PHYSICAL REVIEW B VOLUME 17, NUMBER 2 15 JANUARY 1978

Dynamic Jahn-Teller vibronic coupling for an orbital triplet: $T \times \tau_2$ and $T \times (\tau_2 + \epsilon)$

N. Sakamoto and S. Muramatsu

Department of Electronic Engineering, Utsunomiya University, Utsunomiya, Japan

(Received 1 November 1976; revised manuscript received 30 June 1977)

Numerical solutions of the vibronic problem for an electronic triplet state coupled to τ_2 vibrations in cubic symmetry have been investigated in detail by Lanczos's method for the diagonalization of a sparse matrix. Ham's reduction factors and zero-phonon intensity have been calculated and compared with the previous results. Good agreement between our results and the previous ones has been found. Our method has been sucessfully extended to the general problem of a $T \times (\tau_2 + \epsilon)$ system in which the coupling to the two modes is assumed different. The vibronic energy scheme for the lower states of this system are obtained in the intermediate-coupling region. The properties of the lowest state are also investigated.

I. INTRODUCTION

Analysis of vibronic states has been one of the important problems in the theory of the Jahn-Teller effect. Its study was initiated by Moffitt and co-workers[1,2] and independently by Longuet-Higgins *et al.*[3] A purely quantum-mechanical solution for an electronic doublet (E) state coupled to a doubly degenerate vibrational ϵ mode ($E\times\epsilon$) has been first obtained numerically by them.[3,4] The vibronic state in this system can be specified by a quantum number J corresponding to a fictitious angular momentum operator commuting with a total Hamiltonian. Existence of this operator makes the treatment elegant. The matrix of the vibronic Hamiltonian to be diagonalized has a tridiagonal form, of which matrix elements are given analytically, once one specifies the quantum number J.

Thorson and Moffitt[5] presented numerical solutions of the vibronic energy levels for the dynamic Jahn-Teller coupling of the fourfold degenerate Γ_8 state with a triply degenerate vibration (τ_2). This problem is similar to that of the $E\times\epsilon$ in some points: It has a good quantum number J and its secular equation is identical to that of the $E\times\epsilon$ except that matrix elements in it are expressed by a half integer instead of an integer in the latter.

The vibronic system where we cannot find an operator analogous to J is much more complicated than the one which has it. This typical example is an electronic triplet state (T) coupled to a triply degenerate vibrational τ_2 mode in cubic symmetry ($T\times\tau_2$). Caner and Englman have first succeeded in analyzing this problem numerically.[6] In order to reduce the order of the matrix to be diagonalized, Caner and Englman classified vibronic basis functions, so that they transformed as the irreducible representations of the cubic group. They set up the matrix of the Hamiltonian in these symmetry-adapted basis functions constructed from cubic harmonics which are obtained from spherical harmonics up to order 12.

Recently, the specific system in which an electronic triplet T state in cubic symmetry equally couples to both ϵ and τ_2 modes has been studied by O'Brien[7] and by Romestain and D'Aubigné[8] (hereafter referred to as D-mode model). The assumption about equal frequency, equal effective mass, and equal coupling allows the ϵ and τ_2 vibrations of the different symmetry to behave as if they were components of a single mode (D mode), so that a triplet state couples to a fivefold degenerate vibration. In this special case a good quantum number J exists. A general treatment of the $T\times(\tau_2+\epsilon)$ vibronic problem has not yet been done without the assumption used in the analysis of the D-mode model, because of the complexity which derives mainly from the high degeneracies in the vibrational states.

The objective of this work is to investigate a further challenge from a different approach to the fundamental problem ($T\times\tau_2$) first analyzed numerically by Caner and Englman,[6] and to extend it to a general problem of a triplet state linearly coupled to both ϵ and τ_2 modes. Our method is a direct application of recent numerical analysis for diagonalization of a sparse matrix. We have found that the Lanczos method[9] can be applied effectively to the vibronic Hamiltonian matrix with which we are concerned, even if the order of its matrix is very large. This method has the advantage of easy inclusion of the vibrational states up to the higher order, since we have no need to construct the symmetry-adapted basis functions. The Lanczos method consists of the following two steps: The first step is tridiagonalization of the original matrix, and the second is final diagonalization of the resulting tridiagonal matrix.

In Sec. II we briefly describe our method, taking the case of $T\times\tau_2$ as an example. In Sec. III the results for vibronic energy levels, Ham's reduction factors and optical absorption intensity are presented in the case of $T\times\tau_2$. The extension to $T\times(\tau_2+\epsilon)$ is made in Sec. IV. The results of the present calculation will be compared with those previously studied.

II. METHOD

We assume that a T_1 electronic state in cubic symmetry is linearly coupled to a vibrational τ_2 mode. The effective vibronic Hamiltonian is expressed as a matrix in the electronic T_1 wave functions $|x\rangle$, $|y\rangle$, and $|z\rangle$:

$$\mathcal{H}=(1/2\mu_\tau)(P_\xi^2+P_\eta^2+P_\zeta^2)+\tfrac{1}{2}\mu_\tau\omega_\tau(Q_\xi^2+Q_\eta^2+Q_\zeta^2)+V_\tau\begin{bmatrix}0 & Q_\zeta & Q_\eta\\ Q_\zeta & 0 & Q_\xi\\ Q_\eta & Q_\xi & 0\end{bmatrix}. \tag{1}$$

Q_α $(\alpha=\xi,\eta,\zeta)$ is the vibrational coordinate of τ_2 mode; P_α the momentum conjugate to Q_α; μ_τ is the effective mass of the mode and ω_τ its angular frequency; V_τ is the Jahn-Teller coupling coefficient. The vibronic Hamiltonian matrix H to be diagonalized is that expressed in vibronic basis functions, which are direct products of electronic wave functions and harmonic oscillator wave functions in the τ_2 mode. The vibrational basis functions are those of the isotropic harmonic oscillator, written as

$$[n_\xi n_\eta n_\zeta]=\chi_{n_\xi}(Q_\xi)\chi_{n_\eta}(Q_\eta)\chi_{n_\zeta}(Q_\zeta), \tag{2}$$

where $\chi_n(Q)$ is a normalized harmonic oscillator function of order n.

The vibronic Hamiltonian matrix H can be tridiagonalized by a similarity transformation matrix P. The resulting transformed Hamiltonian matrix H' has the form

$$H'=P^{-1}HP=\begin{bmatrix}H'(T_1,x) & & & & & \\ & H'(T_1,y) & & & & \\ & & \ddots\, H'(T_2,\xi) & & & \\ & & & H'(T_2,\eta) & & \\ & & & & \ddots\, H'(E,\theta) & \\ & & & & & \ddots\end{bmatrix}, \tag{3}$$

where the submatrix $H'(\Gamma,\gamma)$ $(\Gamma=A_1,A_2,E,T_1,T_2)$ is a symmetric tridiagonal one,

$$H'(\Gamma,\gamma)=\begin{bmatrix}\alpha_1(\Gamma) & \beta_1(\Gamma) & 0 & 0\dots\\ \beta_1(\Gamma) & \alpha_2(\Gamma) & \beta_2(\Gamma) & 0\dots\\ 0 & \beta_2(\Gamma) & \alpha_3(\Gamma) & \beta_3(\Gamma)\dots\\ 0 & 0 & \beta_3(\Gamma) & \alpha_4(\Gamma)\dots\\ \vdots & \vdots & \vdots & \vdots\end{bmatrix}. \tag{4}$$

The basis function of the submatrix $H'(\Gamma,\gamma)$ should transform as the γth component of the Γ irreducible representation of the cubic group. Matrix elements α and β depend on the coupling strength, but are independent of γ.

The eigenvalues of the original Hamiltonian are identical with those of the submatrices of the transformed matrix H'. The corresponding vibronic wave function belonging to the γth component of the Γ irreducible representation can be written as

$$\Psi(\Gamma,\gamma)=\phi_x(\Gamma,\gamma)|x\rangle+\phi_y(\Gamma,\gamma)|y\rangle+\phi_z(\Gamma,\gamma)|z\rangle, \tag{5a}$$

$$\phi_\lambda(\Gamma,\gamma)=\sum_n\sum_j a^\lambda_{nj}[n_\tau;j], \tag{5b}$$

where $[n_\tau;j]$ stands for the vibrational wave function $[n_\xi n_\eta n_\zeta]$, with $n_\tau=n_\xi+n_\eta+n_\zeta$, j being the number labeling the degenerate vibrational states with the energy $(n_\tau+\frac{3}{2})\hbar\omega_\tau$. The coefficients a are determined by the eigenvector of the transformed matrix H' and the transformation matrix P.

In actual process of the similarity transformation of (3), the Lanczos algorithm[9] is used to construct a matrix P such that the result of the similarity transformation

$$T=P^{-1}HP$$

is a tridiagonal matrix. A sequence of vectors

$(P_1, P_2, \ldots)$, as the column vectors of P, is generated by the Lanczos algorithm:

$$
\begin{aligned}
&\|P_1\| = 1, \\
&\alpha_i = (P_i, HP_i) \quad (i = 1, 2, \ldots), \\
&d_{i+1} = HP_i - \alpha_i P_i - \beta_{i-1} P_{i-1} \quad (\beta_0 = 0), \qquad (6)\\
&\beta_i = \|d_{i+1}\|, \\
&P_{i+1} = d_{i+1}/\beta_i,
\end{aligned}
$$

where $\|\ \|$ indicates Euclidean norm. In order to obtain the physically interesting solutions, the initial vector (P_1) must be chosen from a symmetry consideration (see the Appendix for details).

In the case of $T\times(\tau_2+\epsilon)$, we must solve the effective Hamiltonian which consists of Eq. (1) and the following one for the Jahn-Teller coupling to ϵ mode:

$$
\mathcal{H} = (1/2\mu_\epsilon)(P_\theta^2 + P_\epsilon^2) + \tfrac{1}{2}\mu_\epsilon\omega_\epsilon^2(Q_\theta^2 + Q_\epsilon^2)
+ V_\epsilon \begin{bmatrix} \frac{1}{2}Q_\theta - \frac{\sqrt{3}}{2}Q_\epsilon & 0 & 0 \\ 0 & \frac{1}{2}Q_\theta + \frac{\sqrt{3}}{2}Q_\epsilon & 0 \\ 0 & 0 & -Q_\theta \end{bmatrix}. \qquad (7)
$$

Therefore, the vibrational basis function has the form

$$
[n_\xi n_\eta n_\zeta n_\theta n_\epsilon] = \chi_{n_\xi}(Q_\xi)\chi_{n_\eta}(Q_\eta)\chi_{n_\zeta}(Q_\zeta) \times \chi_{n_\theta}(Q_\theta)\chi_{n_\epsilon}(Q_\epsilon), \qquad (8)
$$

instead of (2).

Before leaving this section, we define dimensionless coupling constants k_τ and k_ϵ by

$$k_\tau^2 = V_\tau^2/\mu_\tau\hbar\omega_\tau^3, \qquad (9a)$$

$$k_\epsilon^2 = V_\epsilon^2/\mu_\epsilon\hbar\omega_\epsilon^3. \qquad (9b)$$

The Jahn-Teller stabilization energies for τ_2 and ϵ modes are expressed as

$$E_{\mathrm{JT}}(\tau) = \tfrac{2}{3}k_\tau^2\hbar\omega_\tau = S_\tau\hbar\omega_\tau, \qquad (10a)$$

$$E_{\mathrm{JT}}(\epsilon) = \tfrac{1}{2}k_\epsilon^2\hbar\omega_\epsilon = S_\epsilon\hbar\omega_\epsilon. \qquad (10b)$$

These equations define the Huang-Rhys factors S_τ and S_ϵ.

III. RESULTS FOR $T\times\tau_2$

A. Energy level

We obtain the vibronic energy levels solving secular equations for the symmetric tridiagonal matrices such as Eq. (4). The results of the vibronic energy levels for the lower ones are shown in Fig. 1 as a function of k_τ. The energy unit is $\hbar\omega_\tau$.

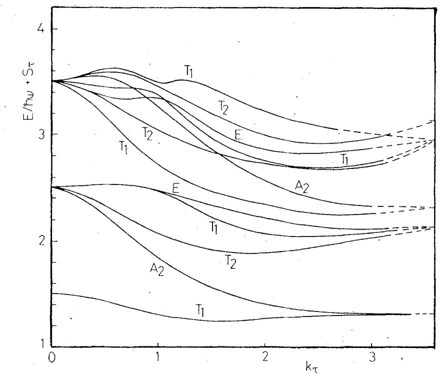

FIG. 1. Vibronic energy levels for $T\times\tau_2$ vs coupling constant k_τ. The levels are labeled according to the irreducible representation of the cubic group.

In order to demonstrate the validity of our method, we have checked whether our results give correct ones in limiting cases. In very weak coupling ($k_\tau \lesssim 0.2$), we can compare the results with the perturbation calculation of Moffitt and Thorson,[2] and at other extreme limit ($k_\tau \to \infty$), with asymptotic expression given by them (on the extreme right in Fig. 1). Our results are in reasonably good accord with those in two limiting cases, and also in very good agreement with those of Caner and Englman.[6] Our results have been obtained by taking into account up to vibrational states corresponding to the phonon number $N_\tau = 20$ at maximum. The convergence of the calculation for the lower vibronic levels shown in Fig. 1 was checked by taking the energy difference (ΔE) between the energy obtained from the calculation taken up to the phonon number N_τ and that from the one up to $N_\tau + 1$. Roughly speaking, the lower vibronic levels originating in $n_\tau = 0$ or $n_\tau = 1$ converge within an accuracy of the order of $|\Delta E/\hbar\omega_\tau| = 10^{-2}$, if we consider the vibrational states up to the phonon number $N_\tau = 5$ for $k_\tau \simeq 1.0$, $N_\tau = 10$ for $k_\tau \simeq 2.0$, and $N_\tau = 18$ for $k_\tau \simeq 3.0$.

B. Reduction factors

Using our vibronic wave functions, $\Psi(T_1, x)$ and $\Psi(T_1, y)$ in Eq. (5), we calculate reduction factors $K(E)$, $K(T_1)$, and $K(T_2)$ first introduced by Ham.[10] From the definition of the reduction factor, they are expressed as

$$K(E) = 1 - 3f(z, z), \qquad (11a)$$

$$K(T_1) = f(x, y) - f(y, x), \qquad (11b)$$

$$K(T_2) = f(x, y) + f(y, x), \qquad (11c)$$

where

$$f(z,z)=\langle\phi_z(T_1,x)|\,\phi_z(T_1,x)\rangle\,,\ f(x,y)=\langle\phi_x(T_1,x)|\,\phi_y(T_1,y)\rangle,$$

and

$$f(y,x)=\langle\phi_y(T_1,x)|\,\phi_x(T_1,y)\rangle\,.$$

The $\phi_x(T_1,y)$ and $\phi_y(T_1,y)$ are obtained from $\phi_z(T_1,x)$ and $\phi_x(T_1,x)$, respectively, by a symmetry consideration.

Leung and Kleiner[11] have derived the expressions for these reduction factors from a group-theoretical analysis, and pointed out that they are related by

$$K(F)+\tfrac{3}{2}[K(T_2)-K(T_1)]=1-3f(T_1). \qquad (12)$$

The $f(T_1)$ measures the contribution of T_1 vibrational part to the vibronic ground state. In our notations, it is given by $f(z,z)-f(y,x)$.

The numerical result of the reduction factors of the vibronic ground state has been already given by Caner and Englman.[6] Our result agrees with theirs very well. Instead of showing respective result for three reduction factors, we have plotted $3f(T_1)$ as a function of k_τ in Fig. 2. Leung and Kleiner argued that this factor was probably small and that $f(T_1)$ is zero both for weak coupling and in the strong coupling limit.[11] Our result in Fig. 2 confirms the smallness of $f(T_1)$, but does not show that it passes through a maximum at some k_τ. We are now doing calculations which are accurate enough to predict the correct behavior of $f(T_1)$ in the strong coupling limit.

C. Absorption intensity

The intensity of the zero-phonon line of a transition from a S-like ground state is given by $|a^x_{01}(T_1,x)|^2=|a^y_{01}(T_1,y)|^2=|a^z_{01}(T_1,z)|^2$. The parameter S', which is plotted against k_τ^2 in Fig. 3, is such that $e^{-S'}$ is the fraction of the total intensity in the zero-phonon line. An analytical expression for S' has been derived by Nasu[12] in a weak coupling approximation. Our result coincides with the value of his expression, $S'=k_\tau^2(1-\frac{1}{8}k_\tau^2)/(1+\frac{1}{4}k_\tau^2)^2$, if $k_\tau^2\lesssim 0.3$.

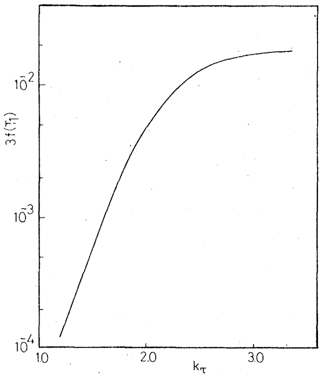

FIG. 2. Factor $3f(T_1)$ is plotted as a function of k_τ.

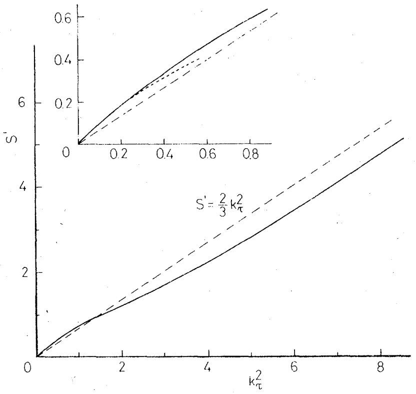

FIG. 3. Plot of S' against k_τ^2. The upper curve shows S' for small values of k_τ^2 on an expanded scale. The dotted curve is $S'=k_\tau^2(1-k_\tau^2/8)/(1+k_\tau^2/4)^2$.

IV. RESULTS FOR $T\times(\tau_2+\epsilon)$

We have extended our calculation to the problem for a triplet state linearly coupled to both τ_2 and ϵ modes. We assume that frequencies of the τ_2 and ϵ modes are equal, throughout the present calculation. The assumption of equal frequencies for both modes is not essential in our method, but only helpful to making the treatment simple.

A. Energy level

The vibronic energy levels for the lower states are presented for three values fo the Huang-Rhys factor ratio (S_ϵ/S_τ) as a function of k_τ or k_ϵ in Fig. 4. When $\omega_\tau=\omega_\epsilon$, the ordinary perturbation theory is applicable only to energies for the T_1 state originating from $n_\tau=n_\epsilon=0$, and A_2, E states from $n_\tau=1$ and $n_\epsilon=0$.[13] To second order, the energy corrections for these states are given by the sum of Eqs. (12) and (14) in Ref. 2. Our results agree with them, when k_τ and k_ϵ are smaller than about 0.2.

The convergency of the calculation has been checked by the same method as that used for the case of the $T\times\tau_2$. Unfortunately, we could not carry out the accurate calculation for large coupling, because extending the order of the Hamiltonian matrix to too large a matrix introduces numerical errors into α's and β's in Eq. (4). It is due to that the Hamiltonian matrix in this case is less sparse than that for the $T\times\tau_2$. These errors

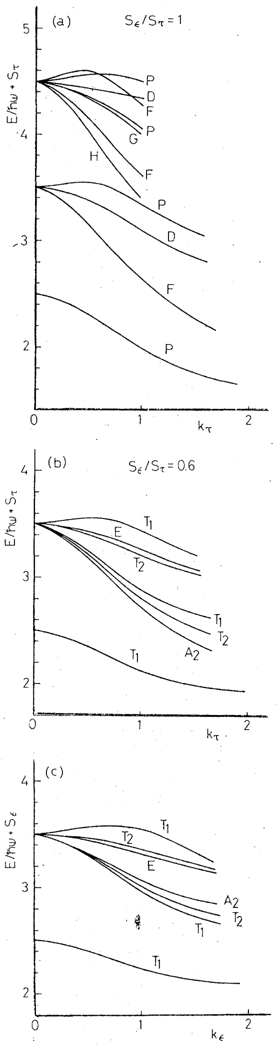

FIG. 4. Vibronic energy levels for $T\times(\tau_2+\epsilon)$ vs k_τ or k_ϵ for (a) $S_\epsilon/S_\tau=1.0$, (b) $S_\epsilon/S_\tau=0.6$, and (c) $S_\epsilon/S_\tau=1.65$. In the case of D-mode model, spectroscopic symbols are used to label the energy levels.

spoil the orthogonality of the column vectors of P and bring about poor results. This is a weak point in the Lanczos method. If we want to remove this weakness, we must take steps of reorthogonalization of the column vectors. In this paper, we are content to confine ourselves to the intermediate coupling region, where the calculation taken up to the phonon number $N(=N_\tau+N_\epsilon)=7$ gives reasonable results to the lower states.

$S_\epsilon/S_\tau=1$ corresponds to the D-mode model. In this special case, the effective Hamiltonian is invariant under the three-dimensional rotation group R_3. The vibronic wave functions transform under R_3 according to an irreducible representation $D^{(L)}$, $L=0,1,\ldots$. O'Brien has analyzed numerically P vibronic states, which are of interest in comparison of the theory to experiment. The available data for comparison between our result and hers is the energy level of the lowest P state. The agreement is very good up to $k_\tau=1.8$. In the strong coupling limit, the vibronic states associated with the lower potential energy surface are $P, F, H, \ldots$ states with odd values of quantum number (L).[14,15] Their energies are given by[7,14]

$$[-S+\tfrac{3}{2}+\tfrac{1}{12}L(L+1)S^{-1}]\hbar\omega+O(S^{-2}),$$

where $S\equiv S_\epsilon=S_\tau$ and $\omega\equiv\omega_\epsilon=\omega_\tau$. The P, F, and H levels in Fig. 4(a) should approach these values. Indeed, they proceed in those directions. The vibronic states in the strong coupling limit are studied sufficiently by Judd and Vogel.[15]

From Figs. 4(b) and 4(c), we can see how the energy levels split, as the effective Hamiltonian has the lower symmetry, that is, cubic one. They split in the same way as atomic levels in the cubic crystal field. Our result is physically reasonable, according with the fact pointed out by O'Brien: Trigonal distortions are favored if the sign of the fourth-order cubic field term is positive and the negative sign favors tetragonal distortions.[14] The magnitude of the level splitting is not so sensitive to the deviation of S_ϵ/S_τ from unity, being at most about $\frac{1}{5}$ of the vibrational energy $\hbar\omega$. However, the energy scheme for the $T\times(\tau_2+\epsilon)$ is different from that for the $T\times\tau_2$, even apart from new vibronic levels introduced by the effect of the ϵ mode interaction.

O'Brien[7,14] concludes that the ground state is a T_1 state originating from $n_\tau=n_\epsilon=0$ throughout, as long as ω_τ and ω_ϵ are not largely different from each other. Without removing the assumption of equal frequencies, we cannot completely rule out the possibility that in a certain vibronic coupling, other state is the ground state rather than the T_1 state, but it also seems improbable to us.

B. Properties of the lowest state

In the D-mode model, properties of the lowest state such as reduction factors and absorption zero zero-phonon intensity have been already studied by O'Brien.[7] She also qualitatively discussed how the reduction factors changed in the strong coupling limit, as S_ϵ/S_τ deviated from unity.[14]

Here we can calculate the reduction factors and zero-phonon intensity for an arbitrary value of S_ϵ/S_τ, except in the strong coupling. The expressions for the reduction factors have the same forms as those of Eqs. (11) except that $\phi_\lambda(\Gamma,\gamma)$ is expressed in terms of the vibrational basis function in (8). Examples of the numerical calculation of reduction factors for three values of the Huang-Rhys factor ratio: $S_\epsilon/S_\tau=0.6$, 1.0, and 1.65 are shown in Fig. 5. The results show physically reasonable behavior:

$$K(E)\gtreqless K(T_2)\quad\text{for}\quad S_\epsilon\gtreqless S_\tau.$$

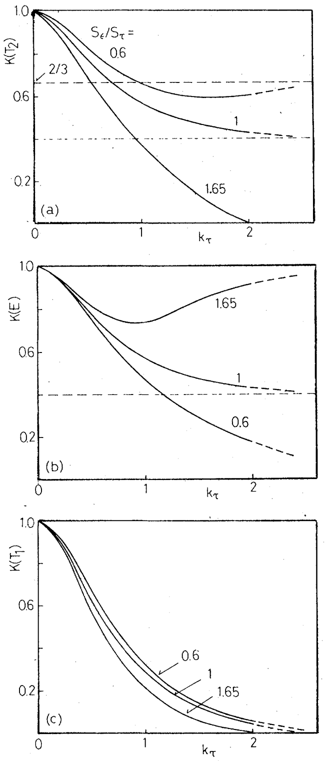

FIG. 5. Reduction factors $K(T_1)$, $K(T_2)$, and $K(E)$ in $T\times(\tau_2+\epsilon)$ for three values of S_ϵ/S_τ: $S_\epsilon/S_\tau=1.65$, 1.0, and 0.6.

The $K(T_1)$ hardly depends on S_ϵ/S_τ, while the other two factors have strong dependence. As discussed by O'Brien,[14] the $K(E)$ and $K(T_2)$ get close to the values appropriate to $S_\epsilon=0$ or $S_\tau=0$ in moderately strong coupling, even when S_ϵ and S_τ are not largely different.

Figure 6 is a plot of the parameter S' for fixed values of total Huang-Rhys factor $(=S_\tau+S_\epsilon)$ against $\Delta\equiv(S_\tau-S_\epsilon)/(S_\tau+S_\epsilon)$. This figure shows that the zero-phonon intensity has the greatest value when S_ϵ and S_τ are nearly equal.

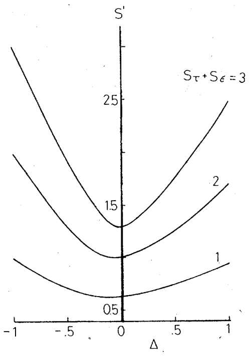

FIG. 6. Parameter S' for fixed values of total Huang-Rhys factor against $\Delta=(S_\tau-S_\epsilon)/(S_\tau+S_\epsilon)$.

V. CONCLUSION

We have studied vibronic systems for a triplet state in cubic symmetry that is more complicated than the others. Firstly, the fundamental problem, $T\times\tau_2$ is solved numerically in detail from a rather different approach from that used by Caner and Englman.[6] We have considered vibrational states up to the phonon number 20. Our results for the vibronic energy levels and reduction factors agree very well with those of Caner and Englman.

It is shown that our method is successfully applied to a more complicated system where a triplet state linearly couples to both ϵ and τ_2 vibrations of different symmetry. We have first solved this problem without the assumption of equal coupling, and obtained the energy scheme for the lower states in the intermediate coupling region. This energy scheme is different from that for the coupling of the τ_2 mode alone.

We should like to emphasize that the method can be applied to other systems, even when one cannot find a good quantum number. A doublet state in tetragonal symmetry that involves competing modes of different symmetry is such an example. Although this system is much simpler than $T\times(\tau_2+\epsilon)$, it has properties similar to those of the latter.[16]

The calculation without the assumption of equal frequency $(\omega_\tau=\omega_\epsilon)$ and application of our calculation to experiment[17] are left for the future.

ACKNOWLEDGMENT

A part of the calculation was performed on a HITAC 8800/8700 computer at the Computer Center of the University of Tokyo.

APPENDIX: USE OF THE LANCZOS ALGORITHM FOR VIBRONIC PROBLEMS

Our approach to the fundamental problems of the dynamic Jahn-Teller effect is to find an algorithm for solving the vibronic Hamiltonian matrix without any assumption about values of parameters involved. The vibronic Hamiltonian matrix is infinite, so that exact solutions cannot be obtained.

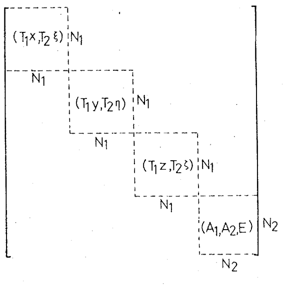

FIG. 7. Block form reduced by row and column permutations from the original matrix.

in a strict sense. In order to obtain the accurate approximate solutions which are of interest to us, we must do a calculation with such large basis that the effect of truncation of the matrix is negligible. For the $T\times\tau_2$ problem, if one includes vibrational states up to the phonon number $N_\tau=20$, the order of the truncated matrix is 5313. The matrix is very large but sparse. It is well known that the principal technique employed in handling a large sparse matrix is permutation of rows and columns to transform it to some proper form so that the problem is reduced to the determination of eigenvalues of several matrices of small dimensions. For the vibronic Hamiltonian matrix in cubic symmetry, it is possible to transform the matrix to four diagonal blocks by row and column permutation, as shown in Fig. 7. One of the diagonal blocks, which we call $(T_1x, T_2\xi)$, is

$$\begin{array}{ccccccc} [000]\,|x\rangle & [001]\,|y\rangle & [010]\,|z\rangle & [101]\,|z\rangle & [002]\,|x\rangle & [020]\,|x\rangle & \cdots \\ \end{array}$$
$$\left[\begin{array}{ccccccc} 3/2 & k_\tau/\sqrt{2} & k_\tau/\sqrt{2} & 0 & 0 & 0 & \cdots \\ k_\tau/\sqrt{2} & 5/2 & 0 & k_\tau/\sqrt{2} & k_\tau & 0 & \cdots \\ k_\tau/\sqrt{2} & 0 & 5/2 & 0 & 0 & k_\tau & \cdots \\ 0 & k_\tau/\sqrt{2} & 0 & 7/2 & 0 & 0 & \cdots \\ 0 & k_\tau & 0 & 0 & 7/2 & 0 & \cdots \\ 0 & 0 & k_\tau & 0 & 0 & 7/2 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \end{array}\right],$$

where matrix elements are in units of $\hbar\omega_\tau$.

It is not difficult to write the positions and values of the matrix elements in a FORTRAN function statement. The next step is to decompose $(T_1x, T_2\xi)$ matrix into (T_1x) and $(T_2\xi)$ matrices using the Lanczos algorithm with tridiagonalization. This process is an essential part of our method.

In computing the eigenvalues and corresponding eigenvectors which transform as the T_1 irreducible representation of the cubic group, we can find, from a symmetry consideration, that the initial vector for the Lanczos process should be chosen as $P_1^\tau=(1,0,0\ldots)$, where τ denotes the transpose. If the Lanczos process is carried out by using Eq. (6), the process breaks down at some stage, since the number of the generated orthogonal vectors which couple to the T_1 vector cannot exceed the number of eigenvectors (k) belonging to the T_1 representation. In principle, once the initial vector is taken as $P_1^\tau=(1,0,0\ldots)$, the Lanczos process proceeds until $\beta_k=0$, and all solutions belonging to the T_1 are obtained. However, in an actual computation a loss of significant bits in finite precision causes destruction of orthogonality of the generated vectors. This is an instability in the Lanczos algorithm. We can overcome this difficulty in the actual process by reorthogonalization of the generated vectors.

To compute the eigenvalues belonging to the T_2 representation, it is necessary to find a new initial vector which is orthogonal to all the previously generated vectors. This vector is $P_1^\tau=(0, -1/\sqrt{2}, 1/\sqrt{2}, 0, 0\ldots)$. The components of this vector are just the Clebsch-Gordan coefficients $\langle T_1\gamma_1T_2\gamma_2\,|\,T_2\xi\rangle$, for vibrational basis functions, [001] and [010] transform as ζ and η rows of the T_2 representation, respectively. The initial vectors for (A_1, A_2, E) matrix are obtained in the same way.

For solving the $T\times(\tau_2+\epsilon)$ vibronic problem, we use the same technique. It is important to arrange the additional matrix elements in appropriate positions. When we apply our method to the problem of the D-mode model, some symmetry considerations are necessary. As pointed out by O'Brien[7]

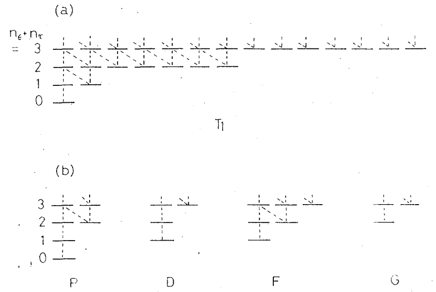

FIG. 8. Coupling scheme for (a) a general case (only T_1 state) and (b) D-mode model. The dotted line joins a pair of coupling levels.

and by Romestain and D'Aubigné,[8] the character of the ground state in this model is P like rather than T_1 like, and the first excited states are P, D, and F like rather than T_1, E, T_2, A_2, T_1, and T_2 like. If we choose the initial vector as done for the $T\times\tau_2$ problem, we can obtain from $(T_1x, T_2\xi)$ matrix only eigenvalues of P- and D-like states. In order to determine the eigenvalues of $F, G, H, I, \ldots$ states, new initial vectors must be chosen step by step from symmetry considerations of the vibronic basis states. Very similar situation occurs in $E\times(\beta_1+\beta_2)$ vibronic problem in tetragonal symmetry.[16] To show the difference of the Lanczos process between a general case and the D-mode model, coupling schemes for some of the lowest levels are illustrated in Fig. 8.

We think that the Lanczos algorithm is one of the effective methods for solutions of the vibronic problem if we handle with care for the reason mentioned before. A progressive understanding for usefulness of the Lanczos algorithm in other problems will be emerging.

---

[1] W. Moffitt and A. D. Liehr, Phys. Rev. 106, 1195 (1957).

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

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

[4] M. Moffitt and W. Thorson, Colloq. Int. Cent. Natl. Rech. Sci. 82, 141 (1958).

[5] W. Thorson and W. Moffitt, Phys. Rev. 168, 362 (1968).

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

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

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

[9] C. Lanczos, J. Res. Natl. Bur. Stand. 45, 255 (1950).

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

[11] C. H. Leung and W. H. Kleiner, Phys. Rev. B 10, 4434 (1974).

[12] K. Nasu, Z. Naturforsch. 30, 1060 (1975).

[13] I. B. Bersuker and V. Z. Polinger, Phys. Status Solidi B 60, 85 (1973).

[14] M. C. M. O'Brien, Phys. Rev. 187, 407 (1969).

[15] B. R. Judd and E. E. Vogel, Phys. Rev. B 11, 2427 (1975).

[16] S. Muramatsu and N. Sakamoto (unpublished).

[17] M. D. Sturge, Phys. Rev. 140, A880 (1965).