Comparison of the T_1 and D_1 Diagnostics: A New Definition for the Open-Shell D_1 Diagnostic

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Abstract

It is shown that the T_1 operator used in a previous study to define the open-shell D_1 diagnostic is invalid, and leads to an arbitrary definition of the open-shell D_1 diagnostic. A new definition is proposed that eliminates this ambiguity and approximately restores the mathematical relationship previously noted between the closed-shell D_1 and T_1 diagnostics. Statistical comparison of the T_1 and D_1 diagnostics shows a very high degree of correlation between them, although it is argued that both diagnostics used together can provide more information than either can separately.

Introduction

Recently, Leininger et al. [1] defined the open-shell version of the D_1 diagnostic, the closed-shell version of which was defined by Janssen and Nielsen in 1998 [2]. The D_1 diagnostic is based on the matrix 2-norm of the coupled-cluster t_1 amplitudes, and, like the T_1 diagnostic [3-6] which is based on the Frobenius norm, it is designed to give an indication of the quality of results to be expected from a singles and doubles coupled-cluster (CCSD) calculation. Janssen and Nielsen showed that there was a rigorous mathematical relationship between the D_1 and T_1 diagnostics for closed-shell theory, which is due to the fact that they are both based on the coupled-cluster t_1 amplitudes. For the open-shell version, however, no such relationship exists even though both the D_1 and T_1 open-shell diagnostics were defined for coupled-cluster wavefunctions based on restricted Hartree-Fock reference functions. There is a difference, however, since the open-shell T_1 diagnostic was defined using an open-shell coupled-cluster wavefunction that is an S_x eigenfunction [6] based on symmetric spin-orbitals [7], whereas Leininger et al. defined a new T_1 operator based on symmetric and antisymmetric combinations of annihilation and creation operators. This T_1 operator was not actually used in calculating the wavefunction, rather the standard S_z spin-orbital equations were used, and the resulting t_1 amplitudes transformed into those for the newly defined T_1 operator. We show below, however, that the new T_1 operator is not valid and that the relationship between the S_z open-shell t_1 amplitudes and the new amplitudes is arbitrary. Hence, the definition of the open-shell D_1 diagnostic is also arbitrary.

One of the purposes of this study is to eliminate the ambiguity in the open-shell D_1 diagnostic by basing it on the S_x restricted open-shell coupled-cluster wavefunction developed in Ref. [6]. The mathematical relationship between the D_1 and T_1 diagnostics is now valid for both the open- and closed-shell versions. We provide test examples of

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Relationships between the coupled-cluster amplitudes in the S_x and the usual S_z basis were also given in Ref. [6]. For current purposes, a brief summary is given here. The T_1 operator, spin rotated into an S_z basis, is given by Eq. (45) in Ref. [6] and is

$$T_1 = f_i^a E_{ai} + v_i^a A_{ai} + \sqrt{2} f_x^a \left[(a\alpha)^\dagger (x\alpha)\right] + \sqrt{2} f_i^x \left[(x\beta)^\dagger (i\beta)\right] , \tag{3}$$

where **f** and **v** are the t_1 amplitudes in the S_x basis. The **f** amplitudes correspond to orbital relaxation parameters whereas the **v** amplitudes correspond to a type of double excitation in the S_x basis (see Ref. [6] for a more complete discussion). Equating Eq. (1) and Eq. (3) allows us to determine relationships between the **f** and **t** amplitudes:

$$f_i^a = \left(t_{i\alpha}^{a\alpha} + t_{i\beta}^{a\beta}\right)/2 \ , \tag{4}$$

$$f_x^a = t_{x\alpha}^{a\alpha} / \sqrt{2} \ , \tag{5}$$

$$f_i^x = t_{i\beta}^{x\beta} / \sqrt{2} \ , \tag{6}$$

$$v_i^a = \left(t_{i\alpha}^{a\alpha} - t_{i\beta}^{a\beta}\right)/2 \ , \tag{7}$$

where Eq. (7) is given for completeness. The open-shell D_1 diagnostic is then defined as the matrix 2-norm of the **f** amplitudes analogous to the procedure used in Ref. [1]. That is, the three open-shell amplitude blocks are treated separately and the maximum matrix 2-norm is taken as the D_1 diagnostic in order to preserve the energy invariance properties of the open-shell D_1 diagnostic (see Ref. [1]).

$$D_1 = \max\left(\left\|f_i^a\right\|_2, \left\|f_x^a\right\|_2, \left\|f_i^x\right\|_2\right) \ . \tag{8}$$

Again, following Ref. [1], the matrix 2-norm is computed according to

$$\left\|\mathbf{R}\right\|_2 = \sqrt{\lambda_{\max}} = \sigma_{\max} \ , \tag{9}$$

where $\lambda_{\max}$ is the largest eigenvalue of the matrix $\mathbf{RR}^{\mathrm{T}}$ and $\sigma_{\max}$ is the largest singular value of **R**. Similar to the relationship between the open- and closed-shell T_1 diagnostics, if there are no open-shell orbitals x, then the open-shell D_1 diagnostic is identical to the closed-shell definition [2]. Defining the open-shell D_1 diagnostic in this way has the additional advantage that the equation relating the closed-shell D_1 and T_1 diagnostics, $\sqrt{2}T_1 \le D_1$, now approximately holds for the open-shell diagnostics in the limit of the number of open-shell electrons being much smaller than the total number of electrons. Test case examples of the new D_1 diagnostic are given in the next section followed by a critical comparison to the T_1 diagnostic.

Results and Discussion

A. New Open-Shell D_1 Values

Test case examples of the new open-shell D_1 diagnostic together with the openboth the closed-shell and open-shell molecules included in these two studies. To give an idea of how strong the correlation between T_1 and D_1 is, we can compare to the correlation coefficient between the T_1 and S_2 diagnostics (S_2 is the perturbation theory equivalent of the T_1 diagnostic [11]), as well as to the correlation coefficient between the coupled-cluster and perturbation theory D_1 diagnostics [2]. Using the data for closed-shell molecules contained in Ref. [2], we obtain a correlation coefficient of 0.98 between the T_1 and S_2 values, and a correlation coefficient of 0.95 between the coupled-cluster and perturbation theory D_1 diagnostics. This shows that the correlation between the D_1 and T_1 coupled-cluster diagnostics is almost as strong as the correlation with their respective second-order perturbation theory analogues.

Perhaps this high degree of correlation is to be expected because of the similarities between the two diagnostics. Both the T_1 and D_1 diagnostics are based on the orbital relaxation parts of the t_1 amplitudes, both were designed to exhibit the same orbital invariance properties that the CCSD energy possesses, and in spite of suggestions to the contrary [1,2], they were both designed to exhibit the mathematical property of size-intensivity. For example, both diagnostics will yield the same value for a single helium atom as for any number of non-interacting helium atoms. However, it was pointed out in Ref. [5] that the T_1 diagnostic may fail to indicate that a small region of a large molecule is difficult to describe properly if the rest of the molecule is well described at the CCSD level of theory, and in Ref. [2] Janssen and Nielsen gave a numerical example of this phenomenon. In essence, the T_1 diagnostic is an average over the whole molecule, and the contribution from the small problem area is swamped by that from the majority of the molecule, which is well described. This can be viewed as a failure of the T_1 diagnostic or it can also be viewed as a success since the majority of the molecule is well described and the T_1 diagnostic indicates this. Conversely, the D_1 diagnostic is designed to yield a large value for a large molecule with only a small problem area. Again, this could be viewed as a success or a failure since most of the molecule is well described, which the D_1 diagnostic does not suggest, but there is one problem area which the D_1 diagnostic does indicate. Another situation where the two diagnostics could give conflicting information is when there is an accumulation of correlation effects wherein there is no one orbital relaxation parameter or excited state that is very important, but rather there are several states or orbital relaxation parameters that are moderately important. In this case, the T_1 diagnostic would be larger than usual, indicating the need to treat higher-order correlation, which would be missed by the D_1 diagnostic. The important point, is that together the T_1 and D_1 diagnostics provide more information than either does alone, and it is best to use both. We stress, however, that we also believe that diagnostics based on two-particle components of the wavefunction, such as the D_2 diagnostic [12], can provide additional, important information in assessing the quality of a particular calculation.

Another quantity to consider is the ratio T_1/D_1, and these are included in Table 1 for the open-shell molecules studied here. In a perfectly homogeneous system, this ratio can be derived from the approximate mathematical relationship between the T_1 and D_1 diagnostics to be $1/\sqrt{2}$. A homogeneous system in this sense is defined as one in which the contribution from all of the **f** amplitudes is identical. Thus, the further the T_1/D_1 ratio deviates from $1/\sqrt{2}$, the greater the non-homogeneity of the electronic structure of the molecule being studied. We note that the T_1/D_1 ratio will deviate from a perfectly

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