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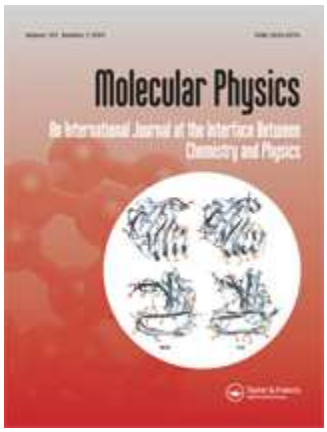
Monika Agnieszka Musial



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The excited, ionized and electron attached states within the EOM-CC approach with full inclusion of connected triple excitations

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Abstract

A full inclusion of the connected single (S), double (D) and triple (T) excitations into the equation-of-motion (EOM) coupled cluster (CC) approach is discussed in the context of the calculations of excitation energies (EE), ionization potentials (IP) and electron affinity (EA). The EOM-CC formalism relies on the diagonalization of the CI-like matrix representing similarity transformed Hamiltonian $\bar{H}$, defined as $\bar{H} = e^{-T}He^{T}$ where T is a cluster operator. The $\bar{H}$ operator is non-Hermitian and – in the case of the EOM-CCSDT model – includes also three- and four-body elements which have to be treated in a special factorized manner to avoid very high scaling of the method and — at the same time — to keep the method fully rigorous. An analysis of the results indicates that the inclusion of triples for the EE reduces the average error twice and for the IP - three times. The performance of the

EOM-CCSDT scheme for the electron affinity is more difficult to assess due to scarcity of the experimental data.

1 Introduction

In this work we focus on the equation-of-motion (EOM) [1–4] coupled cluster (CC) [5–12] approach in the context of its application to the calculations of excitation energies (EE), ionization potentials (IP) and electron affinities (EA). The main topic of the article is connected with the triple excitation operator and its role in the theoretical evaluation of the above quantities.

The idea of extending the EOM-CC scheme to the full triples originated in the Bartlett's group in Quantum Theory Project, University of Florida. The inclusion of the full triple excitation operator into the EOM theory has been a long term project realized on the basis of previous works done in this group concerning incorporation of the higher clusters (quadruples [13,14] and pentuples [15,16]) into the CC theory of the ground state. Most of the work has been done during my numerous inspiring visits to Quantum Theory Project.

The original formulation of the time-dependent CC theory goes back to the works of Monkhorst [17], Emrich [18] and Mukherjee [19] (see also paper by Paldus [20]). This approach, known also as a linear response theory (LRT) [1, 21, 22], is — for the full CC models — entirely equivalent to the EOM formulation. The latter scheme has been intensively studied in the Bartlett's group which resulted in the first general purpose computer code developed by Stanton and Bartlett [3] in the

elegant way exploiting an Abelian symmetry of a molecule. This was the EOM-CC model with single and double excitations applied to the description of the excited states. There were also several successful attempts to include the connected triples in the partial, i.e., approximate manner [23–25]. The results show that the triples are important to the proper description of the transition energies in general and crucial for the correct reproduction of the energies of the states dominated by doubly excited configurations.

The CCSD model has been successfully implemented also for the IP [10] and EA [26, 27] calculations and the results indicate its great usefulness also in the description of the ionized and electron attached states. Both for the EE and IP/EA quantities the EOM-CCSD model generates results with average deviation from the experimental data of ca 0.2 - 0.3 eV.

The central problem in the EOM-CC calculations is a construction of the similarity transformed Hamiltonian $\bar{H}$ ($\equiv e^{-T}He^{T}$) the diagonalization of which provides the eigenvalues related to the studied process. The full inclusion of the triple excitations makes the EOM-CC approach by far more complicated as compared to the CCSD model. At the implementation stage the new features include:

- the reference (ground state) function must be constructed at the full CCSDT level;
- the $\bar{H}$ matrix includes new terms, usually much more complicated than those constructed at the CCSD level;

- several $\bar{H}$ elements, present already at the CCSD level, include new terms dependent on the triple excitation amplitudes;
- the $\bar{H}$ operator must be diagonalized within the significantly larger configurational subspace (now consisting of singles, doubles and triples).

In addition the application of the EOM-CCSDT scheme [28–30] is connected with the significantly higher scaling than that for the EOM-CCSD method: n^8 vs. n^6 which requires very careful analysis of each coded term to make the whole method feasible.

In practical realization we benefited from the fact that the ground state program at the CCSDT level has been available for us [31, 32]. In addition the new $\bar{H}$ elements — three- and four-body components — have been coded when developing the coupled cluster version including the T_5 operator in the approximate [15] and full [16] model. The latter scheme has been constructed in the so called quasi-linear formulation in which all nonlinear terms were included into the amplitude equations via $\bar{H}$ elements. Due to that the complicated amplitude equations assumed relatively simple linear form which, however, required prior evaluation of the $\bar{H}$ element (see also [13, 14]) and they were available at the start of the EOM-CCSDT project.

Another important factor which also had to be taken into consideration was a feasibility of the EOM-CCSDT calculations. A straightforward introduction of the three- and four-body $\bar{H}$ elements would create a prohibitive demand concerning both the disk storage as well as the cost of the calculations. In order to avoid these limitations the inclusion of all four-body elements and most of the three-

body ones required reorganization of the equations to avoid explicit constructions of the latter terms – on one hand – and to keep the method fully rigorous – on the other. An efficient and precise implementation was possible when using the diagrammatic formalism to derive and code all the equations. All variants of the EOM-CC approach were introduced into the ACES II [33] program system developed in Quantum Theory Project.

In next section we give a short description of the EOM-CC theory in the form applicable to all studied processes: EE, IP and EA.

1.1 Theory

We look for the solution of the Schrödinger equation:

$$H_N|\Psi_k\rangle = \Delta E_k|\Psi_k\rangle \quad k = 1, 2, ... \tag{1}$$

where H_N is a normal ordered Hamiltonian with respect to a Φ_o vacuum. Within the EOM formalism the k-state wave function $|\Psi_k\rangle$ is obtained by the action of the $R(k)$ operator on the ground state wave function $|\Psi_o\rangle$:

$$|\Psi_k\rangle = R(k)|\Psi_o\rangle \tag{2}$$

The $R(k)$ is a linear (CI-like) excitation, electron-attachment and/or ionization operator limited in this approach to the single, double and triple excitations (see Fig. 1):

$$R(k) = R_o(k) + R_1(k) + R_2(k) + R_3(k) \tag{3}$$

or in the expanded form:

$$R(k)^{EE} = r_0 + \sum_{ia} r_i^a(k) a^\dagger i + \frac{1}{4}\sum_{ab}\sum_{ij} r_{ij}^{ab}(k) a^\dagger b^\dagger j i + \frac{1}{36}\sum_{abc}\sum_{ijl} r_{ijl}^{abc}(k) a^\dagger b^\dagger c^\dagger l j i \quad (4)$$

$$R(k)^{IP} = \sum_{i} r_i(k) i + \frac{1}{2}\sum_{a}\sum_{ij} r_{ij}^{a}(k) a^\dagger j i + \frac{1}{12}\sum_{ab}\sum_{ijl} r_{ijl}^{ab}(k) a^\dagger b^\dagger l j i \quad (5)$$

$$R(k)^{EA} = \sum_{a} r^a(k) a^\dagger + \frac{1}{2}\sum_{ab}\sum_{i} r_{i}^{ab}(k) a^\dagger b^\dagger i + \frac{1}{12}\sum_{abc}\sum_{ij} r_{ij}^{abc}(k) a^\dagger b^\dagger c^\dagger j i \quad (6)$$

where $a, b, ...$ run over unoccupied levels and $i, j, ...$ run over occupied levels in the Φ_o. Inserting the $|\Psi_k\rangle$ wave function, Eq. (2), into the Schrödinger equation, Eq. (1), we have:

$$H_N R(k)|\Psi_o\rangle = \Delta E_k R(k)|\Psi_o\rangle \quad (7)$$

Multiplying the Schrödinger equation for the ground state by $R(k)$ we obtain:

$$R(k) H_N|\Psi_o\rangle = \Delta E_o R(k)|\Psi_o\rangle \quad (8)$$

and then subtracting from Eq. (7) gives the EOM:

$$(H_N R(k) - R(k) H_N)|\Psi_o\rangle = (\Delta E_k - \Delta E_o) R(k)|\Psi_o\rangle \quad (9)$$

$$[H_N, R(k)]|\Psi_o\rangle = \omega_k R(k)|\Psi_o\rangle \quad (10)$$

where $\omega_k = \Delta E_k - \Delta E_o = E_k - E_o$ is the energy change connected with the excitation, ionization or electron attachment process. Since $|\Psi_o\rangle = e^T|\Phi_o\rangle$ we have:

$$[H_N, R(k)] e^T|\Phi_o\rangle = \omega_k R(k) e^T|\Phi_o\rangle \quad (11)$$

Multiplying from the left with e^{-T} we obtain:

$$e^{-T}H_N R(k)e^T|\Phi_o\rangle - e^{-T}R(k)H_N e^T|\Phi_o\rangle = \omega_k e^{-T}R(k)e^T|\Phi_o\rangle \quad (12)$$

Since T and R commute:

$$[\bar{H}_N, R(k)]|\Phi_o\rangle = \omega_k R(k)|\Phi_o\rangle \quad (13)$$

where $\bar{H}_N$ is a similarity transformed Hamiltonian

$$\bar{H}_N = e^{-T}H_N e^T = (\bar{H}_N e^T)_c \quad (14)$$

which includes also three-, four- and, in general, higher-body elements. Expanding $\bar{H}_N$ into one-body, two-body, three-body, ... etc. contributions we get:

$$\bar{H}_N = I^o + \sum_{k=0}^{2} I_k^1 + \sum_{k=0}^{4} I_k^2 + \sum_{k=0}^{3} I_k^3 + \sum_{k=0}^{3} I_k^4 + \cdots \quad (15)$$

where I_k^n represents the n-body element of $\bar{H}_N$ with k annihilation lines (lines below the vertex, see Fig. 2). So, the $\bar{H}_N$ contains also closed diagrams ($= \Delta E_o$) which are eliminated by the commutator. Indicating open diagrams within $\bar{H}_N$ by $\bar{H}_{N,o}$ we may get rid of commutator:

$$\bar{H}_{N,o}R(k) = \omega_k R(k) \quad (16)$$

$$\bar{H}_{N,o} = (e^{-T}H_N e^T)_o = (H_N e^T)_{c,o} \quad (17)$$

In the matrix form we may write out a CI-like matrix eigenvalue equation:

$$\bar{\mathbf{H}}\mathbf{R}(\mathbf{k}) = \omega_{\mathbf{k}}\mathbf{R}(\mathbf{k}) \quad (18)$$

where $\bar{\mathbf{H}}$ – for the CCSDT case – represents matrix of the $\bar{H}_{N,o}$ operator in the configurational subspace of single, double, and triple excitations:

$$\bar{\mathbf{H}} = \begin{bmatrix} \langle \mathbf{S}|\bar{\mathbf{H}}|\mathbf{S}\rangle & \langle \mathbf{S}|\bar{\mathbf{H}}|\mathbf{D}\rangle & \langle \mathbf{S}|\bar{\mathbf{H}}|\mathbf{T}\rangle \\ \langle \mathbf{D}|\bar{\mathbf{H}}|\mathbf{S}\rangle & \langle \mathbf{D}|\bar{\mathbf{H}}|\mathbf{D}\rangle & \langle \mathbf{D}|\bar{\mathbf{H}}|\mathbf{T}\rangle \\ \langle \mathbf{T}|\bar{\mathbf{H}}|\mathbf{S}\rangle & \langle \mathbf{T}|\bar{\mathbf{H}}|\mathbf{D}\rangle & \langle \mathbf{T}|\bar{\mathbf{H}}|\mathbf{T}\rangle \end{bmatrix}$$

Since $\bar{\mathbf{H}}$ is a non-Hermitian matrix, it has different left ($\mathbf{L}(\mathbf{k})$) and right ($\mathbf{R}(\mathbf{k})$) eigenvectors, both corresponding to the same eigenvalue. Moreover, both are needed to obtain density matrices.

To solve the EOM-CC equations we have to diagonalize $\bar{\mathbf{H}}$ matrix. We use the generalized Davidson diagonalization procedure [34,35]. A crucial step in this procedure is taking product of the amplitude vector R and the matrix to be diagonalized, i.e., $x = (\bar{H}_N R)_c$. So, the schematic EE-EOM-CCSDT equations look like:

$$x_i^a(k) = \langle \Phi_i^a | (\bar{H}_{N,o} R^{EE}(k))_c | \Phi_o \rangle \tag{19}$$

$$x_{ij}^{ab}(k) = \langle \Phi_{ij}^{ab} | (\bar{H}_{N,o} R^{EE}(k))_c | \Phi_o \rangle \tag{20}$$

$$x_{ijl}^{abc}(k) = \langle \Phi_{ijl}^{abc} | (\bar{H}_{N,o} R^{EE}(k))_c | \Phi_o \rangle \tag{21}$$

This is the standard form of the equations (see Fig. 3). So we may say that in practice the EOM equations are identical to the familiar configuration interaction (CI) problem with one modification which is the replacement of the Hamiltonian operator with the similarity transformed Hamiltonian and this is an important difference since H_N has only one- and two-body contributions while $\bar{H}_N$ consists also of higher-body contributions (see Fig. 2). Thus the form of the matrix $\bar{\mathbf{H}}$ is:

	S	D	T
S	I_1^1 $I_2^{2'}$	I_2^1 I_3^2	I_4^2
D	I_1^2 $I_2^{3'}$	I_1^1 I_2^2 I_3^3	I_2^1 I_3^2
T	I_1^3 $I_2^{4'}$	I_1^2 I_2^3 I_3^4	I_1^1 I_2^2 I_3^3

where prime indicates that some of the $\bar{H}_N$ elements are not complete, e.g., in $I_2^{4'}$ component we take only $hole - particle$ type (for annihilation lines, see Fig. 2) for CCSDT case and we do not take $particle - particle$ and $hole - hole$ types of this element. They enter EOM-CCSDTQ variant.

As we can see the standard way of derivation of the EOM-CC equations assumes that we use in the equation all required $\bar{H}_N$ elements regardless of the complexity of the considered term. This means that in the standard version we employ all required three- and four-body terms (see Fig. 2). Such a formulation of the EOM-CC problem, although the most natural one, would result in the high rank of the computational procedure (n^9 for CCSDT case). The remedy invented to solve this problem, which is the crucial point in creation of the efficient code, is a *factorization scheme* [13, 36].

We can describe the factorization with following scheme. The X quantity, see left hand side of Eqs. (19)-(21), depends on both T and R operators. If we evaluate

the X via $\bar{H}_N$ then we have:

$$X(T,R) = \bar{H}_N(T)R \tag{22}$$

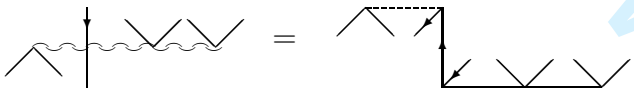
Here in the first step we construct $\bar{H}_N(T)$ while in the second one we take product of the $\bar{H}_N$ and R (realized in the EOM equation).

The other possibility is presented in the equation:

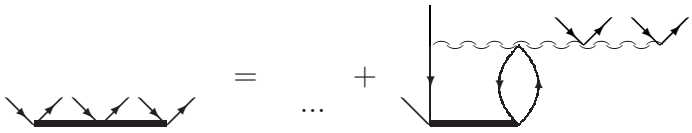
$$X(T,R) = Z(R)T \tag{23}$$

In the first step we construct the intermediate Z depending on R and in the second step we contract Z and T to obtain X. The drawback of the second-possibility is that the Z intermediate must be constructed in each iteration while the $\bar{H}_N$ operator is obtained only once (as a follow up of the ground state solution).

Here we present example of such factorization for I_3^4 element of $\bar{H}_N$ in EE-EOM-CCSDT model. So in order to omit construction of this element:

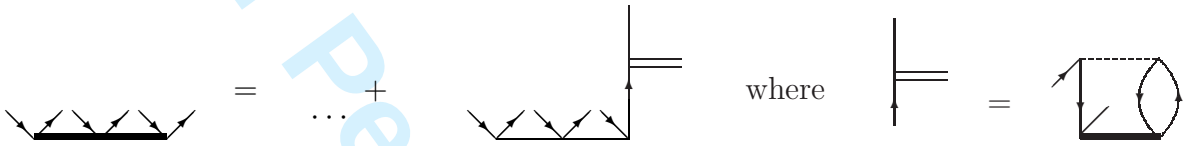


which requires the scaling factor equal to n^9 with the CI-type step scaling also as n^9:



we rewrite the R_3 with the expanded form of the I_3^4 element:

and now we factorize the above diagram, i.e., we cut the diagram along the vertical line obtaining the final contribution to the equation (scaling as n^7) with the new intermediate (scaling as n^5).



The difficult terms (i.e., those engaging the three- and four-body $\bar{H}_N$ elements) are indicated in Fig. 3 by the rectangles. Their construction is omitted by the factorization procedure as described above. The factorized form of the EE-EOM-CCSDT equations is presented in Fig. 4 with intermediates shown in Fig. 5.

The factorization procedure, i.e., replacement of some $\bar{H}_N$ elements contracted with the R operators with the appropriate intermediates contracted with the T operator makes the evaluation of the $\bar{H}_N R$ quantities much more efficient. Moreover, the factorization does not introduce any approximation, the method is fully rigorous.

It should be explained that the $\bar{H}_N$ elements as presented in Fig. 2 enter the EOM-CCSDT scheme — in a standard or factorized form — only for the EE case. For the IP formulation only one I_3^4 element for which two out of three annihilation lines are of the hole type, denoted as I_{aklm}^{ijbc}, is involved. For the EA, vice versa, the I_3^4 having one hole and two particle annihilation lines, I_{aejk}^{ibcd}, survives. Similarly, out

of seven three-body elements one, I_2^3 with two particle lines, denoted in Fig. 2 as I_{cjk}^{aib} is excluded from the IP treatment, while its two-hole line counterpart, I_{klm}^{ija}, is excluded from the EA-EOM-CCSDT model. Note that it follows from the Fig. 3 and Fig. 6 that only two three-body elements of the $\bar{H}_N$ enter the EOM equations in the standard, i.e., not factorized form, namely those which have the annihilation lines exclusively of the hole type, i.e., I_{jkl}^{iab} and I_{klm}^{ija}. This means that, e.g., for the EA case all three- and four-body terms are treated in a factorized way.

The factorization makes it possible to achieve for the EOM part a scaling no worse than n^8 for EE-EOM-CCSDT and n^7 for IP-EOM-CCSDT and EA-EOM-CCSDT case. Thus for the EE case the EOM part scales identically as the ground state, i.e., n^8, while for the IP and EA cases the ground state solution is the slowest step and becomes a bottleneck of the whole procedure.

Moreover, the IP-EOM-CC formalism in its standard formulation (see Fig. 6) [29] formally parallels the EA-EOM-CCSDT theory [30]. Diagrammatically it is just reverting directions of all lines, but replacing the hole indices with particle ones changes the scaling (IP: $n_{occ}^3 n_{vir}^4$; EA: $n_{occ}^2 n_{vir}^5$ for factorized variants).

All the resulting equations for the IP and EA variants (standard and factorized ones) are presented in Refs. [29, 30], respectively. Note, that the *sine qua non* condition of efficient performance of EOM-CC is a very careful implementation of the method with systematic factorization of the difficult terms.

Summing up, we may consider each of these processes as a special case of the general EOM-CC theory. However, the detailed equations are slightly different (con-

firm Figs. 3 and 6) in their form but entirely different when writing computer code. In particular when we want to apply factorization technique, which turns out to be different for each case (see Fig. 3 and Refs. [29, 30]).

It should be indicated that the most crucial quantity in all these theories is a similarity transformed Hamiltonian which plays essential role in the construction of the EOM-CC method.

2 Results and discussion

The incorporation of the connected triples into the EOM-CC scheme creates much more reliable method than the EOM-CCSD model. The price we pay for the higher accuracy is a significantly larger cost of calculations. Although at the EOM step we have different scaling for each type of the EOM problem, i.e., for EE we have $n^8(n_{occ}^3 n_{virt}^5)$, for IP — $n^7(n_{occ}^3 n_{vir}^4)$ and for EA — $n^7(n_{occ}^2 n_{vir}^5)$, the general scaling for all EOM-CC schemes is assumed to be n^8 since the bottle neck of the calculations is a ground state wave function and this step scales as n^8.

The EOM-CCSDT results were compared to the reference data in two ways: for small basis sets they were related to available full Configuration Interaction (FCI) results, and for majority of examples — to the existing experimental data.

We are not going to repeat the description of the results reported in the original papers [29, 30, 37–44], but we want to reiterate the general conclusions concerning performance of the SDT variant of the EOM-CC approach. In Table 1 we report the mean absolute deviations (MAD) from the FCI results for the computed EE

and IP values [37, 38]. We compare MAD for the five systems when the electronic excitations are considered (N_2, C_2, H_2O, HF, Ne) and for three systems (C_2, BH, H_2O) in connection with IP results. The MAD were computed on the basis of 2 to 5 excited/ionized states depending on the molecule. We observe a significant improvement of the EEresults obtained upon inclusion of connected triples. For the EE values the MAD is smaller by the order of magnitude for the N_2 and 2 to 8 times for the remaining systems. The improvement for the IP values is even more spectacular with MAD for C_2 and BH lower more than the order of magnitude and five times for the H_2O system. The results quoted in Table 1 relate — for obvious reasons — to the small basis sets and we may expect that for the larger systems and basis sets we cannot keep the same proportion of the errors for the EOM-CCSD and EOM-CCSDT methods. Nevertheless it indicates that the inclusion of the connected triple excitations is an important factor reducing errors of the computed quantities.

In Table 2 we analyze the performance of the EOM-CCSDT in the description of the excited states for two molecules: N_2 and CO. We quote the mean absolute deviations from the experimental values for excitations energies and selected properties. In cases when the theoretical values are being compared with the experimental data an important factor to be eliminated are deficiencies of the basis set to be sure that the possible errors are not caused by the inadequacies of the basis set. The results cited in Table 2 were obtained for the aug-cc-pVQZ basis set (160 functions per molecule) which is relatively large to make basis set error small compared to the inaccuracies in the correlation treatment. The quantities listed in Table 2 are

vertical (VEE) and adiabatic excitation energies (AEE), equilibrium geometry and harmonic frequencies. In all cases we note a considerable amelioration of the results. For VEE values the MAD goes down from 0.234 eV to 0.024 eV for N_2 molecule and from 0.171 eV to 0.077 eV for C_2, respectively for EOM-CCSD and EOM-CCSDT models. Even larger changes occur for the adiabatic EEs where for both molecules we observe a reduction in MAE by more than the order of magnitude. The similar improvement is observed for the equilibrium bond lengths: at the CCSD level we achieve the accuracy of 0.02 Å which goes down by nearly an order of magnitude to 0.002 - 0.003 Å for the CCSDT model. Finally, a significant increase in the accuracy of the EOM-CCSDT results is observed also for the harmonic frequencies: the MAD is reduced from 177 and 114 wavenumbers to 42 and 14 wavenumbers for N_2 and C_2 molecules, respectively.

The quality of the theoretical results is easy to assess when the reference values are obtained with the well defined accuracy. In Table 3 we compare the electron affinity of the C_2 molecule obtained with the EOM-CCSD and EOM-CCSDT methods. We quote the values extrapolated from triple and quadruple zeta to the basis set limit both for the regular and augmented Dunning basis set [45–47]. In both cases an extension of the EOM-CC model results in lowering the EA value by 0.13 - 0.15 eV. Since the experimental value is measured with an accuracy of 0.1 eV it is difficult to conclude on the quality of the computed number. Nevertheless we would rather point out to the value close to 3.25 eV than to that indicated by the experiment.

Moreover, in the paper [44] we compare the data computed for the ozone molecule. For that system we were limited to the smaller basis sets (POL1 [48] and aug-cc-pVTZ [46]) and, consequently the larger discrepancies between computed and experimental values may be due to the basis set inadequacies. Nevertheless, what catches our attention is a dramatic change in the computed excitation energy for the 2^1A_1 state where the inclusion of triples reduces the theoretical value by ca 5 eV. This is due to the fact that the 2^1A_1 state is dominated by doubly excited configurations and in that case the EOM-CCSD scheme fails. However, also for the remaining EEs the effect of the connected triples is well pronounced and lowers the computed value by 0.2 – 0.4 eV. In all cases it is a desired result since it brings down the deviation from the experiment.

More erratic behavior is observed for the IP values. An inclusion of triples lowers the theoretical values, however the T_3 effect is smaller, ranging from 0.2 to 0.02 eV and is more basis set sensitive, e.g., the POL1 values are in significantly larger error than those due to aug-cc-pVTZ basis set. Thus the apparent relatively larger deviations from the experiment, e.g., $^2B_2$ state, can be explained by the basis set limitations. The same observation applies to the electron affinity calculations.

To make more general conclusion we presented in Fig. 7 a histogram indicating the mean absolute deviations of the computed excitation energies from the reference values for the EOM-CCSD and EOM-CCSDT models. The data considered in Fig. 7 where taken from the papers [39–41]. Analogous data, referring to the ionization potential calculations [29, 42, 43] are presented in Fig. 8. For the EE calculations

the average error for the EOM-CCSDT results amounts to 0.1 eV, for the IP – it is slightly lower and goes down to 0.06 eV. The histograms show that the gain in accuracy due to the inclusion of connected triples into the EOM-CC schemes is substantial and the EOM-CCSDT method may be considered as the source of reliable reference data for the more approximate theoretical tools in case where the experimental data are scarce or unavailable.

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Figure caption

Figure 1. Diagrammatic form of the R operators.

Figure 2. Diagrammatic representation of the $\bar{H}_N$ components entering the EOM-CCSDT equations.

Figure 3. Diagrammatic form of the EE-EOM-CCSDT equations in an antisymmetrized formalism for the standard version.

Figure 4. Diagrammatic picture of the factorization of selected contributions to the EE-EOM-CCSDT equations.

Figure 5. Diagrammatic form of the intermediates used in factorized contributions to the EE-EOM-CCSDT equations in Fig. 4.

Figure 6. Diagrammatic form of the IP-EOM-CCSDT equations in an antisymmetrized formalism for the standard version.

Figure 7. (Color online) Mean absolute deviation (eV) from the experimental data for excitation energies.

Figure 8. (Color online) Mean absolute deviation (eV) from the experimental data for ionization potentials.

Fig. 1.

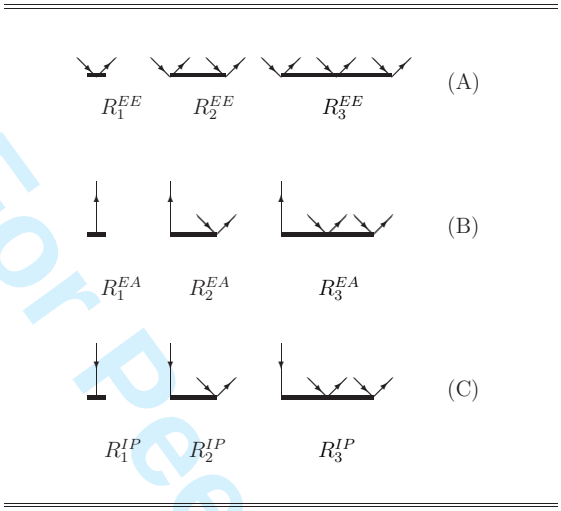

Fig. 2.

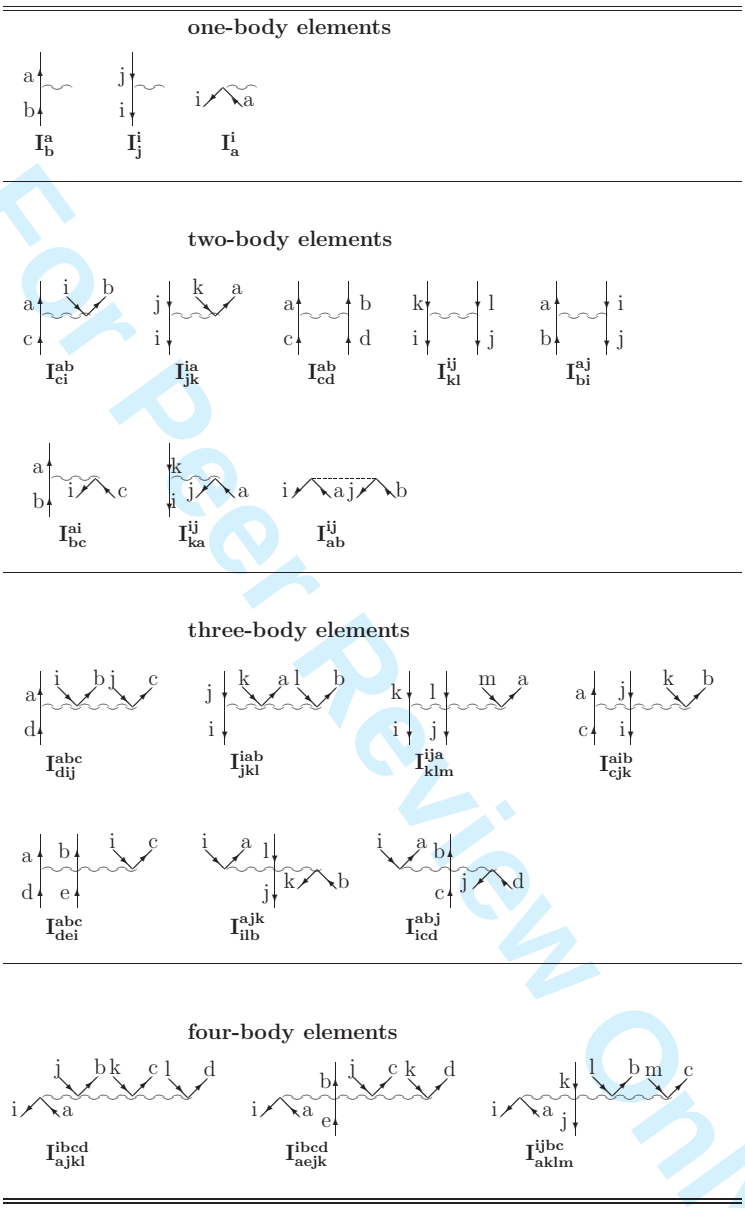

Fig. 3.

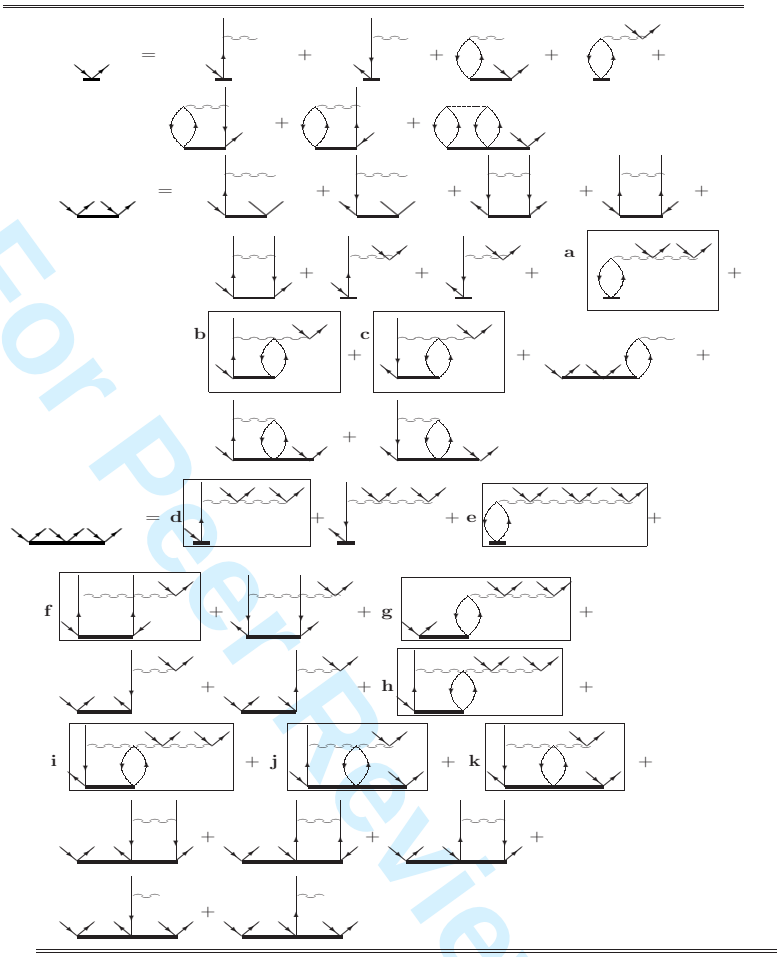

Fig. 4.

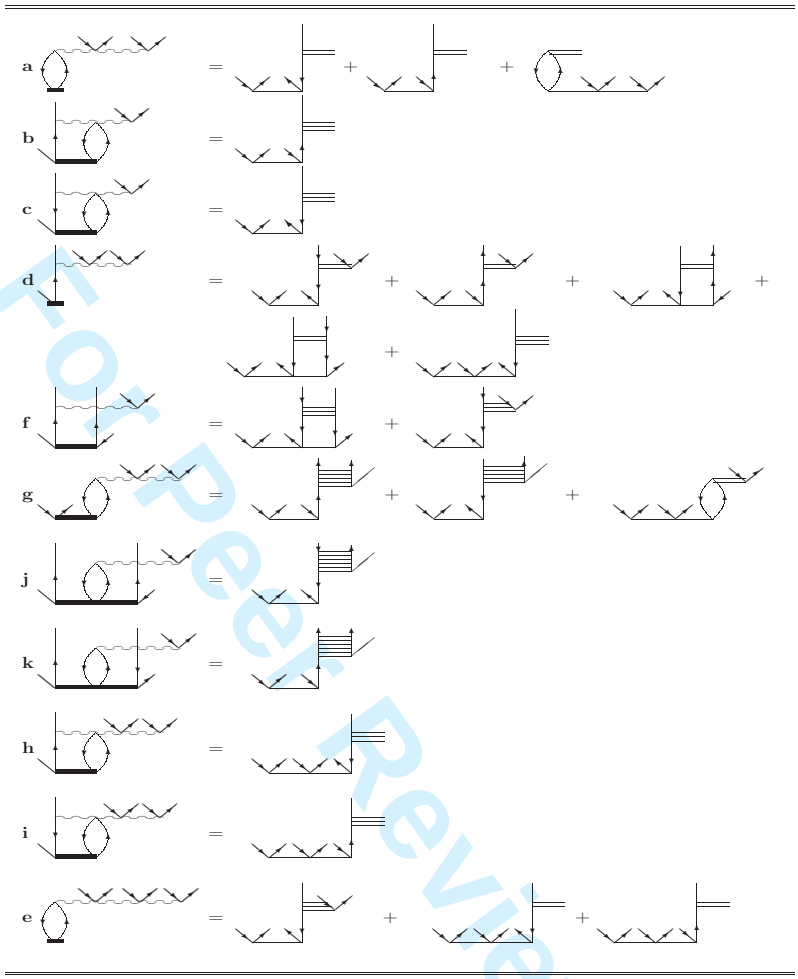

Fig. 5.

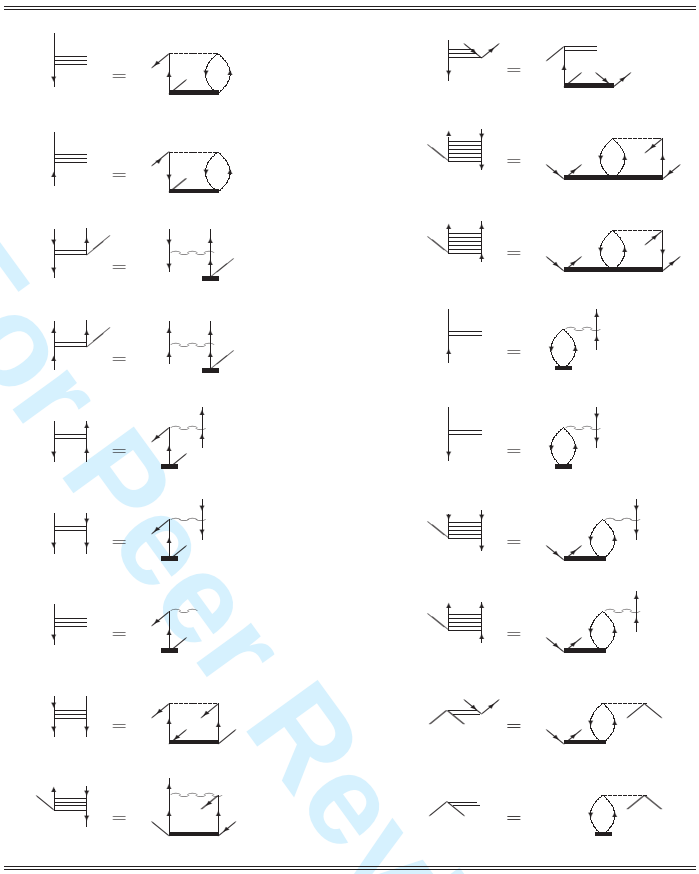

Fig. 6.

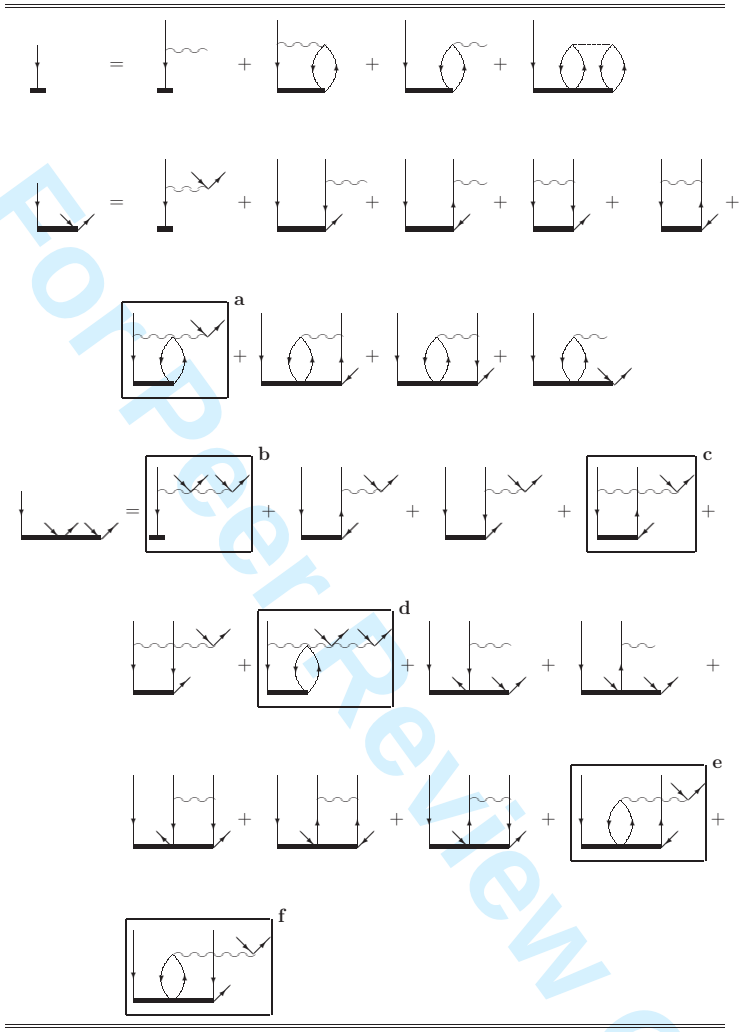

Fig. 7.

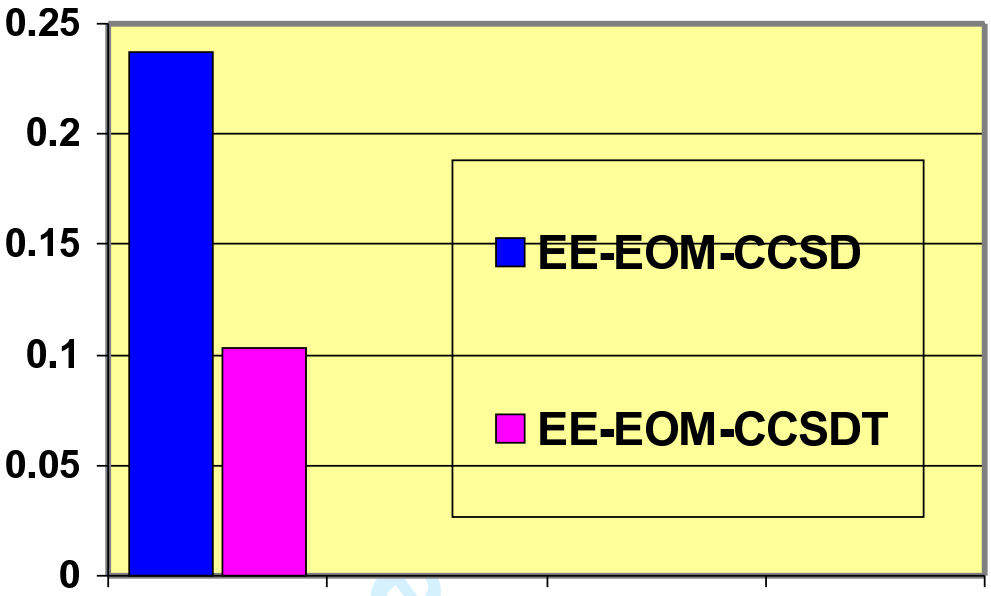

Fig. 8.

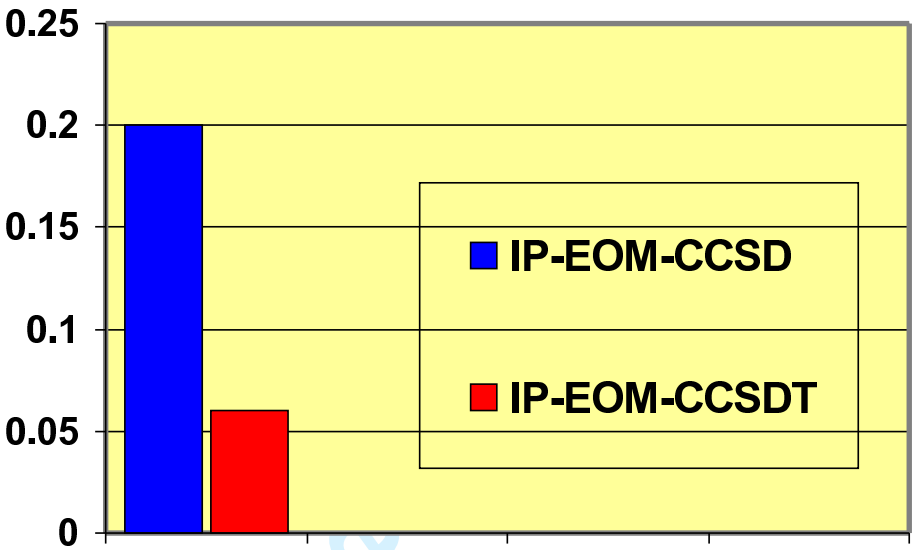

Table 1. Mean absolute deviation (eV) from the FCI values for the excitation energies and ionization potentials.

Mol./Atom	EOM-CCSD	EOM-CCSDT
excitation energies		
N_2	0.13	0.01
C_2	0.14	0.07
H_2O	0.08	0.03
HF	0.16	0.04
Ne	0.25	0.03
ionization potentials		
C_2	0.50	0.04
BH	0.19	0.01
H_2O	0.10	0.02

Table 2. Mean absolute deviations from experiment. EOM-CC methods with aug-cc-pVQZ basis set and core electrons frozen (Ref. [39]).

$VEE^{a)}$ (eV)			$AEE^{b)}$ (eV)		
Molecule	*SD*	**SDT**	*Molecule*	*SD*	**SDT**
$\mathbf{N_2}$	0.234	**0.024**	$\mathbf{N_2}$	0.313	**0.026**
CO	0.171	**0.077**	**CO**	0.221	**0.011**
R_e (Å)			ω (cm^{-1})		
Molecule	*SD*	**SDT**	*Molecule*	*SD*	**SDT**
$\mathbf{N_2}$	0.022	**0.003**	$\mathbf{N_2}$	177	**42**
CO	0.024	**0.002**	**CO**	114	**14**

[a)] VEE – vertical excitation energies.

[b)] AEE – adiabatic excitation energies.

Table 3. Extrapolated electron affinity (eV) for the C_2 molecule within EOM-CC methods (Ref. [30]).

Sym.	cc-pV∞Z		aug-cc-pV∞Z		
	CCSD	**CCSDT**	CCSD	**CCSDT**	*Exp.*[a)]
$^2\Sigma_g^+$	3.36	**3.23**	3.39	**3.24**	*3.30±0.1*

[a)] Ref. [49].

Gainesville, 07/14/10

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"The excited, ionized and electron attached states within the EOM-CC approach with full inclusion of connected triple excitations" by Monika Musial.

Dear Editors,
Please, find attached the revised version of the MS.

In response to the referee comments:

1. in abstract (p. 1) we corrected sentence, i.e instead of:
...triples reduces the average error for the EE by 2 anf for the IP by 3...
we have:
...triples for the EE reduces the average error twice and for the IP – three times...
2. p. 5: we added after Eq. (1):
where H_N is a normal ordered Hamiltonian with respect to the Φ_o vacuum.
3. p. 6 after Eq. (6) we added "in the Φ_o" so instead of:
where $a, b, ...$ run over unoccupied levels and $i, j, ...$ run over occupied levels
we have:
where $a, b, ...$ run over unoccupied levels and $i, j, ...$ run over occupied levels in the Φ_o.
4. p. 7 we added "lines below the vertex" so instead of:
....annihilation lines (see Fig. 2).
we have:
....annihilation lines (lines below the vertex, see Fig. 2).
5. and 6. fixed notation
7. fixed
8. fixed
9. fixed
10. p. 14 instead of:
... of the results ...
we have:
...of the EE results obtained upon inclusion of connected triples.
11. p. 14 insted of "discuss" we used "analyze"
12. p. 15 we added "extrapolated **from triple and quadruple zeta**"...

Sincerely yours,

Monika Musial