Relations among reduction factors in Jahn-Teller systems*

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A group-theoretical method for construction of vibronic wave functions of required symmetry is developed. The method is applied to investigate relations among Ham's reduction factors in Jahn-Teller systems of cubic (or tetrahedral) symmetry. Three special cases are discussed in detail: (i) in the case of linear Jahn-Teller coupling of an E electronic level with many E-type crystal vibrational modes, it is shown, on the basis of a detailed symmetry analysis, that the relation $q = (1 + p)/2$ between the reduction factors holds for linear coupling to a single mode pair (in agreement with Ham's result) but not in general otherwise; a detailed symmetry analysis made for this system allows dynamic effects to be disentangled from effects of symmetry; (ii) for Jahn-Teller coupling of a T electronic level with many E vibrational modes, it is found that the relations among the reduction factors, as given by Ham for linear Jahn-Teller coupling, are valid under general vibronic coupling; (iii) in the case of coupling of a T electronic level with a single vibrational mode triplet of T_2 symmetry, the relation $K(E) = 1 - 3[K(T_2) - K(T_1)]/2$ is shown to be valid in the weak-coupling regime for vibronic states correct to fourth order in the vibronic coupling constant but not for vibronic states correct to fifth order.

I. INTRODUCTION AND CONCLUSIONS

Our understanding of the Jahn-Teller effect has been greatly increased recently.[1] In particular, the reduction factors first introduced by Ham[2,3] play an important role in various experimental investigations of the Jahn-Teller effect in crystals. The importance stems from the fact that the effect of Jahn-Teller coupling on the response of a system to weak perturbations can usually be described adequately in terms of reduction factors.

The reduction factors for the (nearest-neighbor) cluster model have been studied by various authors, and also reviewed in recent years.[4-7] In the case of linear Jahn-Teller coupling of an orbital electronic doublet in cubic symmetry, Ham[3] was able to establish a relationship between the reduction factors p and q, namely, $q = \frac{1}{2}(1 + p)$. More recently, interest in the Jahn-Teller effect has been directed mainly toward the case in which the coupling is with a continuous spectrum of phonons rather than with just a few vibrational modes. In a many-mode variational calculation, Fletcher[8] pointed out that the relation $q = \frac{1}{2}(1 + p)$ is valid for his choice of the variational ground-state wave functions. Subsequently, O'Brien[9] concluded that this relation is in general valid also for the many-mode linear Jahn-Teller interaction. More recently, Halperin and Englman[10] as well as Gauthier and Walker[11] have found that $q = \frac{1}{2}(1 + p)$ holds generally only for the single mode-pair case.

It is the purpose of this paper to investigate the relations among the reduction factors under very general conditions, which include coupling with a continuous spectrum of phonons as well as higher-order Jahn-Teller interactions. We use a common approach, involving two steps. The first, which our work emphasizes, is to find the symmetry restrictions on a property, in this case the reduction factors, using the full symmetry of the Hamiltonian including dynamical symmetry (symmetry in addition to space-time symmetry). The second step involves using considerations beyond symmetry.

A group-theoretical approach for constructing vibronic wave functions of required symmetry, introduced by Abragam and Bleaney (p. 814–815 of Ref. 5) for application in the case of an E electronic doublet coupled to a single E-type vibrational mode pair, is developed for a general system in Sec. II. By a general and detailed group-theoretical analysis the symmetry restrictions on the vibrational parts of a vibronic wave function are determined, and a method for constructing vibronic wave functions consistent with these restrictions is described. The method is applied in Sec. III to the Jahn-Teller effect of an orbital electronic doublet in cubic symmetry. We find that under very general vibronic coupling mentioned above, Ham's relation $q = \frac{1}{2}(1 + p)$ is in general not satisfied; rather, $q \leq \frac{1}{2}(1 + p)$; these results were obtained by Abragam and Bleaney.[5] Although their brief discussion was given in terms of a cluster model, it applies when the coupling is to any number of modes. Further analysis shows that $q \leq \frac{1}{2}(1 + p)$ remains true even in the special case of linear Jahn-Teller coupling to many modes, contrary to O'Brien's conclusion,[9] but in agreement with the conclusions, obtained by different approaches, of Halperin and Englman[10] and of Gauthier and Walker.[11] A detailed analysis of the symmetry of a system with a linear Jahn-Teller Hamil-

tonian is presented in Appendix A. The results of this analysis can be used to disentangle dynamic effects from effects of symmetry.

In Sec. IV, we treat the case of a triplet electronic level in a cubic environment. Again we begin with a general analysis of the relations among the reduction factors, and then examine some particular cases. In the case of coupling to E-type vibrational modes only, we find that the relations $K(E) = 1$ and $K(T_1) = K(T_2)$, first discovered by Ham,[2] are valid quite generally. In the case of coupling to a single vibrational mode triplet of T_2 symmetry, no simple exact relation among the three reduction factors $K(E)$, $K(T_2)$, and $K(T_1)$ exists for the ground vibronic triplet; however, the relation $K(E) = 1 - \frac{3}{2}[K(T_2) - K(T_1)]$ is shown to be a good approximation in the weak coupling regime. The case of equal linear coupling to an E-mode pair and a T_2-mode triplet of equal frequency is also discussed.

We have limited ourselves in this paper to the discussion of relations among the reduction factors in Jahn-Teller systems of cubic symmetry. We should emphasize that the method can be applied to various other systems. Also, the method for construction of vibronic wave functions is of general applicability for the study of vibronic interaction.

II. CONSTRUCTION OF VIBRONIC WAVE FUNCTIONS

The vibronic Hamiltonian incorporates the Jahn-Teller interaction of the vibrational modes with a set of degenerate electronic wave functions $\psi_1^{(\mu)}, \psi_2^{(\mu)}, \ldots, \psi_{n_\mu}^{(\mu)}$ which transform as basis functions for the μth irreducible representation of the group G. This Hamiltonian is necessarily invariant with respect to G. It follows that the vibronic eigenfunctions belonging to a given energy eigenvalue can be chosen to be partners forming a basis for one of the irreducible representations of G (apart from accidental degeneracy). Within the Born-Oppenheimer approximation, extended in the usual way to allow for degenerate electronic states, the vibronic wave function which transforms as the lth row of the λth irreducible representation can be written

$$\Psi_l^{(\lambda)}(Q, q) = \sum_{m=1}^{n_\mu} \chi_{lm}(Q) \psi_m^{(\mu)}(q).$$ (1)

Here, $\chi_{lm}(Q)$ is the vibrational factor associated with the electronic wave function $\psi_m^{(\mu)}(q)$, and we have denoted the electronic coordinates and the vibrational coordinates collectively by q and Q, respectively. We want to determine the most general form that the χ_{lm} and hence the $\Psi_l^{(\lambda)}$ can assume consistent with the symmetry.

Following Hamermesh,[12] we define the unitary operator $\hat{O}_R$ corresponding to an element R of the group G as,

$$\hat{O}_R f(Q, q) = f(R^{-1}Q, R^{-1}q),$$ (2)

where $f(q, Q)$ is any function of Q and q, and R^{-1} denotes the inverse of R. Accordingly, we have

$$\hat{O}_R \Psi_l^{(\lambda)} = \sum_{l'=1}^{n_\lambda} \Psi_{l'}^{(\lambda)} D^{(\lambda)}(R)_{l'l}$$

$$= \sum_{l'=1}^{n_\lambda} \sum_{m'=1}^{n_\mu} \chi_{l'm'} \psi_{m'}^{(\mu)} D^{(\lambda)}(R)_{l'l},$$ (3)

where $D^{(\lambda)}(R)$ is the matrix in the λth irreducible representation corresponding to the symmetry operation R. On the other hand, operating on the right-hand side of Eq. (1) with $\hat{O}_R$ gives

$$\hat{O}_R \Psi_l^{(\lambda)} = \sum_{m=1}^{n_\mu} \chi_{lm}(R^{-1}Q) \hat{O}_R \psi_m^{(\mu)}$$

$$= \sum_{m=1}^{n_\mu} \sum_{m'=1}^{n_\mu} \chi_{lm}(R^{-1}Q) \psi_{m'}^{(\mu)} D^{(\mu)}(R)_{m'm}.$$ (4)

Since Q and q are independent coordinate spaces, it follows from Eqs. (3) and (4) and the linear independence of the $\psi_m^{(\mu)}, m = 1, 2, \ldots, n_\mu$, that

$$\sum_{m=1}^{n_\mu} \chi_{lm}(R^{-1}Q) D^{(\mu)}(R)_{m'm} = \sum_{l'=1}^{n_\lambda} \chi_{l'm'}(Q) D^{(\lambda)}(R)_{l'l}.$$

(5)

Multiplying by $D^{(\mu)}(R)_{m''m'}^{-1}$ and summing over m', we obtain

$$\hat{O}_R \chi_{lm} = \sum_{l'}^{n_\lambda} \sum_{m'}^{n_\mu} \chi_{l'm'} D^{(\lambda)}(R)_{l'l} D^{(\mu)}(R)_{mm'}^{-1}.$$ (6)

We see that χ_{lm} transforms according to the Kronecker-product representation $D^{(\lambda)} \times \bar{D}^{(\mu)}$, where $\bar{D}^{(\mu)}$ is the representation adjoint[12] to $D^{(\mu)}$; $\bar{D}^{(\mu)}(R)_{m'm} = D^{(\mu)}(R)_{mm'}^{-1}$. The product representation can be decomposed into irreducible representations in the usual way[12]

$$D^{(\lambda)} \times \bar{D}^{(\mu)} = \sum_\sigma c_\sigma D^{(\sigma)},$$ (7)

where c_σ is the number of times that $D^{(\sigma)}$ is contained in $D^{(\lambda)} \times \bar{D}^{(\mu)}$. Accordingly, linear combinations of the χ_{lm} can be formed which transform as the $D^{(\sigma)}$ appearing in Eq. (7),

$$\bar{\chi}_{s, \tau_\sigma}^{(\sigma)} = \sum_l^{n_\lambda} \sum_m^{n_\mu} \chi_{lm} c(lm, \sigma s \tau_\sigma), \quad s = 1, \ldots, n_\sigma,$$

(8a)

where $\tau_\sigma = 1, 2, \ldots, c_\sigma$ and the $c(lm, \sigma s \tau_\sigma)$ are constants. It is possible, and often convenient, to choose the $c(lm, \sigma s \tau_\sigma)$ so that all the $\bar{\chi}_{s, \tau_\sigma}^{(\sigma)}$ are mutually orthogonal. The inverse of the transformation (8a) gives the χ_{lm} in terms of $\bar{\chi}_{s, \tau_\sigma}^{(\sigma)}$,

$$\chi_{lm} = \sum_{\sigma} \sum_{\tau_\sigma} \sum_{s} \bar{\chi}_{s,\tau_\sigma}^{(\sigma)} \bar{U}_{sml,\tau_\sigma}^{\sigma\mu\lambda}. \qquad (8b)$$

Substituting Eq. (8b) into (1), we obtain

$$\Psi_l^{(\lambda)} = \sum_{\sigma} \sum_{\tau_\sigma}^{c_\sigma} \Psi_{l,\sigma\tau_\sigma}^{(\lambda)}, \qquad (9a)$$

$$\Psi_{l,\sigma\tau_\sigma}^{(\lambda)} = \sum_{m}^{n_\mu} \sum_{s}^{n_\sigma} \bar{\chi}_{s,\tau_\sigma}^{(\sigma)} \psi_m^{(\mu)} \bar{U}_{sml,\tau_\sigma}^{\sigma\mu\lambda}. \qquad (9b)$$

Since for given σ and τ_σ the $\bar{\chi}_{s,\tau_\sigma}^{(\sigma)}$, $s = 1, 2, \ldots, n_\sigma$ transform only among themselves, we see that not only $\Psi_l^{(\lambda)}$ but also $\Psi_{l,\sigma\tau_\sigma}^{(\lambda)}$ must transform as the lth row of the λth irreducible representation. It also follows that the matrix elements $\bar{U}_{sml,\tau_\sigma}^{\sigma\mu\lambda}$ are closely related to the (Clebsch-Gordan) coupling coefficients.[12]

It can be readily verified that c_σ is also equal to the number of times that $D^{(\lambda)}$ is contained in $D^{(\sigma)} \times D^{(\mu)}$. This shows that for given σ and τ_σ, c_σ independent sets of partners $\{\Phi_{l,\tau_\sigma,\tau_\lambda}^{(\lambda)}, l = 1, \ldots, n_\lambda\}$, $\tau_\lambda = 1, \ldots, c_\sigma$, each transforming as $D^{(\lambda)}$, can be constructed from the set of product functions $\{\bar{\chi}_{s,\tau_\sigma}^{(\sigma)} \psi_m^{(\mu)}\}$ by means of the coupling coefficients

$$\Phi_{l,\tau_\sigma,\tau_\lambda}^{(\lambda)} = \sum_{m}^{n_\mu} \sum_{s}^{n_\sigma} \bar{\chi}_{s,\tau_\sigma}^{(\sigma)} \psi_m^{(\mu)} U_{sml,\tau_\lambda}^{\sigma\mu\lambda}. \qquad (10)$$

Here $\{U_{sml,\tau_\lambda}^{\sigma\mu\lambda}\}$, $\tau_\lambda = 1, \ldots, c_\sigma$, are the c_σ distinct sets of coupling coefficients associated with the decomposition of the direct product $D^{(\sigma)} \times D^{(\mu)}$ into $c_\sigma D^{(\lambda)}$; they have been chosen to couple orthonormal functions to produce orthonormal functions and have been extensively tabulated by Koster et al.[13] for crystallographic point groups. The most general basis set which transforms as $D^{(\lambda)}$ and which can be constructed from the $\{\bar{\chi}_{s,\tau_\sigma}^{(\sigma)} \psi_m^{(\mu)}\}$ with given σ and τ_σ is then a linear combination of the $\Phi_{l,\tau_\sigma,\tau_\lambda}^{(\lambda)}$. As a special case $\Psi_{l,\sigma\tau_\sigma}^{(\lambda)}$ in Eq. (9b) can be represented this way; thus, a (possibly singular) matrix $a_{\tau_\sigma\tau_\lambda}^{\sigma}$ can be chosen so that

$$\bar{U}_{sml,\tau_\sigma}^{\sigma\mu\lambda} = \sum_{\tau_\lambda}^{c_\sigma} a_{\tau_\sigma\tau_\lambda}^{\sigma} U_{sml,\tau_\lambda}^{\sigma\mu\lambda}. \qquad (11)$$

In case $c_\sigma = 1$, the matrix can be chosen unity by suitably redefining $\bar{\chi}_s^{(\sigma)}$.

Combining Eqs. (9a), (9b), and (11), we obtain

$$\Psi_l^{(\lambda)} = \sum_{\sigma} \sum_{\tau_\lambda}^{c_\sigma} \sum_{s}^{n_\sigma} \sum_{m}^{n_\mu} \chi_{s,\tau_\lambda}^{(\sigma)} \psi_m^{(\mu)} U_{sml,\tau_\lambda}^{\sigma\mu\lambda}, \qquad (12a)$$

where

$$\chi_{s,\tau_\lambda}^{(\sigma)} = \sum_{\tau_\sigma} \bar{\chi}_{s,\tau_\sigma}^{(\sigma)} a_{\tau_\sigma\tau_\lambda}^{\sigma}. \qquad (12b)$$

The most general form for the vibronic wave function $\Psi_l^{(\lambda)}$ consistent with the symmetry is thus given by (12a) in which the $\{\chi_{s,\tau_\lambda}^{(\sigma)}\}$, $\tau_\lambda = 1, \ldots, c_\sigma$ are independent basis sets each having the most

general form. The $\chi_{s,\tau_\lambda}^{(\sigma)}$ can be specialized according to (12b) so as to express the actual vibronic wave function.

It is sometimes convenient to deal with vibronic wave functions containing orthogonal vibrational parts. The function $\Psi_l^{(\lambda)}$ takes this form if the $\bar{\chi}_{s,\tau_\sigma}^{(\sigma)}$ are chosen mutually orthogonal and (12b) is substituted into (12a). In this form the coefficients $a_{\tau_\sigma\tau_\lambda}^{\sigma}$ appear explicitly.

The method just described can be generalized to construct the most general form of vibronic wave function of given symmetry involving N electronic levels, each of which belongs to a certain irreducible representation of G. This form consists simply of a summation of terms of the type (12a), one for each electronic level. This form can be applied, e.g., in the study of the pseudo-Jahn-Teller effect. Even more generally, exact vibronic wave functions can, in principle, be represented in this form if the summation includes all electronic levels.

III. ORBITAL DOUBLET LEVEL IN CUBIC SYMMETRY

In this section the electronic level coupled to the crystal vibrational modes belongs to the irreducible representation E of the cubic group O (or the tetrahedral group T_d) and has eigenstates $(|\psi_\theta^E\rangle, |\psi_\epsilon^E\rangle)$. Within the framework of the Born-Oppenheimer approximation, the vibronic Hamiltonian, which must necessarily be invariant under the group O (or T_d), takes the following form:

$$\mathcal{K}(E) = \mathcal{K}(A_1)\mathcal{S} + \mathcal{K}(\theta)\mathcal{U}_\theta + \mathcal{K}(\epsilon)\mathcal{U}_\epsilon + \mathcal{K}(A_2)\mathcal{Q}_2. \qquad (13)$$

Here $\mathcal{S}$, $\mathcal{U}_\theta$, $\mathcal{U}_\epsilon$, and $\mathcal{Q}_2$ are the electronic operators or their corresponding matrices $[\mathcal{S} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$, $\mathcal{U}_\theta = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$, $\mathcal{U}_\epsilon = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\mathcal{Q}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}]$, defined by Ham,[3,6] while $\mathcal{K}(A_1)$, $\mathcal{K}(\theta)$, $\mathcal{K}(\epsilon)$, and $\mathcal{K}(A_2)$ are operators in the vibrational coordinate space, which transform under the group O (or T_d), respectively, as A_1, E_θ, E_ϵ, and A_2. We remark that $\mathcal{K}(E)$ is the most general form consistent with the symmetry and includes as special cases the Hamiltonians discussed by various authors.[3,5,8,9,14] We consider only vibronic E levels, since they are of particular interest as ground levels.

The normalized eigenfunctions of $\mathcal{K}(E)$ for an E level must, according to the method of Sec. II, take the form

$$\Psi_\theta^E = (\chi^{A_1} - \chi_\theta^E)\psi_\theta^E + (\chi^{A_2} + \chi_\epsilon^E)\psi_\epsilon^E, \qquad (14a)$$

$$\Psi_\epsilon^E = (-\chi^{A_2} + \chi_\epsilon^E)\psi_\theta^E + (\chi^{A_1} + \chi_\theta^E)\psi_\epsilon^E, \qquad (14b)$$

where χ^{A_1}, χ^{A_2}, and $(\chi_\theta^E, \chi_\epsilon^E)$ are, respectively, basis functions of the irreducible representations A_1, A_2, and E of the group O (or T_d). Following Ham,[3] the reduction factors p and q for a vibronic

E level can be defined as

$$p = i\langle \Psi_\theta^E | \mathcal{C}_2 | \Psi_\epsilon^E \rangle, \qquad (15a)$$

$$q = -\langle \Psi_\theta^E | \mathcal{U}_\theta | \Psi_\theta^E \rangle. \qquad (15b)$$

It can be seen immediately on using Eqs. (14a) and (14b) that

$$p = \langle \chi^{A_1} | \chi^{A_1} \rangle + \langle \chi^{A_2} | \chi^{A_2} \rangle - \langle \chi_\theta^E | \chi_\theta^E \rangle - \langle \chi_\epsilon^E | \chi_\epsilon^E \rangle, \qquad (16a)$$

$$q = \langle \chi^{A_1} | \chi^{A_1} \rangle - \langle \chi^{A_2} | \chi^{A_2} \rangle, \qquad (16b)$$

$$1 = \langle \chi^{A_1} | \chi^{A_1} \rangle + \langle \chi^{A_2} | \chi^{A_2} \rangle + \langle \chi_\theta^E | \chi_\theta^E \rangle + \langle \chi_\epsilon^E | \chi_\epsilon^E \rangle, \qquad (16c)$$

which yields the following relation:

$$q = \tfrac{1}{2}(1 + p) - 2\langle \chi^{A_2} | \chi^{A_2} \rangle. \qquad (17)$$

Thus, quite generally, $q \leq \tfrac{1}{2}(1 + p)$, and $q = \tfrac{1}{2}(1 + p)$ if, and only if, $\chi^{A_2} = 0$.[15] Equations (14)–(17) correspond to equations (21.61), (21.63), (21.64), and (21.65) of Abragam and Bleaney,[5] and extend the scope of the latter to apply to general vibronic coupling to many modes of all symmetries. In particular, one can be assured that $q \leq \tfrac{1}{2}(1 + p)$ holds not only for an XY_6-type cluster, but also quite generally for more realistic models of a Jahn-Teller ion embedded in a crystal.

Linear coupling

In order to examine how χ^{A_2} enters into the vibronic wave function, we have made a more detailed analysis for the case when only linear Jahn-Teller interaction is present. In this case additional symmetry which is present allows the vibrational functions χ^{A_1}, χ^{A_2}, χ_θ^E, and χ_ϵ^E appearing in (14a) and (14b) to be expressed in more explicit form.

The Hamiltonian $\mathcal{H}(E)$ in Eq. (13) now assumes the form

$$\mathcal{H}_L(E) = \sum_{i=1}^{N} (2\mu_i)^{-1}[P_{\theta i}^2 + P_{\epsilon i}^2 + \mu_i^2 \omega_i^2 (Q_{\theta i}^2 + Q_{\epsilon i}^2)]\mathcal{S}$$
$$+ \left(\sum_{i=1}^{N} V_i Q_{\theta i}\right) \mathcal{U}_\theta + \left(\sum_{i=1}^{N} V_i Q_{\epsilon i}\right) \mathcal{U}_E, \qquad (18)$$

where $(Q_{\theta i}, Q_{\epsilon i} ; i = 1, \ldots, N)$ are the vibrational coordinates with each pair $(Q_{\theta i}, Q_{\epsilon i})$ belonging to E; $(P_{\theta i}, P_{\epsilon i})$ are the momenta conjugate to $(Q_{\theta i}, Q_{\epsilon i})$; μ_i is the effective mass of the ith mode pair and ω_i is its frequency; and V_i is the linear Jahn-Teller coupling coefficient between the degenerate electronic states and the modes with coordinates $Q_{\theta i}$ and $Q_{\epsilon i}$.

We observe that the pseudo-angular-momentum operator

$$J = \sum_{i=1}^{N} l_i - \tfrac{1}{2}\mathcal{C}_2, \qquad (19)$$

with $l_i = (Q_{\theta i} P_{\epsilon i} - Q_{\epsilon i} P_{\theta i})/\hbar$ commutes with $\mathcal{H}_L(E)$. Also, the operator

$$\mathcal{P} = -\mathcal{R}\mathcal{U}_\theta \qquad (20)$$

commutes with $\mathcal{H}_L(E)$ and anticommutes with J, $\mathcal{R}$ being a reflection in the $Q_{\theta i}$ axis in each of the $(Q_{\theta i}, Q_{\epsilon i})$ subspaces $[\mathcal{R}: (Q_{\theta i}, Q_{\epsilon i}) \rightarrow (Q_{\theta i}, -Q_{\epsilon i})]$. Finally, the Hamiltonian $\mathcal{H}_L(E)$, being real, is invariant under time reversal and hence commutes with the complex-conjugation operator K. A detailed analysis of the symmetry properties of the Hamiltonian is included in Appendix A.

Since $[\mathcal{H}_L(E), J] = 0$, eigenstates of $\mathcal{H}_L(E)$ can be chosen to be also eigenstates of J. Solving the eigenvalue problem for J we find that eigenvalues of J are half odd integers given by $M = L \pm \tfrac{1}{2}$, where L is an integer, one of the eigenvalues of $\sum_i l_i$. An eigenfunction of J with eigenvalue M has the form

$$\Psi_M = (f_{M-1/2} + g_{M+1/2})\psi_\theta^E + (-i f_{M-1/2} + i g_{M+1/2})\psi_\epsilon^E, \qquad (21)$$

where f_L and g_L are eigenfunctions of $\sum_i l_i$ with eigenvalues L. In terms of polar coordinates $(Q_{\theta i} = \rho_i \cos\theta_i, Q_{\epsilon i} = \rho_i \sin\theta_i ; i = 1, \ldots, N)$, they have the form

$$f_L(\ldots, \rho_i, \theta_i, \ldots) = \sum_{\{m_j\}}^{L} c(\{m_j\}) \prod_{j=1}^{N} e^{im_j\theta_j}, \qquad (22a)$$

$$g_L(\ldots, \rho_i, \theta_i, \ldots) = \sum_{\{m_j\}}^{L} d(\{m_j\}) \prod_{j=1}^{N} e^{im_j\theta_j}, \qquad (22b)$$

where the m_j's are integers, the c's and d's depend on $\{\rho_i\}$, and the summation is restricted so that $\sum_j m_j = L$. It is shown in Appendix A that the c's and d's can be chosen to be real. It is further shown in Appendix A that (Ψ_M, Ψ_M^*) is a vibronic doublet belonging to E of the cubic group for $M = \tfrac{1}{2} + 3k$ and $\tfrac{5}{2} + 3k$, k being a non-negative integer.

The $M = \tfrac{1}{2}$ case is of special interest since the ground vibronic level of $\mathcal{H}_L(E)$ has been found to have $M = \tfrac{1}{2}$ in the one frequency case,[16,17] and evidence presented by other authors[8,9] suggests that this is true in the many-frequency case. As shown in Eqs. (A34a) and (A34b) in Appendix A, the wave functions for the E vibronic doublet with $M = \tfrac{1}{2}$ can be chosen to have the forms (14a) and (14b) with

$$\chi^{A_1} = \sqrt{2} \ \text{Re}f_0, \quad \chi^{A_2} = \sqrt{2} \ \text{Im}f_0, \qquad (23a)$$

$$\chi_\theta^E = -\sqrt{2} \ \text{Re}g_1, \quad \chi_\epsilon^E = -\sqrt{2} \ \text{Im}g_1. \qquad (23b)$$

Hence the relation $q = \tfrac{1}{2}(1 + p)$ is valid if and only if

$$\text{Im}f_0 = 0. \qquad (24)$$

We shall first examine the case of coupling to a single mode pair ($N=1$). Then,

$$\mathrm{Im} f_0 = \sum_{m_1}^{0} c(m_1)\sin m_1\theta_1 = 0, \tag{25}$$

which shows that $q = \frac{1}{2}(1 + p)$ is valid for the single mode-pair case. This provides an alternative proof of Ham's relation, and shows clearly that Ham's relation is purely a consequence of symmetry. However, for the many mode-pair case, no such conclusion about $\mathrm{Im} f_0$ can be drawn by symmetry argument alone.[18] Moreover, for the ground level, dynamic properties of the system also do not lead in general to $\mathrm{Im} f_0 = 0$, since $\mathrm{Im} f_0$ is, in fact, nonzero unless all frequencies are equal, as can be seen from a perturbation calculation described in Appendix C. This calculation shows that the second-order perturbed ground E-level wave functions (with the coupling as a perturbation) contain a nonzero A_2 vibrational part of second order in the coupling coefficients, demonstrating that $\mathrm{Im} f_0 \neq 0$.[19] This agrees with the fact that p and q, expressed to fourth order in the coupling coefficients on the basis of a perturbation calculation,[10] explicitly satisfy $q < \frac{1}{2}(1 + p)$.

For an E level with $M > \frac{1}{2}$, symmetry does not require $\chi^{A_2} = 0$ [as can be seen from Eqs. (A34a), (A35a), and the form of (A9b)], so that $q < \frac{1}{2}(1 + p)$ unless $\chi^{A_2} = 0$ results as a special dynamical property of the system. In addition, the reduction factor q is zero. From Eq. (16b) this is equivalent to $\langle \chi^{A_1} | \chi^{A_1} \rangle = \langle \chi^{A_2} | \chi^{A_2} \rangle$, which follows from the expressions (A34a) and (A35a) for χ^{A_1} and χ^{A_2}, and the fact that if $L \neq 0$, the transformation $\theta_j \rightarrow \theta_j + \pi/2L$ converts $\langle \mathrm{Re} f_L | \mathrm{Re} f_L \rangle$ into $\langle \mathrm{Im} f_L | \mathrm{Im} f_L \rangle$ and converts $\langle \mathrm{Re} g_L | \mathrm{Re} g_L \rangle$ into $\langle \mathrm{Im} g_L | \mathrm{Im} g_L \rangle$. On the other hand, in case $M = \frac{1}{2}$, q can be expressed as

$$q = 2(2\pi)^N \sum_{\{m_j\}}^{0} \int_0^\infty \cdots$$

$$\times \int_0^\infty c(\{m_j\})c(\{-m_j\})\rho_1 \cdots \rho_N\, d\rho_1 \cdots d\rho_N, \tag{26}$$

which is, in general, not equal to zero. We thus conclude, on using $q = 0$ in Eq. (17), that for an E level, with $M > \frac{1}{2}$,

$$p = 2\langle \chi^{A_2} | \chi^{A_2} \rangle - 1 \geqslant -1, \tag{26'}$$

where the inequality holds unless $\chi^{A_2} = 0$ as a special dynamical property of the system.

An immediate consequence of $q = 0$ is that the Zeeman effect of an E vibronic level with $M > \frac{1}{2}$ is isotropic. This appears to have interesting implications for experiment, e.g., (i) a vibronic level observed to have an isotropic Zeeman effect is not necessarily a vibronic singlet, and (ii) if an observed vibronic level identified as an E level with $M > \frac{1}{2}$ is found to have $q \neq 0$, the magnitude of q may be interpretable as a measure of the extent of nonlinear coupling.

By choosing energy eigenfunctions of the form (21) the Schrödinger equation for the Hamiltonian (18) can be expressed as a system of partial differential equations in the c's and d's of Eq. (22). The Schrödinger equation written in this form takes explicit account of the symmetry, which includes the fact that the c's and d's can be chosen real. The same is true of an expression [such as Eq. (26)] for a physical property given in terms of the c's and d's. The dynamic properties of the system are determined by determining the c's and d's as functions of $\rho_1, \rho_2, \ldots, \rho_N$, and these functions are determined as solutions of the differential equations. Study of the properties of these functions should be a useful approach to understanding the dynamic properties of the system.

IV. TRIPLET ELECTRONIC LEVEL IN CUBIC SYMMETRY

In this section we treat the case of a T_1 or T_2 electronic level in cubic (or tetrahedral) symmetry, coupled to the crystal vibrational modes. We assume the most general form for the vibronic coupling within the framework of the Born-Oppenheimer approximation, so that our discussion would be applicable for a vibronic Hamiltonian of the form

$$\mathcal{H}(T) = H(A_1)\mathcal{S} + H(\theta)\mathcal{S}_\theta + H(\epsilon)\mathcal{S}_\epsilon + H(\xi)\mathcal{T}_\xi$$
$$+ H(\eta)\mathcal{T}_\eta + H(\zeta)\mathcal{T}_\zeta + H(x)\mathcal{L}_x + H(y)\mathcal{L}_y + H(z)\mathcal{L}_z \tag{27}$$

Here, $H(A_1)$, $(H(\theta), H(\epsilon))$, $(H(\xi), H(\eta), H(\zeta))$, and $(H(x), H(y), H(z))$ are operators in the vibrational coordinate space belonging, respectively, to A_1, E, T_2, and T_1, while the electronic operators (or their matrix representations with respect to the electronic triplet) $\mathcal{S}$, $\mathcal{S}_\theta$, $\mathcal{S}_\epsilon$, $\mathcal{T}_\xi$, $\mathcal{T}_\eta$, $\mathcal{T}_\zeta$, $\mathcal{L}_x$, $\mathcal{L}_y$, and $\mathcal{L}_z$ have been defined by Ham.[6]

We confine our discussion to vibronic levels of $\mathcal{H}(T)$ of T_1 (or T_2) symmetry for the case when the electronic level is T_1 (or T_2); such vibronic levels are of particular interest as ground levels.[2,20] To be specific we assume a T_1 electronic triplet in O symmetry[21] and investigate the relation among the reduction factor $K(E)$, $K(T_1)$, and $K(T_2)$ defined below. In accordance with Sec. II, the most general form for the normalized vibronic wave functions $\Psi_x^{T_1}$, $\Psi_y^{T_1}$, and $\Psi_z^{T_1}$ transforming as partners for the T_1 irreducible representation are given by Eq. (1) with the $\chi_{lx}, \chi_{ly}, \chi_{lz}$ given in column matrix form by

$$\Psi_x^{T_1} = \begin{pmatrix} \chi^{A_1} - \tfrac{1}{2}\chi_\theta^E + \tfrac{1}{2}\sqrt{3}\,\chi_\epsilon^E \\ -(1/\sqrt{2})\chi_z^{T_1} + (1/\sqrt{2})\chi_\zeta^{T_2} \\ (1/\sqrt{2})\chi_y^{T_1} + (1/\sqrt{2})\chi_\eta^{T_2} \end{pmatrix}, \tag{28a}$$

$$\Psi_y^{T_1} = \begin{pmatrix} (1/\sqrt{2})\chi_z^{T_1} + (1/\sqrt{2})\chi_\zeta^{T_2} \\ \chi^{A_1} - \tfrac{1}{2}\chi_\theta^E - \tfrac{1}{2}\sqrt{3}\,\chi_\epsilon^E \\ -(1/\sqrt{2})\chi_x^{T_1} + (1/\sqrt{2})\chi_\xi^{T_2} \end{pmatrix}, \tag{28b}$$

$$\Psi_z^{T_1} = \begin{pmatrix} -(1/\sqrt{2})\chi_y^{T_1} + (1/\sqrt{2})\chi_\eta^{T_2} \\ (1/\sqrt{2})\chi_x^{T_1} + (1/\sqrt{2})\chi_\xi^{T_2} \\ \chi^{A_1} + \chi_\theta^E \end{pmatrix}. \tag{28c}$$

Here the χ's denote functions in the vibrational coordinate space; χ^{A_1}, $(\chi_\theta^E, \chi_\epsilon^E)$, $(\chi_x^{T_1}, \chi_y^{T_1}, \chi_z^{T_1})$, and $(\chi_\xi^{T_2}, \chi_\eta^{T_2}, \chi_\zeta^{T_2})$ transform according to A_1, (θ, ϵ) in E, (T_x, T_y, T_z) in T_1, and (T_ξ, T_η, T_ζ) in T_2, respectively. As a consequence of their transformation properties, we have

$$\langle \chi_i^\alpha | \chi_j^\beta \rangle = f(\alpha)\delta_{\alpha\beta}\delta_{ij}, \tag{29}$$

where $f(\alpha)$ is a normalization parameter depending on α only.

Following Ham,[2,6] the reduction factors $K(E)$, $K(T_1)$, and $K(T_2)$ for a T_1 vibronic state are defined as

$$K(E) = -\langle \Psi_z^{T_1} | \mathcal{S}_\theta | \Psi_z^{T_1} \rangle, \tag{30}$$

$$K(T_1) = i\langle \Psi_x^{T_1} | \mathcal{L}_z | \Psi_y^{T_1} \rangle, \tag{31}$$

$$K(T_2) = -\langle \Psi_x^{T_1} | \mathcal{T}_\zeta | \Psi_y^{T_1} \rangle. \tag{32}$$

Making use of the expressions (28a)–(28c) for the vibronic wave functions and (29), we obtain

$$K(E) = f(A_1) + f(E) - \tfrac{1}{2}f(T_1) - \tfrac{1}{2}f(T_2), \tag{33}$$

$$K(T_1) = f(A_1) - \tfrac{1}{2}f(E) + \tfrac{1}{2}f(T_1) - \tfrac{1}{2}f(T_2), \tag{34}$$

$$K(T_2) = f(A_1) - \tfrac{1}{2}f(E) - \tfrac{1}{2}f(T_1) + \tfrac{1}{2}f(T_2). \tag{35}$$

Using these and the normalization condition

$$1 = f(A_1) + f(E) + f(T_1) + f(T_2) \tag{36}$$

to eliminate $f(A_1)$, $f(E)$, and $f(T_2)$, we arrive at the following relation between the reduction factors:

$$K(E) = 1 - \tfrac{3}{2}[K(T_2) - K(T_1)] - 3f(T_1). \tag{37}$$

This is analogous to (17) for the electronic doublet; T_1 is the antisymmetric part of the direct product $T_1 \times T_1$ just as A_2 is the antisymmetric part of $E \times E$. If

$$f(T_1) = 0 \quad \text{(i.e., } \chi_x^{T_1} = \chi_y^{T_1} = \chi_z^{T_1} = 0\text{)}, \tag{38}$$

Eq. (37) reduces to the relation

$$K(E) = 1 - \tfrac{3}{2}[K(T_2) - K(T_1)] \tag{39}$$

among the three reduction factors. This is analogous to Ham's relation $q = \tfrac{1}{2}(1 + p)$. The question of when $f(T_1) = 0$ holds, is of some interest. This question is discussed below for two special cases.

In the case of coupling only to vibrational modes of E symmetry, denoted by $(Q_{\theta 1}, Q_{\epsilon 1})$, $(Q_{\theta 2}, Q_{\epsilon 2})$, ..., $(Q_{\theta N}, Q_{\epsilon N})$, no function of $(Q_{\theta 1}, Q_{\epsilon 1}, Q_{\theta 2}, ..., Q_{\epsilon N})$ of T_1 or T_2 symmetry can be constructed (Appendix B). Accordingly, in Eqs. (28a)–(28c),

$$\chi_x^{T_1} = \chi_y^{T_1} = \chi_z^{T_1} = \chi_\xi^{T_2} = \chi_\eta^{T_2} = \chi_\zeta^{T_2} = 0, \tag{40}$$

and hence $f(T_1) = f(T_2) = 0$. In this case not only is (39) satisfied but also, from (33) to (36),

$$K(E) = 1, K(T_1) = K(T_2). \tag{41}$$

The results (41) were first derived by Ham[2,6] for the ground vibronic level in the case of linear Jahn-Teller coupling to E-type vibrational mode pairs. The above analysis shows that these results apply as well to any T_1 vibronic states depending on T_1 electronic states, even if the coupling is nonlinear.

We next consider the special case of linear coupling to only one T_2 vibrational-mode triplet (Q_ξ, Q_η, Q_ζ) described by the Hamiltonian[2]

$$\mathcal{H}_L(T) = \mathcal{H}_0 \mathcal{I} + V_T(Q_\xi \mathcal{T}_\xi + Q_\eta \mathcal{T}_\eta + Q_\zeta \mathcal{T}_\zeta), \tag{42}$$

where $\mathcal{H}_0$ is given by

$$\mathcal{H}_0 = (1/2\mu)(P_\xi^2 + P_\eta^2 + P_\zeta^2)$$
$$+ \tfrac{1}{2}\mu\omega^2(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2). \tag{43}$$

We note that the reduction factors $K(E)$, $K(T_1)$, and $K(T_2)$ for the T_1 ground vibronic level as calculated by Ham[2,22] to second order in V_T satisfy the relation (39), which indicates that $f(T_1) = 0$ for the first-order perturbed vibronic wave function. This suggests the possibility of finding an operator, analogous to J of Eq. (19), which commutes with the Hamiltonian (42). Such an operator might be expected, for example, to lead (by an analysis similar to that in Sec. III) to the conclusion that for a ground vibronic T_1 level, the T_1 vibrational parts in Eqs. (28a)–(28c) do not appear, so that $f(T_1) = 0$. We have not been able to find such an operator. Nevertheless, there is some evidence suggesting that such an operator "almost exists," that is, an operator exists whose commutator with $\mathcal{H}_L(T)$ of Eq. (42) is small in some sense.

With the vibronic coupling as the perturbation, the perturbed ground-level wave functions contain a T_1 vibrational part in fifth order, but not in lower order. This result, derived in Appendix D, extends to fourth-order Ham's result that $f(T_1) = 0$ to first order, but demonstrates that the relation $f(T_1) = 0$ is not exact. The fact that $f(T_1) = 0$ for wave functions correct to fourth order indicates

that the relation (39) is a good approximation in the weak coupling regime.

We note that according to Caner and Englman,[20]

$$K(E) = K(T_1) = 0, K(T_2) = \tfrac{2}{3} \qquad (44)$$

in the strong-coupling limit; these values also satisfy Eq. (39).

Finally, we consider a special case of (27) for which $\mathcal{H}(T)$ is invariant under the three-dimensional proper rotation group $O^+(3)$. In this case the vibronic wave functions transform under $O^+(3)$ according to an irreducible representation $D^{(L)}$, $L = 0, 1, \ldots$. We consider here only vibronic states which belong to $D^{(1)}$. Regarding the electronic T_1 states as belonging to $D^{(1)}$, we conclude that the vibrational functions $(\chi^{A_1}, \chi_\theta^E, \chi_\epsilon^E, \chi_x^{T_1}, \chi_y^{T_1},$ $\chi_z^{T_1}, \chi_\xi^{T_2}, \chi_\eta^{T_2}, \chi_\zeta^{T_2})$ of (28) must form a basis for the representation $\Gamma = D^{(0)} + D^{(1)} + D^{(2)}$ of $O^+(3)$, with the correspondence $D^{(0)} \to A_1$, $D^{(1)} \to T_1$, and $D^{(2)} \to E + T_2$. This determines $f(T_2)/f(E)$. The functions $(\chi_\theta^E, \chi_\epsilon^E,$ $\chi_\xi^{T_2}, \chi_\eta^{T_2}, \chi_\zeta^{T_2})$ then form a basis for $D^{(2)}$ and transform as $[2z^2 - x^2 - y^2, \sqrt{3}\,(x^2 - y^2), 2\sqrt{3}\,yz, 2\sqrt{3}\,zx, 2\sqrt{3}\,xy]$. Consequently, $f(T_2)/f(E) = \tfrac{3}{2}$ and, from (33) and (35), $K(E) = K(T_2)$.

A particular case for which $\mathcal{H}(T)$ is invariant under $O^+(3)$ occurs for equal linear coupling to an E mode pair and a T_2 mode triplet of equal frequency and equal effective mass. In this case the function space of the vibrational factors in Eqs. (28a)–(28c) does not contain a $D^{(1)}$ component, as pointed out by O'Brien[23] and by Romestain and d'Aubigné,[24] so that $f(T_1) = 0$ and (39) holds. Combining (39) with $K(E) = K(T_2)$, we obtain $K(E) = \tfrac{2}{5} + \tfrac{3}{5}K(T_1)$, a result found earlier.[23,24] In case of more than one such linearly coupled $D^{(2)} = E + T_2$ vibrational mode quintet, $K(E) = K(T_2)$, but the above symmetry argument[23,24] used to conclude that $f(T_1) = 0$ does not apply.

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APPENDIX A: SYMMETRY PROPERTIES OF THE LINEAR JAHN-TELLER HAMILTONIAN FOR ORBITAL ELECTRONIC DOUBLET

We shall study in detail the symmetry properties of the Hamiltonian $\mathcal{H}_L(E)$, given by (18), on the basis[25,26] that the operators $J, \mathcal{P}$, and K commute with $\mathcal{H}_L(E)$, where [see Eq. (19) and following text]

$$J = \sum_{i=1}^{N} l_i - \tfrac{1}{2}\alpha_2, \qquad (A1)$$

$$\mathcal{P} = -\mathcal{R}\mathcal{U}_\theta = \begin{pmatrix} \mathcal{R} & 0 \\ 0 & -\mathcal{R} \end{pmatrix}, \qquad (A2)$$

$$K = \text{complex-conjugation operator}, \qquad (A3)$$

which can readily be shown to have the following properties:

$$\mathcal{P}^2 = \mathcal{I}, \quad K^2 = \mathcal{I}, \qquad (A4)$$

$$[\mathcal{P}, K] = 0, \qquad (A5)$$

$$[J, \mathcal{P}]_+ = 0, \quad [J, K]_+ = 0. \qquad (A6)$$

A. Eigenfunctions of $\mathcal{H}_L(E)$, J, $\mathcal{P}$, and K

Eigenfunctions Ψ_M of J with eigenvalues M $(M = L + \tfrac{1}{2}, L$ an integer) are discussed in Sec. III; their form is given by Eqs. (21), (22a), and (22b). Since $[\mathcal{H}_L(E), J] = 0$, an eigenfunction of $\mathcal{H}_L(E)$ can be chosen to have the form of Ψ_M.

Eigenfunctions of $\mathcal{P}$ even and odd under $\mathcal{P}$ can be constructed by using the projection operators $\tfrac{1}{2}(1 \pm \mathcal{P})$. In particular, we have

$$\Psi_M^+ \equiv 2^{-1/2}(1 + \mathcal{P})\Psi_M, \quad \Psi_M^- \equiv -i2^{-1/2}(1 - \mathcal{P})\Psi_M. \qquad (A7)$$

These functions are given explicitly by

$$2^{-1/2}\Psi_M^+ = (f_{M-1/2}^c + g_{M+1/2}^c)\psi_\theta^E + (f_{M-1/2}^s - g_{M+1/2}^s)\psi_\epsilon^E, \qquad (A8a)$$

$$2^{-1/2}\Psi_M^- = (f_{M-1/2}^s + g_{M+1/2}^s)\psi_\theta^E + (-f_{M-1/2}^c + g_{M+1/2}^c)\psi_\epsilon^E, \qquad (A8b)$$

where

$$f_L^c \equiv \sum_{\{m_j\}}^{L} c(\{m_j\}) \cos\left(\sum_j m_j \theta_j\right), \qquad (A9a)$$

$$f_L^s \equiv \sum_{\{m_j\}}^{L} c(\{m_j\}) \sin\left(\sum_j m_j \theta_j\right), \qquad (A9b)$$

and g_L^c and g_L^s are defined similarly. If Ψ_M is an eigenfunction of $\mathcal{H}_L(E)$, then so are Ψ_M^+ and Ψ_M^-, since $\tfrac{1}{2}(1 \pm \mathcal{P})$ commutes with $\mathcal{H}_L(E)$.

Similarly, if Ψ_M is an eigenfunction of $\mathcal{H}_L(E)$, then so is $\mathcal{P}\Psi_M$; moreover, $J\mathcal{P} = -\mathcal{P}J$ implies that $\mathcal{P}\Psi_M$ is an eigenfunction of J with eigenvalue $-M$, and is orthogonal to Ψ_M.

Time inversion symmetry, $[K, \mathcal{H}_L(E)] = 0$, implies in addition that if Ψ_M is an eigenfunction of $\mathcal{H}_L(E)$, then the c's and d's in (22a) and (22b) can be chosen to be real. This can be seen as follows. Since $\mathcal{H}_L(E)$, $\mathcal{P}$, and K commute with each other, an eigenfunction Ψ_M^+ of $\mathcal{H}_L(E)$ and $\mathcal{P}$ can also be chosen to be an eigenfunction of K, that is, real or imaginary. From the linear independence of the trigonometric functions appearing in the f's and the g's in (A8a), one can show that for Ψ_M^+ to be real, the c's and d's must be real functions. If one requires

Ψ_M^+ to be imaginary, the result differs only by a phase factor. We shall henceforth assume that the c's and d's are real. With this choice of phase,

$$f_L^c = \mathrm{Re}f_L, \quad f_L^s = \mathrm{Im}f_L,$$

$$g_L^c = \mathrm{Re}g_L, \quad g_L^s = \mathrm{Im}g_L. \tag{A10}$$

Also, Ψ_M is invariant under $K\mathcal{P}$, so that

$$\Psi_M^* = K\Psi_M = \mathcal{P}\Psi_M, \tag{A11}$$

$$\Psi_M^+ = \sqrt{2} \, \mathrm{Re}\Psi_M, \quad \Psi_M^- = \sqrt{2} \, \mathrm{Im}\Psi_M. \tag{A12}$$

B. Symmetry group of $\mathcal{K}_L(E)$

The group[27] $\mathcal{G}$ of the Hamiltonian $\mathcal{K}_L(E)$ is generated by the elements $e^{-iJ\phi}$, $\mathcal{P}$, and K,

$$\mathcal{G} = \left\{ e^{-iJ\phi}, \mathcal{P}, K \right\}, \tag{A13}$$

where ϕ is any real number. The group element $e^{-iJ\phi}$ has the explicit form

$$U(\phi) = \exp(-iJ\phi) = \exp\left[-i\left(\sum l_i\right)\phi\right]\exp(\tfrac{1}{2}i\mathcal{Q}_2\phi)$$

$$= \exp\left[-i\left(\sum l_i\right)\phi\right](\cos\tfrac{1}{2}\phi + i\mathcal{Q}_2\sin\tfrac{1}{2}\phi), \tag{A14}$$

showing that

$$\bar{U}(\phi) \equiv U(\phi + 2\pi) = -U(\phi), \quad U(\phi + 4\pi) = U(\phi). \tag{A15}$$

Also, as a consequence of Eq. (A6), we have

$$U(\phi)\mathcal{P} = \mathcal{P}U(-\phi), \tag{A16}$$

$$U(\phi)K = KU(\phi). \tag{A17}$$

The subgroup of $\mathcal{G}$ generated by $U(\phi)$ is isomorphic to the double group $\bar{C}_\infty$ of the two-dimensional rotation group C_∞. However, the group

$$\mathcal{G}' = \left\{ e^{-iJ\phi}, \mathcal{P} \right\} \tag{A18}$$

is not isomorphic to the double group $\bar{C}_{\infty v}$ of $C_{\infty v}$ = $\{C(\phi), \sigma_v\}$, even though the property $C(\phi)\sigma_v$ = $\sigma_v C(-\phi)$, analogous to (A16), holds. The order of the group element $\mathcal{P}$ is two: $\mathcal{P}^2 = \mathcal{G}$, while the order of σ_v in $\bar{C}_{\infty v}$ is four: $\sigma_v^2 = \bar{E}$, $\sigma_v^4 = E$. Thus, the correspondence $\mathcal{P} \to \sigma_v$ does not yield an isomorphism. The difference between the groups arises from the fact that $\bar{C}_{\infty v}$ is related to two-valued representations of $C_{\infty v}$ and to spinors, while the state space of $\mathcal{K}_L(E)$ involves no spinors.

The character table for $\mathcal{G}'$ is given in Table I. Every irreducible representation of $\mathcal{G}'$ can be chosen real by suitable selection of basis functions. Table I also gives the irreducible representations of $\bar{C}_{\infty v}$ if $U(\phi) \to C(\phi), \mathcal{P} \to \sigma_v$, even though $\mathcal{G}'$ and $\bar{C}_{\infty v}$ are not isomorphic. In contrast, in the case of the analogous finite groups $\mathcal{G}_3' = \{U(\tfrac{2}{3}\pi), \mathcal{P}\}$ and $\bar{C}_{3v}$, the character tables are different.

C. Symmetry of the eigenfunctions of $\mathcal{K}_L(E)$

We now regard (Ψ_M, Ψ_M^*) as a pair of degenerate orthogonal eigenfunctions of $\mathcal{K}_L(E)$ such that $\Psi_M^* = \mathcal{P}\Psi_M$ and $J\Psi_M^* = -M\Psi_M^*$. Thus, each energy level is doubly degenerate (barring accidental degeneracy).

We first identify the irreducible representations of $\mathcal{G}'$ generated by the basis functions (Ψ_M, Ψ_M^*). From $U(\phi)\Psi_M = e^{-iM\phi}\Psi_M$, $\mathcal{P}\Psi_M = \Psi_M^*$, etc., we determine the representation and its characters, and that (Ψ_M, Ψ_M^*) transform according to the irreducible representation E_M' of $\mathcal{G}'$ shown in Table I.

We next make connection between $\mathcal{G}'$ and the cubic point group (O or T_d). We show that each operator representing an element of the cubic group can be expressed as an element of $\mathcal{G}'$, as far as the operator's effect on a vibronic wave function is concerned. In this sense the cubic group can be represented by a subgroup of $\mathcal{G}'$. To show this, we examine the effect of the operator O_R on a general vibronic wave function

$$\Psi(Q, q) = \chi_1(Q)\psi_\theta(q) + \chi_2(Q)\psi_\epsilon(q) \tag{A19}$$

appropriate to $\mathcal{K}_L(E)$; R is an element of the cubic group, $Q = \{Q_{\theta 1}, Q_{\epsilon 1}, \ldots, Q_{\epsilon N}\}$, and q represents the electronic coordinates. Accordingly, we write

$$O_R = O_R(Q)O_R(q), \tag{A20}$$

where $O_R(Q)$ and $O_R(q)$ operate respectively on the vibrational and electronic coordinate spaces. Both the basis sets $(\psi_\theta, \psi_\epsilon)$ and $(Q_{\theta i}, Q_{\epsilon i})$ generate the irreducible representation E of the cubic group (with the same representation matrices). We have

$$O_R(q)\psi_M = \sum_{m'=1}^{2} \psi_{m'} D^E(R)_{m'm}, \tag{A21}$$

where $\psi_1 = \psi_\theta$, $\psi_2 = \psi_\epsilon$ and $D^E(R)$ is the representation matrix. Operating on (A19) with (A20) and using (A21), we obtain

$$O_R\Psi(Q, q) = [D^E(R)_{11}O_R(Q)\chi_1 + D^E(R)_{12}O_R(Q)\chi_2]\psi_1$$

$$+ [D^E(R)_{21}O_R(Q)\chi_1 + D^E(R)_{22}O_R(Q)\chi_2]\psi_2. \tag{A22}$$

If we write the vibronic wave function $\Psi(Q, q)$ in

TABLE I. Character tables for $\mathcal{G}'$ and $\bar{C}_{\infty v}$; $\bar{E}$ = $U(2\pi)$; L is a positive integer and M is a positive half-odd integer.

$\bar{C}_{\infty v}$ $\mathcal{G}'$	E E	$\bar{E}$ $\bar{E}$	$C(\phi), C(-\phi)$ $U(\phi), U(-\phi)$	$C(\phi)\sigma_v$ $U(\phi)\mathcal{P}$
A_1	1	1	1	1
A_2	1	1	1	−1
E_L	2	2	$2\cos L\phi$	0
E_M'	2	−2	$2\cos M\phi$	0

the form of a column matrix, Eq. (A22) takes the form

$$O_R \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = D^E(R) O_R(Q) \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix}. \tag{A23}$$

We assume that the representation D^E has been chosen real unitary, so that every element R of the cubic group can be represented as a rotation $(\mathcal{S}\phi_0)$ in the electronic function space (ψ_1, ψ_2) and in each $(Q_{\theta i}, Q_{\epsilon i})$ vibrational coordinate space, where ϕ_0 specifies the angle of rotation and $\mathcal{S}$ takes the values 1 or 2 denoting respectively proper or improper rotations. Thus,

$$D^E(R) = D^E(\mathcal{S}\phi_0) = \tau(\mathcal{S}) \begin{pmatrix} \cos\phi_0 & -\sin\phi_0 \\ \sin\phi_0 & \cos\phi_0 \end{pmatrix}$$

$$= \tau(\mathcal{S}) e^{-i\phi_0 \alpha_2}, \tag{A24}$$

with

$$\tau(1) = \mathcal{S}, \quad \tau(2) = -\mathcal{U}_\theta. \tag{A25}$$

Next, we introduce polar coordinates (ρ_i, θ_i) for each $(Q_{\theta i}, Q_{\epsilon i})$. Consistent with the specification of $D^E(\mathcal{S}\phi_0)$ in (A24), we find that

$$O_R(Q)\chi = O_{(\mathcal{S}\phi_0)}(Q)\chi(\theta_1, \ldots, \theta_i, \ldots, \theta_N)$$

$$= \chi(\pm\theta_1 - \phi_0, \ldots, \pm\theta_i - \phi_0, \ldots, \pm\theta_N - \phi_0), \tag{A26}$$

where the upper and lower signs correspond respectively to proper and improper rotations. Hence,

$$O_R(Q) = O_{(\mathcal{S}\phi_0)}(Q) = \mathcal{S}(\mathcal{S})\exp\left[-i\phi_0\left(\sum_i l_i\right)\right], \tag{A27}$$

with

$$\mathcal{S}(1) = 1, \quad \mathcal{S}(2) = \mathcal{R}. \tag{A28}$$

Combining Eqs. (A23)-(A25), (A27), and (A28) gives

$$O_R = O_{(\mathcal{S}\phi_0)} = \mathcal{W}(\mathcal{S})\exp\left[-i\phi_0\left(\sum_i l_i\right)\right]\exp(-i\phi_0\alpha_2), \tag{A29}$$

with

$$\mathcal{W}(1) = \mathcal{S}, \quad \mathcal{W}(2) = -\mathcal{R}\mathcal{U}_\theta = \mathcal{P}. \tag{A30}$$

Since χ in Eq. (A26) is a periodic function in each θ_i with period 2π [consistent for example with Eqs. (22a) and (22b)] and since $D^E(\mathcal{S}\phi_0)$ is periodic in ϕ_0, we can write $O_{(\mathcal{S}\phi_0)}$ in the more general form

$$O_{(\mathcal{S}\phi_0)} = \mathcal{W}(\mathcal{S})\exp\left[-i\left(\sum_i l_i \phi' + \alpha_2 \phi''\right)\right], \tag{A31}$$

where $\phi' = \phi_0 + 2\pi n'$, $\phi'' = \phi_0 + 2\pi n''$, and n' and n'' are integers. In the form (A31), $O_{(1\phi_0)}$ can be ex-

pressed as $U(\phi) = e^{-iJ\phi}$, if $\phi = \phi' = -2\phi''$, that is, if $\phi_0 = -\frac{2}{3}\pi(n' + 2n'')$. This is a necessary condition for expressing O_R as an element of $\mathcal{S}'$.

We need not consider all elements of the cubic group; it suffices to treat the generators of the group, since these determine the group. Suitable generators for the groups O and T_d are listed in Table II. The threefold rotation C_3 is taken to be about the [111] axis: $C_3 = C_{3[111]}$, so that $O_R f(x,y,z) = f(y,z,x)$, where f is some function. Similarly for $R = C_{4z}$, $O_R f(x,y,z) = f(y,-x,z)$.

Values of $(\mathcal{S}\phi_0)$ for operators O_R corresponding to generators of O and T_d are also given in Table II. For each of these values, $(1, \frac{2}{3}\pi)$ and $(2,0)$, it is possible to express O_R as an element of $\mathcal{S}'$; such elements are also shown in Table II. These elements of $\mathcal{S}'$, $O_{(1,2\pi/3)} = U(-\frac{4}{3}\pi)$ and $O_{(2,0)} = \mathcal{P}$, generate a subgroup $\mathcal{S}''$ of $\mathcal{S}'$; $\mathcal{S}''$ is isomorphic to D_3, a subgroup of O, and to C_{3v}, a subgroup of T_d. The irreducible representations of $\mathcal{S}'$ can be decomposed with respect to those of its subgroup $\mathcal{S}''$. Proceeding in the usual way using character tables, we find that $E'_{1/2+3k}$, $E'_{3/2+3k}$, and $E'_{5/2+3k}$ with k a non-negative integer decompose respectively into E, $A_1 + A_2$, and E. Basis functions for A_1, A_2, and E of $\mathcal{S}''$ generate representations of O and T_d which are also irreducible and denoted by A_1, A_2, and E.

As a further step we use the projection operator

$$\mathcal{P}_{nm}^{(\mu)} = \frac{n_\mu}{g}\sum_R D^{(\mu)}(R)_{mn}^* O_R \tag{A32}$$

to obtain the transformation properties of Ψ_M^+ and Ψ_M^- given by Eqs. (A8a) and (A8b). We find that for $M = \frac{1}{2} + 3k$, $(\Psi_M^+, -\Psi_M^-)$ transform as basis functions (E_θ, E_ϵ) of E; for $M = \frac{3}{2} + 3k$, Ψ_M^+ belongs to A_1, and Ψ_M^- to A_2; and for $M = \frac{5}{2} + 3k$, (Ψ_M^+, Ψ_M^-) transform as partners (E_θ, E_ϵ).

The analysis for the group O_h differs from that for O only in that $(\psi_\theta, \psi_\epsilon)$ transform as E_g or E_u while only (Q_θ, Q_ϵ) which transform as E_g can occur in $\mathcal{K}_L(E_g)$ and $\mathcal{K}_L(E_u)$.

D. Transformation properties of the vibrational parts in Ψ_M^+ and Ψ_M^-

The vibrational parts of Ψ_M^+ and Ψ_M^- are shown in Eqs. (A8a) and (A8b). According to Eqs. (A9a),

TABLE II. Generators for O and T_d with corresponding values of $(\mathcal{S}\phi_0)$ and elements of $\mathcal{S}'$.

Generators R		$(\mathcal{S}\phi_0)$	$\mathcal{S}'$
T_d	O		
C_3	C_3	$(1, \frac{2}{3}\pi)$	$U(-\frac{4}{3}\pi)$
iC_{4z}	C_{4z}	$(2, 0)$	$\mathcal{P}$

(A9b), and (A26), f_L^c and f_L^s transform under $C_{\infty v}$ as

$$O_{(\delta\phi)}(Q)f_L^c = f_L^c \cos L\phi \pm f_L^s \sin L\phi, \qquad \text{(A33a)}$$

$$O_{(\delta\phi)}(Q)f_L^s = -f_L^c \sin L\phi \pm f_L^s \cos L\phi, \qquad \text{(A33b)}$$

where the upper and lower signs correspond to $\mathcal{E} = 1$ and $\mathcal{E} = 2$, respectively. g_L^c and g_L^s transform in the same way. We see from (A33) and Table I that f_0^c, f_0^s, and (f_L^c, f_L^s) belong to the irreducible representations A_1, A_2, and E_L of $C_{\infty v}$, where L is a positive integer. With the aid of Table II we see also that (f_L^c, f_L^s) generate a representation of the cubic group. By working out the characters for different classes we find that for $L = 3k$, $1 + 3k$, and $2 + 3k$ (k is a non-negative integer), (f_L^c, f_L^s) belong, respectively, to $A_1 + A_2$, E, and E of O and T_d.

Next, we again use the projection operator (A32), but with O_R replaced by $O_R(Q)$. We find that for $L = 3k$, f_L^c transforms as A_1 and f_L^s transforms as A_2 of O and T_d; for $L = 1 + 3k$, (f_L^c, f_L^s) and for $L = 2 + 3k$, $(-f_L^c, f_L^s)$ transform as partners (E_θ, E_ϵ).

We are now in a position to express the E vibronic wave functions in the forms (14a) and (14b). We find by inspection that for $M = \frac{1}{2} + 3k$, $(\Psi_M^+, -\Psi_M^-)$ have the forms of (14a) and (14b) with

$$\chi^{A_1} = \sqrt{2}\, f_{3k}^c, \quad \chi^{A_2} = \sqrt{2}\, f_{3k}^s, \qquad \text{(A34a)}$$

$$\chi_\theta^E = -\sqrt{2}\, g_{3k+1}^c, \quad \chi_\epsilon^E = -\sqrt{2}\, g_{3k+1}^s, \qquad \text{(A34b)}$$

while for $M = \frac{5}{2} + 3k$, (Ψ_M^+, Ψ_M^-) have the forms of Eqs. (14a) and (14b) with

$$\chi^{A_1} = \sqrt{2}\, g_{3k+3}^c, \quad \chi^{A_2} = -\sqrt{2}\, g_{3k+3}^s, \qquad \text{(A35a)}$$

$$\chi_\theta^E = -\sqrt{2}\, f_{3k+2}^c, \quad \chi_\epsilon^E = \sqrt{2}\, f_{3k+2}^s. \qquad \text{(A35b)}$$

Recall that from (A10), $f_L^c = \text{Re} f_L$ and $f_L^s = \text{Im} f_L$.

APPENDIX B: SYMMETRY OF FUNCTIONS OF E-MODE COORDINATES

We show here that no function of $(Q_{\theta 1}, Q_{\epsilon 1}, \ldots, Q_{\theta N}, Q_{\epsilon N})$ can transform as a basis function of T_1 or T_2 symmetry for either of the cubic point groups O or T_d. Consider the multiple Fourier series expansion of a function F of $(Q_{\theta 1}, Q_{\epsilon 1}, \ldots, Q_{\theta N}, Q_{\epsilon N})$ in terms of polar coordinates $(\rho_1, \theta_1, \ldots, \rho_N, \theta_N)$,

$$F(\rho_1, \theta_1, \ldots, \rho_N, \theta_N) = \sum_{\{m_j\}} h(\{m_j\}) \prod_{j=1}^{N} e^{im_j\theta_j}, \qquad \text{(B1)}$$

where $\sum_{\{m_j\}}$ denotes summation over distinct sets of integers $\{m_1, m_2, \ldots, m_N\}$, and the h's are functions of the ρ_i's. F is a linear combination of the functions

$$\cos\sum_j m_j\theta_j \quad \text{and} \quad \sin\sum_j m_j\theta_j, \qquad \text{(B2)}$$

where $\sum_j m_j = L$, and L takes on integer values. These functions, for given L, are special cases of f_L^c and f_L^s defined in Eqs. (A9a) and (A9b). We saw in Appendix A, subsection D, that the latter functions can form basis functions only for the irreducible representations A_1, A_2, and E of O or of T_d.

APPENDIX C: $\chi^{A_2} \neq 0$ FOR A TWO-FREQUENCY $\mathcal{H}_L(E)$

The Hamiltonian for two-frequency linear Jahn-Teller coupling is given by

$$\mathcal{H} = \mathcal{H}_0\, \mathcal{S} + (V_1 Q_{\theta 1} + V_2 Q_{\theta 2})\mathcal{U}_\theta + (V_1 Q_{\epsilon 1} + V_2 Q_{\epsilon 2})\mathcal{U}_\epsilon, \text{(C1)}$$

where

$$H_0 = \tfrac{1}{2}(P_{\theta 1}^2 + P_{\epsilon 1}^2) + \tfrac{1}{2}\omega_1^2(Q_{\theta 1}^2 + Q_{\epsilon 1}^2)$$
$$+ \tfrac{1}{2}(P_{\theta 2}^2 + P_{\epsilon 2}^2) + \tfrac{1}{2}\omega_2^2(Q_{\theta 2}^2 + Q_{\epsilon 2}^2). \qquad \text{(C2)}$$

To simplify the notation, we denote by $|n_1, n_2; n_3, n_4\rangle$ the normalized eigenfunction $\chi_{n_1}(Q_{\theta 1})\chi_{n_2}(Q_{\epsilon 1})\chi_{n_3}(Q_{\theta 2}) \times \chi_{n_4}(Q_{\epsilon 2})$ of $\mathcal{H}_0$ with eigenvalue $(n_1 + n_2 + 1)\omega_1 + (n_3 + n_4 + 1)\omega_2$, where $\hbar = 1$ and the χ's are the usual simple harmonic oscillator type wave functions. Using the method of Raleigh-Schrödinger perturbation theory, we find the following expression for the second-order perturbed ground vibronic wave function $|\Psi_\theta^E\rangle^{(2)}$ of $\mathcal{H}$:

$$|\Psi_\theta^E\rangle^{(2)} = \begin{pmatrix} |\psi_1\rangle \\ |\psi_2\rangle \end{pmatrix}, \qquad \text{(C3)}$$

$$|\psi_1\rangle = |0000\rangle + \beta_1|1000\rangle + \beta_2|0010\rangle$$
$$+ \beta_1^2(|2000\rangle + |0200\rangle)/\sqrt{2}$$
$$+ \beta_2^2(|0002\rangle + |0020\rangle)/\sqrt{2}$$
$$+ \beta_1\beta_2(|0101\rangle + |1010\rangle), \qquad \text{(C3a)}$$

$$|\psi_2\rangle = -\beta_1|0100\rangle - \beta_2|0001\rangle$$
$$- [(\omega_1 - \omega_2)/(\omega_1 + \omega_2)]\beta_1\beta_2(|0110\rangle - |1001\rangle), \qquad \text{(C3b)}$$

and a similar expression for $|\Psi_\epsilon^E\rangle^{(2)}$; here $\beta_i = (V_i^2/2\omega_i^3)^{1/2}$, $i = 1, 2$.

Comparing with Eq. (14a) we see that χ^{A_2} to second order is the term in $|\psi_2\rangle$ involving $|0110\rangle - |1001\rangle$, which is proportional to

$$Q_{\epsilon 1}Q_{\theta 2} - Q_{\theta 1}Q_{\epsilon 2} = \rho_1\rho_2 \sin(\theta_1 - \theta_2).$$

This shows that, if $\omega_1 \neq \omega_2$, then $\chi^{A_2} \neq 0$ already in second order, and $q = \tfrac{1}{2}(1 + p)$ is not satisfied.

APPENDIX D: PERTURBED TRIPLET VIBRONIC GROUND STATES WITH $f(T_1) \neq 0$

In this appendix, we describe a calculation of the perturbed ground vibronic wave functions of $\mathcal{H}_L(T)$ [see Eq. (42)] to show that vibrational parts

of T_1 symmetry actually enter in the fifth-order perturbed wave functions. We first express the linear Jahn-Teller perturbation υ as follows:

$$\upsilon = 2^{-1/2} k (A + A^\dagger), \tag{D1}$$

$$A = a_\xi \mathcal{T}_\xi + a_\eta \mathcal{T}_\eta + a_\zeta \mathcal{T}_\zeta, \tag{D2}$$

where $a_\xi, a_\xi^\dagger$, etc., are the usual annihilation and creation operators $[a_\xi = i(2\mu\hbar\omega)^{-1/2}(P_\xi - i\mu\omega Q_\xi)]$ of the simple harmonic oscillators, and $k = (\hbar/\mu\omega)^{1/2} V_T$. Next, we observe that the vibronic states of the unperturbed Hamiltonian $\mathcal{K}_0 \mathcal{S}$, given by Eq. (43), can be classified into discrete energy levels characterized by the eigenvalue n of the number operator

$$N = (\hbar\omega)^{-1}(\mathcal{K}_0 - \tfrac{3}{2}\hbar\omega)\mathcal{S}$$

$$= (a_\xi^\dagger a_\xi + a_\eta^\dagger a_\eta + a_\zeta^\dagger a_\zeta)\mathcal{S}. \tag{D3}$$

It is not difficult to verify that if $N|\Psi_n\rangle = n|\Psi_n\rangle$, then $A^\dagger|\Psi_n\rangle$ and $A|\Psi_n\rangle$ are respectively eigenstates of N with eigenvalues $n+1$ and $n-1$. This shows that the perturbation mixes only states with n differing by one, which greatly simplifies the analysis.

The ground vibronic level of $\mathcal{K}_0 \mathcal{S}$ is a vibronic triplet transforming as T_1 (assuming that the electronic triplet is T_1), and is given by

$$|T_{1x}\rangle^{(0)} = \begin{pmatrix} |0\rangle \\ 0 \\ 0 \end{pmatrix}, \quad |T_{1y}\rangle^{(0)} = \begin{pmatrix} 0 \\ |0\rangle \\ 0 \end{pmatrix}, \quad |T_{1z}\rangle^{(0)} = \begin{pmatrix} 0 \\ 0 \\ |0\rangle \end{pmatrix},$$

$$\tag{D4}$$

where $|0\rangle$ denotes the ground state of $\mathcal{K}_0$. Since the perturbation υ is of cubic symmetry, the states $|T_{1x}\rangle^{(0)}$, $|T_{1y}\rangle^{(0)}$, and $|T_{1z}\rangle^{(0)}$ are not mixed by the perturbation, and nondegenerate perturbation theory can be applied to each of the three unperturbed states.

We now proceed to find the perturbed state $|T_{1x}\rangle$ to fifth order. With $|\Psi\rangle^{(s)}$ and W_s the sth-order contribution to the perturbed state and energy, respectively, we have from standard perturbation theory

$$(\mathcal{K}_0 \mathcal{S} - W_0)|\Psi\rangle^{(s)} = (W_1 - \upsilon)|\Psi\rangle^{(s-1)} + W_2|\Psi\rangle^{(s-2)}$$

$$+ \cdots + W_s|T_{1x}\rangle^{(0)}. \tag{D5}$$

Using the properties of υ mentioned above, it can be proved by induction that $|\Psi\rangle^{(s)}$ is a linear combination of unperturbed states with n equal to $s, s-2, s-4, \ldots, 2$ or 1, and $W_s = 0$ for odd s. Moreover, it is convenient to work directly with the set of equations (D5). We shall illustrate the method for the first and second order. In first order, we have

$$(\mathcal{K}_0 \mathcal{S} - W_0)|\Psi\rangle^{(1)} = -2^{-1/2} k (A + A^\dagger)|T_{1x}\rangle^{(0)}, \tag{D6}$$

which yields the solution for $|\Psi\rangle^{(1)}$ given by

$$|\Psi\rangle^{(1)} = -\lambda A^\dagger |T_{1x}\rangle^{(0)} \tag{D7}$$

where $\lambda = k/\sqrt{2}\,\hbar\omega$. The second-order equation is given by

$$(\mathcal{K}_0 \mathcal{S} - W_0)|\Psi\rangle^{(2)} = 2^{-1/2} k \lambda (A + A^\dagger) A^\dagger |T_{1x}\rangle^{(0)}$$

$$+ W_2|T_{1x}\rangle^{(0)} \tag{D8}$$

and has the solution

$$W_2 = -k^2/\hbar\omega, \tag{D9}$$

$$|\Psi\rangle^{(2)} = \tfrac{1}{2}\lambda^2 A^{\dagger 2}|T_{1x}\rangle^{(0)}. \tag{D10}$$

Here we have used the fact that $A A^\dagger |T_{1x}\rangle^{(0)} = 2|T_{1x}\rangle^{(0)}$. Continuing our calculation to fifth order, we find

$$|\Psi\rangle^{(3)} = \tfrac{1}{6}\lambda^3 [-A^{\dagger 3} + 3A^\dagger]|T_{1x}\rangle^{(0)}, \tag{D11}$$

$$|\Psi\rangle^{(4)} = \tfrac{1}{24}\lambda^4 [A^{\dagger 4} + 2A A^{\dagger 3} - 18A^{\dagger 2}]|T_{1x}\rangle^{(0)}, \tag{D12}$$

$$W_4 = \tfrac{1}{4} k^4/(\hbar\omega)^3, \tag{D13}$$

$$|\Psi\rangle^{(5)} = \tfrac{1}{360}\lambda^5 [-3A^{\dagger 5} - 5A A^{\dagger 4} - 10A^\dagger A A^{\dagger 3}$$

$$+ 130A^{\dagger 3} - 270A^\dagger]|T_{1x}\rangle^{(0)}. \tag{D14}$$

By expressing the perturbed wave functions in terms of the unperturbed wave functions, one can readily see that they have the form of Eq. (28a).

The only contributions through fifth order to T_1 vibrational parts of $|\Psi\rangle$ arise from the terms in $|\Psi\rangle^{(5)}$ proportional to

$$|\Psi\rangle^{\prime(5)} = [A A^{\dagger 4} + 2A^\dagger A A^{\dagger 3}]|T_{1x}\rangle^{(0)}; \tag{D15}$$

to see this we first use the following result.

For n a non-negative integer, $A^{\dagger n}|T_{1x}\rangle^{(0)}$ contains no T_1 vibrational part. This can be understood as follows. Since $|T_{1x}\rangle^{(0)}$ involves only an A_1 vibrational part, $A^{\dagger n}|T_{1x}\rangle^{(0)}$ can have a T_1 vibrational part only if $A^{\dagger n}$ does. Now $A^\dagger$ is a cubic invariant with a symmetric matrix representation. Consequently, $A^{\dagger n}$ is also, and can therefore be represented as

$$A^{\dagger n} = \hat{O}(A_1)\mathcal{S} + \hat{O}(\theta)\mathcal{E}_\theta + \hat{O}(\epsilon)\mathcal{E}_\epsilon + \hat{O}(\xi)\mathcal{T}_\xi$$

$$+ \hat{O}(\eta)\mathcal{T}_\eta + \hat{O}(\zeta)\mathcal{T}_\zeta. \tag{D16}$$

There is no T_1 electronic part in (D16) because the matrix is symmetric. To be a cubic invariant, the vibrational operators $\hat{O}(A_1)$, $(\hat{O}(\theta), \hat{O}(\epsilon))$, and $(\hat{O}(\xi), \hat{O}(\eta), \hat{O}(\zeta))$ must transform as basis functions for A_1, E, and T_2, respectively. Thus, $A^{\dagger n}$ has no T_1 vibrational part and neither does $A^{\dagger n}|T_{1x}\rangle^{(0)}$.

Through fifth order the only terms in $|\Psi\rangle$ not of the form $A^{\dagger n}|T_{1x}\rangle^{(0)}$ are the terms in $|\Psi\rangle^{(4)}$ proportional to $A A^{\dagger 3}|T_{1x}\rangle^{(0)}$ and the terms in $|\Psi\rangle^{(5)}$ proportional to $|\Psi\rangle^{\prime(5)}$, as is seen by inspection. An examination of the explicit form of $A A^{\dagger 3}|T_{1x}\rangle^{(0)}$

in terms of harmonic-oscillator wave functions reveals that it has the form of (28a) with non-vanishing A_1, E, and T_2 vibrational parts, but no T_1 vibrational part. Consequently, only the terms $|\Psi\rangle^{(5)}$ proportional to $|\Psi\rangle'^{(5)}$ can contribute T_1 vibrational parts to $|\Psi\rangle$ through fifth order. In terms of standard harmonic oscillator wave functions χ_n we have

$$|\Psi\rangle'^{(5)} = \begin{pmatrix} 28\chi_1\,\chi_1\,\chi_1 \\ 13\sqrt{6}\,\chi_0\,\chi_0\,\chi_3 + 15\sqrt{2}\,\chi_0\,\chi_2\,\chi_1 + 17\sqrt{2}\,\chi_2\,\chi_0\,\chi_1 \\ 13\sqrt{6}\,\chi_0\,\chi_3\,\chi_0 + 15\sqrt{2}\,\chi_0\,\chi_1\,\chi_2 + 17\sqrt{2}\,\chi_2\,\chi_1\,\chi_0 \end{pmatrix},$$

(D17)

where $\chi_{n_1}\,\chi_{n_2}\,\chi_{n_3}$ is an abbreviation for $\chi_{n_1}(Q_\xi)\chi_{n_2}(Q_\eta) \times \chi_{n_3}(Q_\zeta)$. The vibronic wave function (D17) can be

expressed in the form (28a) with

$$\chi^{A_1} = 28\chi_1\,\chi_1\,\chi_1, \quad \chi_\theta^E = \chi_\epsilon^E = 0,$$

$$-2^{-1/2}\chi_z^{T_1} = -\sqrt{2}\,(\chi_0\,\chi_2\,\chi_1 - \chi_2\,\chi_0\,\chi_1),$$

$$2^{-1/2}\chi_\zeta^{T_2} = 13\sqrt{6}\,\chi_0\,\chi_0\,\chi_3 + 16\sqrt{2}\,(\chi_0\,\chi_2\,\chi_1 + \chi_2\,\chi_0\,\chi_1),$$

$$2^{-1/2}\chi_y^{T_1} = \sqrt{2}\,(-\chi_0\,\chi_1\,\chi_2 + \chi_2\,\chi_1\,\chi_0),$$

$$2^{-1/2}\chi_\eta^{T_2} = 13\sqrt{6}\,\chi_0\,\chi_3\,\chi_0 + 16\sqrt{2}\,(\chi_0\,\chi_1\,\chi_2 + \chi_2\,\chi_1\,\chi_0).$$

(D18)

We thus conclude that in the case of linear Jahn-Teller coupling to a single T_2 vibrational-mode triplet, the ground-state wave functions actually assume the most general form (28), so that $f(T_1) \neq 0$.

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[1] F. S. Ham, Int. J. Quant. Chem. 5, 191 (1971).

[2] F. S. Ham, Phys. Rev. 138, A1727 (1965).

[3] F. S. Ham, Phys. Rev. 166, 307 (1968).

[4] M. D. Sturge, Solid State Phys. 20, 91 (1967).

[5] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Metal Ions (Oxford U. P., London, 1970).

[6] F. S. Ham, in Electron Paramagnetic Resonance, edited by S. Geschwind (Plenum, New York, 1972).

[7] R. Englman, The Jahn-Teller Effect in Molecules and Crystals (Wiley, New York, 1972).

[8] J. R. Fletcher, J. Phys. C 5, 852 (1972).

[9] M. C. M. O'Brien, J. Phys. C 5, 2045 (1972).

[10] B. Halperin and R. Englman, Phys. Rev. Lett. 31, 1052 (1973).

[11] N. Gauthier and M. B. Walker, Phys. Rev. Lett. 31, 1211 (1973).

[12] M. Hamermesh, Group Theory and its Application to Physical Problems (Addison-Wesley, Reading, Mass., 1962).

[13] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, Properties of the Thirty-Two Point Groups (M. I. T. Press, Cambridge, 1963).

[14] J. C. Slonczewski, Phys. Rev. 131, 1596 (1963).

[15] The variational ground level functions used by Fletcher (Ref. 8) do not contain vibrational parts of A_2 symmetry, i.e., $\chi^{A_2} = 0$. This leads to $q = \frac{1}{2}(1+p)$ in his calculation.

[16] H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, and R. A. Sack, Proc. R. Soc. A 244, 1 (1958).

[17] W. Moffitt and W. Thorson, in Calcul des Functions d'Onde Moleculaire, edited by R. Dundel (Rec. Mem. Centre Nat. Rech. Sci., Paris, 1958), p. 141.

[18] It should be noted $\text{Im} f_0 = 0$ in the special case when all the frequencies of the vibrational modes are

equal, since in this case, $\mathcal{H}_L(E)$ can be transformed (see Ref. 14) so that the Jahn-Teller coupling involves only a single vibrational mode pair. Thus, this conclusion reached in Ref. 10 to fourth order in the coupling coefficients for the ground level actually holds for arbitrary coupling strength and for any $M = \frac{1}{2}$ level.

[19] This is contrary to O'Brien's conclusion (Ref. 9) mentioned earlier. In O'Brien's proof, the $|f_0\rangle$ in Eq. (46), which corresponds to the f_0 in our (23a) and (22a), has been implicitly assumed to be real. This assumption leads to $\chi^{A_2} = 0$ [see Eq. (23a)], and hence the validity of $q = \frac{1}{2}(1+p)$.

[20] M. Caner and R. Englman, J. Chem. Phys. 44, 4054 (1966).

[21] Exactly the same discussion and conclusion will hold for electronic triplet states T_1 or T_2 in either cubic or tetrahedral symmetry. In particular, Eqs. (28a)–(28c) represent T_1 (or T_2) vibronic wave functions when the electronic state is T_1 (or T_2) in either cubic (O) or tetrahedral (T_d) environment. Further, for the group O_h, Eqs. (28a)–(28c) would also represent vibronic states which transform in the same way as the electronic triplet provided that g-type vibrational factors are used (e.g., $\chi_x^{T_1}$ becomes $\chi_x^{T_1 g}$, $\chi_\xi^{T_2}$ becomes $\chi_\xi^{T_2 g}$, etc.).

[22] For convenience, Ham introduced extrapolation formulas (Ref. 2) for the reduction factors, based on the second order perturbation results; these formulas satisfy Eq. (39) for all values of the coupling constants.

[23] M. C. M. O'Brien, J. Phys. C 4, 2524 (1971).

[24] R. Romestain and Y. Merle d'Aubigné, Phys. Rev. B 4, 4611 (1971).

[25] W. Moffitt and W. Thorson, Phys. Rev. 108, 1251 (1957).

[26] In a cluster-model case of $\mathcal{H}_L(E)$, Moffitt and Thorson (Ref. 23) pointed out that J and $\mathcal{P}$ commute with $\mathcal{H}_L(E)$. For the many-frequency case, an operator related to J was discussed by Slonczewski (Ref. 14). The symmetry was discussed recently by Fletcher (Ref. 8) on the basis of J and K commuting with $\mathcal{H}_L(E)$. However, the full implications of the symmetry of $\mathcal{H}_L(E)$

have apparently not hitherto been developed.

[27]Strictly speaking one may regard the group of $\mathcal{K}_L(E)$ to be the group generated by $\mathcal{G}$ and the spatial symmetry group of the system, the cubic point group; $\mathcal{G}$ is a proper subgroup of the group so generated. However, it so happens that some elements of the cubic group affect neither the electronic wave functions nor the vibrational coordinates associated with $\mathcal{K}_L(E)$, and as discussed below, the effect of any element of the cubic group can be represented by an element of $\mathcal{G}$. Consequently, we regard $\mathcal{G}$ as the group of $\mathcal{K}_L(E)$.