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Effective Hamiltonian approach to doubly degenerate electronic states

I — Theory and applications to $\mathbf{E} \otimes (\mathbf{b_1} + \mathbf{b_2})$ and related Jahn-Teller systems

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Abstract. Several problems in vibronic spectroscopy are solved within the effective Hamiltonian formalism combined with Lie algebraic methods. We consider mainly vibronic interactions in orbital doublets for molecules with a principal symmetry axis of order $n = 4k$ (or n even for D_{nd} symmetry groups). Effective Hamiltonian models for $E \otimes (b_1 + b_2)$, $E \otimes (b_i + a_j)$ and $E \otimes (b_i + e)$ Jahn-Teller dynamical systems are discussed as well as some correlations with previous studies established.

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1 Introduction

Since the seminal paper by Longuet-Higgins et al. [1] giving the energy levels of $E \otimes e$ Jahn-Teller (JT) systems in symmetrical molecules, many studies have been devoted to this kind of vibronic systems, especially in cubic symmetry. In such situations an electronic orbital doublet is coupled to a doubly degenerate vibration (or to a pair of phonon modes). Extensions are the multimode $E \otimes \sum e$ cases and a nearby problem is the so-called $E \otimes (b_1 + b_2 + \cdots)$ case in which two non-degenerate vibrations are involved. The theory of the static and dynamical JT effects in localized systems has been discussed in several monographs or review articles [2–4]. More recent reviews about the current status of JT theory with extensive bibliographies can be found in [5–9].

For some times there has been a renewed interest in the search of analytical approximate solutions since they allow to explore areas which are not reachable through purely numerical methods [10–13]. However the well recognized [3,4,14–16] high symmetry of the zeroth order problem is rarely used to its full extent.

The aim of the present work is to establish a framework for a unified treatment of rovibronic interactions in doubly degenerate electronic states. This is possible if one starts with a complete sets of electronic and rovibrational operators built from the knowledge of the zeroth order symmetry algebras. The space of states span well defined irreducible representations (*irreps*) of these algebras and all the necessary matrix elements are obtained through standard methods. Symmetry adaptation in the molecular point group G can be made through various methods and heavily relies on physical assumptions concerning the dominant interactions breaking the zeroth order symmetry. As an aside it appears that the various forms of vibronic Hamiltonians given in the literature describing linear couplings in such systems are simply related through a change of the orientation for the E *irrep* of G.

The general features of our formalism are presented in the first part of this paper. Our assumptions are clearly specified and the restriction to doubly degenerate electronic states is developed next. The preliminary results obtained in a previous work [17] lead us to a natural division in two main cases determined by the reduction of the symmetrized product $[E \times E]$.

The following sections deal with electronic states for which $[E \times E]$ is of type $A_1 + B_1 + B_2$. Several zeroth-order effective Hamiltonian models are considered for $E \otimes (b_1 + b_2)$, $E \otimes (b_i + a_j)$ and $E \otimes (b_i + e)$ JT systems. In each case exact eigenvalues and symmetry adapted vibronic eigenstates are obtained. The determination of these symmetry adapted states is important for the inclusion of higher order interactions or intensity calculations. Whenever possible the relation between our approach and previous studies is made. In two cases the exact unitary transformation between the untransformed vibronic Hamiltonian and the effective associated model is found.

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2 Working assumptions

In what follows we restrict ourselves to semi-rigid non linear molecular systems in a degenerate electronic state to which is associated an *irrep* Γ_e of the molecular point symmetry group G. We assume that in first approximation the Hamiltonian which includes electronic, vibrational and rotational degrees of freedom is invariant with respect to transformations of a certain Lie group or more precisely that it admits a certain Lie symmetry algebra $\mathcal{A}$. We further assume that $\mathcal{A}$ may be taken as as a direct sum of Lie algebras associated with each degrees of freedom: $\mathcal{A} = \mathcal{A}_e \oplus \mathcal{A}_v \oplus \mathcal{A}_r$. This is probably not the most general solution but it reflects the orders of magnitude for the various interactions commonly found for the considered molecular systems. When we go beyond the zeroth order the preceding high symmetry is usually broken and we have a chain

$$\mathcal{A}_e \oplus \mathcal{A}_v \oplus \mathcal{A}_r \supset \cdots \supset G, \tag{1}$$

where the dots $\cdots$ mean that in general we have several possibilities. $\mathcal{A}$ must have one (or several) *irrep* $\Lambda_e \times \Lambda_v \times \Lambda_r$ which generate the space of states and whose subduction in the chain (1) gives appropriate symmetry adapted states.

At this point, reminding that all classical Lie algebras admit bosonic (or fermionic) realizations, the construction of all possible operators acting within $\Lambda_e \times \Lambda_v \times \Lambda_r$ can be made. This is not necessarily an easy step especially if one wants to build operators which are symmetry adapted in the whole chain. Rovibronic states and operators can be written in a general manner

$$\begin{aligned}&[[^{\{\gamma_e\}}\Psi^{(\Gamma_e)} \times^{\{\gamma_v\}} \Psi^{(\Gamma_v)}]^{(\Gamma_{ev})} \times^{\{\gamma_r\}} \Psi^{(\Gamma_r)}]^{\{\gamma\}(\Gamma_{evr})} \equiv \\ &\qquad |\{\gamma_e\}\Gamma_e, \{\gamma_v\}\Gamma_v, \Gamma_{ev}, \{\gamma_r\}\Gamma_r; \{\gamma\}\Gamma_{evr}\rangle \\ &\qquad\qquad \equiv |^{\{\gamma\}}\Psi^{(\Gamma_{evr})}\rangle, \end{aligned} \tag{2}$$

$$\begin{aligned}{}^{\{\kappa\}}O^{(C_{evr})} &= [[^{\{\kappa_e\}}E^{(C_e)} \times^{\{\kappa_v\}} V^{(C_v)}]^{(C_{ev})} \\ &\qquad \times^{\{\kappa_r\}} R^{(C_r)}]^{\{\kappa\}(C_{evr})}, \end{aligned} \tag{3}$$

where the indices γ_i and κ_i represent the additional labels needed to fully specify states and operators. In equation (3) C_{evr} is the scalar representation Γ_0 of G for an Hamiltonian operator or one of the appropriate *irrep* of G for transition moments. Besides we assume that these operators satisfy the usual properties of hermiticity and invariance upon time reversal. All the necessary matrix elements are calculated by standard techniques. The Wigner-Eckart theorem gives

$$\begin{aligned}&\langle^{\{\gamma'\}}\Psi^{(\Gamma'_{evr})}_{\sigma'}|^{\{\kappa\}}O^{(C_{evr})}_{\theta}|^{\{\gamma\}}\Psi^{(\Gamma_{evr})}_{\sigma}\rangle = \\ &\qquad [\Gamma'_{evr}]^{-\frac{1}{2}} F \begin{matrix} \theta & \sigma & (\Gamma'_{evr})* \\ (C_{evr} & \Gamma_{evr}) & \sigma' \end{matrix} \\ &\qquad\qquad \times (\{\gamma'\}\Gamma'_{evr}||^{\{\kappa\}}O^{(C_{evr})}||\{\gamma\}\Gamma_{evr}), \end{aligned} \tag{4}$$

where the F coefficients are Clebsch-Gordan coefficients (CGC) for G and the reduced matrix elements given by

$$\begin{aligned}&(\{\gamma'\}\Gamma'_{evr}||^{\{\kappa\}}O^{(C_{evr})}||\{\gamma\}\Gamma_{evr}) = \\ &\quad ([\Gamma'_{evr}][\Gamma_{evr}][C_{evr}][\Gamma'_{ev}][\Gamma_{ev}][C_{ev}])^{\frac{1}{2}} \left\{ \begin{matrix} C_{ev} & \Gamma_{ev} & \Gamma'_{ev} \\ C_r & \Gamma_r & \Gamma'_r \\ C_{evr} & \Gamma_{evr} & \Gamma'_{evr} \end{matrix} \right\} \\ &\quad \times \left\{ \begin{matrix} C_e & \Gamma_e & \Gamma'_e \\ C_v & \Gamma_v & \Gamma'_v \\ C_{ev} & \Gamma_{ev} & \Gamma'_{ev} \end{matrix} \right\} (\{\gamma'_e\}\Gamma'_e||^{\{\kappa_e\}}E^{(C_e)}||\{\gamma_e\}\Gamma_e) \\ &\qquad \times (\{\gamma'_v\}\Gamma'_v||^{\{\kappa_v\}}V^{(C_v)}||\{\gamma_v\}\Gamma_v) \\ &\qquad\qquad \times (\{\gamma'_r\}\Gamma'_r||^{\{\kappa_r\}}R^{(C_r)}||\{\gamma_r\}\Gamma_r), \end{aligned} \tag{5}$$

where $\{...\}$ are $9-C$ symbols of G. At this point a few remarks are in order:

(i) in the preceding equations (4, 5) the Wigner-Eckart theorem has been applied at the G level; this is not always the best option but it simplifies the presentation of the method. We also assume that all products of *irrep* of G involved are multiplicity free, as it will be the case in this paper. Non multiplicity free cases can be handled along the same lines with the addition of multiplicity indices appropriately;

(ii) the coupling schemes in equations (2, 3) assume a preponderant interaction between electronic and vibrational degrees of freedom. Other situations could be considered and treated either directly through a different coupling scheme or obtained from this one through standard recoupling techniques;

(iii) if the algebras $\mathcal{A}_i$ and *irreps* Λ_i have been appropriately chosen with a formal expansion of the form

$$\begin{aligned}H = \sum_{\kappa_i, C_i} t^{\{\kappa_i\}}_{\{C_i\}} &[[^{\{\kappa_e\}}E^{(C_e)} \times^{\{\kappa_v\}} V^{(C_v)}]^{(C_{ev})} \\ &\qquad \times^{\{\kappa_r\}} R^{(C_r)}]^{\{\kappa\}(\Gamma_0)}, \end{aligned} \tag{6}$$

one must be able to represent any "untransformed" Hamiltonian as well as any effective one. This point will be illustrated in the following for the specific systems under study.

3 Further restrictions

For all molecular systems the treatment of rotational degrees of freedom is rather well established, even if different approaches are used [18,19]. The simplest algebraic chains

$$\begin{matrix} O(3)_r \supset O(2)_r & \text{or} & O(3)_r \supset & G \\ j_\tau \qquad\quad m & & j_\tau \qquad & n_r C_r \sigma_r \end{matrix}$$

are commonly used and allow to get a set of rotational operators

$$R^{\Omega(K_g)}_{q} \quad \text{or} \quad R^{\Omega(K_g)}_{p_r} = R^{\Omega(K_g, n_r C_r)}_{\sigma_r},$$

where Ω is the degree with respect to the $so(3)$ generators. Compact dynamical algebras and their bosonic realizations have also been proposed [20]; they allow more general operators to be built.

In this paper we will restrict to vibronic interactions, which amounts to take $R^{(C_r)}$ as the identity operator in equation (2). We thus write vibronic states and operators as

$$\begin{aligned}&[{}^{\{\gamma_e\}}\Psi^{(\Gamma_e)} \times {}^{\{\gamma_v\}}\,\Psi^{(\Gamma_v)}]^{\{\gamma_{ev}\}(\Gamma_{ev})} \equiv \\ &\qquad |\{\gamma_e\}\Gamma_e,\{\gamma_v\}\Gamma_v;\{\gamma_{ev}\}\Gamma_{ev}\rangle \equiv {}^{\{\gamma_{ev}\}}\Psi^{(\Gamma_{ev})}, \end{aligned} \tag{7}$$

$${}^{\{\kappa\}}O^{(C_{ev})} = [[{}^{\{\kappa_e\}}E^{(C_e)} \times {}^{\{\kappa_v\}}\,V^{(C_v)}]^{\{\kappa_{ev}\}(C_{ev})}, \tag{8}$$

and equations (4, 5) reduce to

$$\begin{aligned}&\langle {}^{\{\gamma'_{ev}\}}\Psi^{(\Gamma'_{ev})}_{\sigma'_{ev}}|{}^{\{\kappa_{ev}\}}O^{(C_{ev})}_{\theta}|{}^{\{\gamma_{ev}\}}\Psi^{(\Gamma_{ev})}_{\sigma_{ev}}\rangle = \\ &\qquad [\Gamma'_{ev}]^{-\frac{1}{2}} F \begin{matrix} \theta & \sigma_{ev} & (\Gamma'_{ev})* \\ (C_{ev} & \Gamma_{ev}) & \sigma'_{ev} \end{matrix} \\ &\qquad \times (\{\gamma'_{ev}\}\Gamma'_{ev}||{}^{\{\kappa_{ev}\}}O^{(C_{ev})}||\{\gamma_{ev}\}\Gamma_{ev}), \end{aligned} \tag{9}$$

with for the reduced matrix elements

$$\begin{aligned}&(\{\gamma'_{ev}\}\Gamma'_{ev}||{}^{\{\kappa_{ev}\}}O^{(C_{ev})}||\{\gamma_{ev}\}\Gamma_{ev}) = \\ &\qquad \times \left\{ \begin{matrix} C_e & \Gamma_e & \Gamma'_e \\ C_v & \Gamma_v & \Gamma'_v \\ C_{ev} & \Gamma_{ev} & \Gamma'_{ev} \end{matrix} \right\} (\{\gamma'_e\}\Gamma'_e||{}^{\{\kappa_e\}}E^{(C_e)}||\{\gamma_e\}\Gamma_e) \\ &\quad \times ([\Gamma'_{ev}][\Gamma_{ev}][C_{ev}])^{\frac{1}{2}} (\{\gamma'_v\}\Gamma'_v||{}^{\{\kappa_v\}}V^{(C_v)}||\{\gamma_v\}\Gamma_v)\,. \end{aligned} \tag{10}$$

In the following section we specify the electronic operators and states adapted to cases where Γ_e is of the E type and the vibrational operators we will use.

4 The case of electronic states with E symmetry type

As we shall consider only electronic states of type E (and G' in part II) it is better to refine the classification of groups introduced in [17,21]. In fact if we denote E_r (or $E_{r\alpha}$) the *irrep* of G spanned by the electronic states of type E it follows that we have fundamentally two cases according as the reduction of the symmetrized square $[E_r \times E_r] = [E_r]^2 = \Gamma_0 + \Gamma$ contains either an E type *irrep* or two one dimensional B_1 and B_2 type *irreps*. This is summarized in Table 1 for groups in $G_{(I)} = C_{nv}, D_n, D_{nd}$ (n even), T_d, O. For groups in $G_{(II)}$ we have the rules:

- $D_{2p+1h} = D_{2p+1} \times C_s$: for $E_r = E'_r$ or $E_r = E''_r$ add a $'$ to Γ in column for D_{2p+1},
- $D_{2ph} = D_{2p} \times C_i$: for $E_r = E_{rg}$ or $E_r = E_{ru}$ add a g to Γ in column for D_{2p},
- $D_{2p+1d} = D_{2p+1} \times C_i$: for $E_r = E_{rg}$ or $E_r = E_{ru}$ add a g to Γ in column for D_{2p+1},
- $O_h = O \times C_i$: for $E_r = E_g$ or $E_r = E_u$ add a g to Γ in column for O.

(11)

Table 1. $\Gamma \subset [E_r]^2$ for groups in $G_{(I)}$.

Γ	D_{2p+1} C_{2p+1v} T_d, O	D_{2p} C_{2pv}	D_{2pd}	Case
$B_1 + B_2$		$r = \frac{p}{2}$	$r = p$	(i)
E_{2r}	$r \leq \frac{p}{2}$	$r \leq \frac{p-1}{2}$ p odd $r < \frac{p}{2}$ p even	$r < p$	(ii)
E_{n-2r}	$r > \frac{p}{2}$	$r > \frac{p-1}{2}$ p odd $r > \frac{p}{2}$ p even		(iii)
E_{2n-2r}			$r > p$	(iii)

We have thus two main cases according as Γ is of type $B_1 + B_2$ or E. This latter case also includes cubic groups for which there is only one E type *irrep* (two in O_h differing in parity only) and which are the only ones which admit G' electronic states also[1].

4.1 Electronic operators and states

For an orbital doublet or E term it is well-known that an $u(2)$ algebra is appropriate [4]. Whatever G we shall denote E_r the *irrep* spanned by the electronic states. So, from the results of [17] the electronic space of states is a carrier space for the *irrep* [10] of $u(2)_e$ which subduces to E_r in G with different possible bases mainly determined by the orientation chosen for the E type *irreps* of G.

A complete set of electronic operators writes ${}^{[1\,-1]}\mathcal{E}^{(k)}_{p_e}$. In fact as ${}^{[1\,-1]}\mathcal{E}^{(0)} = (N_1 + N_2)/\sqrt{2}$ reduces to the linear invariant which is a constant within [10] we are left with ${}^{[1\,-1]}\mathcal{E}^{(1)} = {}^{[1\,-1]}E^{(1)}$. The indices p_e depend upon the algebraic chain used:

$$\begin{array}{ll} u(2)_e \supset su(2)_e \supset so(2)_e & \\ p_e = m_e \quad m_e = 0, \pm 1 & \\ u(2)_e \supset su^*(2)_e \supset G & \\ p_e = \ell_e C_e \sigma_e & \begin{cases} \ell_e = 0 \; C_e\sigma_e = A_2 \\ \ell_e = 2 \; C_e\sigma_e = \Gamma\sigma_e \end{cases} \end{array} \tag{12}$$

where the Γ values are those in table 1 and equation (11); A_2 is A'_2 or A_{2g} for groups in $G_{(II)}$. Depending upon the orientation of the *irreps* of type E the index σ_e is denoted σ, $\bar{\sigma}$ or $\bar{\bar{\sigma}}$ for orientations I, II and III, respectively [17].

For each cases the expressions of the symmetry adapted electronic operators in terms of the $su(2)_e$ generators have been given in Table II of [17] and their matrix elements calculated in the various bases:

$$\begin{array}{ccccc} u(2)_e & \supset & su(2)_e & \supset & so(2)_e \\ [10] & \downarrow & \frac{1}{2} & \downarrow & m_e \\ u(2)_e & \supset & su^*(2)_e & \supset & G \\ [10] & \downarrow & \frac{1}{2} & \downarrow & 1E_r\sigma_e \end{array} \tag{13}$$

with $\sigma_e = \sigma$ or $\bar{\sigma}, \bar{\bar{\sigma}}$.

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[1] Icosahedral molecules have G' electronic states but no E type *irrep* and as such no E electronic states.

4.2 Vibrational operators and states

An arbitrary vibrational operator involving several modes $s_1, s_2, \cdots, s_k$ with symmetry $C_{s_1}, C_{s_2}, \cdots, C_{s_k}$ may be denoted:

$$ {}^{\{\kappa_v\}}_{\{s\}}V^{(C_v)} = [\ {}^{\{\kappa_1\}}_{s_1}V^{(C_1)} \times {}^{\{\kappa_2\}}_{s_2}V^{(C_2)} \times \cdots {}^{\{\kappa_k\}}_{s_k}V^{(C_k)}]^{(C_v)}. \tag{14} $$

As icosahedral molecules are not considered here[1] we can restrict to oscillators with dimension at most equal to three. We also note that molecules with symmetry other than that of cubic or icosahedral groups have at most two dimensional vibrational modes. We give in Appendix A the various forms of the vibrational operators we use. The general expression (14) is restricted there to one and two mode operators which should be sufficient in most applications for the systems under consideration. In any case higher order interaction terms could be built along the same line. With this assumption vibrational basis states will mainly be of one of the two basic forms:

$$ {}^{\{\gamma_{v_s}\}}\Psi^{(\Gamma_v)}_{\sigma_v} = |\{\gamma_{v_s}\}\Gamma_v\sigma_v\rangle, \text{ or} $$

$$ [\ {}^{\{\gamma_{v_{s_1}}\}}\Psi^{(\Gamma_{v_{s_1}})} \times {}^{\{\gamma_{v_{s_2}}\}}\ \Psi^{(\Gamma_{v_{s_2}})}]^{(\Gamma_v)}_{\sigma_v} = |\{\gamma_{v_{s_1}}\gamma_{v_{s_2}}\}\Gamma_v\sigma_v\rangle, $$

where the γ_{v_s} indices depend also upon the vibrational algebraic chain used.

5 Formal vibronic Hamiltonian

The most general formal vibronic Hamiltonian may first be written as a linear combination with real parameters of Hermitian and time reversal invariant operators:

$$ H_F = \sum_{\text{all indices}} {}_{\{s\}}t^{\{\kappa_e\kappa_v\}}\ [{}^{[1\,-1]}\mathcal{E}^{(k_e,\ell_e C_e)} \times {}^{\{\kappa_v\}}_{\{s\}}V^{(C_v)}]^{(\Gamma_0)}. $$

The $\{s\} = s_1, s_2 \cdots$ set may include arbitrary vibrational operators built from the elementary ones associated with any mode s_i appearing in the full vibrational representation. Taking into account that electronic operators with $k_e = 0$ are proportional to the identity operator H_F may also be written

$$ \begin{aligned} H_F = I_e &\sum_{\{s\},\{\kappa_v\}} {}_{\{s\}}t^{\Gamma_0\{\kappa_v\}}\ {}^{\{\kappa_v\}}_{\{s\}}V^{(\Gamma_0)} \\ &+ \sum_{\text{all indices}} {}_{\{s\}}t^{\{\kappa_e\kappa_v\}}\ [{}^{[1\,-1]}E^{(1_e,\ell_e C_e)} \times {}^{\{\kappa_v\}}_{\{s\}}V^{(C_v)}]^{(\Gamma_0)}, \end{aligned} \tag{15} $$

where the first term represents the purely vibrational Hamiltonian. For practical purposes the previous expansion has to be specialized. Basically we define two categories:

(a) the expansion is used to represent what we call the *untransformed* vibronic Hamiltonian (although it is already an effective one) for the considered degenerate electronic state. Its expression is commonly written in the form

$$ \begin{aligned} H(r,Q) &= T(Q) + U(r,Q) \\ &= T(Q) + H(r) + V(r,Q_0) + \sum_{s,C} [{}_sV^{(C)} \times {}_sQ^{(C)}]^{(\Gamma_0)} \\ &\quad + \frac{1}{2}\sum_{s_i,C_i,C} [{}_{s_1,s_2}W^{C_1C_2(C)} \times [{}_{s_1}Q^{(C_1)} \\ &\quad \times {}_{s_2}Q^{(C_2)}]^{(C)}]^{(\Gamma_0)} + \cdots \end{aligned} \tag{16} $$

With respect to the equivalent expression given in [4] we only slightly change the notations; in particular we allow for non trivial CGC. The ${}_sV^{(C)}$ and ${}_{s_1,s_2}W^{C_1C_2(C)}$ operators are related to the first and second derivatives with respect to normal coordinates ${}_sQ^{(C)}$ of the potential. The projection of (16) onto the considered electronic state determines the *vibronic Hamiltonian matrix*

$$ \begin{aligned} P_eHP_e &= H^{\langle P_e\rangle} \\ &= \widehat{H}_0 + \sum_{s,C} {}_sV_C[\widehat{C}^{(C)} \times {}_sQ^{(C)}]^{(\Gamma_0)} \\ &\quad + \frac{1}{2}\sum_{s_i,C_i,C} {}_{s_1,s_2}W_C(C_1 \times C_2) \\ &\quad \times [[\widehat{C}^{(C)} \times [{}_{s_1}Q^{(C_1)} \times {}_{s_2}Q^{(C_2)}]^{(C)}]^{(\Gamma_0)} + \cdots \end{aligned} \tag{17} $$

Usually only terms which are at most quadratic in the normal coordinates are retained;

(b) the expansion (15) is to represent an effective Hamiltonian obtained from the untransformed one through a (usually unknown) unitary transformation. Thus it is mainly determined by the polyad scheme appropriate to the particular molecular system under study [19,22,23]. In a general way, if we denote by P_k the projector onto an arbitrary vibrational subspace Ω_k of the complete vibrational Hilbert space $\mathcal{H}_v$

$$ P_kH_FP_k = \widetilde{H}^{\langle P_k\rangle}, $$

contains only vibrational operators acting within the set of levels contained in Ω_k; if the set of all vibrational operators is appropriately chosen the effective Hamiltonian for a given *vibronic polyad* N_e is then given by

$$ \widetilde{H}^{\langle P_N\rangle} = \sum_{k=1}^{N_e} \widetilde{H}^{\langle P_k\rangle}_{\{P_k\}}, $$

where the summation is over the lowest polyads, including the ground state.

In the following sections the preceding ideas are applied to specific E electronic states.

6 The $\mathbf{E \otimes (b_1 + b_2 + \cdots)}$ case

6.1 General expansions

This corresponds to case (i) of Section 4 for which $[E_r]^2 = A_1 + B_1 + B_2$ with $r = n/4$ for groups in $G_{(I)}$ except for D_{nd} groups with n even for which it is $r = n/2$. For other groups, $[E_{r\alpha}]^2 = A_{1\alpha^2} + B_{1\alpha^2} + B_{2\alpha^2}$ with $\alpha^2 = {}'$ or g. Since in general, parities can easily be added they will be omitted in the following except in a few cases; in particular for groups in $G_{(II)}$ all Hamiltonian terms are of symmetry $'$ or g. The expansion (15) writes then

$$\begin{aligned} H_F = I_e &\sum_{\{s\}\{\kappa_v\}} {}_{\{s\}}t^{A_1\{\kappa_v\}}\ {}^{\{\kappa_v\}}_{\{s\}}V_+^{(A_1)} \\ &+ \sum_{\{s\}\{\kappa_v\}} {}_{\{s\}}t^{A_2\{\kappa_v\}} \left[{}^{[1\,-1]}E^{(1,0A_2)} \times {}^{\{\kappa_v\}}_{\{s\}}V_-^{(A_2)}\right]^{(A_1)} \\ &+ \sum_{t=1,2} \sum_{\{s\}\{\kappa_v\}} {}_{\{s\}}t^{B_t\{\kappa_v\}} \left[{}^{[1\,-1]}E^{(1,2B_t)} \times {}^{\{\kappa_v\}}_{\{s\}}V_+^{(B_t)}\right]^{(A_1)}, \end{aligned} \tag{18}$$

where $+$ $(-)$ stands for time-reversal invariant (non invariant) operators. As all CGC reduce to unity (18) may also be written

$$\begin{aligned} H_F = I_e &\sum_{\{s\}\{\kappa_v\}} {}_{\{s\}}t^{A_1\{\kappa_v\}}\ {}^{\{\kappa_v\}}_{\{s\}}V_+^{(A_1)} \\ &+ {}^{[1\,-1]}E^{(1,0A_2)} \sum_{\{s\}\{\kappa_v\}} {}_{\{s\}}t^{A_2\{\kappa_v\}}\ {}^{\{\kappa_v\}}_{\{s\}}V_-^{(A_2)} \\ &+ \sum_{t=1,2} {}^{[1\,-1]}E^{(1,2B_t)} \sum_{\{s\}\{\kappa_v\}} {}_{\{s\}}t^{B_t\{\kappa_v\}}\ {}^{\{\kappa_v\}}_{\{s\}}V_+^{(B_t)}. \end{aligned} \tag{19}$$

To facilitate practical applications and further comparisons with previous approaches we detail below the preceding expansion taking into account that molecules entering this case have vibrational modes which are at most doubly degenerate. Also we keep only one and two modes vibrational operators. Setting

$$H_F = H_{vib} + H(A_2) + H(B_t) \quad t = 1, 2,$$

we have with the notations of Appendix A

$$\begin{aligned} H_{vib} = I_e \Bigg\{ &\sum_s \Big\{ {}_s t^{CC(A_1)}_{n_1n_2}\ {}^0_s V^{CC(A_1)}_{n_1n_2} \\ &+ {}_s t^{j\ell(A_1)}_{m_1m_2}\ {}^{[m_1\,-m_2]}_{s}\mathcal{V}^{(j,\ell A_1)} \Big\} \\ &+ \sum_{s\neq s'} \Big\{ {}_{ss'}t^{\{C_i\}\{C'_i\}(A_1)}_{n_in'_i}\ {}^0_{ss'}V^{\{C_i\}\{C'_i\}(A_1)}_{\{n_i\}\{n'_i\}} \\ &+ {}_{ss'}t^{\{C_ij_i\ell_i\}\{C'_ij'_i\ell'_i\}(A_1)}_{n_im_i}\ {}^0_{ss'}V^{\{C_ij_i\ell_i\}\{C'_ij'_i\ell'_i\}(A_1)}_{n_1n_2,m_1m_2} \\ &+ {}_{ss'}t^{\{j_i\ell_iC_i\}\{j'_i\ell'_iC'_i\}(A_1)}_{n_im_i}\ {}^0_{ss'}V^{\{j_i\ell_iC_i\}\{j'_i\ell'_iC'_i\}(A_1)}_{n_1n_2,m_1m_2} \Big\} + \cdots \Bigg\}, \end{aligned} \tag{20}$$

$$\begin{aligned} H(A_2) = {}^{[1\,-1]}E^{(1,0A_2)} \Bigg\{ &\sum_s \Big\{ {}_s t^{C_1C_2(A_2)}_{n_1n_2}\ {}^1_s V^{C_1C_2(A_2)}_{n_1n_2} \\ &+ {}_s t^{j\ell(A_2)}_{m_1m_2}\ {}^{[m_1\,-m_2]}_{s}\mathcal{V}^{(j,\ell A_2)} \Big\} \\ &+ \sum_{s\neq s'} \Big\{ {}_{ss'}t^{\{C_i\}\{C'_i\}(A_2)}_{n_in'_i}\ {}^1_{ss'}V^{\{C_i\}\{C'_i\}(A_2)}_{\{n_i\}\{n'_i\}} \\ &+ {}_{ss'}t^{\{C_ij_i\ell_i\}\{C'_ij'_i\ell'_i\}(A_2)}_{n_im_i}\ {}^1_{ss'}V^{\{C_ij_i\ell_i\}\{C'_ij'_i\ell'_i\}(A_2)}_{n_1n_2,m_1m_2} \\ &+ {}_{ss'}t^{\{j_i\ell_iC_i\}\{j'_i\ell'_iC'_i\}(A_2)}_{n_im_i}\ {}^1_{ss'}V^{\{j_i\ell_iC_i\}\{j'_i\ell'_iC'_i\}(A_2)}_{n_1n_2,m_1m_2} \Big\} + \cdots \Bigg\}, \end{aligned} \tag{21}$$

$$\begin{aligned} H(B_t) = {}^{[1\,-1]}E^{(1,2B_t)} \Bigg\{ &\sum_s \Big\{ {}_s t^{CC(B_t)}_{n_1n_2}\ {}^0_s V^{CC(B_t)}_{n_1n_2} \\ &+ {}_s t^{j\ell(B_t)}_{m_1m_2}\ {}^{[m_1\,-m_2]}_{s}\mathcal{V}^{(j,\ell B_t)} \Big\} \\ &+ \sum_{s\neq s'} \Big\{ {}_{ss'}t^{\{C_i\}\{C'_i\}(B_t)}_{n_in'_i}\ {}^0_{ss'}V^{\{C_i\}\{C'_i\}(B_t)}_{\{n_i\}\{n'_i\}} \\ &+ {}_{ss'}t^{\{C_ij_i\ell_i\}\{C'_ij'_i\ell'_i\}(B_t)}_{n_im_i}\ {}^0_{ss'}V^{\{C_ij_i\ell_i\}\{C'_ij'_i\ell'_i\}(B_t)}_{n_1n_2,m_1m_2} \\ &+ {}_{ss'}t^{\{j_i\ell_iC_i\}\{j'_i\ell'_iC'_i\}(B_t)}_{n_im_i}\ {}^0_{ss'}V^{\{j_i\ell_iC_i\}\{j'_i\ell'_iC'_i\}(B_t)}_{n_1n_2,m_1m_2} \Big\} + \cdots \Bigg\}. \end{aligned} \tag{22}$$

From now on the electronic operators will be simply denoted $E^{(1,\ell_eC_e)}$.

6.2 Representing the untransformed Hamiltonian

In such a case it is better to take vibrational operators defined in terms of coordinates as in equations (A.1) and (A.6); also we restrict to terms which are at most quadratic in the coordinates. From equations (20–22) we then obtain

$$\begin{aligned} H = I_e &\sum_s \Big\{ \hbar\omega_s \left(N_s + \frac{g_s}{2}\right) \\ &+ {}_s t^{B_1} E^{(1,2B_1)}\ {}_sQ^{(B_1)} + {}_s t^{B_2} E^{(1,2B_2)}\ {}_sQ^{(B_2)} \Big\} \\ &+ \sum_{t,i,j} \sum_{s\neq s'} {}_{ss'}t^{A_jB_i(B_t)} E^{(1,2B_t)} \left({}_sQ^{(A_j)} \times {}_{s'}Q^{(B_i)}\right)^{(B_t)} \\ &+ \sum_t \Bigg\{ \sum_{s,s'} {}_{ss'}t^{E_{\frac{n}{4}}E_{\frac{n}{4}}(B_t)} E^{(1,2B_t)} \left({}_sQ^{(E_{\frac{n}{4}})} \times {}_{s'}Q^{(E_{\frac{n}{4}})}\right)^{(B_t)} \\ &+ \sum_{s\neq s'} {}_{ss'}t^{E_kE_{\frac{n}{2}-k}(B_t)} E^{(1,2B_t)} \left({}_sQ^{(E_k)} \times {}_{s'}Q^{(E_{\frac{n}{2}-k})}\right)^{(B_t)} \Bigg\}, \end{aligned} \tag{23}$$

with $A_j \times B_i = B_t$ $(t = 1, 2)$. For D_{nd} (n even) groups the substitution $n \to 2n$ must be made in the last two terms. For groups in $G_{(II)}$ $','' $ (or g, u) indices must be added in such a way that the global vibrational operator be of type $'$ (or g). We also note that the last term in (23) require $n \geq 8$ ($n \geq 4$) in D_n type groups (D_{nd}).

Standard treatments of vibronic interactions in such cases can be recovered by selecting appropriate terms in the Hamiltonian (23); often the last two terms, which do not involve the active coordinates, are neglected. As an illustration we give below for some cases how well-known results can be recovered and eventually extended.

$E \otimes (b_1 + b_2)$ case: denoting s_1 and s_2 the active coordinates we obtain

$$\begin{aligned} H = I_e \Bigg\{ & \sum_{i=1,2} \hbar\omega_{s_i}\left(N_{s_i} + \frac{1}{2}\right) + \sum_{s \neq s_1, s_2} \hbar\omega_s \left(N_s + \frac{1}{2}\right)\Bigg\} \\ & + {}_{s_1}t^{B_1} E^{(1,2B_1)} {}_{s_1}Q^{(B_1)} + {}_{s_2}t^{B_2} E^{(1,2B_2)} {}_{s_2}Q^{(B_2)} \\ & + \sum_s \Big\{ {}_{ss_1}t^{A_1B_1(B_1)} E^{(1,2B_1)} \big({}_sQ^{(A_1)} \times {}_{s_1}Q^{(B_1)}\big)^{(B_1)} \\ & + {}_{ss_2}t^{A_1B_2(B_2)} E^{(1,2B_2)} \big({}_sQ^{(A_1)} \times {}_{s_2}Q^{(B_2)}\big)^{(B_2)} \Big\} \\ & + \sum_s \Big\{ {}_{ss_2}t^{A_2B_2(B_1)} E^{(1,2B_1)} \big({}_sQ^{(A_2)} \times {}_{s_2}Q^{(B_2)}\big)^{(B_1)} \\ & + {}_{ss_1}t^{A_2B_1(B_2)} E^{(1,2B_2)} \big({}_sQ^{(A_2)} \times {}_{s_1}Q^{(B_1)}\big)^{(B_2)} \Big\} + \cdots , \end{aligned} \tag{24}$$

where the summation over s involves only modes with significant coupling with b_1 and b_2 vibrational modes. The multimode $E \otimes (nb_1 + n'b_2)$ problem is obtained with a summation over s_1 and (or) s_2 indices.

For the $E \otimes b_1$ case (resp. $E \otimes b_2$) only terms with indices s_1 (resp. s_2) are retained. Likewise for a $E \otimes (b_1 + b_1 + \cdots)$ (resp. $E \otimes (b_2 + b_2 + \cdots)$) case one would introduces a s_1 (resp. s_2) summation.

In the preceding equations (23, 24) we could replace the electronic operators $E^{(1,2B_i)}$ by their expression in terms of the components of the pseudo-spin S_α. However the relations between our parameters and conventional ones can only be made through the vibronic matrix. The latter is most easily obtained with the results of reference [17]. We only give its expression for the general expansion (23), those associated with particular cases being easily deduced.

- *Vibronic matrix in orientation I.* The projector onto the electronic subspace E_r writes

$$P_e = \sum_\sigma \left| [1\,0]\frac{1}{2}1E_r\sigma \right\rangle\!\!\right\rangle \left\langle\!\!\left\langle [1\,0]\frac{1}{2}1E_r\sigma \right| .$$

For the quadratic terms in (23) we set

$$\begin{aligned} {}^{(2)}V^{(B_t)} = & \sum_{i,j} \sum_{s \neq s'} {}_{ss'}t^{A_jB_i(B_t)} \big({}_sQ^{(A_j)} \times {}_{s'}Q^{(B_i)}\big)^{(B_t)} \\ & + \sum_{s,s'} {}_{ss'}t^{E_{\frac{n}{4}}E_{\frac{n}{4}}(B_t)} \big({}_sQ^{(E_{\frac{n}{4}})} \times {}_{s'}Q^{(E_{\frac{n}{4}})}\big)^{(B_t)} \\ & + \sum_{s \neq s'} {}_{ss'}t^{E_kE_{\frac{n}{2}-k}(B_t)} \big({}_sQ^{(E_k)} \times {}_{s'}Q^{(E_{\frac{n}{2}-k})}\big)^{(B_t)}, \end{aligned}$$

then the vibronic matrix is given in terms of Pauli matrices $\widehat{\sigma}_\alpha$ by

$$\begin{aligned} \widehat{H} = \sum_s \Big\{ & \hbar\omega_s \widehat{\sigma}_0 \left(N_s + \frac{g_s}{2}\right) \\ & + \frac{1}{2}\, \widehat{\sigma}_z \; {}_st^{B_1} {}_sQ^{(B_1)} - \frac{1}{2}\, \widehat{\sigma}_x \; {}_st^{B_2} {}_sQ^{(B_2)} \Big\} \\ & + \frac{1}{2}\, \widehat{\sigma}_z \; {}^{(2)}V^{(B_1)} - \frac{1}{2}\, \widehat{\sigma}_x \; {}^{(2)}V^{(B_2)} + \cdots \end{aligned} \tag{25}$$

expression which shows that this orientation is suitable when the vibronic coupling with the b_2 vibration is small or in a $E \otimes (b_1 + b_1 + \cdots)$ multimode problem. The terms in the first and second line are those commonly found [4,24,25] for such systems even with the equal coupling approximation.

- *Vibronic matrix in orientation II.* For the same subspace we have now

$$P_e = \sum_{\bar{\sigma}} \left| [1\,0]\frac{1}{2}1E_r\bar{\sigma} \right\rangle\!\!\right\rangle \left\langle\!\!\left\langle [1\,0]\frac{1}{2}1E_r\bar{\sigma} \right| ,$$

and the vibronic matrix reads

$$\begin{aligned} \widehat{H} = \sum_s \Big\{ & \hbar\omega_s \widehat{\sigma}_0 \left(N_s + \frac{g_s}{2}\right) \\ & - \frac{1}{2}\, \widehat{\sigma}_x \; {}_st^{B_1} {}_sQ^{(B_1)} + \frac{1}{2}\, \widehat{\sigma}_y \; {}_st^{B_2} {}_sQ^{(B_2)} \Big\} \\ & - \frac{1}{2}\, \widehat{\sigma}_x \; {}^{(2)}V^{(B_1)} + \frac{1}{2}\, \widehat{\sigma}_y \; {}^{(2)}V^{(B_2)} + \cdots \end{aligned} \tag{26}$$

The terms on the first two lines of equation (26) are in a form similar to that used when discussing adiabatic potentials [4] and in the equal coupling case [26,27].

- *Vibronic matrix in orientation III.* In this case the projector onto the electronic subspace E_r is:

$$P_e = \sum_{\bar{\bar{\sigma}}} \left| [1\,0]\frac{1}{2}1E_r\bar{\bar{\sigma}} \right\rangle\!\!\right\rangle \left\langle\!\!\left\langle [1\,0]\frac{1}{2}1E_r\bar{\bar{\sigma}} \right| ,$$

and the vibronic matrix given by

$$\begin{aligned} \widehat{H} = \sum_s \Big\{ & \hbar\omega_s \widehat{\sigma}_0 \left(N_s + \frac{g_s}{2}\right) \\ & + \frac{1}{2}\, \widehat{\sigma}_x \; {}_st^{B_1} {}_sQ^{(B_1)} + \frac{1}{2}\, \widehat{\sigma}_z \; {}_st^{B_2} {}_sQ^{(B_2)} \Big\} \\ & + \frac{1}{2}\, \widehat{\sigma}_x \; {}^{(2)}V^{(B_1)} + \frac{1}{2}\, \widehat{\sigma}_z \; {}^{(2)}V^{(B_2)} + \cdots \end{aligned} \tag{27}$$

This case is similar to that in equation (25) in the sense that this orientation is appropriate when the vibronic coupling with the b_1 vibration is small or for a multimode $E \otimes (b_2 + b_2 + \cdots)$ problem.

Relations with usual parameters used in the literature can be summarized by

$$\left\langle {}^{e}\Psi^{(E_r)}_{\alpha'}\left|\frac{\partial V}{\partial_s Q^{(B_t)}}\right|{}^{e}\Psi^{(E_r)}_{\alpha}\right\rangle = {}_s t^{B_t}\frac{1}{\sqrt{2}}\left(-i\sqrt{\frac{3}{2}}\right)F\begin{array}{ccc} 2B_t & 1E_r\alpha & ([1\,0]1/2)* \\ ([1\;-1]1\;[1\,0]1/2) & & 1E_r\alpha' \end{array}, \tag{28}$$

where the coefficient $-i\sqrt{3/2}$ is the reduced matrix element $([1\,0]\frac{1}{2}||\,{}^{[1\,-1]}E^{(1)}||[1\,0]\frac{1}{2})$ of our electronic operators and $r = n/4$ or $n/2$ depending on the group involved. The F symbols, which are CGC for the chain $u_e(2) \supset su_e^*(2) \supset G$ have been defined in [17].

Likewise for quadratic coupling constants we have

$$\frac{1}{2}\left\langle {}^{e}\Psi^{(E_r)}_{\alpha'}\left|\frac{\partial^2 V}{\partial_s Q^{(C_1)}_{\alpha_1}\partial_{s'} Q^{(C_2)}_{\alpha_2}}\right|{}^{e}\Psi^{(E_r)}_{\alpha}\right\rangle = {}_{ss'}t^{C_1C_2(B_t)}\frac{1}{\sqrt{2}}\left(-\,i\sqrt{\frac{3}{2}}\right)F\begin{array}{ccc} \alpha_1 & \alpha_2 & (B_t) \\ (C_1 & C_2) & \end{array} \times F\begin{array}{ccc} 2B_t & 1E_r\alpha & ([1\,0]1/2)* \\ ([1\;-1]1\;[1\,0]1/2) & & 1E_r\alpha' \end{array}, \tag{29}$$

where the indices α_1, α_2 can be omitted when C_1 and C_2 are one dimensional. The first F symbols in (29) are CGC for the group G. Up to now these symbols were not explicitly needed since all computations have been made in the full chain starting from $u(2)$. If they are introduced through

$$F\begin{array}{ccc} 2B_t & 1E_r\alpha & ([1\,0]1/2) \\ ([1\;-1]1\;[1\,0]1/2) & & 1E_r\alpha' \end{array} = K\begin{array}{ccc} 2B_t & 1E_r & ([1\,0]1/2) \\ ([1\;-1]1\;[1\,0]1/2) & & 1E_r \end{array} F\begin{array}{ccc} & \alpha & (E_r) \\ (B_t\;E_r) & & \alpha' \end{array},$$

equations (28, 29) may be given a somewhat more familiar form:

$$\left\langle {}^{e}\Psi^{(E_r)}_{\alpha'}\left|\frac{\partial V}{\partial_s Q^{(B_t)}}\right|{}^{e}\Psi^{(E_r)}_{\alpha}\right\rangle = {}_s t^{B_t}\,c(B_t,E_r)F\begin{array}{ccc} & \alpha & (E_r)* \\ (B_t\;E_r) & & \alpha' \end{array}, \tag{30}$$

$$\frac{1}{2}\left\langle {}^{e}\Psi^{(E_r)}_{\alpha'}\left|\frac{\partial^2 V}{\partial_s Q^{(C_1)}_{\alpha_1}\partial_{s'} Q^{(C_2)}_{\alpha_2}}\right|{}^{e}\Psi^{(E_r)}_{\alpha}\right\rangle = {}_{ss'}t^{C_1C_2(B_t)}\,c(B_t,E_r)\,F\begin{array}{ccc} \alpha_1 & \alpha_2 & (B_t) \\ (C_1 & C_2) & \end{array} F\begin{array}{ccc} & \alpha & (E_r)* \\ (B_t\;E_r) & & \alpha' \end{array}, \tag{31}$$

where we set

$$K\begin{array}{ccc} 2B_i & 1E_r & ([1\,0]1/2)* \\ ([1\;-1]1\;[1\,0]1/2) & 1E_r & \end{array}\left(-i\frac{\sqrt{3}}{2}\right) = c(B_i,E_r),$$

the K coefficients being isoscalar factors for the chain $u_e(2) \supset su_e^*(2) \supset G$ and as such independent of the orientation chosen for the *irreps* of G.

7 Examples with effective Hamiltonians

The usual approach to the dynamical Jahn-Teller effect is to set up the Hamiltonian matrix in the basis of the vibrational modes involved with a truncation of the space of states to a sufficiently high value of the vibrational quantum numbers. This works well in the single mode case and as far as the rotational degrees of freedom are not taken into account. We shall not illustrate this approach, since the computation of matrix elements of the Hamiltonians in section 6 is rather straightforward (Eqs. (9, 10)) in the coupled bases

$$|[1\,0]E_r, \{\gamma_{v_s}\}\Gamma_v; \Gamma_{ev}\sigma_{ev}\rangle$$

for a one mode case or

$$|[1\,0]E_r, \{\gamma_{v_s}\}\Gamma_1, \{\gamma_{v_{s'}}\}\Gamma_2; \Gamma_v; \Gamma_{ev}\sigma_{ev}\rangle,$$

when two modes are involved.

Rather we choose to illustrate the effective Hamiltonian approach, already used in spherical tops [19,22,23] and in some symmetric and asymmetric molecules [28,29], which allows to deal in most cases with matrices of reasonable size. However a meaningful model can only be proposed if the vibronic polyad scheme, which should differ from the usually known vibrational polyad scheme, for the molecule under study is approximately known. Thus there is no general solution and the cases we consider rely on definite choices. In fact, so as to establish comparisons, among the examples developed below some have already been treated by conventional techniques, mainly of the perturbative type and usually only eigenvalues have been given to first or second order.

We consider two modes in the full vibrational representation with frequencies ω_s and $\omega_{s'}$ for which quadratic vibronic coupling terms are allowed (Eq. (23)). Also, we may expect a significant interaction if these modes are coupled through cubic terms in the potential energy. If we ask moreover that the latter involve the active coordinate, then simple symmetry arguments reveal that there are only two possibilities

$$\left(q_s^{(B_i)}\right)^2 q_{s'}^{(A_1)} \quad , \quad q_s^{(B_i)}\left(q_{s'}^{(E_{\frac{n}{4}})}\right)^2$$

with the substitution $n/4 \to n/2$ for D_{nd} groups. The effective Hamiltonian expansion is obtained from the results in Appendix A retaining only those vibrational operators which have non zero matrix elements within a polyad which we assume to be characterized by the quantum number $N = v_s + v'_{s'}$. We consider separately below various JT systems meeting these requirements and discuss the properties of their zeroth order spectrum.

7.1 $\mathbf{E} \otimes (\mathbf{b}_1 + \mathbf{b}_2)$ case

The most general effective vibronic Hamiltonian is of the form

$$\begin{aligned}\widetilde{H}_{vibr} = I_e \Bigg\{ &\sum_{n} {}_{s_1}\tilde{t}^{C_1C_1(A_1)}_{\{n\}\{n\}}\ {}^{0}_{s_1}V^{C_1C_1(A_1)}_{\{n\}\{n\}} \\ &+ {}_{s_2}\tilde{t}^{C_2C_2(A_1)}_{\{n\}\{n\}}\ {}^{0}_{s_2}V^{C_2C_2(A_1)}_{\{n\}\{n\}} \\ &+ \sum_{\{n_i,n_i'\}} {}_{s_1s_2}\tilde{t}^{C_1C_2\,C_1'C_2'(A_1)}_{\{n_1n_2\}\{n_1'n_2'\}}\ {}^{0}_{s_1s_2}V^{C_1C_2\,C_1'C_2'(A_1)}_{\{n_1n_2\}\{n_1'n_2'\}} \Bigg\} \\ &+ E^{(1,0A_2)} \sum_{\{n_i,n_i'\}} {}_{s_1s_2}\tilde{t}^{C_1C_2\,C_1'C_2'(A_2)}_{\{n_1n_2\}\{n_1'n_2'\}}\ {}^{1}_{s_1s_2}V^{C_1C_2\,C_1'C_2'(A_2)}_{\{n_1n_2\}\{n_1'n_2'\}}, \end{aligned} \tag{32}$$

with $C_1(C_2) = B_1(B_2)$ for $n_1(n_2)$ odd and $C_1(C_2) = A_1$ for $n_1(n_2)$ even. Also we have the condition $n_1 + n_2 = n_1' + n_2'$ and the matrix elements are non-zero only if $n_1' + n_2' \leq N$. In Appendix B equation (32) is detailed for the cases $N \leq 2$.

For the computation of matrix elements one usually resorts to the mathematically convenient coupled basis of the general form (7) and given for the special case considered here by

$$\left|[1\,0]\frac{1}{2}1E_r, (v\Gamma_1, N - v\Gamma_2)\Gamma_v; E_r\sigma_{ev}\right\rangle = |{}^{\{\gamma\}}\Psi^{(E_r)}_{\sigma_{ev}}\rangle, \tag{33}$$

where we took into account that in all cases the overall symmetry of states is E_r since $A_1 \times E_r = B_i \times E_r = E_r$. However, as we will show, this is not necessarily the interesting basis for the prediction of zeroth order spectrum properties.

We can already note that, since the electronic operator $E^{(1,0A_2)}$ is proportional to the z-component of the pseudo-spin S_z [17], symmetry adapted electronic states in orientation II are appropriate. In order to obtain the dominant features the Hamiltonian expansion given in Appendix B can be simplified. We take the following approximate expression

$$\begin{aligned}\widetilde{H}^{(0)}_{vibr} = {} & \tilde{t}^{A_1A_1(A_1)}_{\{0\}\{0\}} I_v + {}_{s_1}\tilde{t}^{B_1B_1(A_1)}_{\{1\}\{1\}}\ {}^{0}_{s_1}V^{B_1B_1(A_1)}_{\{1\}\{1\}} \\ & + {}_{s_2}\tilde{t}^{B_2B_2(A_1)}_{\{1\}\{1\}}\ {}^{0}_{s_2}V^{B_2B_2(A_1)}_{\{1\}\{1\}} \\ & + E^{(1,0A_2)}\ {}_{s_1s_2}\tilde{t}^{B_1A_1\,A_1B_2(A_2)}_{\{10\}\{01\}}\ {}^{1}_{s_1s_2}V^{B_1A_1\,A_1B_2(A_2)}_{\{10\}\{01\}}, \end{aligned} \tag{34}$$

which amounts to consider as predominant the terms which have the lowest degree in vibrational variables. Equation (34) may also be written simplifying the notations for the effective parameters

$$\begin{aligned}\widetilde{H}^{(0)}_{vibr} = {} & \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_{s_1}\left(N_1 + \frac{1}{2}\right) + \hbar\tilde{\omega}_{s_2}\left(N_2 + \frac{1}{2}\right) \\ & + \hbar\tilde{\lambda} S_z i({}_{s_2}a^{+(B_2)}\,{}_{s_1}a^{(B_1)} - {}_{s_1}a^{+(B_1)}\,{}_{s_2}a^{(B_2)}). \end{aligned} \tag{35}$$

Using the coupled basis (33) we obtain the matrix elements within the polyad N

$$\begin{aligned} & \left\langle {}^{\{\gamma'\}}\Psi^{(E_r)}_{\sigma_{ev}'} | \widetilde{H}^{(0)}_{vibr} | {}^{\{\gamma\}}\Psi^{(E_r)}_{\sigma_{ev}} \right\rangle = \\ & \delta_{\sigma_{ev},\sigma_{ev}'} \Bigg[\left[\hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_{s_1}\left(v + \frac{1}{2}\right) + \hbar\tilde{\omega}_{s_2}\left(N - v + \frac{1}{2}\right) \right] \delta_{v',v} \\ & + \hbar\tilde{\lambda}\frac{(-1)^{\Gamma_v}}{\sqrt{2}} \begin{Bmatrix} \Gamma_{v'}' & E_r & E_r \\ E_r & \Gamma_v & A_2 \end{Bmatrix} \begin{Bmatrix} B_1 & \Gamma_1 & \Gamma_1' \\ B_2 & \Gamma_2 & \Gamma_2' \\ A_2 & \Gamma_v & \Gamma_{v'}' \end{Bmatrix} \\ & \times \left\{ [(v+1)(N-v)]^{\frac{1}{2}} \delta_{v',v+1} - [v(N-v+1)]^{\frac{1}{2}} \delta_{v',v-1} \right\} \Bigg], \end{aligned} \tag{36}$$

and nothing special appears apart from the usual selection rules contained in the recoupling coefficients and $\sigma_{ev} = \sigma_{ev}'$ which implies that one only needs to diagonalize one matrix of dimension $N + 1$.

If instead we use the unsymmetrized basis

$$\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle |v\Gamma_1, N - v\Gamma_2; \Gamma_v\rangle,$$

and perform first a projection onto the considered electronic state we obtain

$$\begin{aligned}\left\langle \widetilde{H}^{(0)}_{vibr} \right\rangle_{E_r} = {} & \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_{s_1}\left(N_1 + \frac{1}{2}\right) + \hbar\tilde{\omega}_{s_2}\left(N_2 + \frac{1}{2}\right) \\ & - \hbar\frac{\tilde{\lambda}}{2}(-1)^{\bar{\sigma}+1} i({}_{s_2}a^{+(B_2)}\,{}_{s_1}a^{(B_1)} - {}_{s_1}a^{+(B_1)}\,{}_{s_2}a^{(B_2)}), \end{aligned}$$

where we took into account the important property, established in [17]:

$$\left\langle\!\!\left\langle [1\,0]\frac{1}{2}1E_r\bar{\sigma}' \right| E^{(1,0A_2)} \left| [1\,0]\frac{1}{2}1E_r\bar{\sigma} \right\rangle\!\!\right\rangle = \frac{(-1)^{\bar{\sigma}+1}}{2}\delta_{\bar{\sigma},\bar{\sigma}'},$$

if *orientation II* is used. The eigenvalues are the same for both values $\bar{\sigma} = \bar{1}, \bar{2}$ since we have upon time reversal

$$\mathcal{K}\langle \tilde{H}^{(0)}_{vibr} \rangle_{E_r} \mathcal{K}^{-1}(\bar{\sigma} = \bar{1}) = \langle \tilde{H}^{(0)}_{vibr} \rangle_{E_r}(\bar{\sigma} = \bar{2}),$$

and within this orientation

$$\begin{aligned} & \mathcal{K}\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle |v\Gamma_1, N - v\Gamma_2; \Gamma_v\rangle = \\ & \qquad \left|[1\,0]\frac{1}{2}1E_r - \bar{\sigma}\right\rangle\!\!\right\rangle |v\Gamma_1, N - v\Gamma_2; \Gamma_v\rangle, \end{aligned}$$

with $-\bar{1} = \bar{2}$ and conversely. This results will also naturally appear in the following.

7.1.1 Eigenvalues and symmetry adapted states

We give a rather detailed account of the method we use to solve the eigenequation for the present problem since other vibronic cases to be considered in the next sections appeal to similar techniques. Also we wish to establish precisely the connection with previous results [26,27] for the same $E \otimes (b_1 + b_2)$ case. First we simplify temporarily the notation setting ${}_{s_2}a^{(B_2)} = a_2$ and ${}_{s_1}a^{(B_1)} = a_1$. Equation (35) becomes

$$\widetilde{H}^{(0)}_{vibr} = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_{s_1}\left(N_1 + \frac{1}{2}\right) + \hbar\tilde{\omega}_{s_2}\left(N_2 + \frac{1}{2}\right) + \hbar\tilde{\lambda}S_z i(a_2^+ a_1 - a_1^+ a_2), \quad (37)$$

and appears naturally as a function of the generators of an $u(2)$ algebra:

$$J_+ = J_+^{(A_2)} = a_1^+ a_2, \quad J_- = J_-^{(A_2)} = a_2^+ a_1,$$
$$J_z = J_z^{(A_1)} = \frac{1}{2}(N_1 - N_2). \quad (38)$$

With the results of [17] the polyad states can be written as $u(2) \supset su(2) \supset G$ covariant symmetry adapted states ($j = N/2$, $m = N/2 - v$):

$$|[N\,0]jm(\Gamma_v)\rangle\rangle = (-1)^{j-m}|j - m(\Gamma_1), j + m(\Gamma_2); \Gamma_v\rangle$$
$$= (-1)^{j-m}[(j-m)!(j+m)!)]^{-\frac{1}{2}} a_1^{+(j-m)} a_2^{+(j+m)}|0,0\rangle, \quad (39)$$

and the Hamiltonian (37) writes

$$\widetilde{H}^{(0)}_{vibr} = \hbar\tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_{s_1} + \tilde{\omega}_{s_2})}{2}(N+1) + \hbar(\tilde{\omega}_{s_1} - \tilde{\omega}_{s_2})J_z + \hbar 2\tilde{\lambda}S_z J_y. \quad (40)$$

We note here that the operator $J_y = i(a_2^+ a_1 - a_1^+ a_2)/2$ may be interpreted as the angular momentum operator, expressed in a Cartesian basis, of a pseudo two dimensional harmonic oscillator associated with the b_1 and b_2 modes. We may thus consider the unitary transformation to the pseudo-angular momentum basis [21,30]:

$$c_1 = \frac{1}{\sqrt{2}}(a_1 + ia_2); \qquad c_1^+ = \frac{1}{\sqrt{2}}(a_1^+ - ia_2^+),$$
$$c_2 = \frac{1}{\sqrt{2}}(a_1 - ia_2); \qquad c_2^+ = \frac{1}{\sqrt{2}}(a_1^+ + ia_2^+). \quad (41)$$

The set of operators $c_i^+ c_j$ span an equivalent $su(2)$ algebra with generators

$$J'_+ = c_1^+ c_2, \quad J'_- = c_2^+ c_1,$$
$$J'_z = \frac{1}{2}(N'_1 - N'_2), \quad (42)$$

which are unsymmetrized, except for J'_z with symmetry A_2; the $u(2)$ invariant is conserved $N = N_1 + N_2 = N'_1 + N'_2$. As before covariant but unsymmetrized states are obtained through:

$$|[N\,0]jm\rangle\rangle' = (-1)^{j-m}|j - m, j + m\rangle =$$
$$(-1)^{j-m}[(j-m)!(j+m)!)]^{-\frac{1}{2}} c_1^{+(j-m)} c_2^{+(j+m)}|0,0\rangle, \quad (43)$$

and the Hamiltonian (37) writes

$$\widetilde{H}^{(0)}_{vibr} = \hbar\tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_{s_1} + \tilde{\omega}_{s_2})}{2}(N+1) + \hbar(\tilde{\omega}_{s_1} - \tilde{\omega}_{s_2})J'_x - \hbar 2\tilde{\lambda}S_z J'_z. \quad (44)$$

Within orientation II for the pseudo-spin operator $S_z = \sigma_z/2$ we can use the concept of extended generators introduced in [31] to solve the eigenvalue equation for $\widetilde{H}^{(0)}_{vibr}$ in (40, 44). This determines unitary operators $U(\sigma_z J_\alpha)$ and $U'(\sigma_z J'_\alpha)$ such that

$$U(\sigma_z J_\alpha)\widetilde{H}^{(0)}_{vibr}U(\sigma_z J_\alpha)^{-1} = {}^{U}\widetilde{H}^{(0)}_{vibr}$$
$$= \hbar\tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_{s_1} + \tilde{\omega}_{s_2})}{2}(N+1) + \hbar\Omega(\sigma_z)J_z,$$
$$U'(\sigma_z J'_\alpha)\widetilde{H}^{(0)}_{vibr}U'(\sigma_z J'_\alpha)^{-1} = {}^{U'}\widetilde{H}'^{(0)}_{vibr}$$
$$= \hbar\tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_{s_1} + \tilde{\omega}_{s_2})}{2}(N+1) + \hbar\Omega(\sigma_z)J'_z, \quad (45)$$

with, in this case,

$$\Omega(\sigma_z) = [\tilde{\lambda}^2 + (\tilde{\omega}_{s_1} - \tilde{\omega}_{s_2})^2]^{1/2} \quad (46)$$

independent of σ_z. The operator $U(\sigma_z J_\alpha)$ is given by

$$U(\sigma_z J_\alpha) = \exp\left[-i\frac{(\Omega - \omega_0)}{\tilde{\lambda}}\sigma_z J_+\right]\exp\left[\ln(\frac{2\Omega}{\Omega + \omega_0})J_z\right]$$
$$\times \exp\left[-i\frac{(\Omega - \omega_0)}{\tilde{\lambda}}\sigma_z J_-\right]$$
$$= \exp[-2i\xi\sigma_z J_x], \quad (47)$$

where we set $\omega_0 = \tilde{\omega}_{s_1} - \tilde{\omega}_{s_2}$ and with

$$\tan\xi = \frac{(\Omega - \omega_0)}{\tilde{\lambda}}, \quad \cos\xi = \left[\frac{\Omega + \omega_0}{2\Omega}\right]^{1/2}.$$

For the $U'(\sigma_z J'_\alpha)$ operator we have

$$U'(\sigma_z J'_\alpha) = \exp\left[\frac{(\Omega + \tilde{\lambda}\sigma_z)}{\omega_0}J'_+\right]\exp\left[\ln\left(\frac{2\Omega}{\Omega - \tilde{\lambda}\sigma_z}\right)J'_z\right]$$
$$\times \exp\left[-\frac{(\Omega + \tilde{\lambda}\sigma_z)}{\omega_0}J'_-\right]$$
$$= \exp[2i\xi' J'_y], \quad (48)$$

with

$$\tan\xi' = \frac{\Omega + \tilde{\lambda}\,\sigma_z}{\omega_0}, \quad \cos\xi' = \left[\frac{\Omega - \tilde{\lambda}\,\sigma_z}{2\Omega}\right]^{1/2}.$$

Thus within the vibronic bases

$$\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle|[N\,0]jm(\Gamma_v)\rangle\rangle, \quad \left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle|[N\,0]jm\rangle\rangle',$$

for ${}^{U}\widetilde{H}^{(0)}_{vibr}$ and ${}^{U'}\widetilde{H}'^{(0)}_{vibr}$, respectively, we obtain the eigenvalues

$$E^{(0)}_{vibr} = \hbar\tilde{\lambda}_0 + \frac{(\tilde{\omega}_{s_1} + \tilde{\omega}_{s_2})}{2}(N+1) + \hbar[(\tilde{\omega}_{s_1} - \tilde{\omega}_{s_2})^2 + \tilde{\lambda}^2]^{\frac{1}{2}}\,m, \quad m\colon -j, \cdots + j. \quad (49)$$

This expression shows, as predicted, that these eigenvalues are independent of $\bar{\sigma}$. The symmetrized vibronic eigenstates are obtained through a two steps procedure.

Firstly from the expressions of the $U(\sigma_z J_\alpha)$ and $U'(\sigma_z J'_\alpha)$ operators (47, 48) we obtain unsymmetrized eigenstates of $\widetilde{H}^{(0)}_{vibr}$:

$$\begin{aligned}
&\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle|[N\,0]jm(\theta_e)\rangle\rangle\\
&\quad= U(\sigma_z J_\alpha)^{-1}\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle|[N\,0]jm(\Gamma_v)\rangle\rangle\\
&\quad= \exp[2i\xi\sigma_z J_x]\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle|[N\,0]jm(\Gamma_v)\rangle\rangle\\
&\quad= \sum_{m'} e^{i(m-m')\frac{\pi}{2}} d^{(j)}_{m'm}(2\xi(-1)^{\bar{\sigma}})\\
&\qquad\times\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle|[N\,0]jm'(\Gamma')\rangle\rangle,
\end{aligned}\tag{50}$$

with $\theta_e = \theta_1$ ($\theta_e = \theta_2 = -\theta_1$) when $\bar{\sigma} = \bar{1}$ ($\bar{\sigma} = \bar{2}$) and

$$\cos\theta_e = \frac{\omega_0}{\Omega},\quad \sin\theta_e = \frac{\tilde{\lambda}}{\Omega}(-1)^{\bar{\sigma}}.\tag{51}$$

Likewise with the $U'(\sigma_z J'_\alpha)$ operator we obtain the eigenstates in the form

$$\begin{aligned}
&\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle|[N\,0]jm(\theta'_e)\rangle\rangle'\\
&\quad= U'(\sigma_z J'_\alpha)^{-1}\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle|[N\,0]jm\rangle\rangle'\\
&\quad= \exp[-2i\xi' J'_y]\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle|[N\,0]jm\rangle\rangle'\\
&\quad= \sum_{m'} d^{(j)}_{mm'}(2\xi'(\bar{\sigma}))\\
&\qquad\times\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle|[N\,0]jm'\rangle\rangle',
\end{aligned}\tag{52}$$

with $\theta'_e = \theta'_1$ ($\theta'_e = \theta'_2 = \pi - \theta'_1$) when $\bar{\sigma} = \bar{1}$ ($\bar{\sigma} = \bar{2}$) and

$$\cos\theta'_e = \frac{\tilde{\lambda}}{\Omega}(-1)^{\bar{\sigma}+1},\quad \sin\theta'_e = \frac{\omega_0}{\Omega}.\tag{53}$$

In equations (50, 52) the $d^{(j)}$ Wigner matrices are those given for instance in [32]. In a second step, starting from the preceding states (50, 52) and using techniques similar to those presented in [17] we obtain the symmetrized vibronic eigenstates

$$\begin{aligned}
&\left|[1\,0]\frac{1}{2}1E_r,[N\,0]jm(\theta_e);E_r\bar{\sigma}\right\rangle\!\!\right\rangle =\\
&\qquad e^{i\varphi(\tau)}\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}_e\right\rangle\!\!\right\rangle|[N\,0]jm(\theta_e)\rangle\rangle,
\end{aligned}\tag{54}$$

$$\begin{aligned}
&\left|[1\,0]\frac{1}{2}1E_r,[N\,0]jm(\theta'_e);E_r\bar{\sigma}\right\rangle\!\!\right\rangle' =\\
&\qquad e^{i\varphi'(\tau')}\left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}_e\right\rangle\!\!\right\rangle|[N\,0]jm(\theta'_e)\rangle\rangle',
\end{aligned}\tag{55}$$

which are respectively eigenstates of the sets $\widetilde{H}^0_{vibr}, S_z, \tilde{J}_z$ and $\widetilde{H}^0_{vibr}, S_z, \tilde{J}'_z$. The values for the phase factors $e^{i\varphi(\tau)}$ and $e^{i\varphi'(\tau')}$ as a function of the other quantum numbers are given by:

$$\begin{array}{cccccc}
j & j-m & \bar{\sigma}_e & \theta_e & e^{i\varphi(\tau)} & \bar{\sigma}\\
\text{integer} & \text{even} & \bar{1} & \theta_1 & 1 & \bar{1}\\
 & & \bar{2} & -\theta_1 & 1 & \bar{2}\\
 & \text{odd} & \bar{1} & \theta_1 & i & \bar{1}\\
 & & \bar{2} & -\theta_1 & -i & \bar{2}\\
\text{half- integer} & \text{even} & \bar{1} & \theta_1 & i & \bar{2}\\
 & & \bar{2} & -\theta_1 & -i & \bar{1}\\
 & \text{odd} & \bar{1} & \theta_1 & 1 & \bar{2}\\
 & & \bar{2} & -\theta_1 & 1 & \bar{1}
\end{array}\tag{56}$$

for the states (54). On the other hand for the states (55) we have

$$\begin{aligned}
&\left|[1\,0]\frac{1}{2}1E_r,[N\,0]jm(\theta'_1);E_r\bar{1}\right\rangle\!\!\right\rangle' \quad j\text{ integer}\\
&\quad= \left|[1\,0]\frac{1}{2}1E_r\bar{1}\right\rangle\!\!\right\rangle|[N\,0]jm(\theta'_1)\rangle\rangle'\\
&\left|[1\,0]\frac{1}{2}1E_r,[N\,0]jm(\theta'_2);E_r\bar{2}\right\rangle\!\!\right\rangle'\\
&\quad= (-1)^{j+m}\left|[1\,0]\frac{1}{2}1E_r\bar{2}\right\rangle\!\!\right\rangle|[N\,0]jm(\theta'_2)\rangle\rangle'
\end{aligned}\tag{57}$$

$$\begin{aligned}
&\left|[1\,0]\frac{1}{2}1E_r,[N\,0]jm(\theta'_2);E_r\bar{1}\right\rangle\!\!\right\rangle' \quad j\text{ half-integer}\\
&\quad= \left|[1\,0]\frac{1}{2}1E_r\bar{2}\right\rangle\!\!\right\rangle|[N\,0]jm(\theta'_2)\rangle\rangle'\\
&\left|[1\,0]\frac{1}{2}1E_r,[N\,0]jm(\theta'_1);E_r\bar{2}\right\rangle\!\!\right\rangle'\\
&\quad= (-1)^{j+m}\left|[1\,0]\frac{1}{2}1E_r\bar{1}\right\rangle\!\!\right\rangle|[N\,0]jm(\theta'_1)\rangle\rangle'.
\end{aligned}\tag{58}$$

To conclude we note that the algebraic chain adapted to the considered case allowing to find the exact eigenvalues is

$$\begin{array}{ccccccccc}
u(2)_e & \oplus & u(2)_{s_1s_2} & \supset & su^*(2)_e & \oplus & su^*(2)_{s_1s_2} & \supset & G\\
[1\,0] & \times & [N\,0] & \downarrow & \frac{1}{2} & \times & j & \downarrow & \Gamma_{ev}\sigma_{ev}
\end{array}\tag{59}$$

instead of the common $u(2)_e \oplus (u(1)_{s_1} \oplus u(1)_{s_2}) \supset G$ associated with basis (33).

7.1.2 Correlations with previous studies

One of the very first study of the dynamical JT effect in molecules with a four-fold axis of symmetry is that of Child [33]; it was then reconsidered in [26] and by Hougen [27]. The standard starting point is given by the terms in equation (26) in terms of Pauli matrices

$$\begin{aligned}
\widehat{H}^{(0)} = \widehat{\sigma}_0\left\{\hbar\omega_{s_1}\left(N_{s_1}+\frac{1}{2}\right)+\hbar\omega_{s_2}\left(N_{s_2}+\frac{1}{2}\right)\right\}\\
+\widehat{\sigma}_x\ V_{1\ s_1}Q^{(B_1)}+\widehat{\sigma}_y\ V_{2\ s_2}Q^{(B_2)}.
\end{aligned}\tag{60}$$

The notation in equation (60) is that of [4] and related to those in [26,27] by

$$V_1 = k_1 = f, \quad V_2 = k_2 = -g; \quad \hbar\omega_i D_i = \frac{V_i^2}{2\omega_i^2}. \tag{61}$$

Approximate solutions of equation (60), for the eigenvalues only, have been given in several limiting cases:

(i) $\omega_{s_1} \simeq \omega_{s_2}$
With this assumption equation (49) may be written as

$$\begin{aligned} E^{(0)}_{vibr} &\approx \tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_{s_1} + \tilde{\omega}_{s_2})}{2}(N+1) \\ &\quad + \hbar\tilde{\lambda}\left[1 + \frac{(\tilde{\omega}_{s_1} - \tilde{\omega}_{s_2})^2}{2\tilde{\lambda}^2} + \cdots\right] m, \end{aligned} \tag{62}$$

with $2m = N, N-2 \cdots - N$. The limiting case considered in [26] $\omega_{s_1} = \omega_{s_2} = \omega$ amounts to keep only the zeroth-order term in the preceding expansion and leads to the relations between parameters

$$\begin{aligned} &\tilde{\lambda}_0 = -(D_1 + D_2)\,\omega, \quad \frac{(\tilde{\omega}_{s_1} + \tilde{\omega}_{s_2})}{2} = \omega, \\ &\frac{\tilde{\lambda}}{2} = 2\sqrt{D_1 D_2}\,\omega. \end{aligned} \tag{63}$$

The additional assumption of equal couplings $V_1 = V_2$ in equation (60) transforms the $E \otimes (b_1 + b_2)$ case to an equivalent $E \otimes e$ one [4,27]. The energies have been given, within the same order of approximation, by several authors [1,4,34,35] in the form ($\omega \equiv \omega_E$)

$$\begin{aligned} E^{(0)} &= \hbar\omega_E(n+1) - \frac{V_E^2}{\omega_E^2}(1 \pm \ell_2) \\ &= \hbar\omega_E(n+1) - \frac{V_E^2}{\omega_E^2}\left(j_2^2 - \ell_2^2 + \frac{3}{4}\right), \end{aligned} \tag{64}$$

where ℓ_2 is the pseudo doubly degenerate oscillator angular momentum and $j_2 = \ell_2 \pm 1/2$. We find then from (62, 63):

$$\begin{aligned} &\tilde{\lambda}_0 = -2D\omega = -\frac{V_E^2}{\hbar\omega_E^2}, \quad \frac{(\tilde{\omega}_{s_1} + \tilde{\omega}_{s_2})}{2} = \omega, \\ &\frac{\tilde{\lambda}}{2} = 2D\omega = \frac{V_E^2}{\hbar\omega_E^2}. \end{aligned} \tag{65}$$

In this case where $\omega_{s_1} \simeq \omega_{s_2}$ it is clear that the appropriate form for $\widetilde{H}^0_{vibr}$ is that given by equation (44). It can easily be checked from equations (46, 53) that

$$\cos\theta'_e \to \mp 1, \quad \sin\theta'_e \to 0.$$

So in the limiting case $\omega_{s_1} = \omega_{s_2}$ the vibrational functions in (52) reduce to the usual oscillator states in the angular momentum basis (43):

$$\begin{aligned} &|[N\,0]jm(\theta'_1 = 0)\rangle\rangle' = |[N\,0]jm\rangle\rangle', \\ &|[N\,0]jm(\theta'_2 = \pi)\rangle\rangle' = (-1)^{j-m}|[N\,0]j-m\rangle\rangle'. \end{aligned}$$

The associated symmetry adapted vibronic states are given by (57) with $\theta'_1 = 0$, $\theta'_2 = \pi$.

(ii) $(\omega_{s_1} - \omega_{s_2})/(\omega_{s_1} + \omega_{s_2}) \gg \sqrt{D_1 D_2}$
In this case we write equation (49):

$$\begin{aligned} E^{(0)}_{vibr} &\approx \tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_{s_1} + \tilde{\omega}_{s_2})}{2}(N+1) \\ &\quad + \hbar(\tilde{\omega}_{s_1} - \tilde{\omega}_{s_2})\left[1 + \frac{\tilde{\lambda}^2}{2(\tilde{\omega}_{s_1} - \tilde{\omega}_{s_2})^2} + \cdots\right] m. \end{aligned} \tag{66}$$

Keeping terms up to the first order, the comparison with the corresponding result in [26] gives

$$\begin{aligned} &\tilde{\lambda}_0 = -D_1\,\omega_1 - D_2\,\omega_2, \quad \tilde{\omega}_{s_1} = \omega_1, \\ &\frac{\tilde{\lambda}}{2} = \sqrt{D_1 D_2}(\,\omega_1 + \,\omega_2), \quad \tilde{\omega}_{s_2} = \omega_2. \end{aligned} \tag{67}$$

The appropriate form for $\widetilde{H}^0_{vibr}$ is now that given by equation (40) and we deduce from equations (46, 51) that

$$\cos\theta_e \to 1, \quad \sin\theta_e \to 0.$$

So for large $\omega_{s_1} - \omega_{s_2}$ values the vibrational functions in (50) reduce to the usual oscillator states in the Cartesian basis (39):

$$\begin{aligned} |[N\,0]jm(\theta_1 = 0)\rangle\rangle &= |[N\,0]jm(\theta_2 = 0)\rangle\rangle \\ &= |[N\,0]jm\rangle\rangle. \end{aligned}$$

The associated symmetry adapted vibronic states are given by (54, 56) with $\theta_1 = \theta_2 = 0$.

7.2 E ⊗ (b$_\mathsf{i}$ + a$_\mathsf{j}$) case

In such a case we have one active coordinate b_i ($i = 1$ or 2) and we assume a non zero coupling with a non-active mode with symmetry A_j ($j = 1$ or 2) (Eq. (23)). Most of the time only totally symmetric modes are considered but all cases can be treated within a unique formalism. The importance of taking into account such quadratic couplings was first established by Bacci [24]. More recently the influence of large quadratic couplings in $E \otimes e$ problems has been investigated [9,36]. The most general effective vibronic Hamiltonian is of the form

$$\begin{aligned} \widetilde{H}_{vibr} = I_e \Bigg\{ &\sum_n {}_s\tilde{t}^{C_iC_i(A_1)}_{\{n_i\}\{n_i\}}\; {}^0_sV^{C_iC_i(A_1)}_{\{n_i\}\{n_i\}} \\ &+ {}_{s'}\tilde{t}^{C_jC_j(A_1)}_{\{n_j\}\{n_j\}}\; {}^0_{s'}V^{C_jC_j(A_1)}_{\{n_j\}\{n_j\}} \\ &+ \sum_{\{n\}\{n'\}} {}_{ss'}\tilde{t}^{C_iC_j\,C_iC_j(A_1)}_{\{n_in_j\}\{n'_in'_j\}}\; {}^0_{ss'}V^{C_iC_j\,C_iC_j(A_1)}_{\{n_in_j\}\{n'_in'_j\}} \Bigg\} \\ &+ E^{(1,2B_k)} \sum_n {}_{ss'}\tilde{t}^{C_iC_j\,C'_iC'_j(B_k)}_{\{n_in_j\}\{n'_in'_j\}}\; {}^0_{ss'}V^{C_iC_j\,C'_iC'_j(B_k)}_{\{n_in_j\}\{n'_in'_j\}}, \end{aligned} \tag{68}$$

with $C_i(C'_i) = B_i$ for $n_i(n'_i)$ odd and $C_i(C'_i) = A_1$ for $n_i(n'_i)$ even; likewise $C_j(C'_j) = A_j$ for $n_j(n'_j)$ odd and

$C_j(C'_j) = A_1$ for $n_j(n'_j)$ even. As before we have the conditions $n_i + n_j = n'_i + n'_j$ and the matrix elements are nonzero only if $n'_i + n'_j \leq N$. In Appendix C.1 equation (68) is detailed for the cases $N \leq 2$.

In order to obtain the dominant features of the zeroth-order spectrum as well as good symmetry adapted basis functions we take the following approximate expression:

$$\begin{aligned}\widetilde{H}^{(0)}_{vibr} = {} & \tilde{t}^{A_1A_1(A_1)}_{\{0\}\{0\}} I_v + {}_s\tilde{t}^{B_iB_i(A_1)}_{\{1\}\{1\}}\ {}^0_sV^{B_iB_i(A_1)}_{\{1\}\{1\}} \\ & + {}_{s'}\tilde{t}^{A_jA_j(A_1)}_{\{1\}\{1\}}\ {}^0_{s'}V^{A_jA_j(A_1)}_{\{1\}\{1\}} \\ & + E^{(1,2B_k)}\ {}_{ss'}\tilde{t}^{B_iA_1\,A_1A_j(B_k)}_{\{10\}\{01\}}\ {}^0_{ss'}V^{B_iA_1\,A_1A_j(B_k)}_{\{10\}\{01\}}. \end{aligned} \tag{69}$$

All matrix elements can be computed straightforwardly in the coupled basis $|[1\,0]\frac{1}{2}1E_r, (v_s\Gamma_i, v'_{s'}\Gamma_j)\Gamma_v; E_r\sigma_{ev}\rangle$ (in all cases the overall symmetry of states is E_r since $A_j \times E_r = B_i \times E_r = E_r$) and are given in Appendix C.2. However for our purpose it is not the best choice. Equation (69) may also be written

$$\begin{aligned}\widetilde{H}^{(0)}_{vibr} = {} & \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s\left(N_s + \frac{1}{2}\right) + \hbar\tilde{\omega}_{s'}\left(N'_{s'} + \frac{1}{2}\right) \\ & + \hbar\tilde{\lambda}S_\alpha({}_sa^{+(B_i)}\,{}_{s'}a^{(A_j)} + {}_{s'}a^{+(A_j)}\,{}_sa^{(B_i)}), \end{aligned} \tag{70}$$

with $\alpha = x$ (resp. y) when $k = 1$ (resp. $k = 2$) in equation (69). Although the symmetries of electronic operators are different from that of Section 7.1 (Eq. (34)) we can take advantage of the various orientations for the E *irreps* defined in [17] if we start from the unsymmetrized vibronic bases

$$\left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\Big\rangle |v\Gamma_i, N - v\Gamma_j; \Gamma_v\rangle,$$

since we have

$$\left\langle\!\!\left\langle [1\,0]\frac{1}{2}1E_r\sigma'_e \right| E^{(1,2B_k)} \left| [1\,0]\frac{1}{2}1E_r\sigma_e \right\rangle\!\!\right\rangle = \frac{(-1)^{\sigma_e+1}}{2}\,\delta_{\sigma_e,\sigma'_e},$$

if and only if *orientation I* ($\sigma_e = \sigma$) is used when $B_k = B_1$ and *orientation III* ($\sigma_e = \bar{\bar{\sigma}}$) when $B_k = B_2$ in (69). We note that these symmetries are those of the active coordinate only for totally symmetric $A_j = A_1$ modes.

Setting ${}_sa^{(B_i)} = a_1$ and ${}_{s'}a^{(A_j)} = a_2$ equation (70) takes a form similar to one of those encountered previously (see Eq. (44))

$$\begin{aligned}\widetilde{H}^{(0)}_{vibr} & = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s\left(N_1 + \frac{1}{2}\right) + \hbar\tilde{\omega}_{s'}\left(N_2 + \frac{1}{2}\right) \\ & \quad + \hbar\tilde{\lambda}S_\alpha(a_1^+a_2 + a_2^+a_1) \\ & = \hbar\tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_s + \tilde{\omega}_{s'})}{2}(N + 1) \\ & \quad + \hbar(\tilde{\omega}_s - \tilde{\omega}_{s'})J_z + \hbar 2\tilde{\lambda}S_\alpha J_x, \end{aligned} \tag{71}$$

and is again a function of the generators of an $u(2)$ algebra:

$$\begin{aligned} & J_+ = J_+^{(B_k)} = a_1^+a_2, \quad J_- = J_-^{(B_k)} = a_2^+a_1, \\ & J_z = J_z^{(A_1)} = \frac{1}{2}(N_1 - N_2). \end{aligned} \tag{72}$$

But this time the last term in equation (71) involving $J_x = (a_1^+a_2 + a_2^+a_1)/2$ cannot be interpreted as the angular momentum of a pseudo two-dimensional oscillator associated with the b_i and a_j modes. As before the polyad states are given by $u(2) \supset su(2) \supset G$ covariant symmetry adapted states built from the a_i^+ ($j = N/2$, $m = N/2 - v$):

$$\begin{aligned}|[N\,0]jm(\Gamma_v)\rangle\rangle = {} & (-1)^{j-m}[(j-m)!(j+m)!]^{-1/2} \\ & \times |j - m(\Gamma_i), j + m(\Gamma_j); \Gamma_v\rangle. \end{aligned}$$

Keeping in mind the discussion of the preceding section, this basis may be seen as adapted to a small coupling regime. A new basis may be defined for the case $\tilde{\omega}_s \simeq \tilde{\omega}_{s'}$. Among the various possible unitary transformations we choose the orthogonal one

$$\begin{aligned} & c_1 = \frac{1}{\sqrt{2}}(a_1 + a_2); \quad c_1^+ = \frac{1}{\sqrt{2}}(a_1^+ + a_2^+), \\ & c_2 = \frac{1}{\sqrt{2}}(a_1 - a_2); \quad c_2^+ = \frac{1}{\sqrt{2}}(a_1^+ - a_2^+), \end{aligned} \tag{73}$$

which keeps the Hamiltonian (71) in the same form

$$\begin{aligned}\widetilde{H}^{(0)}_{vibr} & = \hbar\tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_s + \tilde{\omega}_{s'})}{2}(N + 1) \\ & \quad + \hbar\frac{(\tilde{\omega}_s - \tilde{\omega}_{s'})}{2}(c_1^+c_2 + c_2^+c_1) + \hbar\tilde{\lambda}S_\alpha(c_1^+c_1 - c_2^+c_2) \\ & = \hbar\tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_s + \tilde{\omega}_{s'})}{2}(N + 1) + \hbar(\tilde{\omega}_s - \tilde{\omega}_{s'})J'_x + \hbar 2\tilde{\lambda}S_\alpha J'_z, \end{aligned} \tag{74}$$

with corresponding basis states of the form (43). We can thus proceed as in Section 7.1.1 with unitary operators $U(\sigma_\alpha J_\beta)$ and $U'(\sigma_\alpha J'_\beta)$ [31] ($\sigma_\alpha = 2S_\alpha$) to solve the eigenvalue equation for $\widetilde{H}^{(0)}_{vibr}$. In particular it appears that, within the considered order of approximation, the eigenvalues are given by equation (49) with the substitution $s_1 \to s$, $s_2 \to s'$ and the appropriate algebraic chain for the $E\otimes(b_i + a_j)$ problem is similar to that in equation (59). The symmetry adapted eigenbasis is obtained with a procedure identical to that in Section 7.1.1 using electronic states whose orientation is determined by the k value in the product $B_i \times A_j = B_k$; these are explicitly given together with the U and U' operators in Appendix C.3.

7.3 E ⊗ b_i cases

If in the two previous models we assume a negligible vibronic coupling for one of the two modes we are left with an $E\otimes b_i$ problem or two uncoupled such cases (accidental

Born-Oppenheimer case [27]). As can be seen from equations (32, 68) the effective Hamiltonian reduces to a polynomial expansion in the number operator which writes, keeping only one b_i mode

$$\begin{aligned}\widetilde{H}_{vibr} &= I_e \left\{ \sum_n {}_{s_i}\tilde{t}^{C_iC_i(A_1)}_{\{n\}\{n\}}\ {}^{0}_{s_i}V^{C_iC_i(A_1)}_{\{n\}\{n\}} \right\} \\ &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_{s_i}\left(N_{s_i} + \frac{1}{2}\right) + \sum_{n>1} {}_{s_i}\tilde{t}^{C_iC_i(A_1)}_{\{n\}\{n\}}\ {}^{0}_{s_i}V^{C_iC_i(A_1)}_{\{n\}\{n\}},\end{aligned} \tag{75}$$

where the electronic operators reduce to the identity. Within the same order of approximation than previously (Sects. 7.1.1, 7.2) we simply have

$$\widetilde{H}^0_{vibr} = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_{s_i}\left(N_{s_i} + \frac{1}{2}\right), \tag{76}$$

and we will show that this reflects the known exact solvability of the linear $E \otimes b_i$ JT system [4]. Also it is one of the very few cases where the effective operators can be given a precise interpretation.

The untransformed Hamiltonian is given by (Eq. (23))

$$\begin{aligned} H &= \hbar\omega_{s_i}\left(N_s + \frac{1}{2}\right) + \ {}_{s_i}t^{B_i}\ {}^{[1\,-1]}E^{(1,2B_i)}\ {}_sQ^{(B_i)} \\ &= \hbar\omega_{s_i}\left({}_{s_i}a^{+(B_i)}\,{}_{s_i}a^{(B_i)} + \frac{1}{2}\right) \\ &\quad + \hbar\delta\left({}_{s_i}a^{+(B_i)} + {}_{s_i}a^{(B_i)}\right)S_\alpha, \end{aligned} \tag{77}$$

with $\hbar\delta = \ {}_{s_i}t^{B_i}\sqrt{\hbar/2\omega_{s_i}}$. Usually [4,27] H is projected onto the electronic subspace which leads to two uncoupled eigenvalue equations for the vibronic matrix $\widehat{H}$. We prefer to use the formalism developed in [31] which allows to treat both symmetries b_1 and b_2 simultaneously; also it gives through a unique transformation both the eigenvalues and eigenstates. With the unitary operator

$$\begin{aligned} &U(S_\alpha, {}_{s_i}a^{+(B_i)}, {}_{s_i}a^{(B_i)}) = \\ &\qquad \exp\left[\frac{\delta}{\omega_{s_i}}({}_{s_i}a^{+(B_i)} - {}_{s_i}a^{(B_i)})S_\alpha\right], \end{aligned} \tag{78}$$

function of the extended generators of the harmonic oscillator algebra, we obtain

$${}^UH = UHU^{-1} = \hbar\omega_{s_i}\left({}_{s_i}a^{+(B_i)}\,{}_{s_i}a^{(B_i)} + \frac{1}{2}\right) - \hbar\frac{\delta^2}{4\omega_{s_i}}, \tag{79}$$

with doubly degenerate energies

$$E_{n_i\pm} = \hbar\omega_{s_i}\left(n_i + \frac{1}{2}\right) - \hbar\frac{\delta^2}{4\omega_{s_i}}, \tag{80}$$

in the vibronic bases

$$\begin{aligned} |n_i\Gamma_i\rangle|\pm\rangle &= |n_i\Gamma_i\rangle\left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\right\rangle \\ &= (n_i!)^{-1/2}\,{}_{s_i}a^{+(B_i)n_i}|0\rangle\left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\right\rangle, \end{aligned} \tag{81}$$

with $\sigma_e = 1, 2$ (resp. $\sigma_e = \bar{\bar{1}}, \bar{\bar{2}}$) when $B_i = B_1$ and $\alpha = x$ (resp. $B_i = B_2$ and $\alpha = y$). With equations (76, 80) we obtain

$$\tilde{\omega}_{s_i} = \omega_{s_i}, \quad \tilde{\lambda}_0 = -\frac{\delta^2}{4\omega_{s_i}}.$$

The corresponding degenerate eigenstates of H (77) are next obtained with

$$\begin{aligned} |\widetilde{n_i\Gamma_i\pm}\rangle &= \exp\left[-\frac{\delta}{\omega_{s_i}}({}_{s_i}a^{+(B_i)} - {}_{s_i}a^{(B_i)})S_\alpha\right]|n_i\Gamma_i\rangle|\pm\rangle \\ &= (n_i!)^{-\frac{1}{2}}\left({}_{s_i}a^{+(B_i)} + \frac{\delta}{\omega_{s_i}}S_\alpha\right)^{n_i}|\widetilde{0A_1\pm}\rangle \\ &= (n_i!)^{-\frac{1}{2}}\left({}_{s_i}a^{+(B_i)} + \frac{\delta}{\omega_{s_i}}S_\alpha\right)^{n_i}\left|\mp\frac{\delta}{2\omega_i}A_1\right\rangle||\pm\rangle, \end{aligned} \tag{82}$$

where $|\mp(\delta/2\omega_i)A_1\rangle$ are two totally symmetric oscillator coherent states [37,38]. We note that we may alternatively write the Hamiltonian (77) in term of generalized displaced creation and annihilation operators

$$\begin{aligned} &{}_{s_i}b^{+(B_i)} = {}_{s_i}a^{+(B_i)} + \frac{\delta}{\omega_{s_i}}S_\alpha, \quad {}_{s_i}b^{(B_i)} = {}_{s_i}a^{(B_i)} + \frac{\delta}{\omega_{s_i}}S_\alpha, \\ &H = \hbar\omega_{s_i}\left({}_{s_i}b^{+(B_i)}\,{}_{s_i}b^{(B_i)} + \frac{1}{2}\right) - \hbar\frac{\delta^2}{4\omega_{s_i}}. \end{aligned}$$

With both approaches symmetry adapted eigenstates are easily obtained since, within the appropriate orientation, all CGC reduce to a phase (Appendix A.4, Tab. 2)

$$F\begin{matrix} \sigma_e & (E_r) \\ (E_r\ \Gamma_i) & \sigma'_e \end{matrix} = e^{i\varphi}\,\delta_{\sigma_e,\sigma'_e},$$

and the operator entering the exponential in (78) is totally symmetric in G.

We note that for a $E \otimes (b_i + b_i)$ case, within the same order of approximation, the effective Hamiltonian is of the form

$$\begin{aligned} \widetilde{H}^{(0)}_{vibr} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s\left(N_s + \frac{1}{2}\right) + \hbar\tilde{\omega}_{s'}\left(N'_{s'} + \frac{1}{2}\right) \\ &\quad + \hbar\tilde{\lambda}({}_sa^{+(B_i)}\,{}_{s'}a^{(B_i)} + {}_{s'}a^{+(B_i)}\,{}_sa^{(B_i)}), \end{aligned} \tag{83}$$

where the electronic operators reduce once again to the identity. It can also be written

$$\begin{aligned} \widetilde{H}^{(0)}_{vibr} &= \hbar\tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_s + \tilde{\omega}_{s'})}{2}(N+1) \\ &\quad + \hbar\frac{(\tilde{\omega}_s - \tilde{\omega}_{s'})}{2}(N_s - N'_{s'}) \\ &\quad + \hbar\tilde{\lambda}({}_sa^{+(B_i)}\,{}_{s'}a^{(B_i)} + {}_{s'}a^{+(B_i)}\,{}_sa^{(B_i)}) \\ &= \hbar\tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_s + \tilde{\omega}_{s'})}{2}(N+1) \\ &\quad + \hbar(\tilde{\omega}_s - \tilde{\omega}_{s'})J_z + \hbar 2\tilde{\lambda}J_x, \end{aligned} \tag{84}$$

and diagonalized through a standard unitary transformation of the $su(2)$ algebra [37] built from the elementary boson operators associated with s and s' modes:

$$J_+ = J_+^{(A_1)} = {}_{s}a^{+(B_i)}{}_{s'}a^{(B_i)},\ J_z = J_z^{(A_1)} = \frac{1}{2}(N_s - N'_{s'}),$$
$$J_- = J_-^{(A_1)} = {}_{s'}a^{+(B_i)}{}_{s}a^{(B_i)}.$$

However since this time the untransformed vibronic Hamiltonian contains, besides the linear terms as in (77), cubic ones involving ${}_{s}(Q^{(B_i)})^2{}_{s'}Q^{(B_i)}$ and ${}_{s}Q^{(B_i)}{}_{s'}(Q^{(B_i)})^2$, one cannot expect to find the exact transformation between the two approaches.

7.4 $\mathbf{E \otimes (b_i + e_r)}$ and $\mathbf{E \otimes e_r}$

For the electronic states considered in this paper it can be seen from equation (23) that vibronic coupling terms involving modes with the same E symmetry type as the electronic state are possible; also purely vibrational cubic couplings are allowed in the untransformed Hamiltonian expansion. We recall that r equals $n/4$ for C_{nv} and D_n groups and $n/2$ for D_{nd} groups. In both cases the vibrational operators for the doubly degenerate mode are of the form [17]:

$$\begin{aligned} &{}^{[m_1\ -m_2]}_{\qquad\ \ s}\mathcal{V}^{(j_v)}_{\ell_v\Gamma_v\sigma_v} = {}^{[m_1\ -m_2]}_{\qquad\ \ s}\mathcal{V}^{(j_v,\ell_v\Gamma_v)}_{\sigma_v} \\ &\text{with}\quad \begin{array}{ll} \ell_v = 4p & \Gamma_v = A_1, A_2 \\ \ell_v = 4p+2 & \Gamma_v = B_1, B_2\,, \\ \ell_v = 4p+1, 4p+3 & \Gamma_v = E_r \end{array} \end{aligned} \tag{85}$$

and the most general effective vibronic Hamiltonian writes (Appendix A)

$$\begin{aligned} \widetilde{H}_{vibr} = I_e \Bigg\{ & \sum_n {}_{s'}\tilde{t}^{C_iC_i(A_1)}_{\{n_i\}\{n_i\}}\ {}^{0}_{s'}V^{C_iC_i(A_1)}_{\{n_i\}\{n_i\}} \\ & + {}_{s}\tilde{t}^{j_v,4pA_1(A_1)}_{\{n\}\{n\}}\ {}^{[n\ -n]}_{\quad\ s}\mathcal{V}^{(j_v,4p\,A_1)} \\ + & \sum_{\{n\}\{n'\}} {}_{s's}\tilde{t}^{\gamma_i\gamma_v(C)\,\gamma'_i\gamma'_v(C)(A_1)}_{\{n_in\}\{n'_in'\}}\ {}^{\ 0}_{s's}V^{\gamma_i\gamma_v(C)\,\gamma_i\gamma_v(C)(A_1)}_{\{n_in\}\{n'_in'\}} \Bigg\} \\ & + E^{(1,0A_2)} \Bigg\{ \sum_{\{n\}\{n'\}} {}_{s}\tilde{t}^{j_v,4pA_2(A_2)}_{\{n\}\{n\}}\ {}^{[n\ -n]}_{\quad\ s}\mathcal{V}^{(j_v,4p\,A_2)} \\ & + {}_{s's}\tilde{t}^{\gamma_i\gamma_v(C)\,\gamma'_i\gamma'_v(C')(A_2)}_{\{n_in\}\{n'_in'\}}\ {}^{\ 1}_{s's}V^{\gamma_i\gamma_v(C)\,\gamma'_i\gamma'_v(C')(A_2)}_{\{n_in\}\{n'_in'\}} \Bigg\} \\ + & \sum_{t=1,2} E^{(1,2B_t)} \Bigg\{ \sum_{\{n\}\{n'\}} {}_{s}\tilde{t}^{j_v,4p+2B_t(B_t)}_{\{n\}\{n\}}\ {}^{[n\ -n]}_{\quad\ s}\mathcal{V}^{(j_v,4p+2\,B_t)} \\ & + {}_{s's}\tilde{t}^{\gamma_i\gamma_v(C)\,\gamma'_i\gamma'_v(C')(B_t)}_{\{n_in\}\{n'_in'\}}\ {}^{\ 0}_{s's}V^{\gamma_i\gamma_v(C)\,\gamma'_i\gamma'_v(C')(B_t)}_{\{n_in\}\{n'_in'\}} \Bigg\}, \end{aligned} \tag{86}$$

where we set $\gamma_i\gamma_v = C_ij_v\ell_v\Gamma_v$; s' is associated with the b_i active coordinate and s with the e_r mode. In (86) we have $n_i + n = n'_i + n' \leq N$ and the summation over the other indices is implied. In Appendix D.1 the Hamiltonian (86) is detailed for the cases $N \leq 2$.

As in the previous sections the computation of matrix elements can be made in the coupled basis

$$\left|[1\,0]\frac{1}{2}1E_r; v'_{s'}\Gamma_i, [v_s\,0]j\ell\Gamma; \Gamma_v; \Gamma_{ev}\sigma_{ev}\right\rangle, \tag{87}$$

with $v'_{s'} + v_s = N$ and associated with the algebraic chain:

$$\begin{array}{ccccccccc} u(2)_e & \oplus & (u(1)_{s'} & \oplus & u(2)_s) & \supset & & & \\ [1\,0] & \times & v'_{s'} & \times & [v_s\,0] & \downarrow & & & \\ & & su^*(2)_e & \oplus & (u(1)_{s'} & \oplus & su^*(2)_s) & \supset & G \\ & & \frac{1}{2} & \times & v'_{s'} & \times & j & \downarrow & \Gamma_{ev}\sigma_{ev} \end{array}\ . \tag{88}$$

In view of potential applications we prefer to look at properties of different possible zeroth order models and for this the uncoupled basis is often a more convenient starting point. Restricting as before to dominant terms we find the approximate expansion:

$$\begin{aligned} \widetilde{H}^0_{vibr} = {} & \tilde{t}^{A_1A_1(A_1)}_{\{0\}\{0\}} I_v + {}_{s'}\tilde{t}^{B_iB_i(A_1)}_{\{1\}\{1\}}\ {}^{0}_{s'}V^{B_iB_i(A_1)}_{\{1\}\{1\}} \\ & + {}_{s}\tilde{t}^{0,0A_1(A_1)}_{\{1\}\{1\}}\ {}^{[1\ -1]}_{\quad\ s}\mathcal{V}^{(0,0\,A_1)} \\ & + E^{(1,0A_2)}\ {}_{s}\tilde{t}^{1,0A_2(A_2)}_{\{1\}\{1\}}\ {}^{[1\ -1]}_{\quad\ s}\mathcal{V}^{(1,0\,A_2)} \\ & + \sum_{t=1,2} E^{(1,2B_t)}\ {}_{s}\tilde{t}^{1,2B_t(B_t)}_{\{1\}\{1\}}\ {}^{[1\ -1]}_{\quad\ s}\mathcal{V}^{(1,2\,B_t)}. \end{aligned} \tag{89}$$

The expression for the matrix elements of the various operators in (89), within basis (87), is given in Appendix D.2. We could also keep in the expansion some anharmonicity operators without changing the results of the discussion to follow. On the first two lines of (89) we have the harmonic terms

$$\widetilde{H}^{(0)}_{vib} = \hbar\tilde{\omega}_{s'}\left(N'_{s'} + \frac{1}{2}\right) + \hbar\tilde{\omega}_s(N_s + 1). \tag{90}$$

The dimension of each N polyad is thus $g = (N+1)(N+2)/2$. The levels splitting is determined by the other three vibronic operators which may be written [17]

$$\widetilde{H}^{(1)}_{vibr} = \hbar\tilde{\lambda}_x S_x J_x + \hbar\tilde{\lambda}_y S_y J_y + \hbar\tilde{\lambda}_z S_z J_z, \tag{91}$$

where we recall that the pseudo-spin operators S_α are associated with the electronic $su(2)_e$ subalgebra and the J_α with the vibrational $su(2)_s$ subalgebra for mode s. For arbitrary values of the coupling constants $\tilde{\lambda}_\alpha$ nothing can be deduced concerning the energy level patterns. However there are some limiting cases for which exact solutions can be found. These correspond to situations where two of the coupling constants satisfy $|\tilde{\lambda}_\alpha| \simeq |\tilde{\lambda}_\beta|$ which implies

$$\widetilde{H}^{(1)}_{vibr} \simeq \hbar\tilde{\lambda}_\alpha(S_\alpha J_\alpha \pm S_\beta J_\beta) + \hbar\tilde{\lambda}_\gamma S_\gamma J_\gamma. \tag{92}$$

Additional special cases arise when all three effective vibronic constants $\tilde{\lambda}_\alpha$ are nearly equal which leads to

$$\widetilde{H}^{(1)}_{vibr} \simeq \tilde{\lambda}\sum_\alpha S_\alpha J_\alpha = \tilde{\lambda}\boldsymbol{S}\cdot\boldsymbol{J}, \tag{93}$$

or when $|\tilde{\lambda}_\alpha| \simeq |\tilde{\lambda}_\beta| \simeq 0$ and then

$$\widetilde{H}^{(1)}_{vibr} \simeq \hbar\tilde{\lambda}_\gamma S_\gamma J_\gamma. \tag{94}$$

We discuss below these possible limiting cases and determine the eigenvalues and symmetry adapted vibronic kets.

7.4.1 Eigenvalues and symmetry adapted states: equal coupling case

We begin with the most degenerate case for which the quite simple form of the zeroth-order model

$$\widetilde{H}^{(0)}_{vibr} = \hbar\tilde{\omega}_{s'}\left(N'_{s'}+\frac{1}{2}\right)+\hbar\tilde{\omega}_s(N_s+1)+\hbar\tilde{\lambda}\boldsymbol{S}\cdot\boldsymbol{J} \tag{95}$$

suggests the introduction of the diagonal subalgebra $su(2)_D$ of $su(2)_e \oplus su(2)_s$ with generators $J'_\alpha = S_\alpha + J_\alpha$. In the chain $su(2)_e \oplus su(2)_s \supset su(2)_D \supset so(2)_D$ the coupled basis ($j' = j \pm \frac{1}{2}$)

$$\left|[1\,0]\frac{1}{2},[v_s\,0]j;j'm'\right\rangle\!\!\Big\rangle = \sum_{m_e,m} C^{\,m_e\ m\ (j')}_{(\frac{1}{2}\ j)\ m'} \left|[1\,0]\frac{1}{2}m_e\right\rangle\!\!\Big\rangle |[v_s\,0]jm\rangle\rangle, \tag{96}$$

is an eigenbasis of $\boldsymbol{S}\cdot\boldsymbol{J}$. Within the total vibronic basis

$$|N-v_s\Gamma_i\rangle\left|[1\,0]\frac{1}{2},[v_s\,0]j;j'm'\right\rangle\!\!\Big\rangle, \tag{97}$$

we thus obtain the zeroth order energies, setting $v_s = v$:

$$\begin{aligned}E^0_{vibr} &= \hbar\tilde{\omega}_{s'}\left(N-v+\frac{1}{2}\right)+\hbar\tilde{\omega}_s(v+1)\\ &\quad+\hbar\frac{\tilde{\lambda}}{2}\left[j'(j'+1)-j(j+1)-\frac{3}{4}\right]\\ &= \hbar\frac{(\tilde{\omega}_{s'}+\tilde{\omega}_s)}{2}\left(N+\frac{3}{2}\right)\\ &\quad+\hbar\frac{(\tilde{\omega}_{s'}-\tilde{\omega}_s)}{2}\left(N-2v-\frac{1}{2}\right)\\ &\quad+\hbar\frac{\tilde{\lambda}}{2}\left[j'(j'+1)-\frac{v}{2}\left(\frac{v}{2}+1\right)-\frac{3}{4}\right]\end{aligned} \tag{98}$$

where the last form shows the levels splitting within the polyad the organization of which depends upon the relative order of magnitudes of $(\tilde{\omega}_{s'}-\tilde{\omega}_s)/2$ and $\tilde{\lambda}$. Each level has a degeneracy of $2j'+1$. The symmetry of these degenerate states is obtained with the symmetry rules given in (85) with $m_1 = v$, $m_2 = 0$ ($j = v/2$) and standard multiplication rules $A_i \times E_r = B_i \times E_r = E_r$, $E_r \times E_r = A_1 + A_2 + B_1 + B_2$. Using the same techniques as described in [17] and [21] one can also find the expressions of the symmetry adapted states. We first determine those $|[1\,0]\frac{1}{2},[v\,0]j;j'|m'|\Gamma\sigma\rangle\rangle$ arising from the states (96) and obtain ($\varepsilon = \frac{1}{2}+j-j'$):

- for v odd, j' integer:

$$\begin{aligned}&|[1\,0]\tfrac{1}{2},[v\,0]j;j'|m'|\Gamma_1\rangle\rangle = \frac{i^{v+1}}{\sqrt{2}}\\ &\times\{|[1\,0]\tfrac{1}{2},[v\,0]j;j'm'\rangle\rangle+(-1)^\varepsilon|[1\,0]\tfrac{1}{2},[v\,0]j;j'-m'\rangle\rangle\}\\ &|[1\,0]\tfrac{1}{2},[v\,0]j;j'|m'|\Gamma_2\rangle\rangle = \frac{i^{v}}{\sqrt{2}}\\ &\times\{|[1\,0]\tfrac{1}{2},[v\,0]j;j'm'\rangle\rangle-(-1)^\varepsilon|[1\,0]\tfrac{1}{2},[v\,0]j;j'-m'\rangle\rangle\}\end{aligned}$$

  with $\Gamma_1, \Gamma_2 = A_1, A_2$ for m' even and $\Gamma_1, \Gamma_2 = B_1, B_2$ for m' odd;
- for v even, j' half integer:

$$\begin{aligned}&|[1\,0]\tfrac{1}{2},[v\,0]j;j'|m'|E_r1\rangle\rangle = \frac{i^{v+1}}{\sqrt{2}}\\ &\times\{|[1\,0]\tfrac{1}{2},[v\,0]j;j'm'\rangle\rangle-(-1)^\varepsilon|[1\,0]\tfrac{1}{2},[v\,0]j;j'-m'\rangle\rangle\}\\ &|[1\,0]\tfrac{1}{2},[v\,0]j;j'|m'|E_r2\rangle\rangle = i^{2|m'|-1}\frac{i^{v}}{\sqrt{2}}\\ &\times\{|[1\,0]\tfrac{1}{2},[v\,0]j;j'm'\rangle\rangle+(-1)^\varepsilon|[1\,0]\tfrac{1}{2},[v\,0]j;j'-m'\rangle\rangle\}.\end{aligned}$$

The total zeroth order vibronic states symmetrized in the chain

$$\begin{array}{cccccccc} u(1)_{s'} & \oplus & (u(2)_e & \oplus & u(2)_s) & & & \\ N-v & \times & [1\,0] & \times & [v\,0] & & & \\ & \supset & u(1)_{s'} & \oplus & (su^*(2)_e & \oplus & su^*(2)_s) & \\ & \downarrow & N-v & \times & \frac{1}{2} & \times & j & \\ & \supset & u(1)_{s'} & \oplus & su^*(2)_D & \supset & G & \\ & \downarrow & N-v & \times & j' & \downarrow & \Gamma_{ev}\sigma_{ev} & \end{array} \tag{99}$$

are built with

$$\begin{aligned}&\left|N-v\Gamma_i,[1\,0]\frac{1}{2},[v\,0]j;j'|m'|\Gamma;\Gamma_{ev}\sigma_{ev}\right\rangle\!\!\Big\rangle =\\ &\qquad F^{\ \ \sigma\ \ (\Gamma_{ev})}_{(\Gamma_i\ \Gamma)\ \ \sigma_{ev}}|N-v\Gamma_i\rangle\left|[1\,0]\frac{1}{2},[v\,0]j;j'|m'|\Gamma\sigma\right\rangle\!\!\Big\rangle.\end{aligned} \tag{100}$$

When $N-v$ is odd $\Gamma_i = B_i$ and the states may be obtained with the values of the CGC given in Table 2; when $N-v$ is even so $\Gamma_i = A_1$ and

$$F^{\ \ \sigma\ \ (\Gamma_{ev})}_{(A_1\ \Gamma)\ \ \sigma_{ev}} = \delta_{\Gamma_{ev},\Gamma}\,\delta_{\sigma_{ev},\sigma}.$$

7.4.2 Eigenvalues and symmetry adapted states: $\tilde{\lambda}_\alpha = \pm\tilde{\lambda}_\beta$, $\tilde{\lambda}_\gamma \neq 0$ with $\alpha \neq \beta \neq \gamma$

We consider first the values $(\alpha,\beta,\gamma) = (x,y,z)$ in equation (92) and we will show next how other cases can be deduced. Introducing the ladder operators $S_\pm$ and $J_\pm$ of $su(2)_e$ and $su(2)_s$ respectively, the Hamiltonian for our system writes:

$${}^{+}\widetilde{H}^0_{vibr} = \widetilde{H}^0_{vib}+\hbar\tilde{\lambda}_x\left[\frac{1}{2}(S_+J_-+S_-J_+)+\tilde{\delta}_zS_zJ_z\right], \tag{101}$$

or

$${}^{-}\widetilde{H}^0_{vibr} = \widetilde{H}^0_{vib}+\hbar\tilde{\lambda}_x\left[\frac{1}{2}(S_+J_++S_-J_-)+\tilde{\delta}_zS_zJ_z\right], \tag{102}$$

where we have set $\tilde{\delta}_z = \tilde{\lambda}_z/\tilde{\lambda}_x$ ($\tilde{\lambda}_x \neq 0$). In both cases a basis for the space of states is given by

$$\begin{aligned}|\pm\rangle\rangle|[v\,0]j\,m\rangle\rangle &\equiv \left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\Big\rangle|[v\,0]j\,m\rangle\rangle \\ &\equiv \left|[1\,0]\frac{1}{2}m_e\right\rangle\!\!\Big\rangle|[v\,0]j\,m\rangle\rangle,\end{aligned} \tag{103}$$

where $|\pm\rangle\rangle$ are the electronic states in orientation II and $|[v\,0]j\,m\rangle\rangle$ the standard $su(2)_s$ covariant states for the e_r mode [17]. For clarity we temporarily omit the states $|N - v\,\Gamma_i\rangle$ associated with the b_i mode. In order to solve the eigenvalue equations we appeal to the formalism developed in [31] which allows first to write the Hamiltonian in terms of the generators of a new $su(2)$ algebra.

Case (a) ${}^{+}\widetilde{H}^0_{vibr}$ (Eq. (101))

We introduce the $\mathcal{F}$ operator function

$$\mathcal{F} = (S_+J_- + S_-J_+)^2 = J^2 - J_z^2 - 2S_zJ_z, \tag{104}$$

which is easily shown to commute with ${}^{+}\widetilde{H}^0_{vibr}$ and the eigenvalues of which $f(j,m) = (j-m)(j+m+1)$ have a fourfold degeneracy in the basis (103) the degenerate states being

$$\begin{aligned} &|+\rangle\rangle|[v\,0]j\,m\rangle\rangle, \quad |-\rangle\rangle|[v\,0]j\,m+1\rangle\rangle,\\ &|+\rangle\rangle|[v\,0]j\,-m-1\rangle\rangle, \quad |-\rangle\rangle|[v\,0]j\,-m\rangle\rangle, \end{aligned} \tag{105}$$

with $m = -j, -j+1 \cdots j-1$. Next we build an $su(2)(M)$ algebra which is isomorphic to that of a spin 1/2 and with generators:

$$M_+ = \frac{1}{\sqrt{\mathcal{F}}}S_+J_-,\ M_- = \frac{1}{\sqrt{\mathcal{F}}}S_-J_+,\ M_z = S_z. \tag{106}$$

In particular we have, using our conventions for covariant states [17]

$$\begin{aligned} &M_+|+\rangle\rangle|[v\,0]j\,m\rangle\rangle = |-\rangle\rangle|[v\,0]j\,m+1\rangle\rangle,\\ &M_+|-\rangle\rangle|[v\,0]j\,m+1\rangle\rangle = 0,\\ &M_-|-\rangle\rangle|[v\,0]j\,m+1\rangle\rangle = |+\rangle\rangle|[v\,0]j\,m\rangle\rangle,\\ &M_-|+\rangle\rangle|[v\,0]j\,m\rangle\rangle = 0. \end{aligned} \tag{107}$$

The operator

$$\Delta = S_z + J_z = S_z - \frac{1}{2}\,{}_s\ell_z = \frac{1}{2}(\sigma_z - {}_s\ell_z), \tag{108}$$

${}_s\ell_z$ being the angular momentum of the doubly degenerate oscillator, has the eigenvalues $\Delta(m) = -(m+\frac{1}{2})$ (resp. $\Delta(m) = (m+\frac{1}{2})$) on the states $|+\rangle\rangle|[v\,0]j\,m\rangle\rangle$, $|-\rangle\rangle|[v\,0]j\,m+1\rangle\rangle$ (resp. $|+\rangle\rangle|[v\,0]j\,-m-1\rangle\rangle$, $|-\rangle\rangle|[v\,0]j\,-m\rangle\rangle$), and commutes with the $su(2)(M)$ generators together with ${}^{+}\widetilde{H}^0_{vibr}$. The latter can then be written as

$$\begin{aligned} {}^{+}\widetilde{H}^0_{vibr} = \widetilde{H}^0_{vib} - \hbar\frac{\tilde{\lambda}_z}{4}\\ + \hbar\tilde{\lambda}_x\left\{\frac{1}{2}\sqrt{\mathcal{F}}(M_+ + M_-) + \tilde{\delta}_z\Delta M_z\right\}, \end{aligned} \tag{109}$$

and diagonalized through a unitary transformation of the $su(2)(M)$ algebra. Explicitly, we obtain:

$$U^+\widetilde{H}^0_{vibr}U^{-1} = \widetilde{H}^0_{vib} - \hbar\frac{\tilde{\lambda}_z}{4} + \hbar 2\tilde{\lambda}_x\Omega(\mathcal{F},\Delta)S_z, \tag{110}$$

where the operator function $\Omega(\mathcal{F},\Delta)$ is given by

$$\Omega(\mathcal{F},\Delta) = \frac{1}{2}[\mathcal{F} + \tilde{\delta}_z^2\Delta^2]^{1/2}. \tag{111}$$

Within basis (105) we thus have the doubly degenerate eigenvalues (except for $m = -1/2$)

$${}^{+}E_{jm\pm} = \hbar\tilde{\omega}_s(2j+1) - \hbar\frac{\tilde{\lambda}_z}{4} + \hbar\tilde{\lambda}_x\Omega_\pm(j,m), \tag{112}$$

with

$$\begin{aligned} \Omega_\pm(j,m) &= \pm\Omega(j,m)\\ &= \pm\frac{1}{2}\left[(j-m)(j+m+1) + \tilde{\delta}_z^2\left(m+\frac{1}{2}\right)^2\right]^{1/2}\\ &= \pm\frac{1}{4}[(v\mp\ell)(v\pm\ell+2) + \tilde{\delta}_z^2(\pm\ell+1)^2]^{1/2}, \end{aligned} \tag{113}$$

where we used [17] $j = v/2$, $\ell = 2|m|$. The U^{-1} operator is given by

$$\begin{aligned} U^{-1} &= (I + k^\dagger M_+)\exp[k_zM_z](I - kM_-)\\ &= (I - kM_-)\exp[-k_zM_z](I + k^\dagger M_+), \end{aligned} \tag{114}$$

with

$$\begin{aligned} k &= -\frac{2\Omega(\mathcal{F},\Delta) - \tilde{\delta}_z\Delta}{\sqrt{\mathcal{F}}}\\ &= -\left[\frac{\Omega(\mathcal{F},\Delta) - \tilde{\delta}_z\Delta/2}{\Omega(\mathcal{F},\Delta) + \tilde{\delta}_z\Delta/2}\right]^{1/2}, \end{aligned} \tag{115}$$

and

$$k_z = \ln\left[\frac{2\Omega(\mathcal{F},\Delta)}{\Omega(\mathcal{F},\Delta) + \tilde{\delta}_z\Delta/2}\right]. \tag{116}$$

Unsymmetrized eigenstates of ${}^{+}\widetilde{H}^0_{vibr}$ (101) are next obtained with U^{-1} acting on the states (m: $j-1\cdots 1/2$ or 0) (105):

$$\begin{aligned} {}^{+}\widetilde{\Psi}^{(1)}_{jm-} &= U^{-1}|+\rangle\rangle|[v\,0]j\,m\rangle\rangle\\ &= \cos[\theta(j,m)]|+\rangle\rangle|[v\,0]j\,m\rangle\rangle\\ &\quad - \sin[\theta(j,m)]|-\rangle\rangle|[v\,0]j\,m+1\rangle\rangle\\ {}^{+}\widetilde{\Psi}^{(1)}_{jm+} &= U^{-1}|-\rangle\rangle|[v\,0]j\,m+1\rangle\rangle\\ &= \cos[\theta(j,m)]|-\rangle\rangle|[v\,0]j\,m+1\rangle\rangle\\ &\quad + \sin[\theta(j,m)]|+\rangle\rangle|[v\,0]j\,m\rangle\rangle\\ {}^{+}\widetilde{\Psi}^{(2)}_{jm-} &= U^{-1}|+\rangle\rangle|[v\,0]j\,-m-1\rangle\rangle\\ &= \sin[\theta(j,m)]|+\rangle\rangle|[v\,0]j\,-m-1\rangle\rangle\\ &\quad - \cos[\theta(j,m)]|-\rangle\rangle|[v\,0]j\,-m\rangle\rangle\\ {}^{+}\widetilde{\Psi}^{(2)}_{jm+} &= U^{-1}|-\rangle\rangle|[v\,0]j\,-m\rangle\rangle\\ &= \sin[\theta(j,m)]|-\rangle\rangle|[v\,0]j\,-m\rangle\rangle\\ &\quad + \cos[\theta(j,m)]|+\rangle\rangle|[v\,0]j\,-m-1\rangle\rangle \end{aligned} \tag{117}$$

with

$$\cos[\theta(j,m)] = \left[\frac{\Omega(j,m) - \tilde{\delta}_z(m+1/2)/2}{2\Omega(j,m)}\right]^{1/2}$$
$$\sin[\theta(j,m)] = \left[\frac{\Omega(j,m) + \tilde{\delta}_z(m+1/2)/2}{2\Omega(j,m)}\right]^{1/2} \qquad (118)$$

and

$$\cos[\theta(j,m)] = \sin[\theta(j,-m-1)].$$

The associated symmetry adapted states are listed below in the form

$$\left|[1\,0]\frac{1}{2}1E_r,[v\,0]j;\Omega_\pm,\Gamma_{ev}\bar{\sigma}\right\rangle\!\!\right\rangle, \qquad (119)$$

with all phases settled so that under time reversal

$$\mathcal{K}\left|[1\,0]\frac{1}{2}1E_r,[v\,0]j;\Omega_\pm,\Gamma_{ev}\bar{\sigma}\right\rangle\!\!\right\rangle = \left|[1\,0]\frac{1}{2}1E_r,[v\,0]j;\Omega_\pm,\Gamma_{ev}-\bar{\sigma}\right\rangle\!\!\right\rangle.$$

- $\ell = 2|m| = 4q, 4q+2$

$$\begin{aligned}
|[1\,0]\tfrac{1}{2}1E_r,[v\,0]j;\Omega_+,E_r\bar{\sigma}\rangle\rangle &= i^{v}\,{}^{+}\widetilde{\Psi}^{(1)}_{jm+}\\
|[1\,0]\tfrac{1}{2}1E_r,[v\,0]j;\Omega_+,E_r-\bar{\sigma}\rangle\rangle &= i^{v}\,{}^{+}\widetilde{\Psi}^{(2)}_{jm+}\\
|[1\,0]\tfrac{1}{2}1E_r,[v\,0]j;\Omega_-,E_r\bar{\sigma}\rangle\rangle &= i^{v}\,{}^{+}\widetilde{\Psi}^{(1)}_{jm-}\\
|[1\,0]\tfrac{1}{2}1E_r,[v\,0]j;\Omega_-,E_r-\bar{\sigma}\rangle\rangle &= -i^{v}\,{}^{+}\widetilde{\Psi}^{(2)}_{jm-}
\end{aligned} \qquad (120)$$

with $(\bar{\sigma},-\bar{\sigma}) = (\bar{1},\bar{2})$ (resp. $(\bar{\sigma},-\bar{\sigma}) = (\bar{2},\bar{1})$) for $\ell = 4q$ (resp. $\ell = 4q+2$).

- $\ell = 2|m| = 4q+1, 4q+3$

$$\begin{aligned}
|[1\,0]\tfrac{1}{2}1E_r,[v\,0]j;\Omega_+,\Gamma_1\rangle\rangle &= \frac{i^{v+1}}{\sqrt{2}}({}^{+}\widetilde{\Psi}^{(1)}_{jm+} + {}^{+}\widetilde{\Psi}^{(2)}_{jm+})\\
|[1\,0]\tfrac{1}{2}1E_r,[v\,0]j;\Omega_+,\Gamma_2\rangle\rangle &= \frac{i^{v}}{\sqrt{2}}({}^{+}\widetilde{\Psi}^{(1)}_{jm+} - {}^{+}\widetilde{\Psi}^{(2)}_{jm+})\\
|[1\,0]\tfrac{1}{2}1E_r,[v\,0]j;\Omega_-,\Gamma_1\rangle\rangle &= \frac{i^{v+1}}{\sqrt{2}}({}^{+}\widetilde{\Psi}^{(1)}_{jm-} - {}^{+}\widetilde{\Psi}^{(2)}_{jm-})\\
|[1\,0]\tfrac{1}{2}1E_r,[v\,0]j;\Omega_-,\Gamma_2\rangle\rangle &= \frac{i^{v}}{\sqrt{2}}({}^{+}\widetilde{\Psi}^{(1)}_{jm-} + {}^{+}\widetilde{\Psi}^{(2)}_{jm-})
\end{aligned} \qquad (121)$$

with $\Gamma_1, \Gamma_2 = B_1, B_2$ for $\ell = 4q+1$ and A_1, A_2 for $\ell = 4q+3$.

Special cases

- For $m = -1/2$ the states in (105) reduce to two and we have a degeneracy of one for the energy levels (112). In these cases we may take

$$\begin{aligned}
|[1\,0]\tfrac{1}{2}1E_r,[v\,0]j;\Omega_+,A_1\rangle\rangle &= i^{v+1}U^{-1}|-\rangle\rangle|[v\,0]j\,\tfrac{1}{2}\rangle\rangle\\
|[1\,0]\tfrac{1}{2}1E_r,[v\,0]j;\Omega_-,A_2\rangle\rangle &= i^{v}U^{-1}|+\rangle\rangle|[v\,0]j\,-\tfrac{1}{2}\rangle\rangle
\end{aligned}$$

- The states $|+\rangle\rangle|[v\,0]j\,j\rangle\rangle \equiv |[1\,0]\frac{1}{2}1E_r\bar{1}\rangle\rangle|[v\,0]j\,j\rangle\rangle$ and $|-\rangle\rangle|[v\,0]j\,-j\rangle\rangle \equiv |[1\,0]\frac{1}{2}1E_r\bar{2}\rangle\rangle|[v\,0]j\,-j\rangle\rangle$ which are uncoupled by $\widetilde{H}^{(1)}_{vibr}$ (101) and also associated with the zero eigenvalues of the $\mathcal{F}$ function (104) are eigenstates of ${}^{+}\widetilde{H}^{(0)}_{vibr}$ with eigenvalues

$${}^{+}E_j = \hbar\tilde{\omega}_s(2j+1) + \hbar\frac{\tilde{\lambda}_z}{2}j. \qquad (122)$$

The corresponding symmetry adapted states are given by:

$$\begin{aligned}
\left|[1\,0]\frac{1}{2}1E_r,[v\,0]j;{}^{+}E_j,E_r\bar{\sigma}\right\rangle\!\!\right\rangle &= |+\rangle\rangle|[v\,0]j\,j\rangle\rangle\\
\left|[1\,0]\frac{1}{2}1E_r,[v\,0]j;{}^{+}E_j,E_r-\bar{\sigma}\right\rangle\!\!\right\rangle &= |-\rangle\rangle|[v\,0]j\,-j\rangle\rangle
\end{aligned} \qquad (123)$$

with $\bar{\sigma} = \bar{1}$ (resp. $\bar{\sigma} = \bar{2}$) for v even and j even (resp. j odd) and

$$\begin{aligned}
&\left|[1\,0]\frac{1}{2}1E_r,[v\,0]j;{}^{+}E_j,\Gamma_1\right\rangle\!\!\right\rangle = \\
&\quad \frac{i^{v+1}}{2}(|+\rangle\rangle|[v\,0]j\,j\rangle\rangle + |-\rangle\rangle|[v\,0]j\,-j\rangle\rangle)\\
&\left|[1\,0]\frac{1}{2}1E_r,[v\,0]j;{}^{+}E_j,\Gamma_2\right\rangle\!\!\right\rangle = \\
&\quad \frac{i^{v}}{2}(|+\rangle\rangle|[v\,0]j\,j\rangle\rangle - |-\rangle\rangle|[v\,0]j\,-j\rangle\rangle)
\end{aligned} \qquad (124)$$

with $\Gamma_1 = B_1$, $\Gamma_2 = B_2$ (resp. $\Gamma_1 = A_1$, $\Gamma_2 = A_2$) for v odd and $2j = 4q+1$ (resp. $2j = 4q+3$).

Case (b) ${}^{-}\widetilde{H}^{0}_{vibr}$ (Eq. (102))

The eigenvalue equation for ${}^{-}\widetilde{H}^{0}_{vibr}$ (101) is solved with a method similar to that used for ${}^{+}\widetilde{H}^{0}_{vibr}$. This time we introduce the $\overline{\mathcal{F}}$ operator function

$$\overline{\mathcal{F}} = (S_+J_+ + S_-J_-)^2 = J^2 - J_z^2 + 2S_zJ_z, \qquad (125)$$

and the operator

$$\overline{\Delta} = -S_z + J_z = -S_z - \frac{1}{2}\,{}_s\ell_z = -\frac{1}{2}(\sigma_z + {}_s\ell_z). \qquad (126)$$

Both commute with ${}^{-}\widetilde{H}^{0}_{vibr}$ and the degenerate states (105) are replaced by ($m = -j, -j+1, \cdots j-1$)

$$\begin{aligned}
&|-\rangle\rangle|[v\,0]j\,m\rangle\rangle,\ |+\rangle\rangle|[v\,0]j\,m+1\rangle\rangle\\
&|-\rangle\rangle|[v\,0]j\,-m-1\rangle\rangle,\ |+\rangle\rangle|[v\,0]j\,-m\rangle\rangle.
\end{aligned} \qquad (127)$$

They are associated with the eigenvalues $\bar{f}(j,m) = (j-m)(j+m+1) = f(j,m)$ of $\overline{\mathcal{F}}$ and $\overline{\Delta}(m) = \Delta(m)$ of $\overline{\Delta}$. The $su(2)(M)$ algebra (106) is replaced by an $su(2)(N)$ one with generators

$$N_+ = \frac{1}{\sqrt{\overline{\mathcal{F}}}}S_+J_+\ ,\ N_- = \frac{1}{\sqrt{\overline{\mathcal{F}}}}S_-J_-\ ,\ N_z = S_z, \qquad (128)$$

with which ${}^{-}\widetilde{H}^{0}_{vibr}$ can be written

$$\begin{aligned}
{}^{-}\widetilde{H}^{0}_{vibr} &= \widetilde{H}^{0}_{vib} + \hbar\frac{\tilde{\lambda}_z}{4}\\
&+\ \hbar\tilde{\lambda}_x\left\{\frac{1}{2}\sqrt{\overline{\mathcal{F}}}(N_+ + N_-) + \tilde{\delta}_z\overline{\Delta}N_z\right\},
\end{aligned} \qquad (129)$$

and diagonalized with a unitary operator U' of the $su(2)(N)$ algebra:

$$U'^{-}\widetilde{H}^{0}_{vibr}U'^{-1} = \widetilde{H}^{0}_{vib} + \hbar\frac{\tilde{\lambda}_z}{4} + \hbar 2\tilde{\lambda}_x \Omega(\overline{\mathcal{F}}, \overline{\Delta})S_z. \quad (130)$$

The operator function $\Omega(\overline{\mathcal{F}}, \overline{\Delta})$ is given by (111) with the substitutions $\mathcal{F} \rightarrow \overline{\mathcal{F}}$ and $\Delta \rightarrow \overline{\Delta}$. Within the basis (127) we obtain the eigenvalues

$${}^{-}E_{jm\pm} = \hbar\tilde{\omega}_s(2j+1) + \hbar\frac{\tilde{\lambda}_z}{4} + \hbar\tilde{\lambda}_x\Omega_{\pm}(j,m) \quad (131)$$

with $\Omega_{\pm}(j,m)$ given by (113). The corresponding unsymmetrized eigenstates of ${}^{-}\widetilde{H}^{0}_{vibr}$ (101) are obtained with U'^{-1} acting on the states (127) with U'^{-1} deduced from U^{-1} in equations (114–116) with the substitutions $M_{\pm} \rightarrow N_{\pm}$, $M_z \rightarrow N_z$, $\mathcal{F} \rightarrow \overline{\mathcal{F}}$ and $\Delta \rightarrow \overline{\Delta}$. This leads to states ${}^{-}\widetilde{\Psi}^{(i)}_{jm\pm}$ $(i = 1, 2)$ which can be deduced from those ${}^{+}\widetilde{\Psi}^{(i)}_{jm\pm}$ (117) with the substitutions

$$\begin{aligned}
&|\pm\rangle\rangle|[v\,0]j\ \pm m\rangle\rangle \rightarrow |\pm\rangle\rangle|[v\,0]j\ \pm(m+1)\rangle\rangle,\\
&|\mp\rangle\rangle|[v\,0]j\ \pm(m+1)\rangle\rangle \rightarrow |\mp\rangle\rangle|[v\,0]j\ \pm m\rangle\rangle.
\end{aligned}$$

$\cos[\theta(j,m)]$ and $\sin[\theta(j,m)]$ are still given by (118). Likewise symmetry adapted states are obtained from those in equations (120, 121) with the substitutions ${}^{+}\widetilde{\Psi}^{(1)}_{jm\pm} \rightarrow {}^{-}\widetilde{\Psi}^{(2)}_{jm\pm}$, ${}^{+}\widetilde{\Psi}^{(2)}_{jm\pm} \rightarrow {}^{-}\widetilde{\Psi}^{(1)}_{jm\pm}$ and with $\Gamma_1 = A_1$, $\Gamma_2 = A_2$ (resp. $\Gamma_1 = B_1$, $\Gamma_2 = B_2$) for v odd and $\ell = 4q+1$ (resp. $\ell = 4q+3$). The same rules apply for the special cases considered in equations (122–124) with (122) replaced by

$${}^{-}E_{j} = \hbar\tilde{\omega}_s(2j+1) - \hbar\frac{\tilde{\lambda}_z}{2}j. \quad (132)$$

All other cases $\tilde{\lambda}_\alpha = \pm\tilde{\lambda}_\beta$, $\tilde{\lambda}_\gamma \neq 0$ can be deduced from the previous two with appropriate unitary operators so in all cases the eigenvalues are identical. However for an easy determination of symmetry adapted vibronic eigenstates it is better not to choose them arbitrarily. We set (Eq. (92))

$$\begin{aligned}
\widetilde{H}^{(1)}_{vibr} &= \widetilde{H}^{(1)}_{vibr}(\alpha,\beta,\gamma)\\
&= T(\alpha,\beta,\gamma)\widetilde{H}^{(1)}_{vibr}(x,y,z)T^{-1}(\alpha,\beta,\gamma)\\
&= \hbar\tilde{\lambda}_\alpha[(\widehat{S}_x\widehat{J}_x \pm \widehat{S}_y\widehat{J}_y) + \frac{\tilde{\lambda}_\gamma}{\tilde{\lambda}_\alpha}\widehat{S}_z\widehat{J}_z]\\
&= \hbar\tilde{\lambda}_\alpha[(\widehat{S}_x\widehat{J}_x \pm \widehat{S}_y\widehat{J}_y) + \hat{\delta}_z\widehat{S}_z\widehat{J}_z], \qquad (133)
\end{aligned}$$

where $T(\alpha,\beta,\gamma)$ is a unitary operator which performs the change of reference configuration $(x,y,z) \rightarrow (\alpha,\beta,\gamma)$. The operators $\widehat{W}_{\pm} = \widehat{W}_x \pm i\widehat{W}_y$, $\widehat{W}_z$ ($\widehat{W} = \widehat{S}$ or $\widehat{J}$) still satisfy the usual $su(2)$ commutation rules $[\widehat{W}_z, \widehat{W}_{\pm}] = \pm\widehat{W}_{\pm}$, $[\widehat{W}_+, \widehat{W}_-] = 2\widehat{W}_z$ and $\widehat{W}^2 = W^2$. The normal covariant standard basis is replaced by ($w = 1/2$ or j)

$$\begin{aligned}
|\widehat{w,m}\rangle\rangle &= T(\alpha,\beta,\gamma)|w,m\rangle\rangle,\\
\widehat{W}_z|\widehat{w,m}\rangle\rangle &= -m|\widehat{w,m}\rangle\rangle, .\\
\widehat{W}^2|\widehat{w,m}\rangle\rangle &= w(w+1)|\widehat{w,m}\rangle\rangle. \qquad (134)
\end{aligned}$$

With the previous operators we have
Case (a)

$${}^{+}\widetilde{H}^{0}_{vibr}(\alpha,\beta,\gamma) = \widetilde{H}^{0}_{vib} + \hbar\tilde{\lambda}_\alpha\left[\frac{1}{2}(\widehat{S}_+\widehat{J}_- + \widehat{S}_-\widehat{J}_+) + \hat{\delta}_z\widehat{S}_z\widehat{J}_z\right]$$

Case (b)

$${}^{-}\widetilde{H}^{0}_{vibr}(\alpha,\beta,\gamma) = \widetilde{H}^{0}_{vib} + \hbar\tilde{\lambda}_\alpha\left[\frac{1}{2}(\widehat{S}_+\widehat{J}_+ + \widehat{S}_-\widehat{J}_-) + \hat{\delta}_z\widehat{S}_z\widehat{J}_z\right]$$

and the method used for $(\alpha,\beta,\gamma) = (x,y,z)$ applies in terms of $\widehat{W}_{\pm}$, $\widehat{W}_z$ operators.

One may show that convenient choices are:

- for $(x,y,z) \rightarrow (y,z,x)$: case (i)

$$T = P_R = \exp\left[i\frac{\pi}{2}(S_y + J_y)\right]\exp\left[-i\frac{\pi}{2}(S_z + J_z)\right] \quad (135)$$

and

- for $(x,y,z) \rightarrow (x,z,y)$: case (ii)

$$\begin{aligned}
T = P_{R'} &= \exp\left[i\frac{\pi}{2}(S_z + J_z)\right]\\
&\times \exp\left[-i\frac{\pi}{2}(S_y + J_y)\right]\exp\left[i\frac{\pi}{2}(S_z + J_z)\right] \qquad (136)
\end{aligned}$$

and the electronic rotation amounts, within an overall unessential phase, to a change from orientation II to orientation I in case (i) and to orientation III for case (ii). Thus the basis states (103) are replaced by:

$$|\widehat{\pm}\rangle\rangle|\widehat{[v\,0]j\,m}\rangle\rangle \equiv |[1\,0]\tfrac{1}{2}1E_r\sigma\rangle\rangle|\widehat{[v\,0]jm}\rangle\rangle \quad \text{in case (i)}$$

$$|\widehat{\widehat{\pm}}\rangle\rangle|\widehat{\widehat{[v\,0]j\,m}}\rangle\rangle \equiv |[1\,0]\tfrac{1}{2}1E_r\bar{\bar{\sigma}}\rangle\rangle|\widehat{\widehat{[v\,0]jm}}\rangle\rangle \quad \text{in case (ii)}$$

where we set for the rotated vibrational parts

$$\begin{aligned}
|\widehat{[v\,0]jm}\rangle\rangle &= \exp\left(i\frac{\pi}{2}J_y\right)\exp\left(-i\frac{\pi}{2}J_z\right)|[v\,0]jm\rangle\rangle\\
&= e^{im\frac{\pi}{2}}\sum_{m'} d^{(j)}_{m'm}\left(\frac{\pi}{2}\right)|[v\,0]jm'\rangle\rangle, \qquad (137)
\end{aligned}$$

and

$$\begin{aligned}
|\widehat{\widehat{[v\,0]jm}}\rangle\rangle &= \exp\left(i\frac{\pi}{2}J_z\right)\exp\left(-i\frac{\pi}{2}J_y\right)\\
&\times \exp\left(i\frac{\pi}{2}J_z\right)|[v\,0]jm\rangle\rangle\\
&= \sum_{m'} e^{-i(m+m')\frac{\pi}{2}} d^{(j)}_{mm'}\left(\frac{\pi}{2}\right)|[v\,0]jm'\rangle\rangle. \qquad (138)
\end{aligned}$$

Thus the equivalents of the eigenstates (117) in case (a) are simply obtained with the substitutions $|\pm\rangle\rangle|[v\,0]jm\rangle\rangle \rightarrow |\widehat{\pm}\rangle\rangle|\widehat{[v\,0]j\,m}\rangle\rangle$ in case (i) (or $|\pm\rangle\rangle|[v\,0]jm\rangle\rangle \rightarrow |\widehat{\widehat{\pm}}\rangle\rangle|\widehat{\widehat{[v\,0]jm}}\rangle\rangle$ in case (ii)). The same rules apply for case (b). The symmetry adaptation is then straightforward. We underline that this procedure is preferable to a direct action of the rotation operators onto the symmetry adapted states, for instance (120, 121), since the R operations are not and cannot be elements of G.

For all cases considered in this section inclusion of the b_i mode amounts, within the considered order of approximation, to the replacement of $\hbar\tilde{\omega}_s(2j+1) = \hbar\tilde{\omega}_s(v+1)$ by

$$\begin{aligned} E^0_{vib} &= \hbar\tilde{\omega}_{s'}\left(N - v + \frac{1}{2}\right) + \hbar\tilde{\omega}_s(v+1) \\ &= \hbar\frac{(\tilde{\omega}_{s'} + \tilde{\omega}_s)}{2}\left(N + \frac{3}{2}\right) \\ &\quad + \hbar\frac{(\tilde{\omega}_{s'} - \tilde{\omega}_s)}{2}\left(N - 2v - \frac{1}{2}\right), \end{aligned}$$

in equations (112, 122, 131, 132). The associated symmetrized vibronic eigenstates are built with

$$\begin{aligned} &\left|N - v\Gamma_i, [1\,0]\frac{1}{2}1E_r, [v\,0]j; \Lambda_\pm, \Gamma; \Gamma_{ev}\sigma_{ev}\right\rangle\!\!\right\rangle = \\ &\qquad F^{\theta\quad(\Gamma_{ev})}_{(\Gamma_i\ \Gamma)\quad\sigma_{ev}} |N - v\Gamma_i\rangle \left|[1\,0]\frac{1}{2}1E_r, [v\,0]j; \Lambda_\pm, \Gamma\theta\right\rangle\!\!\right\rangle \end{aligned} \tag{139}$$

where $\Lambda_\pm = \Omega_\pm$ or ${}^\pm E_j$. In the CGC $\theta = \sigma$, $\bar{\sigma}$ or $\bar{\bar{\sigma}}$ according to the case when $\Gamma = E_r$ (Tab. 2).

7.4.3 Eigenvalues and symmetry adapted states: $\tilde{\lambda}_\alpha = \tilde{\lambda}_\beta = 0$, $\tilde{\lambda}_\gamma \neq 0$

Finally we consider the situation in which one of the effective coupling constants is preponderant which gives three mathematically equivalent cases. For $\tilde{\lambda}_\gamma = \tilde{\lambda}_z$ the interaction operator in equation (89)

$${}^{[1\,-1]}E^{(1,0A_2)}\,{}^{[1\,-1]}_{\ \ s}\mathcal{V}^{(1,0\,A_2)} = S_z J_z = -\frac{1}{2} S_z\, {}_s\ell_z,$$

represents the interaction between the electronic pseudo-spin and the vibrational angular momentum of the twofold degenerate oscillator. We thus have a zeroth order vibronic Hamiltonian in the form

$$\widetilde{H}^0_{vibr} = \hbar\tilde{\omega}_{s'}\left(N'_{s'} + \frac{1}{2}\right) + \hbar\tilde{\omega}_s(N_s + 1) - \hbar\frac{\tilde{\lambda}_z}{2} S_z\, {}_s\ell_z.$$

The eigenvalues are most easily obtained if one uses electronic and vibrational functions for the s mode in the standard $u(2) \supset su(2) \supset so(2)$ chain:

$$\begin{aligned} &\left|N - v\,\Gamma_i\rangle|[1\,0]\frac{1}{2}m_e\right\rangle\!\!\right\rangle |[v\,0]jm\rangle\rangle \equiv \\ &\qquad |N - v\,\Gamma_i\rangle \left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle |[v\,0]jm\rangle\rangle, \end{aligned}$$

$$\begin{aligned} E^0_{vibr} &= \hbar\tilde{\omega}_{s'}\left(N - v + \frac{1}{2}\right) + \hbar\tilde{\omega}_s(v+1) + \hbar\tilde{\lambda}_z\, m_e m \\ &= \hbar\frac{(\tilde{\omega}_{s'} + \tilde{\omega}_s)}{2}\left(N + \frac{3}{2}\right) \\ &\quad + \hbar\frac{(\tilde{\omega}_{s'} - \tilde{\omega}_s)}{2}\left(N - 2v - \frac{1}{2}\right) \pm \hbar\frac{\tilde{\lambda}_z}{2}\frac{\ell}{2}. \end{aligned} \tag{140}$$

For each value of $\ell = 4q, 4q+2, 4q+1, 4q+3$ there remains a degeneracy of two. The symmetry of these degenerate states is obtained with the symmetry rules given in (85) with $m_1 = v$, $m_2 = 0$ ($j = v/2$) and standard multiplication rules. The associated symmetry adapted vibronic eigenstates are given in Appendix D.3 in a form which allows to take easily into account the neglected vibronic terms in the Hamiltonian expansion.

The other cases $\tilde{\lambda}_\alpha = \tilde{\lambda}_\beta = 0$, $\tilde{\lambda}_\gamma \neq 0$ in which the coupling with one of the pseudo-spin components is strong are solved using techniques similar to those in Section 7.4.2. They can be seen as situations in which the contribution of the term involving the symmetry of one active coordinate dominates the other one.

$\tilde{\lambda}_\gamma = \tilde{\lambda}_x$ (resp. $\tilde{\lambda}_\gamma = \tilde{\lambda}_y$) which corresponds to $B_t = B_1$ (resp. $B_t = B_2$) in equation (89) give respectively with the same assumptions

$$\widetilde{H}^0_{vibr} = \hbar\tilde{\omega}_{s'}\left(N'_{s'} + \frac{1}{2}\right) + \hbar\tilde{\omega}_s(N_s + 1) + \hbar\tilde{\lambda}_x S_x J_x, \tag{141}$$

$$\widetilde{H}^0_{vibr} = \hbar\tilde{\omega}_{s'}\left(N'_{s'} + \frac{1}{2}\right) + \hbar\tilde{\omega}_s(N_s + 1) + \hbar\tilde{\lambda}_y S_y J_y. \tag{142}$$

Although the vibrational operators J_x and J_y cannot be associated with vibrational angular momentum components we can again take advantage of the $su(2)$ properties to find both the spectrum and the symmetry adapted states. With the same rotation operators as in equations (135–138) the states

$$\begin{aligned} &|N - v\,\Gamma_i\rangle P_R \left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\rangle\rangle|[v\,0]jm\right\rangle\!\!\right\rangle = \\ &\qquad |N - v\,\Gamma_i\rangle \left|[1\,0]\frac{1}{2}1E_r\sigma\right\rangle\!\!\right\rangle |\widehat{[v\,0]jm}\rangle\rangle \end{aligned} \tag{143}$$

$$\begin{aligned} &|N - v\,\Gamma_i\rangle P_{R'} \left|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\right\rangle\!\!\right\rangle |[v\,0]jm\rangle\rangle = \\ &\qquad |N - v\,\Gamma_i\rangle \left|[1\,0]\frac{1}{2}1E_r\bar{\bar{\sigma}}\right\rangle\!\!\right\rangle |\widehat{\widehat{[v\,0]jm}}\rangle\rangle \end{aligned} \tag{144}$$

are unsymmetrized eigenstates of (141) and (142) respectively with eigenvalues given by equation (140) with the replacements $\tilde{\lambda}_z \to \tilde{\lambda}_x$ and $\tilde{\lambda}_z \to \tilde{\lambda}_y$. Explicit expressions of the symmetry adapted vibronic eigenstates are given in Appendix D.4.

7.4.4 Correlations with previous studies

Some of our results can be related to those obtained in a previous study of an $E \otimes e$ case in D_{4h} molecules by

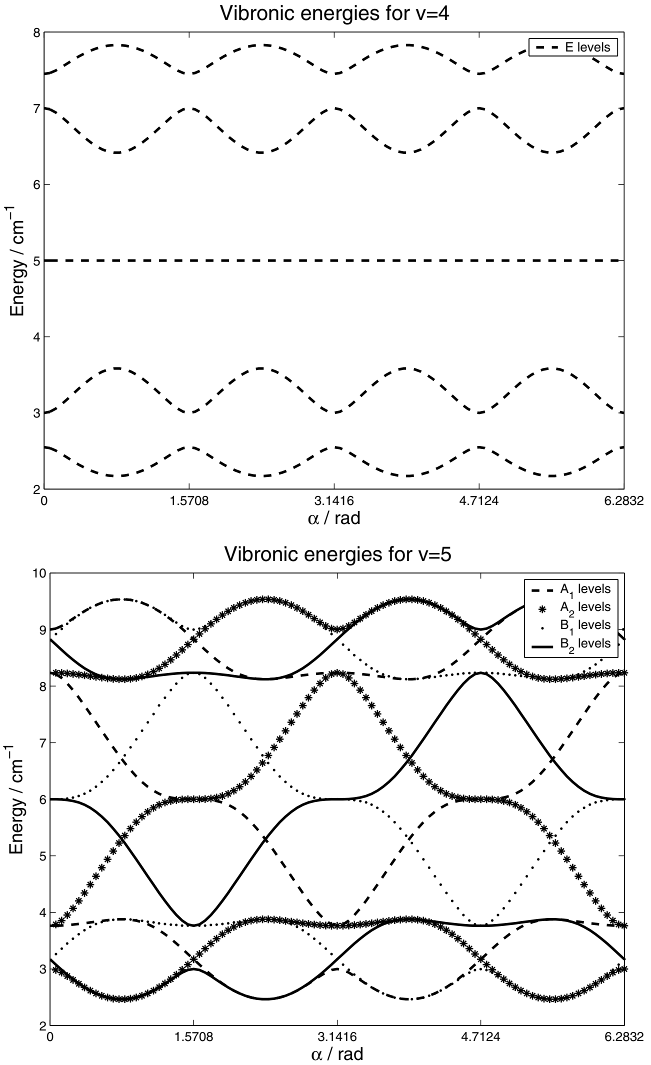

Fig. 1. Vibronic energies for a $E \otimes e$ system in D_{4h} (for $v = 4$ and $v = 5$) as a function of α (see text).

Hougen [27]. The approximate models discussed in Sections 7.4.1–7.4.3 neglect vibronic interaction operators involving the b_i mode since these are at least of degree four in the elementary creation and annihilation operators. As a result the $E \otimes e_r$ problem is recovered by setting $\tilde{\omega}_{s'} = 0$ in the Hamiltonian expansions and in the corresponding energy expressions. The associated symmetry adapted states are obtained with the omission of the kets $|N - v(\Gamma_i)\rangle$.

In the general case of arbitrary coupling constants the energies, obtained through a first order perturbation calculation, have been given in [27] up to $v = 4$. They can be recovered from our model with equation (D.3) for the matrix elements and equations (90, 91) with $\tilde{\lambda}_z = 0$. Results for higher v values can easily be obtained since from the outset we work in a fully symmetry adapted basis $|\Psi\rangle = |[1\,0]\frac{1}{2}1E_r; [v\,0]j\ell\Gamma; \Gamma_{ev}\sigma_{ev}\rangle\rangle$. This is illustrated in Figure 1 for $v = 4$ and $v = 5$. The vibronic energies have been calculated with parameters $\tilde{\lambda}_x/2 = (\cos\alpha + \sin\alpha)$ and $\tilde{\lambda}_y/2 = (\cos\alpha - \sin\alpha)$ in order to make the link with previous results [27].

Special cases considered in [27] and associated with a "Renner effect" [39] correspond to those studied in Section 7.4.2. When $\tilde{\lambda}_x = \tilde{\lambda}_y$ ($\tilde{\lambda}_x = -\tilde{\lambda}_y$) and $\tilde{\lambda}_z = 0$ if we denote j_z (j'_z) the eigenvalues of $\Delta = S_z + J_z$ (Eq. (108)) ($\overline{\Delta} = -S_z + J_z$ (Eq. (126))) then:

$$j_z = -\frac{1}{2}K, \quad j'_z = \frac{1}{2}\widetilde{K},$$

where K and $\widetilde{K}$ are the quantum numbers used in [27][2]. Direct comparison of (112), (113), (131) with equation (11) of [27] leads to

$$\hbar\tilde{\omega}_s = \hbar\omega\left(1 - \frac{p^2}{8\hbar^2\omega^2}\right), \qquad \hbar\tilde{\lambda}_x = \pm 2p.$$

We note that the energies in [27] are expressed in terms of K and $\widetilde{K}$; however these are no longer good quantum numbers for symmetry adapted states (except for E_r ones (120, 121)): the true conserved quantum numbers are, besides the overall symmetry labels, $\Omega_\pm$.

The "accidental Born-Oppenheimer" cases discussed in the last section of [27] correspond to $\tilde{\lambda}_z = \tilde{\lambda}_y = 0$ and $\tilde{\lambda}_z = \tilde{\lambda}_x = 0$ of Section 7.4.3. As in Section 7.3 it is a situation where a relation between the effective Hamiltonian approach and the traditional one can be established. We start from the untransformed vibronic Hamiltonian (23) written in terms of dimensionless normal coordinates:

$$\begin{aligned} H &= I_e\hbar\omega_s(N_s + 1) + \hbar\lambda_x S_x({}_sq^{(E_r)} \times {}_sq^{(E_r)})^{(B_1)} \\ &= I_e\hbar\omega_s(N_s + 1) + \hbar\frac{\lambda_x}{\sqrt{2}}\, S_x({}_sq_1^{(E_r)2} - {}_sq_2^{(E_r)2}), \end{aligned} \quad (145)$$

$$\begin{aligned} H &= I_e\hbar\omega_s(N_s + 1) + \hbar\lambda_y S_y({}_sq^{(E_r)} \times {}_sq^{(E_r)})^{(B_2)} \\ &= I_e\hbar\omega_s(N_s + 1) - \hbar\frac{\lambda_y}{\sqrt{2}}\, S_y({}_sq_{\bar{\bar{1}}}^{(E_r)2} - {}_sq_{\bar{\bar{2}}}^{(E_r)2}). \end{aligned} \quad (146)$$

Equation (145) (resp. (146)) uses orientation I (resp. III) in which the electronic operator ${}^{[1\,-1]}E^{(1,2B_1)} = S_x$ (resp. ${}^{[1\,-1]}E^{(1,2B_2)} = S_y$) is diagonal and correspond respectively to cases (iii) (resp. (iv)) of [27] with $\hbar\lambda_x = 4\sqrt{2}f\hbar\omega_s/k$ (resp. $\hbar\lambda_y = -4\sqrt{2}f\hbar\omega_s/k$) where f is the vibronic coupling constant and k the force constant associated with the e_r mode.

In order to treat both cases simultaneously we set:

$$\begin{aligned} &{}_sa_1^+ = {}_sb_1^{+(E_r)}, \quad {}_sa_2^+ = {}_sb_2^{+(E_r)} \quad \text{(Eq. (145))} \\ &{}_sa_1^+ = {}_sb_{\bar{\bar{1}}}^{+(E_r)}, \quad {}_sa_2^+ = {}_sb_{\bar{\bar{2}}}^{+(E_r)} \quad \text{(Eq. (146))} \end{aligned} \quad (147)$$

where the notation for the symmetrized elementary operators associated with mode e_r is that of [17]. Equations (145, 146) can then be written

$$\begin{aligned} H_\alpha &= \hbar\omega_s({}_sa_1^+{}_sa_1 + {}_sa_2^+{}_sa_2 + 1) \\ &\quad + \hbar\frac{\delta_\alpha}{2\sqrt{2}}S_\alpha[({}_sa_1^+ + {}_sa_1)^2 - ({}_sa_2^+ + {}_sa_2)^2], \end{aligned} \quad (148)$$

---

[2] The $\ell = 2m$ quantum number in [27] differs from ours which is $\ell = 2|m|$.

with $\delta_\alpha = \lambda_x$ or $\delta_\alpha = -\lambda_y$ according to the case. As shown in [31] the eigenvalues and eigenstates may be obtained through a unitary transformation which is a product of two one mode generalized Bogoliubov transformations

$$\begin{aligned}\widetilde{H}_\alpha &= B_1(\sigma_\alpha)B_2(\sigma_\alpha)HB_2^{-1}(\sigma_\alpha)B_1^{-1}(\sigma_\alpha)\\ &= \hbar\omega_s[1+\frac{\delta_\alpha}{\sqrt{2}\omega_s}\sigma_\alpha]^{1/2}\left({}_sa_1^+{}_sa_1+\frac{1}{2}\right)\\ &\quad+\hbar\omega_s[1-\frac{\delta_\alpha}{\sqrt{2}\omega_s}\sigma_\alpha]^{1/2}\left({}_sa_2^+{}_sa_2+\frac{1}{2}\right)\\ &= \hbar\frac{[\Omega_+(\sigma_\alpha)+\Omega_-(\sigma_\alpha)]}{2}(N_s+1)\\ &\quad+\hbar\frac{[\Omega_+(\sigma_\alpha)-\Omega_-(\sigma_\alpha)]}{2}({}_sa_1^+{}_sa_1-{}_sa_2^+{}_sa_2),\end{aligned} \quad (149)$$

where

$$\Omega_\pm(\sigma_\alpha) = \omega_s\left[1\pm\frac{\delta_\alpha}{\sqrt{2}\omega_s}\sigma_\alpha\right]^{1/2}.$$

Within bases $|n_1,n_2\rangle|\pm\rangle$ the doubly degenerate eigenvalues are given by

$$\begin{aligned}E_{n_1n_2} &= \hbar\omega_+\left(n_1+\frac{1}{2}\right)+\hbar\omega_-\left(n_2+\frac{1}{2}\right)\\ &= \hbar\frac{(\omega_++\omega_-)}{2}(v+1)+\hbar\frac{(\omega_+-\omega_-)}{2}(n_1-n_2),\end{aligned} \quad (150)$$

with $v = n_1+n_2$ and where we set

$$\omega_+ = \Omega_+(+) = \Omega_-(-), \quad \omega_- = \Omega_+(-) = \Omega_-(+).$$

The corresponding degenerate states are for $\alpha = x$

$$\begin{aligned}|n_1,n_2\rangle|+\rangle &= |\widehat{[v\,0]jm}\rangle\rangle\left|[1\,0]\frac{1}{2}1E_r1\right\rangle\!\!\right\rangle\\ &= [n_1!n_2!]^{-1/2}({}_sb^{+(E_r)}_{1})^{n_1}({}_sb^{+(E_r)}_{2})^{n_2}|0,0\rangle\left|[1\,0]\frac{1}{2}1E_r1\right\rangle\!\!\right\rangle,\\ |n_2,n_1\rangle|-\rangle &= |\widehat{[v\,0]j-m}\rangle\rangle\left|[1\,0]\frac{1}{2}1E_r2\right\rangle\!\!\right\rangle\\ &= [n_1!n_2!]^{-1/2}({}_sb^{+(E_r)}_{1})^{n_2}({}_sb^{+(E_r)}_{2})^{n_1}|0,0\rangle\left|[1\,0]\frac{1}{2}1E_r2\right\rangle\!\!\right\rangle,\end{aligned}$$

with $j = (n_1+n_2)/2$ and $m = (n_1-n_2)/2$ and for $\alpha = y$

$$\begin{aligned}|n_1,n_2\rangle|+\rangle &= |\widehat{\widehat{[v\,0]jm}}\rangle\rangle\left|[1\,0]\frac{1}{2}1E_r\bar{\bar{1}}\right\rangle\!\!\right\rangle\\ &= [n_1!n_2!]^{-1/2}({}_sb^{+(E_r)}_{\bar{\bar{1}}})^{n_1}({}_sb^{+(E_r)}_{\bar{\bar{2}}})^{n_2}|0,0\rangle\left|[1\,0]\frac{1}{2}1E_r\bar{\bar{1}}\right\rangle\!\!\right\rangle,\\ |n_2,n_1\rangle|-\rangle &= |\widehat{\widehat{[v\,0]j-m}}\rangle\rangle\left|[1\,0]\frac{1}{2}1E_r\bar{\bar{2}}\right\rangle\!\!\right\rangle\\ &= [n_1!n_2!]^{-1/2}({}_sb^{+(E_r)}_{\bar{\bar{1}}})^{n_2}({}_sb^{+(E_r)}_{\bar{\bar{2}}})^{n_1}|0,0\rangle\left|[1\,0]\frac{1}{2}1E_r\bar{\bar{2}}\right\rangle\!\!\right\rangle,\end{aligned}$$

where the states $|\widehat{[v\,0]jm}\rangle\rangle$ and $|\widehat{\widehat{[v\,0]jm}}\rangle\rangle$ are those defined in equations (137, 138). Knowing that $({}_sa_1^+{}_sa_1-{}_sa_2^+{}_sa_2) = 2J_x$ (resp. $({}_sa_1^+{}_sa_1-{}_sa_2^+{}_sa_2) = 2J_y$) within orientation I (resp. orientation III) and with the property

$$\begin{aligned}\left[1\pm\frac{\delta_\alpha}{\sqrt{2}\omega_s}\sigma_\alpha\right]^{1/2} &= \frac{1}{2}\left\{\left[(1+\frac{\delta_\alpha}{\sqrt{2}\omega_s})^{1/2}+(1-\frac{\delta_\alpha}{\sqrt{2}\omega_s})^{1/2}\right]\right.\\ &\quad\left.\pm\,\sigma_\alpha\left[\left(1+\frac{\delta_\alpha}{\sqrt{2}\omega_s}\right)^{1/2}-\left(1-\frac{\delta_\alpha}{\sqrt{2}\omega_s}\right)^{1/2}\right]\right\},\end{aligned}$$

straightforward identification of equations (141–149) leads for $\alpha = x$ to:

$$\begin{aligned}\tilde{\omega}_s &= \frac{\omega_++\omega_-}{2} = \frac{\omega_s}{2}\left[\left(1+\frac{\lambda_x}{\sqrt{2}\omega_s}\right)^{1/2}+\left(1-\frac{\lambda_x}{\sqrt{2}\omega_s}\right)^{1/2}\right],\\ \frac{\tilde{\lambda}_x}{4} &= \frac{\omega_+-\omega_-}{2} = \frac{\omega_s}{2}\left[\left(1+\frac{\lambda_x}{\sqrt{2}\omega_s}\right)^{1/2}-\left(1-\frac{\lambda_x}{\sqrt{2}\omega_s}\right)^{1/2}\right].\end{aligned}$$

Likewise for $\alpha = y$ with equations (142)-(149) the correlation is given by the preceding equation with the substitutions $\tilde{\lambda}_x \to \tilde{\lambda}_y$ and $\lambda_x \to -\lambda_y$. Also with equation (150) and equation (14) of [27] we find:

$$\begin{aligned}\tilde{\omega}_s &= \frac{\omega_s}{2}\left\{\left(1+\frac{4f}{k}\right)^{\frac{1}{2}}+\left(1-\frac{4f}{k}\right)^{\frac{1}{2}}\right\},\\ \frac{\tilde{\lambda}_x}{4} &= \frac{\omega_s}{2}\left\{\left(1+\frac{4f}{k}\right)^{\frac{1}{2}}-\left(1-\frac{4f}{k}\right)^{\frac{1}{2}}\right\},\end{aligned} \quad (151)$$

and $\tilde{\omega}_s\tilde{\lambda}_x = \omega_+^2-\omega_-^2 = \sqrt{2}\lambda_x\omega_s$.

The correlation between eigenvectors of $\widetilde{H}^0_{vibr}$ (141, 142) and those of H (145, 146) is obtained with the expressions for the $B_i(\sigma_\alpha)$ unitary operators given in [31]:

$$\begin{aligned}|\tilde{\Psi}_{n_1n_2+}\rangle &= B_1^{-1}(\sigma_\alpha)B_2^{-1}(\sigma_\alpha)|n_1,n_2\rangle|+\rangle,\\ |\tilde{\Psi}_{n_1n_2-}\rangle &= B_1^{-1}(\sigma_\alpha)B_2^{-1}(\sigma_\alpha)|n_2,n_1\rangle|-\rangle,\end{aligned}$$

are eigenstates of H (145, 146) with eigenvalues (150). Various expressions can be given for these states; in particular they can be expressed in terms of generalized boson operators obtained from the initial ones through the Bogoliubov transformation:

$$\begin{aligned}{}_sc_1^+(\sigma_\alpha) &= \frac{1}{2}\left\{\left[\kappa_+(\sigma_\alpha)-\frac{1}{\kappa_+(\sigma_\alpha)}\right]e^{i\phi_1}{}_sa_1\right.\\ &\quad\left.+\left[\kappa_+(\sigma_\alpha)+\frac{1}{\kappa_+(\sigma_\alpha)}\right]e^{i\phi_1}{}_sa_1^+\right\},\\ {}_sc_2^+(\sigma_\alpha) &= \frac{1}{2}\left\{\left[\kappa_-(\sigma_\alpha)-\frac{1}{\kappa_-(\sigma_\alpha)}\right]e^{i\phi_2}{}_sa_2\right.\\ &\quad\left.+\left[\kappa_-(\sigma_\alpha)+\frac{1}{\kappa_-(\sigma_\alpha)}\right]e^{i\phi_2}{}_sa_2^+\right\},\end{aligned} \quad (152)$$

with $\kappa_\pm^2(\sigma_\alpha) = [1 \pm \delta_\alpha\sigma_\alpha/\sqrt{2}\omega_s]^{1/2}$, which gives

$$\begin{aligned}|\widetilde{\Psi}_{n_1n_2+}\rangle &= |n_1, n_2\rangle_+|+\rangle \\ &= (n_1!n_2!)^{-1/2}[{}_sc_1^+(+)]^{n_1}[{}_sc_2^+(+)]^{n_2}|0,0\rangle_+|+\rangle, \\ |\widetilde{\Psi}_{n_1n_2-}\rangle &= |n_2n_1\rangle_-|-\rangle \\ &= (n_1!n_2!)^{-1/2}[{}_sc_1^+(-)]^{n_2}[{}_sc_2^+(-)]^{n_1}|0,0\rangle_-|-\rangle. \end{aligned} \tag{153}$$

We underline that in each subspace we have two different vibrational ground states, made of two harmonic oscillator squeezed vacuum states [37,38], and given in terms of the initial ones by

$$|0,0\rangle_+ = \mathcal{N}_+\mathcal{N}_- \exp\left[-\frac{\xi_+}{2}({}_sa_1^+)^2\right]\exp\left[-\frac{\xi_-}{2}({}_sa_2^+)^2\right]|0,0\rangle,$$

$$|0,0\rangle_- = \mathcal{N}_+\mathcal{N}_- \exp\left[-\frac{\xi_-}{2}({}_sa_1^+)^2\right]\exp\left[-\frac{\xi_+}{2}({}_sa_2^+)^2\right]|0,0\rangle,$$

where, setting $\kappa_+(+) = \kappa_-(-) = \kappa_+$, $\kappa_+(-) = \kappa_-(+) = \kappa_-$, we have

$$\xi_+ = \frac{\kappa_+^2 - 1}{\kappa_+^2 + 1}, \quad \xi_- = \frac{\kappa_-^2 - 1}{\kappa_-^2 + 1},$$

and

$$\begin{aligned}\mathcal{N}_+\mathcal{N}_- &= \exp\left[\frac{i(\phi_1+\phi_2)}{2}\right]\left[\frac{4\kappa_+\kappa_-}{(\kappa_+^2+1)(\kappa_-^2+1)}\right]^{1/2} \\ &= \exp\left[\frac{i(\phi_1+\phi_2)}{2}\right](1-\xi_+^2)^{1/4}(1-\xi_-^2)^{1/4}.\end{aligned}$$

Also in order to take into account interactions with other vibrational modes or molecular rotation care should be taken since the sets $\{c_i(\pm), c_i^+(\pm)\}$ are not independent as it appears from equation (152). For completeness we give below the symmetry adapted eigenstates

$$\Big|[1\,0]\frac{1}{2}1E_r; n_1n_2; \Gamma_{ev}\sigma_{ev}\Big\rangle\!\!\Big\rangle$$

of H (145, 146) obtained with the matrices for the *irrep* E_r [17] in orientation I when $\alpha = x$ and orientation III when $\alpha = y$. The corresponding realization of the elementary boson operators is in each case that given in equation (147). All phases have been settled so that upon time reversal

$$\mathcal{K}\Big|[1\,0]\frac{1}{2}1E_r; n_1n_2; \Gamma_{ev}\sigma_{ev}\Big\rangle\!\!\Big\rangle = \Big|[1\,0]\frac{1}{2}1E_r; n_1n_2; \Gamma_{ev}\sigma_{ev}\Big\rangle\!\!\Big\rangle.$$

Also we set below

$$e^{i\theta_1} = \exp\left[-i\left(n_1+\frac{1}{2}\right)\phi_1\right]\exp\left[-i\left(n_2+\frac{1}{2}\right)\phi_2\right],$$

$$e^{i\theta_2} = \exp\left[-i\left(n_2+\frac{1}{2}\right)\phi_1\right]\exp\left[-i\left(n_1+\frac{1}{2}\right)\phi_2\right].$$

- $\alpha = x$

$$\begin{aligned}\Big|[1\,0]\frac{1}{2}1E_r; n_1n_2; E_r\sigma\Big\rangle\!\!\Big\rangle &= e^{i\theta_1}|\widetilde{\Psi}_{n_1n_2+}\rangle \\ \Big|[1\,0]\frac{1}{2}1E_r; n_1n_2; E_r-\sigma\Big\rangle\!\!\Big\rangle &= e^{i\theta_2}|\widetilde{\Psi}_{n_1n_2-}\rangle\end{aligned} \tag{154}$$

with $(\sigma, -\sigma) = (1,2)$ (resp. $(\sigma, -\sigma) = (2,1)$) for n_1 and n_2 even (resp. odd).

$$\begin{aligned}\Big|[1\,0]\frac{1}{2}1E_r; n_1n_2; \Gamma_1\Big\rangle\!\!\Big\rangle &= \frac{e^{i\theta_1}}{\sqrt{2}}(e^{i\theta_1}|\widetilde{\Psi}_{n_1n_2+}\rangle + e^{i\theta_2}|\widetilde{\Psi}_{n_1n_2-}\rangle) \\ \Big|[1\,0]\frac{1}{2}1E_r; n_1n_2; \Gamma_2\Big\rangle\!\!\Big\rangle &= \frac{e^{i\theta_1}}{\sqrt{2}}(e^{i\theta_1}|\widetilde{\Psi}_{n_1n_2+}\rangle - e^{i\theta_2}|\widetilde{\Psi}_{n_1n_2-}\rangle)\end{aligned} \tag{155}$$

with $(\Gamma_1, \Gamma_2) = (B_2, A_2)$ (resp. $(\Gamma_1, \Gamma_2) = (A_1, B_1)$) for n_1 even and n_2 odd (resp. n_1 odd and n_2 even).

- $\alpha = y$

All results for this case are deduced from those in equations (154, 155) with the substitutions $E_r\sigma \rightarrow E_r\bar{\bar{\sigma}}$ and $(\Gamma_1, \Gamma_2) = (B_1, A_2)$ (resp. $(\Gamma_1, \Gamma_2) = (A_1, B_2)$) for n_1 even and n_2 odd (resp. n_1 odd and n_2 even).

8 Conclusion

Through several examples we showed that the effective Hamiltonian approach combined with Lie algebraic methods allows to obtain exact solutions for various zeroth order models to which additional higher order interaction terms can next be added. Also the usual technique of projection of the eigenvalue equation onto separate pseudospin subspaces is completely avoided.

In the following paper we will consider $E \otimes e$ JT dynamical systems for cases where $[E \times E]$ is of the $A_1 + E$ type and the closely related $G' \otimes e$ case in cubic molecules. Clearly many other JT molecular systems can be considered with a similar approach, a natural extension of our work being ${}^kE$ terms.

Appendix A: Vibrational states and operators

Vibrational operators as defined in equation (14) are built below taking into account that for the molecules considered in this paper we can restrict to oscillators with dimension at most equal to two. This covers the groups D_n, C_{nv}, D_{nd} *(n even)* in $G_{(I)}$; D_{nh}, D_{nd} *(n odd)* in $G_{(II)}$; groups in $G_{(III)}$ are somewhat special since their full vibrational representation admits only E_r (or $E_{r\alpha}$) modes with $r = 1$. In view of our applications, detailed properties are given for operators involving at most two modes in (14).

Results below are first given assuming matrices for the *irrep* of type E in real form (orientation I of [17]). This implies that all CGC may be taken real. We also use:

$$(-1)^{A_2} = -1, \quad (-1)^{B_1} = (-1)^{B_2} = 1$$

since A_2 is odd and B_1, B_2 even. For E symmetry we choose in all cases $(-1)^E = 1$. The modifications to bring when we consider orientations II or III of [17] are indicated in Section A.3 of this appendix.

A.1 One mode operators

A.1.1 Non degenerate modes $g_s = 1$

For a non degenerate mode with symmetry C we simply have the operator set

$$ {}_{s}X^{n(C_n)} = [\,{}_{s}X^{(C)}]^n, \tag{A.1}$$

with $C_n = \Gamma_0$ for n even and $C_n = C$ for n odd. In (A.1) we may take for ${}_{s}X^{(C)}$ the normal coordinates ${}_{s}Q^{(C)}$ or their conjugate momentum ${}_{s}P^{(C)}$, their dimensionless counterparts ${}_{s}q^{(C)}$, ${}_{s}p^{(C)}$, annihilation ${}_{s}a^{(C)}$ or creation ${}_{s}a^{+(C)}$ operators for mode s. We may build Hermitian operators in normal form with:

$$\begin{aligned} {}^{\epsilon}_{s}V^{C_1C_2(C_v)}_{\{n_1\}\{n_2\}} &= i^{\epsilon}\{[\,{}_{s}a^{+n_1(C_1)} \times \,{}_{s}a^{n_2(C_2)}]^{(C_v)} \\ &\quad + (-1)^{\epsilon}[\,{}_{s}a^{+n_2(C_2)} \times \,{}_{s}a^{n_1(C_1)}]^{(C_v)}\}. \end{aligned} \tag{A.2}$$

$\epsilon = 0$ (or 1) gives the behavior upon time reversal + (or −). In particular when $n_1 = n_2 = n$ we have the scalar operators

$$\begin{aligned} {}^{0}_{s}V^{C_nC_n(\Gamma_0)}_{\{n\}\{n\}} &= 2[\,{}_{s}a^{+n(C_n)} \times \,{}_{s}a^{n(C_n)}]^{(\Gamma_0)} \\ &= 2N_s^{[n]} = 2N_s(N_s-1)\cdots(N_s-n+1). \end{aligned}$$

The space of states is spanned by the kets

$$|v\,\Gamma\rangle = (v!)^{-\frac{1}{2}}[\,{}_{s}a^{+(C)}]^v|0\rangle,$$

and for the matrix elements we have

$$\begin{aligned} \langle v'\,\Gamma'|\,{}_{s}a^{+n(C_n)}|v\,\Gamma\rangle &= \langle v\,\Gamma|\,{}_{s}a^{n(C_n)}|v'\,\Gamma'\rangle \\ &= [\Gamma']^{-\frac{1}{2}}F\begin{matrix} & (\Gamma')* \\ (C_n\;\Gamma) & \end{matrix}(v'\,\Gamma'||\,{}_{s}a^{+n(C_n)}||v\,\Gamma) \\ &= \delta_{\Gamma',C_n\times\Gamma}\left[\frac{(v+n)!}{v!}\right]^{\frac{1}{2}}\delta_{v',v+n}, \end{aligned} \tag{A.3}$$

from which those of the general operators (A.2) are deduced:

$$\begin{aligned} \langle v'\,\Gamma'|{}^{\epsilon}_{s}V^{C_1C_2(C_v)}_{\{n_1\}\{n_2\}}|v\,\Gamma\rangle &= (v'\,\Gamma'||{}^{\epsilon}_{s}V^{C_1C_2(C_v)}_{n_1n_2}||v\,\Gamma) \\ &\times i^{\epsilon}\delta_{\Gamma',C_v\times\Gamma}\left\{\frac{[v!(v+n_1-n_2)!]^{\frac{1}{2}}}{(v-n_2)!}\,\delta_{v',v+n_1-n_2}\right. \\ &\left. +(-1)^{\epsilon}\frac{[v!(v-n_1+n_2)!]^{\frac{1}{2}}}{(v-n_1)!}\,\delta_{v',v-n_1+n_2}\right\}. \end{aligned} \tag{A.4}$$

In equations (A.3, A.4) we took into account that all CGC can be chosen equal to one.

A.1.2 Doubly degenerate modes $g_s = 2$

For a vibrational mode with symmetry E_k in G we take the operators introduced previously [17] for the chains $u(2) \supset su(2) \supset so(2)$ or $u(2) \supset su^*(2) \supset G$:

$$ {}^{[m_1-m_2]}_{\qquad s}\mathcal{V}^{(j)}_{m} \quad \text{or} \quad {}^{[m_1-m_2]}_{\qquad s}\mathcal{V}^{(j)}_{\ell\Gamma\sigma} = {}^{[m_1-m_2]}_{\qquad s}\mathcal{V}^{(j,\ell\Gamma)}_{\sigma}. \tag{A.5}$$

Depending on the chain used the space of states is spanned by the kets

$$|[v\,0]jm\rangle\rangle \quad \text{or} \quad |[v\,0]j\,\ell\Gamma\sigma\rangle\rangle,$$

and all matrix elements and properties have been given in [17].

A.2 Two mode operators

In our applications of Sections 6 and 7 the vibronic terms involve at most two mode operators. These are detailed below for various possible cases.

A.2.1 $g_s = 1$ and $g_{s'} = 1$

Depending upon the case at hand we have several possibilities. For operators based on coordinates and momenta we can simply take $(s \neq s')$ (Eq. (A.1)):

$$ {}_{ss'}V^{C_1C_2(C_v)}_{n_1n_2} = [{}_{s}X^{n_1(C_1)} \times {}_{s'}Y^{n_2(C_2)}]^{(C_v)}, \tag{A.6}$$

whose behavior upon time reversal is determined by the choice for X and Y and the powers n_i. We may also perform a coupling of the operators (A.2) built from creation and annihilation operators:

$$ {}^{\epsilon+\epsilon'}_{\;\;ss'}V^{\{C_iC'_i\}(C_v)}_{\{n_in'_i\}} = [\,{}^{\epsilon}_{s}V^{C_1C_2(C_{12})}_{\{n_1\}\{n_2\}} \times {}^{\epsilon'}_{s'}V^{C'_1C'_2(C'_{12})}_{\{n'_1\}\{n'_2\}}]^{(C_v)},$$

but the latter are not directly in normal form and not convenient within a polyad scheme. If we define [19,40]

$$ {}_{ss'}A^{+C_1C_2(C_{12})}_{n_1n_2} = [\,{}_{s}a^{+n_1(C_1)} \times \,{}_{s'}a^{+n_2(C_2)}]^{(C_{12})},$$

and an identical expression in terms of annihilation operators we obtain normal ordered Hermitian operators with

$$\begin{aligned} {}^{\epsilon}_{ss'}V^{\{C_i\}\{C'_i\}(C_v)}_{\{n_i\}\{n'_i\}} &= i^{\epsilon}\{[{}_{ss'}A^{+C_1C_2(C_{12})}_{n_1n_2} \times {}_{ss'}A^{C'_1C'_2(C'_{12})}_{n'_1n'_2}]^{(C_v)} \\ &\quad + (-1)^{\epsilon'}[{}_{ss'}A^{+C'_1C'_2(C'_{12})}_{n'_1n'_2} \times {}_{ss'}A^{C_1C_2(C_{12})}_{n_1n_2}]^{(C_v)}\} \end{aligned} \tag{A.7}$$

where $\epsilon' = \epsilon + C_{12} + C'_{12} + C_v$. All matrix elements can be computed from those in equations (A.3) or (A.4).

A.2.2 $\mathsf{g_s} = 1$ and $\mathsf{g_{s'}} = 2$

Likewise we mainly have two solutions. Firstly through a coupling of one mode operators defined in (A.2, A.5):

$$
\begin{aligned}
&{}^{\mu}_{ss'}V^{C_1C_2(C_{12})j\ell C'_{12}(C_v)}_{n_1n_2,m_1m_2} = \\
&\qquad i^{\epsilon'}\{[{}^{\epsilon}_{s}V^{C_1C_2(C_{12})}_{\{n_1\}\{n_2\}} \times {}^{[m_1\,-m_2]}_{s'}\mathcal{V}^{(j,\ell C'_{12})}]^{(C_v)} \\
&\qquad + (-1)^{\epsilon'}[{}^{\epsilon}_{s}V^{C_1C_2(C_{12})}_{n_1n_2} \times {}^{[m_2\,-m_1]}_{s'}\mathcal{V}^{(j,\ell C'_{12})}]^{(C_v)}\}, \qquad \text{(A.8)}
\end{aligned}
$$

with $\mu = \epsilon' + \epsilon + j - \ell/2$, secondly with a construction similar to that of the previous section which leads to operators in normal form. We set

$$
{}_{ss'}A^{+C_1,j\ell C_2(C_{12})}_{n_1n_2} = [{}_{s}a^{+n_1(C_1)} \times {}^{[n_2\,0]}_{s'}V^{(j,\ell C_2)}]^{(C_{12})},
$$

and

$$
{}_{ss'}A^{C_1,j\ell C_2(C_{12})}_{n_1n_2} = [{}_{s}a^{n_1(C_1)} \times {}^{[0\,-n_2]}_{s'}V^{(j,\ell C_2)}]^{(C_{12})},
$$

from which we build:

$$
\begin{aligned}
&{}^{\mu}_{ss'}V^{\{C_ij_i\ell_i\}\{C'_ij'_i\ell'_i\}(C_v)}_{\{n_i\}\{n'_i\}} = \\
&\qquad i^{\epsilon}\{[{}_{ss'}A^{+C_1,j\ell C_2(C_{12})}_{n_1n_2} \times {}_{ss'}A^{C'_1,j'\ell' C'_2(C'_{12})}_{n'_1n'_2}]^{(C_v)} \\
&\qquad + (-1)^{\epsilon'}[{}_{ss'}A^{+C'_1,j'\ell' C'_2(C'_{12})}_{n'_1n'_2} \times {}_{ss'}A^{C_1,j\ell C_2(C_{12})}_{n_1n_2}]^{(C_v)}\}, \qquad \text{(A.9)}
\end{aligned}
$$

with $\mu = \epsilon + j - \ell/2 + j' - \ell'/2$ and $\epsilon' = \epsilon + C_{12} + C'_{12} + C_v$.

A.2.3 $\mathsf{g_s} = 2$ and $\mathsf{g_{s'}} = 2$

Similarly from the coupling of one mode operators (A.5) we determine Hermitian operators (not in normal form):

$$
\begin{aligned}
&{}^{\mu}_{ss'}V^{j\ell\Gamma,j'\ell'\Gamma'(C_v)}_{m_1m_2,m'_1m'_2} = \\
&\qquad i^{\epsilon}\{[{}^{[m_1\,-m_2]}_{s}\mathcal{V}^{(j,\ell\Gamma)} \times {}^{[m'_1\,-m'_2]}_{s'}\mathcal{V}^{(j',\ell'\Gamma')}]^{(C_v)} \\
&\qquad + (-1)^{\epsilon}[{}^{[m_2\,-m_1]}_{s}\mathcal{V}^{(j,\ell\Gamma)} \times {}^{[m'_2\,-m'_1]}_{s'}\mathcal{V}^{(j',\ell'\Gamma')}]^{(C_v)}\}, \qquad \text{(A.10)}
\end{aligned}
$$

with $\mu = \epsilon + j - \ell/2 + j' - \ell'/2$.

We can also define

$$
\begin{aligned}
&{}_{ss'}A^{+j_1\ell_1C_1,j_2\ell_2C_2(C_{12})}_{n_1n_2} = \\
&\qquad [{}^{[n_1\,0]}_{s}V^{(j_1,\ell_1C_1)} \times {}^{[n_2\,0]}_{s'}V^{(j_2,\ell_2C_2)}]^{(C_{12})},
\end{aligned}
$$

and

$$
\begin{aligned}
&{}_{ss'}A^{j_1\ell_1C_1,j_2\ell_2C_2(C_{12})}_{n_1n_2} = \\
&\qquad [{}^{[0\,-n_1]}_{s}V^{(j_1,\ell_1C_1)} \times {}^{[0\,-n_2]}_{s'}V^{(j_2,\ell_2C_2)}]^{(C_{12})},
\end{aligned}
$$

from which we built setting $j_i\ell_iC_i = j_1\ell_1C_1, j_2\ell_2C_2$:

$$
\begin{aligned}
&{}^{\mu}_{ss'}V^{\{j_i\ell_iC_i\}\{j'_i\ell'_iC'_i\}(C_v)}_{\{n_i\}\{n'_i\}} = \\
&\qquad i^{\epsilon}\{[{}_{ss'}A^{+j_i\ell_iC_i(C_{12})}_{n_1n_2} \times {}_{ss'}A^{j'_i\ell'_iC'_i(C'_{12})}_{n'_1n'_2}]^{(C_v)} \\
&\qquad + (-1)^{\epsilon'}[{}_{ss'}A^{+j'_i\ell'_iC'_i(C'_{12})}_{n'_1n'_2} \times {}_{ss'}A^{j_i\ell_iC_i(C_{12})}_{n_1n_2}]^{(C_v)}\} \qquad \text{(A.11)}
\end{aligned}
$$

with $\mu = \epsilon + j_1 - \ell_1/2 + j'_1 - \ell'_1/2 + j_2 - \ell_2/2 + j'_2 - \ell'_2/2$ and $\epsilon' = \epsilon + C_{12} + C'_{12} + C_v$.

We note that when other degrees of freedom are involved, the previously defined coupling schemes may be modified.

A.3 Changing the orientation of an irreducible representation

In a general way a change of orientation $\sigma \to \kappa$ of an *irrep* C is performed through a unitary transformation:

$$
T^{(C)}_{\kappa} = {}^{(C)}U^{\sigma}_{\kappa}T^{(C)}_{\sigma},
$$

where the quantities denoted T may be tensor operators or kets. When the transformation ${}^{(C)}U$ is determined the modification rules to be applied to the new symmetry adapted quantities are easily obtained. For instance starting from an Hermitian operator we have:

$$
T^{(C)\dagger}_{\kappa} = {}^{(C)}U^{\sigma *}_{\kappa}T^{(C)}_{\sigma},
$$

and under time reversal the new quantities transform as

$$
\mathcal{K}_tT^{(C)}_{\kappa}\mathcal{K}_t^{-1} = {}^{(C)}U^{\sigma *}_{\kappa}\mathcal{K}_tT^{(C)}_{\sigma}\mathcal{K}_t^{-1},
$$

For the cases considered in the paper, only E type *irrep* are involved, and we have from [17]:

$$
{}^{(C)}U^{\sigma *}_{\bar{\sigma}} = {}^{(C)}U^{\sigma}_{-\bar{\sigma}},
$$

when going from orientation I to orientation II ($\kappa = \bar{\sigma}$) and

$$
{}^{(C)}U^{\sigma *}_{\bar{\bar{\sigma}}} = {}^{(C)}U^{\sigma}_{\bar{\bar{\sigma}}}
$$

when going from orientation I to orientation III ($\kappa = \bar{\bar{\sigma}}$). So the modification rules are particularly simple to apply.

A.4 Coupling coefficients

For the groups and irreducible representations considered in our applications, Sections 6 and 7, we give in Table 2 non-zero $3 - \Gamma$ coefficients satisfying the usual symmetry properties with respect to permutation of their columns [41,42] with

$$
(-1)^{A_1} = (-1)^{B_1} = (-1)^{B_2} = (-1)^{E_r} = 1, (-1)^{A_2} = -1.
$$

The associated CGC are deduced, for these cases, with

$$
F\,\begin{matrix} \sigma_1 & \sigma_2 & (\Gamma_3) \\ (\Gamma_1 & \Gamma_2) & \sigma_3 \end{matrix} = [\Gamma_3]^{1/2}\begin{pmatrix} & \Gamma_3 \\ \sigma_3 & \sigma'_3 \end{pmatrix} F\,\begin{matrix} \sigma_1 & \sigma_2 & \sigma'_3 \\ (\Gamma_1 & \Gamma_2 & \Gamma_3) \end{matrix},
$$

Table 2. $3-\Gamma$ coefficients in various orientations.

	Γ_1	Γ_2	Γ_3	σ_1	σ_2	σ_3	$3-\Gamma$	Γ_1	Γ_2	Γ_3	σ_1	σ_2	σ_3	$3-\Gamma$
	E_r	E_r	A_1	1	1		$1/\sqrt{2}$	E_r	E_r	B_1	1	1		$1/\sqrt{2}$
I	E_r	E_r	A_1	2	2		$1/\sqrt{2}$	E_r	E_r	B_1	2	2		$-1/\sqrt{2}$
	E_r	E_r	A_2	1	2		$1/\sqrt{2}$	E_r	E_r	B_2	1	2		$1/\sqrt{2}$
	Γ_1	Γ_2	Γ_3	$\bar{\sigma}_1$	$\bar{\sigma}_2$	$\bar{\sigma}_3$	$3\Gamma-\sigma$	Γ_1	Γ_2	Γ_3	$\bar{\sigma}_1$	$\bar{\sigma}_2$	$\bar{\sigma}_3$	$3\Gamma-\sigma$
	E_r	E_r	A_1	$\bar{1}$	$\bar{2}$		$1/\sqrt{2}$	E_r	E_r	B_1	$\bar{2}$	$\bar{2}$		$-1/\sqrt{2}$
II	E_r	E_r	A_2	$\bar{1}$	$\bar{2}$		$i/\sqrt{2}$	E_r	E_r	B_2	$\bar{1}$	$\bar{1}$		$i/\sqrt{2}$
	E_r	E_r	B_1	$\bar{1}$	$\bar{1}$		$-1/\sqrt{2}$	E_r	E_r	B_2	$\bar{2}$	$\bar{2}$		$-i/\sqrt{2}$
	Γ_1	Γ_2	Γ_3	$\bar{\bar{\sigma}}_1$	$\bar{\bar{\sigma}}_2$	$\bar{\bar{\sigma}}_3$	$3\Gamma-\sigma$	Γ_1	Γ_2	Γ_3	$\bar{\bar{\sigma}}_1$	$\bar{\bar{\sigma}}_2$	$\bar{\bar{\sigma}}_3$	$3\Gamma-\sigma$
	E_r	E_r	A_1	$\bar{\bar{1}}$	$\bar{\bar{1}}$		$1/\sqrt{2}$	E_r	E_r	B_1	$\bar{\bar{1}}$	$\bar{\bar{2}}$		$1/\sqrt{2}$
III	E_r	E_r	A_1	$\bar{\bar{2}}$	$\bar{\bar{2}}$		$1/\sqrt{2}$	E_r	E_r	B_2	$\bar{\bar{1}}$	$\bar{\bar{1}}$		$-1/\sqrt{2}$
	E_r	E_r	A_2	$\bar{\bar{1}}$	$\bar{\bar{2}}$		$1/\sqrt{2}$	E_r	E_r	B_2	$\bar{\bar{2}}$	$\bar{\bar{2}}$		$1/\sqrt{2}$

where the $1-\Gamma$ symbol reduces to the identity except for E_r *irrep* in orientation II for which it is

$$\begin{pmatrix} E_r \\ \bar{\sigma}\ \bar{\sigma}' \end{pmatrix} = \delta_{\bar{\sigma}',-\bar{\sigma}},$$

with $-\bar{1} = \bar{2}$ and $-\bar{2} = \bar{1}$. In all orientations we have $(i = 1, 2)$:

$$^{F}(A_i\ A_i\ A_1) = {}^{F}(B_i\ B_i\ A_1) = {}^{F}(B_1\ B_2\ A_2) = 1.$$

Appendix B: Effective Hamiltonian for $\mathbf{E \otimes (b_1 + b_2)}$

The expansion (32) is restricted to terms whose total degree in annihilation and creation operators is at most equals to four. The indices s_1, s_2 refer respectively to the b_1 and b_2 active modes and the operators are those defined in equations (A.2, A.7).

$$\begin{aligned}
\widetilde{H}_{vibr} = I_e \Bigg\{ & \sum_{n=0,1,2} {}_{s_1}\tilde{t}^{C_1C_1(A_1)}_{\{n_1\}\{n_1\}}\ {}^{0}_{s_1}V^{C_1C_1(A_1)}_{\{n_1\}\{n_1\}} \\
& + {}_{s_2}\tilde{t}^{C_2C_2(A_1)}_{\{n_2\}\{n_2\}}\ {}^{0}_{s_2}V^{C_2C_2(A_1)}_{\{n_2\}\{n_2\}} \\
& + {}_{ss'}\tilde{t}^{A_1A_1\,A_1A_1(A_1)}_{\{20\}\{02\}}\ {}^{0}_{s_1s_2}V^{A_1A_1\,A_1A_1(A_1)}_{\{20\}\{02\}} \\
& + {}_{s_1s_2}\tilde{t}^{B_1B_2\,B_1B_2(A_1)}_{\{11\}\{11\}}\ {}^{0}_{s_1s_2}V^{B_1B_2\,B_1B_2(A_1)}_{\{11\}\{11\}} \Bigg\} \\
& + {}^{[1\,-1]}E^{(1,0A_2)} \Bigg\{ {}_{s_1s_2}\tilde{t}^{B_1A_1\,A_1B_2(A_2)}_{\{10\}\{01\}}\ {}^{1}_{s_1s_2}V^{B_1A_1\,A_1B_2(A_2)}_{\{10\}\{01\}} \\
& + {}_{s_1s_2}\tilde{t}^{A_1A_1\,B_1B_2(A_2)}_{\{20\}\{11\}}\ {}^{1}_{s_1s_2}V^{A_1A_1\,B_1B_2(A_2)}_{\{20\}\{11\}} \\
& + {}_{s_1s_2}\tilde{t}^{A_1A_1\,B_1B_2(A_2)}_{\{02\}\{11\}}\ {}^{1}_{s_1s_2}V^{A_1A_1\,B_1B_2(A_2)}_{\{02\}\{11\}} \Bigg\}
\end{aligned}$$

Appendix C: Vibronic Hamiltonian for $\mathbf{E \otimes (b_i + a_j)}$

C.1 Restricted expansion for the effective Hamiltonian

The expansion (68) is restricted to terms whose total degree in annihilation and creation operators is at most equals to four. The indices s, s' refer respectively to the b_i and a_j modes.

$$\begin{aligned}
\widetilde{H}_{vibr} = I_e \Bigg\{ & \sum_{n=0,1,2} {}_{s}\tilde{t}^{C_iC_i(A_1)}_{\{n_i\}\{n_i\}}\ {}^{0}_{s}V^{C_iC_i(A_1)}_{\{n_i\}\{n_i\}} \\
& + {}_{s'}\tilde{t}^{C_jC_j(A_1)}_{\{n_j\}\{n_j\}}\ {}^{0}_{s'}V^{C_jC_j(A_1)}_{\{n_j\}\{n_j\}} \\
& + {}_{ss'}\tilde{t}^{A_1A_1\,A_1A_1(A_1)}_{\{20\}\{02\}}\ {}^{0}_{ss'}V^{A_1A_1\,A_1A_1(A_1)}_{\{20\}\{02\}} \\
& + {}_{ss'}\tilde{t}^{B_iA_j\,B_iA_j(A_1)}_{\{11\}\{11\}}\ {}^{0}_{ss'}V^{B_iA_j\,B_iA_j(A_1)}_{\{11\}\{11\}} \Bigg\} \\
& + {}^{[1\,-1]}E^{(1,2B_k)} \Bigg\{ {}_{ss'}\tilde{t}^{B_iA_1\,A_1A_j(B_k)}_{\{10\}\{01\}}\ {}^{0}_{ss'}V^{B_iA_1\,A_1A_j(B_k)}_{\{10\}\{01\}} \\
& + {}_{ss'}\tilde{t}^{A_1A_1\,B_iA_j(B_k)}_{\{20\}\{11\}}\ {}^{0}_{ss'}V^{A_1A_1\,B_iA_j(B_k)}_{\{20\}\{11\}} \\
& + {}_{ss'}\tilde{t}^{A_1A_1\,B_iA_j(B_k)}_{\{02\}\{11\}}\ {}^{0}_{ss'}V^{A_1A_1\,B_iA_j(B_k)}_{\{02\}\{11\}} \Bigg\}
\end{aligned}$$

C.2 Matrix elements in the coupled basis

Within the coupled basis

$$\left|[1\,0]\frac{1}{2}1E_r,(v\Gamma_i,N-v\Gamma_j)\Gamma_v;E_r\sigma_{ev}\right\rangle \equiv |^{\{\gamma_{ev}\}}\Psi^{(E_r)}_{\sigma_{ev}}\rangle,$$

the matrix elements of the zeroth-order model in equations (69, 70) are given within the polyad N by

$$\begin{aligned}
&\langle^{\{\gamma'_{ev}\}}\mathit{\Psi}^{(E_r)}_{\sigma'_{ev}}|\widetilde{H}^{(0)}_{vibr}|^{\{\gamma_{ev}\}}\mathit{\Psi}^{(E_r)}_{\sigma_{ev}}\rangle = \delta_{\sigma_{ev},\sigma'_{ev}} \\
&\quad\times\left[\left[\hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s\left(v+\frac{1}{2}\right) + \hbar\tilde{\omega}_{s'}\left(N-v+\frac{1}{2}\right)\right]\delta_{v',v}\right. \\
&\quad+\ \hbar(-1)^{k+1}\tilde{\lambda}\frac{(-1)^{\mathit{\Gamma}_v}}{\sqrt{2}}\begin{Bmatrix}\mathit{\Gamma}'_{v'} & E_r & E_r \\ E_r & \mathit{\Gamma}_v & B_k\end{Bmatrix}\begin{Bmatrix}B_i & \mathit{\Gamma}_i & \mathit{\Gamma}'_i \\ A_j & \mathit{\Gamma}_j & \mathit{\Gamma}'_j \\ B_k & \mathit{\Gamma}_v & \mathit{\Gamma}'_{v'}\end{Bmatrix} \\
&\left.\times\left\{[(v+1)(N-v)]^{\frac{1}{2}}\delta_{v',v+1} + [v(N-v+1)]^{\frac{1}{2}}\delta_{v',v-1}\right\}\right]. \qquad \text{(C.1)}
\end{aligned}$$

Most selection rules are contained in the $6-C$ and $9-C$ symbols of G. The usual rule $\sigma_{ev} = \sigma'_{ev}$ linked to the A_1 symmetry of Hamiltonian terms implies that the matrix to diagonalize is of dimension $N+1$.

C.3 Symmetry adapted eigenstates for $\widetilde{\mathbf{H}}^{(0)}_{\mathbf{vibr}}$

The vibronic Hamiltonians (71, 74) are respectively transformed as

$$\begin{aligned}
U(\sigma_\alpha J_\beta)\widetilde{H}^{(0)}_{vibr}U(\sigma_\alpha J_\beta)^{-1} &= {}^{U}\widetilde{H}^{(0)}_{vibr} \\
&= \hbar\tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_s+\tilde{\omega}_{s'})}{2}(N+1) + \hbar\mathit{\Omega}(\sigma_\alpha)J_z, \\
U'(\sigma_\alpha J'_\beta)\widetilde{H}^{(0)}_{vibr}U'(\sigma_\alpha J'_\beta)^{-1} &= {}^{U'}\widetilde{H}'^{(0)}_{vibr} \\
&= \hbar\tilde{\lambda}_0 + \hbar\frac{(\tilde{\omega}_s+\tilde{\omega}_{s'})}{2}(N+1) + \hbar\mathit{\Omega}(\sigma_\alpha)J'_z, \qquad \text{(C.2)}
\end{aligned}$$

with

$$\mathit{\Omega}(\sigma_\alpha) = [\tilde{\lambda}^2 + (\tilde{\omega}_s - \tilde{\omega}_{s'})^2]^{1/2}.$$

The operator $U(\sigma_\alpha J_\beta)$ is given by

$$\begin{aligned}
U(\sigma_\alpha J_\beta) &= \exp\left[\frac{(\mathit{\Omega}-\omega_0)}{\tilde{\lambda}}\sigma_\alpha J_+\right]\exp\left[\ln\left(\frac{2\mathit{\Omega}}{\mathit{\Omega}+\omega_0}\right)J_z\right] \\
&\quad\times\exp\left[-\frac{(\mathit{\Omega}-\omega_0)}{\tilde{\lambda}}\sigma_\alpha J_-\right] \\
&= \exp[2i\xi\sigma_\alpha J_y], \qquad \text{(C.3)}
\end{aligned}$$

where we set $\omega_0 = \tilde{\omega}_s - \tilde{\omega}_{s'}$ and with

$$\tan\xi = \frac{(\mathit{\Omega}-\omega_0)}{\tilde{\lambda}}, \quad \cos\xi = \left[\frac{\mathit{\Omega}+\omega_0}{2\mathit{\Omega}}\right]^{1/2}.$$

For the $U'(\sigma_\alpha J'_\beta)$ operator we have

$$\begin{aligned}
U'(\sigma_\alpha J'_\beta) &= \exp\left[\frac{(\mathit{\Omega}-\tilde{\lambda}\,\sigma_\alpha)}{\omega_0}J'_+\right]\exp\left[\ln\left(\frac{2\mathit{\Omega}}{\mathit{\Omega}+\tilde{\lambda}\,\sigma_\alpha}\right)J'_z\right] \\
&\quad\times\exp\left[-\frac{(\mathit{\Omega}-\tilde{\lambda}\,\sigma_\alpha)}{\omega_0}J'_-\right] \\
&= \exp[2i\xi' J'_y], \qquad \text{(C.4)}
\end{aligned}$$

with

$$\tan\xi' = \frac{\mathit{\Omega}-\tilde{\lambda}\,\sigma_\alpha}{\omega_0}\ ,\ \cos\xi' = \left[\frac{\mathit{\Omega}+\tilde{\lambda}\,\sigma_\alpha}{2\mathit{\Omega}}\right]^{1/2}.$$

Eigenstates for the Hamiltonian $\widetilde{H}^{0}_{vibr}$ (70) are obtained starting from the vibronic bases

$$\left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\right\rangle|[N\,0]jm(\mathit{\Gamma}_v)\rangle\rangle,\ \left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\right\rangle|[N\,0]jm\rangle\rangle',$$

with $\sigma_e = 1, 2$ (orientation I) when $B_i \times A_j = B_k = B_1$ and $\sigma_e = \bar{\bar{1}}, \bar{\bar{2}}$ (orientation III) when $B_i \times A_j = B_k = B_2$. $|[N\,0]jm(\mathit{\Gamma}_v)\rangle\rangle$ (resp. $|[N\,0]jm\rangle\rangle'$) are $u(2) \supset su(2) \supset so(2)$ covariant states built with the sets $a_1^+ = {}_s a^{+(B_i)}$, $a_2^+ = {}_{s'}a^{+(A_j)}$ (Eq. (39))(resp. c_1^+, c_2^+ (Eq. (43))).

From the expressions of the $U(\sigma_\alpha J_\beta)$ and $U'(\sigma_\alpha J'_\beta)$ operators (C.3, C.4) we obtain unsymmetrized eigenstates of $\widetilde{H}^{(0)}_{vibr}$:

$$\begin{aligned}
&\left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\right\rangle|[N\,0]jm(\theta_e)\rangle\rangle \\
&= U(\sigma_\alpha J_\beta)^{-1}\left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\right\rangle|[N\,0]jm(\mathit{\Gamma}_v)\rangle\rangle \\
&= \exp[-2i\xi\sigma_\alpha J_y]\left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\right\rangle|[N\,0]jm(\mathit{\Gamma}_v)\rangle\rangle \\
&= \sum_{m'} d^{(j)}_{mm'}(2\xi(-1)^{\sigma_e+1})\left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\right\rangle|[N\,0]jm'(\mathit{\Gamma}'_v)\rangle\rangle, \qquad \text{(C.5)}
\end{aligned}$$

with $\theta_e = \theta_1$ ($\theta_e = \theta_2 = -\theta_1$) when $\sigma_e = 1$ or $\sigma_e = \bar{\bar{1}}$ ($\sigma_e = 2$ or $\sigma_e = \bar{\bar{2}}$) and

$$\cos\theta_e = \frac{\omega_0}{\mathit{\Omega}}, \quad \sin\theta_e = \frac{\tilde{\lambda}}{\mathit{\Omega}}(-1)^{\sigma_e+1}.$$

Likewise from $U'(\sigma_z J'_\alpha)$ we obtain the eigenstates in the form:

$$\begin{aligned}
&\left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\right\rangle|[N\,0]jm(\theta'_e)\rangle\rangle' \\
&= U'(\sigma_\alpha J'_\beta)^{-1}\left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\right\rangle|[N\,0]jm\rangle\rangle' \\
&= \exp[-2i\xi' J'_y]\left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\right\rangle|[N\,0]jm\rangle\rangle' \\
&= \sum_{m'} d^{(j)}_{mm'}(2\xi'(\sigma_e))\left|[1\,0]\frac{1}{2}1E_r\sigma_e\right\rangle\!\!\right\rangle|[N\,0]jm'\rangle\rangle', \qquad \text{(C.6)}
\end{aligned}$$

with $\theta'_e = \theta'_1$ ($\theta'_e = \theta'_2 = \pi - \theta'_1$) when $\sigma_e = \bar{1}$ or $\sigma_e = \bar{\bar{1}}$ ($\sigma_e = \bar{2}$ or $\sigma_e = \bar{\bar{2}}$) and

$$\cos\theta'_e = \frac{\tilde{\lambda}}{\mathit{\Omega}}(-1)^{\sigma_e+1}, \quad \sin\theta'_e = \frac{\omega_0}{\mathit{\Omega}}.$$

Next symmetrized vibronic eigenstates are obtained from (C.5, C.6) with the method presented in [17]:

$$\left|[1\,0]\frac{1}{2}1E_r,[N\,0]jm(\theta_e);E_r\sigma_{ev}\right\rangle\!\!\right\rangle = e^{i\varphi(\tau)}\left|[1\,0]\frac{1}{2}1E_r\sigma_e\rangle\!\rangle|[N\,0]jm(\theta_e)\right\rangle\!\!\right\rangle, \tag{C.7}$$

or

$$\left|[1\,0]\frac{1}{2}1E_r,[N\,0]jm(\theta'_e);E_r\sigma_{ev}\right\rangle\!\!\right\rangle' = e^{i\varphi'(\tau')}\left|[1\,0]\frac{1}{2}1E_r\sigma_e\rangle\!\rangle|[N\,0]jm(\theta'_e)\right\rangle\!\!\right\rangle'. \tag{C.8}$$

The phase factors in (C.7) are given below for the various cases:

$$\begin{array}{cccccc}
(B_i,A_j) & j & \theta_e & \sigma_e & \sigma_{ev} & e^{i\varphi(\tau)} \\
(B_1,A_1) & \text{integer and} & \theta_1 & 1 & 1 & (-1)^{j-m} \\
 & \text{half-integer} & -\theta_1 & 2 & 2 & 1 \\
(B_2,A_2) & \text{integer} & \theta_1 & 1 & 1 & (-1)^{j-m} \\
 & & -\theta_1 & 2 & 2 & 1 \\
 & \text{half-integer} & \theta_1 & 1 & 2 & -1 \\
 & & -\theta_1 & 2 & 1 & (-1)^{j-m} \\
(B_2,A_1) & \text{integer and} & \theta_1 & \bar{\bar{1}} & \bar{\bar{1}} & (-1)^{j-m} \\
 & \text{half-integer} & -\theta_1 & \bar{\bar{2}} & \bar{\bar{2}} & 1 \\
(B_1,A_2) & \text{integer} & \theta_1 & \bar{\bar{1}} & \bar{\bar{1}} & (-1)^{j-m} \\
 & & -\theta_1 & \bar{\bar{2}} & \bar{\bar{2}} & 1 \\
 & \text{half-integer} & \theta_1 & \bar{\bar{1}} & \bar{\bar{2}} & -1 \\
 & & -\theta_1 & \bar{\bar{2}} & \bar{\bar{1}} & (-1)^{j-m}
\end{array} \tag{C.9}$$

For the phase factors in (C.8) we have $e^{i\varphi'(\tau')} = e^{i\varphi(\tau)}$ as given in (C.9) with the substitutions $\theta_1 \rightarrow \theta'_1$ and $-\theta_1 \rightarrow \pi - \theta'_1$.

Appendix D: Vibronic Hamiltonian for $\mathbf{E_r \otimes (b_i + e_r)}$

D.1 Restricted expansion for the effective Hamiltonian

The expansion (86) limited to terms with $n_i + n_j = n'_i + n'_j \leq 2$ writes $\widetilde{H}_{vibr} = \widetilde{H}_{vib} + \widetilde{H}'_{vibr}$ with:

$$\begin{aligned}
\widetilde{H}_{vib} = I_e\Bigg\{ & I_v + \sum_{n=1,2} {}_{s'}\tilde{t}^{C_iC_i(A_1)}_{\{n_i\}\{n_i\}}\ {}^{0}_{s'}V^{C_iC_i(A_1)}_{\{n_i\}\{n_i\}} \\
& + {}_{s}\tilde{t}^{0,0A_1(A_1)}_{\{1\}\{1\}}\,{}^{[1\,-1]}_{\quad s}\mathcal{V}^{(0,0\,A_1)} + {}_{s}\tilde{t}^{0,0A_1(A_1)}_{\{2\}\{2\}}\,{}^{[2\,-2]}_{\quad s}\mathcal{V}^{(0,0\,A_1)} \\
& + {}_{s}\tilde{t}^{2,0A_1(A_1)}_{\{2\}\{2\}}\,{}^{[2\,-2]}_{\quad s}\mathcal{V}^{(2,0\,A_1)} + {}_{s}\tilde{t}^{2,4A_1(A_1)}_{\{2\}\{2\}}\,{}^{[2\,-2]}_{\quad s}\mathcal{V}^{(2,4\,A_1)} \\
& + {}_{s's}\tilde{t}^{A_1 00A_1\,A_1 10A_1(A_1)}_{\{20\}\{02\}}\ {}^{0}_{s's}V^{A_1 00A_1\,A_1 10A_1(A_1)}_{\{20\}\{02\}} \\
& + {}_{s's}\tilde{t}^{B_i\frac{1}{2}1E_k\,B_i\frac{1}{2}1E_k(A_1)}_{\{11\}\{11\}}\ {}^{0}_{s's}V^{B_i\frac{1}{2}1E_k\,B_i\frac{1}{2}1E_k(A_1)}_{\{11\}\{11\}}\Bigg\}
\end{aligned}$$

$$\begin{aligned}
\widetilde{H}'_{vibr} = {}^{[1\,-1]}E^{(1,0A_2)}\Bigg\{ & {}_{s}\tilde{t}^{1,0A_2(A_2)}_{\{1\}\{1\}}\,{}^{[1\,-1]}_{\quad s}\mathcal{V}^{(1,0\,A_2)} \\
& + {}_{s}\tilde{t}^{1,0A_2(A_2)}_{\{2\}\{2\}}\,{}^{[2\,-2]}_{\quad s}\mathcal{V}^{(1,0\,A_2)} \\
& + {}_{s's}\tilde{t}^{B_i\frac{1}{2}1E_k\,B_i\frac{1}{2}1E_k(A_2)}_{\{11\}\{11\}}\ {}^{1}_{s's}V^{B_i\frac{1}{2}1E_k\,B_i\frac{1}{2}1E_k(A_2)}_{\{11\}\{11\}}\Bigg\} \\
+ \sum_{t=1,2} {}^{[1\,-1]}E^{(1,2B_t)}\Bigg\{ & {}_{s}\tilde{t}^{1,2B_t(B_t)}_{\{1\}\{1\}}\,{}^{[1\,-1]}_{\quad s}\mathcal{V}^{(1,2\,B_t)} \\
& + {}_{s}\tilde{t}^{1,2B_t(B_t)}_{\{2\}\{2\}}\,{}^{[2\,-2]}_{\quad s}\mathcal{V}^{(1,2\,B_t)} \\
& + {}_{s's}\tilde{t}^{A_1 00A_1\,A_1 12B_t(B_t)}_{\{20\}\{02\}}\ {}^{0}_{s's}V^{A_1 00A_1\,A_1 12B_t(B_t)}_{\{20\}\{02\}} \\
& + {}_{s's}\tilde{t}^{B_i\frac{1}{2}1E_k\,B_i\frac{1}{2}1E_k(B_t)}_{\{11\}\{11\}}\ {}^{0}_{s's}V^{B_i\frac{1}{2}1E_k\,B_i\frac{1}{2}1E_k(B_t)}_{\{11\}\{11\}}\Bigg\}.
\end{aligned}$$

D.2 Matrix elements in the coupled basis

We give below the matrix elements for the various operators in $\widetilde{H}^0_{vibr}$ (89) within the coupled basis

$$|\varPsi\rangle = \left|[1\,0]\frac{1}{2}1E_r;(v_{s'}\varGamma_i,[v\,0]j\ell\varGamma)\varGamma_v;\varGamma_{ev}\sigma_{ev}\right\rangle\!\!\right\rangle,$$

using the simplified notation

$$\mathcal{O}_{vibr} = [E^{(C)} \times [{}_{s'}V^{(A_1)} \times {}_{s}V^{(C)}]]^{(A_1)},$$

for the vibronic operators. With equations (9, 10) we obtain

$$\begin{aligned}
\langle\varPsi'|\mathcal{O}_{vibr}|\varPsi\rangle = {} & \delta_{\varGamma'_{ev},\varGamma_{ev}}\delta_{\sigma'_{ev},\sigma_{ev}}\delta_{v'_{s'},v_{s'}}\delta_{\varGamma'_i,\varGamma_i}\delta_{v',v} \\
& \times (-1)^{\varGamma_{ev}+\varGamma_i+\varGamma'}([\varGamma_v][\varGamma'_v])^{1/2}\begin{Bmatrix}\varGamma'_v & E_r & \varGamma_{ev}\\ E_r & \varGamma_v & C\end{Bmatrix} \\
& \times \begin{Bmatrix}\varGamma'_v & \varGamma' & \varGamma_i\\ \varGamma & \varGamma_v & C\end{Bmatrix}\left([1\,0]\frac{1}{2}1E_r||E^{(C)}||[1\,0]\frac{1}{2}1E_r\right) \\
& \times (v_{s'}\varGamma_i||{}_{s'}V^{(A_1)}||v_{s'}\varGamma_i)([v\,0]j\ell'\varGamma'||{}_{s}V^{(C)}||[v\,0]j\ell\varGamma).
\end{aligned} \tag{D.1}$$

Special cases

- $E^{(C)} = I_e^{(A_1)}$, ${}_{s}V^{(C)} = {}_{s}I^{(A_1)}$ that is for operators involving the b_i mode only we have (Eq. (A.4)), omitting the Kronecker symbols

$$\begin{aligned}
\langle\varPsi'|\mathcal{O}_{vibr}|\varPsi\rangle &= \langle\varPsi'|\,{}^{0}_{s}V^{C_iC_i(A_1)}_{\{n_i\}\{n_i\}}|\varPsi\rangle \\
&= (v_{s'}\varGamma_i||{}_{s'}V^{(A_1)}||v_{s'}\varGamma_i) = 2\frac{v_{s'}!}{(v_{s'}-n)!}.
\end{aligned}$$

- $E^{(C)} = I_e^{(A_1)}$, ${}_{s'}V^{(A_1)} = {}_{s'}I^{(A_1)}$ that is for operators involving the e_r mode only:

$$\begin{aligned}
\langle\varPsi'|\mathcal{O}_{vibr}|\varPsi\rangle &= \langle\varPsi'|\,{}^{[k\,-k]}_{\quad s}\mathcal{V}^{(k_v)}_{\ell_v C\sigma}|\varPsi\rangle \\
&= \frac{1}{[\varGamma]^{1/2}}([v\,0]j\ell'\varGamma||{}_{s}V^{(A_1)}||[v\,0]j\ell\varGamma),
\end{aligned}$$

where the reduced matrix elements, as well as those of the electronic operators $E^{(C)}$, can be obtained from the results in [17].

- ${}_{s'}V^{(C)} = {}_{s'}I^{(A_1)}$ that is for vibronic operators involved in (91)

$$\begin{aligned}\langle\Psi'|\mathcal{O}_{vibr}|\Psi\rangle &= \delta_{\Gamma'_{ev},\Gamma_{ev}}\delta_{\sigma'_{ev},\sigma_{ev}}\delta_{v'_{s'},v_{s'}}\delta_{\Gamma'_i,\Gamma_i}\delta_{v',v}\\ &\times(-1)^{\Gamma_{ev}+\Gamma'}([\Gamma_v][\Gamma'_v])^{1/2}\begin{Bmatrix}\Gamma'_v & E_r & \Gamma_{ev}\\ E_r & \Gamma_v & C\end{Bmatrix}\begin{Bmatrix}\Gamma'_v & \Gamma' & \Gamma_i\\ \Gamma & \Gamma_v & C\end{Bmatrix}\\ &\times\left([1\,0]\frac{1}{2}1E_r||E^{(C)}||[1\,0]\frac{1}{2}1E_r\right)\\ &\times([v\,0]j\ell'\Gamma'||{}_sV^{(C)}||[v\,0]j\ell\Gamma). \qquad \text{(D.2)}\end{aligned}$$

We note that in the special case $\Gamma_i = A_1$ the preceding equation reduces to:

$$\begin{aligned}\langle\Psi'|\mathcal{O}_{vibr}|\Psi\rangle &= \delta_{\Gamma'_{ev},\Gamma_{ev}}\delta_{\sigma'_{ev},\sigma_{ev}}\delta_{v'_{s'},v_{s'}}\delta_{v',v}\delta_{\Gamma,\Gamma_v}\delta_{\Gamma',\Gamma'_v}\\ &\times(-1)^{\Gamma_{ev}+\Gamma+C}\begin{Bmatrix}\Gamma' & E_r & \Gamma_{ev}\\ E_r & \Gamma & C\end{Bmatrix}\\ &\times\left([1\,0]\frac{1}{2}1E_r||E^{(C)}||[1\,0]\frac{1}{2}1E_r\right)\\ &\times([v\,0]j\ell'\Gamma'||{}_sV^{(C)}||[v\,0]j\ell\Gamma). \qquad \text{(D.3)}\end{aligned}$$

This gives, within the same assumptions, all matrix elements for an $E_r \otimes e_r$ case with basis states of the form $|\Psi\rangle = |[1\,0]\frac{1}{2}1E_r;[v\,0]j\ell\Gamma;\Gamma_{ev}\sigma_{ev}\rangle\rangle$.

D.3 Pseudo-spin vibration interaction

The operator considered as dominant in Section 7.4.3 writes

$${}_s\tilde{t}^{1,0A_2(A_2)}_{\{11\}}\;{}^{[1\,-1]}E^{(1,0A_2)[1\,-1]}{}_s\mathcal{V}^{(1,0\,A_2)} = \hbar\tilde{\lambda}_z S_z J_z = -\hbar\frac{\tilde{\lambda}_z}{2}S_z\,{}_s\ell_z.$$

Its eigenvalues in the unsymmetrized standard basis are obtained from:

$$\begin{aligned}S_zJ_z\left|[1\,0]\frac{1}{2}m_e,[v\,0]jm\right\rangle\!\!\right\rangle &= m_e m\left|[1\,0]\frac{1}{2}m_e,[v\,0]jm\right\rangle\!\!\right\rangle\\ &= \pm\frac{\ell}{4}\left|[1\,0]\frac{1}{2}m_e,[v\,0]jm\right\rangle\!\!\right\rangle.\end{aligned}$$

The space of states can thus be divided into two subspaces $\mathcal{H}_+$ and $\mathcal{H}_-$ associated respectively with eigenvalues $\pm\ell/4$ and stable under the action of the elements of the molecular point symmetry group G. For the basis vectors in $\mathcal{H}_+$ we set:

$$\left|[1\,0]\frac{1}{2}\frac{1}{2},[v\,0]j\frac{\ell}{2}\right\rangle\!\!\right\rangle = {}^{(+)}\varphi_+,$$

$$\left|[1\,0]\frac{1}{2}-\frac{1}{2},[v\,0]j-\frac{\ell}{2}\right\rangle\!\!\right\rangle = {}^{(+)}\varphi_-,$$

and for those in $\mathcal{H}_-$

$$\left|[1\,0]\frac{1}{2}\frac{1}{2},[v\,0]j-\frac{\ell}{2}\right\rangle\!\!\right\rangle = {}^{(-)}\varphi_+,$$

$$\left|[1\,0]\frac{1}{2}-\frac{1}{2},[v\,0]j\frac{\ell}{2}\right\rangle\!\!\right\rangle = {}^{(-)}\varphi_-,$$

and we note that under time-reversal we have $\mathcal{K}\,{}^{(+)}\varphi_+ = {}^{(+)}\varphi_-$ and $\mathcal{K}\,{}^{(-)}\varphi_+ = {}^{(-)}\varphi_-$. Using the methods described in [17] we build the symmetry adapted states in orientation II listed below in the form

$$\left|[1\,0]\frac{1}{2}1E_r,[v\,0]j\ell;\kappa,\,\Gamma\bar{\sigma}\right\rangle\!\!\right\rangle,$$

where $\kappa = \pm1$ is associated with the eigenvalues $\pm\ell/4$ of S_zJ_z. All phases have been settled so that under time reversal

$$\mathcal{K}\left|[1\,0]\frac{1}{2}E_r,[v\,0]j\ell;\kappa,\,\Gamma\bar{\sigma}\right\rangle\!\!\right\rangle = \left|[1\,0]\frac{1}{2}E_r,[v\,0]j\ell;\kappa,\,\Gamma-\bar{\sigma}\right\rangle\!\!\right\rangle$$

- $\ell = 4q, 4q+2$

$$\begin{aligned}|[1\,0]\tfrac{1}{2}1E_r,[v\,0]j\ell;+,E_r\bar{\sigma}\rangle\rangle &= i^{v(+)}\varphi_+\\ |[1\,0]\tfrac{1}{2}1E_r,[v\,0]j\ell;+,E_r-\bar{\sigma}\rangle\rangle &= i^{v(+)}\varphi_-\\ |[1\,0]\tfrac{1}{2}1E_r,[v\,0]j\ell;-,E_r\bar{\sigma}\rangle\rangle &= i^{v(-)}\varphi_+\\ |[1\,0]\tfrac{1}{2}1E_r,[v\,0]j\ell;-,E_r-\bar{\sigma}\rangle\rangle &= i^{v(-)}\varphi_-\end{aligned} \qquad \text{(D.4)}$$

where $(\bar{\sigma},-\bar{\sigma}) = (\bar{1},\bar{2})$ for $\ell = 4q$ and $(\bar{\sigma},-\bar{\sigma}) = (\bar{2},\bar{1})$ for $\ell = 4q+2$. In the special case $\ell = 0$ only states $+$ or $-$ in equation (D.4) are retained.

- $\ell = 4q+1, 4q+3$

$$\begin{aligned}|[1\,0]\tfrac{1}{2}1E_r,[v\,0]j\ell;+,\Gamma_1\rangle\rangle &= \frac{i^{v+1}}{\sqrt{2}}({}^{(+)}\varphi_+ + {}^{(+)}\varphi_-)\\ |[1\,0]\tfrac{1}{2}1E_r,[v\,0]j\ell;+,\Gamma_2\rangle\rangle &= \frac{i^{v}}{\sqrt{2}}({}^{(+)}\varphi_+ - {}^{(+)}\varphi_-)\\ |[1\,0]\tfrac{1}{2}1E_r,[v\,0]j\ell;-,\Gamma'_1\rangle\rangle &= \frac{i^{v+1}}{\sqrt{2}}({}^{(-)}\varphi_+ + {}^{(-)}\varphi_+)\\ |[1\,0]\tfrac{1}{2}1E_r,[v\,0]j\ell;-,\Gamma'_2\rangle\rangle &= \frac{i^{v}}{\sqrt{2}}({}^{(-)}\varphi_+ - {}^{(-)}\varphi_+)\end{aligned}$$

with $\Gamma_1,\Gamma_2,\Gamma'_1,\Gamma'_2 = B_1,B_2,A_1,A_2$ for $\ell = 4q+1$ and A_1,A_2,B_1,B_2 for $\ell = 4q+3$.

The complete vibronic eigenbasis, including states associated with the b_i mode, is obtained with

$$\begin{aligned}&\left|N-v\,\Gamma_i;[1\,0]\frac{1}{2}1E_r,[v\,0]j\ell;\kappa,\,\Gamma;\Gamma_{ev}\bar{\sigma}_{ev}\right\rangle\!\!\right\rangle =\\ &\qquad F\,{}^{\bar{\sigma}}_{(\Gamma_i\;\Gamma)}\,{}^{(\Gamma_{ev})}_{\bar{\sigma}_{ev}}\,|N-v\,\Gamma_i\rangle\left|[1\,0]\frac{1}{2}1E_r,[v\,0]j\ell;\kappa\Gamma\bar{\sigma}\right\rangle\!\!\right\rangle.\end{aligned} \qquad \text{(D.5)}$$

When $N-v$ is even we simply have

$$\begin{aligned}&\left|N-v\,A_1\rangle|[1\,0]\frac{1}{2}E_r,[v\,0]j\ell;\kappa\,\Gamma\bar{\sigma}\right\rangle\!\!\right\rangle =\\ &\qquad\left|N-v\,A_1;[1\,0]\frac{1}{2}E_r,[v\,0]j\ell;\kappa\Gamma;\Gamma\bar{\sigma}\right\rangle\!\!\right\rangle \quad N-v \text{ even,}\end{aligned}$$

since all CGC equal one. When $N-v$ is odd $\Gamma_i = B_i$ and the states are obtained with the values of the CGC given in Table 2. We note that the transformation (D.5) reduces in all cases to a phase (no $\bar{\sigma}$ summation).

D.4 Symmetry adapted states for other cases

For an active coordinate with symmetry B_1 the operator considered as dominant in Section 7.4.3 writes

$$ {}_s\tilde{t}^{1,2B_1(B_1)}_{\{11\}}\ {}^{[1\,-1]}E^{(1,2B_1)}{}^{[1\,-1]}_{\quad s}\mathcal{V}^{(1,2\,B_1)} = \tilde{\lambda}_x S_x\, J_x. $$

We know that within orientation I the symmetry adapted electronic states are eigenstates of ${}^{[1\,-1]}E^{(1,2B_1)} = S_x$:

$$ S_x \left|[1\,0]\frac{1}{2}1E_r\sigma\right\rangle\!\!\rangle = \frac{1}{2}(-1)^{\sigma+1}\left|[1\,0]\frac{1}{2}1E_r\sigma\right\rangle\!\!\rangle \quad \sigma = 1,2, $$

and that the rotated states $|\widehat{[v\,0]jm}\rangle\rangle$ given in equation (137) are eigenstates of J_x. The space of states is again split into two subspaces $\mathcal{H}_+$ and $\mathcal{H}_-$ associated respectively with eigenvalues $\pm\ell/4$ of S_xJ_x. For the basis vectors in $\mathcal{H}_+$ we set:

$$ \left|[1\,0]\frac{1}{2}1E_r1\right\rangle\!\!\rangle\left|\widehat{[v\,0]j\frac{\ell}{2}}\right\rangle\!\!\rangle = {}^{(+)}\widehat{\varphi}_+ $$

$$ \left|[1\,0]\frac{1}{2}1E_r2\right\rangle\!\!\rangle\left|\widehat{[v\,0]j-\frac{\ell}{2}}\right\rangle\!\!\rangle = {}^{(+)}\widehat{\varphi}_- $$

and for those in $\mathcal{H}_-$

$$ \left|[1\,0]\frac{1}{2}1E_r1\right\rangle\!\!\rangle\left|\widehat{[v\,0]j-\frac{\ell}{2}}\right\rangle\!\!\rangle = {}^{(-)}\widehat{\varphi}_+ $$

$$ \left|[1\,0]\frac{1}{2}1E_r2\right\rangle\!\!\rangle\left|\widehat{[v\,0]j\frac{\ell}{2}}\right\rangle\!\!\rangle = {}^{(-)}\widehat{\varphi}_-. $$

Under time reversal we have $\mathcal{K}^{(+)}\widehat{\varphi}_\pm = i^v\ {}^{(+)}\widehat{\varphi}_\pm$ and $\mathcal{K}^{(-)}\widehat{\varphi}_\pm = i^v\ {}^{(-)}\widehat{\varphi}_\pm$. The associated symmetry adapted states are listed below in the form:

$$ \left|[1\,0]\frac{1}{2}E_r,[v\,0]j\ell;\kappa,\Gamma\sigma\right\rangle\!\!\rangle, $$

with $\kappa = \pm 1$ associated with the eigenvalues $\pm\ell/4$ of S_xJ_x.

- v even (j integer)

$$ \begin{aligned} &|[1\,0]\tfrac{1}{2}E_r,[v\,0]j\ell;+,E_r\sigma\rangle\rangle = i^j\ {}^{(+)}\widehat{\varphi}_+ \\ &|[1\,0]\tfrac{1}{2}E_r,[v\,0]j\ell;+,E_r-\sigma\rangle\rangle = i^j\ {}^{(+)}\widehat{\varphi}_- \\ &|[1\,0]\tfrac{1}{2}E_r,[v\,0]j\ell;-,E_r\sigma\rangle\rangle = i^j\ {}^{(-)}\widehat{\varphi}_+ \\ &|[1\,0]\tfrac{1}{2}E_r,[v\,0]j\ell;-,E_r-\sigma\rangle\rangle = i^j\ {}^{(-)}\widehat{\varphi}_- \end{aligned} \qquad \text{(D.6)} $$

where $(\sigma,-\sigma) = (1,2)$ for $j+\ell/2$ even and $(\sigma,-\sigma) = (2,1)$ for $j+\ell/2$ odd. In the special case $\ell = 0$ only states $+$ or $-$ in equation (D.6) are retained.

- v odd (j half integer)

$$ \begin{aligned} &\left|[1\,0]\frac{1}{2}E_r,[v\,0]j\ell;+\Gamma_1\right\rangle\!\!\rangle = \frac{i^j}{\sqrt{2}}({}^{(+)}\widehat{\varphi}_+ +\ {}^{(+)}\widehat{\varphi}_-) \\ &\left|[1\,0]\frac{1}{2}E_r,[v\,0]j\ell;+\Gamma_2\right\rangle\!\!\rangle = \frac{i^j}{\sqrt{2}}({}^{(+)}\widehat{\varphi}_+ -\ {}^{(+)}\widehat{\varphi}_-) \\ &\left|[1\,0]\frac{1}{2}E_r,[v\,0]j\ell;-\Gamma_1'\right\rangle\!\!\rangle = \frac{i^j}{\sqrt{2}}({}^{(-)}\widehat{\varphi}_+ +\ {}^{(-)}\widehat{\varphi}_-) \\ &\left|[1\,0]\frac{1}{2}E_r,[v\,0]j\ell;-\Gamma_2'\right\rangle\!\!\rangle = \frac{i^j}{\sqrt{2}}({}^{(-)}\widehat{\varphi}_+ -\ {}^{(-)}\widehat{\varphi}_+) \end{aligned} \qquad \text{(D.7)} $$

with $\Gamma_1,\Gamma_2,\Gamma_1',\Gamma_2' = B_2,A_2,A_1B_1$ for $j+\ell/2$ even and $\Gamma_1,\Gamma_2,\Gamma_1',\Gamma_2' = A_1,B_1,B_2,A_2$ for $j+\ell/2$ odd.

In a similar manner for an active coordinate with symmetry B_2 the operator considered as dominant is

$$ {}_s\tilde{t}^{1,2B_1(B_2)}_{\{11\}}\ {}^{[1\,-1]}E^{(1,2B_2)}{}^{[1\,-1]}_{\quad s}\mathcal{V}^{(1,2\,B_2)} = \tilde{\lambda}_y S_y\, J_y. $$

Within orientation III the symmetry adapted electronic states are eigenstates of ${}^{[1\,-1]}E^{(1,2B_2)} = S_y$:

$$ S_y \left|[1\,0]\frac{1}{2}1E_r\bar{\bar{\sigma}}\right\rangle\!\!\rangle = \frac{1}{2}(-1)^{\bar{\bar{\sigma}}+1}\left|[1\,0]\frac{1}{2}1E_r\bar{\bar{\sigma}}\right\rangle\!\!\rangle \quad \bar{\bar{\sigma}} = 1,2, $$

and the rotated states $|\widehat{\widehat{[v\,0]jm}}\rangle\rangle$ given in equation (138) are eigenstates of J_y. As previously the space of states can be split into two subspaces $\mathcal{H}_+$ and $\mathcal{H}_-$ associated respectively with eigenvalues $\pm\ell/4$ of $S_y\,J_y$. For the basis vectors in $\mathcal{H}_+$ we set this time:

$$ \left|[1\,0]\frac{1}{2}1E_r\bar{\bar{1}}\right\rangle\!\!\rangle\left|\widehat{\widehat{[v\,0]j\frac{\ell}{2}}}\right\rangle\!\!\rangle = {}^{(+)}\widehat{\widehat{\varphi}}_+ $$

$$ \left|[1\,0]\frac{1}{2}1E_r\bar{\bar{2}}\right\rangle\!\!\rangle\left|\widehat{\widehat{[v\,0]j-\frac{\ell}{2}}}\right\rangle\!\!\rangle = {}^{(+)}\widehat{\widehat{\varphi}}_- $$

and for those in $\mathcal{H}_-$

$$ \left|[1\,0]\frac{1}{2}1E_r\bar{\bar{1}}\right\rangle\!\!\rangle\left|\widehat{\widehat{[v\,0]j-\frac{\ell}{2}}}\right\rangle\!\!\rangle = {}^{(-)}\widehat{\widehat{\varphi}}_+ $$

$$ \left|[1\,0]\frac{1}{2}1E_r\bar{\bar{2}}\right\rangle\!\!\rangle\left|\widehat{\widehat{[v\,0]j\frac{\ell}{2}}}\right\rangle\!\!\rangle = {}^{(-)}\widehat{\widehat{\varphi}}_-. $$

With the same techniques as previously one builds symmetry adapted states

$$ \left|[1\,0]\frac{1}{2}1E_r,[v\,0]j\ell;\kappa,\Gamma\bar{\bar{\sigma}}\right\rangle\!\!\rangle, $$

the expressions of which can be deduced from those in equations (D.6, D.7) with the substitutions

$$ {}^{(\pm)}\widehat{\varphi}_\pm \to {}^{(\pm)}\widehat{\widehat{\varphi}}_\pm, \quad \bar{\sigma} \to \bar{\bar{\sigma}} $$

and for the cases in equation (D.7) $\Gamma_1,\Gamma_2,\Gamma_1',\Gamma_2' = B_1,A_2,A_1,B_2$ for $j+\ell/2$ even and $\Gamma_1,\Gamma_2,\Gamma_1',\Gamma_2' = A_1,B_2,B_1,A_2$ for $j+\ell/2$ odd.

For both cases just treated inclusion of the b_i mode can be made with equation (D.5) with F coefficients in the appropriate orientation.

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