	0.056			0.3
RuBr	0.040	0.084	0.999	0.997	3.2	$NbBr_3$	0.026	0.067			0.4
RhCl	0.038	0.140	0.997	0.995	8.9	$MoCl_3$	0.025	0.068			4.9
PdF	0.021	0.044	0.996	0.992	7.4	TcF_3	0.034	0.123			5.3
PdCl	0.017	0.047	0.996	0.992	7.9	RuF_3	0.033	0.084			4.0
PdBr	0.018	0.048	0.996	0.992	9.9	$RuCl_3$	0.028	0.078			5.1
YF_2	0.018	0.041	0.988	0.976	1.9	$RuBr_3$	0.049	0.143			5.6
ZrF_2	0.022	0.046	0.981	0.962	2.1	$RhCl_3$	0.024	0.093			7.7
$ZrCl_2$	0.017	0.036	0.990	0.980	6.0	ZrF_4	0.019	0.052			2.3
$ZrBr_2$	0.018	0.038	0.989	0.979	23.5	$ZrCl_2Br_2$	0.017	0.048			2.9
$NbCl_2$	0.035	0.101	0.989	0.978	1.0	$ZrClBr_3$	0.018	0.050			3.0
$NbBr_2$	0.046	0.136	0.989	0.978	1.5	$ZrCl_3Br$	0.016	0.046			2.8
MoF_2	0.024	0.079	0.986	0.972	3.8	$NbBr_4$	0.025	0.078			0.7
$MoCl_2$	0.026	0.084	0.987	0.975	4.6	$NbCl_4$	0.021	0.066			0.6
$MoBr_2$	0.029	0.103	0.990	0.980	4.5	$MoCl_4$	0.028	0.094			6.8
TcF_2	0.023	0.054	0.966	0.934	2.6	MoF_4	0.026	0.083			4.7
$TcCl_2$	0.023	0.058	0.982	0.964	2.3	$MoBr_4$	0.032	0.111			8.2
$TcBr_2$	0.026	0.067	0.982	0.965	2.4	TcF_4	0.037	0.148			11.2
RuF_2	0.028	0.070	0.992	0.984	−4.6						

Table 4. Diagnostics for Metal Dimers Calculated by CCSD, CCSD(T), or CASSCF in Combination with the cc-PVTZ-DK Basis Set

molecule	T_1	D_1	C_0	C_0^2	TAE CCSD	TAE CCSD(T)	exptl. D_0[a]	%TAE
Y_2	0.098	0.202	0.883	0.780	14.824	20.669	37.36	28.3
Zr_2	0.047	0.095	0.831	0.690	−2.221	11.666	70.38	119.0
Nb_2	0.150	0.438	0.520	0.271	4.289	4.661	126.37	8.0
Mo_2	0.043	0.106	0.810	0.656	−0.598	−0.133	98.93	−349.6
Tc_2	0.043	0.135	0.860	0.739	−43.173	−30.568		−41.2
Ru_2	0.156	0.586	0.856	0.733	0.418	12.807	73.56	96.7
Rh_2	0.109	0.406	0.741	0.549	−30.505	−42.325	67.34	27.9
Pd_2	0.034	0.097	0.790	0.624	−22.018	−40.857	23.75	46.1

[a]Experimental data from refs 71−77.

less than 0.045. All of the monohalides have D_1 less than 0.120, except for RhCl (D_1 = 0.140). The amplitude of %TAE diagnostics is less than 10% for all monohalides except ZrF (14.0%). Values of the D_1 diagnostic increase from fluorine to bromine for all of the metal monohalides. Additionally, the values of the T_1 diagnostic increase from fluorine to bromine for the TM species considered, with the exception of Mo and Pd species. Overall, the nondynamic correlation is increasingly important for heavier halides. The same trends for the T_1 and D_1 diagnostics have been found for the 3d TM monohalides in

previous work.[25] The values of %TAE decrease from fluorine to bromine for Zr, Mo, and Tc species.

For the dihalides, the C_0^2 values are consistently greater than 0.90, which implies SR character for these dihalides. All of the considered dihalides have T_1 less than 0.045 and D_1 less than 0.120, except $NbBr_2$ (T_1 = 0.046, D_1 = 0.136). Most of the SR dihalides have %TAE less than 10%, except for $ZrBr_2$, $RhCl_2$, $RhBr_2$, $PdCl_2$, and $PdBr_2$, despite the presence of relatively small T_1 (less than 0.045) and D_1 (less than 0.120). Similar to the trends found for monohalides, from fluorine to bromine,
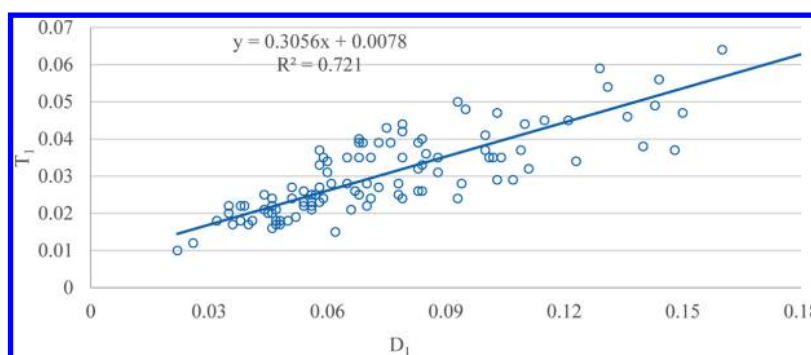
Figure 1. Scatter plot of T_1 and D_1 diagnostics for 110 4d TM-containing molecules without TM dimers.

the values of the T_1 and D_1 diagnostics increase for Nb, Mo, Tc, and Pd dihalides, but they decrease for Zr and Ru dihalides.

As mentioned earlier, the C_0^2 was not determined for most trihalides and tetrahalides due to the impracticality of the large full-valence CASSCF calculations. For trihalides of the early TMs, the T_1 diagnostic values are between 0.010 and 0.034, the D_1 diagnostic values are between 0.022 and 0.068, and the %TAE values are between 0.3% and 4.9% for Y, Zr, Nb, and Mo. The values of all considered diagnostics increase from the late TM trihalides to the early TM trihalides, which suggests that nondynamic correlation effects have increasing prominence. Although RuCl$_3$ and RhCl$_3$ have T_1 values less than 0.045, these two molecules have very large %TAE values (18.9% and 28.9%, respectively), which implies that the triples correction to the CCSD results is considerable; thus, CCSD is not recommended for calculating their bonding energies. The tetrahalides of Zr and Nb have T_1 less than 0.045, D_1 less than 0.120, and %TAE less than 10%, which suggests that a single-reference treatment may be suitable. The Mo tetrahalides have T_1, D_1, and %TAE less than 0.045, 0.120, and 10%, respectively. The D_1 diagnostic of 0.148 and the (T) contribution to TAE are relatively large (%TAE = 11.2%) for TcF$_4$ despite the relatively small T_1 diagnostic of 0.037.

3.1.4. Metal Dimers. The T_1, D_1, C_0^2, and %TAE diagnostics are presented for TM dimers in Table 4. The values of C_0^2 (less than 0.8) imply that all TM dimers are dominated by significant nondynamic correlation effects. All of the dimers have the T_1 diagnostics greater than or near 0.045 (except for Pd$_2$) and D_1 diagnostics much greater than 0.120 (except for Zr$_2$, Mo$_2$, and Pd$_2$). The values of %TAE for the 4d TM dimers are much greater than 10% (except Nb$_2$), indicating that CCSD is not reliable for calculating bonding energies of the 4d TM dimers. After further investigation of TAE values, a large difference was found between the D_e (=TAE for diatomic molecules) of CCSD(T) calculations and the D_0 of the experimental data of 4d TM dimers. Also, the negative values of CCSD(T) TAEs indicate that Tc$_2$, Ru$_2$, Rh$_2$, and Pd$_2$ are dissociative, whereas the positive experimental D_0 data show that extra energies are needed to dissociate all of the 4d TM dimers. Therefore, coupled cluster calculations should not be applied to obtain qualitatively correct bonding energies for 4d TM dimers.

3.2. Discussion. T_1, D_1, and %TAE diagnostics based on coupled cluster calculations are more accessible for large molecules than C_0^2 based on large full-valence CASSCF calculations. Each diagnostic (T_1, D_1, and %TAE) has been compared to predictions made using the C_0^2 coefficient alone, since the square of the leading coefficient, C_0^2 in the large full-valence CASSCF wave function, directly shows the extent to which the configuration state functions (CSFs) correlate within

the CAS. If a strong linear correlation exists between each diagnostic (T_1, D_1, and %TAE) and the C_0^2 coefficient, then each diagnostic alone has the ability to indicate likely MR character. The C_0^2 values have been determined for 83 4d TM-containing molecules composed of three or fewer atoms. In considering these species, the small squared correlation coefficient values (R^2 less than 0.3) in the relationships T_1 vs C_0^2, D_1 vs C_0^2, and %TAE vs C_0^2 (Figures S1–S3, Supporting Information) suggest that there is very little correlation between each diagnostic and the C_0^2 coefficient. The correlation between T_1 and D_1 diagnostics for 110 4d TM-containing molecules without TM dimers shows a moderate linear correlation with an R^2 value of 0.721 (Figure 1).

The average values of the T_1, D_1, and %TAE diagnostics (Table 5) are 0.030, 0.076, and 4.9%, respectively, for the 110

Table 5. Average Diagnostic Values for Different Molecule Classifications

classification	T_1	D_1	%TAE
Hydrides (8)	0.031	0.069	−1.9
Chalcogenides (21)	0.042	0.090	6.4
Monohalides (20)	0.026	0.059	4.7
Dihalides (20)	0.028	0.079	5.9
Trihalides (14)	0.025	0.068	3.2
Tetrahalides (10)	0.024	0.078	4.3
TM-Dimers (8)	0.085	0.259	−8.1
Other small coordination complexes (17)	0.036	0.086	11.5
Overall (118)	0.037	0.098	3.25
Overall without TM-Dimers (110)	0.030	0.076	4.9

4d TM-containing molecules (TM dimers are not included), whereas the 3d set has larger average values of 0.044, 0.127, and 7.5%, respectively.[25] As shown in Section 3.1, despite the wide range of metal–ligand bonding in the systems analyzed, similar cutoffs for SR calculations are found for T_1, D_1, and %TAE based on calibration from C_0^2. Most molecules, which are suggested to be dominated by dynamic correlation with $C_0^2 \geq$ 0.9, have $T_1 < 0.045$, $D_1 < 0.120$, and %TAE < 10%. By considering the consistency of the predictions from the considered diagnostics (T_1, D_1, and %TAE) with predictions from C_0^2 for 83 4d TM-containing molecules as well as the average values of the considered diagnostics for 110 4d TM-containing molecules, $T_1 < 0.045$, $D_1 < 0.120$, and %TAE < 10% are suggested as the diagnostic criteria for reliable calculations by SR methods for 4d TM-containing molecules.

Utilization of only one diagnostic cannot identify pathological systems sufficiently.[66−68] Additionally, the combined use of various diagnostics can provide a more reliable prediction of

MR character.[38,69,70] As shown in Figure 2, 13 molecules have $T_1 \geq 0.045$, 13 molecules have $D_1 \geq 0.120$, and 20 molecules
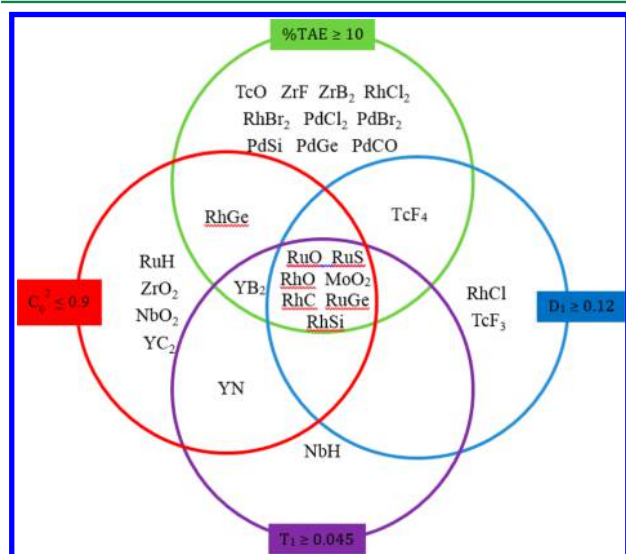

Figure 2. TM-containing molecules that may be dominated by nondynamic correlation effects (TM dimers are not included, and C_0^2 is considered only for molecules with three or fewer atoms), as gauged by noted diagnostic criteria.

have %TAE $\geq$ 10%. Twenty-five molecules (Figure 3) in total $(T_1 \geq 0.045 \cup D_1 \geq 0.120 \cup \%\text{TAE} \geq 10\%)$ potentially have nondynamic correlation based on the union of the diagnostic criteria. Using the union of the diagnostic criteria sets provides inconsistent prediction with C_0^2: only 10 of the 25 molecules have $C_0^2 < 0.90$ (YB$_2$, YN, MoO$_2$, RuO, RuS, RuGe, RhC, RhO, RhSi, and RhGe), and the remaining 15 have primarily dynamic correlation. Instead, with the intersection of all three criteria, 7 molecules (RuO, RuS, RhO, MoO$_2$, RhC, RuGe, and RhSi) were found with $T_1 \geq 0.045 \cap D_1 \geq 0.120 \cap \%\text{TAE} \geq 10\%$ (Figure 3). All 7 molecules also have $C_0^2 < 0.90$. 58 molecules were found that have $T_1 < 0.045 \cap D_1 < 0.120 \cap \%\text{TAE} < 10\%$. Of the 58 molecules that are not predicted to have significant nondynamic correlation by the diagnostic criteria, four

molecules (ZrO$_2$ ($C_0^2 = 0.886$), YC$_2$ ($C_0^2 = 0.885$), NbO$_2$ ($C_0^2 = 0.858$), and RuH ($C_0^2 = 0.483$)) have $C_0^2 < 0.9$. Therefore, while the union of all three diagnostic criteria sets can suggest that multireference methods may be necessary for a particular system, the combined intersection of the three diagnostic criteria sets can identify that a particular system most likely requires multireference methods.

With T_1, D_1, and %TAE criteria established based on C_0^2 values, the criteria are applied to 27 molecules for which C_0^2 has not been calculated (Figure 3). The criteria predict that RuBr$_3$ requires multireference methods. TcF$_3$ and TcF$_4$ are near the threshold criteria and may require multireference methods.

Additional metrics are recommended when the full-valence CASSCF calculation is prohibitive and the considered diagnostics cannot provide consistent predictions of MR character for molecular systems. For instance, RuCl$_3$ and RhCl$_3$ were predicted to be dominated by dynamic correlation effects by T_1 (less than 0.045) and D_1 (less than 0.120), but they were predicted to have severe nondynamic correlation effects by %TAE (greater than 10%), as shown in Figure 3. In this case, the spin contamination ($\langle S^2 - S_z^2 - S_z \rangle$) can be used to consider the reliability of the diagnostics.[25] Since strong nondynamic correlation effects may lead to a mixture of strongly correlated high-spin states with the ground states, significant spin contamination, which has been eliminated by the ROHF reference wave function, may reappear with UCCSD calculations. The value of spin contamination for each of the molecules is less than 0.1 (RuCl$_3$ = 0.007; RhCl$_3$ = 0.008), a factor that is used to gauge nondynamical correlation effects;[25] thus, nondynamical correlation may not be critical for these molecules.

4. CONCLUSIONS

In this study, four widely used diagnostics (T_1, D_1, C_0^2, and %TAE) were examined to consider their utility in indicating the nondynamic correlation of 4d TM-containing molecules with representative bonding types (hydrides, chalcogenides, halides, metal dimers, and several other TM species).

The historical criteria $T_1 \leq 0.02$ and $D_1 \leq 0.05$ for main group species are not practical for 4d TM-containing species. Thus, instead, new T_1, D_1, and %TAE diagnostic criteria are
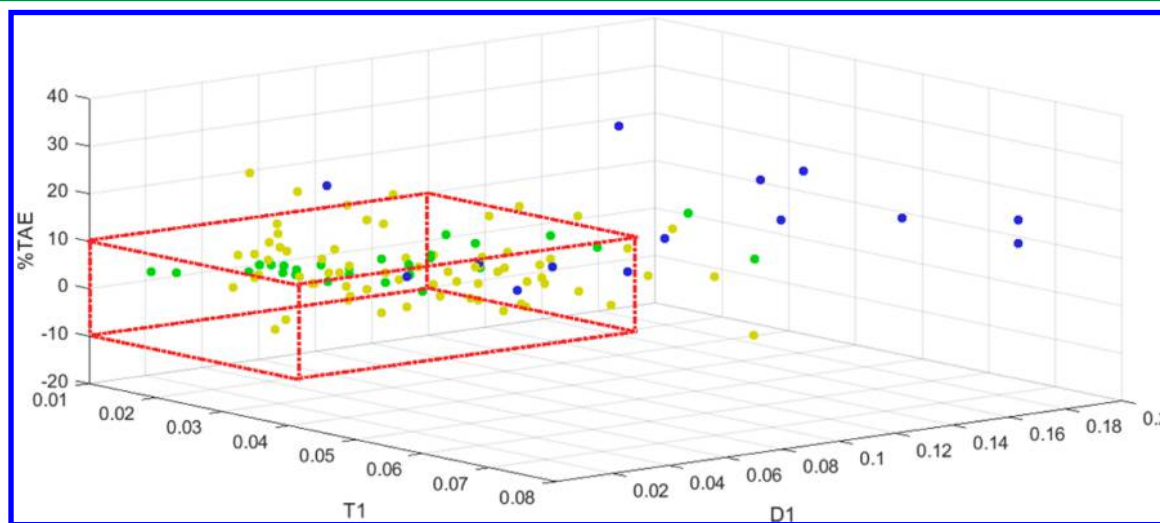

Figure 3. 3D scatter plot of T_1, D_1, and %TAE diagnostics for 110 4d TM-containing molecules without TM dimers. Points that are yellow have $C_0^2 \geq 0.90$; blue points have $C_0^2 < 0.90$. Green points are for predicted data with no C_0^2 value calculated. The red box indicates the SR criteria selected.

suggested for 4d TM-containing species. While the recent criteria of $T_1 \leq 0.05$, $D_1 \leq 0.15$, and %TAE $\leq 10\%$ for 3d TM-containing species can be utilized for most 4d TM-containing species, the criteria $T_1 < 0.045$, $D_1 < 0.120$, and %TAE < 10 are proposed as a more fine-tuned set of criteria to aid in identifying the significance of nondynamic correlation for 4d TM-containing species.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00861.

> Scatter plots of diagnostics for 83 4d TM-containing molecules and diagnostics for the metal dimers and other metal species calculated by CCSD, CCSD(T), or CASSCF in combination with the cc-pVTZ-DK basis set (PDF)

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Notes

The authors declare no competing financial interest.

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