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ABSTRACT
This work presents the formalism and implementation for calculations of spin–orbit couplings (SOCs) using the Breit–Pauli Hamiltonian and non-relativistic wave functions described by the restricted active space configuration interaction (RASCI) method with general excitation operators of spin-conserving spin-flipping, ionizing, and electron-attaching types. The implementation is based on the application of the Wigner–Eckart theorem within the spin space, which enables the calculation of the entire SOC matrix based on the explicit calculation of just one transition between the two spin multiplets. Numeric results for a diverse set of atoms and molecules highlight the importance of a balanced treatment of correlation and adequate basis sets and illustrate the overall robust performance of RASCI SOCs. The new implementation is a useful addition to the methodological toolkit for studying spin-forbidden processes and molecular magnetism.

I. INTRODUCTION
The time-independent electronic Schrödinger equation provides a central framework for the theoretical description and analysis of a vast variety of molecular phenomena. Regarded as the first-principles foundation of quantum chemistry, the Schrödinger equation is itself an approximation that assumes instantaneous Coulomb interactions between charged particles. Hence, it is valid in the non-relativistic limit of quantum mechanics. Relativistic effects, neglected in non-relativistic quantum-chemical treatments, affect chemistry in profound ways.¹ Although more pronounced in molecules composed of heavier elements, relativistic effects¹ are also important in light molecules. In particular, spin–orbit coupling (SOC) facilitates many processes that are forbidden in the non-relativistic description. SOC mixes electronic states of different spins that do not interact in the non-relativistic picture. This interaction manifests itself spectroscopically as spin–orbit splitting of energy levels and intensity redistribution (intensity borrowing). For example, the electronic transition responsible for the purple color of iodine is formally spin-forbidden but becomes allowed due to strong spin–orbit interaction.¹³ SOC also facilitates non-radiative and radiative transitions between different spin manifolds, leading to inter-system crossing (ISC)¹⁸ and phosphorescence.¹³ These phenomena open spin-forbidden reaction and relaxation pathways, which are relevant in astrochemistry, combustion chemistry, electronics, and catalysis.¹⁶ In single-molecule magnets,¹⁷–¹⁹ SOC introduces magnetic anisotropy and spin-reversal barriers, determining the relaxation time of magnetization, a crucially important property in practical applications of these magnetic materials. In molecules composed of light atoms, SOC can be described by using the so-called perturbative approach, i.e., by computing...
matrix elements of the Breit–Pauli Hamiltonian\cite{5,15,16} using non-relativistic wave functions and diagonalizing the resulting matrix to obtain spin–orbit perturbed states. The set of non-relativistic wave functions form a spin–orbit diabatic representation; they can be described as zero-order states. The perturbed states, resulting from the diagonalization, form a spin–orbit adiabatic representation. Effective algorithms\cite{17–19,20,21} for the calculation of SOC matrix elements often exploit the Wigner–Eckart theorem,\cite{22,23} which enables the evaluation of the entire SOC matrix between two multiplets from just one transition, for example, between a singlet state and the $M = 0$ component of a triplet state. Recently, Pokhilko et al.\cite{24} reported an algorithm for evaluating SOCs by application of the Wigner–Eckart theorem to the reduced spinless density matrix generated for one specific transition. Formulated in the spin-orbital form,\cite{25} this approach is ansatz-agnostic and is applicable to transitions between any types of open-shell states, as long as respective transition density matrices can be obtained.

Pokhilko et al. applied this approach for computing SOCs using equation-of-motion coupled-cluster (EOM-CC) wave functions\cite{26–28,29} within the Q-Chem electronic structure package.\cite{30} Recently, this approach was extended\cite{31} to compute SOCs between core-level states using EOM-CC augmented with core–valence separation.\cite{32,33} This algorithm has also been implemented into a pilot RASCI (restricted active space configuration interaction) code within Psi4.\cite{34–40} Here, we extend the implementation of Pokhilko et al.\cite{41,64} to a production-level implementation of the RASCI family of methods\cite{41,64} within Q-Chem, which enables the calculation of a large variety of open-shell and electronically excited states. In addition to the calculation of SOCs, we also implemented the calculation of natural transition orbitals (NTOs) of the spinless transition density matrix (1TDM) to provide insight into the mechanism of the spin–orbit interactions.\cite{35,36}

Among the various flavors of RASCI methods, the spin-flip (SF) variant, RASCI-SF or simply RAS-SF, is of special interest. The SF approach\cite{37,38} extends single-reference methods to strongly correlated states, traditionally treated by multi-reference methods. SF treatment uses a carefully chosen high-spin reference state, in which all strongly correlated electrons have the same spin, and then employs spin-flipping operators to access the desired low-spin manifold, providing a low-cost yet accurate description of the states of interest. Among various variants of SF methods,\cite{42–46} the RAS-SF approach\cite{47,48} has particular utility. In RAS-SF, a small active space is defined to include the most strongly correlated electrons (i.e., the high-spin reference electrons and orbitals), which are treated at the complete active space (CAS) level of theory. A small subset of electronic configurations outside of this space is added to ensure balanced treatment of states with different characters, as described below. Since its introduction in 2009, RAS-SF methods have been employed to treat a variety of phenomena featuring a challenging electronic structure. Examples include diradicals,\cite{49,50} polyradicals,\cite{51–53} excited states in multichromophoric systems,\cite{54,55} catalysis,\cite{56} singlet fission processes,\cite{57–61} and charge transfer.\cite{62,63}

Following the EOM-CC philosophy,\cite{23} the RAS-SF approach has been generalized to employ other (non-SF) types of excitation operators, such as excitation energy (EE), ionization potential (IP), and electron attachment (EA) operators, giving rise to the RASCI family of methods.\cite{24} The present work further extends the scope of applications of the RASCI hierarchy of methods by enabling calculations of SOCs using any type of RASCI wave function. We describe a general framework for the calculation of SOCs with RASCI wave functions and illustrate the utility of the new approach by application to selected atoms and molecules.

This paper is organized as follows. We begin by briefly reviewing the RASCI formalism and describing the key steps of computing SOCs with the Breit–Pauli Hamiltonian. The essential computational details are given in Sec. III. Section IV illustrates the performance of RASCI SOCs in doublet radicals, atoms, small diradicals, conjugated ketones and alcohols, and along the molecular torsion of tetramethyleneethane. Section V summarizes the main findings of this study.

II. THEORY

A. The RASCI method

The RASCI ansatz\cite{41,64} is defined by choosing a reference configuration ($\Phi_0$, usually a Hartree–Fock determinant) and dividing the orbital space into three subspaces: RAS1, RAS2, and RAS3. The three RAS subspaces usually span the entire set of molecular orbitals, although the space can be reduced by freezing low-energy occupied and/or high-energy virtual orbitals. The RASCI wave function is produced by the action of an excitation operator that includes all possible electronic promotions within RAS2 ($\hat{R}_h$) and specified hole and particle excitations, i.e., configurations with vacancies (holes) and electrons (particles), in RAS1 and RAS3, respectively,

$$\hat{R} = \hat{R}_h + \hat{R}_p + \hat{R}_{hp} + \hat{R}_{2h} + \hat{R}_{2p} + \hat{R}_{2hp} + \cdots. \quad (1)$$

The configuration expansion within the RAS2 space is equivalent to full CI (FCI), whereas the truncated excitation set in RAS1 and RAS2 brings the essential electronic correlation while keeping the expansion compact (Fig. 1). The excitation operator connects the reference configuration $\Phi_0$ with the target states $|Y\rangle$.

![FIG. 1. RASCI electronic configurations within the hole and particle approximation generated by the excitation operator $\hat{R} = \hat{R}_h + \hat{R}_p + \hat{R}_{hp}$ acting on a reference $\Phi_0$.](image-url)
Several flavors of $\hat{R}$ can be used, i.e., excitation energy (EE), spin-flip (SF) operators performing single or multiple excitations of spin-$\alpha$ electrons to empty spin-$\beta$ orbitals (or the other way around), as well as ionization potential (IP) and electron attachment (EA) operators connecting the reference configuration with states with fewer and more electrons, respectively.78,63 In particular, the action of a SF operator with $\Delta M < 0$ on a high-spin reference within the hole and particle approximation ($\hat{R} = \hat{r}_0 + \hat{r}_3 + \hat{r}_5$) has been successfully applied to a variety of strongly correlated systems, such as diradicals35,43 and polyradicals44–46 multie excitons in multichromophoric systems,47,48 and electronic states involved in singlet fission.29,65

The implementation of the RASCI ansatz within effective algorithms, such as analytic integral evaluation35,43 and the resolution-of-identity (RI) approximation36 resulted in effective computer codes capable of handling extended systems, such as carbon nanotubes67 and organic macrocycles.45,46,68

**B. The Breit–Pauli spin–orbit Hamiltonian**

The Breit–Pauli spin–orbit Hamiltonian, originally introduced by Pauli,35,69 is commonly employed in calculations of the spin–orbit interaction between the electronic states computed by nonrelativistic quantum chemistry methods. In atomic units, the one- and two-electron spin–orbit terms of the Breit–Pauli Hamiltonian are

$$H_{SO}^{\beta} = \frac{1}{2c^2} \left[ \sum_i h^{SO}(i) \cdot s(i) + \sum_{i<j} h^{SO}(i,j) \cdot (s(i) + 2s(j)) \right],$$

where $c$ is the speed of light, $r_i$ and $p_i$ are the coordinates and momentum of the $i$th electron, respectively, $Z_i$ is the atomic charge of the $i$th nucleus, and $r_j$ and $p_j$ are the relative coordinates of electron $i$ and electron $j$ or nucleus $I$, respectively.

The Breit–Pauli spin–orbit operator has one- and two-electron parts, which, in the second quantization form, can be written as follows:

$$H^{SO} = \frac{1}{2c^2} \left[ \sum_{pq} h^{SO}_{pq} a_p^\dagger a_q + \sum_{pqrs} h^{SO}_{pqrs} a_p^\dagger a_q a_s^\dagger a_r \right],$$

$$I_{pq} = \langle \phi_p | h^{SO} (1) \cdot s(1) | \phi_q \rangle,$$

$$I_{pqrs} = (\phi_p (1) \phi_q (2) | h^{SO} (1,2) \cdot (s(1) + 2s(2)) | \phi_r (1) \phi_s (2)), \tag{8}$$

where $h^{SO}$ and $h^{SO}_{pqrs}$ operators are defined in Eqs. (4) and (5) and $\phi_p(i)$ denotes the $i$th spin-orbital with $r_i$ and $s_i$ spatial and spin coordinates, respectively. Details for computing one- and two-electron spin–orbit integrals ($I_{pq}$ and $I_{pqrs}$) can be found elsewhere.70

Evaluation of the SOC between two electronic states requires the contraction of $I_{pq}$ and $I_{pqrs}$ with one- and two-particle transition density matrices. This expression can be reduced by invoking SOMF (spin–orbit mean-field) approximation,2

$$H_{SOMF}^{SO} = \frac{1}{2} \sum_{pq} \left[ I_{pq} + \sum_{rs} \rho_{rs} (I_{pqrs} - I_{pqs} - I_{qps} + I_{qsr}) \right] a_p^\dagger a_q, \tag{9}$$

where $\rho_{rs}$ is a density matrix of a vacuum determinant (see derivation based on the separable part of the two-particle density matrix in Ref. 71), and with spin–orbit–mean-field matrices defined as

$$H_{SOMF}^{SO} = I_{pq}^{1SO} + I_{pq}^{2SO}, \tag{10}$$

$$I_{pq}^{1SO} = I_{pq}, \tag{11}$$

$$I_{pq}^{2SO} = \sum_{rs} \rho_{rs} (I_{pqrs} - I_{pqs} - I_{qps}). \tag{12}$$

Expanding the contractions and integrating over spin variables in Eqs. (7) and (8), the mean-field Hamiltonian can be written as

$$H_{SOMF}^{SO} = \frac{1}{2} \sum_{pq} \left[ h_{L_pq}^{SOMF} a_p^\dagger a_q + h_{z-pq}^{SOMF} a_p^\dagger a_q + h_{L_pq}^{SOMF} a_p a_q + h_{z-pq}^{SOMF} a_p a_q \right], \tag{13}$$

where we assume restricted spin orbitals, with the creation and annihilation of $\alpha$ and $\beta$ spin-orbitals indicated with orbital indices without and with overbars, respectively. The spherical components $L_+$ and $L_-$ are defined as

$$h_{L_p}^{SOMF} = h_{x}^{SOMF} + ih_{y}^{SOMF}, \tag{14}$$

$$h_{L_z}^{SOMF} = h_{x}^{SOMF} - ih_{y}^{SOMF}. \tag{15}$$

and where $h_{x}^{SOMF}$, $h_{y}^{SOMF}$, and $h_{z}^{SOMF}$ denote the sum of one-electron and mean-field two-electron components.19

$$h_{x}^{SOMF} = -h_{y}^{SOMF}, \tag{16}$$

then Eq. (13) can be written in terms of triplet excitation operators as2

$$H_{SOMF}^{SO} = \frac{1}{2} \sum_{pq} \left[ T_{pq}^{1 SO} + \sqrt{2} h_{L}^{SOMF} T_{pq}^{2 SO} + h_{z}^{SOMF} T_{pq}^{3 SO} \right], \tag{17}$$

$$T_{pq}^{1 SO} = a_p^\dagger a_q, \tag{18}$$

$$T_{pq}^{2 SO} = \frac{1}{\sqrt{2}} (a_p^\dagger a_q - a_q^\dagger a_p), \tag{19}$$

$$T_{pq}^{3 SO} = -a_p^\dagger a_q. \tag{20}$$

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In the case of restricted orbital spaces, condition (16) is satisfied by the one-electron terms, but for the two-electron mean-field part, it is ensured only for reference density matrices \( \rho \) with equal \( \alpha \) and \( \beta \) occupancies. The use of different spin-projected \( \rho_n \) densities in Eq. (8) results in \( \tilde{h}_{pq}^\text{SOMF} = -\tilde{h}_{pq}^\text{SOMF} \), introducing unphysical contributions to the couplings. Only the densities from spin-pure states with the same number of \( \alpha \) and \( \beta \) electrons \((M = 0)\) guarantee the proper symmetry of the operator.

1. The Wigner–Eckart theorem in the space of tensor operators

The evaluation of Eq. (17) can be implemented by the application of the Wigner–Eckart theorem to the \( T_{pq}^{\text{LM}''} \) matrices

\[
\langle IS | T_{pq}^{\text{LM}''} | I'S'M' \rangle = \langle S' M' ; 1M'' | SM \rangle \langle IS' T^L || I'S' \rangle,
\]

where \( I, S, M \) indices indicate the \( I \)th electronic state with spin \( S \) and spin projection \( M \), \((S'M'; 1M''|SM)\) is a Clebsh–Gordan coefficient, and \((IS|T^L || I'S'\rangle\) is a spinless triplet transition density matrix, which we denote by \( \upsilon \), following the nomenclature from Ref. 19,

\[
\upsilon \equiv \langle IS|T^L || I'S' \rangle = \langle IS|T_{pq}^{\text{LM}''} | I'S'M' \rangle / \langle SM | S'M' ; 1M'' \rangle.
\]

We construct \( \upsilon \) following the prescription given by Pokhilo et al., through the spin-conserving \( \alpha \alpha \) and \( \beta \beta \) parts of the 1TDM \((\gamma)\) between the states with the same spin projection,

\[
\upsilon_{pq} = \frac{1}{\sqrt{2}} (\upsilon_{pq} - \upsilon_{qp}) / \langle SM | S'M' ; 10 \rangle,
\]

\[
\upsilon_{pq} = \langle IS|a_p a_q | I'S'M' \rangle.
\]

The SOC between the two (spin-pure) electronic states is obtained as the contraction of the spinless \( \upsilon \) matrix with the appropriate one- and two-electron mean-field spin–orbit terms scaled by the associated Clebsh–Gordan coefficients,

\[
\langle IS | H^\text{SOMF} | I'S'M' \rangle = \frac{1}{2} \sum_p \left( \langle S'M' ; 1 - 1 | SM \rangle \tilde{h}_{pq}^\text{SOMF} + \langle S'M' ; 10 | SM \rangle \sqrt{2} h_{pq}^\text{SOMF} \right) \upsilon_{pq}.
\]

Importantly, the spinless \( \upsilon \) matrix can be computed between two specific states from the interacting spin multiplets, \(|SM\rangle\) and \(|S'M'\rangle\), and then used to obtain the entire SOC matrix for all pairs of the \(-S \leq M \leq S\) and \(-S' \leq M' \leq S'\) states. The simultaneous calculation of \( N \) electronic states is normally performed for the same spin projection \((M' = M)\) of states, as used in Eq. (23). For systems with an even number of electrons, the \( M = 0 \) solutions are preferred, since they afford the computation of \( S \geq 0 \) states, i.e., spin singlets, triplets, and quintets. However, the Clebsh–Gordan coefficients \((S'M'; 10 | SM)\) vanish for \( S' = S \) with \( M = 0 \), precluding the computation of SOCs between same-spin states, e.g., triplet–triplet or quintet–quintet. In these cases, a different spin projection needs to be used.74

2. Spin–orbit coupling constant

The evaluation of key properties related to spin-forbidden processes, e.g., ISC rates, oscillator strengths, or magnetic anisotropies, require the calculation of SOCs for all multiplet components. While different Cartesian contributions and multiplet components depend on spatial orientation, the SOC constant \((\text{SOCC})\) is rotationally invariant. In molecules, this constant can be obtained by taking the sum over all spin projections as follows:

\[
|\text{SOCC}|^2 = \sum_{M,M'} \|\langle IS | H^\text{SOMF} | S'M' \rangle \|^2.
\]

For atoms, one needs to sum over orbital angular momentum \((M_L)\) and spin \((M)\) projections,

\[
|\text{SOCC}|^2 = \sum_{M_L,M_L'} \sum_{M,M'} \|\langle L M_L | H^\text{SOMF} | L'M_L' S'M' \rangle \|^2.
\]

In atoms, the relationship between coupling constants and energy splittings can be obtained through the Landé interval rule,77

\[
E_J - E_{J-1} = \lambda J,
\]

where \( \lambda \) is a constant proportional to the one-electron spin–orbit coupling constant \( \zeta \) \((\lambda = \pm \sqrt{2} \zeta)\).75 From the invariance of the (Frobenius) norm of the spin–orbit matrix with respect to unitary transformations and setting the non-relativistic energy to zero, i.e., \( \sum_j (2J + 1)E_J = 0 \), \(|\text{SOCC}|^2\) in Eq. (27) can be expressed in terms of relative energies of \( J \) states \((E_J)\) as

\[
|\text{SOCC}|^2 = \sum_{J} (2J + 1)E_J^2.
\]

Combining Eqs. (28) and (29) enables comparison between the calculated SOCC and the experimental level splittings in atoms. For the triplet \((^3P)\) and doublet \((^1P)\) atoms studied in Sec. IV B,

\[
|\text{SOCC}|^2 = 3\zeta^2.
\]

For easy comparisons with previous studies,71,29 the values for C, O, S, Si, F, and Cl presented in Table II correspond to \( \zeta/2 \).

III. COMPUTATIONAL DETAILS

We implemented the computation of SOCs within the RASCI framework in a development version of the Q-Chem electronic structure package,7 using general libraries developed for SOC calculations within EOM-CC.7 The required integrals are evaluated using the King–Furlani algorithm,7 as implemented by Epifanovsky et al.7 Spin–orbit NTOs are computed and analyzed using the libwfa library.7 RASCI calculations were carried out with RAS1...
and RAS3 subspaces including all occupied and virtual orbitals, respectively. Unless otherwise indicated, the core electrons were kept frozen.

Details about molecular geometries are given in Sec. IV and in the supplementary material. SOC calculations were carried out with Dunning’s correlation-consistent basis sets: cc-pCVXZ (X = D, T, Q, 5) and aug-cc-pVXZ (X = D, T, Q), and the polarized core–valence bases: cc-pCVXZ (X = D, T, Q, 5).

We note that, depending on molecular orientation, symmetry labels corresponding to the same orbital (or vibrational mode) may differ. Q-Chem’s standard molecular orientation is different from that of Mulliken. For example, Q-Chem places the water molecule in the xz-plane instead of yz. Consequently, for C2v symmetry, b1 and b2 labels are flipped. More details can be found at http://openshell.usc.edu/resources/howto/symmetry. All reported symmetry labels follow the Q-Chem convention, which needs to be kept in mind when reading Secs. III B and IV E.

IV. RESULTS

A. Doublet radicals

We begin by considering a simple example of doublet radicals OH, SH, and SeH with a doubly degenerate 2Π ground state derived by distributing three electrons in the πg and πu orbitals, as shown in Fig. 2. Spin–orbit interaction between the two degenerate doublet states lifts the degeneracy and splits the interacting states, yielding the energy gap twice the magnitude of the interstate SOC.

We computed SOCs using structures from Ref. 88 (R(OH) = 0.9697 Å, R(SH) = 1.3409 Å, and R(SeH) = 1.5811 Å). To preserve orbital and state degeneracy, we describe these systems by the RAS-IP variant using the closed-shell Hartree–Fock reference configuration with an additional electron: [core] (σg)² (σu)² (πg)² (πu)². We carried out calculations including a variable treatment of electron correlation, by varying the size of the RAS2 orbital space. To investigate the basis-set dependence of the results, we considered the cc-pVXZ and cc-pCVXZ series of bases (with X = D, T, Q, and 5).

The computed SO splittings are shown in Table I, along with the corresponding experimental values. In agreement with the previous study using multi-reference coupled-cluster method,88 we observe that the double-zeta results are far from the basis-set limit. The computed SO splittings for OH obtained with cc-pVXZ and cc-pCVXZ (X = T, Q, and 5) agree well with the experimental value, with errors less than 2%. The splittings in SH and SeH, computed with the full correlation of the highest ns and np electrons (n = 3 and n = 4 for SH and SeH), i.e., [7e, 4o], show no differences between the cc-pVXZ and cc-pCVXZ values, but the errors relative to the experiment are larger (8%–10%). Correlation of the internal electrons affects the magnitude of SOCs in SH and SeH. Inclusion of the (n = 1) electrons, i.e., [15e, 8o] in SH and [25e, 13o] in SeH, increases the magnitude of the splitting and reduces the error relative to the experiment. The improvement is more significant when using a polarized core–valence family of bases (cc-pCVXZ) because of the better description of the internal electrons. Correlating 2s2p electrons in SeH ([33e, 17o]) further improves the results, with errors of ≤1% for all bases in the cc-pCVXZ series.

We note that the SOCs are rather sensitive to the treatment of electron correlation and that using unbalanced active spaces deteriorates the results. Increasing the RAS2 space (or the active space in CASSCF) does not necessarily improve the accuracy, unless electron correlation effects are properly handled, as shown by the results presented in Figs. S1–S5, where partial addition of atomic shells increases the errors with respect to the experimental values. Finally, we note that in all three molecules, full correlation of the 1s electrons has a minor effect on the computed SOCs.

The two-electron contribution to the SOC (and, consequently, to the splittings) is much smaller than the one-electron part and has an opposite sign due to the charge signs of interacting particles (Fig. 3). The relative weight of the two-electron part in SeH is only 10%, but it is larger in lighter systems, i.e., 19% in SH and 35% in OH, illustrating, once again, the importance of two-electron SOC contributions in typical organic molecules.

B. Spin–orbit splittings in atoms

Table II shows the computed coupling constants for first- (carbon, oxygen, and fluorine) and second-row (silicon, sulfur, and chlorine) atoms. For a balanced description of the 3P multiplet, we used RAS-nIP with a high-spin quartet anion (n = 1) reference for carbon and silicon atoms, and a singlet anion (n = 2) reference for oxygen and sulfur. To describe the 3P states of chlorine and atoms, we used a singlet anion reference state (with fully occupied valence shell).

Because triplet–triplet SOCs cannot be evaluated by the Wigner–Eckart theorem from the M = 0 component of the triplet states, we compute SOCs from the three high-spin (M = 1) 3P RAS-nIP solutions. Comparison of computed results with experimental splittings must be done with caution, since the spin–spin interaction can contribute to the energy splittings, especially for light atoms. The results are shown in Table II, together with pure SOC values derived from the experimental J = 0, 1, 2 state energy splittings by removing spin–spin interactions.

The results show minor differences between the two considered basis sets (cc-pCVTZ and cc-pCVQZ). The RAS-nIP couplings for the C and O atoms are within 6%–8% of the experimental values. The accuracy for the second-row atoms is sensitive to the treatment of electron correlation. The SOCCs for the 3P second-row atoms with the [3s3p] correlated space exhibit larger errors (17% and 14% for Si and S, respectively) than their first-row counterparts. Correlation of the 2p electrons increases the magnitude of the SOCC in silicon...
TABLE I. Spin–orbit splittings (cm$^{-1}$) for OH, SH, and SeH doublet radicals computed with RAS-IP with the cc-pVXZ and cc-pCVXZ (X = D, T, Q, and 5) basis sets. Correlated orbital space (RAS2) indicated in square brackets. The splittings are computed by considering SOCs between the two $^2$Π states.

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<th>OH</th>
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<th>SeH</th>
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<tr>
<td></td>
<td>[7e, 4o]</td>
<td>[7e, 4o]</td>
<td>[15e, 8o]</td>
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$^a$ Functions with g and higher angular momentum omitted.
$^b$ Values from Ref. 89.
$^c$ Values from Ref. 90.

by $\sim 9$ cm$^{-1}$, reducing the errors to 4%–5%. The effect of correlating 2p electrons is also large for sulfur; it increases the couplings by $\sim 35$ cm$^{-1}$ and reduces the error to 3%–4%. Correlating 2s electrons yields an additional 0.5 cm$^{-1}$ increase of the SOCC for Si and S atoms. Correlating 1s electrons has practically no effect on the couplings, so that frozen-core approximation can be safely used in SOCCs calculations (Table S1).

To quantify the effect of higher electronic states on the state energies, we computed SOCCs between the $^3$P states with the low-lying $^1$D and $^1$S singlets in C, O, Si, and S (at the RAS-IP/cc-pCVTZ level). Table III compares the energy distribution of $J = 0, 1, 2$ obtained through the diagonalization of the SOC matrix of the nine-dimensional triplet space (RAS-IP[9s]) and including the couplings to $^1$D and $^1$S (RAS-IP[12s]). These second-order contributions to the energy splittings of the $^3$P states are very small in all four atoms: less than 1%–2% of the RAS-IP[9s] values, in agreement with earlier multireference calculations.

C. Singlet-triplet couplings in diradicals

The SF excitation operator is particularly suitable for describing molecules with the diradical (or polyradical) character. Below, we...
investigate the performance of RAS-SF in the calculation of SOCs between the lowest singlet and triplet states of diatomic (BH and AlH) and triatomic (CH\textsubscript{2}, NH\textsubscript{2}+, SiH\textsubscript{2}, and PH\textsubscript{2}+) diradicals.

### 1. Spin-orbit couplings in BH and AlH

The interest in BH and AlH molecules is motivated by their presence in stellar atmospheres.\textsuperscript{95–98} More recently, small diatomics have been attracting considerable attention in the context of laser-cooling experiments and quantum information science.\textsuperscript{99} BH and AlH have been investigated using different spectroscopies\textsuperscript{96–98} and simulations.\textsuperscript{99} These studies corroborated the diradical nature of their ground states. Hence, RAS-SF is expected to be a good approach for the description of their electronic properties, including the SOCCs for the 1\textsuperscript{1}\Sigma^+ \rightarrow 1\textsuperscript{1}\Pi transition.

The calculations were carried out using the geometries from Ref. 99 (R\textsubscript{BH} = 2.3289 bohrs and R\textsubscript{AlH} = 3.1103 bohrs). In RAS-SF and EOM-SF-CCSD calculations, we used a ROHF (1\textsuperscript{1}\Pi) triplet reference. The RAS\textsubscript{2} space included four electrons in five orbitals, i.e., the 2s2p orbitals of B (3s3p of Al) and 1s of H. Core orbitals were frozen in the RAS-SF and EOM-SF-CCSD calculations. Tables IV and V show the computed singlet–triplet energy gaps and SOCCs. The RAS\textsubscript{SF} SOCCs agree well with the EOM-SF-CCSD values for BH, with a mean-absolute-percentage-error (MAPE) of 1.5% for the one-electron part and 2.7% for mean-field SOCCs. For AlH, the RAS\textsubscript{SF} values are lower than EOM-SF-CCSD ones (both 1e and mean-field SOCCs), with an MAPE of ~3.0%. The effect of the basis set is similar for both methods, giving rise to differences of up to 10% (0.5 cm\textsuperscript{-1}) for BH and 5% (1.1 cm\textsuperscript{-1}) for AlH.

Overall, these results indicate that RAS-SF provides accurate SOCCs for these diatomic diradicals with relatively weak basis-set dependence. This benchmark also suggests that accurate SOCCs can be computed at a low cost in a triple-zeta basis, provided that the frontier orbitals are included in the RAS\textsubscript{2} space.

### 2. Spin-orbit couplings in CH\textsubscript{2}, NH\textsubscript{2}+, SiH\textsubscript{2}, and PH\textsubscript{2}+

Here, we analyze the SOCC between the lowest triplet (\textsuperscript{3}\Pi) and singlet (\textsuperscript{1}\Sigma) states in triatomic XH\textsubscript{2} (XH\textsubscript{2}+) with X = C and Si (N and P) molecules. The calculations were carried out at the equilibrium triplet-state (\textsuperscript{3}\Pi) geometries.\textsuperscript{99–103} Optimized structures are given in Table S2 of the supplementary material. RAS-SF calculations used the ROHF \textsuperscript{3}\Pi reference and various RAS\textsubscript{2} spaces. RAS1 and RAS3 include all occupied and all virtual orbitals, respectively. The results are collected in Table VI.

The computed RAS-SF SOCCs agree well with the EOM-SF-CCSD results. The differences between the RAS-SF and EOM-SF-CCSD singlet–triplet SOCCs are on the order of 1 cm\textsuperscript{-1} (error of 9%–14%) in CH\textsubscript{2} and are slightly larger in NH\textsubscript{2}+ (15%–20% of error). Interestingly, the increase in the RAS\textsubscript{2} size, which increases the amount of correlation included in RAS-SF, considerably reduces the differences between the RAS-SF and EOM-SF-CCSD values in SiH\textsubscript{2} and PH\textsubscript{2}+.

The \textsuperscript{3}\Pi/\textsuperscript{1}\Sigma A\textsubscript{1} couplings increase with the atomic number of the central atom. The ratio between the one- and two-electron parts grows linearly with Z (Fig. 4), with the absolute magnitude of the one-electron contribution being twice larger than the two-electron...
part in CH$_2$ and nearly five times in PH$_2^\text{+}$. This behavior is expected, since one- and two-electron SO terms grow as $Z^4$ and $Z^3$, respectively.\(^\text{15}\) The slope of the linear fit could be used to extrapolate the two-electron contribution for larger $Z$ values in the series. In general, the linear behavior in Fig. 4 justifies the use of effective $Z$ in one-electron approximations to recover two-electron effects in heavy elements in which the one-electron term is dominant.

As noted above, the use of different $\alpha$ and $\beta$ densities ($\rho$) in Eq. (12), such as for open-shell Hartree–Fock reference in RAS-SF, might violate $L/L_\text{c}$ symmetry. The proper symmetry can be recovered by averaging between the two spin densities. Symmetrization of $\alpha/\beta$ Hartree–Fock densities has a minor impact on the computed singlet–triplet couplings in CH$_2$, NH$_2^\text{+}$, SiH$_2$, and PH$_2^\text{+}$, with changes with respect to (non-averaged) SOCs being around $0.01 \text{ cm}^{-1}$ or smaller (Table S3).

**D. Spin-orbit couplings between $\pi\pi^\text{+}$ and $n\pi^\text{+}$ states**

In this section, we investigate the performance of RASCI in describing the SOCs between singlet and triplet states of different character. We choose three organic compounds with $\pi\pi^\text{+}$ and $n\pi^\text{+}$ excited states (Fig. 5): a diketone, biacetyl, or butanedione (BIA), butanone, also known as methyl ethyl ketone (MEK), and one of its isomers (2E)-2-buten-2-ol (BOL). Conjugated ketones and alcohols can exhibit strong SOCs even without the presence of heavy atoms. Carbonyl groups support low-lying $n\pi^\text{+}$ states, which can effectively couple to the $n\pi^\text{+}$ states with different spins, as explained by El-Sayed’s rules.\(^\text{15}\) In particular, BIA shows phosphorescent emission\(^\text{104}\) due to the efficient ISC and radiative decay from the triplet manifold.\(^\text{105}\)

Ground-state geometries of these molecules were optimized with B3LYP/cc-pVDZ and are given in the supplementary material. Vertical excitation energies and the SOCs were computed with the cc-pVTZ basis set for the TDDFT/TDA (Tamm–Dancoff approximation) with the B3LYP functional, EOM-CCSD, and RASCI methods.

The planar structure of the BIA, MEK, and BOL backbone results in a clear separation between $\sigma$- and $\pi$-type orbitals. The highest occupied molecular orbitals (HOMOs) of the ketone and diketone compounds have important contributions of the oxygen ($n$) lone pairs (Fig. 6) and $\pi$-type occupied orbitals are energetically below them. This orbital ordering leads to low-energy $n \rightarrow \pi^\text{+}$ excited states, with $\pi \rightarrow \pi^\text{+}$ states being higher in energy. The $n$-type orbital in BOL is lower in energy than the $\pi$-HOMO, which is mainly localized on the C=C double bond. Consequently, the lowest singlet and triplet excitations in BOL are of $\pi\pi^\text{+}$ character. In all

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**TABLE VI. Singlet-triplet SOCC (cm$^{-1}$) between $^3\text{B}_2$ and $^1\text{A}_1$ states computed with RAS-SF and EOM-SF-CCSD with the cc-pVTZ basis set.** Fully correlated electrons and orbitals (RAS2) are indicated in square brackets.

<table>
<thead>
<tr>
<th>Method</th>
<th>CH$_2$</th>
<th>NH$_2^+$</th>
<th>SiH$_2$</th>
<th>PH$_2^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RAS[2e, 2o]-SF</td>
<td>9.73</td>
<td>15.27</td>
<td>50.28</td>
<td>110.31</td>
</tr>
<tr>
<td>RAS[4e, 3o]-SF</td>
<td>9.87</td>
<td>15.50</td>
<td>51.65</td>
<td>112.82</td>
</tr>
<tr>
<td>RAS[6e, 5o]-SF</td>
<td>9.36</td>
<td>14.51</td>
<td>51.28</td>
<td>109.46</td>
</tr>
<tr>
<td>RAS[6o, 6o]-SF</td>
<td>9.54</td>
<td>14.96</td>
<td>53.55</td>
<td>113.96</td>
</tr>
<tr>
<td>RAS[12e, 7o]-SF</td>
<td>...</td>
<td>...</td>
<td>58.56</td>
<td>119.38</td>
</tr>
<tr>
<td>RAS[14e, 8o]-SF</td>
<td>...</td>
<td>...</td>
<td>58.73</td>
<td>119.66</td>
</tr>
<tr>
<td>EOM-SF-CCSD</td>
<td>10.86</td>
<td>18.26</td>
<td>56.74</td>
<td>119.97</td>
</tr>
</tbody>
</table>

EOM-SF-CCSD values are from Ref. 19.
three molecules, the LUMO (lowest unoccupied molecular orbital) corresponds to a π-orbital (π∗).

Table VII shows vertical excitation energies to the lowest nπ* and ππ* states of BIA, MEK, and BOL computed at the TDDFT/TDA (B3LYP), EOM-CCSD, and RASCI levels. The states of interest can be described as one-electron excitations from the ground state, as indicated by the norms of the respective one-particle transition density matrix (||y||), both for EOM-CCSD and for RASCI. Therefore, we regard EOM-CCSD as the reference method, as it has been shown to deliver accurate results for singly excited states.

We observe that B3LYP energies are systematically red-shifted with respect to EOM-CCSD. On the other hand, the limited account of the dynamic correlation in RASCI results in the overestimation of the transition energies, by two orders of magnitude with respect to the EOM-CCSD energies, and up to ~1 eV.

Due to the limitation of the current Q-Chem implementation, the spin–orbit calculations with TDDFT/TDA (B3LYP) only include one-electron contributions of the Breit–Pauli Hamiltonian. The RASCI and EOM-CCSD calculations include both one-electron and mean-field two-electron couplings. Overall, the couplings between the states of different character (π∗/π) are much larger than the couplings between the states with similar orbital occupations (ππ*/ππ′ and nπ*/nπ′), in accordance with El-Sayed’s rules. Despite the limited account of dynamic correlation, the RASCI SOCCs agree rather well with the EOM-CCSD values (Table VII). The strong nπ*/ππ* couplings in BIA, MEK, and BOL molecules are of the order of several tens of cm−1, with relative errors of RASCI with respect to the EOM-CCSD SOCCs of <8% for BIA and MEK. We observe larger differences for BOL, which can be related to larger differences between the EOM-CCSD and RASCI wave functions.

The BIA molecule has C₂ᵥ symmetry in which L₆ and L₇ belong to the B₂g irreducible representation (irrep), and L₈ is invariant under all the operations of the group (A₂). Therefore, only the triplet states from the A₅ and B₅ irreps can couple to the ground-state singlet (X¹A₁) via the spin–orbit operator. The 3 nπ* and 3 ππ* states are antisymmetric with respect to inversion (A₅ and B₅, respectively); hence, the SOC to the ground state is symmetry-forbidden. On the other hand, the spin–orbit coupling of 3 ππ* (B₅) is strong. These trends are nicely reproduced by all three methods, with one-electron SOCCs around 130 cm−¹ and the mean-field (total) couplings in the 80 cm−¹–90 cm−¹ range. Similarly, non-vanishing couplings between the excited singlets and triplets are restricted to those for which the symmetry product of the two states belongs to the A₅ or B₅ irreps. In other words, only the states with the same parity, gerade (g) or ungerade (u), can interact through the spin–orbit Hamiltonian (this can also be seen from the pseudovector nature of L). Therefore, non-zero couplings are obtained for nπ*/ππ*, n’π*/n’π′, nπ*/ππ*, and n’π*/nπ′ pairs of states, in which the coupling strength is strongly dependent on the orbital occupations. Singlet–triplet couplings of the nπ*/ππ* type are rather strong, whereas all the others are much weaker (<1 cm−¹).

As described by Pokhilkov and Krylov, the strength of the computed SOCs can be rationalized in terms of the NTO pairs of the

<table>
<thead>
<tr>
<th>State</th>
<th>B3LYP</th>
<th>EOM-CCSD</th>
<th>RASCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIA</td>
<td>ΔE</td>
<td>ΔE</td>
<td></td>
</tr>
<tr>
<td>3nπ*</td>
<td>2.15</td>
<td>2.68</td>
<td>0.939</td>
</tr>
<tr>
<td>3ππ*</td>
<td>3.90</td>
<td>4.35</td>
<td>0.941</td>
</tr>
<tr>
<td>3ππ*</td>
<td>5.00</td>
<td>5.36</td>
<td>0.958</td>
</tr>
<tr>
<td>1nπ*</td>
<td>2.71</td>
<td>3.11</td>
<td>0.932</td>
</tr>
<tr>
<td>1n’π*</td>
<td>4.50</td>
<td>4.78</td>
<td>0.932</td>
</tr>
<tr>
<td>1ππ*</td>
<td>7.76</td>
<td>8.37</td>
<td>0.927</td>
</tr>
</tbody>
</table>

| MEK   | ΔE    | ΔE       | ||y||  |
|-------|-------|----------|-------|
| 3nπ*  | 3.87  | 4.18     | 0.944  | 4.83  | 0.982  |
| 3ππ*  | 5.97  | 6.21     | 0.963  | 6.90  | 0.994  |
| 1nπ*  | 4.47  | 4.58     | 0.937  | 5.34  | 0.976  |
| 1ππ*  | 8.14  | 9.50     | 0.935  | 10.50 | 0.971  |

| BOL   | ΔE    | ΔE       | ||y||  |
|-------|-------|----------|-------|
| 3ππ*  | 3.97  | 4.14     | 0.962  | 4.20  | 0.997  |
| 3ππ*  | 8.28  | 9.14     | 0.938  | 10.30 | 0.976  |
| 1nπ*  | 6.70  | 7.06     | 0.944  | 8.07  | 0.980  |
| 1ππ*  | 8.70  | 9.45     | 0.934  | 10.72 | 0.971  |

*Norm of the one-particle transition density matrix averaged between A → B and B → A: ||y|| = ||yAB|| = ||yBA||.
The results for BIA and MEK are similar to those for BIA, but with only one low-lying singlet and one triplet of the \( n \rightarrow \pi^* \) character. It is worth noting that while the RASCI and EOM-CCSD couplings are in very good quantitative agreement, the one-electron \( n n^*/\pi^* \) and \( \pi^*/\pi^* \) SOCCs obtained with B3LYP are considerably smaller, especially for the \( n n^*/\pi^* \) pairs. This can be related to the mixing of electronic configurations in the B3LYP states, in contrast to the EOM-CCSD and RASCI states, which exhibit nearly pure \( n n^* \) or \( \pi^* \) characters. The largest differences between the RASCI and EOM-CCSD SOCCs are obtained in BOL. RASCI couplings (1e and SOMF) follow the same trends as the EOM-CCSD values, but they are systematically smaller, while the (one-electron) SOCs computed with B3LYP are close to EOM-CCSD. These results suggest that, in this case, the lack of dynamic correlation in RASCI negatively affects the accuracy of the computed SOCs. The leading spinless triplet NTOs and their weights between singlet and triplet states of MEK and BOL can be found in Figs. S5 and S6, respectively.

### E. Molecular torsion in tetramethyleneethane

Tetramethyleneethane (TME), which is one of the simplest non-Kekulé disjoint diradicals, has attracted interest as a potential organic magnet\(^{112,113}\) as a building block for electrically conductive polymers\(^{112,113}\) and has also been used to generate organoruthenium complexes with unique dianionic character.\(^{114}\) Highly accurate electronic structure calculations\(^{115–117}\) established that the ground-state singlet and the lowest triplet in TME are very close in energy, with a singlet–triplet gap that varies with the molecular conformation due to the subtle changes in the interaction between the two radical electrons. These studies concluded that reliable calculations of singlet and triplet electronic states of TME require the inclusion of electron correlations between all six \( p \)-electrons.

Here, we evaluate the profile of the SOCC between the nearly degenerate singlet and triplet states of TME along the torsional rotation about the central C–C bond with dihedral angles from 0 to 90°. We use geometries from Ref. 115, optimized at the CASSCF(6,6)/cc-pVTZ level for the ground-state singlet and the lowest triplet for different dihedral angles (supplementary material).
RAS-SF calculations were carried out with the lowest ROHF septet as the reference, with six electrons in the six π-orbitals in RAS2 [Fig. 8(a)], and with the cc-pVTZ basis set.

At the planar and fully twisted structures, TME has $D_{2h}$ and $D_{2d}$ symmetry, respectively. Only the three twofold symmetry rotations are preserved for any other torsional angle ($D_{2d}$ symmetry). For the sake of clarity, unless otherwise indicated, below we use the $D_{2h}$ labels ($1A$ and $3B_1$) to mark the two states of interest along the molecular torsion. Symmetry axes have been chosen by considering the $D_{2h}$ structure on the $xz$-plane and the central bond aligned with the $z$ axis.

At the planar geometry ($D_{2h}$ symmetry), the two states have $1A_g$ and $3B_{1u}$ symmetries, while $L_z$, $L_y$, and $L_x$ operators belong to the $B_{1g}$, $B_{2g}$, and $B_{3g}$ irreps. At the $D_{2d}$ symmetry, the singlet and triplet have $1A_1$ and $3B_2$ symmetries, while the angular momentum operators belong to the $A_2$ and $E$ irreps. Therefore, symmetry selection rules forbid singlet–triplet spin–orbit interaction at the planar and orthogonal structures of TME, resulting in zero SOCCs.

These symmetry restrictions for the singlet–triplet ($1A/3B_1$) SOCs are lifted at the reduced $D_2$ symmetry at intermediate dihedral angles ($L_z$, $L_y$, and $L_x \in B_1$, $B_2$, and $B_3$). Figure 8(b) shows that the $1A/3B_1$ SOCC increases as soon as the molecule becomes bent.

The computed SOCCs reach a maximum at $\sim 20^\circ$ of $\sim 0.35$ cm$^{-1}$ for the one-electron spin–orbit contribution and $\sim 0.20$ cm$^{-1}$ for the total SOCCs computed for the singlet and triplet geometries. Beyond this point, the SOCCs drop to nearly zero at $\sim 45^\circ$. At this structure, the $7a$ and $6b_1$ orbitals are nearly degenerate and the $1A/3B_1$ energy gap reaches the smallest value along the torsion coordinate. At $45^\circ$ twist, the triplet state is dominated by a single electronic configuration: $(7a)^{(6b_1)}$. In contrast, the singlet state, $1A$, is multiconfigurational, with two determinants with nearly equal central contribution, as indicated by the approximately equal RAS-SF weights of the $(7a)^2(6b_1)$ and $(7a)^3(6b_1)^2$ configurations (44% and 40%, respectively). Contributions to the $1A/3B_1$ SOCC due to the interaction of $(7a)^2(6b_1)$ and $(7a)^3(6b_1)$ with $(7a)^3(6b_1)$ cancel each other, similar to the SOCC couplings observed in C$_2$H$_4$O intermediate. Thus, the similar weight of the two configurations in $1A$ at $45^\circ$ results in nearly zero SOCCs. The magnitude of the cancellation effect depends on the relative weights of the two most dominant NTO pairs, which exhibit similar values at $45^\circ$ [$\omega_1$ and $\omega_2$ in Fig. 8(c)]. The profile of the SOCCs in the $45^\circ$–$90^\circ$ torsion range is rather similar to the one in the $0^\circ$–$45^\circ$ region, but with lower SOCC maxima of $\sim 0.10$ cm$^{-1}$ ($\sim 0.22$ cm$^{-1}$) for the total mean-field (or one-electron) SOCCs.

**FIG. 8.** (a) π orbitals of TME (isovalue of 0.05) obtained from the ROHF septet reference on the $3B_1$ optimized geometry with a $0^\circ$ torsion angle. (b) One-electron and mean-field SOCCs along torsion angles calculated for the two optimized geometries. (c) Dominant NTO pairs of the spinless transition matrix of TME involved in the $3B_1$ ↔ $1A$ transitions at different torsion angles, with isovalue of 0.05. The two largest singular values ($\omega_1$ and $\omega_2$) between the NTO pairs at different torsion angles are presented in the table on the right.
Figure 8(c) shows the NTOs responsible for the $^1{A}_1 \leftrightarrow ^3{B}_1$ SOCs at different torsion angles, indicating that the $^1{A}/^3{B}_1$ couplings arise mainly due to the $7a \rightarrow 6b_1$ orbital transition.

V. CONCLUSIONS

The present contribution expands the capabilities of the RASCI family of methods to the computation of SOCs using the Breit–Pauli Hamiltonian. SOCs are evaluated within the spin–orbit mean-field approximation, which considerably reduces the computational cost while introducing negligible errors relative to the full two-electron treatment. Our implementation is based on the application of the Wigner–Eckart theorem to triplet excitation operators and the generation of a spinless triplet transition density matrix to obtain the entire SOC matrix for all spin projections.

We tested the performance of RASCI SOCs in a variety of atomic and molecular systems. The results demonstrate that the RASCI method captures the key details of the electronic structure of correlated states, enabling accurate computations of SOCs within the limitations of the Breit–Pauli approximation. The level of correlation treatment in the RASCI ansatz affects the accuracy of the results. In particular, the correlation of inner electrons ($n - 1$ level) improves the computed values. On the other hand, core electrons can be safely disregarded in the computation of SOCs of valence states by using the frozen core approximation. Double-zeta basis sets are not sufficient, and triple-zeta or larger basis sets should be used for accurate results. The polarized core–valence family of bases (cc-pCVXZ) delivers a faster convergence with the size of the valence orbital space ($X = D, T, Q, 5, \ldots$) than the cc-pVXZ family.

The reported methodological developments broaden the scope of applications of the RASCI family of methods to include studies of spin-forbidden processes. Incorporating the SOC analysis into RASF methods and utilizing the detailed wave function analysis of the spin–orbit perturbed RASCI states can provide deeper insight into the complicated strongly correlated systems.

SUPPLEMENTARY MATERIAL

See the supplementary material for the study of the basis-set dependence of SOCs in doublet radicals and atoms, optimized geometries for triatomic diradicals, spinless NTOs and optimized geometries of BIA, MEK, and BOL molecules, and SOCCs and optimized geometries of TME.

ACKNOWLEDGMENTS

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We thank the anonymous reviewer for pointing out a mistake in the prefactor of the two-electron part of SOMF.

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

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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70 A number of papers erroneously show a factor \( \frac{1}{2} \) in front of the two-electron SOMF part. The two-particle part of the Breit–Pauli spin–orbit Hamiltonian does not have a \( \frac{1}{2} \) prefactor. Consequently, it should not be present in the second-quantized expression. In our implementation, we use spin-integrated expressions from Appendix B of Ref. 71, which are correct and do not contain this prefactor.


