

# A Diagnostic for Determining the Quality of Single-Reference Electron Correlation Methods

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## Abstract

It was recently proposed that the Euclidian norm of the  $t_1$  vector of the coupled cluster wave function (normalized by the number of electrons included in the correlation procedure) could be used to determine whether a single-reference-based electron correlation procedure is appropriate. This diagnostic,  $\mathcal{T}_1$ , is defined for use with self-consistent-field molecular orbitals and is invariant to the same orbital rotations as the coupled cluster energy.  $\mathcal{T}_1$  is investigated for several different chemical systems which exhibit a range of multireference behavior, and is shown to be an excellent measure of the importance of non-dynamical electron correlation and is far superior to  $C_0$  from a singles and doubles configuration interaction wave function. It is further suggested that when the aim is to recover a large fraction of the dynamical electron correlation energy, a large  $\mathcal{T}_1$  (i.e.,  $> 0.02$ ) probably indicates the need for a multireference electron correlation procedure.

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## Introduction

It was recently proposed<sup>1</sup> that the Euclidian norm of the vector of  $t_1$  amplitudes in the closed-shell coupled cluster singles and doubles wave function could be used as a diagnostic for the *a priori* prediction of the reliability of results obtained from a single-reference-based electron correlation procedure. The  $t_1$  amplitudes in coupled cluster theory are closely related to the coefficients of singly excited configurations in configuration interaction theory. It is well documented<sup>2</sup> that the singly excited configurations in an electron correlation procedure allow molecular orbital relaxation to occur. For many years quantum chemists have used  $C_0$ , the reference configuration coefficient in a configuration interaction wave function, as a diagnostic. As is widely recognized, however, if  $C_0$  is taken from a self-consistent-field (SCF) singles and doubles configuration interaction (CISD) wave function, then it is of limited utility since the molecular orbitals are strongly biased towards the SCF reference function. Thus it is not uncommon for a known multireference system to yield an SCF-CISD  $C_0$  which is 0.95 or larger (i.e., the SCF determinant comprises 90% of the wave function). A reliable diagnostic which is more sensitive to the importance of non-dynamical electron correlation would therefore be of great utility.

Laidig, Purvis and Bartlett<sup>3,4</sup> have investigated the use of localized molecular orbitals in coupled cluster methods, specifically the doubles and the singles and doubles coupled cluster methods (CCD and CCSD, respectively). We note that the particular localization technique investigated by Laidig *et al.* does not leave the SCF energy unaffected<sup>3,4</sup>. They found that the use of localized molecular orbitals greatly improved the CCD results, but that the CCSD energies were little affected by the different reference molecular orbitals. The inclusion of  $e^{T_1}$  in the CCSD wave function thus accounts for the important orbital relaxation effects which were incorporated by localizing the molecular orbitals. In addition, Scuseria and Schaefer<sup>5</sup> have investigated the use of Brueckner-like molecular orbitals in CCSD and CCD calculations and arrive at essentially the same conclusions.

The purpose of the present study is to further investigate the use of the Euclidian norm of  $t_1$  as a diagnostic; applying this test to chemical systems exhibiting a range of bonding situations and known multireference and strongly single-reference

dominated problems. In this way the actual value and utility of the Euclidian norm of  $t_1$  as a diagnostic tool will become evident. To begin, it must be emphasized that the diagnostic reported here

$$\mathcal{T}_1 = \frac{\|t_1\|}{N_{elec}^{1/2}} \quad (1)$$

was always determined using SCF molecular orbitals. As the results of references 3 through 5 clearly demonstrate, it is possible to obtain a similar CCSD energy with different molecular orbitals which will give a different  $t_1$  vector and a different Euclidian norm. In fact, the Euclidian norm of  $t_1$  for the ‘optimized orbitals’ of reference 5 should be very close to zero. Thus, in order to compare  $\mathcal{T}_1$  from different chemical systems, the diagnostic must be uniquely defined for each system. The most straightforward approach is to require that restricted Hartree-Fock SCF molecular orbitals are used to determine the CCSD wave function and diagnostic for each system, and this is therefore the approach which has been adopted in the present study. In addition, we point out that since the CCSD energy is invariant to unitary transformations of occupied-occupied or virtual-virtual molecular orbitals the  $\mathcal{T}_1$  diagnostic will also be invariant to these types of orbital rotations.

The next section contains a brief summary of the theoretical methods used together with a description of the method we have devised to judge the  $\mathcal{T}_1$  diagnostic. The results, including a discussion, are presented in the third section. Our conclusions are presented in the final section.

## Methods

All of the chemical systems included in this study have been investigated previously<sup>1,6,7</sup> and these reports include a detailed description of the basis sets and geometries. We therefore include only a brief description of the basis sets. Table 1 contains the size of the primitive basis, our designation and the reference from which the orbital exponents and contraction coefficients may be obtained. In forming the designation for each basis two rules have been followed. Firstly, a generally contracted atomic natural orbital (ANO) basis set is denoted by square brackets, e.g., [4321], where the numbers enumerate the number of contracted  $s$ ,  $p$ ,  $d$  and  $f$  functions, respectively. Secondly, a basis set which utilizes a segmented

contraction scheme is designated as 7s3p2d1f, for example. In most cases where a segmented contraction is used, the contraction has been performed over the core atomic orbitals, allowing maximum flexibility in the valence region. For those cases where the polarization function orbital exponents are not given in the reference the exponents are listed in Table 1. In addition, where more than one level of polarization function has been included (e.g., 7s3p2d1f Be) the levels are separated by a semicolon.

Bond lengths are given in atomic units,  $a_0$ . The unique bond length is specified for the  $\text{Be}_3$ ,  $\text{Mg}_3$ ,  $\text{Be}_4$  and  $\text{Mg}_4$  clusters. The trimers form an equilateral triangle and the tetramers adopt a tetrahedral structure. The pentamer,  $\text{Be}_5$ , is defined by two bond lengths since it conforms to a trigonal bipyramidal geometry. For this system, the first bond length refers to a side of the triangular base while the second refers to the distance from an apex atom to one contained in the base. The bond lengths and bond angles for FOOF,  $(\text{NO})_2$  and FNNF are the TZ2P MP2 structures reported in reference 1.

Since the definition of  $\mathcal{T}_1$  depends upon the number of electrons correlated it is clearly important to consider which electrons should be included in this definition. It is expected that only the valence electrons should be important for non-dynamical electron correlation effects and therefore we have chosen to freeze the core-like molecular orbitals in all procedures. It is possible that even if the core electrons are included in the correlation procedure, then the definition of  $\mathcal{T}_1$  should include only the number of valence electrons (see note added in proof in reference 1). However, as several studies have demonstrated<sup>2,8,9</sup> the basis set requirements for the adequate treatment of core-valence and core-core correlation effects are quite severe. Therefore, for our initial investigations of  $\mathcal{T}_1$  only the valence electrons are considered. Additionally, for basis sets which utilize segmented contractions the virtual molecular orbitals which are the core-counterparts were deleted from the correlation procedure. The CCSD wave functions were determined with a vectorized closed-shell CCSD method<sup>10</sup> and the CI wave functions were evaluated with either the Berkeley shape-driven graphical unitary group CI program<sup>11</sup> or the MOLECULE-SWEDEN codes<sup>12,13</sup>.

## Results and Discussion

The  $\mathcal{T}_1$  diagnostic together with  $C_0$  from CISD and full CI wave functions are presented for several systems in Table 2. Note that only two electrons are correlated for the first five systems. Comparing  $\mathcal{T}_1$  with  $C_0$  for these systems it is clear that there is a good correspondence between  $\mathcal{T}_1$  and the total weight of the reference in the full CI wave function. Thus for He and  $H_2$ , where  $C_0$  is greater than 0.99, the  $\mathcal{T}_1$  diagnostic is 0.0029 and 0.0050, respectively, whereas for the other three systems (Be, Mg and  $Li_2$ )  $\mathcal{T}_1$  is greater than 0.015 and  $C_0$  is less than 0.965. Be and Mg are known to exhibit multireference behaviour due to the  $s - p$  near degeneracy.  $Li_2$  possesses a  $\sigma - \sigma^*$  near degeneracy in addition to the  $s - p$  near degeneracy.

Since the remaining molecules in Table 2 ( $He_2$ ,  $Be_2$ ,  $Mg_2$  and HF) all contain more than two valence electrons it is possible to compare  $\mathcal{T}_1$ , the  $C_0$  from CISD, and the  $C_0$  from full CI. As expected,  $He_2$  is strongly dominated by a single reference function and so there is not a significant difference between the CISD and full CI  $C_0$ . Consistently,  $\mathcal{T}_1$  is again very small and is actually the same (to the precision reported) as for the single He atom. However, for the  $Be_2$ ,  $Mg_2$  and HF diatomics there is a significant difference between the full CI and CISD  $C_0$ . In fact, for  $Be_2$  the difference amounts to 4.5% of the full CI wave function. An important point which should be emphasized is that due to the lack of size-extensivity the discrepancy between the full CI and CISD  $C_0$  is expected to become larger as the number of electrons correlated increases.  $\mathcal{T}_1$  is greater than 0.013 for  $Be_2$ ,  $Mg_2$  and HF demonstrating that a large degree of orbital relaxation occurs. Thus, the results of Table 2 demonstrate two important points: 1) there is a good correspondence between  $\mathcal{T}_1$  and the full CI  $C_0$  when a modest number of electrons are correlated and 2) for chemical systems with more than two electrons there may be a large difference between the CISD and full CI  $C_0$ .

$\mathcal{T}_1$  and the CISD  $C_0$  for several different chemical systems with a large number of valence electrons are collected in Table 3. The  $\mathcal{T}_1$  diagnostic and the  $C_0$  for the Be and Mg clusters (at their equilibrium structures) indicates that these systems are probably not well described by a single-reference method and that a large degree of orbital relaxation is taking place. Binding energies and equilibrium bond lengths for the clusters, for example, would be expected to be substantially in error when

a single-reference-based treatment is used, and it is doubtful that binding energy predictions would be reliable to within even 10 kcal/mol. However, the large  $C_0$  for these systems might tempt many observers to believe that a single-reference-based electron correlation procedure is adequate. Conversely, the  $\mathcal{T}_1$  value is larger than 0.02 for each cluster with the exception of  $\text{Mg}_3$ . The comparisons made in Table 2 together with multireference CI (MRCI) results<sup>6</sup> suggest that multireference techniques are required for Be and Mg clusters, and thus that a  $\mathcal{T}_1$  value larger than 0.02 is a clear indication that other important configurations exist and may be needed as references in a treatment of dynamical electron correlation. The infinite separation results for the Be and Mg clusters also demonstrate the inadequacy of using  $C_0$  from a CISD wave function since the  $C_0$  suggests that as the number of atoms increases the ‘super-molecule’ is more difficult to describe whereas the size-extensive CCSD method correctly shows that these systems are all equivalently described (in fact, since only valence electrons are correlated the CCSD results correspond to a full CI).

The FOOF,  $(\text{NO})_2$  and FNNF molecules are included in Table 3 since these were the systems investigated in the study<sup>1</sup> which first suggested the use of  $\mathcal{T}_1$ . These systems are very difficult to describe — the geometry of FOOF is not even qualitatively correct at the CISD level, for example. The  $C_0$  values for FOOF and  $(\text{NO})_2$  are very similar although  $\mathcal{T}_1$  indicates that non-dynamical electron correlation is much more important for FOOF. The results of several single-reference methods for these two systems<sup>1</sup> provide additional evidence that the electron correlation of FOOF is indeed even more difficult to describe than that for  $(\text{NO})_2$ . The  $C_0$  for the isomers of FNNF suggests that these systems are more strongly dominated by a single reference than either FOOF or  $(\text{NO})_2$  and that they are all nearly equally well described by a single-reference-based method. However, while the  $\mathcal{T}_1$  diagnostic does suggest that non-dynamical electron correlation is less important in the cis and trans isomers, it also indicates that the transition state is strongly affected by non-dynamical electron correlation and thus, single-reference-based methods will not work as well for TS-FNNF as they do for cis and trans FNNF. Again, the latter conclusions are consistent with the results of reference 1.

The last four molecules of Table 3 are all known to be strongly dominated

by a single determinant reference function and both  $C_0$  and  $\mathcal{T}_1$  are consistent with this observation. However, the fine details of relating  $C_0$  and  $\mathcal{T}_1$  exhibit small inconsistencies. For example, for the first-row closed-shell hydrides it is generally accepted that the reliability of a single-reference-based electron correlation method decreases in the order  $\text{CH}_4 > \text{H}_2\text{O} > \text{HF}$ . The  $\mathcal{T}_1$  diagnostic is consistent with this empirical observation whereas the  $C_0$  from a CISD wave function exhibits exactly the opposite trend.

Perhaps the molecule which best exhibits the superiority of  $\mathcal{T}_1$  over  $C_0$  as a diagnostic is the CuH diatomic. It has been shown<sup>14</sup> that the bonding of CuH is complicated because of the importance of both the  $d^9s^2$  and  $d^{10}s^1$  atomic occupations of Cu. Thus there are several important configurations which differ from the closed shell single determinant reference by a single excitation. The  $C_0$  for this diatomic is 0.96, which is very similar to that obtained for  $\text{CH}_4$ . However, the  $\mathcal{T}_1$  value, 0.046, is the largest found in this study. Thus, the important non-dynamical electron correlation effects present in the bonding of CuH are completely missed by the single-reference CISD method whereas the  $\mathcal{T}_1$  diagnostic correctly indicates the importance of these effects.

Table 4 contains  $\mathcal{T}_1$  and  $C_0$  (from CISD) for  $\text{Be}_3$  and  $\text{H}_2\text{O}$  using several basis sets in order to determine the one-particle basis set effect. In order for this diagnostic to be generally useful it should exhibit a certain degree of invariance with respect to the choice of a one-particle basis set. This statement assumes, of course, that the smallest basis sets at least contain proper correlating functions. On the other hand, it is well known that the one-particle and n-particle basis sets are inherently coupled though this coupling is usually small. As the one-particle basis set limit is approached, it may be expected that  $\mathcal{T}_1$  will stabilize. This is expected despite the fact that the n-particle basis increases substantially with one-particle basis set augmentations.

The results of Table 4 confirm the above discussion and demonstrate that  $\mathcal{T}_1$  converges to a value near 0.0340 for  $\text{Be}_3$  and near 0.0075 for  $\text{H}_2\text{O}$ . The fact that  $\mathcal{T}_1$  decreases with improvements in the one-particle basis set provides further support for the above discussion. In other words, a larger degree of orbital relaxation is required for the smaller one-particle basis sets (giving a larger  $\mathcal{T}_1$ ) in order to

compensate for the lack of flexibility. Thus the value to which  $\mathcal{T}_1$  converges should give an indication of the inherent importance of non-dynamical electron correlation for the chemical system under investigation. Moreover, the rate of convergence with respect to basis set improvement should give a measure of the interaction between the one- and n-particle basis sets.

## Conclusions

The  $\mathcal{T}_1$  diagnostic has been shown to be a reliable measure of the importance of non-dynamical electron correlation and to be far superior to the use of  $C_0$  from a CISD wave function as an indicator as to whether it is appropriate to use a single-reference-based electron correlation procedure. No doubt a similar type of diagnostic could be defined for the CISD wave function by separating the  $C_1$  coefficients (coefficients from the singly excited configurations). However, there are two problems with this procedure. Because CISD is, in general, not size extensive then the diagnostic would not have the desired property of giving the same result for two non-interacting He atoms as it would for a single He atom. Also, the results for CuH presented in this study clearly indicate that the CISD procedure is incapable of overcoming the bias of using SCF molecular orbitals and thus any diagnostic similar to  $\mathcal{T}_1$  but based on an SCF-CISD wave function would almost certainly suffer from this bias.

Several studies<sup>14,22</sup> have pointed out that the coupled pair functional<sup>23</sup> (CPF), modified CPF<sup>24</sup> (MCPF) and averaged CPF<sup>25</sup> (ACPF) methods are very good at identifying specific configurations which are important and hence should be used as references in a multireference electron correlation procedure. A diagnostic similar to  $\mathcal{T}_1$  could also be constructed for these methods and it is likely that it would give similar results to  $\mathcal{T}_1$  for those situations where the CCSD and the various CPF-type methods gave similar results. Clearly for the situation where the methods give very different results (such as FOOF<sup>1</sup>) the diagnostics would be expected to yield different results also. In addition these observations also indicate that specific important configurations may be identified by analysis of the CCSD  $t_1$  and  $t_2$  amplitudes.

Finally, the results of this study indicate that if  $\mathcal{T}_1$  is greater than 0.02 then



single-reference-based electron correlation methods are probably unreliable and will certainly not yield highly accurate results.

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Table 1

Basis set designations and definitions used in this study.

Atom	Primitive Basis	Designation	Reference	Polarization Exponents
H	4s	DZP	15,16	0.75
H	8s2p	6s2p	17	1.0,0.33
H	8s6p	[32]	18	-
H	8s6p4d	[321]	18	-
H	8s6p4d	[432]	18	-
He	8s2p	6s2p	17	1.0,0.33
Li	9s4p	4s3p	17	-
Be	12s5p2d	7s3p2d	17	0.3,0.1
Be	12s5p2d1f	7s3p2d1f	17	0.3,0.1;0.26
Be	12s7p4d2f	[5321]	18	-
Be	12s7p4d2f	[6432]	18	-
C	10s6p2d	TZ2P <sup>a</sup>	15,19	1.5,0.35
N	10s6p2d	TZ2P <sup>a</sup>	15,19	1.5,0.35
O	10s6p2d	TZ2P <sup>a</sup>	15,19	1.5,0.35
O	13s8p6d	[432]	18	-
O	13s8p6d4f	[4321]	18	-
O	13s8p6d4f2g	[54321]	18	-
F	9s5p1d	DZP	15,16	1.6
F	10s6p2d	TZ2P <sup>a</sup>	15,19	1.5,0.35
Ne	10s6p2d	TZ2P <sup>b</sup>	17	4.5,1.3
Mg	12s9p2d	6s5p2d	20	0.3,0.1
Cu	14s11p6d3f	8s6p4d1f	7	-

a. The 5s3p contraction of reference 19 was used.

b. A 5s3p contraction, similar to those given in reference 19, was constructed.

Table 2

The  $\mathcal{T}_1$  diagnostic together with the  $C_0$  obtained from a full CI and a CISD wave function<sup>a</sup>.

Molecule	Basis Set	$r$	$\mathcal{T}_1$	$C_0^b$	$C_0^c$
He	6s2p	-	0.0029	0.9960	0.9960
H <sub>2</sub>	6s2p	1.361	0.0050	0.9912	0.9912
Be	7s3p2d	-	0.0210	0.9523	0.9523
Mg	6s5p2d	-	0.0159	0.9640	0.9640
Li <sub>2</sub>	4s3p	5.11	0.0165	0.9510	0.9510
He <sub>2</sub>	6s2p	5.61	0.0029	0.9920	0.9921
Be <sub>2</sub>	7s3p2d	4.75	0.0282	0.8901	0.9150
Mg <sub>2</sub>	6s5p2d	7.35	0.0138	0.9268	0.9401
HF <sup>d</sup>	DZP	2.5995	0.0187	0.9583	0.9680

a. All correlated wave functions are based upon SCF molecular orbitals. Only valence electrons have been included in the correlation procedure. Bond lengths are in atomic units,  $a_0$ .

b. FCI.

c. CISD.

d. FCI and CISD results from reference 21.

Table 3

The  $\mathcal{T}_1$  diagnostic together with  $C_0$  obtained from a CISD wave function<sup>a</sup>.

Molecule	Basis Set	Geometry	$\mathcal{T}_1$	$C_0$
CuH	b	2.850	0.0461	0.9621
Be <sub>3</sub>	7s3p2d	4.273	0.0360	0.9133
Be <sub>4</sub>	7s3p2d	3.915	0.0318	0.9189
Be <sub>5</sub>	7s3p2d	3.831,3.929	0.0290	0.9094
Be <sub>3</sub>	7s3p2d	$\infty$	0.0210	0.9067
Be <sub>4</sub>	7s3p2d	$\infty$	0.0210	0.8933
Be <sub>5</sub>	7s3p2d	$\infty$	0.0210	0.8828
Mg <sub>3</sub>	6s5p2d	7.522	0.0127	0.9235
Mg <sub>4</sub>	6s5p2d	6.102	0.0204	0.9102
Mg <sub>3</sub>	6s5p2d	$\infty$	0.0159	0.9240
Mg <sub>4</sub>	6s5p2d	$\infty$	0.0159	0.9111
FOOF	TZ2P	see text	0.0313	0.9189
(NO) <sub>2</sub>	TZ2P	see text	0.0203	0.9177
cis-FNNF	TZ2P	see text	0.0187	0.9303
trans-FNNF	TZ2P	see text	0.0166	0.9308
TS-FNNF <sup>c</sup>	TZ2P	see text	0.0277	0.9283
HF	TZ2P	1.734	0.0104	0.9775
H <sub>2</sub> O	TZ2P	1.809,104.8°	0.0096	0.9720
CH <sub>4</sub>	TZ2P	2.052	0.0073	0.9672
Ne	TZ2P	-	0.0065	0.9850

a. All correlated wave functions are based upon SCF molecular orbitals. Only valence electrons have been included in the correlation procedure. Bond lengths are in atomic units,  $a_0$ .

b. The Cu basis is as described in Table 1 and the H basis is the [32] ANO basis set.

c. Transition state to cis-trans isomerization.

**Table 4**

The  $\mathcal{T}_1$  diagnostic for  $\text{Be}_3$  and  $\text{H}_2\text{O}$  using several different basis sets. The  $C_0$  value is obtained from a CISD wave function.

Molecule	Basis Set	$\mathcal{T}_1$	$C_0$
$\text{Be}_3$	7s3p2d	0.0360	0.9133
$\text{Be}_3$	7s3p2d1f	0.0339	0.9149
$\text{Be}_3$	[421]	0.0386	0.9107
$\text{Be}_3$	[5321]	0.0341	0.9148
$\text{Be}_3$	[6432]	0.0341	0.9157
$\text{H}_2\text{O}$	TZ2P	0.0096	0.9720
$\text{H}_2\text{O}$	[432/32]	0.0076	0.9721
$\text{H}_2\text{O}$	[4321/321]	0.0071	0.9714
$\text{H}_2\text{O}$	[54321/432]	0.0078	0.9713

a. The geometries are the same as those listed in Table 2. Only valence electrons have been correlated.