

Equation-of-motion coupled cluster method with full inclusion of the connected triple excitations for ionized states: IP-EOM-CCSDT

Monika Musiał

Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida 32611

Stanisław A. Kucharski

Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland

Rodney J. Bartlett

Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida 32611

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The equation-of-motion (EOM) coupled cluster (CC) method with full inclusion of the connected triple excitations for ionization energies has been formulated and implemented. Using proper factorization of the three- and four-body parts of the effective Hamiltonian, an efficient computational procedure has been proposed for IP-EOM-CCSDT which at the EOM level requires no-higher-than $n_{\text{occ}}^3 n_{\text{vir}}^4$ scaling. The method is calibrated by the evaluation of the valence vertical ionization potentials for CO, N₂, and F₂ molecules for several basis sets up to 160 basis functions. At the basis set limit, errors vary from 0.0 to 0.2 eV, compared to “experimental” vertical ionization potentials. © 2003 American Institute of Physics. [DOI: 10.1063/1.1527013]

INTRODUCTION

The coupled cluster (CC) (Refs. 1–12) theory, originally developed as a method for the calculation of ground state properties, has been further generalized for the description of the excited, ionized and electron-attached states via the equation-of-motion (EOM) CC philosophy.¹³ This elegant, very general, time independent method exploits the left- and right-hand eigenfunctions of the non-Hermitian operator $\bar{H} = e^{-T} H e^T$. When solved in a space of $N \pm p$ electrons, this equation yields ionized or electron attached states and for $p = 0$ gives electronic excited states. A related time-dependent method for excited states is the CC linear response (CCLR) approach of Monkhorst.^{14–17}

The EOM method is a useful tool since it provides, directly, the sought quantity [excitation energy (EE),^{13,18–22} ionization potential (IP),^{23–27} or electron affinity (EA)^{28,29}]. The CC scheme most commonly used in combination with the EOM approach is the CCSD model and its performance is well documented in the literature.^{13,23–26,28,29} This approach has been successfully used for the description of excited states dominated by single excitations. Nowadays several efforts have been made to improve its accuracy for the states with large double excitation character by developing CC schemes with inclusion of the higher-than-double excitation operators.³⁰ The implementation of EE-EOM-CCSDT with full inclusion of the connected triple excitations for the evaluation of the excited states energies is an example.^{21,22} The program developed in Ref. 22 is coded very efficiently both at the CCSDT level (with quasilinear formulation of the CC equations) and at the CI step, where most of the terms engaging three- and four-body elements of the \bar{H} operator were factorized. Due to this the program was successfully

applied to basis sets using over 90 functions. In addition to this there have been proposed a number of variants for EE and/or IP calculations including triple excitations in approximate ways, either iterative or noniterative.^{18–21,27} The latter, in particular, have not been found to be very successful. Hence, it is helpful to have full triple benchmark results. In this paper we report the initial results of a general purpose diagrammatic implementation of the benchmark EOM-CCSDT method for calculation of the ionization potentials.

In the EOM-CC approach an excited state is created by the action of an elementary excitation operator R on the CC reference state Ψ_0 which—within the CC formalism—is obtained with an exponential e^T operating on the Hartree–Fock reference, Φ_0 . The expansion coefficients for the excited state are defined by the solution of the matrix eigenvalue equation obtained by the projection of the eigenvalue problem upon a suitable set of configurations. The diagonalization also yields directly the excitation energies. In other words, EOM-CC may be viewed as a diagonalization of the CC similarity transformed Hamiltonian, \bar{H} , in the CI configuration space. On the other hand, in the ionization potential studies the wave functions that correspond to the ionized states can be obtained by diagonalizing \bar{H} in a basis of determinants containing $N - 1$ electrons (N refers to the number of electrons in Φ_0). It is also possible to view the ionization process as an excitation in which one electron is promoted to a continuum orbital. Likewise one can obtain electron affinities, together with the associated $(N + 1)$ -electron eigenstates by using operators that create an electron.

The resulting IP-EOM-CC and EA-EOM-CC approaches are intimately connected to the Fock space CC

(FSCC) approaches for the (0,1) and (1,0) sectors, respectively. FSCC and EOM-CC are known to give identical results for the principal IP and EA sectors.^{31,32} The comparison between these two methods for the EE sector has also been analyzed.^{33,34}

In this paper we will present the EOM-CC formalism developed for ionization potential calculations. Detailed IP-EOM-CCSDT working equations will be given explicitly in algebraic and diagrammatic form for standard and factorized version. The factorization procedure makes it possible to maintain the rank of the computational procedure to be $n_{\text{occ}}^3 n_{\text{vir}}^4$ for the EOM part. We stress that this procedure does not introduce any approximation. The factorization strategy plus the real abelian symmetry implementation, makes it possible to apply the method to larger (>150) basis sets, offering near benchmark quality for full triples.

THEORY

Let us consider the Schrödinger equation,

$$H|\Psi_k\rangle = E_k|\Psi_k\rangle \quad k = 1, 2, \dots \quad (1)$$

assuming that Ψ_k describes the k th ionized state obtained by the removal of the electron from the reference ground state Ψ_0 . Within the coupled-cluster formalism the reference wave function Ψ_0 is obtained by action of the exponential e^T ,

$$|\Psi_0\rangle = e^T|\Phi_0\rangle, \quad (2)$$

where Φ_0 is the reference determinant and T is the cluster operator. Within the CCSDT model, the cluster operator is approximated as

$$T = T_1 + T_2 + T_3 \quad (3)$$

and T_k is defined as

$$T_k = (k!)^{-2} \sum_{ab\dots} \sum_{ij\dots} t_{ij\dots}^{ab\dots} a^\dagger b^\dagger \dots ji, \quad (4)$$

where the indices $a, b, \dots (i, j, \dots)$ refer to virtual (occupied) one-particle levels. The cluster amplitudes, $t_{ij\dots}^{ab\dots}$, are obtained by solving the CC equations,

$$\langle \Phi_{ij\dots}^{ab\dots} | (He^T)_c | \Phi_0 \rangle = 0. \quad (5)$$

$\langle \Phi_{ij\dots}^{ab\dots} |$ is a k -tuply excited determinant and subscript c in the above equation indicates that only connected diagrams should be considered.

Within the EOM formalism the k -state wave function for IP (Ψ_k) is obtained by operating with the $R(k)$ operator on the ground state wave function (Ψ_0),

$$|\Psi_k\rangle = R(k)|\Psi_0\rangle. \quad (6)$$

The $R(k)$ is a linear (CI-like) ionization operator limited in this approach to single, double, and triple excitations,

$$R(k) = R_1(k) + R_2(k) + R_3(k) \quad (7)$$

expressed through the elementary creation-annihilation operators in the following way:

$$R(k) = \sum_i r_i(k) i + \frac{1}{2} \sum_a \sum_{ij} r_{ij}^a(k) a^\dagger ji + \frac{1}{12} \sum_{ab} \sum_{ijl} r_{ijl}^{ab}(k) a^\dagger b^\dagger lji. \quad (8)$$

Inserting the Ψ_k wave function, Eq. (6), into the Schrödinger equation, Eq. (1), we obtain the equation-of-motion,

$$[\bar{H}R(k)]_c = \omega_k R(k), \quad (9)$$

where \bar{H} is the similarity transformed Hamiltonian, formally defined as

$$\bar{H} = e^{-T} H e^T \quad (10)$$

and ω_k is the energy change connected with the ionization process. For ionization although the operator R is presented as linear in Eq. (6), it can equally well be recognized as the appropriate exponential operator in Fock space CC, since all

TABLE I. IP-EOM-CCSDT equations in Goldstone formalism for standard and factorized version.

Expression ^a
$(\bar{H})_i = -r_{mi}^m - 2r_{nm}^e I_{ie}^{mn} + r_{nm}^e I_{ie}^{mn} + 2r_{mi}^e I_{ie}^m - r_{im}^e I_{ie}^m + 2r_{mni}^{ef} v_{ef}^{mn} - 2r_{inm}^{ef} v_{ef}^{mn} - r_{mni}^{ef} v_{fe}^{mn} + r_{min}^{ef} v_{fe}^{nm}$
$(\bar{H}R)_{ji}^b = -r_{mi}^m I_{ij}^{mb} - r_{mi}^b I_{ij}^m + r_{jm}^b I_{ij}^m + r_{nm}^e I_{ij}^{mn} + 2r_{mi}^e I_{ej}^{mb} - r_{im}^e I_{ej}^{mb} - r_{mi}^e I_{ej}^{mb} v_{jm}^e v_{ie}^{mb} + 2r_{mji}^{ef} I_{ef}^{mb} - r_{jmi}^{ef} I_{ef}^{mb} - r_{ijm}^{ef} I_{ef}^{mb} - 2r_{mni}^{eb} I_{ej}^{mn} + r_{mni}^{be} I_{ej}^{mn} + r_{inm}^{eb} I_{ej}^{mn} - 2r_{njm}^{eb} I_{ie}^{mn} + r_{mjm}^{eb} I_{ie}^{mn} + 2r_{mji}^{eb} I_{ie}^m - r_{jmi}^{eb} I_{ie}^m - r_{ijm}^{eb} I_{ie}^m + F_{ji}^b$
$F_{ji}^b = -2r_{nm}^e I_{iej}^{mnb} + r_{mn}^e I_{jei}^{bnm}$
$F_{ji}^{bc} = t_{ji}^{bc} \chi_e$
$(\bar{H}R)_{jki}^{bc} = P(jb/kc)[r_{ji}^e I_{ek}^{bc} - r_{km}^b I_{jk}^{mc} - r_{mi}^c I_{jk}^{mb} + r_{nm}^c I_{ij}^{mnc}] - r_{jkm}^{bc} I_{ie}^m - P(jb/kc)[r_{mki}^{bc} I_{ij}^m - r_{jki}^{ec} I_{ie}^b - r_{nkm}^{bc} I_{ij}^{mn}] + r_{mni}^{bc} I_{jk}^{mn} + r_{jki}^{ef} I_{ef}^{bc} - P(jb/kc)[r_{jkm}^{ec} I_{ie}^{mb} + r_{jmi}^{ec} I_{ek}^{mb} + r_{mki}^{ec} I_{ej}^{mb} - 2r_{mki}^{ec} I_{ej}^{mb} + r_{jmi}^{ec} I_{ek}^{mb} + r_{ikm}^{ec} I_{ej}^{mb}] + F_{jki}^{bc}$
$F_{jki}^{bc} = -r_{mi}^m I_{ijk}^{mbc} + 2r_{mi}^e I_{ejk}^{mbc} - r_{im}^e I_{ejk}^{mbc} - P(jb/kc)[r_{mi}^e I_{ejk}^{mbc} + r_{jm}^e I_{iek}^{mbc}] - 2r_{mn}^e I_{iekj}^{nmc} + r_{nm}^e I_{eikj}^{nmc} + P(jb/kc)[2r_{mji}^{ef} I_{efk}^{mbc} - r_{jmi}^{ef} I_{efk}^{mbc} - 2r_{ijm}^{ef} I_{efk}^{mbc} - 2r_{mni}^{eb} I_{ejk}^{mnc} + r_{mni}^{be} I_{jek}^{mnc} + r_{inm}^{eb} I_{ejk}^{mnc} - 2r_{njm}^{eb} I_{iek}^{mnc} + r_{mjm}^{eb} I_{iek}^{mnc} + r_{njm}^{be} I_{ike}^{mnc}]$
$F_{jki}^{bc} = -r_{mi}^m I_{ijk}^{mbc} + P(jb/kc)[r_{ji}^e I_{ek}^{bc} \chi_e^c + 2r_{mi}^e I_{ejk}^{mbc} - r_{im}^e I_{ejk}^{mbc} - P(jb/kc)[r_{mi}^e I_{ejk}^{mbc} + r_{jm}^e I_{iek}^{mbc} + r_{jmi}^{bce} I_{ie}^m - t_{kjm}^{bce} \chi_{ie}^m + 2t_{jkm}^{bce} \chi_{ie}^m - P(jb/kc)t_{jmk}^{bce} \chi_{ie}^m + t_{ijk}^{bce} \chi_e^m - P(jb/kc)[t_{mk}^{bc} \chi_{ji}^m - t_{jk}^{ec} \chi_{ie}^b - t_{ik}^{bc} \chi_{je}^b]]$

^aSummation over repeated indices assumed on the right-hand side; summation indices belong to the set {e,f,m,n}; $P(jb/kc)$ implies sum of two components differing by permutation of jb and kc . All elements of \bar{H} ($I_{tu}^{s\dots}$) and intermediates ($\chi_t^{s\dots}$) are defined in Tables 2 and 3, respectively.

^bStandard version.

^cFactorized version.

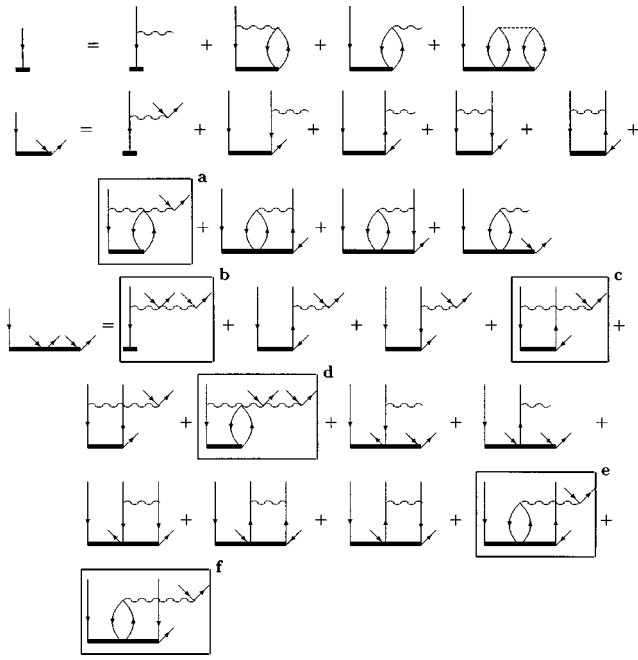


FIG. 1. Diagrammatic form of the IP-EOM-CCSDT equations in an anti-symmetrized formalism for the standard version.

products of $S^{(0,1)}$ in $\exp(S^{(0,1)})$ vanish, leaving just $S^{(0,1)} = R$. This makes IP-EOM-CC entirely linked, connected and extensive, unlike that for excited states that derive from $\exp(S^{(1,1)})$.^{35–39} Because \bar{H} is non-Hermitian, we also have the left-hand eigenvector, $L(k)$, $L(k)\bar{H} = \omega_k L(k)$, where $L(k)\bar{H}$ is not connected. Both $L(k)$ and $R(k)$ are needed to obtain density matrices.

IP-EOM-CCSDT WORKING EQUATIONS

In this section we present explicit working equations for the IP-EOM-CCSDT method. This requires solution of the CCSDT equations, Eq. (5), for the T_1 , T_2 , and T_3 amplitudes and then the construction of the \bar{H} operator, according to Eq. (10). To obtain the eigenvalues and eigenvectors we employ a direct diagonalization scheme⁴⁰ analogous to the Davidson method⁴¹ for symmetric matrices. In case of the solution for the right-hand side eigenvectors we require the results of the IP-EOM-CC matrix right multiplying an arbitrary vector R , i.e., $\bar{H}R$. Using the direct CI-like formalism the components of the $(\bar{H}R)_c$ vector are constructed according to the equations presented in the diagrammatic form in Fig. 1, or, in the algebraic form, in Table I. To each term in Table I (and also in Table II) the proper permutation of the external indices should be applied indicated by the symbol $P(\dots/\dots)$ (see the explanation given at the footnote to Table I). Note that in Tables I, II, and III we adopt the tensor notation with implied summation over repeated indices.

The form of \bar{H} which is required for the construction and solution of the IP-EOM-CCSDT equations in their standard form involves up to four-body elements. Emphasizing the many-body structure of \bar{H} , we may decompose it into individual contributions as follows:

TABLE II. Algebraic expression for the elements of \bar{H} used in the IP-EOM-CCSDT model.

	Expression ^a
I_a^i	$f_a^i + 2t_n^e v_{ae}^{in} - t_n^e v_{ea}^{in}$
I_b^a	$f_b^a + 2t_n^e v_{be}^{an} - t_n^e v_{be}^{na} - 2t_{no}^{ea} v_{eb}^{no} + t_{no}^{ea} v_{be}^{no} - t_n^a I_n^b$
I_j^i	$f_j^i + 2t_n^e v_{je}^{in} - t_n^e v_{ej}^{in} + 2t_{nj}^{ef} v_{ef}^{ni} - t_{nj}^{ef} v_{ef}^{in} + t_j^e I_e^i$
I_{bc}^{ai}	$I_{bc}^{ai} - \frac{1}{2} t_n^a v_{bc}^{ni}$
I_{bc}^{ai}	$v_{bc}^{ai} - \frac{1}{2} t_n^a v_{bc}^{ni}$
I_{ka}^{ij}	$I_{ka}^{ij} + \frac{1}{2} t_k^e v_{ea}^{ij}$
I_{ka}^{ij}	$v_{ka}^{ij} + \frac{1}{2} t_k^e v_{ea}^{ij}$
I_{cd}^{ab}	$v_{cd}^{ab} - P(ac/bd) t_{n'cd}^{b'an} + t_{no}^{ab, no}$
I_{kl}^{ij}	$v_{kl}^{ij} + P(ik/jl) t_{l'ke}^{e'ij} + t_{kl}^{ef} v_{ef}^{ij}$
I_{bi}^{aj}	$I_{bi}^{aj} - t_{ni}^{ae} v_{be}^{nj} + \frac{1}{2} t_i^e t_{be}^{aj}$
I_{bi}^{aj}	$v_{bi}^{aj} - \frac{1}{2} t_n^a v_{bi}^{nj} + t_i^e t_{be}^{aj}$
I_{bi}^{naj}	$v_{bi}^{aj} - t_n^a v_{bi}^{nj} + \frac{1}{2} t_i^e t_{be}^{aj}$
I_{ib}^{aj}	$I_{ib}^{aj} + 2t_{ni}^{ea} v_{eb}^{nj} - t_{in}^{ae} v_{eb}^{jn} - t_{ni}^{ae} v_{eb}^{nj} + \frac{1}{2} t_i^e I_{eb}^{aj}$
I_{ib}^{aj}	$v_{ib}^{aj} - \frac{1}{2} t_n^a v_{ib}^{nj} + t_i^e t_{eb}^{aj}$
I_{ib}^{naj}	$v_{ib}^{aj} - t_n^a v_{ib}^{nj} + \frac{1}{2} t_i^e t_{eb}^{aj}$
I_{ci}^{ab}	$v_{ci}^{ab} + t_i^e v_{ce}^{ab} - t_{ni}^{a'ci} t_{ci}^{anb} - t_{ni}^{a'ci} I_{ci}^{an} + 2t_{ni}^{eb} v_{an}^{in} - t_{ni}^{eb} v_{na}^{in} - t_{ni}^{ae} v_{ce}^{no} - t_{noi}^{ae} v_{ce}^{no} + t_{noi}^{ae} v_{ce}^{no}$
I_{jk}^{ia}	$v_{jk}^{ia} - t_n^a v_{jk}^{in} + t_k^e v_{je}^{nia} + t_j^e v_{ek}^{nia} + t_{jk}^{ea} v_{ie}^{in} + 2t_{nk}^{ea} v_{je}^{in} - t_{nk}^{ea} v_{ej}^{in} - t_{jn}^{ea} v_{ek}^{in} + t_{jk}^{ef} I_{ef}^{ia} + 2t_{jnk}^{ef} v_{ef}^{in} - t_{jkn}^{ef} v_{ef}^{in} - t_{jnk}^{ef} v_{ef}^{in}$
I_{jkl}^{iab}	$I_{jkl}^{iab} + P(ka/lb) t_{jkl}^{ef} I_{ef}^{ia}$
I_{jkl}^{iab}	$-P(ka/lb) [t_{n'l'jk}^{ab} v_{in}^{jn} - t_{kl'je}^{eb} v_{ia}^{in} - t_{jl'ek}^{eb} v_{ia}^{in}] + t_{jkl}^{ef} I_e^{iab} - P(ka/lb) \times [t_{jnl}^{eab} v_{in}^{in} + t_{nkl}^{eab} v_{jn}^{in} + 2t_{nkl}^{eab} v_{je}^{in} - t_{nkl}^{eab} v_{ej}^{in}]$
I_{klm}^{ija}	$P(ik/jl) t_{lm}^{eaij} + t_{klm}^{efa} v_{ij}^{ef}$
I_{cjk}^{aib}	$I_{cjk}^{aib} - t_{njc}^{aeb} v_{ce}^{ni}$
I_{cjk}^{aib}	$t_{jkc}^{eb} v_{ce}^{ai} - t_{nk}^{ab} v_{cj}^{ni}$
I_{cjk}^{iab}	$I_{cjk}^{iab} + 2t_{njc}^{eab} v_{ce}^{in} - P(ja/kb) t_{jnk}^{eab} v_{ce}^{in} - t_{njc}^{eab} v_{ce}^{ni}$
I_{cjk}^{iab}	$P(ja/kb) [t_{jkc}^{eb} v_{ce}^{ia} - t_{nk}^{ab} v_{cj}^{in}]$
I_{ilb}^{ajk}	$t_{il}^{ae} v_{eb}^{jk}$
I_{icd}^{abj}	$-t_{in}^{ab} v_{cd}^{nj}$
I_{aklm}^{ijbc}	$t_{klm}^{ebc} v_{ae}^{ij}$

^aSummation over repeated indices assumed; summation indices belong to the set $\{e, f, n, o\}$.

$$\bar{H} = I^1 + I^2 + I^3 + I^4. \quad (11)$$

We may rewrite the particular element, I^n , as the sum over components I_k^n , where k indicates the number of annihilation lines

$$\begin{aligned} I^1 &= I_1^1 + I_2^1, \\ I^2 &= I_1^2 + I_2^2 + I_3^2 + I_4^2, \\ I^3 &= I_1^3 + I_2^3 + I_3^3, \\ I^4 &= I_3^4. \end{aligned} \quad (12)$$

We skipped the \bar{H} components with 0 annihilation lines since they cannot be contracted with the R operators. Similarly in the last equation the I_1^4 and I_2^4 terms are omitted since they do not enter the IP-EOM-CCSDT model.

The many-body type of the \bar{H} elements expressed through the I_{\dots}^{\dots} amplitudes are determined by the number of indices, i.e., I_s^1 , I_{tu}^{rs} , I_{uvw}^{rst} , and I_{vwxy}^{rstu} corresponding to the I^1 ,

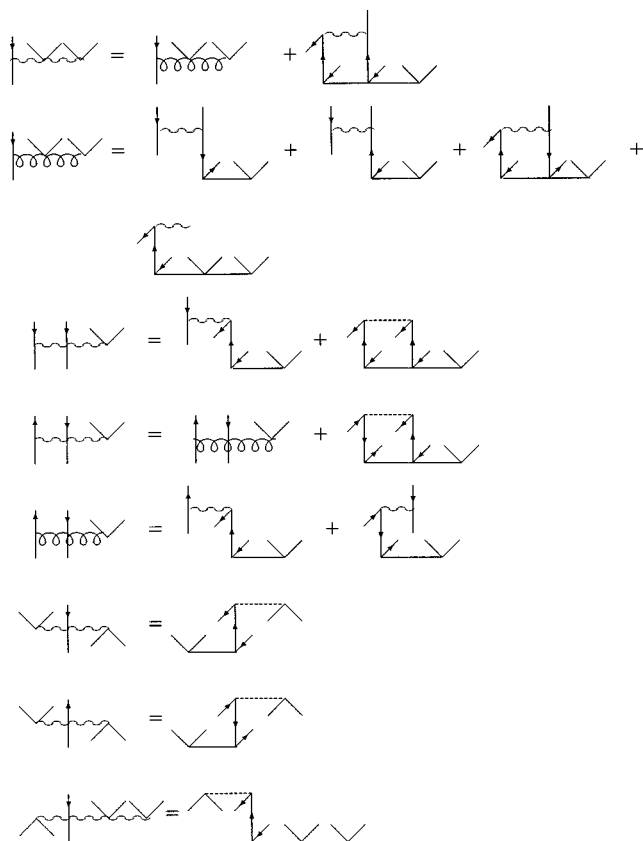


FIG. 2. Diagrammatic form of the three- and four-body elements of \bar{H} used in the IP-EOM-CCSDT equations in the antisymmetrized formalism.

I^2 , I^3 , and I^4 operators, respectively. Note that the r, s, \dots symbols indicate general indices being of either hole or particle character.

It is easy to also assign creation—annihilation character to the particular $I_{s\dots}^r$ amplitude. The index referring to the annihilation (creation) line is represented by the presence of the hole (particle) symbol as a superscript or the particle (hole) symbol as the subscript. Thus, e.g., the I_{bj}^{ia} element corresponds to two annihilation lines: indicated with the indices i (hole and superscript) and b (particle and subscript) and two creation lines: a and j , so the I_{bj}^{ia} amplitude is connected with the I_2^2 operator.

All elements of \bar{H} are defined in Goldstone formulation in Table II. The three- and four-body components are presented also in diagrammatic form within the antisymmetrized formalism in Fig. 2. The one- and two-body components of \bar{H} are well documented in diagrammatic form in Refs. 11 and 42 and are used to define the higher rank terms in Fig. 2.

The standard derivation of the IP-EOM equations assumes that we use all required \bar{H} elements regardless of the complexity of a particular term. This means that we would employ all appropriate three- and four-body terms. Such a form of the IP-EOM equations is presented diagrammatically in Fig. 1 and in algebraic form in Table I.

Such a formulation of the IP-EOM problem, although perhaps the most natural one, would result in high scaling of the computational procedure either in the \bar{H} construction or in the solution of the EOM equations. To avoid this we apply

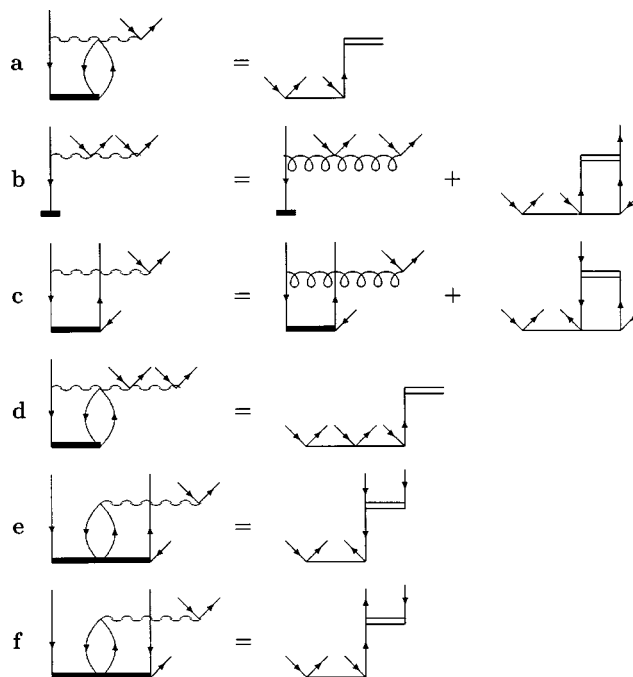


FIG. 3. Diagrammatic picture of the factorization of selected contributions to the IP-EOM equations.

a factorization scheme which would eliminate the difficult terms, i.e., those engaging the four-body \bar{H} element and some of the three-body ones, without any loss of rigor. The difficult terms are indicated in Fig. 1 by the rectangles and their construction in a factorized way is explained in Figs. 3 and 4. Hence, the diagram indicated by the letter a in the R_2 equation in Fig. 1 is replaced by the contribution given in Fig. 3(a), where the heavy horizontal line corresponds to the R amplitude and the thin one—to the T amplitude. Thus we may avoid using the three-body \bar{H} element in the R_2 equa-

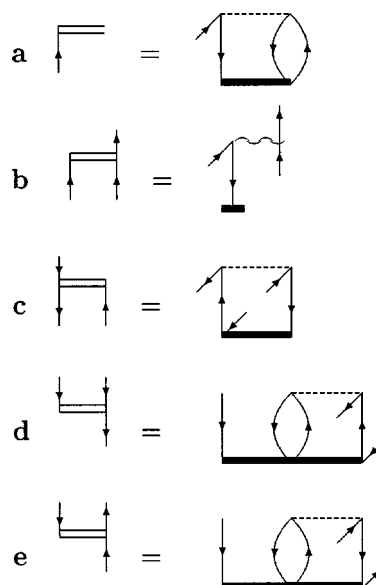


FIG. 4. Diagrammatic form of the intermediates used in the IP-EOM-CCSDT equations in the antisymmetrized formalism.

TABLE III. Algebraic expression for the intermediates used in the IP-EOM-CCSDT model.

Intermediate	Expression ^a
χ_a	$-2r_{on}^e v_{ae}^{no} + r_{on}^e v_{ea}^{no}$
χ_{jk}^i	$2r_{nj}^{ef} v_{ef}^{ni} - r_{nj}^{ef} v_{ef}^{in} - r_{kj}^{ef} v_{ef}^{ni}$
χ_{ca}^b	$-r_n I_{ac}^{nb}$
χ_{bi}^a	$-2r_{noi}^{ea} v_{eb}^{no} + r_{noi}^{ea} v_{be}^{no} + r_{ion}^{ea} v_{eb}^{no}$
χ_{ja}^i	$-r_{jn}^e v_{ae}^{ni}$
χ_{ib}^a	$-2r_{oin}^{ea} v_{be}^{no} + r_{oin}^{ea} v_{eb}^{no} + r_{oin}^{ae} v_{be}^{no}$
χ_{aj}^i	$2r_{nj}^e v_{ea}^{ni} - r_{nj}^e v_{ae}^{ni} - r_{jn}^e v_{ae}^{in}$

^aSummation over repeated indices assumed; summation indices belong to the set $\{e, f, n, o\}$.

tion by construction of the intermediate shown in Fig. 4(a) and then by employing it in the diagram on the right-hand side of the equation in Fig. 3(a). By the intermediate we understand throughout the paper the quantity obtained by the contraction of the integral or \bar{H} element with the R operator. The diagram, a , engaging the three-body \bar{H} element in the R_2 equation in Fig. 1 as well as the \bar{H} element itself, both require n^7 scaling. On the other hand the same term computed via the diagram in the Fig. 3(a) with the intermediate in Fig. 4(a) requires two n^4 steps, so we see a definite gain in computational efficiency.

The same refers to the diagrams contributing to the R_3 equation in Fig. 1 labeled with letters b, c, d, e, f . In actual calculations they are evaluated according to the scheme shown in Fig. 3: b, c, d, e, f , respectively. The diagram d in Fig. 1 requires n^8 scaling while the four-body \bar{H} element engaged in it— n^9 scaling (see the last line of Fig. 2). Instead we have an n^6 scheme with the same intermediate as that used in the case of the diagram in Fig. 3(a). A similar situation occurs in cases e and f of Fig. 3, where the two n^8 contributions are replaced with the n^6 ones. A slightly different procedure has been applied to the c and d diagrams in Fig. 3. Here we do not eliminate the respective contributions in the R_3 equation of Fig. 2, but avoid only the most difficult contribution to the three-body \bar{H} element. So in this case the savings occurs since we do not take the contribution to the I_1^3 \bar{H} element shown in first line of Fig. 2 and analogous term in the fourth line of the same figure (both contributions require

n^8 scaling), but instead we include the contributions shown in Figs. 3(b) and 3(c) which scale as n^7 .

The factorization procedure shown diagrammatically in Figs. 3 and 4 is accounted for also in Table I, where the contributions denoted by $F_{ji}^{b(b)}$ and $F_{jki}^{b(c)}$ refer to the nonfactorized version engaging only \bar{H} elements and R amplitudes whereas the terms $F_{ji}^{b(c)}$ and $F_{jki}^{b(c)}$ represent the factorized variant engaging also the intermediates χ_a and χ_{st}^r defined in Table III.

The factorization procedure, i.e., replacement of some \bar{H} elements contracted with the R operators with the appropriate intermediates contracted with the T operator makes the evaluation of the $(\bar{H}R)$ quantities much more efficient. We should remember, however, that the \bar{H} elements are computed only once in the whole process while the intermediates must be recomputed in each iteration. However, it does not change the general conclusion concerning significant saving of the computational effort due to this procedure.

We should mention also that there exists a very simple formula to evaluate the rank of the computational procedure for each term. Namely, for the general term $I_k^n R_m$ the rank of the computational procedure (scaling) is equal to $n^{2(n+m)-k}$.⁴³

RESULTS

In order to verify the correctness of the program as a first step we have reproduced the IP-EOM-CCSDT results of Hirata, Nooijen, and Bartlett,⁴⁴ obtained with a FCI program for BH and C_2 molecules at the 6-31G** and 6-31G basis set level, respectively.

To test the performance of the EOM-CCSDT model in ionization potential calculations we selected three molecules: N_2 , CO, and F_2 and assume the validity of the “experimental” vertical ionization potentials (see Ref. 45 for a discussion). We use two types of the correlation consistent basis sets of Dunning:⁴⁶ cc-pVXZ and aug-cc-pVXZ, where X denotes D, T, and Q. The results are collected in Table IV (N_2), Table V (CO), and Table VI (F_2). For each basis set we run calculations with all electrons correlated (see rows with AE headings in Tables IV–VI) or with the core electrons frozen (rows with VE headings). As we see the exclusion of the core electrons from the correlation treatment has a very small effect on the calculated “valence,” potentials. The same is true

TABLE IV. Vertical ionization potentials of N_2 molecule with IP-EOM-CC methods (eV) ($R = 1.097\ 685\ \text{\AA}$).

Nominal state		cc-pVDZ		aug-cc-pVDZ		cc-pVTZ		aug-cc-pVTZ		cc-pVQZ		aug-cc-pVQZ		Expt. ^a
		CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	
$3\sigma_g$	AE ^b	15.18	15.10	15.43	15.34	15.58	15.46	15.66	15.54	15.71	15.57	15.75	15.60	15.60
	VE ^c	15.18	15.10	15.43	15.34	15.56	15.44	15.65	15.52	15.68	15.55	15.71	15.58	
$1\pi_u$	AE ^b	16.93	16.64	17.12	16.84	17.19	16.92	17.27	16.99	17.31	17.02	17.34	17.05	16.98
	VE ^c	16.93	16.64	17.11	16.84	17.18	16.90	17.25	16.98	17.28	16.99	17.31	17.03	
$2\sigma_u$	AE ^b	18.47	18.35	18.70	18.57	18.82	18.66	18.91	18.74	18.94	18.76	18.98	18.79	18.78
	VE ^c	18.47	18.36	18.71	18.57	18.83	18.67	18.92	18.75	18.94	18.77	18.98	18.80	

^aReference 49.

^bAll electrons correlated.

^cValence electrons correlated.

TABLE V. Vertical ionization potentials of CO molecule with IP-EOM-CC methods (eV) ($R = 1.128\ 323\ \text{\AA}$).

Nominal state		cc-pVDZ		aug-cc-pVDZ		cc-pVTZ		aug-cc-pVTZ		cc-pVQZ		aug-cc-pVQZ		Expt. ^a
		CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	
5 σ	AE ^b	13.81	13.58	13.99	13.76	14.14	13.90	14.19	13.95	14.24	13.99	14.26	14.01	14.01
	VE ^c	13.81	13.58	13.99	13.76	14.13	13.89	14.18	13.94	14.22	13.98	14.23	14.00	
1 π	AE ^b	16.74	16.71	16.92	16.90	17.04	16.98	17.10	17.03	17.16	17.07	17.18	17.09	16.91
	VE ^c	16.74	16.71	16.92	16.89	17.02	16.96	17.08	17.02	17.13	17.05	17.15	17.07	
4 σ	AE ^b	19.47	19.33	19.67	19.52	19.74	19.55	19.80	19.60	19.87	19.64	19.89	19.66	19.72
	VE ^c	19.47	19.33	19.67	19.52	19.74	19.55	19.80	19.60	19.86	19.64	19.88	19.66	

^aReference 49.^bAll electrons correlated.^cValence electrons correlated.

when the explicit core functions are included in the basis set. We performed calculations for the cc-pCVTZ basis with all electron correlated and obtained negligible changes, e.g., 15.47, 16.92, and 18.68 eV for the three states of N₂ molecule which differ from the AE cc-pVTZ values by 0.01, 0.00, and 0.02 eV, respectively. For CO the analogous changes are 0.01, 0.00, and 0.01 eV for the 5 σ , 1 π , and 4 σ states, respectively. While for the F₂ molecule the cc-pCVTZ values differ by 0.01 eV for all states. For double zeta basis sets the effect of core functions is below the accuracy of the quoted results for most cases, for the triple zeta basis it ranges from 0.00 to 0.02 eV and for the quadruple zeta we observe the largest effects amounting to 0.02–0.03 eV. Some states, e.g., the σ_u state of N₂ or the σ state of CO are practically insensitive to the presence of core correlation functions in the correlation treatment. This indicates that even in high accuracy calculations we may limit the correlation treatment to the valence electrons only which, for the very sophisticated approaches, can significantly lower the cost of calculations. Of course, it is another question whether the core functions have a significant effect on core ionizations.

The main feature to note is the importance of the T_3 operator in the CC calculations of the ionization potentials. The general effect of the T_3 operator is to lower the value of the ionization energy, and its magnitude depends upon the molecule and the state studied. For the N₂ molecule the largest effect is observed for the π_u state for which the T_3 correction is equal to 0.29 eV, whereas for the remaining two states, σ_g and σ_u it is equal to 0.15 and 0.18 eV, respectively. For the CO molecule the effect of T_3 is slightly smaller

amounting to 0.23, 0.22, and 0.08 eV for 5 σ , 4 σ , and π states, respectively. Note that here the smallest effect refers to the π state, unlike the N₂ molecule. In the F₂ case we should note the different behavior of the π_g state for which the T_3 operator increases the IP value. For the remaining two states the T_3 effect is similar to that for the other molecules, i.e., it lowers the energy by 0.12 and 0.09 eV, respectively, for π_u and σ_g states. All values quoted above refer to the aug-cc-pVQZ results with all electrons correlated. For the majority of cases the small basis sets underestimate the T_3 effect, i.e., by increasing the size of the basis set the T_3 gives a larger contribution, e.g., for σ_g and σ_u states of N₂ it increases from 0.08 and 0.12 to 0.15 and 0.18 eV, respectively. For one case, the π_u state of N₂, the effect of triples is stable, remaining close to 0.3 eV for all basis sets. A more peculiar behavior is observed for the π states of the F₂ molecule; for the double zeta basis the T_3 effect is positive, i.e., it increases the IP value. For the larger basis set it reduces from -0.20 to -0.04 eV for the π_g state while for the π_u state the T_3 correction changes sign from -0.06 eV for double zeta to $+0.12$ eV for augmented quadruple zeta. The above results indicate that in some cases one has to be cautious when discussing the effect of the higher clusters on the basis of calculations done for very small basis sets.

When comparing the computed values with experiment one should observe that the final IP value is a result of two opposite trends: An increase in the basis set size always moves the calculated IP's up whereas the inclusion of the T_3 operator lowers their values in all but one case. So one can see that for a double zeta basis set the computed values are smaller than those for the largest basis set (aug-cc-pVQZ) by

TABLE VI. Vertical ionization potentials of F₂ molecule with IP-EOM-CC methods (eV) ($R = 1.411\ 93$).

Nominal state		cc-pVDZ		aug-cc-pVDZ		cc-pVTZ		aug-cc-pVTZ		cc-pVQZ		aug-cc-pVQZ		Expt. ^a
		CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	
1 π_g	AE ^b	15.10	15.30	15.40	15.59	15.50	15.58	15.63	15.69	15.69	15.73	15.75	15.79	15.83
	VE ^c	15.10	15.30	15.40	15.59	15.49	15.57	15.61	15.68	15.66	15.71	15.72	15.76	
1 π_u	AE ^b	18.41	18.47	18.77	18.81	18.83	18.75	18.97	18.89	19.03	18.90	19.09	18.97	18.8
	VE ^c	18.40	18.47	18.76	18.81	18.81	18.74	18.96	18.88	19.00	18.89	19.06	18.95	
3 σ_g	AE ^b	20.77	20.70	21.16	21.12	21.06	20.97	21.19	21.11	21.21	21.11	21.27	21.18	21.1
	VE ^c	20.77	20.70	21.16	21.12	21.05	20.96	21.18	21.10	21.19	21.09	21.25	21.16	

^aReference 49.^bAll electrons correlated.^cValence electrons correlated.

TABLE VII. Extrapolated^a ionization potential values (eV) (AE).^b

Molecule	Nominal state	cc-pV ∞ Z		aug-cc-pV ∞ Z		Expt. ^c
		CCSD	CCSDT	CCSD	CCSDT	
N ₂	3 σ_g	15.78	15.63	15.80	15.63	15.60
	1 π_u	17.38	17.08	17.38	17.09	16.98
	2 σ_u	19.01	18.82	19.02	18.82	18.78
CO	5 σ	14.30	14.04	14.30	14.04	14.01
	1 π	17.23	17.12	17.23	17.13	16.91
	4 σ	19.95	19.69	19.95	19.70	19.72
F ₂	1 π_g	15.80	15.82	15.82	15.85	15.83
	1 π_u	19.15	18.99	19.16	19.02	18.8
	3 σ_g	21.30	21.20	21.32	21.23	21.1

^aAn extrapolation formula was taken from Ref. 50.^bAll electrons correlated.^cReference 49.

≈ 0.4 – 0.6 eV for the CCSD scheme and by 0.3 – 0.5 eV for the CCSDT one. Thus the effect of the basis set is more pronounced than that due to the T_3 operator.

Comparing the AE EOM-CCSDT values for the aug-cc-pVQZ basis set with experiment for the N₂ molecule we observe perfect agreement for the σ_g and σ_u states (0.01 eV error). For the π_u state the error is slightly larger (0.07 eV) which would indicate that the T_4 operator could play a more significant role here than for the previous states, although further basis set extension in the core and mid-valence region cannot be discounted.

The CO molecule shows perfect agreement for the 5 σ state (0.01 eV difference) and is slightly worse for the π state. Here the computed value is 0.18 eV larger than the experimental one. There is no immediate explanation for this discrepancy; one can hardly assign this exclusively to the T_4 operator. For the remaining σ state the theoretical IP value is 0.06 eV lower than the experimental one.

For the F₂ molecule two states, π_g and σ_g , are reasonably (as for that level of sophistication) close to the experimental data. The π_g state is lower by 0.04 eV while the σ_g one is higher by 0.08 eV than the experimental value. Apparently the experimental value for the σ_g state is less accu-

rately measured, so this discrepancy potentially could be reduced. The same is true for the π_u state, but here the deviation from experiment is larger, 0.19 eV, i.e., of the order of error that occurred for the π state of CO molecule. Generally it looks as if the full CCSDT level has more difficulty with the π states than the σ_g ones.

In the next table, Table VII, we list the CCSD and CCSDT IP values extrapolated to the complete basis set (CBS) limit. We explore two series of basis sets: standard and augmented ones. For both cases we obtained the same CBS limit with an accuracy up to 0.01 eV (the only exception is the σ_g state of the F₂ molecule where the difference in the limit amounts to 0.03 eV) (at infinity both basis sets should converge to the same limit). The CBS values are somewhat (0.03–0.04 eV) higher than the aug-cc-pVQZ ones (0.05–0.06 eV for F₂) which were used above for comparison to experiment. The confrontation of the extrapolated values with experiment does not change the conclusions presented above. The σ states remain in excellent agreement whereas the difference for the π states is insignificantly higher. One may expect that the comparison of the CCSDT basis set limit values with experiment will permit estimating the importance of the higher (T_4, T_5, \dots) clusters.

It is also of interest to discuss the performance of the approximate T_3 models by comparison with the complete approach. Noniterative T_3 corrections to IP-EOM-CCSD or its Fock space equivalent, have generally been unsatisfactory.⁴⁷ Iterative T models, e.g., CCSDT-3, have been more satisfactory.^{27,44} Short of the full EOM-CCSDT, EOM-CCSDT-3 is the most complete method available. In Table VIII we list the CCSD and CCSDT values for the aug-cc-pVTZ and aug-cc-pVQZ basis sets and we also quote the CCSDT-3 and CC3 results taken from Ref. 27. We observe that both approximate T_3 schemes behave in a similar manner. The largest error occurs for the 4 σ state of CO: 0.18 and 0.16 eV, respectively, compared to 0.23 eV for CCSD (aug-cc-pVQZ values). For the majority of states the errors stay below 0.1 eV which is reflected by the average deviation of 0.08 and 0.07 eV for the CCSDT-3 and CC3 approaches,

TABLE VIII. Comparison of the full and approximate T_3 models in the IP calculations (eV) (AE).^a

Molecule	Nominal state	aug-cc-pVTZ				aug-cc-pVQZ				Expt. ^b
		CCSD	CCSDT-3	CC3	CCSDT	CCSD	CCSDT-3	CC3	CCSDT	
N ₂	3 σ_g	15.66	15.58	15.54	15.54	15.75	15.64	15.60	15.60	15.60
	1 π_u	17.27	16.95	16.88	16.99	17.34	17.00	16.94	17.05	16.98
	2 σ_u	18.91	18.87	18.82	18.74	18.98	18.92	18.87	18.79	18.78
CO	5 σ	14.19	13.94	13.86	13.95	14.26	13.99	13.91	14.01	14.01
	1 π	17.10	17.10	17.09	17.03	17.18	17.16	17.15	17.09	16.91
	4 σ	19.80	19.77	19.76	19.60	19.89	19.84	19.82	19.66	19.72
F ₂	1 π_g	15.63	15.80	15.75	15.69	15.75	15.88	15.83	15.79	15.83
	1 π_u	18.97	19.04	18.94	18.89	19.09	19.11	19.01	18.97	18.8
	3 σ_g	21.19	21.13	21.15	21.11	21.27	21.19	21.20	21.18	21.1
	a.e. T_3 ^c	0.14	0.08	0.07	0.00	0.16	0.08	0.07	0.00	
	a.e. expt. ^d	0.16	0.08	0.09	0.07	0.22	0.12	0.10	0.07	

^aAll electrons correlated.^bReference 49.^cAverage error with respect to the T_3 values.^dAverage error with respect to the experimental values.

respectively, compared to 0.14–0.15 eV for the CCSD model. In the last row we have an average error with respect to the experimental values. We observe that the CCSD error grows significantly with the size of the basis set while the CCSDT value stays unchanged (full model) or increases only slightly (0.01–0.04 eV). The question of core ionization is also interesting particularly due to their very large orbital relaxation. We will report on this issue in a future study.

CONCLUSIONS

A new, rigorous EOM-CC method with full inclusion of the connected triple excitations has been formulated and implemented for calculations of ionization potentials. By adopting the proper factorization strategy all terms involving the evaluation of the four-body elements of the \bar{H} operators were bypassed via a rigorous factorization procedure as well as the most time-consuming three-body ones. It should be emphasized that such diagram factorization does not introduce any approximation. The factorization makes it possible to achieve for EOM a scaling no worse than $n_{\text{occ}}^3 n_{\text{vir}}^4$. All the resulting equations were presented in both diagrammatic and algebraic form with detailed presentation of the factorization scheme. The program developed, part of ACES II,⁴⁸ has been subsequently applied to the calculation of the low-lying ionization potentials for three molecules N₂, CO, and F₂. The bottleneck of the calculation occurs in the solution of the neutral state CCSDT equations, an $n_{\text{occ}}^3 n_{\text{vir}}^5$ procedure. By exploiting spatial symmetry it has been possible to implement the calculations for quite sizable basis sets reaching 160 basis functions (aug-cc-pVQZ basis set) for the most difficult case.

The results indicate that for accurate values of the ionization potentials one should definitely go beyond the CCSD model. The effect of the T_3 operator is reflected in the lowering of the CCSD IP value by 0.1–0.3 eV (except for the π_g state of F₂, where it raises the IP by 0.04 eV). Comparison with experiment shows that the values computed for the largest basis set (aug-cc-pVQZ) are quite close to experiment, e.g., for the N₂ molecule they differ by 0.00, 0.07, and 0.01 eV for the three valence states. The largest discrepancy occurs for the π state of the CO molecule for which the computed value is too large by 0.18 eV; part of the error is probably due to the neglect of the T_4 and higher cluster operators. Nevertheless the proposed method provides the most accurate and rigorous evaluation of valence ionization potentials in the literature, and offers a high level correlation treatment applicable for relatively large basis sets.

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