Hamiltonian formalisms of spin-orbit Jahn-Teller and pseudo-Jahn-Teller problems in trigonal and tetragonal symmetries

Kun Wang and Tao Zeng

Department of Chemistry, York University,

Toronto, Ontario M3J1P3, Canada and

Department of Chemistry, Carleton University, Ottawa, Ontario K1S5B6, Canada

Abstract

A formalism for expansions of all bimodal spin-orbit Jahn-Teller and pseudo-Jahn-Teller Hamiltonian operators in trigonal and tetragonal symmetries is presented. With the formalism, we can easily obtain expansion formulas of the Hamiltonian matrix elements in symmetry-adapted vibrational coordinates up to arbitrary order. The formalism is presented as a set of generic matrices and lookup tables, which are convenient to use even without understanding the derivation of the formalism. Three examples are used to demonstrate the correctness, completeness, and conciseness of the formalism. One of the examples is also used to demonstrate how to obtain expansion formulas in more than two vibrational modes by using the bimodal formalism. This work lays a foundation for deriving a unified formalism for spin-orbit and non-spin-orbit (pseudo-)Jahn-Teller Hamiltonians in general axial symmetries.

I. INTRODUCTION

The Jahn-Teller (JT) effect was proposed about 80 years ago.[1] Nonlinear polyatomic systems with a principal axis $\geq$ 3-fold can have orbital degeneracy. Paradoxically, the orbital degeneracy forces the systems to distort to lower symmetries and lose the degeneracy. The distortion arises from the fact that electronic Hamiltonian matrix elements of the degenerate states depend on non-totally-symmetric vibrations.[2–4] Such a vibronic coupling also occurs between non-degenerate states and leads to the pseudo-Jahn-Teller (pJT) distortion of systems in non-degenerate electronic states.[5] JT and pJT interactions are ubiquitous in chemistry and physics, leading to numerous phenomena in spectroscopy, structural chemistry, solid-state physics, and materials science.[6–12] The JT and pJT interactions are important as they provide the only source of spontaneous symmetry breaking in polyatomic systems.[13]

Spin-orbit coupling (SOC) is another type of interaction that is closely related to orbital degeneracy of electronic states.[14–22] Orbital degeneracy implies nonzero orbital angular momentum of electrons, which interacts with electronic spin and gives SOC. There is an intimate interplay between SOC and JT/pJT interactions[23–37] since they are both connected to electronic orbital degeneracy. They in general quench each other (e.g., through the Ham reduction factors[38]).[2–4,39] SOC at high symmetry configuration can split degenerate states and convert JT to pJT interaction. Reversely, JT/pJT distortion to lower symmetry lifts orbital degeneracy, quenches orbital angular momentum, and consequently reduces magnitude of SOC. On the other hand, they may enhance each other if there is a constructive interference between the vibronic couplings of non-SOC and SOC origins.[33] SOC can even induce JT interaction. For instance, the $E \otimes t_2$ interaction in T_d symmetry and the $E \otimes e$ interaction in D_{2d} symmetry are JT-active in first order expansion in vibrational coordinates only when SOC is considered.[40,41] The interplay of the two types of interaction is especially pronounced for systems with heavy elements, whose SOC strength is comparable to electrostatic interaction.[14–16,22,34,42–44] It is necessary to treat SOC and JT/pJT interactions on an equal footing for those systems.

In studying a JT/pJT problem, the Hamiltonian operator of the system is resolved in a set of electronic states that are supposed to interact significantly along nuclear distortion. In a diabatic representation of the states,[45–48] the Hamiltonian matrix elements are smooth, differentiable functions of vibrational coordinates. They are expanded as Taylor series of the vibrational coordinates, taking the high-symmetry, undistorted structure as the origin. In standard JT/pJT model, the expansions are truncated at the second order.[3,4] For a long time, when SOC is included in the Hamiltonian, the SO matrix elements had been assumed to be constants along nuclear distortion and only adopt values obtained at the high-symmetry structure. The first attempt to include linear dependence of SOC on vibrational coordinate was made by Moffitt and Thorson in their study of SO JT effect in octahedral complexes.[49] Half a century later, Poluyanov and Domcke and their coworkers carried out a series of studies on SO JT/pJT interactions in trigonal, tetragonal, and cubic systems using SO Hamiltonian expanded to the first order in vibrational coordinates.[33,40,41,50] They pointed out the relativistic origins of some JT interactions in tetragonal and cubic systems.

In the past 15 years, more and more studies on electrostatic (i.e., non-SO) JT/pJT systems showed the inadequacy of the standard second order model Hamiltonians,[51–59] especially in simulating vibronic spectra. The main source of the inadequacy is the anharmonicity in the potential energy surfaces of the diabatic states, which is often induced by large amplitude motion of nuclei.[54] There is no reason to assume exemption from this inadequacy in SO JT/pJT problems that involve heavy elements. Therefore, high-order expansion formulas of SO JT/pJT Hamiltonian matrix elements in vibrational coordinates are highly desired, as much as the high-order formulas of non-SO JT/pJT Hamiltonians.

The first attempts to derive high-order expansion formulas for SO JT/pJT Hamiltonians were made in 2016 by the Domcke group[60] and the Eisfeld group.[61] Domcke and coworkers derived expansion formulas for a set of p orbitals in the tetrahedral and trigonal environments. They derived the relations between SO and non-SO JT/pJT Hamiltonian matrix elements of the p orbitals. One can then adapt non-SO JT/pJT expansion formulas to express SO JT/pJT expansions. Weike and Eisfeld derived expansion formulas for the $(E + A_1) \otimes (e + a_1)$ and $(E + A_1) \otimes (3e + 3a_1)$ JT/pJT problems in C_{3v} symmetry, with the purpose to study the SO JT/pJT interactions in CH_3I^+.

These pioneering and enlightening works motivate us to perform the present study to derive general expansion formulas for SO JT/pJT Hamiltonians in trigonal and tetragonal symmetries. The two classes of symmetries are chosen because: (1) trigonal symmetries are the lowest symmetries that allow for orbital degeneracy and thus JT effect; (2) tetragonal symmetries are the lowest symmetries that possess all three types of irreducible representations (irreps) of axial symmetries (i.e., symmetries with only one principal symmetry axis),

A-, B-, and E-type; (3) tetragonal symmetries are the lowest symmetries that feature purely SO-induced JT effect. Our objective is to obtain bimodal expansion formulas up to arbitrary order for all SO JT/pJT problems in all 6 trigonal symmetries (C_3, C_{3v}, D_3, C_{3h}, D_{3h}, and D_{3d}) and all 7 (C_4, S_4, C_{4v}, D_{2d}, D_4, C_{4h}, and D_{4h}) tetragonal symmetries. This objective is attained by our efficient derivation, which is based on the idea of "descent in symmetry",[62] the root-branch approach, and the modularized approach. The idea and approaches have been employed in our recent derivations of arbitrarily high order expansion formulas for non-SO JT/pJT problems in trigonal, tetragonal, and cubic symmetries.[63–67] They can be equally employed in deriving SO JT/pJT formulas, and the resultant formulas can be similarly summarized in a set of look-up tables. Each independent Hamiltonian matrix element of a SO JT/pJT problem carries a set of symmetry eigenvalues, which guide us to retrieve the element's expansion formulas in the tables. We focus on bimodal problems because: (1) it is usually adequate to consider up to two vibrational modes; (2) problems involving more than two modes can be approximated as composites of bimodal sub-problems; (3) it is straightforward to extend the bimodal expansions to formulas for more vibrational modes. One example of the extension is given in Section VII C.

II. SETTING, SYMBOLS, AND TERMINOLOGIES

Following the tradition in the JT community, we use upper case Mulliken symbols to label electronic states and lower case symbols to label vibrations. As shown later, only one-electron states (i.e., orbitals) need to be considered in the derivation. We label the two real-valued components of an E state as $|X\rangle$ and $|Y\rangle$, and the two components of an e vibrational mode as e_x and e_y. The component states are so oriented that they transform under $\hat{C}_n$ ($n = 3, 4$) as

$$\hat{C}_n |X\rangle = \cos\frac{2\pi}{n} |X\rangle + \sin\frac{2\pi}{n} |Y\rangle ; \hat{C}_n |Y\rangle = \cos\frac{2\pi}{n} |Y\rangle - \sin\frac{2\pi}{n} |X\rangle , \tag{1}$$

and the component modes transform similarly. The component states are combined to form eigenstates of $\hat{C}_n$,

$$(|+\rangle\, |-\rangle) = (|X\rangle\, |Y\rangle) \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix} ; \hat{C}_3 |\pm\rangle = e^{\mp i \frac{2\pi}{3}} |\pm\rangle ; \hat{C}_4 |\pm\rangle = \mp i |\pm\rangle . \tag{2}$$

In D_3, D_{3h}, D_{3d}, D_4, D_{4h}, and D_{2d} symmetries, $|X\rangle$ and $|Y\rangle$ are further defined so that the former is symmetric with respect to one $\hat{C}_2'$, while the latter is antisymmetric. In C_{nv} symmetry, the component states follow the same transformation but with $\hat{C}_2'$ being replaced by $\hat{\sigma}_v$. The two e component modes transform similarly under $\hat{C}_2'$ and $\hat{\sigma}_v$ in the respective symmetries. Such a setting of the E component states and e component modes is exemplified in Figures S.1 and S.2 in the Supporting Information, for trigonal and tetragonal symmetries, respectively. A consequence of such an orientation setting of the real-valued E component states is

$$\hat{C}_2' \left|\pm\right\rangle = \left|\mp\right\rangle = \left(\left|\pm\right\rangle\right)^* ; \hat{\sigma}_v \left|\pm\right\rangle = \left|\mp\right\rangle = \left(\left|\pm\right\rangle\right)^* . \tag{3}$$

For these states, the actions fo the two symmetry operators give the same results as the time-reversal operator (*vide infra*).

x and y and their polar counterparts ρ and ϕ ($x = \rho\cos\phi$; $y = \rho\sin\phi$) are used to label vibrational coordinates of the e_x and e_y component modes, z for a mode, and w for b mode. SOC and JT interaction between states arising from the same term symbol are called intra-term couplings. They are labelled as $\Gamma \otimes \left(\gamma_{(1)} + \gamma_{(2)}\right)$ and correspond to SO JT interactions. The interactions between states from different term symbols are called inter-term couplings. They are labelled as $(\Gamma_I + \Gamma_{II}) \otimes \left(\gamma_{(1)} + \gamma_{(2)}\right)$ and correspond to SO pJT interactions. As the multi-electronic states reduce to one-electron orbitals in the following derivation, the terminologies of "intra-shell coupling" and "inter-shell coupling" are used instead.

α and β are used to label the two electronic spin functions with spin-up and -down. The z axis for spin quantization is chosen to be the principal C_n axis. This setting leads to the transformation

$$\hat{C}_3 \left|\pm\frac{1}{2}\right\rangle = e^{\mp i\frac{\pi}{3}} \left|\pm\frac{1}{2}\right\rangle ; \hat{C}_4 \left|\pm\frac{1}{2}\right\rangle = e^{\mp i\frac{\pi}{4}} \left|\pm\frac{1}{2}\right\rangle . \tag{4}$$

Here, $\left|\frac{1}{2}\right\rangle$ and $\left|-\frac{1}{2}\right\rangle$ are used represent the α and β spin functions. In D_3, D_{3h}, D_{3d}, D_4, D_{2d}, and D_{4h} (C_{3v} and C_{4v}) symmetries, we need to consider the transformations of the spin functions under the actions of $\hat{C}_2'$ ($\hat{\sigma}_v$). Therefore, we also need to consider spin quantizations along directions perpendicular to the z axis. The most convenient setting is that the C_2' axis in D_3, D_{3h}, D_{3d}, D_4, D_{2d}, and D_{4h} symmetries is chosen to be the x axis, along which the Pauli matrix

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{5}$$

is used to represent the $\hat{s}_x$ component of the spin operator $\hat{\vec{s}}$. "$\hat{C}_2'$" and "$\hat{C}_2^x$" are used interchangeably in the text below. In C_{3v} and C_{4v} symmetries, the x axis is defined to be perpendicular to the principal axis and contained by the σ_v plane. The y axis is obtained by the cross product $\vec{y} = \vec{z} \times \vec{x}$. Such a setting of the spin quantization axes is exemplified in Figure S.3. With this setting, the spin functions transform under $\hat{\sigma}_v$ and $\hat{C}_2'$ as

$$\hat{\sigma}_v (\alpha, \beta) = \hat{I}\hat{C}_2^y (\alpha, \beta) = \hat{C}_2^y (\alpha, \beta) = (\alpha, \beta) \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}; \tag{6}$$

$$\hat{C}_2' (\alpha, \beta) = \hat{C}_2^x (\alpha, \beta) = (\alpha, \beta) \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}. \tag{7}$$

$\hat{I}$ is the inversion operator. The σ_h plane in C_{3h}, D_{3h}, C_{4h}, and D_{4h} symmetries is the xy plane. Under the action of $\hat{\sigma}_h$, the spin functions transform as

$$\hat{\sigma}_h (\alpha, \beta) = \hat{I}\hat{C}_2^z (\alpha, \beta) = \hat{C}_2^z (\alpha, \beta) = (\alpha, \beta) \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}. \tag{8}$$

III. SPIN-ORBIT HAMILTONIAN AND ITS APPROXIMATION AS AN EFFECTIVE ONE-ELECTRON OPERATOR

Under the Breit-Pauli approximation, SOC operator in atomic unit reads

$$\begin{aligned} \hat{H}_{SO} &= \frac{1}{2c^2}\left[\sum_i \sum_A \frac{Z_A}{r_{iA}^3} \hat{\vec{l}}_{iA} \cdot \hat{\vec{s}}_i - \sum_{i \neq j} \frac{1}{r_{ij}^3} \hat{\vec{l}}_{ij} \cdot (\hat{\vec{s}}_i + 2\hat{\vec{s}}_j)\right] \\ &= \sum_i \hat{\vec{z}}_i^{(1)} \cdot \hat{\vec{s}}_i + \sum_{i \neq j} \hat{\vec{z}}_{ij}^{(2)} \cdot \left(\hat{\vec{s}}_i + 2\hat{\vec{s}}_j\right) \\ &= \sum_i \hat{h}_{SO}^{1e}(i) + \sum_{i \neq j} \hat{h}_{SO}^{2e}(i, j), \end{aligned} \tag{9}$$

Symbols in the first row are commonly used in literatures and are not re-introduced here. Definitions of the symbols in the second and third rows become clear when the rows are compared with the first row. $\hat{H}_{SO}$ contains both one- and two-electron components, corresponding to the electronic orbital motions around nuclei and other electrons, i.e., $\vec{l}_{iA}$ and $\vec{l}_{ij}$, respectively. $\hat{H}_{SO}$ under other approximations, e.g., Douglas-Kroll-Hess,[68,69] infinite-order two-component,[70] and relativistic elimination of small components,[71,72] carry the same symmetry properties. Since only these symmetry properties matter in the following derivation, the resultant formalism is applicable regardless of the approximation in obtaining $\hat{H}_{SO}$.

The main body of the two-electron SO interaction can be viewed as the screening of the one-electron SO interaction. Consequently, the matrix element between two multi-electronic states $|\Psi_I\rangle$ and $|\Psi_J\rangle$ can be safely approximated as a summation of integrals of the mean-field one-electron SO operator $\hat{h}^{1e}_{eff}$:[73–77]

$$H^{SO}_{IJ} = \langle\Psi_I|\,\hat{H}_{SO}\,|\Psi_J\rangle \approx \sum_i \sum_j P^{IJ}_{ij}\,\langle\psi_i|\,\hat{h}^{1e}_{eff}\,|\psi_j\rangle = \sum_i \sum_j P^{IJ}_{ij}\,\langle\phi_i|\,\hat{\vec{z}}^{(1)}_{eff}\,|\phi_j\rangle \cdot \langle\sigma_i|\,\hat{\vec{s}}\,|\sigma_j\rangle\,, \tag{10}$$

where i and j loop over all molecular spin orbitals ψ_i, ψ_j, and P^{IJ} stands for the transition density matrix between the two states. The spin orbitals are products of spatial orbitals ϕ_i, ϕ_j and spin functions σ_i, σ_j

Eq. 10 represents an important simplification. Any multi-electronic SO matrix element can be eventually expressed using one-electron SO matrix elements. It is for this reason that the expansion formulas obtained in Refs. 60 and 61, in which the derivations were based on the one-electron Pauli SOC operator and spin orbitals, are also applicable in expanding SO matrix elements of multi-electronic states. The procedure is as follows. Given a pair of diabatic states $|\Psi_I\rangle$ and $|\Psi_J\rangle$ that are built using a common set of diabatic spin orbitals $\{\psi\}$, one first calculates its transition density matrix P^{IJ}. A few pairs of ψ_i and ψ_j that correspond to P^{IJ}_{ij} elements with large magnitude are selected. The expansions of the one-electron elements $\langle\psi_i|\,\hat{h}^{1e}_{eff}\,|\psi_j\rangle$s in vibrational coordinates are then linearly combined with the P^{IJ}_{ij} coefficients to give the expansion of H^{SO}_{IJ}. Clearly, the derivation of H^{SO}_{IJ} expansion formulas has been reduced to deriving expansion formulas for $\langle\psi_i|\,\hat{h}^{1e}_{eff}\,|\psi_j\rangle$s, which are the focus of this work. Henceforth, the term "matrix element" is reserved for $\langle\psi_i|\,\hat{h}^{1e}_{eff}\,|\psi_j\rangle$. The actual forms of $\hat{h}^{1e}_{eff}$ and $\hat{\vec{z}}^{(1)}_{eff}$ are not of importance. We only need to know that they share the same structures and symmetries with the $\hat{h}^{1e}_{SO}$ and $\sum_A \frac{Z_A}{r^3_{iA}}\hat{\vec{l}}_{iA}$ operators in Eq. 9, respectively.

IV. SYMMETRY

Symmetry properties of $\hat{H}_{SO}$ have been thoroughly discussed in Refs. 15 and 78. In short, the operator is invariant with respect to the time-reversal operator and all symmetry operators of a system. Furthermore, the Wigner-Eckart Theorem (WET) allows us to obtain a set of $\langle\Psi_I\,(M_S)|\,\hat{H}_{SO}\,|\Psi_J\,(M'_S)\rangle$s with a constant $\Delta M_S = M_S - M'_S$, from one element of the set. In this set of elements, all bra states only differ in the projection of total spin (i.e., the M_S quantum number), and so do all the ket states. Also, an element is nonzero only for $\Delta M_S = 0, \pm 1$. All these symmetry properties are transferrable to $\hat{h}^{1e}_{eff}$, which is just a one-electron special case of $\hat{H}_{SO}$. In this section, we will discuss how the time-reversal symmetry and WET simplify the structure of the $\langle \psi_i | \hat{h}^{1e}_{eff} | \psi_j \rangle$ matrix.

A. Time-Reversal Symmetry

General aspects of time-reversal symmetry and the time-reversal operator $\hat{\mathcal{T}}$, especially those that are relevant to our derivation, are detailed in Ref. 79. They are recapitulated here:

1. $\hat{\mathcal{T}}$ converts all imaginary unit i in its operand to $-i$, α to β, and β to $-\alpha$;

2. each state $|X\rangle$ has its time-reversal counterpart $|X'\rangle = \hat{\mathcal{T}} |X\rangle$. $|X'\rangle$ may be equal to $|X\rangle$ when it is a state of an even number of electrons. In this situation, we may multiply i to the $|X\rangle$. The resultant $|Y\rangle = i |X\rangle$ satisfies $\hat{\mathcal{T}} |Y\rangle = - |Y\rangle$;

3. for a Hamiltonian operator $\hat{H}$ that is time-reversal symmetric, its matrix elements between states of even numbers of electrons satisfy $\langle X_i | \hat{H} | X_j \rangle = \langle X'_j | \hat{H} | X'_i \rangle$ and $\langle X_i | \hat{H} | X'_j \rangle = \langle X_j | \hat{H} | X'_i \rangle$;

4. its matrix elements between states of odd numbers of electrons satisfy $\langle X_i | \hat{H} | X_j \rangle = \langle X'_j | \hat{H} | X'_i \rangle$ and $\langle X_i | \hat{H} | X'_j \rangle = - \langle X_j | \hat{H} | X'_i \rangle$;

Point 3 determines that a Hamiltonian matrix of a set of time-reversal-adapted states of an even number of electrons adopt the block structure shown in Figure 1(a). The states are ordered so that the first $2k$ states are k pairs of $|X_i\rangle$s and $|X'_i\rangle$s, the k $|X_i\rangle$s first, followed by the k $|X'_i\rangle$s; then n $|Y_i\rangle$s that are invariant under the action of $\hat{\mathcal{T}}$; then m $|Z_i\rangle$s that change their signs under the action of $\hat{\mathcal{T}}$. The whole set of the adapted states can be transformed to all $|Y_i\rangle$-type or all $|Z_i\rangle$-type states. We keep the form of Figure 1(a) to maintain generality.

Point 4 determines that a Hamiltonian matrix of a set of time-reversal-adapted states of an odd number of electrons adopt the block structure in Figure 1(b). For a system with an odd number of electrons, the $|Y_i\rangle$-type and $|Z_i\rangle$-type states do not exist. All states in the set must be paired into the $|X_i\rangle$-type and $|X'_i\rangle$-type states, underlying the Kramer

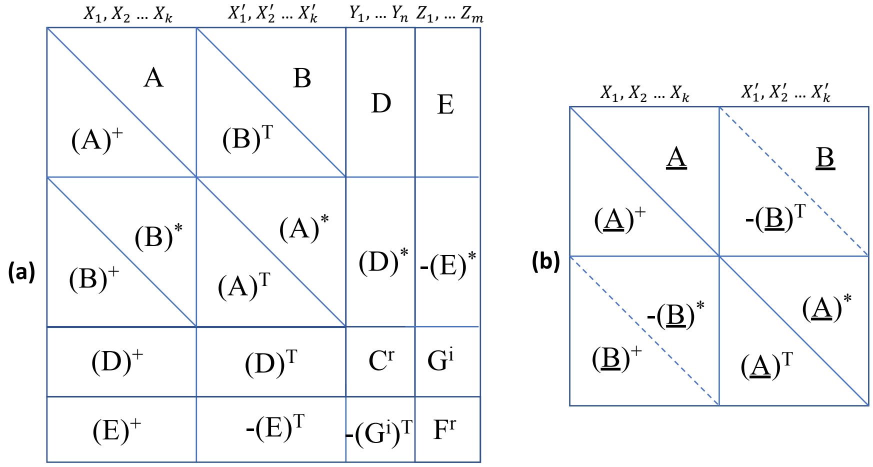

FIG. 1. Block structures of general matrices of a time-reversal symmetric Hamiltonian in a set of time-reversal-adapted states with (a) an even number and (b) an odd number of electrons. Superscripted asterisk, T and dagger indicate taking the complex conjugate, the transpose, and both for the denoted block of matrix. Superscripted i indicates that the denoted block is purely imaginary. Superscripted r indicates that that the denoted square block is real and symmetric. The two dashed lines in (b) indicate that the "diagonal" elements of the two off-diagonal blocks are zero.

doublet degeneracy.[80] Putting $i = j$ in the second equality in Point 4, we immediately see $\langle X_i| \hat{H} |X_i'\rangle = 0$, which gives the dashed lines in Figure 1(b), which indicate zero "diagonal" elements on the off-diagonal blocks. The block structure in Figure 1(b) is most relevant to our derivation. We are deriving expansion formulas for $\langle\psi_i| \hat{h}^{1e}_{eff} |\psi_j\rangle$s, with $|\psi_i\rangle$ and $|\psi_j\rangle$ being one-electron states (i.e., spin orbitals or spinors). Clearly, given a time-reversal-adapted set of $2k$ spin orbitals, we only need to consider the $\frac{k(k+1)}{2}$ elements in the A triangle block and the $\frac{k(k-1)}{2}$ elements in the B triangle block. Henceforth, all matrices discussed adopt the form of Figure 1(b). And there are only k^2 independent matrix elements. Compared to the $\frac{2k(2k+1)}{2}$ independent matrix elements in a $2k \times 2k$ hermitian matrix, the time-reversal symmetry has reduced the number of independent matrix elements by more than one half. The terms "A block" and "B block" are frequently used below. We emphasize that they denote the different triangle blocks in Figure 1(b), *and one shall not associate the A and B in the terms to A- and B-type irreps.*

The connections between $\hat{\mathcal{T}}$, $\hat{\sigma}_v$, and $\hat{C}_2'$ are important. It has been pointed out under Eq. 3 that for the complex-valued E component states, the operations of $\hat{\sigma}_v$ and $\hat{C}_2'$ give the same result as acting $\hat{\mathcal{T}}$. The comparison of Point 1 and Eqs. 6 and 7 clearly shows that for the spin functions, the operation of $\hat{\sigma}_v$ is equivalent to $\hat{\mathcal{T}}$. $\hat{C}_2'$ is also closely related to $\hat{\mathcal{T}}$ by swapping the two functions. The three operators all reverse the direction of the angular momentum along the principal axis, and that is why they are connected. As shown below, the close connections between $\hat{\mathcal{T}}$, $\hat{\sigma}_v$, and $\hat{C}_2'$ allow us to derive the expansion formulas without resorting to constructing eigenfunctions of $\hat{\sigma}_v$, and $\hat{C}_2'$. This is one technical difference between the present work and Ref. 61.

B. Symmetry Relation Dictated by the Wigner-Eckart Theorem

Now, we order a time-reversal-adapted set of spin orbitals so that the $|X_i\rangle$-type states all have α spin functions, and the $|X_i'\rangle$-type states all have β spin functions, i.e.,

$$\phi_1\alpha, \phi_2\alpha, \cdots \phi_k\alpha, \phi_1^*\beta, \phi_2^*\beta, \cdots \phi_k^*\beta. \tag{11}$$

ϕ_i indicates the spatial part of a spin orbital. According to WET, the matrix element $\langle X_i|\,\hat{h}^{1e}_{eff}\,|X_j\rangle$ can be written as[78]

$$\langle X_i|\,\hat{h}^{1e}_{eff}\,|X_j\rangle = \langle \phi_i\alpha|\,\hat{h}^{1e}_{eff}\,|\phi_j\alpha\rangle = \langle \phi_i|\,|\hat{z}^{1e}_{eff,0}\hat{\vec{s}}|\,|\phi_j\rangle \left(\frac{1}{2}, 1, \frac{1}{2}, 0\middle|\frac{1}{2}, \frac{1}{2}\right), \tag{12}$$

where $\left(\frac{1}{2}, 1, \frac{1}{2}, 0\middle|\frac{1}{2}, \frac{1}{2}\right)$ is the Clebsch-Gordan coefficient with the format $\left(j_1, j_2, m_1, m_2\middle|j, m\right)$, and $\langle \phi_i|\,|\hat{z}^{1e}_{eff,0}\hat{s}|\,|\phi_j\rangle$ the reduced matrix element of the one-electron spin operator $\hat{\vec{s}}$, along with the 0 spherical component of the rank-1 tensor operator $\hat{\vec{z}}^{1e}_{eff}$. Since $\left(\frac{1}{2}, 1, \frac{1}{2}, 0\middle|\frac{1}{2}, \frac{1}{2}\right) = -\left(\frac{1}{2}, 1, -\frac{1}{2}, 0\middle|\frac{1}{2}, -\frac{1}{2}\right)$,

$$\langle X_i|\,\hat{h}^{1e}_{eff}\,|X_j\rangle = -\langle \phi_i|\,|\hat{z}^{1e}_{eff,0}\hat{\vec{s}}|\,|\phi_j\rangle \left(\frac{1}{2}, 1, -\frac{1}{2}, 0\middle|\frac{1}{2}, -\frac{1}{2}\right) = -\langle \phi_i\beta|\,\hat{h}^{1e}_{eff}\,|\phi_j\beta\rangle\,. \tag{13}$$

If $\phi_i\beta$ and $\phi_j\beta$ happen to be in the set of $|X_i'\rangle$-type states, i.e., $\phi_i\beta = X_m'$ and $\phi_j\beta = X_l'$ (or equivalently, $\phi_i = \phi_m^*$ and $\phi_j = \phi_l^*$), then

$$\langle X_i|\,\hat{h}^{1e}_{eff}\,|X_j\rangle = -\langle X_m'|\,\hat{h}^{1e}_{eff}\,|X_l'\rangle\,. \tag{14}$$

and this equality reduces the number of independent matrix elements in the A block in Figure 1(b). Eq. 14 is used in all considered cases below to further simplify the derivation.

For one-electron spin orbitals, WET can only be used through Eqs. 13 and 14, i.e., to connect the $\langle \phi_i\alpha|\,\hat{h}^{1e}_{eff}\,|\phi_j\alpha\rangle$ and $\langle \phi_i\beta|\,\hat{h}^{1e}_{eff}\,|\phi_j\beta\rangle$ elements by a sign change. Given two spatial orbitals ϕ_i and ϕ_j, there are two more $\hat{h}^{1e}_{eff}$ matrix elements:

$$\langle\phi_i\alpha|\,\hat{h}^{1e}_{eff}\,|\phi_j\beta\rangle = \langle\phi_i|\,|\hat{z}^{1e}_{eff,-1}\hat{\vec{s}}|\,|\phi_j\rangle\left(\frac{1}{2},1,-\frac{1}{2},1\Big|\frac{1}{2},\frac{1}{2}\right);$$
$$\langle\phi_i\beta|\,\hat{h}^{1e}_{eff}\,|\phi_j\alpha\rangle = \langle\phi_i|\,|\hat{z}^{1e}_{eff,+1}\hat{\vec{s}}|\,|\phi_j\rangle\left(\frac{1}{2},1,\frac{1}{2},-1\Big|\frac{1}{2},-\frac{1}{2}\right). \quad (15)$$

The reduced matrix elements of the 0, +1 and −1 spherical component of $\hat{\vec{z}}^{1e}_{eff}$ are in general independent of each other. Therefore, we can only associate $\langle\phi_i\alpha|\,\hat{h}^{1e}_{eff}\,|\phi_j\alpha\rangle$ and $\langle\phi_i\beta|\,\hat{h}^{1e}_{eff}\,|\phi_j\beta\rangle$, which share a reduced matrix element. The spatial symmetry of a polyatomic system may impose relations between the reduced matrix elements $\langle\phi_i|\,|\hat{z}^{1e}_{eff,0,\pm1}\hat{\vec{s}}|\,|\phi_j\rangle$ or nullify some of them. However, the symmetry lowering due to JT/pJT distortion in general alleviates such constraints. We hence do not consider any symmetry relations between the reduced matrix elements.

Before ending this section, we note that with the spin orbitals ordering convention in Eq. 11, SOC matrix elements of the $\hat{z}^{(1)}_{eff,z}\hat{s}_z$ component in the dot product in Eq. 10 are in the A block, while those of the $\hat{z}^{(1)}_{eff,x}\hat{s}_x$ and $\hat{z}^{(1)}_{eff,y}\hat{s}_y$ components are in the B block.

C. Spatial Symmetry of $\hat{H}_{SO}$

Spatial symmetry means the actual symmetry of the system under consideration. While the system's symmetry is fully represented by a point group, it in general requires us to consider the associated double group in discussing $\hat{H}_{SO}$, since spin is involved. Here, we show that we only need to consider the point group symmetry in deriving expansion formulas of the matrix elements of $\hat{H}_{SO}$.

The two spin functions α and β gain a minus sign under any 2π rotation (labelled as $\hat{R}$), instead of returning to themselves like usual objects do. Only when they are rotated by 4π they return to themselves.[42] The pair of spin functions hence form a new irreducible representation, and correspondingly, the number of symmetry elements is doubled. Any product of $\hat{S}\hat{R}$, with $\hat{S}$ being a symmetry operation of the original point group, is a new symmetry operation. The extended group is the double group of the original point group. In general, any electronic states with an even number of electrons return to themselves under the action of $\hat{R}$, and those with an odd number of electrons change their signs. The former belong to Boson irreps while the latter belong to Fermion irreps of the relevant double groups.[15]

Resolving $\hat{H}_{SO}$ in a set of electronic states $\{|\Psi_I\rangle\}$, the Hamiltonian becomes

$$\hat{H}_{SO} = |\Psi_I\rangle \, H_{IJ}^{SO} \, \langle\Psi_J| \, . \tag{16}$$

Throughout this work, Einstein's convention of summing over all duplicate indices in a mathematical expression is followed. Under the symmetry operation $\hat{R}$, the Hamiltonian becomes

$$\hat{R}\hat{H}_{SO}\hat{R}^{-1} = \left|\hat{R}\Psi_I\right\rangle \left(\hat{R}H_{SO}^{IJ}\right) \left\langle\hat{R}\Psi_J\right| = p_I p_J \, |\Psi_I\rangle \left(\hat{R}H_{SO}^{IJ}\right) \langle\Psi_J| = |\Psi_I\rangle \left(\hat{R}H_{SO}^{IJ}\right) \langle\Psi_J| \, . \tag{17}$$

p_I and p_J stand for the $+1$ or -1 phases that the Ψ_I and Ψ_J gain under the action of $\hat{R}$. Since $\hat{H}_{SO}$ conserves the number of electrons, Ψ_I and Ψ_J must have the same number of electrons, p_I and p_J must equal, giving $p_I p_J = 1$ and the last equality in Eq. 17. The Hamiltonian belongs to the totally symmetric irrep, which is a Boson irrep. It thus must return to itself under the action of $\hat{R}$. To satisfy this symmetry requirement of $\hat{R}\hat{H}_{SO}\hat{R}^{-1} = \hat{H}_{SO}$, we must have $\hat{R}H_{SO}^{IJ} = H_{SO}^{IJ}$. Therefore, all the matrix elements must belong to Boson irreps, and we only need to consider symmetry operations of normal point groups in deriving expansion formulas for the matrix elements. This conclusion is tenable for the one-electron matrix elements $\langle\psi_i| \, \hat{h}_{eff}^{1e} \, |\psi_j\rangle$s, which are special cases of H_{IJ}^{SO}s. With all these understandings of symmetry properties of SOC matrix elements, we commence deriving their expansion formulas.

We first present detailed derivation and discussion for the trigonal formalism. Many of the results are transferrable to the tetragonal formalism. This transferability lays a foundation for future efficient derivation of general n-gonal formalism.

V. HAMILTONIAN STRUCTURES AND SYMMETRY EIGENVALUES FOR TRIGONAL SYSTEMS

There are A- and E-type irreps in trigonal symmetries, giving the two types of intra-shell coupling and the $(E+E)$, $(E+A)$, and $(A+A)$ three types of inter-shell coupling. It has been well known that angular momentum operator matrix element between identical real-valued functions is zero due to the purely imaginary nature and hermiticity of the operator. Since the A-type spatial orbitals can always be taken real-valued, the A-type intra-shell

SOC is null. We only need to consider the other four types of SOC. The essence of the modularized approach[64–67] to obtain expansion formulas for Hamiltonian matrix elements is to first derive the symmetry eigenvalues of the matrix elements. Expansions in vibrational coordinates that feature these symmetry eigenvalues are modules. They are selected by matching their eigenvalues with those of the matrix elements. This efficient approach allows us to derive expansion formulas for thousands of non-SO JT/pJT problems in one work.[65] In this section, we set out the first step to identify independent matrix elements in each of the four types of SOC, and also derive their symmetry eigenvalues.

A. E-type Hamiltonian

We start with the intra-shell SOC of a set of E-type orbitals. It is the most common type of SOC in trigonal symmetries. There are in total four spin orbitals, $|X\alpha\rangle$, $|Y\alpha\rangle$, $|X\beta\rangle$, and $|Y\beta\rangle$ with the real-valued spatial orbitals, or those with complex-valued spatial orbitals obtained using the transformation in Eq. 2. Our derivation is based on the complex-valued orbitals: $|+\alpha\rangle$, $|-\alpha\rangle$, $|+\beta\rangle$, and $|-\beta\rangle$. $|+\alpha\rangle$ and $|-\beta\rangle$ together transform as $E_{3/2}$-type irreps in any trigonal and tetragonal double groups except S_4^2, while the other two transform as $E_{1/2}$-type irreps. In the S_4^2 double group, the former transform as the $E_{1/2}$ irrep, while the latter as the $E_{3/2}$ irrep. The SOC matrix of these spinors is shown in Figure 2(a). Clearly, it takes the structure in Figure 1(b), as the spinors are properly ordered. Henceforth, we just use $\hat{H}$ to label the one-electron effective SOC operator and H_{ij} to label its matrix elements between spin orbitals. There is only one element in the B block, $H_{+\alpha+\beta}$. For the A block, $H^r_{+\beta+\beta} = -H^r_{+\alpha+\alpha}$ due to WET. Consequently, the four real-valued (denoted by the superscript r) diagonal elements are all connected to $H^r_{+\alpha+\alpha}$. WET also determines $H_{+\beta-\beta} = -H_{+\alpha-\alpha}$. The block structure in Figure 1(b) (i.e., time-reversal symmetry) determines $H_{+\beta-\beta} = H_{+\alpha-\alpha}$. The last two equalities together determine $H_{+\alpha-\alpha} = 0$. Therefore, $H^r_{+\alpha+\alpha}$ is the only independent matrix element in the A block.

Expressed using the two independent matrix elements, the intra-shell SO Hamiltonian reads

$$\hat{H} = (|+\alpha\rangle\langle+\alpha| + |-\beta\rangle\langle-\beta| - |-\alpha\rangle\langle-\alpha| - |+\beta\rangle\langle+\beta|)\, H^r_{+\alpha+\alpha} + (|+\alpha\rangle\langle+\beta| - |-\alpha\rangle\langle-\beta|)\, H_{+\alpha+\beta} + (|+\beta\rangle\langle+\alpha| - |-\beta\rangle\langle-\alpha|)\, H^*_{+\alpha+\beta}. \tag{18}$$

We start with the lowest symmetry in the trigonal class, C_3 symmetry. This is the essence of the root-branch approach. There is only one representative symmetry operator in this point group, which is $\hat{C}_3$. With the $\hat{C}_3$-transformations in Eqs. 2 and 4, we easily obtain the $\hat{C}_3$-transformed Hamiltonian:

$$\begin{aligned}\hat{C}_3\hat{H}\hat{C}_3^{-1} = &\left(\left|+\alpha\right\rangle\left\langle+\alpha\right| + \left|-\beta\right\rangle\left\langle-\beta\right| - \left|-\alpha\right\rangle\left\langle-\alpha\right| - \left|+\beta\right\rangle\left\langle+\beta\right|\right)\hat{C}_3 H^r_{+\alpha+\alpha} \\ &+ \left(\left|+\alpha\right\rangle\left\langle+\beta\right| - \left|-\alpha\right\rangle\left\langle-\beta\right|\right)e^{-i\frac{2\pi}{3}}\hat{C}_3 H_{+\alpha+\beta} \\ &+ \left(\left|+\beta\right\rangle\left\langle+\alpha\right| - \left|-\beta\right\rangle\left\langle-\alpha\right|\right)e^{i\frac{2\pi}{3}}\hat{C}_3 H^*_{+\alpha+\beta}. \end{aligned} \tag{19}$$

In order to let $\hat{C}_3\hat{H}\hat{C}_3^{-1} = \hat{H}$, $H^r_{+\alpha+\alpha}$ and $H_{+\alpha+\beta}$ need to be eigenfunctions of $\hat{C}_3$, with eigenvalues $\chi^{C_3} = 1$ and $e^{i\frac{2\pi}{3}}$, respectively.

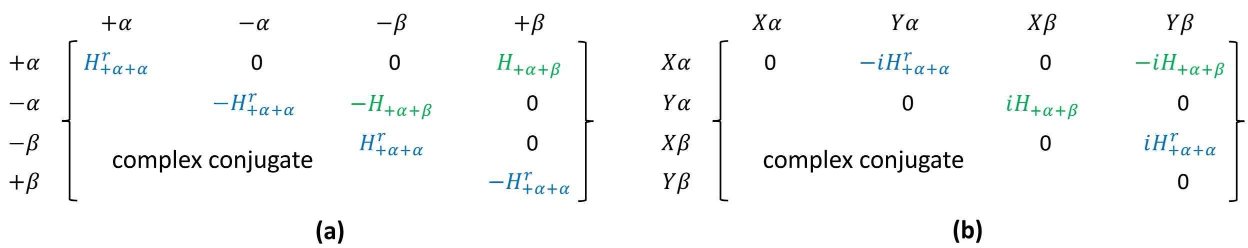

FIG. 2. Structures of the intra-shell spin-orbit coupling matrices within a set of e-type orbitals in (a) the complex-valued and (b) the real-valued bases. Only the elements in the upper triangle of each matrix are given. The lower triangle is just the complex conjugate of the upper triangle. Matrix elements that are derived from one independent matrix element by time-reversal symmetry and WET are given in the same color.

In C_{3v} symmetry, we need to consider the action of σ_v. The $\hat{\sigma}_v$-transformations in Eqs. 3 and 6 leads to the $\hat{\sigma}_v$-transformed $\hat{H}$:

$$\begin{aligned}\hat{\sigma}_v\hat{H}\hat{\sigma}_v{}^{-1} = &\left(\left|-\beta\right\rangle\left\langle-\beta\right| + \left|+\alpha\right\rangle\left\langle+\alpha\right| - \left|+\beta\right\rangle\left\langle+\beta\right| - \left|-\alpha\right\rangle\left\langle-\alpha\right|\right)\hat{\sigma}_v H^r_{+\alpha+\alpha} \\ &+ \left(-\left|-\beta\right\rangle\left\langle-\alpha\right| + \left|+\beta\right\rangle\left\langle+\alpha\right|\right)\hat{\sigma}_v H_{+\alpha+\beta} \\ &+ \left(-\left|-\alpha\right\rangle\left\langle-\beta\right| + \left|+\alpha\right\rangle\left\langle+\beta\right|\right)\hat{\sigma}_v H^*_{+\alpha+\beta}. \end{aligned} \tag{20}$$

In order to have the required symmetry for the Hamiltonian, $\hat{\sigma}_v\hat{H}\hat{\sigma}_v^{-1} = \hat{H}$, we must have $\hat{\sigma}_v H^r_{+\alpha+\alpha} = H^r_{+\alpha+\alpha}$ and $\hat{\sigma}_v H_{+\alpha+\beta} = H^*_{+\alpha+\beta}$. The two equalities point to the following σ_v-eigenvalues for the real and imaginary parts of the matrix elements: $(\chi^{\sigma_v}_{Re}, \chi^{\sigma_v}_{Im}) = (1, 0)$ and $(1, -1)$ for $H^r_{+\alpha+\alpha}$ and $H_{+\alpha+\beta}$, respectively. $\chi^{\sigma_v}_{Im} = 0$ indicates that the matrix element is real-valued.

A difference between the present work and Ref. 61 is noted. We here show that it is unnecessary to transform the spin orbitals to $\hat{\sigma}_v$-eigenstates in deriving symmetry properties of the matrix elements in C_{3v} symmetry. $\hat{\sigma}_v$ converts each ket-bra dyad to its time-reversal counterpart (see the last paragraph in Section IV A). According to the general block structure in Figure 1(b), the matrix element of a dyad and that of the time-reversal dyad are complex conjugates of each other. Therefore, to have the Hamiltonian invariant with respect to $\hat{\sigma}_v$, it is necessary to have $\hat{\sigma}_v H_{ij} = H_{ij}^*$, resulting in the requirement of $(\chi_{Re}^{\sigma_v}, \chi_{Im}^{\sigma_v}) = (1, -1)$. This is the only constraint on the matrix element induced by $\hat{\sigma}_v$. $(\chi_{Re}^{\sigma_v}, \chi_{Im}^{\sigma_v}) = (1, 0)$ is a special case of this general requirement for real-valued matrix elements. This rationale also applies in the derivation for the $(E + E)$ and $(E + A)$ inter-shell SOC below. Therefore, it is also unnecessary to construct $\hat{\sigma}_v$-eigenstates in those cases.

In D_3 symmetry, whose point group is isomorphic with C_{3v}, we need to consider the action of $\hat{C}_2^x$ on $\hat{H}$. With the $\hat{C}_2'$-transformations in Eqs 3 and 7, we have:

$$\begin{aligned}\hat{C}_2^x \hat{H} \left(\hat{C}_2^x\right)^{-1} &= \left(\left|-\beta\right\rangle\left\langle-\beta\right| + \left|+\alpha\right\rangle\left\langle+\alpha\right| - \left|+\beta\right\rangle\left\langle+\beta\right| - \left|-\alpha\right\rangle\left\langle-\alpha\right|\right)\hat{C}_2^x H_{+\alpha+\alpha}^r \\ &+ \left(\left|-\beta\right\rangle\left\langle-\alpha\right| - \left|+\beta\right\rangle\left\langle+\alpha\right|\right)\hat{C}_2^x H_{+\alpha+\beta} \\ &+ \left(\left|-\alpha\right\rangle\left\langle-\beta\right| - \left|+\alpha\right\rangle\left\langle+\beta\right|\right)\hat{C}_2^x H_{+\alpha+\beta}^*. \end{aligned} \tag{21}$$

In order to have $\hat{C}_2^x \hat{H} \left(\hat{C}_2^x\right)^{-1} = \hat{H}$, the matrix elements need to satisfy $\hat{C}_2^x H_{+\alpha+\alpha}^r = H_{+\alpha+\alpha}^r$ and $\hat{C}_2^x H_{+\alpha+\beta} = -H_{+\alpha+\beta}^*$. These equalities point to the following C_2'-eigenvalues of the matrix elements: $\left(\chi_{Re}^{C_2'}, \chi_{Im}^{C_2'}\right) = (1, 0)$ and $(-1, 1)$ for $H_{+\alpha+\alpha}^r$ and $H_{+\alpha+\beta}$, respectively. Similarly to $\hat{\sigma}_v$ in C_{3v} symmetry, $\hat{C}_2'$ convert each ket-bra dyad to its time-reversal counterpart (again, the last paragraph in Section IV A), but with an extra sign change for the dyads that involve one α and one β spin function, i.e., those whose elements are in the B block. Correspondingly, the elements in the A block must be converted to their complex conjugates by $\hat{C}_2'$, while those in the B block must be converted to the negative of their complex conjugates. These are the only constraints imposed by $\hat{C}_2'$ to the matrix elements. And it is unnecessary to construct $\hat{C}_2'$-eigenstates out of the spin orbitals to obtain the constraints. Similar arguments apply in the derivation for the $(E + E)$ and $(E + A)$ inter-shell SOC below.

In C_{3h} symmetry, the E orbitals are addressed by the prime or double-prime, depending on whether they are σ_h-even or -odd. Using p and q to express the generic superscript of prime and double-prime, the SO Hamiltonian reads

$$\hat{H} = \left(|+^p\alpha\rangle \langle +^p\alpha| + |-^p\beta\rangle \langle -^p\beta| - |-^p\alpha\rangle \langle -^p\alpha| - |+^p\beta\rangle \langle +^p\beta| \right) H^r_{+^p\alpha +^p\alpha} + \left(|+^p\alpha\rangle \langle +^p\beta| - |-^p\alpha\rangle \langle -^p\beta| \right) H_{+^p\alpha +^p\beta} + \left(|+^p\beta\rangle \langle +^p\alpha| - |-^p\beta\rangle \langle -^p\alpha| \right) H^*_{+^p\alpha +^p\beta} \quad (22)$$

The same superscript for the spatial orbitals + and − determines that their phase flippings (if there are) cancel. With the $\hat{\sigma}_h$-transformations of spin functions in Eq. 8, we have

$$\hat{\sigma}_h \hat{H} \hat{\sigma}_h^{-1} = \left(|+^p\alpha\rangle \langle +^p\alpha| + |-^p\beta\rangle \langle -^p\beta| - |-^p\alpha\rangle \langle -^p\alpha| - |+^p\beta\rangle \langle +^p\beta| \right) \hat{\sigma}_h H^r_{+^p\alpha +^p\alpha} + \left(- |+^p\alpha\rangle \langle +^p\beta| + |-^p\alpha\rangle \langle -^p\beta| \right) \hat{\sigma}_h H_{+^p\alpha +^p\beta} + \left(- |+^p\beta\rangle \langle +^p\alpha| + |-^p\beta\rangle \langle -^p\alpha| \right) \hat{\sigma}_h H^*_{+^p\alpha +^p\beta}. \quad (23)$$

To have $\hat{\sigma}_h \hat{H} \hat{\sigma}_h^{-1} = \hat{H}$, we need $\hat{\sigma}_h H^r_{+^p\alpha +^p\alpha} = H^r_{+^p\alpha +^p\alpha}$ and $\hat{\sigma}_h H_{+^p\alpha +^p\beta} = -H_{+^p\alpha +^p\beta}$. The matrix elements need to be σ_h-eigenfunctions with the eigenvalues $\chi^{\sigma_h} = 1$ and -1, respectively. It is interesting to note that even for this intra-shell SOC, the σ_h-eigenvalue of the matrix elements is not always 1, which is the case for the corresponding non-SOC intra-shell (and intra-term too) elements. The reason is related to the different σ_h-eigenvalues of $|\alpha\rangle$ and $|\beta\rangle$ (Eq. 8).

$\chi^{C_3} = e^{i\frac{2\pi}{3}}$ and $\chi^{\sigma_h} = -1$ for $H_{+^p\alpha +^p\beta}$ indicates that e''-type (e') modes are SO JT-active (-inactive) in first order expansion. This is because the *linear* monomial $\rho e^{-i\phi}$ of a set of e'' coordinates has the specific χ^{C_3} and χ^{σ_h}, while any functions of e' coordinates must have $\chi^{\sigma_h} = 1$. On the contrary, when SOC is not considered, only e'-type modes are JT active. The JT-activity of e''-type modes is thus a purely relativistic effect. Please note that this relativistic JT-activity is in terms of the original E-type spatial orbitals. If we consider that SOC has split the E-type shell to the two sets of $E_{1/2}$- and $E_{3/2}$-type spinors, the e''-type modes is pJT-active in coupling the non-degenerate spinors (recalling that $|+\alpha\rangle$ and $|+\beta\rangle$ transform as $E_{3/2}$- and $E_{1/2}$-type irreps, respectively).

D_{3h} is the composite of D_3 and C_{3h}. Correspondingly, the matrix elements need to adopt all four (three sets of) symmetry eigenvalues, $\left(\chi^{C_3}, \left(\chi^{C_2'}_{Re}, \chi^{C_2'}_{Im}\right), \chi^{\sigma_h}\right)$. Although the D_{3d} point group is isomorphic to D_{3h}, we cannot directly transplant the D_{3h} symmetry eigenvalues directly to D_{3d}. This is because the spin functions α and β are invariant under

$\hat{I}$, but they gain phases under $\hat{\sigma}_h$. Under the action of $\hat{I}$,

$$\begin{aligned}\hat{I}\hat{H}\hat{I}^{-1} = &(|+_p\alpha\rangle\langle +_p\alpha| + |-_p\beta\rangle\langle -_p\beta| - |-_p\alpha\rangle\langle -_p\alpha| - |+_p\beta\rangle\langle +_p\beta|)\, H^r_{+_p\alpha+_p\alpha} \\ &+ (|+_p\alpha\rangle\langle +_p\beta| - |-_p\alpha\rangle\langle -_p\beta|)\, H_{+_p\alpha+_p\beta} \\ &+ (|+_p\beta\rangle\langle +_p\alpha| - |-_p\beta\rangle\langle -_p\alpha|)\, H^*_{+_p\alpha+_p\beta}.\end{aligned} \tag{24}$$

Certainly, $\chi^I = 1$ for both $H^r_{+_p\alpha+_p\alpha}$ and $H_{+_p\alpha+_p\beta}$. Here, the subscript p has been used to represent the g and u symmetry of the E orbitals.

Our derivation for symmetry eigenvalues of all matrix elements in E-type intra-shell SOC problems in all six trigonal symmetries is finished. The eigenvalues are summarized in the E block of Table I. As discussed later, these eigenvalues guide us to look up appropriate expansion formulas for the matrix elements.

In Section IV C, we show that only point group symmetry operations shall be considered in deriving expansion formulas of the SOC matrix elements. However, while the D_{3h} and D_{3d} point groups are isomorphic, with $\hat{\sigma}_h$ in the former being replaced by $\hat{I}$ in the latter, different symmetry eigenvalues are obtained for the two operators. Specifically, $\chi^{\sigma_h} = 1$ for $H_{+^p\alpha+^p\beta}$, but $\chi^{\sigma_I} = -1$ for $H_{+_p\alpha+_p\beta}$. This seems inconsistent to our conclusion in Section IV C: if only point group symmetries matter, the isomorphism between point groups shall strictly apply, and the matrix elements in isomorphic correspondence shall have the same eigenvalues for the corresponding symmetry elements. A further clarification is necessary.

The isomorphism between the matrix elements of the two point groups is applicable only when the two sets of ket-bra dyads transform as the corresponding irreps. For instance, in the E-type non-SO JT couplings in D_{3h} symmetry, the ket-bra dyad $(|+^p\rangle\langle +^p| + |-^p\rangle\langle -^p|)$ transforms as A'_1, $(|+^p\rangle\langle +^p| - |-^p\rangle\langle -^p|)$ as A'_2, $|+^p\rangle\langle -^p|$ and $|-^p\rangle\langle +^p|$ together as E'. In the corresponding D_{3d} problem, $(|+_p\rangle\langle +_p| + |-_p\rangle\langle -_p|)$ transforms as A_{1g}, $(|+_p\rangle\langle +_p| - |-_p\rangle\langle -_p|)$ transforms as A_{2g}, $|+_p\rangle\langle -_p|$ and $|-_p\rangle\langle +_p|$ together as E_g. In the isomorphic relation between the two point groups, A'_1 corresponds to A_{1g}, A'_2 to A_{2g}, and E' to E_g. These correspondences guarantee the isomorphism between the matrix elements of the two sets of dyads.

Now let's consider the dyads of the spin functions. $(|\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta|)$ transforms as A'_1 in D_{3h} and A_{1g} in D_{3g}, $(|\alpha\rangle\langle\alpha| - |\beta\rangle\langle\beta|)$ as A'_2 in D_{3h} and A_{2g} in D_{3d}. Good correspondences between the irreps of the two sets of dyads maintain so far. $|\alpha\rangle\langle\beta|$ and $|\beta\rangle\langle\alpha|$, however, transform as E'' in D_{3h} and E_g in D_{3d}. However, E_g corresponds to E', not E''. This inconsistence is carried to the dyads of spin orbitals, which are the direct products of the ket-bra dyads of the spatial orbitals and the dyads of the spin functions. It is this inconsistence that eliminates the isomorphism between the $H_{+^p\alpha+^p\beta}$ and $H_{+_p\alpha+_p\beta}$ elements. The further underlying reason for this inconsistence is that the D_{3h}^2 and D_{3d}^2 double groups are not isomorphic, although their normal point groups are. The non-isomorphism arises from that the spin functions are invariant under $\hat{I}$ but gain the opposite phases $-i$ and i under $\hat{\sigma}_h$ (Eq. 8). The characters of the fundamental Fermion irreps composed of the spin functions are thus different: 2 in D_{3d}^2 and 0 in D_{3h}^2. The different character tables of the D_{3h}^2 and D_{3d}^2 double groups can be seen in Pages 260-261 in Ref. 42. Similar non-trivial differences in symmetry eigenvalues of matrix elements between D_{3h} and D_{3d} symmetries also exist in the $(E+E)$-type and $(E+A)$-type inter-shell SOC below. The rationalization here also applies in those cases and is hence not repeated. We only need to consider symmetry operations in normal point groups in deriving symmetry properties of each matrix element. However, this conclusion does not mean the irrelevance of double group symmetry to SOC. Double group symmetry matters for this intrinsically spin-related interaction.

With all these understandings, we come back to the opposite symmetry eigenvalues of $H_{+\alpha+\beta}$ in C_{3v} and D_3: $(\chi_{Re}^{\sigma_v}, \chi_{Im}^{\sigma_v}) = (1, -1)$ in the former and $(-1, 1)$ in the latter. However, the C_{3v}^2 and D_{3h}^2 double groups are isomorphic and the spin ket-bra dyads transform as corresponding irreps in the two symmmetries. Such an inconsistence should not occur. The inconsistence arises from the different transformations of the spin functions with respect to $\hat{\sigma}_v$ and $\hat{C}_2'$ (Eq. 6 vs Eq. 7). And this difference can be removed. Replacing β by $-i\beta$, i.e., rotating β by $-\pi$ about the C_3 axis and using the resultant spin function as the spin-down basis, the C_2'-transformation matrix is identical to the σ_v matrix in Eq. 6. Consequently, with such a new β, $H_{+\alpha+\beta}$ in D_3 has the same $(\chi_{Re}^{\sigma_v}, \chi_{Im}^{\sigma_v}) = (1, -1)$ as in C_{3v} symmetry. This phase multiplication to β does not change the $|\beta\rangle\langle\beta|$ dyad, as the phases in the bra and ket cancel. The symmetry eigenvalues of $H_{+\beta+\beta}^r$ (equivalently $H_{+\alpha+\alpha}^r$) are hence not affected by the phase, and the equivalence between the symmetry eigenvalues of $H_{+\alpha+\alpha}^r$ in the two symmetries maintain. Overall, the isomorphism of the SOC operators in C_{3v} and D_3 symmetries is regained with such a $-i$ phase multiplication to β. In short, the difference in the symmetry eigenvalues of $H_{+\alpha+\beta}$ in C_{3v} and D_3 symmetries is trivial and can be eliminated by a phase adjustment to the spin basis. Similar trivial differences in symmetry eigenvalues between C_{3v} and D_3 also exist in the $(E+E)$- and $(E+A)$-type SOC below.

The rationalization will not be repeated.

B. $(E+E)$-type Hamiltonian

This type of inter-shell SOC can be seen in many transition metal compounds. For instance, the d_{xz} and d_{yz} orbitals of the central metal form one set of E-type orbitals, and the $d_{x^2-y^2}$ and d_{xy} oribtals form another set. Superscripts p and q are used to differentiate the two sets. They also label the $'$ and $''$ σ_h-parities of the orbitals in D_{3h} symmetry, as well as the g and u I-parities in D_{3d} symmetry. The inter-shell SOC matrix takes the structure shown in Figure 3(a), which is consistent with the one shown in Figure 1(b), since the eight spinors are properly ordered. WET determines $H_{+^p\beta+^q\beta} = -H_{+^p\alpha+^q\alpha}$ and $H_{+^p\beta-^q\beta} = -H_{+^p\alpha-^q\alpha}$. Time-reversal symmetry determines $H_{+^p\beta+^q\beta} = H^*_{-^p\alpha-^q\alpha}$ and $H_{+^p\beta-^q\beta} = H^*_{-^p\alpha+^q\alpha}$. These four equalities together lead to $H_{-^p\alpha-^q\alpha} = -H^*_{+^p\alpha+^q\alpha}$ and $H_{-^p\alpha+^q\alpha} = -H^*_{+^p\alpha-^q\alpha}$. Therefore, only two independent elements remain in the A block and they are colored in blue and green in Figure 3(a). As discussed in Section IV B, WET cannot be used to reduce the number of independent elements in the B block. There are hence in total six independent matrix elements.

With the six independent matrix elements shown in Figure 3(a), the inter-shell Hamiltonian reads

$$\begin{aligned}\hat{H} &= \left(|+^p\alpha\rangle\langle+^q\alpha| - |+^p\beta\rangle\langle+^q\beta| + |-^q\beta\rangle\langle-^p\beta| - |-^q\alpha\rangle\langle-^p\alpha|\right) H_{+^p\alpha+^q\alpha} + hc \\ &+ \left(|+^p\alpha\rangle\langle-^q\alpha| - |+^p\beta\rangle\langle-^q\beta| + |+^q\beta\rangle\langle-^p\beta| - |+^q\alpha\rangle\langle-^p\alpha|\right) H_{+^p\alpha-^q\alpha} + hc \\ &+ \left(|+^p\alpha\rangle\langle-^q\beta| - |+^q\alpha\rangle\langle-^p\beta|\right) H_{+^p\alpha-^q\beta} + hc \\ &+ \left(|+^p\alpha\rangle\langle+^q\beta| - |-^q\alpha\rangle\langle-^p\beta|\right) H_{+^p\alpha+^q\beta} + hc \\ &+ \left(|-^p\alpha\rangle\langle-^q\beta| - |+^q\alpha\rangle\langle+^p\beta|\right) H_{-^p\alpha-^q\beta} + hc \\ &+ \left(|-^p\alpha\rangle\langle+^q\beta| - |-^q\alpha\rangle\langle+^p\beta|\right) H_{-^p\alpha+^q\beta} + hc.\end{aligned} \tag{25}$$

Here, each hc stands for the hermitian conjugate of the operator component in front of it.

(a)

$$
\begin{array}{c|cccccccc}
 & +^{p}\alpha & -^{p}\alpha & +^{q}\alpha & -^{q}\alpha & -^{p}\beta & +^{p}\beta & -^{q}\beta & +^{q}\beta \\
\hline
+^{p}\alpha & \multicolumn{2}{c}{E_{I}\ \text{intra-shell SOC}} & H_{+^{p}\alpha+^{q}\alpha} & H_{+^{p}\alpha-^{q}\alpha} & \multicolumn{2}{c}{E_{I}\ \text{intra-shell SOC}} & H_{+^{p}\alpha-^{q}\beta} & H_{+^{p}\alpha+^{q}\beta} \\
-^{p}\alpha & & & -H^{*}_{+^{p}\alpha-^{q}\alpha} & -H^{*}_{+^{p}\alpha+^{q}\alpha} & & & H_{-^{p}\alpha-^{q}\beta} & H_{-^{p}\alpha+^{q}\beta} \\
+^{q}\alpha & & & \multicolumn{2}{c}{E_{II}\ \text{intra-shell SOC}} & -H_{+^{p}\alpha-^{q}\beta} & -H_{-^{p}\alpha-^{q}\beta} & \multicolumn{2}{c}{E_{II}\ \text{intra-shell SOC}} \\
-^{q}\alpha & & & & & -H_{+^{p}\alpha+^{q}\beta} & -H_{-^{p}\alpha+^{q}\beta} & & \\
-^{p}\beta & & & & & \multicolumn{2}{c}{E_{I}\ \text{intra-shell SOC}} & H^{*}_{+^{p}\alpha+^{q}\alpha} & H^{*}_{+^{p}\alpha-^{q}\alpha} \\
+^{p}\beta & \multicolumn{4}{c}{\text{complex conjugate}} & & & -H_{+^{p}\alpha-^{q}\alpha} & -H_{+^{p}\alpha+^{q}\alpha} \\
-^{q}\beta & & & & & & & \multicolumn{2}{c}{E_{II}\ \text{intra-shell SOC}} \\
+^{q}\beta & & & & & & & &
\end{array}
$$

(b)

$$
\begin{array}{c|cc}
 & X^{q}\alpha & Y^{q}\alpha \\
\hline
X^{p}\alpha & iIm(H_{+^{p}\alpha+^{q}\alpha}) + iIm(H_{+^{p}\alpha-^{q}\alpha}) & -iRe(H_{+^{p}\alpha+^{q}\alpha}) + iRe(H_{+^{p}\alpha-^{q}\alpha}) \\
Y^{p}\alpha & iRe(H_{+^{p}\alpha+^{q}\alpha}) + iRe(H_{+^{p}\alpha-^{q}\alpha}) & iIm(H_{+^{p}\alpha+^{q}\alpha}) - iIm(H_{+^{p}\alpha-^{q}\alpha})
\end{array}
$$

(c)

$$
\begin{array}{c|cc}
 & X^{q}\beta & Y^{q}\beta \\
\hline
X^{p}\beta & -iIm(H_{+^{p}\alpha+^{q}\alpha}) - iIm(H_{+^{p}\alpha-^{q}\alpha}) & iRe(H_{+^{p}\alpha+^{q}\alpha}) - iRe(H_{+^{p}\alpha-^{q}\alpha}) \\
Y^{p}\beta & -iRe(H_{+^{p}\alpha+^{q}\alpha}) - iRe(H_{+^{p}\alpha-^{q}\alpha}) & -iIm(H_{+^{p}\alpha+^{q}\alpha}) + iIm(H_{+^{p}\alpha-^{q}\alpha})
\end{array}
$$

(d)

$$
\begin{array}{c|cc}
 & X^{q}\beta & Y^{q}\beta \\
\hline
X^{p}\alpha & \frac{1}{2}(H_{+^{p}\alpha+^{q}\beta} + H_{-^{p}\alpha-^{q}\beta} + H_{+^{p}\alpha-^{q}\beta} + H_{-^{p}\alpha+^{q}\beta}) & \frac{i}{2}(-H_{+^{p}\alpha+^{q}\beta} + H_{-^{p}\alpha-^{q}\beta} + H_{+^{p}\alpha-^{q}\beta} - H_{-^{p}\alpha+^{q}\beta}) \\
Y^{p}\alpha & \frac{i}{2}(H_{+^{p}\alpha+^{q}\beta} - H_{-^{p}\alpha-^{q}\beta} + H_{+^{p}\alpha-^{q}\beta} - H_{-^{p}\alpha+^{q}\beta}) & \frac{1}{2}(H_{+^{p}\alpha+^{q}\beta} + H_{-^{p}\alpha-^{q}\beta} - H_{+^{p}\alpha-^{q}\beta} - H_{-^{p}\alpha+^{q}\beta})
\end{array}
$$

(e)

$$
\begin{array}{c|cc}
 & X^{p}\beta & Y^{p}\beta \\
\hline
X^{q}\alpha & -\frac{1}{2}(H_{+^{p}\alpha+^{q}\beta} + H_{-^{p}\alpha-^{q}\beta} + H_{+^{p}\alpha-^{q}\beta} + H_{-^{p}\alpha+^{q}\beta}) & -\frac{i}{2}(H_{+^{p}\alpha+^{q}\beta} - H_{-^{p}\alpha-^{q}\beta} + H_{+^{p}\alpha-^{q}\beta} - H_{-^{p}\alpha+^{q}\beta}) \\
Y^{q}\alpha & -\frac{i}{2}(-H_{+^{p}\alpha+^{q}\beta} + H_{-^{p}\alpha-^{q}\beta} + H_{+^{p}\alpha-^{q}\beta} - H_{-^{p}\alpha+^{q}\beta}) & -\frac{1}{2}(H_{+^{p}\alpha+^{q}\beta} + H_{-^{p}\alpha-^{q}\beta} - H_{+^{p}\alpha-^{q}\beta} - H_{-^{p}\alpha+^{q}\beta})
\end{array}
$$

FIG. 3. (a) Structure of the inter-shell spin-orbit coupling matrix between two sets of E-type orbitals in the complex-valued bases. Only the inter-shell elements in the upper triangle of the matrix are given. The lower triangle is just the complex conjugate of the upper triangle. Matrix elements that are derived from one independent matrix element by time-reversal symmetry and WET are given in the same color. The blocks of the E-type intra-shell SOC matrix elements are indicated by text and they take the same structure as in Figure 2(a). Given in (b)-(d) are the blocks of the inter-shell SOC matrix in the real-valued bases. (b) and (c) are complex conjugates of each other. (d) and (e) are the negative of the transpose of each other.

$\hat{C}_3$ transforms the Hamiltonian as

$$\begin{aligned}\hat{C}_3\hat{H}\hat{C}_3^{-1} = & \left(\left|+^p\alpha\right\rangle\left\langle+^q\alpha\right| - \left|+^p\beta\right\rangle\left\langle+^q\beta\right| + \left|-^q\beta\right\rangle\left\langle-^p\beta\right| - \left|-^q\alpha\right\rangle\left\langle-^p\alpha\right|\right)\hat{C}_3 H_{+^p\alpha+^q\alpha} + hc \\ & + e^{i\frac{2\pi}{3}}\left(\left|+^p\alpha\right\rangle\left\langle-^q\alpha\right| - \left|+^p\beta\right\rangle\left\langle-^q\beta\right| + \left|+^q\beta\right\rangle\left\langle-^p\beta\right| - \left|+^q\alpha\right\rangle\left\langle-^p\alpha\right|\right)\hat{C}_3 H_{+^p\alpha-^q\alpha} + hc \\ & + \left(\left|+^p\alpha\right\rangle\left\langle-^q\beta\right| - \left|+^q\alpha\right\rangle\left\langle-^p\beta\right|\right)\hat{C}_3 H_{+^p\alpha-^q\beta} + hc \\ & + e^{-i\frac{2\pi}{3}}\left(\left|+^p\alpha\right\rangle\left\langle+^q\beta\right| - \left|-^q\alpha\right\rangle\left\langle-^p\beta\right|\right)\hat{C}_3 H_{+^p\alpha+^q\beta} + hc \\ & + e^{-i\frac{2\pi}{3}}\left(\left|-^p\alpha\right\rangle\left\langle-^q\beta\right| - \left|+^q\alpha\right\rangle\left\langle+^p\beta\right|\right)\hat{C}_3 H_{-^p\alpha-^q\beta} + hc \\ & + e^{i\frac{2\pi}{3}}\left(\left|-^p\alpha\right\rangle\left\langle+^q\beta\right| - \left|-^q\alpha\right\rangle\left\langle+^p\beta\right|\right)\hat{C}_3 H_{-^p\alpha+^q\beta} + hc. \end{aligned} \tag{26}$$

Clearly, the C_3-eigenvalues of the six matrix elements are: $\chi^{C_3} = 1$ for $H_{+^p\alpha+^q\alpha}$ and $H_{+^p\alpha-^q\beta}$; $\chi^{C_3} = e^{-i\frac{2\pi}{3}}$ for $H_{+^p\alpha-^q\alpha}$ and $H_{-^p\alpha+^q\beta}$; $\chi^{C_3} = e^{i\frac{2\pi}{3}}$ for $H_{+^p\alpha+^q\beta}$ and $H_{-^p\alpha-^q\beta}$, so that $\hat{C}_3\hat{H}\hat{C}_3^{-1} = \hat{H}$.

In C_{3v} symmetry, under the action of $\hat{\sigma}_v$,

$$\begin{aligned}\hat{\sigma}_v\hat{H}\hat{\sigma}_v^{-1} = & \left(\left|-^p\beta\right\rangle\left\langle-^q\beta\right| - \left|-^p\alpha\right\rangle\left\langle-^q\alpha\right| + \left|+^q\alpha\right\rangle\left\langle+^p\alpha\right| - \left|+^q\beta\right\rangle\left\langle+^p\beta\right|\right)\hat{\sigma}_v H_{+^p\alpha+^q\alpha} + hc \\ & + \left(\left|-^p\beta\right\rangle\left\langle+^q\beta\right| - \left|-^p\alpha\right\rangle\left\langle+^q\alpha\right| + \left|-^q\alpha\right\rangle\left\langle+^p\alpha\right| - \left|-^q\beta\right\rangle\left\langle+^p\beta\right|\right)\hat{\sigma}_v H_{+^p\alpha-^q\alpha} + hc \\ & + \left(-\left|-^p\beta\right\rangle\left\langle+^q\alpha\right| + \left|-^q\beta\right\rangle\left\langle+^p\alpha\right|\right)\hat{\sigma}_v H_{+^p\alpha-^q\beta} + hc \\ & + \left(-\left|-^p\beta\right\rangle\left\langle-^q\alpha\right| + \left|+^q\beta\right\rangle\left\langle+^p\alpha\right|\right)\hat{\sigma}_v H_{+^p\alpha+^q\beta} + hc \\ & + \left(-\left|+^p\beta\right\rangle\left\langle+^q\alpha\right| + \left|-^q\beta\right\rangle\left\langle-^p\alpha\right|\right)\hat{\sigma}_v H_{-^p\alpha-^q\beta} + hc \\ & + \left(-\left|+^p\beta\right\rangle\left\langle-^q\alpha\right| + \left|+^q\beta\right\rangle\left\langle-^p\alpha\right|\right)\hat{\sigma}_v H_{-^p\alpha+^q\beta} + hc. \end{aligned} \tag{27}$$

Evidently, to have $\hat{\sigma}_v\hat{H}\hat{\sigma}_v^{-1} = \hat{H}$, we need $\hat{\sigma}_v H_{+^p\alpha+^q\alpha} = H^*_{+^p\alpha+^q\alpha}$; $\hat{\sigma}_v H_{+^p\alpha-^q\alpha} = H^*_{+^p\alpha-^q\alpha}$; $\hat{\sigma}_v H_{+^p\alpha-^q\beta} = H^*_{+^p\alpha-^q\beta}$; $\hat{\sigma}_v H_{+^p\alpha+^q\beta} = H^*_{+^p\alpha+^q\beta}$; $\hat{\sigma}_v H_{-^p\alpha-^q\beta} = H^*_{-^p\alpha-^q\beta}$; $\hat{\sigma}_v H_{-^p\alpha+^q\beta} = H^*_{-^p\alpha+^q\beta}$. Therefore, all six independent matrix elements have $(\chi^{\sigma_v}_{Re}, \chi^{\sigma_v}_{Im}) = (1, -1)$.

In D_3 symmetry, under the action of $\hat{C}_2^x$,

$$\begin{aligned}\hat{C}_2^x\hat{H}\left(\hat{C}_2^x\right)^{-1} = & \left(\left|-^p\beta\right\rangle\left\langle-^q\beta\right| - \left|-^p\alpha\right\rangle\left\langle-^q\alpha\right| + \left|+^q\alpha\right\rangle\left\langle+^p\alpha\right| - \left|+^q\beta\right\rangle\left\langle+^p\beta\right|\right)\hat{C}_2^x H_{+^p\alpha+^q\alpha} + hc \\ & + \left(\left|-^p\beta\right\rangle\left\langle+^q\beta\right| - \left|-^p\alpha\right\rangle\left\langle+^q\alpha\right| + \left|-^q\alpha\right\rangle\left\langle+^p\alpha\right| - \left|-^q\beta\right\rangle\left\langle+^p\beta\right|\right)\hat{C}_2^x H_{+^p\alpha-^q\alpha} + hc \\ & + \left(\left|-^p\beta\right\rangle\left\langle+^q\alpha\right| - \left|-^q\beta\right\rangle\left\langle+^p\alpha\right|\right)\hat{C}_2^x H_{+^p\alpha-^q\beta} + hc \\ & + \left(\left|-^p\beta\right\rangle\left\langle-^q\alpha\right| - \left|+^q\beta\right\rangle\left\langle+^p\alpha\right|\right)\hat{C}_2^x H_{+^p\alpha+^q\beta} + hc \\ & + \left(\left|+^p\beta\right\rangle\left\langle+^q\alpha\right| - \left|-^q\beta\right\rangle\left\langle-^p\alpha\right|\right)\hat{C}_2^x H_{-^p\alpha-^q\beta} + hc \\ & + \left(\left|+^p\beta\right\rangle\left\langle-^q\alpha\right| - \left|+^q\beta\right\rangle\left\langle-^p\alpha\right|\right)\hat{C}_2^x H_{-^p\alpha+^q\beta} + hc. \end{aligned} \tag{28}$$

To have $\hat{C}_2^x \hat{H} \left(\hat{C}_2^x\right)^{-1} = \hat{H}$, we need $\hat{C}_2^x H_{+^p\alpha+^q\alpha} = H^*_{+^p\alpha+^q\alpha}$; $\hat{C}_2^x H_{+^p\alpha-^q\alpha} = H^*_{+^p\alpha-^q\alpha}$; $\hat{C}_2^x H_{+^p\alpha-^q\beta} = -H^*_{+^p\alpha-^q\beta}$; $\hat{C}_2^x H_{+^p\alpha+^q\beta} = -H^*_{+^p\alpha+^q\beta}$; $\hat{C}_2^x H_{-^p\alpha-^q\beta} = -H^*_{-^p\alpha-^q\beta}$; $\hat{C}_2^x H_{-^p\alpha+^q\beta} = -H^*_{-^p\alpha+^q\beta}$. Therefore, $\left(\chi_{Re}^{C_2'}, \chi_{Im}^{C_2'}\right) = (1, -1)$ for $H_{+^p\alpha+^q\alpha}$ and $H_{+^p\alpha-^q\alpha}$, and $(-1, 1)$ for $H_{+^p\alpha-^q\beta}$, $H_{+^p\alpha+^q\beta}$, $H_{-^p\alpha-^q\beta}$, and $H_{-^p\alpha+^q\beta}$.

In C_{3h} symmetry, the spatial orbitals are addressed by the prime and double-prime, which are symbolically represented by the superscripts p and q. Under the action of $\hat{\sigma}_h$,

$$\begin{aligned}
\hat{\sigma}_h \hat{H} \hat{\sigma}_h^{-1} = {} & (-1)^{\delta_{pq}+1} \left(|+^p\alpha\rangle \langle +^q\alpha| - |+^p\beta\rangle \langle +^q\beta| + |-^q\beta\rangle \langle -^p\beta| - |-^q\alpha\rangle \langle -^p\alpha|\right) \hat{\sigma}_h H_{+^p\alpha+^q\alpha} + hc \\
& + (-1)^{\delta_{pq}+1} \left(|+^p\alpha\rangle \langle -^q\alpha| - |+^p\beta\rangle \langle -^q\beta| + |+^q\beta\rangle \langle -^p\beta| - |+^q\alpha\rangle \langle -^p\alpha|\right) \hat{\sigma}_h H_{+^p\alpha-^q\alpha} + hc \\
& + (-1)^{\delta_{pq}} \left(|+^p\alpha\rangle \langle -^q\beta| - |+^q\alpha\rangle \langle -^p\beta|\right) \hat{\sigma}_h H_{+^p\alpha-^q\beta} + hc \\
& + (-1)^{\delta_{pq}} \left(|+^p\alpha\rangle \langle +^q\beta| - |-^q\alpha\rangle \langle -^p\beta|\right) \hat{\sigma}_h H_{+^p\alpha+^q\beta} + hc \\
& + (-1)^{\delta_{pq}} \left(|-^p\alpha\rangle \langle -^q\beta| - |+^q\alpha\rangle \langle +^p\beta|\right) \hat{\sigma}_h H_{-^p\alpha-^q\beta} + hc \\
& + (-1)^{\delta_{pq}} \left(|-^p\alpha\rangle \langle +^q\beta| - |-^q\alpha\rangle \langle +^p\beta|\right) \hat{\sigma}_h H_{-^p\alpha+^q\beta} + hc.
\end{aligned} \tag{29}$$

The $(-1)^{\delta_{pq}+1}$ factor with the symbolic Kronecker delta arises from the product of the two E sets' $\hat{\sigma}_h$-parities. This factor becomes $(-1)^{\delta_{pq}}$ when the spin orbitals are different in bra and ket. Clearly, $\chi^{\sigma_h} = (-1)^{\delta_{pq}+1}$ for $H_{+^p\alpha+^q\alpha}$ and $H_{+^p\alpha-^q\alpha}$ and $(-1)^{\delta_{pq}}$ for $H_{+^p\alpha-^q\beta}$, $H_{+^p\alpha+^q\beta}$, $H_{-^p\alpha-^q\beta}$, and $H_{-^p\alpha+^q\beta}$, to give a $\hat{\sigma}_h$-invariant Hamiltonian.

The matrix elements in D_{3h} symmetry must have all four symmetry eigenvalues, $\left(\chi^{C_3}, \left(\chi_{Re}^{C_2'}, \chi_{Im}^{C_2'}\right), \chi^{\sigma_h}\right)$. In D_{3d} symmetry, the orbitals are dressed by the g and u subscripts. The I-parities are still symbolically represented by the p and q superscripts, just for convenience, so that we can still use the Hamiltonian in Eq. 25 in the following derivation. Under the action of $\hat{I}$,

$$\begin{aligned}
\hat{I} \hat{H} \hat{I}^{-1} = {} & (-1)^{\delta_{pq}+1} \left(|+^p\alpha\rangle \langle +^q\alpha| - |+^p\beta\rangle \langle +^q\beta| + |-^q\beta\rangle \langle -^p\beta| - |-^q\alpha\rangle \langle -^p\alpha|\right) \hat{I} H_{+^p\alpha+^q\alpha} + hc \\
& + (-1)^{\delta_{pq}+1} \left(|+^p\alpha\rangle \langle -^q\alpha| - |+^p\beta\rangle \langle -^q\beta| + |+^q\beta\rangle \langle -^p\beta| - |+^q\alpha\rangle \langle -^p\alpha|\right) \hat{I} H_{+^p\alpha-^q\alpha} + hc \\
& + (-1)^{\delta_{pq}+1} \left(|+^p\alpha\rangle \langle -^q\beta| - |+^q\alpha\rangle \langle -^p\beta|\right) \hat{I} H_{+^p\alpha-^q\beta} + hc \\
& + (-1)^{\delta_{pq}+1} \left(|+^p\alpha\rangle \langle +^q\beta| - |-^q\alpha\rangle \langle -^p\beta|\right) \hat{I} H_{+^p\alpha+^q\beta} + hc \\
& + (-1)^{\delta_{pq}+1} \left(|-^p\alpha\rangle \langle -^q\beta| - |+^q\alpha\rangle \langle +^p\beta|\right) \hat{I} H_{-^p\alpha-^q\beta} + hc \\
& + (-1)^{\delta_{pq}+1} \left(|-^p\alpha\rangle \langle +^q\beta| - |-^q\alpha\rangle \langle +^p\beta|\right) \hat{I} H_{-^p\alpha+^q\beta} + hc.
\end{aligned} \tag{30}$$

Evidently, only when $\chi^I = (-1)^{\delta_{pq}+1}$ for all the six matrix elements, the Hamiltonian is $\hat{I}$-invariant. All symmetry eigenvalues of the $(E+E)$-type SOC matrix elements have been derived and they are summarized in the $(E+E)$ block in Table I.

C. $(A+E)$-type Hamiltonian

This is also a common type of inter-shell SOC in trigonal systems.[55] For instance, it can occur in transition metal compounds with E-type orbitals of d_{xz} and d_{yz} character and an A-type orbital of d_{z^2} character. Or similarly, but in main group compounds, between E-type orbitals of p_x and p_y character and an A-type orbital of p_z character.[60,61] $|A\alpha\rangle$ and $|A\beta\rangle$ transform as $E_{1/2}$-type irreps in any trigonal and tetragonal double groups except S_4^2. In the S_4^2 double group, they transform as the $E_{3/2}$ irrep. The SOC matrix in the complex-valued bases adopts the structure in Figure 4(a), which is consistent with the structure in Figure 1(b). WET determines $H_{+\beta A\beta} = -H_{+\alpha A\alpha}$. The time-reversal symmetry determines $H_{+\beta A\beta} = H^*_{-\alpha A\alpha}$. They together lead to $H_{-\alpha A\alpha} = -H^*_{+\alpha A\alpha}$. There is thus only one independent matrix element in the A block of the SOC matrix, and three in the whole matrix.

Expressed using the three independent matrix elements in Figure 4(a), the Hamiltonian reads

$$\begin{aligned}\hat{H} = &\left(|{+\alpha}\rangle\langle A\alpha| - |A\alpha\rangle\langle{-\alpha}| + |A\beta\rangle\langle{-\beta}| - |{+\beta}\rangle\langle A\beta|\right) H_{+\alpha A\alpha} + hc \\ &+ \left(|{+\alpha}\rangle\langle A\beta| - |A\alpha\rangle\langle{-\beta}|\right) H_{+\alpha A\beta} + hc \\ &+ \left(|{-\alpha}\rangle\langle A\beta| - |A\alpha\rangle\langle{+\beta}|\right) H_{-\alpha A\beta} + hc. \end{aligned} \tag{31}$$

Under $\hat{C}_3$,

$$\begin{aligned}\hat{C}_3\hat{H}\hat{C}_3^{-1} = &\, e^{-i\frac{2\pi}{3}}\left(|{+\alpha}\rangle\langle A\alpha| - |A\alpha\rangle\langle{-\alpha}| + |A\beta\rangle\langle{-\beta}| - |{+\beta}\rangle\langle A\beta|\right) \hat{C}_3 H_{+\alpha A\alpha} + hc \\ &+ e^{i\frac{2\pi}{3}}\left(|{+\alpha}\rangle\langle A\beta| - |A\alpha\rangle\langle{-\beta}|\right) \hat{C}_3 H_{+\alpha A\beta} + hc \\ &+ \left(|{-\alpha}\rangle\langle A\beta| - |A\alpha\rangle\langle{+\beta}|\right) \hat{C}_3 H_{-\alpha A\beta} + hc. \end{aligned} \tag{32}$$

Therefore, to have $\hat{C}_3\hat{H}\hat{C}_3^{-1} = \hat{H}$, we need to have $\chi^{C_3} = e^{i\frac{2\pi}{3}}$, $e^{-i\frac{2\pi}{3}}$, and 1 for $H_{+\alpha A\alpha}$, $H_{+\alpha A\beta}$, and $H_{-\alpha A\beta}$, respectively.

In C_{3v} symmetry, the A-type orbital is dressed by a subscript 1 or 2, which is symbolically represented by k. The action of $\hat{\sigma}_v$ transforms the Hamiltonian to

$$\begin{aligned}\hat{\sigma}_v\hat{H}\hat{\sigma}_v^{-1} = &\, (-1)^{\delta_{k2}}\left(|{-\beta}\rangle\langle A_k\beta| - |A_k\beta\rangle\langle{+\beta}| + |A_k\alpha\rangle\langle{+\alpha}| - |{-\alpha}\rangle\langle A_k\alpha|\right) \hat{\sigma}_v H_{+\alpha A_k\alpha} + hc \\ &+ (-1)^{\delta_{k1}}\left(|{-\beta}\rangle\langle A_k\alpha| - |A_k\beta\rangle\langle{+\alpha}|\right) \hat{\sigma}_v H_{+\alpha A_k\beta} + hc \\ &+ (-1)^{\delta_{k1}}\left(|{+\beta}\rangle\langle A_k\alpha| - |A_k\beta\rangle\langle{-\alpha}|\right) \hat{\sigma}_v H_{-\alpha A_k\beta} + hc. \end{aligned} \tag{33}$$

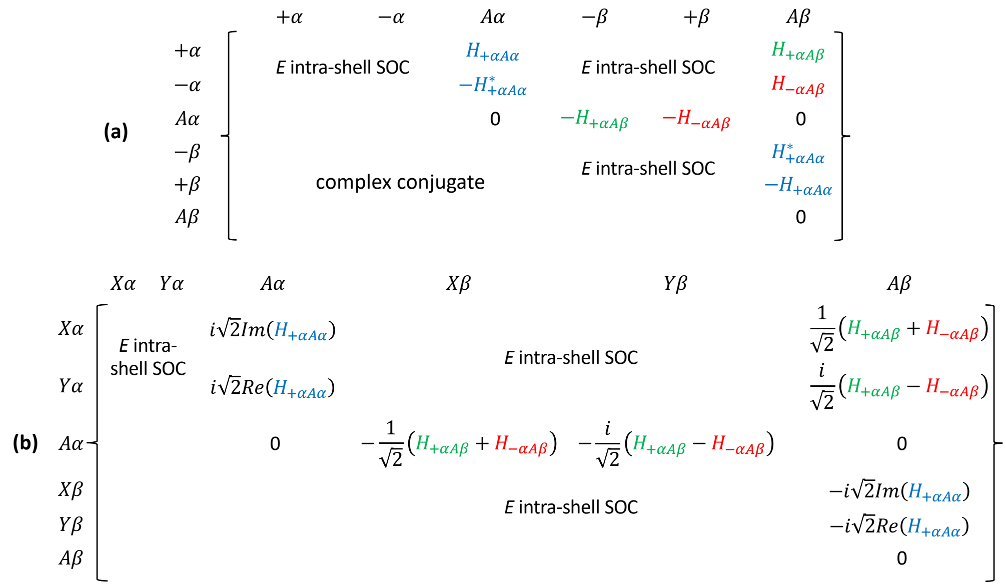

FIG. 4. Structures of the inter-shell spin-orbit coupling matrix between a set of E-type orbitals and an A-type orbital in (a) the complex-valued and (b) the real-valued bases. Only the inter-shell elements in the upper triangle of the matrix are given. The lower triangle is just the complex conjugate of the upper triangle. Matrix elements that are derived from one independent matrix element by time-reversal symmetry and WET are given in the same color. The blocks of the E-type intra-shell SOC matrix elements are indicated by text and they take the same structure as in Figure 2(a).

$\hat{\sigma}_v \hat{H} \hat{\sigma}_v^{-1} = \hat{H}$ requires $\hat{\sigma}_v H_{+\alpha A_k \alpha} = (-1)^{\delta_{k2}} H^*_{+\alpha A_k \alpha}$; $\hat{\sigma}_v H_{+\alpha A_k \beta} = (-1)^{\delta_{k2}} H^*_{+\alpha A_k \beta}$; $\hat{\sigma}_v H_{-\alpha A_k \beta} = (-1)^{\delta_{k2}} H^*_{-\alpha A_k \beta}$. Therefore, $(\chi_{Re}^{\sigma_v}, \chi_{Im}^{\sigma_v}) = \left((-1)^{\delta_{k2}}, (-1)^{\delta_{k1}}\right)$ for all three matrix elements.

In D_3 symmetry,

$$\begin{aligned} \hat{C}_2^x \hat{H} \left(\hat{C}_2^x\right)^{-1} &= (-1)^{\delta_{k2}} \left(\left|-\beta\right\rangle \left\langle A_k\beta\right| - \left|A_k\beta\right\rangle \left\langle +\beta\right| + \left|A_k\alpha\right\rangle \left\langle +\alpha\right| - \left|-\alpha\right\rangle \left\langle A_k\alpha\right|\right) \hat{C}_2^x H_{+\alpha A_k \alpha} + hc \\ &+ (-1)^{\delta_{k2}} \left(\left|-\beta\right\rangle \left\langle A_k\alpha\right| - \left|A_k\beta\right\rangle \left\langle +\alpha\right|\right) \hat{C}_2^x H_{+\alpha A_k \beta} + hc \\ &+ (-1)^{\delta_{k2}} \left(\left|+\beta\right\rangle \left\langle A_k\alpha\right| - \left|A_k\beta\right\rangle \left\langle -\alpha\right|\right) \hat{C}_2^x H_{-\alpha A_k \beta} + hc. \end{aligned} \quad (34)$$

$\hat{C}_2^x \hat{H} \left(\hat{C}_2^x\right)^{-1} = \hat{H}$ requires $\left(\chi_{Re}^{C_2'}, \chi_{Im}^{C_2'}\right) = \left((-1)^{\delta_{k2}}, (-1)^{\delta_{k1}}\right)$ for $H_{+\alpha A_k \alpha}$ and $\left((-1)^{\delta_{k1}}, (-1)^{\delta_{k2}}\right)$ for $H_{+\alpha A_k \beta}$ and $H_{-\alpha A_k \beta}$.

In C_{3h} symmetry, the $(E+A)$-type SO Hamiltonian reads

$$\begin{aligned}\hat{H} &= \left(\left|+^{p}\alpha\right\rangle\left\langle A^{q}\alpha\right| - \left|A^{q}\alpha\right\rangle\left\langle -^{p}\alpha\right| + \left|A^{q}\beta\right\rangle\left\langle -^{p}\beta\right| - \left|+^{p}\beta\right\rangle\left\langle A^{q}\beta\right|\right) H_{+^{p}\alpha A^{q}\alpha} + hc \\ &+ \left(\left|+^{p}\alpha\right\rangle\left\langle A^{q}\beta\right| - \left|A^{q}\alpha\right\rangle\left\langle -^{p}\beta\right|\right) H_{+^{p}\alpha A^{q}\beta} + hc \\ &+ \left(\left|-^{p}\alpha\right\rangle\left\langle A^{q}\beta\right| - \left|A^{q}\alpha\right\rangle\left\langle +^{p}\beta\right|\right) H_{-^{p}\alpha A^{q}\beta} + hc.\end{aligned} \tag{35}$$

p and q denote the $'$ and $''$ σ_h-parities. Under the action of $\hat{\sigma}_h$,

$$\begin{aligned}\hat{\sigma}_h\hat{H}\hat{\sigma}_h^{-1} &= (-1)^{\delta_{pq}+1}\left(\left|+^{p}\alpha\right\rangle\left\langle A^{q}\alpha\right| - \left|A^{q}\alpha\right\rangle\left\langle -^{p}\alpha\right| + \left|A^{q}\beta\right\rangle\left\langle -^{p}\beta\right| - \left|+^{p}\beta\right\rangle\left\langle A^{q}\beta\right|\right)\hat{\sigma}_h H_{+^{p}\alpha A^{q}\alpha} + hc \\ &+ (-1)^{\delta_{pq}}\left(\left|+^{p}\alpha\right\rangle\left\langle A^{q}\beta\right| - \left|A^{q}\alpha\right\rangle\left\langle -^{p}\beta\right|\right)\hat{\sigma}_h H_{+^{p}\alpha A^{q}\beta} + hc \\ &+ (-1)^{\delta_{pq}}\left(\left|-^{p}\alpha\right\rangle\left\langle A^{q}\beta\right| - \left|A^{q}\alpha\right\rangle\left\langle +^{p}\beta\right|\right)\hat{\sigma}_h H_{-^{p}\alpha A^{q}\beta} + hc.\end{aligned} \tag{36}$$

To have $\hat{\sigma}_h\hat{H}\hat{\sigma}_h^{-1} = \hat{H}$, we need $\chi^{\sigma_h} = (-1)^{\delta_{pq}+1}$ for $H_{+^{p}\alpha A^{q}\alpha}$ and $(-1)^{\delta_{pq}}$ for $H_{+^{p}\alpha A^{q}\beta}$ and $H_{-^{p}\alpha A^{q}\beta}$. The $(E+A)$-type Hamiltonians in D_{3h} symmetry simply adopt all four symmetry eigenvalues, $\left(\chi^{C_3}, \left(\chi^{C_2'}_{Re}, \chi^{C_2'}_{Im}\right), \chi^{\sigma_h}\right)$.

In D_{3d} symmetry, the $(E+A)$-type SO Hamiltonian reads

$$\begin{aligned}\hat{H} &= \left(\left|+_{p}\alpha\right\rangle\left\langle A_{kq}\alpha\right| - \left|A_{kq}\alpha\right\rangle\left\langle -_{p}\alpha\right| + \left|A_{kq}\beta\right\rangle\left\langle -_{p}\beta\right| - \left|+_{p}\beta\right\rangle\left\langle A_{kq}\beta\right|\right) H_{+_{p}\alpha A_{kq}\alpha} + hc \\ &+ \left(\left|+_{p}\alpha\right\rangle\left\langle A_{kq}\beta\right| - \left|A_{kq}\alpha\right\rangle\left\langle -_{p}\beta\right|\right) H_{+_{p}\alpha A_{kq}\beta} + hc \\ &+ \left(\left|-_{p}\alpha\right\rangle\left\langle A_{kq}\beta\right| - \left|A_{kq}\alpha\right\rangle\left\langle +_{p}\beta\right|\right) H_{-_{p}\alpha A_{kq}\beta} + hc.\end{aligned} \tag{37}$$

p and q denote the g and u I-parities.

$$\begin{aligned}\hat{I}\hat{H}\hat{I}^{-1} &= (-1)^{\delta_{pq}+1}\left(\left|+_{p}\alpha\right\rangle\left\langle A_{kq}\alpha\right| - \left|A_{kq}\alpha\right\rangle\left\langle -_{p}\alpha\right| + \left|A_{kq}\beta\right\rangle\left\langle -_{p}\beta\right| - \left|+_{p}\beta\right\rangle\left\langle A_{kq}\beta\right|\right)\hat{I} H_{+_{p}\alpha A_{kq}\alpha} + hc \\ &+ (-1)^{\delta_{pq}+1}\left(\left|+_{p}\alpha\right\rangle\left\langle A_{kq}\beta\right| - \left|A_{kq}\alpha\right\rangle\left\langle -_{p}\beta\right|\right)\hat{I} H_{+_{p}\alpha A_{kq}\beta} + hc \\ &+ (-1)^{\delta_{pq}+1}\left(\left|-_{p}\alpha\right\rangle\left\langle A_{kq}\beta\right| - \left|A_{kq}\alpha\right\rangle\left\langle +_{p}\beta\right|\right)\hat{I} H_{-_{p}\alpha A_{kq}\beta} + hc.\end{aligned} \tag{38}$$

To have $\hat{I}\hat{H}\hat{I}^{-1} = \hat{H}$, we need $\chi^{I} = (-1)^{\delta_{pq}+1}$ for all three matrix elements. All the symmetry eigenvalues derived in this section are summarized in the $E+A$ block of Table I.

D. $(A+A)$-type Hamiltonian

SOC between two A-type orbitals is less common than the others. But it can occur, e.g., in coupling the $f_{x^3-3xy^2}$ and $f_{y^3-3yx^2}$ orbitals of an f-block atom at the trigonal center (exemplified in Figure 5(a)). This coupling is induced by the $\hat{z}^{(1)}_{eff,z}\hat{s}_z$ component in the dot product operator in Eq. 10. As mentioned in the end of Section IV B, matrix elements of this type of coupling appear in the A block. At any undistorted trigonal structures, the $\hat{z}^{(1)}_{eff,x}\hat{s}_x$ and $\hat{z}^{(1)}_{eff,y}\hat{s}_y$ components cannot couple any A-type orbitals, because $\hat{z}^{(1)}_{eff,x}$ and $\hat{z}^{(1)}_{eff,y}$ belong to an E-type irrep, which is not contained by the direct product of two A-type irreps. However, this symmetry argument does not hold when the structure is distorted by JT/pJT interaction, which is our main concern. For instance, the two A-type orbitals shown in Figure 5(b) are composed of peripheral p orbitals in a D_{3h} framework. At the undistorted trigonal structure, the $\hat{z}^{(1)}_{eff,x}$ and $\hat{z}^{(1)}_{eff,y}$ matrix elements of the orbitals are zero due to cancellation of the contributions from the three peripheral atoms. As the structure is distorted along an e mode, the exact cancellation is alleviated, resulting in nonzero SOC. This type of coupling contributes elements in the B block. With all these considerations, we should not leave behind the $(A + A)$-type SOC.

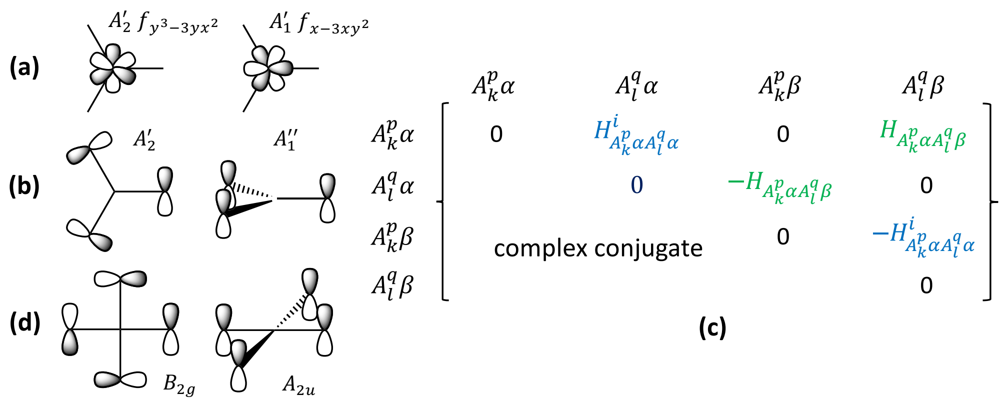

FIG. 5. (a) $f_{y^3-3yx^2}$ and $f_{x^3-3xy^2}$ orbitals at the center of a D_{3h} framework, with their irrep symbols; (b) two A-type orbitals that can have nonzero SOC along e' distortion from the D_{3h} structure; (c) structures of the inter-shell spin-orbit coupling matrix between two A-type orbitals. The lower triangle in (c) is just the complex conjugate of the upper triangle. Matrix elements that are derived from one independent matrix element by time-reversal symmetry and WET are given in the same color. The trivial zero A-type intra-shell SOC matrix elements are also given; (d) a B- and an A-type orbital that can have nonzero SOC along e_u distortion from the D_{4h} structure.

The $(A + A)$-type SOC matrix adopts the structure in Figure 5(b), with the A and B blocks each containing one element. k and l denote the 1 and 2 parities, and p and q the $'$ and $''$ parities and g and u parities, whenever the parities are applicable. WET determines $H_{A^p_k\beta A^q_l\beta} = -H_{A^p_k\alpha A^q_l\alpha}$. The time-reversal symmetry determines $H_{A^p_k\beta A^q_l\beta} = \left(H_{A^p_k\alpha A^q_l\alpha}\right)^*$. These two equalities determine $H_{A^p_k\alpha A^q_l\alpha}$ to be purely imaginary, which is denoted by the superscript i in Figure 5(c). The $(A+A)$-type SOC Hamiltonian reads

$$\hat{H} = \left(\left|A_k^p\alpha\right\rangle\left\langle A_l^q\alpha\right| + \left|A_l^q\beta\right\rangle\left\langle A_k^p\beta\right| - \left|A_l^q\alpha\right\rangle\left\langle A_k^p\alpha\right| - \left|A_k^p\beta\right\rangle\left\langle A_l^q\beta\right|\right) H^i_{A_k^p\alpha A_l^q\alpha} + \left(\left|A_k^p\alpha\right\rangle\left\langle A_l^q\beta\right| - \left|A_l^q\alpha\right\rangle\left\langle A_k^p\beta\right|\right) H_{A_k^p\alpha A_l^q\beta} + hc. \tag{39}$$

Under the action of $\hat{C}_3$, the Hamiltonian becomes

$$\hat{C}_3\hat{H}\hat{C}_3^{-1} = \left(\left|A_k^p\alpha\right\rangle\left\langle A_l^q\alpha\right| + \left|A_l^q\beta\right\rangle\left\langle A_k^p\beta\right| - \left|A_l^q\alpha\right\rangle\left\langle A_k^p\alpha\right| - \left|A_k^p\beta\right\rangle\left\langle A_l^q\beta\right|\right) \hat{C}_3 H^i_{A_k^p\alpha A_l^q\alpha} + e^{-i\frac{2\pi}{3}}\left(\left|A_k^p\alpha\right\rangle\left\langle A_l^q\beta\right| - \left|A_l^q\alpha\right\rangle\left\langle A_k^p\beta\right|\right) \hat{C}_3 H_{A_k^p\alpha A_l^q\beta} + hc. \tag{40}$$

To have $\hat{C}_3\hat{H}\hat{C}_3^{-1} = \hat{H}$, we need $\chi^{C_3} = 1$ and $e^{i\frac{2\pi}{3}}$ for $H^i_{A_k^p\alpha A_l^q\alpha}$ and $H_{A_k^p\alpha A_l^q\beta}$, respectively.

In C_{3v} symmetry, $\hat{\sigma}_v$ transforms the Hamiltonian to

$$\hat{\sigma}_v\hat{H}\hat{\sigma}_v^{-1} = (-1)^{\delta_{kl}+1}\left(\left|A_k^p\beta\right\rangle\left\langle A_l^q\beta\right| + \left|A_l^q\alpha\right\rangle\left\langle A_k^p\alpha\right| - \left|A_l^q\beta\right\rangle\left\langle A_k^p\beta\right| - \left|A_k^p\alpha\right\rangle\left\langle A_l^q\alpha\right|\right) \hat{\sigma}_v H^i_{A_k^p\alpha A_l^q\alpha} + (-1)^{\delta_{kl}}\left(\left|A_k^p\beta\right\rangle\left\langle A_l^q\alpha\right| - \left|A_l^q\beta\right\rangle\left\langle A_k^p\alpha\right|\right) \hat{\sigma}_v H_{A_k^p\alpha A_l^q\beta} + hc. \tag{41}$$

In order to have $\hat{\sigma}_v\hat{H}\hat{\sigma}_v^{-1} = \hat{H}$, the matrix elements need to satisfy $\hat{\sigma}_v H^i_{A_k^p\alpha A_l^q\alpha} = (-1)^{\delta_{kl}+1} H^i_{A_k^p\alpha A_l^q\alpha}$ and $\hat{\sigma}_v H_{A_k^p\alpha A_l^q\beta} = (-1)^{\delta_{kl}+1} H^*_{A_k^p\alpha A_l^q\beta}$, i.e., $(\chi^{\sigma_v}_{Re}, \chi^{\sigma_v}_{Im}) = \left(0, (-1)^{\delta_{kl}+1}\right)$ and $\left((-1)^{\delta_{kl}+1}, (-1)^{\delta_{kl}}\right)$ for the two elements, respectively. Similar to the $\chi_{Im} = 0$ cases above, $\chi_{Re} = 0$ arises from that the element is purely imaginary.

In D_3 symmetry, $\hat{C}_2^x$ transforms the Hamiltonian to

$$\hat{C}_2^x\hat{H}\left(\hat{C}_2^x\right)^{-1} = (-1)^{\delta_{kl}+1}\left(\left|A_k^p\beta\right\rangle\left\langle A_l^q\beta\right| + \left|A_l^q\alpha\right\rangle\left\langle A_k^p\alpha\right| - \left|A_l^q\beta\right\rangle\left\langle A_k^p\beta\right| - \left|A_k^p\alpha\right\rangle\left\langle A_l^q\alpha\right|\right) \hat{C}_2^x H^i_{A_k^p\alpha A_l^q\alpha} + (-1)^{\delta_{kl}+1}\left(\left|A_k^p\beta\right\rangle\left\langle A_l^q\alpha\right| - \left|A_l^q\beta\right\rangle\left\langle A_k^p\alpha\right|\right) \hat{C}_2^x H_{A_k^p\alpha A_l^q\beta} + hc. \tag{42}$$

In order to have $\hat{C}_2^x\hat{H}\left(\hat{C}_2^x\right)^{-1} = \hat{H}$, we need $\hat{C}_2^x H^i_{A_k^p\alpha A_l^q\alpha} = (-1)^{\delta_{kl}+1} H^i_{A_k^p\alpha A_l^q\alpha}$ and $\hat{C}_2^x H_{A_k^p\alpha A_l^q\beta} = (-1)^{\delta_{kl}} H^*_{A_k^p\alpha A_l^q\beta}$, i.e., $\left(\chi^{C_2'}_{Re}, \chi^{C_2'}_{Im}\right) = \left(0, (-1)^{\delta_{kl}+1}\right)$ and $\left((-1)^{\delta_{kl}}, (-1)^{\delta_{kl}+1}\right)$ for the two elements, respectively.

In C_{3h} symmetry, $\hat{\sigma}_h$ transforms $\hat{H}$ to

$$\hat{\sigma}_h\hat{H}\hat{\sigma}_h^{-1} = (-1)^{\delta_{pq}+1}\left(\left|A_k^p\alpha\right\rangle\left\langle A_l^q\alpha\right| + \left|A_l^q\beta\right\rangle\left\langle A_k^p\beta\right| - \left|A_l^q\alpha\right\rangle\left\langle A_k^p\alpha\right| - \left|A_k^p\beta\right\rangle\left\langle A_l^q\beta\right|\right) \hat{\sigma}_h H^i_{A_k^p\alpha A_l^q\alpha} + (-1)^{\delta_{pq}}\left(\left|A_k^p\alpha\right\rangle\left\langle A_l^q\beta\right| - \left|A_l^q\alpha\right\rangle\left\langle A_k^p\beta\right|\right) \hat{\sigma}_h H_{A_k^p\alpha A_l^q\beta} + hc. \tag{43}$$

In order to have $\hat{\sigma}_h\hat{H}\hat{\sigma}_h^{-1} = \hat{H}$, we need $\hat{\sigma}_h H^i_{A_k^p\alpha A_l^q\alpha} = (-1)^{\delta_{pq}+1} H_{A_k^p\alpha A_l^q\alpha}$ and $\hat{\sigma}_h H_{A_k^p\alpha A_l^q\beta} = (-1)^{\delta_{pq}} H_{A_k^p\alpha A_l^q\beta}$, i.e., $\chi^{\sigma_h} = (-1)^{\delta_{pq}+1}$ and $(-1)^{\delta_{pq}}$ for the two elements, respectively.

Matrix elements in D_{3h} symmetry need to be characterized by all four (three sets of) symmetry eigenvalues. In D_{3d} symmetry, $\hat{I}$ transforms the Hamiltonian to

$$\hat{I}\hat{H}\hat{I}^{-1} = (-1)^{\delta_{pq}+1} \left(|A_k^p\alpha\rangle \langle A_l^q\alpha| + |A_l^q\beta\rangle \langle A_k^p\beta| - |A_l^q\alpha\rangle \langle A_k^p\alpha| - |A_k^p\beta\rangle \langle A_l^q\beta| \right) \hat{I}H^i_{A_k^p\alpha A_l^q\alpha} + (-1)^{\delta_{pq}+1} \left(|A_k^p\alpha\rangle \langle A_l^q\beta| - |A_l^q\alpha\rangle \langle A_k^p\beta| \right) \hat{I}H_{A_k^p\alpha A_l^q\beta} + hc. \quad (44)$$

Evidently, we need $\chi^I = (-1)^{\delta_{pq}+1}$ for both elements. All symmetry eigenvalues of the $(A + A)$-type SOC matrix elements have been derived and they are summarized in the $(A + A)$ block in Table I.

E. The Table of Symmetry Eigenvalues

Table I is the central contribution of this work. This table allows us to identify symmetry eigenvalues of matrix elements of all bimodal SO JT/pJT problems in trigonal symmetries. When E-type orbitals are involved, the symmetry eigenvalues are for the elements in the complex-valued E components. In practice, quantum chemistry calculations generate data for real-valued E components. To facilitate the use of our expansion formulas in actual simulations, the structures of the SOC matrices in the real-valued E orbitals representations are also given in Figures 2 to 4. The matrices in the complex-valued spinors are more relevant to systems with strong SO interaction, since the spinors are symmetry-adapted for the relevant double groups. The matrices in the real-valued spin orbitals are more relevant to systems with weak to intermediate SO interaction, since the real-valued spatial orbitals are adapted for the relevant point groups.

VI. HAMILTONIAN STRUCTURES AND SYMMETRY EIGENVALUES FOR TETRAGONAL SYSTEMS

Symmetry-wise, the spatial orbitals in tetragonal and trigonal symmetries ONLY differ in their C_n-eigenvalues. *Consequently, the results derived above for trigonal problems, which are obtained without explicitly consideration of C_3-eigenvalues, are directly applicable to tetragonal problems.* These results include the matrix structures in Figures 2 to 4, the σ_v-eigenvalues, the C_2-eigenvalues, and the I-eigenvalues. In short, the only additional derivation for tetragonal SOC problems is to obtain C_4- and S_4-eigenvalues of the relevant independent matrix elements.

TABLE I. The eigenvalues of symmetry operators of the independent elements in trigonal and tetragonal vibronic Hamiltonian matrices. The σ_v- and C_2-eigenvalues are given for the real and imaginary parts of the matrix elements separately. The heading $(E+E)$ means the matrix elements underneath are relevant to the $(E+E)$ problems, etc. k and l stand for the 1 and 2 subscripts when σ_v or C_2' are relevant. p and q stand for the $'$ and $''$ superscripts when σ_h is relevant. Although p and q are placed as superscripts, they also stand for possible g and u subscripts when I is relevant.

		$\chi^{C_3\,a}$	$\chi^{C_4\,b}$	χ^{S_4}	$(\chi^{\sigma_v}_{Re}, \chi^{\sigma_v}_{Im})^c$	$\left(\chi^{C_2'}_{Re}, \chi^{C_2'}_{Im}\right)^d$	$(\chi^{\sigma_h})^e$	$(\chi^I)^f$
E	$H^r_{+\alpha+\alpha}$	1	1	1	$(1,0)$	$(1,0)$	1	1
	$H_{+\alpha+\beta}$	$e^{i\frac{2\pi}{3}}$	i	$-i$	$(1,-1)$	$(-1,1)$	-1	1
$(E+E)^g$	$H_{+^p\alpha+^q\alpha}$	1	1	1	$\left(1,-1\right)$	$\left(1,-1\right)$	$\left((-1)^{\delta_{pq}+1}\right)$	$\left((-1)^{\delta_{pq}+1}\right)$
	$H_{+^p\alpha-^q\alpha}$	$e^{-i\frac{2\pi}{3}}$	-1	-1				
	$H_{+^p\alpha-^q\beta}$	1	$-i$	i		$\left(-1,1\right)$	$\left((-1)^{\delta_{pq}}\right)$	
	$H_{+^p\alpha+^q\beta}$	$e^{i\frac{2\pi}{3}}$	i	$-i$				
	$H_{-^p\alpha-^q\beta}$	$e^{i\frac{2\pi}{3}}$	i	$-i$				
	$H_{-^p\alpha+^q\beta}$	$e^{-i\frac{2\pi}{3}}$	$-i$	i				
$(E+A)^g$	$H_{+^p\alpha A^q_k\alpha}$	$e^{i\frac{2\pi}{3}}$	i	i	$\left((-1)^{\delta_{k2}},(-1)^{\delta_{k1}}\right)$	$\left((-1)^{\delta_{k2}},(-1)^{\delta_{k1}}\right)$	$(-1)^{\delta_{pq}+1}$	$\left((-1)^{\delta_{pq}+1}\right)$
	$H_{+^p\alpha A^q_k\beta}$	$e^{-i\frac{2\pi}{3}}$	-1	1		$\left((-1)^{\delta_{k1}},(-1)^{\delta_{k2}}\right)$	$\left((-1)^{\delta_{pq}}\right)$	
	$H_{-^p\alpha A^q_k\beta}$	1	1	-1				
$(A+A)^g$	$H^i_{A^p_k\alpha A^q_l\alpha}$	1	1	1	$\left(0,(-1)^{\delta_{kl}+1}\right)$	$\left(0,(-1)^{\delta_{kl}+1}\right)$	$(-1)^{\delta_{pq}+1}$	$\left((-1)^{\delta_{pq}+1}\right)$
	$H_{A^p_k\alpha A^q_l\beta}$	$e^{i\frac{2\pi}{3}}$	i	$-i$	$\left((-1)^{\delta_{kl}+1},(-1)^{\delta_{kl}}\right)$	$\left((-1)^{\delta_{kl}},(-1)^{\delta_{kl}+1}\right)$	$(-1)^{\delta_{pq}}$	
$(E+B)^g$	$H_{+^p\alpha B^q_k\alpha}$		$-i$	$-i$	$\left((-1)^{\delta_{k2}},(-1)^{\delta_{k1}}\right)$	$\left((-1)^{\delta_{k2}},(-1)^{\delta_{k1}}\right)$	$(-1)^{\delta_{pq}+1}$	$\left((-1)^{\delta_{pq}+1}\right)$
	$H_{+^p\alpha B^q_k\beta}$		1	-1		$\left((-1)^{\delta_{k1}},(-1)^{\delta_{k2}}\right)$	$\left((-1)^{\delta_{pq}}\right)$	
	$H_{-^p\alpha B^q_k\beta}$		-1	1				
$(B+B)^g$	$H^i_{B^p_k\alpha B^q_l\alpha}$		1	1	$\left(0,(-1)^{\delta_{kl}+1}\right)$	$\left(0,(-1)^{\delta_{kl}+1}\right)$	$(-1)^{\delta_{pq}+1}$	$\left((-1)^{\delta_{pq}+1}\right)$
	$H_{B^p_k\alpha B^q_l\beta}$		i	$-i$	$\left((-1)^{\delta_{kl}+1},(-1)^{\delta_{kl}}\right)$	$\left((-1)^{\delta_{kl}},(-1)^{\delta_{kl}+1}\right)$	$(-1)^{\delta_{pq}}$	
$(A+B)^g$	$H^i_{A^p_k\alpha B^q_l\alpha}$		-1	-1	$\left(0,(-1)^{\delta_{kl}+1}\right)$	$\left(0,(-1)^{\delta_{kl}+1}\right)$	$(-1)^{\delta_{pq}+1}$	$\left((-1)^{\delta_{pq}+1}\right)$
	$H_{A^p_k\alpha B^q_l\beta}$		$-i$	i	$\left((-1)^{\delta_{kl}+1},(-1)^{\delta_{kl}}\right)$	$\left((-1)^{\delta_{kl}},(-1)^{\delta_{kl}+1}\right)$	$(-1)^{\delta_{pq}}$	

[a] Applicable for trigonal symmetries. [b] Applicable for tetragonal symmetries except S_4. [c] Applicable for C_{3v} and C_{4v} problems. $\chi^{\sigma_v}_{Im} = 0$ ($\chi^{\sigma_v}_{Re} = 0$) means only the real (imaginary) part of the expansion formula formula is taken. [d] Applicable for D_3, D_{3h}, D_{3d}, D_4, D_{2d}, and D_{4h} problems. $\chi^{C_2'}_{Im} = 0$ ($\chi^{C_2'}_{Re} = 0$) means only the real (imaginary) part of the expansion is taken. [e] Applicable for C_{3h} and D_{3h} problems. [f] Applicable for D_{3d}, C_{4h}, and D_{4h} problems. [g] The superscripts p and q represent the prime and double-prime in C_{3h} and D_{3h} symmetries. The also represent the g and u *subscripts* in D_{3d}, C_{4h}, and D_{4h} symmetries. For $(A+A)$-, $(E+E)$-, and $(B+B)$-type (only applicable for tetragonal symmetries) problems in C_3, C_{3v}, D_3, C_4, S_4, C_{4v}, D_4, and D_{2d} symmetries, they simply denote the two sets of orbitals that transform as the same irrep.

The orbitals with $\chi^{C_4} = 1, -1, (i, -i)$ transform as A-, B-, and E-type irreps in tetragonal symmetries, respectively. Given the extra B-type irrep, there are the following additional types of SOC in tetragonal symmetries: B intra-shell coupling, $(A+B)$, $(B+B)$, and $(B+E)$ inter-shell coupling. $|B\alpha\rangle$ and $|B\beta\rangle$ transform as $E_{3/2}$-type irreps in any tetragonal double groups except S_4^2, in which as the $E_{1/2}$ irrep. With the real-valued $\chi^{C_4} = -1$, B-type orbitals can always be taken real-valued, just like A-type orbitals. Therefore, the B-type intra-shell SOC is null. The $(B+E)$ inter-shell coupling adopts the same matrix form as the $(A+E)$ coupling in Figure 4, only with the A orbital label being replaced by B. An example of the $(B+E)$ coupling is between a d_{xy} orbital (or $d_{x^2-y^2}$ orbital) and a (d_{xz}, d_{yz}) set of orbitals at a tetragonal center. The $(A+B)$ and $(B+B)$ couplings adopt the same matrix form as the $(A+A)$ coupling in Figure 5(c), only with one and both A orbital labels being replaced by B, respectively. The $(B+B)$ inter-shell coupling is commonly seen between a $d_{x^2-y^2}$ orbital and a d_{xy} orbital at a tetragonal center. A- and B-type orbitals that can be SO coupled through e-type distortion are exemplified in Figure 5(d).

The C_4-eigenvalues of the tetragonal matrix elements are derived in a similar way as for the C_3-eigenvalues above. Skipping the details, the resultant C_4-eigenvalues are all summarized in Table I. It is not accidental that the χ^{C_4}s of the $(E+A)$ and $(E+B)$ tetragonal problems differ by a sign change, and so do those of the $(A+A)$ and $(A+B)$ tetragonal problems. This is related to the $\chi^{C_4} = 1$ and -1 for A- and B-type orbitals, respectively. Also, the $(A+A)$ and $(B+B)$ type problems share the same χ^{C_4}s, since the sign changes of the two B-type orbitals cancel. We note again that the same set of σ_v-, C_2-, and I-eigenvalues are shared by the same type of trigonal and tetragonal problems. The $(E+A)$ and $(E+B)$ tetragonal problems share the same set of σ_v-, C_2-, and I-eigenvalues, since the two types of problems only differ in χ^{C_4}s of their independent matrix elements. For the same reason, The $(A+A)$, $(A+B)$ and $(B+B)$ tetragonal problems share the same set of σ_v-, C_2-, and I-eigenvalues.

Summarized in Table I are also S_4-eigenvalues, which are relevant for problems in S_4 symmetry. The C_4^2 and S_4^2 double groups are isomorphic. However, the C_4- and S_4-eigenvalues are not all identical. Those for the B block elements have opposite signs. The fundamental reason for this difference is that the α and β spin functions transform as the $E_{1/2}$ irrep in the C_4^2 double group, while as the $E_{3/2}$ irrep in the S_4^2 double group. This is because the $\hat{\sigma}_h$ hidden in the $\hat{S}_4$ operator brings an extra rotation of π to the spin functions. Consequently, the action of $\hat{S}_4$ on the $|\alpha\rangle\langle\beta|$ dyad results in an extra -1 factor compared to the action of $\hat{C}_4$. All derivation work in this study has been finished. Again, Table I is our central contribution.

VII. EXPANSION FORMULAS AND COMPARISONS WITH PREVIOUS RESULTS

All bimodal expansion formulas that feature the symmetry eigenvalues summarized in Table I, except $\left(\chi_{Re}^{\sigma_v,C_2'}, \chi_{Im}^{\sigma_v,C_2'}\right) = (0, \pm 1)$, have been derived before in the context of non-SO pJT/JT interactions in trigonal[63,67] and tetragonal[65] symmetries. The trigonal formulas are summarized in Tables S.I to S.VI in Section S.III, and the tetragonal formulas in Tables S.VII to S.XV in Section S.IV. Given the symmetry eigenvalues in Table I, one can easily look up symmetry-adapted expansions for a specific SO JT/pJT problem. Here we use three examples to show how to obtain expansion formulas for specific SO pJT/JT problems, and compare our formulas with those obtained in previous studies.

A. $(E + A_1) \otimes (e + a_1)$ in C_{3v} Symmetry

This specific SO pJT problem is considered because the expansions of its matrix elements were derived in Ref. 61. Comparison with those results confirms the correctness of our general formalism.

In Figure 4 we see that there are three independent matrix elements for this problem: $H_{+\alpha A_1\alpha}$, $H_{+\alpha A_1\beta}$, and $H_{-\alpha A_1\beta}$. From Table I, we see that $\left(\chi^{C_3}, (\chi_{Re}^{\sigma_v}, \chi_{Im}^{\sigma_v})\right) = \left(e^{i\frac{2\pi}{3}}, (1, -1)\right)$, $\left(e^{-i\frac{2\pi}{3}}, (1, -1)\right)$, and $(1, (1, -1))$ for the three elements in order. $\chi^{C_3} = e^{i\frac{2\pi}{3}}$ of $H_{+\alpha A_1\alpha}$ directs us to Table S.II, whose $(e + a)$-row gives the root expansion:

$$H_{+\alpha A\alpha} = \rho^{|3n-1|+2K} \left[b_{I_1,2K}^{r,3n-1} z^{I_1} \cos((3n-1)\phi) - b_{I_2,2K}^{i,3n-1} z^{I_2} \sin((3n-1)\phi) + i \left(b_{I_1,2K}^{r,3n-1} z^{I_1} \sin((3n-1)\phi) + b_{I_2,2K}^{i,3n-1} z^{I_2} \cos((3n-1)\phi)\right)\right] \quad (45)$$

Throughout this work, all summation (power) indices that are in the absolute value symbol take all integer values, while the others only take nonnegative integer values. Also, Einstein's convention of summing over duplicate indices is followed. In the expansion formula, the subscript 1 of the a_1 orbital has been dropped because this is the expansion in the lowest (in correspondence to "root") C_3 symmetry among all trigonal symmetries. $\chi^{C_3} = e^{i\frac{2\pi}{3}}$ also directs us to Table S.IV, and the $(e + a_1)$-$(1, -1)$ entry there is "b^r nz", i.e., only the terms with the b^r coefficients in Eq. 45 shall be nonzero. Therefore, the final expansion for $H_{+\alpha A_1\alpha}$ is obtained:

$$H_{+\alpha A_1 \alpha} = b^{r,3n-1}_{I_1,2K} z^{I_1} \rho^{|3n-1|+2K} e^{i(3n-1)\phi} \tag{46}$$

The symmetry eigenvalues of $H_{+\alpha A_1\beta}$ are identical to those of $H_{+\alpha A_1\alpha}$ except for the χ^{C_3} takes the complex conjugate. Therefore, the $H_{+\alpha A_1\beta}$ expansion takes the complex conjugate of the $H_{+\alpha A_1\alpha}$ expansion:

$$H_{+\alpha A_1 \beta} = c^{r,3n-1}_{I_1,2K} z^{I_1} \rho^{|3n-1|+2K} e^{-i(3n-1)\phi}. \tag{47}$$

Please note that the expansion formulas of $H_{+\alpha A_1\alpha}$ and $H_{+\alpha A_1\beta}$ are connected by taking complex conjugate. The coefficients in the two expansions are not correlated. That is why we use c^r to label the coefficients in the $H_{+\alpha A_1\beta}$ expansion.

The $\chi^{C_3} = 1$ of $H_{-\alpha A_1\beta}$ directs us to Table S.I, whose $(e + a)$ row gives the root expansion

$$\begin{aligned} H_{-\alpha A\beta} = \rho^{|3m|+2K} \Big[& a^{r,3m}_{I_1,2K} z^{I_1} \cos(3m\phi) - a^{i,3m}_{I_2,2K} z^{I_2} \sin(3m\phi) \\ & + i \left(a^{r,3m}_{I_1,2K} z^{I_1} \sin(3m\phi) + a^{i,3m}_{I_2,2K} z^{I_2} \cos(3m\phi) \right) \Big] \end{aligned} \tag{48}$$

The $\chi^{C_3} = 1$ also directs us to Table S.III. Applying the "a^r nz" constraint in the $(e + a_1)$-$(1, -1)$ entry there to the root formula, we have the final expansion

$$H_{-\alpha A_1 \beta} = a^{r,3m}_{I_1,2K} z^{I_1} \rho^{|3m|+2K} e^{i3m\phi}. \tag{49}$$

Figure 4(b) shows that the three complex-valued independent matrix elements become four real-valued independent matrix elements in the real basis set. They take the following expansion formulas:

$$\begin{aligned} H_{X\alpha A_1\alpha} &= i\sqrt{2} Im \left(H_{+\alpha A_1\alpha} \right) = i b^{r,3n-1}_{I_1,2K} z^{I_1} \rho^{|3n-1|+2K} \sin\left(3n-1\right)\phi; \\ H_{Y\alpha A_1\alpha} &= i\sqrt{2} Re \left(H_{+\alpha A_1\alpha} \right) = i b^{r,3n-1}_{I_1,2K} z^{I_1} \rho^{|3n-1|+2K} \cos\left(3n-1\right)\phi; \\ H_{X\alpha A_1\beta} &= \frac{1}{\sqrt{2}} \left(H_{+\alpha A_1\beta} + H_{-\alpha A_1\beta} \right) = c^{r,3n-1}_{I_1,2K} z^{I_1} \rho^{|3n-1|+2K} e^{-i(3n-1)\phi} + a^{r,3m}_{I_1,2K} z^{I_1} \rho^{|3m|+2K} e^{i3m\phi}; \\ H_{Y\alpha A_1\beta} &= \frac{i}{\sqrt{2}} \left(H_{+\alpha A_1\beta} - H_{-\alpha A_1\beta} \right) = i c^{r,3n-1}_{I_1,2K} z^{I_1} \rho^{|3n-1|+2K} e^{-i(3n-1)\phi} - i a^{r,3m}_{I_1,2K} z^{I_1} \rho^{|3m|+2K} e^{i3m\phi}. \end{aligned} \tag{50}$$

The common factors $\sqrt{2}$ and $\frac{1}{\sqrt{2}}$ have been absorbed in the coefficients b^r, a^r, and c^r. Up to 4th order, the term-by-term expansions are

$$
\begin{aligned}
H_{X\alpha A_1\alpha} &= -ib_{0,0}^{r,-1}y + ib_{0,0}^{r,2}2xy - ib_{1,0}^{r,-1}zy - ib_{0,2}^{r,-1}\left(x^2+y^2\right)y + ib_{1,0}^{r,2}z2xy - ib_{2,0}^{r,-1}z^2y \\
&\quad -ib_{0,0}^{r,-4}4xy\left(x^2-y^2\right) + ib_{0,2}^{r,2}\left(x^2+y^2\right)2xy - ib_{1,2}^{r,-1}z\left(x^2+y^2\right)y + ib_{2,0}^{r,2}z^2 2xy - ib_{3,0}^{r,-1}z^3y \\
H_{Y\alpha A_1\alpha} &= ib_{0,0}^{r,-1}x + ib_{0,0}^{r,2}\left(x^2-y^2\right) + ib_{1,0}^{r,-1}zx + ib_{0,2}^{r,-1}\left(x^2+y^2\right)x + ib_{1,0}^{r,2}z\left(x^2-y^2\right) + ib_{2,0}^{r,-1}z^2x \\
&\quad +ib_{0,0}^{r,-4}\left(x^4+y^4-6x^2y^2\right) + ib_{0,2}^{r,2}\left(x^4-y^4\right) + ib_{1,2}^{r,-1}z\left(x^2+y^2\right)x + ib_{2,0}^{r,2}z^2\left(x^2-y^2\right) \\
&\quad +ib_{3,0}^{r,-1}z^3x \\
H_{X\alpha A_1\beta} &= a_{0,0}^{r,0} + a_{1,0}^{r,0}z + c_{0,0}^{r,-1}\left(x-iy\right) + a_{0,2}^{r,0}\left(x^2+y^2\right) + a_{2,0}^{r,0}z^2 + c_{0,0}^{r,2}\left(x^2-y^2+i2xy\right) \\
&\quad +c_{1,0}^{r,-1}z\left(x-iy\right) + a_{0,0}^{r,-3}\left(x^3-3xy^2-i3x^2y+iy^3\right) + a_{0,0}^{r,3}\left(x^3-3xy^2+i3x^2y-iy^3\right) \\
&\quad +a_{1,2}^{r,0}z\left(x^2+y^2\right) + a_{3,0}^{r,0}z^3 + c_{0,2}^{r,-1}\left(x^2+y^2\right)\left(x-iy\right) + c_{1,0}^{r,2}z\left(x^2-y^2+i2xy\right) \\
&\quad +c_{2,0}^{r,-1}z^2\left(x-iy\right) + a_{0,4}^{r,0}\left(x^2+y^2\right)^2 + a_{1,0}^{r,-3}z\left(x^3-3xy^2-i3x^2y+iy^3\right) \\
&\quad +a_{1,0}^{r,3}z\left(x^3-3xy^2+i3x^2y-iy^3\right) + a_{2,2}^{r,0}z^2\left(x^2+y^2\right) + a_{4,0}^{r,0}z^4 \\
&\quad +c_{0,0}^{r,-4}\left(x^4+y^4-6x^2y^2-i4xy\left(x^2-y^2\right)\right) + c_{0,2}^{r,2}\left(x^2+y^2\right)\left(x^2-y^2+i2xy\right) \\
&\quad +c_{1,2}^{r,-1}z\left(x^2+y^2\right)\left(x-iy\right) + c_{2,0}^{r,2}z^2\left(x^2-y^2+i2xy\right) + c_{3,0}^{r,-1}z^3\left(x-iy\right). \qquad (51)
\end{aligned}
$$

Replacing c^r by ic^r and a^r by $-ia^r$ in the $H_{X\alpha A_1\beta}$ expansion, we obtain the $H_{Y\alpha A_1\beta}$ expansion. The three expansions in Eq. 51 are identical to those given in Ref. 61 except for some trivial phase differences. The correctness of our general formalism is confirmed.

B. The $(E'+A_2'')\otimes(e'+a_2'')$ Problem in D_{3h} Symmetry

Another example is the $(E'+A_2'')\otimes(e'+a_2'')$ SO pJT problem in D_{3h} symmetry, whose expansion formulas were derived in Ref. 60 under the assumption that the E' and A_2'' orbitals arise from one set of p orbitals that are located at the D_{3h} center. From Table I, we immediately obtain the symmetry eigenvalues of the three independent matrix elements: $\left(\chi^{C_3}, \left(\chi_{Re}^{C_2'}, \chi_{Im}^{C_2'}\right), \chi^{\sigma_h}\right) = \left(e^{i\frac{2\pi}{3}}, (-1,1), -1\right)$ for $H_{+'\alpha A_2''\alpha}$, $\left(e^{-i\frac{2\pi}{3}}, (1,-1), 1\right)$ for $H_{+'\alpha A_2''\beta}$, and $(1,(1,-1),1)$ for $H_{-'\alpha A_2''\beta}$. Guided by these eigenvalues and consulting the root formulas table and constraints tables, we obtain the general expansion formulas of the elements:

$$
\begin{aligned}
H_{+'\alpha A_2''\alpha} &= b^{r,3n-1}_{2I_1+1,2K} z^{2I_1+1}\rho^{|3n-1|+2K}e^{i(3n-1)\phi};\\
H_{+'\alpha A_2''\beta} &= c^{r,3n-1}_{2I_1,2K} z^{2I_1}\rho^{|3n-1|+2K}e^{-i(3n-1)\phi};\\
H_{-'\alpha A_2''\beta} &= a^{r,3m}_{2I_1,2K} z^{2I_1}\rho^{|3m|+2K}e^{i3m\phi}.
\end{aligned}
\tag{52}
$$

They differ from the counterparts in Eqs 46, 47, and 49 in the selections of the z powers. We can hence obtain the $H_{X'\alpha A_2''\alpha}$ and $H_{X'\alpha A_2''\beta}$ expansions up to 4th order by taking only the terms with odd powers of z in the $H_{X\alpha A_1\alpha}$ and $H_{Y\alpha A_1\beta}$ expansions in Eq. 51, respectively:

$$
\begin{aligned}
H_{X'\alpha A_2''\alpha} &= -ib^{r,-1}_{1,0}zy + ib^{r,2}_{1,0}z2xy - ib^{r,-1}_{1,2}z\left(x^2+y^2\right)y - ib^{r,-1}_{3,0}z^3y;\\
H_{Y'\alpha A_2''\alpha} &= ib^{r,-1}_{1,0}zx + ib^{r,2}_{1,0}z(x^2-y^2) + ib^{r,-1}_{1,2}z\left(x^2+y^2\right)x + ib^{r,-1}_{3,0}z^3x.
\end{aligned}
\tag{53}
$$

They are identical to the expansions given in Eqs. 39(b) and 39(c) in Ref. 60, except for a trivial sign difference in $H_{Y'\alpha A_2''\alpha}$.

Similarly, we obtain the $H_{X'\alpha A_2''\beta}$ expansion up to 4th order by taking the terms with even powers of z in the $H_{X\alpha A_1\beta}$ expansion in Eq. 51:

$$
\begin{aligned}
H_{X'\alpha A_2''\beta} = {} & a^{r,0}_{0,0} + c^{r,-1}_{0,0}(x-iy) + a^{r,0}_{0,2}\left(x^2+y^2\right) + a^{r,0}_{2,0}z^2 + c^{r,2}_{0,0}\left(x^2-y^2+i2xy\right)\\
&+(a^{r,3}_{0,0}+a^{r,-3}_{0,0})\left(x^3-3xy^2\right) + (a^{r,3}_{0,0}+a^{r,-3}_{0,0})i\left(3x^2y-y^3\right)\\
&+c^{r,-1}_{0,2}\left(x^2+y^2\right)(x-iy) + c^{r,-1}_{2,0}z^2(x-iy) + a^{r,0}_{0,4}\left(x^2+y^2\right)^2 + a^{r,0}_{2,2}z^2\left(x^2+y^2\right) + a^{r,0}_{4,0}z^4\\
&+c^{r,-4}_{0,0}\left(x^4+y^4-6x^2y^2-i4xy\left(x^2-y^2\right)\right) + c^{r,2}_{0,2}\left(x^2+y^2\right)\left(x^2-y^2+i2xy\right)\\
&+c^{r,2}_{2,0}z^2\left(x^2-y^2+i2xy\right).
\end{aligned}
\tag{54}
$$

Discrepancy is seen between this expansion and the one given in Eq. 39(e) in Ref. 60, which lacks the term corresponds to the $i\left(3x^2y-y^3\right)$ monomial. The assumption there that all three orbitals arise from a common set of p orbitals imposes higher symmetry to the $(E'+A_2'')$ problem, and naturally keeps fewer terms in the expansions. Specifically, this assumption excludes all terms with the $i\sin 3m\phi$ angular factor in the $H_{X'\alpha A_2''\beta}$ expansion. Under this assumption, the $H_{X'\alpha A_2''\beta}$ expansion takes a form of $iH_{X'Y'} - H_{X'X'} - H_{A_2''A_2''}$ (see Eqs. 14(b), 14(e), and 21(e) in Ref. 60), where the real-valued H_{IJ} stands for the electrostatic, non-SO coupling between states I and J. The component that is totally symmetric with respect to $\hat{C}_3$ is $H_{A_2''A_2''}$, which contains terms with $\cos 3m\phi$ but not those with $i\sin 3m\phi$.

We have no attempt to criticize the work of Ref. 60. As mentioned in Section I, this excellent work motivates us to derive the present formalism. The authors of Ref. 60 have clearly discussed the approximation nature of the formulas therein and the limits of their use. The comparison here is only to highlight the capacity of the present formalism. It provides both the terms that are included and not included by the three-p-approximation.

C. The $(E_u + A_{2u}) \otimes (e_u + b_{1g} + b_{2g})$ Problem in D_{4h} Symmetry

First order expansion formulas of this SO pJT problem are given in Ref. 81 in the context of studying Ng^+F_4 cations (Ng: a nobel gas atom). We take this problem as an example to show how to obtain trimodal expansions from the presented bimodal formalism. First, we identify the three independent matrix elements and their symmetry eigenvalues $\left(\chi^{C_4}, \left(\chi^{C_2'}_{Re}, \chi^{C_2'}_{Im}\right), \chi^I\right)$ in Table I: $H_{+_u\alpha A_{2u}\alpha}$, $(i, (-1,1), 1)$; $H_{+_u\alpha A_{2u}\beta}$, $(-1, (1,-1), 1)$; $H_{-_u\alpha A_{2u}\beta}$, $(1, (1,-1), 1)$. Second, we recognize that there are four types of products of monomials of the two b coordinates, $w_1^{2I_1+1}w_2^{2I_2+1}$, $w_1^{2I_1+1}w_2^{2I_2}$, $w_1^{2I_1}w_2^{2I_2+1}$, and $w_1^{2I_1}w_2^{2I_2}$, which transform as a_{2g}, b_{1g}, b_{2g}, and a_{1g} coordinates, respectively. w_1 and w_2 are used to label the the actual b_{1g} and b_{2g} coordinates. Third, using the symmetry eigenvalues and from Tables S.VII to S.XV, we extract the $(e_u + a_{2g})$, $(e_u + b_{1g})$, $(e_u + b_{2g})$, and $(e_u + a_{1g})$ expansion formulas for the three matrix elements. We call these the intermediate expansions.

The $(e_u + b_g)$-$(i, 1)$ and $(e_u + a_g)$-$(i, 1)$ entries in Table S.XV are both "na" (not applicable) and therefore, the intermediate expansions for $H_{+_u\alpha A_{2u}\alpha}$ are null and so is the $(e_u + b_{1g} + b_{2g})$ expansion. This is consistent with the null $H_{W_1V_1}$ element in Eq. (21) of Ref. 81. The $(e_u + a_{2g})$ intermediate expansion for $H_{+_u\alpha A_{2u}\beta}$ is

$$b^{r,4k+2}_{2I,2K} z^{2I} \rho^{|4k+2|+2K} e^{i(4k+2)\phi} + i b^{i,4k+2}_{2I+1,2K} z^{2I+1} \rho^{|4k+2|+2K} e^{i(4k+2)\phi}, \tag{55}$$

where z is used to label the symbolic a_{2g} coordinate. The other three intermediate expansions for this matrix element and all four intermediate expansions for $H_{-_u\alpha A_{2u}\beta}$ are not shown. The fourth step is to replace the symbolic coordinates by the corresponding products of the two b coordinates. For instance, in Eq. 55, z is replaced by $w_1^{2I_1+1}w_2^{2I_2+1}$, and after some simple algebraic manipulation, the expansion becomes

$$b^{r,4k+2}_{2I_1,2I_2,2K} w_1^{2I_1} w_2^{2I_2} \rho^{|4k+2|+2K} e^{i(4k+2)\phi} + i b^{i,4k+2}_{2I_1+1,2I_2+1,2K} w_1^{2I_1+1} w_2^{2I_2+1} \rho^{|4k+2|+2K} e^{i(4k+2)\phi}. \tag{56}$$

The other three intermediate expansions for $H_{+_u\alpha A_{2u}\beta}$ become

$$b^{r,4k}_{2I_1+1,2I_2,2K} w_1^{2I_1+1} w_2^{2I_2} \rho^{|4k|+2K} e^{i4k\phi} + b^{r,4k+2}_{2I_1,4I_2,2K} w_1^{2I_1} w_2^{4I_2} \rho^{|4k+2|+2K} e^{i(4k+2)\phi};$$
$$b^{r,4k+2}_{4I_1,2I_2,2K} w_1^{4I_1} w_2^{2I_2} \rho^{|4k+2|+2K} e^{i(4k+2)\phi} + ib^{i,4k}_{2I_1,2I_2+1,2K} w_1^{2I_1} w_2^{2I_2+1} \rho^{|4k|+2K} e^{i4k\phi};$$
$$b^{r,4k+2}_{2I_1,2I_2,2K} w_1^{2I_1} w_2^{2I_2} \rho^{|4k+2|+2K} e^{i(4k+2)\phi}. \tag{57}$$

The analogue expansions for $H_{-_u\alpha A_{2u}\beta}$ are not shown.

The fifth and final step is to sum all the four expansions corresponding to the four types of b monomial products. Combining duplicate terms, the final expansion formulas are

$$\begin{aligned} H_{+_u\alpha A_{2u}\beta} = {} & b^{r,4k+2}_{2I_1,2I_2,2K} w_1^{2I_1} w_2^{2I_2} \rho^{|4k+2|+2K} e^{i(4k+2)\phi} + b^{r,4k}_{2I_1+1,2I_2,2K} w_1^{2I_1+1} w_2^{2I_2} \rho^{|4k|+2K} e^{i4k\phi} \\ & + ib^{i,4k+2}_{2I_1+1,2I_2+1,2K} w_1^{2I_1+1} w_2^{2I_2+1} \rho^{|4k+2|+2K} e^{i(4k+2)\phi} \\ & + ib^{r,4k}_{2I_1,2I_2+1,2K} w_1^{2I_1} w_2^{2I_2+1} \rho^{|4k|+2K} e^{i4k\phi}; \end{aligned} \tag{58}$$

$$\begin{aligned} H_{-_u\alpha A_{2u}\beta} = {} & a^{r,4k}_{2I_1,2I_2,2K} w_1^{2I_1} w_2^{2I_2} \rho^{|4k|+2K} e^{i4k\phi} + a^{r,4k+2}_{2I_1+1,2I_2,2K} w_1^{2I_1+1} w_2^{2I_2} \rho^{|4k+2|+2K} e^{i(4k+2)\phi} \\ & + ia^{i,4k}_{2I_1+1,2I_2+1,2K} w_1^{2I_1+1} w_2^{2I_2+1} \rho^{|4k|+2K} e^{i4k\phi} \\ & + ia^{i,4k+2}_{2I_1,2I_2+1,2K} w_1^{2I_1} w_2^{2I_2+1} \rho^{|4k+2|+2K} e^{i(4k+2)\phi}. \end{aligned} \tag{59}$$

Keeping up to the linear terms, $H_{+_u\alpha A_{2u}\beta} = b^{r,0}_{1,0,0} w_1 + ib^{r,0}_{0,1,0} w_2$ and $H_{-_u\alpha A_{2u}\beta} = a^{r,0}_{0,0,0}$, which are consistent with $H_{W_1V_2} = -\sqrt{2}\,(\gamma q_1 - i\delta q_2)$ and $H_{U_2V_2} = \sqrt{2}\beta$ in Eq. (21) of Ref. 81, respectively.

Expansion formulas involving more vibrational modes can be obtained in a similar fashion. For non-degenerate modes (a- and b-type modes), we can always combine their monomials to have symbolic single mode coordinates. For problems with more e-type modes, we can always decompose single e mode's monomials to products of multiple e modes' monomials. For example, to obtain the $(b_{1g} + b_{2g} + 2e_u)$ expansions for the two matrix elements above, we simply need to replace $\rho^{|4k|+2K} e^{i4k\phi}$ by $\rho_1^{|4k-m|+2K_1} \rho_2^{|m|+2K_2} e^{i[(4k-m)\phi_1 + m\phi_2]}$ and $\rho^{|4k+2|+2K} e^{i(4k+2)\phi}$ by $\rho_1^{|4k+2-m|+2K_1} \rho_2^{|m|+2K_2} e^{i[(4k+2-m)\phi_1 + m\phi_2]}$, and then to add the extra summation indices to the coefficient labels. Depending on the parities of the matrix elements and the modes, further constraints on the summation indices may be applicable.

VIII. CONCLUSIONS

In this work, we present a general formalism for all bimodal spin-orbit (pseudo-)Jahn-Teller problems in trigonal and tetragonal symmetries. The formalism gives us expansion formulas of spin-orbit matrix elements in symmetry-adapted vibrational coordinates up to arbitrary order. The derivation is based on the fundamental symmetry requirements of the spin-orbit vibronic Hamiltonian operator and does not rely on a specific form of the operator. The root-branch approach and the modularized approach facilitate the derivation so much that thousands of problems in the two classes of symmetries are covered in this work. The formalism is presented as four generic matrices, one table of symmetry eigenvalues, two tables of root expansion formulas, and ten tables of constraints. We can identify independent matrix elements and look up their expansion formulas using the tables. With the generic matrix structures, we can easily construct the total spin-orbit vibronic Hamiltonian operator from the independent matrix elements. With all these features, the formalism is programmable. The correctness, completeness, and conciseness of the formalism is demonstrated by comparisons with formulas derived in earlier studies. Given the ubiquity of trigonal and tetragonal spin-orbit (pseudo-)Jahn-Teller problems, especially for heavy element compounds of the symmetries, the applicability of the presented formalism is broad.

The derivation in this work also lays a solid foundation for future derivation for the spin-orbit (pseudo-)Jahn-Teller formalism for general axial symmetries with arbitrary n-fold principal axes. The generic matrix structures and the σ_v-, C_2-, and I-eigenvalues are transferable. We will still need to derive C_n- and S_n-eigenvalues, and some extra root expansion formulas and the constraints onto them. Since spin-orbit and non-spin-orbit (pseudo-)Jahn-Teller formalisms only differ in symmetry eigenvalues of independent matrix elements, we can combine the two formalisms into one. It will be an interesting future study to derive the unified formalism for spin-orbit and non-spin-orbit (pseudo-)Jahn-Teller problems in arbitrary axial symmetries.

ACKNOWLEDGEMENTS

T.Z. is thankful to the Natural Sciences and Engineering Research Council (NSERC) of Canada (RGPIN-2016-06276), Carleton University (186853), and York University (481333) for research funding.

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