

COMMUNICATIONS

Coupled-cluster theory for excited electronic states: The full equation-of-motion coupled-cluster single, double, and triple excitation method

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The equation-of-motion coupled-cluster method with the full inclusion of the single, double, and triple excitations (EOM-CCSDT) has been formulated and implemented. The proper factorization procedure ensures that the method scales as n^8 , i.e., in the same manner as the standard CCSDT method for ground states. The method has been tested on the vertical excitation energies of the N_2 and CO molecules for several basis sets up to 92 basis functions. The full inclusion of the triple excitations improves the EOM-CCSD results by up to 0.2 eV for considered systems. © 2001 American Institute of Physics. [DOI: 10.1063/1.1416173]

I. INTRODUCTION

In the treatment of excited states, EOM-CC¹⁻¹¹ has the enviable property for application that, like ground state CC,^{2,12-16} the only decisions required are basis set and level of correlation. This makes it possible to calibrate the method for routine application. However, just as CCSD can be significantly improved by triples excitations as in CCSDT,¹⁴ there are reasons to expect the role of triples to be even greater for excited states. Primary among these is that the first correlation effects to excited states can be viewed as arising from double excitations from a zeroth-order single excitation approximation, so triple excitations can play a similar role to double excitations in the ground state. The ultimate such method is EOM-CCSDT. This note reports the initial results of a general purpose diagrammatic implementation of EOM-CCSDT.

EOM-CC may be viewed as a diagonalization of the CC effective Hamiltonian, $\bar{H} = e^{-T}He^T$, in the CI configuration space. It depends upon the CC model selected to construct the \bar{H} and on the type of configuration space chosen.¹⁷ Consistent approximations use the same excitation space for both the ground and excited states, like EOM-CCSD.¹ In addition, there are a number of variants that include triples approximately, noniteratively and iteratively.^{3,4,7,10,11} For the full EOM-CCSDT, after solving the standard CCSDT equations, the complete \bar{H} operator is constructed and subsequently diagonalized in the single, double, and triple excitation subspace. This minimal $\sim n^8$ procedure is computationally quite demanding. There have been full EOM-CCSDT results and the related CCSDT linear response results reported for some small basis set examples where full CI comparisons are usually possible.¹⁷⁻¹⁹ These also use CI-like ideas in their implementation. However, we fully use diagrammatic theory to derive the formulas and to organize an efficient implementa-

tion. The latter is only possible by extensively using a factorization procedure for the relevant diagrammatic intermediates. This allows us to perform EOM-CCSDT calculations at the same scaling of $\sim n^8$ as in the underlying CCSDT method. It also permits us to report here results from large (>90 functions) basis sets.

II. THEORY

The ground state wave function within the coupled-cluster formalism is expressed as

$$\Psi_g = e^T |\Phi_o\rangle, \quad (1)$$

where $|\Phi_o\rangle$ is an arbitrary single Slater determinant, usually chosen to be the SCF solution, and T is the cluster operator. Within the CCSDT model, the cluster operator is approximated as

$$T = T_1 + T_2 + T_3 \quad (2)$$

and T_n is defined as $T_n = (n!)^{-2} \sum t_{ij\dots}^{ab\dots} \{a^\dagger b^\dagger \dots ji\}$.

The cluster amplitudes, $t_{ij\dots}^{ab\dots}$, are determined by solving the CC equations

$$\langle \Phi_{ij\dots}^{ab\dots} | (He^T)_c | \Phi_o \rangle = 0. \quad (3)$$

In the EOM-CC method the wave function for the k th excited state is given by

$$|\Psi_k\rangle = R |\Psi_g\rangle, \quad (4)$$

and R is a linear (CI-like) excitation operator, defined as

$$R = R_0 R_1 + R_2 + R_3, \quad (5)$$

with R_n defined analogously as T_n , i.e., $R_n = (n!)^{-2} \sum r_{ij\dots}^{ab\dots} \{a^\dagger b^\dagger \dots ji\}$.

Inserting the $|\Psi_k\rangle$ wave function, Eq. (4), into the Schrödinger equation we obtain

TABLE I. Definitions of intermediates used in the EOM-CCSDT model.

Intermediate	Definition ^{a,b}	Scaling
I_1^1	$I_{ba}^a v_a^b + I_{ji}^i v_j^i$	$n_o^2 n_v^3, n_o^3 n_v^2$
I_2^1	$I_{a1}^i v_1^a$	$n_o^2 n_v^2$
I_1^2	$I_{ci}^{ab} v_{ab}^{ci} + I_{jk}^{ia} v_{ja}^{ik}$	$n_o^3 n_v^4, n_o^4 n_v^3$
I_2^2	$I_2^2 + I_{cd}^{ab} v_{ab}^{cd} + I_{kl}^{ij} v_{ij}^{kl}$	$n_o^3 n_v^3, n_o^2 n_v^4, n_o^4 n_v^2$
I_1^2	$I_{ib}^{aj} v_{aj}^{ib}$	$n_o^3 n_v^3$
I_2^3	$I_{bc}^{ai} v_{ai}^{bc} + I_{ka}^{ij} v_{ij}^{ka}$	$n_o^2 n_v^3, n_o^3 n_v^2$
I_1^3	$I_{dij}^{abc} v_{abc}^{dij} + I_{jkl}^{iab} v_{iab}^{jkl}$	$n_o^3 n_v^5, n_o^4 n_v^4$
I_2^3	$I_2^3 + I_{dei}^{abc} v_{abc}^{dei} + I_{klm}^{ija} v_{ija}^{klm}$	$n_o^4 n_v^4, n_o^3 n_v^5, n_o^5 n_v^3$
I_1^3	$I_{ejk}^{aib} v_{aib}^{ejk}$	$n_o^4 n_v^4$
I_2^3	$I_{ilb}^{ajk} v_{ajk}^{ilb} + I_{icd}^{abj} v_{abj}^{icd}$	$n_o^3 n_v^4, n_o^4 n_v^3$
I_1^4	$I_{ajkl}^{ibcd} v_{ibcd}^{ajkl}$	$n_o^4 n_v^5$
I_2^4	$I_{ajkl}^{ibcd} v_{ibcd}^{ajkl} + I_{aklm}^{ijbc} v_{ijbc}^{aklm} + I_{aejk}^{ibcd} v_{ibcd}^{aejk}$	$n_o^5 n_v^4, n_o^4 n_v^5$

^a $v_{tu\dots}^{rs\dots} = t^\dagger u^\dagger \dots s r$ ^bSummation over repeated indices assumed.

$$H R e^T |\Phi_o\rangle = E R e^T |\Phi_o\rangle, \quad (6)$$

or, since the R and T operators commute,

$$\bar{H} R |\Phi_o\rangle = E R |\Phi_o\rangle, \quad (7)$$

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

$$\bar{H} = e^{-T} H e^T. \quad (8)$$

The full EOM-CCSDT method requires solution of the CCSDT equations, Eq. (3), for T_1 , T_2 , and T_3 amplitudes, and then construction of the \bar{H} operator, according to Eq. (8). The form of \bar{H} which is required for the construction and solution of the EOM equations involves up to four-body intermediates. Emphasizing the many-body structure of \bar{H} , we may decompose it into individual contributions as follows:

$$\bar{H} = I^1 + I^2 + I^3 + I^4. \quad (9)$$

We may rewrite the particular intermediate, I^n ($\equiv \bar{H}$ element) as the sum over elements I_k^n , where k indicates the number of annihilation lines

$$\begin{aligned} I^1 &= I_1^1 + I_2^1, \\ I^2 &= I_1^2 + I_2^2 + I_3^2 + I_4^2, \\ I^3 &= I_1^3 + I_2^3 + I_3^3, \\ I^4 &= I_2^4 + I_3^4. \end{aligned} \quad (10)$$

In the last equation we skipped the I_1^4 component since it is not needed within the EOM-CCSDT model. In Table I, we specify the forms of the particular intermediate, assuming their antisymmetrized form. We note that some of them are not complete, e.g., I_2^4 , in which only a particle-hole component is included, is responsible for connecting the single and triple excitation subspaces. The other two components, i.e., particle-particle and hole-hole components, enter the CI part upon inclusion of the quadruple excitation subspace. On the other hand, we may expand the \bar{H} by its underlining CI-like structure and rewrite it in its matrix form:

$$\bar{H} = \begin{pmatrix} \bar{H}_{SS} & \bar{H}_{SD} & \bar{H}_{ST} \\ \bar{H}_{DS} & \bar{H}_{DD} & \bar{H}_{DT} \\ \bar{H}_{TS} & \bar{H}_{TD} & \bar{H}_{TT} \end{pmatrix}. \quad (11)$$

Note the constant term in Eq. (5) gives a zero column decoupling it from the matrix of Eq. (11). The interrelation between the matrix elements are given in Eq. (11) and the intermediates, Eq. (10), are presented in Table II. In column 2 of this table we specify the intermediates contributing to a given matrix element. We observe that in order to construct the complete EOM-CCSDT method, the four-body \bar{H} elements must be considered, as they enter the H_{TS} and H_{TD} matrix elements (see Table II). However, their conventional construction requires an n^9 computational procedure, slowing down the computations markedly. Thus, the construction of the four-body part of \bar{H} must be avoided in an efficient computational scheme. This procedure is analogous to that for avoiding construction of the three-body \bar{H} elements within the EOM-CCSD approach. As we see from Table II, in order to obtain the H_{DD} and H_{DS} matrix elements, which are present in the EOM-CCSD method, the three-body \bar{H} components are formally required. However, within the existing implementations, their construction is avoided. A similar procedure is applied here with respect to the four-body part of \bar{H} . Within the current implementation, we do not compute the I_2^3 intermediate which involves five particle indices (see the second component of I_2^3 in Table I)

TABLE II. Intermediates contributing to CI matrix elements.

Matrix element	Contributing intermediates ^a
H_{SS}	$\langle S I_1^1 + I_2^2 S \rangle$
H_{DD}	$\langle D I_1^1 + I_2^2 + I_3^3 D \rangle$
H_{TT}	$\langle T I_1^1 + I_2^2 + I_3^3 T \rangle$
H_{SD}	$\langle S I_2^1 + I_3^3 D \rangle$
H_{DS}	$\langle D I_2^1 + I_3^3 S \rangle$
H_{ST}	$\langle S I_4^2 T \rangle^b$
H_{TS}	$\langle T I_1^3 + I_2^4 S \rangle$
H_{DT}	$\langle D I_2^1 + I_3^3 T \rangle$
H_{TD}	$\langle T I_1^2 + I_2^3 + I_3^4 D \rangle$

^a S , D , T represent single-, double-, and triple-excited determinants, respectively.^b I_4^2 is a two-electron integral based operator: $I_4^2 = \langle ij || ab \rangle i^\dagger j^\dagger b a$.

TABLE III. Excitation energies of N₂ with EOM-CC methods [eV] ($R=2.068$ au).

Excited state	DZP		PBS ^a		PVDZ+ ^b		PVTZ		PVTZ+ ^b		Experiment ^c
	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	
¹ Π _g	9.602	9.528	9.600	9.519	9.583	9.506	9.559	9.482	9.497	9.417	9.31
¹ Σ _u	10.460	10.299	10.308	10.165	10.324	10.188	10.185	10.087	10.124	10.019	9.92
¹ Δ _u	10.885	10.680	10.726	10.549	10.729	10.561	10.636	10.500	10.567	10.427	10.27

^aPolarized basis of Sadlej, Ref. 25.^bPVXZ+ indicates aug-cc-pVXZ basis set, Ref. 24.^cReference 27 ¹Π_u and ¹Σ_u⁺ states are from Ref. 28.

in order to avoid large storage problems. This component, as well as the four-body part, are included by the proper factorization procedure. We stress that this procedure does not introduce any approximation. Thus, the computational scheme can be described as follows:

- Solve the standard CCSDT equations for the ground state problem.
- Using the converged T_1 , T_2 and T_3 amplitudes, construct all \bar{H} elements listed in Table I, except for the two four-body and one three-body pieces.
- Apply a generalized, non-Hermitian Davidson diagonalization procedure^{20,21} taking care to properly modify the CI-vector construction to account for the \bar{H} elements whose explicit construction is avoided.

The detailed description of the adopted computational scheme together with complete formulas for the intermediates will be given elsewhere.²²

III. RESULTS

The performance of the newly implemented method has been tested for two example molecules: N₂ and CO. Five different basis sets have been employed for each system: standard DZP,²³ three examples of the correlation-consistent basis sets of Dunning:²⁴ aug-cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ; and the polarized basis set of Sadlej.²⁵ The results, i.e., vertical excitation energies, have been listed in Table III (N₂) and in Table IV (CO) along with the experimental results. First, we note that all three states of N₂ are dominated by singles, hence the EOM-CCSD should give reasonably good agreement with experiment. The largest T_3 effect is observed for the ¹Δ_u state. For the ¹Σ_u state, T_3 produces a somewhat smaller difference, reducing the error relative to experiment by 0.14–0.16 eV for the double zeta sets and by

0.10 eV for the triple zeta ones. Finally, for the ¹Π_g state, the T_3 contribution is nearly constant amounting to 0.08 eV.

It is obvious from Table III that one source of discrepancies between the theoretical and experimental values is inadequacies in the basis sets. We observe that at the DZP level the CCSD error amounts to 0.3, 0.5, and 0.6 eV for the three states considered. When going to the augmented triple zeta basis set—the largest used in this work—the errors are reduced to 0.2 eV (¹Π_g and ¹Σ_u) and 0.3 eV (¹Δ_u). By doing the full triples calculations for the latter basis set the error is reduced by half to approximately 0.1 eV (¹Π_g and ¹Σ_u) and 0.16 eV (¹Δ_u).

For the CO molecule, we consider four excited states: ¹Π, ¹Σ[−], ¹Δ, and ¹Σ⁺. Within the computational scheme adopted in this work, which uses the CIS solution as an initial guess for the Davidson diagonalization, we were unable to locate the ¹Σ⁺ state for the DZP and cc-pVTZ basis sets. We observe for the present example a similar behavior of the T_3 contributions as in the case of N₂ molecule; they lower the energy of each state bringing it closer to experiment. The largest T_3 effect occurs for the ¹Σ⁺ state improving—relative to experiment—its energy by ca. 0.23 eV. A significant improvement of 0.10 eV is obtained also for the ¹Π state. For the other two states the T_3 effect is smaller, 0.02 to 0.05 eV. Generally, for the largest basis set considered, the complete inclusion of the triple excitations reduces the EOM-CCSD error from 0.13 to 0.03 eV for the ¹Π state, from 0.21 to 0.16 eV for the ¹Σ[−] state, from 0.43 to 0.20 eV for the ¹Σ⁺ state. For the ¹Δ state, the CCSD result accidentally matches the experimental value while the T_3 moves it away by 0.05 eV.

Part of the error occurring at the aug-cc-pVTZ level is due to the basis set inadequacies. It is difficult to say how much improvement would be obtained by higher correlation treatments. In the full CI analysis of the EOM-CC methods by Hirata *et al.*,¹⁷ the T_4 effect was observed to amount to

TABLE IV. Excitation energies of CO with EOM-CC methods [eV] ($R=2.132$ au).

Excited state	DZP		PBS ^a		PVDZ+ ^b		PVTZ		PVTZ+ ^b		Experiment ^c
	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	CCSD	CCSDT	
¹ Π	8.841	8.746	8.764	8.664	8.719	8.621	8.736	8.648	8.636	8.541	8.51
¹ Σ [−]	10.291	10.269	10.193	10.162	10.202	10.168	10.140	10.097	10.093	10.045	9.88
¹ Δ	10.415	10.389	10.314	10.285	10.317	10.283	10.287	10.240	10.230	10.182	10.23
¹ Σ ⁺			11.154	10.931	11.164	10.939			11.215	10.983	10.78

^aSee footnote in Table III.^bSee footnote in Table III.^cReference 29.

10% of that due to triples. Although one might expect that for larger systems the same proportions will not necessarily apply.

The vertical excitation energies obtained with the full EOM-CCSDT method, indicate that the triple excitations significantly reduce the error introduced at the EOM-CCSD level. Even for the states which are dominated by single excitations, the T_3 effect amounts to 0.1–0.2 eV. For states dominated by double excitations, T_3 has been shown to be absolutely essential,^{4,17,26} and even the EOM-CCSDT-3 method, the most complete to date, falls short for some difficult examples.^{4,17} These states will be considered in future work.

To make the program applicable to larger basis sets, the explicit consideration of all the four-body elements as well as certain three-body pieces were factorized, at the expense of the introduction of more complicated equations within the CI-like part of the code. The factorization procedure makes it possible to maintain the rank of the computational procedure as n^8 for the whole method, the same as CCSDT for the ground state.

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