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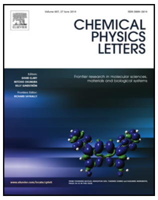

Approximate account of connected triply and quadruply excited clusters in single reference coupled cluster theory via cluster analysis of projected unrestricted coupled cluster with single and double wave function

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ABSTRACT

The projected unrestricted coupled cluster wave function with singly and doubly excited clusters (PUCCSD) has been used as a source of information about the T_3 and T_4 cluster contributions in the externally corrected CCSD approach. In order to remove the spin contamination of the UCCSD wave function the group invariant average of the unitary group was adapted. Preliminary results presented here for the DZ H8 model system show surprisingly good agreement with the exact results, particularly in the case of the energy contribution of the T_4 cluster to the quasidegenerate region with errors of less than 0.1 milihartree.

1. Introduction

Extension of the applicability of the closed-shell coupled cluster (CC) theory [1] to a qualitatively proper description of single and multiple bond breaking phenomena requires the inclusion of highly excited cluster components. Since an explicit consideration of such clusters is still computationally very demanding, there is a need to find some alternative solutions of these limitations. The perturbative estimates of the highly excited clusters, mainly triply [2–8] and quadruply [9,10], may help here but the resulting CC approaches are often limited to near equilibrium geometries yielding incorrect shapes of PES at larger internuclear distances. Replacing the single-reference (SR) space by its multi-reference (MR) counterparts leads to the various types of the MR CC approaches [11–14] which can help in the quasidegenerate situations but their practical application is still rather far from being routine.

Another interesting proposal to solve the above-mentioned problem is suggested by Paldus the RMR CCSD method [15] that requires the cluster analysis of the MR CISD wave function in order to obtain the cluster amplitudes of the T_3 and T_4 operators which are then used to correct the absolute term in the standard CCSD [16–18] equations. Generally, the RMR CCSD method is one of the possible variants of the whole family of methods referred to as the externally corrected CCSD (*ec*CCSD) approaches [19] for which different kinds of wave functions, such as UHF [20,21], VB [19,22,23] and CASSCF [24], are used as a source of information about the needed T_3 and T_4 contributions. Contrary to the standard SR CCSDTQ [25–27] approach the *ec*CCSD methods treat the amplitudes of the T_3 and T_4 operators as independent variables when solving the CC equations.

Performance of the RMR CCSD method depends heavily on the applied reference space in the MR CISD calculation. And only in the case of suitably selected reference configurations in the MR CISD calculation the RMR CCSD method offers good results [28]. And in this way, the applicability of this approach is restricted to the situations where the correct MR CISD calculations are feasible. This feature makes the method not so easy to use in cases such as breaking multiple bonds in order to properly describe the process of dissociation of molecular systems such as the C_2 and BN molecules, not to mention the need to include in the reference space the twelve-body excitations in the case of the calculation for the Cr_2 molecule. Therefore, there is still a method needed that operates on the wave function of a rich cluster structure and simultaneously offers low cost related calculations.

Replacing the restricted Hartree–Fock (RHF) reference by its unrestricted broken spin and symmetry [29–32] counterpart generally may help in the CCSD calculation yielding, for example, good dissociation energies with the computational costs of such calculations being slightly higher. However, in the intermediate bond-breaking region incorrect shapes of PES are often found [33].

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These effects are among others a consequence of spin contamination which is relatively large even in the highly correlated UHF-base CCSD (UCCSD) wave function.

Qualitatively correct description of the quasidegenerate electronic ground state for the DZP H4 model [34,35] by the CCSDQ' [20,21] method, where a single determinant UHF wave function was used to estimate the T_4 contribution in the *ec*CCSD equations, gives reason to believe that much more complex UCCSD wave function can be a good source of information about cluster contributions to the *ec*CCSD approach offering simultaneously the final results without shortcomings, which appear in the calculations using the original UCCSD method due to the spin contamination.

2. Theory

The externally corrected CCSD approach relies on a decoupling of the full CC (FCC) closed-shell equations spanned on singly excited,

$$\langle\Phi_{I_1}^{(1)}|[H_N(e^{T_1+T_2})]_C|\Phi_0\rangle + \Theta_{I_1}^{(1)} = 0, \tag{1}$$

and doubly excited configurations,

$$\langle\Phi_{I_2}^{(2)}|[H_N(e^{T_1+T_2})]_C|\Phi_0\rangle + \Theta_{I_2}^{(2)} = 0, \tag{2}$$

by treating the cluster amplitudes of the T_3^X and T_4^X operators given in the $\Theta_{I_1}^{(1)} \equiv \langle\Phi_{I_1}^{(1)}|H_N T_3^X|\Phi_0\rangle$ and $\Theta_{I_2}^{(2)} \equiv \langle\Phi_{I_2}^{(2)}|[H_N(T_3^X + T_1^X T_3^X + T_4^X)]_C|\Phi_0\rangle$ terms [19] as independent variables when solving CC equations. The down index I_i with $i=1$, 2 represents the set of the hole and particle one electron states defining i-body excitation, while the down index I determines any excitation. The upper index X represents the PUCCSD, PUHF and FCI wave function. In the *ec*CCSD approach the terms $\Theta_{I_1}^{(1)}$ and $\Theta_{I_2}^{(2)}$ are calculated only once and correct accordingly the absolute term in the CCSD equations [19]. The *ec*CCSD energies can be next calculated from the standard CCSD formula [16] with the cluster amplitudes obtained by solving the above *ec*CCSD equations. The missing amplitudes of the T_1^X, T_3^X, and T_4^X cluster operators can be obtained, for example, via standard cluster analysis of the CI-type wave function.

The energy calculated directly from the T_1^X and T_2^X cluster operators employing the standard CCSD formula [16] is indicated in this Letter by the CCSD(X) acronym.

Let us consider two examples for better understanding of the *ec*CCSD method. Namely, performing the cluster analysis of the FCI wave function we can obtain the T_1^{FCI}, T_2^{FCI}, T_3^{FCI} and T_4^{FCI} cluster contributions. Calculating then the CCSD(FCI) energy using the T_1^{FCI} and T_2^{FCI} cluster contributions we obtain the exact (FCI) energy. In the case of the *ec*CCSD calculation the result will be the same, namely exact energy. A totally different situation we have in the case of any approximate wave functions is; for example, when we use the MR CISD wave function then the CCSD(MR CISD) energy will be the same as the MR CISD energy obtained by digitalization of the CI matrix due to the unitarity of the CI wave function. However, in the case of the RMR CCSD calculation the final energy will represent significant improvement compared to the MR CISD calculation [28]. This observation is a key reason for which we mainly concentrate on the higher excited T_3^X and T_4^X cluster operators.

3. Cluster analysis

In the CCSD theory [1,16] the wave operator has an exponential form and for this reason we obtain up to the N-electron excited disconnected excitations when acting on the reference configuration. Unfortunately, most of these excitations do not correspond to the real coupling between the cluster amplitudes while solving the CCSD equations. Thus, in further deliberations on the cluster analysis of the UCCSD wave function we will focus only on those connected and disconnected excitations that directly correspond to the relevant diagrammatic expressions [16,36] in the CCSD equations.

In order to simplify further considerations, it would be desirable to transform the UCCSD wave function defined by the $\hat{T}_1$ and $\hat{T}_2$ cluster excitations into the CI-representation by suitably grouping of the connected and disconnected excitations into the one CI-excitation. Finally, we have the wave function with up to the four-body CI-amplitudes and the UHF configurations $|\Xi_{J_j}^{(j)}\rangle$, namely,

$$|\Psi_0\rangle = \sum_{j=0}^{4} \hat{C}_j\,|\Xi_0\rangle, \quad \hat{C}_j\,|\Xi_0\rangle = \sum_{J_j} c_{J_j}^{(j)}\,|\Xi_{J_j}^{(j)}\rangle, \tag{3}$$

where $\hat{C}_0 \equiv 1$, $\hat{C}_1 = \hat{T}_1$ and $\hat{C}_2 = \hat{T}_2 + \frac{1}{2}\hat{T}_1^2$ represent a typical relationship between the CC and the CI theory. In the case of the $\hat{C}_3$ and $\hat{C}_4$ excitations we have a slightly different situation because of the lack of the $\hat{T}_3$ and $\hat{T}_4$ cluster operators in the standard CCSD equations [16], namely,

$$\hat{C}_3 = \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3\,, \tag{4}$$

$$\hat{C}_4 = \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{24}\hat{T}_1^2\,. \tag{5}$$

The next step is the projection in such way obtained wave function on the RHF configurations $|\Phi_{J_j}^{(j)}\rangle$ through the use of the Thouless' theorem [37] for a single determinantal wave function which states that,

$$|\Xi_J\rangle = \lambda_J \exp(\hat{R}_1^{(J)})\,|\Phi_J\rangle, \tag{6}$$

with $\lambda_J \equiv \langle\Xi_J|\Phi_J\rangle$ representing the overlap between the UHF and RHF configurations. The singly excited $\hat{R}_1^{(J)}$ operator in Eq. (6) is defined as

$$\hat{R}_1^{(J)} = \sum_{\alpha,\sigma} \langle\sigma|\hat{R}_1^{(J)}|\alpha\rangle X_\sigma^\dagger X_\alpha, \tag{7}$$

where the summation indices represent here the hole α and particle σ one electron states determined with respect to each reference $|\Phi_J\rangle$ configuration [37]. Scalar part of this operator, namely $\mathbf{R}^{(J)} \equiv \langle\rho|\hat{R}_1^{(J)}|\alpha\rangle$, is given by the matrix product $\mathbf{G}^{(J)}[\mathbf{F}^{(J)}]^{-1}$, where matrices $\mathbf{F}^{(J)} \equiv ||f_{ij}^{(J)}||_{i,j=1}^{N} = ||c_{ij}^{(J)}||_{i,j=1}^{N}$ and $\mathbf{G}^{(J)} \equiv ||g_{ij}^{(J)}||_{i,j=1}^{M-N,N} = ||c_{ij}^{(J)}||_{i=N+1,j=1}^{M,N}$ are defined by the transformation matrix $\mathbf{C}^{(J)} \equiv ||c_{ij}^{(J)}||_{i,j=1}^{M,N}$ between the UHF and RHF spin–orbitals [21]. Indices M and N denote here the total number of molecular spin–orbitals and the number of electrons, respectively.

After this transformation, the wave function takes the following form,

$$|\Psi_0\rangle = \sum_J \tilde{c}_J \exp(\hat{R}_1^{(J)})|\Phi_J\rangle,\ \tilde{c}_J \equiv \lambda_J c_J\,. \tag{8}$$

When we choose any $|\Phi_J\rangle$ configuration belonging to the full symmetric representation of the special symmetry group as the reference configuration $|\Phi_0\rangle$, the remaining configurations will be presented as the effect of excitation operator G_J on the reference configuration $|\Phi_0\rangle$ and the wave function will be expressed as follows:

$$|\Psi_0\rangle = \sum_J \exp(\hat{R}_1^{(J)})\,\tilde{c}_J G_J|\Phi_0\rangle. \tag{9}$$