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Effective Hamiltonian approach to doubly degenerate electronic states

II-Applications to $\mathrm{E_r} \otimes \mathrm{e_{r'}}$ and $\mathrm{G'} \otimes \mathrm{e}$ dynamical Jahn-Teller systems

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Abstract. Effective vibronic Hamiltonian models are built for $E \otimes e$ Jahn-Teller systems and analytical solutions are obtained through Lie algebraic methods. Although approximate, we show that these models allow in particular to recover the possible ground state crossover when quadratic couplings are present. The equivalence of $E \otimes e$ and $G' \otimes e$ vibronic systems in cubic symmetry is precisely established through a particular realization of the electronic operators for an orbital quadruplet. We show how this equivalence is broken by a rovibronic interaction which, for a $G' \otimes e$ system, still gives an exactly solvable model.

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1 Introduction

In a previous paper [1], hereafter referred as (I), the effective Hamiltonian approach to doubly degenerate electronic states has been presented and applied to several Jahn-Teller (JT) systems when the symmetrized product of the E irreducible representation (*irrep*) spanned by the electronic states is of type $A_1 + B_1 + B_2$. We consider now the more widespread case when this product contains a true E-type *irrep*, together with the nearby $G' \otimes e$ system in cubic molecules involving a fourfold degenerate electronic state.

Over the last 40 years these $E \otimes e$ systems have been studied by numerous authors and from many different points of view (for reviews and many references see for instance [2–9]). Our approach differ from previous ones in several aspects. Firstly, we maintain our aim to give a unified framework for the study of dynamical rovibronic interactions in doubly degenerate electronic states whatever the molecular point symmetry group G. This is possible through the use of the underlying algebraic symmetry together with a tensor formalism. We thus built formal Hamiltonian models which can be next specialized to represent untransformed Hamiltonians or effective ones. Secondly, we put special emphasis on exactly solvable effective models for various $E \otimes e$ dynamical JT systems a classification of which is established first.

Somewhat curiously the possibility of an analytical treatment appears more easily if one works within an uncoupled vibronic basis. These models should be in most cases only zeroth-order approximations for a more refined treatment; eventually they furnish the necessary ingredients for a perturbative treatment of higher-order interactions. This is especially important if the experimental data are rare; a good zeroth-order model being essential before including these higher-order interactions.

In Section 2 we briefly recall the bases of our formalism and obtain general expansions for $E \otimes e$ dynamical JT systems. The possible terms which may appear in the expansion of an untransformed Hamiltonian are detailed up to quadratic terms in Section 3. This allows to establish correlations with standard forms through the vibronic matrix. The general form of an effective Hamiltonian is obtained in Section 4 and the matrix elements of an arbitrary vibronic operator are given in a symmetry adapted basis.

Approximate models are detailed next after a classification in five types of $E \otimes e$ systems has been made. Their eigenvalues are determined and we indicate for each type how symmetry adapted eigenstates may be built. These are explicitly given in two cases. For the $E \otimes e$ systems usually considered in the literature it appears that, although approximate, these models allow to recover the property, recently proved numerically [8,10–12], that the ground state may have a degeneracy and a symmetry different from that of the electronic state. We discuss next

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the introduction of additional vibronic operators which still allow to retain the exact solvability of each model.

$G' \otimes e$ dynamical JT systems in cubic symmetry are discussed in Section 5. The equivalence of $E \otimes e$ and $G' \otimes e$ vibronic systems mentioned in the literature [4,13–16] is precisely established. Further we show how this equivalence is broken when rovibronic interactions are introduced: a rovibronic model for $G' \otimes e$ is exactly solved.

Finally in the last section approximate correlations between our effective parameters and standard ones are established in a few limiting cases.

2 Theoretical background

As explained in (I) a formal vibronic Hamiltonian may be written as a linear combination with real parameters of hermitian and time reversal invariant operators built from electronic and vibrational operators

$$\begin{aligned} H_F = I_e \sum_{\{s\},\{\kappa_v\}} {}_{\{s\}}t^{\Gamma_0\{\kappa_v\}}\, {}^{\{\kappa_v\}}_{\{s\}}V^{(\Gamma_0)} \\ + \sum_{all\, indices} {}_{\{s\}}t^{C_e\{\kappa_e\kappa_v\}} \left[{}^{\{\kappa_e\}}E^{(C_e)} \times {}^{\{\kappa_v\}}_{\{s\}}V^{(C_e)}\right]^{(\Gamma_0)}, \quad (1) \end{aligned}$$

where the first term represents the purely vibrational Hamiltonian and Γ_0 is the scalar *irrep* of G which we shall simply denote A_1 in the following. The set $\{s\} = s_1, s_2 \cdots$ may include any mode s_i appearing in the full vibrational representation and the κ_i indices represent the additional labels needed to fully specify the operators. The electronic operators are partly determined from the symmetry properties of the considered electronic states. For a given system the expansion (1) may be used to represent an untransformed Hamiltonian, for instance that of the adiabatic approximation [4], or an effective one adapted to the study of a given vibronic polyad [17,18]. The main preliminary step is thus the determination of a complete set of electronic operators and states.

2.1 Electronic operators and states

For the cases considered in this paper the electronic algebras are the unitary algebras $u(2)_e$ for an orbital doublet and $u(4)_e$ for a G' (or Γ_8) quadruplet in cubic molecules [15,16,19,20].

2.1.1 E-type electronic states

Whatever G we shall denote E_r the *irrep* spanned by the electronic states and we keep the classification of point groups introduced in [21,22] and recalled in Appendix A, together with a summary of our conventions for $u(2)$ algebras associated with electronic and vibrational degrees of freedom. For an orbital doublet 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 is of the form ${}^{[1\,-1]}\mathcal{E}^{(k)}_{p_e}$, but as ${}^{[1\,-1]}\mathcal{E}^{(0)}$ reduces to the linear invariant $(N_1 + N_2)/\sqrt{2}$ 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:

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

where the E_k symmetries are those in Table A.3. For groups in $G_{(I)}$ we have mainly two cases:

$$\text{(ii) } k = 2r \quad , \quad \text{(iii) } k = n - 2r \; (k = 2n - 2r), \qquad (3)$$

where the substitution $n \to 2n$ is for D_{nd} (n even) groups. Groups in $G_{(II)}$ being direct products of groups in $G_{(I)}$ with C_s or C_I in all cases the electronic operators are of $'$ or g type; likewise for these groups A_2 in (2) is replaced by A'_2 or A_{2g}. Groups in $G_{(III)}$ associated with linear molecules will not be explicitly considered since their full vibrational representation contains only E_1 or $E_{1\alpha}$ modes.

Depending upon the orientation of the *irreps* of type E the index σ_e is denoted σ or $\bar{\sigma}$ for orientations I and II respectively. For each case the expressions of the symmetry adapted electronic operators in terms of the $su(2)_e$ generators are given in Appendix A together with their matrix elements calculated in the various bases:

$$\begin{array}{ccccc} u(2)_e \supset & su(2)_e & \supset & so(2)_e \\ [10] \;\; \downarrow & \frac{1}{2} & \downarrow & m_e \\ u(2)_e \supset & su^*(2)_e & \supset & G \\ [10] \;\; \downarrow & \frac{1}{2} & \downarrow & 1E_r\sigma_e \end{array} \qquad (4)$$

with $\sigma_e = \sigma$ or $\bar{\sigma}$. From now on the electronic operators will be simply denoted $E^{(1,\ell_e C_e)}$.

2.1.2 G′ electronic states in spherical tops

It has been shown [20] that two algebraic chains are convenient for the study of rovibronic interactions in G' states of spherical top molecules. Both use the fact that the electronic states span an *irrep* $[1\dot{0}]$ of $u(4)_e$ which can be symmetry adapted in different chains. The first one introduces the “natural” $su(2) \approx so(3)$ sub-algebra via the $sp(4) \approx so(5)$ algebra:

$$\begin{array}{ccccccccc} u(4)_e & \supset & su(4)_e & \supset & sp(4)_e & \supset & su(2)_e & \supset & X \\ [1\dot{0}] & \downarrow & [1\dot{0}] & \downarrow & \langle 10 \rangle & \downarrow & \frac{3}{2} & \downarrow & p \end{array} \qquad (5)$$

where X is $so(2)_e$ when dealing with the standard basis ($p = m_e$) or O^S, T^S_d when working in a basis symmetrized in the molecular symmetry group ($p = G'\sigma$ or $p = G'\bar{\sigma}$ depending on the orientation chosen for the *irrep* G'). O^S and T^S_d denote respectively the octahedral and tetrahedral groups with their spinorial *irreps*. A complete set of electronic tensor operators may be built through a bosonic realization of $u(4)_e$ [23]:

$$^{[1\dot{0}-1]}E^{\langle\lambda_1\lambda_2\rangle(k_e)}_{m_e} \quad \text{or} \quad ^{[1\dot{0}-1]}E^{\langle\lambda_1\lambda_2\rangle(k_e)}_{C_e\sigma_e}, \tag{6}$$

with the $sp(4)$, $su(2)$ and C_e labels

$$\begin{array}{ccl} \langle\lambda_1\lambda_2\rangle & k_e & C_e \\ \langle 20\rangle & 1 & F_1 \\ & 3 & A_2, F_1, F_2 \\ \langle 11\rangle & 2 & E, F_2 \end{array} \tag{7}$$

and $m_e = k_e, k_e - 1 \cdots - k_e$ when $X = so(2)_e$. The scalar operator $^{[1\dot{0}-1]}E^{\langle 00\rangle(0)}$ is proportional to the $u(4)_e$ linear invariant and thus reduces to a constant within $[1\,\dot{0}]$.

The second possibility uses the direct product property $E \times E'_1 = G'$ and the known fact that E and E'_1 can be embedded in two $su(2)$ algebras:

$$\begin{array}{ccccccl} u(4)_e & \supset & su(4)_e & \supset & so(4)_e & \approx & su(2)_S \oplus su(2)_\Sigma \\ [1\dot{0}] & \downarrow & [1\dot{0}] & \downarrow & & & (\tfrac{1}{2} \quad , \quad \tfrac{1}{2}) \\ & & & & & \supset & so(2)_S \oplus so(2)_\Sigma \\ & & & & & \downarrow & (m_e \quad , \quad m'_e) \end{array} \tag{8}$$

$$\begin{array}{ccccccl} u(4)_e & \supset & su(4)_e & \supset & so(4)_e & \approx & su^*(2)_S \oplus su(2)_\Sigma \\ [1\dot{0}] & \downarrow & [1\dot{0}] & \downarrow & & & (\tfrac{1}{2} \quad , \quad \tfrac{1}{2}) \\ & & & & & \supset & G^S \\ & & & & & \downarrow & E\bar{\sigma}_e, E'_1\bar{\sigma}'_e \end{array} \tag{9}$$

In fact, for the electronic states, both chains (8, 9) are identical:

$$\begin{aligned} &|[1\dot{0}], [10]\tfrac{1}{2}\, m_e, [10]\tfrac{1}{2}\, m'_e\rangle\rangle \equiv |[1\dot{0}], [10]\tfrac{1}{2}1E\bar{\sigma}_e, [10]\tfrac{1}{2}E'_1\bar{\sigma}'_e\rangle\rangle \\ &\equiv |[1\dot{0}], [10]\tfrac{1}{2}1E, [10]\tfrac{1}{2}E'_1; G'\overline{\sigma}\rangle\rangle, \end{aligned} \tag{10}$$

since the orientations of the E and E'_1 *irreps* have been chosen so that the Clebsch-Gordan coefficients matrix reduces to the identity:

$$F\begin{array}{ccc} \bar{\sigma}_e & \bar{\sigma}'_e & (G') \\ (E & E'_1) & \bar{\sigma} \end{array} \equiv \mathbf{I}. \tag{11}$$

Besides the scalar operator, the electronic operators are now of the form

$$^{[1\dot{0}-1]}E^{([\lambda_1\mu_1]k_1, [\lambda_2\mu_2]k_2)}_{m_1 m_2} \quad \text{or} \quad ^{[1\dot{0}-1]}E^{([\lambda_1\mu_1]k_1 \quad, [\lambda_2\mu_2]k_2)}_{l_1C_e\overline{\sigma}_1 \quad C'_e\overline{\sigma}_2}, \tag{12}$$

according as one works either in chain (8) or in chain (9), with symmetry labels:

$$\begin{array}{l} [\lambda_1\mu_1]k_1l_1C_e,\ [\lambda_2\mu_2]k_2C'_e \\ [1-1]1, 0A_2, [0\ \ 0]0A_1 \\ [1-1]1, 2E,\ [0\ \ 0]0A_1 \\ [0\ \ 0]0, 0A_1,\ [1-1]1F_1 \\ [1-1]1, 0A_2, [1-1]1F_1 \\ [1-1]1, 2E,\ [1-1]1F_1\,. \end{array} \tag{13}$$

In particular those needed in the following are the symmetry adapted generators of $su^*(2)_S$

$$\begin{aligned} ^{[1\dot{0}-1]}E^{([1-1]1,\ [00]0)}_{2E\overline{1} \quad\ A_1} &= i\,\mathbf{S}_+/\sqrt{2} \\ ^{[1\dot{0}-1]}E^{([1-1]1,\ [00]0)}_{2E\overline{2} \quad\ A_1} &= -i\,\mathbf{S}_-/\sqrt{2} \\ ^{[1\dot{0}-1]}E^{([1-1]1,\ [00]0)}_{0A_2 \quad\ A_1} &= -\mathbf{S}_z, \end{aligned} \tag{14}$$

and those of $su(2)_\Sigma$

$$\begin{aligned} ^{[1\dot{0}-1]}E^{([00]0,\ [1-1]1)}_{0A_1 \quad\ F_1x} &= -(\Sigma_- + \Sigma_+)/2 \\ ^{[1\dot{0}-1]}E^{([00]0,\ [1-1]1)}_{0A_1 \quad\ F_1y} &= -i(\Sigma_- - \Sigma_+)/2 \\ ^{[1\dot{0}-1]}E^{([00]0,\ [1-1]1)}_{0A_1 \quad\ F_1z} &= -\Sigma_z, \end{aligned} \tag{15}$$

where the pseudo-spin electronic operators $\mathbf{S}_\alpha$ and Σ_α satisfy the usual $su(2)$ commutation rules. Bold face letters are used for the first pseudo-spin electronic operator to distinguish it from its counterpart for an E-type electronic state. In both cases the bosonic realizations of the generators together with their matrix elements have been given in [20]. In the following the $u(4)_e$ label $[1\dot{0} - 1]$ will be omitted in the electronic operators.

2.2 Formal Hamiltonian expansions

With the operators introduced in the preceding section the expansion (1) may be specialized to E and G' electronic states.

- *H_F for E_r electronic states*

With equation (2) we obtain the expansion

$$\begin{aligned} H_F = I_e &\sum_{\{s\}\{\kappa_v\}} {}_{\{s\}}t^{A_1\{\kappa_v\}}\ {}^{\{\kappa_v\}}_{\{s\}}V^{(A_1)}_{+} \\ &+ \sum_{\{s\}\{\kappa_v\}} {}_{\{s\}}t^{A_2\{\kappa_v\}}\, [E^{(1,0A_2)} \times {}^{\{\kappa_v\}}_{\{s\}}V^{(A_2)}_{-}]^{(A_1)} \\ &+ \sum_{\{s\}\{\kappa_v\}} {}_{\{s\}}t^{E_k\{\kappa_v\}}\, [E^{(1,2E_k)} \times {}^{\{\kappa_v\}}_{\{s\}}V^{(E_k)}_{+}]^{(A_1)}, \end{aligned} \tag{16}$$

where $+$ (resp. $-$) stands for time reversal invariant (resp. non-invariant) operators and for a given E_r state, the k values are those in equation (3). This form also includes groups which have only one E-type *irrep*, such as $C_{3v}, D_3, D_{3h}, D_{3d}$ and cubic point groups, for which we have a (iii) case with $k = 1$ and $n = 3$.

- *H_F for G' electronic states*

Several expressions can be given depending upon the electronic chain used. With chain (5) we may write

$$\begin{aligned} H_F = I_e &\sum_{\{s\}\{\kappa_v\}} {}_{\{s\}}t^{A_1\{\kappa_v\}}\ {}^{\{\kappa_v\}}_{\{s\}}V^{(A_1)}_{+} \\ &+ \sum_{\{s\}\{\kappa_v\}} {}_{\{s\}}t^{F_1\{\kappa_v\}}\, [E^{\langle 20\rangle(1,F_1)} \times {}^{\{\kappa_v\}}_{\{s\}}V^{(F_1)}_{-}]^{(A_1)} \\ &+ \sum_{\{s,C\}\{\kappa_v\}} {}_{\{s\}}t^{C\{\kappa_v\}}\, [E^{\langle 20\rangle(3,C)} \times {}^{\{\kappa_v\}}_{\{s\}}V^{(C)}_{-}]^{(A_1)} \\ &+ \sum_{\{s,C\}\{\kappa_v\}} {}_{\{s\}}t^{C\{\kappa_v\}}\, [E^{\langle 11\rangle(2,C)} \times {}^{\{\kappa_v\}}_{\{s\}}V^{(C)}_{+}]^{(A_1)}, \end{aligned} \tag{17}$$

where the C symmetries are those specified in equation (7). When no doubly degenerate modes are involved the couplings can also be performed at the $su(2)$ level [20]. Using chain (9) gives ($C = F_1,\ F_2$):

$$\begin{aligned} H_F = I_e \sum_{\{s,C\}\{\kappa_v\}} \Big[& {}_{\{s\}}t^{A_1\{\kappa_v\}}\, {}^{\{\kappa_v\}}_{\{s\}}V_+^{(A_1)} \\ & + {}_{\{s\}}t^{A_2\{\kappa_v\}} [E^{([1-1]1,0A_2,\,[00]0A_1)(A_2)} \times {}^{\{\kappa_v\}}_{\{s\}}V_-^{(A_2)}]^{(A_1)} \\ & + {}_{\{s\}}t^{E\{\kappa_v\}} [E^{([1-1]1,2E,\,[00]0A_1)(E)} \times {}^{\{\kappa_v\}}_{\{s\}}V_+^{(E)}]^{(A_1)} \\ & + {}_{\{s\}}t^{F_1\{\kappa_v\}} [E^{([00]0,0A_1,\,[1-1]1F_1)(F_1)} \times {}^{\{\kappa_v\}}_{\{s\}}V_-^{(F_1)}]^{(A_1)} \\ & + {}_{\{s\}}t^{F_2\{\kappa_v\}} [E^{([1-1]1,0A_2,\,[1-1]1F_1)(F_2)} \times {}^{\{\kappa_v\}}_{\{s\}}V_+^{(F_2)}]^{(A_1)} \\ & + {}_{\{s\}}t^{C\{\kappa_v\}} [E^{([1-1]1,2E,\,[1-1]1F_1)(C)} \times {}^{\{\kappa_v\}}_{\{s\}}V_-^{(C)}]^{(A_1)} \Big]. \end{aligned} \tag{18}$$

3 Untransformed Hamiltonian expansion for an $\mathsf{E_r}$ state

With equation (16) we can represent either an untransformed or an effective vibronic Hamiltonian. However the allowed values for $\ell_e C_e$ in equation (2) as well as the structure of the vibrational factor depend upon the model to be built. For a vibronic term in the untransformed Hamiltonian ${}^{\{\kappa_v\}}V^{(C_v)}$ is a function of normal coordinates ${}_sQ^{(C_s)}$ and we have only $\ell_e C_e = 2E_k$ since for $\ell_e C_e = 0A_2$ the electronic operator is associated with the z component of the pseudo-spin and is not invariant upon time reversal. Restricting to terms which are at most quadratic in the coordinates we can thus write

$$\begin{aligned} H_{vibr} = I_e \sum_s \Big\{ & \hbar\omega_s \Big(N_s + \frac{g_s}{2}\Big) \\ & + {}_st^{E_k}[E^{(1,2E_k)} \times {}_sQ^{(E_k)}]^{(A_1)} \Big\} \\ & + \sum_{s,s'} {}_{ss'}t^{C_1C_2(E_k)}[E^{(1,2E_k)} \times ({}_sQ^{(C_1)} \times {}_{s'}Q^{(C_2)})^{(E_k)}]^{(A_1)} \\ & + \cdots \end{aligned} \tag{19}$$

For a given molecule, with symmetry group G, the active coordinates, associated with the linear JT terms on the second line, are determined for a given E_r electronic state by the k values and with the knowledge of the full vibrational representation which can be found for instance in [4]. Likewise the possible quadratic terms are first fixed through the analysis of direct products $C_1 \times C_2$ of two *irreps* of G. These products are given in Appendix B. In all cases we have terms

$$\sum_{s \neq s',i} {}_{ss'}t^{A_iE_k(E_k)}[E^{(1,2E_k)} \times ({}_sQ^{(A_i)} \times_{s'} Q^{(E_k)})^{(E_k)}]^{(A_1)},$$

involving nondegenerate modes A_i ($i = 1, 2$). For D_n, C_{nv}, D_{nd} groups with n even which admit B_i ($i = 1, 2$) *irreps* we find

$$\sum_{s \neq s',i} {}_{ss'}t^{B_iE_{\frac{n}{2}-k}(E_k)}[E^{(1,2E_k)} \times ({}_sQ^{(B_i)} \times_{s'} Q^{(E_{\frac{n}{2}-k})})^{(E_k)}]^{(A_1)}$$

for D_n, C_{nv} and

$$\sum_{s \neq s',i} {}_{ss'}t^{B_iE_{n-k}(E_k)}[E^{(1,2E_k)} \times ({}_sQ^{(B_i)} \times_{s'} Q^{(E_{n-k})})^{(E_k)}]^{(A_1)}$$

for D_{nd}.

Terms involving doubly degenerate modes are of the form

$$\sum_{s,s'} {}_{ss'}t^{E_{k_1}E_{k_2}(E_k)}[E^{(1,2E_k)} \times ({}_sQ^{(E_{k_1})} \times {}_{s'}Q^{(E_{k_2})})^{(E_k)}]^{(A_1)},$$

with the following conditions for the possible k_1, k_2 values for a given k:

- $k_1 \neq k_2$, hence $s \neq s'$, $k_1 + k_2 \neq n/2$ (n)
  $$k = |k_1 - k_2| \text{ or } n - (k_1 + k_2)\ (2n - (k_1 + k_2)),$$
- $k_1 = k_2$, $s \neq s'$ or $s = s'$, $k_1 \neq n/4$ $(n/2)$
  $$k = 2k_1 \text{ or } n - 2k_1\ (2n - 2k_1),$$

where the values in parenthesis refer to D_{nd} (n even) groups.

For cubic point groups we simply have

$$\sum_{s,s'} {}_{ss'}t^{EE(E)}[E^{(1,2E)} \times ({}_sQ^{(E)} \times {}_{s'}Q^{(E)})^{(E)}]^{(A_1)}.$$

This same expression applies to groups D_3, C_{3v} having only one E *irrep* whose symmetrized product contains E. Cubic molecules also admit three dimensional vibrational modes which give the additional quadratic terms

$$\sum_{s,s',i,j} {}_{ss'}t^{F_iF_j(E)}[E^{(1,2E)} \times ({}_sQ^{(F_i)} \times {}_{s'}Q^{(F_j)})^{(E)}]^{(A_1)},$$

with ($i, j = 1, 2$). We note that quadratic terms involving modes with the symmetry of the active coordinate

$${}_{ss'}t^{E_kE_k(E_k)}[E^{(1,2E_k)} \times ({}_sQ^{(E_k)} \times {}_{s'}Q^{(E_k)})^{(E_k)}]^{(A_1)},$$

are possible only for E_r electronic states as summarized below:

$$\begin{array}{rlll} & E_r & E_k & \text{case} \\ D_n, C_{nv} & r = n/6 & k = n/3 & \text{(ii)} \\ & r = n/3 & k = n/3 & \text{(iii)} \\ D_{nd} & r = n/3 & k = 2n/3 & \text{(ii)} \\ n \text{ even} & r = 2n/3 & k = 2n/3 & \text{(iii)} \end{array} \tag{20}$$

with n such that r and k be integers. We thus obtain three possible expansions for the untransformed vibronic Hamiltonian for an E_r electronic state.

- D_n, C_{nv}, n odd

$$\begin{aligned} & H_{vibr} = \\ & \quad I_e \sum_s \Big\{\hbar\omega_s \Big(N_s + \frac{g_s}{2}\Big) + {}_st^{E_k}[E^{(1,2E_k)} \times {}_sQ^{(E_k)}]^{(A_1)}\Big\} \\ & \quad + \Big[E^{(1,2E_k)} \times \Big\{ \sum_{s \neq s',i} {}_{ss'}t^{A_iE_k(E_k)}({}_sQ^{(A_i)} \times {}_{s'}Q^{(E_k)})^{(E_k)} \\ & \quad + \sum_{s,s'} {}_{ss'}t^{E_{k_1}E_{k_2}(E_k)}\, ({}_sQ^{(E_{k_1})} \times {}_{s'}Q^{(E_{k_2})})^{(E_k)}\Big\}\Big]^{(A_1)} + \cdots, \end{aligned} \tag{21}$$

- D_n, C_{nv}, D_{nd}, n even

$$\begin{aligned}H_{vibr} = I_e\sum_s\Big\{&\hbar\omega_s\left(N_s+\frac{g_s}{2}\right)+{}_st^{E_k}[E^{(1,2E_k)}\times{}_sQ^{(E_k)}]^{(A_1)}\Big\}\\
&+\Big[E^{(1,2E_k)}\times\Big\{\sum_{s\neq s',i}{}_{ss'}t^{A_iE_k(E_k)}({}_sQ^{(A_i)}\times{}_{s'}Q^{(E_k)})^{(E_k)}\\
&+\sum_{s\neq s',i}{}_{ss'}t^{B_iE_{\frac{n}{2}-k}(E_k)}({}_sQ^{(B_i)}\times{}_{s'}Q^{(E_{\frac{n}{2}-k})})^{(E_k)}\\
&+\sum_{s,s'}{}_{ss'}t^{E_{k_1}E_{k_2}(E_k)}\left({}_sQ^{(E_{k_1})}\times{}_{s'}Q^{(E_{k_2})}\right)^{(E_k)}\Big\}\Big]^{(A_1)}+\cdots,\end{aligned}\tag{22}$$

with the substitution $n/2 \rightarrow n$ for terms involving B_i modes for D_{nd} n even groups.

- O, T_d

$$\begin{aligned}H_{vibr} = I_e\sum_s\Big\{&\hbar\omega_s\left(N_s+\frac{g_s}{2}\right)+{}_st^{E}[E^{(1,2E)}\times{}_sQ^{(E)}]^{(A_1)}\Big\}\\
&+\Big[E^{(1,2E)}\times\Big\{\sum_{s\neq s',i}{}_{ss'}t^{A_iE(E)}({}_sQ^{(A_i)}\times{}_{s'}Q^{(E)})^{(E)}\\
&+\sum_{s,s'}{}_{ss'}t^{EE(E)}({}_sQ^{(E)}\times{}_{s'}Q^{(E)})^{(E)}\\
&+\sum_{s,s',i,j}{}_{ss'}t^{F_iF_j(E)}\left({}_sQ^{(F_i)}\times{}_{s'}Q^{(F_j)}\right)^{(E)}\Big\}\Big]^{(A_1)}+\cdots\end{aligned}\tag{23}$$

For groups in $G_{(II)}$ $','' $ or u, g labels are added following the rules given after equation (3) and in Appendix B.

3.1 Vibronic Hamiltonian for E$_r$ electronic states

The expressions commonly found in the literature for the so-called $E \otimes e$ JT systems usually neglect all coupling terms involving non active vibrational coordinates and most often apply to molecules with symmetry group C_{3v}, D_3, D_{3h} or one of the cubic groups. Sometimes $E_k = E_{2r}$ systems are mentioned [4]. Relations between our parameters and some conventional ones are obtained through the vibronic matrix

$$\begin{aligned}\widehat{H} &= \langle {}^e\Psi^{(E_r)}_{\sigma'_e}|H_{vibr}|{}^e\Psi^{(E_r)}_{\sigma_e}\rangle\\
&= \langle\langle[1\,0]\frac{1}{2}1E_r\sigma'_e|H_{vibr}|[1\,0]\frac{1}{2}1E_r\sigma_e\rangle\rangle.\end{aligned}\tag{24}$$

Various expressions are obtained depending on the orientation used for operators and states.

- Orientation I

Both cases (ii) and (iii) (Eq. (3)) can be treated simultaneously. From the expression (A.6) of the electronic operators and with

$$F\begin{matrix}\sigma & \sigma' \\ (E_k & E_k)\end{matrix}^{(A_1)} = \frac{1}{\sqrt{2}}\,\delta_{\sigma',\sigma}\,,\tag{25}$$

equation (19) can be written

$$\begin{aligned}H_{vibr} = I_e\sum_s&\hbar\omega_s\left(N_s+\frac{g_s}{2}\right)\\
&+\frac{1}{\sqrt{2}}S_x\,V^{(E_k)}_1-\frac{\eta}{\sqrt{2}}S_y\,V^{(E_k)}_2,\end{aligned}\tag{26}$$

with $\eta = +1$ (resp. $\eta = -1$) for case (ii) (resp. (iii)) and where we set

$$\begin{aligned}V^{(E_k)}_\sigma = &\sum_s {}_st^{E_k}{}_sQ^{(E_k)}_\sigma\\
&+\sum_{s,s'}{}_{ss'}t^{C_1C_2(E_k)}({}_sQ^{(C_1)}\times{}_{s'}Q^{(C_2)})^{(E_k)}_\sigma+\cdots\end{aligned}\tag{27}$$

The possible C_1, C_2 symmetries are those in equations (21–23) according to the case. Within the unsymmetrized standard $u(2)_e \supset su(2)_e \supset so(2)_e$ basis the vibronic matrix writes in terms of Pauli matrices

$$\begin{aligned}\widehat{H} = \widehat{\sigma}_0&\sum_s\hbar\omega_s\left(N_s+\frac{g_s}{2}\right)\\
&-\frac{1}{2\sqrt{2}}\,\widehat{\sigma}_x\,V^{(E_k)}_1-\frac{\eta}{2\sqrt{2}}\,\widehat{\sigma}_y\,V^{(E_k)}_2,\end{aligned}\tag{28}$$

where we used our conventions for $|[1\,0]\frac{1}{2}m\rangle\rangle$ covariant states. Projection of equation (26) onto the E_r state using this time the $u(2)_e \supset su^*(2)_e \supset G$ symmetry adapted basis associated with orientation I gives (Eq. (A.7))

$$\begin{aligned}\widehat{H} = \widehat{\sigma}_0&\sum_s\hbar\omega_s\left(N_s+\frac{g_s}{2}\right)\\
&+\frac{1}{2\sqrt{2}}\,\widehat{\sigma}_z\,V^{(E_k)}_1+\frac{\eta}{2\sqrt{2}}\,\widehat{\sigma}_x\,V^{(E_k)}_2.\end{aligned}\tag{29}$$

- Orientation II

Likewise with the expressions (A.9) of the electronic operators and with

$$F\begin{matrix}\bar{\sigma} & \bar{\sigma}' \\ (E_k & E_k)\end{matrix}^{(A_1)} = \frac{1}{\sqrt{2}}\,\delta_{\bar{\sigma}',-\bar{\sigma}}\tag{30}$$

where $-\bar{\sigma} = 2, 1$ for $\bar{\sigma} = 1, 2$, we obtain for equation (19):
–for case (ii) $\eta = +1$

$$\begin{aligned}H_{vibr} &= I_e\sum_s\hbar\omega_s\left(N_s+\frac{g_s}{2}\right)+\frac{i}{2}(S_-\,V^{(E_k)}_{\bar{2}}-S_+\,V^{(E_k)}_{\bar{1}})\\
&= I_e\sum_s\hbar\omega_s\left(N_s+\frac{g_s}{2}\right)+\frac{1}{2}(S_-V^{(E_k)}_{-}+S_+V^{(E_k)}_{+}),\end{aligned}\tag{31}$$

where we set for the vibrational operators (27) in orientation II

$$\begin{aligned}V^{(E_k)}_{\bar{1}} &= \frac{i}{\sqrt{2}}\left(V^{(E_k)}_1+iV^{(E_k)}_2\right) = iV^{(E_k)}_{+}\\
V^{(E_k)}_{\bar{2}} &= -\frac{i}{\sqrt{2}}\left(V^{(E_k)}_1-iV^{(E_k)}_2\right) = -iV^{(E_k)}_{-}.\end{aligned}\tag{32}$$

The projection of H_{vibr} (31) onto the E_r state using the $u(2)_e \supset su^*(2)_e \supset G$ symmetry adapted basis associated with orientation II gives (Eq. (A.10))

$$\widehat{H} = \widehat{\sigma}_0 \sum_s \hbar\omega_s \left(N_s + \frac{g_s}{2}\right) - \frac{1}{2}(\widehat{\sigma}_+ V^{(E_k)}_{-} + \widehat{\sigma}_- V^{(E_k)}_{+}), \tag{33}$$

–for case (iii) $\eta = -1$ we obtain

$$\begin{aligned} H_{vibr} &= I_e \sum_s \hbar\omega_s \left(N_s + \frac{g_s}{2}\right) + \frac{i}{2}(S_+ V^{(E_k)}_{\bar{2}} - S_- V^{(E_k)}_{\bar{1}}) \\ &= I_e \sum_s \hbar\omega_s \left(N_s + \frac{g_s}{2}\right) + \frac{1}{2}(S_+ V^{(E_k)}_{-} + S_- V^{(E_k)}_{+}), \end{aligned} \tag{34}$$

which gives for the vibronic matrix within the same basis than for case (ii)

$$\widehat{H} = \widehat{\sigma}_0 \sum_s \hbar\omega_s \left(N_s + \frac{g_s}{2}\right) - \frac{1}{2}(\widehat{\sigma}_- V^{(E_k)}_{-} + \widehat{\sigma}_+ V^{(E_k)}_{+}). \tag{35}$$

3.2 Correlations with standard forms

3.2.1 Linear and quadratic vibronic coupling constants

We take equation (19), assuming that the conditions in equation (3) are satisfied, and with the Wigner-Eckart theorem we obtain for the linear coupling constants:

$$\left\langle {}^e\Psi^{(E_r)}_{\sigma'_e} \left| \frac{\partial V}{\partial_s Q^{(E_k)}_{\alpha'}} \right| {}^e\Psi^{(E_r)}_{\sigma_e} \right\rangle =_s t^{E_k} \left(-i\frac{\sqrt{3}}{2}\right) \times \sum_\alpha F \begin{matrix} \alpha & \alpha' & (A_1) \\ (E_k & E_k) & \end{matrix} F \begin{matrix} 2E_k\alpha & 1E_r\sigma_e & ([1\,0]1/2)* \\ ([1\,-1]1 & [1\,0]1/2) & 1E_r\sigma'_e \end{matrix},$$

and for quadratic ones

$$\left\langle {}^e\Psi^{(E_r)}_{\sigma'_e} \left| \frac{\partial^2 V}{\partial_s Q^{(C_1)}_{\sigma_1} \partial_{s'} Q^{(C_2)}_{\sigma_2}} \right| {}^e\Psi^{(E_r)}_{\sigma_e} \right\rangle = {}_{ss'}t^{C_1C_2(E_k)}(-i\sqrt{3}) \sum_{\alpha,\alpha'} F \begin{matrix} \alpha & \alpha' & (A_1) \\ (E_k & E_k) & \end{matrix} F \begin{matrix} \sigma_1 & \sigma_2 & (E_k) \\ (C_1 & C_2) & \alpha' \end{matrix} \times F \begin{matrix} 2E_k\alpha & 1E_r\sigma_e & ([1\,0]1/2)* \\ ([1\,-1]1 & [1\,0]1/2) & 1E_r\sigma'_e. \end{matrix}$$

The preceding expressions may be simplified with the introduction of the isoscalar factors for the chain $u(2)_e \supset su^*(2)_e \supset G$

$$F \begin{matrix} 2E_k\alpha & 1E_r\sigma_e & ([1\,0]1/2) \\ ([1\,-1]1 & [1\,0]1/2) & 1E_r\sigma'_e \end{matrix} = K \begin{matrix} 2E_k & 1E_r & ([1\,0]1/2) \\ ([1\,-1]1 & [1\,0]1/2) & 1E_r \end{matrix} F \begin{matrix} \alpha & \sigma_e & (E_r) \\ (E_k & E_r) & \sigma'_e \end{matrix},$$

and taking into account equation (25) or (30).

3.2.2 Special case of the linear JT problem

As shown by equations (28, 29) the usual forms [2–4] for the linear vibronic JT models are included within our approach. Some differences can be explained by our particular conventions for $su(2)$ covariant states; others come from different phase conventions for symmetry adapted electronic states. From equations (27, 31, 34) we have in terms of the pseudo-spin electronic operators and of dimensionless normal coordinates (${}_sD^{E_k} = {}_st^{E_k}/2\sqrt{\hbar\omega_s}$)

$$H_{JTL}/\hbar = I_e\omega_s(N_s+1) + {}_sD^{E_k}(S_{-\,s}q^{(E_k)}_{-} + S_{+\,s}q^{(E_k)}_{+}) \tag{36}$$

for an (ii) case and

$$H_{JTL}/\hbar = I_e\omega_s(N_s+1) + {}_sD^{E_k}(S_{+\,s}q^{(E_k)}_{-} + S_{-\,s}q^{(E_k)}_{+}) \tag{37}$$

for an (iii) one. They commute respectively with

$$\begin{aligned} \bar{j}_z &= {}_s\ell_z - S_z = -2J_z - S_z \quad \text{case (ii)} \\ j_z &= {}_s\ell_z + S_z = -2J_z + S_z \quad \text{case (iii)} \end{aligned} \tag{38}$$

where ${}_s\ell_z = -2J_z$ is the oscillator angular momentum and J_z one of the generators of the $u(2)_v$ vibrational algebra. The second case is that usually considered in the literature [6]. We first take as basis for the space of states ($v = 2j$)

$$\{|\Psi_{vibr}\rangle\} = |[1\,0]\frac{1}{2}m_e\rangle\rangle|[v\,0]j\,m\rangle\rangle \equiv |[1\,0]\frac{1}{2}1E_r\bar{\sigma}\rangle\rangle|[v\,0]j\,m\rangle\rangle,$$

whose members are eigenstates of j_z (resp. $\bar{j}_z$) with eigenvalues $\mu = 2m - m_e$ (resp. $\bar{\mu} = 2m + m_e$). The properties under time reversal

$$\begin{aligned} &\mathcal{K}H_{JTL}\mathcal{K}^{-1} = H_{JTL},\ \mathcal{K}j_z\mathcal{K}^{-1} = -j_z,\ \mathcal{K}\bar{j}_z\mathcal{K}^{-1} = -\bar{j}_z, \\ &\mathcal{K}|[1\,0]\frac{1}{2}m_e\rangle\rangle|[v\,0]j\,m\rangle\rangle = |[1\,0]\frac{1}{2} - m_e\rangle\rangle|[v\,0]j\ -m\rangle\rangle, \\ &\mathcal{K}|[1\,0]\frac{1}{2}1E_r\bar{\sigma}\rangle\rangle|[v\,0]j\,m\rangle\rangle = |[1\,0]\frac{1}{2}1E_r - \bar{\sigma}\rangle\rangle|[v\,0]j\ -m\rangle\rangle, \end{aligned}$$

allow to recover the known properties [13,24] that the eigenvalues of H_{JTL} only depend upon $|\mu|$ (resp. $|\bar{\mu}|$) and that each one is at least doubly degenerate. Thus the eigenstates of H_{JTL} for case (ii) are linear combinations of the states ($\bar{\mu} \geq 1/2$)

$$\begin{aligned} |[1\,0]\frac{1}{2}\frac{1}{2}\rangle\rangle|[v\,0]j\ \frac{\bar{\mu}-\frac{1}{2}}{2}\rangle\rangle &= \overline{\varphi}_{j\bar{\mu}+} \\ |[1\,0]\frac{1}{2} - \frac{1}{2}\rangle\rangle|[v\,0]j\ \frac{\bar{\mu}+\frac{1}{2}}{2}\rangle\rangle &= \overline{\phi}_{j\bar{\mu}+}, \end{aligned} \tag{39}$$

and of those obtained with the time reversal operator

$$\begin{aligned} \mathcal{K}\overline{\varphi}_{j\bar{\mu}+} &= |[1\,0]\frac{1}{2} - \frac{1}{2}\rangle\rangle|[v\,0]j\ -\frac{\bar{\mu}-\frac{1}{2}}{2}\rangle\rangle = \overline{\varphi}_{j\bar{\mu}-} \\ \mathcal{K}\overline{\phi}_{j\bar{\mu}+} &= |[1\,0]\frac{1}{2}\frac{1}{2}\rangle\rangle|[v\,0]j\ -\frac{\bar{\mu}+\frac{1}{2}}{2}\rangle\rangle = \overline{\phi}_{j\bar{\mu}-}. \end{aligned} \tag{40}$$

Likewise for an (iii) case we have ($\mu \geq 1/2$):

$$|[1\,0]\frac{1}{2}\frac{1}{2}\rangle\rangle|[v\,0]j\;\frac{\mu+\frac{1}{2}}{2}\rangle\rangle = \varphi_{j\mu+}$$
$$|[1\,0]\frac{1}{2} - \frac{1}{2}\rangle\rangle|[v\,0]j\;\frac{\mu-\frac{1}{2}}{2}\rangle\rangle = \phi_{j\mu+}, \tag{41}$$

$$\mathcal{K}\varphi_{j\mu+} = |[1\,0]\frac{1}{2} - \frac{1}{2}\rangle\rangle|[v\,0]j\; - \frac{\mu+\frac{1}{2}}{2}\rangle\rangle = \varphi_{j\mu-}$$
$$\mathcal{K}\phi_{j\mu+} = |[1\,0]\frac{1}{2}\frac{1}{2}\rangle\rangle|[v\,0]j\; - \frac{\mu-\frac{1}{2}}{2}\rangle\rangle = \phi_{j\mu-}. \tag{42}$$

We can write

$$ {}_sq^{(E_k)}_{+} = -i\ {}_sq^{(E_k)}_{\bar{1}} = \frac{i}{\sqrt{2}}({}^{[10]}V^{(\frac{1}{2})}_{\frac{1}{2}} + i^{[0-1]}V^{(\frac{1}{2})}_{\frac{1}{2}})$$
$$ {}_sq^{(E_k)}_{-} = i\ {}_sq^{(E_k)}_{\bar{2}} = -\frac{i}{\sqrt{2}}({}^{[10]}V^{(\frac{1}{2})}_{-\frac{1}{2}} - i^{[0-1]}V^{(\frac{1}{2})}_{-\frac{1}{2}})$$

where ${}^{[10]}V^{(\frac{1}{2})}$ and ${}^{[0-1]}V^{(\frac{1}{2})}$ are $su(2)_v$ irreducible tensor operators with $su(2)$ reduced matrix elements

$$([v'\,0]j'||{}^{[10]}V^{(\frac{1}{2})}||[v\,0]j) = i([v\,0]j||{}^{[0-1]}V^{(\frac{1}{2})}||[v'\,0]j')$$
$$= [(2j+1)(2j+2)]^{\frac{1}{2}}\ \delta_{v',v+1}.$$

This allows to obtain close expressions for the matrix elements of H_{JTL} for arbitrary $E_r \times e_k$ cases in the form

$$\langle\overline{\phi}_{j+\frac{1}{2}\bar{\mu}+}|H_{JTL}|\overline{\varphi}_{j\bar{\mu}+}\rangle = -i\hbar\ {}_sD^{E_k}/\sqrt{2}$$
$$\times(2j+1)^{\frac{1}{2}}\ C^{\left(\frac{1}{2}\quad j\ \right)\quad \frac{\bar{\mu}+\frac{1}{2}}{2}}_{\frac{1}{2}\quad \frac{\bar{\mu}-\frac{1}{2}}{2}\quad (j+\frac{1}{2})}, \tag{43}$$

$$\langle\overline{\phi}_{j-\frac{1}{2}\bar{\mu}+}|H_{JTL}|\overline{\varphi}_{j\bar{\mu}+}\rangle = -i\hbar\ {}_sD^{E_k}/\sqrt{2}$$
$$\times(2j+1)^{\frac{1}{2}}\ C^{\left(\frac{1}{2}\quad j\ \right)\quad \frac{\bar{\mu}+\frac{1}{2}}{2}}_{\frac{1}{2}\quad \frac{\bar{\mu}-\frac{1}{2}}{2}\quad (j-\frac{1}{2})}, \tag{44}$$

where the $su(2)$ Clebsch-Gordan coefficients can be found for instance in [25]. The matrix elements (43, 44) have been given for cases of type (ii). It can be shown that those for cases (iii) can be deduced from the preceding ones with the substitutions $\bar{\mu} \rightarrow \mu$, $\overline{\varphi} \rightarrow \phi$ and $\overline{\phi} \rightarrow \varphi$. However we will see that this equivalence between both cases is lost when higher order interactions are taken into account. Also it is easily checked that with (43, 44) one recovers, within a phase, the famous tri-diagonal matrices of Longuet-Higgins et al. [24].

For completeness we give below the symmetry of the degenerate states and indicate how symmetry adapted bases can be built for all cases. To our knowledge only special cases have been considered so far. We note that under the action of the P_R operators associated with the generators X and Y (Appendix A) for groups in $G_{(I)}$ we have

$$P_X\overline{\varphi}_{j\bar{\mu}+} = e^{i2r\bar{\mu}\psi}\ \overline{\varphi}_{j\bar{\mu}+}, \qquad P_X\varphi_{j\mu+} = e^{-i2r\mu\psi}\ \varphi_{j\mu+},$$
$$P_Y\overline{\varphi}_{j\bar{\mu}+} = (-1)^{2j+1}\ \overline{\varphi}_{j\bar{\mu}-}, \quad P_Y\varphi_{j\mu+} = (-1)^{2j+1}\ \varphi_{j\mu-},$$

and identical relations in terms of $\overline{\phi}$ and ϕ. This allows first to determine the symmetry $\varGamma_{ev}$ of the degenerate states associated with the sets $\overline{\varphi}_{j\bar{\mu}\pm}, \overline{\phi}_{j\bar{\mu}\pm}$ and $\varphi_{j\mu\pm}, \phi_{j\mu\pm}$. These are given in Table 1 for groups in $G_{(I)}$. For groups in $G_{(II)}$ since the active coordinates are always of type $'$ or g the overall symmetry is always that $'$, $''$, g or u, according to the case, of the electronic state. Next with the matrices for the *irreps* in orientation II symmetry adapted states are built. We obtain:

- When μ or $\bar{\mu}$ are associated with an E-type *irrep* of G

$$\varPhi_{j\kappa E_t\bar{\sigma}} = i^{2j}\ \varPhi_{j\kappa+}\ ,\quad \varPhi_{j\kappa E_t-\bar{\sigma}} = i^{-2j}\ \varPhi_{j\kappa-} \tag{45}$$

where $\kappa = \bar{\mu}$ (resp. $\kappa = \mu$) when $\varPhi = \overline{\varphi}$ or $\overline{\phi}$ (Eqs. (39, 40)) (resp. $\varPhi = \varphi$ or ϕ (Eqs. (41, 42))). The $\kappa, E_t, \bar{\sigma}$ values are those in Table 1 and $-\bar{\sigma} = 2, 1$ for $\bar{\sigma} = 1, 2$.

- When μ or $\bar{\mu}$ are linked with an A or B-type *irrep* of G

$$\varPhi_{j\kappa\varGamma_1} = i^{2j+1}(\varPhi_{j\kappa+} + (-1)^{2j+1}\ \varPhi_{j\kappa-})/\sqrt{2}$$
$$\varPhi_{j\kappa\varGamma_2} = i^{2j}(\varPhi_{j\kappa+} - (-1)^{2j+1}\ \varPhi_{j\kappa-})/\sqrt{2} \tag{46}$$

$\varPhi$ and κ have the same meaning as before and the $\kappa, \varGamma$ (A or B) values given in Table 1. We note that all phases have been settled so that under time reversal

$$\mathcal{K}\varPhi_{j\kappa E_t\bar{\sigma}} = \varPhi_{j\kappa E_t-\bar{\sigma}},\quad \mathcal{K}\varPhi_{j\kappa\varGamma_i} = \varPhi_{j\kappa\varGamma_i}\quad i = 1, 2$$

which leads to real matrix elements (Eqs. (43, 44)) for H_{JTL} when expressed in the symmetry adapted bases (45, 46).

4 Effective Hamiltonian for $\mathbf{E_r \otimes e_{r'}}$ dynamical JT systems

We first underline that we extend somewhat the usual terminology for $E \otimes e$ cases in that we do not assume that the twofold degenerate mode is associated with an active coordinate. This will allow a more general approach and also to discuss systems similar to those $E_r \otimes e_r$ encountered in our previous work (I). Following the method presented there we can write quite generally

$$\widetilde{H}_{vibr} = \sum_{\{n_v, j_v, \ell_v\}} \Big\{ {}_s\tilde{t}^{j_v,\ell_v A_1(A_1)}_{\{n_v\}\{n_v\}} I_e\ {}^{[n_v\ -n_v]}_{\quad\ \ s}\mathcal{V}^{(j_v,\ell_v\ A_1)}$$
$$+\ {}_s\tilde{t}^{j_v,\ell_v A_2(A_2)}_{\{n_v\}\{n_v\}}[E^{(1,0A_2)} \times {}^{[n_v\ -n_v]}_{\quad\ \ s}\mathcal{V}^{(j_v,\ell_v\ A_2)}]^{(A_1)}$$
$$+\ {}_s\tilde{t}^{j_v,\ell_v E_k(E_k)}_{\{n_v\}\{n_v\}}[E^{(1,2E_k)} \times {}^{[n_v\ -n_v]}_{\quad\ \ s}\mathcal{V}^{(j_v,\ell_v\ E_k)}]^{(A_1)} \Big\} \tag{47}$$

where ${}^{[m_1\ -m_2]}_{\quad\ \ s}\mathcal{V}^{(j_v,\ell_v\ E_k)}$ are vibrational operators for the $e_{r'}$ mode, with $m_1 = m_2 = n_v$ for those appearing in the effective Hamiltonian and we recall that j_v can take the values $0, 1 \cdots, n_v$ and hence that ℓ_v is even. In equation (47) operators with symmetry A_1 and E_k (resp. A_2) must satisfy $(-1)^{j_v-\ell_v/2} = +1$ (resp. $(-1)^{j_v-\ell_v/2} = -1$). The matrix elements of the various operators in $\widetilde{H}_{vibr}$ can be computed within a coupled vibronic basis

$$|[1\,0]\frac{1}{2}1E_r, [v\,0]j\ell\varGamma_v; \varGamma_{ev}\sigma_{ev}\rangle\rangle\ \ (\varGamma_{ev} = E_r \times \varGamma_v), \tag{48}$$

Table 1. Symmetry of degenerate states of H_{JTL}.

G	$E_r \otimes e_k$	κ	Γ_{ev}	$\bar{\sigma}$	G	$E_r \otimes e_k$	κ	Γ_{ev}	$\bar{\sigma}$
C_{3v}, D_3	$E \otimes e$	$\mu = 3p + \frac{1}{2}$	E	$\bar{2}$	C_{6v}, D_6	$E_2 \otimes e_2$	$\mu = 3p + \frac{1}{2}$	E_2	$\bar{2}$
O, T_d		$\mu = 3p + \frac{3}{2}$	A_1, A_2				$\mu = 3p + \frac{3}{2}$	A_1, A_2	
		$\mu = 3p + \frac{5}{2}$	E	$\bar{1}$			$\mu = 3p + \frac{5}{2}$	E_2	$\bar{1}$
D_{4d}	$E_1 \otimes e_2$	$\bar{\mu} = 4p + \frac{1}{2}$	E_1	$\bar{1}$	D_{6d}	$E_1 \otimes e_2$	$\bar{\mu} = 6p + \frac{1}{2}$	E_1	$\bar{1}$
		$\bar{\mu} = 4p + \frac{3}{2}$	E_3	$\bar{1}$			$\bar{\mu} = 6p + \frac{3}{2}$	E_3	$\bar{1}$
		$\bar{\mu} = 4p + \frac{5}{2}$	E_3	$\bar{2}$			$\bar{\mu} = 6p + \frac{5}{2}$	E_5	$\bar{1}$
		$\bar{\mu} = 4p + \frac{7}{2}$	E_1	$\bar{2}$			$\bar{\mu} = 6p + \frac{7}{2}$	E_5	$\bar{2}$
	$E_3 \otimes e_2$	$\mu = 4p + \frac{1}{2}$	E_3	$\bar{2}$			$\bar{\mu} = 6p + \frac{9}{2}$	E_3	$\bar{2}$
		$\mu = 4p + \frac{3}{2}$	E_1	$\bar{2}$			$\bar{\mu} = 6p + \frac{11}{2}$	E_1	$\bar{2}$
		$\mu = 4p + \frac{5}{2}$	E_1	$\bar{1}$		$E_2 \otimes e_4$	$\bar{\mu} = 3p + \frac{1}{2}$	E_2	$\bar{1}$
		$\mu = 4p + \frac{7}{2}$	E_3	$\bar{1}$			$\bar{\mu} = 3p + \frac{3}{2}$	B_1, B_2	
C_{5v}, D_5	$E_1 \otimes e_2$	$\bar{\mu} = 5p + \frac{1}{2}$	E_1	$\bar{1}$			$\bar{\mu} = 3p + \frac{5}{2}$	E_2	$\bar{2}$
		$\bar{\mu} = 5p + \frac{3}{2}$	E_2	$\bar{2}$		$E_4 \otimes e_4$	$\mu = 3p + \frac{1}{2}$	E_4	$\bar{2}$
		$\bar{\mu} = 5p + \frac{5}{2}$	A_1, A_2				$\mu = 3p + \frac{3}{2}$	A_1, A_2	
		$\bar{\mu} = 5p + \frac{7}{2}$	E_2	$\bar{1}$			$\mu = 3p + \frac{5}{2}$	E_4	$\bar{1}$
		$\bar{\mu} = 5p + \frac{9}{2}$	E_1	$\bar{2}$		$E_5 \otimes e_2$	$\mu = 6p + \frac{1}{2}$	E_5	$\bar{2}$
	$E_2 \otimes e_1$	$\mu = 5p + \frac{1}{2}$	E_2	$\bar{2}$			$\mu = 6p + \frac{3}{2}$	E_3	$\bar{2}$
		$\mu = 5p + \frac{3}{2}$	E_1	$\bar{2}$			$\mu = 6p + \frac{5}{2}$	E_1	$\bar{2}$
		$\mu = 5p + \frac{5}{2}$	A_1, A_2				$\mu = 6p + \frac{7}{2}$	E_1	$\bar{1}$
		$\mu = 5p + \frac{7}{2}$	E_1	$\bar{1}$			$\mu = 6p + \frac{9}{2}$	E_3	$\bar{1}$
		$\mu = 5p + \frac{9}{2}$	E_2	$\bar{1}$			$\mu = 6p + \frac{11}{2}$	E_5	$\bar{1}$
C_{6v}, D_6	$E_1 \otimes e_2$	$\bar{\mu} = 3p + \frac{1}{2}$	E_1	$\bar{1}$					
		$\bar{\mu} = 3p + \frac{3}{2}$	B_1, B_2						
		$\bar{\mu} = 3p + \frac{5}{2}$	E_1	$\bar{2}$					

associated with the algebraic chain

$$\begin{array}{ccccc} u(2)_e \oplus u(2)_v & \supset & su^*(2)_e \oplus su^*(2)_v & \supset & G \\ [10] \qquad [v\,0] & & \frac{1}{2} \qquad j = \frac{v}{2} & & \Gamma_{ev}\sigma_{ev} \end{array} \tag{49}$$

and are given in Appendix C. We note that this approach would also allow to take easily into account, within a polyad scheme, the coupling of the $e_{r'}$ mode with another one. However as in (I) we look for exact solutions of approximate models to which higher order interaction terms can next be added and for this the coupled basis is inappropriate.

For a given E_r electronic state and an arbitrary $e_{r'}$ mode the terms on the first two lines of equation (47) always exist but such is not the case for those on the third line. We thus established first a classification of JT systems for common point groups.

4.1 Classification of $\mathsf{E_r \otimes e_{r'}}$ systems

We first notice that for a given E_r symmetry we have in general at least one vibrational mode with the same symmetry type in the full vibrational representation. This means that quadratic terms involving that mode are allowed in the untransformed Hamiltonian expansion and that the operators of degree one with respect to the $u(2)_v$ algebra generators

$${}^{[1\,-1]}_{\quad s}\mathcal{V}^{(1,2\,E_k)} = {}^{[1\,-1]}_{\quad s}V^{(1,2\,E_k)}, \tag{50}$$

enter the expansion (47). This determines $E_r \otimes e_r$ systems which are classical ones only if $r = n/3$ ($r = 2n/3$ for D_{2pd} groups) (see Appendix B and Eq. (20)). This also includes the standard $E \otimes e$ cases (and $E_\alpha \otimes e_\beta$, $\beta = {}'$ or g) for $C_{3v}, D_3, D_{3h}, D_{3d}, O, O_h, T_d$.

We also have in general the possibility $r' = n/2 - r$ for C_{2p}, D_{2p} groups in $G_{(I)}$ and associated ones in $G_{(II)}$ since

$$E_{\frac{n}{2}-r} \times E_{\frac{n}{2}-r} = A_1 + A_2 + E_k.$$

For D_{2pd} groups the substitution $n/2 \rightarrow n$ must be made. We thus have a second class of JT systems $E_r \otimes e_{n/2-r}$ (n even) (resp. $E_r \otimes e_{n-r}$) for which the operator (50) exists but these are classical ones only if $r = n/6$ (resp. $r = n/3$) (see Appendix B and Eq. (20)).

It can be shown that for all other $E_r \otimes e_{r'}$ systems either there is no term

$$[E^{(1,2E_k)} \times {}^{[n_v\,-n_v]}_{\quad s}\mathcal{V}^{(j_v,\ell_v\,E_k)}]^{(A_1)} \tag{51}$$

at any order in the effective Hamiltonian expansion (47), or it requiers a minimum n_v value (hence one of j_v) greater

Table 2. $E_r \otimes e_{r'}$ JT systems for groups in $G_{(I)}$.

Group	$E_r \otimes e_{r'}$	E_k	JTL	Case type	j_{min}, ℓ_{min}	Group	$E_r \otimes e_{r'}$	E_k	JTL	Case type	j_{min}, ℓ_{min}
C_{3v}, D_3	$E \otimes e$	E	*	A	(1,2)	D_{6d}	$E_1 \otimes e_3$	E_2		X	-
O, T_d	$E \otimes e$	E	*	A	(1,2)	$r \neq 3$	$E_1 \otimes e_4$	E_2		X	-
D_{4d}	$E_1 \otimes e_1$	E_2		A	(1,2)		$E_1 \otimes e_5$	E_2		B	(1,2)
$r \neq 2$	$E_1 \otimes e_2$	E_2	*	X	-		$E_2 \otimes e_1$	E_4		C	(2,4)
	$E_1 \otimes e_3$	E_2		B	(1,2)		$E_2 \otimes e_2$	E_4		A	(1,2)
	$E_3 \otimes e_1$	E_2		B	(1,2)		$E_2 \otimes e_3$	E_4		X	-
	$E_3 \otimes e_2$	E_2	*	X	-		$E_2 \otimes e_4$	E_4	*	B	(1,2)
	$E_3 \otimes e_3$	E_2		A	(1,2)		$E_2 \otimes e_5$	E_4		D	(2,4)
C_{5v}, D_5	$E_1 \otimes e_1$	E_2		A	(1,2)		$E_4 \otimes e_1$	E_4		D	(2,4)
	$E_1 \otimes e_2$	E_2	*	D	(2,4)		$E_4 \otimes e_2$	E_4		B	(1,2)
	$E_2 \otimes e_1$	E_1	*	C	(2,4)		$E_4 \otimes e_3$	E_4		X	-
	$E_2 \otimes e_2$	E_1		A	(1,2)		$E_4 \otimes e_4$	E_4	*	A	(1,2)
C_{6v}, D_6	$E_1 \otimes e_1$	E_2		A	(1,2)		$E_4 \otimes e_5$	E_4		C	(2,4)
	$E_1 \otimes e_2$	E_2	*	B	(1,2)		$E_5 \otimes e_1$	E_2		B	(1,2)
	$E_2 \otimes e_1$	E_2		B	(1,2)		$E_5 \otimes e_2$	E_2	*	X	-
	$E_2 \otimes e_2$	E_2	*	A	(1,2)		$E_5 \otimes e_3$	E_2		X	-
D_{6d}	$E_1 \otimes e_1$	E_2		A	(1,2)		$E_5 \otimes e_4$	E_2		X	-
$r \neq 3$	$E_1 \otimes e_2$	E_2	*	X	-		$E_5 \otimes e_5$	E_2		A	(1,2)

than one. These various possible cases are summarized in the first columns of Table 2 (the $*$ indicate the active coordinates).

- $E_r \otimes e_r$ cases.

We first remind that the expressions of the symmetry adapted $su(2)$ generators based on an E symmetry type differ according as we deal with an (ii) or (iii) case (Eq. (3), Appendix A). For an $E_r \otimes e_r$ system as the electronic and vibrational E symmetries are the same we have $\eta\eta' = -\mu(2)\mu'(2) = 1$ and the interaction operator of lowest degree in elementary operators takes the form

$$\begin{aligned}[E^{(1,2E_k)} \times {}^{[1\,-1]}_{\quad s}V^{(1,2\,E_k)}]^{(A_1)} &= (S_x J_x + S_y J_y) \\ &= \frac{1}{2}(S_+ J_- + S_- J_+)\end{aligned}$$

where we introduced the ladder operators $S_\pm$ and $J_\pm$ of $su(2)_e$ and $su(2)_v$ respectively. As a consequence a zeroth-order model

$$\begin{aligned}\widetilde{H}^0_{vibr} = {}& {}_s\tilde{t}^{A_1 A_1 (A_1)}_{\{0\}\{0\}} I_v + {}_s\tilde{t}^{0,0 A_1 (A_1)}_{\{1\}\{1\}} {}^{[1\,-1]}_{\quad s}\mathcal{V}^{(0,0\,A_1)} \\ &+ {}_s\tilde{t}^{1,0 A_2 (A_2)}_{\{1\}\{1\}} [E^{(1,0A_2)} \times {}^{[1\,-1]}_{\quad s}V^{(1,0\,A_2)}]^{(A_1)} \\ &+ {}_s\tilde{t}^{1,2E_k (E_k)}_{\{1\}\{1\}} [E^{(1,2E_k)} \times {}^{[1\,-1]}_{\quad s}V^{(1,2\,E_k)}]^{(A_1)}, \quad (52)\end{aligned}$$

is given, omitting temporarily the constant term, by:

$$^{+}\widetilde{H}^0_{vibr}/\hbar = \tilde{\omega}_s(N_s+1) + \tilde{\lambda}_z S_z J_z + \frac{\tilde{\lambda}_x}{2}(S_+ J_- + S_- J_+). \quad (53)$$

Systems with $\widetilde{H}^0_{vibr}$ of the form (53) will be referred to as A-type cases in the following.

- $E_r \otimes e_{n/2-r}$ ($E_r \otimes e_{n-r}$).

This time the electronic and vibrational operators are necessarily of different species ($\eta\eta' = -\mu(2)\mu'(2) = -1$) and we have

$$\begin{aligned}[E^{(1,2E_k)} \times {}^{[1\,-1]}_{\quad s}V^{(1,2\,E_k)}]^{(A_1)} &= (S_x J_x - S_y J_y) \\ &= \frac{1}{2}(S_+ J_+ + S_- J_-),\end{aligned}$$

hence for $\widetilde{H}^0_{vibr}$ (52) we obtain

$$^{-}\widetilde{H}^0_{vibr}/\hbar = \tilde{\omega}_s(N_s+1) + \tilde{\lambda}_z S_z J_z + \frac{\tilde{\lambda}_x}{2}(S_+ J_+ + S_- J_-). \quad (54)$$

This will be referred to as B-type case in the following.

- Other $E_r \otimes e_{r'}$ cases.

For the common point groups we see from Table 2 that the first allowed vibronic interaction term of type (51) is characterized by $(j_v, \ell_v) = (2,4)$. Thus in the zeroth order model (52) the last term is replaced by

$${}_s\tilde{t}^{2,4E_k (E_k)}_{\{2\}\{2\}} [E^{(1,2E_k)} \times {}^{[2\,-2]}_{\quad s}V^{(2,4\,E_k)}]^{(A_1)},$$

with

$$\begin{aligned}{}^{[2\,-2]}_{\quad s}V^{(2,4\,E_k)}_{1} &= (J_-^2 + J_+^2)/2\sqrt{2}, \\ {}^{[2\,-2]}_{\quad s}V^{(2,4\,E_k)}_{2} &= \mu'(4)(J_-^2 - J_+^2)/2\sqrt{2}.\end{aligned}$$

In fact within the same order of approximation we should include terms involving the vibrational operators

$${}^{[2\,-2]}_{\quad s}\mathcal{V}^{(0,0\,A_1)}, \quad {}^{[2\,-2]}_{\quad s}\mathcal{V}^{(2,0\,A_1)}, \quad {}^{[2\,-2]}_{\quad s}\mathcal{V}^{(1,0\,A_2)}$$

which represent anharmonicity corrections to those included in $\widetilde{H}^0_{vibr}$. We postpone their introduction to Section 4.5 where we consider the additional terms which may be taken into account without breaking the exact solvability of the various zeroth-order models.

Depending on the r, r' values it appears that we have again two different expressions for $\widetilde{H}^0_{vibr}$.
When $\mu(2)\mu'(4) = -1$

$$^{+}\widetilde{H}^0_{vibr}/\hbar = \tilde{\omega}_s(N_s+1)+\tilde{\lambda}_z S_z J_z+\frac{\tilde{\delta}}{2}(S_+J_-^2+S_-J_+^2), \quad (55)$$

and when $\mu(2)\mu'(4) = 1$

$$^{-}\widetilde{H}^0_{vibr}/\hbar = \tilde{\omega}_s(N_s+1)+\tilde{\lambda}_z S_z J_z+\frac{\tilde{\delta}}{2}(S_+J_+^2+S_-J_-^2), \quad (56)$$

which will be denoted case C and D respectively.

Finally the X-type cases for which no operator (51) can be built simply give

$$\widetilde{H}^0_{vibr} = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(N_s + 1) + \hbar\tilde{\lambda}_z S_z J_z. \quad (57)$$

The lack of any vibronic interaction term with E_k symmetry type is explained by the analysis of the powers of $E_{r'}$ *irreps* [22]. It covers two different physical situations. One in which the untransformed vibronic Hamiltonian contains only odd powers in the (active) coordinate $_sQ^{(E_{r'})}$, the other in which no power in this coordinate can be of E_k symmetry type. In both cases vibronic terms involving the $^{[1\,-1]}E^{(1,2E_k)}$ electronic operators can only appear in a multimode case.

4.2 Eigenvalues and eigenstates for A and B cases

For both problems it appears that the Hamiltonians $^{\pm}\widetilde{H}^0_{vibr}$ (53, 54) have exactly the same forms as in the $E\otimes e$ cases studied in Section 7.4.2 of (I) and denoted there cases *a)* and *b)* respectively. So, they can be diagonalized through the same unitary transformation U expressed in terms of two conserved quantities [26]

$$\begin{aligned} \varDelta &= S_z + J_z \;; & \mathcal{F} &= (S_+J_- + S_-J_+)^2 \quad \text{for case A} \\ \overline{\varDelta} &= -S_z + J_z \;; & \overline{\mathcal{F}} &= (S_+J_+ + S_-J_-)^2 \quad \text{for case B.} \end{aligned} \quad (58)$$

The eigenvalues as well as the unsymmetrized eigenstates have identical expressions which we recall below:

$$^{\pm}E_{jm\pm} = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) \mp \hbar\frac{\tilde{\lambda}_z}{4} + \hbar\tilde{\lambda}_x\varOmega_\pm(j,m), \quad (59)$$

with

$$\begin{aligned} \varOmega_\pm(j,m) &= \pm\varOmega(j,m) \\ &= \pm\frac{1}{2}[(j-m)(j+m+1) + \tilde{\delta}_z^2\left(m+\frac{1}{2}\right)^2]^{1/2} \\ &= \pm\frac{1}{4}[(v\mp\ell)(v\pm\ell+2) + \tilde{\delta}_z^2(\pm\ell+1)^2]^{1/2}, \end{aligned} \quad (60)$$

and where $\tilde{\delta}_z = \tilde{\lambda}_z/\tilde{\lambda}_x$ and $j = v/2$, $\ell = 2|m|$. In terms of the basis states

$$\begin{aligned} |\pm\rangle\rangle|[v\,0]j\,m\rangle\rangle &\equiv |[1\,0]\frac{1}{2}1E_r\bar{\sigma}\rangle\rangle|[v\,0]j\,m\rangle\rangle \\ &\equiv |[1\,0]\frac{1}{2}m_e\rangle\rangle|[v\,0]j\,m\rangle\rangle, \end{aligned} \quad (61)$$

where $|\pm\rangle\rangle$ are the E_r electronic states in orientation II and $|[v\,0]j\,m\rangle\rangle$ the standard $su(2)_v$ covariant states for the $e_{r'}$ mode, the unsymmetrized vibronic eigenstates for A-type systems read ($m : j-1, \cdots 1/2$ or 0)

$$\begin{aligned} ^{+}\widetilde{\varPsi}^{(1)}_{jm-} &= U^{-1}|+\rangle\rangle|[v\,0]j\,m\rangle\rangle \\ &= \cos[\theta(j,m)]|+\rangle\rangle|[v\,0]j\,m\rangle\rangle \\ &\quad - \sin[\theta(j,m)]|-\rangle\rangle|[v\,0]j\,m+1\rangle\rangle \\ ^{+}\widetilde{\varPsi}^{(1)}_{jm+} &= U^{-1}|-\rangle\rangle|[v\,0]j\,m+1\rangle\rangle \\ &= \cos[\theta(j,m)]|-\rangle\rangle|[v\,0]j\,m+1\rangle\rangle \\ &\quad + \sin[\theta(j,m)]|+\rangle\rangle|[v\,0]j\,m\rangle\rangle \end{aligned} \quad (62)$$

$$\begin{aligned} ^{+}\widetilde{\varPsi}^{(2)}_{jm-} &= U^{-1}|+\rangle\rangle|[v\,0]j\;-m-1\rangle\rangle \\ &= \sin[\theta(j,m)]|+\rangle\rangle|[v\,0]j\;-m-1\rangle\rangle \\ &\quad - \cos[\theta(j,m)]|-\rangle\rangle|[v\,0]j\;-m\rangle\rangle \\ ^{+}\widetilde{\varPsi}^{(2)}_{jm+} &= U^{-1}|-\rangle\rangle|[v\,0]j\;-m\rangle\rangle \\ &= \sin[\theta(j,m)]|-\rangle\rangle|[v\,0]j\;-m\rangle\rangle \\ &\quad + \cos[\theta(j,m)]|+\rangle\rangle|[v\,0]j\;-m-1\rangle\rangle \end{aligned} \quad (63)$$

with

$$\begin{aligned} \cos[\theta(j,m)] &= \left[\frac{\varOmega(j,m) - \tilde{\delta}_z(m+1/2)/2}{2\varOmega(j,m)}\right]^{1/2} \\ \sin[\theta(j,m)] &= \left[\frac{\varOmega(j,m) + \tilde{\delta}_z(m+1/2)/2}{2\varOmega(j,m)}\right]^{1/2} \end{aligned} \quad (64)$$

and

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

Those for B-type systems $^{-}\widetilde{\varPsi}^{(i)}_{jm\pm}$ ($i = 1, 2$) can be deduced from the previous ones with the substitutions

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

The uncoupled states are still

$$\begin{aligned} |+\rangle\rangle|[v\,0]j\,j\rangle\rangle &\equiv |[1\,0]\frac{1}{2}1E_r\bar{1}\rangle\rangle|[v\,0]j\,j\rangle\rangle, \\ |-\rangle\rangle|[v\,0]j\;-j\rangle\rangle &\equiv |[1\,0]\frac{1}{2}1E_r\bar{2}\rangle\rangle|[v\,0]j\;-j\rangle\rangle, \end{aligned}$$

for $^{+}\widetilde{H}^0_{vibr}$ and

$$\begin{aligned} |-\rangle\rangle|[v\,0]j\,j\rangle\rangle &\equiv |[1\,0]\frac{1}{2}1E_r\bar{2}\rangle\rangle|[v\,0]j\,j\rangle\rangle, \\ |+\rangle\rangle|[v\,0]j\;-j\rangle\rangle &\equiv |[1\,0]\frac{1}{2}1E_r\bar{1}\rangle\rangle|[v\,0]j\;-j\rangle\rangle, \end{aligned}$$

for $^{-}\widetilde{H}^0_{vibr}$, with respective eigenvalues

$$^{\pm}E_j = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) \pm \hbar\frac{\tilde{\lambda}_z}{2}j. \quad (65)$$

Table 3. Transformation laws for A type eigenstates.

$P_X {}^{+}\widetilde{\Psi}^{(1)}_{jm\pm} = e^{ir(\ell+1)\psi}\ {}^{+}\widetilde{\Psi}^{(1)}_{jm\pm}$	$P_X {}^{+}\widetilde{\Psi}^{(2)}_{jm\pm} = e^{-ir(\ell+1)\psi}\ {}^{+}\widetilde{\Psi}^{(2)}_{jm\pm}$
$P_Y {}^{+}\widetilde{\Psi}^{(1)}_{jm+} = (-1)^{2j+1}\ {}^{+}\widetilde{\Psi}^{(2)}_{jm+}$	$P_Y {}^{+}\widetilde{\Psi}^{(2)}_{jm+} = (-1)^{2j+1}\ {}^{+}\widetilde{\Psi}^{(1)}_{jm+}$
$P_Y {}^{+}\widetilde{\Psi}^{(1)}_{jm-} = (-1)^{2j}\ {}^{+}\widetilde{\Psi}^{(2)}_{jm-}$	$P_Y {}^{+}\widetilde{\Psi}^{(2)}_{jm-} = (-1)^{2j}\ {}^{+}\widetilde{\Psi}^{(1)}_{jm-}$
$\mathcal{K}^{+}\widetilde{\Psi}^{(1)}_{jm+} = {}^{+}\widetilde{\Psi}^{(2)}_{jm+}$	$\mathcal{K}^{+}\widetilde{\Psi}^{(2)}_{jm+} = {}^{+}\widetilde{\Psi}^{(1)}_{jm+}$
$\mathcal{K}^{+}\widetilde{\Psi}^{(1)}_{jm-} = -{}^{+}\widetilde{\Psi}^{(2)}_{jm-}$	$\mathcal{K}^{+}\widetilde{\Psi}^{(2)}_{jm-} = -{}^{+}\widetilde{\Psi}^{(1)}_{jm-}$

Table 4. Transformation laws for B type eigenstates.

$P_X {}^{-}\widetilde{\Psi}^{(1)}_{jm\pm} = e^{i\ell\pi} e^{-ir(\ell+1)\psi}\ {}^{-}\widetilde{\Psi}^{(1)}_{jm\pm}$	$P_X {}^{-}\widetilde{\Psi}^{(2)}_{jm\pm} = e^{i\ell\pi} e^{ir(\ell+1)\psi}\ {}^{-}\widetilde{\Psi}^{(2)}_{jm\pm}$
$P_Y {}^{-}\widetilde{\Psi}^{(1)}_{jm+} = (-1)^{2j+1}\ {}^{-}\widetilde{\Psi}^{(2)}_{jm+}$	$P_Y {}^{-}\widetilde{\Psi}^{(2)}_{jm+} = (-1)^{2j+1}\ {}^{-}\widetilde{\Psi}^{(1)}_{jm+}$
$P_Y {}^{-}\widetilde{\Psi}^{(1)}_{jm-} = (-1)^{2j}\ {}^{-}\widetilde{\Psi}^{(2)}_{jm-}$	$P_Y {}^{-}\widetilde{\Psi}^{(2)}_{jm-} = (-1)^{2j}\ {}^{-}\widetilde{\Psi}^{(1)}_{jm-}$
$\mathcal{K}^{-}\widetilde{\Psi}^{(1)}_{jm+} = {}^{-}\widetilde{\Psi}^{(2)}_{jm+}$	$\mathcal{K}^{-}\widetilde{\Psi}^{(2)}_{jm+} = {}^{-}\widetilde{\Psi}^{(1)}_{jm+}$
$\mathcal{K}^{-}\widetilde{\Psi}^{(1)}_{jm-} = -{}^{-}\widetilde{\Psi}^{(2)}_{jm-}$	$\mathcal{K}^{-}\widetilde{\Psi}^{(2)}_{jm-} = -{}^{-}\widetilde{\Psi}^{(1)}_{jm-}$

We note that, assuming $\tilde{\lambda}_z \gg \tilde{\lambda}_x$, we obtain in first approximation $\cos[\theta(j,m)] \simeq 0$, $\sin[\theta(j,m)] \simeq 1$ (Eqs. (60, 64)). The eigenvalues (59) for all pair of states

$$|\pm\rangle\rangle|[v\,0]j\ \pm m\rangle\rangle, \tag{66}$$

may be written ${}^{\pm}E_{jm\pm} \simeq E^{(0)}_{vibr} + \Delta^{\pm}E_{vibr}$ where

$$E^{(0)}_{vibr} = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar\frac{\tilde{\lambda}_z}{2}m, \tag{67}$$

is the usual expression [13] for the energies in the weak coupling limit (see also Sect. 6) and in first order

$$\begin{aligned}
\Delta^{+}E_{vibr} &= \frac{\hbar}{4}\frac{\tilde{\lambda}_x^2}{\tilde{\lambda}_z}\frac{(j-m)(j+m+1)}{(m+1/2)} + \cdots \quad m \neq -1/2\\
\Delta^{-}E_{vibr} &= \frac{\hbar}{4}\frac{\tilde{\lambda}_x^2}{\tilde{\lambda}_z}\frac{(j-m+1)(j+m)}{(m-1/2)} + \cdots \quad m \neq 1/2.
\end{aligned}$$

We give in Tables 3 and 4 the general relations which allow to build, for arbitrary systems of A or B-type, symmetrized vibronic eigenstates for groups in $G_{(I)}$. When dealing with groups in $G_{(II)}$ with $E_{r\alpha}$ electronic states and $e_{r'\beta}$ modes we have for the third Z generator the additional relation:

$$P_Z {}^{\pm}\widetilde{\Psi}^{(i)}_{jm\pm} = (-1)^{\alpha}[(-1)^{\beta}]^{2j}\ {}^{\pm}\widetilde{\Psi}^{(i)}_{jm\pm} \tag{68}$$

where ($\tau = \alpha$ or β) $(-1)^{\tau} = +1$ (resp.$(-1)^{\tau} = -1$) for $'$ or g (resp. $''$ or u) *irreps*. As an illustration these functions are detailed in Appendix D for C_{3v}, D_3, D_{3h}, D_{3d}, O, O_h, T_d. Moreover we underline the special case $m = -1/2$ for which we have two nondegenerate eigenvalues

$$\begin{aligned}
{}^{+}E_{j-\frac{1}{2}\pm} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) - \hbar\frac{\tilde{\lambda}_z}{4} \pm \hbar\frac{\tilde{\lambda}_x}{4}(2j+1)\\
{}^{-}E_{j-\frac{1}{2}\pm} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar\frac{\tilde{\lambda}_z}{4} \pm \hbar\frac{\tilde{\lambda}_x}{4}(2j+1)
\end{aligned} \tag{69}$$

with corresponding symmetry adapted eigenstates

$$\begin{aligned}
&|[1\,0]\tfrac{1}{2}1E_r, [v\,0]j; \Omega_+, A_1\rangle\rangle = \\
&\qquad i^{v+1}[|+\rangle\rangle|[v\,0]j\ -1/2\rangle\rangle + |-\rangle\rangle|[v\,0]j\,1/2\rangle\rangle]/\sqrt{2}\\
&|[1\,0]\tfrac{1}{2}1E_r, [v\,0]j; \Omega_-, A_2\rangle\rangle = \\
&\qquad i^{v}[|+\rangle\rangle|[v\,0]j\ -1/2\rangle\rangle - |-\rangle\rangle|[v\,0]j\,1/2\rangle\rangle]/\sqrt{2},
\end{aligned} \tag{70}$$

for ${}^{+}\widetilde{H}^{0}_{vibr}$ and

$$\begin{aligned}
&|[1\,0]\tfrac{1}{2}1E_r, [v\,0]j; \Omega_+, B_1\rangle\rangle = \\
&\qquad i^{v+1}[|-\rangle\rangle|[v\,0]j\ -1/2\rangle\rangle + |+\rangle\rangle|[v\,0]j\,1/2\rangle\rangle]/\sqrt{2}\\
&|[1\,0]\tfrac{1}{2}1E_r, [v\,0]j; \Omega_-, B_2\rangle\rangle = \\
&\qquad i^{v}[|-\rangle\rangle|[v\,0]j\ -1/2\rangle\rangle - |+\rangle\rangle|[v\,0]j\,1/2\rangle\rangle]/\sqrt{2},
\end{aligned} \tag{71}$$

for ${}^{-}\widetilde{H}^{0}_{vibr}$. For groups in $G_{(II)}$ one must add a τ label in equations (70, 71). We will show in Section 6 that these results allow to recover in a straightforward manner that the ground state may be of A_i or B_i symmetry for these JT systems.

4.3 Eigenvalues and eigenstates for C and D cases

The method used to solve the eigenvalue equation for ${}^{\pm}\widetilde{H}^{0}_{vibr}$ (55, 56) is similar to that used for A and B cases and is detailed in [26]. In both cases the Hamiltonian is written as a linear combination in the generators of an $su(2)(P)$ algebra and as a function of an operator Δ (or $\overline{\Delta}$) which commutes with the $su(2)$ generators and ${}^{\pm}\widetilde{H}^{0}_{vibr}$. For case C the Δ operator is given by

$$\Delta = -E^{(1,0A_2)} - 2^{[1\,\underset{s}{-1}]}\mathcal{V}^{(1,0\,A_2)} = J_z + 2S_z \tag{72}$$

and for the $su(2)(P)$ algebra, isomorphic to that of a spin 1/2, we have

$$P_+ = \frac{1}{\sqrt{\mathcal{F}}}S_+J_-^2\ ,\ P_- = \frac{1}{\sqrt{\mathcal{F}}}S_-J_+^2\ ,\ P_z = S_z, \tag{73}$$

where the $\mathcal{F}$ operator is expressed as

$$\begin{aligned}\mathcal{F} = (S_+J_-^2 + S_-J_+^2)^2 = \\ (\frac{1}{2} + S_z)[J^2 - (J_z+1)J_z][J^2 - (J_z+2)(J_z+1)] \\ + (\frac{1}{2} - S_z)[J^2 - (J_z-1)J_z][J^2 - (J_z-1)(J_z-2)].\end{aligned} \tag{74}$$

The vibronic states ($m = -j, -j+1 \cdots j-2$)

$$|+\rangle\rangle|[v\,0]j\,m\rangle\rangle \quad , |-\rangle\rangle|[v\,0]j\,m+2\rangle\rangle \tag{75a}$$
$$|-\rangle\rangle|[v\,0]j\ -m\rangle\rangle \ , |+\rangle\rangle|[v\,0]j\ -m-2\rangle\rangle \tag{75b}$$

are associated with the eigenvalues $\Delta(m) = -(m+1)$ for (75a) and $\Delta(m) = (m+1)$ for (75b) of Δ and both with the eigenvalue

$$f(j,m) = \frac{(j-m)!(j+m+2)!}{(j+m)!(j-m-2)!} \tag{76}$$

of $\mathcal{F}$. We can then write ${}^+\widetilde{H}^0_{vibr}$ (55) as

$$\begin{aligned}{}^+\widetilde{H}^0_{vibr} = \hbar\tilde{\omega}_s(N_s+1) - \frac{\tilde{\lambda}_z}{2} \\ + \hbar\tilde{\delta}\left\{\frac{1}{2}\sqrt{\mathcal{F}}(P_+ + P_-) + \tilde{\delta}_z\Delta P_z\right\},\end{aligned} \tag{77}$$

with $\tilde{\delta}_z = \tilde{\lambda}_z/\tilde{\delta}$. A unitary transformation of the $su(2)(P)$ algebra leads to [26,27]

$$U^+\widetilde{H}^0_{vibr}U^{-1} = \hbar\tilde{\omega}_s(N_s+1) - \hbar\frac{\tilde{\lambda}_z}{2} + \hbar 2\tilde{\delta}\Omega(\mathcal{F},\Delta)S_z, \tag{78}$$

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

$$\Omega(\mathcal{F},\Delta) = \frac{1}{2}[\mathcal{F} + \tilde{\delta}_z^2\Delta^2]^{1/2}. \tag{79}$$

Within basis (75) we obtain the doubly degenerate eigenvalues (except for $m = -1$)

$${}^+E_{jm\pm} = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) - \hbar\frac{\tilde{\lambda}_z}{2} + \hbar\tilde{\delta}\Omega_\pm(j,m), \tag{80}$$

where $\tilde{\lambda}_0$ is associated with the first term in equation (52) and with

$$\begin{aligned}\Omega_\pm(j,m) &= \pm\Omega(j,m) \\ &= \pm\frac{1}{2}\left[\frac{(j-m)!(j+m+2)!}{(j+m)!(j-m-2)!} + \tilde{\delta}_z^2(m+1)^2\right]^{1/2}\end{aligned} \tag{81}$$

which can also be expressed in terms of the quantum numbers $v = 2j$ and $\ell = 2|m|$. The U^{-1} operator is given by

$$\begin{aligned}U^{-1} &= (I + k^\dagger P_+)\exp[k_zP_z](I - kP_-) \\ &= (I - kP_-)\exp[-k_zP_z](I + k^\dagger P_+),\end{aligned} \tag{82}$$

where

$$\begin{aligned}k &= -\frac{2\Omega(\mathcal{F},\Delta) - \tilde{\delta}_z\Delta}{\sqrt{\mathcal{F}}} = -\left[\frac{\Omega(\mathcal{F},\Delta) - \tilde{\delta}_z\Delta/2}{\Omega(\mathcal{F},\Delta) + \tilde{\delta}_z\Delta/2}\right]^{1/2} \\ k_z &= \ln\left[\frac{2\Omega(\mathcal{F},\Delta)}{\Omega(\mathcal{F},\Delta) + \tilde{\delta}_z\Delta/2}\right].\end{aligned} \tag{83}$$

Unsymmetrized eigenstates of ${}^+\widetilde{H}^0_{vibr}$ (55) are obtained with U^{-1} acting on the states (75) (m: $j-2, j-3 \cdots 1/2$ or 0):

$$\begin{aligned}{}^+\widetilde{\Psi}^{(1)}_{jm-} &= U^{-1}|+\rangle\rangle|[v\,0]j\,m\rangle\rangle \\ &= \cos[\theta(j,m)]|+\rangle\rangle|[v\,0]j\,m\rangle\rangle \\ &\quad - \sin[\theta(j,m)]|-\rangle\rangle|[v\,0]j\,m+2\rangle\rangle \\ {}^+\widetilde{\Psi}^{(1)}_{jm+} &= U^{-1}|-\rangle\rangle|[v\,0]j\,m+2\rangle\rangle \\ &= \cos[\theta(j,m)]|-\rangle\rangle|[v\,0]j\,m+2\rangle\rangle \\ &\quad + \sin[\theta(j,m)]|+\rangle\rangle|[v\,0]j\,m\rangle\rangle\end{aligned} \tag{84}$$

$$\begin{aligned}{}^+\widetilde{\Psi}^{(2)}_{jm-} &= U^{-1}|+\rangle\rangle|[v\,0]j\ -m-2\rangle\rangle \\ &= \sin[\theta(j,m)]|+\rangle\rangle|[v\,0]j\ -m-2\rangle\rangle \\ &\quad - \cos[\theta(j,m)]|-\rangle\rangle|[v\,0]j\ -m\rangle\rangle \\ {}^+\widetilde{\Psi}^{(2)}_{jm+} &= U^{-1}|-\rangle\rangle|[v\,0]j\ -m\rangle\rangle \\ &= \sin[\theta(j,m)]|-\rangle\rangle|[v\,0]j\ -m\rangle\rangle \\ &\quad + \cos[\theta(j,m)]|+\rangle\rangle|[v\,0]j\ -m-2\rangle\rangle\end{aligned} \tag{85}$$

with

$$\begin{aligned}\cos[\theta(j,m)] &= \left[\frac{\Omega(j,m) - \tilde{\delta}_z(m+1)/2}{2\Omega(j,m)}\right]^{1/2} \\ \sin[\theta(j,m)] &= \left[\frac{\Omega(j,m) + \tilde{\delta}_z(m+1)/2}{2\Omega(j,m)}\right]^{1/2}\end{aligned} \tag{86}$$

and $\cos[\theta(j,m)] = \sin[\theta(j,-m-2)]$.

Special cases

- For $m = -1$ the states in (75) reduce to two and we have one-fold degenerate energy levels

$${}^+E_{j-1\pm} = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) - \hbar\frac{\tilde{\lambda}_z}{2} \pm \hbar\frac{\tilde{\delta}}{2}j(j+1), \tag{87}$$

with the corresponding eigenstates

$$\begin{aligned}{}^+\widetilde{\Psi}_{j-1+} &= \frac{1}{\sqrt{2}}[\,|+\rangle\rangle|[v\,0]j\ -1\rangle\rangle + |-\rangle\rangle|[v\,0]j\,1\rangle\rangle] \\ {}^+\widetilde{\Psi}_{j-1-} &= \frac{1}{\sqrt{2}}[\,|+\rangle\rangle|[v\,0]j\ -1\rangle\rangle - |-\rangle\rangle|[v\,0]j\,1\rangle\rangle].\end{aligned} \tag{88}$$

- There are two sets of uncoupled states, associated with the zero eigenvalues of the $\mathcal{F}$ function (74):

$$\begin{aligned}&|+\rangle\rangle|[v\,0]j\,j\rangle\rangle \ , \ |-\rangle\rangle|[v\,0]j\ -j\rangle\rangle \\ &|+\rangle\rangle|[v\,0]j\,j-1\rangle\rangle \ , \ |-\rangle\rangle|[v\,0]j\ -j+1\rangle\rangle.\end{aligned} \tag{89}$$

These are eigenstates of ${}^{+}\widetilde{H}^{(0)}_{vibr}$ with eigenvalues respectively given by

$$\begin{aligned}{}^{+}E_{jj} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar\frac{\tilde{\lambda}_z}{2}j\\ {}^{+}E_{jj-1} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar\frac{\tilde{\lambda}_z}{2}(j-1). \qquad (90)\end{aligned}$$

Case D is treated along the same lines through an $su(2)(P')$ algebra realized as

$$P'_+ = \frac{1}{\sqrt{\overline{\mathcal{F}}}}S_+J_+^2\ ,\ P'_- = \frac{1}{\sqrt{\overline{\mathcal{F}}}}S_-J_-^2\ ,\ P'_z = S_z \qquad (91)$$

where the $\overline{\mathcal{F}}$ invariant operator

$$\overline{\mathcal{F}} = (S_+J_+^2 + S_-J_-^2)^2 \qquad (92)$$

can be obtained from $\mathcal{F}$ (74) with the interchange $1/2 + S_z \leftrightarrow 1/2 - S_z$. The degenerate states (75) are replaced by ($m = -j, -j+1 \cdots j-2$)

$$\begin{aligned}&|-\rangle\rangle|[v\,0]j\,m\rangle\rangle \quad , \ |+\rangle\rangle|[v\,0]j\,m+2\rangle\rangle \qquad (93a)\\ &|+\rangle\rangle|[v\,0]j\ -m\rangle\rangle\ , \ |-\rangle\rangle|[v\,0]j\ -m-2\rangle\rangle. \qquad (93b)\end{aligned}$$

They are associated with the eigenvalue $\bar{f}(j,m) = f(j,m)$ (76) of $\overline{\mathcal{F}}$ and $\overline{\Delta}(m)$ of $\overline{\Delta}$ given by

$$\overline{\Delta} = -{}^{[1\,-1]}E^{(1,0A_2)} + 2^{[1\,\underset{s}{-}1]}\mathcal{V}^{(1,0\,A_2)} = J_z - 2S_z, \quad (94)$$

with $\overline{\Delta}(m) = -(m+1)$ for (93a) and $\overline{\Delta}(m) = (m+1)$ for (93b). So we have for ${}^{-}\widetilde{H}^0_{vibr}$ (56)

$$\begin{aligned}{}^{-}\widetilde{H}^0_{vibr} = \hbar\tilde{\omega}_s(N_s+1) + \hbar\frac{\tilde{\lambda}_z}{2}\\ + \hbar\tilde{\delta}\left\{\frac{1}{2}\sqrt{\overline{\mathcal{F}}}(P'_+ + P'_-) + \tilde{\delta}_z\overline{\Delta}P'_z\right\}, \qquad (95)\end{aligned}$$

where $\tilde{\delta}_z = \tilde{\lambda}_z/\tilde{\delta}$. It can be diagonalized through a unitary transformation U' of $su(2)(P')$:

$$U'{}^{-}\widetilde{H}^0_{vibr}U'^{-1} = \hbar\tilde{\omega}_s(N_s+1) + \hbar\frac{\tilde{\lambda}_z}{2} + \hbar 2\tilde{\delta}\Omega(\overline{\mathcal{F}}, \overline{\Delta})S_z \quad (96)$$

where the operator $\Omega(\overline{\mathcal{F}}, \overline{\Delta})$ is given by (79) with the substitutions $\mathcal{F} \to \overline{\mathcal{F}}$ and $\Delta \to \overline{\Delta}$. Within the basis (93) we obtain the eigenvalues

$${}^{-}E_{jm\pm} = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar\frac{\tilde{\lambda}_z}{2} + \hbar\tilde{\delta}\Omega_\pm(j,m), \quad (97)$$

where $\Omega_\pm(j,m)$ is given by (81). The corresponding unsymmetrized eigenstates of ${}^{-}\widetilde{H}^0_{vibr}$ (56) are obtained with U'^{-1} acting on the states (93), U'^{-1} being deduced from U^{-1} in equations (82, 83) with the substitutions $P_\pm \to P'_\pm$, $P_z \to P'_z$, $\mathcal{F} \to \overline{\mathcal{F}}$ and $\Delta \to \overline{\Delta}$. This leads to states ${}^{-}\widetilde{\Psi}^{(i)}_{jm\pm}$ $(i = 1,2)$ which can be deduced from those ${}^{+}\widetilde{\Psi}^{(i)}_{jm\pm}$ (84, 85) through the substitutions

$$\begin{aligned}&|\pm\rangle\rangle|[v\,0]j\ \pm m\rangle\rangle \to |\pm\rangle\rangle|[v\,0]j\ \pm(m+2)\rangle\rangle,\\ &|\mp\rangle\rangle|[v\,0]j\ \pm(m+2)\rangle\rangle \to |\mp\rangle\rangle|[v\,0]j\ \pm m\rangle\rangle. \qquad (98)\end{aligned}$$

$\cos[\theta(j,m)]$ and $\sin[\theta(j,m)]$ are still given by (86). The same rules apply for the special case $m = -1$ with equation (87) replaced by

$${}^{-}E_{j-1\pm} = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar\frac{\tilde{\lambda}_z}{2} \pm \hbar\frac{\tilde{\delta}}{2}j(j+1). \quad (99)$$

The uncoupled states are now

$$\begin{aligned}&|-\rangle\rangle|[v\,0]j\,j\rangle\rangle,\ |+\rangle\rangle|[v\,0]j\ -j\rangle\rangle,\\ &|-\rangle\rangle|[v\,0]j\,j-1\rangle\rangle,\ |+\rangle\rangle|[v\,0]j\ -j+1\rangle\rangle, \qquad (100)\end{aligned}$$

with associated eigenvalues

$$\begin{aligned}{}^{-}E_{jj} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) - \hbar\frac{\tilde{\lambda}_z}{2}j,\\ {}^{-}E_{jj-1} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) - \hbar\frac{\tilde{\lambda}_z}{2}(j-1). \qquad (101)\end{aligned}$$

As in A and B cases, on the assumption that $\tilde{\lambda}_z \gg \tilde{\delta}$, we obtain for the states (66) the energies (80, 97) in the form ${}^{\pm}E_{jm\pm} \simeq E^{(0)}_{vibr} + \Delta^{\pm}E_{vibr}$, with $E^{(0)}_{vibr}$ as given by (67) and for cases C and D respectively

$$\Delta^{+}E_{vibr} = \frac{\hbar}{4}\frac{\tilde{\delta}^2}{\tilde{\lambda}_z}\frac{f(j,m)}{(m+1)} + \cdots \quad m \neq -1$$

$$\Delta^{-}E_{vibr} = \frac{\hbar}{4}\frac{\tilde{\delta}^2}{\tilde{\lambda}_z}\frac{f(j,-m)}{(m-1)} + \cdots \quad m \neq 1$$

with $f(j,m)$ as defined in (76).

The transformation laws of the eigenstates of ${}^{\pm}\widetilde{H}^0_{vibr}$ under the action of the groups generators are given in Section D.3 of Appendix D with an application to the determination of symmetry adapted vibronic states of C-type JT systems in symmetry $C_{5v}, D_5, D_{5h}, D_{5d}$.

4.4 Eigenvalues and eigenstates for X cases

This case is similar to that considered in Section 7.4.3 of (I) for $\tilde{\lambda}_x = \tilde{\lambda}_y = 0$ since the zeroth-order model (57) reduces to $\widetilde{H}^0_{vibr} = \hbar\tilde{\omega}_s(N_s+1) - \tilde{\lambda}_z S_{z\,s}\ell_z/2$ with a pseudo-spin-vibration interaction term. The subspaces

$$\mathcal{H}_+\begin{cases}|[1\,0]\frac{1}{2}\frac{1}{2}, [v\,0]j\frac{\ell}{2}\rangle\rangle = {}^{(+)}\varphi_+,\\ |[1\,0]\frac{1}{2} - \frac{1}{2}, [v\,0]j - \frac{\ell}{2}\rangle\rangle = {}^{(+)}\varphi_-,\end{cases} \qquad (102)$$

and

$$\mathcal{H}_-\begin{cases}|[1\,0]\frac{1}{2}\frac{1}{2}, [v\,0]j - \frac{\ell}{2}\rangle\rangle = {}^{(-)}\varphi_+,\\ |[1\,0]\frac{1}{2} - \frac{1}{2}, [v\,0]j\frac{\ell}{2}\rangle\rangle = {}^{(-)}\varphi_-,\end{cases} \qquad (103)$$

are respectively associated with the doubly degenerate eigenvalues

$$E^0_{j\ell\pm} = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) \pm \hbar\frac{\tilde{\lambda}_z}{4}\ell \qquad (104)$$

Symmetry adapted eigenstates for all X type cases can be built from the relations

$$\begin{aligned}
&{P_X}^{(+)}\varphi_\pm = e^{\pm i(\ell\, r'+r)\psi(+)}\varphi_+\\
&{P_X}^{(-)}\varphi_\pm = e^{\mp i(\ell\, r'-r)\psi(-)}\varphi_+\\
&{P_Y}^{(+)}\varphi_+ = (-1)^{2j+1\,(+)}\varphi_-\ ,\ \mathcal{K}^{(+)}\varphi_+ = {}^{(+)}\varphi_-\\
&{P_Y}^{(-)}\varphi_+ = (-1)^{2j+1\,(-)}\varphi_-\ ,\ \mathcal{K}^{(-)}\varphi_+ = {}^{(-)}\varphi_-
\end{aligned}$$

It can be checked that for these systems all vibronic levels have an E-type symmetry.

4.5 Introduction of additional terms

At this point it may be asked whether the previous zeroth-order models may be refined without losing their exact solvability. To the next order in elementary creation and annihilation operators we first find the two purely vibrational anharmonicity operators

$$\begin{aligned}
{}^{[2\,\underset{s}{-}2]}\mathcal{V}^{(0,0\,A_1)} &= N_s(N_s-1)/2\sqrt{3},\\
{}^{[2\,\underset{s}{-}2]}\mathcal{V}^{(2,0\,A_1)} &= (J^2-3J_z^2)/\sqrt{6}\\
&= \left[\frac{N_s}{2}\left(\frac{N_s}{2}+1\right)-3J_z^2\right]/\sqrt{6}.
\end{aligned}$$

The operator ${}^{[2\,\underset{s}{-}2]}\mathcal{V}^{(2,4\,A_1)}$ can only appear for e_2 (resp. e_3) modes in D_{4d} (resp. D_{6d}) symmetry and breaks the exact solvability of X-type systems.

Vibronic terms involving

$${}^{[2\,\underset{s}{-}2]}\mathcal{V}^{(1,0\,A_2)} = \frac{1}{2}(N_s-1)^{[1\,\underset{s}{-}1]}V^{(1,0\,A_2)},$$

can also be included in all cases and bring an anharmonicity correction to the pseudo-spin-vibration interaction. Finally for A and B-type systems we also find vibronic interaction terms involving

$${}^{[2\,\underset{s}{-}2]}\mathcal{V}^{(1,2\,E_k)} = \frac{1}{2}(N_s-1)\ {}^{[1\,\underset{s}{-}1]}V^{(1,2\,E_k)}.$$

In some cases, for instance in C_{3v}, D_3, O, T_d symmetry, there exists a vibrational operator ${}^{[2\,\underset{s}{-}2]}\mathcal{V}^{(2,4\,E_k)}$ which is also of degree four in elementary creation and annihilation operators. However the exact solvability is lost when the corresponding vibronic interaction term is included in the Hamiltonian expansion.

For the various types of effective vibronic Hamiltonians we simply give below the modified form of $\widetilde{H}_{vibr}$ and the corresponding eigenvalues.

4.5.1 A and B modified effective Hamiltonians

We set $\widetilde{H}_{vibr} = \widetilde{H}^0_{vibr} + \widetilde{H}^1_{vibr}$ where $\widetilde{H}^0_{vibr}$ is that in equation (52) and $\widetilde{H}^1_{vibr}$ given by

$$\begin{aligned}
\widetilde{H}^1_{vibr} = {}& {}_s\tilde{t}^{0,0A_1(A_1)}_{\{2\}\{2\}}\,{}^{[2\,\underset{s}{-}2]}\mathcal{V}^{(0,0\,A_1)}\\
&+ {}_s\tilde{t}^{2,0A_1(A_1)}_{\{2\}\{2\}}\,{}^{[2\,\underset{s}{-}2]}\mathcal{V}^{(2,0\,A_1)}\\
&+ {}_s\tilde{t}^{1,0A_2(A_2)}_{\{2\}\{2\}}\,[E^{(1,0A_2)} \times {}^{[2\,\underset{s}{-}2]}\mathcal{V}^{(1,0\,A_2)}]^{(A_1)}\\
&+ {}_s\tilde{t}^{1,2E_k(E_k)}_{\{2\}\{2\}}\,[E^{(1,2E_k)} \times {}^{[2\,\underset{s}{-}2]}\mathcal{V}^{(1,2\,E_k)}]^{(A_1)}. \quad (105)
\end{aligned}$$

According as we deal with a A or B case it may be written in the form

$$\begin{aligned}
{}^\pm\widetilde{H}^1_{vibr} = {}& \hbar\tilde{\mu}^{(0)}N_s(N_s-1) + \hbar\tilde{\mu}^{(2)}\left[\frac{N_s}{2}\left(\frac{N_s}{2}+1\right)-3J_z^2\right]\\
&+ \hbar\tilde{\lambda}^{(1)}_z\,(N_s-1)\,S_zJ_z\\
&+ \hbar\tilde{\lambda}^{(1)}_x(N_s-1)\frac{1}{2}(S_+J_\mp + S_-J_\pm). \qquad (106)
\end{aligned}$$

With the property $J_z = \varDelta - S_z$ (resp. $J_z = \overline{\varDelta} + S_z$) we can rewrite $\widetilde{H}_{vibr}$ as

$${}^\pm\widetilde{H}_{vibr} = {}^\pm\widetilde{H}^0_{vibr} + {}^\pm\widetilde{H}^1_{vibr},$$

where ${}^\pm\widetilde{H}^1_{vibr}$ are in a form similar to that used to solve the eigenvalue equation for ${}^\pm\widetilde{H}^0_{vibr}$, that is expressed in terms of the conserved quantities $(\varDelta,\, \mathcal{F})$ (resp. $(\overline{\varDelta},\, \overline{\mathcal{F}})$) (Eq. (58)) and of the generators of two spin 1/2 algebras $su(2)(M)$ (resp. $su(2)(N)$):

$$\begin{aligned}
{}^+\widetilde{H}_{vibr} = {}& \hbar\tilde{\omega}_s(N_s+1) + \hbar\tilde{\mu}^{(0)}N_s(N_s-1)\\
&-\hbar\frac{\tilde{\lambda}_z}{4} - \hbar\frac{\tilde{\lambda}^{(1)}_z}{4}(N_s-1) + \hbar\tilde{\mu}^{(2)}\left[\frac{N_s}{2}\left(\frac{N_s}{2}+1\right) - 3\varDelta^2 - \frac{3}{4}\right]\\
&+\hbar[\tilde{\lambda}_x + \tilde{\lambda}^{(1)}_x(N_s-1)]\left\{\frac{1}{2}\sqrt{\mathcal{F}}(M_+ + M_-) + {}^+\tilde{\delta}^{(1)}_z\varDelta M_z\right\},
\end{aligned}$$

with

$${}^+\tilde{\delta}^{(1)}_z = \frac{\tilde{\lambda}_z + 6\tilde{\mu}^{(2)} + \tilde{\lambda}^{(1)}_z(N_s-1)}{\tilde{\lambda}_x + \tilde{\lambda}^{(1)}_x(N_s-1)}.$$

Likewise for ${}^-\widetilde{H}_{vibr}$ we obtain

$$\begin{aligned}
{}^-\widetilde{H}_{vibr} = {}& \hbar\tilde{\omega}_s(N_s+1) + \hbar\tilde{\mu}^{(0)}N_s(N_s-1)\\
&+\hbar\frac{\tilde{\lambda}_z}{4} + \hbar\frac{\tilde{\lambda}^{(1)}_z}{4}(N_s-1) + \hbar\tilde{\mu}^{(2)}\left[\frac{N_s}{2}\left(\frac{N_s}{2}+1\right) - 3\overline{\varDelta}^2 - \frac{3}{4}\right]\\
&+\hbar[\tilde{\lambda}_x + \tilde{\lambda}^{(1)}_x(N_s-1)]\left\{\frac{1}{2}\sqrt{\overline{\mathcal{F}}}(N_+ + N_-) + {}^-\tilde{\delta}^{(1)}_z\overline{\varDelta}N_z\right\},
\end{aligned}$$

with

$${}^-\tilde{\delta}^{(1)}_z = \frac{\tilde{\lambda}_z - 6\tilde{\mu}^{(2)} + \tilde{\lambda}^{(1)}_z(N_s-1)}{\tilde{\lambda}_x + \tilde{\lambda}^{(1)}_x(N_s-1)}.$$

${}^+\widetilde{H}_{vibr}$ and ${}^-\widetilde{H}_{vibr}$ can then be diagonalized, as described in [26,27], through a unitary transformation of the algebras $su(2)(M)$ and $su(2)(N)$ respectively. This leads to the eigenvalues

$$\begin{aligned}
{}^\pm E_{jm\pm} = {}& \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar\tilde{\mu}^{(0)}2j(2j-1)\\
&\mp \hbar\frac{\tilde{\lambda}_z}{4} \mp \hbar\frac{\tilde{\lambda}^{(1)}_z}{4}(2j-1)\\
&+ \hbar\tilde{\mu}^{(2)}\left[j(j+1) - 3\left(m+\frac{1}{2}\right)^2 - \frac{3}{4}\right]\\
&+ \hbar[\tilde{\lambda}_x + \tilde{\lambda}^{(1)}_x(2j-1)]\varOmega_\pm(j,m), \qquad (107)
\end{aligned}$$

with

$$\begin{aligned}\mathit{\Omega}_{\pm}(j,m) &= \pm\mathit{\Omega}(j,m) \qquad (108)\\ &= \pm\frac{1}{2}\left[(j-m)(j+m+1) + {}^{\pm}\tilde{\delta}_z^{(1)}(j)^2\left(m+\frac{1}{2}\right)^2\right]^{1/2},\end{aligned}$$

and

$${}^{\pm}\tilde{\delta}_z^{(1)}(j) = \frac{\tilde{\lambda}_z \pm 6\tilde{\mu}^{(2)} + \tilde{\lambda}_z^{(1)}(2j-1)}{\tilde{\lambda}_x + \tilde{\lambda}_x^{(1)}(2j-1)}. \qquad (109)$$

The corresponding eigenstates can be obtained with the method presented in [26] or directly from the results in Section 4.2 with $\mathit{\Omega}_{\pm}(j,m)$ as given by (108) and the substitution $\tilde{\delta}_z \to {}^{\pm}\tilde{\delta}_z^{(1)}(j)$ in equation (64).

For the uncoupled states equation (65) is replaced by

$$\begin{aligned}{}^{\pm}E_j &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar(2\tilde{\mu}^{(0)} - \tilde{\mu}^{(2)})j(2j-1)\\ &\quad \pm \frac{\hbar}{2}[\tilde{\lambda}_z + \tilde{\lambda}_z^{(1)}(2j-1)]j, \qquad (110)\end{aligned}$$

and for the special case $m = -1/2$ the energies (69) become

$$\begin{aligned}{}^{+}E_{j-1/2\pm} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar\tilde{\mu}^{(0)}2j(2j-1)\\ &\quad - \frac{\hbar}{4}\left[\tilde{\lambda}_z + \tilde{\lambda}_z^{(1)}(2j-1)\right] + \hbar\tilde{\mu}^{(2)}\left[j(j+1) - \frac{3}{4}\right]\\ &\quad \pm \frac{\hbar}{4}[\tilde{\lambda}_x + \tilde{\lambda}_x^{(1)}(2j-1)](2j+1), \qquad (111)\end{aligned}$$

$$\begin{aligned}{}^{-}E_{j-1/2\pm} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar\tilde{\mu}^{(0)}2j(2j-1)\\ &\quad + \frac{\hbar}{4}[\tilde{\lambda}_z + \tilde{\lambda}_z^{(1)}(2j-1)] + \hbar\tilde{\mu}^{(2)}\left[j(j+1) - \frac{3}{4}\right]\\ &\quad \pm \frac{\hbar}{4}[\tilde{\lambda}_x + \tilde{\lambda}_x^{(1)}(2j-1)](2j+1). \qquad (112)\end{aligned}$$

4.5.2 C and D modified effective Hamiltonians

Within the same order of approximation as previously the zeroth-order model of Section 4.3 is supplemented with the first three terms of equations (105) which gives

$$\begin{aligned}\widetilde{H}^{1}_{vibr} &= \hbar\tilde{\mu}^{(0)}N_s(N_s-1) + \hbar\tilde{\mu}^{(2)}\left[\frac{N_s}{2}\left(\frac{N_s}{2}+1\right) - 3J_z^2\right]\\ &\quad + \hbar\tilde{\lambda}_z^{(1)}(N_s-1)S_zJ_z. \qquad (113)\end{aligned}$$

Taking into account that $J_z = \mathit{\Delta} - 2S_z$ (resp. $J_z = \overline{\mathit{\Delta}} + 2S_z$) for case C (resp. D) we can rewrite $\widetilde{H}_{vibr}$ in a form similar to those of ${}^{\pm}\widetilde{H}^{0}_{vibr}$ (Eqs. (77), (95)). For C-type systems we obtain

$$\begin{aligned}{}^{+}\widetilde{H}_{vibr} &= \hbar\tilde{\omega}_s(N_s+1) + \hbar\tilde{\mu}^{(0)}N_s(N_s-1)\\ &\quad - \hbar\frac{\tilde{\lambda}_z}{2} - \hbar\frac{\tilde{\lambda}_z^{(1)}}{2}(N_s-1) + \hbar\tilde{\mu}^{(2)}\left[\frac{N_s}{2}\left(\frac{N_s}{2}+1\right) - 3\mathit{\Delta}^2 - 3\right]\\ &\quad + \hbar\tilde{\delta}\left\{\frac{1}{2}\sqrt{\mathcal{F}}(P_+ + P_-) + {}^{+}\tilde{\delta}_z^{(1)}\mathit{\Delta}P_z\right\}, \qquad (114)\end{aligned}$$

with

$${}^{+}\tilde{\delta}_z^{(1)} = \frac{1}{\tilde{\delta}}[\tilde{\lambda}_z + 12\tilde{\mu}^{(2)} + \tilde{\lambda}_z^{(1)}(N_s-1)],$$

and for D-type ones

$$\begin{aligned}{}^{-}\widetilde{H}_{vibr} &= \hbar\tilde{\omega}_s(N_s+1) + \hbar\tilde{\mu}^{(0)}N_s(N_s-1)\\ &\quad + \hbar\frac{\tilde{\lambda}_z}{2} + \hbar\frac{\tilde{\lambda}_z^{(1)}}{2}(N_s-1) + \hbar\tilde{\mu}^{(2)}\left[\frac{N_s}{2}\left(\frac{N_s}{2}+1\right) - 3\overline{\mathit{\Delta}}^2 - 3\right]\\ &\quad + \hbar\tilde{\delta}\left\{\frac{1}{2}\sqrt{\overline{\mathcal{F}}}(P'_+ + P'_-) + {}^{-}\tilde{\delta}_z^{(1)}\overline{\mathit{\Delta}}P'_z\right\}, \qquad (115)\end{aligned}$$

with

$${}^{-}\tilde{\delta}_z^{(1)} = \frac{1}{\tilde{\delta}}[\tilde{\lambda}_z - 12\tilde{\mu}^{(2)} + \tilde{\lambda}_z^{(1)}(N_s-1)].$$

The diagonalization is now performed with unitary transformations U and U' having the same form than those in Section 4.3. The eigenvalues (80), (97) become

$$\begin{aligned}{}^{\pm}E_{jm\pm} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar\tilde{\mu}^{(0)}2j(2j-1)\\ &\quad \mp \hbar\frac{\tilde{\lambda}_z}{2} \mp \hbar\frac{\tilde{\lambda}_z^{(1)}}{2}(2j-1)\\ &\quad + \hbar\tilde{\mu}^{(2)}[j(j+1) - 3(m+1)^2 - 3] + \hbar\tilde{\delta}\mathit{\Omega}_{\pm}(j,m), \qquad (116)\end{aligned}$$

where $\mathit{\Omega}_{\pm}(j,m)$ is obtained from equation (81) with the substitution

$$\tilde{\delta}_z \to {}^{\pm}\tilde{\delta}_z^{(1)}(j) = \frac{1}{\tilde{\delta}}[\tilde{\lambda}_z \pm 12\tilde{\mu}^{(2)} + \tilde{\lambda}_z^{(1)}(2j-1)].$$

The eigenstates of ${}^{\pm}\widetilde{H}_{vibr}$ are obtained from those determined in Section 4.3 with the appropriate substitutions for $\mathit{\Omega}_{\pm}(j,m)$ and $\tilde{\delta}_z$.

For the special case $m = -1$ the energies (87, 99) become

$$\begin{aligned}{}^{+}E_{j-1\pm} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar\tilde{\mu}^{(0)}2j(2j-1)\\ &\quad - \frac{\hbar}{2}[\tilde{\lambda}_z + \tilde{\lambda}_z^{(1)}(2j-1)]\\ &\quad + \hbar\tilde{\mu}^{(2)}[j(j+1) - 3] \pm \frac{\hbar}{2}\tilde{\delta}j(j+1), \qquad (117)\end{aligned}$$

$$\begin{aligned}{}^{-}E_{j-1\pm} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar\tilde{\mu}^{(0)}2j(2j-1)\\ &\quad + \frac{\hbar}{2}[\tilde{\lambda}_z + \tilde{\lambda}_z^{(1)}(2j-1)]\\ &\quad + \hbar\tilde{\mu}^{(2)}[j(j+1) - 3] \pm \frac{\hbar}{2}\tilde{\delta}j(j+1). \qquad (118)\end{aligned}$$

For the uncoupled states (89, 100) equations (90, 101) are replaced by

$$\begin{aligned}{}^{\pm}E_{jj} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1) + \hbar(2\tilde{\mu}^{(0)} - \tilde{\mu}^{(2)})j(2j-1)\\ &\quad \pm \frac{\hbar}{2}[\tilde{\lambda}_z + \tilde{\lambda}_z^{(1)}(2j-1)]j, \qquad (119)\\ {}^{\pm}E_{jj-1} &= \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(2j+1)\\ &\quad + \hbar[2\tilde{\mu}^{(0)}j - \tilde{\mu}^{(2)}(j-3)](2j-1)\\ &\quad \pm \frac{\hbar}{2}[\tilde{\lambda}_z + \tilde{\lambda}_z^{(1)}(2j-1)](j-1). \qquad (120)\end{aligned}$$

In spite of these additional terms we observe that, for A-B as well as for C-D cases, there remains some (A_1, A_2) (or (B_1, B_2)) degenerate pairs. These residual degeneracies are lifted if one takes into account, perturbatively or through a numerical diagonalization, either a purely vibrational operator ${}^{[n_v\ -n_v]}_{\quad\ s}\mathcal{V}^{(j_v, \ell_v\, A_1)}$ with $\ell_v \neq 0$ or the next allowed vibronic tensor involving ${}^{[n_v\ -n_v]}_{\quad\ s}\mathcal{V}^{(j_v, \ell_v\, E_k)}$ (see Eq. (47)); vibrational tensors with A_2 symmetry and $\ell_v \neq 0$ require usually higher n_v values [22].

4.5.3 X modified effective Hamiltonians

In this case the additional terms are those in equation (113). Thus within the same subspaces (102, 103) the eigenvalues (104) are replaced by

$$\begin{aligned} E^0_{j\ell\pm} &= \hbar\tilde{\omega}_s(2j+1) + \hbar\tilde{\mu}^{(0)}2j(2j-1) \\ &\quad + \tilde{\mu}^{(2)}[j(j+1) - \frac{3}{4}\ell^2] \pm \hbar[\tilde{\lambda}_z + \tilde{\lambda}^{(1)}_z(2j-1)]\frac{\ell}{4}. \end{aligned} \tag{121}$$

We will not consider here the introduction of effective rovibronic operators which allow to refine the previous vibronic models. This will be presented elsewhere for symmetric top molecules for all five types of $E_r \otimes e_{r'}$ systems.

5 G′ electronic states in cubic symmetry

5.1 Untransformed Hamiltonian expansion

For a G' electronic state we have from equation (17) restricting to terms which are at most of degree two in the coordinates and invariant upon time reversal

$$\begin{aligned} H_{vibr} &= I_e \sum_s \hbar\omega_s \left(N_s + \frac{g_s}{2}\right) \\ &\quad + \sum_C [E^{\langle 11\rangle(2,C)} \times V^{(C)}]^{(A_1)}, \end{aligned} \tag{122}$$

where, to simplify the notation, we set:

$$\begin{aligned} V^{(C)} &= \sum_s {}_s t^C\, {}_s Q^{(C)} \\ &\quad + \sum_{s,s'} {}_{ss'}t^{C_1C_2(C)}({}_sQ^{(C_1)} \times {}_{s'}Q^{(C_2)})^{(C)} + \cdots, \end{aligned} \tag{123}$$

with $C = E$ or F_2 (Eq. (7)). Likewise from (18) we obtain

$$\begin{aligned} H_{vibr} &= I_e \sum_s \hbar\omega_s \left(N_s + \frac{g_s}{2}\right) \\ &\quad + [E^{([1-1]1,2E,\,[00]A_1)(E)} \times V^{(E)}]^{(A_1)} \\ &\quad + [E^{([1-1]1,0A_2,\,[1-1]1F_1)(F_2)} \times V^{(F_2)}]^{(A_1)}. \end{aligned} \tag{124}$$

Various forms for the vibronic matrix may be obtained depending partly on the basis used for the electronic states. We will restrict below to few possibilities chosen for their practical interest.

5.1.1 Vibronic matrix using chain (5)

In that case we choose the symmetry adapted basis defined in [20,32] which takes advantage of the natural subduction $\mathcal{D}^{(3/2)} \downarrow G'$ to define the orientation of the *irrep* G':

$$|[1\,\dot{0}]\langle 10\rangle \frac{3}{2} m_e\rangle\rangle \equiv |[1\,\dot{0}]\langle 10\rangle \frac{3}{2} G'\sigma_e\rangle\rangle, \tag{125}$$

with

$$\begin{array}{ccccc} m_e & \frac{3}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{3}{2} \\ \sigma_e & 1 & 2 & 3 & 4 \end{array} \tag{126}$$

With the results obtained in [20] the vibronic matrix for (122) reads

$$\begin{aligned} \widehat{H} &= \widehat{\sigma}_0 \sum_s \hbar\omega_s \left(N_s + \frac{g_s}{2}\right) - \frac{1}{2\sqrt{2}}(\widehat{\rho}_1 V^{(E)}_1 + \widehat{\rho}_2 V^{(E)}_2) \\ &\quad + \frac{1}{2\sqrt{3}}\,\widehat{\rho}_3[\,\widehat{\rho}_x\ V^{(F_2)}_x + \widehat{\rho}_y\ V^{(F_2)}_y + \widehat{\rho}_z\ V^{(F_2)}_z], \end{aligned} \tag{127}$$

where $\widehat{\rho}_i$ are 4 by 4 matrices given in terms of Pauli matrices by:

$$\widehat{\rho}_1 = \begin{pmatrix} \widehat{\sigma}_z & 0 \\ 0 & -\widehat{\sigma}_z \end{pmatrix},\ \widehat{\rho}_x = \begin{pmatrix} 0 & \widehat{\sigma}_x \\ \widehat{\sigma}_x & 0 \end{pmatrix},$$

$$\widehat{\rho}_2 = \begin{pmatrix} 0 & \widehat{\sigma}_0 \\ \widehat{\sigma}_0 & 0 \end{pmatrix},\ \widehat{\rho}_y = \begin{pmatrix} 0 & \widehat{\sigma}_y \\ \widehat{\sigma}_y & 0 \end{pmatrix},$$

$$\widehat{\rho}_3 = \begin{pmatrix} 0 & -i\widehat{\sigma}_z \\ i\widehat{\sigma}_z & 0 \end{pmatrix},\ \widehat{\rho}_z = \begin{pmatrix} \widehat{\sigma}_z & 0 \\ 0 & \widehat{\sigma}_z \end{pmatrix}.$$

This particular form for the vibronic matrix is due to our choice (125, 126) which differs from that defined in [2,4]. Taking into account that in [4] standard conventions are used for the $su(2)$ *irreps* it may be shown that the symmetry adapted basis given there is related to ours by:

$$\begin{aligned} {}^B\Psi^{(G')}_1 &= \frac{1}{\sqrt{2}}[\,|[1\,\dot{0}]\langle 10\rangle\frac{3}{2}G'3\rangle\rangle + i|[1\,\dot{0}]\langle 10\rangle\frac{3}{2}G'1\rangle\rangle\,] \\ {}^B\Psi^{(G')}_2 &= \frac{1}{\sqrt{2}}[\,|[1\,\dot{0}]\langle 10\rangle\frac{3}{2}G'2\rangle\rangle + i|[1\,\dot{0}]\langle 10\rangle\frac{3}{2}G'4\rangle\rangle\,] \\ {}^B\Psi^{(G')}_3 &= \frac{1}{\sqrt{2}}[-|[1\,\dot{0}]\langle 10\rangle\frac{3}{2}G'3\rangle\rangle + i|[1\,\dot{0}]\langle 10\rangle\frac{3}{2}G'1\rangle\rangle\,] \\ {}^B\Psi^{(G')}_4 &= \frac{1}{\sqrt{2}}[-|[1\,\dot{0}]\langle 10\rangle\frac{3}{2}G'2\rangle\rangle + i|[1\,\dot{0}]\langle 10\rangle\frac{3}{2}G'4\rangle\rangle\,]. \end{aligned}$$

Within this basis the vibronic matrix associated with H_{vibr} (122) takes the form

$$\begin{aligned} {}^B\widehat{H} &= \widehat{\sigma}_0 \sum_s \hbar\omega_s \left(N_s + \frac{g_s}{2}\right) + \frac{1}{2\sqrt{2}}(\widehat{C}_\theta\ V^{(E)}_1 + \widehat{C}_\epsilon\ V^{(E)}_2) \\ &\quad - \frac{1}{2\sqrt{3}}[\widehat{C}_\xi\ V^{(F_2)}_x + \widehat{C}_\eta\ V^{(F_2)}_y + \widehat{C}_\zeta\ V^{(F_2)}_z], \end{aligned} \tag{128}$$

where the $\widehat{C}_\alpha$ matrices are those defined in [4]. This leads in particular to the relations between parameters of linear coupling in equation (123) and those used in [4]:

$${}_sV_E = \frac{1}{2\sqrt{2}}\ {}_st^E \quad , \quad {}_sV_T = -\frac{1}{2\sqrt{3}}\ {}_st^{F_2}.$$

5.1.2 Vibronic matrix using chain (9)

We first note that with equations (14, 15) and (32) we can rewrite H_{vibr} (124) as

$$\begin{aligned} H_{vibr} = I_e \sum_s \hbar\omega_s(N_s + \frac{g_s}{2}) + \frac{1}{2}(\mathbf{S}_+\ V_-^{(E)} + \mathbf{S}_-\ V_+^{(E)}) \\ + \frac{2}{\sqrt{3}}\mathbf{S}_z \sum_\alpha \varSigma_\alpha\ V_\alpha^{(F_2)}, \end{aligned} \tag{129}$$

where we took into account that within the irreducible subspace $[1\,\dot{0}]$ of $u(4)_e$ we have [20]

$$E^{([1-1]1,\,[1-1]1)}_{\;0A_2\quad F_1\alpha} \sim 2E^{([1-1]1,\,[00]0)}_{\;0A_2\quad A_1}\ E^{([00]0,\,[1-1]1)}_{\;0A_1\quad F_1\alpha}$$

with $\alpha = x, y, z$. The vibronic matrix for H_{vibr} (124, 129) is determined in the symmetry adapted basis (10) with kets ordered as:

$$\begin{array}{ccccc} (m_e, m'_e) & (\frac{1}{2},\frac{1}{2}) & (-\frac{1}{2},\frac{1}{2}) & (\frac{1}{2},-\frac{1}{2}) & (-\frac{1}{2},-\frac{1}{2}) \\ E\bar{\sigma}_1, E'_1\bar{\sigma}_2 & \bar{1},\bar{1} & \bar{2},\bar{1} & \bar{1},\bar{2} & \bar{2},\bar{2} \\ G'\bar{\sigma} & G'\bar{1} & G'\bar{2} & G'\bar{3} & G'\bar{4} \end{array} \tag{130}$$

We note that this order differ from the one used in [20] which was chosen in view of applications to $G' \times f_2$ JT systems in octahedral molecules. With the method and results of [20] for (124) or directly from (129) with our conventions (Eq. (A.2)) for $su(2)$ covariant states the vibronic matrix is obtained as

$$\begin{aligned} \widehat{H}_{vibr} = \widehat{\sigma}_0 \sum_s \hbar\omega_s \left(N_s + \frac{g_s}{2}\right) - \frac{1}{2}\left(\widehat{\rho}_-\ V_-^{(E)} + \widehat{\rho}_+\ V_+^{(E)}\right) \\ + \frac{1}{2\sqrt{3}} \sum_\alpha \widetilde{\widehat{\rho}}_\alpha\ V_\alpha^{(F_2)}, \end{aligned} \tag{131}$$

where

$$\widehat{\rho}_- = \begin{pmatrix} \widehat{\sigma}_- & 0 \\ 0 & \widehat{\sigma}_- \end{pmatrix},\ \widehat{\rho}_+ = \begin{pmatrix} \widehat{\sigma}_+ & 0 \\ 0 & \widehat{\sigma}_+ \end{pmatrix}$$
$$\widetilde{\widehat{\rho}}_x = \begin{pmatrix} 0 & \widehat{\sigma}_z \\ \widehat{\sigma}_z & 0 \end{pmatrix},\ \widetilde{\widehat{\rho}}_y = i\begin{pmatrix} 0 & \widehat{\sigma}_z \\ -\widehat{\sigma}_z & 0 \end{pmatrix},\ \widetilde{\widehat{\rho}}_z = \begin{pmatrix} \widehat{\sigma}_z & 0 \\ 0 & -\widehat{\sigma}_z \end{pmatrix}.$$

5.2 The linear G′ ⊗ e system

The analogy between the $E \otimes e$ and $G' \otimes e$ systems in cubic symmetry has been mentioned in several places [4,15] but to our knowledge not precisely established. We will show how the use of chains (8) or (9) to perform the symmetry adaptation of both electronic states and operators allows to recover this result in a straightforward manner together with a complete determination of a symmetry adapted vibronic basis. This already appears if one compares equation (35) with the first line in equation (131) together with the expressions for the matrices $\widehat{\rho}_\pm$.

With equation (124) we have the linear Hamiltonian

$$\begin{aligned} H_{JTL} = I_e\hbar\omega_s(N_s + 1) \\ + {}_{\{s\}}t^E\,[E^{([1-1]1,2E,[00]0A_1)(E)} \times {}_sQ^{(E)}]^{(A_1)}, \end{aligned}$$

or in terms of pseudo-spin operators (14) and with equations (30, 32)

$$H_{JTL}/\hbar = I_e\omega_s(N_s + 1) + {}_sD^{E_k}(\mathbf{S}_{+\,s}q_-^{(E_k)} + \mathbf{S}_{-\,s}q_+^{(E_k)}),$$

that is of the form (37) in a type (iii) case as appropriate for an $E \otimes e$ system in spherical top molecules but with pseudo-spin operators acting in the four dimensional space defined in (10). The property

$$[H_{JTL}, \mathbf{j}_z] = [H_{JTL}, {}_s\ell_z + \mathbf{S}_z] = 0,$$

together with the time reversal invariance of H_{JTL} and the property of the basis states

$$\begin{aligned} &\mathcal{K}|[1\dot{0}], [10]\frac{1}{2}\,m_e, [10]\frac{1}{2}\,m'_e\rangle\rangle = \\ &\qquad (-1)^{\frac{1}{2}-m'_e}|[1\dot{0}], [10]\frac{1}{2}\ -m_e, [10]\frac{1}{2}\ -m'_e\rangle\rangle, \end{aligned}$$

imply that the energies only depend on the eigenvalues $|\mu|$ of $\mathbf{j}_z$ and a fourfold degeneracy of the eigenstates. In the following we will also use the fact that H_{JTL} commutes with the third component $\varSigma_z$ of the pseudo-spin linked to the $su(2)_\varSigma$ algebra (15) of which the basis states (10) are eigenstates. The states (41, 42) are replaced by

$$\begin{aligned} |[1\dot{0}], [1\,0]\frac{1}{2}\frac{1}{2}, [1\,0]\frac{1}{2}m'_e\rangle\rangle|[v\,0]j\,\frac{\mu+\frac{1}{2}}{2}\rangle\rangle = \varphi^{(\pm)}_{j\mu+} \\ |[1\dot{0}], [1\,0]\frac{1}{2} - \frac{1}{2}, [1\,0]\frac{1}{2}m'_e\rangle\rangle|[v\,0]j\,\frac{\mu-\frac{1}{2}}{2}\rangle\rangle = \psi^{(\pm)}_{j\mu+} \\ |[1\dot{0}], [1\,0]\frac{1}{2} - \frac{1}{2}, [1\,0]\frac{1}{2}m'_e\rangle\rangle|[v\,0]j\,-\frac{\mu+\frac{1}{2}}{2}\rangle\rangle = \varphi^{(\pm)}_{j\mu-} \\ |[1\dot{0}], [1\,0]\frac{1}{2}\frac{1}{2}, [1\,0]\frac{1}{2}m'_e\rangle\rangle|[v\,0]j\,-\frac{\mu-\frac{1}{2}}{2}\rangle\rangle = \psi^{(\pm)}_{j\mu-} \end{aligned} \tag{132}$$

where the upper $(\pm)$ indices refer to the eigenvalues $m'_e = \pm 1/2$ of $-\varSigma_z$. With these phase choices it is easily checked that the matrix elements of H_{JTL}

$$\begin{aligned} \langle\varphi^{(\pm)}_{j+\frac{1}{2}\mu+}|H_{JTL}|\psi^{(\pm)}_{j\mu+}\rangle, \\ \langle\varphi^{(\pm)}_{j-\frac{1}{2}\mu+}|H_{JTL}|\psi^{(\pm)}_{j\mu+}\rangle, \end{aligned} \tag{133}$$

are those given in the right member of equations (43, 44) (with $\bar{\mu} \to \mu$). From equations (10, 130, 132) and Table 1 we obtain the symmetry of the degenerate eigenstates of H_{JTL}:

$$\begin{aligned} &|\mu|\varGamma_{ev} \\ &3p + \frac{1}{2}E \times E'1 = G' \\ &3p + \frac{3}{2}(A_1 + A_2) \times E'1 = E'_1 + E'_2 \\ &3p + \frac{5}{2}E \times E'1 = G'. \end{aligned}$$

With the results in equations (45, 46) for $G = O, T_d$ and the properties (11, C.7, C.8) a symmetry adapted vibronic basis is easily obtained and summarized below.

- $\mu = 3p + \frac{1}{2}$

$$\begin{array}{l} \varPhi^{(+)}_{j\mu G'\bar{1}} = i^{-v}\varPhi^{(+)}_{j\mu -}\ ,\ \varPhi^{(+)}_{j\mu G'\bar{2}} = i^{v}\varPhi^{(+)}_{j\mu +} \\ \varPhi^{(-)}_{j\mu G'\bar{3}} = i^{-v}\varPhi^{(-)}_{j\mu -}\ ,\ \varPhi^{(-)}_{j\mu G'\bar{4}} = i^{v}\varPhi^{(-)}_{j\mu +} \end{array}$$

- $\mu = 3p + \frac{3}{2}$

$$\begin{array}{l} \varPhi^{(+)}_{j\mu E'_1\bar{1}} = i^{v+1}(\varPhi^{(+)}_{j\mu +} - (-1)^{2j}\varPhi^{(+)}_{j\mu -})/\sqrt{2} \\ \varPhi^{(-)}_{j\mu E'_1\bar{2}} = i^{v+1}(\varPhi^{(-)}_{j\mu +} - (-1)^{2j}\varPhi^{(-)}_{j\mu -})/\sqrt{2} \\ \varPhi^{(+)}_{j\mu E'_2\bar{1}} = i^{v}(\varPhi^{(+)}_{j\mu +} + (-1)^{2j}\varPhi^{(+)}_{j\mu -})/\sqrt{2} \\ \varPhi^{(-)}_{j\mu E'_2\bar{2}} = i^{v}(\varPhi^{(-)}_{j\mu +} + (-1)^{2j}\varPhi^{(-)}_{j\mu -})/\sqrt{2} \end{array}$$

- $\mu = 3p + \frac{5}{2}$

$$\begin{array}{l} \varPhi^{(+)}_{j\mu G'\bar{1}} = i^{v}\varPhi^{(+)}_{j\mu +}\ ,\ \varPhi^{(+)}_{j\mu G'\bar{2}} = i^{-v}\varPhi^{(+)}_{j\mu -} \\ \varPhi^{(-)}_{j\mu G'\bar{3}} = i^{v}\varPhi^{(-)}_{j\mu +}\ ,\ \varPhi^{(-)}_{j\mu G'\bar{4}} = i^{-v}\varPhi^{(-)}_{j\mu -} \end{array}$$

with $\varPhi^{(\pm)}_{j\mu\pm}$, $\varPhi = \varphi$ or $\varPhi = \psi$ as defined in equation (132). We note that the preceding states satisfy upon time reversal

$$\mathcal{K}\varPhi^{(\pm)}_{j\mu C\bar{\sigma}} = (-1)^{C-\bar{\sigma}}\varPhi^{(\mp)}_{j\mu C-\bar{\sigma}},$$

with

$$\begin{array}{ccccccc} C & & G' & & & E'_i & \\ \bar{\sigma} & \bar{1} & \bar{2} & \bar{3} & \bar{4} & \bar{1} & \bar{2} \\ -\bar{\sigma} & \bar{4} & \bar{3} & \bar{2} & \bar{1} & \bar{2} & \bar{1} \\ (-1)^{C-\bar{\sigma}} & 1 & 1 & -1 & -1 & 1 & -1 \end{array}$$

5.3 G′ ⊗ e dynamical JT systems in spherical tops

We first recall that within our approach an arbitrary effective vibronic operator for an $E\otimes e$ case in cubic symmetry may be written as

$$[E^{(1,\ell_e C_e)} \times {}^{[m_1\ -m_2]}_{\quad\ s}\mathcal{V}^{(j_v,\ell_v\, C_v)}]^{(C_{ev})}, \tag{134}$$

with $C_{ev} = A_1$, A_2 or E and its matrix elements computed in the coupled basis

$$|[1\,0]\frac{1}{2}1E, [v\,0]j\ell\varGamma_v; \varGamma_{ev}\sigma_{ev}\rangle\rangle, \tag{135}$$

associated with chain (49) (see Appendix C). Also in O_h only e_g modes are active.

For a $G' \otimes e$ case we have mainly two possibilities according as chain (5) or (9) is used. In the first case we have the vibronic chain

$$\begin{array}{ccccccc} su(4)_e \oplus & u(2)_v \supset & sp(4)_e \oplus & su^*(2)_v & & & \\ [1\dot{0}] & [v0] & \langle 10\rangle & j & & & \\ & & \supset su(2)_e \oplus & su^*(2)_v \supset & O^S & & \\ & & \frac{3}{2} & j & \varGamma_{ev}\sigma_{ev} & & \end{array} \tag{136}$$

with vibronic operators written as

$$[E^{\langle\lambda_1\lambda_2\rangle(K_e C_e)} \times {}^{[m_1\ -m_2]}_{\quad\ s}\mathcal{V}^{(j_v,\ell_v\, C_v)}]^{(C_{ev})}. \tag{137}$$

Their matrix elements can be computed in the vibronic basis

$$|[1\dot{0}]\langle 10\rangle\frac{3}{2}G', [v\,0]j\ell\varGamma_v; \varGamma_{ev}\sigma_{ev}\rangle\rangle \quad (\varGamma_{ev} = G' \times \varGamma_v), \tag{138}$$

associated with (136). In the second case we have

$$\begin{array}{ccccc} su(4)_e \oplus & u(2)_v \supset & (su^*(2)_S \oplus & su^*(2)_v) \oplus & su(2)_\varSigma \\ [1\dot{0}] & [v0] & \frac{1}{2} & j & \frac{1}{2} \\ & & & \supset & O^S \\ & & & & \varLambda_{ev}\sigma_{ev} \end{array} \tag{139}$$

with $\varLambda_{ev} = (E\times\varGamma_v)\varGamma_{ev}\times E'_1$. The vibronic operators (137) are replaced by

$$[[E^{([\lambda_1\mu_1]k_1,\ell_1 C_e,[\lambda_2\mu_2]k_2 C'_e)} \times {}^{[m_1\ -m_2]}_{\quad\ s}\mathcal{V}^{(j_v,\ell_v\, C_v;A_1)}]^{(C_{ev},k_2 C'_e)}]^{(C)}, \tag{140}$$

and this time the associated symmetry adapted basis is

$$|[1\dot{0}], [10]\frac{1}{2}1E, [10]\frac{1}{2}E'_1; [v\,0]j\ell\varGamma_v; \varGamma_{ev}, E'_1; \varLambda_{ev}\sigma_{ev}\rangle\rangle. \tag{141}$$

Other coupling schemes could be considered. Although both formalisms are mathematically equivalent we will see that, as before, the second possibility is more suitable to establish the connection between $G' \otimes e$ and $E \otimes e$ problems. Matrix elements for operators (140) within basis (141) are given in Appendix C.

We notice that whenever C is of species A_1, A_2 or E we can only have $k_2 = 0$, $C'_e = A_1$ in (140). This comes from the fact that C_{ev} can only be A_1, A_2 or E and from the symmetries (13) of the electronic operators. In such cases the operators (140) take the form

$$\begin{array}{l} [E^{([\lambda_1\mu_1]k_1,\ell_1 C_e,[00]0A_1)} \times {}^{[m_1\ -m_2]}_{\quad\ s}\mathcal{V}^{(j_v,\ell_v\, C_v;A_1)}]^{(C_{ev},A_1)} \equiv \\ \qquad [E^{([\lambda_1\mu_1]k_1,\ell_1 C_e,[00]0A_1)} \times {}^{[m_1\ -m_2]}_{\quad\ s}\mathcal{V}^{(j_v,\ell_v\, C_v;A_1)}]^{(C_{ev})}, \end{array}$$

where we used the property

$$F\begin{array}{cc} \sigma_{ev} & (C) \\ (C_{ev}\ A_1) & \sigma'_{ev} \end{array} = \delta_{C_{ev},C}\,\delta_{\sigma_{ev},\sigma'_{ev}}.$$

This means that, since the electronic operators

$$E^{([\lambda_1\mu_1]k_1,\ell_1 C_e,[00]0A_1)}$$

are proportional to the pseudo-spin components $\mathbf{S}_\pm$, $\mathbf{S}_z$ associated with the $su^*(2)_S$ algebra (14), to all orders in the effective Hamiltonian expansions both $E\otimes e$ and $G'\otimes e$ problems are formally identical. We underline that this is true if no triply degenerate mode is involved and as far as rovibronic interactions are neglected. This last point will be further illustrated in the following.

In particular the expansion equivalent to that in equation (47) writes ($kC = 0A_2, 2E$)

$$\begin{array}{l} \widetilde{H}_{vibr} = \displaystyle\sum_{\{n_v,j_v,\ell_v\}} \Big\{ {}_s\tilde{t}^{j_v,\ell_v A_1(A_1)}_{\{n_v\}\{n_v\}} I_e\, {}^{[n_v\ -n_v]}_{\quad\ s}\mathcal{V}^{(j_v,\ell_v\, A_1)} \\ \qquad + \displaystyle\sum_{\{k,C\}} {}_s\tilde{t}^{j_v,\ell_v C(C)}_{\{n_v\}\{n_v\}} \Big[E^{([1-1]1,kC,[00]0A_1)} \\ \qquad\qquad \times {}^{[n_v\ -n_v]}_{\quad\ s}\mathcal{V}^{(j_v,\ell_v\, C;A_1)}\Big]^{(A_1)} \Big\}. \end{array}$$

When expressed in terms of the pseudo-spin electronic operators $\mathbf{S}_\pm$, $\mathbf{S}_z$ and with the same assumptions than in Section 4 we are led to a A-type case (53) associated with the corresponding $E \otimes e$ problem in cubic symmetry:

$$ {}^{+}\widetilde{H}^{0}_{vibr}/\hbar = \tilde{\omega}_s(N_s+1) + \tilde{\lambda}_z \mathbf{S}_z J_z + \frac{\tilde{\lambda}_x}{2}(\mathbf{S}_+ J_- + \mathbf{S}_- J_+). \tag{142}$$

Thus the eigenvalues are identical to those ${}^{+}E_{jm\pm}$ in equations (59, 60) with this time a degeneracy of four in general. The unsymmetrized eigenstates ${}^{+}\widetilde{\Psi}^{(i)(\pm)}_{jm\pm}$ are obtained from those in equations (62, 63) with the substitution

$$|\pm\rangle\rangle \to |\pm, m'_e\rangle\rangle \equiv |[1\dot{0}], [10]\frac{1}{2}\, m_e, [10]\frac{1}{2}\, m'_e\rangle\rangle$$

for the electronic states which can also be expressed as in (10). As before the notation $(\pm)$ for the upper indices underline that they are also eigenstates of the pseudo-spin operator Σ_z.

Special cases

- We have four uncoupled states

$$|+,\pm\rangle\rangle|[v\,0]j\,j\rangle\rangle, \quad |-,\pm\rangle\rangle|[v\,0]j\, -j\rangle\rangle,$$

associated with the energy ${}^{+}E_j$ in equation (65);

- for $m = -1/2$ we have two doubly degenerate eigenstates with eigenvalues ${}^{+}E_{j-1/2\pm}$ as given by (69). Equation (70) for the corresponding symmetry adapted eigenstates is replaced by:

$$\begin{aligned}
&|[1\,\dot{0}][1\,0]\tfrac{1}{2}1E, [1\,0]\tfrac{1}{2}E'_1, [v\,0]j; \Omega_+, E'_1\bar{1}\rangle\rangle \\
&= i^{v+1}[|+,+\rangle\rangle|[v\,0]j\, -1/2\rangle\rangle + |-,+\rangle\rangle|[v\,0]j\,1/2\rangle\rangle]/\sqrt{2} \\
&|[1\,\dot{0}][1\,0]\tfrac{1}{2}1E, [1\,0]\tfrac{1}{2}E'_1, [v\,0]j; \Omega_+, E'_1\bar{2}\rangle\rangle \\
&= i^{v+1}[|+,-\rangle\rangle|[v\,0]j\, -1/2\rangle\rangle + |-,-\rangle\rangle|[v\,0]j\,1/2\rangle\rangle]/\sqrt{2} \\
&|[1\,\dot{0}][1\,0]\tfrac{1}{2}1E, [1\,0]\tfrac{1}{2}E'_1, [v\,0]j; \Omega_-, E'_2\bar{1}\rangle\rangle \\
&= i^{v}[|+,+\rangle\rangle|[v\,0]j\, -1/2\rangle\rangle - |-,+\rangle\rangle|[v\,0]j\,1/2\rangle\rangle]/\sqrt{2} \\
&|[1\,\dot{0}][1\,0]\tfrac{1}{2}1E, [1\,0]\tfrac{1}{2}E'_1, [v\,0]j; \Omega_-, E'_2\bar{2}\rangle\rangle \\
&= i^{v}[|+,-\rangle\rangle|[v\,0]j\, -1/2\rangle\rangle - |-,-\rangle\rangle|[v\,0]j\,1/2\rangle\rangle]/\sqrt{2}.
\end{aligned}$$

The expressions of the symmetry adapted vibronic eigenstates for other $\ell = 2|m|$ values are given in Section D.2 of Appendix D together with those of the $E \otimes e$ system.

5.4 Additional terms in the effective Hamiltonian expansion

As discussed in Section 4.5 higher order terms can be included and still lead to a solvable effective model. The formal equivalence of the $G' \otimes e$ and $E \otimes e$ systems discussed before imply that we can also add ${}^{+}\widetilde{H}^{1}_{vibr}$ (106), in which $\{S_\pm, S_z\}$ are replaced by the pseudo-spin components $\{\mathbf{S}_\pm, \mathbf{S}_z\}$ (14), to the previous zeroth-order model (142) since we have a A-type case. The corresponding eigenvalues are ${}^{+}E_{jm\pm}$ as determined through equations (107–112).

As mentioned previously we may expect that this equivalence disappears when rovibronic interactions are taken into account. This is confirmed when one looks for the possible rovibronic interaction operators of lowest degree in rotational variables which may appear in both Hamiltonian expansions.

- For an $E \otimes e$ case these are at least of degree two in the $so(3)_R$ generators $R^{1(1)}$ [28,29]:

$$[E^{(1,2E)} \times R^{2(2,E)}]^{(A_1)}\ ,\ [E^{(1,0A_2)} \times R^{3(3,A_2)}]^{(A_1)} \cdots \tag{143}$$

and unfortunately the introduction of any of them breaks the exact solvability.

- But for a $G' \otimes e$ system appears a pseudo-spin rotation interaction operator which commutes with ${}^{+}\widetilde{H}^{0}_{vibr} + {}^{+}\widetilde{H}^{1}_{vibr}$:

$$\begin{aligned}
&[E^{([00]0,[1-1]1)} \times R^{1(1)}]^{(0)}_{A_1} = \\
&\qquad - [E^{([00]0,0A_1,[1-1]1F_1)} \times R^{1(1,F_1)}]^{(A_1)} = -\frac{1}{\sqrt{3}}\vec{R}\cdot\vec{\Sigma},
\end{aligned}$$

where the coupling in the electronic operator involves the $su(2)_\Sigma$ label only. Thus the usual $su(2)_\Sigma \oplus su(2)_R \supset su(2)_W$ algebra associated with the standard theory of angular momentum addition $\vec{R} + \vec{\Sigma} = \vec{W}$ can be introduced. This leads first to two possible bases for the space of rovibronic states:

$$\begin{aligned}
&|[1\dot{0}], [10]\frac{1}{2}m_e, ([10]\frac{1}{2}, J)Wq\rangle\rangle|[v\,0]jm\rangle\rangle = \\
&\qquad \sum_{m'_e, K} C\,\begin{matrix} m'_e & K & (W) \\ (\,\frac{1}{2} & J) & q \end{matrix}\ |[1\dot{0}], [10]\frac{1}{2}m_e, [10]\frac{1}{2}m'_e\rangle\rangle \\
&\qquad\qquad \times |JM, JK\rangle\rangle|[v\,0]jm\rangle\rangle,
\end{aligned} \tag{144}$$

within an $su(2) \supset so(2)$ orientation; $|JM, JK\rangle\rangle$ are the usual symmetric top rotational covariant states [25,30,31] which satisfy upon time reversal

$$\mathcal{K}|JM, JK\rangle\rangle = (-1)^{M-K}|J-M, J-K\rangle\rangle.$$

Alternatively we may use as rovibronic basis

$$\begin{aligned}
&|[1\dot{0}], [10]\frac{1}{2}m_e, ([10]\frac{1}{2}, J)W\bar{p}\rangle\rangle|[v\,0]jm\rangle\rangle = \\
&\qquad \sum_{\bar{\sigma}, \bar{p}'} F\,\begin{matrix} E'_1\bar{\sigma} & \bar{p}' & (W) \\ (\frac{1}{2} & J) & \bar{p} \end{matrix}\ |[1\dot{0}], [10]\frac{1}{2}m_e, [10]\frac{1}{2}E'_1\bar{\sigma}\rangle\rangle \\
&\qquad\qquad \times |JM, J\bar{p}'\rangle\rangle|[v\,0]jm\rangle\rangle
\end{aligned} \tag{145}$$

with $su(2) \supset G^S$ ($G = O, T_d$ or O_h) symmetry adapted bases [17,32] for the pseudo-spin Σ and the rotational operators. In equation (145) $\bar{p} = n_r C_r \bar{\sigma}_r$ and the F symbols are symmetry adapted Clebsch-Gordan coefficients [28,33,34]. The expressions of both basis states (144, 145) show that the procedure used in Sections 4.2, 4.5.1 applies to the diagonalization of

$$\widetilde{H}_{rvibr} = {}^{+}\widetilde{H}^{0}_{vibr} + {}^{+}\widetilde{H}^{1}_{vibr} + \hbar\tilde{\beta}R^2 + \hbar\tilde{\lambda}_{\Sigma r}\vec{R}\cdot\vec{\Sigma},$$

the eigenvalues of which are given by ($W = J \pm \frac{1}{2}$):

$$\begin{aligned}
E_{jm\pm,J,W} &= {}^{+}E_{jm\pm} + \hbar\tilde{\beta}J(J+1) \\
&\quad + \hbar\tilde{\lambda}_{\Sigma r}\frac{1}{2}\left[W(W+1) - J(J+1) - \frac{3}{4}\right].
\end{aligned} \tag{146}$$

The associated unsymmetrized eigenstates ${}^{+}\widetilde{\Psi}^{(i)(Wq)}_{jm\pm}$ or ${}^{+}\widetilde{\Psi}^{(i)(W\bar{p})}_{jm\pm}$ of $\widetilde{H}_{rvibr}$ are first obtained from those in equations (62,63) with the substitutions

$$|\pm\rangle\rangle \to |\pm, Wq\rangle\rangle \equiv |[1\dot{0}], [10]\frac{1}{2}\, m_e, ([10]\frac{1}{2}, J)W\, q\rangle\rangle,$$

or

$$|\pm\rangle\rangle \to |\pm, W\bar{p}\rangle\rangle \equiv |[1\dot{0}], [10]\frac{1}{2}\, m_e, ([10]\frac{1}{2}, J)W\, \bar{p}\rangle\rangle,$$

and the values of $\cos\theta(j,m)$, $\sin\theta(j,m)$ as given in (64) with appropriate values for $\Omega(j,m)$ and $\tilde{\delta}_z$ according to the terms retained in the vibronic part. Symmetrized rovibronic eigenstates are determined through a two steps procedure. Firstly with the results in Section D.1 of Appendix D for an $E \otimes e$ system we obtain states

$$|[1\dot{0}], [1\,0]\frac{1}{2}, \left([1\,0]\frac{1}{2}, J\right) W\bar{p}; [v\,0]j; \Omega_{\pm}, \Gamma_{ev}\bar{\sigma}_{ev}\rangle\rangle$$

given by equations (D.2–D.5) in which the substitution

$${}^{+}\widetilde{\Psi}^{(i)}_{jm\pm} \to {}^{+}\widetilde{\Psi}^{(i)(W\bar{p})}_{jm\pm}$$

is made. Secondly a standard coupling in O^S

$$|[1\dot{0}], [1\,0]\frac{1}{2}, \left([1\,0]\frac{1}{2}, J\right) W n_r C_r; [v\,0]j; \Omega_{\pm}, \Delta_{ev}\bar{\theta}_{ev}\rangle\rangle =$$
$$\sum_{\bar{\sigma}_r, \bar{\sigma}_{ev}} F\begin{matrix} \bar{\sigma}_r & \bar{\sigma}_{ev} & (\Delta_{ev}) \\ (C_r & \Gamma_{ev}) & \bar{\theta}_{ev} \end{matrix}$$
$$\times |[1\dot{0}], [1\,0]\frac{1}{2}, ([1\,0]\frac{1}{2}, J)W\bar{p}; [v\,0]j; \Omega_{\pm}, \Gamma_{ev}\bar{\sigma}_{ev}\rangle\rangle,$$

leads to symmetrized rovibronic eigenstates associated with the eigenvalues $E_{jm\pm,J,W}$ (146).

6 Correlations with previous studies

As explained below correlations with previous studies are not straightforward and must be made with some caution. Let us first recall that in a general way a formal effective Hamiltonian (for instance for a given vibronic polyad) is linked to an untransformed Hamiltonian through a usually unknown unitary transformation. In addition our expansions in normal order form for the vibrational operators imply that all equivalent contributions coming from different powers in normal coordinates are included. Also, different physical effects which may contribute to the same effective operator are automatically taken into account. A similar situation arises in rovibrational effective Hamiltonians [29]. This is illustrated, for instance, by some X-type systems, such as $E_1 \otimes e_3$ in D_{6d} symmetry, which show that the effective operator $\hbar\tilde{\lambda}_z S_z J_z$ associated with a pseudo-spin vibration interaction necessarily includes a contribution coming from the rotational terms [6,35]. Also Table 2 and the results in Section 4 show that, within the considered orders of approximation, we may have similar formal effective Hamiltonians whether or not there exists a JT active coordinate. The effective models in Sections 4.2–4.5 and 5.3, 5.4, for which exact analytical expressions for the energies and eigenstates have been obtained, are thus difficult to relate to existing studies of similar systems. The latter are often the result of a numerical diagonalization of Hamiltonian matrices truncated to some v_{max} value and associated with untransformed Hamiltonians such as those presented in Section 3. The few analytical expressions for the energies appearing in the literature are related to A and B-type cases for $E \otimes e$ systems and usually arise from a second order perturbation calculation of the linear and (or) quadratic JT terms. We will thus mainly consider these cases with the zeroth-order models described by $\widetilde{H}^0_{vibr}$ for limiting values of the effective parameters.

We consider first, for $E_r \otimes e_{r'}$ systems admitting an active coordinate, the first order expansions in equations (53, 54, 55, 56, 57) with $\tilde{\lambda}_x = 0$ in (53, 54) and $\tilde{\delta} = 0$ in (55, 56). In all cases, with these assumptions, the eigenvalues reduce to:

$$E^{(0)}_{vibr} = \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(v+1) \pm \hbar\frac{\tilde{\lambda}_z}{4}\ell, \tag{147}$$

all levels being doubly degenerate. This means that we may associate these restricted models with standard ones in which the linear JT term only is included to second order in perturbation theory [4,13,36] (see also Sect. 3.2.2). This leads to

$$\hbar\tilde{\lambda}_0 \approx -2\hbar D\omega = -\frac{V_E^2}{\omega_E^2}, \quad \tilde{\omega}_s \approx \omega_E,$$
$$\hbar\frac{\tilde{\lambda}_z}{4} \approx \mp 2\hbar D\omega = \mp\frac{V_E^2}{\omega_E^2} = \mp\hbar\omega k^2, \tag{148}$$

where the upper (lower) sign corresponds to $r' = 2r$ ($r' = n - 2r(2n - 2r)$); D, V_E and k are the linear coupling constants used in [36], [4] and [11] respectively. We note that contributions to the vibronic energies of the linear JT term, up to sixth order in perturbation theory have recently been reported [37] for molecules in C_{3v} or D_{3h} symmetry; some second order contributions from the quadratic JT effect were also calculated. Within our approach these results may be modeled by an Hamiltonian with eight parameters, involving only terms with

$$\begin{aligned} &{}^{[n_v \, \underset{s}{-} n_v]}\mathcal{V}^{(j_v,\ell_v=0\,A_1)} && j_v \text{ even } n_v \leq 2 \\ &{}^{[n_v \, \underset{s}{-} n_v]}\mathcal{V}^{(j_v,\ell_v=0\,A_2)} && j_v \text{ odd } n_v \leq 3 \end{aligned} \tag{149}$$

in equation (47). The corresponding eigenvalues are easily obtained since there is no vibrational factors with $\ell_v \neq 0$ and no tensor interaction term with E species involved. The eigenbasis is simply $|\pm\rangle|[v\,0]jm\rangle\rangle$ and the eigenvalues are a polynomial in the quantum numbers j (or v) and

$\pm\ell = \mathit{\Lambda}\ell$ which extends (147) (see also (121)):

$$\begin{aligned} E_{v\mathit{\Lambda}\ell} = {} & \hbar\tilde{\lambda}_0 + \hbar\tilde{\omega}_s(v+1) \\ & + \hbar\tilde{\mu}^{(0)}v(v-1) + \hbar\tilde{\mu}^{(2)}[v(v+2) - 3\ell^2] \\ & + \frac{\hbar}{4}\Big\{\tilde{\lambda}_z + \tilde{\lambda}_z^{(1)}(v-1) + \tilde{\lambda}_z^{(2)}(v-1)(v-2) \\ & + \tilde{\lambda}_z^{(3)}[5\ell^2 - 3v(v+2) + 4]/16\Big\}\mathit{\Lambda}\ell. \end{aligned} \tag{150}$$

In addition to the reasons already given at the beginning of this section, the difference between the number of parameters (eight instead of three) is partly due to contributions from cubic and quartic terms in the potential energy neglected in [37]. Although we could relate both sets of parameters we doubt that this would be meaningful. We simply note that including the fourth order contribution from the linear JT coupling changes (148) for these $E \otimes e$ systems to:

$$\begin{aligned} & \hbar\tilde{\lambda}_0 \approx -2\hbar D\omega, \quad \tilde{\omega}_s \approx \omega_E(1 + 2D^2), \\ & \hbar\frac{\tilde{\lambda}_z}{4} \approx \hbar\omega(2D - 8D^2). \end{aligned} \tag{151}$$

As an aside it may be noted that operators in (149) and similar ones of higher orders which lead to an expansion of $\widetilde{\mathcal{H}}_{vibr}$ of the form

$$\widetilde{\mathcal{H}}_{vibr} = \sum_k \{f(N_s)J_z^{2k} + g(N_s)S_z\,J_z^{2k+1}\},$$

where $f(N_s)$ and $g(N_s)$ are polynomials in the oscillator number operator N_s will never raise the degeneracy of A_1, A_2 (or B_1, B_2) sub-levels for A (resp. B) type cases.

Now if we make the assumption that for A and B-type cases we have $\tilde{\lambda}_z = 0$ in the low order expansions (53, 54), the eigenvalues in equations (59, 60) reduce to those obtained from a second order perturbation calculation for the Renner effect [38–41]:

$$\begin{aligned} & {}^{+}E_{jK\pm}/\hbar = \tilde{\lambda}_0 + \tilde{\omega}_s(v+1) \pm \frac{\tilde{\lambda}_x}{4}[(v+1)^2 - K^2]^{1/2} \\ & {}^{-}E_{j\widetilde{K}\pm}/\hbar = \tilde{\lambda}_0 + \tilde{\omega}_s(v+1) \pm \frac{\tilde{\lambda}_x}{4}[(v+1)^2 - \widetilde{K}^2]^{1/2} \end{aligned} \tag{152}$$

where we introduced the quantum numbers K (resp. $\widetilde{K}$) for A-type (resp. B-type) cases associated with the operators $2\mathit{\Delta}$ (resp. $2\overline{\mathit{\Delta}}$). A similar situation was encountered in (I) and it is known that a zero value of the linear vibronic coupling constant reduces the quadratic $E \otimes e$ system to that of the Renner effect [2,4]. Relating (152) with known expressions [39] gives one additional contribution to the effective parameter $\tilde{\omega}_s$ and a rough estimate for $\tilde{\lambda}_x$:

$$\begin{aligned} & \hbar\tilde{\omega}_s \approx \hbar\omega_E\left(1 - \frac{p^2}{8\hbar^2\omega^2}\right), \quad \hbar\tilde{\lambda}_x \approx \pm 2p \\ & \frac{p}{\hbar\omega_E} = g = \frac{W_E}{\omega_E^2}, \end{aligned} \tag{153}$$

where p, g and W_E are the parameters of quadratic coupling used respectively in [39], [11] and [4]. Although approximate it can be checked that these relations taken with ${}^{+}E_j$ (65) for $j = 0$ and ${}^{+}E_{j-1/2\pm}$ for $j = 1/2$ (69) gives a crossing of the lowest E and A levels for $g = 0.899$ which is close to the value $g = 0.918$ obtained in [11] through a numerical diagonalization of a truncated Hamiltonian matrix. The lowest level being A_1 (resp. A_2) for $\tilde{\lambda}_x < 0$ (resp. $\tilde{\lambda}_x > 0$) in agreement with [41]. For a $G' \otimes e$ system in cubic symmetry the substitution $A_1, A_2 \to E'_1, E'_2$ must be made and for a B-type case ${}^{+}E$ is replaced by ${}^{-}E$ and species A_1, A_2 by B_1, B_2 ones.

When combined, equations (148) (or (151)) and (153) give a rough estimate of our effective parameters in the zeroth-order models (53, 54) for A-B cases and for systems admitting an active coordinate only. We doubt that these correlations apply for arbitrary values of the effective parameters in the energy expressions determined by equations (59) and (60). Still more work should be done to give a precise physical meaning to those appearing in the extended models (Eqs. (107–112)) and for cases when the $e_{r'}$ mode is not associated with an active coordinate. The same apply to C-D and X models solved in Sections 4.3, 4.4 and their modified forms in Sections 4.5.2 and 4.5.3.

7 Conclusion

Assuming in first approximation the existence of electronic $\mathcal{A}_e$ and vibrational $\mathcal{A}_v$ invariance algebras allows to build complete sets of electronic and vibrational operators, their matrix elements being calculated within appropriate symmetry adapted bases. One may next build effective vibronic Hamiltonians the form of which depends upon additional physical assumptions.

In this series of two papers this approach has been applied to JT dynamical systems of the $E \otimes e$ type for arbitrary molecular point symmetry group G and to $G' \otimes e$ systems in cubic symmetry. Our main concern has been in the study of exactly solvable models which, besides the common invariants of the invariance algebras, include vibronic interaction operators the characteristics of which are mainly determined, for a given molecular point group, by the symmetry of the vibrational mode. We thus obtained new analytical expressions for the energies and corresponding eigenstates for models including several vibronic interaction parameters. Even the simplest of these models account for a possible ground-state crossover for some of these systems.

In a future work we will show that for symmetric top molecules one may also introduce some rovibronic interaction operators while keeping the exact solvability. We also look at further extensions to other $\mathit{\Gamma}_e \otimes \gamma_v$ systems as well as to situations in which spin-orbit interactions are present.

Table A.1. Conventions for groups in $G_{(I)}$.

G	X	Y	r	ψ
D_n	C_n^z	$C_2'(Ox)$	$1 \dots \frac{n-1}{2}$ n odd $1 \dots \frac{n}{2} - 1$ n even	$\frac{2\pi}{n}$
C_{nv}	C_n^z	$\sigma_v(Ox)$	$1 \dots \frac{n-1}{2}$ n odd $1 \dots \frac{n}{2} - 1$ n even	$\frac{2\pi}{n}$
D_{nd} (n even)	S_{2n}^z	$C_2'(Ox)$	$1 \dots n-1$	$\frac{\pi}{n}$
O	$C_{3(1,1,1)}$	C_4^z	1	$\frac{2\pi}{3}$
T_d	$C_{3(1,1,1)}$	$S_4^{z\,3}$	1	$\frac{2\pi}{3}$

Appendix A: Summary of previous results

A.1 Classification of point groups

The various point groups admitting integer E-type *irrep* are separated into three categories:

- groups in $G_{(I)}$ are finite subgroups of $O(3)$ of rank two. We have thus the groups D_n, C_{nv}, D_{nd} (n even), O and T_d with generators, denoted X and Y, characterized by an angle ψ;
- groups in $G_{(II)}$ are direct product groups of an element in $G_{(I)}$ with C_s or C_I thus introducing a third generator Z whose matrix representative is always of the form:
$$D^{(E_{r\alpha})}(Z) = \pm \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \tag{A.1}$$
- groups in $G_{(III)}$ are $C_{\infty v}$ and $D_{\infty h}$ and not considered in this paper.

The chosen X, Y, Z elements, the appropriate angle ψ, the possible r and α values are given, for groups in $G_{(I)}$ and $G_{(II)}$, in Tables A.1 and A.2.

A.2 Conventions for generic su(2) states and operators

For an arbitrary $su(2)$ algebra with generators $\{J_z, J_\pm\}$ satisfying $[J_z, J_\pm] = \pm J_\pm$, $[J_+, J_-] = 2J_z$, our conventions for $su(2) \supset so(2)$ covariant states read:

$$\begin{aligned} J_z \; |\{\gamma\}jm\rangle\rangle &= -m \; |\{\gamma\}jm\rangle\rangle, \qquad m : -j, \cdots, j \\ J_\pm \; |\{\gamma\}jm\rangle\rangle &= -[(j \pm m)(j \mp m + 1)]^{1/2} \; |\{\gamma\}jm \mp 1\rangle\rangle. \end{aligned} \tag{A.2}$$

Likewise covariant components of irreducible tensor operators, with rank k, ${}^{\{\kappa\}}T_q^{(k)}$ satisfy:

$$\begin{aligned} [J_z, \; {}^{\{\kappa\}}T_q^{(k)}] &= -q \; {}^{\{\kappa\}}T_q^{(k)} \\ [J_\pm, \; {}^{\{\kappa\}}T_q^{(k)}] &= -[(k \pm q)(k \mp q + 1)]^{1/2} \; {}^{\{\kappa\}}T_{q\mp1}^{(k)}. \end{aligned} \tag{A.3}$$

In equations (A.2, A.3) the indices $\{\gamma\}$ and $\{\kappa\}$ refer to all additional labels needed to fully specify states and operators, including those which may appear when higher algebras are introduced.

Table A.2. Conventions for groups in $G_{(II)}$.

G	Z	α	sign (Eq. (A.1))
$D_{nh} = D_n \times C_s$ (n odd)	σ_h	$'$ $''$	$+$ $-$
$D_{nh} = D_n \times C_i$ (n even)	I	g u	$+$ $-$
$D_{nd} = D_n \times C_i$ (n odd)	I	g u	$+$ $-$
$O_h = O \times C_i$	I	g u	$+$ $-$

A.3 u(2) algebras for $\mathbf{E_r \otimes e_{r'}}$ systems

In a previous work [22] we showed that a full treatment of doubly degenerate vibrational modes, as well as orbital doublets, can be performed starting from a Schwinger realization of an $u(2)$ algebra. This comes from the fact that symmetrized powers $E^{\otimes n}$ of E species in common point groups span an *irrep* $[n\,0]$ of $u(2)$ with $n = 2j$.

Within the standard $u(2)_i \supset su(2)_i \supset so(2)_i$ ($i = e, v$) chains the basis states are thus labeled $|[n\,0]jm_i\rangle\rangle$ with $n = 1$, $j = 1/2$ for an E_r electronic state and we set $n = v$ for the vibrational states associated with an $e_{r'}$ mode. Symmetry adapted states

$$|[n\,0]j\;\ell_i\Gamma_i\sigma_i\rangle\rangle = \sum_{m_i} \; {}^{[n\,0]}G^{\;m_i}_{\ell_i\Gamma_i\sigma_i} \; |[n\,0]jm_i\rangle\rangle,$$

have been built in three orientations of which only two are used in this paper. The corresponding algebraic chains are denoted $u(2)_i \supset su^*(2)_i \supset G$ where the notation $su^*(2)$ is used to emphasize that we deal with a non canonical symmetry adaptation. In orientation I the matrices $D^{(E)}(R)$ ($R \in G$) for E-type *irreps* are real with, for the generators X and Y:

$$D^{(E_r)}(X) = \begin{pmatrix} \cos r\psi & \sin r\psi \\ -\sin r\psi & \cos r\psi \end{pmatrix}, \quad D^{(E_r)}(Y) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

In orientation II they are complex with:

$$D^{(E_r)}(X) = \begin{pmatrix} e^{-ir\psi} & 0 \\ 0 & e^{ir\psi} \end{pmatrix}, \quad D^{(E_r)}(Y) = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$$

and the notation $\bar{\sigma}_i$, instead of σ_i, is used for the kets and tensors components.

General tensor operators ${}^{[m_1\,-m_2]}\mathcal{T}^{(k)}$, where $[m_1 - m_2]$ is an $u(2)$ label, have been built[1] and their matrix elements computed in the previously described bases. We recall below the main results needed in this paper.

---

[1] In Appendix B of [22] in D_{6d} for the E_5 *irrep* the $\mu(\ell)$ factors must be replaced by their conjugate for E_2 and E_4 symmetries.

Table A.3. $E_k \subset [E_r]^2$ for groups in $G_{(I)}$.

E_k	D_{2p+1} C_{2p+1v} T_d, O	D_{2p} C_{2pv}	D_{2pd}	Case
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)

A.3.1 u(2)$_\mathsf{e}$ for E$_\mathsf{r}$ electronic states

The standard components of the electronic operators are:

$$\begin{aligned} &{}^{[1\,-1]}\mathcal{E}^{(0)}_{0} = (N_1 + N_2)/\sqrt{2}, \quad {}^{[1\,-1]}E^{(1)}_{0} = -iS_z, \\ &{}^{[1\,-1]}E^{(1)}_{1} = iS_-/\sqrt{2}, \quad {}^{[1\,-1]}E^{(1)}_{-1} = -iS_+/\sqrt{2} \end{aligned} \tag{A.4}$$

where the notation S_z, $S_\pm$ is used for the pseudo-spin electronic operators spanning the $su(2)_e$ algebra; $N_1 + N_2$ is the $u(2)_e$ linear invariant. Within the $u(2)_e \supset su(2)_e \supset so(2)_e$ orientation their matrix representatives are given by:

$$\begin{aligned} &{}^{[1\,-1]}\widehat{E}^{(1)}_{1} = -\frac{i}{\sqrt{2}}\,\hat{\sigma}_+, \quad {}^{[1\,-1]}\widehat{E}^{(1)}_{-1} = \frac{i}{\sqrt{2}}\,\hat{\sigma}_- \\ &{}^{[1\,-1]}\widehat{E}^{(1)}_{0} = \frac{i}{2}\,\hat{\sigma}_z, \quad {}^{[1\,-1]}\widehat{\mathcal{E}}^{(0)} = \frac{1}{\sqrt{2}}\,\hat{\sigma}_0 \end{aligned} \tag{A.5}$$

where $\hat{\sigma}_\alpha$ ($\alpha = x, y, z$), $\hat{\sigma}_\pm = (\hat{\sigma}_x \pm i\hat{\sigma}_y)/2$ are the usual Pauli matrices and $\hat{\sigma}_0$ is the two dimensional identity matrix.

- *The $u(2)_e \supset su^*(2)_e \supset G$ chain with orientation I*

For a given E_r electronic state the possible E_k *irrep* appearing in the symmetrized product $[E_r \times E_r]$ are summarized in Table A.3 for groups in $G_{(I)}$. Setting $\eta = i\mu(2) = 1$ (resp. $\eta = -1$) for a (ii) (resp. (iii)) case, the symmetry adapted generators are then given by

$$\begin{aligned} &{}^{[1\,-1]}E^{(1)}_{0A_2} = -S_z, \quad {}^{[1\,-1]}E^{(1)}_{2E_k1} = S_x, \\ &{}^{[1\,-1]}E^{(1)}_{2E_k2} = -\eta S_y, \end{aligned} \tag{A.6}$$

and their matrix representatives, within the symmetry adapted electronic basis $|[10]\frac{1}{2}E_r\,\sigma\rangle\rangle$ are:

$$\begin{aligned} &{}^{[1\,-1]}\widehat{E}^{(1)}_{2E_k1} = \frac{1}{2}\,\hat{\sigma}_z, \quad {}^{[1\,-1]}\widehat{E}^{(1)}_{2E_k2} = \frac{\eta}{2}\,\hat{\sigma}_x, \\ &{}^{[1\,-1]}\widehat{E}^{(1)}_{0A_2} = \frac{1}{2}\,\hat{\sigma}_y. \end{aligned} \tag{A.7}$$

- *The $u(2)_e \supset su^*(2)_e \supset G$ chain with orientation II*

In a general way the change from orientation I to that called II for E-type species is performed through the unitary transformation

$$\begin{aligned} T^{(E)}_{\bar{1}} &= \frac{i}{\sqrt{2}}(T^{(E)}_{1} + i\,T^{(E)}_{2}), \\ T^{(E)}_{\bar{2}} &= -\frac{i}{\sqrt{2}}(T^{(E)}_{1} - i\,T^{(E)}_{2}), \end{aligned} \tag{A.8}$$

where the quantities denoted T may be tensor operators or states. As a result orientation II is characterized by the fact that, for the electronic states, the symmetrized basis is identical to the standard one's:

$$|[10]\frac{1}{2}E_r\,\bar{\sigma}\rangle\rangle \equiv |[1\,0]\frac{1}{2}m_e\rangle\rangle.$$

The symmetry adapted electronic operators are then:

$$\begin{aligned} &\text{Case (ii)} && \text{Case (iii)} \\ &{}^{[1\,-1]}E^{(1)}_{0A_2} = -S_z, && {}^{[1\,-1]}E^{(1)}_{0A_2} = -S_z, \\ &{}^{[1\,-1]}E^{(1)}_{2E_k\bar{1}} = \frac{i}{\sqrt{2}}\,S_-, && {}^{[1\,-1]}E^{(1)}_{2E_k\bar{1}} = \frac{i}{\sqrt{2}}\,S_+, \\ &{}^{[1\,-1]}E^{(1)}_{2E_{r'}\bar{2}} = -\frac{i}{\sqrt{2}}\,S_+, && {}^{[1\,-1]}E^{(1)}_{2E_k\bar{2}} = -\frac{i}{\sqrt{2}}\,S_-, \end{aligned} \tag{A.9}$$

and their associated matrix representation:

$$\begin{aligned} &\text{Case (ii)} && \text{Case (iii)} \\ &{}^{[1\,-1]}\widehat{E}^{(1)}_{0A_2} = \frac{1}{2}\,\hat{\sigma}_z, && {}^{[1\,-1]}\widehat{E}^{(1)}_{0A_2} = \frac{1}{2}\,\hat{\sigma}_z, \\ &{}^{[1\,-1]}\widehat{E}^{(1)}_{2E_{r'}\bar{1}} = -\frac{i}{\sqrt{2}}\,\hat{\sigma}_+, && {}^{[1\,-1]}\widehat{E}^{(1)}_{2E_{r'}\bar{1}} = -\frac{i}{\sqrt{2}}\,\hat{\sigma}_-, \\ &{}^{[1\,-1]}\widehat{E}^{(1)}_{2E_{r'}\bar{2}} = \frac{i}{\sqrt{2}}\,\hat{\sigma}_-, && {}^{[1\,-1]}\widehat{E}^{(1)}_{2E_{r'}\bar{2}} = \frac{i}{\sqrt{2}}\,\hat{\sigma}_+. \end{aligned} \tag{A.10}$$

A.3.2 u(2)$_\mathsf{v}$ for e$_\mathsf{r'}$ vibrational modes

For a given s vibrational mode with symmetry $E_{r'}$ in G the associated operators are written:

$${}^{[m_1\,-m_2]}_{\quad s}\mathcal{V}^{(j_v)}_{m_v} \quad \text{or} \quad {}^{[m_1\,-m_2]}_{\quad s}\mathcal{V}^{(j_v)}_{\ell_v C_v \sigma_v} = {}^{[m_1\,-m_2]}_{\quad s}\mathcal{V}^{(j_v, \ell_v C_v)}_{\sigma_v},$$

according as one works within chain $u(2)_v \supset su(2)_v \supset so(2)_v$ or $u(2)_v \supset su^*(2)_v \supset G$ with respective bases $|[v\,0]jm\rangle\rangle$ or $|[v\,0]j\,\ell\Gamma_v\sigma_v\rangle\rangle$.

In particular for the $su(2)_v$ generators we keep the notation $\{J_z, J_\pm\}$ and the corresponding symmetry adapted generators in orientation I are given by:

$$\begin{aligned} &{}^{[1\,-1]}V^{(1)}_{0A_2} = -\sqrt{2}J_z, \\ &{}^{[1\,-1]}V^{(1)}_{2E_{k'}1} = \sqrt{2}J_x, \quad {}^{[1\,-1]}V^{(1)}_{2E_{k'}2} = -i\sqrt{2}\mu'(2)J_y \end{aligned} \tag{A.11}$$

where the symmetry $E_{k'}$ is also obtained from Table A.3 in which the substitutions $r \to r'$, $k \to k'$ are made and $\mu'(2) = -i$ (resp. $\mu'(2) = i$) for an (ii) (resp. (iii)) case. Also we note that $J_z = -\frac{1}{2}\,{}_s\ell_z$ where ${}_s\ell_z$ is the doubly degenerate oscillator angular momentum. Other vibrational tensors used in this work are specified where they appear.

Appendix B: Direct products analysis

The analysis of direct products $E_{k_1} \times E_{k_2}$ can be made in a general manner with the results in [21,22]. This is useful for instance for the determination of active coordinates in E-type electronic states as well as to find possible terms in the untransformed vibronic Hamiltonian. The results are detailed below following our classification (Sect. A.1) for molecular point symmetry groups admitting integer E-type *irreps*.

B.1 Groups in $\mathsf{G}_{(\mathsf{I})}$

B.1.1 Groups $\mathsf{D}_{2p+1}, \mathsf{C}_{2p+1v}$

These groups have *irreps* E_k with $k = 1, \cdots p$ and we have ($n = 2p + 1$):
- $k_1 \neq k_2$

$$\begin{aligned} E_{k_1} \times E_{k_2} &= E_{|k_1-k_2|} + E_{k_1+k_2} && k_1 + k_2 \leq p \\ &= E_{|k_1-k_2|} + E_{n-(k_1+k_2)} && p+1 \leq k_1+k_2 \leq 2p \end{aligned}$$

- $k_1 = k_2$

$$\begin{aligned} E_k \times E_k &= A_1 + A_2 + E_{2k} && k \leq p/2 \\ &= A_1 + A_2 + E_{n-2k} && (p+1)/2 \leq k \leq p. \end{aligned}$$

We note the special case of $D_3 \approx C_{3v}$ which admits only one type E *irrep* with $E \times E = A_1 + A_2 + E$.

B.1.2 Groups in $\mathsf{D}_{2p}, \mathsf{C}_{2pv}$

These groups have *irreps* E_k with $k = 1, \cdots p - 1$ and we have ($n = 2p$):
- $k_1 \neq k_2$ and $k_1 + k_2 \neq n/2 = p$

$$E_{k_1} \times E_{k_2} = E_{|k_1-k_2|} + E_{k_1+k_2}$$

for $k_1 + k_2 \leq p - 1$ and

$$E_{k_1} \times E_{k_2} = E_{|k_1-k_2|} + E_{n-(k_1+k_2)}$$

for $p + 1 \leq k_1 + k_2 \leq 2p - 2$.
- Special case $k_1 \neq k_2$ and $k_1 + k_2 = n/2 = p$

$$E_{k_1} \times E_{k_2} = B_1 + B_2 + E_{|k_1-k_2|}$$

- $k_1 = k_2$ and p odd

$$\begin{aligned} E_k \times E_k &= A_1 + A_2 + E_{2k} && k \leq (p-1)/2 \\ &= A_1 + A_2 + E_{n-2k} && (p+1)/2 \leq k \leq p - 1 \end{aligned}$$

- $k_1 = k_2$ and p even

$$\begin{aligned} E_k \times E_k &= A_1 + A_2 + E_{2k} && k < p/2 \\ &= A_1 + A_2 + B_1 + B_2 && k = p/2 \\ &= A_1 + A_2 + E_{n-2k} && p/2 < k \leq p - 1. \end{aligned}$$

We have the special case of $D_4 \approx C_{4v}$ which admits only one type E *irrep* with $E \times E = A_1 + A_2 + B_1 + B_2$.

B.1.3 Groups $\mathsf{D}_{\mathsf{nd}} = \mathsf{D}_{\mathsf{2pd}}$

These groups have *irreps* E_k with $k = 1, \cdots 2p - 1$ and we have ($n = 2p$):
- $k_1 \neq k_2$ and $k_1 + k_2 \neq n = 2p$

$$E_{k_1} \times E_{k_2} = E_{|k_1-k_2|} + E_{k_1+k_2}$$

for $k_1 + k_2 \leq n - 1$ and

$$E_{k_1} \times E_{k_2} = E_{|k_1-k_2|} + E_{2n-(k_1+k_2)}$$

for $n + 1 \leq k_1 + k_2 \leq 2n - 2$.
- Special case $k_1 \neq k_2$ and $k_1 + k_2 = n = 2p$

$$E_{k_1} \times E_{k_2} = B_1 + B_2 + E_{|k_1-k_2|}$$

- $k_1 = k_2$

$$\begin{aligned} E_k \times E_k &= A_1 + A_2 + E_{2k} && k < p \\ &= A_1 + A_2 + B_1 + B_2 && k = p \\ &= A_1 + A_2 + E_{2n-2k} && p < k \leq 2p - 1. \end{aligned}$$

We have the special case of D_{2d} which admits only one type E *irrep* with $E \times E = A_1 + A_2 + B_1 + B_2$.

B.1.4 Cubic groups O, T_d

We have only one E *irrep* with $E \times E = A_1 + A_2 + E$ as in $D_3 \approx C_{3v}$.

B.2 Groups in $\mathsf{G}_{(\mathsf{II})}$

- $D_{2p+1\,h} = D_{2p+1} \times C_s$

$$E_{k_1\alpha} \times E_{k_2\beta} = \sum_i C_{i\gamma}$$

with C_i as given in Section B.1.1 and $\alpha \times \beta = \gamma$, the indices α, β being of type $'$ or $''$.
- $D_{2p\,h} = D_{2p} \times C_i$

$$E_{k_1\alpha} \times E_{k_2\beta} = \sum_i C_{i\gamma}$$

with C_i as given in Section B.1.2 and $\alpha \times \beta = \gamma$, the indices α, β being of type g or u.
- $D_{2p+1d} = D_{2p+1} \times C_i$

$$E_{k_1\alpha} \times E_{k_2\beta} = \sum_i C_{i\gamma}$$

with C_i as given in Section B.1.1 and $\alpha \times \beta = \gamma$, the indices α, β being of type g or u.
- $O_h = O \times C_i$

$$E_\alpha \times E_\beta = A_{1\gamma} + A_{2\gamma} + E_\gamma$$

$\alpha \times \beta = \gamma$, the indices α, β being of type g or u.

B.3 Groups in $\mathrm{G}_{(\mathrm{III})}$

- $C_{\infty v}$

$$\begin{aligned} E_{k_1} \times E_{k_2} &= E_{|k_1-k_2|} + E_{k_1+k_2} && k_1 \neq k_2 \\ &= A_1 + A_2 + E_{2k} && k_1 = k_2 = k \\ &= \Sigma^+ + \Sigma^- + E_{2k} \end{aligned}$$

- $D_{\infty h}$

$$\begin{aligned} E_{k_1\alpha} \times E_{k_2\beta} = &= E_{|k_1-k_2|\gamma} + E_{(k_1+k_2)\gamma} && k_1 \neq k_2 \\ &= A_{1\gamma} + A_{2\gamma} + E_{2k\gamma} && k_1 = k_2 = k \\ &= \Sigma^+_\gamma + \Sigma^-_\gamma + E_{2k\gamma} \end{aligned}$$

$\alpha \times \beta = \gamma$, the indices α, β being of type g or u.

In all cases we have for products involving one dimensional *irreps*

$$A_i \times E_r = E_r \quad \text{or} \quad A_{i\alpha} \times E_{r\beta} = E_{r\gamma}$$

and when n is even

$$B_i \times E_r = E_{\frac{n}{2}-r} \quad \text{or} \quad B_{i\alpha} \times E_{r\beta} = E_{(\frac{n}{2}-r)\gamma}$$

and $B_i \times E_r = E_{n-r}$ for D_{nd} (n even) groups.

Appendix C: Matrix elements

We give below matrix elements for an arbitrary vibronic operator which may appear in an effective rovibronic Hamiltonian or in transition moments for an $E_r \otimes e_{r'}$ JT system. We set for the coupled vibronic basis states

$$|\Psi_{vibr}\rangle = |[1\,0]\frac{1}{2}1E_r; [v\,0]j\ell\Gamma_v; \Gamma_{ev}\sigma_{ev}\rangle\rangle,$$

and we use the simplified notation

$$\mathcal{O}^{(C_{ev})} = [E^{(C_e)} \times {}^{[m_1\ -m_2]}_{\quad s}\mathcal{V}^{(j_v,\ell_v\,C_v)}]^{(C_{ev})},$$

for the vibronic operators. The vibrational operators associated with the doubly degenerate $e_{r'}$ mode are those defined in [22]. The Wigner-Eckart theorem leads to

$$\begin{aligned} \langle\Psi'_{vibr}|\mathcal{O}^{(C_{ev})}_{\theta_{ev}}|\Psi_{vibr}\rangle &= ([\Gamma_{ev}][C_{ev}])^{\frac{1}{2}} F \begin{array}{ccc} \theta_{ev} & \sigma_{ev} & (\Gamma'_{ev})* \\ (C_{ev} & \Gamma_{ev}) & \sigma'_{ev} \end{array} \\ &\times \begin{Bmatrix} C_e & E_r & E_r \\ C_v & \Gamma_v & \Gamma'_v \\ C_{ev} & \Gamma_{ev} & \Gamma'_{ev} \end{Bmatrix} \left([1\,0]\frac{1}{2}1E_r||E^{(C_e)}||[1\,0]\frac{1}{2}1E_r\right) \\ &\times([v'\,0]j'\ell'\Gamma'_v||{}^{[m_1\ -m_2]}_{\quad s}\mathcal{V}^{(j_v,\ell_v\,C_v)}||[v\,0]j\ell\Gamma_v). \qquad (C.1) \end{aligned}$$

This expression can be used in any of the orientations defined in [22], the Clebsch-Gordan coefficients being chosen accordingly.

Special cases

- $E^{(C_e)} = I_e^{(A_1)}$ that is for purely vibrational operators (C.1) reduces to

$$\begin{aligned} \langle\Psi'_{vibr}|\mathcal{O}^{(C_{ev})}_{\theta_{ev}}|\Psi_{vibr}\rangle &= \delta_{C_v,C_{ev}}(-1)^{C_v+\Gamma_{ev}+\Gamma'_v} \\ &\times([\Gamma_{ev}])^{\frac{1}{2}} F \begin{array}{ccc} \theta_{ev} & \sigma_{ev} & (\Gamma'_{ev})* \\ (C_{ev} & \Gamma_{ev}) & \sigma'_{ev} \end{array} \begin{Bmatrix} \Gamma'_{ev} & \Gamma'_v & E_r \\ \Gamma_v & \Gamma_{ev} & C_v \end{Bmatrix} \\ &\times([v'\,0]j'\ell'\Gamma'_v||{}^{[m_1\ -m_2]}_{\quad s}\mathcal{V}^{(j_v,\ell_v\,C_v)}||[v\,0]j\ell\Gamma_v)\,. \qquad (C.2) \end{aligned}$$

- Vibronic scalar operators as considered in this paper are characterized by $C_{ev} = A_1$ hence $C_v = C_e$ which gives

$$\begin{aligned} \langle\Psi'|\mathcal{O}^{(A_1)}|\Psi\rangle &= \delta_{\Gamma'_{ev},\Gamma_{ev}}\delta_{\sigma'_{ev},\sigma_{ev}}[C_e]^{-\frac{1}{2}}(-1)^{\Gamma_{ev}+\Gamma_v+C_e} \\ &\times \begin{Bmatrix} \Gamma'_v & E_r & \Gamma_{ev} \\ E_r & \Gamma_v & C_e \end{Bmatrix} \left([1\,0]\frac{1}{2}1E_r||E^{(C_e)}||[1\,0]\frac{1}{2}1E_r\right) \\ &\times([v'\,0]j'\ell'\Gamma'_v||{}^{[m_1\ -m_2]}_{\quad s}\mathcal{V}^{(j_v,\ell_v\,C_e)}||[v\,0]j\ell\Gamma_v). \qquad (C.3) \end{aligned}$$

For those used in this work we have in addition $m_1 = m_2 = n_v$ which leads to the additional $v' = v$, $j' = j$ selection rules. Reduced matrix elements for the vibrational operators may be obtained as described in [22]. Those for the electronic operators are given below for cases (ii) ($\eta = +1$) and (iii) ($\eta = -1$)

$$\begin{aligned} &([1\,0]\tfrac{1}{2}1E_r||{}^{[1\,-1]}E^{(1,0A_2)}||[1\,0]\tfrac{1}{2}1E_r) = i/\sqrt{2}\ \forall\, r \\ &([1\,0]\tfrac{1}{2}1E_r||{}^{[1\,-1]}E^{(1,2E_k)}||[1\,0]\tfrac{1}{2}1E_r) = \eta. \end{aligned}$$

- Vibronic matrix elements for $E \otimes e$ and $G' \otimes e$ systems in cubic molecules.

For an $E \otimes e$ case in cubic symmetry the matrix elements are those given by the preceding equations with $E_r = E$ and $\eta = -1$. For vibronic operators associated with a $G' \otimes e$ case we only consider below those built with the algebraic chain (9) for the electronic operators. For the coupled vibronic basis we set

$$\begin{aligned} &|[1\dot{0}], [10]\frac{1}{2}1E, [10]\frac{1}{2}E'_1; [v\,0]j\ell\Gamma_v; \Gamma_{ev}, E'_1; \Lambda_{ev}\lambda_{ev}\rangle\rangle = \\ &\quad |\{\gamma_e\}E, E'_1; [v\,0]j\ell\Gamma_v; \Gamma_{ev}, E'_1; \Lambda_{ev}\lambda_{ev}\rangle\rangle = |\Psi_{vibr}\rangle \qquad (C.4) \end{aligned}$$

with the implied $(E \times \Gamma_v)\Gamma_{ev}$ and $(\Gamma_{ev} \times E'_1)\Lambda_{ev}$ coupling schemes. The vibronic operators are built following the same coupling scheme:

$$\begin{aligned} \mathcal{O}^{(C)} = [&E^{([\lambda_1\mu_1]k_1,\ell_1C_e\ ,\ [\lambda_2\mu_2]k_2C'_e)} \\ &\times {}^{[m_1\ -m_2]}_{\quad s}\mathcal{V}^{(j_v,\ell_v\,C_v;A_1)}]^{(C_{ev},k_2C'_e)(C)}. \end{aligned}$$

The Wigner-Eckart theorem for double tensors [31,42] leads then to

$$\begin{aligned} \langle\Psi'_{vibr}|\mathcal{O}^{(C)}_{\theta_{ev}}|\Psi_{vibr}\rangle &= ([\Lambda_{ev}][C])^{\frac{1}{2}}\sum_\beta {}_\beta F \begin{array}{ccc} \theta_{ev} & \lambda_{ev} & (\Lambda'_{ev})* \\ (C & \Lambda_{ev}) & \lambda'_{ev} \end{array} \\ &\times([\Gamma'_{ev}][\Gamma_{ev}][C_{ev}])^{\frac{1}{2}} \begin{Bmatrix} C_{ev} & C'_e & C \\ \Gamma_{ev} & E'_1 & \Lambda_{ev} \\ \Gamma'_{ev} & E'_1 & \Lambda'_{ev} \end{Bmatrix}_\beta \begin{Bmatrix} C_e & E & E \\ C_v & \Gamma_v & \Gamma'_v \\ C_{ev} & \Gamma_{ev} & \Gamma'_{ev} \end{Bmatrix} \\ &\times(\{\gamma_e\}E, E'_1||E^{([\lambda_1\mu_1]k_1,\ell_1C_e,\ [\lambda_2\mu_2]k_2C'_e)}||\{\gamma_e\}E, E'_1) \\ &\times([v'\,0]j'\ell'\Gamma'_v||{}^{[m_1\ -m_2]}_{\quad s}\mathcal{V}^{(j_v,\ell_v\,C_v)}||[v\,0]j\ell\Gamma_v), \qquad (C.5) \end{aligned}$$

where β is a multiplicity index for the product $C \times \Lambda_{ev}$. We note two special cases. Firstly when $C'_e = A_1$, hence $C = C_{ev}$, as discussed in Section 5.3 for which we have for (C.5):

$$\langle \Psi'_{vibr}|\mathcal{O}^{(C_{ev})}_{\theta_{ev}}|\Psi_{vibr}\rangle = \frac{1}{\sqrt{2}}\,(-1)^{C_{ev}+E'_1+\varLambda'_{ev}+\varGamma_{ev}}$$
$$\times([\varLambda_{ev}][C_{ev}][\varGamma'_{ev}][\varGamma_{ev}])^{\frac{1}{2}}\,F^{\;\theta_{ev}\quad\lambda_{ev}\quad(\varLambda'_{ev})*}_{(C_{ev}\;\varLambda_{ev})\quad\lambda'_{ev}}$$
$$\times\begin{Bmatrix}\varGamma'_{ev} & \varGamma_{ev} & C_{ev}\\ \varLambda_{ev} & \varLambda'_{ev} & E'_1\end{Bmatrix}\begin{Bmatrix}C_e & E & E\\ C_v & \varGamma_v & \varGamma'_v\\ C_{ev} & \varGamma_{ev} & \varGamma'_{ev}\end{Bmatrix}$$
$$\times(\{\gamma_e\}E,E'_1||E^{([\lambda_1\mu_1]k_1,\ell_1C_e,\;[00]0A_1)}||\{\gamma_e\}E,E'_1)$$
$$\times([v'\,0]j'\ell'\varGamma'_v||^{[m_1\;\underset{s}{-}m_2]}\mathcal{V}^{(j_v,\ell_v\,C_v)}||[v\,0]j\ell\varGamma_v). \quad (C.6)$$

Although this expression hides somewhat the equivalence of both systems (Eq. (C.1) with $E_r = E$) it can be recovered if one notes that in fact the basis (C.4) we used and that defined by

$$|\varPsi_{vibr}\rangle = |[1\dot{0}],[10]\frac{1}{2}1E,[10]\frac{1}{2}E'_1\bar{\sigma}'_e;[v\,0]j\ell\varGamma_v;\varGamma_{ev}\sigma_{ev}\rangle\rangle$$

are identical due to the properties (11) and the values

$$F^{\;\;\bar{\sigma}'_e\quad(\varLambda_{ev})}_{(A_1\;E'_1)\quad\lambda_{ev}} = \delta_{\varLambda_{ev},E'_1}\,\delta_{\lambda_{ev},\bar{\sigma}'_e}, \quad (C.7)$$

$$F^{\;\;\bar{\sigma}'_e\quad(\varLambda_{ev})}_{(A_2\;E'_1)\quad\lambda_{ev}} = \delta_{\varLambda_{ev},E'_2}\,\delta_{\lambda_{ev},\bar{\sigma}'_e}, \quad (C.8)$$

of the Clebsch-Gordan coefficients of O^S [20,32]. Secondly for scalar vibronic operators as considered in this paper $C = C_{ev} = A_1$ equations (C.5, C.6) give

$$\langle \varPsi'_{vibr}|\mathcal{O}^{(A_1)}|\varPsi_{vibr}\rangle = \delta_{\varLambda'_{ev},\varLambda_{ev}}\delta_{\lambda'_{ev},\lambda_{ev}}\delta_{\varGamma'_{ev},\varGamma_{ev}}[C_e]^{-\frac{1}{2}}$$
$$\times(-1)^{C_e+\varGamma_{ev}+\varGamma_v}\,\frac{1}{\sqrt{2}}\begin{Bmatrix}\varGamma'_v & E & \varGamma_{ev}\\ E & \varGamma_v & C_e\end{Bmatrix}$$
$$\times(\{\gamma_e\}E,E'_1||E^{([\lambda_1\mu_1]k_1,\ell_1C_e\;,\;[00]0A_1)}||\{\gamma_e\}E,E'_1)$$
$$\times([v'\,0]j'\ell'\varGamma'_v||^{[m_1\;\underset{s}{-}m_2]}\mathcal{V}^{(j_v,\ell_v\,C_v)}||[v\,0]j\ell\varGamma_v). \quad (C.9)$$

The reduced matrix elements of electronic operators are given by:

$k_1\ell_1C_e$	; $k_2C'_e$	$r.m.e$
$1,0A_2$	; $0A_1$	i
$1,2E$	; $0A_1$	$-\sqrt{2}$
$0,0A_1$	; $1F_1$	$i\sqrt{3}$
$1,0A_2$	; $1F_1$	$-\sqrt{3}$
$1,2E$	; $1F_1$	$-i\sqrt{6}$

Appendix D: Symmetrized vibronic eigenstates for $^{\pm}\widetilde{\mathrm{H}}_{\mathrm{vibr}}$

D.1 $\mathrm{C_{3v}, D_3, D_{3h}, D_{3d}, O, T_d, O_h}$

For these groups we have only one $E\otimes e$ or $E_\alpha\times e_\beta$ system of A-type. Table 3 is used with $r = 1$ together with the matrices for the E type *irreps* in orientation II. The symmetry adapted eigenstates denoted

$$|[1\,0]\frac{1}{2}1E;[v\,0]j;\varOmega_\pm,\varGamma_{ev}\bar{\sigma}_{ev}\rangle\rangle,$$

are listed below in terms of those defined in equations (62–64) taking into account the relation $\ell = 2|m|$. All phases have been chosen so that under time reversal

$$\mathcal{K}|[1\,0]\frac{1}{2}1E;[v\,0]j;\varOmega_\pm,\varGamma_{ev}\bar{\sigma}_{ev}\rangle\rangle =$$
$$|[1\,0]\frac{1}{2}1E;[v\,0]j;\varOmega_\pm,\varGamma_{ev}-\bar{\sigma}_{ev}\rangle\rangle, \quad (D.1)$$

with for E *irreps* $-\bar{1} = \bar{2}$ and conversely.

- $\ell = 3p, 3p+1$

$$|[1\,0]\frac{1}{2}1E;[v\,0]j;\varOmega_+,E\bar{1}\rangle\rangle = i^{2j}\;{}^+\widetilde{\varPsi}^{(i)}_{jm+}$$
$$|[1\,0]\frac{1}{2}1E;[v\,0]j;\varOmega_+,E\bar{2}\rangle\rangle = i^{-2j}\;{}^+\widetilde{\varPsi}^{(i')}_{jm+}$$
$$|[1\,0]\frac{1}{2}1E;[v\,0]j;\varOmega_-,E\bar{1}\rangle\rangle = i^{2j}\;{}^+\widetilde{\varPsi}^{(i)}_{jm-}$$
$$|[1\,0]\frac{1}{2}1E;[v\,0]j;\varOmega_-,E\bar{2}\rangle\rangle = -i^{-2j}\;{}^+\widetilde{\varPsi}^{(i')}_{jm-} \quad (D.2)$$

with $(i,i') = (1,2)$ (resp. $(i,i') = (2,1)$) for $\ell = 3p$ (resp. $\ell = 3p+1$).

- $\ell = 3p+2$

$$|[1\,0]\frac{1}{2}1E;[v\,0]j;\varOmega_\pm,A_1\rangle\rangle =$$
$$i^{2j+1}(\;{}^+\widetilde{\varPsi}^{(1)}_{jm\pm}\mp(-1)^{2j}\;{}^+\widetilde{\varPsi}^{(2)}_{jm\pm})/\sqrt{2}$$
$$|[1\,0]\frac{1}{2}1E;[v\,0]j;\varOmega_\pm,A_2\rangle\rangle =$$
$$i^{2j}(\;{}^+\widetilde{\varPsi}^{(1)}_{jm\pm}\pm(-1)^{2j}\;{}^+\widetilde{\varPsi}^{(2)}_{jm\pm})/\sqrt{2}. \quad (D.3)$$

For $E_\alpha\times e_\beta$ systems in D_{3h}, D_{3d}, O_h the additional τ label in $\varGamma_{ev}$ is determined according to the rule given in equation (68).

We underline that the values $\ell = 3p, 3p+1, 3p+2$ correspond to the absolute values $(3p+1)/2$, $(3p+2)/2$, $(3p+3)/2$ respectively of the eigenvalues of the $\varDelta$ operator.

- The symmetrized eigenstates built from the uncoupled states associated with the eigenvalue ${}^+E_j$ (65) are given by:

$$|[1\,0]\tfrac{1}{2}1E;[v\,0]j;{}^+E_j,E\bar{\sigma}\rangle\rangle = i^{2j}|[1\,0]\tfrac{1}{2}1E\bar{1}\rangle\rangle|[v\,0]jj\rangle\rangle$$
$$|[1\,0]\tfrac{1}{2}1E;[v\,0]j;{}^+E_j,E-\bar{\sigma}\rangle\rangle = i^{-2j}|[1\,0]\tfrac{1}{2}1E\bar{2}\rangle\rangle|[v\,0]j-j\rangle\rangle \quad (D.4)$$

where $(\bar{\sigma},-\bar{\sigma}) = (\bar{1},\bar{2})$ (resp. $(\bar{2},\bar{1})$) for $2j = v = 3p$ (resp. $2j = v = 3p+1$). For $2j = v = 3p+2$ we find

$$|[1\,0]\frac{1}{2}1E;[v\,0]j;{}^+E_j,A_1\rangle\rangle = i^{2j+1}\Big\{|[1\,0]\frac{1}{2}1E\bar{1}\rangle\rangle|[v\,0]jj\rangle\rangle$$
$$-(-1)^{2j}|[1\,0]\frac{1}{2}1E\bar{2}\rangle\rangle|[v\,0]j-j\rangle\rangle\Big\}/\sqrt{2}$$
$$|[1\,0]\frac{1}{2}1E;[v\,0]j;{}^+E_j,A_2\rangle\rangle = i^{2j}\Big\{|[1\,0]\frac{1}{2}1E\bar{1}\rangle\rangle|[v\,0]jj\rangle\rangle$$
$$+(-1)^{2j}|[1\,0]\frac{1}{2}1E\bar{2}\rangle\rangle|[v\,0]j-j\rangle\rangle\Big\}/\sqrt{2}. \quad (D.5)$$

D.2 Symmetrized eigenstates for $\mathbf{G' \otimes e}$

As shown in Section 5.3 to each unsymmetrized eigenstate ${}^{+}\widetilde{\varPsi}^{(i)}_{jm\pm}$ of ${}^{+}\widetilde{H}_{vibr}$ for an $E \otimes e$ system are associated two, also unsymmetrized, eigenstates ${}^{+}\widetilde{\varPsi}^{(i)(\pm)}_{jm\pm}$ for $G' \otimes e$. The upper $(\pm)$ indices refer to the eigenvalues of the third component of the pseudo-spin $\overrightarrow{\varSigma}$ operator and are also symmetry labels with the correspondences $+ \rightarrow E'_1\bar{1}$ and $- \rightarrow E'_1\bar{2}$. The symmetrized eigenstates for $G' \otimes e$ denoted

$$|[1\dot{0}],[1\,0]\frac{1}{2}1E,[1\,0]\frac{1}{2}E'_1;[v\,0]j;\varOmega_\pm,\varGamma_{ev}\bar{\sigma}_{ev}\rangle\rangle \equiv$$

$$|[1\dot{0}],[1\,0]\frac{1}{2},[1\,0]\frac{1}{2};[v\,0]j;\varOmega_\pm,\varGamma_{ev}\bar{\sigma}_{ev}\rangle\rangle$$

$$\equiv |\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_\pm,\varGamma_{ev}\bar{\sigma}_{ev}\rangle\rangle,$$

can be deduced from the corresponding ones for an $E \otimes e$ case in the following way. From the property

$$\varphi^{(E)}_{\bar{\sigma}_1}\chi^{(E'_1)}_{\bar{\sigma}_2} \equiv [\varphi^{(E)} \times \chi^{(E'_1)}]^{(G')}_{\bar{\sigma}} \quad \forall\ \varphi,\chi,$$

associated with equation (11) and the basis kets order in (130) we obtain first the states with $\varGamma_{ev} = G'$ from those in equation (D.2):

- $\ell = 3p, 3p+1$

$$\begin{aligned}
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_+,G'\bar{1}\rangle\rangle = i^{2j}\ {}^{+}\widetilde{\varPsi}^{(i)(+)}_{jm+}\\
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_+,G'\bar{2}\rangle\rangle = i^{-2j}\ {}^{+}\widetilde{\varPsi}^{(i')(+)}_{jm+}\\
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_+,G'\bar{3}\rangle\rangle = i^{2j}\ {}^{+}\widetilde{\varPsi}^{(i)(-)}_{jm+}\\
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_+,G'\bar{4}\rangle\rangle = i^{-2j}\ {}^{+}\widetilde{\varPsi}^{(i')(-)}_{jm+}\\
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_-,G'\bar{1}\rangle\rangle = i^{2j}\ {}^{+}\widetilde{\varPsi}^{(i)(+)}_{jm-}\\
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_-,G'\bar{2}\rangle\rangle = -i^{-2j}\ {}^{+}\widetilde{\varPsi}^{(i')(+)}_{jm-}\\
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_-,G'\bar{3}\rangle\rangle = i^{2j}\ {}^{+}\widetilde{\varPsi}^{(i)(-)}_{jm-}\\
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_-,G'\bar{4}\rangle\rangle = -i^{-2j}\ {}^{+}\widetilde{\varPsi}^{(i')(-)}_{jm-} \qquad \text{(D.6)}
\end{aligned}$$

with $(i,i') = (1,2)$ (resp. $(i,i') = (2,1)$) for $\ell = 3p$ (resp. $\ell = 3p+1$).

Next from the properties (C.7, C.8) of the Clebsch-Gordan coefficients the states with $\varGamma_{ev} = E'_1$ and $\varGamma_{ev} = E'_2$ are easily obtained from those in equation (D.3):

- $\ell = 3p+2$

$$\begin{aligned}
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_\pm,E'_1\bar{1}\rangle\rangle =\\
&\quad \frac{i^{2j+1}}{\sqrt{2}}({}^{+}\widetilde{\varPsi}^{(1)(+)}_{jm\pm} \mp (-1)^{2j}\ {}^{+}\widetilde{\varPsi}^{(2)(+)}_{jm\pm})\\
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_\pm,E'_1\bar{2}\rangle\rangle =\\
&\quad \frac{i^{2j+1}}{\sqrt{2}}({}^{+}\widetilde{\varPsi}^{(1)(-)}_{jm\pm} \mp (-1)^{2j}\ {}^{+}\widetilde{\varPsi}^{(2)(-)}_{jm\pm})\\
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_\pm,E'_2\bar{1}\rangle\rangle =\\
&\quad \frac{i^{2j}}{\sqrt{2}}({}^{+}\widetilde{\varPsi}^{(1)(+)}_{jm\pm} \pm (-1)^{2j}\ {}^{+}\widetilde{\varPsi}^{(2)(+)}_{jm\pm})\\
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_\pm,E'_2\bar{2}\rangle\rangle =\\
&\quad \frac{i^{2j}}{\sqrt{2}}({}^{+}\widetilde{\varPsi}^{(1)(-)}_{jm\pm} \pm (-1)^{2j}\ {}^{+}\widetilde{\varPsi}^{(2)(-)}_{jm\pm}). \qquad \text{(D.7)}
\end{aligned}$$

The same procedure applies to the uncoupled states in equations (D.4, D.5).

Also for $m = -1/2$ the states (70) associated with the energy ${}^{+}E_{j-1/2\pm}$ (69) are now given by

$$\begin{aligned}
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_+,E'_1\bar{\sigma}\rangle\rangle =\\
&\quad i^{v+1}\{|[1\dot{0}],[1\,0]\frac{1}{2}1E\bar{1},[1\,0]\frac{1}{2}E'_1\bar{\sigma}\rangle\rangle|[v\,0]j\ -1/2\rangle\rangle\\
&\quad + |[1\dot{0}],[1\,0]\frac{1}{2}1E\bar{2},[1\,0]\frac{1}{2}E'_1\bar{\sigma}\rangle\rangle|[v\,0]j\,1/2\rangle\rangle\}/\sqrt{2}\\
&|\{\gamma_e\}E,E'_1;[v\,0]j;\varOmega_-,E'_2\bar{\sigma}\rangle\rangle =\\
&\quad i^{v}\{|[1\dot{0}],[1\,0]\frac{1}{2}1E\bar{1},[1\,0]\frac{1}{2}E'_1\bar{\sigma}\rangle\rangle|[v\,0]j\ -1/2\rangle\rangle\\
&\quad - |[1\dot{0}],[1\,0]\frac{1}{2}1E\bar{2},[1\,0]\frac{1}{2}E'_1\bar{\sigma}\rangle\rangle|[v\,0]j\,1/2\rangle\rangle\}/\sqrt{2}.\\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(D.8)}
\end{aligned}$$

Alternatively they can be expressed in terms of the states $|[1\dot{0}],[1\,0]\frac{1}{2},[1\,0]\frac{1}{2};G'\bar{\sigma}\rangle\rangle$ using equation (10) and the correspondences in equation (130).

D.3 Symmetrized eigenstates for type C and D cases

The transformation laws for the eigenstates (84, 85) under the action of the generators X for groups in $G_{(I)}$ are given by:

$$\begin{aligned}
P_X\,{}^{+}\widetilde{\varPsi}^{(1)}_{jm\pm} &= e^{i(\ell r'+r)\psi}\ {}^{+}\widetilde{\varPsi}^{(1)}_{jm\pm},\\
P_X\,{}^{+}\widetilde{\varPsi}^{(2)}_{jm\pm} &= e^{-i(\ell r'+r)\psi}\ {}^{+}\widetilde{\varPsi}^{(2)}_{jm\pm}.
\end{aligned}$$

Those associated with the Y generator and the time reversal operator are as given in Table 3 for A-type systems. These relations are sufficient, together with the matrices for the E-type *irreps* in orientation II, to built symmetry adapted eigenstates for ${}^{+}\widetilde{H}_{vibr}$ of $E_r \otimes e_{r'}$ systems of type C. For $E_{r\alpha} \otimes e_{r'\beta}$ systems for groups in $G_{(II)}$ equation (68) is unchanged.

Similarly for type D cases, remembering that the eigenstates ${}^{-}\widetilde{\varPsi}^{(i)}_{jm\pm}$ are obtained from those in equation (84,85) with the substitutions (98), we have

$$\begin{aligned} P_X\,{}^{-}\widetilde{\Psi}^{(1)}_{jm\pm} &= e^{i(\ell r'-r)\psi}\ {}^{-}\widetilde{\Psi}^{(1)}_{jm\pm}, \\ P_X\,{}^{-}\widetilde{\Psi}^{(2)}_{jm\pm} &= e^{-i(\ell r'-r)\psi}\ {}^{-}\widetilde{\Psi}^{(2)}_{jm\pm}. \end{aligned}$$

The transformation laws associated with the Y generator and the time reversal operator are as given in Table 4 for B-type systems.

Special cases

- $m=-1$. From the relations

$$\begin{aligned} &P_X|+\rangle\rangle|[v\,0]j\ \pm 1\rangle\rangle = e^{i(r\pm 2r')\psi}\,|+\rangle\rangle|[v\,0]j\ \pm 1\rangle\rangle \\ &P_X|-\rangle\rangle|[v\,0]j\ \pm 1\rangle\rangle = e^{-i(r\mp 2r')\psi}\,|-\rangle\rangle|[v\,0]j\ \pm 1\rangle\rangle \\ &P_Y|+\rangle\rangle|[v\,0]j\ \pm 1\rangle\rangle = -|-\rangle\rangle|[v\,0]j\ \mp 1\rangle\rangle \\ &P_Y|-\rangle\rangle|[v\,0]j\ \pm 1\rangle\rangle = -|+\rangle\rangle|[v\,0]j\ \mp 1\rangle\rangle \end{aligned}$$

one may check with Table 2 that for all (r,r') cases associated with C or D-types we have $e^{i(r\pm 2r')\psi}=\pm 1$ and that the states ${}^{\pm}\widetilde{\Psi}_{j-1+}$ (resp. ${}^{\pm}\widetilde{\Psi}_{j-1-}$) associated with the energies (87, 99) are of symmetry A_2 or B_2 (resp. A_1 or B_1) depending on the (r,r') values.

- The sets of uncoupled states (89, 100)

$$\begin{aligned} &|\pm\rangle\rangle|[v\,0]j\,j\rangle\rangle = \varphi_{(\pm)j} \\ &|\mp\rangle\rangle|[v\,0]j\ -j\rangle\rangle = \varphi_{(\mp)-j} \\ &|\pm\rangle\rangle|[v\,0]j\,j-1\rangle\rangle = \varphi_{(\pm)j-1} \\ &|\mp\rangle\rangle|[v\,0]j\ -j+1\rangle\rangle = \varphi_{(\mp)-j+1} \end{aligned}$$

associated with the eigenvalues ${}^{\pm}E_{jj}$, ${}^{\pm}E_{jj-1}$ (Eqs. (90, 101)) transform as

$$\begin{aligned} &P_X\varphi_{(\pm)j} = e^{i(2jr'\pm r)\psi}\,\varphi_{(\pm)j} \\ &P_X\varphi_{(\mp)-j} = e^{-i(2jr'\pm r)\psi}\,\varphi_{(\mp)-j} \\ &P_X\varphi_{(\pm)j-1} = e^{i(2(j-1)r'\pm r)\psi}\,\varphi_{(\pm)j-1} \\ &P_X\varphi_{(\mp)-j+1} = e^{-i(2(j-1)r'\pm r)\psi}\,\varphi_{(\mp)-j+1} \\ &P_Y\varphi_{(\pm)j} = (-1)^{2j+1}\,\varphi_{(\mp)-j} \\ &P_Y\varphi_{(\pm)j-1} = (-1)^{2j+1}\,\varphi_{(\mp)-j+1} \\ &\mathcal{K}\varphi_{(\pm)j} = \varphi_{(\mp)-j} \\ &\mathcal{K}\varphi_{(\pm)j-1} = \varphi_{(\mp)-j+1}. \end{aligned}$$

As an example the symmetrized eigenstates for a $E_2\otimes e_1$ system of C-type in C_{5v}, D_5 symmetry are given below in the form

$$|[1\,0]\frac{1}{2}1E_2;[v\,0]j;\Omega_{\pm},\Gamma_{ev}\bar{\sigma}_{ev}\rangle\rangle,$$

with phases fixed as in equation (D.1).

$$\begin{aligned} |[1\,0]\frac{1}{2}1E_2;[v\,0]j;\Omega_{+},E_i\bar{\sigma}\rangle\rangle &= i^{2j}\ {}^{+}\widetilde{\Psi}^{(1)}_{jm+} \\ |[1\,0]\frac{1}{2}1E_2;[v\,0]j;\Omega_{+},E_i-\bar{\sigma}\rangle\rangle &= i^{-2j}\ {}^{+}\widetilde{\Psi}^{(2)}_{jm+} \\ |[1\,0]\frac{1}{2}1E_2;[v\,0]j;\Omega_{-},E_i\bar{\sigma}\rangle\rangle &= i^{2j}\ {}^{+}\widetilde{\Psi}^{(1)}_{jm-} \\ |[1\,0]\frac{1}{2}1E_2;[v\,0]j;\Omega_{-},E_i-\bar{\sigma}\rangle\rangle &= -i^{-2j}\ {}^{+}\widetilde{\Psi}^{(2)}_{jm-} \end{aligned} \tag{D.9}$$

with

$$\begin{array}{ccc} (\bar{\sigma},-\bar{\sigma}) & \ell & E_i \\ (\bar{1},\bar{2}) & 5p & E_2 \\ (\bar{2},\bar{1}) & 5p+1 & E_2 \\ (\bar{2},\bar{1}) & 5p+2 & E_1 \\ (\bar{1},\bar{2}) & 5p+4 & E_1 \end{array} \tag{D.10}$$

For $\ell = 5p+3$

$$\begin{aligned} &|[1\,0]\frac{1}{2}1E_2;[v\,0]j;\Omega_{\pm},A_1\rangle\rangle = \\ &\qquad i^{2j+1}({}^{+}\widetilde{\Psi}^{(1)}_{jm\pm} \mp (-1)^{2j}\ {}^{+}\widetilde{\Psi}^{(2)}_{jm\pm})/\sqrt{2} \\ &|[1\,0]\frac{1}{2}1E_2;[v\,0]j;\Omega_{\pm},A_2\rangle\rangle = \\ &\qquad i^{2j}({}^{+}\widetilde{\Psi}^{(1)}_{jm\pm} \pm (-1)^{2j}\ {}^{+}\widetilde{\Psi}^{(2)}_{jm\pm})/\sqrt{2}. \end{aligned} \tag{D.11}$$

For $m=-1$ the states ${}^{+}\widetilde{\Psi}_{j-1+}$ and ${}^{+}\widetilde{\Psi}_{j-1-}$ (88) are respectively of symmetry A_2 and A_1. Finally from the uncoupled states (89) associated with the eigenvalues (90) we built the symmetry adapted states

$$\begin{aligned} |[1\,0]\frac{1}{2}1E_2;[v\,0]j;^{+}E_{jk},E_i\bar{\sigma}\rangle\rangle &= i^{2j}\,|+\rangle\rangle|[v\,0]j\,k\rangle\rangle \\ |[1\,0]\frac{1}{2}1E_2;[v\,0]j;^{+}E_{jk},E_i-\bar{\sigma}\rangle\rangle &= i^{-2j}\,|-\rangle\rangle|[v\,0]j\ -k\rangle\rangle \end{aligned}$$

where the labels are specified as in equation (D.10) with ℓ replaced by $2j$ (resp. $2(j-1)$) for $k=j$ (resp. $k=j-1$). Likewise the states with symmetry A_1, A_2 are given by

$$\begin{aligned} &|[1\,0]\frac{1}{2}1E_2;[v\,0]j;^{+}E_{jk},A_1\rangle\rangle = \\ &\qquad i^{2j+1}\{|+\rangle\rangle|[v\,0]j\,k\rangle\rangle - (-1)^{2j}\,|-\rangle\rangle|[v\,0]j\ -k\rangle\rangle\}/\sqrt{2} \\ &|[1\,0]\frac{1}{2}1E_2;[v\,0]j;^{+}E_{jk},A_2\rangle\rangle = \\ &\qquad i^{2j}\{|+\rangle\rangle|[v\,0]j\,k\rangle\rangle + (-1)^{2j}\,|-\rangle\rangle|[v\,0]j\ -k\rangle\rangle\}/\sqrt{2} \end{aligned}$$

for $2k=5p+3$.

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