Equation-of-motion coupled cluster method for ionized states with partial inclusion of connected triples: Assessment of the accuracy in regular and explicitly-correlated approaches

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ABSTRACT

Equation-of-motion coupled cluster method for ionized states with partial inclusion of connected triples is implemented within both regular and explicitly-correlated approaches. The computational scaling of proposed scheme is N^6, so the IP-EOM part is not more expensive than the underlying neutral-state CCSD calculation. Numerical results for the set of molecules and their ionized states are in good agreement with highly-accurate IP-EOM-CCSDT results. Comparison of predicted and experimental results for target ionization potentials shows an agreement between two sets with average deviation of ∼0.2 eV. Better agreement with IP-EOM-CCSDT results indicate that the most significant discrepancies may be related to the not enough accurate values of vertical ionization potentials, restored from experimental data.

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1. Introduction

The EOM-CC methodology is a convenient tool for the calculation of differential energies, such as ionization potentials (IP-EOM-CC) [1], electron affinities (EA-EOM-CC) [2], excitation energies (EE-EOM-CC) [3] double ionization potential (DIP) [4], and double electron attached (DEA) [5] states, and some other properties [6]. The key step of any EOM-CC calculation is the diagonalization of a non-Hermitian effective Hamiltonian $\overline{H} = e^{-\widehat{T}}\widehat{H}e^{\widehat{T}}$ based upon the ground or reference state amplitudes, T, in the corresponding sector of Fock space. The N-h and N+p spaces of $\overline{H}$ are used to obtain IPs and EAs, while the N-electron sector gives excitation energies. The IP-EOM-CC and EA-EOM-CC are directly related to the 1h and 1p sectors of the Fock-space coupled-cluster approach but provide a far better computational procedure. Thus they exhibit exact size-extensivity [7–9]. The related similarly-transformed EOM-CC (STEOM-CC) method has been developed by Nooijen and Bartlett [10] as a computationally less demanding alternative to EE-EOM-CC.

Nowadays, the EOM-CC algorithm [11,12], based on coupled-cluster singles and doubles (CCSD) has become a standard tool in quantum chemical calculations and can be routinely used for the treatment of molecular systems. The calculation of the principal IPs with the IP-EOM-CCSD method can provide an accuracy of a few tenths of electron-volt (eV) with respect to experimental data if reasonably augmented Gaussian bases are used [6]. The IP-EOM-CCSDT method, developed by Musiał et al. [13] significantly improves the accuracy, but the computational cost of this method is proportional to N^8, and, thus, can be applied only for small systems. On the other hand, the accuracy of the ionization potentials obtained is known to be quite dependent upon the chosen basis set. In order to circumvent this problem, the explicitly-correlated IP-EOM-CCSD(F12) was developed [14]. Results, reported in Ref. [14] indicate significant acceleration of convergence of target ionization potentials with the maximal angular momentum of the basis set, but comparison with experimental results shows an increase in the error with the number of electrons in the system which should not happen for a size-extensive method. Such inaccuracy can potentially be eliminated by the inclusion of triple excitations into the IP-EOM-CCSD(F12) scheme, which would have a computational cost proportional to N^7. In this Letter we explore an even more approximate method, IP-EOM(R3)-CCSD(F12) which scales

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like N^6 and includes both short-range Slater geminals and triple excitations to offer a balanced treatment of differential correlation energies. Following a discussion of the theory, a numerical test for a set of molecules and assessment is presented in the subsequent sections.

2. Theory

2.1. General considerations

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

$$\Psi_0 = e^{(\widehat{T_1} + \widehat{T_2} + \cdots)}\Phi_0, \tag{1}$$

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:

$$\Psi_0(\text{CCSD}) = e^{(\widehat{T_1} + \widehat{T_2})}\Phi_0. \tag{2}$$

The linearly approximated explicitly-correlated extension of CCSD, known as CCSD(F12) [15] includes an additional operator, $\widehat{T_2'}$ which takes care of short-range correlation effects:

$$\Psi_0(\text{CCSD(F12)}) = e^{(\widehat{T_1} + \widehat{T_2} + \widehat{T_2'})}\Phi_0. \tag{3}$$

The $\widehat{T_2'}$ operator has the form:

$$\widehat{T_2'} = \frac{1}{2}\sum_{ijkl} t_{kl}^{'ij}\left(\sum_{\alpha\beta}\langle\alpha\beta|f_{12}|kl\rangle\widehat{E}_{\alpha i}\widehat{E}_{\beta j} - \sum_{ab}\langle ab|f_{12}|kl\rangle\widehat{E}_{ai}\widehat{E}_{bj}\right). \tag{4}$$

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

$$\widehat{E}_{pq} = a_{p\uparrow}^+ a_{q\uparrow} + a_{p\downarrow}^+ a_{q\downarrow} \tag{5}$$

and f_{12} are Slater-type geminals [16]:

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

The symbols $i, j, \ldots, a, b, \ldots, \alpha, \beta, \ldots, p, q, \ldots$ are used respectively for occupied, virtuals, virtuals from the complete basis and all possible spin–orbitals. In our approach the IP-EOM-CC wave function of the target ionized state assumes the following form:

$$\Psi_{ion} = \widehat{R}\Psi_0(\text{CCSD/CCSD(F12)}) \tag{7}$$

where $\widehat{R} = (\widehat{R_1} + \widehat{R_2} + \widehat{R_3})$, and

$$\widehat{R_1} = \sum_i r_i a_i \tag{8}$$

$$\widehat{R_2} = \sum_{i,j,a} r_{ij}^a \{a_a^\dagger a_i a_j\} \tag{9}$$

$$\widehat{R_3} = \sum_{i,j,k,a,b} r_{ijk}^{ab}\{a_a^\dagger a_b^\dagger a_i a_j a_k\} \tag{10}$$

and $\Psi_0(\text{CCSD/CCSD(F12)})$ stands for either the regular or the explicitly-correlated CCSD solution.

Introducing the effective Hamiltonian

$$\overline{H} = e^{-\widehat{T}}He^{\widehat{T}} = \widetilde{H} + [\widetilde{H}, T_3] \tag{11}$$

$$\widetilde{H} = e^{(-T_1 - T_2)}He^{(T_1 + T_2)} \tag{12}$$

the IP-EOM-CC equations can be written as

$$[\widetilde{H}, \widehat{R}]|\Phi_0\rangle = \omega_k \widehat{R}|\Phi_0\rangle, \tag{13}$$

where ω_n is the ionization potential. The explicitly-correlated version of Eq. (13) has the same form as regular IP-EOM, but elements of $\widetilde{H}$ will be augmented by terms originating from geminals; detailed description is given in Ref. [14]. There is no direct contribution of (F12) to the R-equations for the IP problem.

Traditionally, IP-EOM methods are formulated in such a way that the excitation levels of the $\widehat{T}$ and $\widehat{R}$ operators are the same. The IP-EOM-CCSD and IP-EOM-CCSDT are examples of that. However, In our IP-EOM(R3)-CCSD approach the $\widehat{T}$ operator is taken from CCSD, while the $\widehat{R}$ operator is truncated at the level of triples. Even though $\widetilde{H}$ does not satisfy the coupled cluster T_3 equation, the structure of the EOM-CC equations is preserved for the case of ionization potentials and electron affinities, while for excitation energies an extra term will appear due to the presence of the r_0 term.

The main idea of an IP-EOM approach is to describe ionized states in terms of neutral state orbitals and cluster amplitudes and each term of Eq. (7) has its purpose. The $\widehat{R_1}$ operator creates ionized states by annihilation of one electron (one hole, 1h). The $\widehat{R_2}$ operator (2h1p) provides partial orbital relaxation in the ionized state, while for more complete inclusion of relaxation effects higher-order terms would be necessary. The double excitations of $\widehat{R_3}$ (3h2p) take into account correlation effects in the ionized state, thus, helping to provide a proper description of differential correlation effects.

2.2. Working equations

Eq. (13) can be written in terms of projections:

$$\langle\Phi_i|[\widetilde{H}, \widehat{R}]|\Phi_0\rangle = \omega_k\langle\Phi_i|\widehat{R}|\Phi_0\rangle \tag{14}$$

$$\langle\Phi_{ij}^a|[\widetilde{H}, \widehat{R}]|\Phi_0\rangle = \omega_k\langle\Phi_{ij}^a|\widehat{R}|\Phi_0\rangle \tag{15}$$

$$\langle\Phi_{ijk}^{ab}|[\widetilde{H}, \widehat{R}]|\Phi_0\rangle = \omega_k\langle\Phi_{ijk}^{ab}|\widehat{R}|\Phi_0\rangle \tag{16}$$

of which those due to $\widehat{R_3}$ are of interest, the rest simply being the IP-EOM-CCSD part of the equations. These $\widehat{R_3}$ specific terms are

$$\langle\Phi_i|[\widetilde{H}, \widehat{R_3}]|\Phi_0\rangle = \omega_k\langle\Phi_i|\widehat{R_1}|\Phi_0\rangle$$

$$\langle\Phi_{ij}^a|[\widetilde{H}, \widehat{R_3}]|\Phi_0\rangle = \omega_k\langle\Phi_{ij}^a|\widehat{R_2}|\Phi_0\rangle$$

$$\langle\Phi_{ijk}^{ab}|[\widetilde{H}, (\widehat{R_1} + \widehat{R_2} + \widehat{R_3})]|\Phi_0\rangle = \omega_k\langle\Phi_{ijk}^{ab}|\widehat{R_3}|\Phi_0\rangle$$

In our treatment of the $\widehat{R_3}$ operator we choose to exclude any terms that scale worse than N^6 to be consistent with the computational dependence of the CCSD reference state. We also eliminate the $\widehat{R_3}$ contributions to $\widehat{R_2}$ and the $\widehat{R_2}$ contribution to $\widehat{R_3}$ as a part of this approximation. So far, in the framework of our approach only $\widehat{R_3}$ and $\widehat{R_1}$ related terms are coupled directly, i.e. equations for $\widehat{R_1}$ contain contribution from $\widehat{R_3}$ and equations for $\widehat{R_3}$ contain only contribution from $\widehat{R_1}$. Such coupling provides account of influence of differential correlation effects on ionization amplitudes in $\widehat{R_1}$ operator, and, thus more accurate vertical ionization potentials are expected. Decoupling of $\widehat{R_3}$ and $\widehat{R_2}$ preserves N^6 computational scaling, but description of interference of relaxation and differential correlation effects cannot be done in such imbalanced scheme. As a consequence, results for ionized states with significant relaxation, like inner valence or core states may suffer from errors. Nevertheless, the IP-EOM(R3)-CCSD should be less imbalanced and more accurate then the traditional IP-EOM-CCSD method without any inclusion of $\widehat{R_3}$ terms.