General formalism of vibronic Hamiltonians for tetrahedral and octahedral systems: problems that involve T, E states and t, e vibrations

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Abstract

We derive expansion formulas up to arbitrary order in vibrational coordinates for the tetrahedral and octahedral vibronic Hamiltonians that involve T and E states, and t and e vibrations. These states feature both Jahn-Teller (JT) and pseudo-Jahn-Teller (pJT) effects, and the vibrations are the most JT and pJT active. We first derive the formulas for 92 problems of T and T_d symmetries involving up to two vibrational modes. The formulas can be easily generalized to problems of T_h, O, and O_h symmetries, and problems involving more than two vibrational modes. They can also be adapted to describe spin-orbit vibronic Hamiltonians of tetrahedral p-type problems. Overall, this work makes crucial preparations for future studies on vibronic coupling problems of tetrahedral and octahedral systems. Most importantly, a new, simple, modularized approach to construct vibronic Hamiltonians for a set of related problems, instead of particular problems one by one, is presented.

1 Introduction

Highly symmetric nonlinear polyatomic systems with the principal axis (proper or improper) equal to or higher than three fold allow for orbital degeneracy. Paradoxically, this degeneracy forces the systems to abandon their high symmetry structures and eliminate the degeneracy itself. This is because the degenerate states are linearly coupled by non-totally symmetric vibrations. This interesting spontaneous symmetry breaking was first proposed and explained by Jahn and Teller in 1937,[1] through *a bit of spade work* (Teller's words[2]). All effects related to this symmetry breaking are consequently called Jahn-Teller (JT) effects. When the distortion-induced coupling between a non-degenerate state and other states is strong enough, the non-degenerate state is also subject to symmetry lowering, and all relevant effects are termed pseudo-Jahn-Teller (pJT) effects. The JT and pJT effects are ubiquitous in photochemistry, stereochemistry, solid-state chemistry, and material chemistry. A plethora of studies, experimental and theoretical, have been dedicated to those effects since they were proposed 80 years ago.[3–12]

Since the JT (and often the pJT) effects are closely related to orbital (pseudo)degeneracy in electronic states, the Born-Oppenheimer approximation of adiabatically separating the electronic and vibrational motions is not applicable; we need to consider the intimate coupling of the two types of motions and treat them on an equal footing. Therefore, an accurate vibronic Hamiltonian is indispensable to describe and understand a JT/pJT problem. A vibronic Hamiltonian is usually expanded at a high-symmetry reference structure using a subset of strongly coupled electronic states and the vibrational modes that mediate their couplings. (Quasi-)diabatic electronic states[13] are used so that the Hamiltonian matrix elements are smooth functions of the vibrational coordinates and support a Taylor expansion. Traditionally, the expansion is truncated at the second order. This is often deemed adequate: the linear terms provide the symmetry-breaking force and the quadratic terms have given all qualitative features of the relevant adiabatic potential energy surfaces (PESs).[14]

However, the importance of higher order expansions has been demonstrated by more and

more studies. The diabatic energies can be highly anharmonic.[15–18] This is especially true when the so-called intramolecular collision occurs:[19] when JT-active bending modes bring atoms close to each other, it is necessary to use higher order expansions to describe the positive anharmonicity.[20,21] For instance, up to 12th order expansion in the t_2 H-C-H bending coordinates is needed to describe the $T_2 \otimes t_2$ Hamiltonian of the ground state of CH_4^+.[22] The anharmonicity is also important for JT/pJT problems that involve bond dissociation.[18] It is noteworthy that high-order expansions are not only of concern to theoreticians. They are needed to give satisfactory interpretation for complicated vibronic spectrum.[23–26] They are also needed to fit spectra and obtain reasonable empirical JT/pJT parameters, e.g., JT stabilization energy, barrier for hindered pseudo-rotation, etc.[27] Unfortunately, our knowledge of general expansions of vibronic Hamiltonians up to arbitrary order is highly limited. While state-of-the-art quantum chemistry calculations and the latest developed diabatization schemes[28–33] bring us highly accurate numerical values for vibronic matrix elements, we very often can only fit them using low-order functions of vibrational coordinates, regretfully compromising the accuracy. In this sense, the development of vibronic coupling modelling lags behind the development of quantum chemistry and diabatization schemes.

Early attempts to derive high-order formalism for vibronic Hamiltonians were dedicated to textbook problems, e.g., the $E\otimes e$ problem in C_{3v} symmetry, the $T_2\otimes t_2$, and $T_2\otimes e$ problems in T_d symmetry.[15,22,34] Inspired by these case-specific pioneering works, we recently managed to derive vibronic Hamiltonian expansions up to arbitrary order for 153 $(E + A) \otimes (e + a)$ problems for systems with trigonal symmetry.[35] The expansions are *c*oncise, *c*omplete, and *c*onvenient to use (CCC). Encouraged by this success, we, in this study, move on to derive general expansion formulas for the more challenging tetrahedral and octahedral systems, whose importance in chemistry can never be overstated. Our derivations are focused on the states and vibrations of T and E irreducible representations (irreps) because they are the most JT and pJT active. Vibronic problems with up to two sets of vibrational modes are considered because: (1) this is usually enough, with one set of stretching and one set

of bending mode; (2) a problem with more than two modes (e.g., $T_1 \otimes (t_1 + t_2 + e)$ can be decomposed into several double-mode problems (e.g., $T_1 \otimes (t_1 + t_2)$, $T_1 \otimes (t_1 + e)$, and $T_1 \otimes (t_2 + e)$). Terms with more than two modes' coordinates are believed to be of less significance and can usually be neglected; (3) even when these terms are needed, it is straightforward (e.g., see Eq. 24) to extend double-mode expansion formulas to include more modes. Our derived formulas apply to both molecules and local formations in solids. Therefore, the more generic term "systems" is used.

However, do we need the general expansion formalism? For any vibronic problem that involves N vibrational coordinates (Q_{1-N}), one can first construct the n-th order preliminary Hamiltonian as

$$\hat{H}_0^{(n)} = |\chi_I\rangle \langle\chi_J| h^{IJ}_{i_1 i_2 \cdots i_N} Q_1^{i_1} Q_2^{i_2} \cdots Q_N^{i_N}. \quad (1)$$

Throughout this paper, Einstein's convention of summing over duplicated indices is followed, unless the summation sign is explicitly used. In Eq. 1, $\{\chi\}$ denote the diabatic states (diabats), $\left\{h^{IJ}_{i_1 i_2 \cdots i_N}\right\}$ stand for expansion coefficients, and the power indices $\{i_k\}$ run over all possible values that satisfy $\sum_{k=1}^{N} i_k = n$. In diabatic representation, the nuclear kinetic operator does not take part in vibronic coupling, and is hence not discussed. The *S*ymmetry-*A*dapted Hamiltonian ($\hat{H}_{SA}$) at the same order can be obtained as

$$\hat{H}_{SA}^{(n)} = \sum_S \hat{S} \hat{H}_0^{(n)} \hat{S}^{-1}, \quad (2)$$

where the summation runs over all symmetry operators $\left\{\hat{S}\right\}$ of the point group. This is just to extract the totally symmetric component in $\hat{H}_0^{(n)}$ using projection operator, and we call it the brute-force method. A large number of terms need to be handled as the order and the number of vibrational modes increase. This makes the brute-force method vulnerable to numerical errors and redundant terms in the final expansion. More elegant methods based on the same projection strategy have been proposed to alleviate these drawbacks.[36,37] Another

more traditional way to construct symmetry-adapted Hamiltonians is to employ Clebsch-Gordan coefficients and elementary polynomials of vibrational coordinates that transform following the irreps of the relevant point group.[2,38] All these methods can be programmed, and we can leave the construction of vibronic Hamiltonians to computer; the derivation of the general expansion formalism seems unnecessary. However, the hand-written formalism features the aforementioned CCC advantages. It is immune to any numerical errors and redundancy, it saves the efforts of programming to symmetrize the Hamiltonian, and furthermore, it clearly reveals connections between vibronic problems. Overall, derived formalism vs. program-generated expansion is analogous to analytical vs. numerical solution. We can always gain from knowing the analytical solution.

This paper is organized as follows. Section 2 gives a preparation for the derivation, in which we introduce the notation to be used and the transformations of the diabats and functions of vibrational coordinates under the tetrahedral symmetry operations. In Section 3 we present the derivations for 92 important tetrahedral vibronic Hamiltonian expansions. A numerical example is given in Section 4 to examine our formalism. Some of the derived formulas can be adapted to describe spin-orbit vibronic Hamiltonians of tetrahedral p-type problems. This is discussed in Section 5. Section 6 extends the formalism to octahedral systems and concludes the paper.

2 Settings

Shown in Figure 1 is a neopentane molecule model of T_d symmetry, with a standard molecular-fixed frame being attached to it. The C_3 axis pointing from C_1 to C_5 trisects the x-, y-, and z-axes and we call it the C_3^{xyz} axis. The x-, y-, and z-axes are the three C_2 axes, called C_2^x, C_2^y, and C_2^z, respectively. When an object is symmetric with respect to the $\hat{C}_3^{xyz}$ and the $\hat{C}_2^z$ operations, it is symmetric with respect to all 12 symmetry operations of the T point group. Therefore, $\hat{C}_3^{xyz}$ and $\hat{C}_2^z$ are two representative symmetry operators of T symmetry. They

are randomly chosen to be the representatives and are not different from the other $\hat{C}_3$ and $\hat{C}_2$ operators of the point group. For T_h symmetry, the center-inversion $\hat{I}$ is an additional representative symmetry operator. For T_d symmetry, the $\hat{\sigma}_d^x$ reflection is chosen as the additional representative symmetry operator. In the neopentane model, such a reflection is with respect to the C_2-C_1-C_5 plane that contains the x-axis, which explains the meaning of the superscript "x". The C_3-C_1-C_4 plane also contains the x-axis. However, in this paper, σ_d^x is reserved for the plane that bisects the first and third quadrants of the y-z plane. Similarly, σ_d^z is defined to be the symmetric plane that contains the z-axis and bisects the first and third quadrants of the x-y plane.

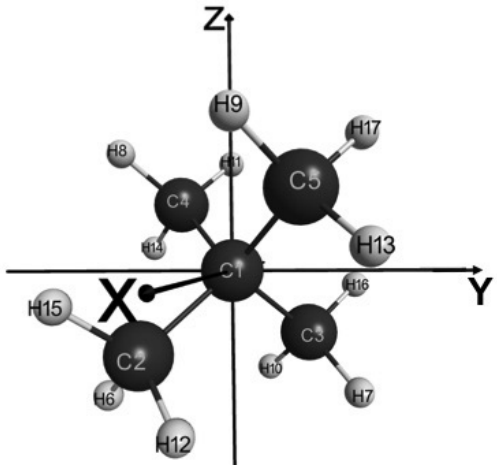

Figure 1: A model neopentane molecule that demonstrates the symmetry elements of the T_d point group.

For a generic T degenerate state (including $T_{1,2}$ in T_d and $T_{g,u}$ in T_h) or a generic t degenerate mode (also including the subscript-dressing ones), we set its three components to transform as the three polar (e.g., momentum) or axial (e.g., angular momentum) vectors with the same length along the x-, y-, and z-axes under $\hat{C}_3^{xyz}$ and $\hat{C}_2^z$. Correspondingly, we label the three T diabats as $|X\rangle$, $|Y\rangle$, and $|Z\rangle$, and the coordinates of the t mode x, y, and z. For an E state or an e mode, we set its two components to transform as the $2x^2 - y^2 - z^2$ and $\sqrt{3}\,(y^2 - z^2)$ functions, and correspondingly label the diabats as $|\Theta\rangle$ and $|\Xi\rangle$, and the vibrational coordinates q_θ and q_ξ, respectively. Sometimes it is convenient to use the complex

representation for the E state and the polar coordinates for the e vibration in the derivation:

$$\begin{pmatrix} |+\rangle \\ |-\rangle \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ 1 & -i \end{pmatrix} \begin{pmatrix} |\Theta\rangle \\ |\Xi\rangle \end{pmatrix}; q_\theta = \rho\cos\phi, q_\xi = \rho\sin\phi. \tag{3}$$

With these settings, the E and T diabats and a generic function of an arbitrary number of sets of e and t coordinates, $f\left(\{\rho,\phi\},\{x,y,z\}\right)$, transform under the symmetry operations as:

$$\begin{aligned}
\hat{C}_3^{xyz}\left(|+\rangle,|-\rangle,|X\rangle,|Y\rangle,|Z\rangle\right) &= \left(e^{-i\frac{2\pi}{3}}|+\rangle, e^{i\frac{2\pi}{3}}|-\rangle,|Y\rangle,|Z\rangle,|X\rangle\right); \\
\hat{C}_3^{xyz} f\left(\{\rho,\phi\},\{x,y,z\}\right) &= f\left(\left\{\rho,\phi-\frac{2\pi}{3}\right\},\{y,z,x\}\right); \\
\hat{C}_2^{z}\left(|+\rangle,|-\rangle,|X\rangle,|Y\rangle,|Z\rangle\right) &= \left(|+\rangle,|-\rangle,-|X\rangle,-|Y\rangle,|Z\rangle\right); \\
\hat{C}_2^{x} f\left(\{\rho,\phi\},\{x,y,z\}\right) &= f\left(\{\rho,\phi\},\{x,-y,-z\}\right); \\
\hat{C}_2^{y} f\left(\{\rho,\phi\},\{x,y,z\}\right) &= f\left(\{\rho,\phi\},\{-x,y,-z\}\right); \\
\hat{C}_2^{z} f\left(\{\rho,\phi\},\{x,y,z\}\right) &= f\left(\{\rho,\phi\},\{-x,-y,z\}\right),
\end{aligned} \tag{4}$$

In T_h symmetry,

$$\begin{aligned}
\hat{I}\left(|+\rangle,|-\rangle,|X\rangle,|Y\rangle,|Z\rangle\right) &= \left(\pm^E|+\rangle,\pm^E|-\rangle,\pm^T|X\rangle,\pm^T|Y\rangle,\pm^T|Z\rangle\right); \\
\hat{I} f\left(\{\rho,\phi\},\{x,y,z\}\right) &= f\left(\{\pm^e\rho,\phi\},\left\{\pm^t x,\pm^t y,\pm^t z\right\}\right).
\end{aligned} \tag{5}$$

The "+" ("−") of "±" applies to gerade (ungerade) states and modes. State and mode irrep symbols are added as superscripts to the "±"s to clarify to which states or coordinates the

sign selections apply. In T_d symmetry,

$$\hat{\sigma_d^x}\left(|+\rangle, |-\rangle, |X\rangle, |Y\rangle, |Z\rangle\right) = \left(|-\rangle, |+\rangle, \pm^T |X\rangle, \pm^T |Z\rangle, \pm^T |Y\rangle\right);$$

$$\hat{\sigma_d^x} f\left(\{q_\theta, q_\xi\}, \{\rho, \phi\}, \{x, y, z\}\right) = f\left(\{q_\theta, -q_\xi\}, \{\rho, -\phi\}, \left\{\pm^t x, \pm^t z, \pm^t y\right\}\right);$$

$$\hat{\sigma}_d^z f\left(\{q_\theta, q_\xi\}, \{\rho, \phi\}, \{x, y, z\}\right) =$$

$$f\left(\left\{-\frac{1}{2}q_\theta + \frac{\sqrt{3}}{2}q_\xi, \frac{1}{2}q_\xi + \frac{\sqrt{3}}{2}q_\theta\right\}, \left\{\rho, -\phi + \frac{2\pi}{3}\right\}, \left\{\pm^t y, \pm^t x, \pm^t z\right\}\right). \tag{6}$$

The "+" ("−") of "$\pm^T$" and "$\pm^t$" applies to states and modes of T_2 (T_1) irrep. The transformations of both the cartesian and polar coordinates of e vibrations under $\hat{\sigma}_d^x$ are shown. Transformations in Eqs. 4 to 6 are used frequently in the following derivations. Throughout this paper, upper case symbols are reserved for electronic states, and lower case for modes and orbitals. Unless further specified, symbols starting with i, j, k, l, m, n and their upper case analogues stand for integers. However, "i" itself is reserved for the imaginary unit. We would like to emphasize that all derivations below adopt the settings here. In order to use the resultant expansion formulas in actual vibronic calculations, one needs to orient the components of the degenerate states and modes so that they transform following Eqs. 4 to 6.

When subscripts of Mulliken symbols are not given in the text below, "T", "E", and their lower case analogues are used generically to denote all relevant states and modes containing the letters. For instance, "$(T + E) \otimes (t + e)$ problems in T_d" refers to problems with all possible combinations of the subscripts 1 and 2 for the T and t symbols in T_d symmetry. The subscripts "α", "β", etc. are used to differentiate states or modes with the same irrep symbols. The greek subscripts on states and coordinates are independent: the same α of $|X_\alpha\rangle$ and x_α does not mean that the state and the mode share the same irrep. In the derivations, we separate the discussions for *inter*- and *intra*-term couplings. "*Inter*-term coupling" means the part of the vibronic Hamiltonian that couples states of two term symbols and corresponds to pJT interaction. "*Intra*-term coupling" couples states within one term symbol and corresponds to JT interaction. One example of a vibronic Hamiltonian among

two T term symbols is given in Figure 2 to show the difference between the two types of coupling.

$$\left(\left(\left|T^{\alpha}\right\rangle\right)_{1\times3},\left(\left|T^{\beta}\right\rangle\right)_{1\times3}\right)\begin{pmatrix} H^{\alpha\alpha}_{3\times3} & H^{\alpha\beta}_{3\times3} \\ \left(H^{\alpha\beta}_{3\times3}\right)^{\dagger} & H^{\beta\beta}_{3\times3} \end{pmatrix}\begin{pmatrix} \left(\left\langle T^{\alpha}\right|\right)_{3\times1} \\ \left(\left\langle T^{\beta}\right|\right)_{3\times1} \end{pmatrix}$$

Figure 2: The matrix form of the vibronic coupling Hamiltonian that involve two T term symbols. The green and blue diagonal blocks of the H matrix give the *intra*-term couplings, and the red off-diagonal blocks give the *inter*-term coupling.

3 Derivations and Results

The derivation follows the same "root-branch" procedure as in our previous work:[35] we first tackle the problems of T symmetry, whose expansion formulas are called the *root* formulas. We then impose constraints on the root formulas to obtain *branch* formulas for the higher T_h and T_d symmetries. As shown below, it is straightforward to obtain *intra*-term formulas from *inter*-term formulas. We hence first derive *inter*-term formulas and then impose constraints to obtain *intra*-term formulas.

3.1 $(T+T)$ coupling

The most general form of the *inter*-term coupling Hamiltonian between two T states reads

$$\begin{aligned}\hat{H} \;=\; & \left(|X_\alpha\rangle\langle X_\beta| + |X_\beta\rangle\langle X_\alpha|\right) H_{X_\alpha X_\beta} + \left(|Y_\alpha\rangle\langle Y_\beta| + |Y_\beta\rangle\langle Y_\alpha|\right) H_{Y_\alpha Y_\beta} + \left(|Z_\alpha\rangle\langle Z_\beta| + |Z_\beta\rangle\langle Z_\alpha|\right) H_{Z_\alpha Z_\beta} \\ & + \left(|X_\alpha\rangle\langle Y_\beta| + |Y_\beta\rangle\langle X_\alpha|\right) H_{X_\alpha Y_\beta} + \left(|Y_\alpha\rangle\langle Z_\beta| + |Z_\beta\rangle\langle Y_\alpha|\right) H_{Y_\alpha Z_\beta} + \left(|Z_\alpha\rangle\langle X_\beta| + |X_\beta\rangle\langle Z_\alpha|\right) H_{Z_\alpha X_\beta} \\ & + \left(|X_\beta\rangle\langle Y_\alpha| + |Y_\alpha\rangle\langle X_\beta|\right) H_{X_\beta Y_\alpha} + \left(|Y_\beta\rangle\langle Z_\alpha| + |Z_\alpha\rangle\langle Y_\beta|\right) H_{Y_\beta Z_\alpha} + \left(|Z_\beta\rangle\langle X_\alpha| + |X_\alpha\rangle\langle Z_\beta|\right) H_{Z_\beta X_\alpha}.\end{aligned} \tag{7}$$

All matrix elements are real since the diabats are real. Under the $\hat{C}_3^{xyz}$ operation (henceforth abbreviated as $\hat{C}_3$),

$$\begin{aligned}
\hat{C}_3\hat{H}\hat{C}_3^{-1} &= \left(|Y_\alpha\rangle\langle Y_\beta| + |Y_\beta\rangle\langle Y_\alpha|\right)\hat{C}_3 H_{X_\alpha X_\beta} + \left(|Z_\alpha\rangle\langle Z_\beta| + |Z_\beta\rangle\langle Z_\alpha|\right)\hat{C}_3 H_{Y_\alpha Y_\beta} \\
&+ \left(|X_\alpha\rangle\langle X_\beta| + |X_\beta\rangle\langle X_\alpha|\right)\hat{C}_3 H_{Z_\alpha Z_\beta} + \left(|Y_\alpha\rangle\langle Z_\beta| + |Z_\beta\rangle\langle Y_\alpha|\right)\hat{C}_3 H_{X_\alpha Y_\beta} \\
&+ \left(|Z_\alpha\rangle\langle X_\beta| + |X_\beta\rangle\langle Z_\alpha|\right)\hat{C}_3 H_{Y_\alpha Z_\beta} + \left(|X_\alpha\rangle\langle Y_\beta| + |Y_\beta\rangle\langle X_\alpha|\right)\hat{C}_3 H_{Z_\alpha X_\beta} \\
&+ \left(|Y_\beta\rangle\langle Z_\alpha| + |Z_\alpha\rangle\langle Y_\beta|\right)\hat{C}_3 H_{X_\beta Y_\alpha} + \left(|Z_\beta\rangle\langle X_\alpha| + |X_\alpha\rangle\langle Z_\beta|\right)\hat{C}_3 H_{Y_\beta Z_\alpha} \\
&+ \left(|X_\beta\rangle\langle Y_\alpha| + |Y_\alpha\rangle\langle X_\beta|\right)\hat{C}_3 H_{Z_\beta X_\alpha}. \qquad (8)
\end{aligned}$$

The transformations of the ket-bra dyad simply follow the $\hat{C}_3$-transformations in Eq. 4. The Hamiltonian is required to satisfy $\hat{C}_3\hat{H}\hat{C}_3^{-1} = \hat{H}$. Through equating the matrix elements associated with the same dyads in Eqs. 7 and 8, we readily see that the symmetry requirement imposes the following relations between the matrix elements:

$$H_{X_\alpha X_\beta} = \hat{C}_3^2 H_{Y_\alpha Y_\beta} = \hat{C}_3 H_{Z_\alpha Z_\beta}; H_{X_\alpha Y_\beta} = \hat{C}_3^2 H_{Y_\alpha Z_\beta} = \hat{C}_3 H_{Z_\alpha X_\beta}; H_{X_\beta Y_\alpha} = \hat{C}_3^2 H_{Y_\beta Z_\alpha} = \hat{C}_3 H_{Z_\beta X_\alpha}. \qquad (9)$$

Evidently, $\hat{H}$ involves only three independent matrix elements: $H_{X_\alpha X_\beta}$, $H_{X_\alpha Y_\beta}$, and $H_{X_\beta Y_\alpha}$, written as W, V, and U, respectively. $\hat{H}$ can then be rewritten as

$$\begin{aligned}
\hat{H} &= \left(|X_\alpha\rangle\langle X_\beta| + |X_\beta\rangle\langle X_\alpha|\right)W + \left(|Y_\alpha\rangle\langle Y_\beta| + |Y_\beta\rangle\langle Y_\alpha|\right)\hat{C}_3 W + \left(|Z_\alpha\rangle\langle Z_\beta| + |Z_\beta\rangle\langle Z_\alpha|\right)\hat{C}_3^2 W \\
&+ \left(|X_\alpha\rangle\langle Y_\beta| + |Y_\beta\rangle\langle X_\alpha|\right)V + \left(|Y_\alpha\rangle\langle Z_\beta| + |Z_\beta\rangle\langle Y_\alpha|\right)\hat{C}_3 V + \left(|Z_\alpha\rangle\langle X_\beta| + |X_\beta\rangle\langle Z_\alpha|\right)\hat{C}_3^2 V \\
&+ \left(|X_\beta\rangle\langle Y_\alpha| + |Y_\alpha\rangle\langle X_\beta|\right)U + \left(|Y_\beta\rangle\langle Z_\alpha| + |Z_\alpha\rangle\langle Y_\beta|\right)\hat{C}_3 U + \left(|Z_\beta\rangle\langle X_\alpha| + |X_\alpha\rangle\langle Z_\beta|\right)\hat{C}_3^2 U. \qquad (10)
\end{aligned}$$

The fact that symmetry reduces the number of independent matrix elements is related to the Wigner-Eckart Theorem: only the reduced matrix elements are needed.[39] Note that W,

V, and U are not the actual reduced matrix elements, as the vibrational part of the vibronic problem has not been specified yet.

Under the $\hat{C}_2^z$ operation, $\hat{H}$ becomes (see the $\hat{C}_2^z$-transformation in Eq. 4)

$$\begin{aligned}
\hat{C}_2^z \hat{H} \left(\hat{C}_2^z\right)^{-1} &= \left(|X_\alpha\rangle \langle X_\beta| + |X_\beta\rangle \langle X_\alpha|\right) \hat{C}_2^z W + \left(|Y_\alpha\rangle \langle Y_\beta| + |Y_\beta\rangle \langle Y_\alpha|\right) \hat{C}_2^z \hat{C}_3 W \\
&+ \left(|Z_\alpha\rangle \langle Z_\beta| + |Z_\beta\rangle \langle Z_\alpha|\right) \hat{C}_2^z \hat{C}_3^2 W + \left(|X_\alpha\rangle \langle Y_\beta| + |Y_\beta\rangle \langle X_\alpha|\right) \hat{C}_2^z V \\
&- \left(|Y_\alpha\rangle \langle Z_\beta| + |Z_\beta\rangle \langle Y_\alpha|\right) \hat{C}_2^z \hat{C}_3 V - \left(|Z_\alpha\rangle \langle X_\beta| + |X_\beta\rangle \langle Z_\alpha|\right) \hat{C}_2^z \hat{C}_3^2 V \\
&+ \left(|X_\beta\rangle \langle Y_\alpha| + |Y_\alpha\rangle \langle X_\beta|\right) \hat{C}_2^z U - \left(|Y_\beta\rangle \langle Z_\alpha| + |Z_\alpha\rangle \langle Y_\beta|\right) \hat{C}_2^z \hat{C}_3 U \\
&- \left(|Z_\beta\rangle \langle X_\alpha| + |X_\alpha\rangle \langle Z_\beta|\right) \hat{C}_2^z \hat{C}_3^2 U. \qquad (11)
\end{aligned}$$

By equating the matrix elements of the corresponding dyads in Eqs. 10 and 11, we find the following symmetry constraints on W, V, and U in order to satisfy $\hat{C}_2^z \hat{H} \left(\hat{C}_2^z\right)^{-1} = \hat{H}$:

$$W = \hat{C}_2^x W = \hat{C}_2^y W = \hat{C}_2^z W; V = -\hat{C}_2^x V = -\hat{C}_2^y V = \hat{C}_2^z V; U = -\hat{C}_2^x U = -\hat{C}_2^y U = \hat{C}_2^z U. \qquad (12)$$

Multiplication relations of symmetry operators are used to obtain these equalities. For instance, to equate the matrix elements of the $\left(|Y_\alpha\rangle \langle Y_\beta| + |Y_\beta\rangle \langle Y_\alpha|\right)$ dyads in Eqs. 10 and 11, we need $\hat{C}_3 W = \hat{C}_2^z \hat{C}_3 W$, i.e., $W = \hat{C}_3^2 \hat{C}_2^z \hat{C}_3 W$. And because $\hat{C}_3^2 \hat{C}_2^z \hat{C}_3 = \hat{C}_2^y$, we need $W = \hat{C}_2^y W$.

Extending the vibronic formalism from T to T_h symmetry is trivial (see the paragraph

following Eq. 24). For T_d symmetry (see the σ_d^x-transformations in Eq. 6),

$$\begin{aligned}
\hat{\sigma}_d^x \hat{H} \left(\hat{\sigma}_d^x\right)^{-1} &= \pm^{TT} \left(|X_\alpha\rangle \langle X_\beta| + |X_\beta\rangle \langle X_\alpha|\right) \hat{\sigma}_d^x W \pm^{TT} \left(|Z_\alpha\rangle \langle Z_\beta| + |Z_\beta\rangle \langle Z_\alpha|\right) \hat{\sigma}_d^x \hat{C}_3 W \\
&\pm^{TT} \left(|Y_\alpha\rangle \langle Y_\beta| + |Y_\beta\rangle \langle Y_\alpha|\right) \hat{\sigma}_d^x \hat{C}_3^2 W \pm^{TT} \left(|X_\alpha\rangle \langle Z_\beta| + |Z_\beta\rangle \langle X_\alpha|\right) \hat{\sigma}_d^x V \\
&\pm^{TT} \left(|Z_\alpha\rangle \langle Y_\beta| + |Y_\beta\rangle \langle Z_\alpha|\right) \hat{\sigma}_d^x \hat{C}_3 V \pm^{TT} \left(|Y_\alpha\rangle \langle X_\beta| + |X_\beta\rangle \langle Y_\alpha|\right) \hat{\sigma}_d^x \hat{C}_3^2 V \\
&\pm^{TT} \left(|X_\beta\rangle \langle Z_\alpha| + |Z_\alpha\rangle \langle X_\beta|\right) \hat{\sigma}_d^x U \pm^{TT} \left(|Z_\beta\rangle \langle Y_\alpha| + |Y_\alpha\rangle \langle Z_\beta|\right) \hat{\sigma}_d^x \hat{C}_3 U \\
&\pm^{TT} \left(|Y_\beta\rangle \langle X_\alpha| + |X_\alpha\rangle \langle Y_\beta|\right) \hat{\sigma}_d^x \hat{C}_3^2 U. \qquad (13)
\end{aligned}$$

"+" of "$\pm^{TT}$" applies to $(T_1 + T_1)$ and $(T_2 + T_2)$ problems, while "$-$" to $(T_1 + T_2)$ problems. Since the sign selection is determined by a pair of T states, it is dressed by the "TT" superscript. This sign selection clearly indicates that all $(T_1 + T_1)$ *inter*-term problems share the same expansion formalism as their $(T_2 + T_2)$ conterparts. This is also true for T_1 and T_2 *intra*-term problems. Obviously, the formula-sharings result from the equality of the direct products: $T_1 \otimes T_1 = T_2 \otimes T_2 = A_1 + E + T_1 + T_2$, and the symmetrized products: $[T_1 \otimes T_1] = [T_2 \otimes T_2] = A_1 + E + T_2$. Comparing Eqs. 10 and 13 and employing the multiplication relations between symmetry elements, we see that in order to have $\hat{\sigma}_d^x \hat{H} \left(\hat{\sigma}_d^x\right)^{-1} = \hat{H}$, we need

$$\hat{\sigma}_d^x W = \pm^{TT} W; \hat{\sigma}_d^z V = \pm^{TT} U. \qquad (14)$$

All constraints on the matrix elements are now known. We can start to derive their expansion formulas for specific vibronic problems.

3.1.1 $(T + T) \otimes (t + t)$, $(T + T) \otimes t$, $T \otimes (t + t)$, and $T \otimes t$

For generic $(T + T) \otimes (t + t)$ problems, W, V, and U are now functions of two sets of t coordinates, e.g., $W\left(x_\alpha, y_\alpha, z_\alpha, x_\beta, y_\beta, z_\beta\right)$. The monomials that contribute to their expansions

have the most general form

$$x_\alpha^{l_1} x_\beta^{l_2} y_\alpha^{m_1} y_\beta^{m_2} z_\alpha^{n_1} z_\beta^{n_2}. \tag{15}$$

All these monomials are eigenfunctions of $\hat{C}_2^{x,y,z}$:

$$\begin{aligned}
\hat{C}_2^x x_\alpha^{l_1} x_\beta^{l_2} y_\alpha^{m_1} y_\beta^{m_2} z_\alpha^{n_1} z_\beta^{n_2} &= (-1)^{mod(m_1+m_2,2)+mod(n_1+n_2,2)}\, x_\alpha^{l_1} x_\beta^{l_2} y_\alpha^{m_1} y_\beta^{m_2} z_\alpha^{n_1} z_\beta^{n_2}; \\
\hat{C}_2^y x_\alpha^{l_1} x_\beta^{l_2} y_\alpha^{m_1} y_\beta^{m_2} z_\alpha^{n_1} z_\beta^{n_2} &= (-1)^{mod(l_1+l_2,2)+mod(n_1+n_2,2)}\, x_\alpha^{l_1} x_\beta^{l_2} y_\alpha^{m_1} y_\beta^{m_2} z_\alpha^{n_1} z_\beta^{n_2}; \\
\hat{C}_2^z x_\alpha^{l_1} x_\beta^{l_2} y_\alpha^{m_1} y_\beta^{m_2} z_\alpha^{n_1} z_\beta^{n_2} &= (-1)^{mod(l_1+l_2,2)+mod(m_1+m_2,2)}\, x_\alpha^{l_1} x_\beta^{l_2} y_\alpha^{m_1} y_\beta^{m_2} z_\alpha^{n_1} z_\beta^{n_2}.
\end{aligned} \tag{16}$$

$mod\,(N,2)$ means the modulo function to obtain the remainder of $N/2$. Obviously, only the monomials with

$$mod\,(l_1+l_2,2) = mod\,(m_1+m_2,2) = mod\,(n_1+n_2,2) = 1 \text{ or } 0 \tag{17}$$

are symmetric with respect to all $\hat{C}_2^{x,y,z}$. They can contribute to W to make it satisfy Eq. 12. These monomials have the general form

$$\begin{aligned}
&\left(x_{\alpha/\beta} y_{\alpha/\beta} z_{\alpha/\beta}\right)^K x_\alpha^l x_\beta^{2k_1-l} y_\alpha^m y_\beta^{2k_2-m} z_\alpha^n z_\beta^{2k_3-n}, \\
&K = 0,1; l,m,n,k_{1,2,3} = 0,1,2,\cdots; l \le 2k_1; m \le 2k_2; n \le 2k_3.
\end{aligned} \tag{18}$$

The ranges of indices are maintained in the text below unless further specified. Throughout this paper, "α/β" means either α or β can be taken. $K = 0$ and 1 correspond to the 0 and 1 cases in Eq. 17, respectively. W of the $(T+T)\otimes(t+t)$ problem in T symmetry hence takes the following expansion formula:

$$W = a_{l,2k_1,m,2k_2,n,2k_3}^{x_{\alpha/\beta}y_{\alpha/\beta}z_{\alpha/\beta},K} \left(x_{\alpha/\beta} y_{\alpha/\beta} z_{\alpha/\beta}\right)^K x_\alpha^l x_\beta^{2k_1-l} y_\alpha^m y_\beta^{2k_2-m} z_\alpha^n z_\beta^{2k_3-n}. \tag{19}$$

When $K = 0$, the "α/β" subscripts are trivial and we simply set them all to be α. Please note that all monomials in the expansion in Eq. 19 differ in power(s) of the vibrational coordinate(s); there is no linear dependency among them and the expansion is redundancy-free. This redundancy-free argument is applicable to the other expansion formulas below that consist of similar, straightforward combinations of monomials.

The monomials with

$$mod\,(l_1 + l_2, 2) = mod\,(m_1 + m_2, 2) = 0 \text{ and } mod\,(n_1 + n_2, 2) = 1 \tag{20}$$

and

$$mod\,(l_1 + l_2, 2) = mod\,(m_1 + m_2, 2) = 1 \text{ and } mod\,(n_1 + n_2, 2) = 0 \tag{21}$$

are antisymmetric with respect to $\hat{C}_2^{x,y}$ and symmetric with respect to $\hat{C}_2^z$. They have the form

$$\left(z_{\alpha/\beta}\right) x_\alpha^l x_\beta^{2k_1-l} y_\alpha^m y_\beta^{2k_2-m} z_\alpha^n z_\beta^{2k_3-n} \text{ or } \left(x_{\alpha/\beta} y_{\alpha/\beta}\right) x_\alpha^l x_\beta^{2k_1-l} y_\alpha^m y_\beta^{2k_2-m} z_\alpha^n z_\beta^{2k_3-n}. \tag{22}$$

Only these monomials contribute to the V and U expansions:

$$V(U) \;=\; \left[b^{z_{\alpha/\beta}}_{l,2k_1,m,2k_2,n,2k_3}\left(z_{\alpha/\beta}\right) + b^{x_{\alpha/\beta}y_{\alpha/\beta}}_{l,2k_1,m,2k_2,n,2k_3}\left(x_{\alpha/\beta}y_{\alpha/\beta}\right)\right] x_\alpha^l x_\beta^{2k_1-l} y_\alpha^m y_\beta^{2k_2-m} z_\alpha^n z_\beta^{2k_3-n}. \tag{23}$$

Note that the V and U formulas take different expansion coefficients. Eqs 10, 19, and 23 give the general expansion formulas of the $(T+T)\otimes(t+t)$ Hamiltonian in T symmetry.

Extending the formulas to the $(T+T)\otimes(t+t+t)$ problem in T symmetry (and even

with more t modes) is straightforward:

$$\begin{aligned} W &= a^{x_{\alpha/\beta/\gamma}y_{\alpha/\beta/\gamma}z_{\alpha/\beta/\gamma},K}_{l_1,l_2,2k_1,m_1,m_2,2k_2,n_1,n_2,2k_3} \left(x_{\alpha/\beta/\gamma}y_{\alpha/\beta/\gamma}z_{\alpha/\beta/\gamma}\right)^K x_\alpha^{l_1}x_\beta^{l_2}x_\gamma^{2k_1-l_1-l_2}y_\alpha^{m_1}y_\beta^{m_2}y_\gamma^{2k_2-m_1-m_2}z_\alpha^{n_1} \\ & \quad z_\beta^{n_2}z_\gamma^{2k_3-n_1-n_2}; \\ V(U) &= \left[b^{z_{\alpha/\beta/\gamma}}_{l_1,l_2,2k_1,m_1,m_2,2k_2,n_1,n_2,2k_3}\left(z_{\alpha/\beta/\gamma}\right) + b^{x_{\alpha/\beta/\gamma}y_{\alpha/\beta/\gamma}}_{l_1,l_2,2k_1,m_1,m_2,2k_2,n_1,n_2,2k_3}\left(x_{\alpha/\beta/\gamma}y_{\alpha/\beta/\gamma}\right)\right] \\ & \quad x_\alpha^{l_1}x_\beta^{l_2}x_\gamma^{2k_1-l_1-l_2}y_\alpha^{m_1}y_\beta^{m_2}y_\gamma^{2k_2-m_1-m_2}z_\alpha^{n_1}z_\beta^{n_2}z_\gamma^{2k_3-n_1-n_2}. \end{aligned} \tag{24}$$

Due to this simplicity, we will not discuss similar mode extensions in the text below.

Obviously, Eqs. 19 and 23 can be used for the $(T_{g,u}+T_{g,u})\otimes(t_g+t_g)$ problems in T_h. Throughout the paper, the composite subscripts of Mulliken symbols match in order, e.g., $(T_{g,u}+T_{g,u})$ means (T_g+T_g) and (T_u+T_u). The expansions can be easily adapted for the other T_h cases. For the $(T_{g,u}+T_{g,u})\otimes(t_u+t_u)$ problems, only the even order terms shall be kept, while for the $(T_g+T_u)\otimes(t_u+t_u)$ problem, only the odd order terms remain. For the $(T_{g,u}+T_{g,u})\otimes(t_g+t_u)$ ($(T_g+T_u)\otimes(t_g+t_u)$) problems, only the terms with an even (odd) summation of the powers of the t_u coordinates shall be kept. The rule is that the parities of the monomials and the dyads must match. Keeping this simple rule in mind, we will not discuss any problems in T_h symmetry below.

It is only slightly more involved to obtain the expansions for problems in T_d symmetry following the constraints in Eq. 14. According to Eq. 6, acting σ_d^x on the monomials in Eq. 18 results in

$$\left(\left(\pm^{t^x_{\alpha/\beta}}x_{\alpha/\beta}\right)\left(\pm^{t^z_{\alpha/\beta}}z_{\alpha/\beta}\right)\left(\pm^{t^y_{\alpha/\beta}}y_{\alpha/\beta}\right)\right)^K\left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n}x_\alpha^l x_\beta^{2k_1-l}z_\alpha^m z_\beta^{2k_2-m}y_\alpha^n y_\beta^{2k_3-n}. \tag{25}$$

Since there are two t modes, "$\pm^t$"s are differentiated by "$\pm^{t_\alpha}$" and "$\pm^{t_\beta}$". When the sign selection is determined by one specific coordinate that may belong to the α or β mode, e.g., $x_{\alpha/\beta}$, symbols like "$\pm^{t^x_{\alpha/\beta}}$" are used. The monomials in Eqs. 18 and 25 are then symmetrized

to expand W for T_d problems:

$$\begin{aligned} W &= a_{l,2k_1,m,2k_2,n,2k_3}^{x_{\alpha/\beta}y_{\alpha/\beta}z_{\alpha/\beta},K}\left[\left(x_{\alpha/\beta}y_{\alpha/\beta}z_{\alpha/\beta}\right)^K x_\alpha^l x_\beta^{2k_1-l} y_\alpha^m y_\beta^{2k_2-m} z_\alpha^n z_\beta^{2k_3-n}\right. \\ &\left.\pm^{TT}\left(\left(\pm^{t^x_{\alpha/\beta}}x_{\alpha/\beta}\right)\left(\pm^{t^z_{\alpha/\beta}}z_{\alpha/\beta}\right)\left(\pm^{t^y_{\alpha/\beta}}y_{\alpha/\beta}\right)\right)^K\left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n} x_\alpha^l x_\beta^{2k_1-l} z_\alpha^m z_\beta^{2k_2-m} y_\alpha^n y_\beta^{2k_3-n}\right], \\ &k_3 \le k_2. \end{aligned} \tag{26}$$

$k_3 \le k_2$ is introduced to avoid double-counting the terms, so that the expansion is redundancy-free. Similar constraints on the summation (power) indices are introduced below for some expansion formulas for the same reason; the rationalization is not repeated, except for several cases whose constraints require further explanations, or even derivations (given in the Supporting Information (SI)). T_d symmetry does not impose further constraints on V, but connects it to U through $\hat{\sigma}_d^z$ (Eq. 14). Therefore, V takes the same expansion as in Eq. 23, and correspondingly

$$\begin{aligned} U &= \pm^{TT}\left[b_{l,2k_1,m,2k_2,n,2k_3}^{z_{\alpha/\beta}}\left(\pm^{t^z_{\alpha/\beta}}z_{\alpha/\beta}\right) + b_{l,2k_1,m,2k_2,n,2k_3}^{x_{\alpha/\beta}y_{\alpha/\beta}}\left(\left(\pm^{t^y_{\alpha/\beta}}y_{\alpha/\beta}\right)\left(\pm^{t^x_{\alpha/\beta}}x_{\alpha/\beta}\right)\right)\right] \\ &\left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n} y_\alpha^l y_\beta^{2k_1-l} x_\alpha^m x_\beta^{2k_2-m} z_\alpha^n z_\beta^{2k_3-n}. \end{aligned} \tag{27}$$

Please note that the order of the $y_{\alpha/\beta}x_{\alpha/\beta}$ factor in Eq. 27 and the $x_{\alpha/\beta}y_{\alpha/\beta}$ factor in Eq. 23 are connected by an $x \leftrightarrow y$ swapping while maintaining the α/β selection.

The general expansions for all $(T+T)\otimes(t+t)$ problems in T and T_d symmetries have been derived. $(T+T)\otimes t$ problems are their subproblems with one set of the t coordinates being zero; their expansion formulas are immediately obtained. Please note that setting one set of coordinates to be zero does not alter the redundancy-free nature of the expansion formulas. For the $(T+T)\otimes t$ problem in T symmetry,

$$\begin{aligned} W &= a_{2k_1,2k_2,2k_3}^K (xyz)^K x^{2k_1} y^{2k_2} z^{2k_3}; \\ V(U) &= \left[b_{2k_1,2k_2,2k_3}^z(z) + b_{2k_1,2k_2,2k_3}^{xy}(xy)\right] x^{2k_1} y^{2k_2} z^{2k_3}, \end{aligned} \tag{28}$$

Again V and U share the same expansion formula but with different expansion coefficients. For $(T+T)\otimes t$ problems in T_d symmetry:

$$W = a^K_{2k_1,2k_2,2k_3}\left(xyz\right)^K x^{2k_1}\left[y^{2k_2}z^{2k_3}\pm^{TT}\left(\pm^t\right)^K z^{2k_2}y^{2k_3}\right], k_3\leq k_2, \tag{29}$$

V takes the same expansion in Eq. 28, and correspondingly,

$$U = \pm^{TT}\left[b^z_{2k_1,2k_2,2k_3}\left(\pm^t z\right)+b^{xy}_{2k_1,2k_2,2k_3}\left(xy\right)\right]y^{2k_1}x^{2k_2}z^{2k_3}. \tag{30}$$

It is straightforward to obtain the expansions for the *intra*-term $T\otimes(t+t)$ coupling from the *inter*-term $(T+T)\otimes(t+t)$ formulas. The *intra*-term Hamiltonian reads

$$\begin{aligned}\hat{H} &= |X\rangle\langle X|W+|Y\rangle\langle Y|\hat{C}_3W+|Z\rangle\langle Z|\hat{C}_3^2W+\left(|X\rangle\langle Y|+|Y\rangle\langle X|\right)V\\ &+\left(|Y\rangle\langle Z|+|Z\rangle\langle Y|\right)\hat{C}_3V+\left(|Z\rangle\langle X|+|X\rangle\langle Z|\right)\hat{C}_3^2V.\end{aligned} \tag{31}$$

The $\hat{C}_3$- and $\hat{C}_2^{x,y,z}$-transformations of the *intra*-term ket-bra dyads are identical to those of the *inter*-term analogues and that is why the *intra*-term Hamiltonian has the same form as in Eq. 10, except that only two independent elements, W and V, are needed. Also, W and V have the same symmetry properties as in Eq. 12, and hence are expanded in the monomials in Eqs. 18 and 22. The only difference is in T_d symmetry,

$$\hat{\sigma}_d^x W=W;\hat{\sigma}_d^z V=V. \tag{32}$$

Obviously, the *intra*-term dyads can only take the + of the "$\pm^{TT}$" in Eq. 14, and the role of U has been replaced by V .

Given these considerations, we know that the $T\otimes(t+t)$ problem in T symmetry takes the same expansions as in Eqs. 19 and 23. For problems in T_d, W takes the "+" (of the

"$\pm^{TT}$") expansion in Eq. 26. V takes the symmetrized version of Eq. 23:

$$\begin{aligned} V &= b^{z_{\alpha/\beta}}_{l,2k_1,m,2k_2,n,2k_3}\left[\left(z_{\alpha/\beta}\right)x_\alpha^l x_\beta^{2k_1-l}y_\alpha^m y_\beta^{2k_2-m}+\left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n}\left(\pm^{t^z_{\alpha/\beta}}z_{\alpha/\beta}\right)y_\alpha^l y_\beta^{2k_1-l}x_\alpha^m x_\beta^{2k_2-m}\right]z_\alpha^n z_\beta^{2k_3-n} \\ &\quad +b^{x_{\alpha/\beta}y_{\alpha/\beta}}_{l,2k_1,m,2k_2,n,2k_3}\left[\left(x_{\alpha/\beta}y_{\alpha/\beta}\right)x_\alpha^l x_\beta^{2k_1-l}y_\alpha^m y_\beta^{2k_2-m}\right. \\ &\quad \left.+\left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n}\left(\left(\pm^{t^y_{\alpha/\beta}}y_{\alpha/\beta}\right)\left(\pm^{t^x_{\alpha/\beta}}x_{\alpha/\beta}\right)\right)y_\alpha^l y^{2k_1-l}x_\alpha^m x^{2k_2-m}\right]z_\alpha^n z_\beta^{2k_3-n}, k_2\le k_1. \end{aligned} \tag{33}$$

Setting one set of t coordinates to be zero in these $T\otimes(t+t)$ expansions gives us the corresponding $T\otimes t$ expansions. The $T\otimes t$ problem in T symmetry takes the expansions in Eq. 28. For the analogous problems in T_d, W takes the "+" of "$\pm^{TT}$" in Eq. 29. V takes the symmetrized version of the expansion in Eq. 28:

$$\begin{aligned} V &= b^z_{2k_1,2k_2,2k_3}\left[x^{2k_1}y^{2k_2}+\left(\pm^t\right)y^{2k_1}x^{2k_2}\right]z^{2k_3+1} \\ &\quad +b^{xy}_{2k_1,2k_2,2k_3}\left[x^{2k_1}y^{2k_2}+y^{2k_1}x^{2k_2}\right]xyz^{2k_3}, k_2\le k_1. \end{aligned} \tag{34}$$

We have finished deriving the general expansions up to arbitrary order for all $(T+T)\otimes(t+t)$, $(T+T)\otimes t$, $T\otimes(t+t)$,and $T\otimes t$ problems. Most of them are presented for the first time, except those of the $T_2\otimes(t_2+t_2)$ and $T_2\otimes t_2$ problems in T_d, which were derived using Weyl's polarization method.[22,40] Explicit expansions of all 29 of the four classes of Hamiltonians in T and T_d symmetries are given up to 4th order in Section S.1 in SI. The robustness of our derivations is demonstrated by the perfect agreement between our formulas for the $T_2\otimes(t_2+t_2)$ and $T_2\otimes t_2$ problems and those derived in Ref. 22 (see Section S.1.15 and Section S.1.18).

3.1.2 $(T+T)\otimes(e+e)$, $(T+T)\otimes e$, $T\otimes(e+e)$, and $T\otimes e$

W, V, and U are now functions of two sets of e coordinates, $W\left(\rho_\alpha,\phi_\alpha,\rho_\beta,\phi_\beta\right)$, etc. Eqs. 4 and 12 impose the following condition on V (and likewise U):

$$V\left(\rho_\alpha,\phi_\alpha,\rho_\beta,\phi_\beta\right)=-V\left(\rho_\alpha,\phi_\alpha,\rho_\beta,\phi_\beta\right). \tag{35}$$

Therefore, $V = U = 0$. This nullification arises from the fact that the e vibrations are invariant with respect to $\hat{C}_2^{x,y,z}$. For the same invariance, any arbitrary $W(\rho_\alpha, \phi_\alpha, \rho_\beta, \phi_\beta)$ function satisfies Eq. 12. The *inter*-term vibronic Hamiltonian hence adopts the following form:

$$\begin{aligned}\hat{H} &= (|X_\alpha\rangle\langle X_\beta| + |X_\beta\rangle\langle X_\alpha|) W(\rho_\alpha, \phi_\alpha, \rho_\beta, \phi_\beta) + (|Y_\alpha\rangle\langle Y_\beta| + |Y_\beta\rangle\langle Y_\alpha|) W\left(\rho_\alpha, \phi_\alpha - \frac{2\pi}{3}, \rho_\beta, \phi_\beta - \frac{2\pi}{3}\right) \\ &\quad + (|Z_\alpha\rangle\langle Z_\beta| + |Z_\beta\rangle\langle Z_\alpha|) W\left(\rho_\alpha, \phi_\alpha + \frac{2\pi}{3}, \rho_\beta, \phi_\beta + \frac{2\pi}{3}\right), \end{aligned} \tag{36}$$

and W has a free expansion. In cartesian e-coordinates:

$$W = a_{k_1,k_2,k_3,k_4} q_{\theta_\alpha}^{k_1} q_{\xi_\alpha}^{k_2} q_{\theta_\beta}^{k_3} q_{\xi_\beta}^{k_4}, k_{1-4} = 0, 1, 2, \cdots \tag{37}$$

The $\phi - \frac{2\pi}{3}$ ($\phi + \frac{2\pi}{3}$) rotation in the second (third) term in Eq. 36 corresponds to replacing q_θ and q_ξ in Eq. 37 by $-\frac{1}{2}q_\theta + \frac{\sqrt{3}}{2}q_\xi$ and $-\frac{\sqrt{3}}{2}q_\theta - \frac{1}{2}q_\xi$ ($-\frac{1}{2}q_\theta - \frac{\sqrt{3}}{2}q_\xi$ and $\frac{\sqrt{3}}{2}q_\theta - \frac{1}{2}q_\xi$), respectively.

Following the $\hat{\sigma}_d^x$-transformation in Eq. 6, we simply keep the terms with $k_2 + k_4$ being even, i.e.,

$$W = a_{k_1,k_2,k_3,k_4} q_{\theta_\alpha}^{k_1} q_{\xi_\alpha}^{k_2} q_{\theta_\beta}^{k_3} q_{\xi_\beta}^{2k-k_2}, 2k \geq k_2, \tag{38}$$

for the "+" case of "$\pm^{TT}$" in Eq. 14, and those with $k_2 + k_4$ being odd, i.e.,

$$W = a_{k_1,k_2,k_3,k_4} q_{\theta_\alpha}^{k_1} q_{\xi_\alpha}^{k_2} q_{\theta_\beta}^{k_3} q_{\xi_\beta}^{2k+1-k_2}, 2k+1 \geq k_2, \tag{39}$$

for the "−" case. Expansions of W for all $(T+T) \otimes (e+e)$ problems in T_d are obtained.

The expansions for $(T+T) \otimes e$ problems are obtained by setting $q_{\theta_\beta} = q_{\xi_\beta} = 0$ in Eqs. 37 to 39: for the $(T+T) \otimes e$ problem in T symmetry,

$$W = a_{k_1,k_2} q_\theta^{k_1} q_\xi^{k_2}; \tag{40}$$

for $(T+T)\otimes e$ problems in T_d symmetry,

$$W = a_{k_1,k_2} q_\theta^{k_1} q_\xi^{2k_2} \tag{41}$$

for the "+" case of "$\pm^{TT}$" in Eq. 14, and

$$W = a_{k_1,k_2} q_\theta^{k_1} q_\xi^{2k_2+1} \tag{42}$$

for the "−" case.

The *intra*-term $T\otimes(e+e)$ Hamiltonian reads

$$\begin{aligned}\hat{H} &= |X\rangle\langle X| W(\rho_\alpha,\phi_\alpha,\rho_\beta,\phi_\beta) + |Y\rangle\langle Y| W\left(\rho_\alpha,\phi_\alpha-\frac{2\pi}{3},\rho_\beta,\phi_\beta-\frac{2\pi}{3}\right)\\ &\quad + |Z\rangle\langle Z| W\left(\rho_\alpha,\phi_\alpha+\frac{2\pi}{3},\rho_\beta,\phi_\beta+\frac{2\pi}{3}\right).\end{aligned} \tag{43}$$

Eq. 37 also applies to the W of the $T\otimes(e+e)$ problem in T symmetry. For $T\otimes(e+e)$ problems in T_d symmetry, only the "+" of "$\pm^{TT}$" in Eq. 14 applies, and therefore, it takes the W expansion in Eq. 38. Following the same route, the W expansions for $T\otimes e$ problems are readily obtained. The $T\otimes e$ problem in T symmetry takes the W expansion in Eq. 40, and for $T\otimes e$ problems in T_d symmetry, the W expansion in Eq. 41 applies.

General expansions for all $(T+T)\otimes(e+e)$, $(T+T)\otimes e$, $T\otimes(e+e)$, and $T\otimes e$ problems have thus been derived. This derivation clearly demonstrates the origin of the well-known diagonal vibronic Hamiltonian of the $T\otimes(e+e+\cdots)$ problems with an arbitrary number of e modes: the invariance of the e vibration with respect to $\hat{C}_2^{x,y,z}$ (Eq. 4) is incompatible with the sign-flipping of the off-diagonal ket-bra dyads (Eq. 35). Explicit expansions up to 4th order of all 14 of these problems are given in Section S.2. Again, it is encouraging to see that our $T_2\otimes e$ expansion in T_d symmetry is in perfect agreement with the one derived by Opalka et al.[34] (see Section S.2.10). In this pioneering work, the authors employed a set of nonorthogonal e coordinates to tackle the problem in order to have a compact expansion and

to avoid square roots in the Hamiltonian matrix. We hereby show that using the conventional orthogonal coordinates also leads to a compact (maybe the most compact) expansion (see Eq. 41). As mentioned above, square roots emerge in H_{YY} and H_{ZZ} after carrying out the $\phi \mp \frac{2\pi}{3}$ rotations. Nevertheless, they do not complicate our derivation, since H_{XX} (W) is the only independent matrix element that we need to work on.

Before ending this part, let us examine the $T \otimes (e+e)$ Hamiltonian in T_d symmetry in Eq. 43, with the W expansion in Eq. 38:

$$\begin{aligned}
\hat{H} &= |X\rangle\langle X| a_{k_1,k_2,k_3,2k} q_{\theta_\alpha}^{k_1} q_{\xi_\alpha}^{k_2} q_{\theta_\beta}^{k_3} q_{\xi_\beta}^{2k-k_2} \\
&+ |Y\rangle\langle Y| a_{k_1,k_2,k_3,2k} \left(-\frac{1}{2}q_{\theta_\alpha} + \frac{\sqrt{3}}{2}q_{\xi_\alpha}\right)^{k_1} \left(-\frac{1}{2}q_{\xi_\alpha} - \frac{\sqrt{3}}{2}q_{\theta_\alpha}\right)^{k_2} \left(-\frac{1}{2}q_{\theta_\beta} + \frac{\sqrt{3}}{2}q_{\xi_\beta}\right)^{k_3} \left(-\frac{1}{2}q_{\xi_\beta} - \frac{\sqrt{3}}{2}q_{\theta_\beta}\right)^{2k-k_2} \\
&+ |Z\rangle\langle Z| a_{k_1,k_2,k_3,2k} \left(-\frac{1}{2}q_{\theta_\alpha} - \frac{\sqrt{3}}{2}q_{\xi_\alpha}\right)^{k_1} \left(-\frac{1}{2}q_{\xi_\alpha} + \frac{\sqrt{3}}{2}q_{\theta_\alpha}\right)^{k_2} \left(-\frac{1}{2}q_{\theta_\beta} - \frac{\sqrt{3}}{2}q_{\xi_\beta}\right)^{k_3} \left(-\frac{1}{2}q_{\xi_\beta} + \frac{\sqrt{3}}{2}q_{\theta_\beta}\right)^{2k-k_2} \quad (44)
\end{aligned}$$

Setting $q_{\xi_\alpha} = q_{\xi_\beta} = 0$ in the equation above,

$$\hat{H} = a_{k_1,k_2,k_3,2k} \left[|X\rangle\langle X| q_{\theta_\alpha}^{k_1} q_{\theta_\beta}^{k_3} + \left(-\frac{1}{2}\right)^{k_1+k_3} \left(\frac{3}{4}\right)^{k} q_{\theta_\alpha}^{k_1+k_2} q_{\theta_\beta}^{k_3+2k-k_2} \left(|Y\rangle\langle Y| + |Z\rangle\langle Z|\right) \right]. \quad (45)$$

This is the Hamiltonian when the system is distorted only along the e_θ directions. Certainly, $|Y\rangle$ and $|Z\rangle$ are degenerate in this distorted Hamiltonian. This is consistent with the well-known fact that the e_θ distortion lowers the symmetry to the D_{2d} epikernel and then partially lifts the 3-fold degeneracy of a T_2 (T_1) state to a non-degenerate B_2 (A_2) and a 2-fold degenerate E state.[41] Our expansion formula fully captures this partial degeneracy-lifting. Following a similar route, the $T \otimes (e+e)$ Hamiltonian in T symmetry along the e_θ distortions reads

$$\hat{H} = a_{k_1,k_2,k_3,k_4} \left[|X\rangle\langle X| q_{\theta_\alpha}^{k_1} q_{\theta_\beta}^{k_3} + \left(-\frac{1}{2}\right)^{k_1+k_3} \left(\frac{\sqrt{3}}{2}\right)^{k_2+k_4} q_{\theta_\alpha}^{k_1+k_2} q_{\theta_\beta}^{k_3+k_4} \left((-1)^{k_2+k_4} |Y\rangle\langle Y| + |Z\rangle\langle Z|\right) \right]. \quad (46)$$

The $(-1)^{k_2+k_4}$ factor breaks the degeneracy between $|Y\rangle$ and $|Z\rangle$. This is consistent with the fact that the e_θ distortion itself has lowered the T symmetry to the abelian D_2 kernel and fully lifts the 3-fold symmetry of the T state.

3.1.3 $(T+T)\otimes(t+e)$ and $T\otimes(t+e)$

Due to the $\hat{C}_2^{x,y,z}$-invariance of the e coordinates, we can simply multiply the monomials of the t coordinates in Eq. 28 by any monomials of the e coordinates to obtain symmetry-adapted monomials to expand W, V, and U of the $(T+T)\otimes(t+e)$ problem in T symmetry:

$$\begin{aligned} W &= a^K_{2k_1,2k_2,2k_3,k_4,k_5}\,(xyz)^K\,x^{2k_1}y^{2k_2}z^{2k_3}q_\theta^{k_4}q_\xi^{k_5}; \\ V(U) &= \left(b^z_{2k_1,2k_2,2k_3,k_4,k_5}\,(z)+b^{xy}_{2k_1,2k_2,2k_3,k_4,k_5}\,(xy)\right)x^{2k_1}y^{2k_2}z^{2k_3}q_\theta^{k_4}q_\xi^{k_5}. \end{aligned} \tag{47}$$

Recalling Eq. 35, $b^z_{0,0,0,k_4,k_5}=b^{xy}_{0,0,0,k_4,k_5}=0$. For $(T+T)\otimes(t+e)$ problems in T_d, we can modify Eq. 29 according to the power of q_ξ to have the symmetry-adapted W:

$$W = a^K_{2k_1,2k_2,2k_3,k_4,k_5}\,(xyz)^K\,x^{2k_1}\left(y^{2k_2}z^{2k_3}\pm^{TT}\left(\pm^t\right)(-1)^{k_5}\,z^{2k_2}y^{2k_3}\right)q_\theta^{k_4}q_\xi^{k_5}, k_2\geq k_3 \tag{48}$$

V retains its expansion in Eq. 47. Given the $\hat{\sigma}_d^z$-transformation in Eq. 6 and following Eq. 14, we have

$$U = \pm^{TT}V\left(-\frac{1}{2}q_\theta+\frac{\sqrt{3}}{2}q_\xi,\frac{1}{2}q_\xi+\frac{\sqrt{3}}{2}q_\theta,\pm^t y,\pm^t x,\pm^t z\right). \tag{49}$$

The U expansion formula is readily obtained through changing the arguments in the V in Eq. 47.

For the $T\otimes(t+e)$ *intra*-term problem in T symmetry (see Eq. 31 for the Hamiltonian), W and V take the same expansions as in Eq. 47, while U is not applicable. For $T\otimes(t+e)$ problems in T_d symmetry, W can only take the "+" of "$\pm^{TT}$" in Eq. 48. For the V expansion,

it is more convenient to define a new set of e coordinates, $\left(q'_\theta, q'_\xi\right)$, whose bases transform as the $2z^2 - x^2 - y^2$ and $\sqrt{3}\left(x^2 - y^2\right)$ functions. The new coordinates are adapted to $\hat{\sigma}_d^z$:

$$\hat{\sigma}_d^z f\left(q'_\theta, q'_\xi\right) = f\left(q'_\theta, -q'_\xi\right), \tag{50}$$

and they are related to the original e coordinates as

$$f\left(q'_\theta, q'_\xi\right) = f\left(-\frac{1}{2}q_\theta - \frac{\sqrt{3}}{2}q_\xi, -\frac{1}{2}q_\xi + \frac{\sqrt{3}}{2}q_\theta\right). \tag{51}$$

Eq. 34 can now be slightly modified and multiplied by $q_\theta'^{k_4} q_\xi'^{k_5}$ monomials to give the expansion for $T \otimes (e + t)$ problems in T_d symmetry:

$$\begin{aligned} V &= b^z_{2k_1,2k_2,2k_3,k_4,k_5}\left[x^{2k_1}y^{2k_2} + (-1)^{k_5}\left(\pm^t\right)y^{2k_1}x^{2k_2}\right] z^{2k_3+1} q_\theta'^{k_4} q_\xi'^{k_5} \\ &\quad + b^{xy}_{2k_1,2k_2,2k_3,k_4,k_5}\left[x^{2k_1}y^{2k_2} + (-1)^{k_5}\, y^{2k_1}x^{2k_2}\right] xyz^{2k_3} q_\theta'^{k_4} q_\xi'^{k_5}, k_1 \geq k_2. \end{aligned} \tag{52}$$

It can be easily converted to a function of the original e coordinates using Eq. 51 (see Section S.3.7 and Section S.3.8).

We believe that none of the general expansion formulas derived in this subsection have been presented. The $T_2 \otimes (t_2 + e)$ is one of the most important tetrahedral vibronic problems.[41–49] The ground state of CH_4^+ features such a JT interaction. When a linear JT model is used to simulate the CH_4 photoelectron spectrum, only qualitative agreement with experiment is obtained.[45] A quadratic model including bilinear terms of the e and t_2 coordinates substantially improves the agreement to semi-quantitative.[46] Higher order terms are needed to achieve even higher accuracy. The formulas presented here will certainly facilitate future studies of this class of problems. Explicit expansions of all 12 $(T + T) \otimes (t + e)$ and $T \otimes (t + e)$ problems up to 4th order are given in Section S.3.

3.2 A summary of our derivations, a modularized approach

Before entering the discussions for the E-related problems, let us summarize the procedure of our derivations: (1) for the class of $(T+T)$ *inter*-term coupling, we first infer the number of independent matrix elements and the generic Hamiltonian expressed using the elements. This is the process of obtaining Eq. 10; (2) we infer the symmetry requirements on the independent matrix elements (eq. Eqs. 12 and 14). These two steps do not require information of the vibrations that mediate the coupling. Therefore, their results are applicable for all $(T+T)$ problems; (3) for a particular $(T+T)$ vibronic problem whose mediating vibrations are specified, symmetry-adapted monomials of the vibrational coordinates are selected (e.g., Eqs. 18 and 22) or linearly combined (e.g., Eq. 26) following the requirements in Step (2). The vibronic Hamiltonian expansion is hence obtained; (4) the T *intra*-term coupling inherits the generic Hamiltonian from the $(T+T)$ *inter*-term coupling, with slight modification and additional symmetry requirements (e.g., Eqs. 31 and 32). The *inter*-term Hamiltonian formulas can then be adopted or adapted to describe the corresponding *intra*-term Hamiltonian with the same mediating vibrations; (5) single-mode problems are subproblems of double-mode problems and their Hamiltonians are obtained through allowing only the set of interesting vibrational coordinates to be nonzero.

The advantage of this five-step procedure is to separate the considerations of the electronic (Steps 1, 2, and 4) and vibrational parts (3 and 5). The symmetry-adapted monomials and symmetrized combinations of monomials can be considered as modules that meet the needs of the electronic part. Problems that share the same symmetry requirements (e.g., (T_1+T_1) and (T_2+T_2)) adopt the same modules. For problems that differ by a sign-flipping (e.g., (T_1+T_2) vs. (T_2+T_2)), one can easily adapt the modules for one problem to the other. Such a modularization strategy significantly increases the efficiency in deriving the Hamiltonians and clearly reveals connections between different problems. It enables us to construct vibronic Hamiltonians for a set of related problems in one shot, instead of particular problems one by one. It is universally applicable, regardless of the electronic states that are

coupled, the vibrations that couple them, and the fundamental symmetry (all point groups, including the highest symmetries O_h, I_h, etc.). We consider this modularized approach as the most important theoretical advance of this work. Please note that we are not the first to consider the electronic and vibrational parts separately.[15,16] We exploit this strategy to maximize the efficiency in deriving vibronic Hamiltonians.

3.3 $(E + E)$ coupling

The $(E + E)$ JT and pJT problems mediated by a set of e modes already exist in trigonal systems. We therefore leave those problems to future work dedicated to trigonal systems. Here, we only consider the $(E + E)$ problems that are relevant to tetrahedral systems, i.e., those involving at least one t mode. In the complex representation of the E states, the *inter*-term Hamiltonian reads

$$\hat{H} = \left(|+_\alpha\rangle\langle+_\beta| + |-_\beta\rangle\langle-_\alpha|\right) H_{+_\alpha+_\beta} + \left(|+_\alpha\rangle\langle-_\beta| + |+_\beta\rangle\langle-_\alpha|\right) H_{+_\alpha-_\beta} + c.c. \quad (53)$$

"*c.c.*" means taking the complex conjugate of the matrix elements and swapping the bra and ket of each dyad in the explicitly given part of the operator. There are only two independent matrix elements: the time-reversal symmetry forces the dyads within each pair of parentheses to share the same matrix element (see Eqs. 6 and 7 in Ref. 35 for more discussion on the similar sharing of matrix elements). We set $H_{+_\alpha+_\beta} = W$ and $H_{+_\alpha-_\beta} = V$. Since complex-valued diabats are used, W and V are complex, unlike in the $(T + T)$ problems above.

The transformations of the E states in Eq. 4 indicate that

$$\hat{C}_3\hat{H}\hat{C}_3^{-1} = \left(|+_\alpha\rangle\langle+_\beta| + |-_\beta\rangle\langle-_\alpha|\right)\hat{C}_3 W + e^{i\frac{2\pi}{3}}\left(|+_\alpha\rangle\langle-_\beta| + |+_\beta\rangle\langle-_\alpha|\right)\hat{C}_3 V + c.c \quad (54)$$

$\hat{C}_3\hat{H}\hat{C}_3^{-1} = \hat{H}$ requires

$$\hat{C}_3 W = W; \hat{C}_3 V = e^{-i\frac{2\pi}{3}} V. \quad (55)$$

Since the E states are invariant to $\hat{C}_2^{x,y,z}$,

$$\hat{C}_2^{x,y,z}\hat{H}\left(\hat{C}_2^{x,y,z}\right)^{-1} = \left(|+_\alpha\rangle\langle+_\beta| + |-_\beta\rangle\langle-_\alpha|\right)\hat{C}_2^{x,y,z}W + \left(|+_\alpha\rangle\langle-_\beta| + |+_\beta\rangle\langle-_\alpha|\right)\hat{C}_2^{x,y,z}V + c.c. \tag{56}$$

$\hat{C}_2^{x,y,z}\hat{H}\left(\hat{C}_2^{x,y,z}\right)^{-1} = \hat{H}$ requires

$$\hat{C}_2^{x,y,z}W = W; \hat{C}_2^{x,y,z}V = V. \tag{57}$$

Note that being symmetric with respect to $\hat{C}_3$ and all three $\hat{C}_2$ operators is equivalent to being symmetric with respect to $\hat{C}_3$ and one of the $\hat{C}_2$ operators. We here consider all three $\hat{C}_2$ operators because the derivation is easier. In T_d symmetry,

$$\hat{\sigma}_d^x\hat{H}\left(\hat{\sigma}_d^x\right)^{-1} = \left(|-_\alpha\rangle\langle-_\beta| + |+_\beta\rangle\langle+_\alpha|\right)\hat{\sigma}_d^x W + \left(|-_\alpha\rangle\langle+_\beta| + |-_\beta\rangle\langle+_\alpha|\right)\hat{\sigma}_d^x V + c.c. \tag{58}$$

$\hat{\sigma}_d^x\hat{H}\left(\hat{\sigma}_d^x\right)^{-1} = \hat{H}$ requires

$$\hat{\sigma}_d^x W = W^*; \hat{\sigma}_d^x V = V^*. \tag{59}$$

3.3.1 $(E+E)\otimes(t+e)$, $(E+E)\otimes e$, $E\otimes(t+e)$, and $E\otimes t$

Since monomials of e coordinates are invariant with respect to $\hat{C}_2^{x,y,z}$, we can multiply the t monomials that are $C_2^{x,y,z}$-invariant with arbitrary e monomials to give the $t+e$ monomials that make W and V satisfy Eq. 57. Such t monomials are all contained in the W expansion in Eq. 28. Acting the projection operators of the three irreps of the C_3 point group onto

those monomials, we obtain the eigenfunctions of $\hat{C}_3$:

$$\begin{aligned} F^0_{m,2k_1,2k_2} &= (xyz)^m \left(x^{2k_1}y^{2k_2} + y^{2k_1}z^{2k_2} + z^{2k_1}x^{2k_2}\right); \\ F^{\pm}_{m,2k_1,2k_2} &= (xyz)^m \left(x^{2k_1}y^{2k_2} + e^{\mp\frac{i2\pi}{3}}y^{2k_1}z^{2k_2} + e^{\pm\frac{i2\pi}{3}}z^{2k_1}x^{2k_2}\right), \\ & \quad m, k_1, k_2 = 0, 1, 2, \cdots \end{aligned} \tag{60}$$

A further constraint on the summation indices is that if $k_1 = 0$, then $k_2 = 0$. This is to avoid redundancy when k_1 or $k_2 = 0$: $F^0_{m,2k,0} = F^0_{m,0,2k}$; $F^{\pm}_{m,2k,0} = e^{\mp i\frac{2\pi}{3}}F^{\pm}_{m,0,2k}$. The functions have the following eigenvalues:

$$\hat{C}_3 F^0_{m,2k_1,2k_2} = F^0_{m,2k_1,2k_2}; \hat{C}_3 F^{\pm}_{m,2k_1,2k_2} = e^{\pm\frac{i2\pi}{3}}F^{\pm}_{m,2k_1,2k_2}. \tag{61}$$

The $F^{0/\pm}$ functions still satisfy Eq. 57 because the projection operators (specifically, the underlying $\hat{C}_3$ operator) only permute the powers of x, y, and z (say l, m, n respectively); the equalities (see Eq. 17 for their origin) of

$$mod(l, 2) = mod(m, 2) = mod(n, 2) = 1 \text{ or } 0 \tag{62}$$

are unaltered by $\hat{C}_3$.

The similar eigenfunctions in the e coordinates read:

$$\begin{aligned} G^0_{3N,2M} = \rho^{|3N|+2M}e^{i3N\phi}; G^{\pm}_{3N,2M} = \rho^{|3N\mp1|+2M}e^{i(3N\mp1)\phi}, \\ N = \cdots, -1, 0, 1, \cdots; M = 0, 1, 2, \cdots; \\ \hat{C}_3 G^0_{3N,2M} = G^0_{3N,2M}; \hat{C}_3 G^{\pm}_{3N,2M} = e^{\pm\frac{i2\pi}{3}}G^{\pm}_{3N,2M}. \end{aligned} \tag{63}$$

The $|3N| + 2M$ and $|3N \mp 1| + 2M$ powers of ρ guarantee that these functions can be expressed as polynomials of (q_θ, q_ξ) (see Eq. 24 and the relevant discussion in Ref. 35). The $G^{0/\pm}$ functions with different $\hat{C}_3$-eigenvalues are linearly independent, and the functions with

the same eigenvalue differ in either the angular phase factor of ϕ or the power of ρ; there is no redundancy among the $G^{0/\pm}$ functions. With the F and G functions, the W and V expansions that satisfy Eq. 55 are readily obtained:

$$\begin{aligned} W &= a^{+-,3N,2M}_{m,2k_1,2k_2} G^{+}_{3N,2M} F^{-}_{m,2k_1,2k_2} + a^{00,3N,2M}_{m,2k_1,2k_2} G^{0}_{3N,2M} F^{0}_{m,2k_1,2k_2} + a^{-+,3N,2M}_{m,2k_1,2k_2} G^{-}_{3N,2M} F^{+}_{m,2k_1,2k_2} \\ V &= b^{-0,3N,2M}_{m,2k_1,2k_2} G^{-}_{3N,2M} F^{0}_{m,2k_1,2k_2} + b^{0-,3N,2M}_{m,2k_1,2k_2} G^{0}_{3N,2M} F^{-}_{m,2k_1,2k_2} + b^{++,3N,2M}_{m,2k_1,2k_2} G^{+}_{3N,2M} F^{+}_{m,2k_1,2k_2}. \end{aligned} \tag{64}$$

The a and b coefficients are complex. These are the expansion formulas for the $(E+E)\otimes(t+e)$ problem in T symmetry. The direct product of the respectively linearly independent $F^{0/\pm}$ and $G^{0/\pm}$ functions give a set of linear independent functions. Therefore, the expansions in Eq. 64 are redundancy-free. This argument is applicable to any expansions that consist of products of two sets of linearly independent functions, and is not repeated.

To facilitate the derivation for problems in T_d symmetry, we separate each set of the F functions in Eq. 60 into two groups:

$$\begin{aligned} F^{0}_{m,2k_1,2k_2,y} &= (xyz)^m \left(x^{2k_1}y^{2k_2} + y^{2k_1}z^{2k_2} + z^{2k_1}x^{2k_2}\right); \\ F^{0}_{m,2k_1,2k_2,z} &= (xyz)^m \left(x^{2k_1}z^{2k_2} + y^{2k_1}x^{2k_2} + z^{2k_1}y^{2k_2}\right); \\ F^{\pm}_{m,2k_1,2k_2,y} &= (xyz)^m \left(x^{2k_1}y^{2k_2} + e^{\mp\frac{i2\pi}{3}}y^{2k_1}z^{2k_2} + e^{\pm\frac{i2\pi}{3}}z^{2k_1}x^{2k_2}\right); \\ F^{\pm}_{m,2k_1,2k_2,z} &= (xyz)^m \left(x^{2k_1}z^{2k_2} + e^{\mp\frac{i2\pi}{3}}y^{2k_1}x^{2k_2} + e^{\pm\frac{i2\pi}{3}}z^{2k_1}y^{2k_2}\right); \\ & \quad k_2 \le k_1. \end{aligned} \tag{65}$$

Function redundancies occur: (1) when $k_1 = k_2$, $F^{0}_{m,2k_1,2k_1,y} = F^{0}_{m,2k_1,2k_1,z}$ and $F^{\pm}_{m,2k_1,2k_1,y} = e^{\pm i\frac{2\pi}{3}} F^{\pm}_{m,2k_1,2k_1,z}$; (2) when $k_2 = 0$, $F^{0/\pm}_{m,2k_1,0,y} = F^{0/\pm}_{m,2k_1,0,z}$. The redundancies are trivial because those duplicated pairs are always added or subtracted in the final expansion formulas (Eqs. 71 and 72), which are redundancy-free. With the $\hat{\sigma}^x_d$-transformation in Eq. 6, we readily see

that

$$\hat{\sigma}_d^x F^{0/\pm}_{m,2k_1,2k_2,y/z} \;=\; \left(\pm^t\right)^m F^{0/\mp}_{m,2k_1,2k_2,z/y}; \hat{\sigma}_d^x G^{0/\pm}_{3N,2M} = {G^{0/\pm}_{3N,2M}}^* = G^{0/\mp}_{-3N,2M}. \tag{66}$$

Written as an expansion in the new set of F functions, W in Eq. 64 becomes

$$\begin{aligned} W \;=\; & G^+_{3N,2M}\left(a^{+-,3N,2M}_{m,2k_1,2k_2,y}F^-_{m,2k_1,2k_2,y} + a^{+-,3N,2M}_{m,2k_1,2k_2,z}F^-_{m,2k_1,2k_2,z}\right) + G^0_{3N,2M}\left(a^{00,3N,2M}_{m,2k_1,2k_2,y}F^0_{m,2k_1,2k_2,y}\right. \\ & \left. + a^{00,3N,2M}_{m,2k_1,2k_2,z}F^0_{m,2k_1,2k_2,z}\right) + G^-_{3N,2M}\left(a^{-+,3N,2M}_{m,2k_1,2k_2,y}F^+_{m,2k_1,2k_2,y} + a^{-+,3N,2M}_{m,2k_1,2k_2,z}F^+_{m,2k_1,2k_2,z}\right). \end{aligned} \tag{67}$$

Using Eq. 66,

$$\begin{aligned} \hat{\sigma}_d^x W \;=\; & G^-_{-3N,2M}\left(\pm^t\right)^m\left(a^{+-,3N,2M}_{m,2k_1,2k_2,y}F^+_{m,2k_1,2k_2,z} + a^{+-,3N,2M}_{m,2k_1,2k_2,z}F^+_{m,2k_1,2k_2,y}\right) \\ & + G^0_{-3N,2M}\left(\pm^t\right)^m\left(a^{00,3N,2M}_{m,2k_1,2k_2,y}F^0_{m,2k_1,2k_2,z} + a^{00,3N,2M}_{m,2k_1,2k_2,z}F^0_{m,2k_1,2k_2,y}\right) \\ & + G^+_{-3N,2M}\left(\pm^t\right)^m\left(a^{-+,3N,2M}_{m,2k_1,2k_2,y}F^-_{m,2k_1,2k_2,z} + a^{-+,3N,2M}_{m,2k_1,2k_2,z}F^-_{m,2k_1,2k_2,y}\right), \end{aligned} \tag{68}$$

while

$$\begin{aligned} W^* \;=\; & G^-_{-3N,2M}\left({a^{+-,3N,2M}_{m,2k_1,2k_2,y}}^* F^+_{m,2k_1,2k_2,y} + {a^{+-,3N,2M}_{m,2k_1,2k_2,z}}^* F^+_{m,2k_1,2k_2,z}\right) \\ & + G^0_{-3N,2M}\left({a^{00,3N,2M}_{m,2k_1,2k_2,y}}^* F^0_{m,2k_1,2k_2,y} + {a^{00,3N,2M}_{m,2k_1,2k_2,z}}^* F^0_{m,2k_1,2k_2,z}\right) \\ & + G^+_{-3N,2M}\left({a^{-+,3N,2M}_{m,2k_1,2k_2,y}}^* F^-_{m,2k_1,2k_2,y} + {a^{-+,3N,2M}_{m,2k_1,2k_2,z}}^* F^-_{m,2k_1,2k_2,z}\right). \end{aligned} \tag{69}$$

To have $\hat{\sigma}_d^x W = W^*$, we need

$$a^{+-/00/-+,3N,2M}_{m,2k_1,2k_2,z} = \left(\pm^t\right)^m {a^{+-/00/-+,3N,2M}_{m,2k_1,2k_2,y}}^*. \tag{70}$$

Implementing these constraints in Eq. 67, we obtain the symmetry-adapted W expansion

for $(E+E)\otimes(t+e)$ problems in T_d symmetry:

$$\begin{aligned} W &= G^{+}_{3N,2M}\left(a^{+-,3N,2M}_{m,2k_1,2k_2}F^{-}_{m,2k_1,2k_2,y}+\left(\pm^{t}\right)^{m}a^{+-,3N,2M^*}_{m,2k_1,2k_2}F^{-}_{m,2k_1,2k_2,z}\right)\\ &+G^{0}_{3N,2M}\left(a^{00,3N,2M}_{m,2k_1,2k_2}F^{0}_{m,2k_1,2k_2,y}+\left(\pm^{t}\right)^{m}a^{00,3N,2M^*}_{m,2k_1,2k_2}F^{0}_{m,2k_1,2k_2,z}\right)\\ &+G^{-}_{3N,2M}\left(a^{-+,3N,2M}_{m,2k_1,2k_2}F^{+}_{m,2k_1,2k_2,y}+\left(\pm^{t}\right)^{m}a^{-+,3N,2M^*}_{m,2k_1,2k_2}F^{+}_{m,2k_1,2k_2,z}\right). \end{aligned} \tag{71}$$

The V expansion is obtained through a similar route:

$$\begin{aligned} V &= G^{-}_{3N,2M}\left(b^{-0,3N,2M}_{m,2k_1,2k_2}F^{0}_{m,2k_1,2k_2,y}+\left(\pm^{t}\right)^{m}b^{-0,3N,2M^*}_{m,2k_1,2k_2}F^{0}_{m,2k_1,2k_2,z}\right)\\ &+G^{0}_{3N,2M}\left(b^{0-,3N,2M}_{m,2k_1,2k_2}F^{-}_{m,2k_1,2k_2,y}+\left(\pm^{t}\right)^{m}b^{0-,3N,2M^*}_{m,2k_1,2k_2}F^{-}_{m,2k_1,2k_2,z}\right)\\ &+G^{+}_{3N,2M}\left(b^{++,3N,2M}_{m,2k_1,2k_2}F^{+}_{m,2k_1,2k_2,y}+\left(\pm^{t}\right)^{m}b^{++,3N,2M^*}_{m,2k_1,2k_2}F^{+}_{m,2k_1,2k_2,z}\right). \end{aligned} \tag{72}$$

Setting the e coordinates to zero in the formulas above give the W and V expansions for $(E+E)\otimes t$ problems. For $(E+E)\otimes t$ problem in T symmetry,

$$W = a_{m,2k_1,2k_2}F^{0}_{m,2k_1,2k_2}; V = b_{m,2k_1,2k_2}F^{-}_{m,2k_1,2k_2}. \tag{73}$$

For $(E+E)\otimes t$ problems in T_d symmetry,

$$\begin{aligned} W &= a_{m,2k_1,2k_2}F^{0}_{m,2k_1,2k_2,y}+\left(\pm^{t}\right)^{m}a_{m,2k_1,2k_2}{}^{*}F^{0}_{m,2k_1,2k_2,z};\\ V &= b_{m,2k_1,2k_2}F^{-}_{m,2k_1,2k_2,y}+\left(\pm^{t}\right)^{m}b_{m,2k_1,2k_2}{}^{*}F^{-}_{m,2k_1,2k_2,z}. \end{aligned} \tag{74}$$

The a and b coefficients in Eqs. 73 and 74 are, in general, complex.

The $E\otimes(t+e)$ *intra*-term Hamiltonian in T symmetry reads

$$\hat{H} = \left(|+\rangle\langle+|+|-\rangle\langle-|\right)W+|+\rangle\langle-|\,V+|-\rangle\langle+|\,V^{*}, \tag{75}$$

with W and V satisfying Eqs. 55 and 57, and W being real. Therefore, V takes the same

expansion as in Eq. 64, while W only takes the real part of the W expansion there:

$$W = Re\left(a^{+-,3N,2M}_{m,2k_1,2k_2} G^{+}_{3N,2M} F^{-}_{m,2k_1,2k_2} + a^{00,3N,2M}_{m,2k_1,2k_2} G^{0}_{3N,2M} F^{0}_{m,2k_1,2k_2}\right). \quad (76)$$

Since the G^+F^- and G^-F^+ terms are complex conjugate to each other, we only keep the former in taking the real part. A more explicit W formula is given in Eq. S.68. For $E\otimes(t+e)$ problems in T_d symmetry, V also needs to satisfy Eq. 59, and it takes the same expansion as in Eq. 72. Since W is real, it simply takes the real part of Eq. 71:

$$\begin{aligned} W = Re\Big[& G^{+}_{3N,2M}\left(a^{+-,3N,2M}_{m,2k_1,2k_2,y} F^{-}_{m,2k_1,2k_2,y} + \left(\pm^t\right)^m a^{+-,3N,2M\ *}_{m,2k_1,2k_2,y} F^{-}_{m,2k_1,2k_2,z}\right) \\ & + G^{0}_{3N,2M}\left(a^{00,3N,2M}_{m,2k_1,2k_2,y} F^{0}_{m,2k_1,2k_2,y} + \left(\pm^t\right)^m a^{00,3N,2M\ *}_{m,2k_1,2k_2,y} F^{0}_{m,2k_1,2k_2,z}\right)\Big]. \end{aligned} \quad (77)$$

Again, the G^-F^+ terms have been dropped. A more explicit W formula is given in Eq. S.71. $E\otimes t$ *intra*-term problems take the expansions for $E\otimes(t+e)$ problems with the e coordinates set to zero. The $E\otimes t$ problem in T symmetry takes the same W and V expansions as in Eq. 73, with the a coefficients being real. $E\otimes t$ problems in T_d take the same W and V expansions as in Eq. 74, with the a coefficients being real.

All general expansions for $(E+E)\otimes(t+e)$, $(E+E)\otimes t$, $E\otimes(t+e)$, and $E\otimes t$ problems have thus been derived and they can be transformed to the expansions in the real representation of the E states using the matrix in Eq. 3. Explicit expansions of vibronic Hamiltonians of all 12 of these problems are given up to 4th order in Section S.4, in both the complex and the real representations.

3.3.2 $(E+E)\otimes(t+t)$ and $E\otimes(t+t)$

The monomials of two sets of t coordinates that satisfy Eq. 57 are given in Eq. 18, and they can be rewritten and separated into two groups:

$$f^{e,l,m,n}_{k_1,k_2,k_3}=x^l_\alpha x^{2k_1-l}_\beta y^m_\alpha y^{2k_2-m}_\beta z^n_\alpha z^{2k_3-n}_\beta; f^{o,l,m,n}_{k_1,k_2,k_3}=x^l_\alpha x^{2k_1-l+1}_\beta y^m_\alpha y^{2k_2-m+1}_\beta z^n_\alpha z^{2k_3-n+1}_\beta,$$
$$l,m,n,k_1,k_2,k_3=0,1,2,\cdots;l\leq 2k_1\,(+1)\,;m\leq 2k_2\,(+1)\,;n\leq 2k_3\,(+1)\ \text{for}\ f^e\,(f^o)\,. \quad (78)$$

The "e,o" superscripts indicate the even or odd total power of the monomials. The functions are constructed to be eigenfunctions of $\hat{C}_3$:

$$\begin{aligned}
F^{e/o,0,l,m,n}_{k_1,k_2,k_3} &= f^{e/o,l,m,n}_{k_1,k_2,k_3}+\hat{C}_3 f^{e/o,l,m,n}_{k_1,k_2,k_3}+\hat{C}_3^2 f^{e/o,l,m,n}_{k_1,k_2,k_3}=f^{e/o,l,m,n}_{k_1,k_2,k_3}+f^{e/o,n,l,m}_{k_3,k_1,k_2}+f^{e/o,m,n,l}_{k_2,k_3,k_1}\\
F^{e/o,\pm,l,m,n}_{k_1,k_2,k_3} &= f^{e/o,l,m,n}_{k_1,k_2,k_3}+e^{\mp i\frac{2\pi}{3}}\hat{C}_3 f^{e/o,l,m,n}_{k_1,k_2,k_3}+e^{\pm i\frac{2\pi}{3}}\hat{C}_3^2 f^{e/o,l,m,n}_{k_1,k_2,k_3}\\
&= f^{e/o,l,m,n}_{k_1,k_2,k_3}+e^{\mp i\frac{2\pi}{3}} f^{e/o,n,l,m}_{k_3,k_1,k_2}+e^{\pm i\frac{2\pi}{3}} f^{e/o,m,n,l}_{k_2,k_3,k_1}. \qquad (79)
\end{aligned}$$

The following constraints on the summation indices are imposed on $F^{e/o,0/\pm,l,m,n}_{k_1,k_2,k_3}$ to remove function redundancies (see Section S.5): (1) $k_3\leq k_1,k_2$; (2) if $k_1=0$, then $k_2=0$; (3) in the situation of $k_1=k_2=k_3$, $n\leq l,m$ and if $l=0$, then $m=0$. $F^{e/o,0,l,m,n}_{k_1,k_2,k_3}$ are the two modes analogues of $F^{0/\pm}_{m,2k_1,2k_2,2k_3}$ in Eq. 60 and are obtained following a similar procedure. These functions form a basis set to expand W and V satisfying Eq. 55:

$$W=a^{e/o,l,m,n}_{k_1,k_2,k_3}F^{e/o,0,l,m,n}_{k_1,k_2,k_3};V=b^{e/o,l,m,n}_{k_1,k_2,k_3}F^{e/o,-,l,m,n}_{k_1,k_2,k_3}. \qquad (80)$$

The a and b coefficients are complex. They are the expansions for the $(E+E)\otimes(t+t)$ problem in T symmetry.

The $f^{e/o,l,m,n}_{k_1,k_2,k_3}$ monomials can be further separated into two groups:

$$f^{e,l,m,n}_{k_1,k_2,k_3,y} = x^l_\alpha x^{2k_1-l}_\beta y^m_\alpha y^{2k_2-m}_\beta z^n_\alpha z^{2k_3-n}_\beta; f^{e,l,m,n}_{k_1,k_2,k_3,z} = x^l_\alpha x^{2k_1-l}_\beta z^m_\alpha z^{2k_2-m}_\beta y^n_\alpha y^{2k_3-n}_\beta,$$
$$k_3 \leq k_2, \qquad (81)$$

and similar for $f^{o,l,m,n}_{k_1,k_2,k_3,y}$ and $f^{o,l,m,n}_{k_1,k_2,k_3,z}$. The two groups are related by $\hat{\sigma}^x_d$:

$$\hat{\sigma}^x_d f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} = \left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n}\left(\pm^{t_\beta}\right)^{I_{eo}} f^{e/o,l,m,n}_{k_1,k_2,k_3,z/y}. \qquad (82)$$

$I_{eo} = 0$ for f^e and 1 for f^o. The functions are symmetrized to be $\hat{C}_3$-eigenfunctions:

$$\begin{aligned}
F^{e/o,0,l,m,n}_{k_1,k_2,k_3,y/z} &= f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} + \hat{C}_3 f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} + \hat{C}^2_3 f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} = f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} + f^{e/o,n,l,m}_{k_3,k_1,k_2,y/z} + f^{e/o,m,n,l}_{k_2,k_3,k_1,y/z};\\
F^{e/o,\pm,l,m,n}_{k_1,k_2,k_3,y/z} &= f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} + e^{\mp i\frac{2\pi}{3}}\hat{C}_3 f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} + e^{\pm i\frac{2\pi}{3}}\hat{C}^2_3 f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z}\\
&= f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} + e^{\mp i\frac{2\pi}{3}} f^{e/o,n,l,m}_{k_3,k_1,k_2,y/z} + e^{\pm i\frac{2\pi}{3}} f^{e/o,m,n,l}_{k_2,k_3,k_1,y/z}.
\end{aligned} \qquad (83)$$

In addition to the constraints introduced below Eq. 79, $k_2 \leq k_1$ (see Section S.5). These functions are the two-mode analogues of Eq. 65 and satisfy

$$\hat{\sigma}^x_d F^{e/o,0/\pm,l,m,n}_{k_1,k_2,k_3,y/z} = \left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n}\left(\pm^{t_\beta}\right)^{I_{eo}} F^{e/o,0/\mp,l,m,n}_{k_1,k_2,k_3,z/y}. \qquad (84)$$

It is straightforward to use these functions to construct W and V for $(E+E)\otimes(t+t)$ problems in T_d symmetry:

$$\begin{aligned}
W &= a^{e/o,l,m,n}_{k_1,k_2,k_3} F^{e/o,0,l,m,n}_{k_1,k_2,k_3,y} + \left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n}\left(\pm^{t_\beta}\right)^{I_{eo}} a^{e/o,l,m,n^*}_{k_1,k_2,k_3} F^{e/o,0,l,m,n}_{k_1,k_2,k_3,z};\\
V &= b^{e/o,l,m,n}_{k_1,k_2,k_3} F^{e/o,-,l,m,n}_{k_1,k_2,k_3,y} + \left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n}\left(\pm^{t_\beta}\right)^{I_{eo}} b^{e/o,l,m,n^*}_{k_1,k_2,k_3} F^{e/o,-,l,m,n}_{k_1,k_2,k_3,z},
\end{aligned} \qquad (85)$$

which satisfy Eq. 59.

As discussed in Section 3.3.1, the V expansions are invariant when switching from

$(E+E)\otimes(t+t)$ to the corresponding $E\otimes(t+t)$ problems, while the W expansions only keep the real parts. Therefore, $E\otimes(t+t)$ problems in T and T_d symmetries take the W and V expansions in Eqs. 80 and 85, respectively, but with all a coefficients being real. Explicit expansions up to 4th order are given for all 8 $(E+E)\otimes(t+t)$ and $E\otimes(t+t)$ problems in Section S.6. Even up to 4th order, the expansions are already cumbersome. This arises from the large number of the summation indices in the $F^{e/o,0/\pm,l,m,n}_{k_1,k_2,k_3}$ and $F^{e/o,0/\pm,l,m,n}_{k_1,k_2,k_3,y/z}$ functions and their consequently large number of combinations.

3.4 $(E+T)$ coupling

Lastly, we investigate the *inter*-term coupling between an E and a T state. The generic Hamiltonian in the complex representation of the E state and real representation of the T state reads

$$\begin{aligned}\hat{H} &= \left(|+\rangle\langle X| + |X\rangle\langle -|\right) H_{+X} + \left(|+\rangle\langle Y| + |Y\rangle\langle -|\right) H_{+Y} + \left(|+\rangle\langle Z| + |Z\rangle\langle -|\right) H_{+Z} \\ &\quad + c.c. \end{aligned} \tag{86}$$

The time-reversal symmetry forces the ket-bra dyads within each pair of parentheses to share the same matrix element. The matrix elements are complex. Following the $\hat{C}_3$-transformations in Eq. 4,

$$\begin{aligned}\hat{C}_3\hat{H}\hat{C}_3^{-1} &= e^{-i\frac{2\pi}{3}}\Big[\left(|+\rangle\langle Y| + |Y\rangle\langle -|\right)\hat{C}_3 H_{+X} + \left(|+\rangle\langle Z| + |Z\rangle\langle -|\right)\hat{C}_3 H_{+Y} \\ &\quad + \left(|+\rangle\langle X| + |X\rangle\langle -|\right)\hat{C}_3 H_{+Z}\Big] + c.c. \end{aligned} \tag{87}$$

Clearly, $\hat{C}_3\hat{H}\hat{C}_3^{-1} = \hat{H}$ requires

$$H_{+X} = e^{i\frac{2\pi}{3}}\hat{C}_3^2 H_{+Y} = e^{-i\frac{2\pi}{3}}\hat{C}_3 H_{+Z}. \tag{88}$$

There is only one independent matrix element, $H_{+X} = V$, and

$$\begin{aligned}\hat{H} &= \left(|+\rangle\langle X| + |X\rangle\langle -|\right) V + \left(|+\rangle\langle Y| + |Y\rangle\langle -|\right) e^{-i\frac{2\pi}{3}} \hat{C}_3 V + \left(|+\rangle\langle Z| + |Z\rangle\langle -|\right) e^{i\frac{2\pi}{3}} \hat{C}_3^2 V \\ &\quad + c.c. \end{aligned} \tag{89}$$

Following the $\hat{C}_2^z$-transformations in Eq. 4,

$$\begin{aligned}\hat{C}_2^z \hat{H} \left(\hat{C}_2^z\right)^{-1} &= -\left(|+\rangle\langle X| + |X\rangle\langle -|\right) \hat{C}_2^z V - \left(|+\rangle\langle Y| + |Y\rangle\langle -|\right) e^{-i\frac{2\pi}{3}} \hat{C}_2^z \hat{C}_3 V \\ &\quad + \left(|+\rangle\langle Z| + |Z\rangle\langle -|\right) e^{i\frac{2\pi}{3}} \hat{C}_2^z \hat{C}_3^2 V + c.c. \\ &= -\left(|+\rangle\langle X| + |X\rangle\langle -|\right) \hat{C}_2^z V - \left(|+\rangle\langle Y| + |Y\rangle\langle -|\right) e^{-i\frac{2\pi}{3}} \hat{C}_3 \hat{C}_2^y V \\ &\quad + \left(|+\rangle\langle Z| + |Z\rangle\langle -|\right) e^{i\frac{2\pi}{3}} \hat{C}_3^2 \hat{C}_2^x V + c.c. \end{aligned} \tag{90}$$

$\hat{C}_2^z \hat{C}_3 = \hat{C}_3 \hat{C}_2^y$ and $\hat{C}_2^z \hat{C}_3^2 = \hat{C}_3^2 \hat{C}_2^x$ have been used to obtain the second equality. Clearly, $\hat{C}_2^z \hat{H} \left(\hat{C}_2^z\right)^{-1} = \hat{H}$ requires

$$V = \hat{C}_2^x V = -\hat{C}_2^y V = -\hat{C}_2^z V. \tag{91}$$

In T_d symmetry, the $\hat{\sigma}_d^x$-transformations in Eq. 6 lead to

$$\begin{aligned}\hat{\sigma}_d^x \hat{H} \left(\hat{\sigma}_d^x\right)^{-1} &= \pm^T \left(|-\rangle\langle X| + |X\rangle\langle +|\right) \hat{\sigma}_d^x V \pm^T \left(|-\rangle\langle Z| + |Z\rangle\langle +|\right) e^{-i\frac{2\pi}{3}} \hat{\sigma}_d^x \hat{C}_3 V \\ &\quad \pm^T \left(|-\rangle\langle Y| + |Y\rangle\langle +|\right) e^{i\frac{2\pi}{3}} \hat{\sigma}_d^x \hat{C}_3^2 V + c.c. \end{aligned} \tag{92}$$

$\hat{\sigma}_d^x \hat{H} \left(\hat{\sigma}_d^x\right)^{-1} = \hat{H}$ requires $\hat{\sigma}_d^x V = \pm^T V^*$. All symmetry requirements on V are now known.

3.4.1 $(E+T) \otimes (t+t)$ and $(E+T) \otimes t$

Switching x and z in Eq. 22, we obtain the monomials of two sets of t coordinates that satisfy Eq. 91. This is a manifestation of the module-adaptation mentioned in Section 3.2.

Therefore, for the $(E+E)\otimes(t+t)$ problem in T symmetry,

$$V = \left(b^{x_{\alpha/\beta}}_{l,2k_1,m,2k_2,n,2k_3} x_{\alpha/\beta} + b^{y_{\alpha/\beta}z_{\alpha/\beta}}_{l,2k_1,m,2k_2,n,2k_3} y_{\alpha/\beta}z_{\alpha/\beta}\right) x^l_\alpha x^{2k_1-l}_\beta y^m_\alpha y^{2k_2-m}_\beta z^n_\alpha z^{2k_3-n}_\beta, \quad (93)$$

with complex b coefficients. For problems in T_d symmetry, we again separate each of the x and yz types of monomials into two groups:

$$\begin{aligned}
F^{x_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,y} &= \left(x_{\alpha/\beta}\right) x^l_\alpha x^{2k_1-l}_\beta y^m_\alpha y^{2k_2-m}_\beta z^n_\alpha z^{2k_3-n}_\beta;\\
F^{x_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,z} &= \left(x_{\alpha/\beta}\right) x^l_\alpha x^{2k_1-l}_\beta z^m_\alpha z^{2k_2-m}_\beta y^n_\alpha y^{2k_3-n}_\beta;\\
F^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,y} &= \left(y_{\alpha/\beta}z_{\alpha/\beta}\right) x^l_\alpha x^{2k_1-l}_\beta y^m_\alpha y^{2k_2-m}_\beta z^n_\alpha z^{2k_3-n}_\beta;\\
F^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,z} &= \left(z_{\alpha/\beta}y_{\alpha/\beta}\right) y^l_\alpha x^{2k_1-l}_\beta z^m_\alpha z^{2k_2-m}_\beta y^n_\alpha y^{2k_3-n}_\beta,\\
& \quad k_3 \le k_2. \qquad (94)
\end{aligned}$$

Please note the $\left(y_{\alpha/\beta}z_{\alpha/\beta}\right)$ and $\left(z_{\alpha/\beta}y_{\alpha/\beta}\right)$ factors in $F^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,y}$ and $F^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,z}$ are related by the $y \leftrightarrow z$ swapping but maintaining the α/β selection. The two groups of functions are connected by $\hat{\sigma}^x_d$:

$$\begin{aligned}
\hat{\sigma}^x_d F^{x_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,y} &= \left(\pm^{t^x_{\alpha/\beta}}\right)\left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n} F^{x_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,z};\\
\hat{\sigma}^x_d F^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,y} &= \left(\pm^{t^y_{\alpha/\beta}}\pm^{t^z_{\alpha/\beta}}\right)\left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n} F^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,z}. \qquad (95)
\end{aligned}$$

Please note that the sign of $\pm^{t^{y,z}_{\alpha/\beta}}$ is determined by whether the $y_{\alpha/\beta}$ and $z_{\alpha/\beta}$ coordinates in the $F^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,y}$ functions, NOT in the $F^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,z}$ functions, are t_1 or t_2 coordinates. Using these functions, we can construct the V expansion:

$$\begin{aligned}
V = {} & b^{x_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3} F^{x_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,y} \pm^T \left(\pm^{t^x_{\alpha/\beta}}\right)\left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n} b^{x_{\alpha/\beta},l,m,n\ *}_{2k_1,2k_2,2k_3} F^{x_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,z}\\
& + b^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3} F^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,y} \pm^T \left(\pm^{t^y_{\alpha/\beta}}\pm^{t^z_{\alpha/\beta}}\right)\left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n} b^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n*}_{2k_1,2k_2,2k_3} F^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,z}, \qquad (96)
\end{aligned}$$

which satisfy $\hat{\sigma}_d^x V = \pm^T V^*$.

As usual, setting one set of t coordinates to be zero in the expansion formulas above give those for $(E+T)\otimes t$ problems: for the $(E+T)\otimes t$ problem in T symmetry,

$$V = \left(b^x_{2k_1,2k_2,2k_3} x + b^{yz}_{2k_1,2k_2,2k_3} yz\right) x^{2k_1} y^{2k_2} z^{2k_3}; \tag{97}$$

for $(E+T)\otimes t$ problems in T_d,

$$\begin{aligned} V &= \left(b^x_{2k_1,2k_2,2k_3} x + b^{yz}_{2k_1,2k_2,2k_3} yz\right) x^{2k_1} y^{2k_2} z^{2k_3} \\ &\quad \pm^T \left(\left(\pm^t\right) {b^x_{2k_1,2k_2,2k_3}}^* x + {b^{yz}_{2k_1,2k_2,2k_3}}^* yz\right) x^{2k_1} z^{2k_2} y^{2k_3}, k_3 \le k_2. \end{aligned} \tag{98}$$

Explicit expansions up to 4th order of all 12 $(E+T)\otimes(t+t)$ and $(E+T)\otimes t$ problems are given in Section S.7.

3.4.2 $(E+T)\otimes(t+e)$ and $(E+T)\otimes e$

Following the same procedure of getting Eq. 47 from Eq. 28, we obtain from Eq. 97 the V expansion for the $(E+T)\otimes(t+e)$ problem in T symmetry,

$$V = \left(b^x_{2k_1,2k_2,2k_3,k_4,k_5} x + b^{yz}_{2k_1,2k_2,2k_3,k_4,k_5} yz\right) x^{2k_1} y^{2k_2} z^{2k_3} q_\theta^{k_4} q_\xi^{k_5}. \tag{99}$$

All coefficients are complex. This expansion formula is symmetrized as

$$\begin{aligned} V &= \left(b^x_{2k_1,2k_2,2k_3,k_4,k_5} y^{2k_2} z^{2k_3} \pm^T \left(\pm^t\right) (-1)^{k_5} {b^x_{2k_1,2k_2,2k_3,k_4,k_5}}^* z^{2k_2} y^{2k_3}\right) x^{2k_1+1} q_\theta^{k_4} q_\xi^{k_5} \\ &\quad + \left(b^{yz}_{2k_1,2k_2,2k_3,k_4,k_5} y^{2k_2} z^{2k_3} \pm^T (-1)^{k_5} {b^{yz}_{2k_1,2k_2,2k_3,k_4,k_5}}^* z^{2k_2} y^{2k_3}\right) yz x^{2k_1} q_\theta^{k_4} q_\xi^{k_5}, k_3 \le k_2, \end{aligned} \tag{100}$$

to satisfy $\hat{\sigma}_d^x V = \pm^T V^*$. This is the general V expansion formula for $(E+T)\otimes(t+e)$ problems in T_d symmetry.

Setting the t coordinates to zero gives the expansion formulas for $(E+T)\otimes e$ problems. However, all those expansions only contain odd powers of the t coordinates and therefore, $V=0$ for $(E+T)\otimes e$ problems: an e mode does not mediate vibronic interaction between an E and a T state. This is because the direct product $E\otimes T = T+T$ in T symmetry. It does not contain E and A, which arise from self-products of E. It can hence be generalized that there are no $(E+T)\otimes(e+e+\cdots)$ *inter*-term vibronic couplings, regardless of the number of e modes. Explicit expansions up to 4th order are given for all 5 $(E+T)\otimes(t+e)$ problems in Section S.8.

4 A numerical example

Within this paper, it is unfeasible to give numerical examples for all 92 problems whose expansion formulas are just derived. Here, we examine one representative yet simple case whose formulas are unknown prior to this work, the $T_1\otimes t_1$ problem in T_d symmetry. This JT problem can occur for neopentane. Removing an electron from neopentane's t_1 HOMO-1 set results in a $^2T_1$ state. Since the t_1 orbital contains substantial C-H σ-bonding character, the $^2T_1$ state is expected to experience a substantial vibronic coupling along the t_1 H-C-H bending mode. The x components of the t_1 orbital and mode are shown in Figure 3. We are more interested in the correctness of our formalism than the actual $^2T_1\otimes t_1$ problem. Therefore, we put aside the full vibronic problem and only examine a 1-electron model problem: the t_1 orbital forms the 1-electron T_1 state and the Hamiltonian contains the 1-electron kinetic operator and the nuclei-electron attraction. All t_1 orbital components are frozen against the t_1 nuclear vibration; they are strict diabatic states. The Hamiltonian matrix elements of the frozen t_1 orbital are calculated on a 3-D grid of the t_1 bending normal mode coordinates (x,y,z). Both the orbital and the normal mode are obtained from the B3LYP density functional theory calculation of the ground state neopentane, using the GAMESS-US package.[50,51]

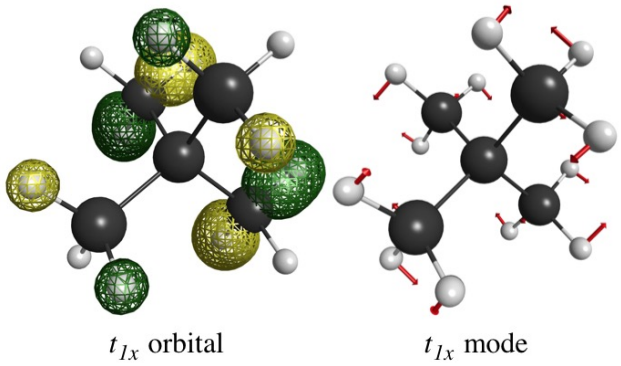

Figure 3: The x component of the t_1 HOMO-1 degenerate orbital and the x component of the t_1 H-C-H bending normal mode of neopentane. The molecule has a similar orientation as in Figure 1 and therefore, the axes are not shown.

The calculated H_{XX} (W) and H_{XY} (V) are fitted using a polynomial with all 34 $x^l y^m z^n$ monomials up to 4th order. The W value at the undistorted structure is taken to be zero. The fitting results are:

$$\begin{aligned} W &= 0.098778x^2 + 0.150010y^2 + 0.149999z^2 - 0.012058x^4 - 0.018998y^4 - 0.018998z^4 \\ &\quad -0.035637x^2y^2 - 0.035625x^2z^2 - 0.055627y^2z^2; \\ V &= -0.229226xy + 0.175309x^2z - 0.175235y^2z - 0.043888x^3y - 0.043885y^3x \\ &\quad +0.612812z^2xy. \end{aligned} \tag{101}$$

The other terms have coefficients that are too small to be considered. W and V are in Hartree and the mass-weighted normal mode coordinates are in $\sqrt{\text{u}}$Å. Evidently, with numerical errors $< 10^{-4}$, the fitted W and V bear the following expressions:

$$\begin{aligned} W^{(1-4)} &= a^0_{2,0,0}x^2 + a^0_{0,2,0}\left(y^2+z^2\right) + a^0_{4,0,0}x^4 + a^0_{0,4,0}\left(y^4+z^4\right) + a^0_{2,2,0}x^2\left(y^2+z^2\right) \\ &\quad +a^0_{0,2,2}\left(y^2z^2+z^2y^2\right); \\ V^{(1-4)} &= b^{xy}_{0,0,0}xy + b^z_{0,0,0}\left(x^2-y^2\right)z + b^{xy}_{2,0,0}\left(x^2+y^2\right)xy + b^{xy}_{0,0,2}xyz^2, \end{aligned} \tag{102}$$

which are obtained by taking $\pm^t = -1$ for the t_1 mode in Eqs. 29 and 34, respectively.

Our formulas fully capture the symmetries of the matrix elements. Please note that the $a^0_{0,2,2}\,(y^2z^2 + z^2y^2)$ term in the W expansion manifests the trivial redundancy mentioned under Eq. 65: the two identical terms y^2z^2 and z^2y^2 are (always) added (or subtracted in other expansions) so that the redundancy does not occur.

Similar calculations and fittings have been carried out for the $(T_1 + T_2)\otimes t_1$ and $(T_1 + T_2)\otimes e$ *inter*-term problems, with the same T_1 state and t_1 mode, the T_2 state being the t_2 HOMO, and the e mode being the e H-C-H bending. The fitted expansions are all in good agreement with the analytical formulas (see Section S.9). These numerical examples are far from being complete. Nevertheless, their agreements with analytical formulas do reflect the robustness of our derivations.

5 Expansion of spin-orbit matrix elements in the p-type tetrahedral vibronic problems

Spin-orbit coupling (SOC) is another mechanism that couples different electronic states and its magnitude increases along with the nuclear charge.[52–54] The interplay between SOC and JT/pJT effects has been a long lasting research subject.[55–70] For JT/pJT systems with heavy nuclei, it is necessary to include the spin-orbit interaction in the vibronic Hamiltonian expansion. Very recently, Domcke et al.[71] showed that there is a neat connection between the SOC and the electrostatic Hamiltonian matrix elements for a set of p Gaussian orbitals. This finding facilitates the construction of the spin-orbit vibronic Hamiltonians for the relevant problems.

The Domcke formalism applies to SOC problems that can be approximately described using spin-orbit matrix elements between a set of $p_{x,y,z}$ Gaussian orbitals, which we term the "p-type problems". Tetrahedral systems with a heavy p-block atoms at the centre, e.g., PbH_4, fall into this class of problems. The p-orbitals are of t, t_u, and t_2 irreps in T, T_h, and T_d symmetries, respectively. Correspondingly, we can use the W and V expansion formulas

of the T, T_u, and T_2 *intra*-term couplings to describe the spin-orbit vibronic Hamiltonians of tetrahedral p-type problems. These two elements are generically labelled as W_{T_p} and V_{T_p} below. Another element is needed, and it corresponds to the Φ_{00} in Eq. 16 in Ref. 71. This element is symmetric with respect to all symmetry operations. Certainly, it should have the same expansion formula as the W in the E *intra*-term coupling (see Section 3.3.1), which is labeled as W_E below. Substituting W_{T_p}, V_{T_p}, and W_E into Eqs 14 to 21 of Ref. 71, we obtain the following expressions for the six fundamental p-type SOC matrix elements:

$$\begin{aligned}
h^{SO}_{p_x p_y} &= i\left(W_{T_p} + \hat{C}_3 W_{T_p}\right) - W_E; \\
h^{SO}_{p_x p_z} &= i\hat{C}_3 V_{T_p}; \\
h^{SO}_{p_y p_z} &= -i\hat{C}_3^2 V_{T_p}; \\
h^{SO}_{p_x \bar{p}_y} &= -i\hat{C}_3^2 V_{T_p} - \hat{C}_3 V_{T_p}; \\
h^{SO}_{p_x \bar{p}_z} &= iV_{T_p} - W_{T_p} - \hat{C}_3^2 W_{T_p} + W_E; \\
h^{SO}_{p_y \bar{p}_z} &= i\hat{C}_3 W_{T_p} + i\hat{C}_3^2 W_{T_p} - iW_E - V_{T_p}.
\end{aligned} \tag{103}$$

The other elements are either zero or related to the six by sign-flipping and/or taking the complex conjugate.[71] In the expressions above, orbitals with β spin are denoted by overhead bar, while those with α spin are not denoted. One can substitute the corresponding W_{T_p}, V_{T_p}, and W_E formulas into the expressions above and use the $\hat{C}_3$-transformation in Eq. 4 to obtain the SOC matrix elements' expansions in different tetrahedral vibronic problems. Clearly, the calculation of all SOC matrix elements in a vibrational basis set is reduced to the calculation of the W_{T_p}, V_{T_p}, and W_E matrix elements. This is a substantial saving in computing time.

6 Further Discussion and Conclusion

We have derived general, redundancy-free expansion formulas up to arbitrary order for 92 vibronic coupling problems in T and T_d symmetries. These problems include the Jahn-Teller problems of an E or a T term, as well as the $(T+T)$, $(E+E)$, and $(E+T)$ type pseudo-Jahn-Teller problems, coupled by up to two t and/or e vibrational modes. They cover the most interesting vibronic problems of tetrahedral systems. This work has thus laid a solid foundation for future studies of tetrahedral vibronic problems. Let us take the simplest tetrahedral system CH_4 as an example and consider its double ionization that leaves two holes in the t_2 HOMO set. It results in a $^3T_1$, a $^1T_2$, a ^1E, and a $^1A_1$ state; the first three experience both JT and pJT interactions. Prior to this work, only the general expansion formulas of handling the T_2 JT problem were available. This work sets a cornerstone for investigating all the other vibronic problems of the three states by offering their Hamiltonian formulas. The formulas for T symmetries can be readily adapted to the problems in T_h symmetry, and it is straightforward to generalize the formulas to include more vibrational modes. Also, the formulas derived for electrostatic vibronic Hamiltonians can be adapted to describe spin-orbit vibronic Hamiltonians.

We have not derived any formulas for octahedral systems yet. However, this is unnecessary. The T_d and O point groups are isomorphic; they share the same expansion formulas. Please note that this formula-sharing critically relies on the consistency in settings. The x-, y-, and z-axes coincide with the three C_2 axes of T_d symmetry (e.g., see Figure 1). Correspondingly, they need to coincide with the three C_4 axes of O symmetry. The same procedure used to obtain T_h expansion formulas from T formulas can be used to obtain O_h formulas from O formulas. Therefore, this work has also laid a solid foundation for vibronic studies of octahedral systems. Overall, the applicability of the results in this work extends far beyond the 92 problems.

Most of the formulas are presented for the first time, except those for the $T_2 \otimes t_2$, $T_2 \otimes (t_2+t_2)$, and $T_2 \otimes e$ problems. For these three problems, our formulas are in perfect agreement

with those derived using the Weyl's polarization method. This agreement corroborates the correctness of our formalism. Our formalism is concise. Fewer than two expansion formulas (W and/or V; U, when applicable, is related to V) are needed for each problem, and most of them can be written within two lines. The formulas are convenient to use in actual vibronic calculations. With the help of a spreadsheet, all allowed summation indices are easily generated, and explicit expansions are readily obtained. This is how we prepared the explicit expansions up to 4th order for the 92 problems in SI. Our derivations are simple and transparent to chemists. They require no more than point group theory and a few algebraic tricks. Most importantly, we present a modularized approach to construct vibronic Hamiltonians for a set of related problems in one shot, instead of particular problems one by one. The knowledge acquired in this work has paved the way for deriving Hamiltonian formulas for the even more complicated icosahedral vibronic problems.

The derivations clearly demonstrate connections between different problems. For instance, all $(t+t)$ problems involve the three monomials in Eqs. 18 and 22 (which are the most adaptable modules). The same set of matrix elements of those monomials in vibrational basis are hence applicable in simulating all those problems. Many problems are shown to share identical vibronic Hamiltonians (e.g., $T_1 \otimes (t_2 + t_2)$ and $T_2 \otimes (t_2 + t_2)$), or only have a sign difference (e.g., $(T_1 + T_2) \otimes (t_2 + t_2)$ vs. $(T_1 + T_1) \otimes (t_2 + t_2)$). Guided by the formulas, one can easily adapt a program designed for one problem to another problem, or connect the interpretation of one vibronic spectrum to another. These are the gainings from knowing the analytical formulas. More gainings will be perceived in using the formulas in actual vibronic studies.

ASSOCCIATED CONTENT

Supporting Information The Supporting Information is available free of charge on the ACS Publication Website at http://pubs.acs.org. Explicit expansion formulas up to 4th order for the 92 vibronic Hamiltonians that are derived in this work; derivation for the

constraints on the power indices for the $F^{e/o,0/\pm,l,m,n}_{k_1,k_2,k_3}$ and $F^{e/o,0/\pm,l,m,n}_{k_1,k_2,k_3,y/z}$ functions; numerical examples of the $(T_1 + T_2) \otimes t_1$ and $(T_1 + T_2) \otimes e$ problems.

Notes The authors declare no competing financial interest.

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References

(1) Jahn, H. A.; Teller, E. Stability of Polyatomic Molecules in Degenerate Electronic States. *Proc. Roy. Soc. A* **1937**, *161*, 220–235.

(2) Englman, R. *Jahn-Teller Effect in Molecules and Crystals*; John Wiley and Sons, Ltd.: London, 1972.

(3) Goodenough, J. B. Jahn-Teller Phenomena in Solids. *Ann. Rev. Mater. Sci.* **1998**, *28*, 1–27.

(4) Barckholtz, T. A.; Miller, T. A. Quantitative Insights about Molecules Exhibiting Jahn-Teller and Related Effects. *Int. Rev. Phys. Chem.* **1998**, *17*, 435–524.

(5) Bersuker, I. B. Modern Aspects of the Jahn?Teller Effect Theory and Applications To Molecular Problems. *Chem. Rev.* **2001**, *101*, 1067–1114.

(6) Applegate, B. E.; Barckholtz, T. A.; Miller, T. A. Explorations of Conical Intersections and Their Ramifications for Chemistry through the Jahn-Teller Effect. *Chem. Soc. Rev.* **2003**, *32*, 38–49.

(7) Bersuker, I. A Unique Jahn-Teller Mechanism of All the Symmetry Breakings in Molecular Systems and Condensed Matter. *Adv. Quantum Chem.* **2003**, *44*, 1–12.

(8) Köppel, H. Jahn-Teller and Pseudo-Jahn-Teller Intersections: Spectroscopy and Vibronic Dynamics. In *Conical Intersections: Electronic Structure, Dynamics and Spectroscopy*; Domcke, W., Yarkony, D. R., Köppel, H., Eds.; World Scientific: New Jersey, 2004; Chapter 10, pp 429–472.

(9) Bersuker, I. B. *The Jahn-Teller Effect*; Cambridge University Press: Cambridge, UK, 2006.

(10) Domcke, W.; Yarkony, D. R. Role of Conical Intersections in Molecular Spectroscopy and Photoinduced Chemical Dynamics. *Annu. Rev. Phys. Chem.* **2012**, *63*, 325–352.

(11) Bersuker, I. B. Pseudo-Jahn-Teller Effect—A Two-State Paradigm in Formation, Deformation, and Transformation of Molecular Systems and Solids. *Chem. Rev.* **2013**, *113*, 1351–1390.

(12) Halcrow, M. A. Jahn-Teller Distortion in Transition Metal Compounds, and Their Importance in Functional Molecular and Inorganic Materials. *Chem. Soc. Rev.* **2013**, *42*, 1784–1795.

(13) Köppel, H.; Domcke, W.; Cederbaum, L. S. Multi-mode Molecular Dynamics beyond the Born-Oppenheimer Approximation. *Adv. Chem. Phys.* **1984**, *59*, 57–246.

(14) Bersuker, I. B.; Polinger, V. Z. *Vibronic Interactions in Molecules and Crystals*; Springer-Verlag, 1989.

(15) Viel, A.; Eisfeld, W. Effects of Higher Order Jahn-Teller Coupling on the Nuclear Dynamics. *J. Chem. Phys.* **2004**, *120*, 4603–4613.

(16) Eisfeld, W.; Viel, A. Higher Order $(A + E) \times e$ Pseudo-Jahn-Teller Coupling. *J. Chem. Phys.* **2005**, *122*, 204317.

(17) Bhattacharyya, S.; Opalka, D.; Poluyanov, L. V.; Domcke, W. The $(E + A) \times (e + a)$ Jahn-Teller and Pseudo-Jahn-Teller Hamiltonian Including Spin-Orbit Coupling for Trigonal Systems. *J. Phys. Chem. A* **2014**, *118*, 11962–11970.

(18) Eisfeld, W.; Vieuxmaire, O.; Viel, A. Full-Dimensional Diabatic Potential Energy Surfaces Including Dissociation: the $^2E''$ State of NO_3. *J. Chem. Phys.* **2014**, *140*, 224109.

(19) Bhattacharyya, S.; Opalka, D.; Poluyanov, L. V.; Domcke, W. Jahn-Teller Theory beyond the Standard Model. *J. Phys. Conf. Series* **2013**, *428*, 012015.

(20) Mondal, P.; Opalka, D.; Poluyanov, L. V.; Domcke, W. Jahn-Teller and Spin-Orbit Coupling Effects in Transition-Metal Trifluorides. *Chem. Phys.* **2011**, *387*, 56–65.

(21) Mondal, P.; Opalka, D.; Poluyanov, L. V.; Domcke, W. Ab Initio Study of Dynamical $E \times e$ Jahn-Teller and Spin-Orbit Coupling Effects in the Transition-Metal Trifluorides TiF_3, CrF_3 and NiF_3. *J. Chem. Phys.* **2012**, *136*, 084308.

(22) Opalka, D.; Domcke, W. High-Order Expansion of $T_2 \times t_2$ Jahn-Teller Potential-Energy Surfaces in Tetrahedral Molecules. *J. Chem. Phys.* **2010**, *132*, 154108.

(23) Weaver, A.; Arnold, D. W.; Bradforth, S. E.; Neumark, D. M. Examination of the $^2A_2'$ and $^2E'$ States of NO_3 by Ultraviolet Photoelectron Spectroscopy of NO_3^-. *J. Chem. Phys.* **1991**, *94*, 1740–1751.

(24) Faraji, S.; Köppel, H.; Eisfeld, W.; Mahapatra, S. Towards a Higher-Order Description of Jahn-Teller Coupling Effects in Molecular Spectroscopy: the A^2E'' State of NO_3. *Chem. Phys.* **2008**, *347*, 110–109.

(25) Shao, Z.; Li, H.; Zhang, S.; Li, J.; Dai, Z.; Mo, Y. The Jahn-Teller Effect in $CH_3Cl^+(X^2E)$: A Combined High-Resolution Experimental Measurement and *Ab Initio* Theoretical Study. *J. Chem. Phys.* **2012**, *136*, 064308.

(26) Gao, S.; Dai, Z.; Sun, W.; Li, H.; Wang, J.; Mo, Y. Tunneling Splittings in Vibronic Energy Levels of CH_3F^+ X^2E Studied by High Resolution Photoelectron Spectroscopy and *Ab Initio* Calculation. *J. Chem. Phys.* **2013**, *139*, 064302.

(27) Codd, T.; Chen, M.-W.; Roudjane, M.; Stanton, J. F.; Miller, T. A. Jet Cooled Cavity Ringdown Spectroscopy of the $A^2E'' \leftarrow X^2A_2'$ Transition of the NO_3 Radical. *J. Chem. Phys.* **2015**, *142*, 184305.

(28) Li, S. L.; Truhlar, D. G.; Schmidt, M. W.; Gordon, M. S. Model Space Diabatization for Quantum Photochemistry. *J. Chem. Phys.* **2015**, *142*, 064106.

(29) Subotnik, J. E.; Alguire, E. C.; Ou, Q.; Landry, B. R.; Fatehi, S. The Requisite Electronic Structure Theory To Describe Photoexcited Nonadiabatic Dynamics: Nonadia-

batic Derivative Couplings and Diabatic Electronic Couplings. *Acc. Chem. Res.* **2015**, *48*, 1340–1350.

(30) Wittenbrink, N.; Venghaus, F.; Williams, D.; Eisfeld, W. A New Approach for the Development of Diabatic Potential Energy Surfaces: Hybrid Block-Diagonalization and Diabatization by Ansatz. *J. Chem. Phys.* **2016**, *145*, 184108.

(31) Tamura, H. Diabatization for Time-Dependent Density Functional Theory: Exciton Transfers and Related Conical Intersections. *J. Phys. Chem. A* **2016**, *120*, 9341–9347.

(32) Zeng, T. A Diabatization Protocol that Includes Spin-Orbit Coupling. *J. Chem. Phys.* **2017**, *146*, 144103.

(33) Grofe, A.; Qu, Z.; Truhlar, D. G.; Li, H.; Gao, J. Diabatic-At-Construction Method for Diabatic and Adiabatic Ground and Excited States Based on Multistate Density Functional Theory. *J. Chem. Theory Comput.* **2017**, *13*, 1176–1187.

(34) Opalka, D.; Domcke, W. High-Order Expansion of $T_2 \otimes e$ Jahn-Teller Potential-Energy Surfaces in Tetrahedral Systems. *Chem. Phys. Lett.* **2010**, *494*, 134–138.

(35) Zeng, T.; Seidu, I. Revisiting the $(E + A) \otimes (e + a)$ Problems of Polyatomic Systems with Trigonal Symmetry: General Expansions of Their Vibronic Hamiltonians. *Phys. Chem. Chem. Phys.* **2017**, *19*, 11098–11110.

(36) Dillon, J.; Yarkony, D. R.; Schuurman, M. S. On the Construction of Quasidiabatic State Representations of Bound Adiabatic State Potential Energy Surfaces Coupled by Accidental Conical Intersections: Incorporation of Higher Order Terms. *J. Chem. Phys.* **2011**, *134*, 044101.

(37) Robertson, C.; Worth, G. A. Generating Symmetry-Adapted Bases for Non-Abelian Point Groups to Be Used in Vibronic Coupling Hamiltonians. *Chem. Phys.* **2015**, *460*, 125–134.

(38) Griffith, J. S. *The Irreducible Tensor Method for Molecular Symmetry Group*; Dover Publications, Inc., 2006.

(39) Wigner, E. P. *Group Theory and Its Applications to the Quantum Mechanics of Atomic Spectra*; Academic Press: New York, 1959.

(40) Weyl, H. *The Classical Groups, Their Invariants and Representations*; Princeton University Press: New Jersey, 1946.

(41) Ceulemans, A.; Beyens, D.; Vanquickenborne, L. G. Symmetry Aspects of Jahn-Teller Activity: Structure and Reactivity. *J. Am. Chem. Soc.* **1984**, *106*, 5824–5837.

(42) Moffitt, W.; Thorson, W. Vibronic States of Octahedral Complexes. *Phys. Rev.* **1957**, *108*, 1251–1255.

(43) Baker, S.; Robinson, J. S.; Haworth, C. A.; Teng, H.; Smith, R. A.; Chirilă, C. C.; Lein, M.; Tisch, J. W. G.; Marangos, J. P. Probing Proton Dynamics in Molecules on an Attosecond Time Scale. *Science* **2006**, *312*, 424–427.

(44) Wörner, H. J.; Merkt, F. Jahn-Teller Effects in Molecular Cations Studied by Photoelectron Spectroscopy and Group Theory. *Angew. Chem. Int. Ed.* **2009**, *48*, 6404–6424.

(45) Mondal, T.; Varandas, A. J. C. The Jahn-Teller Effect in the Triply Degenerate Electronic State of Methane Radical Cation. *J. Chem. Phys.* **2011**, *135*, 174304.

(46) Mondal, T.; Varandas, A. J. C. Quadratic Coupling Treatment of the Jahn-Teller Effect in the Triply-Degenerate Electronic State of CH_4^+: Can One Account for Floppiness? *J. Chem. Phys.* **2012**, *137*, 214320.

(47) Mondal, T.; Varandas, A. J. C. On Extracting Subfemtosecond Data from Femtosecond Quantum Dynamics Calculations: the Methane Cation. *J. Chem. Theory Comput.* **2014**, *10*, 3606–3616.

(48) Mondal, T.; Varandas, A. J. C. Structural Evolution of the Methane Cation in Subfemtosecond Photodynamics. *J. Chem. Phys.* **2015**, *143*, 014304.

(49) Mondal, T. Origin of Distinct Structural Symmetry of the Neopentane Cation in the Ground Electronic State Compared to the Methane Cation. *Phys. Chem. Chem. Phys.* **2016**, *18*, 10459–10472.

(50) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery Jr., J. A. General Atomic and Molecular Electronic Structure System. *J. Comput. Chem.* **1993**, *14*, 1347–1363.

(51) Gordon, M. S.; Schmidt, M. W. Advances in Electronic Structure Theory: GAMESS a Decade Later. In *Theory and Applications of Computational Chemistry: The First Forty Years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G. E., Eds.; Elsevier: Amsterdam, 2005; Chapter 41, pp 1167-1189.

(52) Pyykkö, P.; Desclaux, J. P. Summary of Relativistic Effects in Heavy-Element Chemistry. *C. R. Acad. Sci. Paris* **1981**, *II 292*, 1513–1515.

(53) Pyykkö, P. Relativistic Effects in Structural Chemistry. *Chem. Rev.* **1988**, *88*, 563–594.

(54) Zeng, T.; Fedorov, D. G.; Klobukowski, M. Performance of Dynamically Weighted Multiconfiguration Self-Consistent Field and Spin-Orbit Coupling Calculations of Diatomic Molecules of Group 14 Elements. *J. Chem. Phys.* **2011**, *134*, 024108.

(55) Chau, F. T.; Karlsson, L. Vibronic Interaction in Molecules and Ions. *Phys. Scripta.* **1977**, *16*, 258–267.

(56) Opalka, D.; Segado, M.; Poluyanov, L. V.; Domcke, W. Relativistic Jahn-Teller Effect in Tetrahedral Systems. *Phys. Rev. A* **2010**, *81*, 042501.

(57) Poluyanov, L. V.; Mishra, S.; Domcke, W. Quasistationary Upper-Well States of $E \times e$ Jahn-Teller Systems with Spin-Orbit Coupling. *Chem. Phys.* **2007**, *332*, 243–248.

(58) Poluyanov, L. V.; Mishra, S.; Domcke, W. Quasiclassical Theory of the Dynamical $E \times e$ Jahn-Teller Effect Including Spin-Orbit Interaction. *Mol. Phys.* **2007**, *105*, 1471–1485.

(59) Poluyanov, L. V.; Domcke, W. Relativistic $E \times t$ Jahn-Teller Effect in Tetrahedral Systems. *J. Chem. Phys.* **2008**, *129*, 224102.

(60) Matsika, S.; Yarkony, D. R. Conical Intersections and the Spin-Orbit Interaction. *Adv. Chem. Phys.* **2003**, *124*, 557–583.

(61) Domcke, W.; Mishra, S.; Poluyanov, L. V. The Relativistic $E \times e$ Jahn-Teller Effect Revisited. *Chem. Phys.* **2006**, *322*, 405–410.

(62) Schuurman, M. S.; Yarkony, D. R. On the Vibronic Coupling Approximation: A Generally Applicable Approach for Determining Fully Quadratic Quasi Diabatic Coupled Electronic State Hamiltonians. *J. Chem. Phys.* **2007**, *127*, 094104.

(63) Zeng, T.; Fedorov, D. G.; Schmidt, M. W.; Klobukowski, M. Effects of Spin-Orbit Coupling on Covalent Bonding and the Jahn-Teller Effect are Revealed with the Natural Language of Spinors. *J. Chem. Theory Comput.* **2011**, *7*, 2864–2875.

(64) Zeng, T.; Fedorov, D. G.; Schmidt, M. W.; Klobukowski, M. Nautral Spinors Reveal How the Spin-Orbit Coupling Affects the Jahn-Teller Distortions in the Hexafluorotungstate(V) Anion. *J. Chem. Theory Comput.* **2012**, *8*, 3061–3071.

(65) Poluyanov, L. V.; Domcke, W. Relativistic Jahn-Teller and pseudo-Jahn-Teller Couplings in D_{2d} Systems. *Chem. Phys.* **2012**, *407*, 1–8.

(66) Marquez, S.; Dillon, J.; Yarkony, D. R. On the photoionization spectrum of propyne. A Fully *Ab Initio* Simulation of the Low-Energy Spectrum Including the Jahn-Teller and the Spin-Orbit Interaction. *J. Phys. Chem. A* **2013**, *117*, 12002–12010.

(67) Ndome, H.; Welsch, R.; Eisfeld, W. A New Method to Generate Spin-Orbit Coupled Potential Energy Surfaces: Effective Relativistic Coupling by Asymptotic Representation. *J. Chem. Phys.* **2012**, *136*, 034103.

(68) Ndome, H.; Eisfeld, W. Spin-Orbit Coupled Potential Energy Surfaces and Properties using Effective Relativistic Coupling by Asymptotic Reprentation. *J. Chem. Phys.* **2012**, *137*, 064101.

(69) Wittenbrink, N.; Ndome, H.; Eisfeld, W. Toward Spin-Orbit Coupled Diabatic Potential Energy Surfaces for Methyl Iodide Using Effective Relativistic Coupling by Asymptotic Representation. *J. Phys. Chem. A* **2013**, *117*, 7408–7420.

(70) Weike, T.; Eisfeld, W. Development of Multi-Mode Diabatic Spin-Orbit Models at Arbitrary Order. *J. Chem. Phys.* **2016**, *144*, 104108.

(71) Domcke, W.; Opalka, D.; Poluyanov, L. V. Relativistic Theory of the Jahn-Teller Effect: *p*-Orbital in Tetrahedral and Trigonal Systems. *J. Chem. Phys.* **2016**, *144*, 124101.

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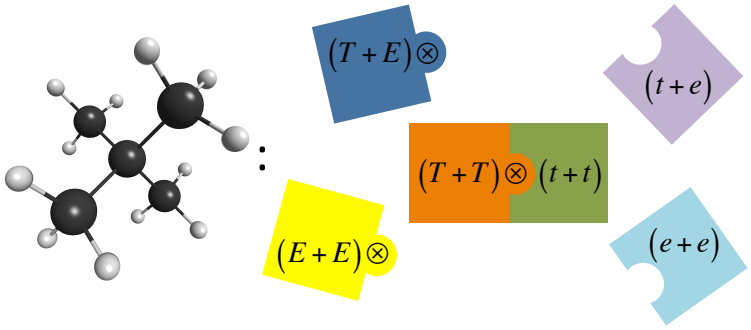

Table of Contents Graphic: expansion formulas of 92 tetrahedral vibronic problems are derived in a modularized approach.