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Explicitly-correlated ring-coupled-cluster-doubles theory: Including exchange for computations on closed-shell systems



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ABSTRACT

Random-phase-approximation (RPA) methods have proven to be powerful tools in electronic-structure theory, being non-empirical, computationally efficient and broadly applicable to a variety of molecular systems including small-gap systems, transition-metal compounds and dispersion-dominated complexes. Applications are however hindered due to the slow basis-set convergence of the electron-correlation energy with the one-electron basis. As a remedy, we present approximate explicitly-correlated RPA approaches based on the ring-coupled-cluster-doubles formulation including exchange contributions. Test calculations demonstrate that the basis-set convergence of correlation energies is drastically accelerated through the explicitly-correlated approach, reaching 99% of the basis-set limit with triple-zeta basis sets. When implemented in close analogy to early work by Szabo and Ostlund [36], the new explicitly-correlated ring-coupled-cluster-doubles approach including exchange has the perspective to become a valuable tool in the framework of symmetry-adapted perturbation theory (SAPT) for the computation of dispersion energies of molecular complexes of weakly interacting closed-shell systems.

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1. Introduction

Wave-function methods based on molecular orbitals suffer from the slow convergence of the correlation energy with respect to the size of the basis set. While the reference energy converges exponentially with increasing cardinal number X [1], much slower asymptotics proportional to X^{-3} are found for the correlation energy [2],

$$|E_c(X) - E_c(\infty)| \propto a/X^3. \quad (1)$$

The power law describes the convergence of the correlation energy $E_c(X)$, obtained within a basis of cardinal number X , towards the basis-set limit $E_c(\infty)$. It was shown to fit for a variety of perturbation-theory and coupled-cluster methods [3] as well as for the random-phase approximation (RPA), which is a post-Kohn-Sham (KS) approach relying on molecular orbitals and which has recently attracted much attention [4–7]. RPA has become popular as a computationally efficient and broadly applicable method, capturing long-range dynamic [8,9] as well as static correlation [10]. Applications on larger molecules are however hindered due to its slow basis-set convergence. In general, basis sets of quadruple-zeta quality are found to be necessary if at all sufficient to reach satis-

fyng accuracy [11,12]. However, several strategies to accelerate convergence and thus avoid the use of high angular momentum basis functions exist.

Firstly, as convergence is smooth, asymptotic laws like in Eq. (1) allow to set up extrapolation schemes [3,13–15]. Fabiano et al. for example applied various extrapolation formula to post-KS RPA calculations [12], investigating test sets of first- and second-row molecules using Dunning's correlation-consistent basis sets cc-pVXZ [16–18]. They showed that two-point extrapolation schemes using quintuple- and sextuple-zeta basis sets with optimized parameters achieve an accuracy of 2 mE_h for RPA correlation energies, which has to be compared with an error of 10 mE_h for standard septuple-zeta results. Extrapolation including quadruple-zeta basis sets is however found to be of too low quality, and Fabiano et al. therefore recommend to use either semiempirical extrapolations or basis sets with higher cardinal numbers.

Secondly, another strategy to circumvent the intrinsically slow basis-set convergence of wave-function methods is given by range separation [19]. Range-separated RPA methods [20–22] partition the Coulomb electron–electron interaction into a short-range density-functional-theory (DFT) and a long-range RPA contribution. Convergence is accelerated as the short-range part of the correlation hole, whose accurate description requires high-angular momentum basis functions, is now treated within density-functional theory. Franck et al. showed that, for range-separated

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approaches, both the short- and long-range parts converge exponentially with the maximum angular momentum quantum number [23]. However, modifying the Hamiltonian by range separation always implicates a change of the corresponding basis-set limit.

Hence, aiming to accelerate convergence without changing the underlying correlation method requires to go for a third strategy: explicitly-correlated (or F12) wave-function methods [24]. The idea of F12 methods is to improve the description of the Coulomb hole by taking into account geminals which explicitly depend on the inter-electronic distance [25,26]. By doing so, correlation energies converge proportional to X^{-7} [27], which allows to investigate basis-set limits without falling back onto large basis sets. In our recent paper on explicitly-correlated direct RPA (dRPA) [28], we demonstrate that triple-zeta basis sets are sufficient to reach sextuple-zeta accuracy for atomization energies. For interaction energies, the gain in terms of the possible reduction of the basis-set size is about one cardinal number. For interaction energies, for example, quadruple-zeta quality is reached with triple-zeta basis-set size.

Our investigations presented in Ref. [28] were restricted to the dRPA approach, in which exchange contributions are neglected. In consequence, the method suffers from the self-interaction error leading to an incorrect description of bond dissociation as well as a strong overestimation of correlation energies. For conventional RPA, different exchange RPA methods have been developed as a remedy, based on perturbation theory [29–31], the adiabatic connection [32,33], or the equivalence of RPA with ring-coupled-cluster-doubles theory [34–39]. Among the latter approaches are two approximate rCCD variants developed by Szabo and Ostlund in the 1970s to calculate correlation energies for interacting closed-shell systems [36,37]. Recently, Toulouse and Mussard et al. adopted Szabo and Ostlund's ideas to set up analogous rCCD variants with range separation [40,41]. Their findings, based on the examination of rare-gas dimers, weakly interacting complexes, atomization energies and reaction barrier heights, proved these approximate rCCD approaches as very promising for general chemical applications.

Based on the work by Toulouse and Mussard et al., we have developed analogous explicitly-correlated rCCD approaches for closed- and open-shell systems, denoted rCCD(F12). In contrast to the direct counterpart, drCCD(F12) [28], spin-flipped excitations have to be taken into account for open-shell rCCD(F12) theory, and spin adaptation in terms of singlet and triplet amplitudes is required for the corresponding closed-shell formulation based on spatial orbitals (cf. Section 2.1). The thereby entailed triplet and spin-flipped instabilities can however be avoided when introducing the approximations suggested by Szabo and Ostlund (cf. Section 2.2). Furthermore, the geminal amplitudes account for antisymmetry (cf. Section 2.3) in such a way that all rCCD(F12) variants yield the MP2-F12 correlation energy at second-order perturbation theory (cf. Section 2.4). The derived rCCD(F12) approaches were implemented in the Turbomole program package based on the already available drCCD(F12) code [42], allowing for the analysis of the basis-set convergence of correlation and atomization energies for an exemplary test set of small molecules (cf. Section 3).

For the future, we plan to employ rCCD(F12)-based approaches for the computation of dispersion-energy contributions in the framework of (KS-based) symmetry-adapted perturbation theory (SAPT) [43–46]. In some of our recent work [47,48], we have corrected the basis-set-incompleteness error in SAPT dispersion energies by adding corrections computed at the level of explicitly-correlated second-order perturbation theory (MP2-F12) [49], but rCCD(F12)-based approaches could provide much more accurate corrections for basis set incompleteness.

2. Theory

2.1. Symmetry of the ring-coupled-cluster-doubles amplitudes

In their 1977 papers [36,37], Szabo and Ostlund start from a reformulation of the RPA eigenvalue problem that is based on double-excitation amplitudes \mathbf{T} and the corresponding residual equation $\Omega = \mathbf{0}$, with

$$\Omega = \mathbf{T}\mathbf{D} + \mathbf{B} + \mathbf{A}\mathbf{T} + \mathbf{T}\mathbf{A} + \mathbf{T}\mathbf{B}\mathbf{T}. \quad (2)$$

All terms in Eq. (2) bear the important characteristic that they solely represent particle-hole interactions which correspond to ring diagrams. The method is therefore, often synonymously to RPA, called “ring-coupled-cluster-doubles” (rCCD) approach. Depending on the definition of the matrices \mathbf{A} and \mathbf{B} , it is furthermore common to discriminate between the *direct* ring-coupled-cluster-doubles (drCCD) and full ring-coupled-cluster-doubles (rCCD) approaches. The direct approach neglects exchange and the matrices \mathbf{A} and \mathbf{B} therefore only include Coulomb contributions, $A_{ib}^{aj} = \langle aj||ib \rangle$ and $B_{ij}^{ab} = \langle ab||ij \rangle$. The rCCD approach, in contrast, assumes *antisymmetrized* two-electron integrals,

$$\bar{A}_{ib}^{aj} = \langle aj||ib \rangle = \langle aj||ib \rangle - \langle aj||bi \rangle, \quad (3)$$

$$\bar{B}_{ij}^{ab} = \langle ab||ij \rangle = \langle ab||ij \rangle - \langle ab||ji \rangle. \quad (4)$$

Here and in the following, antisymmetrized matrices are indicated with an overline and, to distinguish the direct-ring CCD amplitudes from the ring CCD ones, we use the matrix \mathbf{T} for the *direct-ring* CCD and $\bar{\mathbf{T}}$ for the *ring* CCD amplitudes. All spin orbitals are assumed to be real, and $\{i, j, \dots\}$ denote occupied spin orbitals while $\{a, b, \dots\}$ denote virtual spin orbitals, respectively. The matrix \mathbf{D} represents for both drCCD and rCCD the zeroth-order term $D_{ijab} = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j$, with the (Kohn–Sham) molecular orbital energies ε . Note that the above notation should be understood in such a manner that the row (ia) and column (jb) indices of the matrices in Eq. (2) are, for example, as follows: $(\mathbf{A})_{ia,jb} = A_{ib}^{aj}$, $(\mathbf{T})_{ia,jb} = T_{ij}^{ab}$ and so on, where T_{ij}^{ab} is a direct ring-coupled-cluster amplitude for the double substitution of the occupied spin-orbital pair ij with the virtual pair ab .

The restriction to ring diagrams in the residual equation has the consequence that neither the so-determined drCCD nor the rCCD amplitudes are antisymmetric with respect to the individual exchange of the index i with j or the index a with b , that is, $t_{ij}^{ab} \neq -t_{ji}^{ab} = -t_{ij}^{ba}$ and $\bar{t}_{ij}^{ab} \neq -\bar{t}_{ji}^{ab} = -\bar{t}_{ij}^{ba}$. This “missing antisymmetry” imposes important restrictions on the implementation of open- and closed-shell rCCD, as we will see in the following.

First of all, the drCCD and rCCD correlation-energy equations,

$$E_c^{\text{drCCD}} = \frac{1}{2} \text{tr}[\mathbf{B}\mathbf{T}], \quad (5)$$

$$E_c^{\text{rCCD}} = \frac{1}{4} \text{tr}[\bar{\mathbf{B}}\bar{\mathbf{T}}], \quad (6)$$

are not equivalent and the rCCD correlation energy can – in contrast to standard coupled-cluster schemes like coupled-cluster-doubles CCD – only be formulated in terms of the antisymmetrized matrix $\bar{\mathbf{B}}$. This furthermore implies that open-shell rCCD implementations have to rely on the spin-integrated formulation of Eq. (6),

$$E_c^{\text{rCCD}} = \frac{1}{4} \sum_{IJAB} \sum_{\sigma, \sigma' \neq \sigma} \left[\bar{B}_{A\sigma B\sigma'}^{I\sigma J\sigma'} \bar{t}_{J\sigma I\sigma'}^{B\sigma A\sigma'} + B_{A\sigma B\sigma'}^{I\sigma J\sigma'} \bar{t}_{J\sigma I\sigma'}^{B\sigma A\sigma'} - B_{A\sigma B\sigma'}^{I\sigma J\sigma'} \bar{t}_{J\sigma I\sigma'}^{B\sigma A\sigma'} \right], \quad (7)$$

requiring to take into account spin-flipped excitations, parameterized by the amplitudes $\bar{t}_{I\sigma' J\sigma}^{A\sigma B\sigma'}$ [50]. For spin integration, spin orbitals

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