

# Equation-of-Motion Coupled-Cluster Theory for Excitation Energies of Closed-Shell Systems with Spin–Orbit Coupling

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**ABSTRACT:** Excitation energies of closed-shell systems based on the equation-of-motion (EOM) coupled-cluster theory at the singles and doubles (CCSD) level with spin–orbit coupling (SOC) included in the post-Hartree–Fock treatment are implemented in the present work. SOC can be included in both the CC and EOM steps (EOM-SOC-CCSD) or only in the EOM part (SOC-EOM-CCSD). The latter approach is an economical way to account for SOC effects, but excitation energies with this approach are not size-intensive. When the unlinked term in the latter approach is neglected (cSOC-EOM-CCSD), size-intensive excitation energies can be obtained. Time-reversal symmetry and spatial symmetry are exploited to reduce the computational effort. Imposing time-reversal symmetry results in a real matrix representation for the similarity-transformed Hamiltonian, which facilitates the requirement of time-reversal symmetry for new trial vectors in Davidson's algorithm. Results on some closed-shell atoms and molecules containing heavy elements show that EOM-SOC-CCSD can provide excitation energies and spin–orbit splittings with reasonable accuracy. On the other hand, the SOC-EOM-CCSD approach is able to afford accurate estimates of SOC effects for valence electrons of systems containing elements up to the fifth row, while cSOC-EOM-CCSD is less accurate for spin–orbit splittings of transitions involving  $p_{1/2}$  spinors, even for Kr.

## EOMEE-SOC-CCSD

$$\langle \Phi_\mu | [\bar{H}_0 + \bar{H}_{SO}, R] | \Phi_0 \rangle = E_{excit} r_\mu$$

## I. INTRODUCTION

It has been well-established that excitation energies can be calculated accurately with equation-of-motion coupled-cluster (EOM-CC) theory.<sup>1–9</sup> In the EOM-CC method, excitation energies are calculated by means of a configuration interaction (CI)-like approach from eigenvalues of a similarity-transformed Hamiltonian. A closely related method for excitation energies based on CC theory is linear-response CC (LR-CC) theory,<sup>10–12</sup> where excitation energies are determined from poles of the corresponding linear response function. The equations for excitation energies adopted in the EOM-CC method and LR-CC theory are the same, but these two approaches differ in the calculation of transition properties such as transition dipole moment and rotational strength. LR-CC theory can provide size-intensive transition properties, while the EOM-CC method does not.<sup>13</sup> However, Caricato et al.<sup>14</sup> recently demonstrated that this difference may not be as pronounced as previously thought. Other approaches based on CC theory that are capable of calculating excitation energies also exist, such as Fock-space CC (FS-CC) theory,<sup>15</sup> the similarity-transformed equation-of-motion CC (STEOM-CC) method,<sup>16,17</sup> and the symmetry-adapted-cluster configuration interaction (SAC-CI) method.<sup>18–20</sup> One of the most commonly used EOM-CC methods is the EOM-CC approach at the CC singles and doubles level (CCSD),<sup>21</sup> which can provide reasonable descriptions of excited states with dominant single-excitation character. It should also be noted that ionization energies and electron affinities<sup>7–9</sup> can be calculated as well by means of these approaches for excitation energies. In

fact, they can readily be obtained by including a basis function with a nearly zero exponent and calculating excitations from or to this orbital with the existing programs for excitation energies.<sup>22</sup>

For molecules containing heavy elements, relativistic effects<sup>23–26</sup> must be included to achieve reliable excitation energies, and spin–orbit coupling (SOC) is an important part of such relativistic effects. SOC is generally more significant for excited states than for ground states of closed-shell molecules containing heavy elements since the energy gaps between excited states are usually much smaller than those between the ground state and excited states. Furthermore, SOC results in splitting of degenerate spin-triplet excited states and mixing of spin-singlet and spin-triplet states, which is the origin of phosphorescence and intersystem crossing. Excitation energies based on CC theory including SOC have previously been reported using the EOM-CC method,<sup>27,28</sup> FS-CC theory,<sup>29–31</sup> and multireference CC theory<sup>32–34</sup> with either a four-component or two-component relativistic Hamiltonian.<sup>35–38</sup> In most of these implementations, SOC is included at the self-consistent field (SCF) level, and these approaches are thus computationally expensive and mainly useful for rather small molecules.

In our previous works,<sup>39–41</sup> we proposed and implemented a CC approach for closed-shell molecules using relativistic effective core potentials (RECPs)<sup>42</sup> to treat relativistic effects,

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with SOC included in the CC part. Total energies<sup>39</sup> and analytic first<sup>40</sup> and second-order derivatives<sup>41</sup> of this CC approach with SOC were implemented at the CCSD level as well as at the CCSD level augmented by a perturbative treatment of triple excitations (CCSD(T)).<sup>43</sup> This approach can provide rather accurate estimates of properties of compounds containing heavy or even superheavy elements.<sup>39,44</sup> Furthermore, because of the use of real molecular spinorbitals as well as the exploitation of time-reversal and spatial symmetry, this CC approach is computationally efficient.<sup>45</sup> Ionization energies<sup>46</sup> and electron affinities<sup>47</sup> with EOM-CCSD based on this CC approach have been reported. In the present work, we report the implementation of excitation energies using the EOM-CCSD method based on this CC approach with SOC. It should be noted that a similar implementation of excitation energies in the framework of FS-CC theory with SOC included at the post-Hartree–Fock level has also been reported previously.<sup>29</sup>

In the EOM-CC approach with SOC, it is possible to turn on SOC only in the EOM step, in which case the effects of SOC on the ground and excited states are taken into account only in the EOM step. One then only needs to solve the CC equations without SOC, which can reduce the computational effort significantly since solving the CCSD equations with SOC is about 10 times more expensive than that without SOC.<sup>19</sup> Orbital relaxation effects are taken into account via single-excitation operators in the cluster operator<sup>48,49</sup> when SOC is included in CC step. On the other hand, one would expect that including SOC only in the EOM step may result in large errors for molecules with significant SOC effects because of an insufficient description of orbital relaxation unless high excitation levels are included in the calculations. It should be noted that the approach with SOC included in both the CC and EOM steps is similar to the one-step spin–orbit configuration interaction (SOCi) approach, where SOC and electron correlation are calculated simultaneously. On the other hand, the approach with SOC included only in the EOM step is conceptually similar to the two-step approach where SOC is taken into account in a basis of correlated molecular wave functions,<sup>50</sup> except that all of the possible correlated wave functions in single- and double-excitation space are included in the present approach.

This paper is organized in the following manner: Basic equations required in the EOM-CCSD method with SOC included in both the CC and EOM steps or only in the EOM step are discussed in section II. Implementation details and symmetry exploitation are presented in section III. In section IV, excitation energies for some closed-shell atoms and molecules based on these EOM-CCSD approaches with SOC are reported.

## II. THEORY

To calculate excitation energies using the EOM-CC method, CC equations must first be solved. In CC theory, the ground-state wave function is represented by  $e^T|\Phi_0\rangle$ , where  $\Phi_0$  is the Hartree–Fock (HF) wave function and  $T$  is the cluster operator, which is defined as follows in CCSD:

$$T = \sum_{i,a} t_i^a a_a^\dagger a_i + \frac{1}{4} \sum_{a,b,i,j} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_i a_j \quad (1)$$

where  $i, j, \dots$  and  $a, b, \dots$  are indices for occupied and virtual spin orbitals, respectively. The cluster amplitudes  $t$  in eq 1 are determined by the following equations:

$$\langle \Phi_i | e^{-T} H e^T | \Phi_0 \rangle = 0, \quad \langle \Phi_{ij}^{ab} | e^{-T} H e^T | \Phi_0 \rangle = 0 \quad (2)$$

where  $\Phi_i^a$  and  $\Phi_{ij}^{ab}$  are single- and double-excitation determinants with respect to  $\Phi_0$ . The ground-state energy is then given by

$$E_{\text{CCSD}} = \langle \Phi_0 | H e^T | \Phi_0 \rangle = \langle \Phi_0 | e^{-T} H e^T | \Phi_0 \rangle \quad (3)$$

In EOM-CCSD, the excited-state wave function is represented as  $R e^T |\Phi_0\rangle$ , where  $R$  is the excitation operator, defined as

$$R = r_0 + \sum_{i,a} r_i^a a_a^\dagger a_i + \frac{1}{4} \sum_{a,b,i,j} r_{ij}^{ab} a_a^\dagger a_b^\dagger a_i a_j \quad (4)$$

Excited-state energies can be calculated using the following equation:

$$e^{-T} H e^T R |\Phi_0\rangle = \bar{H} R |\Phi_0\rangle = E R |\Phi_0\rangle \quad (5)$$

where  $\bar{H} = e^{-T} H e^T$  is the similarity-transformed Hamiltonian and  $E$  is the energy for some excited state. Similar to the CCSD equations in eq 2, eq 5 is satisfied only in the space spanned by  $\{\Phi_0, \Phi_i^a, \Phi_{ij}^{ab}\}$  in the EOM-CCSD method. Both  $R|\Phi_0\rangle$  and  $|\Phi_0\rangle$  are eigenfunctions of  $\bar{H}$  in this space, and the fact that  $\bar{H}$  is non-Hermitian means that  $R|\Phi_0\rangle$  and  $|\Phi_0\rangle$  are nonorthogonal to each other. Thus,  $r_0$  would be nonzero for excited states with the same symmetry as the ground state. Equation 5 can be readily written in the following way on the basis of eq 2:

$$\langle \Phi_0 | [\bar{H}, R] | \Phi_0 \rangle = E_{\text{excit}} \langle \Phi_0 | R | \Phi_0 \rangle = E_{\text{excit}} r_0 \quad (6)$$

$$\langle \Phi_i^a | [\bar{H}, R] | \Phi_0 \rangle = E_{\text{excit}} \langle \Phi_i^a | R | \Phi_0 \rangle = E_{\text{excit}} r_i^a \quad (7)$$

$$\langle \Phi_{ij}^{ab} | [\bar{H}, R] | \Phi_0 \rangle = E_{\text{excit}} \langle \Phi_{ij}^{ab} | R | \Phi_0 \rangle = E_{\text{excit}} r_{ij}^{ab} \quad (8)$$

where  $E_{\text{excit}}$  is the excitation energy. Using the fact that the commutator between  $\bar{H}$  and  $r_0$  is zero, one can see from these equations that only eqs 7 and 8 are needed to calculate excitation energies and that  $r_0$  is not required. This is equivalent to finding eigenvalues of the similarity-transformed Hamiltonian  $\bar{H}$  in the space spanned by  $\{\Phi_i^a, \Phi_{ij}^{ab}\}$ . Detailed algebraic expressions for left-hand sides of eqs 7 and 8 are given in eqs 9 and 10, respectively:

$$\begin{aligned} \langle \Phi_i^a | [\bar{H}, R] | \Phi_0 \rangle &= \sum_e F_{ae} r_i^e - \sum_m F_{mi} r_m^a + \sum_{me} F_{me} r_{im}^{ae} \\ &+ \sum_{em} W_{ame} r_m^e - \frac{1}{2} \sum_{em} W_{mie} r_{mn}^{ae} \\ &+ \frac{1}{2} \sum_{em} W_{amef} r_{im}^{ef} \end{aligned} \quad (9)$$

$$\begin{aligned}
\langle \Phi_{ij}^{ab} | [\bar{H}, R] | \Phi_0 \rangle &= P_{-}(ab) \sum_e F_{be} r_{ij}^{ae} \\
&- P_{-}(ij) \sum_m F_{mj} r_{im}^{ab} + \frac{1}{2} \sum_{mn} W_{mnij} r_{mn}^{ab} + \frac{1}{2} \sum_{ef} W_{abef} r_{ij}^{ef} \\
&- \frac{1}{2} P_{-}(ab) \sum_{efmn} \langle mnll ef \rangle t_{ij}^{ae} r_{mn}^{bf} - \frac{1}{2} P_{-}(ij) \sum_{efmn} \langle mnll ef \rangle \\
&t_{im}^{ab} r_{jn}^{ef} + P_{-}(ab) P_{-}(ij) \sum_{em} W_{mbej} r_{im}^{ae} \\
&+ P_{-}(ij) \sum_e W_{abef} r_i^e - P_{-}(ab) \sum_m W_{mbij} r_m^a \\
&+ P_{-}(ab) \sum_{efm} W_{maef} t_{ij}^{fb} r_m^e - P_{-}(ij) \sum_{efm} W_{mnei} t_{nj}^{ab} r_m^e \\
&- P_{-}(ab) \sum_{efmn} t_{ij}^{ae} r_{mn}^{bf} \langle mnll ef \rangle - P_{-}(ij) \sum_{efmn} t_{im}^{ab} r_{jn}^{ef} \langle mnll ef \rangle
\end{aligned} \quad (10)$$

The intermediates  $F_{ae}$ ,  $F_{mi}$ ,  $W_{amie}$ ,  $W_{mnie}$ , etc., involved in eqs 9 and 10 are the one- and two-electron parts of  $\bar{H}$ , and algebraic expressions for these quantities can be found in ref 51. If SOC is introduced in the CC part, the HF wave function  $\Phi_0$  corresponds to the Hamiltonian without SOC, while the Hamiltonian as well as the intermediates in eqs 2–10 include contributions from SOC. The SOC operator adopted here is taken from the RECP operator and represented by a one-electron operator. One can thus conclude that the SOC matrix directly contributes only to  $F_{ae}$ ,  $F_{mi}$ ,  $F_{me}$ ,  $W_{mbij}$ , and  $W_{abef}$  while the other intermediates depend indirectly on the SOC matrix through the cluster operator. This EOM-CCSD approach is denoted as EOM-SOC-CCSD in this paper.

If SOC is turned on only in the EOM-CCSD equations (i.e., eq 5), then the Hamiltonian without SOC is used to solve the CCSD equations, while the Hamiltonian employed in the EOM-CCSD equation as in eq 5 contains the SOC operator. The Hamiltonian used to solve the CCSD equations is thus different from that in the EOM-CCSD equations. The EOM-CCSD equations cannot be written in the same form as those in eqs 6–8 in this case, and eq 5 has to be used to calculate the excited-state energies directly. The EOM-CCSD equations in this case then read

$$\bar{H} = e^{-T_0} (H_0 + h^{\text{SO}}) e^{T_0}, \quad \bar{H}_{\text{SO}} = e^{-T_0} h^{\text{SO}} e^{T_0} \quad (11)$$

$$\begin{aligned}
\langle \Phi_0 | \bar{H} R | \Phi_0 \rangle &= E_{\text{CCSD}}^0 r_0 + \sum_{ia} t_i^a h_{ia}^{\text{SO}} + \sum_{ai} r_i^a F_{ia} + \frac{1}{4} \\
&\sum_{abij} r_{ij}^{ab} \langle ij || ab \rangle \\
&= E_i r_0
\end{aligned} \quad (12)$$

$$\begin{aligned}
\langle \Phi_i^a | \bar{H} R | \Phi_0 \rangle &= E_i r_i^a \\
&= \langle \Phi_i^a | [\bar{H}, R] | \Phi_0 \rangle + E_{\text{CCSD}}^0 r_i^a + (\bar{H}_{\text{SO}})_{ai} r_0
\end{aligned} \quad (13)$$

$$\begin{aligned}
\langle \Phi_{ij}^{ab} | \bar{H} R | \Phi_0 \rangle &= E_i r_{ij}^{ab} \\
&= \langle \Phi_{ij}^{ab} | [\bar{H}, R] | \Phi_0 \rangle + E_{\text{CCSD}}^0 r_{ij}^{ab} + (\bar{H}_{\text{SO}})_{abij} r_0 \\
&+ P_{-}(ab) P_{-}(ij) r_i^a (\bar{H}_{\text{SO}})_{bj}
\end{aligned} \quad (14)$$

$$\begin{aligned}
(\bar{H}_{\text{SO}})_{ai} &= h_{ai}^{\text{SO}} + \sum_e t_i^e (h_{ae}^{\text{SO}} - \sum_m t_m^a h_{me}^{\text{SO}}) - \sum_m t_m^a h_{mi}^{\text{SO}} \\
&+ \sum_{me} t_{im}^{ae} h_{me}^{\text{SO}}
\end{aligned} \quad (15)$$

$$\begin{aligned}
(\bar{H}_{\text{SO}})_{abij} &= P_{-}(ab) \sum_e t_{ij}^{ae} (h_{be}^{\text{SO}} - \sum_m t_m^b h_{me}^{\text{SO}}) \\
&- P_{-}(ij) \sum_m t_{im}^{ab} (h_{mj}^{\text{SO}} + \sum_e t_j^e h_{me}^{\text{SO}})
\end{aligned} \quad (16)$$

where  $H_0$  is the scalar relativistic Hamiltonian,  $T_0$  is the cluster operator in the CCSD equations without SOC,  $h^{\text{SO}}$  is the one-electron SOC operator, and  $E_{\text{CCSD}}^0$  is the scalar relativistic ground state energy. It should be noted that the cluster amplitudes in eqs 12–16 correspond to those in  $T_0$ . The algebraic expressions for  $\langle \Phi_i^a | [\bar{H}, R] | \Phi_0 \rangle$  and  $\langle \Phi_{ij}^{ab} | [\bar{H}, R] | \Phi_0 \rangle$  in eqs 13 and 14 are the same as those in eqs 9 and 10 except that the intermediates involved are calculated using the cluster operator  $T_0$ . This implies that only the intermediates  $F_{ae}$ ,  $F_{mi}$ ,  $F_{me}$ ,  $W_{mbij}$ , and  $W_{abef}$  are complex and spin cases such as  $F_{a\bar{\alpha}} F_{m\bar{\beta}}$  and  $F_{m\bar{\alpha}}$  have to be considered, where orbitals without (with) a bar denote orbitals with spin  $\alpha$  ( $\beta$ ). The other intermediates are real, and their nonzero-spin cases are the same as those without SOC. This results in a further reduction in computational effort. Unlike the case of EOM-SOC-CCSD, the EOM-CCSD equations must be solved in the space spanned by  $\{\Phi_0, \Phi_i^a, \Phi_{ij}^{ab}\}$  since  $r_0$  is required in eqs 13 and 14 if SOC is included only in the EOM-CCSD equations. A correction to the ground-state energy due to SOC can thus be obtained by turning on SOC only in the EOM-CCSD equations, and this approach could be used to calculate SOC effects on both the ground-state and excited-state energies. It should be noted that  $r_0$  is zero for excited states whose symmetries are different from that of the ground state. One can see from eqs 12–14 that  $E_{\text{CCSD}}^0$  appears only in diagonal elements of the  $\bar{H}$  matrix and can thus be neglected. It should be noted that energy obtained from eqs 12–14 by neglecting the  $E_{\text{CCSD}}^0$  term is not the excitation energy but rather is the energy difference between the excited state *with* SOC and the ground state *without* SOC. To calculate excitation energies with SOC, the SOC correction to the ground-state energy must be included. However, because of the appearance of the unlinked term (i.e., the last term in eq 14), excitation energies based on this approach are not size-intensive and the ground-state energy is not size-extensive. In the following, this approach with SOC included only in the EOM part will be denoted as SOC-EOM-CCSD.

As for SOC effects on the ground-state properties, the previous CC approach with SOC included in the CC part can account for orbital relaxation effectively via single-excitation operators in the cluster operator.<sup>48,49</sup> On the other hand, the SOC-EOM-CCSD approach may result in large errors when SOC effects are pronounced as a result of an insufficient description of orbital relaxation. When SOC is included only in the EOM-CCSD equation, the correction to the ground-state energy due to SOC can be estimated by treating the operator  $\bar{H}_{\text{SO}}$  as a perturbation to the original operator  $\bar{H}_0 = e^{-T_0} H_0 e^{T_0}$  in the EOM-CCSD equation. From the fact that the first-order energy correction due to SOC is zero, the SOC correction to the ground-state energy can be estimated by means of second-order perturbation theory as follows:



$$\Delta E_{\text{SO}} = \sum_K \frac{\langle \Phi_0 | (1 + \Lambda) \bar{H}_{\text{SO}} | \Phi_{\text{EOM}}^{K,0} \rangle \langle \tilde{\Phi}_{\text{EOM}}^{K,0} | \bar{H}_{\text{SO}} | \Phi_0 \rangle}{E_{\text{CCSD}}^0 - E_K^0} \quad (17)$$

where  $\Lambda$  is the de-excitation operator introduced in CC gradient theory,<sup>49,51</sup> which is also the left-hand eivector of the operator  $\bar{H}_0$  corresponding to the ground state;  $|\Phi_{\text{EOM}}^{K,0}\rangle$  and  $\langle \tilde{\Phi}_{\text{EOM}}^{K,0}|$  are the  $K$ -th right-hand and left-hand eigenvectors of  $\bar{H}_0$  in the space of  $\{\Phi_0, \Phi_i^a, \Phi_{ij}^{ab}\}$ , respectively; and  $E_K^0$  is the  $K$ -th eigenvalue of  $\bar{H}_0$ . It should be noted that  $\bar{H}_0$  and  $\bar{H}$  are non-Hermite, so their left-hand eigenvectors are not simply the complex conjugates of their right-hand eigenvectors for a given eigenvalue. In the present EOM-CCSD implementation, only the right-hand eigenvectors of  $\bar{H}$  are calculated.

The effect of SOC on the ground-state energy can be calculated alternatively using analytic derivative techniques<sup>52,53</sup> in CC theory by treating SOC as a perturbation. Unlike the energy correction obtained in the SOC-EOM-CCSD approach, the derivative of the ground-state CC energy is size-consistent. The correction to the ground-state CCSD energy due to SOC using analytic derivative techniques up to second order can be written as follows:<sup>54</sup>

$$\begin{aligned} \Delta E_{\text{SO}} &= \frac{1}{2} \frac{d^2 E_{\text{CCSD}}}{dh_{\text{SO}}^2} \\ &= \sum_K \frac{\langle \Phi_0 | (1 + \Lambda) \bar{H}_{\text{SO}} | \Phi_{\text{EOM}}^{K,1} \rangle \langle \tilde{\Phi}_{\text{EOM}}^{K,1} | \bar{H}_{\text{SO}} | \Phi_0 \rangle}{E_{\text{CCSD}}^0 - E_K^0} \\ &\quad - \frac{\partial E_{\text{CCSD}}}{\partial h_{\text{SO}}} \langle \Phi_0 | (1 + \Lambda) \frac{\partial T}{\partial h_{\text{SO}}} | \Phi_0 \rangle \\ &\quad + \frac{1}{2} \sum_q \langle \Phi_0 | (1 + \Lambda) e^{-T_0} H_0 e^{T_0} | \Phi_q \rangle \\ &\quad \langle \Phi_q | \frac{\partial T}{\partial h_{\text{SO}}} \frac{\partial T}{\partial h_{\text{SO}}} | \Phi_0 \rangle \end{aligned} \quad (18)$$

where  $|\Phi_{\text{EOM}}^{K,1}\rangle$  and  $\langle \tilde{\Phi}_{\text{EOM}}^{K,1}|$  are the  $K$ -th right-hand and left-hand eigenvectors of  $\bar{H}_0$  in the space of  $\{\Phi_i^a, \Phi_{ij}^{ab}\}$ , respectively; the  $\Phi_q$  are determinants with excitation levels higher than double excitation; and  $(\partial T / \partial h_{\text{SO}})$  represents the first-order change in the cluster operator with respect to the SOC operator. It should be noted that orbital relaxation due to SOC is neglected in eq 18. The relation between  $|\Phi_{\text{EOM}}^{K,0}\rangle$ ,  $\langle \tilde{\Phi}_{\text{EOM}}^{K,0}|$  and  $|\Phi_{\text{EOM}}^{K,1}\rangle$ ,  $\langle \tilde{\Phi}_{\text{EOM}}^{K,1}|$  is

$$|\Phi_{\text{EOM}}^{K,0}\rangle = r_K^0 |\Phi_0\rangle + |\Phi_{\text{EOM}}^{K,1}\rangle, \quad \langle \tilde{\Phi}_{\text{EOM}}^{K,0}| = \langle \tilde{\Phi}_{\text{EOM}}^{K,1}| \quad (19)$$

Using the relations

$$\langle \Phi_0 | (1 + \Lambda) | \Phi_{\text{EOM}}^{K,0} \rangle = r_0^K + \langle \Phi_0 | (1 + \Lambda) | \Phi_{\text{EOM}}^{K,1} \rangle = 0 \quad (20)$$

$$\frac{\partial T}{\partial h_{\text{SO}}} | \Phi_0 \rangle = \sum_K \frac{|\Phi_{\text{EOM}}^{K,1}\rangle \langle \tilde{\Phi}_{\text{EOM}}^{K,1} | \bar{H}_{\text{SO}} | \Phi_0 \rangle}{E_{\text{CCSD}}^0 - E_K^0} \quad (21)$$

$$\frac{\partial E_{\text{CCSD}}}{\partial h_{\text{SO}}} = \langle \Phi_0 | (1 + \Lambda) \bar{H}_{\text{SO}} | \Phi_0 \rangle \quad (22)$$

one can see from eqs 17 and 18 that these two energy corrections due to SOC are exactly the same except for the additional last term in eq 18, regardless of whether the first-order energy correction is zero or nonzero. It should be noted that  $r_0^K$  in eqs 4 and 19 is actually determined from eq 20

instead of eq 6. By inclusion of the last term in eq 18, a size-consistent energy correction can be achieved, and this term may be used to alleviate the size-inconsistency problem for the ground-state energy correction due to SOC based on the SOC-EOM-CCSD method by replacing  $(\partial T / \partial h_{\text{SO}})$  with the excitation operator. On the other hand, SOC effects should be better taken into account using the SOC-EOM-CCSD method than those based on the second-order perturbation treatment as in eq 18, since higher-order contributions are also included in SOC-EOM-CCSD.

In fact, size-intensive excitation energies can be restored in the SOC-EOM-CCSD method simply by neglecting the unlinked terms. This is equivalent to solving eqs 7 and 8 with the effective Hamiltonian  $\bar{H}$  defined in eq 11. A similar approach has been proposed previously for calculation of excitation energies or ionization potentials with an approximate cluster operator.<sup>55,56</sup> SOC effects on the ground state are not taken into account with this approach, and interactions between double-excitation determinants and single-excitation determinants through SOC are not fully considered because of the neglect of the  $\langle \Phi_{ij}^{ab} | \bar{H}_{\text{SO}} | \Phi_i^a \rangle$  term. In the following, this approach will be denoted as cSOC-EOM-CCSD.

### III. IMPLEMENTATION

The EOM-CCSD approaches with SOC for excitation energies described in section II for closed-shell molecules are implemented through an interface to the CFOUR program package.<sup>57</sup> The implementation of eqs 9 and 10 is similar to those in the solution of the perturbed cluster amplitude equations required in analytic second derivatives.<sup>53</sup> The efficiency of the SOC-EOM-CCSD and cSOC-EOM-CCSD approaches has not been fully exploited since we presently intend to evaluate only the accuracy of these approaches in accounting for SOC effects. SOC-EOM-CCSD and cSOC-EOM-CCSD are implemented using the EOM-SOC-CCSD program with slight modifications, such as setting the SOC operator to zero in solving the CCSD equations and turning it on when solving the EOM-CCSD equations. In SOC-EOM-CCSD, the additional terms in eqs 13 and 14 are also included, while they are not required in cSOC-EOM-CCSD.

In our implementation, time-reversal symmetry is imposed on both the ground-state and excited-state wave functions. Although not essential, one can always require the wave function of a system with an even number of electrons to be invariant under time reversal as long as the Hamiltonian is time-reversible. For a ground-state wave function of the form  $e^T | \Phi_0 \rangle$ , where  $\Phi_0$  is the scalar relativistic HF wave function of a closed-shell system, time-reversal symmetry means that the  $t$  amplitudes for different spin cases must satisfy the following expressions:<sup>39,58</sup>

$$t_i^a = (t_i^{\bar{a}})^*, \quad t_i^{\bar{a}} = -(t_i^a)^* \quad (23)$$

$$t_{ij}^{ab} = (t_{ij}^{\bar{a}\bar{b}})^*, \quad t_{ij}^{\bar{a}\bar{b}} = (t_{ij}^{ab})^*, \quad t_{i\bar{j}}^{ab} = -(t_{i\bar{j}}^{\bar{a}\bar{b}})^*,$$

$$t_{i\bar{j}}^{\bar{a}\bar{b}} = -(t_{i\bar{j}}^{ab})^*, \quad t_{i\bar{j}}^{ab} = (t_{i\bar{j}}^{\bar{a}\bar{b}})^* \quad (24)$$

For excited-state wave functions, the same relations hold for  $r_i^a$  and  $r_{ij}^{ab}$  besides the requirement that  $r_0$  must be real. Following our previous works,<sup>39</sup> we chose to calculate  $r$  amplitudes for the following spin cases:  $\{r_i^a, r_i^{\bar{a}}, r_{ij}^{ab}, r_{ij}^{\bar{a}\bar{b}}, r_{i\bar{j}}^{ab}, r_{i\bar{j}}^{\bar{a}\bar{b}}, r_{i\bar{j}}^{ab}, r_{i\bar{j}}^{\bar{a}\bar{b}}\}$  and the other spin cases of  $r$  amplitudes were determined either by time-reversal symmetry or permutation symmetry. It should also be

**Table 1.**  $ns \rightarrow np$  Excitation Energies of Zn, Cd, and Hg; Values in Parentheses Are Splittings of the States with Respect to the Average of the Triplet States (All Values in eV)<sup>a</sup>

	EOM-CCSD	EOM-SOC-CCSD	SOC-EOM-CCSD	cSOC-EOM-CCSD	exptl <sup>b</sup>
Zn					
(a) triplet state avg	3.946	3.946	3.950	3.945	4.054
$^3P_0$		3.900 (−0.047)	3.903 (−0.047)	3.898 (−0.047)	4.006 (−0.048)
$^3P_1$		3.922 (−0.023)	3.926 (−0.024)	3.921 (−0.024)	4.03 (−0.024)
$^3P_2$		3.969 (0.023)	3.974 (0.024)	3.969 (0.024)	4.078 (0.024)
$^1P_1$	5.789	5.789 (1.843)	5.796 (1.950)	5.788 (1.843)	5.796 (1.742)
(b) triplet state avg	3.942	3.941	3.941	3.941	
$^3P_0$		3.896 (−0.045)	3.896 (−0.045)	3.894 (−0.046)	
$^3P_1$		3.918 (−0.023)	3.918 (−0.023)	3.917 (−0.023)	
$^3P_2$		3.963 (0.022)	3.964 (0.023)	3.964 (0.023)	
$^1P_1$	5.792	5.792 (1.851)	5.792 (1.851)	5.791 (1.851)	
Cd					
(a) triplet state avg	3.832	3.829	3.851	3.823	3.874
$^3P_0$		3.690 (−0.139)	3.709 (−0.142)	3.677 (−0.146)	3.734 (−0.140)
$^3P_1$		3.757 (−0.072)	3.777 (−0.074)	3.747 (−0.076)	3.801 (−0.073)
$^3P_2$		3.900 (0.071)	3.924 (0.073)	3.898 (0.075)	3.946 (0.072)
$^1P_1$	5.501	5.503 (1.674)	5.537 (1.686)	5.499 (1.676)	5.417 (1.543)
(b) triplet state avg	3.804	3.797	3.799	3.796	
$^3P_0$		3.660 (−0.138)	3.660 (−0.139)	3.653 (−0.142)	
$^3P_1$		3.726 (−0.072)	3.727 (−0.072)	3.722 (−0.074)	
$^3P_2$		3.868 (0.071)	3.870 (0.071)	3.869 (0.073)	
$^1P_1$	5.474	5.474 (1.677)	5.477 (1.678)	5.473 (1.677)	
Hg					
(a) triplet state avg	5.178	5.136	5.411	5.052	5.181
$^3P_0$		4.641 (−0.495)	4.888 (−0.523)	4.473 (−0.579)	4.667 (−0.514)
$^3P_1$		4.858 (−0.278)	5.116 (−0.295)	4.718 (−0.334)	4.886 (−0.295)
$^3P_2$		5.402 (0.266)	5.693 (0.282)	5.368 (0.316)	5.461 (0.280)
$^1P_1$	6.737	6.765 (1.629)	7.102 (1.691)	6.724 (1.672)	6.704 (1.523)
(b) triplet state avg	5.150	5.050	5.076	5.030	
$^3P_0$		4.499 (−0.551)	4.518 (−0.558)	4.457 (−0.574)	
$^3P_1$		4.732 (−0.317)	4.754 (−0.322)	4.698 (−0.333)	
$^3P_2$		5.351 (0.301)	5.381 (0.305)	5.344 (0.314)	
$^1P_1$	6.715	6.721 (1.671)	6.753 (1.677)	6.705 (1.675)	

<sup>a</sup>For each species, (a) shows results of all-electron calculations and (b) shows results of calculation in which the  $(n-1)s(n-1)p$  electrons were frozen. <sup>b</sup>From ref 73.

noted that the real part of  $r_i^a$  corresponds to the spin-singlet component in the excited-state wave function, while  $r_i^a$  and the imaginary part of  $r_i^a$  are associated with the spin-triplet component. In the following, we will show that the matrix representation of  $\bar{H}$  in a space spanned by time-reversible wave functions will always be real. The similarity-transformed Hamiltonian  $\bar{H}$  is time-reversible since both the Hamiltonian  $H$  and the  $T$  operator are invariant under time reversal. The wave function resulting from the action of  $\bar{H}$  on a time-reversible wave function will thus also be time-reversible. The inner product of two time-reversible wave functions must be a real number since this inner product must be invariant under time reversal and the time reverse of a number is just its complex conjugate. This simply means the matrix element of  $\bar{H}$  between two time-reversible wave functions is real. A similar conclusion was drawn previously in ref 59.

Exploitation of spatial symmetry will result in a significant reduction in computational effort, especially in electron correlation calculations, where the computational savings can be as much as  $h^2$ , where  $h$  is the order of the molecular point group.<sup>60,61</sup> It should be noted that to facilitate implementation, Abelian groups (i.e.,  $D_{2h}$  and its subgroups) are generally adopted in electron correlation calculations. When SOC is

present, double-group symmetry has to be used, and the  $D_{2h}^*$ ,  $D_{2v}^*$ , and  $C_{2v}^*$  double groups are non-Abelian. On the other hand, the molecular orbitals employed here were calculated from the scalar-relativistic Hamiltonian and thus transform as bases of the irreducible representations (IRs) of the corresponding single-point groups, which are also boson IRs of the related double groups. Furthermore, we are dealing with systems having an even number of electrons, and the wave function for such a system also transforms as a boson IR. With these facts, it was shown previously that only single-point-group symmetry is required for closed-shell ground-state calculations using the present CC approach with SOC, and the symmetries of the  $t$  amplitudes for different spin cases can be determined as follows:<sup>45</sup> the real and imaginary parts of  $t$  amplitudes with an even number of  $\beta$  spin orbital indices should transform as the totally symmetric representation and  $\Gamma_{I_y}$ , respectively, while for  $t$  amplitudes with an odd number of  $\beta$  spin orbital indices, the real part should transform as  $\Gamma_{I_y}$  and the imaginary part as  $\Gamma_{I_z}$ , where  $\Gamma_{I_x}$ ,  $\Gamma_{I_y}$ ,  $\Gamma_{I_z}$  are the IRs of the angular momentum operator along the  $x$ ,  $y$ , and  $z$  directions, respectively. For excited states that can be classified according to the IR  $\Gamma_i$ , the symmetries of the corresponding  $r$  amplitudes for different spin cases can be

**Table 2.**  $(n-1)d \rightarrow ns$  Excitation Energies of  $\text{Cu}^+$ ,  $\text{Ag}^+$ , and  $\text{Au}^+$ ; Values in Parentheses Are Splittings of the States with Respect to the Average of the Triplet States (All Values in eV)<sup>a</sup>

	EOM-CCSD	EOM-SOC-CCSD	SOC-EOM-CCSD	cSOC-EOM-CCSD	exptl <sup>b</sup>
<b><math>\text{Cu}^+</math></b>					
(a) triplet state avg	2.395	2.386	2.392	2.386	2.808
$^3D_3$		2.299 (−0.087)	2.304 (−0.088)	2.307 (−0.080)	2.719 (−0.089)
$^3D_2$		2.414 (0.028)	2.421 (0.028)	2.413 (0.027)	2.833 (0.025)
$^3D_1$		2.542 (0.156)	2.551 (0.158)	2.527 (0.141)	2.975 (0.167)
$^1D_2$	2.864	2.895 (0.509)	2.903 (0.511)	2.889 (0.502)	3.256 (0.448)
(b) triplet state avg	2.657	2.648	2.649	2.649	
$^3D_3$		2.568 (−0.080)	2.568 (−0.081)	2.573 (−0.075)	
$^3D_2$		2.675 (0.026)	2.675 (0.026)	2.674 (0.025)	
$^3D_1$		2.792 (0.144)	2.794 (0.145)	2.782 (0.133)	
$^1D_2$	3.101	3.129 (0.481)	3.131 (0.482)	3.125 (0.477)	
<b><math>\text{Ag}^+</math></b>					
(a) triplet state avg	4.845	4.828	4.875	4.783	5.034
$^3D_3$		4.656 (−0.172)	4.699 (−0.176)	4.616 (−0.166)	4.855 (−0.179)
$^3D_2$		4.855 (0.026)	4.901 (0.026)	4.810 (0.027)	5.051 (0.017)
$^3D_1$		5.185 (0.357)	5.242 (0.367)	5.125 (0.342)	5.323 (0.389)
$^1D_2$	5.384	5.525 (0.697)	5.583 (0.708)	5.469 (0.687)	5.709 (0.675)
(b) triplet state avg	5.360	5.338	5.350	5.296	
$^3D_3$		5.167 (−0.171)	5.177 (−0.173)	5.134 (−0.162)	
$^3D_2$		5.359 (0.022)	5.371 (0.021)	5.320 (0.024)	
$^3D_1$		5.700 (0.363)	5.718 (0.368)	5.634 (0.339)	
$^1D_2$	5.867	6.014 (0.676)	6.032 (0.682)	5.955 (0.659)	
<b><math>\text{Au}^+</math></b>					
(a) triplet state avg	2.312	2.142	2.468	2.104	2.288
$^3D_3$		1.714 (−0.428)	2.035 (−0.433)	1.679 (−0.425)	1.865 (−0.423)
$^3D_2$		2.080 (−0.062)	2.414 (−0.054)	2.035 (−0.069)	2.187 (−0.101)
$^3D_1$		3.243 (1.101)	3.568 (1.100)	3.212 (1.107)	3.443 (1.155)
$^1D_2$	3.036	3.598 (1.457)	3.953 (1.485)	3.574 (1.470)	3.673 (1.385)
(b) triplet state avg	2.713	2.530	2.548	2.510	
$^3D_3$		2.091 (−0.429)	2.108 (−0.441)	2.087 (−0.424)	
$^3D_2$		2.441 (−0.088)	2.459 (−0.090)	2.428 (−0.082)	
$^3D_1$		3.701 (1.171)	3.725 (1.177)	3.636 (1.126)	
$^1D_2$	3.388	4.021 (1.492)	4.049 (1.500)	3.966 (1.456)	

<sup>a</sup>For each species, (a) shows results of all-electron calculations and (b) shows results of calculation in which the  $(n-1)s(n-1)p$  electrons were frozen. <sup>b</sup>From ref 73.

determined similarly: for  $r$  amplitudes with an even number of  $\beta$  spin orbital indices, i.e.,  $r_i^a$ ,  $r_{ij}^{ab}$ ,  $r_{ij}^{a\bar{b}}$  and  $r_{ij}^{ab}$ , the real and imaginary parts should transform as  $\Gamma_I$  and  $\Gamma_{I_c} \otimes \Gamma_D$ , respectively, while for  $r$  amplitudes with an odd number of  $\beta$  spin orbital indices, i.e.,  $r_i^a$ ,  $r_{ij}^{ab}$  and  $r_{ij}^{a\bar{b}}$ , the real and imaginary parts should transform as  $\Gamma_{I_c} \otimes \Gamma_I$  and  $\Gamma_{I_c} \otimes \Gamma_D$ , respectively. Once the symmetries for  $r$  amplitudes of different spin cases have been decided, the direct product decomposition (DPD) method<sup>60</sup> is employed in the implementation.

Davidson's algorithm with a slight modification<sup>62,63</sup> for non-Hermite matrices was adopted in the present work to find the lowest several or specified eigenvalues and eigenvectors of  $\bar{H}$ . The diagonal elements of the  $\bar{H}$  matrix required in Davidson's algorithm were approximated by the corresponding orbital energy differences in our implementation. In Davidson's algorithm,  $\bar{H}$  is diagonalized in a small subspace. To make use of the real nature of the  $\bar{H}$  matrix in a space spanned by time-reversible wave functions, one must make sure that the  $r$  amplitudes corresponding to the trial wave functions satisfy relations similar to those shown in eqs 23 and 24. It should be noted that the real nature of the  $\bar{H}$  matrix does not mean that

the  $r$  amplitudes are real, since the time-reversible wave functions on which the  $\bar{H}$  matrix acts are generally complex when SOC is present. Furthermore, the savings in computational effort are mainly due to exploitation of time-reversal and spatial symmetry instead of the real nature of the  $\bar{H}$  matrix, since a matrix with a rather small dimension has to be diagonalized in Davidson's algorithm. On the other hand, the real nature of the  $\bar{H}$  matrix in a subspace usually means that the corresponding eigenvectors are real, which significantly eases the requirement of time-reversal symmetry for new trial wave functions.

#### IV. RESULTS

As a first application of the EOM-CCSD approaches with SOC, we calculated transition energies to the lowest several excited states of the following closed-shell atoms or ions:  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Au}^+$ , Zn, Cd, Hg, Kr, Xe, and Rn. The energy-consistent pseudopotentials developed by the Stuttgart/Cologne groups<sup>64</sup> were used for these atoms, i.e., ECP10MDF for  $\text{Cu}^+$ , Zn, and Kr, ECP28MDF for  $\text{Ag}^+$ , Cd, and Xe, and ECP60MDF for  $\text{Au}^+$ , Hg, and Rn.<sup>65,66</sup> To achieve reliable results with SOC, the employed basis set must be able to describe the spin-orbit splitting of the inner-shell orbitals  $((n-1)p$  and  $(n-1)d$

**Table 3.**  $np \rightarrow (n + 1)s$  Excitation Energies of Kr, Xe, and Rn; Values in Parentheses Are Splittings of the States with Respect to the Lowest Excited States (All Values in eV)<sup>a</sup>

	EOM-CCSD	EOM-SOC-CCSD	SOC-EOM-CCSD	cSOC-EOM-CCSD	exptl <sup>b</sup>
Kr					
(a) $(^3/2, ^1/2)_2$	10.279 <sup>c</sup>	10.069	10.092	10.078	9.915
$(^3/2, ^1/2)_1$		10.221 (0.152)	10.244 (0.152)	10.225 (0.147)	10.032 (0.117)
$(^1/2, ^1/2)_0$		10.709 (0.488)	10.732 (0.487)	10.662 (0.437)	10.562 (0.530)
$(^1/2, ^1/2)_1$	10.548 <sup>d</sup>	10.827 (0.118)	10.852 (0.120)	10.784 (0.122)	10.643 (0.081)
(b) $(^3/2, ^1/2)_2$	10.309 <sup>c</sup>	10.107	10.112	10.115	
$(^3/2, ^1/2)_1$		10.257 (0.150)	10.262 (0.150)	10.261 (0.146)	
$(^1/2, ^1/2)_0$		10.729 (0.471)	10.732 (0.470)	10.689 (0.428)	
$(^1/2, ^1/2)_1$	10.576 <sup>d</sup>	10.847 (0.118)	10.851 (0.119)	10.811 (0.122)	
Xe					
(a) $(^3/2, ^1/2)_2$	8.825 <sup>c</sup>	8.429	8.549	8.429	8.315
$(^3/2, ^1/2)_1$		8.583 (0.154)	8.706 (0.157)	8.579 (0.149)	8.436 (0.121)
$(^1/2, ^1/2)_0$		9.573 (0.990)	9.678 (0.972)	9.472 (0.893)	9.447 (1.011)
$(^1/2, ^1/2)_1$	9.083 <sup>d</sup>	9.718 (0.146)	9.828 (0.151)	9.611 (0.139)	9.569 (0.122)
(b) $(^3/2, ^1/2)_2$	8.837 <sup>c</sup>	8.454	8.507	8.457	
$(^3/2, ^1/2)_1$		8.607 (0.153)	8.660 (0.154)	8.605 (0.148)	
$(^1/2, ^1/2)_0$		9.596 (0.989)	9.637 (0.977)	9.503 (0.897)	
$(^1/2, ^1/2)_1$	9.093 <sup>d</sup>	9.740 (0.144)	9.783 (0.146)	9.641 (0.138)	
Rn					
(a) $(^3/2, ^1/2)_2$	7.848 <sup>c</sup>	6.804	7.769	6.669	6.772
$(^3/2, ^1/2)_1$		7.003 (0.199)	7.980 (0.211)	6.852 (0.182)	6.942 (0.170)
$(^1/2, ^1/2)_0$		10.607 (3.604)	11.456 (3.475)	9.822 (2.970)	10.660 (3.718)
$(^1/2, ^1/2)_1$	8.149 <sup>d</sup>	10.645 (0.038)	11.507 (0.051)	9.859 (0.037)	10.794 (0.134)
(b) $(^3/2, ^1/2)_2$	7.851 <sup>c</sup>	6.820	7.145	6.737	
$(^3/2, ^1/2)_1$		7.017 (0.197)	7.344 (0.199)	6.919 (0.182)	
$(^1/2, ^1/2)_0$		10.966 (3.948)	11.195 (3.851)	10.037 (3.118)	
$(^1/2, ^1/2)_1$	8.150 <sup>d</sup>	11.003 (0.037)	11.238 (0.043)	10.072 (0.035)	

<sup>a</sup>For each species, (a) shows results of all-electron calculations and (b) shows results of calculations in which the  $(n - 1)s(n - 1)p$  electrons were frozen. <sup>b</sup>From ref 73. <sup>c</sup>spin-triplet state. <sup>d</sup>spin-singlet state.

orbitals) of heavy elements.<sup>67–69</sup> Furthermore, correlation of inner-shell orbitals could also be important, and the cc-pwCVQZ basis set,<sup>70,71</sup> which has been shown previously to afford a reliable description of SOC effects, was employed with augmentation of a set of diffuse basis functions.<sup>65,70,72</sup> The calculated excitation energies and spin–orbit splittings for these atoms or ions obtained using the present approaches are listed in Tables 1–3. The excited states for Cu<sup>+</sup>, Ag<sup>+</sup>, Au<sup>+</sup>, Zn, Cd, and Hg were represented by an LS coupling scheme, and the spin–orbit splitting was obtained from the energy difference between the excited state and the average of the triplet states. On the other hand, a JJ coupling scheme was adopted for Kr, Xe, and Rn, and the spin–orbit splitting was calculated from the energy difference between adjacent states. Excitation energies based on EOM-CCSD without SOC and experimental data<sup>73</sup> are also listed in these tables for comparison.

According to these tables, the excitation energies from the scalar relativistic approach are in good agreement with the average energies of the triplet states and the energies of the  $^1P_1$  states when SOC is present. This indicates that the LS coupling scheme is suitable to describe the  $(ns)^1(np)^1$  configuration of Zn, Cd, and Hg. The differences are somewhat larger for Cu<sup>+</sup>, Ag<sup>+</sup>, and Au<sup>+</sup>. For Kr, Xe, and Rn, the difference between the excitation energy of the spin-singlet state and that of the  $(^1/2, ^1/2)_1$  state is already significant even for Kr, which means that the LS coupling scheme not applicable to these states. It can be seen from these tables that the excitation energies obtained from SOC-EOM-CCSD are always larger than those from EOM-SOC-CCSD, while those from cSOC-EOM-CCSD are

smaller in most cases. This could be the case because SOC for the ground state is better described than that for excited states with SOC-EOM-CCSD while it is treated in a more balanced way in EOM-SOC-CCSD. On the other hand, SOC for the ground state is not considered at all in cSOC-EOM-CCSD, which would result in underestimation of the excitation energies. Furthermore, the agreement between these approaches is improved if the inner-shell  $(n - 1)s(n - 1)p$  electrons are kept frozen. This is especially the case for SOC-EOM-CCSD. One can see from Table 1 that the excitation energies from EOM-SOC-CCSD agree well with the experimental data, with a difference of less than 0.1 eV, and that the spin–orbit splittings are also consistent with experimental values when all of the electrons (those not treated via ECPs) are included in the calculations. The excitation energies and spin–orbit splittings from SOC-EOM-CCSD and cSOC-EOM-CCSD are in good agreement with those from EOM-SOC-CCSD, with differences smaller than 0.01 eV in most cases for Zn and Cd, where SOC effects are rather small. For Hg, the excitation energies with SOC-EOM-CCSD are overestimated by about 0.3 eV compared with the EOM-SOC-CCSD results, while the cSOC-EOM-CCSD excitation energies are about 0.15 and 0.04 eV smaller for the lower two and higher two states, respectively. The observation that the errors in the excitation energies to  $^3P_0$  and  $^3P_1$  states is larger than those to  $^3P_2$  and  $^1P_1$  states with cSOC-EOM-CCSD can be rationalized from the JJ coupling scheme.  $^3P_0$  and  $^3P_1$  states mainly stem from transitions to  $p_{1/2}$  spinors, where SOC has the largest effect, while  $^3P_2$  and  $^1P_1$  states come from



Table 4. Excitation Energies of  $I_3^-$  (in eV) from the EOM-SOC-CCSD and SOC-EOM-CCSD Approaches

state	$\Omega$	EOM-SOC-CCSD	SOC-EOM-CCSD	cSOC-EOM-CCSD	CASPT2 <sup>a</sup>	IHFSCC <sup>a</sup>
1	$2_g$	2.215	2.362	2.159	2.24	2.05
2	$0_u^-$	2.336	2.486	2.289	2.47	2.2
3	$1_u$	2.343	2.492	2.296	2.47	2.2
4	$1_g$	2.349	2.498	2.292	2.32	2.18
5	$0_g^-$	2.813	2.957	2.724	2.76	2.64
6	$0_g^+$	2.858	2.991	2.746	2.82	2.69
7	$1_g$	3.042	3.196	2.962	2.85	2.86
8	$2_u$	3.304	3.465	3.250	3.1	3.17
9	$1_u$	3.390	3.554	3.336	3.11	3.24
10	$0_u^+$	3.645	3.790	3.560	3.52	3.51
11	$0_u^-$	4.047	4.183	3.909	3.79	3.91
12	$2_g$	4.043	4.191	3.980	3.98	3.88
13	$1_u$	4.151	4.293	4.014	3.8	4
14	$1_g$	4.166	4.315	4.100	4.06	4
15	$0_u^+$	4.504	4.670	4.418	4.51	4.33
16	$0_g^-$	4.645	4.763	4.507	4.51	4.48
17	$0_g^+$	4.652	4.821	4.510	4.53	4.48
18	$1_g$	4.862	4.990	4.730	4.6	4.68

<sup>a</sup>From ref 77.

transitions to  $p_{3/2}$  spinors, which are less affected by SOC. Excitation energies from SOC-EOM-CCSD and cSOC-EOM-CCSD are in reasonable agreement with the EOM-SOC-CCSD results for Hg when inner-shell electrons are frozen. One can also see from Table 1 that inner-shell electrons have only a minor effect on the investigated excitation energies of Zn, Cd, and Hg with EOM-SOC-CCSD, except for the  $^3P_0$  and  $^3P_1$  states of Hg, whose excitation energies are reduced by 0.14 eV when inner-shell electrons are frozen. The excitation energies for these two states of Hg are in better agreement with the experimental data when the inner-shell electrons are included in calculations.

According to Table 2, these three approaches provide results that agree well with each other for  $Cu^+$ , while the differences between these approaches are somewhat larger for  $Ag^+$  (i.e., 0.05 eV for excitation energies and 0.01 eV for spin–orbit splittings). For  $Au^+$ , the SOC-EOM-CCSD excitation energies are overestimated by about 0.3 eV compared with the EOM-SOC-CCSD results. On the other hand, the cSOC-EOM-CCSD results are consistent with the EOM-SOC-CCSD results. When the  $(n-1)s(n-1)p$  electrons are frozen, the differences in the excitation energies from these three approaches are reduced to about 0.02 eV for  $Ag^+$  and  $Au^+$ . One can see from Table 2 that the  $(n-1)s(n-1)p$  electrons have a pronounced effect on the excitation energies of the  $(n-1)d \rightarrow ns$  transitions. In addition, the excitation energies from EOM-SOC-CCSD are about 0.4, 0.2, and 0.1 eV smaller than the experimental results for  $Cu^+$ ,  $Ag^+$ , and  $Au^+$ , respectively. By inspecting the corresponding  $r$  amplitudes for the calculated excited states of  $Cu^+$ , we find that these excited states are mainly of single-excitation character. This large difference is probably due to the multireference nature of the ground state of  $Cu^+$ , which could not be described properly at the CCSD level. Test calculations without SOC showed that the excitation energy for the spin-singlet state with the CC3 approach<sup>11</sup> is about 0.5 eV larger than that with EOM-CCSD.

For Kr, Xe, and Rn, the excitation energies from EOM-SOC-CCSD are usually 0.1–0.2 eV larger than the experimental results when the inner-shell electrons are included. One would expect these three approaches to provide similar

excitation energies for Kr. However, the excitation energies from cSOC-EOM-CCSD for the higher two states are about 0.04 eV smaller than results from the EOM-SOC-CCSD approach. This sizable difference stems from the fact that the higher two excited states originate from transitions out of  $p_{1/2}$  spinors. The energy difference between  $(^1/2, ^1/2)_0$  and  $(^3/2, ^1/2)_1$  from cSOC-EOM-CCSD is thus underestimated by about 0.05 eV, while the spin–orbit splittings from SOC-EOM-CCSD are in good agreement with those from the EOM-SOC-CCSD approach for Kr. For Xe, the excitation energies for all four states from SOC-EOM-CCSD are overestimated by about 0.1 eV compared with the EOM-SOC-CCSD results. On the other hand, the excitation energies of the lower two states from cSOC-EOM-CCSD agree very well with the EOM-SOC-CCSD results, while the higher two states are calculated to be 0.1 eV lower. When the  $(n-1)s(n-1)p$  electrons are frozen, the agreement between SOC-EOM-CCSD and EOM-SOC-CCSD is improved, while the cSOC-EOM-CCSD results are not affected much. A similar situation was also found for Rn, where the SOC-EOM-CCSD results are about 1 eV larger than those from EOM-SOC-CCSD and the excitation energies from cSOC-EOM-CCSD are 0.15 eV smaller for the lower two states and 0.8 eV smaller for the higher two states. For the splittings between these excited states, the SOC-EOM-CCSD results are in good agreement with the EOM-SOC-CCSD results, while the splittings obtained from cSOC-EOM-CCSD are usually underestimated to some extent. This could be due to the neglect of the  $\langle \Phi_{ij}^{ab} | \bar{H}_{SO} | \Phi_i^a \rangle$  term in cSOC-EOM-CCSD. According to Table 3, the investigated excitation energies for Kr, Xe, and Rn from EOM-SOC-CCSD are not affected much by the inner-shell electrons, except for the higher two states of Rn. The excitation energies for these two states of Rn are increased by 0.36 eV when the  $(n-1)s(n-1)p$  electrons are frozen. Similar to the case of Hg, better agreement with the experimental data is achieved when the inner-shell electrons are included in calculations. This indicates that to provide reliable excitation energies involving  $p_{1/2}$  spinors of heavy elements, the inner-shell electrons should be included with the present approach.



Besides these atoms or ions, the lowest 18 excitation energies for  $I_3^-$  with SOC were also calculated, and the results are listed in Table 4. Previous theoretical results obtained using complete-active-space perturbation theory to second order (CASPT2) and the intermediate-Hamiltonian Fock-space coupled-cluster (IHFS-CC) method with SOC<sup>52</sup> are also listed for comparison. In these calculations, ECP28MDF for  $I^{65,74}$  and the cc-pwCVQZ basis set augmented by a set of diffuse basis functions<sup>74</sup> were employed. The  $4s^2 4p^6$  electrons of I were kept frozen in the calculation. From Table 4, it can be seen that the ordering of the excited states for  $I_3^-$  provided by SOC-EOM-CCSD is the same as that from EOM-SOC-CCSD except for states 11 and 12, whose energy difference is smaller than 0.01 eV. Furthermore, the excitation energies from SOC-EOM-CCSD are always about 0.15 eV larger than those from EOM-SOC-CCSD. This means the SOC-EOM-CCSD approach is able to provide a reasonable description of SOC effects for excited states of this molecule compared with the EOM-SOC-CCSD approach. The excitation energies obtained from cSOC-EOM-CCSD are about 0.05–0.1 eV smaller for the first 11 states and about 0.15 eV smaller for the other states compared with the EOM-SOC-CCSD results. Furthermore, the relative energies of states 3 and 4 as well as those for states 11 and 12 also disagree with the EOM-SOC-CCSD results. The energy of state 11 is calculated to be 0.08 eV larger than that of state 12 with cSOC-EOM-CCSD, while it is about 0.004 eV lower with EOM-SOC-CCSD. It can also be seen from Table 4 that the excitation energies obtained from the present EOM-SOC-CCSD approach are always 0.15–0.2 eV larger than the IHFS-CC results. This is consistent with previous findings that EOM-CC generally produces larger excitation energies compared with IHFS-CC.<sup>75</sup> In comparison with the CASPT2 results, except for the lowest  $2g$ ,  $1u$ , and  $0_u^-$  states, EOM-SOC-CCSD generally overestimates the excitation energies. Unlike the case for IHFS-CC, the difference between the CASPT2 and EOM-SOC-CCSD results ranges from 0.01 to 0.3 eV. It can also be seen from this table that except for the second, third, and fourth states, the ordering of the excited states produced by IHFS-CC is similar to that from the present work. In fact, the energy differences between these states are less than 0.02 eV.

## V. CONCLUSION

We have reported the implementation of excitation energies with SOC for closed-shell systems using the EOM-CCSD approach based on a previously developed CC approach using ECPs to treat scalar relativistic effects and with SOC included in the post-Hartree–Fock treatment. SOC can be included in both the CC and the EOM steps or only in the EOM part in the EOM-CC calculations. The latter approach is conceptually similar to the two-step CI approaches to deal with SOC and provides a computationally economical way to calculate SOC effects on both the ground- and excited-state properties. However, the ground-state energy is not size-consistent and the excitation energies are not size-intensive with the latter approach. Size-intensive excitation energies can be achieved simply by neglecting unconnected terms. In the implementations, both time-reversal symmetry and spatial symmetry are exploited to reduce the computational effort. Imposing time-reversal symmetry on the excited-state wave functions results in a real  $\bar{H}$  matrix, which significantly eases the requirement of time-reversal symmetry for new trial vectors.

Excitation energies for some closed-shell atoms and molecules have been calculated using these three EOM-

CCSD approaches. EOM-SOC-CCSD affords excitation energies that agree well with the experimental data except for  $Cu^+$ , where the multiconfiguration nature of the ground state may be significant. In addition, inner-shell electrons are necessary to achieve reliable excitation energies using EOM-SOC-CCSD for transitions involving  $p_{1/2}$  spinors of heavy elements. The excitation energies obtained from SOC-EOM-CCSD are in reasonable agreement with the EOM-SOC-CCSD results up to the fifth-row elements, and large errors occur for the sixth-row elements, especially when inner-shell electrons are included in the calculations. However, splittings of the excited states can still be computed rather accurately with EOM-SOC-CCSD even for heavy p-block elements. On the other hand, the excitation energies based on cSOC-EOM-CCSD are generally in reasonable agreement with the EOM-SOC-CCSD results even for sixth-row elements as long as  $p_{1/2}$  spinors are not involved, whereas the spin–orbit splittings are less accurate even for transitions involving  $p_{1/2}$  spinors of Kr. It would be interesting to study the performance of EOM-CCSD approaches based on some approximate treatment of SOC or using approximate cluster operators such as  $CC2^{76}$  with SOC. Work in this direction is underway.

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### Notes

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