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# A theoretical study of the strongly coupled $T \times t$ Jahn–Teller system\*

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We investigate the Jahn–Teller effect for strong coupling between a triply degenerate electronic state and a triply degenerate vibrational mode ( $T \times t$ ). We derive approximate analytical expressions for the lowest energy levels for finite but large coupling constant  $k$ , and have calculated the splitting between these levels. Our splitting between the lowest  $T$  and  $A$  states agrees well with the numerical data. We also have derived approximate analytical expressions for the absorption spectrum for all  $k$ . Our spectra are in reasonable agreement with the numerically calculated spectra.

## I. INTRODUCTION

The Jahn–Teller effect is a member of a larger class of physical phenomena which depend on the interaction between the nuclear and electronic motions for their existence. Also included in this class are the relaxation of spins in a lattice, superconductivity, and non-radiative transitions. The theoretical treatment of these problems is difficult owing to the breakdown of the traditional Born–Oppenheimer or adiabatic approximation. In this paper, we will calculate the energy levels and absorption spectrum of a Jahn–Teller system, using the many-body techniques developed to understand other similar phenomena.

In 1937, Jahn and Teller<sup>1</sup> showed that if a nonlinear polyatomic system has a degenerate electronic state, then there exists at least one asymmetric displacement of the nuclei which will lower the energy of the system. The Jahn–Teller effect arises from the fact that for all nonlinear molecules, there is at least one non-totally-symmetric vibrational mode whose irreducible representation is contained in the symmetric square of the irreducible representation of the degenerate electronic states. Thus, there exists a nonzero matrix element between the degenerate electronic states which splits the degeneracy in first order. The result is a mixing of the electronic and vibrational motions accompanied by an alteration of the energy levels.

In this paper we are interested in the Jahn–Teller coupling between a triply degenerate electronic state and a triply degenerate vibrational mode ( $T \times t$ ). This problem arises, for example, when an electronic  $p$  state occurs in octahedral symmetry. A number of investigators have looked at this problem. Van Vleck<sup>2</sup> and Opik and Pryce<sup>3</sup> calculated the static potential surface; Moffitt and Thorson<sup>4</sup> calculated the eigenvalues for weak coupling using perturbation theory; and finally, Caner and Englman<sup>5a</sup> and Englman *et al.*<sup>5b</sup> calculated the eigenvalues and absorption spectrum for *weak to moderate* coupling using numerical techniques. We extend this work with an approximate, yet analytical, calculation of the eigenvalues for strong coupling<sup>6,7c</sup> (Sec. II) and with an approximate analytical calculation of the spectrum for all coupling strengths (Sec. III).

## II. ENERGY LEVELS FOR STRONG COUPLING

In this section we derive an analytical expression for the energy levels in the strong coupling limit. We begin with a presentation of the Hamiltonian and the infinite coupling limit of the eigenvalues in Sec. II. A. In Sec. II. B we perform unitary transformations which allow the Hamiltonian to be written in a form appropriate for strong coupling. Then in Sec. II. C we derive the expressions for the eigenvalues, and finally, in Sec. II. D we calculate the singlet–triplet splitting.

### A. The Hamiltonian

The Hamiltonian for the  $T \times t$  Jahn–Teller problem has been calculated using group theory by earlier authors.<sup>2</sup> In the octahedral point group, the triply degenerate vibrational mode belongs to the  $t_{2g}$  irreducible representation which transforms like  $(yz, xz, xy)$ . Therefore, in the  $T_{1u}(x, y, z)$  electronic basis the Hamiltonian is

$$H = \left[ \frac{1}{2} (P_4^2 + P_5^2 + P_6^2) + \frac{1}{2} (\omega^2) (Q_4^2 + Q_5^2 + Q_6^2) \right] 1 + K(Q_4\tau_1 + Q_5\tau_2 + Q_6\tau_3),$$

$$1 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \tau_1 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix},$$

$$\tau_2 = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}, \quad \tau_3 = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

Since the matrices  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  do not commute, this Hamiltonian entails a nontrivial coupling between the electronic and vibrational modes.

We begin our calculation by second quantizing this Hamiltonian. That is, define

$$b_i = (1/\sqrt{2\omega}) (\omega Q_i + iP_i)$$

and

$$b_i^* = (1/\sqrt{2\omega}) (\omega Q_i - iP_i),$$

where  $b_i$  ( $b_i^*$ ) creates (destroys) an excitation in mode  $i$ .

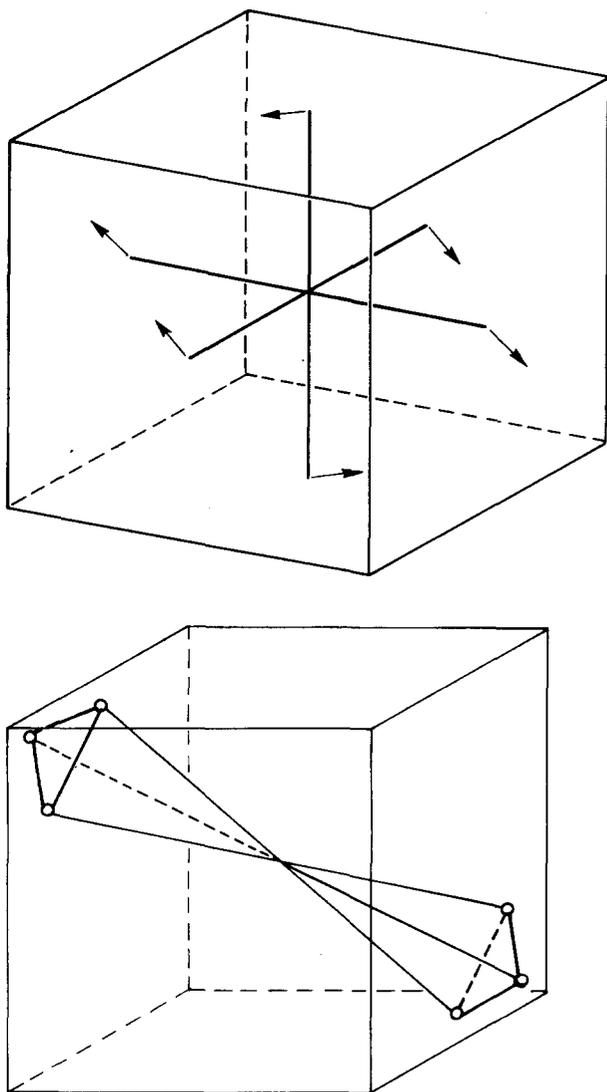


FIG. 1. (a) Octahedron enclosed in a cube with the (1, 1, 1) vibration indicated. (b) Distorted octahedron in an equilibrium position for large finite  $k$ .

With these definitions the Hamiltonian becomes

$$H = \omega(b_4^* b_4 + b_5^* b_5 + b_6^* b_6 + \frac{3}{2}) \mathbf{1} + [k\omega/\sqrt{2}] \{ (b_4 + b_4^*) \tau_1 + (b_5 + b_5^*) \tau_2 + (b_6 + b_6^*) \tau_3 \}. \quad (1)$$

We also define electronic state creation and destruction operators,  $C_i^*$  and  $C_i$ , where the index  $i(=1, 2, 3)$  refers to the  $T_{1u}$  electronic basis.

The asymptotic eigenvalues of this Hamiltonian have been known since the calculation of the static potential surface.<sup>2,3</sup> The potential surface has four minima in  $Q_4, Q_5, Q_6$  space displaced from the origin in the directions  $I = (1, 1, 1)$ ,  $II = (-1, -1, 1)$ ,  $III = (-1, 1, -1)$ , and

$IV = (1, -1, -1)$  by an amount proportional to  $k$  and separated by a barrier of height proportional to  $k^2$ . Thus, for infinite  $k$ , the four minima are well separated and the eigenvalues are those of a three-dimensional harmonic oscillator. Physically, these minima correspond to a distortion of the octahedron by squeezing the axes toward one of the four diagonals of the cube as illustrated in Fig. 1. For infinite  $k$ , the molecule then vibrates about one distorted configuration with no inter-configurational conversion. The ratio of the oscillation frequency in the direction of the displacement to the oscillation frequency perpendicular to the displacement may be calculated by perturbation theory, and is  $1:\sqrt{2/3}$ . Therefore, the asymptotic eigenvalues are

$$E \sim (n_{ii} + 1/2)\omega + (n_{\perp} + 1)\sqrt{2/3}\omega - (2/3)k^2\omega. \quad (2)$$

For all finite values of  $k$  the Hamiltonian has octahedral symmetry; therefore, the lowest state is a triplet throughout. When  $k$  becomes infinite, however, the system assumes a symmetry of  $C_{\infty}$  along any one of the four body diagonals, the lowest singlet becomes degenerate with the triplet, and the lowest state is a quartet. Caner and Englman<sup>5a</sup> give the formula  $0.8k^2 \exp(-0.8k^2)$  as a reasonable fit of their numerical data for  $k \leq 2.5$ . We will now present an approximate calculation of the energy levels for  $k$  large but finite. Our calculation for the separation between the lowest singlet and triplet states agrees reasonably well with the above work, even though only the lowest state is taken into account.

## B. The unitary transformations

For large  $k$ , the problem is basically one of four weakly interacting wells. We will therefore solve for the motion in a single well, e.g.,  $I = (1, 1, 1)$ , and treat the interwell interaction as a perturbation.

First we change the origin of the vibrational coordinate system to  $(1, 1, 1)$  with the unitary transformation  $\exp(S_1)$ , where

$$S_1 = [-k(2)^{1/2}/3] [(b_4 - b_4^*) + (b_5 - b_5^*) + (b_6 - b_6^*)].$$

To perform the unitary transformation, we use the fact that

$$\exp(S)\mathcal{K}\exp(-S) = \mathcal{K} + [S, \mathcal{K}] + \frac{1}{2!}[S, [S, \mathcal{K}]] + \dots$$

Also, for notational simplicity, we define new electronic and vibrational coordinates as follows:

$$\bar{C}_1 = (1/\sqrt{3})(C_1 + C_2 + C_3), \quad \bar{C}_2 = (1/\sqrt{2})(C_1 - C_3),$$

$$\bar{C}_3 = (1/\sqrt{6})(C_1 - 2C_2 + C_3),$$

and

$$\alpha_1 = (1/\sqrt{6})(-b_4 + 2b_5 - b_6), \quad \alpha_2 = (1/\sqrt{2})(-b_4 + b_5),$$

$$\alpha_3 = (1/\sqrt{3})(b_4 + b_5 + b_6).$$

Then

$$H = \omega(\alpha_1^* \alpha_1 + \alpha_2^* \alpha_2 + \alpha_3^* \alpha_3 + 3/2) \mathbf{1} + (k\omega/\sqrt{6})(\bar{\tau}_3 - 2)(\alpha_3 + \alpha_3^*) + (2k^2\omega/3)(1 - \bar{\tau}_3) + (k\omega/\sqrt{6})[(\alpha_1 + \alpha_1^*)\bar{\tau}_1 + (\alpha_2 + \alpha_2^*)\bar{\tau}_2],$$

where

$$\bar{\tau}_1 = \begin{bmatrix} 0 & 0 & 1 \\ 0 & -\sqrt{2} & 0 \\ 1 & 0 & \sqrt{2} \end{bmatrix}, \quad \bar{\tau}_2 = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & -\sqrt{2} \\ 0 & -\sqrt{2} & 0 \end{bmatrix}, \quad \bar{\tau}_3 = \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}.$$

Notice that  $\bar{C}_1^*$  has no linear interaction with the vibrations. To remove the linear interaction between the states  $\bar{C}_2^*$  and  $\bar{C}_3^*$  and the  $\alpha_3$  vibrational mode, we further transform the Hamiltonian with  $e^{S_2}$ , where

$$S_2 = (-k/\sqrt{6})(\bar{\tau}_3 - 2)(\alpha_3 - \alpha_3^*) .$$

Then,  $H = H_0 + V$ , where

$$H_0 = \omega(\alpha_1^* \alpha_1 + \alpha_2^* \alpha_2 + \alpha_3^* \alpha_3 + \frac{3}{2}) - \frac{k^2 \omega}{6} \bar{\tau}_3^2 \quad (3a)$$

and

$$V = (k\omega/\sqrt{6}) [(\bar{C}_1^* \bar{C}_3 \theta + \theta^* \bar{C}_3^* \bar{C}_1)(\alpha_1 + \alpha_1^*) + (\bar{C}_1^* \bar{C}_2 \theta + \theta^* \bar{C}_2^* \bar{C}_1)(\alpha_2 + \alpha_2^*) - \sqrt{2}(\bar{C}_2^* \bar{C}_2 - \bar{C}_3^* \bar{C}_3)(\alpha_1 + \alpha_1^*) - \sqrt{2}(\bar{C}_2^* \bar{C}_3 + \bar{C}_3^* \bar{C}_2)(\alpha_2 + \alpha_2^*)] , \quad (3b)$$

where

$$\theta = \exp[(-3k/\sqrt{6})(\alpha_3 - \alpha_3^*)] .$$

The eigenstates of  $H_0$  are easily seen to be

$$\psi_{i n m l} = (\alpha_1^*)^n (\alpha_2^*)^m (\alpha_3^*)^l \bar{C}_i^* |0\rangle / \sqrt{n! m! l!} ,$$

and the eigenvalues are

$$E_{i n m l}^{(0)} = \begin{cases} (n+m+l+\frac{3}{2})\omega - \frac{2}{3}k^2\omega & i=1 \\ (n+m+l+\frac{3}{2})\omega - \frac{1}{6}k^2\omega & i=2, 3 . \end{cases}$$

### C. The asymptotic eigenvalues

Observe that the separation between the states  $\psi_{1 n m l}$  and  $\psi_{2 n m l}$  or  $\psi_{3 n m l}$  is proportional to  $k^2$ . Therefore, for  $k \gg 1$ , the lowest states are  $\psi_{1 n m l}$ . Proceeding with perturbation theory, we notice that the first order correction

$$\epsilon_1 = \langle \psi_{1 n m l} | V | \psi_{1 n m l} \rangle = 0$$

for all  $n, m$ , and  $l$ . A lengthy but straightforward calculation shows<sup>7c</sup> that

$$\lim_{k \rightarrow \infty} \epsilon_2 = \lim_{k \rightarrow \infty} \sum_{j n' m' l'} \frac{|\langle 1 n m l | V | j n' m' l' \rangle|^2}{E_{1 n m l} - E_{j n' m' l'}} = -(1/6)(n+m+1)\omega .$$

Thus,  $\epsilon_2$  is small for  $n+m$  small, and the energy correction to the second order is

$$E_{1 n m l}^{(2)} = (l + \frac{1}{2})\omega + (n+m+1)(1 - \frac{1}{6})\omega - \frac{2}{3}k^2\omega . \quad (4)$$

It is instructive to compare this energy with the  $k = \infty$  energy levels known from the static calculation [Eq. (2)]. First notice that the Jahn-Teller stabilization energy,  $-(2/3)k^2\omega$ , appears explicitly in the second order energies [Eq. (4)]. Observe further that the static calculation shows that the frequency of the perpendicular mode is  $\sqrt{(2/3)}\omega$ , while Eq. (4) has the frequency shifted from unity to  $1 - \frac{1}{6} \approx 0.834$ , which is reasonably close to  $\sqrt{2/3} \approx 0.827$ .

Continuing with higher order perturbation theory shows that all odd orders vanish. The fourth order correction, which is calculated in the same manner as  $\epsilon_2$ , is

$$\lim_{k \rightarrow \infty} \epsilon_4 = -(1/72)(n+m+1)\omega .$$

The higher order corrections become very difficult to calculate. However, it is easily seen that we have the first three terms in the expansion of

$$\sqrt{2/3} = \sqrt{1 - (1/3)} = 1 - \frac{1}{6} - \frac{1}{72} - \dots .$$

Using a slight variation on Brillouin-Wigner perturbation theory, Beers<sup>7a</sup> has shown that the frequency of the perpendicular mode converges to  $\sqrt{2/3} + \mathcal{O}(k^{-2})$ . Thus the  $k = \infty$  energy levels are well accounted for using the separate well model.<sup>7b</sup>

### D. Singlet-triplet splitting

For  $k = \infty$  there is no interaction between the wells and the lowest state is a quartet. However, if  $k$  is large but finite, the electron may tunnel between the wells. This tunneling will split the degeneracies. To obtain the splitting, we first form approximate eigenfunctions which transform as irreducible representations of the octahedral group from the separate well wavefunctions, then we calculate the Hamiltonian and overlap matrices and finally calculate the energy matrix.

To calculate the eigenfunctions near a trigonal distortion, we use the states appropriate to infinite  $k$ , which are localized in a single well (e.g., I) (i.e., eigenfunctions of  $H_0$ ) as a basis. We then calculate the wavefunction to second order in  $V$  and find, for example,

$$\psi_I = \left\{ \bar{C}_1^* + (k/\sqrt{6}) \sum_{n=0}^{\infty} (-3k/\sqrt{6})^n [1/n! (n+1 + \frac{1}{2}k^2)] \times (\alpha_3^*)^n (\bar{C}_2^* \alpha_2^* + \bar{C}_3^* \alpha_1^*) \right\} |0\rangle .$$

Note that this wavefunction has a zero-point energy of  $(3/2 - 1/6)\omega$  instead of the exact  $k = \infty$  value of  $(\sqrt{2/3} + 1/2)\omega$ . Second order solutions in the other wells are similarly constructed. We now form appropriate (unnormalized) functions which transform as irreducible representations of the octahedral group by combining the lowest states of the four wells. For the lowest  $A_2$  and  $T_1$  states we have

$$\Phi_{T_1} = \frac{1}{2} \begin{pmatrix} \psi_I + \psi_{II} - \psi_{III} - \psi_{IV} \\ \psi_I - \psi_{II} + \psi_{III} - \psi_{IV} \\ \psi_I - \psi_{II} - \psi_{III} + \psi_{IV} \end{pmatrix} , \quad (5)$$

and

$$\Phi_{A_2} = \frac{1}{2} (\psi_I + \psi_{II} + \psi_{III} + \psi_{IV}) .$$

We now calculate the singlet and triplet energies using the second order wavefunctions from each well. For example,

$$E_{A_2}^{(2)} = \frac{\langle \Phi_{A_2} | H | \Phi_{A_2} \rangle}{\langle \Phi_{A_2} | \Phi_{A_2} \rangle} \quad (6)$$

The normalization factor  $\langle \Phi_{A_2} | \Phi_{A_2} \rangle$  is not unity; thus, it is important to include it. Now we let  $|0_J\rangle$  be the zeroth order wavefunction in well  $J$  and  $|1_J\rangle$  be the first order correction, then using Eq. (5) above, Eq. (6) becomes

$$E_{A_2}^{(2)} = \frac{E_0 \langle 0_J + 1_J | 0_J + 1_J \rangle + \epsilon_2 + 3E_0 \langle 0_J + 1_J | 0_K + 1_K \rangle + 3\kappa + 3\kappa'}{\langle 0_J + 1_J | 0_J + 1_J \rangle + 3 \langle 0_J + 1_J | 0_K + 1_K \rangle},$$

where  $E_0 = (1 - 1/6)\omega$ ,  $\kappa = \langle 0_K | V | 1_K \rangle$ , and  $\kappa' = \langle 1_K | V_J | 1_J \rangle$ .  $\kappa$  and  $\kappa'$  are calculated in Ref. 7(c), where they are found to be

$$\kappa = \frac{20}{81} k^2 \omega e^{-8k^2/9}, \quad \kappa' = \frac{8}{243} k^2 \omega e^{-8k^2/9}.$$

Thus, to second order the singlet energy is

$$E_{A_2}^{(2)} = E_0 + \epsilon_2 + \frac{204}{243} k^2 \omega e^{-8k^2/9}.$$

Similarly, the triplet energy is found to be

$$E_{T_1}^{(2)} = E_0 + \epsilon_2 - \frac{68}{243} k^2 \omega e^{-8k^2/9}.$$

Thus the splitting is

$$E_{A_2}^{(2)} - E_{T_1}^{(2)} = +\frac{272}{243} k^2 \omega e^{-8k^2/9}.$$

If we neglect the first order correction to the wavefunction, we find

$$E_{A_2}^{(0)} - E_{T_1}^{(0)} = \frac{32}{27} k^2 \omega e^{-8k^2/9}.$$

This agrees with Judd's calculation.<sup>7b</sup>

Finally, we note that if the approximate ground state wavefunctions localized in each trigonal well, i.e., the  $\psi_1$ , etc., are chosen to be harmonic oscillator functions with the exact  $k = \infty$  frequencies  $\omega$ ,  $\sqrt{2/3}\omega$ , and  $\sqrt{2/3}\omega$ , the singlet triplet splitting is

$$E_{A_2} - E_{T_1} = 1.26 k^2 \omega e^{-0.827k^2}.$$

We note that these approximate results are very close to the numerical calculations for  $k \leq 2.3$  of Caner and Englman given above. Since the present calculation is correct asymptotically for  $k \rightarrow \infty$ , we see that the major effect of the mixing of higher states is to push the  $A$  and  $T$  states closer together while keeping the same form for the interwell overlap, and lowering all states by the same small amount.

Since the weakly interacting well model has succeeded in calculating the energy levels and the splittings for large  $k$ , we will now use this model for calculating the spectral line shape.

### III. SPECTRAL LINE SHAPE

In this section we consider the absorption line shape for transition from a nondegenerate ground state to a triply degenerate excited state in octahedral symmetry. For example, this could correspond to an  $S \rightarrow P$  electronic transition localized on the central ion of an octahedral molecule. The triply degenerate excited state will interact with the vibrational modes of the octahedron, giving structure to the absorption spectrum. It is known<sup>8</sup> that the triply degenerate excited state will couple to the  $a_{1g}$ ,  $e_g$ , and  $t_{2g}$  vibrational modes. However,

since coupling to the  $a_{1g}$  and the  $e_g$  modes is trivial, we will treat coupling to the  $t_{2g}$  vibrational mode only. In this case, the Hamiltonian for the excited state is given by (1) above.

In this section, we will calculate the spectral density using Green's function techniques. Section III.A will give the relationship between the Green's function and the spectral density and also will indicate how the projection operator technique of Zwanzig<sup>9</sup> may be used to make a perturbation expansion of the Green's function. In Sec. III.B this projection operator technique is used to calculate the line shape for small coupling strength,  $k$ . Then in Sec. III.C we will calculate the line shape for large  $k$  using two techniques. The first, an equations of motion technique, is an approximate method which is given for illustrative purposes. The results derived by this first method are confirmed by the second, more accurate but more complicated, projection operator technique. Finally, Sec. III.D discusses these results. Those readers not interested in the mathematical details may go directly to Sec. III.D.

#### A. Spectral density, Green's functions, and projection operators

The absorption line shape for a dipole transition is given by

$$I(\Omega) = \int_{-\infty}^{\infty} dt e^{i\Omega t} \epsilon_\mu \cdot \langle \mu(t) \mu(0) \rangle \cdot \epsilon_\nu,$$

where  $\epsilon_\mu$  ( $\epsilon_\nu$ ) is the polarization of the outgoing (incoming) radiation, and  $\langle \mu(t) \mu(0) \rangle$  is the dipole moment autocorrelation function. Since the dipole moment autocorrelation function is difficult to calculate directly, it is useful to relate the integrand to the Green's function  $G_{jj}(t)$  and to calculate the spectral density using the well-known relationship<sup>7c,10</sup>

$$I(\Omega) = 2\text{Re} \int_0^{\infty} dt e^{i\Omega t} \sum_{j=1}^3 G_{jj}(t), \quad (7a)$$

where

$$G_{jj}(t) = -i\theta(t) \langle C_j(t) C_j^* \rangle \quad (7b)$$

and

$$\theta(t) = \begin{cases} 1 & t > 0 \\ 0 & t < 0. \end{cases}$$

Thus the line shape is just the Fourier transform of a sum of Green's functions. The Green's functions in turn are related to the time evolution of the electronic states. Owing to the form of the Hamiltonian, this time evolution is very complicated, so it may appear that we have gained very little. However, as Eq. (7b) indicates, we are only interested in the vibrational (phonon) average of the evolving electronic state. Thus, by making suitable approximations to the electronic autocorrelation functions and by using the projection operator technique of Zwanzig,<sup>9</sup> we will be able to calculate an analytical expression for the line shape.

We will use the projection operator technique to separate the evolution of the electronic state into a relevant

and an irrelevant part, and to make a perturbation expansion of the relevant part (for a discussion of the use of this technique in other many body problems, see Haake<sup>11</sup>). Briefly, we define the projection

$$P \dots \equiv \frac{\text{Tr}_L(e^{-\beta H_L} \dots)}{\text{Tr}_L(e^{-\beta H_L})}$$

The equation of motion for the relevant part,  $PC_j(t)$ , can be shown to be<sup>9</sup>

$$P\dot{C}_j(t) = i[PH, PC_j(t)] - \int_0^t d\tau PL' e^{i\tau(1-P)L} (1-P)L' PC_j(t-\tau),$$

where  $L' \dots = [V, \dots]$ . If  $\langle V \rangle = 0$ , this equation is exact, but it contains the modified propagator  $\exp[i\tau(1-P)L]$ . We will now expand this exponential keeping only the leading term. Then,

$$P\dot{C}_j(t) = i[PH, PC_j(t)] - \int_0^t d\tau PL' e^{i\tau L_0} L' PC_j(t-\tau), \quad (8)$$

where  $L_0 \dots = [H_0, \dots]$ . This equation for the relevant part keeping all terms to the second order in the perturbation will be the starting point of our line shape calculation.

### B. Small $k$ line shape

We will exhibit the method for small  $k$  first since this is the simpler case. For small  $k$ , the term in curly brackets in Eq. (1) is small and is chosen to be the perturbation  $V$ . In this case  $\langle V \rangle = 0$ , and Eq. (8) is the second order perturbation equation. Further, since  $\langle H \rangle \langle C_i(t) \rangle = 0$ , Eq. (8) simplifies to

$$P\dot{C}_1(t) = - \int_0^t d\tau \langle [V, [V(\tau), \langle C_1(t-\tau) \rangle]] \rangle,$$

where  $V(t) = e^{iH_0 t} V e^{-iH_0 t}$ . A sort of closure holds here because, for example,

$$\langle C_1(t) \rangle = f(t) C_1 + g(t) C_2 + h(t) C_3,$$

where  $f$ ,  $g$ , and  $h$  are unknown functions of time. Now, the line shape is related to  $\sum_i \langle 0 | \langle C_i(t) \rangle C_i^* | 0 \rangle$ , so we look, for example, at

$$\begin{aligned} \langle 0 | \langle \dot{C}_1(t) \rangle C_1^* | 0 \rangle &= \dot{f}(t) \\ &= - \int_0^t d\tau \langle 0 | \langle [V, [V(\tau), f(t-\tau) C_1 \\ &\quad + g(t-\tau) C_2 + h(t-\tau) C_3]] \rangle C_1^* | 0 \rangle \\ &= - \frac{k^2 \omega^2}{2} \int_0^t d\tau \Phi_0(\tau) f(t-\tau), \end{aligned} \quad (9)$$

where

$$\begin{aligned} \Phi_0(\tau) &= \langle (b_6 e^{-i\omega\tau} + b_6^* e^{i\omega\tau}) (b_6 + b_6^*) \\ &\quad + (b_5 e^{-i\omega\tau} + b_5^* e^{i\omega\tau}) (b_5 + b_5^*) \rangle \\ &= 2(\bar{n} + 1) e^{-i\omega\tau} + 2\bar{n} e^{i\omega\tau}, \end{aligned}$$

and  $\bar{n} = (e^{\beta\hbar\omega} - 1)^{-1}$ . The integrand is computed by using the Fermion anticommutation relation  $\{C_i, C_j^*\} = \delta_{ij}$ , and the fact that  $C_i | 0 \rangle = 0$ . The phonon averages are computed as in Messiah.<sup>12</sup> Laplace transforming both sides of (9), we find

$$\hat{f}(s) = \left[ s + \frac{k^2 \omega^2}{2} \hat{\Phi}_0(s) \right]^{-1}$$

and

$$\hat{\Phi}_0(s) = 2 \left[ \frac{\bar{n} + 1}{s + i\omega} + \frac{\bar{n}}{s - i\omega} \right].$$

Therefore,

$$\hat{f}(s) = \left[ s + k^2 \omega^2 \left( \frac{\bar{n} + 1}{s + i\omega} \right) + k^2 \omega^2 \left( \frac{\bar{n}}{s - i\omega} \right) \right]^{-1}.$$

Due to symmetry,  $\hat{f}(s) = \hat{g}(s) = \hat{h}(s)$  and the line shape is just proportional to  $\hat{f}(s)$ . Now, at low temperature,  $\bar{n}$  is small and

$$\hat{f}(s) \cong (s + i\omega) [s(s + i\omega) + k^2 \omega^2]^{-1}.$$

Thus,

$$I(\Omega) = 3 \frac{\omega - \lambda_+}{\lambda_+ - \lambda_-} \delta(\Omega - \lambda_-) + 3 \frac{\lambda_+ - \omega}{\lambda_+ - \lambda_-} \delta(\Omega - \lambda_+),$$

where  $\lambda_{\pm} = \frac{1}{2} \omega [1 \pm (1 + 4k^2)^{1/2}]$ . Thus, to second order in  $k$ , the zero temperature spectrum consists of two delta functions—one relatively intense peak near  $-k^2\omega$ , the other much less intense near  $+\omega$ . For finite temperatures the spectrum has three peaks, and as the temperature is raised, the spectrum becomes more symmetrical as expected from the classical results.<sup>8</sup> These results which hold asymptotically as  $k \rightarrow 0$ , are in qualitative agreement with the exact numerical,  $k=1$  spectrum (the smallest value of  $k$  for which a spectrum is reported) of Englman *et al.*<sup>5b</sup> Quantitative comparison of calculated and numerical spectra is reserved for the next section since the second order perturbation treatment is not expected to be qualitatively good for  $k \geq 1$ .

### C. Large $k$ line shape

As in the energy level calculation, our model for the large  $k$  spectral calculation is based on the static potential surface. Recall that the static surface has four minimum points separated by a distance proportional to  $k$  and by a potential barrier of height proportional to  $k^2$ . Thus, as for the energy level calculation, this problem is basically one of four weakly interacting wells, and we will calculate the spectrum perturbatively starting from the infinite  $k$  form.

The energy level calculation for large  $k$  indicates that the partitioning of the Hamiltonian given in Eqs. (3a) and (3b) is very good for determining the energy of the lowest vibronic states. However, the line shape also depends on the energy of the higher vibronic states; thus, the partitioning of the Hamiltonian should be re-examined. In fact we find that the intraorbital term  $(\bar{C}_2^* \bar{C}_2 - \bar{C}_3^* \bar{C}_3)$  makes a large contribution. We might have anticipated this since earlier work with a different Jahn-Teller problem<sup>13</sup> found that the intraorbital coupling played a dominant role in the dynamical Jahn-Teller effect. This intraorbital coupling is now eliminated with the transformation  $e^{S_3}$ , where

$$S_3 = \frac{k}{\sqrt{3}} (\bar{C}_2^* \bar{C}_2 - \bar{C}_3^* \bar{C}_3) (\alpha_1 - \alpha_1^*).$$

(Notice that  $S_3$  does not contain  $\bar{C}_1$ ; therefore, this transformation has no effect on the previous energy level calculation.)

The Hamiltonian is now written as  $H_0 + V$ , where

$$H_0 = \omega(\alpha_1^\dagger \alpha_1 + \alpha_2^\dagger \alpha_2 + \alpha_3^\dagger \alpha_3 + \frac{3}{2}) - \frac{1}{3} k^2 \omega (\bar{C}_2^\dagger \bar{C}_2 + \bar{C}_3^\dagger \bar{C}_3) - \frac{1}{6} k^2 \omega \bar{\tau}_3^2 \quad (10a)$$

and

$$V = k\omega/\sqrt{6} \{(\bar{C}_1^\dagger \bar{C}_3 f_2 + \text{c. c.}) + (\bar{C}_1^\dagger \bar{C}_2 f_3 + \text{c. c.}) + (\bar{C}_2^\dagger \bar{C}_3 f_1 + \text{c. c.})\}, \quad (10b)$$

where

$$f_1 = -\sqrt{2} \exp[(2k/\sqrt{3})(\alpha_1 - \alpha_1^\dagger)] (\alpha_2 + \alpha_2^\dagger), \\ f_2 = \exp[-(3k/\sqrt{6})(\alpha_3 - \alpha_3^\dagger)] (\alpha_1 + \alpha_1^\dagger) \exp[(k/\sqrt{3})(\alpha_1 - \alpha_1^\dagger)], \\ f_3 = \exp[-(3k/\sqrt{6})(\alpha_3 - \alpha_3^\dagger)] \exp[-(k/\sqrt{3})(\alpha_1 - \alpha_1^\dagger)] (\alpha_2 + \alpha_2^\dagger).$$

Now the effect of  $V$  on all vibronic levels is small, and we may proceed.

As before, the line shape is related to the correlation functions  $\langle C_i(t)C_i^\dagger \rangle$ . Since the trace is cyclically invariant and  $e^S e^{-S} = 1$ , we have

$$\langle C_i(t)C_i^\dagger \rangle_H = \langle \bar{C}_i(t)\bar{C}_i^\dagger \rangle_{\bar{H}}$$

where  $\langle \dots \rangle_H$  means trace with respect to the lattice variable of  $H$ , and  $\langle \dots \rangle_{\bar{H}}$  means the trace with respect to the lattice variables of  $\bar{H}$ ,  $S$  is the sum  $S_1 + S_2 + S_3$ . Thus the phonon average of the time evolution of the bare electronic state is the same as the phonon average of the time evolution of the clothed electronic state. Further, the clothed electronic state can be written as a combination of the states  $\bar{C}_i$ , e.g.,

$$\bar{C}_1 \equiv e^S [(1/\sqrt{3})\bar{C}_1 + (1/\sqrt{2})\bar{C}_2 + (1/\sqrt{6})\bar{C}_3] e^{-S} \\ = (1/\sqrt{3}) \exp[(2k/\sqrt{6})(\alpha_3 - \alpha_3^\dagger)] \bar{C}_1 + (1/\sqrt{2}) \\ \times \exp[-(k/\sqrt{6})(\alpha_3 - \alpha_3^\dagger)] \exp[-(k/\sqrt{3})(\alpha_1 - \alpha_1^\dagger)] \bar{C}_2 \\ + (1/\sqrt{6}) \exp[-(k/\sqrt{6})[(\alpha_3 - \alpha_3^\dagger) - \sqrt{2}(\alpha_1 - \alpha_1^\dagger)]] \bar{C}_3$$

and

$$\langle \bar{C}_1(t)\bar{C}_1^\dagger \rangle \approx \frac{1}{3} \Theta_1(t) \langle \bar{C}_1(t)\bar{C}_1^\dagger \rangle + \frac{1}{2} \Theta_2(t) \langle \bar{C}_2(t)\bar{C}_2^\dagger \rangle \\ + \frac{1}{6} \Theta_3(t) \langle \bar{C}_3(t)\bar{C}_3^\dagger \rangle,$$

where

$$\Theta_1(t) = \exp[-(\frac{2}{3}k^2)(2\bar{n}+1)] \exp\{(\frac{2}{3}k^2)[(\bar{n}+1)e^{-t\omega} + \bar{n}e^{t\omega}]\}, \\ \Theta_2(t) = \Theta_3(t) = \exp[-(\frac{1}{2}k^2)(2\bar{n}+1)] \exp\{(\frac{1}{2}k^2)[(\bar{n}+1)e^{-t\omega} + \bar{n}e^{t\omega}]\}.$$

In this last equation, we have assumed that the electron is clothed by an average phonon cloud so that the phonon operators can be removed from the electron correlation functions. This assumption is asymptotically correct for infinite  $k$  because infinite  $k$  implies an infinite barrier between equivalent distorted configurations. This in turn implies no tunneling between configurations, and the molecule will merely oscillate about one distorted configuration. The infinite  $k$  spectrum will thus be that characteristic of the separate wells (at I, II, III, and IV) and will be given by the Fourier transform of  $\exp[-(\frac{2}{3}k^2)(2\bar{n}+1)] \exp\{(\frac{2}{3}k^2)[\bar{n}e^{t\omega} + (\bar{n}+1)e^{-t\omega}]\} e^{-i(2/3)k^2\omega t}$ . This leads to the usual Poisson form which is well approximated by a Gaussian. For  $k$  finite but large, we expect the spectrum to be perturbed from this form by tunneling between the four wells. However, this approximation is still expected to be fairly good because for large  $k$  the molecule will most often be found near

the four minima in configuration space. Each of the minima has an average phonon cloud associated with it, and it is this average cloud which will dress the electron and interact only weakly with the rest of the phonon bath. With this approximation, the line shape for large, finite  $k$  becomes

$$I(\Omega) = \frac{\mu^2}{3} \int_{-\infty}^{\infty} dt e^{i\Omega t} [\Theta_1(t) \langle \bar{C}_1(t)\bar{C}_1^\dagger \rangle \\ + \Theta_2(t) \langle \bar{C}_2(t)\bar{C}_2^\dagger \rangle + \Theta_3(t) \langle \bar{C}_3(t)\bar{C}_3^\dagger \rangle].$$

Owing to the phonon dressing, the calculation of the line shape for large  $k$  is more complicated than the line shape calculation for small  $k$ . We will calculate it using two methods. The second method is the projection operator technique used previously for small  $k$ . This is the preferred method since it automatically keeps all terms to the same order in the perturbation. However, this problem is sufficiently complicated that it is difficult to see what is going on with this projection operator method. Thus, we present the more transparent but less rigorous equations of motion technique first. In this method, the equation of motion for  $\langle \bar{C}_2(t)\bar{C}_2^\dagger \rangle$  is calculated by differentiating twice with respect to time, decoupling the electron and phonon operators, and finally solving the resulting second order differential equation. This method will be shown to give a reasonable fit to the exact numerical spectra.<sup>5b</sup>

### 1. Equation of motion method.

We begin by going into an interaction representation with respect to  $H_0$  given in Eq. (10a). In this representation, the time evolution of the electronic state is given by

$$\bar{C}_i(t) = \mathcal{T} \left\{ \exp \left( i \int_0^t V(\tau) d\tau \right) \right\} \bar{C}_i \mathcal{T} \left\{ \exp \left( i \int_0^t V(\tau) d\tau e^{-i\epsilon_i \tau} \right) \right\},$$

where  $\epsilon_1 = -(2/3)k^2\omega$ ,  $\epsilon_2 = \epsilon_3 = -(1/2)k^2\omega$ , and  $V(t) = e^{iH_0 t} V e^{-iH_0 t}$ . Then, differentiating twice with respect to time, separating the phonon operators from the electron operators, and computing the phonon averages, one can easily show, for example,

$$\frac{d^2}{dt^2} \langle \bar{C}_1(t)\bar{C}_1^\dagger \rangle \cong -(\epsilon_1^2 + k^2\omega^2\sigma/3) \langle \bar{C}_1(t)\bar{C}_1^\dagger \rangle, \quad (11)$$

where  $\sigma = \coth(\beta\omega/2)$ . The initial conditions are  $\langle \bar{C}_1(0)\bar{C}_1^\dagger \rangle = 1$  and  $\langle \dot{\bar{C}}_1(0)\bar{C}_1^\dagger \rangle = -i\epsilon_1$ ; thus the solution of (11) is

$$\langle \bar{C}_1(t)\bar{C}_1^\dagger \rangle = A_1 i \sin\gamma_1 t + \cos\gamma_1 t,$$

where

$$\gamma_1 = k\omega \left[ \frac{4}{9} k^2 + \frac{1}{3} \sigma \right]^{1/2} \text{ and } A_1 = -\epsilon_1/\gamma_1.$$

The solutions for the other two correlation functions,  $\langle \bar{C}_2(t)\bar{C}_2^\dagger \rangle$  and  $\langle \bar{C}_3(t)\bar{C}_3^\dagger \rangle$ , are similarly found to be

$$\langle \bar{C}_2(t)\bar{C}_2^\dagger \rangle = \langle \bar{C}_3(t)\bar{C}_3^\dagger \rangle = A_2 i \sin\gamma_2 t + \cos\gamma_2 t,$$

where  $\gamma_2 = k\omega \left[ \frac{1}{4} k^2 + \frac{1}{2} \sigma \right]^{1/2}$  and  $A_2 = -\epsilon_2/\gamma_2$ .

Now remember that the line shape is related to the product,  $\theta_i(t) \langle \bar{C}_i(t)\bar{C}_i^\dagger \rangle$ . To calculate the line shape, it turns out to be convenient to express  $\theta_1(t)$  and  $\theta_2(t)$  in terms of a sum of modified (hyperbolic) Bessel functions. For example,

$$\Theta_1(t) = \exp\left[-\left(\frac{2}{3}k^2\right)(2\bar{n}+1)\right] \sum_{m=-\infty}^{\infty} e^{-im\omega t} \left[\frac{\bar{n}+1}{\bar{n}}\right]^{m/2} I_m\left[(4/3)k^2\bar{n}^{1/2}(\bar{n}+1)^{1/2}\right].$$

With this expansion, the line shape becomes

$$\begin{aligned} I(\Omega) &= \frac{\mu^2}{3} \int_{-\infty}^{\infty} dt e^{i\Omega t} \left[ \theta_1(t) \langle \bar{C}_1(t) \bar{C}_1^* \rangle + 2\theta_2(t) \langle \bar{C}_2(t) \bar{C}_2^* \rangle \right] \\ &= \frac{\mu^2}{3} \left( \exp\left[-\left(\frac{2}{3}k^2\right)(2\bar{n}+1)\right] \sum_{m=-\infty}^{\infty} \left[\frac{\bar{n}+1}{\bar{n}}\right]^{m/2} I_m\left[(4/3)k^2\bar{n}^{1/2}(\bar{n}+1)^{1/2}\right] \right. \\ &\quad \times \left\{ \left[\frac{A_1+1}{2}\right] \delta(\Omega - m\omega + \gamma_1) + \left[\frac{1-A_1}{2}\right] \delta(\Omega - m\omega - \gamma_1) \right\} \\ &\quad \left. + 2 \exp\left[-\left(\frac{1}{2}k^2\right)(2\bar{n}+1)\right] \sum_{m=-\infty}^{\infty} \left[\frac{\bar{n}+1}{\bar{n}}\right]^{m/2} I_m\left[k^2\bar{n}^{1/2}(\bar{n}+1)^{1/2}\right] \left\{ \left[\frac{A_2+1}{2}\right] \delta(\Omega - m\omega + \gamma_2) + \left[\frac{1-A_2}{2}\right] \delta(\Omega - m\omega - \gamma_2) \right\} \right). \end{aligned} \quad (12)$$

Although this formula looks somewhat formidable, it is really a series of delta functions with intensities depending on  $k^2$  and  $\bar{n}$ . This dependence is complicated in general, but simplifies at low temperatures when only a few values of  $m$  in the sum have a significant intensity. For example, at zero temperature only positive values of  $m$  contribute [because for small  $Z$ ,  $I_m(Z) \sim (\frac{1}{2}Z)^m / (m+1)!]$ . Further, the intensity of the  $m$ th line is proportional to  $(k^2)^m / (m+1)!$ , so the intensity peaks at  $m \approx k^2$ . Figure 2 shows three spectra calculated using this result and compares them to numerically calculated spectra of Englman *et al.*<sup>5b</sup> We find that the spectra agree reasonably well even for fairly small values of  $k$ . It should be emphasized, however, that this method is not rigorous (for example, it does not keep all terms to the same order in the perturbation). We present these results because they are confirmed by the projection operator technique and because it is easier to see where the terms are coming from using this method. We postpone discussion of the spectra until after completion of the projection operator derivation.

## 2. Projection operator method

We now confirm the equations of motion result with the more accurate projection operator method. The Hamiltonian is partitioned into  $H_0 + V$  as given in Eqs. (10a) and (10b). Notice that now  $\langle V \rangle \neq 0$ , but since it is proportional to  $e^{-k^2}$ , for  $k$  very large, it is quite small and we therefore set it equal to zero. With  $\langle V \rangle = 0$ , we may again use Eq. (8) to determine  $\langle \bar{C}_i(t) \bar{C}_i^* \rangle$  to second order in  $V$ . As in the small  $k$  case, a sort of closure holds and, for example

$$\langle \bar{C}_1(t) \rangle = A(t) \bar{C}_1 + B(t) \bar{C}_2 + D(t) \bar{C}_3,$$

where  $A$ ,  $B$ , and  $D$  are unknown functions of time. Us-

ing this relationship, Eq. (8) becomes

$$\langle 0 | \langle \dot{\bar{C}}_1(t) \bar{C}_1^* | 0 \rangle = \dot{A}(t) = -i\epsilon_1 A(t) - \frac{k^2 \omega^2}{3} \int_0^t \Phi(\tau) A(t-\tau) d\tau, \quad (13)$$

where

$$\begin{aligned} \Phi(t) &= e^{-i\epsilon_2 t} \left\{ \exp\left[-\frac{11}{12} \sigma k^2 (2 - e^{i\omega t} - e^{-i\omega t}) + \frac{11}{12} k^2 (e^{-i\omega t} - e^{i\omega t})\right] \right. \\ &\quad \left. \times \left[ 2\sigma \cos \omega t - 2i \sin \omega t + \frac{1}{6} k^2 [(\cos \omega t - 1) - i\sigma \sin \omega t]^2 \right] \right\}. \end{aligned} \quad (14)$$

Now since the spectral density is related to the real part of the Laplace transform of the autocorrelation function [see Eq. (7)], and because the right hand side of Eq. (13) is a convolution, we evaluate  $\hat{A}(s)$  by Laplace transforming (13) and find

$$\hat{A}(s) = [s + i\epsilon_1 + \frac{1}{3} k^2 \omega^2 \hat{\Phi}(s)]^{-1}. \quad (15)$$

Thus, we must calculate  $\hat{\Phi}(s)$ .

As indicated by Eq. (13),  $\hat{\Phi}(s)$  will be fairly complicated in general and certainly will be much more complicated than its small  $k$  counterpart. Thus, for illustrative purposes, we will examine  $\hat{\Phi}(s)$  in the low temperature, moderate  $k$  limit where it will simplify greatly. For low temperatures,  $\hat{\Phi}(s)$  may be expanded as a series of modified (hyperbolic) Bessel functions:

$$\begin{aligned} \hat{\Phi}(s) &= e^{-11k^2/12} \sum_{m=-\infty}^{\infty} \left(\frac{\bar{n}+1}{\bar{n}}\right)^{m/2} \\ &\quad \times I_m\left[(11/6)k^2\bar{n}^{1/2}(\bar{n}+1)^{1/2}\right] [s + i(m\omega + \epsilon_2)]^{-1}. \end{aligned} \quad (16)$$

Now, at zero temperature (i.e.,  $\bar{n} = 0$ ), only the positive terms in the sum contribute. Further, if  $k$  is moderate, only the  $m = 0$  term will be important and  $\hat{\Phi}(s)$  will be

$$\hat{\Phi}(s) \approx e^{-11k^2/12} (s + i\epsilon_2)^{-1}. \quad (17)$$

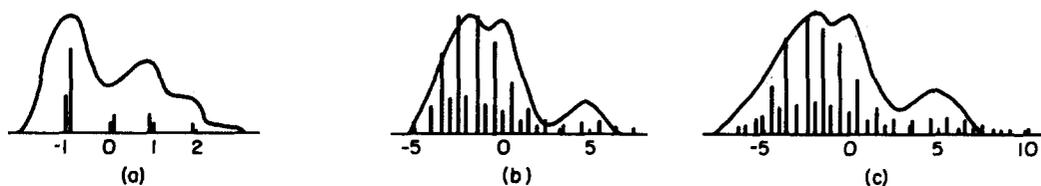


FIG. 2. Absorption spectra for large  $k$ . Solid lines are the numerical results of Englman *et al.*,<sup>5b</sup> and the bar spectra are the results of this calculation. Intensity is in arbitrary units; energy is in units of omega. (a)  $k=1$ ,  $k_B T=0$ ; (b)  $k=2.3$ ,  $k_B T=0$ ; (c)  $k=2.3$ ,  $k_B T=0.5$ .

A simple limit for  $\hat{\Phi}(s)$  has been chosen because the line shape calculation is much less complicated when  $\hat{\Phi}(s)$  is relatively simple. Now, substituting  $\hat{\Phi}(s)$  from Eq. (17) into Eq. (15), we have

$$\hat{A}(s) = [s + i\epsilon_1 + \frac{1}{3}k^2\omega^2 e^{-11k^2/12}(s + i\epsilon_2)^{-1}]^{-1}.$$

Thus, in this limit,  $\hat{A}(s)$  is

$$\hat{A}(s) \approx [(\Lambda_+ + \epsilon_2)/(\Lambda_+ - \Lambda_-)] \delta(s - i\Lambda_+) + [(\Lambda_- + \epsilon_2)/(\Lambda_- - \Lambda_+)] \delta(s - i\Lambda_-),$$

where

$$\Lambda_{\pm} = (\epsilon_1 + \epsilon_2)/2 \pm [\frac{1}{4}(\epsilon_1 - \epsilon_2)^2 + \frac{1}{3}k^2\omega^2 e^{-(11/12)k^2}]^{1/2}.$$

Here we pause a moment to recall that the line shape is not simply related to  $\hat{A}(s)$  as in the small  $k$  case, but rather it is related to the real part of the Laplace transform of

$$\sum_{i=1}^3 \langle \bar{C}_i(t) \bar{C}_i^\dagger \rangle \cong \theta_1(t)A(t) + \theta_2(t)B(t) + \theta_3(t)D(t).$$

Therefore, in the large  $k$  case, the line shape is the Laplace transform of a product of functions. This product may be computed using the complex convolution theorem,<sup>14</sup> i. e.,

$$\int_0^\infty \theta_1(t)A(t)e^{-st} dt = \int_{-i\infty}^{i\infty} \hat{\theta}_1(\sigma)\hat{A}(s-\sigma)d\sigma.$$

Thus, before computing the line shape, we must evaluate  $\hat{\theta}_1(s)$  in the same limit (i. e., low temperature, moderate  $k$ ) used for  $\hat{A}(s)$ . First we expand  $\hat{\theta}_1(s)$  as a sum of Bessel functions:

$$\hat{\theta}_1(s) = \exp[-(\frac{2}{3}k^2)(2\bar{n}+1)] \sum_{m=-\infty}^{\infty} [(\bar{n}+1)/\bar{n}]^m \times I_m[(4/3)k^2\bar{n}^{1/2}(\bar{n}+1)^{1/2}] \delta(s + im\omega). \quad (18)$$

Again, for zero temperature and moderate  $k$ , only the  $m=0$  term in the sum will be important. Since the  $m=0$  term in  $\hat{\theta}_1(s)$  is just a delta function at  $s=0$ , the spectrum due to  $\theta_1 A$  looks like two delta functions, one near  $\Omega = \epsilon_1$ , and the other near  $\Omega = \epsilon_2$ , with the peak near  $\epsilon_1$  being more intense. (A similar analysis for the spectrum due to  $B$  and  $D$  gives a similar result with the more intense peak near  $\epsilon_2$ .)

We have given the above heuristic derivation of the line shape in order to illustrate calculation of the large  $k$  line shape using the projection operator formalism. It should be emphasized that an actual calculation of the spectrum using the above formula is somewhat more complicated since these formulae are valid in the large  $k$  limit. In the large  $k$  limit, the functions  $\hat{\Phi}(s)$  and  $\hat{\theta}(s)$  are more complex than in the above example; however, the line shape calculation follows the above lines. In the next section we will compare spectra calculated using this formalism with those calculated using the previous equations of motion method.

#### D. Discussion of line shape

In the previous section, we presented two methods for calculating the absorption spectra in the strong coupling limit. In this section we will compare these two

methods as well as comparing the spectra calculated with them to the numerically calculated spectra of Englman *et al.*<sup>5b</sup>

The spectra (shown in Fig. 2) were calculated using the equations of motion results [Eq. (12)]. This formula has the advantage of being relatively simple. Even for fairly large values of  $k$ , one may quickly calculate the position and intensity of the spectra lines using only a slide rule and a table of Bessel functions. [In fact, the spectra in Figs. 2(a) and 2(b) were calculated using only a slide rule, since for those values of  $k$ , the approximation,  $I_m(Z) \sim (\frac{1}{2}Z)^m/(m+1)!$  is valid.] However, this formula has the disadvantage of being only approximate, and in some cases one must use the more complicated projection operator from [Eqs. (15), (16), and (18)].

The advantage of the projection operator form is that it keeps all terms to the same order in the perturbation. The major disadvantage is that the functional form is fairly complicated even for relatively small  $k$  and low temperatures, and becomes more complex as  $k$  and  $T$  increase. Thus it is useful to note that in the limit  $k \gg 1$ ,  $k_B T \ll 1$ , the projection operator and equations of motion forms become equivalent. Therefore, for large  $k$  and low  $T$ , one may use the equations of motion form. In fact, for the spectra shown in Fig. 2, the two methods give equivalent spectra.

In Fig. 2 we have also compared our calculated spectra with the exact numerical spectra of Englman *et al.*<sup>5b</sup> We find that even for a fairly small value of  $k$  (i. e.,  $k=1$ ) our spectrum agrees reasonably well with the numerical spectrum. For somewhat larger  $k$  ( $k=2.3$ ) the fit is even better. Also, for finite temperature, we find that our agreement with the numerical spectra is very good. Further, the analytical formula for the spectra has the advantage of being valid for larger values of  $k$ . In fact, since the analytical form is valid asymptotically as  $k \rightarrow \infty$ , this form will be more accurate for larger values of  $k$ .

Figure 2 shows that as  $k$  increases, the width of the spectrum increases. This is very reasonable since a larger value of  $k$  implies a deeper well and hence a larger average number of phonons in the phonon cloud. Also, as the temperature is raised, the spectrum gains intensity on the positive side. This is also reasonable because a higher temperature implies that more phonon states will be thermally populated and hence there will be a greater probability of absorption to the upper leaf of the electronic surface. Also, on classical grounds, the spectrum is expected to become more symmetrical as the temperature is raised.

#### IV. SUMMARY AND CONCLUSIONS

In this work we have applied techniques of many-body theory to the problem of the coupling of a triply degenerate Boson mode to a triply degenerate Fermion state. The particular transformations used in this work were chosen so that the wavefunctions generated by them were closer to the eigenfunctions expected on physical grounds. Alternatively, the transformation can be viewed as replacing the description of the motion of the

strongly coupled individual electrons and nuclei by a description in terms of weakly interacting collective modes. After transformation, the perturbation parameter is  $k^2 e^{-k^2}$ ; therefore, even for large  $k$ , the perturbation is small.

Using the transformed representation of the Hamiltonian we have derived analytic expressions for the asymptotic eigenvalues and find them to be in good agreement with the numerical results of Caner and Englman.<sup>5a</sup> We have also derived an analytic but approximate expression for the spectral density for strong coupling by employing the transformed representation of the Hamiltonian and by taking advantage of the relationship between the spectral density and the Green's functions,  $G_{ii}(t)$ . Line shapes calculated from this expression are in agreement with the earlier numerical results.<sup>5b</sup>

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