



Research paper

Explicitly-correlated double ionization potentials and double electron attachment equation-of-motion coupled cluster methods

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ABSTRACT

Double ionization and double electron attachment equation-of-motion methods, based on linearly approximated explicitly correlated coupled-cluster singles and doubles [CCSD(F12)] are formulated and implemented. An extension of double electron attachment operator is introduced for proper account of short-range correlation effects in states with two additional electrons. Numerical tests for set of doubly ionized and doubly electron attached states of several molecules have shown a good agreement between obtained explicitly-correlated results and the corresponding complete basis set limit values already at double- ζ level.

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1. Introduction

Computational methods, based on the equation-of-motion coupled-cluster methods (EOM-CC) provide a very convenient way to calculate quantities related to differential energies, such as ionization potentials (IP-EOM-CC) [1], electron affinities (EA-EOM-CC) [2], excitation energies (EE-EOM-CC) [3], double ionization potentials (DIP-EOM-CC) [4], double electron attachment (DEA-EOM-CC) [5] and some related properties [6]. These methods are related to the Fock-space coupled-cluster (FS-CC) formalism whose solutions for the $S(p,h)$ sectors of the effective hamiltonian $\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$, $S(0,1)$ and $S(1,0)$, are equivalent to those of IP-EOM-CC and EA-EOM-CC. The former are obtained from a more complicated computational procedure, so that today, the EOM route is preferred. The correspondence, however, ensures exact extensivity and intensity of target ionization potentials and electron affinities [7–9], despite the linear CI-like operator for the target state in EOM-CC, because the Fock space operator is formally an exponential, like in the CC ground. In the case of the $S(0,2)$ and $S(2,0)$, sectors the results are slightly different between Fock-space coupled-cluster and DIP/DEA-EOM-CCSD methods. All the EOM-CC wave functions are pure in spin when based upon a closed shell reference state, enabling \bar{H} to be readily described in terms of spin-free cluster amplitudes. Both FS-CC and DIP/DEA-EOM-CC are widely used for treatment of multireference problems, like bond breaking and calculation of excitation energies of systems with open-shell ground states [10–12]. Also, the calculation of double

ionization potentials are immediately useful to interpret Auger spectra. Yet another application of DIP-EOM-CC is to the ionization spectra of doublet radicals, where a closed-shell anion can be used as a reference state [12]. The excitation spectra of open-shell systems can be obtained from DEA-EOM-CC calculations using the corresponding doubly ionized closed-shell reference in the underlying CC step [12]. The computational cost of such highly applicable DIP-EOM-CCSD and DEA-EOM-CCSD methods is proportional to $nocc^3 nvirt$ and $nvirt^3 nocc$, while the underlying CCSD scheme scales like $nvirt^4 nocc^2$, where $nocc$ and $nvirt$ are numbers of occupied and virtual orbitals in the system. Previous studies for excitation energies, electron affinities and ionization potentials have shown a strong dependence of target quantities upon the quality of used basis sets [13–16]. In the case of the addition and removal of two electrons from the system, the ‘differential’ correlation energies are very large, and the dependence of target double ionization potentials and double electron affinities upon choice of bases can be even larger than that for IPs and EAs. Indeed, in all standard basis methods the difference between the calculated correlation energy and the corresponding complete basis set (CBS) value is proportional to $(L_{max} + 1)^{-3}$ [17], where L_{max} is the highest angular momentum involved in the partial wave expansion. Thus, obtaining highly-accurate converged results might be computationally costly.

The use of an explicitly-correlated approach can be an attractive alternative. After the introduction of even simple linear- r_{12} [18] geminals the convergence of the correlation energy goes as $(L_{max} + 1)^{-7}$ [19]. Consequently, the explicitly correlated coupled-cluster method developed by Kutzelnigg and Noga [20] has become an efficient and convenient approach for the calculation of

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molecular systems. Modern implementations of CC-F12 methods use Kato's cusp conditions for the definition of geminal amplitudes (the so-called SP-*Ansatz*) [21] and utilize short-range Slater geminals, introduced by Ten-no [22]. A linearly approximated F12 coupled cluster singles and doubles method known as CCSD(F12) that retains only linear-F12 terms [23], is computationally less expensive than full CC-F12, but provides similar accuracy for target correlation energies. Explicitly-correlated EOM-CCSD schemes have been presented in the literature for IPs, EAs and excitation energies, the latter by Köhn [24] in the linear response framework. Also, the explicitly-correlated treatment of response properties has been reported recently [25–27]. For the case of excited and electron-attached states an extended XSP-*Ansatz* was introduced in order to describe short-range correlation effects of promoted or attached electrons [24]. Similarly, if two electrons are attached it is necessary to extend the DEA-EOM-CCSD(F12) attachment operator for the proper description of the state with two additional electrons. In this letter we report on the formulation and implementation of explicitly-correlated DIP and DEA-EOM-CCSD(F12) methods. In order to estimate the accuracy of the methods developed, test calculations are conducted for DIPs and DEAs of several molecules.

2. Theory

Henceforth, we denote occupied, virtual, virtuals from the complete basis set and general orbitals in a given basis set as $ij, \dots, ab, \dots, \alpha, \beta, \dots$ and pq, \dots , respectively.

2.1. CCSD(F12) model for the neutral state

Within the coupled-cluster (CC) theory the ground-state wave function of a neutral system has the form

$$\Psi_0 = e^{\widehat{T}_1 + \widehat{T}_2 + \dots} \Phi_0, \quad (1)$$

where \widehat{T}_n are regular cluster operators and Φ_0 – any single determinant reference, but frequently the ground-state Hartree-Fock determinant. The details of CC theory with the corresponding working equations have been presented in numerous articles and textbooks. In this work the coupled cluster singles and doubles (CCSD) neutral-state wave function will be used:

$$\Psi_0(\text{CCSD}) = e^{\widehat{T}_1 + \widehat{T}_2} \Phi_0. \quad (2)$$

The linearly approximated explicitly-correlated extension of CCSD, known as CCSD(F12) [23] includes an additional operator, \widehat{T}'_2 which takes care of short-range correlation effects:

$$\Psi_0(\text{CCSD(F12)}) = e^{\widehat{T}_1 + \widehat{T}_2 + \widehat{T}'_2} \Phi_0, \quad (3)$$

The \widehat{T}'_2 operator has the form:

$$\widehat{T}'_2 = \frac{1}{2} \sum_{ijkl} t_{kl}^{ij} \left(\sum_{\alpha\beta} \langle \alpha\beta | f_{12} | kl \rangle \widehat{E}_{\alpha i} \widehat{E}_{\beta j} - \sum_{ab} \langle ab | f_{12} | kl \rangle \widehat{E}_{a i} \widehat{E}_{b j} \right). \quad (4)$$

Here \widehat{E}_{pq} denote unitary group generators,

$$\widehat{E}_{pq} = a_{p1}^+ a_{q1} + a_{p1}^+ a_{q1}. \quad (5)$$

and f_{12} are Slater-type geminals[22]:

$$f_{12} = -\frac{1}{\gamma} \exp(-\gamma r_{12}). \quad (6)$$

Geminal amplitudes are defined according to Kato's cusp conditions[21]: $t_{ij}^{ij} = \frac{3}{8}$, $t_{ji}^{ij} = \frac{1}{8}$, $t_{ii}^{ii} = \frac{1}{2}$, while all the remaining t_{kl}^{ij} amplitudes are set equal to zero.

2.2. DIP and DEA-EOM-CCSD(F12) methods

Within the DIP-EOM-CCSD(F12) approach the wave function of a doubly-ionized state has the form:

$$\Psi^{2+} = \widehat{R}^{2+} \Psi_0(\text{CCSD(F12)}), \quad (7)$$

where \widehat{R}^{2+} can be presented as:

$$\widehat{R}^{2+} = \widehat{R}_1^{2+} + \widehat{R}_2^{2+}, \quad (8)$$

$$\widehat{R}_1^{2+} = \frac{1}{2} \sum_{ij} r_{ij} \{ a_j a_i \}, \quad (9)$$

$$\widehat{R}_2^{2+} = \frac{1}{6} \sum_{ij,ka} r_{ijk}^a \{ a_a^\dagger a_k a_j a_i \}. \quad (10)$$

Working equations for the DIP-EOM-CCSD(F12) method can be obtained by the projection of \bar{H} onto the proper excitation manifolds:

$$\langle \Phi_{ij} | [\bar{H}, \widehat{R}^{2+}(k)] | \Phi_0 \rangle = \omega_k \langle \Phi_{ij} | \widehat{R}^{2+}(k) | \Phi_0 \rangle, \quad (11)$$

$$\langle \Phi_{ijk}^a | [\bar{H}, \widehat{R}^{2+}(k)] | \Phi_0 \rangle = \omega_k \langle \Phi_{ijk}^a | \widehat{R}^{2+}(k) | \Phi_0 \rangle, \quad (12)$$

where Φ_{ij} and Φ_{ijk}^a are doubly-ionized Slater determinants, index k stands for numbering of doubly-ionized states and ω_k is the corresponding double ionization potential. Detailed diagrammatic representation of these equations can be found in Ref. [10]. The explicitly-correlated version of the Eqs. (11) and (12) has the same form, but the elements of \bar{H} will be augmented by terms originating from geminals[13]. There is no contribution of F(12) to the R-equations for the DIP problem.

The DEA-EOM-CCSD wave function of the target doubly electron attached state assumes the following form:

$$\Psi^{2-} = \widehat{R}^{2-} \Psi_0(\text{CCSD(F12)}), \quad (13)$$

and the \widehat{R}^{2-} operator can be written as:

$$\widehat{R}^{2-} = \widehat{R}_1^{2-} + \widehat{R}_2^{2-} + \widehat{R}_3^{2-}, \quad (14)$$

$$\widehat{R}_1^{2-} = \frac{1}{2} \sum_{a,b} r^{ab} \{ a_a^\dagger a_b^\dagger \}, \quad (15)$$

$$\widehat{R}_2^{2-} = \frac{1}{6} \sum_{a,b,c,i} r_i^{abc} \{ a_a^\dagger a_b^\dagger a_c^\dagger a_i \}, \quad (16)$$

$$\begin{aligned} \widehat{R}_3^{2-} = & \frac{1}{2} \sum_{i,k,c,d,f} (r^{fc}) t_{id}^{kc} \left(\sum_{\alpha,\beta} \langle \alpha\beta | f_{12} | dk \rangle \{ a_\alpha^\dagger a_\beta^\dagger a_i^\dagger a_i \} - \sum_{a,b} \langle ab | f_{12} | dk \rangle \{ a_a^\dagger a_b^\dagger a_i^\dagger a_i \} \right) + \\ & + \frac{1}{2} \sum_{i,k,c,d,f} (r^{fc}) t_{dk}^{ic} \left(\sum_{\alpha,\beta} \langle \alpha\beta | f_{12} | kd \rangle \{ a_\alpha^\dagger a_\beta^\dagger a_i^\dagger a_i \} - \sum_{a,b} \langle ab | f_{12} | kd \rangle \{ a_a^\dagger a_b^\dagger a_i^\dagger a_i \} \right). \end{aligned} \quad (17)$$

Geminal amplitudes in the Eq. (17) are fixed using the known cusp conditions:

$$t_{ia}^{ia} = \frac{3}{8}, t_{ai}^{ia} = \frac{1}{8}, \quad (18)$$

while all the remaining t_{jb}^{ia} and t_{bj}^{ia} amplitudes are set equal to zero. The working equations for r^{ab} and r_i^{abc} amplitudes have form:

$$\langle \Phi^{ab} | [\bar{H}, \widehat{R}^{2-}(k)] | \Phi_0 \rangle = \omega_k \langle \Phi^{ab} | \widehat{R}^{2-}(k) | \Phi_0 \rangle, \quad (19)$$

$$\langle \Phi_i^{abc} | [\bar{H}, \widehat{R}^{2-}(k)] | \Phi_0 \rangle = \omega_k \langle \Phi_i^{abc} | \widehat{R}^{2-}(k) | \Phi_0 \rangle, \quad (20)$$

where Φ^{ab} and Φ_i^{abc} are Slater determinants with two extra electrons and ω_k is the corresponding two-electron affinity. Detailed

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