Quantitative El-Sayed Rules for Many-Body Wave Functions from Spinless Transition Density Matrices

Pavel Pokhilko* and Anna I. Krylov*

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482, United States

Supporting Information

ABSTRACT: One-particle transition density matrices and natural transition orbitals enable quantitative description of electronic transitions and interstate properties involving correlated many-body wave functions within the molecular orbital framework. Here we extend the formalism to the analysis of tensor properties, such as spin–orbit couplings (SOCs), which involve states of different spin projection. By using spinless density matrices and Wigner–Eckart’s theorem, the approach allows one to treat the transitions between states with arbitrary spin projections in a uniform way. In addition to a pictorial representation of the transition, the analysis also yields quantitative contributions of hole–particle pairs into the overall many-body matrix elements. In particular, it helps to rationalize the magnitude of computed SOCs in terms of El-Sayed’s rules. The capabilities of the new tool are illustrated by the analysis of the equation-of-motion coupled-cluster calculations of two transition metal complexes.

Molecular orbital theory is of central importance in chemistry. Chemists use molecular orbital concepts to explain molecular structure and properties.1 Orbitals are used to rationalize systematic trends in series of compounds and chemical reactivity in the ground and electronically excited states.2,3 Molecular orbitals are also commonly invoked to describe electronic transitions and interstate properties, such as transition dipole moments and nonadiabatic and spin–orbit couplings (SOCs).4–7

Molecular orbitals are often associated with (pseudo)-noninteracting electrons. In the Hartree–Fock mean-field theory, an N-electron wave function is given by an antisymmetrized product on N molecular orbitals, and the differences between two electronic states (e.g., neutral and cation or ground and excited) can be described in terms of individual orbitals. Consequently, state and interstate properties can be analyzed in terms of matrix elements between the orbitals.

Yet, a quantitative description of an N-electron system entails multielectronvalent ansätze. Even the simplest excited-state theory, configuration interaction singles (CIS), goes beyond the single-determinant representation. One can analyze such wave functions in terms of molecular orbitals by focusing on the dominant configurations; however, such an approach is imprecise and quickly becomes impractical. Moreover, the choice of individual orbitals (and, consequently, the values of the individual amplitudes in the multiconfigurational wave functions) is not unique. For example, energies and all physical observables of the Hartree–Fock and CIS wave functions are invariant with respect to any unitary orbital transformation within the occupied and virtual orbital spaces. This is also the case for coupled-cluster (CC) and equation-of-motion coupled-cluster (EOM-CC) theories. Despite these unsettling observations, molecular orbital theory and rigorous description of electron correlation are perfectly compatible with each other. Molecular orbital theory can be extended to correlated many-electron wave functions via generalized one-electron quantities such as Dyson8 and natural transition orbitals (NTOs).9–20

In this paper, we focus on one-electron transition properties. The key quantity, which allows one to characterize the differences between two states (e.g., Ψf and Ψi) in terms of one-electron excitations and to compute interstate properties, is a one-particle transition density matrix:

where \( a_p^+ \) and \( a_q^- \) are creation and annihilation operators associated with orbitals \( p \) and \( q \). The interstate matrix element for a one-electron operator \( A \) is then:

where the sum runs over all orbitals. While the value of \( \langle \Psi^f | A | \Psi^i \rangle \) evaluated using the above expression is orbital-invariant, the values of the individual integrals \( A_{pq} = \langle \phi_p | A \phi_q \rangle \) and the respective elements of \( \gamma \) depend on the choice of orbitals. The most compact representation of \( \gamma \) and, consequently, of eq 2 is achieved by using diagonal

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representation of the transition density matrix via singular value decomposition (SVD):\(^{11,14}\)

\[
y^{\text{FI}} = U Z V^T
\]

where \(\Sigma\) is a diagonal matrix with non-negative numbers (\(\sigma_k\)) on the diagonal and the \(k\)th columns of \(U\) and \(V\) are the pair of right and left singular vectors corresponding to the \(k\)th singular value \(\sigma_k\). In this way, one can represent the transition density between states \(F\) and \(I\) as a (usually small) number of particle–hole pairs:

\[
\xi^{\text{FI}}(x_p \rho_h) = \sum_k \sigma_k \phi^p_k(x_p) \phi^h_k(x_h)
\]

where \(x\) denotes spatial and spin coordinates of an electron (\(x \equiv r, s\)) and \(\phi^p_k\) and \(\phi^h_k\), which are called particle and hole NTOs, are defined by the singular vectors from eq 3:

\[
\phi^p_k = \sum_q U_{pq} \phi^p_q
\]

\[
\phi^h_k = \sum_q V_{pq} \phi^p_q
\]

\[
\xi^{\text{FI}}(x_p \rho_h), \text{ which sometimes is called an exciton wave function,}^{11,12,23} \text{ describes the difference between the two many-electron states, } \Psi^* \text{ and } \Psi^0 \text{ in terms of one-electron (i.e., hole–pair) excitations between the orbitals } \phi^p_k \text{ and } \phi^h_k. \text{ In this way, NTOs provide a rigorous extension of molecular orbital theory to general correlated wave functions. In the basis of NTOs, eq 2 becomes}

\[
\langle \Psi^* | A | \Psi^0 \rangle = \sum_k \langle \phi^p_k | A | \phi^h_k \rangle \sigma_k
\]

Thus, an interstate property can be represented as a sum of the matrix elements between the hole and particle orbitals, and the weight of each term is given by the respective singular value.\(^{23}\) Often, only one or two singular values are significant in the expansion, while the contribution of the remaining singular values is small.

NTOs are now routinely used to analyze various aspects of bound\(^{16,19,20,24}\) and metastable\(^{18}\) excited states, including nonlinear optical phenomena.\(^{17}\) In this contribution, we extend the formalism to the analysis of tensor properties, such as SOCs, which involve states of different spin projection.

Qualitative molecular orbital analysis has been used to rationalize the rates of the spin-forbidden transitions since the early days of quantum chemistry.\(^{5,25}\) As succinctly explained by El-Sayed,\(^{5,25}\) the angular momentum operator of the SOC term induces an orbital torque, which means that large values of the SOC matrix element can be attained only when the transitions involve the change of orbital orientation.\(^{26}\) In the context of organic photochemistry, this implies that SOCs between the states that have the same orbital character (e.g., \(\pi\pi^*\) triplet and singlet) are small and SOCs and between the states that have different orbital character (e.g., \(\pi\pi^*\) triplet and \(n\pi^*\) singlet) are large. Known as El-Sayed’s rule, this guideline is often invoked to explain many aspects of spin-forbidden processes, such as diradical reactivity,\(^{27\text{--}29}\) reaction of triplet oxygen with unsaturated compounds,\(^{30\text{--}33}\) and phosphorescent properties of photovoltaic materials.\(^{34\text{--}36}\) Molecular orbital analysis is also invoked to explain the breakdown of El-Sayed’s rules due to vibronic effects.\(^{37}\) For example, since the molecular vibrations affect the shape of molecular orbitals, they can result in mixing of \(n\pi^*\) and \(\pi\pi^*\) states, strongly modulating the magnitude of SOC and the rates of intersystem crossing.

Despite a widespread use of NTOs and natural orbitals to describe characters of the states involved in the spin-forbidden transitions (as in, for example, refs 30, 31, and 38), there have been only a couple of studies reporting the NTOs between spin-coupled states\(^{44}\) or between particular components of a multiplet.\(^{27}\) In this contribution, we introduce a new type of NTOs suitable for the analysis of SOCs. The definition is based on the spinless density matrices and Wigner–Eckart’s theorem, which are used for the calculation of SOCs for the entire multiplet from just one transition.\(^{39,40}\) This approach allows one to treat the transitions between states with arbitrary spin projections in a uniform way and to quantitatively describe the contributions of specific orbital pairs into the overall SOC. We use this tool to rationalize the magnitude of the SOCs computed using EOM-CC wave functions in terms of El-Sayed’s rules.\(^{45}\)

To introduce the key concept, NTOs of the spinless transition density matrix, we first briefly outline the formalism for SOC calculations\(^{46}\) using Wigner–Eckart’s theorem with the Breit–Pauli Hamiltonian and EOM-CC wave functions. It is convenient to describe spin-dependent operators through spin-tensor operators \(\hat{O}^{\alpha, \gamma}\). These operators are defined as a set of \(\hat{O}^{\alpha, \gamma}\), satisfying the following relations:

\[
\hat{S}^\alpha \hat{O}^{\alpha, \gamma} = \sqrt{S(S + 1) - M(M \pm 1)} \hat{O}^{\alpha, \gamma}
\]

where \(S\) and \(M\) label the operator’s spin and spin projection. Spin-independent operators are always singlet operators because they commute with \(\hat{S}_z\) and \(\hat{S}_x\). We can split all one-electron excitation operators into the singlet and triplet substates:\(^{47}\)

\[
\hat{T}_{pq}^{0,0} = \frac{1}{\sqrt{2}}(a^\dag_{pq}a_{q0} + a^\dag_{pq}a_{0q})
\]

\[
\hat{T}_{pq}^{1,1} = -a^\dag_{pq}a_{0q}
\]

\[
\hat{T}_{pq}^{1,0} = \frac{1}{\sqrt{2}}(a^\dag_{pq}a_{q0} - a^\dag_{pq}a_{0q})
\]

\[
\hat{T}_{pq}^{1,-1} = a^\dag_{pq}a_{q0}
\]

\[
\hat{T}_{pq}^{1,1} = a^\dag_{pq}a_{0q}
\]

\[
\hat{T}_{pq}^{0,0}, \hat{T}_{pq}^{1,1}, \hat{T}_{pq}^{1,0}, \text{ and } \hat{T}_{pq}^{1,-1} \text{ form a basis in the space of one-particle excitation operators. Given this partitioning, the transition density matrix } y^{\text{FI}} \text{ can be broken down into the singlet and triplet components. The singlet density matrices have identical } \alpha \alpha \text{ and } \beta \beta \text{ parts, } y^{\alpha, \gamma} = y^{\beta, \gamma} \text{, and } M = 0 \text{ triplet density matrices have the opposite signs of } \alpha \alpha \text{ and } \beta \beta \text{ parts, } y^{\alpha, \gamma} = -y^{\beta, \gamma}. \text{ Because of this property, the singlet and triplet density matrices are orthogonal to each other.}^{44} \text{ To evaluate the transition matrix element, the operators of the singlet type require only the singlet part of the transition density matrix from eq 2, while the triplet operators require only the triplet part. Because different parts of the density matrix give rise to different physical observables, one should analyze the part that is relevant for the investigated property. That is, for rationalizing transition dipole moments or nonadiabatic couplings between spin-coupled states,}^{40} \text{ one should consider the singlet part of } y, \text{ whereas for computing SOC between the nonrelativistic zero-order states one should...
consider the triplet part of $\gamma$. The latter is the key quantity in our analysis.

One-electron and mean-field Breit–Pauli spin–orbit operators have the following form:  

$$
\hat{H}^{SO} = \frac{1}{2} \sum_{pq} h^{SO}_{pq} \hat{\rho}^{pq}_{\mu\nu} + \sum_{pq} h^{SO}_{pq} (\hat{\rho}^{pq}_{\mu\nu} - \hat{\rho}^{pq}_{\nu\mu}) 
+ \sum_{pq} h^{SO}_{pq} \hat{\rho}^{pq}_{\mu\nu}^\dagger + \sqrt{2} \sum_{pq} h^{SO}_{pq} \hat{\rho}^{pq}_{\mu\nu} \hat{\rho}^{pq}_{\nu\mu} 
- \sum_{pq} h^{SO}_{pq} \hat{\rho}^{pq}_{\mu\nu}^\dagger 
$$  

where $L_s$ and $L_e$ parts are spherical components:

$$
\hat{h}_L^{1SO} = h_L^{1SO} + ih_L^{2SO}  \tag{15}
$$

$$
\hat{h}_L^{1SO} = h_L^{1SO} - ih_L^{2SO}  \tag{16}
$$

The spherical components for the spin–orbit mean-field (SOMF) operator are defined in a similar way.  

In practical calculations of SOCs, it is convenient to apply Eckart’s theorem for matrix elements with spin-tensor operators $\hat{S}^2M$:

$$
\langle S'M'|\hat{S}^2M|S'M'\rangle = \langle S'M';SM'S'M'|\hat{S}^2M|S'M'\rangle \tag{17}
$$

where $\langle S'M';SM'S'M'|$ is a Clebsch–Gordan coefficient, $\langle S'\hat{S}^2M'|S'M'\rangle$ is a reduced matrix element, which does not depend on spin projections. Applying Wigner–Eckart’s theorem to the triplet density matrices, we obtain a spinless triplet transition density matrix $u^{1}$:

$$
u^{1}_{pq} = \langle JS'1\hat{T}_{pq}1|\hat{S}'M'\rangle = \langle JS'M'1\hat{T}_{pq}1|\hat{S}'M'1\hat{S}M\rangle \tag{18}
$$

Doing the same for the spin–orbit operator, we obtain the following relations:

$$
\langle JS'1\hat{H}_L1\hat{S}'M'\rangle = -\frac{1}{2} \sum_{pq} h^{SO}_{pq} \hat{\rho}^{pq}_{\mu\nu}^\dagger \tag{19}
$$

$$
\langle JS'1\hat{H}_L1\hat{S}'M'\rangle = \frac{\sqrt{2}}{2} \sum_{pq} h^{SO}_{pq} \hat{\rho}^{pq}_{\mu\nu}^\dagger \tag{20}
$$

$$
\langle JS'1\hat{H}_L1\hat{S}'M'\rangle = \frac{1}{2} \sum_{pq} h^{SO}_{pq} \hat{\rho}^{pq}_{\mu\nu} \tag{21}
$$

As one can see, all relevant matrix elements are computed from $u^{1}$. Thus, to analyze the entire spin–orbit matrix between the two multiplets, we perform SVD of $u^{1}$ and obtain an analog of eq 2. The reduced spin–orbit matrix elements can be then written as

$$
\langle JS'1\hat{H}_L1\hat{S}'M'\rangle = -\frac{1}{2} \sum_{k} \langle \xi^{SO}_{k} | \hat{\rho}^{SO}_{L_sL_s} | \chi^{SO}_{k} \rangle \omega_k \tag{22}
$$

$$
\langle JS'1\hat{H}_L1\hat{S}'M'\rangle = \frac{\sqrt{2}}{2} \sum_{k} \langle \xi^{SO}_{k} | \hat{\rho}^{SO}_{L_sL_s} | \chi^{SO}_{k} \rangle \omega_k \tag{23}
$$

$$
\langle JS'1\hat{H}_L1\hat{S}'M'\rangle = \frac{1}{2} \sum_{k} \langle \xi^{SO}_{k} | \hat{\rho}^{SO}_{L_sL_s} | \chi^{SO}_{k} \rangle \omega_k \tag{24}
$$

where $\xi^{SO}(r)$ and $\omega_k$ are the new spinless NTOs and their respective weights (singular values of $u^{1}$). Because all reduced spin–orbit matrix elements are expressed through the spin–orbit integrals over the spinless NTO pairs and the respective weights $\omega_k$ are the same for all three reduced spin–orbit matrix elements, one can analyze different components of the spin–orbit matrix in a uniform way.

We note that, in contrast to the parent $\gamma$, the norm of $u^{1}$ is not bounded by 1 because of the division by the Clebsch–Gordan coefficient, as per eq 18. Consequently, the magnitude of the respective singular values ($\omega_k$) and their sum can exceed 1. However, the extent of the collectivity of the transition (i.e., the number of significant NTO pairs) can be characterized by the participation ratio computed using the same expression as that for regular NTOs:  

$$
PR_{NTO} = \frac{\left( \sum_k \omega_k^2 \right)}{\sum_k \omega_k^2} \tag{25}
$$

For example, for a transition dominated by a single NTO pair, $PR_{NTO} = 1$, for a transition described by two NTO pairs with equal weights, $PR_{NTO} = 2$, and so on.

Below we illustrate the utility of the spinless NTOs by considering several examples of open-shell species described using EOM-CC wave functions. EOM-CC target electronic states are parametrized using linear excitation (ionization, electron attachment) operators acting on the exponential CC ansatz describing the reference state:

$$
|\Psi_{EOM}\rangle = \hat{R} \hat{T} |\Phi_0\rangle \tag{26}
$$

$$
|\Psi_{EOM}\rangle = |\Phi_0\rangle \hat{L} e^{-\hat{T}} \tag{27}
$$

where $\hat{T}$ is a CC excitation operator and $\hat{R}$ and $\hat{L}$ are the EOM right excitation and left de-excitation operators. In the singles and doubles variant (EOM-CCSD), $\hat{T}$ is truncated after single and double excitations. In the electron excitation (EOM-EE-CCSD) and spin-flip (EOM-SF-CCSD) variants, $\hat{R}$ comprises $1h1p$ (one-hole–one-particle) and $2h2p$ (two-particles–two-holes) operators. In the ionization (EOM-IP-CCSD) and electron-attached (EOM-EA-CCSD) variants, $\hat{R}$ comprises $1h$, $2h1p$ and $1p$, $1h2p$ operators, respectively.

To illustrate the analysis, we consider a tris(pyrrolylmethyl)amine Fe(II) complex (which we hereafter denote as (tpa)Fe), exhibiting a large spin-reversal barrier, and a methylthelyglylamide (EtMeGa) radical, their structures are shown in Figures 1 and 2, respectively. To describe quintet states of (tpa)Fe, we used EOM-EA-MP2/cc-pVDZ from the

Figure 1. Left: Structure of (tpa)Fe ($C_{15}N_{4}H_{15}Fe$). Iron is shown in red, nitrogens in blue, carbons in gray, and hydrogens in white. Right: Frontier MOs and electronic configuration of the $d^5$ hextet reference and relevant target states. The target states are obtained by the attachment of a $\beta$-electron to one of the three MOs marked by the dashed red box: attachment to the two lowest MOs gives rise to degenerate states 1 and 2, and attachment to the next MO gives rise to state 3.
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Figure 2. Left: Structure of the methylethylgalium (EtMeGa) radical (GaC3H7). Gallium is shown in pink, carbons in gray, and hydrogens in white. Right: Electronic configuration of the closed-shell cationic reference and relevant target states. The target states are obtained by electron attachment to the two lowest unoccupied orbitals of the cation marked by the dashed red box.

Figure 3. Spinless triplet NTOs for the transitions between the three lowest quintet states in (tpa)Fe⁺. States 1 and 2 are degenerate. Red, green, and blue axes indicate X, Y, and Z coordinates axes, respectively. The isovalue of 0.050 was used.

Table 1. Spin–Orbit Mean-Field Reduced Matrix Elements of the Considered Systems in the Selected Orientations

<table>
<thead>
<tr>
<th>System</th>
<th>Orientation</th>
<th>Matrix Element</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>(tpa)Fe⁺, 1 → 2</td>
<td>⟨</td>
<td>±</td>
<td>0</td>
</tr>
<tr>
<td>(SiH4)Si</td>
<td>−0.30 + 0.09i</td>
<td>−0.29 + 0.10i</td>
<td></td>
</tr>
<tr>
<td>(SiH4)Si</td>
<td>−209.04</td>
<td>−211.34i</td>
<td></td>
</tr>
<tr>
<td>(SiH4)Si</td>
<td>−0.30 − 0.09i</td>
<td>−0.29 − 0.10i</td>
<td></td>
</tr>
<tr>
<td>(tpa)Fe⁺, 1 → 3</td>
<td>⟨</td>
<td>±</td>
<td>0</td>
</tr>
<tr>
<td>(SiH4)Si</td>
<td>−31.79 + 224.48i</td>
<td>−32.07 + 228.23i</td>
<td></td>
</tr>
<tr>
<td>(SiH4)Si</td>
<td>0.04i</td>
<td>0.07i</td>
<td></td>
</tr>
<tr>
<td>(SiH4)Si</td>
<td>−31.79 − 224.44i</td>
<td>−32.07 − 228.23i</td>
<td></td>
</tr>
<tr>
<td>EtMeGa, 1 → 2</td>
<td>⟨</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>(SiH4)Si</td>
<td>135.87 + 210.65i</td>
<td>132.69 + 205.38i</td>
<td></td>
</tr>
<tr>
<td>(SiH4)Si</td>
<td>−1.68i</td>
<td>−1.80i</td>
<td></td>
</tr>
<tr>
<td>(SiH4)Si</td>
<td>135.87 − 210.65i</td>
<td>132.69 − 205.38i</td>
<td></td>
</tr>
</tbody>
</table>

As per eq 18, the normalization of $u^1$ is different from the normalization of regular one-particle transition densities (γ). Consequently, in contrast to the singular values of γ, the singular values of $u^1$ (ωk) may exceed 1, as it happens in EtMeGa. $u^1$ connects the spin-flip (γff) and spin-preserving triplet ($γ_{\text{EOM}}$) transition density matrices via Clebsch–Gordan coefficients. The numeric consequences of this relationship are analyzed in the SI by using the electronic states of EtMeGa as an example.

Table 1 also illustrates how well the leading NTO pair represents the reduced spin–orbit matrix elements (full EOM-EA values). As one can see, the truncation of the sums from eqs 22–24 by retaining only the first leading term recovers the full value with good accuracy. In other terms, only one spinless NTO pair is needed to describe the physics of these systems and to recover the full SOC matrix with high accuracy in both one-electron and mean-field cases, which is consistent with the respective participation ratios.

We conclude our analysis by discussing the computed NTOs and SOCs in terms of El-Sayed’s rules. Originally introduced on the basis of the selection rules for p-orbitals, El-Sayed’s rule explains why the change in orbital character (e.g., n → n′) is needed for attaining large SOCs. In the context of transition metal photochemistry, following El-Sayed’s reasoning explains why mixing of metal-to-ligand charge-transfer configurations facilitates spin-forbidden transitions on the metal and that large values of SOC can be obtained when the respective singlet and triplet states involve different components of the d-orbital manifold. Here we follow this strategy and generalize El-Sayed’s rules to the case of arbitrary orbitals involved in a localized transition. The generalization is based on the representations of the angular momentum operators in real spherical harmonics. The derivation and the key expressions are given in the SI. This generalization provides selection rules, which can be used to rationalize the magnitude of SOC for a particular transition and to also explain the effect of molecular vibrations on the SOCs. It also explains relative values of different components of the SOC.

Figure 4 shows the leading spinless NTO pair of the type of $p_\text{n} \rightarrow p_\text{p}$, where $p_\text{p}$ is a linear combination of $p_x$ and $p_z$ orbitals in the shown coordinate system. According to the matrix representation of the angular momentum in the basis of p-orbitals, the $(p_\text{n}L_\text{m} | p_\text{p})$ matrix elements are nonzero, which leads to large $\langle \text{SiH4Si} | \text{SiH4Si} \rangle$ and $\langle \text{SiH4Si} | \text{SiH4Si} \rangle$ components of SOC, while $\langle \text{SiH4Si} | \text{SiH4Si} \rangle$ is close to 0.
The generalized El-Sayed’s rules not only predict the transitions with large SOC but also estimate the relative values of SOC for different transitions in the same molecule. For example, the transitions in Figure 3 correspond to the $d_{x^2}$ → $d_{xy}$ and $dy$ → $d_{x^2}$ cases. The case of $d_{x^2}$ → $dx$ is allowed through the $L_x$ operator with a relative magnitude of $X$. The main contribution to the SOC from this transition in this orientation indeed comes from $\langle S|H^0_\alpha|S\rangle$ (Table 1). The $dz$ → $d_{x^2}$ transition is allowed through $L_z$, and $L_x$ with a relative magnitude of $X\sqrt{3}$. The computed spin–orbit matrix elements confirm this expectation: the main contribution to the couplings comes from the imaginary parts of $\langle S|H^0_\alpha|S\rangle$ and $\langle S|H^0_{\alpha\beta}|S\rangle$ and deviation of the shape of the NTOs from ideal d-orbitals, which is especially clear for the $d_{x^2}$-like orbital.

To conclude, we introduced a new type of NTOs, which are suitable for describing spin-forbidden transitions. The new NTOs are obtained by the SVD procedure of the reduced spinless transition density matrix, the quantity determining the SOC values for the entire multiplet by virtue of Wigner–Eckart’s theorem. These spinless NTOs describe the transitions between states with arbitrary spin projections in a uniform way. In addition to pictorial representation of the transition, the analysis also yields quantitative contributions of hole–particle pairs into the overall many-body matrix elements and helps to rationalize the magnitude of computed SOCs in terms of El-Sayed’s rules. By providing a clear orbital picture of the transitions at different geometries, this analysis can also be used to explain vibronic effects on the rate of spin-forbidden transitions. We hope that these tools will be helpful in deriving insight from high-level electronic structure calculations of phenomena facilitated by SOCs.

ASSOCIATED CONTENT

< Supporting Information>

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b02120.

Derivation of generalized El-Sayed’s rules, comparison of one-electron and mean-field values of SOCs, analysis of normalization of the spinless density matrices, and Cartesian coordinates of EtMeGa (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: krylov@usc.edu.

ORCID

Pavel Pokhilko: 0000-0001-5754-9836
Anna I. Krylov: 0000-0001-6788-5016

Notes

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

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REFERENCES

(21) If nonorthogonal orbitals are used, a metric tensor should be introduced in the contraction in eq 2. The equations preserve the same form if contravariant integrals and covariant densities are used, or vice versa. A comprehensive formulation of quantum-chemical methods in nonorthogonal orbital bases is given in ref 54.
If the wave functions are normalized to 1, the Frobenus norm of \( \gamma \) is bounded by 1: 
\[
\| \gamma \|_F^2 = \sum_i \sigma_i^2 \leq 1
\]


Because of the denominator in the Breit–Pauli Hamiltonian, the action of the spin–orbit operator is localized. That is why orbital analysis of SOCs as well as El-Sayed’s rules is framed in terms of atomic orbitals.

