Revisiting the $(E + A) \otimes (e + a)$ problems of polyatomic systems with trigonal symmetry: general expansions of their vibronic Hamiltonians

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Abstract

In this work, we derive general expansions in vibrational coordinates for the $(E + A) \otimes (e + a)$ vibronic Hamiltonians of molecules with one and only one C_3 axis. We first derive the expansion for the lowest C_3 symmetry. Additional symmetry elements systematically eliminate terms in the expansion. We compare our expansions with the previous results for two cases, the D_{3h} $(E' + A_2'') \otimes (e' + a_2'')$ and the C_3 $(E + A) \otimes e$. The first comparison demonstrates the robustness, completeness, conciseness, and convenience of our formalism. There is a systematic discrepancy in the second comparison. We discuss the origin of the discrepancy and use a numerical example to corroborate our expansion. Our formalism covers 153 vibronic problems in 6 point groups. It also gives general expansions for the spin-orbit vibronic Hamiltonians of the p-type $(E + A) \otimes (e + a)$ problems.

I. INTRODUCTION

In any nonlinear molecules, orbital degeneracy induced by symmetry must be lifted along with symmetry lowering. This is the famous Jahn-Teller (JT) effect.[1,2] Such an instability can also be induced by strong interaction between non-degenerate states along symmetry-broken distortion, which is termed the pseudo-Jahn-Teller (pJT) effect.[2] These two effects manifest themselves frequently in molecular physics, solid state physics, and structural chemistry. For instance, they induce line splitting in spectroscopy, internal conversion in quantum dynamics, and phase transition in solid.[2–9] Around the structures of degeneracy or pseudo-degeneracy, the electronic and nuclear motion are strongly coupled. An accurate vibronic Hamiltonian that treats the two types of degrees of freedom on the same footing is the key to describe and understand any phenomena related to the JT and pJT effects.

Non-accidental orbital degeneracy only arises for molecules with at least one n-fold symmetry or improper rotational axis and $n \geq 3$. Trigonal molecules are therefore systems of the lowest symmetry that exhibit the JT effect and have attracted continuous interest. By "trigonal", we mean molecules that feature only one C_3 axis and no other symmetry or improper rotational axes greater than three-fold. Molecules of C_3, C_{3v}, D_3, C_{3h}, D_{3h}, and D_{3d} symmetries belong to this class. The interaction between a doubly degenerate E electronic state and a doubly degenerate e vibrational mode (the $E \otimes e$ problem) in those molecules gives an illustrative example for the JT effect in many classic monographs.[2,10,11] The interaction between an E state and a close-lying A state through an e mode also gives a typical example for the pJT effect.[12] The E-A energy gap and the vibronic coupling strengths among the three states (two E components plus an A state) can be modified by a non-degenerate a mode. The $(E + A) \otimes (e + a)$ interaction in trigonal molecules forms an important class of vibronic problems, including the subproblems of neglecting the A state and/or the a mode[13–34] (also see the references in the cited works). Here, "E" and "A" (the lower case analogues too) cover all irreducible representations (irreps) of the 6 trigonal point groups that have the two respective letters in their symbols. For instance, they include E' and E'' of C_{3h}, A_1', A_2', A_1'', and A_2'' of D_{3h}, etc. Therefore, $(E + A)$ have covered all irreps of the trigonal point groups. We follow the convention of using upper case symbols to denote electronic states and lower case for vibrational modes and orbitals.

A vibronic Hamiltonian is usually expanded in a subspace of interacting electronic states

and relevant vibrational modes. In the electronic degrees of freedom, the Hamiltonians are usually expanded using the (quasi-)diabatic electronic states that preserve their characters along nuclear distortion.[35,36] The character preservation guarantees smoothly changing Hamiltonian matrix elements that are suited for expansion in vibrational coordinates. Traditionally, the expansions in vibrational coordinates stop at the second order. These short expansions are often adequate for stretching modes as their amplitude is relatively small. However, if the vibronically active modes are bending and torsional modes that feature anharmonic large amplitude motion or even tunnelling, higher order expansions are strongly desired.[19,20,29,31,37] The success of the case specific expansions up to 6-th $\sim$ 8-th order for some trigonal $(E+A)\otimes(e+a)$ problems and subproblems in these pioneering works, especially in calculating vibronic and photoelectron spectra, inspires us to pursue the general formalism for this important class of vibronic Hamiltonians. The objective of this work is to derive expansions in the vibrational coordinates for all the trigonal $(E+A)\otimes(e+a)$ Hamiltonians (153 of them in the 6 point groups) to arbitrarily high order. Although our formalism is derived for molecules, it can be readily transplanted to describe the similar vibronic problems of local formations in solids.[2,11] Following the suggestion of a referee, we use "polyatomic systems", instead of "molecules", in the title of this article, to emphasize that the resultant formalism is applicable to a broader range of systems.

In Section II, we first derive the expansion for the least symmetric C_3 $(E+A)\otimes(e+a)$ Hamiltonian. Hamiltonians of higher symmetries have the same mathematical expressions but with case specific constraints on the terms in their expansions. The constraints are derived in Section III. In Section IV, we compare our expansions of two specific cases with previous results and discuss their differences. In Section V, we employ the relation[38] between the electrostatic and the spin-orbit matrix elements to derive concise expressions for the spin-orbit vibronic Hamiltonians of the p-type $(E+A)\otimes(e+a)$ problems. Section VI concludes this work.

II. $(E+A)\otimes(e+a)$ IN C_3 MOLECULES

We use $|X\rangle$ and $|Y\rangle$ to label the two components of the degenerate E state, and $|Z\rangle$ for the non-degenerate A state. Since our focus is the spin-free electrostatic Hamiltonian, the states are chosen to be eigenstates of the $\hat{S}^2$ and $\hat{S}_z$ spin operators with the same $S(S+1)\hbar^2$

and $M_S\hbar$ eigenvalues. x, y, and z are used to label the vibrational coordinates of the e_x, e_y, and a modes. All electronic states in this work are diabatic states. Throughout this paper, we adopt the orientations of the e and E components that they transform under the $\hat{C}_3$ rotation as:

$$\hat{C}_3 e_x = -\frac{1}{2} e_x + \frac{\sqrt{3}}{2} e_y; \hat{C}_3 e_y = -\frac{\sqrt{3}}{2} e_x - \frac{1}{2} e_y;$$
$$\hat{C}_3 |X\rangle = -\frac{1}{2} |X\rangle + \frac{\sqrt{3}}{2} |Y\rangle; \hat{C}_3 |Y\rangle = -\frac{\sqrt{3}}{2} |X\rangle - \frac{1}{2} |Y\rangle . \quad (1)$$

Such orientations are illustrated in Figure 1(a) taking an e stretching and a p-type E state as examples. The orientations of the A state and a mode are immaterial since they do not transform to other states or modes under all symmetry operations considered.

To discuss the effect of $\hat{C}_3$, it is natural to represent the vibronic Hamiltonian using the complex electronic states:[19,20,39,40]

$$(|+\rangle |-\rangle |Z\rangle) = (|X\rangle |Y\rangle |Z\rangle) \underline{\underline{U}}; \underline{\underline{U}} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ \frac{i}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (2)$$

They are eigenstates of $\hat{C}_3$:

$$\hat{C}_3 |\pm\rangle = e^{\mp i 2\pi/3} |\pm\rangle; \hat{C}_3 |Z\rangle = |Z\rangle . \quad (3)$$

The distortion along the e mode can be expressed using the conventional polar coordinates ρ and ϕ that gives

$$x = \rho \cos\phi; y = \rho \sin\phi. \quad (4)$$

Given the transformations of e_x and e_y in Eq. 1, rotating a function of the x and y coordinates by $2\pi/3$ is equivalent to changing ϕ to $\phi - 2\pi/3$, while keeping ρ unchanged.

In the representation of the complex diabatic states, the vibronic Hamiltonian has a general form of

$$\begin{aligned} \hat{H} = & |+\rangle H_{++}(\rho,\phi,z) \langle +| + |-\rangle H_{--}(\rho,\phi,z) \langle -| + |Z\rangle H_{ZZ}(\rho,\phi,z) \langle Z| \\ & + |+\rangle H_{+-}(\rho,\phi,z) \langle -| + |+\rangle H_{+Z}(\rho,\phi,z) \langle Z| + |-\rangle H_{-Z}(\rho,\phi,z) \langle Z| \\ & + c.c. \end{aligned} \quad (5)$$

"*c.c.*" stands for taking the *c*omplex *c*onjugates of the off-diagonal matrix elements and swapping the associated *bra* and *ket* states, e.g., the *c.c.* of $|+\rangle H_{+-}(\rho,\phi,z) \langle -|$ is $|-\rangle H^*_{+-}(\rho,\phi,z) \langle +|$,

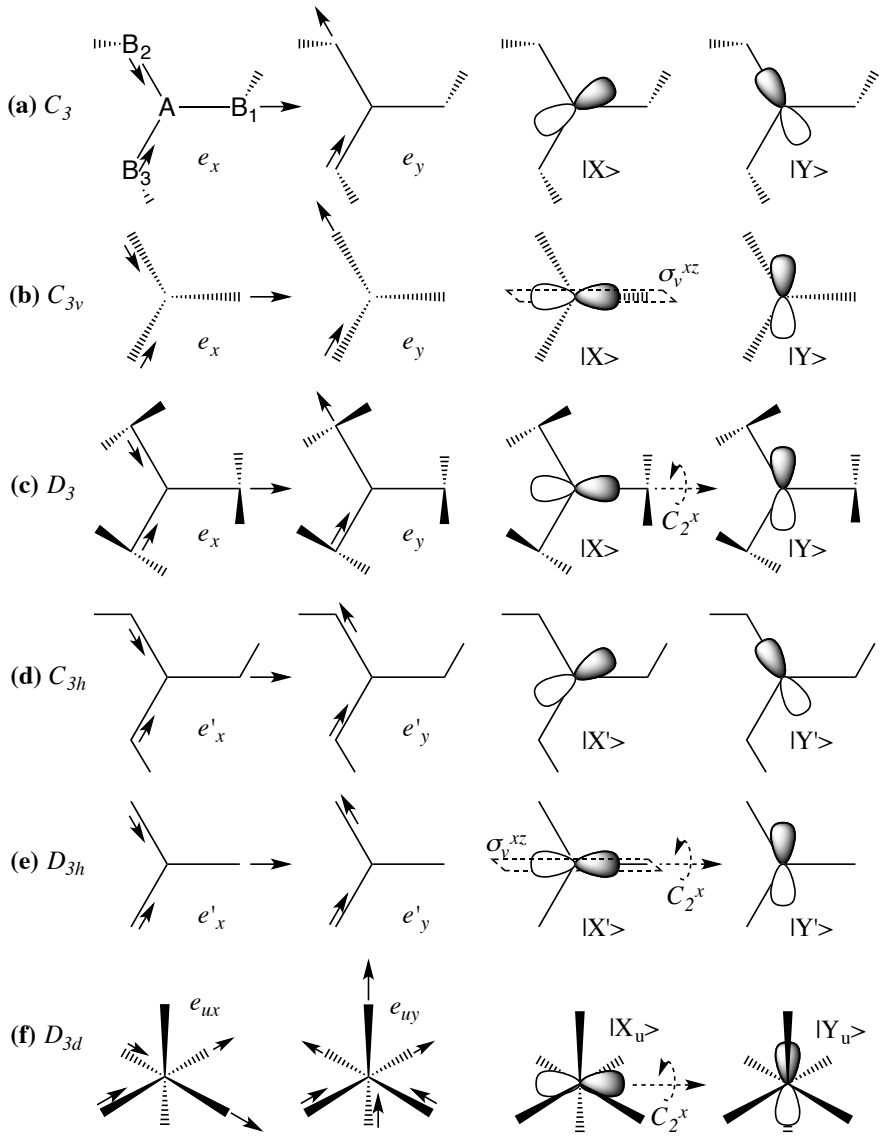

FIG. 1. Examples of orientations of e and E components, on which the derivations are based. Atomic motions in the modes are represented by solid arrows. With the atom labelling in panel (a), $e_x = \sqrt{\frac{1}{6}}\,(2\Delta r_{AB_1} - \Delta r_{AB_2} - \Delta r_{AB_3})$, and $e_y = \sqrt{\frac{1}{2}}\,(\Delta r_{AB_2} - \Delta r_{AB_3})$. Similar definitions apply to the displayed e modes in the other panels. The directions of the arrows are consistent with the e mode transformations in Eq. 1.

etc. Our goal is to derive the expansions of the H_{ij} elements in the vibrational coordinates x, y, and z. Under the action of the time-reversal operator ($\mathcal{T}$), the Hamiltonian becomes

$$\begin{aligned}\hat{\mathcal{T}}\hat{H}\hat{\mathcal{T}}^{-1} = {} & |\tilde{-}\rangle H_{++}(\rho,\phi,z)\langle\tilde{-}| \;+\; |\tilde{+}\rangle H_{--}(\rho,\phi,z)\langle\tilde{+}| \;+\; |\tilde{Z}\rangle H_{ZZ}(\rho,\phi,z)\langle\tilde{Z}| \\ & +\; |\tilde{-}\rangle H^*_{+-}(\rho,\phi,z)\langle\tilde{+}| \;+\; |\tilde{-}\rangle H^*_{+Z}(\rho,\phi,z)\langle\tilde{Z}| \;+\; |\tilde{+}\rangle H^*_{-Z}(\rho,\phi,z)\langle\tilde{Z}|\end{aligned}$$

$$+ \ c.c. \tag{6}$$

$\mathcal{T}$ changes i to $-i$ (i.e., $|+\rangle \leftrightarrow |-\rangle$ and $H_{ij} \rightarrow H_{ij}^*$) and flips spin as $\alpha \rightarrow \beta$ and $\beta \rightarrow -\alpha$ in its operand. The spin-flipped states are denoted by the overhead tilde. Since $\hat{H}$ is spin-independent, the matrix elements for the spin-flipped ket-bra (e.g., $|\tilde{-}\rangle\langle\tilde{-}|$) must be identical to those before spin-flipping (e.g., correspondingly, $|-\rangle\langle-|$). This requirement, and the comparison of Eqs. 5 and 6 determine

$$H_{++} = H_{--}; H_{-Z} = H_{+Z}^*. \tag{7}$$

The two equalities result from the time-reversal symmetry and spin-independence of $\hat{H}$. They simplify $\hat{H}$ to

$$\begin{aligned}\hat{H} = &|+\rangle H_{++}(\rho,\phi,z)\langle+| \ + \ |-\rangle H_{++}(\rho,\phi,z)\langle-| \ + \ |Z\rangle H_{ZZ}(\rho,\phi,z)\langle Z| \\ &+ \ |+\rangle H_{+-}(\rho,\phi,z)\langle-| \ + \ |+\rangle H_{+Z}(\rho,\phi,z)\langle Z| \ + \ |-\rangle H_{+Z}^*(\rho,\phi,z)\langle Z| \\ &+ \ c.c.,\end{aligned} \tag{8}$$

with four independent matrix elements.

$\hat{H}$ commutes with $\hat{C}_3$. Using Eqs. 3 and $\phi \rightarrow \phi - 2\pi/3$ under $\hat{C}_3$, we have

$$\begin{aligned}\hat{C}_3\hat{H}\hat{C}_3^{-1} = &|+\rangle H_{++}(\rho,\phi-2\pi/3,z)\langle+| \ + \ |-\rangle H_{++}(\rho,\phi-2\pi/3,z)\langle-| \\ &+ \ |Z\rangle H_{ZZ}(\rho,\phi-2\pi/3,z)\langle Z| \ + \ e^{i2\pi/3}|+\rangle H_{+-}(\rho,\phi-2\pi/3,z)\langle-| \\ &+ \ e^{-i2\pi/3}|+\rangle H_{+Z}(\rho,\phi-2\pi/3,z)\langle Z| \ + \ e^{i2\pi/3}|-\rangle H_{+Z}^*(\rho,\phi-2\pi/3,z)\langle Z| \\ &+ \ c.c.\end{aligned} \tag{9}$$

The equivalence of Eqs 8 and 9 requires

$$\begin{aligned}&H_{++}(\rho,\phi-2\pi/3,z) = H_{++}(\rho,\phi,z); H_{ZZ}(\rho,\phi-2\pi/3,z) = H_{ZZ}(\rho,\phi,z); \\ &H_{+-}(\rho,\phi-2\pi/3,z) = e^{-i2\pi/3}H_{+-}(\rho,\phi,z); H_{+Z}(\rho,\phi-2\pi/3,z) = e^{i2\pi/3}H_{+Z}(\rho,\phi,z).\end{aligned} \tag{10}$$

Each $H_{ij}(\rho,\phi,z)$ can be expanded as

$$H_{ij}(\rho,\phi,z) = F_m(\rho,z)\,e^{im\phi}, \tag{11}$$

with m being integers to guarantee that the element is invariant under a 2π rotation. Throughout this paper, Einstein's convention of summing over duplicated indices is followed, unless the summation sign is explicitly given. The invariances of H_{++} and H_{ZZ} with

respect to $\phi \to \phi - 2\pi/3$ determine that

$$H_{++} = A_m(\rho, z)\, e^{i3m\phi}; H_{ZZ} = C_m(\rho, z)\, e^{i3m\phi}. \tag{12}$$

They need to be real, and therefore

$$H_{++} = A^r_m(\rho, z)\cos(3m\phi) - A^i_m(\rho, z)\sin(3m\phi); \tag{13}$$

$$H_{ZZ} = C^r_m(\rho, z)\cos(3m\phi) - C^i_m(\rho, z)\sin(3m\phi), \tag{14}$$

with m being nonnegative integers, and $A^{r/i}_m$ and $C^{r/i}_m$ being real functions. The superscript r and i indicate that the functions stem from the real and imaginary parts of the A_m and C_m functions in Eq. 12. Similarly, the respective equalities of H_{+-} and H_{+Z} in Eq. 10 give them the following expansions:

$$H_{+-} = B_n(\rho, z)\, e^{i(3n+1)\phi}; H_{+Z} = \sqrt{\frac{1}{2}} D_n(\rho, z)\, e^{-i(3n+1)\phi}. \tag{15}$$

Here, n can take any integer values, and B_n and D_n are in general complex functions. The $\sqrt{\frac{1}{2}}$ factor is introduced to simplify Eq. 17 below. Allowing the A_m, B_n, C_m, and D_n functions to be complex differentiates our expansions from those in previous studies. Please see Section IV B for discussion in this aspect.

With these angular expansions of the H_{ij} elements, $\hat{H}$ can be written in a matrix form:

$$\hat{H} = (|+\rangle\,|-\rangle\,|Z\rangle) \begin{pmatrix} A^r_m(\rho, z)\cos(3m\phi) & B_n(\rho, z)\, e^{i(3n+1)\phi} & \frac{1}{\sqrt{2}} D_{n'}(\rho, z)\, e^{-i(3n'+1)\phi} \\ -A^i_m(\rho, z)\sin(3m\phi) & & \\ & A^r_m(\rho, z)\cos(3m\phi) & \frac{1}{\sqrt{2}} D^*_{n'}(\rho, z)\, e^{i(3n'+1)\phi} \\ & -A^i_m(\rho, z)\sin(3m\phi) & \\ & & C^r_{m'}(\rho, z)\cos(3m'\phi) \\ & & -C^i_{m'}(\rho, z)\sin(3m'\phi) \end{pmatrix} \begin{pmatrix} \langle +| \\ \langle -| \\ \langle Z| \end{pmatrix}. \tag{16}$$

The complex Hamiltonian matrix is labelled by $\underline{\underline{H}}^c$, and the missing lower triangle is just the complex conjugate of the upper. Throughout the paper, only upper triangles are given for hermitian matrices. Transforming $\hat{H}$ back to the real electronic basis using $\underline{\underline{U}}$ in Eq. 2 (the Hamiltonian matrix transforms as $\underline{\underline{U}}\,\underline{\underline{H}}^c\underline{\underline{U}}^\dagger$; "†" means taking the complex transpose of the denoted matrix),

$\hat{H} = (|X\rangle\,|Y\rangle\,|Z\rangle)$

$$\begin{pmatrix} A_m^r(\rho,z)\cos(3m\phi) & & \\ -A_m^i(\rho,z)\sin(3m\phi) & -Im\left[B_n(\rho,z)\,e^{i(3n+1)\phi}\right] & Re\left[D_{n'}(\rho,z)\,e^{-i(3n'+1)\phi}\right] \\ +Re\left[B_n(\rho,z)\,e^{i(3n+1)\phi}\right] & & \\ & A_m^r(\rho,z)\cos(3m\phi) & \\ & -A_m^i(\rho,z)\sin(3m\phi) & -Im\left[D_{n'}(\rho,z)\,e^{-i(3n'+1)\phi}\right] \\ & -Re\left[B_n(\rho,z)\,e^{i(3n+1)\phi}\right] & \\ & & C_{m'}(\rho,z)\cos(3m'\phi) \\ & & -C_m^i(\rho,z)\sin(3m'\phi) \end{pmatrix} \begin{pmatrix} \langle X| \\ \langle Y| \\ \langle Z| \end{pmatrix}. \tag{17}$$

The resultant Hamiltonian matrix is real and symmetric. Again, m and m' take only non-negative integers, while n and n' take any integers.

Considering the real and imaginary parts of the B_n and D_n functions explicitly:

$$B_n(\rho,z) = B_n^r(\rho,z) + iB_n^i(\rho,z)\,; D_n(\rho,z) = D_n^r(\rho,z) + iD_n^i(\rho,z)\,, \tag{18}$$

we can rewrite $\hat{H}$ as:

$$\hat{H} = (|X\rangle\,|Y\rangle\,|Z\rangle)$$
$$\begin{pmatrix} A_m^r(\rho,z)\cos(3m\phi) & & \\ -A_m^i(\rho,z)\sin(3m\phi) & -B_n^i(\rho,z)\cos((3n+1)\phi) & D_{n'}^r(\rho,z)\cos((3n'+1)\phi) \\ +B_n^r(\rho,z)\cos((3n+1)\phi) & -B_n^r(\rho,z)\sin((3n+1)\phi) & +D_{n'}^i(\rho,z)\sin((3n'+1)\phi) \\ -B_n^i(\rho,z)\sin((3n+1)\phi) & & \\ & A_m^r(\rho,z)\cos(3m\phi) & \\ & -A_m^i(\rho,z)\sin(3m\phi) & -D_{n'}^i(\rho,z)\cos((3n'+1)\phi) \\ & -B_n^r(\rho,z)\cos((3n+1)\phi) & +D_{n'}^r(\rho,z)\sin((3n'+1)\phi) \\ & +B_n^i(\rho,z)\sin((3n+1)\phi) & \\ & & C_{m'}^r(\rho,z)\cos(3m'\phi) \\ & & -C_{m'}^i(\rho,z)\sin(3m\phi) \end{pmatrix} \begin{pmatrix} \langle X| \\ \langle Y| \\ \langle Z| \end{pmatrix}. \tag{19}$$

Each of the functions of ρ and z can be expanded as polynomials of the two variables, e.g.,

$$A_m^r(\rho,z) = a_{I,J}^{r,3m} z^I \rho^J; B_n^i(\rho,z) = b_{I,J}^{i,3n+1} z^I \rho^J. \tag{20}$$

$\left\{a_{I,J}^{r,3m}\right\}$ and $\left\{b_{I,J}^{i,3n+1}\right\}$ are expansion coefficients. The trigonometric functions can be expanded using $\cos\phi$ and $\sin\phi$, e.g.,

$$\cos\left(3m\phi\right)=\sum_{k=0,2,4,\cdots}^{3m}\left(\begin{array}{c}3m\\k\end{array}\right)\left(-1\right)^{k/2}\cos^{3m-k}\phi\sin^{k}\phi; \tag{21}$$

$$\sin\left(\left(3n+1\right)\phi\right)=\mathrm{sgn}\left(3n+1\right)\sum_{k=1,3,5,\cdots}^{|3n+1|}\left(\begin{array}{c}|3n+1|\\k\end{array}\right)\left(-1\right)^{\frac{k-1}{2}}\cos^{|3n+1|-k}\phi\sin^{k}\phi, \tag{22}$$

where $\left(\begin{array}{c}M\\N\end{array}\right)$ stands for binomial coefficient. Since $3n+1$ can be negative, $|3n+1|$ is taken to be the upper limit in the summation over k, and $\mathrm{sgn}\left(3n+1\right)$ is introduced to give the appropriate sign of the expansion. With the expansions of $A_{m}^{r}\left(\rho,z\right)$ and $\cos\left(3m\phi\right)$,

$$\begin{aligned}A_{m}^{r}\left(\rho,z\right)\cos\left(3m\phi\right) & =\sum_{I,J}\sum_{k=0,2,4,\cdots}^{3m}a_{I,J}^{r,3m}\left(\begin{array}{c}3m\\k\end{array}\right)\left(-1\right)^{k/2}z^{I}\rho^{J}\cos^{3m-k}\phi\sin^{k}\phi\\ & =\sum_{I,J}\sum_{k=0,2,4,\cdots}^{3m}a_{I,J}^{r,3m}\left(\begin{array}{c}3m\\k\end{array}\right)\left(-1\right)^{k/2}z^{I}\rho^{J-3m}\left(\rho\cos\phi\right)^{3m-k}\left(\rho\sin\phi\right)^{k}\\ & =\sum_{I,J}\sum_{k=0,2,4,\cdots}^{3m}a_{I,J}^{r,3m}\left(\begin{array}{c}3m\\k\end{array}\right)\left(-1\right)^{k/2}z^{I}\left(x^{2}+y^{2}\right)^{\frac{J-3m}{2}}x^{3m-k}y^{k}.\end{aligned} \tag{23}$$

To expand $A_{m}^{r}\left(\rho,z\right)\cos\left(3m\phi\right)$ and the other similar funcitons as polynomials of x, y, and z, we need positive integer powers of $(x^{2}+y^{2})$, i.e., $J=3m+2K,K=0,1,2,\cdots$ With the constraint on the power of ρ, the expansion can be rewritten as

$$A_{m}^{r}\left(\rho,z\right)\cos\left(3m\phi\right)=a_{I,2K}^{r,3m}z^{I}\rho^{3m+2K}\cos\left(3m\phi\right). \tag{24}$$

With similar expansions for the other terms, $\hat{H}$ can be written as:

$\hat{H}=\left(\left|X\right\rangle\left|Y\right\rangle\left|Z\right\rangle\right)$

$$\left(\begin{array}{ccc}
\begin{array}{c}a_{I_{1},2K}^{r,3m}z^{I_{1}}\rho^{3m+2K}\cos\left(3m\phi\right)\\ -a_{I_{2},2K}^{i,3m}z^{I_{2}}\rho^{3m+2K}\sin\left(3m\phi\right)\\ +b_{I_{3},2K}^{r,3n+1}z^{I_{3}}\rho^{|3n+1|+2K}\cos\left(\left(3n+1\right)\phi\right)\\ -b_{I_{4},2K}^{i,3n+1}z^{I_{4}}\rho^{|3n+1|+2K}\sin\left(\left(3n+1\right)\phi\right)\end{array} & \begin{array}{c}-b_{I_{3},2K}^{r,3n+1}z^{I_{3}}\rho^{|3n+1|+2K}\sin\left(\left(3n+1\right)\phi\right)\\ -b_{I_{4},2K}^{i,3n+1}z^{I_{4}}\rho^{|3n+1|+2K}\cos\left(\left(3n+1\right)\phi\right)\end{array} & \begin{array}{c}d_{I_{5},2K}^{r,3n'+1}z^{I_{5}}\rho^{|3n'+1|+2K}\cos\left(\left(3n'+1\right)\phi\right)\\ +d_{I_{6},2K}^{i,3n'+1}z^{I_{6}}\rho^{|3n'+1|+2K}\sin\left(\left(3n'+1\right)\phi\right)\end{array}\\
\begin{array}{c}a_{I_{1},2K}^{r,3m}z^{I_{1}}\rho^{3m+2K}\cos\left(3m\phi\right)\\ -a_{I_{2},2K}^{i,3m}z^{I_{2}}\rho^{3m+2K}\sin\left(3m\phi\right)\\ -b_{I_{3},2K}^{r,3n+1}z^{I_{3}}\rho^{|3n+1|+2K}\cos\left(\left(3n+1\right)\phi\right)\\ +b_{I_{4},2K}^{i,3n+1}z^{I_{4}}\rho^{|3n+1|+2K}\sin\left(\left(3n+1\right)\phi\right)\end{array} & \begin{array}{c}d_{I_{5},2K}^{r,3n'+1}z^{I_{5}}\rho^{|3n'+1|+2K}\sin\left(\left(3n'+1\right)\phi\right)\\ -d_{I_{6},2K}^{i,3n'+1}z^{I_{6}}\rho^{|3n'+1|+2K}\cos\left(\left(3n'+1\right)\phi\right)\end{array} & \\
 & \begin{array}{c}c_{I_{7},2K}^{r,3m'}z^{I_{7}}\rho^{3m'+2K}\cos\left(3m'\phi\right)\\ -c_{I_{8},2K}^{i,3m'}z^{I_{8}}\rho^{3m'+2K}\sin\left(3m'\phi\right)\end{array} &
\end{array}\right)$$

$$\begin{pmatrix} \langle X| \\ \langle Y| \\ \langle Z| \end{pmatrix}, m, m', K, I_{1-8} = 0, 1, 2, \cdots; n, n' = \cdots, -2, -1, 0, 1, 2, \cdots \tag{25}$$

$\left\{a_{I,2K}^{r/i,3m}\right\}$, $\left\{b_{I,2K}^{r/i,3n+1}\right\}$, $\left\{c_{I,2K}^{r/i,3m'}\right\}$, and $\left\{d_{I,2K}^{r/i,3n'+1}\right\}$ are the expansion coefficients of the functions labelled by the corresponding upper case letters.

Eq. 25 is the central result of the present work. It is the general polynomial expansion for the $(E + A) \otimes (e + a)$ vibronic Hamiltonian for any C_3 molecules, from which we derive the vibronic Hamiltonians for higher symmetries below. All $z^I \rho^L \cos(M\phi)$ and $z^I \rho^L \sin(M\phi)$ monomials in expanding any of the matrix elements differ either in the power of z, the power of ρ, the trigonometric function, or the multiple of ϕ. There is hence no redundancy; Eq. 25 gives the most concise polynomial expansion of the Hamiltonian, which facilitates convergence in numerical fitting to determine the expansion coefficients. The order of expansion is determined by $I + L$ in $z^I \rho^L$ and it can be arbitrarily high. As shown below, the equation can be easily converted to the expansion in x, y, and z. It is ready to be used. We would like to emphasize again that Eq. 25 is derived with the setting in Eq. 1. If instead the e components transform as

$$\hat{C}_3 e_x = -\frac{1}{2} e_x - \frac{\sqrt{3}}{2} e_y; \hat{C}_3 e_y = \frac{\sqrt{3}}{2} e_x - \frac{1}{2} e_y, \tag{26}$$

ϕ should be replaced by $-\phi$ in Eq. 25. If the E components transform as

$$\hat{C}_3 |X\rangle = -\frac{1}{2} |X\rangle - \frac{\sqrt{3}}{2} |Y\rangle; \hat{C}_3 |Y\rangle = \frac{\sqrt{3}}{2} |X\rangle - \frac{1}{2} |Y\rangle, \tag{27}$$

the signs of H_{XY} and H_{YZ} should be flipped.

III. HIGHER SYMMETRIES

A. C_{3v} and D_3

In the following derivation, we adopt the orientations of the E components and e components as shown in Figure 1(b): e_x and $|X\rangle$ are symmetric with respect to one σ_v plane, which is called σ_v^{xz} below. With such natural orientations, all electronic states and vibrational modes are eigenstates of the $\hat{\sigma}_v^{xz}$ operation: $\hat{\sigma}_v^{xz} |X\rangle = |X\rangle$; $\hat{\sigma}_v^{xz} |Y\rangle = -|Y\rangle$;

$\hat{\sigma}_v^{xz}|Z\rangle = \chi_Z^{\hat{\sigma}_v^{xz}}|Z\rangle$; $\hat{\sigma}_v^{xz}e_x = e_x$; $\hat{\sigma}_v^{xz}e_y = -e_y$; $\hat{\sigma}_v^{xz}a = \chi_z^{\hat{\sigma}_v^{xz}}a$. Throughout this paper, the symbol $\chi_i^{\hat{S}}$ is used to label the eigenvalue of the operand i under the symmetry operation $\hat{S}$. The eigenvalues $\chi_Z^{\hat{\sigma}_v^{xz}}$ and $\chi_z^{\hat{\sigma}_v^{xz}}$ are 1 if $|Z\rangle$ and the a mode are of a_1 irrep, and -1 if they are of a_2 irrep. For an e distortion with the (x, y) coordinates,

$$\hat{\sigma}_v^{xz}\left(xe_x + ye_y\right) = \left(xe_x - ye_y\right). \tag{28}$$

In the polar coordinates, correspondingly, the reflection keeps ρ unchanged and changes ϕ to $-\phi$. We can hence associate formal eigenvalues to ρ and ϕ: $\chi_\rho^{\hat{\sigma}_v^{xz}} = 1$ and $\chi_\phi^{\hat{\sigma}_v^{xz}} = -1$. Obviously, under the action of $\hat{\sigma}_v^{xz}$, any function of the mode coordinates transforms as

$$\hat{\sigma}_v^{xz} f\left(\rho, \phi, z\right) = f\left(\left(\chi_\rho^{\hat{\sigma}_v^{xz}}\rho\right), \left(\chi_\phi^{\hat{\sigma}_v^{xz}}\phi\right), \left(\chi_z^{\hat{\sigma}_v^{xz}}z\right)\right). \tag{29}$$

For a C_{3v} vibronic Hamiltonian, we need further constraints on Eq. 25 to make it invariant with respect to $\hat{\sigma}_v^{xz}$. For such a symmetry operation that does not mix the electronic states and does not mix the vibrational modes, it transforms the vibronic Hamiltonian as

$$\hat{S}\hat{H}\hat{S}^{-1} = \hat{S}\left|\Psi_i\right\rangle H_{ij}\left(\rho, \phi, z\right)\left\langle\Psi_j\right|\hat{S}^{-1} = \chi_i^{\hat{S}}\chi_j^{\hat{S}}\left|\Psi_i\right\rangle H_{ij}\left(\left(\chi_\rho^{\hat{S}}\rho\right), \left(\chi_\phi^{\hat{S}}\phi\right), \left(\chi_z^{\hat{S}}z\right)\right)\left\langle\Psi_j\right| \tag{30}$$

Therefore, to have $\hat{S}\hat{H}\hat{S}^{-1} = \hat{H}$, we need

$$\forall\left(i, j\right) : \chi_i^{\hat{S}}\chi_j^{\hat{S}}H_{ij}\left(\left(\chi_\rho^{\hat{S}}\rho\right), \left(\chi_\phi^{\hat{S}}\phi\right), \left(\chi_z^{\hat{S}}z\right)\right) = H_{ij}\left(\rho, \phi, z\right). \tag{31}$$

This is the general requirement on the matrix elements in Eq. 25 for deriving Hamiltonians of all trigonal point groups with higher symmetries than C_3. We need to impose constraints on the expansion coefficients, or in other words, on the summing indices to satisfy Eq. 31. We first consider H_{XX}, H_{ZZ}, and H_{XZ}, since they have included all expansion coefficients. Furthermore, since the expansion of H_{ZZ} has the same form as the $a_{I_1,2K}^{r,3m}z^{I_1}\rho^{3m+2K}\cos\left(3m\phi\right) - a_{I_2,2K}^{i,3m}z^{I_2}\rho^{3m+2K}\sin\left(3m\phi\right)$ part in H_{XX}, and they are both diagonal elements that have $\chi_i^{\hat{S}}\chi_j^{\hat{S}} = 1$ in Eq. 31, the constraints on I_1, I_2, and $3m$ that make H_{XX} satisfy Eq. 31 also apply to I_7, I_8, and $3m'$, in order to make H_{ZZ} symmetry-adapted. There is thus no need to derive constraints on I_7, I_8, and $3m'$ separately.

With the $\chi^{\sigma_v^{\hat{xz}}}$ eigenvalues introduced above Eq. 28, Eq. 31 becomes

$$H_{XX}\left(\rho, -\phi, \left(\chi_z^{\hat{\sigma}_v^{xz}}z\right)\right) = H_{XX}\left(\rho, \phi, z\right); \tag{32}$$

$$H_{XZ}\left(\rho, -\phi, \left(\chi_z^{\hat{\sigma}_v^{xz}}z\right)\right) = \chi_Z^{\hat{\sigma}_v^{xz}}H_{XZ}\left(\rho, \phi, z\right). \tag{33}$$

To satisfy the two equations, we need

$$\left(\chi_z^{\hat{\sigma}_v^{xz}}\right)^{I_1} = 1; \left(\chi_z^{\hat{\sigma}_v^{xz}}\right)^{I_2} = -1; \left(\chi_z^{\hat{\sigma}_v^{xz}}\right)^{I_3} = 1; \left(\chi_z^{\hat{\sigma}_v^{xz}}\right)^{I_4} = -1; \left(\chi_z^{\hat{\sigma}_v^{xz}}\right)^{I_5} = \chi_Z^{\hat{\sigma}_v^{xz}}; \left(\chi_z^{\hat{\sigma}_v^{xz}}\right)^{I_6} = -\chi_Z^{\hat{\sigma}_v^{xz}}. \tag{34}$$

First, for an a_1 mode with $\chi_z^{\hat{\sigma}_v^{xz}} = 1$: there is no constraint on I_1 and I_3, while $a_{I_2,2K}^{i,3m}$ and $b_{I_4,2K}^{i,3n+1}$ need to be zero since the second and fourth equalities cannot be met. If $|Z\rangle$ is an A_1 state, there is no constraint on I_5, and $d_{I_6,2K}^{i,3n'+1}$ need to be zero. If $|Z\rangle$ is an A_2 state, $d_{I_5,2K}^{r,n'} = 0$ and there is no constraint on I_6. Second, for an a_2 mode with $\chi_z^{\hat{\sigma}_v^{xz}} = -1$: I_1 and I_3 need to be even, while I_2 and I_4 odd. If $|Z\rangle$ is an A_1 state, I_5 even and I_6 odd. If $|Z\rangle$ is an A_2 state, I_5 odd and I_6 even. All these constraints are summarized in Table 1. It is straightforward to see that these constraints have made H_{YY}, H_{XY}, and H_{YZ} transform appropriately under $\hat{\sigma}_v^{xz}$. No more constraints are needed.

TABLE 1. Constraints on the summing indices for the $(E + A) \otimes (e + a)$ vibronic Hamiltonian expansions for C_{3v} and D_3 molecules.[a]

	I_1	I_2	I_3	I_4	I_5	I_6
$(E + A_1) \otimes (e + a_1)$	nr	na	nr	na	nr	na
$(E + A_1) \otimes (e + a_2)$	even	odd	even	odd	even	odd
$(E + A_2) \otimes (e + a_1)$	nr	na	nr	na	na	nr
$(E + A_2) \otimes (e + a_2)$	even	odd	even	odd	odd	even

[a] "nr" and "na" stand for "no further restriction" other than indicated in Eq. 25 and "not applicable", respectively. Terms with the "na" indices should be zeroed. $I_{7,8}$ share the same constraints as $I_{1,2}$, respectively, in each case.

The D_3 and C_{3v} point groups are isomorphic. The derivation for the constraints on I_{1-6} above is also applicable to the D_3 $(E + A) \otimes (e + a)$ vibronic Hamiltonian, simply with the σ_v^{xz} plane being replaced by the C_2^x axis. Therefore, Table 1 also applies to D_3 molecules. This transferability is based on that the orientations of the E and e components are consistent with those in the C_{3v} derivation: $|X\rangle$ and e_x are invariant with respect to $\hat{C}_2^x$, while $|Y\rangle$ and e_y antisymmetric. Such orientations and the C_2^x axis are exemplified in Figure 1(c).

B. C_{3h}

The A and E states as well as the a and e modes are dressed by prime and double-prime in the C_{3h} symmetry, according to their being symmetric or antisymmetric with respect to the $\hat{\sigma}_h^{xy}$ operation. In the polar coordinate representation of the e mode, we can associate the prime/double-prime character to ρ, i.e., $\chi_\rho^{\hat{\sigma}_h^{xy}} = 1$ for an e' mode and -1 for an e'' mode. $\chi_\phi^{\hat{\sigma}_h^{xy}} = 1$ regardless of the prime/double-prime character.

The derivation for the C_{3h} vibronic Hamiltonian expansion follows the same route as the C_{3v} above. We need to constrain the summing indices so that H_{XX} and H_{XZ} satisfy Eq. 31 with $\hat{S} = \hat{\sigma}_h^{xy}$. For H_{XX}, the conditions are:

$$\left(\chi_z^{\hat{\sigma}_h^{xy}}\right)^{I_1}\left(\chi_\rho^{\hat{\sigma}_h^{xy}}\right)^{3m} = \left(\chi_z^{\hat{\sigma}_h^{xy}}\right)^{I_2}\left(\chi_\rho^{\hat{\sigma}_h^{xy}}\right)^{3m} = \left(\chi_z^{\hat{\sigma}_h^{xy}}\right)^{I_3}\left(\chi_\rho^{\hat{\sigma}_h^{xy}}\right)^{|3n+1|} = \left(\chi_z^{\hat{\sigma}_h^{xy}}\right)^{I_4}\left(\chi_\rho^{\hat{\sigma}_h^{xy}}\right)^{|3n+1|} = 1. \tag{35}$$

For a' and e' modes, there is simply no constraint, as expected. For a'' and e'' modes, we need $I_{1,2} + 3m$ and $I_{3,4} + |3n+1|$ to be even. For a' and e'' modes, we need $3m$ and $3n+1$ even and there is no constraint on I_{1-4}. For a'' and e' modes, we need I_{1-4} even and there is no constraint on m and n.

The conditions for H_{XZ} to satisfy Eq. 31 are:

$$\left(\chi_z^{\hat{\sigma}_h^{xy}}\right)^{I_5}\left(\chi_\rho^{\hat{\sigma}_h^{xy}}\right)^{|3n'+1|} = \left(\chi_z^{\hat{\sigma}_h^{xy}}\right)^{I_6}\left(\chi_\rho^{\hat{\sigma}_h^{xy}}\right)^{|3n'+1|} = \chi_X^{\hat{\sigma}_h^{xy}}\,\chi_Z^{\hat{\sigma}_h^{xy}}. \tag{36}$$

The $\chi_X^{\hat{\sigma}_h^{xy}}\,\chi_Z^{\hat{\sigma}_h^{xy}}$ factor determines that $(E' + A')$ and $(E'' + A'')$ share the same constraints on the indices; $(E'' + A')$ and $(E' + A'')$ also. Therefore, the 16 C_{3h} $(E + A) \otimes (e + a)$ cases are reduced to 8 sets of constraints. Guided by Eq. 36, it is straightforward to obtain the constraints on $I_{5,6}$ and $3n' + 1$ and the details are skipped. All the constraints derived from H_{XX} and H_{XZ} are summarized in Table 2. These constraints have made the other H_{ij} elements transform appropriately under $\hat{\sigma}_h^{xy}$. The "not applicable"s ("na"s) for $I_{5,6}$ and $3n' + 1$ for the cases of $(E'' + A') \otimes (e' + a')$ and $(E' + A'') \otimes (e' + a')$ simply reflect that primed and double-primed states cannot be coupled by primed vibrational modes.

One can see from Tables 1 and 2 that I_1 and I_3, I_2 and I_4, and $3m$ and $3n + 1$ always share the same constraints pair-wisely. This is because: (1) the constraints of all the $a_{I_1,2K}^{r,3m}$, $a_{I_2,2K}^{i,3m}$, $b_{I_3,2K}^{r,3n+1}$, and $b_{I_4,2K}^{i,3n+1}$ terms are derived from the symmetry requirement on the same matrix element, H_{XX}; (2) the I_1 and I_3 terms have cosine factors, while the I_2 and I_4 terms

have sine factors. Being symmetric with respect to $\hat{C}_2^x$ or $\hat{\sigma}_v^{xz}$ that changes ϕ to $-\phi$ imposes the same constraints on I_1 and I_3, and on I_2 and I_4; (3) both $3m$ and $|3n+1|$ are powers of ρ that follow the same constraints, given the shared constraints of I_1 and I_3, and of I_2 and I_4. The three reasons still apply in the derivation below for higher symmetries, and the constraint-sharings remain. Overall, we have constraint-sharings among (I_1, I_3, I_7), among (I_2, I_4, I_8), and among $(3m, 3n+1, 3m')$.

TABLE 2. Constraints on the summing indices for the $(E+A)\otimes(e+a)$ vibronic Hamiltonian expansions for C_{3h} molecules.[a]

	$I_{1,2}$	$3m$	$I_{3,4}$	$3n+1$	$I_{5,6}$	$3n'+1$
$(E''+A'')\otimes(e'+a')$, $(E'+A')\otimes(e'+a')$	nr	nr	nr	nr	nr	nr
$(E''+A'')\otimes(e''+a')$, $(E'+A')\otimes(e''+a')$	nr	even	nr	even	nr	even
$(E''+A'')\otimes(e'+a'')$, $(E'+A')\otimes(e'+a'')$	even	nr	even	nr	even	nr
$(E''+A'')\otimes(e''+a'')$, $(E'+A')\otimes(e''+a'')$	(ee or oo)		(ee or oo)		(ee or oo)	
$(E''+A')\otimes(e'+a')$, $(E'+A'')\otimes(e'+a')$	nr	nr	nr	nr	na	na
$(E''+A')\otimes(e''+a')$, $(E'+A'')\otimes(e''+a')$	nr	even	nr	even	nr	odd
$(E''+A')\otimes(e'+a'')$, $(E'+A'')\otimes(e'+a'')$	even	nr	even	nr	odd	nr
$(E''+A')\otimes(e''+a'')$, $(E'+A'')\otimes(e''+a'')$	(ee or oo)		(ee or oo)		(eo or oe)	

[a] "nr" and "na" stand for "no further restriction" other than indicated in Eq. 25 and "not applicable", respectively. Terms with the "na" indices should be zeroed. "(ee or oo)" means that the two sets of indices (e.g., $I_{1,2}$ is a set and $3m$ is another set) covered by the parentheses should be both even or both odd. "(eo or oe)" means that one set should be even and the other odd, or the other way around. $I_{7,8}$, and $3m'$ share the same constraints with $I_{1,2}$ and $3m$, respectively, in each case.

C. D_{3h} and D_{3d}

The D_{3h} $(E+A)\otimes(e+a)$ vibronic Hamiltonians should be invariant under $\hat{C}_2^x$ and $\hat{\sigma}_h^{xy}$. They should hence adopt the constraints in both Tables 1 and 2. For instance, for the $(E'+A_1'')\otimes(e'+a_1'')$ Hamiltonian, we need to combine constraints for the $(E+A_1)\otimes(e+a_1)$ case in Table 1, with those for the $(E'+A'')\otimes(e'+a'')$ case in Table 2. The resultant

constraints are: I_1 even, I_2 na, $3m$ nr, I_5 odd, I_6 na, and $3n'+1$ nr (the constraint-shared indices are omitted). The constraints for all 64 $(E+A)\otimes(e+a)$ cases of D_{3h} symmetry are derived in a similar additive way and summarized in Table S.1 in the supporting information (SI). To transfer the D_3 constraints to D_{3h}, the orientations of the states and modes need to be consistent: $|X\rangle$ and e_x are symmetric with respect to one $\hat{C}_2$ operation, while $|y\rangle$ and e_y antisymmetric. Such orientations are exemplified in Figure 1(e).

The D_{3d} point group is isomorphic to the D_{3h} and they have the same number of $(E+A)\otimes(e+a)$ vibronic Hamiltonians. The same derivation follows, with $\hat{\sigma}_h^{xy}$ being replaced by the $\hat{I}$ inversion operation. Naturally, the constraint table of the D_{3d} vibronic Hamiltonians have the same structure and the same entries as the D_{3h} table, simply with the prime on the irrep symbols being replaced by the subscript g (gerade), and the double-prime by the subscript u (ungerade).The D_{3d} constraints are summarized in Table S.2 in SI. Again, the orientations of states and modes need to be consistent with those in deriving the D_3 Hamiltonians, as exemplified in Figure 1(f). Note that the e_{ux} mode there consists of two e_y-type vibrations in the other panels, one for the bold wedged triangle and the other for the hashed wedged triangle. Similarly, the e_{uy} consists of two e_x-type vibrations in the other panels.

In total, there are 153 $(E+A)\otimes(e+a)$ problems for trigonal molecules: 1 for C_3, 4 for C_{3v}, 4 for D_3, 16 for C_{3h}, 64 for D_{3h}, and 64 for D_{3d}. They are all covered by the expansion in Eq. 25 and the constraints summarized in the four tables (Tables 1, 2, S.1, and S.2). The broad applicability of the present formalism is evident.

IV. EXAMPLES

In this section, we show how to obtain expansions of the vibronic Hamiltonians for two cases by using Eq. 25 and the constraint tables. The first example is the D_{3h} $(E'+A_2'')\otimes(e'\otimes a_2'')$ Hamiltonian. This is a thoroughly investigated vibronic problem and its vibronic Hamiltonian expansion up to 8-th order has been derived using Weyl's polarization method[41,42] by Bhattacharyya, Domcke (BD) and coworkers.[29] It provides a reliable reference to benchmark our expansion. The second example is the C_3 $(E+A)\otimes e$ Hamiltonian, for which we compare our expansion with that derived by Eisfeld and Viel.[19,20]

A. The D_{3h} $(E' + A_2'') \otimes (e' \otimes a_2'')$ Hamiltonian

In the text below, the results in Ref. 29 are labelled by "BD". The constraints on the summing indices for the $(E' + A_2'') \otimes (e' \otimes a_2'')$ vibronic Hamiltonian are read from Table S.1: $I_{1,3,7}$ even; $I_{2,4,6,8}$ na; I_5 odd; $3m$, $3m'$ and $3n+1$ nr. With these constraints, one can easily construct a table of allowed indices, e.g., Table 3 for the 5-th to 8-th order expansions of the vibronic Hamiltonian. We first look at the already challenging 5-th order expansion. The possible combinations of summing indices that give $I_1 + 3m + 2K = I_3 + |3n+1| + 2K = I_5 + |3n'+1| + 2K = 5$ are enumerated in the table. Substituting the indices in Eq. 25, we have

$$\begin{aligned}
H_{XX}^{(5)} &= a_{2,0}^{r,3} z^2 \rho^3 \cos 3\phi + a_{0,2}^{r,3} \rho^5 \cos 3\phi + b_{4,0}^{r,1} z^4 \rho \cos\phi + b_{2,0}^{r,1} z^2 \rho^3 \cos\phi + b_{0,4}^{r,1} \rho^5 \cos\phi + b_{0,0}^{r,-5} \rho^5 \cos(-5\phi) \\
&= a_{2,0}^{r,3} z^2 \left(x^3 - 3xy^2\right) + a_{0,2}^{r,3} \left(x^2+y^2\right)\left(x^3 - 3xy^2\right) + b_{4,0}^{r,1} z^4 x + b_{2,2}^{r,1} z^2 \left(x^2+y^2\right) x \\
&\quad + b_{0,4}^{r,1} \left(x^2+y^2\right)^2 x + b_{0,0}^{r,-5} \left(x^5 - 10x^3y^2 + 5y^4 x\right); \qquad (37) \\
H_{XZ}^{(5)} &= d_{3,0}^{r,-2} z^3 \rho^2 \cos(-2\phi) + d_{1,2}^{r,-2} z \rho^4 \cos(-2\phi) + d_{1,0}^{r,4} z \rho^4 \cos 4\phi \\
&= d_{3,0}^{r,-2} z^3 \left(x^2 - y^2\right) + d_{1,0}^{r,-2} z \left(x^2+y^2\right)\left(x^2 - y^2\right) + d_{1,0}^{r,4} z \left(x^4 + y^4 - 6x^2y^2\right); \qquad (38) \\
H_{ZZ}^{(5)} &= c_{2,0}^{r,3} z^2 \rho^3 \cos 3\phi + c_{0,2}^{r,3} \rho^5 \cos 3\phi \\
&= c_{2,0}^{r,3} z^2 \left(x^3 - 3xy^2\right) + c_{0,2}^{r,3} \left(x^2+y^2\right)\left(x^3 - 3xy^2\right). \qquad (39)
\end{aligned}$$

They are consistent with the BD expansions. With the agreements in H_{XX} and H_{XZ}, the expansions of H_{YY}, H_{XY}, and H_{YZ} must also agree.

Similar agreements are found for all lower order and most of the higher order expansions up to the 8-th order, the highest order considered by BD. This overall good agreement corroborates our formalism. However, some inconsistencies do occur in the 6-th to 8th order expansions. The BD $H_{XY}^{(6)}$ contains 3 terms with z^2, while there are only two $I_3 = 2$ entries in the 6-th order $(I_3, 3n+1)$ block in Table 3. The three terms in the BD expansion are

$$\begin{aligned}
&a_7^{(6)} z^2 2xy \left(x^2+y^2\right) - a_8^{(6)} z^2 y \left(x^3 - 3xy^2\right) - 2a_9^{(6)} z^2 2xy \left(x^2 - y^2\right) = \\
&-a_7^{(6)} z^2 \rho^4 \sin(-2\phi) - a_8^{(6)} z^2 \rho^4 \frac{1}{2} \left(\sin 4\phi + \sin(-2\phi)\right) - a_9^{(6)} z^2 \rho^4 \sin 4\phi. \qquad (40)
\end{aligned}$$

The BD notation for the coefficients is used. The first and third terms are consistent with the $(2,-2,2)$ and $(2,4,0)$ entries in the $(I_3, 3n+1)$ block. The second term is a linear combination of the other two and thus redundant. Correspondingly, similar redundancies occur in the BD $H_{XX}^{(6)}$ and $H_{YY}^{(6)}$.

TABLE 3. Allowed summing indices in constructing the D_{3h} $(E' + A_2'') \otimes (e' + a_2'')$ vibronic Hamiltonian expansion at the 5-th to 8-th order.

Order	I_1	$3m$	$2K$	I_3	$3n+1$	$2K$	I_5	$3n'+1$	$2K$	Order	I_1	$3m$	$2K$	I_3	$3n+1$	$2K$	I_5	$3n'+1$	$2K$
5	2	3	0	4	1	0	3	-2	0	6	6	0	0	4	-2	0	5	1	0
	0	3	2	2	1	2	1	-2	2		4	0	2	2	-2	2	3	1	2
				0	1	4	1	4	0		2	0	4	0	-2	4	1	1	4
				0	-5	0					0	6	0	2	4	0	1	-5	0
											0	0	6	0	4	2			
7	4	3	0	6	1	0	5	-2	0	8	8	0	0	6	-2	0	7	1	0
	2	3	2	4	1	2	3	-2	2		6	0	2	4	-2	2	5	1	2
	0	3	4	2	1	4	1	-2	4		4	0	4	2	-2	4	3	1	4
				0	1	6	3	4	0		2	0	6	0	-2	6	1	1	6
				2	-5	0	1	4	2		0	0	8	4	4	0	3	-5	0
				0	-5	2					2	6	0	2	4	2	1	-5	2
				0	7	0					0	6	2	0	4	4	1	7	0
														0	-8	0			

The second inconsistency is seen in $H_{XZ}^{(7)}$ (and correspondingly in $H_{YZ}^{(7)}$). The BD $H_{XZ}^{(7)}$ reads

$$\begin{aligned} H_{XZ}^{(7)} &= c_1^{(7)} z^5 \left(x^2 - y^2\right) + c_2^{(7)} x z^3 \left(x^3 - 3xy^2\right) + c_3^{(7)} z \left(x^2 - y^2\right) \left(x^2 + y^2\right)^2 \\ &= c_1^{(7)} z^5 \rho^2 \cos\left(-2\phi\right) + c_2^{(7)} z^3 \rho^4 \frac{1}{2} \left(\cos\left(-2\phi\right) + \cos 4\phi\right) + c_3^{(7)} z \rho^6 \cos\left(-2\phi\right). \end{aligned} \quad (41)$$

However, there are 5 entries in the 7-th order $(I_5, 3n'+1)$ block in Table 3, giving

$$\begin{aligned} H_{XZ}^{(7)} = {} & d_{5,0}^{r,-2} z^5 \rho^2 \cos\left(-2\phi\right) + d_{3,2}^{r,-2} z^3 \rho^4 \cos\left(-2\phi\right) + d_{1,4}^{r,-2} z \rho^6 \cos\left(-2\phi\right) \\ & + d_{3,0}^{r,4} z^3 \rho^4 \cos\left(4\phi\right) + d_{1,2}^{r,4} z \rho^6 \cos\left(4\phi\right). \end{aligned} \quad (42)$$

The summation in the second term in Eq. 41 becomes two independent terms in Eq. 42. The extra $z\rho^6 \cos\left(4\phi\right)$ term in Eq. 42 shares the same symmetry as the $z^3\rho^4 \cos\left(4\phi\right)$ term and should be included. All terms in Eq. 42 differ either in the trigonometric functions or the powers of z and ρ; none of them is redundant.

The last inconsistency is seen in $H_{XY}^{(8)}$ (and correspondingly in $H_{XX}^{(8)}$ and $H_{YY}^{(8)}$). There are ten terms in the BD $H_{XY}^{(8)}$. However, the 8-th order $(I_3, 3n+1)$ block in Table 3 contains

only 8 entries. There are three z^4 terms and three z^2 terms in the BD expansion, while there are two $I_3 = 4$ and two $I_3 = 2$ entries in the $(I_3, 3n+1)$ block. The z^4 terms in the BD $H^{(8)}_{XY}$ are:

$$a^{(8)}_9 z^4 \left(x^2+y^2\right) 2xy - a^{(8)}_{11} z^4 y \left(x^3 - 3xy^2\right) - 4a^{(8)}_{13} z^4 xy \left(x^2 - y^2\right) = \\ -a^{(8)}_9 z^4 \rho^4 \sin(-2\phi) - a^{(8)}_{11} z^4 \rho^4 \frac{1}{2} \left(\sin 4\phi + \sin(-2\phi)\right) - a^{(8)}_{13} z^4 \rho^4 \sin 4\phi. \tag{43}$$

The second term is redundant. A similarly redundancy is seen in the z^2 terms in the BD $H^{(8)}_{XY}$:

$$a^{(8)}_{10} z^2 \left(x^2+y^2\right)^2 2xy - a^{(8)}_{12} z^2 \left(x^2+y^2\right) y \left(x^3 - 3xy^2\right) - 4a^{(8)}_{14} z^2 \left(x^2+y^2\right) xy \left(x^2 - y^2\right) = \\ -a^{(8)}_{10} z^2 \rho^6 \sin(-2\phi) - a^{(8)}_{12} z^2 \rho^6 \frac{1}{2} \left(\sin 4\phi + \sin(-2\phi)\right) - a^{(8)}_{14} z^2 \rho^6 \sin 4\phi. \tag{44}$$

With all the redundancies removed, the BD expansion and ours are consistent, except for the two missing terms in their $H^{(7)}_{XZ}$ and the corresponding missing terms in their $H^{(7)}_{YZ}$. Please note that our derivation is not oriented towards this specific $(E' + A''_2) \otimes (e' + a''_2)$ Hamiltonian. The close-to-perfect agreement with the BD result demonstrates the robustness, completeness, and conciseness of the present formalism. With the present formalism, constructing vibronic Hamiltonian for any of the 153 $(E+A) \otimes (e+a)$ problems (and their subproblems, *vide infra*) consists of three steps:

1. Read the constraints for the indices for a specific problem from Tables 1, 2, S.1, or S.2;
2. Construct a table of allowed indices following the constraints, order-by-order, like Table 3;
3. Use this table and Eq. 25 to write the Hamiltonian expansion directly.

The 9-th and 10-th order expansions of the D_{3h} $(E' + A''_2) \otimes (e' + a''_2)$ Hamiltonian are presented in Section S.2 in SI. They demonstrate the convenience of using the present formalism to achieve even higher order expansions.

B. The C_3 $(E+A) \otimes e$ Hamiltonian

The $(E+A) \otimes e$ is a subproblem of $(E+A) \otimes (e+a)$ and its Hamiltonian is a special case of Eq. 25 with $I_{1-8} = 0$. The allowed indices for $1 \leq 3m + 2K = |3n+1| + 2K =$

$|3n'+1|+2K \leq 4$ are summarized in Table 4. The $(3n+1, 2K)$ blocks give the following expansion for H_{XY} up to the 4-th order:

$$H_{XY}^{(1)} = -b_{0,0}^{r,1}\rho\sin\phi - b_{0,0}^{i,1}\rho\cos\phi = -b_{0,0}^{r,1}y - b_{0,0}^{i,1}x; \tag{45}$$

$$H_{XY}^{(2)} = -b_{0,0}^{r,-2}\rho^2\sin(-2\phi) - b_{0,0}^{i,-2}\rho^2\cos(-2\phi) = b_{0,0}^{r,-2}2xy - b_{0,0}^{i,-2}\left(x^2-y^2\right); \tag{46}$$

$$H_{XY}^{(3)} = -b_{0,2}^{r,1}\rho^3\sin\phi - b_{0,2}^{i,1}\rho^3\cos\phi = -b_{0,2}^{r,1}\left(x^2+y^2\right)y - b_{0,2}^{i,1}\left(x^2+y^2\right)x; \tag{47}$$

$$\begin{aligned} H_{XY}^{(4)} &= -b_{0,0}^{r,4}\rho^4\sin 4\phi - b_{0,2}^{r,-2}\rho^4\sin(-2\phi) - b_{0,0}^{i,4}\rho^4\cos 4\phi - b_{0,2}^{i,-2}\rho^4\cos(-2\phi) \\ &= -b_{0,0}^{r,4}4xy\left(x^2-y^2\right) + b_{0,2}^{r,-2}\left(x^2+y^2\right)2xy - b_{0,0}^{i,4}\left(x^4+y^4-6x^2y^2\right) \\ &\quad -b_{0,2}^{i,-2}\left(x^2+y^2\right)\left(x^2-y^2\right). \end{aligned} \tag{48}$$

Compared to the expansions derived by Eisfeld and Viel (labelled by "EV" below),[19,20] our expansions contain the extra terms with the $b_{0,2K}^{i,3n+1}$ coefficients. With Table 4, the expansions of H_{XX}, H_{YY}, H_{XZ}, H_{ZZ}, and H_{YZ} can be constructed in a similar way. They are given in Section S.3 in SI, and they all differ from the EV counterparts by having the $a_{0,2K}^{i,3m}$, $b_{0,2K}^{i,3n+1}$, $c_{0,2K}^{i,3m}$, or $d_{0,2K}^{i,3n'+1}$ terms. There is a systematic discrepancy.

TABLE 4. Allowed summing indices in constructing the C_3 $(E+A)\otimes e$ vibronic Hamiltonian expansion at the 1-st to 4-th order. $3n'+1$ has the same allowed values as $3n+1$ for this case and is not listed.

Order	$3m$	$2K$	$3n+1$	$2K$	Order	$3m$	$2K$	$3n+1$	$2K$
1			1	0	2	0	2	-2	0
3	3	0	1	2	4	0	4	4	0
								-2	2

The i-labelled coefficients arise from the imaginary parts of the A_m, C_m, B_n and D_n functions in Eqs. 12 and 15. Assuming those functions to be real, then our expansions are identical to the EV ones. However, we have no reason to make this assumption. Correspondingly, if we allow the $c_{p,q}^{(++)}$ coefficients in Eq. (6) of Ref. 19 (and the other expansion coefficients there too) to take complex values, the EV derivation will result in the same $(E+A)\otimes e$ Hamiltonian as ours. This derivation is given in Section S.3 in SI. We attribute the discrepancy to the unnecessary restriction in Refs. 19 and 20 that the $c_{p,q}^{(++)}$, $c_{p,q}^{(+-)}$, and $c_{p,q}^{(+Z)}$ coefficients in the two works must be real.

The importance of those i-labelled terms is investigated in a numerical example. The three σ lone-pair orbitals of boric acid are shown in Figure 2(a). They are frozen to be one-electron diabatic states, and their matrix elements of the bare nuclei Hamiltonian, i.e., electron kinetic operator plus nucleus-electron attraction operator, are calculated on a grid of e bending and a grid of e stretching coordinates. This model is far from any real systems, but it does reveal the symmetries of the matrix elements. The two components of the e bending are:

$$e_x = \sqrt{\frac{1}{6}} \left(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3\right); e_y = \sqrt{\frac{1}{2}} \left(\Delta\alpha_3 - \Delta\alpha_2\right), \tag{49}$$

and the two components of the e stretching:

$$e_x = \sqrt{\frac{1}{6}} \left(2\Delta r_{BO_1} - \Delta r_{BO_2} - \Delta r_{BO_3}\right); e_y = \sqrt{\frac{1}{2}} \left(\Delta r_{BO_2} - \Delta r_{BO_3}\right). \tag{50}$$

The bond angles $\alpha_{1,2,3}$ and the O atoms numbering are shown in Figure 2(a). The B3LYP[43,44] functional is used to optimize the boric acid structure and the cc-pVDZ[45] basis set is used for all calculations, which are performed using the GAMESS-US program package.[46,47]

Boric acid is a C_{3h} molecule. The electronic states and the vibrational modes are symmetric with respect to $\hat{\sigma}_h$ and hence it is an $(E' + A') \otimes e'$ problem. Its Hamiltonian has the same expansion as the the C_3 $(E + A) \otimes e$ problem (see all the "nr"s in the first row in Table 2). Therefore, the conclusions drawn from this model also apply to the C_3 problem. We first examine the three off-diagonal elements, whose contour plots as functions of the bending coordinates are shown in Figure 2(b). If the EV H_{XY} expansion is correct, that it only contains the $-b_{0,2K}^{r,3n+1} \sin\left((3n+1)\,\phi\right)$ terms (see Eqs 12a-12g in Ref. 19), H_{XY} should be antisymmetric with respect to the straight line corresponding to $\phi = 0$ and $\phi = \pi$. Since the e_x and e_y components of the mode can be arbitrarily oriented (as long as they satisfy the transformation in Eq. 1), there is an arbitrariness in the ϕ value. However, if H_{XY} is antisymmetric with respect to some arbitrary yet fixed ϕ and $\phi + \pi$, its (or one of its) 0 contour line(s) that passes through the origin, which is called "central 0 contour" below, ought to be a straight line. Such a straight central 0 contour is certainly absent in the H_{XY} contour plot. On the other hand, if H_{XY} only contains the $-b_{0,2K}^{i,3n+1} \cos\left((3n+1)\,\phi\right)$ terms, the contour plot should be symmetric with respect to a straight line corresponding to $\phi = 0$ and $\phi = \pi$ (or some arbitrary yet fixed ϕ and $\phi + \pi$). Such a symmetry is not seen either. Therefore, H_{XY} must contain both the $b_{0,2K}^{r,3n+1} \sin\left((3n+1)\,\phi\right)$ and $b_{0,2K}^{i,3n+1} \cos\left((3n+1)\,\phi\right)$ terms.

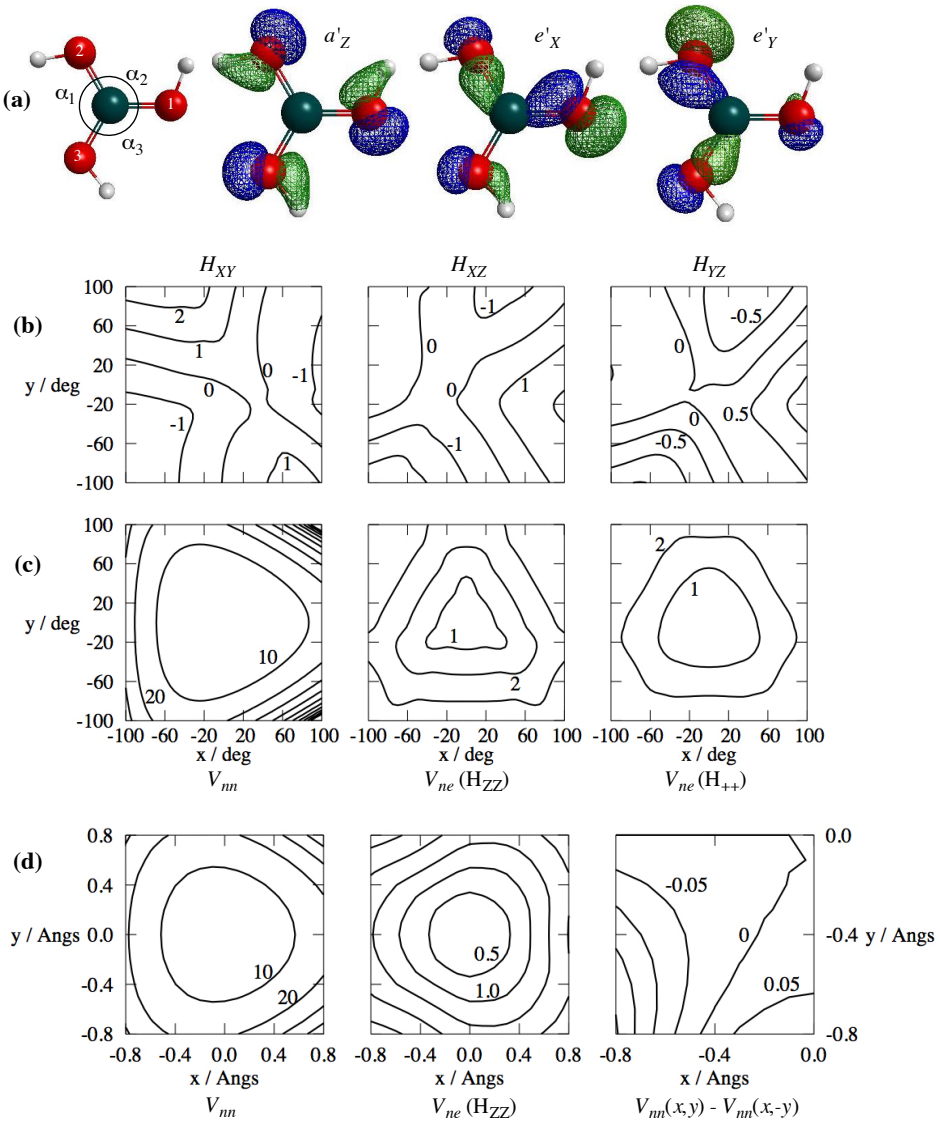

FIG. 2. (a) The three bond angles that define the e' bending, the numbering of the O atoms that define the e' stretching, and the three σ lone pair orbitals that serve as diabatic states; (b) the contour plots of the three off-diagonal matrix elements as functions of the e' bending coordinates; (c) the contour plots of the V_{nn} and V_{ne} components in the diagonal matrix elements; (d) similar counterplots as in (c) but in the e' stretching coordinates. The B, O, and H atoms are represented by dark green, red, and white spheres. The subscripts of the orbital labels indicate the states they make. The contours have equal increments. Some contour values are given (in E_H) so that the others can be obtained through projection. The 0 references of the V_{nn} and V_{ne} contour plots in (c) and (d) are taken to be their values at the undistorted origin.

Similarly, H_{XZ} and H_{YZ}'s central 0 contours are not straight; they are not symmetric with

respect to any straight lines either. H_{XZ} must contain both the $d_{0,2K}^{i,3n'+1}\sin\left(\left(3n'+1\right)\phi\right)$ and $d_{0,2K}^{r,3n'+1}\cos\left(\left(3n'+1\right)\phi\right)$ terms; H_{YZ} must contain both the $d_{0,2K}^{i,3n'+1}\cos\left(\left(3n'+1\right)\phi\right)$ and $d_{0,2K}^{r,3n'+1}\sin\left(\left(3n'+1\right)\phi\right)$ terms.

The importance of the $c_{0,2K}^{i,3m}\sin\left(3m\phi\right)$ terms in H_{ZZ} is shown in the contour plots in Figure 2(c). We can decompose the one-electron H_{ZZ} into two contributions: the nucleus-nucleus repulsion $V_{nn}\left(x,y\right)$ and the nuclei-electron attraction $V_{ne}\left(x,y\right)$ (including electron's kinetic energy in our calculation). V_{nn} is state-independent. For this specific e bending, it can be proved that $V_{nn}\left(x,y\right)$ is symmetric with respect to $y\rightarrow-y$ (see the V_{nn} contour plot in Figure 2(c) and Figure S.2 in SI). $V_{nn}\left(x,y\right)$ hence must take an expansion with only the $\cos\left(3m\phi\right)$ terms. $V_{ne}\left(x,y\right)$ is symmetric with respect to $x\rightarrow-x$ (see the $V_{ne}(H_{ZZ})$ contour plot in Figure 2(c)). Its expansion can only contain the $\sin\left(3m\phi\right)$, $m=1,3,5,\cdots$ and $\cos\left(3m\phi\right)$, $m=0,2,4,\cdots$ terms. Since $V_{ne}\left(x,y\right)$ is asymmetric with respect to $y\rightarrow-y$, it cannot only contain the $\cos\left(3m\phi\right)$ terms. Summing V_{nn} and V_{ne}, the H_{ZZ} expansion must contain both the $c_{0,2K}^{r,3m}\cos\left(3m\phi\right)$ and $c_{0,2K}^{i,3m}\sin\left(3m\phi\right)$ terms. The selection of the $\sin\left(3m\phi\right)$ terms with $m=1,3,5,\cdots$ only applies to the e bending. For the e stretching, the only symmetry is for V_{ne} with respect to $y\rightarrow-y$ (Figure 2(d)). V_{nn} has no symmetry on its contour plot. The apparent symmetry of V_{nn} with respect to $y\rightarrow-y$ in Figure 2(d) is misleading, as clarified by the $V_{nn}\left(x,y\right)-V_{nn}\left(x,-y\right)$ contour plot. The slightly jagged 0 contour in this plot results from the numerical noise of interpolation in generating contour plot from point-wise data. Overall, for the e stretching, V_{ne} contains $\cos\left(3m\phi\right)$ terms and V_{nn} contains $\cos\left(3m\phi\right)$ and $\sin\left(3m\phi\right)$ terms, without selection of the m values. The H_{ZZ} expansion should hence contain both the $c_{0,2K}^{i,3m}\cos\left(3m\phi\right)$ and $c_{0,2K}^{i,3m}\sin\left(3m\phi\right)$ terms. All these symmetry properties of V_{nn} and V_{ne} are proved in Section S.4 in SI. Like $\left|Z\right\rangle$, $\left|+\right\rangle$ gives a totally symmetric electron density. Therefore, the V_{ne}s of the two states share the same symmetry (compare the $V_{ne}\left(H_{++}\right)$ and $V_{ne}\left(H_{ZZ}\right)$ contour plots in Figure 2(c)). The above conclusion about H_{ZZ} can be transferred: H_{++}, and then H_{XX} and H_{YY}, contain both the $a_{0,2K}^{r,3m}\cos\left(3m\phi\right)$ and $a_{0,2K}^{i,3m}\sin\left(3m\phi\right)$ terms.

Overall, the calculated diabatic matrix elements of the boric acid σ lone-pair orbitals corroborate the importance of the $a_{0,2K}^{i,3m}$, $b_{0,2K}^{i,3n+1}$, $c_{0,2K}^{i,3m'}$, and $d_{0,2K}^{i,3n'+1}$ terms in the C_3 and C_{3h} $\left(E+A\right)\otimes e$ Hamiltonian expansion. The symmetry elements that can (but not necessarily) eliminate the i-labelled terms are the σ_v^{xz} reflection plane and the C_2^x axis. For all C_{3v} and D_3 $\left(E+A_1\right)\otimes e$ problems, those i-labelled terms do not contribute, because the $I_{2,4,6,8}$

constraints are either "na" or "odd" in the first two rows of Table 1, and the "odd" constraint is incompatible with the omission of the a mode (i.e., setting $I_{1-8} = 0$). Therefore, the EV expansion can be used for these problems, which are their focuses.[19,20] However, for the $(E + A_2) \otimes e$ problem, the I_6 constraint is "nr" or "even" (see the last two rows of Table 1), which is compatible with $I_6 = 0$. The $d_{0,2K}^{i,3n'+1}$ terms hence contribute to the H_{XZ} and H_{YZ} of the $(E + A_2) \otimes e$ problem. Actually, only the $d_{0,2K}^{i,3n'+1}$ terms contribute to the H_{XZ} and H_{YZ}, since the corresponding I_5 constraint is "na" or "odd", incompatible with $I_5 = 0$. Omitting the i-labelled terms will hence result in no vibronic coupling between the E and A_2 states. Similarly, for the higher symmetry D_{3h} and D_{3d}, only when the A state has a subscript 2 may the $d_{0,2K}^{i,3n'+1}$ terms contribute to the $(E + A) \otimes e$ vibronic Hamiltonian. Those problems correspond to the rows with the I_6 constraint being "nr" or "even" in Tables S.1 and S.2 in SI. The $I_{2,4,8}$ constraints are all "na" or "odd" in the tables; the corresponding i-labelled terms make no contributions to any of the $(E + A) \otimes e$ problems. Again, there is an exclusion between the $d_{0,2K}^{i,3n'+1}$ and $d_{0,2K}^{r,3n'+1}$ terms in the D_{3h} and D_{3d} $(E + A) \otimes e$ problems: whenever the I_6 constraint is "nr" or "even", the I_5 constraint is "na" or "odd", incompatible with $I_5 = 0$. Omitting the i-labelled terms will again result in no coupling between the E and A states in these problems.

V. EXPANSION OF SPIN-ORBIT MATRIX ELEMENTS IN THE p-TYPE $(E + A) \otimes (e + a)$ PROBLEMS

For molecules with heavy atoms, spin-orbit coupling (SOC) becomes significant.[48,49] The spin-orbit interaction can couple states of different symmetries and spins; there is an intricate interplay between SOC and the JT (and pJT) effects.[50–62] The SOC operator should hence be included in the vibronic Hamiltonian expansion for those systems. Very recently, Domcke et al.[38] derived the relations between the SOC matrix elements and the electrostatic Hamiltonian elements for p orbitals. These relations significantly simplify the construction of the spin-orbit vibronic Hamiltonian.

The Domcke formalism is applicable to any SOC problems that can be formally described using spin-orbit matrix elements between a set of $p_{x,y,z}$ Gaussian orbitals (called the "p-type problems" below). Combining the Domcke formalism and Eq. 25, we obtain concise expressions for the SOC matrix elements' expansions for the p-type $(E + A) \otimes (e + a)$ problems.

In the expressions below, orbitals with β spin are denoted by overhead bar, while those with α spin are not denoted; the "=" sign means that its both sides have the same form of expansions, not a true equality; $C_{1,2}$ are common coefficients shared by the last two equations. Expansions for the six basic matrix elements are:

$$h^{SO}_{p_x p_y} = i\left(H_{XX} + H_{YY}\right) = i\epsilon^{r,3m}_{I_1,2K} z^{I_1}\rho^{3m+2K}\cos\left(3m\phi\right) - i\epsilon^{i,3m}_{I_2,2K} z^{I_2}\rho^{3m+2K}\sin\left(3m\phi\right); \tag{51}$$

$$\begin{aligned} h^{SO}_{p_x p_z} &= iH_{YZ} \\ &= i\left(\delta^{r,3n'+1}_{I_5,2K} z^{I_5}\rho^{|3n'+1|+2K}\sin\left((3n'+1)\phi\right) - \delta^{i,3n'+1}_{I_6,2K} z^{I_6}\rho^{|3n'+1|+2K}\cos\left((3n'+1)\phi\right)\right); \end{aligned} \tag{52}$$

$$\begin{aligned} h^{SO}_{p_y p_z} &= -iH_{XZ} \\ &= -i\left(\delta^{r,3n'+1}_{I_5,2K} z^{I_5}\rho^{|3n'+1|+2K}\cos\left((3n'+1)\phi\right) + \delta^{i,3n'+1}_{I_6,2K} z^{I_6}\rho^{|3n'+1|+2K}\sin\left((3n'+1)\phi\right)\right); \end{aligned} \tag{53}$$

$$\begin{aligned} h^{SO}_{p_x \bar{p}_y} &= -iH_{XZ} - H_{YZ} \\ &= -i\zeta^{r,3n'+1}_{I_5,2K} z^{I_5}\rho^{|3n'+1|+2K} e^{-i(3n'+1)\phi} - \zeta^{i,3n'+1}_{I_6,2K} z^{I_6}\rho^{|3n'+1|+2K} e^{i(3n'+1)\phi}; \end{aligned} \tag{54}$$

$$\begin{aligned} h^{SO}_{p_x \bar{p}_z} &= C_1\left(iH_{XY} - H_{XX}\right) - C_2 H_{ZZ} \\ &= \left(\gamma^{r,3n+1}_{I_3,2K} z^{I_3} + i\gamma^{i,3n+1}_{I_4,2K} z^{I_4}\right)\rho^{|3n+1|+2K} e^{i(3n+1)\phi} - \eta^{r,3m}_{I_1,2K} z^{I_1}\rho^{3m+2K}\cos\left(3m\phi\right) \\ &\quad + \eta^{i,3m}_{I_2,2K} z^{I_2}\rho^{3m+2K}\sin\left(3m\phi\right); \end{aligned} \tag{55}$$

$$\begin{aligned} h^{SO}_{p_y \bar{p}_z} &= C_1\left(iH_{YY} - H_{XY}\right) + C_2 iH_{ZZ} \\ &= \left(i\gamma^{r,3n+1}_{I_3,2K} z^{I_3} - \gamma^{i,3n+1}_{I_4,2K} z^{I_4}\right)\rho^{|3n+1|+2K} e^{i(3n+1)\phi} + i\eta^{r,3m}_{I_1,2K} z^{I_1}\rho^{3m+2K}\cos\left(3m\phi\right) \\ &\quad - i\eta^{i,3m}_{I_2,2K} z^{I_2}\rho^{3m+2K}\sin\left(3m\phi\right). \end{aligned} \tag{56}$$

The other p-type SOC elements are either zero or can be readily obtained from the six.[38]

These expansions can be used for any p-type $(E+A)\otimes(e+a)$ spin-orbit vibronic problems for trigonal molecules. The $p_{x,y,z}$ orbitals transform as $(E+A)$ in C_3, $(E+A_1)$ in C_{3v}, $(E+A_2)$ in D_3, $(E'+A'')$ in C_{3h}, $(E'+A''_2)$ in D_{3h}, and (E_u+A_{2u}) in D_{3d}. After dressing the e and a symbols with the prime/double-prime, subscripts 1 and 2, and subscripts g and u, we can look up the corresponding constraints in the four tables and write down the expansions straightforwardly. Implementing the constraints for the D_{3h} $(E'+A''_2)\otimes(e'+a''_2)$ problem and with (ρ,ϕ) being converted to (x,y), our SOC expansions are consistent with those given by Domcke et al.[38] (up to the 4-th order, see Eq. 39 in their paper), except for a trivial sign difference of y.

Despite the conciseness of these expansion formulas of the SO elements, we need to emphasize their nature of approximation. First, they are only applicable for trigonal molecules with one p-block atom at center, whose valence p orbitals provide most of the SO effects. Any polarization of the central p orbitals to d orbitals has been neglected. Second, the derivation of Domcke et al.[38] for the relations between the SOC and non-SOC matrix elements relies on the assumption that the three p components are identical in shape, e.g., the $p_{x,y,z}$ Gaussian components have the same exponent ζ. However, the trigonal symmetry only guarantees the same shape for the central p_x and p_y orbitals, but not for the p_z. Ignoring the shape difference between $p_{x,y}$ and p_z is another approximation. All these approximations are inherited by our expansions. The expansions of the SO matrix elements free from these approximations were recently derived by Weike and Eisfeld for C_{3v} molecules.[62]

VI. CONCLUSIONS

In this work, we revisit the classic $(E + A) \otimes (e + a)$ problems of trigonal molecules and derive the general polynomial expansions for their vibronic Hamiltonians. The symmetry with respect to the three-fold axis rotation leads to the general expansion in Eq. 25. Symmetry requirements with respect to plane reflections, two-fold axis rotation perpendicular to the three-fold axis, and center-inversion impose further constraints on the terms in the expansion. The constraints are additive so that the constraints for a higher symmetry point groups can be readily obtained from those for the lower symmetry subgroups. With the general expansion and the constraints, it is straightforward to construct vibronic Hamiltonians to arbitrarily high order for the 153 $(E + A) \otimes (e + a)$ problems of 6 point groups and their subproblems.

We compare our expansions for the D_{3h} $(E' + A_2'') \otimes (e' + a_2'')$ and the C_3 $(E + A) \otimes e$ Hamiltonians with previous results. For the former, our expansion is in good agreement with that obtained using Weyl's polarization method. The completeness, conciseness, and convenience of our formalism are evident. For the latter, a class of terms emerge in our expansion. They arise from the imaginary parts of the A_m, B_n, C_m, and D_n functions in Eqs. 12 and 15. Those terms are, to the best of our knowledge, the first time derived. Their importance is corroborated by numerical calculation using a boric acid model. The present formalism also brings about concise expansion for the p-type $(E + A) \otimes (e + a)$ spin-

orbit vibronic Hamiltonian. With its completeness, conciseness, convenience, and broad applicability, we anticipate that the formalism will be of extensive use in future vibronic coupling studies.

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