

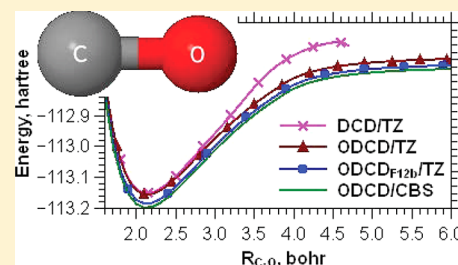
Orbital-Optimized Distinguishable Cluster Theory with Explicit Correlation

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S Supporting Information

ABSTRACT: A combination of orbital-optimized methods with explicit correlation is discussed for the example of the orbital-optimized distinguishable cluster approach. It is shown that the perturbative approach is applicable even in strongly correlated situations, and it is important in these cases to use Lagrange multipliers together with the amplitudes. The partial amplitude relaxation can be applied to relax the amplitudes and makes absolute energies closer to complete basis set results.



1. INTRODUCTION

Orbital relaxation in correlated wave functions parametrizes the response of the mean-field one-particle states to the perturbations resulting from the fluctuation potential and is an essential component of accurate wave function methods. The exponential of the singles excitation operator in coupled-cluster theory^{1,2} as a partial orbital relaxation³ has some advantages compared to orbital optimization techniques, connected to the fact that the orbitals do not change. In particular, the two-electron integrals need only be computed once, and it is straightforward to apply restrictions on the excitation space to exploit the spatial locality of electron correlation in insulators. However, there are situations where orbital relaxation is strong and the partial relaxation of the exponential singles ansatz is not sufficient. Indeed, Brueckner theory^{4,5} and, more notably, fully orbital optimized methods^{6–11} have seen a renaissance in recent years. Orbital-optimized methods that optimize a Lagrangian with respect to orbital rotations are attractive due to the hermiticity of the working equations,^{8,10,12} and the reduction of high-order excitation amplitudes, which simplifies some of the quasi-multireference problems for single-reference methods.⁷

This letter concerns the distinguishable cluster (DC) approach^{13–15} which, despite its single-reference formalism and close resemblance to the coupled-cluster method, provides promising results for strongly correlated systems. In contrast to the coupled-cluster singles and doubles (CCSD) method, DCSD potential energy curves are usually qualitatively correct, dissociating to a constant. However, numerical problems are sometimes encountered for DCSD, where the equations converge to different solutions resulting in unphysical features in the potential energy surface. The orbital optimization in orbital-optimized distinguishable cluster doubles (ODCD) greatly ameliorates these difficulties.¹⁴

The purpose of this letter is to communicate the application of F12 explicitly correlated theory^{16–18} to orbital-optimized

methods such as ODCD to overcome the slow basis-set convergence that plagues electron-correlation methods and approach the basis-set limit of such methods with small orbital basis sets. While F12 theory is straightforwardly applied to DCSD theory through its similarity to CCSD theory, and has been shown to provide the anticipated accelerated basis-set convergence,¹⁹ the application to orbital-optimized theories requires some attention. The primary obstacle is the expense associated with recomputing the two-electron integrals involving the F12 correlation factor and rebuilding the F12 intermediates after every orbital update. As pointed out by one of us in the context of Brueckner theory,²⁰ a practical route to combining explicit correlation with orbital-optimized methods is to use Valeev's perturbative F12 approach,^{21,22} where the F12 contribution enters as a posthoc energy correction and the integrals and intermediates need only be computed once. We have recently shown that the loss of accuracy associated with neglecting the amplitude relaxation due to the coupling between the F12 doubles amplitudes and the T_2 conventional doubles amplitudes can be eliminated with no significant additional cost by employing an approximate Lagrangian estimate for the amplitude relaxation energy.²³

In this letter we report first calculations that demonstrate the utility of the explicitly correlated orbital-optimized distinguishable cluster doubles method for both weakly and strongly correlated molecular systems.

2. THEORY

The working equations for orbital-optimized DCD share a common structure to orbital-optimized quasi-variational coupled-cluster,⁸ density-cumulant,¹² and geminal theories,^{24,25} and the procedure for applying F12 theory presented in this section is transferable to all of these approaches. The

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parameters of the parent (non-F12) theory are determined by optimizing a Lagrangian composed of the projective energy estimator, which depends on the occupied orbitals and correlation parameters, plus each constraint times an associated Lagrange multiplier, where the constraints are the equations for the doubles amplitudes and orbital orthogonality (if required).

$$L[\bar{\mathbf{T}}_2, \bar{\mathbf{c}}, \mathbf{T}_2, \mathbf{c}] = E[\mathbf{T}_2, \mathbf{c}] + \bar{\mathbf{T}}_2 \Omega_2[\mathbf{T}_2, \mathbf{c}] + \bar{\mathbf{c}} W[\mathbf{c}] \quad (1)$$

Here \mathbf{T}_2 , \mathbf{c} , $\bar{\mathbf{T}}_2$, and $\bar{\mathbf{c}}$ denote doubles amplitudes, orbital coefficients, and their Lagrange multipliers, respectively, Ω_2 are the amplitude equations and W are the orthonormality constraints. The optimized orbital coefficients are those that make the Lagrangian stationary with respect to varying the orbitals. Applying Valeev's perturbative F12 approach involves first optimizing the orbitals and amplitudes of the parent method using eq 1 and then computing the explicitly correlated energy by evaluating the corresponding F12 Lagrangian without further refinement of the parameters

$$L[\bar{\mathbf{T}}_2, \mathbf{T}_2, \mathbf{C}] = E[\mathbf{T}_2, \mathbf{C}] + \bar{\mathbf{T}}_2 \Omega_2[\mathbf{T}_2, \mathbf{C}] + \mathbf{C}^\dagger \Omega_{\text{F12}}[\mathbf{T}_2, \mathbf{C}] \quad (2)$$

where Ω_{F12} are the F12 amplitude equations and \mathbf{C} are the F12 amplitudes that satisfy the first-order coalescence conditions, where the optimized reference orbitals define the zeroth-order wave function. Equation 2 contains Lagrange multipliers, which for methods with singles-similarity-transformed and Brueckner orbital relaxations are replaced by contravariant amplitudes to avoid the computational expense of solving for the multipliers. However, for orbital-optimized methods, it is anyway necessary to compute the Lagrange multipliers and these can be used in the F12 correction.

Various low-cost approximations to the full F12 amplitude equations have been proposed in the literature. These include the F12a and F12b approximations,^{26,27} the $(2)_{\text{F12}}$ approximation,^{21,22} and the (F12*) and (F12) approximations.^{28–30} The accuracy and convergence properties of these approximations have recently been studied very carefully and show that the approximation magnitudes follow the ranking F12a > F12b \approx $(2)_{\text{F12}}$ > (F12*) \approx (F12).³¹ All of these approximations can be applied in the context of Valeev's perturbative approach, and in this work we use approximations F12a and F12b for reasons of convenience of implementation in a development version of the MOLPRO package.³² The notation ODCD_{F12b} is used to denote that the F12b approximation is used for a posthoc energy correction.

The posthoc F12 energy correction does not account for the relaxation of the orbitals or T_2 amplitudes induced by coupling to the F12 amplitudes. We have recently presented a Lagrangian-based estimate of the relaxation energy,²³ which improves both absolute and relative energies with virtually no additional cost.

$$E = L[\bar{\mathbf{T}}_2, \mathbf{T}_2, \mathbf{C}] + \delta \mathbf{T}_1 \Omega_1[\mathbf{T}_2, \mathbf{C}] + \delta \mathbf{T}_2 \Omega_2[\mathbf{T}_2, \mathbf{C}] \quad (3)$$

Here the orbital relaxation is treated through the exponentiated T_1 excitation operators and Ω_1 is the F12 contribution to the DCSD-F12 singles residual. Ω_2 is the same as in eq 2. The $\delta \mathbf{T}$ terms in eq 3 should in fact be $\delta \bar{\mathbf{T}}$. However, evaluating $\delta \bar{\mathbf{T}}$ requires one additional evaluation of the Lagrange multiplier residuals, which is an expense we avoided. Instead, we use the (contravariant) amplitude update. Since quality of the correction depends on the accuracy of the update procedure,

and the perturbative update can be rather poor in the strongly correlated case, it is appropriate to modify the update to include an imaginary level shift that eliminates potential singularities in the denominators, a technique also known as Tikhonov regularization^{33,34}

$$\begin{aligned} \delta T_a^i &= -\frac{\Delta_i^a \Omega_a^i}{(\Delta_i^a)^2 + \omega^2} \\ \delta T_{ab}^{ij} &= -\frac{\Delta_{ij}^{ab} \Omega_{ab}^{ij}}{(\Delta_{ij}^{ab})^2 + \omega^2} \end{aligned} \quad (4)$$

with Δ_i^a and Δ_{ij}^{ab} denoting the usual denominators for a perturbative update,

$$\Delta_i^a = \epsilon_a - \epsilon_i, \quad \Delta_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j \quad (5)$$

and a , b , and i , j denoting the virtual and occupied indices, respectively.

The CABS singles correction in F12 theory is derived as a perturbative correction for the basis-set incompleteness error in the HF energy. Here we require a perturbative correction for the basis-set incompleteness error in the reference energy of the optimized orbitals. The appropriate CABS singles correction here is the same as that for Brueckner F12 theory,²⁰ which differs from the standard correction in that the nonzero f_{ai} block of the Fock matrix is set to zero in the equations, which prevents relaxation toward the canonical HF orbitals.

3. TEST CALCULATIONS

We first examine the performance of the F12 correction for the dissociation curve of N_2 , which is a comparably simple case for the DC methods, where both DCSD and ODCD methods work equally well and where DCSD-F12 theory is known to accelerate the basis-set convergence of DCSD theory.¹⁹ We performed ODCD_{F12b} calculations at bond separations between 1.4 and 6 a_u using an aug-cc-pVTZ orbital basis set. The core electrons are frozen in all calculations. The aug-cc-pVTZ/jkfit basis set was used for the complementary auxiliary basis (CABS), and the aug-cc-pVTZ/mp2fit basis set was used for density fitting. A geminal exponent of $\gamma = 1 a_u^{-1}$ was employed for the correlation factor. The complete basis set (CBS) numbers are estimated using Helgakers two point extrapolation³⁵ using the aug-cc-pVQZ and aug-cc-pVSZ basis sets for the correlation energy, and the reference energy is that of the ODCD/aug-cc-pVSZ-optimized orbitals, unless stated otherwise. We performed calculations with and without the partial amplitude relaxation correction and tested the impact of the imaginary shift parameter ω . Calculations without the correction are denoted by [woc]. We also performed calculations where the F12 energy contribution is computed using the contravariant amplitudes rather than using the Lagrange multipliers to assess the impact of this approximation, denoted by $[T_2]$.

In Figure 1 we display the potential energy curves of ODCD_{F12b} with and without the amplitude relaxation correction and include the ODCD/CBS and MRCI+Q-F12³⁶ curves for comparison. All methods produce qualitatively correct curves with no unphysical features. In Figure 2 we display the differences of ODCD_{F12b}[woc] and ODCD_{F12b} to the ODCD/CBS energies. The F12 correction performs slightly better at stretched geometries than at equilibrium. The relaxation correction provides a small but systematic

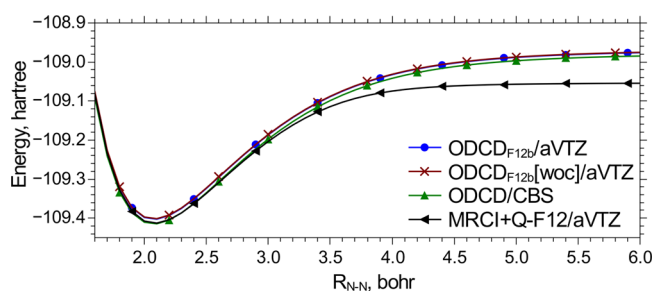


Figure 1. Potential energy curve of N_2 molecule.

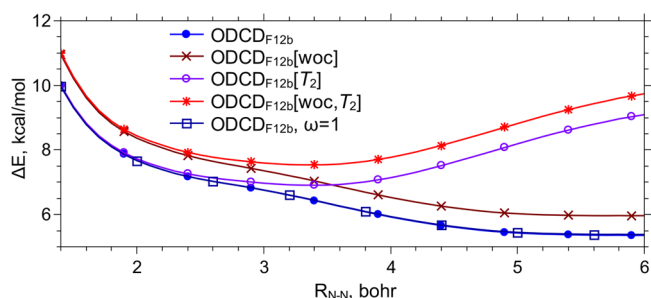


Figure 2. Basis-set incompleteness error (kcal/mol) of $ODCD_{F12b}$ with and without the relaxation correction and using T_2 in place of the Lagrange multipliers. The curve $ODCD_{F12b}$, $\omega = 1$ corresponds to a calculation with the imaginary shift set to one.

reduction in the basis-set error at all geometries and the $ODCD$ and $ODCD_{F12b}[woc]$ curves are parallel to each other even at stretched geometries. We find no evidence of singularities in the perturbative orbital update, and adding an imaginary shift $\omega = 1$ in the correction has no impact on the results.

In Figure 2 we also display the basis-set incompleteness curves obtained when using the contravariant amplitudes in eq 2 in place of the Lagrange multipliers. Approximating the multipliers with contravariant amplitudes is valid in the weakly correlated regime, but introduces substantial errors of nearly 4 kcal/mol at 6 bohr separation and is not recommended in $ODCD$ -F12 theory.

In Figure 3 we plot the basis-set errors for various basis sets for conventional and F12 methods as the function of interatomic distance. To obtain the basis set limit energy, we compute an aug-cc-pV5Z-aug-cc-pV6Z CBS correlation energy, which is added to the reference energy from $ODCD$ /aug-cc-pV6Z-optimized orbitals. As expected, $ODCD_{F12b}$ converges much more quickly to the basis-set

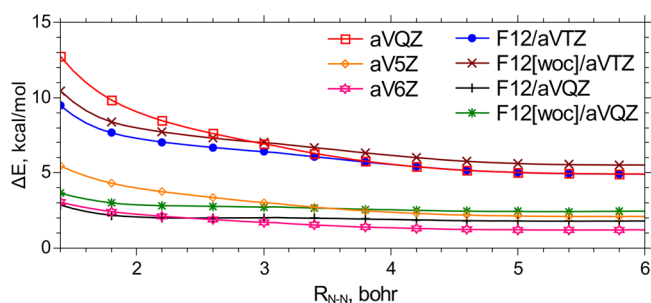


Figure 3. Basis-set incompleteness error (kcal/mol) of $ODCD_{F12b}$, $ODCD_{F12b}[woc]$, and conventional $ODCD$ using aug-cc-pVTZ, aug-cc-pVQZ, aug-cc-pV5Z, and aug-cc-pV6Z basis sets.

limit. Interestingly, the slope of the F12 curves is much flatter, which makes relative basis-set errors along the dissociation curve much smaller than for non-F12 $ODCD$, even with very large basis sets.

The carbon monoxide molecule has been identified previously¹⁴ as one of the problematic cases where the quality of the orbital relaxation treatment plays a critical role in the quality of the results. The DCSD potential energy curve in cc-pVDZ basis is completely wrong for larger interatomic distances, the BDCD curve has an unphysical bump in the region of 4 bohr, but the $ODCD$ method using cc-pVDZ basis set yields a qualitatively correct potential energy curve (see Figure 1 in ref 14). In the following we investigate the behavior of $ODCD_{F12b}$ theory for this molecule, using an aug-cc-pVTZ basis. We experienced severe convergence problems in the $ODCD$ equations for basis sets larger than aug-cc-pVDZ, and the method tends to converge to higher lying solutions. In order to calculate the $ODCD$ potential energy curve, we first converged the BDCD solutions up to a separation of 6 bohr and then calculated $ODCD$ curve by starting from the BDCD 6 bohr solution and reducing the interatomic distance. The $ODCD_{F12b}$ curve is qualitatively correct as can be seen in Figure 4, and as for the nitrogen molecule, both $ODCD_{F12b}$

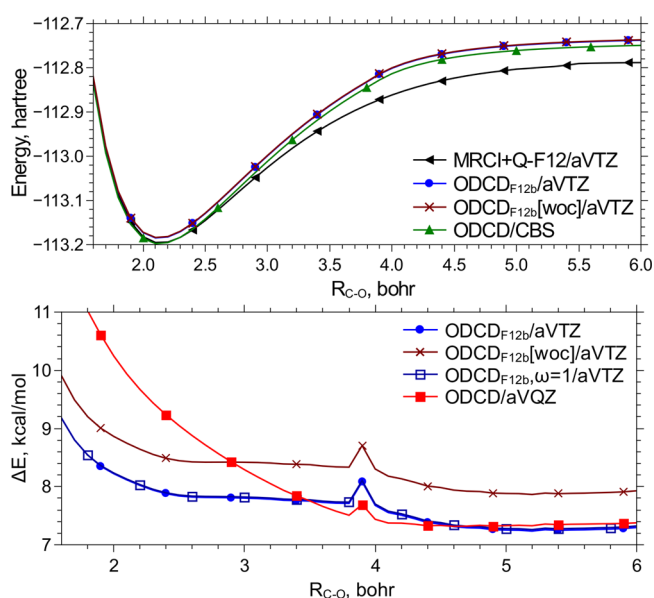


Figure 4. Potential energy curve of CO molecule (above) and basis-set incompleteness error (below).

and $ODCD_{F12b}[woc]$ are quite parallel to the CBS curve, with a nearly constant basis-set error along the dissociation curve. The small bump seen in the basis-set incompleteness curves also occurs in the $ODCD$ without F12 and is a vestige of the problems encountered with DCSD and BDCD at this interatomic separation. The problems arise because there are two low-lying solutions that cross, as shown in the Supporting Information.

The above examples demonstrate that the posthoc F12 correction performs well both at equilibrium and at stretched geometries. To examine the stability of the F12 correction in these regimes, we have investigated the γ dependency of the $ODCD_{F12b}$ energies for N_2 and CO at their equilibrium bond lengths and in the dissociation region. The results are displayed in Figure 5. We find that the optimal γ of $\sim 1.7 a_u^{-1}$ lies at a

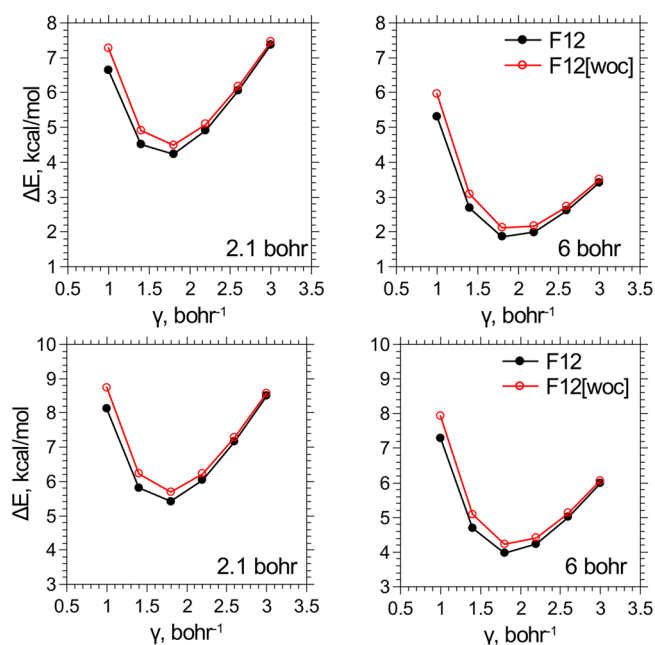


Figure 5. γ dependence of the basis-set incompleteness error for N_2 (above) and CO (below) molecules for interatomic distances of 2.1 and 6 bohr.

higher value than in CCSD-F12 theory for these molecules,³⁷ which is $\sim 1.4 a_u^{-1}$. The fact that short ranged correlation factors perform better is presumably because using the reference orbitals to build geminal basis functions is less physically meaningful in ODCD theory than in CCSD-F12 theory. In both molecules, there is also a slight shift of the optimal γ to larger values for stretched geometries. Nevertheless we find that, just as in CCSD-F12 theory, very good results are obtained for relative energies using the fixed amplitude approach with a correlation length scale of $1 a_u^{-1}$, even for the strongly correlated regime at stretched geometries.

Additionally we have investigated the accuracy of $ODCD_{F12a}$ reaction energies compared to $ODCD/CBS$, approximate $CCSDT(Q)/CBS$, and zero-point-energy back-corrected experimental results for a test set from ref 38, which are all well described by a single-reference determinant. The $ODCD/CBS$ reaction energies have been obtained from a $aug-cc-pVQZ-aug-cc-pV5Z$ extrapolation for most of the reactions. For three reactions involving cyclopropene, cyclobutene, and benzene the basis-set limit has been estimated from a $aug-cc-pVTZ-aug-cc-pVQZ$ extrapolation, and for a reaction involving LiH (for which we do not use frozen-core approximation) we have used a $aug-cc-pwCVQZ-aug-cc-pwCV5Z$ extrapolation. The results can be found in Table 1. Concerning the basis-set incompleteness error, we find that the error from $ODCD_{F12a}$ with an $aug-cc-pVTZ$ basis is smaller than that of $ODCD/aug-cc-pVQZ$. In addition to $ODCD_{F12a}$, we examined the performance of a range of F12 approximations: using the T_2 amplitudes in place of the Lagrange multipliers; not using the amplitude relaxation correction; adding a large imaginary shift to the relaxation amplitude update; using the DCSD singles residual for the amplitude relaxation and the DCSD CABS singles correction, denoted $[f_{ai}]$. For these single-reference systems, all F12 variants perform similarly. The mean absolute error with respect to back-corrected experimental or near basis set limit $CCSDT(Q)$ energies is within 1 kcal/mol for $ODCD_{F12a}$, and maximum errors are 4 kcal/mol. This is very

Table 1. Statistical Measures of Errors in Reaction Energies for a Test Set from Reference 38: Mean Absolute Deviation (MAD), Root Mean Squared Deviation (RMSD), and Maximal Deviation (MAX) in Kilocalories per Mole of $ODCD_{F12a}$ and Various Approximations to It, with Respect to $ODCD/CBS$, Approximate $CCSDT(Q)$ -F12,¹⁵ and Back-Corrected Experimental³⁸ Reaction Energies

Methods	MAD	RMSD	MAX
vs $ODCD/CBS$			
$ODCD_{F12a}$	0.154	0.209	0.59
$ODCD_{F12a}[T_2]$	0.155	0.208	0.53
$ODCD_{F12a}[woc]$	0.161	0.216	0.52
$ODCD_{F12a}, \omega = 1$	0.155	0.210	0.59
$ODCD_{F12a}[f_{ai}]$	0.188	0.308	0.97
$ODCD, aVQZ$	0.216	0.335	1.28
vs $CCSDT(Q)$ -F12			
$ODCD_{F12a}$	0.828	1.268	4.42
$ODCD_{F12a}[T_2]$	0.833	1.272	4.47
$ODCD_{F12a}[woc]$	0.823	1.267	4.47
$ODCD_{F12a}, \omega = 1$	0.827	1.267	4.43
$ODCD_{F12a}[f_{ai}]$	0.819	1.176	3.58
$SCS-ODCD_{F12a}[f_{ai}]$	0.623	0.895	3.30
vs experiment			
$ODCD_{F12a}$	0.947	1.263	3.67
$ODCD_{F12a}[T_2]$	0.954	1.272	3.71
$ODCD_{F12a}[woc]$	0.948	1.263	3.71
$ODCD_{F12a}, \omega = 1$	0.946	1.262	3.67
$ODCD_{F12a}[f_{ai}]$	0.936	1.195	2.96
$SCS-ODCD_{F12a}[f_{ai}]$	0.807	1.040	2.55

impressive accuracy for a doubles theory. Spin-component scaling,³⁹ applied previously to DCSD,⁴⁰ can also be used for ODCD and improves the reaction energies results further.

4. CONCLUSIONS

Orbital-optimized explicitly correlated methods are made practical by using Valeev's perturbative posthoc F12 approach. For strongly correlated electronic structures, the accuracy of the F12 correction is greatly improved by the availability of the Lagrange multipliers in ODCD theory, since they are not well approximated by contravariant amplitudes in this regime. The orbital-optimized explicitly correlated distinguishable cluster approach can be used in situations where orbital relaxation is large and the DCSD-F12 method breaks down. The amplitude relaxation correction introduced in ref 23 that improves the posthoc F12 correction can be applied to explicitly correlated ODCD theory in both weakly and strongly correlated regimes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.8b01047.

Potential energy and dipole moment curves of CO molecule (PDF)

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Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Čížek, J. On the Correlation Problem in Atomic and Molecular Systems. Calculation of Wavefunction Components in Ursell-Type Expansion Using Quantum-Field Theoretical Methods. *J. Chem. Phys.* **1966**, *45*, 4256–4266.
- (2) Purvis, G. D.; Bartlett, R. J. A full coupled-cluster singles and doubles model: The inclusion of disconnected triples. *J. Chem. Phys.* **1982**, *76*, 1910–1918.
- (3) Thouless, D. J. Stability conditions and nuclear rotations in the Hartree-Fock theory. *Nucl. Phys.* **1960**, *21*, 225.
- (4) Brueckner, K. A. Nuclear Saturation and Two-Body Forces. II. Tensor Forces. *Phys. Rev.* **1954**, *96*, 508.
- (5) Nesbet, R. K. Brueckner's Theory and the Method of Superposition of Configurations. *Phys. Rev.* **1958**, *109*, 1632.
- (6) Scuseria, G. E.; Schaefer, H. F., III The optimization of molecular orbitals for coupled cluster wavefunctions. *Chem. Phys. Lett.* **1987**, *142*, 354.
- (7) Kollmar, C.; Heßelmann, A. The role of orbital transformations in coupled-pair functionals. *Theor. Chem. Acc.* **2010**, *127*, 311.
- (8) Robinson, J. B.; Knowles, P. J. Quasi-variational coupled cluster theory. *J. Chem. Phys.* **2012**, *136*, 054114.
- (9) Bozkaya, U.; Turney, J. M.; Yamaguchi, Y.; Schaefer, H. F.; Sherrill, C. D. Quadratically convergent algorithm for orbital optimization in the orbital-optimized coupled-cluster doubles method and in orbital-optimized second-order Møller-Plesset perturbation theory. *J. Chem. Phys.* **2011**, *135*, 104103. 00010.
- (10) Bozkaya, U.; Sherrill, C. D. Orbital-optimized coupled-electron pair theory and its analytic gradients: Accurate equilibrium geometries, harmonic vibrational frequencies, and hydrogen transfer reactions. *J. Chem. Phys.* **2013**, *139*, 054104.
- (11) Bozkaya, U. Orbital-optimized linearized coupled-cluster doubles with density-fitting and Cholesky decomposition approximations: an efficient implementation. *Phys. Chem. Chem. Phys.* **2016**, *18*, 11362–11373.
- (12) Sokolov, A. Y.; Schaefer, H. F., III; Kutzelnigg, W. Density cumulant functional theory from a unitary transformation: N-representability, three-particle correlation effects, and application to O₄⁺. *J. Chem. Phys.* **2014**, *141*, 074111.
- (13) Kats, D.; Manby, F. R. Communication: The distinguishable cluster approximation. *J. Chem. Phys.* **2013**, *139*, 021102.
- (14) Kats, D. Communication: The distinguishable cluster approximation. II. The role of orbital relaxation. *J. Chem. Phys.* **2014**, *141*, 061101.
- (15) Kats, D. The distinguishable cluster approach from a screened Coulomb formalism. *J. Chem. Phys.* **2016**, *144*, 044102.
- (16) Ten-no, S. Explicitly correlated wave functions: summary and perspective. *Theor. Chem. Acc.* **2012**, *131*, 1070.
- (17) Hättig, C.; Klopper, W.; Köhn, A.; Tew, D. P. Explicitly Correlated Electrons in Molecules. *Chem. Rev.* **2012**, *112*, 4–74.
- (18) Kong, L.; Bischoff, F. A.; Valeev, E. F. Explicitly Correlated R12/F12 Methods for Electronic Structure. *Chem. Rev.* **2012**, *112*, 75–107.
- (19) Kats, D.; Kreplin, D.; Werner, H.-J.; Manby, F. R. Accurate thermochemistry from explicitly correlated distinguishable cluster approximation. *J. Chem. Phys.* **2015**, *142*, 064111.
- (20) Tew, D. P. Explicitly correlated coupled-cluster theory with Brueckner orbitals. *J. Chem. Phys.* **2016**, *145*, 074103.
- (21) Valeev, E. F. Coupled-cluster methods with perturbative inclusion of explicitly correlated terms: a preliminary investigation. *Phys. Chem. Chem. Phys.* **2008**, *10*, 106–113.
- (22) Valeev, E. F.; Crawford, T. D. Simple coupled-cluster singles and doubles method with perturbative inclusion of triples and explicitly correlated geminals: The CCSD(T)_{RT} model. *J. Chem. Phys.* **2008**, *128*, 244113.
- (23) Tew, D. P.; Kats, D. Relaxing Constrained Amplitudes: Improved F12 Treatments of Orbital Optimization and Core-Valence Correlation Energies. *J. Chem. Theory Comput.* **2018**, *14*, 5435.
- (24) Boguslawski, K.; Tecmer, P.; Limacher, P. A.; Johnson, P. A.; Ayers, P. W.; Bultinck, P.; De Baerdemacker, S.; Van Neck, D. Projected seniority-two orbital optimization of the antisymmetric product of one-reference orbital geminal. *J. Chem. Phys.* **2014**, *140*, 214114.
- (25) Henderson, T. M.; Bulik, I. W.; Stein, T.; Scuseria, G. E. Seniority-based coupled cluster theory. *J. Chem. Phys.* **2014**, *141*, 244104.
- (26) Adler, T. B.; Knizia, G.; Werner, H.-J. A simple and efficient CCSD(T)-F12 approximation. *J. Chem. Phys.* **2007**, *127*, 221106.
- (27) Knizia, G.; Adler, T. B.; Werner, H.-J. Simplified CCSD(T)-F12 methods: Theory and benchmarks. *J. Chem. Phys.* **2009**, *130*, 054104.
- (28) Tew, D. P.; Klopper, W.; Neiss, C.; Hättig, C. Quintuple-zeta quality coupled-cluster correlation energies with triple-zeta basis sets. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1921–1930.
- (29) Hättig, C.; Tew, D. P.; Köhn, A. Accurate and efficient approximations to explicitly correlated coupled-cluster singles and doubles, CCSD-F12. *J. Chem. Phys.* **2010**, *132*, 231102.
- (30) Köhn, A.; Tew, D. P. Explicitly correlated coupled-cluster theory using cusp conditions. I. Perturbation analysis of coupled-cluster singles and doubles (CCSD-F12). *J. Chem. Phys.* **2010**, *133*, 174117.
- (31) Kesharwani, M. K.; Sylvetsky, N.; Köhn, A.; Tew, D. P.; Martin, J. M. L. Do CCSD and approximate CCSD-F12 variants converge to the same basis set limits? The case of atomization energies. *J. Chem. Phys.* **2018**, *149*, 154109.
- (32) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Györffy, W.; Kats, D.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G.; Shamasundar, K. R.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hesselmann, A.; Hetzer, G.; Hrenar, T.; Jansen, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; O'Neill, D. P.; Palmieri, P.; Peng, D.; Pflüger, K.; Pitzer, R.; Reiher, M.; Shiozaki, T.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M. *MOLPRO*, version 2015.1, a package of ab initio programs; 2015; see <http://www.molpro.net>.
- (33) Forsberg, N.; Malmqvist, P.-Å. Multiconfiguration perturbation theory with imaginary level shift. *Chem. Phys. Lett.* **1997**, *274*, 196.
- (34) Taube, A. G.; Bartlett, R. J. Rethinking linearized coupled-cluster theory. *J. Chem. Phys.* **2009**, *130*, 144112.
- (35) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. Basis-set convergence of correlated calculations on water. *J. Chem. Phys.* **1997**, *106*, 9639.
- (36) Shiozaki, T.; Knizia, G.; Werner, H.-J. Explicitly correlated multireference configuration interaction: MRCl-F12. *J. Chem. Phys.* **2011**, *134*, 034113.
- (37) Tew, D. P.; Klopper, W. New correlation factors for explicitly correlated electronic wave functions. *J. Chem. Phys.* **2005**, *123*, 074101.
- (38) Huntington, L. M. J.; Hansen, A.; Neese, F.; Nooijen, M. Accurate thermochemistry from a parameterized coupled-cluster singles and doubles model and a local pair natural orbital based implementation for applications to larger systems. *J. Chem. Phys.* **2012**, *136*, 064101.
- (39) Grimme, S. Improved second-order Møller-Plesset perturbation theory by separate scaling of parallel- and antiparallel-spin pair correlation energies. *J. Chem. Phys.* **2003**, *118*, 9095–9102.
- (40) Kats, D. Improving the distinguishable cluster results: spin-component scaling. *Mol. Phys.* **2018**, *116*, 1435.