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**Communication: The distinguishable cluster approximation. II. The role of orbital relaxation**

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## Communication: The distinguishable cluster approximation. II. The role of orbital relaxation

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The distinguishable cluster approximation proposed in Paper I [D. Kats and F. R. Manby, *J. Chem. Phys.* **139**, 021102 (2013)] has shown intriguing abilities to accurately describe potential energy surfaces in various notoriously difficult cases. The question that still remained open is to what extent the accuracy and the stability of the method is due to the special choice of orbital-relaxation treatment. In this paper we introduce orbital relaxation in terms of Brueckner orbitals, orbital optimization, and projective singles into the distinguishable cluster approximation and investigate its importance in single- and multireference cases. All three resulting methods are able to cope with many multiple-bond breaking problems, but in some difficult cases where the Hartree-Fock orbitals seem to be entirely inadequate the orbital-optimized version turns out to be superior. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4892792>]

### I. INTRODUCTION

Electron correlation energy, defined as the difference between the exact electronic energy in the given basis and the mean-field Hartree-Fock (HF) energy, represents usually a relatively small contribution, which is, however, essential for an accurate description of chemical processes. In cases where the HF determinant is a good reference the (dynamic) correlation energy can be efficiently captured by the post-HF single-reference techniques, e.g., the coupled-cluster doubles theory (CCD).<sup>1</sup> For molecular systems with large amount of static correlation these methods generally fail, and in this cases usually multireference techniques are employed, which are much more difficult both computationally and methodologically. There are many attempts to develop methods capable to treat strong correlation in the single-reference framework.<sup>2-7</sup> Very recently we have proposed a method named the distinguishable cluster doubles (DCD) approximation,<sup>8</sup> which retains the simplicity and efficiency of the single-reference treatment, but is accurate and robust in the strongly correlated cases, e.g., in bond-breaking processes. Furthermore, even in single-reference cases the accuracy of DCD turned out to be superior to the conventional CCD counterpart.

Generally the main part of dynamic electron correlation can be captured by electron-pair parameters, and pure pair theories like CCD are sufficient for a decent accuracy. However, the uncorrelated HF quasiparticles are generally not entirely appropriate, and in high precision calculations have to be replaced by quasiparticles that include the influence of the electron correlation. In multireference cases the update of the HF orbitals becomes even more vital.

The update of the quasiparticles, i.e., the orbital relaxation, can be achieved by either explicit orbital rotations or by introduction of single excitations in the theory. One way of rotating the orbitals is to demand that the single excitations, if introduced in the wavefunction, would still remain zero. This approach was proposed by Brueckner for nuclear

matter,<sup>9</sup> and was applied to quantum chemistry by Nesbet.<sup>10</sup> These Brueckner orbitals were used later for CCD, and the method is known as Brueckner CCD (BCCD).<sup>11,12</sup> Another way to relax the orbitals is to actually optimize the full Lagrangian with respect to the orbital rotations,<sup>13-15</sup> which is still an exact procedure for a doubles-only theory.<sup>16</sup> The advantage of this approach is that the resulting theory is stationary with respect to orbitals, and therefore it is easier to calculate higher order properties. Even the gradients are somewhat easier, since there are no derivatives of singles terms with respect to orbital coefficients.

Partial orbital relaxation can be achieved by using single excitations.<sup>17</sup> It is advantageous to use them in exponential form, otherwise some parts of the orbital relaxation will be hidden in the higher excitations increasing their importance and thus decreasing the quality of a truncated method. Although it is possible to solve the singles equations variationally<sup>18</sup> a more practical way is to use a projected singles approach as was done in CCD with singles (CCSD).<sup>19</sup> Since this relaxation does not directly affect the actual orbitals, integrals do not have to be recalculated in each iteration. It makes this approach especially useful for local correlation<sup>20-22</sup> methods, where the integral transformations often consume a considerable part of computational time.

In the following we study the performance of all the three mentioned orbital-relaxation approaches in the context of the distinguishable cluster approximation in single- and multireference cases.

### II. THEORY

The distinguishable cluster approximation is derived as a modification of the CCD amplitude equations by imposing distinguishability of particles, belonging to different pairs, and retaining the main desired properties of the CCD: exactness for two-particle systems (more precisely,

HF-quasiparticles), size extensivity, invariance to rotations within occupied and virtual spaces, and particle-hole symmetry. The resulting DCD amplitude equations within the spin-free formalism are shown below and differ from the CCD equations in quadratic terms only,

$$R_{ab}^{ij} = (ai|bj) + (ac|bd)T_{cd}^{ij} + (ki|lj)T_{ab}^{kl} + \tilde{T}_{ac}^{ik}(kc|ld)\tilde{T}_{db}^{lj} \\ + \mathcal{P}(ia; jb)\{x_{ac}T_{cb}^{ij} - x_{ki}T_{ab}^{kj} - (ki|ac)T_{cb}^{kj} \\ - (ki|bc)T_{ac}^{kj} + \tilde{T}_{ac}^{ik}(kc|bj)\} = 0, \quad (1)$$

where

$$x_{ac} = f_{ac} - \frac{1}{2}\tilde{T}_{ad}^{kl}(ld|kc) \quad x_{ki} = f_{ki} + \frac{1}{2}\tilde{T}_{cd}^{il}(ld|kc) \\ \tilde{T}_{ab}^{ij} = 2T_{ab}^{ij} - T_{ba}^{ij} \quad \mathcal{P}(ia; jb)X_{ab}^{ij} = X_{ab}^{ij} + X_{ba}^{ji}, \quad (2)$$

and  $T_{ab}^{ij}$  are the DCD amplitudes,  $(pq|rs)$  – the electron repulsion integrals in the chemical notation, and  $f_{pq}$  – the Fock matrix. The indices  $i, j, k, \dots, a, b, c, \dots$ , and  $p, q, r, \dots$  denote the occupied, virtual, and general orbitals, respectively. In the equations we also assume an implicit summation over repeated indices. The DCD equations can be factorized using density-fitting technique<sup>23–25</sup> even further such that the computation time of quadratic terms would scale with the fifth power of the molecular size only.<sup>26</sup>

The DCD theory is yet not exact for two real particles (but only for the HF-quasiparticles). However, exactness for two real particles can be achieved by allowing for full or partial orbital relaxation. Relaxing orbitals for DCD using Brueckner condition<sup>10–12</sup> was considered in Paper I.<sup>8</sup> Although a DCD wavefunction cannot be properly specified, one can formally assume that there is a DCD wavefunction  $\Psi$  containing only doubles, and then the orbitals are rotated such that the condition

$$\langle \Phi_a^i | \mathbf{H} | \Psi \rangle = 0 \quad (3)$$

is fulfilled.  $\Phi_a^i$  denotes a singly excited determinant and  $\mathbf{H}$  is the Hamilton operator. The resulting BDCD equations differ from the BCCD equations only in the doubles residual, Eq. (1).

In the second method, orbital-optimized DCD (ODCD), the rotated orbitals are obtained by minimizing the DCD Lagrangian with respect to the orbital coefficients. This method is roughly twice as computationally expensive as BDCD, since here one needs to simultaneously calculate the doubles amplitudes and the doubles Lagrange multipliers. The problem of not converging to the exact limit arises only for higher than doubles excitations,<sup>16</sup> and therefore ODCD, as a pair theory, is exact for two-electron systems.

Finally, we consider a partial orbital relaxation using projective singles ansatz. We employ the similarity-transformed Hamiltonian  $\exp(-\mathbf{T}_1)\mathbf{H}\exp(\mathbf{T}_1)$ , which leads to the DCD with singles (DCSD) equations, based on dressed integrals and Fock matrices.<sup>27</sup> It is easy to show that the quadratic terms in the doubles amplitude equations contain only undressed integrals, since all particle/hole lines in the corresponding diagrams are connected to doubles amplitudes. As a result, the DCSD equations differ from the corresponding CCSD equations in the same way as DCD from CCD, i.e., only in the

terms, quadratic in the doubles amplitudes, while all other terms remain the same.

### III. RESULTS

The BDCD, ODCD, and DCSD methods were implemented by modification of the MOLPRO's<sup>28,29</sup> BCCD, OCCD, and CCSD routines,<sup>30,31</sup> respectively. All calculations were based on a restricted HF reference, frozen-core approximation has been employed, and the molecular dissociations were performed using the cc-pVDZ gaussian basis set.

We start by investigating influence of orbital-relaxation techniques on nitrogen dissociation (Figure 1(a)). The BDCD, ODCD, and DCSD curves look very similar; neither of the methods has problems in this otherwise notoriously difficult case for a single-reference theory (see, e.g., the CCSD curve). Even without relaxing orbitals the DCD curve looks smooth and qualitatively correct. The DCSD curve is a little bit lower than other curves, which is somewhat surprising considering the fact that ODCD energy is obtained by minimizing a Lagrangian while the DCSD energy is a projective method.

The next standard example where the coupled-cluster theory has difficulties is a symmetric double dissociation of water (Figure 1(b)). As in the case of nitrogen dissociation, the DC curves with different orbital relaxation schemes are nearly on top of each other. The DCSD curve is again slightly lower, especially in the strong-correlation regime, and

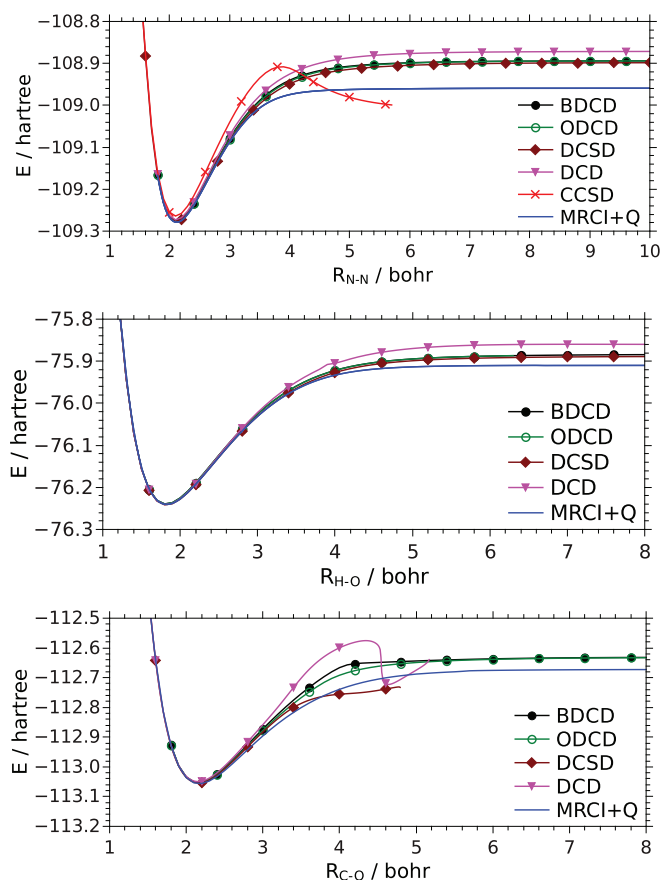
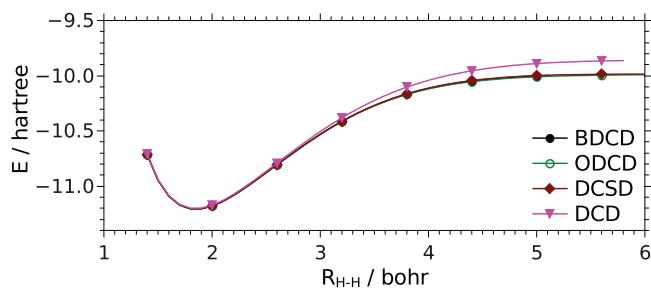


FIG. 1. Potential energy curves. Top:  $N_2$  dissociation. Middle: symmetric double dissociation of  $H_2O$  with  $H-O-H$  angle fixed at  $107.6^\circ$ . Bottom:  $CO$  dissociation.

FIG. 2. Potential energy curves for  $H_{20}$ -chain dissociation.

is therefore closer to the reference curve from the Davidson-corrected internally contracted multireference configuration interaction (MRCI+Q) method.<sup>32</sup> As one would expect, the DCD curve deviates from other curves much stronger for larger O–H distances, manifesting poor quality of the HF reference in this region.

Dissociation of carbon monoxide represents another challenging case for single-reference methods (Figure 1(c)). As expected, the DC methods yield nearly identical results at equilibrium distance. But at stretched geometries the methods start to deviate, and the orbital optimized version of DC provides the smoothest curve. The BDCD curve has a small non-physical bump, while DCSD demonstrates peculiar artifacts after the Coulson-Fischer<sup>33</sup> point. Apparently the orbital relaxation is particularly important for this system, since the DCD method has the biggest problems among all DC schemes considered here, with a jump in the energy of nearly 150 mH at the interatomic distance of 4.55 bohrs (note that this form of the potential curve is exactly reproduced if one starts from 5-bohr values and recalculates the curve in the association direction). Apart from that, we experienced substantial convergence problems in this system. Even the MRCI method was not converging for separations beyond 4 bohrs when for the preceding multi-configurational self-consistent field (MCSCF) calculations the HF orbitals were chosen as a starting guess.

The original BDCD method performed remarkably well in the case of massively correlated hydrogen systems. In order to test the sensitivity of orbital-relaxation techniques to large doubles amplitudes we performed calculations on a linear equidistant  $H_{20}$  chain using all types of DC methods (Figure 2). All three relaxation techniques seem to handle the exploding doubles (with squared norms over 30) very well. Only at large separations the curves start to deviate, although the difference is still very small (less than 12 mH at 5-bohr separation).

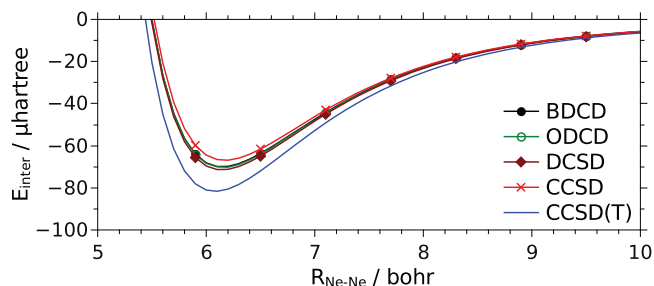


FIG. 3. Interaction energy curves for Ne dimer.

TABLE I. Mean absolute deviation (MAD), root mean squared deviation (RMSD), and maximal deviation (MAX) of reaction energies (aug-cc-pVTZ) from Ref. 35 compared to CCSD(T) calculations.

Methods	MAD	RMSD	MAX
	kJ/mol		
CCSD	5.13	7.14	27.7
BDCD	3.62	4.99	15.6
ODCD	3.41	4.70	14.0
DCSD	3.21	4.40	12.7
DCD	5.01	6.73	19.6

In order to test the quality of the different DC methods also for single-reference problems, we have used them to calculate neon-dimer counterpoise-corrected interaction energies and reaction energies of various molecules in aug-cc-pVTZ basis sets. Neon dimer is a difficult case for CCSD but the perturbative-triples correction (CCSD(T))<sup>34</sup> improves results considerably (Figure 3). It turned out that the DC methods noticeably improve on the CCSD results although the values are still far from the CCSD(T) ones. And as expected for problems for which Hartree-Fock is a good reference the curves for different handling of orbital relaxation are very similar; although at this microhartree scale one can see that the DCSD curve is lower than the other curves resulting in slightly closer agreement with the CCSD(T) reference.

Performance of the orbital-relaxation techniques for calculating relative energies was tested using a set of reactions from Ref. 35 that was already utilised in Paper I.<sup>8</sup> In Table I we have compiled various quality measures of reaction-energy calculations (mean-absolute, root mean squared, and maximal deviations) in comparison to CCSD(T) values. As already noted in Ref. 8 DC provides a better accuracy than BCCD even in single-reference cases. This observation is confirmed also for other orbital-relaxation schemes. The most accurate results are obtained using DCSD, showing an improvement with respect to CCSD by 60% in mean absolute deviation (MAD) and root mean squared deviation (RMSD), and by more than 110% in the maximal deviation. Even the DCD method, which misses the orbital relaxation entirely, outperforms CCSD in all the three statistical measures.

## IV. CONCLUSION

It is generally important to include orbital relaxation when aiming for highly accurate results in the correlated calculations. Moreover, if the HF reference does not provide good description of the molecular system, it can become essential even for qualitative description. We have investigated three ways to introduce orbital relaxation into the recently proposed DCD method:<sup>8</sup> Brueckner orbitals, orbital optimization, and singles similarity transformation. Despite substantial differences in the formalism, all three methods were able to provide qualitatively appropriate potential energy curves for nitrogen, water, and the hydrogen chain. Interestingly, the DC method even without orbital relaxation (i.e., DCD) was providing reasonable results for these systems. The DC methods are thus much less sensitive to orbital relaxation than the



models of Refs. 6 and 7, which generally require a proper choice of orbitals. But in some cases a proper orbital relaxation is indispensable. Carbon monoxide appears to represent a challenging case in this respect. Only orbital optimization was able to reproduce a proper dissociation potential energy curve. The BDCD curve was also reasonable, but with small non-physical deviations. At the same time, DCSD and especially DCD failed to describe dissociation of this molecule.

We also note that DCSD energies are consistently lower than the corresponding BDCD and ODCD ones. Since the DC energies at dissociation are usually somewhat above the exact values, results from similarity-transformation based orbital relaxation come out better compared to the other DC methods. Unfortunately a naive approach to minimize the DCSD energy by rotating orbitals and get even lower values would fail to converge because of the high redundancy in the resulting equations.<sup>13</sup> The DCSD also gives best relative energies (using CCSD(T) as reference), although the difference is tiny and may be caused by the fact that our reference values are biased toward the projective singles approach.

The big advantage of DCSD compared to BDCD or ODCD is the simplicity of extensions to the explicitly correlated<sup>36,37</sup> and linearly scaling local correlation methods. By utilizing density-fitting technique the quadratic doubles diagrams needed in DCSD can be implemented with a nominal  $\mathcal{O}(N^5)$  scaling with respect to the molecular system size resulting in a much faster method for calculations with large pair lists.<sup>26</sup> Further simplifications for weak pairs in the spirit of Ref. 38 and 39 are also feasible.

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