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*J. Chem. Phys.* 164, 124116 (2026)

<https://doi.org/10.1063/5.0316510>



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# Equation-of-motion coupled-cluster methods for doubly ionized and doubly electron-attached states with single, double, and triple substitutions: Theory, implementation, and benchmarks

Cite as: J. Chem. Phys. 164, 124116 (2026); doi: 10.1063/5.0316510

Submitted: 13 December 2025 • Accepted: 19 February 2026 •

Published Online: 27 March 2026



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## ABSTRACT

We present new and computationally efficient implementation of the equation-of-motion (EOM) coupled-cluster methods for doubly ionized (DIP) and doubly electron-attached (DEA) states including single, double, and triple substitutions. In particular, EOM operators include up to 4-hole-2-particle substitutions in EOM-DIP-CCSDT and up to 4-particle-2-holes substitutions in EOM-DEA-CCSDT; both treatments include up to 3-hole-3-particle substitutions in the CC part. These methods have been implemented in the *Q-CHEM* package using effective and open-mp parallel *libtensor* and *libxm* backends. The implementation takes advantage of permutational and point-group symmetries (Abelian subgroups only) and is partially spin-adapted in the case of closed-shell references; it enables both the conventional double-precision and single-precision execution. This paper reports the programmable expressions and details of the implementation. The capabilities of the full EOM-DIP/DEA-CCSDT are demonstrated by application to methylene diradical (CH<sub>2</sub>), water (H<sub>2</sub>O), ammonia (NH<sub>3</sub>), cyclobutadiene (C<sub>4</sub>H<sub>4</sub>), acetylene (C<sub>2</sub>H<sub>2</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), and formaldehyde (CH<sub>2</sub>O), highlighting the utility of these methods for treating diradicals, excited states, and Auger decay.

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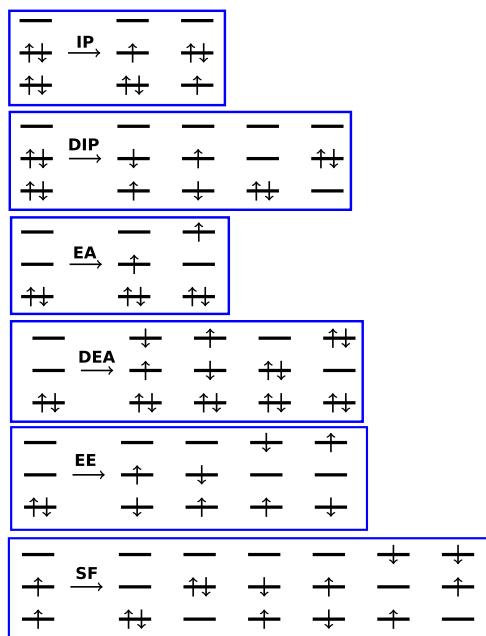
## I. INTRODUCTION

Owing to its ability to accurately treat electronic structure of open-shell and electronically excited species, equation-of-motion (EOM) coupled-cluster (CC) theory became a popular quantum-chemistry method.<sup>1–4</sup> EOM formalism extends CC theory, originally formulated as a single-state approach, to describing multiple states.<sup>5–9</sup> EOM-CC offers an adaptable, robust, and efficient alternative to multi-reference (MR) CC approaches.<sup>10–25</sup>

A specific EOM-CC model is defined by the type of excitation operator, which determines the manifold of the target states accessible from a chosen reference, and by the highest level of excitations included in the ansatz. When all possible excitations are included, EOM-CC is exact, i.e., equivalent to full configuration interaction (FCI). As in other wave-function methods, practical applications

rely on truncated many-body expansions. The truncation reduces computational scaling and costs, but results in lower accuracy. The lowest level of truncation for EOM-CC involves single and double excitations (or, more precisely, substitutions), giving rise to the EOM-CCSD family of methods. In EOM-CCSD, the CC expansion is truncated at singly and doubly excited determinants and EOM-CC expansion is truncated accordingly. EOM-CCSD methods scale as  $N^6$  and yield size-intensive transition energies (excitation, ionization, and electron attachment).<sup>2,4,26,27</sup> Different target states are accessed by choosing different types of EOM operators, as illustrated in Fig. 1.

The most commonly used are EOM-CC methods for electronic excitations (EE),<sup>28–30</sup> ionization potentials (IP), and electron attachment (EA).<sup>31–36</sup> In these variants, the effective EOM Hamiltonian—the similarity-transformed Hamiltonian—is



**FIG. 1.** Different types of target states can be accessed by different combinations of the reference state and EOM operators (only action of the lowest-rank operators is shown). Reproduced with permission from Casanova and Krylov, Phys. Chem. Chem. Phys. **22**, 4326–4342 (2020). Copyright 2020 Royal Society of Chemistry.

diagonalized over the space of the singly and doubly substituted configuration, i.e.,  $1h1p$  (1-hole-1-particle) and  $2h2p$  for EOM-EE,  $1h$  and  $2h1p$  for EOM-IP, and  $1p$  and  $2p1h$  for EOM-EA (here and in the following,  $nh\ mp$  denotes  $n$ -hole- $m$ -particle substituted determinants with respect to the chosen reference determinant). The quality of EOM-CC treatment depends on whether the reference is well-behaved and whether the leading character of the target states is captured by the lowest-rank EOM operator.

To treat systems with electronic degeneracies (such as molecules with small HOMO–LUMO gaps), EOM-CC exploits spin-flipping operators acting on high-spin reference states, giving rise to the EOM-SF family.<sup>27,37–41</sup>

Following a similar strategy, double ionization potential (DIP) and double electron-attachment (DEA) variants can be deployed, where the target states are described by doubly ionized ( $2h, \dots$ ) or doubly electron-attached ( $2p, \dots$ ) configurations, respectively.<sup>34,42–53</sup>

A typical accuracy of EOM-CCSD for transition energies is 0.1–0.3 eV, usually with smaller errors for energy gaps between the target states. However, for states derived by higher excitations, such as doubly excited states ( $2h2p$ ) in EOM-EE or satellite states ( $2h1p$ ) in EOM-IP, the errors are much larger, spoiling the predictive power of these methods in spectroscopic applications.<sup>54–56</sup> Hence, in some cases, the EOM-CCSD ansatz is not sufficient and one needs to incorporate higher-body terms at both the CC and EOM levels. Perturbative approaches, such as CCSD(T),<sup>57</sup> improve the total energies and energy derivatives. However, when the reference and target states differ in the number of electrons and/or

the spin-multiplicity, the extent of correlation recovered by the perturbative (and non-iterative) corrections differs for the two states, resulting in poorer energy gaps between the reference and target states, even though the total energies of the target states and the target-target energy gaps might be improved.<sup>58,59</sup> Properly balanced correlation treatment across multiple electronic states can only be achieved by including full triples in the CC and EOM expansions, resulting in the EOM-CCSDT treatment.<sup>60–68</sup>

In this contribution, we focus on the DIP and DEA variants of EOM-CCSDT. In the DIP and DEA methods, the number of electrons in the target-state manifold differs by 2 from the reference configuration. Hence, the lowest-rank EOM operators are two-electron ones ( $2h$  or  $2p$ ). To be consistent with EOM treatments of excited states, where excitation manifold includes excitations of one or two higher ranks than the lowest level ( $1h1p$ ), EOM-DIP-CCSD includes  $2h$  and  $3h1p$  operators and EOM-DEA-CCSD includes  $2p$  and  $1h3p$  operators in the EOM expansion. Similarly, EOM-DIP-CCSDT and EOM-DEA-CCSDT include, respectively, the  $4h2p$  and  $2h4p$  operators in addition to those already present in the EOM-CCSD analogs. Hence, while the CCSDT amplitudes include the one-, two-, and three-electron operators, in the EOM-DEA/DIP-CCSDT ansatz, we essentially have the two-, three-, and four-electron operators. Alternative choices of truncations of EOM and CC expansions have been also explored, such as using only  $2p$  or  $2h$  EOM operators and the CCSD reference or using up to  $4p2h$  or  $4h2p$  EOM operators and the CCSD reference (see, for example, Refs. 48–50). Although such alternative choices also result in size-intensive energy differences and can yield reasonable (and in some cases even exact) energy differences between the EOM states, they do not provide balanced treatment of the reference and the target states and, therefore, do not yield accurate electron-detachment/attachment energies. In-depth discussion on the size-intensivity of different EOM-CC schemes can be found in Refs. 2, 29, 30, 48, and 69–71.

While full EOM-DIP-CCSDT implementation has been recently reported in the literature,<sup>68</sup> the full EOM-DEA-CCSDT implementation is reported here for the first time, building on our previous EOM-SF-CCSDT work.<sup>67</sup> We have implemented these methods within the *Q-CHEM* electronic structure package<sup>72,73</sup> using general and efficient tensor libraries, *libtensor* and *libxm*.<sup>74,75</sup> The implementation works with both closed-shell and open-shell references, utilizes permutational and Abelian point group symmetries, and, in the case of the closed-shell references, is partially spin-adapted. We implemented these methods both within the conventional double precision and within single precision algorithms.<sup>76</sup> Single precision execution reduces both the storage and memory requirements in the CC and in EOM parts of the computation by ~50%, thereby extending the scope of these methods to bigger molecules for which the double-precision algorithm may be too demanding. Similarly to the EOM-CCSD benchmarks,<sup>76</sup> we observe only insignificant reduction in accuracy due to the use of single precision [ $O(10^{-4})$  eV].

The structure of this paper is as follows: We begin with a brief exposition of the EOM-CCSDT theory, as applied to the DIP and DEA treatments (Sec. II). In Sec. III, we demonstrate the capabilities of our methods through applications to a set of small- and medium-size molecules, including methylene diradical ( $\text{CH}_2$ ), water ( $\text{H}_2\text{O}$ ),

ammonia (NH<sub>3</sub>), cyclobutadiene (C<sub>2</sub>H<sub>4</sub>), acetylene (C<sub>2</sub>H<sub>2</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), and formaldehyde (CH<sub>2</sub>O). Our concluding remarks are given in Sec. IV.

## II. THEORY

The utility of the DEA and DIP variants of the EOM-CC methods has been illustrated by many studies.<sup>42,45,48–50,68,77–85</sup> In the following, we present a concise formulation of the EOM-DIP/DEA-CCSDT methods, followed by the details of our implementation.

Wavefunction  $\Psi_m$  of target state  $m$  is obtained by EOM operator  $\hat{R}$  acting on the reference state,

$$|\Psi_m\rangle = \hat{R}|\Psi_0\rangle = \hat{R}e^{\hat{T}}|\Phi_0\rangle, \quad (1)$$

where  $|\Psi_0\rangle$  is the reference CC wavefunction,

$$|\Psi_0\rangle = e^{\hat{T}}|\Phi_0\rangle \quad (2)$$

and  $\hat{R}$  is the linear excitation operator of a general type (excitation is defined with respect to the reference Slater determinant,  $\Phi_0$ ). In the DIP ansatz, the  $\hat{R}$  operator removes two electrons from the reference determinant, whereas in the DEA ansatz,  $\hat{R}$  adds two electrons to the reference.

The equations for the cluster amplitudes  $\hat{T}$  are obtained by projecting the Schrödinger equation onto the space of the excited determinants,  $\Phi_\mu$ ,

$$e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = (\hat{H}e^{\hat{T}})_C|\Phi_0\rangle = \hat{H}|\Phi_0\rangle = E_0|\Phi_0\rangle, \quad (3)$$

$$E_{CC} = E_0 = \langle\Phi_0|\hat{H}|\Phi_0\rangle, \quad (4)$$

$$0 = \langle\Phi_\mu|\hat{H}|\Phi_0\rangle, \quad \mu = 1, \dots, \mu_{\max}, \quad (5)$$

where  $\mu_{\max}$  is defined by the highest level of excitation included in the ansatz and  $\hat{H}$  is the similarity transformed Hamiltonian,

$$\hat{H} = e^{-\hat{T}}\hat{H}e^{\hat{T}}. \quad (6)$$

Here, we truncate  $\hat{T}$  up to triples, i.e.,  $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$ .

The equations for the amplitudes of the EOM operators  $\hat{R}$  are also obtained by satisfying the Schrödinger equation in the corresponding subspace,

$$\hat{H}|\Psi_m\rangle = \hat{H}\hat{R}e^{\hat{T}}|\Phi_0\rangle = \hat{H}e^{\hat{T}}\hat{R}|\Phi_0\rangle = E_m\hat{R}e^{\hat{T}}|\Phi_0\rangle, \quad (7)$$

$$\hat{H}\hat{R}|\Phi_0\rangle = E_m\hat{R}|\Phi_0\rangle. \quad (8)$$

Action of  $\hat{R}$  on  $\hat{H}$  yields

$$\hat{H}\hat{R}|\Phi_0\rangle = E_{CC}\hat{R}|\Phi_0\rangle. \quad (9)$$

For DEA and DIP, operator  $\hat{R}$  comprises one-body, two-body, and three-body DEA or DIP operators. Figure 1 illustrates the action of different EOM operators on the reference (only the action of the lowest-rank  $\hat{R}$  is shown),

$$\hat{R} = \hat{R}_2 + \hat{R}_3 + \hat{R}_4, \quad (10)$$

$$\begin{aligned} \hat{R}^{DEA} = & \frac{1}{2} \sum_{ab} r^{ab} a^\dagger b^\dagger + \frac{1}{6} \sum_{abc} \sum_i r_i^{abc} a^\dagger b^\dagger c^\dagger i \\ & + \frac{1}{48} \sum_{abcd} \sum_{ij} r_{ij}^{abcd} a^\dagger b^\dagger c^\dagger d^\dagger ji, \end{aligned} \quad (11)$$

$$\hat{R}^{DIP} = \frac{1}{2} \sum_{ij} r_{ij} ij + \frac{1}{6} \sum_{ijk} \sum_a r_{ijk}^a a^\dagger kji + \frac{1}{48} \sum_{ijkl} \sum_{ab} r_{ijkl}^{ab} a^\dagger b^\dagger lkji, \quad (12)$$

where indices  $i, j, k, l, \dots$  denote occupied orbitals and indices  $a, b, c, d, \dots$  denote virtual orbitals (occupied and virtual orbital spaces are defined by the reference determinant,  $\Phi_0$ ).

The above equations for the EOM amplitudes can be cast into matrix eigenvalue form

$$\begin{pmatrix} \hat{H}_{DD} - E_{CC} & \hat{H}_{DT} & \hat{H}_{DQ} \\ \hat{H}_{TD} & \hat{H}_{TT} - E_{CC} & \hat{H}_{TQ} \\ \hat{H}_{QD} & \hat{H}_{QT} & \hat{H}_{QQ} - E_{CC} \end{pmatrix} \begin{pmatrix} R_2 \\ R_3 \\ R_4 \end{pmatrix} = \Omega \begin{pmatrix} R_2 \\ R_3 \\ R_4 \end{pmatrix}. \quad (13)$$

Here, the eigenvalues  $\Omega = E - E_{CC}$  yield the DEA and DIP transition energies of the respective target states relative to the reference state. As illustrated by the following applications, often the reference serves a formal role and one is interested in the transition energies between the target EOM states.

EOM-CC is a non-Hermitian theory, meaning that left eigenvectors of the similarity transformed Hamiltonian are not (complex) conjugates of the right eigenvectors. Left eigenvectors are required only when calculating gradients or properties.

Full diagonalization of the similarity transformed Hamiltonian matrix, Eq. (13), is computationally expensive. Since in most cases, one is interested in a small number of electronic states, Davidson's iterative diagonalization<sup>86–88</sup> is used. The corresponding programmable expressions for EOM-DIP/DEA-CCSDT are given in the Appendix.

We implemented these methods using general tensor libraries (*libxm* and *libtensor*), which afford handling of various symmetries, flexible management of RAM and disk space, and are open-mp parallel.<sup>74,75</sup> Single precision implementation reduces memory footprint by a factor of 2. The methods have been implemented in the *Q-CHEM* package and are available in 6.3 and higher releases.

### A. Computational details

Core orbitals were frozen in all correlated calculations. Symmetry labels for molecular orbitals and electronic states were assigned according to Mulliken's convention.<sup>89</sup> Since this differs from *Q-CHEM*'s standard molecular orientation,<sup>90</sup> we manually relabeled the irreps to match Mulliken's convention.

To describe  $N$ -electron target states, EOM-DEA-CCSDT uses an  $N-2$  reference state whereas EOM-DIP-CCSDT uses an  $N+2$  reference state. Thus, from a closed-shell Hartree-Fock reference of a neutral molecule, the DEA and DIP variants of EOM-CCSDT compute, respectively, the dianionic and dicationic states. In order to compute excited states of a neutral molecule, one can use a suitable dicationic reference and obtain the desired states as DEA target states. Alternatively, one can start with a dianionic reference and obtain the excited states of the neutral molecule as the DIP target states. We note that calculations using dianion references, which are often unstable with respect to electronic detachment,<sup>91</sup> may require

special treatments to stabilize the dianion state, such as using small bases or charge stabilization techniques.<sup>46,47</sup>

Molecular geometries and basis sets were chosen based on previous benchmark studies: methylene geometries and the TZ2P basis set were taken from Ref. 92, cyclobutadiene geometries from Ref. 38, and geometries for water and ammonia from Ref. 93. The structures of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and CH<sub>2</sub>O are from Ref. 50 (where they were taken from the NIST database).

Single-point EOM calculations were carried out using the following basis sets: TZ2P for methylene, cc-pVDZ for cyclobutadiene, and aug-cc-pVDZ for water and ammonia. To compute double ionization energies with EOM-DIP-CCSDT, we used aug-cc-pVTZ for acetylene and aug-cc-pVDZ for the ethylene and formaldehyde, following the protocols from Ref. 50.

In all EOM calculations, the Davidson algorithm was used to solve for the excitation energies, with a convergence threshold of 10<sup>-5</sup> for EOM amplitudes to ensure numerical stability of single precision calculation.<sup>76</sup> All calculations were performed using the *Q-CHEM* software package<sup>73</sup> on high performance computational facilities at BITS Pilani and USC.

### III. RESULTS AND DISCUSSION

#### A. Methylene diradical

Vertical excitation energies of the methylene diradical were computed using its ground-state geometry optimized at the FCI/TZ2P level.<sup>92</sup> Table I summarizes the results. The values obtained using the single-precision algorithm are marked with (SP) and are within 10<sup>-4</sup> eV from the corresponding double-precision values, which is consistent with the previous benchmarks at the EOM-CCSD level.<sup>76</sup>

At the EOM-CCSDT level, the vertical excitation energies calculated by the DIP and DEA approaches differ from those obtained using the SF method by less than 0.02 and 0.004 eV, respectively, both in the single precision and double precision calculations. These differences are small relative to those at the CCSD level. At the CCSD level, the maximum absolute difference of DEA relative to SF is 0.086 eV whereas for DIP, it is 0.205 eV. The difference between the DEA and DIP excitation energies is reduced from 0.12 eV at the CCSD level to just 0.02 eV at the CCSDT level. This is

**TABLE I.** Methylene: total energies (hartree) of ground state ( $\tilde{X}^3B_1$ ) and vertical excitation energies (eV).

Method	$\tilde{X}^3B_1$	$\tilde{a}^1A_1$	$\tilde{b}^1B_1$	$\tilde{c}^1A_1$
SF-CCSD <sup>a</sup>	-39.063 37	0.986	1.585	3.322
DEA-CCSD	-39.052 38	0.900	1.490	3.158
DIP-CCSD	-39.038 28	0.781	1.435	3.171
SF-CCSDT	-39.066 69	0.972	1.566	3.274
SF-CCSDT(SP) <sup>b</sup>	-39.066 69	0.972	1.566	3.274
DEA-CCSDT	-39.066 76	0.972	1.562	3.270
DEA-CCSDT(SP) <sup>b</sup>	-39.066 77	0.972	1.562	3.270
DIP-CCSDT	-39.065 46	0.943	1.545	3.258
DIP-CCSDT(SP) <sup>b</sup>	-39.065 47	0.943	1.545	3.258

<sup>a</sup>UHF reference.

<sup>b</sup>SP: single precision algorithm.

expected behavior, as all EOM methods ultimately converge to the FCI limit.

Table II shows the adiabatic excitation energies (excluding zero-point energy corrections) for the 3 lowest singlet excited states. Here too, the DEA and DIP excitation energies agree well with the SF results, with maximum deviations of 0.02 and 0.009 eV, respectively, at the CCSDT level. These differences are much smaller than those at the CCSD level: 0.184 eV for DEA vs SF and 0.227 eV for DIP vs SF.

#### B. Ammonia and water

We analyze two small molecules, water (H<sub>2</sub>O) and ammonia (NH<sub>3</sub>), from previously used benchmark sets<sup>53,93</sup> to assess the accuracy of EOM-DEA-CCSDT and EOM-DIP-CCSDT for singly excited states. The low-lying excited states in these molecules exhibit significant Rydberg character, which is common in smaller molecules. In contrast to DFT, EOM-CC theory is capable of treating both Rydberg and valence states on the same footing.<sup>94</sup>

Table III summarizes the results for ammonia, where the low-lying excited states primarily involve transitions from the HOMO, which corresponds to the nitrogen's lone pair. Two states from Table III correspond to HOMO-LUMO excitations, and because both DEA and DIP methods are designed to target such states, they are expected to capture these excitations with good accuracy. Indeed, the vertical excitation energies computed using EOM-DEA-CCSDT and EOM-DIP-CCSDT with the aug-cc-pVDZ basis

**TABLE II.** Methylene: adiabatic excitation energies (eV) relative to the ( $\tilde{X}^3B_1$ ) ground state.

Method	$\tilde{a}^1A_1$	$\tilde{b}^1B_1$	$\tilde{c}^1A_1$
FCI <sup>a</sup>	0.483	1.542	2.674
SF-CCSD	0.509	1.563	2.701
DEA-CCSD	0.478	1.461	2.517
DIP-CCSD	0.286	1.404	2.474
SF-CCSDT	0.484	1.544	2.674
SF-CCSDT(SP) <sup>b</sup>	0.484	1.544	2.674
DEA-CCSDT	0.493	1.539	2.668
DEA-CCSDT(SP) <sup>b</sup>	0.493	1.539	2.668
DIP-CCSDT	0.455	1.523	2.650
DIP-CCSDT(SP) <sup>b</sup>	0.455	1.523	2.650

<sup>a</sup>From Ref. 92.

<sup>b</sup>SP: single precision algorithm.

**TABLE III.** Ammonia: vertical excitation energies (eV) for 3 singlet and 1 triplet states computed with different methods; aug-cc-pVDZ.

States	EE-CCSDT	DEA-CCSDT/+2	DIP-CCSDT/-2	Exp-t <sup>a</sup>
<sup>1</sup> A <sub>2</sub> ( <i>n</i> → 3 <i>s</i> )	6.462	6.480	6.500	6.390
<sup>1</sup> A <sub>1</sub> ( <i>n</i> → 3 <i>p</i> )	8.058	8.079	8.245	8.260
<sup>1</sup> A <sub>2</sub> ( <i>n</i> → 4 <i>s</i> )	10.391	10.551	11.621	
<sup>3</sup> A <sub>2</sub> ( <i>n</i> → 3 <i>s</i> )	6.170	6.190	6.210	6.020

<sup>a</sup>From Ref. 95.

**TABLE IV.** Water: vertical excitation energies (eV) for the 2 lowest singlet and 2 lowest triplet states computed with different methods; aug-cc-pVDZ.

States	EE-CCSDT	DEA- CCSDT/+2	DIP- CCSDT/-2	Exp-t <sup>a</sup>
<sup>1</sup> B <sub>1</sub> ( <i>n<sub>y</sub></i> → 3 <i>s</i> )	7.496	7.525	7.520	7.41
<sup>1</sup> A <sub>2</sub> ( <i>n<sub>y</sub></i> → 3 <i>p</i> )	9.278	9.306	9.326	9.20
<sup>3</sup> B <sub>1</sub> ( <i>n<sub>y</sub></i> → 3 <i>s</i> )	7.109	7.135	7.128	7.20
<sup>3</sup> A <sub>2</sub> ( <i>n<sub>y</sub></i> → 3 <i>p</i> )	9.107	9.136	9.154	8.90
<sup>1</sup> A <sub>1</sub> ( <i>n<sub>z</sub></i> → 3 <i>s</i> )	9.792	13.891	14.252	9.67
<sup>3</sup> A <sub>1</sub> ( <i>n<sub>z</sub></i> → 3 <i>s</i> )	9.315	13.500	14.012	9.46

<sup>a</sup>From Ref. 96.

set agree well with the experimental values. Two other states are HOMO–LUMO+1 excitations; they are best described by the EOM-DEA ansatz. Nevertheless, due to the presence of explicit triples, EOM-DIP-CCSD also yields reasonable description of these states. The maximum absolute error relative to the experiment is 0.17 eV for DEA and 0.19 eV for DIP.

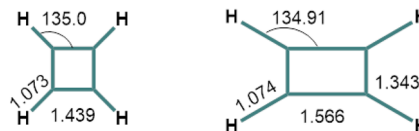
The results for water are shown in Table IV. In contrast to ammonia, some of water's low-lying excited states originate from HOMO-1, which is not the primary manifold of the DEA. At the DIP level, these states can be treated better, provided the reference orbitals capture the Rydberg character of the target state. As a result, these states (of *n<sub>z</sub>* → 3*s* character) have much larger errors, even with the inclusion of triple excitations. For the states derived by excitations from HOMO, both methods yield reasonably accurate excitation energies that differ from the experimental values by 0.24 eV or less for both DEA and DIP.

To highlight the importance of inclusion of full triples, we also report the EOM-CCSD results for these molecules (see Tables S1 and S2 in the supplementary material). In contrast to EOM-EE, EOM-DIP/DEA perform rather poorly at the EOM-CCSD level, with respective RMS errors relative to the experimental values of 1.57 eV/0.46 eV for ammonia and of 2.41 eV/0.51 eV for water for well-behaved states; the errors are even larger for states that are outside primary target manifolds. The large errors may be attributed to the unbalanced treatment of configurations derived by HOMO-1 excitations in the DEA ansatz and configurations derived by excitations to LUMO+N in the DIP ansatz, in addition to orbital relaxation effects. Importantly, inclusion of full triples captures them well, reducing RMS error by ~90% for DIP and by ~70% for DEA, thereby not only taking them closer to the experimental values but also improving the agreement among the DIP, DEA, and EE treatments.

### C. Cyclobutadiene

Cyclobutadiene is a strained antiaromatic molecule with an electron-deficient  $\pi$ -system, making it unstable and reactive. The strain leads to a small HOMO–LUMO gap, which, in turn, results in strong electron correlation, making cyclobutadiene a popular benchmark system in the electronic structure method-development community.

In a square *D*<sub>4h</sub> structure, symmetry dictates that the two frontier orbitals be exactly degenerate, giving rise to a perfect diradical pattern, whereas symmetry lowering to *D*<sub>2h</sub> lifts the degeneracy and

**FIG. 2.** CCSD(T)/cc-pVTZ optimized geometric parameters taken from Ref. 38 for <sup>1</sup>3A<sub>2g</sub> (left) and X<sup>1</sup>A<sub>g</sub> (right) states. The bond lengths are in angstroms, and the angles are in degrees.

results in a closed-shell pattern. The lowest electronic state is a singlet state. Due to the second-order Jahn–Teller effect, the equilibrium ground-state structure is rectangular *D*<sub>2h</sub>, with alternating double and single bonds. The lowest triplet state is not affected by the Jahn–Teller effect; its equilibrium geometry is *D*<sub>4h</sub>. The equilibrium geometries of the molecule in <sup>1</sup>3A<sub>2g</sub> and X<sup>1</sup>A<sub>g</sub> states were taken from an earlier work of Krylov and co-workers,<sup>58</sup> as are shown in Fig. 2. Depending on the geometry, the singlet ground state (X<sup>1</sup>A<sub>g</sub>) of cyclobutadiene exhibits varying degrees of diradical character, which influences the energies and nature of its low-lying excited states.

Table V presents the total energy of the X<sup>1</sup>A<sub>g</sub> ground state, along with vertical excitation energies to the <sup>3</sup>B<sub>1g</sub>, <sup>1</sup>B<sub>1g</sub>, and <sup>2</sup>A<sub>g</sub> states, calculated using the DIP, DEA, and SF variants of EOM-CCSDT. Similarly, Table VI reports the total energy of the X<sup>1</sup>B<sub>1g</sub> ground state and the vertical excitation energies to the <sup>3</sup>A<sub>2g</sub>, <sup>2</sup>A<sub>1g</sub>, and <sup>1</sup>B<sub>2g</sub> states, also computed using DIP, DEA, and SF variants of EOM-CCSDT.

The total EOM-DEA-CCSDT and EOM-DIP-CCSDT ground-state energies are noticeably higher than those obtained using EOM-SF-CCSDT by ~0.003 hartree for DEA and 0.002 hartree for DIP at the ground state geometry, whereas at the triplet state geometry, they are higher by 0.003 hartree for both DIP and DEA methods. We attribute this discrepancy to the orbital relaxation effects, which are much smaller in EOM-SF than in EOM-DIP/DEA. The excitation energies computed by the 3 methods are in good agreement. For both *D*<sub>4h</sub> and *D*<sub>2h</sub> geometries, the vertical excitation energies computed by DEA and DIP differ from those computed by SF

**TABLE V.** Cyclobutadiene: total energies (hartree) of the ground state, X<sup>1</sup>A<sub>g</sub>, and vertical excitation energies (eV) at the X<sup>1</sup>A<sub>g</sub> equilibrium geometry (*D*<sub>2h</sub> symmetry); 4 frozen core orbitals; cc-pVDZ.

Method	X <sup>1</sup> A <sub>g</sub>	<sup>1</sup> 3B <sub>1g</sub>	<sup>1</sup> 1B <sub>1g</sub>	<sup>2</sup> 1A <sub>g</sub>
SF-CCSD <sup>a</sup>	−154.224 37	1.694	3.585	4.415
DIP-CCSD	−154.202 67	1.561	3.356	4.405
DEA-CCSD	−154.199 93	1.434	3.310	4.216
SF-CCSDT	−154.243 58	1.557	3.481	4.229
SF-CCSDT(SP) <sup>b</sup>	−154.243 58	1.557	3.481	4.229
DIP-CCSDT	−154.241 31	1.508	3.404	4.236
DIP-CCSDT(SP) <sup>b</sup>	−154.241 31	1.508	3.404	4.236
DEA-CCSDT	−154.240 11	1.481	3.402	4.205
DEA-CCSDT(SP) <sup>b</sup>	−154.240 12	1.481	3.402	4.205

<sup>a</sup>UHF reference.<sup>b</sup>SP: single precision algorithm.

**TABLE VI.** Cyclobutadiene: total energies (hartree) of the ground state,  $X^1B_{1g}$ , and vertical excitation energies (eV) at the  $1^3A_{2g}$  equilibrium geometry ( $D_{4h}$  symmetry); 4 frozen core orbitals, cc-pVDZ.

Method	$X^1B_{1g}$	$1^3A_{2g}$	$2^1A_{1g}$	$1^1B_{2g}$
SF-CCSD <sup>a</sup>	-154.214 13	0.419	1.902	2.316
DIP-CCSD	-154.186 54	0.121	1.545	1.925
DEA-CCSD	-154.186 17	0.054	1.498	1.933
SF-CCSDT	-154.231 40	0.258	1.683	2.194
SF-CCSDT(SP) <sup>b</sup>	-154.231 40	0.258	1.683	2.194
DIP-CCSDT	-154.227 66	0.182	1.624	2.086
DIP-CCSDT(SP) <sup>b</sup>	-154.227 66	0.182	1.624	2.086
DEA-CCSDT	-154.228 33	0.171	1.628	2.099
DEA-CCSDT(SP) <sup>b</sup>	-154.228 34	0.171	1.628	2.099

<sup>a</sup>UHF reference.<sup>b</sup>SP: single precision algorithm.

by 0.02–0.1 and 0.007–0.09 eV, respectively, with a tendency to underestimate.

#### D. Vertical double ionization energies of acetylene, ethylene, and formaldehyde

Doubly ionized states are relevant in the context of x-ray spectroscopy. In particular, they are produced in Auger decay of core-ionized molecules.<sup>83–85</sup> Table VII presents double ionization energies of acetylene, ethylene, and formaldehyde, computed using EOM-CCSD and EOM-CCSDT methods (labeled according to the character of resulting doubly ionized state). These theoretical results are compared with the experimental values reported in Ref. 50. As one can see, inclusion of full triple excitations via EOM-CCSDT significantly improves the accuracy of the computed double ionization energies. For acetylene, EOM-CCSDT improves double ionization

**TABLE VII.** Vertical double ionization energies (eV) of select molecules; aug-cc-pVDZ.

Molecule	DIP-CCSD <sup>a</sup>	DIP-CCSDT	Exp-t <sup>a</sup>
$C_2H_2$			
$1^1\Delta_g$	33.561	33.374	33.0
$1^1\Pi_u$	38.883	38.576	37.6
$C_2H_4$			
$1^1A_g$	30.913	30.706	30.1
$1^1A_g$	32.571	32.257	32.2
$1^1B_{3u}$	35.321	34.716	34.0
$CH_2O$			
$1^1A_1$	33.328	33.986	
$1^1A_2$	37.190	37.797	
$1^1B_1$	39.116	39.675	

<sup>a</sup>From Ref. 50.

energies by 0.18 eV for the  $1^1\Delta_g$  state and by 0.31 eV for the  $1^1\Pi_u$  state relative to EOM-CCSD. Similarly, in ethylene, the EOM-CCSDT double ionizations corresponding to  $1^1A_g$ ,  $1^1A_g$ , and  $1^1B_{3u}$  states are improved relative to the EOM-CCSD ones by 0.21, 0.31, and 0.61 eV, respectively. In the case of formaldehyde, the EOM-CCSDT double ionizations improve relative to the EOM-CCSD values by 0.66, 0.61, and 0.56 eV for the  $1^1A_1$ ,  $1^1A_2$ , and  $1^1B_1$  states, respectively. Notably, for both acetylene and ethylene, the values computed with EOM-CCSDT show excellent agreement with the experiment, underscoring the importance of including full triple excitations for reliable results of doubly ionized states.

#### IV. CONCLUSION

We presented a new and computationally efficient implementation of EOM-DIP-CCSDT (with  $4h2p$  EOM operators) and EOM-DEA-CCSDT (with  $2h4p$  EOM operators) methods. In addition to the accurate computation of double ionization energies and double electron affinities of molecules, these methods also provide efficient and robust tools for computing excitation energies and tackling multi-configurational wave functions, such as those in systems with small HOMO–LUMO gaps, in addition to the EE and SF variants of EOM-CCSDT. The relative merits of these methods become apparent when inspecting target configurations shown in Fig. 1. Both EOM-DEA and EOM-DIP are suitable for systems with diradical character, providing naturally spin-adapted alternatives to SF. For the states described by two-electrons-in-two-orbitals, DEA, DIP, and SF perform similarly. The advantage of DEA is that it can describe higher excited states of diradicals (see, for example, Refs. 79 and 81), and the advantage of DIP is that it can describe states from double-diradical manifolds, such as those in oxygen-containing diradicals.<sup>97</sup> In closed-shell molecules, DIP and DEA can describe well singly and doubly excited states derived by HOMO–LUMO excitation, providing an alternative to SF and EE. However, the accessible target states in these methods differ. For example, doubly excited states dominated by excitations from HOMO-2 and lower orbitals are best described as  $2h$  DIP states of dianions (see, for example, Ref. 98). Similarly, DEA is best suited for doubly excited states dominated by excitations to LUMO+2 or higher orbitals and can be viewed as  $2p$  dominated DEA states of the respective dications. Moving from EOM-CCSD to EOM-CCSDT, the root mean squared errors and standard deviations in energy gaps computed by different EOM-CC variants are reduced by 70%–90%, thereby improving the general agreement among the DIP, DEA, and SF/EE treatments. The agreement in the total energies computed by DIP/DEA relative to SF improves by an order of magnitude for EOM-CCSDT compared to the EOM-CCSD values. Errors due to the use of single precision vs double precision execution are minute and do not noticeably affect the accuracy of the computed energies and energy gaps while affording substantial computational savings. Our implementation contributes to a growing set of tools for obtaining high-quality reference data for electronically excited and open-shell species.

#### SUPPLEMENTARY MATERIAL

The [supplementary material](#) includes the geometries of the molecules and the other (supporting) [supplementary material](#).

## ACKNOWLEDGMENTS

This work was supported in Los Angeles by the U.S. National Science Foundation (Grant No. CHE-2154482 to A.I.K.). Manisha acknowledges BITS Pilani for providing the institute fellowship and for the central High Performance Computing facility, “Jayant.”

## AUTHOR DECLARATIONS

### Conflict of Interest

The authors declare the following competing financial interest(s): A.I.K. is the president and a part-owner of Q-Chem, Inc.

### Author Contributions

**Manisha:** Data curation (lead); Formal analysis (equal); Software (lead); Validation (lead); Writing – original draft (lead). **Anna I. Krylov:** Formal analysis (equal); Funding acquisition (lead); Supervision (supporting); Writing – review & editing (equal). **Prashant Uday Manohar:** Conceptualization (lead); Formal analysis (equal); Methodology (lead); Project administration (lead); Supervision (lead); Writing – review & editing (equal).

## DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

## APPENDIX: PROGRAMMABLE EXPRESSIONS

In the following, we present the programmable expressions of the right EOM-DEA-CCSDT equations needed for

Davidson’s iterative diagonalization procedure ( $\sigma$ -vectors and intermediates):

$$\begin{aligned}\sigma^{ab} &= ([\tilde{H}_{SS} - E_{CC}]R_1)^{ab} + (\tilde{H}_{SD}R_2)^{ab} + (\tilde{H}_{ST}R_3)^{ab}, \\ \sigma_i^{abc} &= (\tilde{H}_{DS}R_1)_i^{abc} + ([\tilde{H}_{DD} - E_{CC}]R_2)_i^{abc} + (\tilde{H}_{DT}R_3)_i^{abc}, \\ \sigma_{ij}^{abcd} &= (\tilde{H}_{TS}R_1)_{ij}^{abcd} + (\tilde{H}_{TD}R_2)_{ij}^{abcd} + ([\tilde{H}_{TT} - E_{CC}]R_3)_{ij}^{abcd}.\end{aligned}$$

For computational convenience, we express  $\sigma^{ab}$ ,  $\sigma_i^{abc}$ , and  $\sigma_{ij}^{abcd}$  as follows:

$$\begin{aligned}\sigma^{ab} &= \langle \Phi^{ab} | \tilde{H} | R_1 \Phi_0 \rangle + \langle \Phi^{ab} | \tilde{H} | R_2 \Phi_0 \rangle + \langle \Phi^{ab} | \tilde{H} | R_3 \Phi_0 \rangle \\ &= P(ab) \sum_c F_{bc} r_{ac} - \frac{1}{2} P(ab) \sum_{icd} I_{ibcd}^7 r_i^{acd} + \frac{1}{2} \sum_{cd} I_{abcd}^5 r_{cd} \\ &\quad - \sum_{ic} F_{ic} r_i^{bac} + \frac{1}{4} \sum_{ijcd} \langle ij || dc \rangle r_{ij}^{dcab}, \\ \sigma_i^{abc} &= \langle \Phi_i^{abc} | \tilde{H} | R_1 \Phi_0 \rangle + \langle \Phi_i^{abc} | \tilde{H} | R_2 \Phi_0 \rangle + \langle \Phi_i^{abc} | \tilde{H} | R_3 \Phi_0 \rangle \\ &= P(c/ab) \left[ \sum_d F_{cd} r_i^{abd} - \sum_{jd} I_{idjc}^1 r_j^{abd} + \frac{1}{2} \sum_{de} I_{abde}^5 r_i^{dec} \right. \\ &\quad \left. - \sum_j H_{jc}^8 t_{ij}^{ab} + \sum_d I_{idab}^3 r_{dc} \right] - \frac{1}{2} \sum_{nme} I_{mnie}^6 r_{nm}^{eabc} \\ &\quad + \frac{1}{2} P(a/bc) \sum_{mef} I_{mafe}^7 r_{mi}^{feb} + \sum_{ke} F_{ke} r_{ki}^{eabc} \\ &\quad + \frac{1}{2} \sum_{jk} I_{jk}^{4r} t_{ijk}^{abc} - \sum_j F_{ij} r_j^{abc},\end{aligned}$$

$$\begin{aligned}\sigma_{ij}^{abcd} &= \langle \Phi_{ij}^{abcd} | \tilde{H} | R_1 \Phi_0 \rangle + \langle \Phi_{ij}^{abcd} | \tilde{H} | R_2 \Phi_0 \rangle + \langle \Phi_{ij}^{abcd} | \tilde{H} | R_3 \Phi_0 \rangle \\ &= -P(ij) \sum_k F_{jk} r_{ik}^{abcd} + P(a/bcd) \sum_e F_{ae} r_{ij}^{ebcd} - P(a/bcd) \sum_m I_{jima}^2 r_m^{bcd} + P(ij) P(ab|cd) \sum_e I_{ieab}^3 r_j^{ecd} - P(ij) P(b/acd) \sum_{me} I_{iemb}^1 r_{mj}^{aecd} \\ &\quad + \frac{1}{2} \sum_{lk} I_{ijlk}^4 r_{lk}^{abcd} + \frac{1}{2} P(ab/cd) \sum_{ef} I_{cdef}^5 r_{ij}^{abef} + P(a/bcd) \sum_e H_{ebcd}^5 t_{ij}^{ae} - P(ij) P(ab/cd) \sum_m H_{jmcd}^5 t_{im}^{ab} \\ &\quad + \frac{1}{2} P(ij) P(d/abc) \sum_{nl} H_{jnld}^7 t_{nl}^{abc} - P(ad/bc) \sum_{el} H_{ebcl}^6 t_{ijl}^{aed} - P(d/abc) \sum_k H_{kd}^8 t_{ijk}^{abc}.\end{aligned}$$

Intermediates for DEA are

$$\begin{aligned}I_{ij}^{4r} &= \frac{1}{2} \sum_{cb} \langle ij || cb \rangle r_{cb} \quad H_{ia}^{8'} = \frac{1}{2} \sum_{bc} I_{iabc}^7 r_{bc} + \frac{1}{2} \sum_{jbc} \langle ji || bc \rangle r_j^{abc} \quad H_{ia}^8 = \frac{1}{2} \sum_{bc} I_{iabc}^7 r_{bc} + \frac{1}{2} \sum_{jbc} \langle ji || bc \rangle r_j^{abc} + \sum_b F_{ib} r_{ba} \\ H_{edcb}^5 &= \sum_{mf} I_{mdfe}^7 r_m^{fcb} - \sum_f I_{dcef}^5 r_{bf} - \frac{1}{2} \sum_{nmf} \langle nm || fe \rangle r_{nm}^{fcd}, \\ H_{kmba}^{5'} &= P(ab) \sum_e I_{kemb}^1 r_{ea} + \sum_{ne} I_{mkn}^6 r_n^{eba} - \frac{1}{2} P(ab) \sum_{ef} I_{mafe}^7 r_k^{feb} + \frac{1}{2} \sum_{nef} \langle nm || fe \rangle r_{nk}^{feba} + \frac{1}{2} \sum_{nfe} \langle nm || fe \rangle r_{fe} t_{nk}^{ba} \\ H_{bacm}^6 &= -P(ac) \sum_d I_{madb}^7 r_{dc} - \sum_{ne} \langle nm || be \rangle r_n^{ace} \quad H_{ijkb}^7 = \sum_d I_{jkid}^6 r_{db} + \frac{1}{2} \sum_{da} \langle ik || da \rangle r_j^{dab}.\end{aligned}$$

In the following, we present the programmable expressions of EOM-DIP-CCSDT within Davidson’s iterative diagonalization procedure:

$$\begin{aligned}\sigma_{ij} &= ([\tilde{H}_{SS} - E_{CC}]R_1)_{ij} + (\tilde{H}_{SD}R_2)_{ij} + (\tilde{H}_{ST}R_3)_{ij}, \\ \sigma_{ijk}^a &= (\tilde{H}_{DS}R_1)_{ijk}^a + ([\tilde{H}_{DD} - E_{CC}]R_2)_{ijk}^a + (\tilde{H}_{DT}R_3)_{ijk}^a, \\ \sigma_{ijkl}^{ab} &= (\tilde{H}_{TS}R_1)_{ijkl}^a + (\tilde{H}_{TD}R_2)_{ijkl}^{ab} + ([\tilde{H}_{TT} - E_{CC}]R_3)_{ijkl}^{ab}.\end{aligned}$$

For computational convenience, we express  $\sigma^{ij}$ ,  $\sigma_{ijk}^a$ , and  $\sigma_{ijkl}^{ab}$  as follows:

$$\begin{aligned}\sigma_{ij} &= \langle \Phi_{ij} | \tilde{H} | R_1 \Phi_0 \rangle + \langle \Phi_{ij} | \tilde{H} | R_2 \Phi_0 \rangle + \langle \Phi_{ij} | \tilde{H} | R_3 \Phi_0 \rangle \\ &= P(ij) \sum_k F_{ik} r_{jk} + \frac{1}{2} P(ij) \sum_{kla} I_{klia}^6 r_{klj}^a + \frac{1}{2} \sum_{kl} I_{ijkl}^4 r_{kl} + \sum_{ka} F_{ka} r_{ijk}^a + \frac{1}{4} \sum_{klcd} \langle kl || cd \rangle r_{ijkl}^{cd}, \\ \sigma_{ijk}^a &= \langle \Phi_{ijk}^a | \tilde{H} | R_1 \Phi_0 \rangle + \langle \Phi_{ijk}^a | \tilde{H} | R_2 \Phi_0 \rangle + \langle \Phi_{ijk}^a | \tilde{H} | R_3 \Phi_0 \rangle \\ &= P(k/ij) \left[ - \sum_l F_{kl} r_{ijl}^a + \frac{1}{2} \sum_{lm} I_{ijlm}^4 r_{lmk}^a + \sum_b h_{kb}^{9r'} t_{ij}^{ab} - \sum_l I_{ijla}^2 r_{kl} - \sum_{bl} I_{kbla}^1 r_{ij}^b \right] + \sum_b F_{ab} r_{ijk}^b + \sum_{lb} F_{lb} r_{ijk}^{ab} \\ &\quad + \frac{1}{2} \sum_{lcb} I_{labc}^7 r_{ijkl}^{cb} + \frac{1}{2} \sum_{dc} I_{dc}^{5r} t_{ijk}^{dca} - \frac{1}{2} P(k/ij) \sum_{lmb} I_{lmkb}^6 r_{ijlm}^{ab}, \\ \sigma_{ijkl}^{ab} &= \langle \Phi_{ijkl}^{ab} | \tilde{H} | R_1 \Phi_0 \rangle + \langle \Phi_{ijkl}^{ab} | \tilde{H} | R_2 \Phi_0 \rangle + \langle \Phi_{ijkl}^{ab} | \tilde{H} | R_3 \Phi_0 \rangle \\ &= P(ab) \sum_c F_{bc} r_{ijkl}^{ac} - P(l/ijk) F_{lm} r_{ijkm}^{ab} + \frac{1}{2} \sum_{cd} I_{abcd}^5 r_{ijkl}^{cd} + \frac{1}{2} P(ij/kl) \sum_{mn} I_{klmn}^4 r_{ijmn}^{ab} + P(l/ijk) \sum_c I_{lcb}^3 r_{ijk}^c \\ &\quad - P(ab) P(ij/kl) \sum_m I_{klmb}^2 r_{ijm}^a - P(ab) P(l/ijk) \sum_{mc} I_{lcma}^1 r_{ijkm}^{cb} - P(l/ijk) \sum_m H_{ijkm}^{Ar} t_{ml}^{ab} + P(ab) P(ij/kl) \sum_e H_{ijea}^{5r} t_{kl}^{eb} \\ &\quad + P(i/jkl) \sum_d H_{idkn}^{9r} t_{jkl}^{dab} - P(ik/jl) \sum_{nd} H_{idkn}^{6r} t_{jnl}^{dab} + \frac{1}{2} P(i/jkl) P(ab) \sum_{cd} H_{idca}^{7r} t_{jkl}^{dcb}.\end{aligned}$$

Intermediates for DIP are

$$\begin{aligned}I_{cb}^{5r} &= \frac{1}{2} \sum_{ij} \langle ij || cb \rangle r_{ij} \quad H_{ia}^{9r'} = \frac{1}{2} \sum_{jk} I_{jkia}^6 r_{jk} + \frac{1}{2} \sum_{jkb} \langle jk || ba \rangle r_{jki}^b \quad H_{ia}^{9r} = \frac{1}{2} \sum_{jk} I_{jkia}^6 r_{jk} + \frac{1}{2} \sum_{jkb} \langle jk || ba \rangle r_{jki}^b - \sum_k F_{ka} r_{ik} \\ H_{jklm}^{4r} &= P(l/jk) \sum_{ne} I_{mnle}^6 r_{jkn}^e - P(j/kl) \sum_n I_{klmn}^4 r_{jn} + \frac{1}{2} \sum_{nef} \langle nm || fe \rangle r_{jknl}^{fe}, \\ H_{ijec}^{5r} &= -P(ij) \sum_m I_{iemc}^1 r_{mj} - \frac{1}{2} P(ij) \sum_{mn} I_{mnie}^6 r_{jmn}^c + \sum_{mf} I_{mcef}^7 r_{ijm}^f - \frac{1}{2} \sum_{mnf} \langle mn || ef \rangle r_{ijmn}^{cf} - \frac{1}{2} \sum_{mnf} \langle mn || fe \rangle r_{mn} t_{ij}^{cf} \\ H_{jdkn}^{6r} &= -P(kj) \sum_m I_{nmka}^6 r_{jm} - \sum_{mf} \langle mn || df \rangle r_{jmk}^f \quad H_{idca}^{7r} = - \sum_m I_{madc}^7 r_{im} + \frac{1}{2} \sum_{nm} \langle mn || cd \rangle r_{inm}^a.\end{aligned}$$

For the intermediates, one can refer to the works of Levchenko and Krylov<sup>38</sup> (for  $F_{ij}$ ,  $F_{ab}$ ,  $F_{ia}$ ,  $I^1$ ,  $I^4$ ,  $I^5$ ,  $I^6$ , and  $I^7$ ) and Manisha and Manohar<sup>67</sup> (for  $I^2$  and  $I^3$ ).

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