# General formalism of vibronic Hamiltonians for tetrahedral and octahedral systems: problems that involve $A$-type states and $a$-type vibrations

Robert A. Lang, Achini Japahuge, Tao Zeng

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

**Abstract**

In this work, we derive expansion formulas up to arbitrary order in vibrational coordinates for the tetrahedral and octahedral vibronic Hamiltonians that involve $A$-type states and $a$-type vibrations. The root-branch approach and modularized approach enable us to derive vibronic Hamiltonians including up to two vibrational modes for 5 problems in $T$ symmetry and 92 problems in $T_d$ symmetry within one paper. These formulas can be easily adapted to problems of $T_h$, $O$, and $O_h$ symmetries. Finishing this work, we have derived general vibronic Hamiltonians for *all* unimodal and bimodal Jahn-Teller and pseudo-Jahn-Teller problems of cubic group systems. These bimodal formulas can be extended to cover problems that involve more than two modes.

*Keywords:*
Vibronic coupling, Jahn-Teller, Pseudo-Jahn-Teller, Tetrahedral,
Octahedral, Hamiltonian formalism

## 1. Introduction

The Jahn-Teller (JT) effects exist in nonlinear systems with the principal axis, proper or improper, greater than or equal to 3 fold: [1] the orbital degeneracy induced by the high symmetry reversely forces the system to abandon its high symmetry. This is fundamentally because the orbital-degenerate electronic states are coupled linearly (and possibly at higher orders) to non-totally symmetric vibrations. Consequently, the high symmetry configuration is not an extremum on adiabatic potential energy surfaces. [2, 3] Non-totally symmetric vibrations can also couple a non-degenerate state to other

states, leading to a similar energy lowering along the distortions. The relevant effects are called pseudo-Jahn-Teller (pJT) effects. [4] The JT and pJT effects have far-reaching consequences in chemical physics, especially in ultrafast photoinduced processes in polyatomic systems. [5] They have been subjects of a plethora of studies in the past 80 years. [6, 7, 8, 9, 10, 5, 11, 12, 13, 14]

Due to the strong coupling (namely, vibronic coupling) between the electronic and vibrational degrees of freedom in JT (and often pJT) systems, we need to consider the two types of degrees of freedom on an equal footing, i.e., the Born-Oppenheimer approximation [15] is inapplicable. In a vibronic calculation, the molecular Hamiltonian operator is expanded in a subset of strongly coupled electronic states and the vibrational modes that mediate their couplings. The number of states included in the expansion is related to the perturbational approximation of the problem in hand. For a degenerate state, if only all its degenerate components are used to expand the Hamiltonian, it is the first order perturbation treatment of a JT problem. The inclusion of additional states in the expansion, i.e., considering JT and pJT couplings together, exceeds the first order treatment and results in higher accuracy. For instance, the two specific $A_{1g}$ and $A_{2g}$ excited states were found to substantially interact with the ground $E_g$ state of the $RhCl_6^{2-}$ cluster in $O_h$ symmetry. These interactions modify the warping of the cluster's adiabatic potential energy surfaces derived from the $E_g \otimes e_g$ coupling. [16] With this understanding, the vibronic interaction is actually of $(E_g + A_{1g} + A_{2g}) \otimes e_g$ nature. For a nondegenerate state at its optimized structure, only when we consider its interaction with higher-lying states along symmetry-adapted vibrational modes, i.e., through at least a second order perturbation treatment, can we obtain a negative curvature of the nondegenerate state and explain its pJT distortion. [13] The higher accuracy comes at the cost of extra computational resources, as more states are involved in the underlying quantum chemistry calculations.

(Quasi-)diabatic electronic states (diabats) are usually used in constructing vibronic Hamiltonians, [17] so that the vibronic coupling matrix elements are smooth functions of vibrational coordinates and can be expanded as Taylor series. We would like to reiterate the importance of using an adequate number of states in expanding the Hamiltonian. If not enough states are included, the preparation of diabats from adiabatic states, which are the outputs of regular quantum chemistry calculations, will fail. [18, 19, 20, 21] Traditionally, the expansion of the matrix elements in vibrational coordinates is truncated at the second order. [3] Second order expansions have captured

2

the qualitative features and appropriate symmetry of vibronic interaction, and are considered adequate for small amplitude distortions. However, as the distortion amplitude increases, the importance of higher order expansions surges. [22, 23, 24, 25, 26] For example, when JT/pJT-active bending modes bring nuclei close to each other and lead to the so-called intramolecular collision, [27] higher order expansions are needed to describe the resultant anharmonic internuclear repulsion. When JT/pJT-active stretching modes lead to bond dissociation, higher order terms are also needed to describe the anharmonicity in potential energy surfaces. [25] In addition to theoretical studies, high-order expansions find their use in experiments. They are needed to give satisfactory interpretation of complicated vibronic spectrum [28, 29, 30, 31] and reliable empirical JT/pJT parameters, e.g., JT stabilization energy and barrier for pseudo-rotation. [32]

Incommensurate with the importance of the high-order expansions is our limited knowledge of the general expansion formulas up to arbitrary order. Accurate numerical values for vibronic couplings can be obtained using state-of-the-art quantum chemistry methods and the latest developed diabatization schemes. [20, 33, 34, 35, 21, 36] However, if we can only fit the numerical data using low-order functions, the accuracy is regrettably compromised. Along with their importance is the difficulty to fit the high-order expansions to obtain their coefficients. Some solutions of this problem are available, [37, 38, 24] including using Morse type vibrational coordinates to describe dissociative diabatic potentials. [25] Vibronic coupling can be viewed as a perturbative interaction between electronic states and the interaction is induced by vibrational motion. [11] Using the high-order expansions is hence equivalent to include high-order perturbative terms in the interaction. Please note the difference between high-order perturbation treatments and high-order perturbative terms. The former are related to the number of electronic states in resolving the Hamiltonian, and how to implicitly include the effects of the other states, given a perturbative operator. The latter are related to the accuracy of the perturbative operator. The two are different yet connected: when the perturbative operator contains more terms, it couples the electronic states in a more complicated manner. High-order expansions of vibronic matrix elements give more accurate simulation results. However, some neat interpretations of vibronic wave functions based on simple linear coupling models, e.g., the vibronic angular momentum quantum number, are no longer applicable. In short, the gain is of quantitative nature, at the cost of losing a simple picture of vibronic motion.

3

General high-order expansions for vibronic Hamiltonians were first derived for textbook problems, e.g., the $(E + A_1) \otimes e$ in $C_{3v}$ symmetry, the $T_2 \otimes t_2$, and the $T_2 \otimes e$ problem in $T_d$ symmetry. [22, 37, 38] Inspired by these pioneering works, we recently managed to derive general Hamiltonian expansions for 153 $(E + A) \otimes (e + a)$ problems in trigonal symmetry, [39] all 5150 bimodal problems in tetragonal symmetry, [40] and 92 tetrahedral and octahedral problems that involve $E$ and $T$ states and $e$ and $t$ vibrations. [41] The ground of our derivations is the idea of "descent in symmetry". [42] Two generalizing methods enable us to handle such a large number of problems, the root-branch approach and the modularized approach. In the root-branch approach, we first derive *root* expansion formulas for the problem of the lowest symmetry under discussion, e.g., the $(E + A) \otimes (e + a)$ problem in $C_3$ (the lowest trigonal) symmetry. *Branch* formulas for the higher symmetry problems, e.g., the $(E + A_1) \otimes (e + a_2)$ problem in $C_{3v}$ symmetry, are obtained by imposing constraints on the root formulas. In the modularized approach, we decompose a $(\Gamma_1 + \Gamma_2) \otimes (\gamma_1 + \gamma_2 + \cdots)$ vibronic problem into the $(\Gamma_1 + \Gamma_2)$ electronic part and the $(\gamma_1 + \gamma_2 + \cdots)$ vibrational part. The symmetry requirements on matrix elements of a vibronic problem are solely determined by the electronic part. [22, 23] Therefore, we first derive the symmetry requirements only considering the electronic part, and then construct expansions in vibrational coordinates that meet the requirements. The symmetry-adapted expansions are considered as modules. Deriving expansion formulas for a $(\Gamma_1 + \Gamma_2) \otimes (\gamma_1 + \gamma_2 + \cdots)$ problem is equivalent to seeking the appropriate $(\gamma_1 + \gamma_2 + \cdots)$ modules to meet the needs of $(\Gamma_1 + \Gamma_2)$. Very importantly, the modules can be reused or simply modified to meet needs of different electronic parts; the modularized approach is highly efficient.

In this work, we derive general expansion formulas for tetrahedral and octahedral vibronic problems that involve $A$-type states and $a$-type vibrations. Non-degenerate $A$ states are subject to pJT interaction. For instance, a $t_2^2$ or $t_2^4$ electronic configuration of a $T_d$ molecule gives a $^3T_1$, a $^1T_2$, a $^1E$, and a $^1A_1$ state. If the splitting between the three singlet states is not substantial, $(^1A_1 + {}^1T_2)$ and $(^1A_1 + {}^1E)$ vibronic couplings will occur. A more specific example is the $(A_{1g} + T_{1u}) \otimes t_{1u}$ coupling in $O_h$ symmetry. This coupling is essential to understand the phase transitions, ferroelectricity, and electric-field-enhanced permittivity of BaTiO$_3$. [43, 44, 45] Non-totally-symmetric $a_u$ vibrations in $T_h$, $a_2$ vibrations in $T_d$ and $O$, and $a_{1u}$, $a_{2u}$ and $a_{2g}$ vibrations in $O_h$ symmetry may take part in any JT and pJT problems. The complete formalism of tetrahedral and octahedral JT/pJT problems must include the

consideration of $A$-type states and $a$-type vibrations. This requirement motivates us to carry out the present study. In the derivations below, we first focus on tetrahedral problems, as their formulas can be easily transferred to describe octahedral problems. Throughout this paper, when not specified, symbols $A$, $E$, and $T$ and their lower case analogues denote generic Mulliken symbols with all possible subscripts. For instance, $A$ covers $A$ in $T$ symmetry, $A_g$ and $A_u$ in $T_h$ symmetry, and $A_1$ and $A_2$ in $T_d$ symmetry.

With this paper and our previous work [41] (henceforth called Paper I), we have derived expansion formulas for *all* bimodal vibronic problems of cubic groups. We only consider problems with up to two modes because: (1) it is usually adequate to consider two modes of different nature, e.g., one stretching and one bending mode; (2) a $(\gamma_1 + \gamma_2 + \gamma_3)$ triple mode problem (or even with more modes) can be approximated as a composite of double mode problems: $(\gamma_1 + \gamma_2)$, $(\gamma_1 + \gamma_3)$, and $(\gamma_2 + \gamma_3)$; (3) it is straightforward to extend the double-mode formulas to give full $n$-tuple mode expansions with $n > 2$. It is noteworthy that when only linear terms are included in the (p)JT Hamiltonian expansions, one can linearly transform several coupling modes of the same irreducible representation to one effective interaction mode. [11, 46, 47, 48] This transformation substantially reduces the dimension of the potential energy surfaces of the states involved in a (p)JT problem and facilitates the understanding of the relevant structural distortion. Our derived formulas apply to both molecules and local formations in solids. Therefore, we use the more generic term "systems" in the title.

This paper is organized as follows. In Section 2 we introduce the notation of the diabats and vibrational coordinates, and their transformations under the tetrahedral symmetry operations. In Sections 3 and 4, we present the derivations for the $a$- and $A$-related problems, respectively. Our formalism is examined using a numerical example in Section 5. In Section 6, we discuss the extension of the tetrahedral formulas to describe octahedral problems and conclude the paper.

Before moving on to the derivation, we would like to point out the difference between static and dynamic (p)JT effects. [42] When the (p)JT interaction leads to a significant energy lowering along the structural distortion, and the different symmetry-related distorted structures are separated by insurmountable barriers, the system is trapped in one of the distorted structures. This is the so-called static (p)JT effect, as it leads to a stationary structure of lower symmetry. For the static distortions, the Born-Oppenheimer approximation regains its validity and it is natural to discuss the electronic and

vibrational states based on the lowered symmetry. The (p)JT effect is dynamic when the vibronic interaction is not strong enough to trap the system at one lower symmetry configuration. Under such circumstances, the high symmetry conical intersection may still be reached by the nuclear vibration, and the vibrational functions on different low symmetry minima overlap, resulting in tunnelling. It is necessary to consider dynamic (p)JT problems using the parental high symmetry, instead of the distorted lower symmetry, since all the low symmetry configurations are sampled equally by the nuclear vibration. The formulas that we derive in this work are expanded at the origin of high symmetry structure and are hence more relevant to dynamic (p)JT problems. However, they also cover static problems, which are special cases when the formula's expansion coefficients (i.e., (p)JT coupling constants) assume large values.

## 2. Settings

The settings of states and modes have been detailed in Paper I. However, a brief overview is necessary to make this work self-contained. The three $C_2$ axes of a tetrahedral system are called $C_2^x$, $C_2^y$, and $C_2^z$. The three axes set the molecular-fixed frame following the conventional right-hand rule (see Figure 1 in Section 5). The axis that trisects the $C_2$ axes is chosen to be a representative $C_3$ axis, called $C_3^{xyz}$. An object that is symmetric with respect to $\hat{C}_3^{xyz}$ and any of $\hat{C}_2^{x,y,z}$ is of $T$ symmetry. The inversion center $I$ raises the object's symmetry to $T_h$. The symmetry plane $\sigma_d^x$ that contains the $x$-axis and bisects the first and third quadrants of the $y$-$z$ plane raises the symmetry from $T$ to $T_d$. $\sigma_d^y$ and $\sigma_d^z$ are similarly defined, bisecting the first quadrant of the plane made by the two axes not shown in the superscript.

The three components of a $T$ state or a $t$ mode are invariant with respect to the three $\hat{C}_2$ operations, respectively. The three $T$ components are correspondingly labeled as $|X\rangle$, $|Y\rangle$, and $|Z\rangle$, and the $t$ coordinates $x$, $y$, and $z$. The two components of an $E$ state or an $e$ mode are set to transform as the $2x^2 - y^2 - z^2$ and $\sqrt{3}\,(y^2 - z^2)$ functions. The $E$ components are labeled as $|\Theta\rangle$ and $|\Xi\rangle$, and the $e$ coordinates $q_\theta$ and $q_\xi$. It is related to the conventional setting that the components transform as $2z^2 - x^2 - y^2$ and $\sqrt{3}\,(x^2 - y^2)$ by a rotation. By the following transformations we utilize complex-valued $E$ states and polar $e$-coordinates due to their convenient employment in deriva-

tion.

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

An $A$ state is simply denoted as $|A\rangle$, and an $a$ vibrational coordinate as $w$. Greek subscripts "$\alpha$", "$\beta$", etc. are used to differentiate states or modes with the same Mulliken symbol. The Greek subscripts on states and coordinates are independent, e.g., the same $\alpha$ of $|X_\alpha\rangle$ and $x_\alpha$ does not mean that the state and the mode belong to the same $T_d$ or $T_h$ irreducible representation (irrep).

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

$$\hat{C}_3^{xyz} (|A\rangle, |+\rangle, |-\rangle, |X\rangle, |Y\rangle, |Z\rangle) = \left( |A\rangle, e^{-i\frac{2\pi}{3}} |+\rangle, e^{i\frac{2\pi}{3}} |-\rangle, |Y\rangle, |Z\rangle, |X\rangle \right);$$

$$\hat{C}_3^{xyz} f(\{w\}, \{\rho, \phi\}, \{x, y, z\}) = f\left( \{w\}, \left\{\rho, \phi - \frac{2\pi}{3}\right\}, \{y, z, x\} \right);$$

$$\hat{C}_2^z (|A\rangle, |+\rangle, |-\rangle, |X\rangle, |Y\rangle, |Z\rangle) = (|A\rangle, |+\rangle, |-\rangle, -|X\rangle, -|Y\rangle, |Z\rangle);$$
$$\hat{C}_2^x f(\{w\}, \{\rho, \phi\}, \{x, y, z\}) = f(\{w\}, \{\rho, \phi\}, \{x, -y, -z\});$$
$$\hat{C}_2^y f(\{w\}, \{\rho, \phi\}, \{x, y, z\}) = f(\{w\}, \{\rho, \phi\}, \{-x, y, -z\});$$
$$\hat{C}_2^z f(\{w\}, \{\rho, \phi\}, \{x, y, z\}) = f(\{w\}, \{\rho, \phi\}, \{-x, -y, z\}), \quad (2)$$

In $T_h$ symmetry,

$$\hat{I} (|A\rangle, |+\rangle, |-\rangle, |X\rangle, |Y\rangle, |Z\rangle) = \left( \pm^A |A\rangle, \pm^E |+\rangle, \pm^E |-\rangle, \pm^T |X\rangle, \pm^T |Y\rangle, \pm^T |Z\rangle \right);$$
$$\hat{I} f(\{w\}, \{\rho, \phi\}, \{x, y, z\}) = f\left( \{\pm^a w\}, \{\pm^e \rho, \phi\}, \{\pm^t x, \pm^t y, \pm^t z\} \right). \quad (3)$$

The "+" ("−") of "±" applies to gerade (ungerade) states and modes. Superscripts are added to "±"s to differentiate with which states/modes they are associated. In $T_d$ symmetry,

$$\hat{\sigma}_d^x (|A\rangle, |+\rangle, |-\rangle, |X\rangle, |Y\rangle, |Z\rangle) = \left( \pm^A |A\rangle, |-\rangle, |+\rangle, \pm^T |X\rangle, \pm^T |Z\rangle, \pm^T |Y\rangle \right);$$
$$\hat{\sigma}_d^x f(\{w\}, \{q_\theta, q_\xi\}, \{\rho, \phi\}, \{x, y, z\}) = f\left( \{\pm^a w\}, \{q_\theta, -q_\xi\}, \{\rho, -\phi\}, \{\pm^t x, \pm^t z, \pm^t y\} \right);$$
$$\hat{\sigma}_d^z f(\{w\}, \{q_\theta, q_\xi\}, \{\rho, \phi\}, \{x, y, z\}) =$$
$$f\left( \{\pm^a w\}, \left\{-\frac{1}{2}q_\theta + \frac{\sqrt{3}}{2}q_\xi, \frac{1}{2}q_\xi + \frac{\sqrt{3}}{2}q_\theta\right\}, \left\{\rho, -\phi + \frac{2\pi}{3}\right\}, \{\pm^t y, \pm^t x, \pm^t z\} \right). \quad (4)$$

7

The "+" and "−" of "$\pm^{T/t}$" ("$\pm^{A/a}$") apply to $T$ ($A$) states and $t$ ($a$) modes with the subscripts 2 and 1 (1 and 2) in their irrep symbols, respectively. Please note that the same "$\pm^{\Gamma/\gamma}$" symbols are used in $T_h$ and $T_d$ symmetries, but with different meanings. Eqs. 2 to 4 give all transformations needed in the following derivations. Throughout this paper, unless further specified, symbols starting with $I$, $J$, $K$, $L$, $M$, $N$ and their lower case analogues stand for integers, except "$i$", which itself represents the imaginary unit. In order to use our formulas in actual vibronic simulations, one needs to orient the components of the degenerate states and modes so that they transform following Eqs. 2 to 4.

## 3. $a$-involving but not $A$-involving problems

Following the root-branch approach, we first derive formulas for vibronic problems in $T$ symmetry. We separate the derivations for the *inter*-term and *intra*-term problems: the former involve the coupling between states of two term symbols and correspond to pJT interactions, while the latter involve the coupling between states of one term symbol and correspond to JT interactions. It is straightforward to obtain *intra*-term formulas from *inter*-term formulas. The electronic parts of the problems considered in this section have all been considered in Paper I.

### 3.1. $(T + T)$ and $T$ problems involving $a$-type vibration

In Paper I, we have shown:

1. Due to its invariance with respect to $\hat{C}_3^{xyz}$, the $(T + T)$ *inter*-term vibronic Hamiltonian reads

$$
\begin{aligned}
\hat{H} \;=\; & \left( |X_\alpha\rangle \langle X_\beta| + |X_\beta\rangle \langle X_\alpha| \right) W + \left( |Y_\alpha\rangle \langle Y_\beta| + |Y_\beta\rangle \langle Y_\alpha| \right) \hat{C}_3 W + \left( |Z_\alpha\rangle \langle Z_\beta| + |Z_\beta\rangle \langle Z_\alpha| \right) \hat{C}_3^2 W \\
& + \left( |X_\alpha\rangle \langle Y_\beta| + |Y_\beta\rangle \langle X_\alpha| \right) V + \left( |Y_\alpha\rangle \langle Z_\beta| + |Z_\beta\rangle \langle Y_\alpha| \right) \hat{C}_3 V + \left( |Z_\alpha\rangle \langle X_\beta| + |X_\beta\rangle \langle Z_\alpha| \right) \hat{C}_3^2 V \\
& + \left( |X_\beta\rangle \langle Y_\alpha| + |Y_\alpha\rangle \langle X_\beta| \right) U + \left( |Y_\beta\rangle \langle Z_\alpha| + |Z_\alpha\rangle \langle Y_\beta| \right) \hat{C}_3 U + \left( |Z_\beta\rangle \langle X_\alpha| + |X_\alpha\rangle \langle Z_\beta| \right) \hat{C}_3^2 U.
\end{aligned}
\tag{5}
$$

$\hat{C}_3^{xyz}$ is henceforth abbreviated as $\hat{C}_3$. Only three independent matrix elements are needed. They are real because the diabats are real-valued. This reduction of the number of independent matrix elements from 9 to 3 is a reflection of the Wigner-Eckart Theorem, which states that only the reduced matrix elements are needed. [49, 50] However, $W$, $V$, and $U$ are not the actual reduced matrix elements because the vibrational part of the problem has not been specified;

8

2. The matrix elements have the following symmetry properties:

$$W = \hat{C}_2^x W = \hat{C}_2^y W = \hat{C}_2^z W; V = -\hat{C}_2^x V = -\hat{C}_2^y V = \hat{C}_2^z V, \qquad (6)$$

and $U$ shares the same $\hat{C}_2$-transformations with $V$. They are derived from the invariance of $\hat{H}$ with respect to $\hat{C}_2^x$;

3. It is straightforward to extend the vibronic formalism from the $T$ to $T_h$ symmetry (*vide infra*, the paragraph above Eq. 10) and it is unnecessary to derive further symmetry constraints on the matrix elements;

4. For $T_d$ symmetry, we need

$$\hat{\sigma}_d^x W = \pm^{TT} W; \hat{\sigma}_d^z V = \pm^{TT} U. \qquad (7)$$

They are derived from the invariance of $\hat{H}$ with respect to $\hat{\sigma}_d^x$. The sign selections in "$\pm^{TT}$" depends on the pair of $T$ states being coupled: "$+$" applies if they are both $T_1$ or $T_2$ states; "$-$" for $(T_1 + T_2)$.

In Paper I, we have also derived the expansion formulas for the $(T + T) \otimes t$ problem in $T$ symmetry:

$$
\begin{aligned}
W &= a^K_{2k_1, 2k_2, 2k_3} (xyz)^K x^{2k_1} y^{2k_2} z^{2k_3}; \\
V(U) &= \left[ b^z_{2k_1, 2k_2, 2k_3} (z) + b^{xy}_{2k_1, 2k_2, 2k_3} (xy) \right] x^{2k_1} y^{2k_2} z^{2k_3}, \\
& \qquad K = 0, 1; k_{1,2,3} = 0, 1, 2, \cdots
\end{aligned} \qquad (8)
$$

Throughout this paper, Einstein's convention of summing over duplicate indices is followed. The ranges of the indices are maintained in the text below unless further specified. $V$ and $U$ share the same expansion formula but with different expansion coefficients. Since the $a$ mode is totally symmetric in $T$ symmetry, we can simply multiply any $w$ monomials onto the $W$ and $V$ expansions above to obtain the expansion formulas for the $(T + T) \otimes (a + t)$ problem in $T$ symmetry:

$$
\begin{aligned}
W &= a^K_{2k_1, 2k_2, 2k_3, k_4} (xyz)^K x^{2k_1} y^{2k_2} z^{2k_3} w^{k_4}; \\
V(U) &= \left[ b^z_{2k_1, 2k_2, 2k_3, k_4} (z) + b^{xy}_{2k_1, 2k_2, 2k_3, k_4} (xy) \right] x^{2k_1} y^{2k_2} z^{2k_3} w^{k_4}, k_4 = 0, 1, 2, \cdots (9)
\end{aligned}
$$

These two formulas are trivial. They simply demonstrate the well-known fact that the expansion coefficients of the non-totally symmetric modes' coordinates are functions of totally symmetric modes' coordinates. As a matter of fact, only the non-totally symmetric $a_u$ mode in $T_h$ symmetry and $a_2$ mode in $T_d$ symmetry are JT/pJT-active, and only those modes are considered in

9

our derivations. Despite its apparent triviality, Eq. 9 gives the root formulas for the derivations for $a_u$- and $a_2$-involving problems. Please note that all monomials in Eq. 9 differ in power(s) of at least one coordinate and are linearly independent. This expansion is thus free from redundancy, as are all derived expansion formulas in this work. This point will not be repeated unless the linear independency between terms in an expansion is not obvious.

For $(T + T) \otimes (a_u + t)$ problems in $T_h$ symmetry, the parities of $W$, $V$, and $U$ need to be consistent with the parity of the product of the two $T$ states, so that $\hat{H}$ has an even parity. This is the only rule to impose constraints on Eq. 9 to obtain expansion formulas for the $T_h$ problems. For the $(T_g + T_u) \otimes (t_u + a_u)$ problem, to have this consistency in odd parity, only odd order terms are allowed in the $W$ and $V$ expansions; for the $(T_{g,u} + T_{g,u}) \otimes (t_u + a_u)$ problems, only the even order terms are allowed. In this paper, the composite subscripts of Mulliken symbols match in pair, e.g., $(T_{g,u} + T_{g,u})$ means $(T_g + T_g)$ and $(T_u + T_u)$. Similarly, for the $(T_g + T_u) \otimes (t_g + a_u)$ problem, only the terms with odd $k_4$ are allowed in the $W$ and $V$ expansions, while for the $(T_{g,u} + T_{g,u}) \otimes (t_g + a_u)$ problems, only the even $k_4$ terms are allowed. This procedure can be generalized to any other $a_u$-involving problems in $T_h$ symmetry. With the known $(\Gamma_1 + \Gamma_2) \otimes \gamma$ formulas of $T$ symmetry, we can freely multiply $w^k$ monomials to them to obtain $(\Gamma_1 + \Gamma_2) \otimes (\gamma + a)$ formulas. Constraints on power indices are then imposed based on the parity consideration to obtain $(\Gamma_1 + \Gamma_2) \otimes (\gamma + a_u)$ formulas of $T_h$ symmetry. Keeping this simple procedure in mind, we will not (and it is unnecessary to) derive any formulas for problems in $T_h$ symmetry below.

We know from Paper I that for $(T + T) \otimes t$ problems in $T_d$ symmetry:

$$W = a^K_{2k_1,2k_2,2k_3} (xyz)^K x^{2k_1} \left[ y^{2k_2} z^{2k_3} \pm^{TT} \left( \pm^t \right)^K z^{2k_2} y^{2k_3} \right], k_3 \leq k_2 \quad (10)$$

Combining this formula and the antisymmetric character of the $a_2$ coordinate with respect to $\hat{\sigma}^x_d$, we have for $(T + T) \otimes (a_2 + t)$ problems in $T_d$ symmetry

$$W = a^K_{2k_1,2k_2,2k_3,k_4} (xyz)^K x^{2k_1} \left[ y^{2k_2} z^{2k_3} \pm^{TT} (-1)^{k_4} \left( \pm^t \right)^K z^{2k_2} y^{2k_3} \right] w^{k_4}, k_3 \leq k_2. \quad (11)$$

Eq. 7 determines that $V$ takes the same expansion as in Eq. 9 for the $T_d$ problems, while $U$ is connected to $V$ and takes the following expansion,

$$U = \pm^{TT} \left[ b^z_{2k_1,2k_2,2k_3,k_4} \left( \pm^t z \right) + b^{xy}_{2k_1,2k_2,2k_3,k_4} (xy) \right] y^{2k_1} x^{2k_2} z^{2k_3} (-w)^{k_4}. \quad (12)$$

The $b$ coefficients are shared in the $V$ and $U$ expansions.

It is straightforward to obtain the expansion formulas for *intra*-term $T \otimes (a_2 + t)$ problems from the corresponding *inter*-term $(T + T) \otimes (a_2 + t)$ formulas. The *intra*-term Hamiltonian involves only two independent matrix elements:

$$
\begin{aligned}
\hat{H} &= |X\rangle \langle X| W + |Y\rangle \langle Y| \hat{C}_3 W + |Z\rangle \langle Z| \hat{C}_3^2 W + (|X\rangle \langle Y| + |Y\rangle \langle X|) V \\
&\quad + (|Y\rangle \langle Z| + |Z\rangle \langle Y|) \hat{C}_3 V + (|Z\rangle \langle X| + |X\rangle \langle Z|) \hat{C}_3^2 V,
\end{aligned} \tag{13}
$$

and

$$
\hat{\sigma}_d^x W = W; \hat{\sigma}_d^z V = V. \tag{14}
$$

Obviously, for the *intra*-term problem the "$\pm^{TT}$" in Eq. 7 only takes "$+$", and the role of $U$ has been replaced by $V$. Given these considerations, $W$ takes Eq. 11 with $\pm^{TT} = +$. Derived in Paper I, the $V$ expansion for $T \otimes t$ problems in $T_d$ symmetry reads

$$
\begin{aligned}
V &= b_{2k_1,2k_2,2k_3}^z \left[ x^{2k_1} y^{2k_2} + \left(\pm^t\right) y^{2k_1} x^{2k_2} \right] z^{2k_3+1} \\
&\quad + b_{2k_1,2k_2,2k_3}^{xy} \left[ x^{2k_1} y^{2k_2} + y^{2k_1} x^{2k_2} \right] xyz^{2k_3}, k_2 \le k_1.
\end{aligned} \tag{15}
$$

Combining this formula and the antisymmetric character of $w$ with respect to $\hat{\sigma}_d^z$, we immediately obtain the $V$ expansion for $T \otimes (a_2 + t)$ problems in $T_d$ symmetry:

$$
\begin{aligned}
V &= b_{2k_1,2k_2,2k_3,k_4}^z \left[ x^{2k_1} y^{2k_2} + (-1)^{k_4} \left(\pm^t\right) y^{2k_1} x^{2k_2} \right] z^{2k_3+1} w^{k_4} \\
&\quad + b_{2k_1,2k_2,2k_3,k_4}^{xy} \left[ x^{2k_1} y^{2k_2} + (-1)^{k_4} y^{2k_1} x^{2k_2} \right] xyz^{2k_3} w^{k_4}, k_2 \le k_1.
\end{aligned} \tag{16}
$$

Setting the $t$ coordinates in the expansion formulas above to zero brings about the formulas for $(T + T) \otimes a_2$ and $T \otimes a_2$ problems in $T_d$ symmetry:

$$
W = a_{k_4} w^{2k_4} \tag{17}
$$

for the $(T_{1,2} + T_{1,2}) \otimes a_2$ and $T_{1,2} \otimes a_2$ problems ($\pm^{TT} = +$), and

$$
W = a_{k_4} w^{2k_4+1} \tag{18}
$$

for the $(T_1 + T_2) \otimes a_2$ problem ($\pm^{TT} = -$). When substituting $x = y = z = 0$ in the $V$ and $U$ formulas in Eqs. 9, 12, 15, and 16, it is obvious that both $V$ and $U$ are zero for all the $(T + T) \otimes a_2$ and $T \otimes a_2$ problems. This arises from

11

the incompatibility between the $\hat{C}_2^x$-invariance of any $w^{k_4}$ monomials and the $\hat{C}_2^x V = -V$ requirement (and similarly for $U$) in Eq. 6. Following the same rationale, all $V$ and $U$ must be zero for the $(T+T)$ and $T$ problems with any vibrational part that contains only $a$ and $e$ vibrations ($e$ coordinates are also $\hat{C}_2$-invariant, see Eq. 2). This reflects the beauty of the modularized approach. When the different vibrational modules share the same symmetry properties, e.g., the $\hat{C}_2^x$-invariance here, we immediately know that they all do not contribute to matrix elements that are incompatible with these symmetry properties. In the following, we only need to derive $W$ expansions for the leftover $a_2$-involving $(T+T)$ and $T$ problems.

Evidently, $W$ expansions of all $(T+T) \otimes (\gamma + a_2)$ and $T \otimes (\gamma + a_2)$ problems can be easily obtained by: first, multiplying $W$ formulas of the corresponding $(T+T) \otimes \gamma$ and $T \otimes \gamma$ problems with $w^k$ monomials; second, introducing a $(-1)^k$ factor (like in Eq. 16) or selecting the appropriate odd or even $k$ values (like in Eq. 19 below) to let the new formulas satisfy Eqs. 7 and 14. The reason behind this procedure is that all the $W$ elements and the $w^k$ monomials are symmetric or antisymmetric with respect to $\hat{\sigma}_d^x$.

Such simple rules can certainly be applied to derive expansion formulas for $(T+T) \otimes (e + a_2)$ problems in $T_d$ symmetry. As mentioned above, only $W$ can be nonzero for those problems. We have shown in Paper I that $(T+T) \otimes e$ problems in $T_d$ symmetry take $W = a_{k_1, 2k_2} q_\theta^{k_1} q_\xi^{2k_2}$ and $W = a_{k_1, 2k_2+1} q_\theta^{k_1} q_\xi^{2k_2+1}$ for $\pm^{TT} = +$ and $-$ in Eq. 7, respectively. This is related to the fact that $q_\xi$ is antisymmetric with respect to $\hat{\sigma}_d^x$, while $q_\theta$ is symmetric. $W$ formulas of $(T+T) \otimes (e + a_2)$ problems in $T_d$ symmetry are then readily obtained:

$$W = a_{k_1, 2k_2, 2k_4} q_\theta^{k_1} q_\xi^{2k_2} w^{2k_4} + a_{k_1, 2k_2+1, 2k_4+1} q_\theta^{k_1} q_\xi^{2k_2+1} w^{2k_4+1} \qquad (19)$$

for $\pm^{TT} = +$ and

$$W = a_{k_1, 2k_2, 2k_4+1} q_\theta^{k_1} q_\xi^{2k_2} w^{2k_4+1} + a_{k_1, 2k_2+1, 2k_4} q_\theta^{k_1} q_\xi^{2k_2+1} w^{2k_4} \qquad (20)$$

for $\pm^{TT} = -$. $W$ of $T \otimes (e + a_2)$ *intra*-term problems takes Eq. 19.

For $T_d$ $(T+T) \otimes (a_2 + a_2)$ problems in $T_d$ symmetry (again, $V = U = 0$),

$$W = a_{k_1, 2k} w_\alpha^{k_1} w_\beta^{2k-k_1}, 2k \geq k_1 \qquad (21)$$

for $\pm^{TT} = +$ and

$$W = a_{k_1, 2k+1} w_\alpha^{k_1} w_\beta^{2k+1-k_1}, 2k + 1 \geq k_1 \qquad (22)$$

12

for $\pm^{TT} = -$ in Eq. 7. For the $T \otimes (a_2 + a_2)$ *intra*-term problems, $W$ takes the expansion formulas in Eq. 21. Derivations for all $(T + T)$ and $T$ $a$-involving problems have been completed. In total, the derived formulas cover 15 $(T + T)$ and 8 $T$ problems in $T_d$ symmetry.

*3.2. $(E + E)$, $E$, and $(E + T)$ problems involving a-type vibration*

In the complex representation of the $E$ states, the $(E + E)$ *inter*-term Hamiltonian reads

$$\hat{H} = \left(|+_\alpha\rangle \langle +_\beta| + |-_\beta\rangle \langle -_\alpha|\right) W + \left(|+_\alpha\rangle \langle -_\beta| + |+_\beta\rangle \langle -_\alpha|\right) V + c.c. \quad (23)$$

"*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. The time-reversal symmetry has been employed to reduce the number of independent matrix elements to 2 (see Eqs 6 and 7 in Ref. 39 and the relevant discussion there). Since complex-valued diabats are used, $W$ and $V$ are complex. In $T_d$ symmetry, $W$ and $V$ need to satisfy (see Paper I)

$$\hat{\sigma}_d^x W = W^*; \hat{\sigma}_d^x V = V^*. \quad (24)$$

We have shown in Paper I that $(E + E) \otimes t$ problems in $T_d$ symmetry take

$$
\begin{aligned}
W &= a_{m,2k_1,2k_2} F^0_{m,2k_1,2k_2,y} + \left(\pm^t\right)^m a_{m,2k_1,2k_2}{}^* F^0_{m,2k_1,2k_2,z}; \\
V &= b_{m,2k_1,2k_2} F^-_{m,2k_1,2k_2,y} + \left(\pm^t\right)^m b_{m,2k_1,2k_2}{}^* F^-_{m,2k_1,2k_2,z},
\end{aligned}
\quad (25)
$$

with

$$
\begin{aligned}
F^0_{m,2k_1,2k_2,y} &= (xyz)^m \left(x^{2k_1} y^{2k_2} + y^{2k_1} z^{2k_2} + z^{2k_1} x^{2k_2}\right); \\
F^0_{m,2k_1,2k_2,z} &= (xyz)^m \left(x^{2k_1} z^{2k_2} + y^{2k_1} x^{2k_2} + z^{2k_1} y^{2k_2}\right); \\
F^\pm_{m,2k_1,2k_2,y} &= (xyz)^m \left(x^{2k_1} y^{2k_2} + e^{\mp \frac{i2\pi}{3}} y^{2k_1} z^{2k_2} + e^{\pm \frac{i2\pi}{3}} z^{2k_1} x^{2k_2}\right); \\
F^\pm_{m,2k_1,2k_2,z} &= (xyz)^m \left(x^{2k_1} z^{2k_2} + e^{\mp \frac{i2\pi}{3}} y^{2k_1} x^{2k_2} + e^{\pm \frac{i2\pi}{3}} z^{2k_1} y^{2k_2}\right); \\
&\quad k_2 \leq k_1, \quad (26)
\end{aligned}
$$

and complex $a$ and $b$ coefficients. The "+" *before* $\left(\pm^t\right)^m$ in Eq. 25 is introduced to let $W$ and $V$ satisfy Eq. 24. Conversely, "$-$" gives

$$\hat{\sigma}_d^x W = -W^*; \hat{\sigma}_d^x V = -V^*. \quad (27)$$

13

The antisymmetric character of $w$ with respect to $\hat{\sigma}_d^x$ indicates that we shall multiply $w^{2k}$ to the "+" combinations, and $w^{2k+1}$ to the "−" combinations to obtain the expansion formulas for $(E + E) \otimes (t + a_2)$ problems in $T_d$ symmetry:

$$
\begin{aligned}
W &= \left( a_{m,2k_1,2k_2,2k_3} F^0_{m,2k_1,2k_2,y} + \left(\pm^t\right)^m a_{m,2k_1,2k_2,2k_3}{}^* F^0_{m,2k_1,2k_2,z} \right) w^{2k_3} \\
&\quad + \left( a_{m,2k_1,2k_2,2k_3} F^0_{m,2k_1,2k_2,y} - \left(\pm^t\right)^m a_{m,2k_1,2k_2,2k_3}{}^* F^0_{m,2k_1,2k_2,z} \right) w^{2k_3+1}; \\
V &= \left( b_{m,2k_1,2k_2,2k_3} F^-_{m,2k_1,2k_2,y} + \left(\pm^t\right)^m b_{m,2k_1,2k_2,2k_3}{}^* F^-_{m,2k_1,2k_2,z} \right) w^{2k_3} \\
&\quad + \left( b_{m,2k_1,2k_2,2k_3+1} F^-_{m,2k_1,2k_2,y} - \left(\pm^t\right)^m b_{m,2k_1,2k_2,2k_3+1}{}^* F^-_{m,2k_1,2k_2,z} \right) w^{2k_3+1}. \quad (28)
\end{aligned}
$$

The $E$ *intra*-term Hamiltonian reads

$$
\hat{H} = \left( |+\rangle \langle +| + |-\rangle \langle -| \right) W + |+\rangle \langle -| V + |-\rangle \langle +| V^*. \tag{29}
$$

The diagonal element $W$ is real and its symmetry requirement is more stringent than in Eq. 24: $\hat{\sigma}_d^x W = W$, while the symmetry requirement on $V$ is unchanged. Therefore, $E \otimes (t + a_2)$ problems take the same $W$ and $V$ formulas as in Eq. 28 but with the $a$ coefficients being real. The $(E + E) \otimes (t + a_2)$ and $E \otimes (t + a_2)$ problems are the only $a$-involving $(E + E)$ and $E$ problems considered in this work. This is because any $(E + E)$ and $E$ problems not involving a $t$ mode can be viewed as trigonal problems, instead of tetrahedral problems.

In the complex representation of the $E$ state and the real representation of the $T$ state, the $(E + T)$ *inter*-term Hamiltonian reads (see Eq. 89 in Paper I)

$$
\begin{aligned}
\hat{H} &= \left( |+\rangle \langle X| + |X\rangle \langle -| \right) V + \left( |+\rangle \langle Y| + |Y\rangle \langle -| \right) e^{-i\frac{2\pi}{3}} \hat{C}_3 V \\
&\quad + \left( |+\rangle \langle Z| + |Z\rangle \langle -| \right) e^{i\frac{2\pi}{3}} \hat{C}_3^2 V + c.c. \tag{30}
\end{aligned}
$$

The only independent matrix element $V$ needs to satisfy $\hat{\sigma}_d^x V = \pm^T V^*$ in $T_d$ symmetry.

In Paper I, we have derived for $(E + T) \otimes t$ problems in $T_d$ symmetry,

$$
\begin{aligned}
V &= \left( b^x_{2k_1,2k_2,2k_3} x + b^{yz}_{2k_1,2k_2,2k_3} yz \right) x^{2k_1} y^{2k_2} z^{2k_3} \\
&\quad \pm^T \left( \left(\pm^t\right) b^x_{2k_1,2k_2,2k_3}{}^* x + b^{yz}_{2k_1,2k_2,2k_3}{}^* yz \right) x^{2k_1} z^{2k_2} y^{2k_3}, \; k_3 \le k_2. \tag{31}
\end{aligned}
$$

Again, considering the odd $\hat{\sigma}_d^x$-transformation of $w$, this $V$ formula is easily adapted for $(E + T) \otimes (t + a_2)$ problems in $T_d$ symmetry:

$$
\begin{aligned}
V &= \Big[ \left( b^x_{2k_1,2k_2,2k_3,k_4} x + b^{yz}_{2k_1,2k_2,2k_3,k_4} yz \right) x^{2k_1} y^{2k_2} z^{2k_3} \\
&\quad \pm^T (-1)^{k_4} \left( \left(\pm^t\right) b^x_{2k_1,2k_2,2k_3,k_4}{}^* x + b^{yz}_{2k_1,2k_2,2k_3,k_4}{}^* yz \right) x^{2k_1} z^{2k_2} y^{2k_3} \Big] w^{k_4}, \; k_3 \le k_2. \tag{32}
\end{aligned}
$$

14

The $(E + T) \otimes (t + a_2)$ problems are the only $a$-involving $(E + T)$ problems in $T_d$ symmetry. Any other $(a_2 + \gamma)$ vibrational parts involve powers and products of $a_2$ and $e$ coordinates, which give irreps of types $A$ and $E$. These irreps are not contained in $E \otimes T_{1,2} = T_1 + T_2$. In total, we have derived expansion formulas for $2$ $(E + E)$, $2$ $E$, and $4$ $(E + T)$ problems that involve $a_2$ vibrations in $T_d$ symmetry. We have finished deriving expansion formulas for all $a_2$-involving but not $A$-involving problems in $T_d$ symmetry.

## 4. *A*-involving problems

We now move on to derive expansion formulas for the $(A + \Gamma) \otimes (\gamma_1 + \gamma_2)$ type *inter*-term problems. Unlike the problems in the previous section, the electronic parts of these problems were not considered in Paper I. We hence need to derive the generic forms of the vibronic Hamiltonians and the symmetry requirements on their matrix elements. Again, we only focus on the problems with at least one of $\Gamma$, $\gamma_1$, and $\gamma_2$ being a $T$ irrep. All the other problems shall be categorized as trigonal problems. We also skip the derivations for the $T_h$ problems. As mentioned above, their formulas can be readily obtained from those of $T$ symmetry by imposing constraints based on the parity consideration. As shown below, all formulas for the $A$-involving problems are obtained by adopting/adapting the formulas obtained in Paper I. This section showcases the robustness of the modularized approach.

*4.1. $(A + T)$ problems*

The generic $(A + T)$ *inter*-term Hamiltonian in $T$ symmetry reads

$$\hat{H} = (|A\rangle \langle X| + |X\rangle \langle A|) H_{AX} + (|A\rangle \langle Y| + |Y\rangle \langle A|) H_{AY} + (|A\rangle \langle Z| + |Z\rangle \langle A|) H_{AZ}. \tag{33}$$

The diabats are real-valued, and so are the matrix elements. According to the $\hat{C}_3$-transformations in Eq. 2,

$$\begin{aligned} \hat{C}_3 \hat{H} \hat{C}_3^{-1} &= (|A\rangle \langle Y| + |Y\rangle \langle A|) \hat{C}_3 H_{AX} + (|A\rangle \langle Z| + |Z\rangle \langle A|) \hat{C}_3 H_{AY} \\ &\quad + (|A\rangle \langle X| + |X\rangle \langle A|) \hat{C}_3 H_{AZ}. \end{aligned} \tag{34}$$

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

$$H_{AZ} = \hat{C}_3 H_{AY} = \hat{C}_3^2 H_{AX}. \tag{35}$$

Therefore, there is only one independent matrix element. Setting $H_{AX} = V$, $\hat{H}$ is rewritten as

$$
\begin{aligned}
\hat{H} &= (|A\rangle\langle X| + |X\rangle\langle A|)\, V + (|A\rangle\langle Y| + |Y\rangle\langle A|)\, \hat{C}_3 V \\
&\quad + (|A\rangle\langle Z| + |Z\rangle\langle A|)\, \hat{C}_3^2 V.
\end{aligned}
\tag{36}
$$

Under the action of $\hat{C}_2^z$, the Hamiltonian becomes

$$
\begin{aligned}
\hat{C}_2^z \hat{H} \left(\hat{C}_2^z\right)^{-1} &= -(|A\rangle\langle X| + |X\rangle\langle A|)\, \hat{C}_2^z V - (|A\rangle\langle Y| + |Y\rangle\langle A|)\, \hat{C}_2^z \hat{C}_3 V \\
&\quad + (|A\rangle\langle Z| + |Z\rangle\langle A|)\, \hat{C}_2^z \hat{C}_3^2 V.
\end{aligned}
\tag{37}
$$

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

$$
V = \hat{C}_2^x V = -\hat{C}_2^y V = -\hat{C}_2^z V.
\tag{38}
$$

In deriving these requirements, the multiplication relations of the $\hat{C}_2$ and $\hat{C}_3$ operations have been used. For instance, to have equal matrix elements of the $(|A\rangle\langle Z| + |Z\rangle\langle A|)$ dyads in Eqs. 36 and 37, we need $\hat{C}_2^z \hat{C}_3^2 V = \hat{C}_3^2 V$, i.e., $\hat{C}_3 \hat{C}_2^z \hat{C}_3^2 V = V$. Since $\hat{C}_3 \hat{C}_2^z \hat{C}_3^2 = \hat{C}_2^x$, we need $\hat{C}_2^x V = V$.

As the symmetry is increased to $T_d$, we need

$$
\begin{aligned}
\hat{H} &= \hat{\sigma}_d^x \hat{H} (\hat{\sigma}_d^x)^{-1} = \left(\pm^A \pm^T\right) \Big[ (|A\rangle\langle X| + |X\rangle\langle A|)\, \hat{\sigma}_d^x V + (|A\rangle\langle Z| + |Z\rangle\langle A|)\, \hat{\sigma}_d^x \hat{C}_3 V \\
&\quad + (|A\rangle\langle Y| + |Z\rangle\langle Y|)\, \hat{\sigma}_d^x \hat{C}_3^2 V \Big],
\end{aligned}
\tag{39}
$$

which requires

$$
\hat{\sigma}_d^x V = \pm^A \pm^T V.
\tag{40}
$$

The symmetry requirements on $V$ in Eq. 38 are identical to those for the $(E+T)$ problems (derived in Section 3.4 in Paper I). Therefore, the $(A+T)$ and $(E+T)$ problems in $T$ symmetry share the same $V$ expansion formulas, although their Hamiltonian forms are different. We can hence immediately write down the following expansion formulas:

1. For the $(A+T) \otimes (t+t)$ problem in $T$ symmetry,

$$
\begin{aligned}
V &= \left( b_{l,2k_1,m,2k_2,n,2k_3}^{x_{\alpha/\beta}} x_{\alpha/\beta} + b_{l,2k_1,m,2k_2,n,2k_3}^{y_{\alpha/\beta} z_{\alpha/\beta}} y_{\alpha/\beta} z_{\alpha/\beta} \right) \\
&\quad x_\alpha^l x_\beta^{2k_1-l} y_\alpha^m y_\beta^{2k_2-m} z_\alpha^n z_\beta^{2k_3-n}.
\end{aligned}
\tag{41}
$$

"$\alpha/\beta$" means that $\alpha$ or $\beta$ can be selected;

16

2. For the $(A+T) \otimes t$ problem in $T$ symmetry,

$$V = \left( b^x_{2k_1,2k_2,2k_3} x + b^{yz}_{2k_1,2k_2,2k_3} yz \right) x^{2k_1} y^{2k_2} z^{2k_3}; \qquad (42)$$

3. For the $(A+T) \otimes (t+e)$ problem in $T$ symmetry,

$$V = \left( b^x_{2k_1,2k_2,2k_3,k_4,k_5} x + b^{yz}_{2k_1,2k_2,2k_3,k_4,k_5} yz \right) x^{2k_1} y^{2k_2} z^{2k_3} q_\theta^{k_4} q_\xi^{k_5}; \quad (43)$$

4. For the $(A+T) \otimes e$, $(A+T) \otimes (e+e)$, $(A+T) \otimes a$, and $(A+T) \otimes (a+e)$ problems in $T$ symmetry, $V = 0$. $a$ and/or $e$ modes cannot mediate pJT interaction between an $A$ and a $T$ state because $A \otimes T = T$ does not contain $e$, $a$, and any irreps arising from their products and powers.

Please note that all $b$ coefficients in the $V$ expansions above are real. Here, the salient feature of the modularized approach is exhibited. The vibrational monomials like $xx^{2k_1} y^{2k_2} z^{2k_3}$ and $yzx^{2k_1} y^{2k_2} z^{2k_3}$ are symmetry-adapted modules. They contribute to any expansion formulas that are subjected to the requirements in Eq. 38, regardless of whether the underlying electronic part is $(A+T)$ or $(E+T)$.

The symmetry requirement in Eq. 40 is similar to that for $(E+T)$ problems in $T_d$ symmetry:

$$\hat{\sigma}_d^x V = \pm^T V^*. \qquad (44)$$

Therefore, the expansion formulas for the $(E+T)$ problems can be slightly modified to give those for $(A+T)$ problems in $T_d$ symmetry. In Paper I, the following functions:

$$
\begin{aligned}
F^{x_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,y} &= \left( x_{\alpha/\beta} \right) x_\alpha^l x_\beta^{2k_1-l} y_\alpha^m y_\beta^{2k_2-m} z_\alpha^n z_\beta^{2k_3-n}; \\
F^{x_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,z} &= \left( x_{\alpha/\beta} \right) x_\alpha^l x_\beta^{2k_1-l} z_\alpha^m z_\beta^{2k_2-m} y_\alpha^n y_\beta^{2k_3-n}; \\
F^{y_{\alpha/\beta} z_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,y} &= \left( y_{\alpha/\beta} z_{\alpha/\beta} \right) x_\alpha^l x_\beta^{2k_1-l} y_\alpha^m y_\beta^{2k_2-m} z_\alpha^n z_\beta^{2k_3-n}; \\
F^{z_{\alpha/\beta} y_{\alpha/\beta},l,m,n}_{2k_1,2k_2,2k_3,z} &= \left( y_{\alpha/\beta} z_{\alpha/\beta} \right) x_\alpha^l x_\beta^{2k_1-l} z_\alpha^m z_\beta^{2k_2-m} y_\alpha^n y_\beta^{2k_3-n}, \\
& \qquad k_3 \le k_2, \qquad\qquad\qquad\qquad\qquad\qquad\qquad (45)
\end{aligned}
$$

have been used to concisely expand $(E+T)$ Hamiltonians in $T_d$ symmetry. Please note that 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 while maintaining the $\alpha/\beta$

selection. These functions are used here to expand $(A+T)$ Hamiltonians. We simply need to replace "$\pm^T$" and complex expansion coefficients in the $(E+T)$ formulas by "$\pm^A\pm^T$" and real coefficients, consistent with Eq. 44 vs. Eq. 40. The resultant formulas are:

1. For $(A+T)\otimes(t+t)$ problems in $T_d$ symmetry,

$$
\begin{aligned}
V \;=\; & b_{2k_1,2k_2,2k_3}^{x_{\alpha/\beta},l,m,n}\left(F_{2k_1,2k_2,2k_3,y}^{x_{\alpha/\beta},l,m,n} + \left(\pm^A\pm^T\right)\left(\pm^{t_{\alpha/\beta}^x}\right)\left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n}F_{2k_1,2k_2,2k_3,z}^{x_{\alpha/\beta},l,m,n}\right)\\
&+b_{2k_1,2k_2,2k_3}^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}\left(F_{2k_1,2k_2,2k_3,y}^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n} + \left(\pm^A\pm^T\right)\left(\pm^{t_{\alpha/\beta}^y}\pm^{t_{\alpha/\beta}^z}\right)\left(\pm^{t_\alpha}\pm^{t_\beta}\right)^{l+m+n}F_{2k_1,2k_2,2k_3,z}^{y_{\alpha/\beta}z_{\alpha/\beta},l,m,n}\right).
\end{aligned}
$$

$$(46)$$

   The sign of "$\pm^{t_{\alpha/\beta}^x}$" is determined by whether the $x_{\alpha/\beta}$ coordinate is a $t_1$ or $t_2$ coordinate. The sign selection of $\pm^{t_{\alpha/\beta}^{y,z}}$ is determined by whether the $y_{\alpha/\beta}$ and $z_{\alpha/\beta}$ coordinates, before the $y\leftrightarrow z$ swapping, are $t_1$ or $t_2$ coordinates;

2. For $(A+T)\otimes t$ problems in $T_d$ symmetry,

$$
\begin{aligned}
V \;=\; & b_{2k_1,2k_2,2k_3}^{x}x^{2k_1+1}\left(y^{2k_2}z^{2k_3}+\left(\pm^A\pm^T\right)\left(\pm^t\right)z^{2k_2}y^{2k_3}\right)\\
&+b_{2k_1,2k_2,2k_3}^{yz}x^{2k_1}yz\left(y^{2k_2}z^{2k_3}+\left(\pm^A\pm^T\right)z^{2k_2}y^{2k_3}\right),\,k_3\le k_2;\;(47)
\end{aligned}
$$

3. For $(A+T)\otimes(t+e)$ problems in $T_d$ symmetry,

$$
\begin{aligned}
V \;=\; & b_{2k_1,2k_2,2k_3,k_4,k_5}^{x}x^{2k_1+1}q_\theta^{k_4}q_\xi^{k_5}\left(y^{2k_2}z^{2k_3}+\left(\pm^A\pm^T\right)\left(\pm^t\right)(-1)^{k_5}z^{2k_2}y^{2k_3}\right)\\
&+b_{2k_1,2k_2,2k_3,k_4,k_5}^{yz}x^{2k_1}yzq_\theta^{k_4}q_\xi^{k_5}\left(y^{2k_2}z^{2k_3}+\left(\pm^A\pm^T\right)(-1)^{k_5}z^{2k_2}y^{2k_3}\right),\,k_3\le k_2;
\end{aligned}
$$

$$(48)$$

4. Removing $q_\theta$ in Eq. 48 and replacing $q_\xi$ by $w$, we immediately obtain the $V$ expansion for $(A+T)\otimes(a_2+t)$ problems in $T_d$ symmetry:

$$
\begin{aligned}
V \;=\; & b_{2k_1,2k_2,2k_3,k_4}^{x}x^{2k_1+1}w^{k_4}\left(y^{2k_2}z^{2k_3}+\left(\pm^A\pm^T\right)\left(\pm^t\right)(-1)^{k_4}z^{2k_2}y^{2k_3}\right)\\
&+b_{2k_1,2k_2,2k_3,k_4}^{yz}x^{2k_1}yzw^{k_4}\left(y^{2k_2}z^{2k_3}+\left(\pm^A\pm^T\right)(-1)^{k_4}z^{2k_2}y^{2k_3}\right),\,k_3\le k_2;
\end{aligned}
$$

$$(49)$$

   The underlying reason for this adaptation is that both the $e_\xi$ and $a_2$ modes are $\hat{\sigma}_d^x$-odd, while the $e_\theta$ mode is $\hat{\sigma}_d^x$-even;

18

5. $V = 0$ for $(A + T) \otimes e$, $(A + T) \otimes (e + e)$, $(A + T) \otimes a$, and $(A + T) \otimes (a + e)$ problems in $T_d$ symmetry. This is for the same reason as for the analogous problems in $T$ symmetry.

The derivations for all $(A + T)$ expansion formulas have been finished. In total, 2 problems in $T$ symmetry and 34 problems in $T_d$ symmetry are covered, not including those that have null vibronic coupling.

*4.2. $(A + E)$ problems*

The generic $(A + E)$ *inter*-term Hamiltonian in $T$ symmetry has the form

$$\hat{H} = (|+\rangle \langle A| + |A\rangle \langle -|) V + c.c. \tag{50}$$

and $V$ is complex. The $\hat{C}_3$- and $\hat{C}_2$-transformations in Eq. 2 determine that

$$\hat{C}_3 \hat{H} \hat{C}_3^{-1} = e^{-i\frac{2\pi}{3}} (|+\rangle \langle A| + |A\rangle \langle -|) \hat{C}_3 V + c.c.;$$
$$\hat{C}_2^{x,y,z} \hat{H} \left(\hat{C}_2^{x,y,z}\right)^{-1} = (|+\rangle \langle A| + |A\rangle \langle -|) \hat{C}_2^{x,y,z} V + c.c. \tag{51}$$

Therefore, $V$ needs to satisfy

$$\hat{C}_3 V = e^{i\frac{2\pi}{3}} V; \hat{C}_2^{x,y,z} V = V, \tag{52}$$

in order to have $\hat{C}_3 \hat{H} \hat{C}_3^{-1} = \hat{H}$ and $\hat{C}_2^{x,y,z} \hat{H} \left(\hat{C}_2^{x,y,z}\right)^{-1} = \hat{H}$. Please note that it is necessary to consider only one of the $\hat{C}_2$ operations in deriving the expansion formulas. However, for $(A + E)$ problems, considering all three $\hat{C}_2$ operations simplifies the derivations, just like for $(E + E)$ problems in Paper I. In $T_d$ symmetry, the $\hat{\sigma}_d^x$-transformations in Eq. 4 determine that

$$\hat{\sigma}_d^x \hat{H} (\hat{\sigma}_d^x)^{-1} = \pm^A (|-\rangle \langle A| + |A\rangle \langle +|) \hat{\sigma}_d^x V + c.c. \tag{53}$$

In order to have $\hat{\sigma}_d^x \hat{H} (\hat{\sigma}_d^x)^{-1} = \hat{H}$, we need

$$\hat{\sigma}_d^x V = \pm^A V^*. \tag{54}$$

For comparison, the corresponding symmetry requirements on the $V$ (i.e., $H_{+\alpha - \beta}$) of the $(E + E)$ problems are

$$\hat{C}_3 V = e^{-i\frac{2\pi}{3}} V; \hat{C}_2^{x,y,z} V = V; \hat{\sigma}_d^x V = V^*. \tag{55}$$

19

Obviously, the $V$ expansion formula of the $(A + E)$ problem in $T$ symmetry is just the complex conjugate of the corresponding $(E + E)$ formula, and for the problems in $T_d$ symmetry, an additional sign factor "$\pm^A$" is needed. The modularized approach can again be employed to transplant expansion formulas from $(E + E)$ problems to $(A + E)$ problems.

The following functions were used to express the expansion formulas of $(E + E)$ problems in Paper I. They are used here to express $(A + E)$ expansions. The functions are reintroduced to make this paper self-contained.

$$
\begin{aligned}
F^0_{m,2k_1,2k_2} &= (xyz)^m \left( x^{2k_1}y^{2k_2} + y^{2k_1}z^{2k_2} + z^{2k_1}x^{2k_2} \right); \\
F^\pm_{m,2k_1,2k_2} &= (xyz)^m \left( x^{2k_1}y^{2k_2} + e^{\mp \frac{i2\pi}{3}}y^{2k_1}z^{2k_2} + e^{\pm \frac{i2\pi}{3}}z^{2k_1}x^{2k_2} \right), \\
& \qquad m, k_1, k_2 = 0, 1, 2, \cdots \, ; \text{if } k_1 = 0, \, k_2 = 0.
\end{aligned}
\tag{56}
$$

These functions are separated into two groups labeled by the subscripts $y$ and $z$, which have been introduced in Eq. 26.

$$
G^0_{3N,2M} = \rho^{3N+2M}e^{i3N\phi}; \, G^\pm_{3N,2M} = \rho^{|3N\mp 1|+2M}e^{i(3N\mp 1)\phi},
$$
$$
N = \cdots, -1, 0, 1, \cdots \, ; M = 0, 1, 2, \cdots .
\tag{57}
$$

$$
f^{e,l,m,n}_{k_1,k_2,k_3} = x_\alpha^l x_\beta^{2k_1-l} y_\alpha^m y_\beta^{2k_2-m} z_\alpha^n z_\beta^{2k_3-n}; \, f^{o,l,m,n}_{k_1,k_2,k_3} = x_\alpha^l x_\beta^{2k_1-l+1} y_\alpha^m y_\beta^{2k_2-m+1} z_\alpha^n z_\beta^{2k_3-n+1},
$$
$$
l, m, n, k_1, k_2, k_3 = 0, 1, 2, \cdots \, ; l \le 2k_1 \, (+1) \, ; m \le 2k_2 \, (+1) \, ; n \le 2k_3 \, (+1) \, \text{ for } f^e \, (f^o) \,.
\tag{58}
$$

The "$e$" and "$o$" superscripts indicate the even or odd total power of the functions. The $f^{e,l,m,n}_{k_1,k_2,k_3}$ functions are further separated into two groups labeled by the subscripts $y$ and $z$:

$$
f^{e,l,m,n}_{k_1,k_2,k_3,y} = x_\alpha^l x_\beta^{2k_1-l} y_\alpha^m y_\beta^{2k_2-m} z_\alpha^n z_\beta^{2k_3-n}; \, f^{e,l,m,n}_{k_1,k_2,k_3,z} = x_\alpha^l x_\beta^{2k_1-l} z_\alpha^m z_\beta^{2k_2-m} y_\alpha^n y_\beta^{2k_3-n}, \, k_3 \le k_2,
\tag{59}
$$

and similarly for $f^{o,l,m,n}_{k_1,k_2,k_3,y}$ and $f^{o,l,m,n}_{k_1,k_2,k_3,z}$.

$$
\begin{aligned}
F^{e/o,0,l,m,n}_{k_1,k_2,k_3} &= f^{e/o,l,m,n}_{k_1,k_2,k_3} + \hat{C}_3 f^{e/o,l,m,n}_{k_1,k_2,k_3} + \hat{C}_3^2 f^{e/o,l,m,n}_{k_1,k_2,k_3} = f^{e/o,l,m,n}_{k_1,k_2,k_3} + f^{e/o,n,l,m}_{k_3,k_1,k_2} + f^{e/o,m,n,l}_{k_2,k_3,k_1}; \\
F^{e/o,\pm,l,m,n}_{k_1,k_2,k_3} &= f^{e/o,l,m,n}_{k_1,k_2,k_3} + e^{\mp i\frac{2\pi}{3}}\hat{C}_3 f^{e/o,l,m,n}_{k_1,k_2,k_3} + e^{\pm i\frac{2\pi}{3}}\hat{C}_3^2 f^{e/o,l,m,n}_{k_1,k_2,k_3} \\
&= f^{e/o,l,m,n}_{k_1,k_2,k_3} + e^{\mp i\frac{2\pi}{3}} f^{e/o,n,l,m}_{k_3,k_1,k_2} + e^{\pm i\frac{2\pi}{3}} f^{e/o,m,n,l}_{k_2,k_3,k_1}, \\
& \qquad k_3 \le k_1, k_2; \text{ if } k_1 = 0, \, k_2 = 0; \text{ when } k_1 = k_2 = k_3, \, n \le l, m \text{ and if } l = 0, \, m = 0.
\end{aligned}
\tag{60}
$$

The $F^{e/o,0/\pm,l,m,n}_{k_1,k_2,k_3}$ functions are also separated into two groups labeled by the subscripts $y$ and $z$:

$$
\begin{aligned}
F^{e/o,0,l,m,n}_{k_1,k_2,k_3,y/z} &= f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} + \hat{C}_3 f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} + \hat{C}_3^2 f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} \\
&= f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} + f^{e/o,n,l,m}_{k_3,k_1,k_2,y/z} + f^{e/o,m,n,l}_{k_2,k_3,k_1,y/z}; \\
F^{e/o,\pm,l,m,n}_{k_1,k_2,k_3,y/z} &= f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} + e^{\mp i\frac{2\pi}{3}}\hat{C}_3 f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} + e^{\pm i\frac{2\pi}{3}}\hat{C}_3^2 f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} \\
&= f^{e/o,l,m,n}_{k_1,k_2,k_3,y/z} + e^{\mp i\frac{2\pi}{3}} f^{e/o,n,l,m}_{k_3,k_1,k_2,y/z} + e^{\pm i\frac{2\pi}{3}} f^{e/o,m,n,l}_{k_2,k_3,k_1,y/z}, \\
& k_2 \le k_1.
\end{aligned}
\tag{61}
$$

These $F$ and $G$ functions are eigenfunctions of $\hat{C}_3$, with the superscripts $0$ and $\pm$ indicating their eigenvalues $1$ and $e^{\pm i\frac{2\pi}{3}}$. They are needed to expand $V$ as an eigenfunction of $\hat{C}_3$ in Eq. 52. The powers of the $x$, $y$, and $z$ coordinates in these functions guarantee that they are invariant with respect to $\hat{C}_2^{x,y,z}$, another requirement in Eq. 52. With the separations of the $F$ and $f$ functions into the $y$ and $z$ groups, the action of $\hat{\sigma}_d^x$ is to swap the two groups with possible sign flippings; the two groups of functions are needed in the $V$ expansions for problems in $T_d$ symmetry.

With all these functions and the $(E + E)$ formulas expanded in them (see Section 3.3 in Paper I), we immediately obtain:

1. For the $(A + E) \otimes (e + t)$ problem in $T$ symmetry,

$$
\begin{aligned}
V &= b^{+0,3N,2M}_{m,2k_1,2k_2} G^+_{3N,2M} F^0_{m,2k_1,2k_2} + b^{0+,3N,2M}_{m,2k_1,2k_2} G^0_{3N,2M} F^+_{m,2k_1,2k_2} \\
&+ b^{--,3N,2M}_{m,2k_1,2k_2} G^-_{3N,2M} F^-_{m,2k_1,2k_2};
\end{aligned}
\tag{62}
$$

2. For $(A + E) \otimes (e + t)$ problems in $T_d$ symmetry,

$$
\begin{aligned}
V &= G^+_{3N,2M} \left( b^{+0,3N,2M}_{m,2k_1,2k_2} F^0_{m,2k_1,2k_2,y} + (\pm^A)(\pm^t)^m b^{+0,3N,2M*}_{m,2k_1,2k_2} F^0_{m,2k_1,2k_2,z} \right) \\
&+ G^0_{3N,2M} \left( b^{0+,3N,2M}_{m,2k_1,2k_2} F^+_{m,2k_1,2k_2,y} + (\pm^A)(\pm^t)^m b^{0+,3N,2M*}_{m,2k_1,2k_2} F^+_{m,2k_1,2k_2,z} \right) \\
&+ G^-_{3N,2M} \left( b^{--,3N,2M}_{m,2k_1,2k_2} F^-_{m,2k_1,2k_2,y} + (\pm^A)(\pm^t)^m b^{--,3N,2M*}_{m,2k_1,2k_2} F^-_{m,2k_1,2k_2,z} \right);
\end{aligned}
\tag{63}
$$

3. For the $(A + E) \otimes t$ problem in $T$ symmetry,

$$
V = b_{m,2k_1,2k_2} F^+_{m,2k_1,2k_2};
\tag{64}
$$

21

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

$$V = b_{m,2k_1,2k_2} F^+_{m,2k_1,2k_2,y} + \left(\pm^A\right) \left(\pm^t\right)^m b_{m,2k_1,2k_2}{}^* F^+_{m,2k_1,2k_2,z}; \quad (65)$$

5. For the $(A + E) \otimes (t + t)$ problem in $T$ symmetry,

$$V = b^{e/o,l,m,n}_{k_1,k_2,k_3} F^{e/o,+,l,m,n}_{k_1,k_2,k_3}; \quad (66)$$

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

$$V = b^{e/o,l,m,n}_{k_1,k_2,k_3} F^{e/o,+,l,m,n}_{k_1,k_2,k_3,y} + \left(\pm^A\right) \left(\pm^{t_\alpha} \pm^{t_\beta}\right) \left(\pm^{t_\beta}\right)^{I_{eo}} b^{e/o,l,m,n}_{k_1,k_2,k_3}{}^* F^{e/o,+,l,m,n}_{k_1,k_2,k_3,z}. \quad (67)$$

$I_{eo} = 0$ for the $F^e$ functions and 1 for the $F^o$ functions.

Eq. 65 can be adapted to give

$$V = \left[ b_{m,2k_1,2k_2,k_3} F^+_{m,2k_1,2k_2,y} + (-1)^{k_3} \left(\pm^A\right) \left(\pm^t\right)^m b_{m,2k_1,2k_2,k_3}{}^* F^+_{m,2k_1,2k_2,z} \right] w^{k_3} \quad (68)$$

for $(A + E) \otimes (a_2 + t)$ problems in $T_d$ symmetry. All the $b$ coefficients above are complex. The $V$ expansion formulas for all the $(A + E)$ problems that involve at least one $t$ mode have been derived. In total, 3 problems in $T$ symmetry and 18 problems in $T_d$ symmetry are covered. The other $(A + E)$ problems shall be considered in the context of trigonal symmetry.

*4.3. $(A + A)$ problems*

This class of problems are less interesting because two $A$ terms are usually widely separated in energy, implying weak pJT coupling. We here only consider the $(A_1 + A_2)$ problems in $T_d$ symmetry involving at least one $t$ mode. The other $(A_1 + A_2)$ problems are essentially trigonal problems. The $(A + A)$ problem in $T$ symmetry, $(A_{1,2} + A_{1,2})$ problems in $T_d$ symmetry, as well as the $A$-type *intra*-term problems are trivial as they only take totally symmetric real expansions. Such expansion formulas are identical to the $W$ $(H_{++})$ expansions of the $E$ *intra*-term problems in $T$ and $T_d$ symmetries (see Section 3.3 in Paper I). The $(A_1 + A_2)$ Hamiltonian in $T_d$ symmetry reads

$$\hat{H} = \left( |A_1\rangle \langle A_2| + |A_2\rangle \langle A_1| \right) V \quad (69)$$

22

with $V$ being real. It is easy to see that $V$ needs to satisfy

$$\hat{C}_3 V = V; \hat{C}_2^{x,y,z} V = V; \hat{\sigma}_d^x V = -V. \tag{70}$$

These requirements are similar to those of the $W$ ($H_{++}$) in the $E$ *intra*-term problems except that $\hat{\sigma}_d^x W = W$ is needed for the $E$ problems. With a simple sign flipping in the $W$ expansion formulas of the $E$ problems, which change them from being $\hat{\sigma}_d^x$-even to -odd, we have:

1. For $(A_1 + A_2) \otimes (t + t)$ problems,

$$V = b_{k_1,k_2,k_3}^{e/o,l,m,n} \left( F_{k_1,k_2,k_3,y}^{e/o,0,l,m,n} - \left( \pm^{t_\alpha} \pm^{t_\beta} \right)^{l+m+n} \left( \pm^{t_\beta} \right)^{I_{eo}} F_{k_1,k_2,k_3,z}^{e/o,0,l,m,n} \right); \tag{71}$$

2. For $(A_1 + A_2) \otimes t$ problems,

$$V = b_{m,2k_1,2k_2} \left( F_{m,2k_1,2k_2,y}^0 - \left( \pm^t \right)^m F_{m,2k_1,2k_2,z}^0 \right); \tag{72}$$

3. For $(A_1 + A_2) \otimes (e + t)$ problems,

$$V = Re \left[ G_{3N,2M}^+ \left( b_{m,2k_1,2k_2,y}^{+-,3N,2M} F_{m,2k_1,2k_2,y}^- - \left( \pm^t \right)^m b_{m,2k_1,2k_2,y}^{+-,3N,2M\ *} F_{m,2k_1,2k_2,z}^- \right) \right.$$
$$\left. + G_{3N,2M}^0 \left( b_{m,2k_1,2k_2,y}^{00,3N,2M} F_{m,2k_1,2k_2,y}^0 - \left( \pm^t \right)^m b_{m,2k_1,2k_2,y}^{00,3N,2M\ *} F_{m,2k_1,2k_2,z}^0 \right) \right]. \tag{73}$$

A more explicit form of Eq. 73 is given in Eq. S.1 in Supplementary Information.

Note that the $b$ coefficients in Eqs. 71 and 72 are real, and those in Eq. 73 are complex. Eq. 72 can be slightly modified to give

$$V = b_{m,2k_1,2k_2,k_3} \left( F_{m,2k_1,2k_2,y}^0 - (-1)^{k_3} \left( \pm^t \right)^m F_{m,2k_1,2k_2,z}^0 \right) w^{k_3} \tag{74}$$

for $(A_1 + A_2) \otimes (a_2 + t)$ problems in $T_d$ symmetry, with the $b$ coefficients being real. In total, the derived expansion formulas in this subsection cover 9 $(A_1 + A_2)$ problems.

23

## 5. Numerical tests

It is unfeasible to examine all derived formulas by running numerical calculations within this work. Here, we examine two representative problems that involve both an $A$-type state and an $a$-type mode, the $(A_1 + T_{1,2}) \otimes (a_2 + t_1)$ problems. Neopentane is chosen to be the model system in $T_d$ symmetry. The $t_2$ HOMO set of neopentane is chosen to be the 1-electron $T_2$ state, the $t_1$ HOMO$-1$ set is chosen to be the $T_1$ state, and the $2a_1$ orbital in the valence shell is chosen to be the $A_1$ state. The only $a_2$ mode arises from the methyl torsions. Correspondingly, the $t_1$ combination of the methyl torsions is chosen to be the $t_1$ mode. The relevant orbitals and modes are shown in Figure 1. They are obtained from B3LYP density functional theory calculation using the GAMESS-US program package [51, 52] and the cc-pVDZ basis set. [53] The orbitals are frozen when the neopentane is distorted along the $a_2$ and $t_1$ modes; they are strict 1-electron diabatic states and no diabatization is needed. The 1-electron Hamiltonian includes the kinetic and the nuclei-electron attraction operators. The Hamiltonian matrix elements (in eV) of the orbitals are calculated in a 4-D grid with $11^4$ points of the $a_2$ and $t_1$ mass-weighted normal mode coordinates. Each coordinate ranges from $-1$ to $1$ $\sqrt{u}$Å, with a 0.2 $\sqrt{u}$Å step-size.

Fitting a free expansion with all 69 $x^l y^m z^n w^k$ monomials up to 4th order against the calculated matrix elements, we obtain:

$$
\begin{aligned}
V = \ & 0.768108x + 0.012291x^3 + 0.000162xy^2 + 0.000174xz^2 - 0.008155xw^2 - 0.124492xwy^2 \\
& + 0.124564xwz^2 - 0.026700yzw - 0.027095y^3z + 0.027028z^3y
\end{aligned}
\tag{75}
$$

for the $(A_1 + T_1) \otimes (a_2 + t_1)$ problem;

$$
\begin{aligned}
V = \ & 1.698547xw + 0.005093xy^2 - 0.005085xz^2 - 0.144967x^3w - 0.126793xw^3 - 0.385849xwy^2 \\
& - 0.385784xwz^2 + 1.510515yz - 0.099228zy^3 - 0.099206yz^3 - 0.396795x^2yz - 0.329322yzw^2
\end{aligned}
\tag{76}
$$

for the $(A_1 + T_2) \otimes (a_2 + t_1)$ problem. The other terms have too small coefficients to be considered. Except for minute numerical differences, $V$ in Eq. 75 has a form

$$
\begin{aligned}
V = \ & b^x_{0,0,0,0}x + b^x_{2,0,0,0}x^3 + b^x_{0,2,0,0}x\left(y^2 + z^2\right) + b^x_{0,0,0,2}xw^2 + b^x_{0,2,0,1}xw\left(y^2 - z^2\right) \\
& + b^{yz}_{0,0,0,1}yzw + b^{yz}_{0,2,0,0}yz(y^2 - z^2),
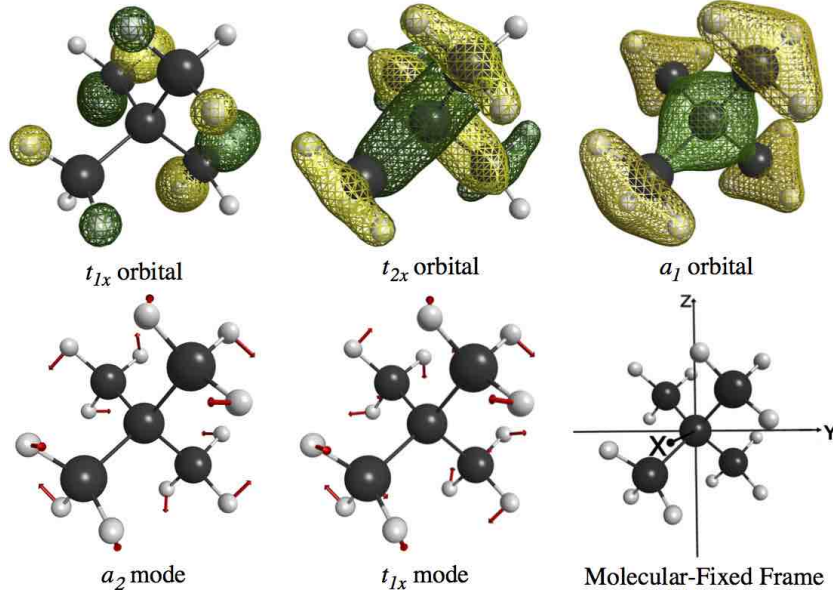\end{aligned}
\tag{77}
$$

24

Figure 1: Orbitals and modes used in the two numerical tests. For the $t_{1,2}$ orbitals and the $t_1$ mode, only the $x$ components are plotted. The molecular-fixed frame is shown to clarify the $x$-direction along which the $x$ components are aligned.

which is consistent with Eq. 49 with $\pm^A = +$, $\pm^T = -$, and $\pm^t = -$. $V$ in Eq. 76 has a form

$$
\begin{aligned}
V &= b^x_{0,0,0,1}xw + b^x_{0,2,0,0}x\left(y^2 - z^2\right) + b^x_{2,0,0,1}x^3w + b^x_{0,0,0,3}xw^3 + b^x_{0,2,0,1}xw\left(y^2 + z^2\right) \\
&\quad + b^{yz}_{0,0,0,0}yz + b^{yz}_{0,2,0,0}yz\left(y^2 + z^2\right) + b^{yz}_{2,0,0,0}yzx^2 + b^{yz}_{0,0,0,2}yzw^2,
\end{aligned} \tag{78}
$$

which is consistent with Eq. 49 with $\pm^A = +$, $\pm^T = +$, and $\pm^t = -$. We also compare a fitted $V$ function of the $(A_1 + T_1) \otimes (a_2 + t_1)$ problem against numerical values in Figure S.1. The fitted function is expanded in the 118 symmetry-adapted terms generated from Eq. 49 up to 10th order. The agreement between the numerical and the fitted results is excellent. All these agreements demonstrate the correctness of Eq. 49 and raise our confidence regarding the other formulas derived in a similar manner.

## 6. Conclusion

We have derived general expansion formulas for all interesting tetrahedral JT/pJT Hamiltonians that involve $A$-type states and $a$-type vibrations.

In total, explicit formulas of 5 problems in $T$ symmetry and 92 problems in $T_d$ symmetry are given, not including the problems that have null vibronic coupling. The derived formulas can be readily adapted to the problems in $T_h$ symmetry. They can also be generalized to include more vibrational modes. Since the $T_d$ and $O$ point groups are isomorphic, the formulas for the $T_d$ problems are also applicable for the corresponding $O$ problems. This transferability of formalism relies critically on the consistency in settings: while the $x$-, $y$-, and $z$-axes coincide with the $C_2$ axes in $T_d$ symmetry, they need to coincide with the $C_4$ axes in $O$ symmetry. The expansion formulas for the $O$ problems can be easily adapted to describe vibronic problems in $O_h$ symmetry, following the same parity consideration as the $T$-to-$T_h$ adaptations. In summary, the formulas derived in this work are also applicable for octahedral JT/pJT problems that involve $A$-type state and $a$-type vibration.

The modularized approach is the key to deriving expansion formulas for such a large number of problems. Symmetry-adapted monomials or elementary functions of vibrational coordinates are taken as modules. The same set of modules are used to expand vibronic matrix elements that need to satisfy the same symmetry requirements. When the symmetry requirements slightly change, e.g., by a sign flipping, the expansion formulas can be easily modified to adjust to the change. In this work, the power of the modularized approach is fully demonstrated, as many of the vibrational modules derived in Paper I can be adopted/adapted to expand the vibronic problems in the $A$-involving problems. This approach has converted the onerous derivations to a matching game. In addition to facilitating the derivations, the modularized approach also reveals the connections between different vibronic problems. Knowing the connections, we can adopt/adapt a simulation program designed for one problem to solve another problem. More benefits of using the modularized approach will be uncovered in future studies.

Combining this work and Paper I, we have derived expansion formulas for all unimodal and bimodal tetrahedral and octahedral vibronic Hamiltonians. They are valuable for future vibronic studies of cubic group systems. Unlike in the Supplementary Information of Paper I, we do not provide explicit term-by-term expansions of full vibronic matrices for the discussed problems, a laborious task that can be performed more readily by computer. We are currently developing a program that converts all general formulas of independent matrix elements derived in the two works to the term-by-term expansions. It will be a highly useful tool in relevant JT/pJT studies.

## 7. Acknowledgements

[1] H. A. Jahn, E. Teller, Stability of polyatomic molecules in degenerate electronic states, Proc. Roy. Soc. A 161 (1937) 220–235.

[2] R. Englman, Jahn-Teller Effect in Molecules and Crystals, John Wiley and Sons, Ltd., London, 1972.

[3] I. B. Bersuker, V. Z. Polinger, Vibronic Interactions in Molecules and Crystals, Springer-Verlag, 1989.

[4] U. Öpik, M. H. L. Pryce, Studies of the Jahn-Teller effect. I. a survey of the static problem., Proc. R. Soc. A 238 (1957) 425–447.

[5] H. Köppel, Jahn-Teller and pseudo-Jahn-Teller intersections: Spectroscopy and vibronic dynamics, in: W. Domcke, D. R. Yarkony, H. Köppel (Eds.), Conical intersections: electronic structure, dynamics and spectroscopy, World Scientific, New Jersey, 2004, Ch. 10, pp. 429–472.

[6] J. B. Goodenough, Jahn-Teller phenomena in solids., Ann. Rev. Mater. Sci. 28 (1998) 1–27.

[7] T. A. Barckholtz, T. A. Miller, Quantitative insights about molecules exhibiting Jahn-Teller and related effects., Int. Rev. Phys. Chem. 17 (1998) 435–524.

[8] I. B. Bersuker, Modern aspects of the Jahn-Teller effect theory and applications to molecular problems, Chem. Rev. 101 (2001) 1067–1114.

[9] B. E. Applegate, T. A. Barckholtz, T. A. Miller, Explorations of conical intersections and their ramifications for chemistry through the Jahn-Teller effect., Chem. Soc. Rev. 32 (2003) 38–49.

[10] I. Bersuker, A unique Jahn-Teller mechanism of all the symmetry breakings in molecular systems and condensed matter, Adv. Quantum Chem. 44 (2003) 1–12.

[11] I. B. Bersuker, The Jahn-Teller Effect, Cambridge University Press, Cambridge, UK, 2006.

[12] W. Domcke, D. R. Yarkony, Role of conical intersections in molecular spectroscopy and photoinduced chemical dynamics., Annu. Rev. Phys. Chem. 63 (2012) 325–352.

[13] I. B. Bersuker, Pseudo-Jahn-Teller effect–a two-state paradigm in formation, deformation, and transformation of molecular systems and solids., Chem. Rev. 113 (2013) 1351–1390.

[14] M. A. Halcrow, Jahn-Teller distortion in transition metal compounds, and their importance in functional molecular and inorganic materials, Chem. Soc. Rev. 42 (2013) 1784–1795.

[15] M. Born, R. Oppenheimer, Zur quantentheorie der molekeln., Ann. Phys. 84 (1927) 457.

[16] P. Garcia-Fernandez, I. B. Bersuker, J. A. Aramburu, M. T. Barriuso, M. Moreno, Origin of warping in the $E \otimes e$ Jahn-Teller problem: quadratic vibronic coupling versus anharmonicity and application to NaCl:$Rh^{2+}$ and triangular molecules., Phys. Rev. B 71 (2005) 184117.

[17] H. Köppel, W. Domcke, L. S. Cederbaum, Multimode molecular dynamics beyond the Born-Oppenheimer approximation., Adv. Chem. Phys. 57 (1984) 59–246.

[18] G. J. Atchity, K. Ruedenberg, Determination of diabatic states through enforcement of configurational uniformity, Theor. Chem. Acc. 97 (1997) 47–58.

[19] H. Köppel, Diabatic representation: methods for the construction of diabatic electronic states, in: W. Domcke, D. R. Yarkony, H. Köppel (Eds.), Conical intersections: electronic structure, dynamics and spectroscopy, World Scientific, New Jersey, 2004, Ch. 4, pp. 175–204.

[20] S. L. Li, D. G. Truhlar, M. W. Schmidt, M. S. Gordon, Model space diabatization for quantum photochemistry, J. Chem. Phys. 142 (2015) 064106.

[21] T. Zeng, A diabatization protocol that includes spin-orbit coupling., J. Chem. Phys. 146 (2017) 144103.

[22] A. Viel, W. Eisfeld, Effects of higher order Jahn-Teller coupling on the nuclear dynamics., J. Chem. Phys. 120 (2004) 4603–4613.

[23] W. Eisfeld, A. Viel, Higher order $(A + E) \times e$ pseudo-Jahn-Teller coupling., J. Chem. Phys. 122 (2005) 204317.

[24] S. Bhattacharyya, D. Opalka, L. V. Poluyanov, W. Domcke, The $(E + A) \times (e + a)$ Jahn-Teller and pseudo-Jahn-Teller hamiltonian including spin-orbit coupling for trigonal systems, J. Phys. Chem. A 118 (2014) 11962–11970.

[25] W. Eisfeld, O. Vieuxmaire, A. Viel, Full-dimensional diabatic potential energy surfaces including dissociation: the $^2E''$ state of $NO_3$., J. Chem. Phys. 140 (2014) 224109.

[26] T. Mondal, On the higher-order $T_2 \otimes (e + t_2)$ Jahn-Teller coupling effects in the photodetachment spectrum of the alanate anion ($AlH_4^+$), Phys. Chem. Chem. Phys. 20 (2018) 9401–9410.

[27] S. Bhattacharyya, D. Opalka, L. V. Poluyanov, W. Domcke, Jahn-Teller theory beyond the standard model, J. Phys. Conf. Series 428 (2013) 012015.

[28] A. Weaver, D. W. Arnold, S. E. Bradforth, D. M. Neumark, Examination of the $^2A_2'$ and $^2E'$ states of $NO_3$ by ultraviolet photoelectron spectroscopy of $NO_3^-$., J. Chem. Phys. 94 (1991) 1740–1751.

[29] S. Faraji, H. Köppel, W. Eisfeld, S. Mahapatra, Towards a higher-order description of Jahn-Teller coupling effects in molecular spectroscopy: the $\tilde{A}^2E''$ state of $NO_3$., Chem. Phys. 347 (2008) 110–109.

[30] Z. Shao, H. Li, S. Zhang, J. Li, Z. Dai, Y. Mo, The Jahn-Teller effect in $CH_3Cl^+(\tilde{X}^2E)$: A combined high-resolution experimental measurement and *ab initio* theoretical study., J. Chem. Phys. 136 (2012) 064308.

[31] S. Gao, Z. Dai, W. Sun, H. Li, J. Wang, Y. Mo, Tunneling splittings in vibronic energy levels of $CH_3F^+$ $\tilde{X}^2E$ studied by high resolution photoelectron spectroscopy and *ab initio* calculation., J. Chem. Phys. 139 (2013) 064302.

[32] T. Codd, M.-W. Chen, M. Roudjane, J. F. Stanton, T. A. Miller, Jet cooled cavity ringdown spectroscopy of the $\tilde{A}^2E'' \leftarrow \tilde{X}^2A_2'$ transition of the $NO_3$ radical., J. Chem. Phys. 142 (2015) 184305.

[33] J. E. Subotnik, E. C. Alguire, Q. Ou, B. R. Landry, S. Fatehi, The requisite electronic structure theory to describe photoexcited nonadiabatic dynamics: Nonadiabatic derivative couplings and diabatic electronic couplings, Acc. Chem. Res. 48 (2015) 1340–1350.

[34] N. Wittenbrink, F. Venghaus, D. Williams, W. Eisfeld, A new approach for the development of diabatic potential energy surfaces: Hybrid block-diagonalization and diabatization by ansatz, J. Chem. Phys. 145 (2016) 184108.

[35] H. Tamura, Diabatization for time-dependent density functional theory: Exciton transfers and related conical intersections, J. Phys. Chem. A 120 (2016) 9341–9347.

[36] A. Grofe, Z. Qu, D. G. Truhlar, H. Li, J. Gao, Diabatic-at-construction method for diabatic and adiabatic ground and excited states based on multistate density functional theory, J. Chem. Theory Comput. 13 (2017) 1176–1187.

[37] D. Opalka, W. Domcke, High-order expansion of $T_2 \times t_2$ Jahn-Teller potential-energy surfaces in tetrahedral molecules., J. Chem. Phys. 132 (2010) 154108.

[38] D. Opalka, W. Domcke, High-order expansion of $T_2 \otimes e$ Jahn-Teller potential-energy surfaces in tetrahedral systems., Chem. Phys. Lett. 494 (2010) 134–138.

[39] T. Zeng, I. Seidu, Revisiting the $(E + A) \otimes (e + a)$ problems of polyatomic systems with trigonal symmetry: General expansions of their vibronic hamiltonians., Phys. Chem. Chem. Phys. 19 (2017) 11098–11110.

[40] R. J. Hickman, R. A. Lang, T. Zeng, General formalism for vibronic hamiltonians in tetragonal symmetry and beyond, Phys. Chem. Chem. Phys. 20 (2018) 12312–12322.

[41] T. Zeng, R. J. Hickman, A. Kadri, I. Seidu, General formalism of vibronic hamiltonians for tetrahedral and octahedral systems: Problems that involve $T$, $E$ states and $t$, $e$ vibrations., J. Chem. Theory Comput. 13 (2017) 5004–5018.

[42] A. D. Liehr, Topological aspects of the conformational stability problem. part i. degenerate electronic states., J. Phys. Chem. 67 (1963) 389–471.

[43] I. B. Bersuker, On the origin of ferroelectricity in perovskite-type crystals., Phys. Lett. 20 (1966) 589–590.

[44] V. Polinger, P. Garcia-Fernandez, I. B. Bersuker, Pseudo Jahn–Teller origin of ferroelectric instability in $BaTiO_3$ type perovskites: The green's function approach and beyond., Physica B 457 (2015) 296–309.

[45] I. B. Bersuker, The Jahn-Teller and pseudo Jahn-Teller effect in materials science., J. Phys.: Conf. Ser. 833 (2017) 012001.

[46] L. S. Cederbaum, E. Gindensperger, I. Burghardt, Short-time dynamics through conical intersections in macrosystems, Phys. Rev. Lett. 94 (2005) 113003.

[47] E. Gindensperger, I. Burghardt, L. S. Cederbaum, Short-time dynamics through conical intersections in macrosystems. ii. applications., J. Chem. Phys. 124 (2006) 144103.

[48] J. Li, L. Joubert-Doriol, A. F. Izmaylov, Geometric phase effects in excited state dynamics through a conical intersection in large molecules: N-dimensional linear vibronic coupling model study., J. Chem. Phys. 147 (2017) 064106.

[49] E. P. Wigner, Group Theory, Academic Press, Inc., 1959.

[50] J. S. Griffith, The Irreducible Tensor Method for Molecular Symmetry Group, Dover Publications, Inc., 2006.

[51] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery Jr., General atomic and molecular electronic structure system, J. Comput. Chem. 14 (1993) 1347–1363.

[52] M. S. Gordon, M. W. Schmidt, Advances in electronic structure theory: GAMESS a decade later, Elsevier, Amsterdam, 2005, Ch. 41, pp. 1167–1189.

[53] T. H. Dunning, Gaussian basis sets for use in correlated molecular calculations. i. the atoms boron through neon and hydrogen, J. Chem. Phys. 90 (1989) 1007–1023.