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One-mode intermediate-coupling calculation of the Jahn-Teller effect for an orbital doublet

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A multistep matrix formulation is used to analyze the intermediate-coupling problem for an orbital doublet coupled to one doubly degenerate vibrational mode. First, the linear-coupling problem is formulated in terms of a basis that reduces the effective Hamiltonian to blocks of tridiagonal matrices. The eigenfunctions for the lower states from this first step are then used as a new basis when including the lowest-order nonlinear coupling and anharmonic terms. The energies are computed and the final eigenfunctions are used to calculate reduction factors and polarizability matrix elements among many of the lower-energy states. Linear coupling, nonlinear coupling, and anharmonicity are varied independently over a wide range. Even though these calculations are accurate (being equivalent to diagonalizing a matrix of order up to 16 000) and cover the intermediate-coupling region on the strong-coupling side, the deviations from strong-coupling theory are primarily in the states whose energies exceed that of the ground state by an amount comparable to or greater than the zero-coupling—mode quantum. The properties of the lowest three states are not significantly different from those in strong coupling.

I. INTRODUCTION

The Jahn-Teller effect[1] occurs because an orbitally degenerate state of a molecule or crystalline defect is unstable against an asymmetric distortion that lowers the energy and removes some of the degeneracy. The effect results from a coupling of vibrational modes with electronic orbital states. The standard approach to the theory of the Jahn-Teller effect[2–4] is to analyze specific cases. The specific case considered in this paper is that of a doubly degenerate electronic orbital state coupled to a single doubly degenerate vibrational mode in cubic (O) symmetry. (The results should also apply for other cubic symmetries and for trigonal or hexagonal symmetries. An additional anharmonic term cubic in the Q's exists for C_3, C_{3i}, T_h, and T, while no anharmonic term cubic in the Q's exist for D_{6h}, D_6, C_{6v}, C_{6h}, C_{3h}, and C_6.)

The vibronic coupling can be classified as linear or nonlinear and the potential energy as harmonic or anharmonic. The nonlinear coupling and anharmonicity have the effect of warping the harmonic plus linear-coupling adiabatic potential energy surfaces. Hereafter, the term warping will mean the nonlinear coupling plus anharmonicity. Longuet-Higgins *et al.*[5] did a comprehensive calculation for the doublet problem considering only linear coupling and a harmonic potential. Their results exhibited a partial lifting of the degeneracies of the uncoupled states and demonstrated the usefulness of a matrix formulation of the problem. O'Brien[6] considered warping (nonlinear coupling and anharmonicity) for the limit of strong linear coupling and showed that, as the warping increases, vibronic singlet states approach the vibronic doublet states in energy. Ham[7] formalized the effect of other perturbations on these vibronic states, and in so doing, defined the reduced effect of orbital operators on vibronic states in terms of reduction factors. Setser and Estle[8] extended the O'Brien and Ham calculations to find energies and reduction factors for more excited states and for larger warping. These calculations are not completely general, in part because the strong—linear-coupling approximation makes the theory inapplicable to intermediate coupling. Other investigations of the orbital-doublet problem suggest that coupling to one vibrational mode is unrealistic and that multimode coupling must be used.[9–21]

Motivated by the desire to examine intermediate-coupling effects and to compare them to strong-coupling calculations, we developed a different approach to the one-mode vibronic coupling problem for an orbital doublet. This new approach allows us to independently vary linear and nonlinear coupling and anharmonicity. It is an exact method (to the accuracy of our computational means) for the Hamiltonian considered and for intermediate coupling on the strong-coupling side. It gives energies and eigenfunctions for many excited states.

The method of computation used in this paper is an extension of the calculation of Longuet-Higgins *et al.*[5] by including warping (higher-order vibronic coupling and anharmonicity) over a range of linear-coupling strengths. The effective Hamiltonian for this doublet problem leads to a sparse Hamiltonian matrix if the basis is properly chosen. The resulting matrix diagonalization problem is best handled in two stages: First, solving the eigenvalue problem with only linear vibronic coupling present and second, including the effects of nonlinear coupling and anharmonicity. Once the eigenfunctions of the final states are obtained, quantities such as the reduction factors and polarizability operator matrix elements (used in finding Raman intensities) can be calculated. This is the approach taken in the present calculations.

In Sec. II we explain the details of how the calculation is done. A method for generating the proper symmetrized basis to give a sparse Hamiltonian matrix is presented. The problem is then formulated so that the various matrix diagonalization steps can be done numerically. The eigenvector components are stored and used to calculate final matrix elements (such as reduction factors). The matrix calculations are done for a wide range of intermediate— and strong—linear-coupling strengths and include warping in the form of the lowest nonlinear coupling and anharmonic terms.

Sections III and IV present some of the results and the conclusions, respectively. The effects of both warping terms, nonlinear coupling and anharmonicity, on the values of the final energies and reduction factors, are found to be virtually the same. Our results show no important deviations from the previous strong-coupling calculations for the lowest three states for all intermediate values of linear-coupling strength on the strong-coupling side. The deviations are significant for energies above the ground state by about an uncoupled vibrational quantum or more. Any significant differences of actual observed behavior of the lowest vibronic doublet and singlet from strong-coupling predictions[6,8] are probably due to other effects (such as multimode coupling) although weak intermediate coupling cannot yet be excluded.

II. COMPUTATIONS

The Hamiltonian for a degenerate orbital state of a molecule or a point defect in a crystal coupled to vibrational modes can be written in the form

$$\mathscr{H}=T_n+V_{\mathrm{vib}}+\mathscr{H}_{\mathrm{JT}}\ ,$$

where T_n is the kinetic energy of the nuclei, V_{vib} is the vibrational potential energy, and $\mathscr{H}_{\mathrm{JT}}$ is the Jahn-Teller interaction or vibronic (vibrational electronic) coupling between the orbital state and the vibrational modes. The specific case considered here is that of a doublet-orbital state coupled to a single doubly degenerate vibrational mode in cubic symmetry. The orbital states transform as partners of the E irreducible representation in cubic symmetry: the $|\theta\rangle$ partner transforming like $3z^2-r^2$, and the $|\epsilon\rangle$ partner transforming like $\sqrt{3}(x^2-y^2)$. Orbital operators connecting these two states can be written in terms of four matrices[7]:

$$\mathscr{I}=\begin{bmatrix}1&0\\0&1\end{bmatrix}\ ,\quad \mathscr{A}_2=i\begin{bmatrix}0&-1\\1&0\end{bmatrix}\ ,$$

$$\mathscr{E}_\theta=\begin{bmatrix}-1&0\\0&1\end{bmatrix}\ ,\quad \mathscr{E}_\epsilon=\begin{bmatrix}0&1\\1&0\end{bmatrix}\ .$$

The first index refers to $|\theta\rangle$ and the second index to $|\epsilon\rangle$. The single vibrational normal mode that couples to the orbital state also transforms as the E representation in cubic symmetry. It is represented by the generalized coordinates Q_θ and Q_ϵ and has an effective mass μ and frequency ω. P_θ and P_ϵ are used to represent the conjugate momenta.

An effective Hamiltonian for this system can be obtained by writing $V_{\mathrm{vib}}+\mathscr{H}_{\mathrm{JT}}$ in a Taylor series in the vibrational coordinates and keeping only the lowest-order terms. Each term is required to transform as the totally symmetric A_1 irreducible representation to guarantee that the Hamiltonian is invariant. The effective Hamiltonian can be written as

$$\mathscr{H}=\mathscr{H}_H+\mathscr{H}_L+\mathscr{H}_N+\mathscr{H}_A+\cdots\ ,$$

where

$$\mathscr{H}_H=\left[\frac{1}{2\mu}(P_\theta^2+P_\epsilon^2)+\tfrac{1}{2}\mu\omega^2(Q_\theta^2+Q_\epsilon^2)\right]\mathscr{I}\ ,$$

$$\mathscr{H}_L=V_1(Q_\theta\mathscr{E}_\theta+Q_\epsilon\mathscr{E}_\epsilon)\ ,$$

$$\mathscr{H}_N=V_2[(Q_\epsilon^2-Q_\theta^2)\mathscr{E}_\theta+2Q_\theta Q_\epsilon\mathscr{E}_\epsilon]\ ,$$

$$\mathscr{H}_A=V_3[Q_\theta(3Q_\epsilon^2-Q_\theta^2)]\mathscr{I}\ .$$

The terms shown are the Hamiltonians for a two-dimensional harmonic oscillator ($\mathscr{H}_H$), a coupling ($\mathscr{H}_L$) which is linear in Q, the lowest-order nonlinear coupling ($\mathscr{H}_N$) which is quadratic in Q, and the lowest-order anharmonicity ($\mathscr{H}_A$) which is cubic in Q. The V's are expansion coefficients serving as parameters indicating the relative strength of each term. V_1 is the same as the V used by other authors.[6,8] We will use the following dimensionless quantities as measures of the strengths of the linear coupling, nonlinear coupling, and anharmonic terms:

$$K_L=(V_1/\hbar\omega)(\hbar/2\mu\omega)^{1/2} ,$$

$$K_N=(V_2/\hbar\omega)(\hbar/2\mu\omega) ,$$

$$K_A=(V_3/\hbar\omega)(\hbar/2\mu\omega)^{3/2} .$$

Note that K_L can be written as

$$K_L=\left[\frac{E_{\rm JT}}{\hbar\omega}\right]^{1/2} ,$$

where $E_{\rm JT}$ is the Jahn-Teller stabilization energy.[3,4]

The Schrödinger equation can be solved as a matrix eigenvalue problem by rewriting the above Hamiltonian in terms of ladder operators (see the Appendix):

$$C^{\dagger}=\frac{1}{\sqrt{2\mu\hbar\omega}}(\mu\omega Q-iP) ,$$

$$C=\frac{1}{\sqrt{2\mu\hbar\omega}}(\mu\omega Q+iP) .$$

By considering only the two-dimensional harmonic oscillator term $\mathscr{H}_H$, the eigenfunctions can be written as $|n_\theta\rangle|n_\epsilon\rangle|S\rangle$, where n_θ and n_ϵ are harmonic excitation numbers for the θ and ϵ partners of the vibrational mode and S signifies the θ or ϵ orbital state. These functions could serve as a basis for solving the whole problem, however, the remaining terms $\mathscr{H}_L+\mathscr{H}_N+\mathscr{H}_A+\cdots$ mix these basis functions, and the total Hamiltonian would be a fairly dense matrix. Choosing a different basis can simplify the problem by making the Hamiltonian matrix sparse (mostly zeros).

A particularly convenient basis which gives a sparse Hamiltonian matrix can be generated using the linear-coupling term $\mathscr{H}_L$. By starting on the lowest state, $|0\rangle|0\rangle|\theta\rangle$ (or $|0\rangle|0\rangle|\epsilon\rangle$), repeated operation with the raising part of $\mathscr{H}_L$ generates a series of zero-coupling functions, all transforming like the E irreducible representation of the group O. Each operation with $\mathscr{H}_L^{\dagger}$ produces a new function with $N=n_\theta+n_\epsilon$ (the vibrational excitation number) larger by 1. Some of these symmetrized zero-coupling functions are shown in Table I. A parallel series of functions is generated by starting with the $N=1$ function which is orthogonal to the $N=1$ function of the first series, then again by starting with a function with $N=2$ orthogonal to the $N=2$ functions in the first two series, etc. (This technique is similar to a Lanczos method applied to a system with high degeneracy.[18,22–25]) Each series is labeled with a quantum number M (equal to 0 for the first series, equal to 1 for the second, etc.), and these are schematically illustrated in Fig. 1. The Appendix gives more detail on this basis generating process.

The linear-coupling term of the Hamiltonian $\mathscr{H}_L$ has matrix elements only between adjacent states with the same M value ($\Delta N=\pm 1, \Delta M=0$). The harmonic oscillator term $\mathscr{H}_H$ has only diagonal matrix elements ($\Delta N=0, \Delta M=0$). As a result the linear-coupling Hamiltonian $\mathscr{H}_H+\mathscr{H}_L$ consists of a semi-infinite number of blocks of semi-infinite tridiagonal matrices. Higher-order terms contribute additional nonzero matrix elements as shown by the selection rules in Table II, but the Hamiltonian remains sparse in this zero-coupling basis.

The matrix elements for $\mathscr{H}_L$, $\mathscr{H}_N$, and $\mathscr{H}_A$ were found inductively. For many states with the lower values of N and M, the matrix elements were com-

TABLE I. Parts of two series of normalized zero-coupling basis functions generated by $[\mathscr{H}_L^{\dagger}]^N|0\rangle|0\rangle|\theta\rangle$ for $M=0$ (θ partner of E representation) states and by $[\mathscr{H}_L^{\dagger}]^{N-1}|N=1,M=1,A_1\rangle$ for $M=1$ (A_1 representation) states. These are referred to as the symmetrized zero-coupling states. The basis functions on the right are written as $|n_\theta\rangle|n_\epsilon\rangle|S\rangle$, where S stands for the partner of the E orbital state (either θ or ϵ), and $N=n_\theta+n_\epsilon$.

N	Zero-coupling basis functions
0	$\|N=0,M=0,\theta\rangle=\|0\rangle\|0\rangle\|\theta\rangle$
1	$\|1,0,\theta\rangle=(1/\sqrt{2})(\|0\rangle\|1\rangle\|\epsilon\rangle-\|1\rangle\|0\rangle\|\theta\rangle)$
2	$\|2,0,\theta\rangle=(1/\sqrt{2})(\|2\rangle\|0\rangle\|\theta\rangle+\|0\rangle\|2\rangle\|\theta\rangle)$
3	$\|3,0,\theta\rangle=(1/2\sqrt{2})[\sqrt{3}(\|0\rangle\|3\rangle\|\epsilon\rangle-\|3\rangle\|0\rangle\|\theta\rangle)+\|2\rangle\|1\rangle\|\epsilon\rangle-\|1\rangle\|2\rangle\|\theta\rangle]$
1	$\|N=1,M=1,A_1\rangle=(1/\sqrt{2})(\|0\rangle\|1\rangle\|\epsilon\rangle+\|1\rangle\|0\rangle\|\theta\rangle)$
2	$\|2,1,A_1\rangle=\frac{1}{2}(\|0\rangle\|2\rangle\|\theta\rangle-\|2\rangle\|0\rangle\|\theta\rangle+\sqrt{2}\|1\rangle\|1\rangle\|\epsilon\rangle)$
3	$\|3,1,A_1\rangle=(1/2\sqrt{2})[\sqrt{3}(\|3\rangle\|0\rangle\|\theta\rangle+\|0\rangle\|3\rangle\|\epsilon\rangle)+\|1\rangle\|2\rangle\|\theta\rangle+\|2\rangle\|1\rangle\|\epsilon\rangle]$

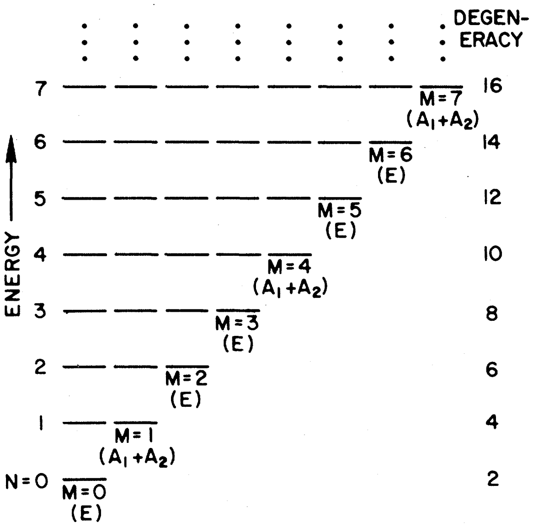

FIG. 1. Labels used for symmetrized zero-coupling basis states.

puted by hand. The resulting values suggested closed-form formulas for the matrix elements (see the Appendix). These formulas were used when solving the eigenvalue problem numerically on a computer.

Our approach to the sparse matrix eigenvalue problem allows consideration of a large number (2000—16 000) of initial basis states using modest amounts of computer time and memory space. Many physical insights also result from this approach. Computing eigenvalues and eigenvectors for a tridiagonal matrix is a straightforward numerical task. So the approach is to first solve the Schrödinger equation including only terms through linear coupling, $\mathscr{H}=\mathscr{H}_H+\mathscr{H}_L$. The Hamiltonian matrix then consists only of blocks of tridiagonal matrices in the zero-coupling basis. The eigenvalue problem is solved numerically for each block to obtain the lower energy states for each M value. This approach was first used for the linear-coupling problem by Longuet-Higgins *et al.*[5] M is a good quantum number which behaves like an angular momentum quantum number and $N-M$ corresponds to the excitation number for radial vibration. Figure 2 shows the variation of the energies of the various linear-coupling states with the strength of the linear coupling. In zero coupling the degeneracy of each level is $2(N+1)$, each pair (θ and ϵ or A_1 and A_2) of the degenerate levels having a different M value. For nonzero linear coupling the degeneracies are reduced to twofold and the lowest radial vibrational state for each N value approaches the lowest state. The second lowest radial vibrational state for each N approaches an energy which is $\hbar\omega$ higher than the lowest state; the third lowest radial vibrational state for each N approaches an energy $2\hbar\omega$ above the ground state, etc. In addition to the energies, the eigenvectors are also calculated for various values of the linear-coupling strength, K_L. For high energies and large values of K_L the clustering of levels predicted by Slonczewski and Moruzzi[26] was observed.

TABLE II. Matrix-element selection rules to illustrate that nonzero matrix elements exist only between certain symmetrized zero-coupling basis functions.

Term from Hamiltonian	Matrix-element selection rules ΔN	ΔM
$\mathscr{H}_H$	0	0
$\mathscr{H}_L$	±1	0
$\mathscr{H}_N$	0, ±2	$2(N$ even, $M=0)$ $0(N$ odd, $M=1)$ $\pm3(N+M$ odd$)$
$\mathscr{H}_A$	±1, ±3	$2(M=0)$ $0(M=1)$ ±3(otherwise)

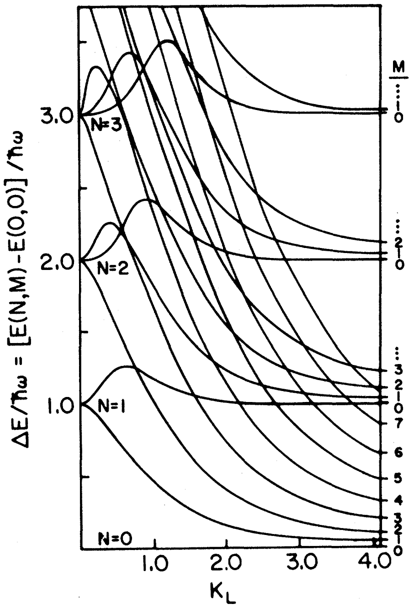

FIG. 2. Linear-coupling energies with respect to the ground level. Units of ΔE are $\hbar\omega$. Most of the levels in the upper right-hand side of the figure were omitted.

The next step is to include the nonlinear coupling $\mathscr{H}_N$ and anharmonicity $\mathscr{H}_A$ in the Hamiltonian. For a given value of K_L, the lowest 5—20 radial vibrational states for each of the lowest 20—40 M values, which result from the linear-coupling solution, are used as a new basis. The Hamiltonian matrix in this basis consists of diagonal terms due to $\mathscr{H}_H+\mathscr{H}_L$ and off-diagonal terms due to $\mathscr{H}_N+\mathscr{H}_A$. The off-diagonal terms mix states of different M values, so M is no longer a good quantum number. However, states of different symmetry are not mixed. Therefore, this final matrix can be reorganized into four blocks, two for the states transforming like the two partners of the E irreducible representation, one for the states transforming like the A_2 representation, and one for the states transforming like the A_1 representation. (The nonlinear coupling and anharmonicity split the A_1+A_2 degeneracy present for pure linear coupling, but the E states remain degenerate.) These final matrices are of a size easily handled on a computer. This two-step approach of first diagonalizing many separate tridiagonal linear-coupling matrices, reordering these states according to energy, and then diagonalizing reasonably sized matrices including nonlinear coupling and anharmonicity allows us to calculate accurately the energies and eigenfunctions of at least the ten lowest-energy states for a wide range of K_L, K_N, and K_A.

The calculations were done on a National Advanced Systems AS/6-II computer using IBM software. Standard EISPACK subroutines[27] were used to tridiagonalize the matrices and obtain eigenvalues and eigenvectors. Various size matrices were used. For each M value in the linear-coupling computation the matrix was truncated at order 200—400, depending on how many of the lower 5—20 eigenstates were to be found. The number of M values considered was between 20—40. After solving the linear-coupling eigenvalue problem, the 100—200 linear-coupling states found were grouped together, reordered according to energy, and used to solve the problem with nonlinear coupling and anharmonicity. Approximately $\frac{1}{3}$ of these states are of A_1+A_2 symmetry and $\frac{2}{3}$ of E symmetry. So the final matrices are of order 65—134 for E states and 34—67 for A_1 or A_2 states.

A wide range of coupling strengths K_L, K_N, and K_A were examined by this approach. By considering how well the eigenfunctions converge as the matrix size varies, one can set limits on the parameters for which this method is valid. Converged results were obtained for $1 \le K_L \le 15$. We did not do valid computations outside this range as excessive amounts of computer time and memory space would have been required for $K_L > 15$ and significant warping could not be introduced by the terms used in $\mathscr{H}_N$ and $\mathscr{H}_A$ for low K_L. More M values (more linear-coupling matrices) had to be included for larger K_L. More linear-coupling eigenfunctions for each value of M had to be used for the cases with smaller K_L values. The warping (nonlinear coupling and/or anharmonicity) is conveniently measured in terms of the parameter β/α,

$$\beta/\alpha = 16K_L^4(K_N - 2K_LK_A) .$$

This β/α corresponds to the β/α parameter introduced by O'Brien[6] for the case of strong coupling. The calculations were valid up to values of β/α of about 100 for K_L greater than 3. For values of K_L less than or equal to 3 the convergence was poor for values of β/α which were about 3 for $K_L=1$, 12 for $K_L=2$, and 60 for $K_L=3$. With only linear and nonlinear coupling, the valid results extended to a slightly larger (by $\sim 10\%$) β/α value than with only linear coupling and anharmonicity. Note that even though β/α is a useful parameter, this method allows K_L, K_N, and K_A to be varied independently.

Once the eigenfunctions of the final states are obtained, other useful quantities can be calculated. Several authors[7,8] have shown quantities called reduction factors to be useful. By denoting a final eigenstate as $|i,S\rangle$, where i is the relative excitation number ($i=1$ at the ground state) and S is the symmetry of the state, reduction factors can be defined in terms of orbital operators as

$$p_{kl} = \langle k,E(\theta) \,|\, i\mathscr{A}_2 \,|\, l,E(\epsilon)\rangle ,$$

$$q_{kl} = -\langle k,E(\theta) \,|\, \mathscr{E}_\theta \,|\, l,E(\theta)\rangle ,$$

$$r_{kl} = \langle k,E(\theta) \,|\, \mathscr{E}_\theta \,|\, l,A_1\rangle ,$$

$$r'_{kl} = \langle k,E(\theta) \,|\, \mathscr{E}_\epsilon \,|\, l,A_2\rangle ,$$

$$s_{kl} = -\langle k,A_1 \,|\, i\mathscr{A}_2 \,|\, l,A_2\rangle .$$

Knowing the effect of an orbital operator on a symmetrized zero-coupling function and the components of a final eigenfunction in terms of the zero-coupling basis, we can easily compute values for the reduction factors. A general formula for the matrix elements of each orbital operator between the symmetrized zero-coupling states was induced by calculating several by hand and observing the resulting pattern of values. (This process is analogous to that for terms in the Hamiltonian as explained in the Appendix.) The zero-coupling components of the final eigenvectors are computed as part of the solution to the eigenvalue problem. Numerical calculation of the reduction factors is then done. Other quantities that can be expressed in terms of orbital and vibrational ladder operators can similarly be calculated. (One example is the polarizability tensor used to calculate transition probabilities and intensities for Raman scattering.[28]) Thus this approach to the orbital-doublet Jahn-Teller calculation allows one to accurately obtain energies, eigenfunctions, and reduction factors (along with other matrix elements) for several different values of the linear and nonlinear coupling, and anharmonicity. More detail on the calculation is contained in Ref. 29.

III. RESULTS

Energies and reduction factors were calculated for several coupling strengths. For a given value of $\beta/\alpha = 16K_L^4(K_N - 2K_L K_A)$ energies were calculated for two cases, the case of only nonlinear coupling and the case of only anharmonicity (in addition to the linear coupling). The differences between the two cases are slight. Figures 3(a)—3(c) are plots of energy differences (excited-state energies minus ground-state energy) versus β/α for given values of linear-coupling strength, K_L. These, in general, are plots for the case of only nonlinear coupling, but in Fig. 3(b) several energy levels are also shown for the case of only anharmonicity. For a given value of K_L, the difference between the nonlinear and anharmonic cases is less at smaller β/α values, but for a given β/α, we found the difference to be less for larger values of K_L. In the limit of strong linear coupling the effects of nonlinear coupling and anharmonicity become identical and β/α serves as a good indicator of warping. This agrees with the strong-coupling approximation used first by O'Brien,[6] in which the warping effects of nonlinear coupling and anharmonicity are considered as one.

Our calculations allowed us to vary the nonlinear coupling and anharmonicity separately. Changing the signs of K_N and K_A gave the same results except that all A_1 symmetry states became A_2 symmetry and vice versa. Calculations with nonzero K_N and K_A such that $\beta/\alpha = 0$ gave virtually the same results as those done with both $K_N = 0$ and $K_A = 0$. This fact also indicates that the effects of nonlinear coupling and anharmonicity are similar.

Comparing the energies we have calculated using our matrix method to energies calculated by others[6,8] using the strong-coupling approximation, no large differences are found for the low-energy states. However, for energies lying approximately $\hbar\omega$ above the ground state or higher, the energies vary with β/α in a manner quite unlike any levels obtained in the strong-coupling approximation. This is because $\hbar\omega$ is effectively infinite in the strong-coupling approximation. For strong coupling ($K_L \gtrsim 6$) there is virtually no difference in values calculated by the

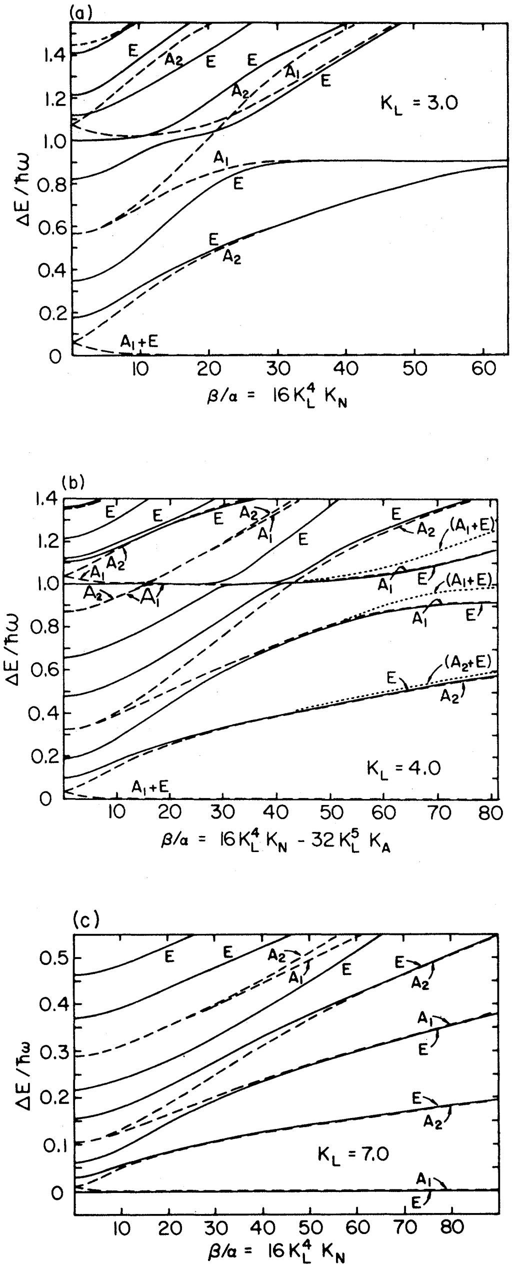

FIG. 3. Energies (with respect to the lowest level) as a function of the warping parameter $\beta/\alpha = 16K_L^4(K_N - 2K_L K_A)$. (a) An intermediate-coupling case with linear-coupling strength $K_L = 3.0$ and only nonlinear coupling added ($K_A = 0$). (b) Cases with $K_L = 4.0$. The solid and dashed lines are for the case of only nonlinear coupling added ($K_A = 0$). The dotted lines illustrate a few levels for the case of only anharmonicity added ($K_N = 0$). The differences between the two cases is small. (c) A (strong-coupling) case with linear-coupling strength $K_L = 7.0$ and only nonlinear coupling added ($K_A = 0$). In all three figures the symmetry of each state is labeled.

two methods for at least the lowest 20 states and for $\beta/\alpha \lesssim 100$. Even for lower coupling, agreement remains good for the lower few energy levels. Figures 3(a)–3(c) demonstrate that the lower levels behave qualitatively the same for different K_L. However, the more highly excited levels mix and behave differently, especially the ones near the first (and higher) radial vibrational energy $(\Delta E/\hbar\omega = 1.0)$. For large $K_L(\gtrsim 6)$, where there are ten or more energy levels below the first radial vibrational energy, behavior is so much like that found by the strong-coupling approximation that this can be called the strong-coupling region. Situations with smaller K_L (down to what we can feasibly calculate, $K_L \sim 1$) can be thought of as being in the intermediate-coupling region but on the strong-coupling side. Though the higher energies are not calculable by the strong-coupling approximation, it agrees well with our exact calculation for the lower energies both in the strong-coupling region and the intermediate-coupling region.

Knowing the eigenvectors permitted us to calculate important matrix elements. Several reduction factors (matrix elements of the orbital operators) were calculated. Figure 4 is a plot of reduction factors as a function of linear-coupling strength only. Their behavior is identical to that shown by Ham,[4] where p_{11} and q_{11} correspond to the p and q of Ham. Figure 5 shows reduction factors for some lower energy states as a function of β/α for $K_L = 3.0$. Their behavior is almost identical to that found by Setser and Estle,[8] who used the strong-coupling approximation. (The differences are on the order of a few percent or less.)

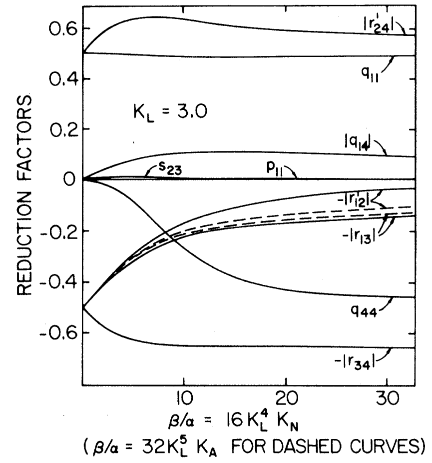

FIG. 5. Some reduction factors calculated as a function of warping, $\beta/\alpha = 16K_L^4(K_N - 2K_LK_A)$, for the inter-intermediate-coupling case of $K_L = 3.0$. The curves for the cases of anharmonicity $(K_N = 0)$ and nonlinear coupling $K_A = 0)$ are indistinguishable except for r'_{12} and r_{13}. In these instances the anharmonic case is shown as dashed lines.

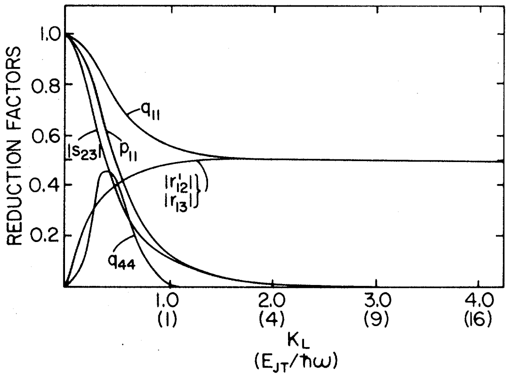

FIG. 4. Some reduction factors calculated as a function of pure linear coupling (strength is equal to K_L). The reduction factors are defined in the text. The labels in parentheses are the Jahn-Teller energies E_{JT} in units of $\hbar\omega$.

The two ground-state reduction factors p_{11} and q_{11} have been of particular interest. For linear coupling to a single E mode, one has $1 - 2q_{11} + p_{11} = 0$. However, if more than one E mode is coupled linearly then this becomes an inequality (Refs. 14 and 15) $1 - 2q_{11} + p_{11} \geq 0$. Slonczewski[30] showed for strong linear coupling that q_{11} varies with warping, β/α, having a maximum value of $\frac{1}{2}$ for β/α zero and very large. The minimum value is about 0.484 and occurs at $\beta/\alpha \simeq 10$. Since $p_{11} = 0$ for strong coupling this gives $2q_{11} - p_{11}$ values from 0.968 to 1. Our intermediate-coupling calculations give virtually identical behavior and therefore confirm that a value of $1 - 2q_{11} - p_{11}$ significantly greater than zero must arise from multimode coupling or from a system in which weak intermediate coupling occurs.

One use of the intermediate-coupling calculations is fitting experimental data. Guha and Chase[28] obtained Raman spectra of a doublet Jahn-Teller system, Cu^{2+} in CaO. They also showed[29] how matrix elements of the polarizability tensor (see the Appendix) can be used to find transition probabilities and intensities. We have tried to fit their data with polarizability operator matrix elements found from our calculations. These efforts have not been successful, but the closest fits occur for $K_L = 3.0$–4.0 and $\beta/\alpha = 4$–5. The system thus appears to be in the intermediate Jahn-Teller coupling range. Guha and Chase[28] found that the strong-coupling approximation of O'Brien does not give a good fit to the data either. A poor fit from our intermediate-coupling calculations is not surprising in light of the fact that for these coupling parameters they have not significantly modified the results of the strong-coupling calculations for other quantities (e.g., the reduction factors) for the lower states. In order to explain the Raman scattering data[28] other considerations, such as orbital coupling to multiple vibrational modes,[9–21] are necessary.

IV. CONCLUSIONS

This paper presents a new approach to numerical calculations for the Jahn-Teller system of an orbital doublet coupled to one doubly degenerate vibrational mode. Several useful features of this approach have been demonstrated. The relative values of the linear and nonlinear vibronic coupling and of the harmonic and anharmonic terms in the potential can be varied independently, allowing one to determine the effects of each contribution. Energies and eigenfunctions of many excited states can be found and used to calculate useful matrix elements such as reduction factors and polarizability operators. The results are valid for intermediate to strong linear coupling and for a wide range of β/α. All results are "exact," being limited only by the size and speed of the computer being used.

Although any other general matrix approach would ultimately be limited by the speed and memory capacity of the computer being used, such limitations are not as severe for the method used here. An extremely large matrix (of order 4000–16 000) is diagonalized by transforming to a new basis, breaking down the first step of the problem into 20–40 smaller tridiagonal matrices (of order 200–400 each). The last step of the problem need only use 100–200 of the eigenstates from the first step to obtain the lower energy states. Thus this method effectively solves a huge (approximately $16\,000\times 16\,000$) eigenvalue problem. The lower 10–20 eigenstates can be found for linear-coupling strengths in the range $1 \lesssim K_L \lesssim 15$ plus a reasonable range of nonlinear coupling and anharmonicity. Significant additional amounts of computer time and memory space would be required to appreciably expand this range, consequently, such calculations were not judged worthwhile.

Although this new, versatile, precise approach extends the range of calculations and has advantages over previous strong-coupling approximation calculations,[6,8] no qualitatively new physical insights have been gained concerning the lowest three states, those of most importance in many experiments. Those states whose energies exceed that of the ground state by about $\hbar\omega$ or more do not occur in strong-coupling calculations. Avoided crossings of states corresponding to differing numbers of radial excitations occur as β/α is varied. These calculations covered the range of E_{JT}, the Jahn-Teller energy, from about $\hbar\omega$ up to about 200 times $\hbar\omega$. The range of values from $E_{\text{JT}}/\hbar\omega$ equal to 1 down to 0.1, the weak coupling side of intermediate coupling was not explored because of the singular nature of the lowest-order term in $\mathscr{H}_A$ and the very small range of β/α which could be considered using the lowest-order term in $\mathscr{H}_N$.

APPENDIX

The effect of various operators on basis functions must be known in order to do matrix calculations such as those in this paper. This information can be used to generate matrices for the operators. Those for operators appearing in the Hamiltonian are needed to calculate energies and eigenfunctions. Knowing final-state eigenfunctions in terms of basis functions and the matrix elements of operators among these basis functions, one can obtain final-state matrix elements like reduction factors (from orbital operators) or Raman transition intensities (from polarizability operators). The first step is to obtain the symmetrized zero-coupling basis functions using the linear-coupling term $\mathscr{H}_L$ from the Hamiltonian. Then the effect of other terms ($\mathscr{H}_N,\mathscr{H}_A$) on these basis functions can be found.

The terms of the effective Hamiltonian written in terms of raising ($C^\dagger$) and lowering (C) ladder operators become

$$\mathscr{H}_L = K_L\hbar\omega[(C_\theta+C_\theta^\dagger)\mathscr{E}_\theta+(C_\epsilon+C_\epsilon^\dagger)\mathscr{E}_\epsilon]\ ,$$

$$\mathscr{H}_N = K_N\hbar\omega\{[(C_\epsilon^{\dagger 2}+C_\epsilon^2)-(C_\theta^{\dagger 2}+C_\theta^2)+2(N_\epsilon-N_\theta)]\mathscr{E}_\theta+2[(C_\theta+C_\theta^\dagger)(C_\epsilon+C_\epsilon^\dagger)]\mathscr{E}_\epsilon\}\ ,$$

$$\mathscr{H}_A = K_A\hbar\omega[3(C_\theta^\dagger+C_\theta)(C_\epsilon^{\dagger 2}+C_\epsilon^2+2N_\epsilon-N_\theta)-C_\theta^{\dagger 3}-C_\theta^3+3C_\theta]\mathscr{I}\ ,$$

where

$$C^\dagger=\frac{1}{\sqrt{2\mu\hbar\omega}}(\mu\omega Q-iP)\ ,\quad C=\frac{1}{\sqrt{2\mu\hbar\omega}}(\mu\omega Q+iP)\ ,\quad N=C^\dagger C\ ,$$

$$C_\theta^\dagger\,|\,n_\theta\rangle=(n_\theta+1)^{1/2}\,|\,n_\theta+1\rangle\ ,\quad C_\theta\,|\,n_\theta\rangle=(n_\theta)^{1/2}\,|\,n_\theta-1\rangle\ ,\quad N_\theta\,|\,n_\theta\rangle=n_\theta\,|\,n_\theta\rangle\ .$$

TABLE III. Matrix elements of $\mathscr{H}_N$ between zero-coupling basis functions.

For $\Delta M=0, M=1, N$ odd (For A_1-symmetry states—with A_2 states the sign is opposite)

$$\langle N',M'=1\,|\,\mathscr{H}_N\,|\,N,M=1\rangle=\hbar\omega K_N\delta_{MM'}[\sqrt{(N-1)(N+1)}\delta_{N',N-2}+2(N+1)\delta_{N',N}+\delta_{N',N+2}\sqrt{(N+1)(N+3)}]$$

For $\Delta M=2, M=0$ or $2, N$ even (For E_θ-symmetry states—with E_ϵ states the sign is opposite)

$$\langle N',M'=2\,|\,\mathscr{H}_N\,|\,N,M=0\rangle=\hbar\omega K_N\delta_{M',M+2}[2\delta_{N',N}\sqrt{N(N+2)}+(\delta_{N,N'+2}+\delta_{N,N'-2})\sqrt{N'(N'+2)}]$$

For $\Delta M=3, N+M$ odd

$$\langle N',M'\,|\,\mathscr{H}_N\,|\,N,M\rangle=-\hbar\omega K_N\delta_{M',M+3}[2\delta_{N,N'}\sqrt{(N-M-1)(N+M+3)}+\delta_{N,N'+2}\sqrt{(N-M-3)(N-M-1)}$$
$$+\delta_{N,N'-2}\sqrt{(N+M+3)(N+M+5)}]$$

Note $\langle N',M'\,|\,\mathscr{H}_N\,|\,N,M\rangle=\langle N,M\,|\,\mathscr{H}_N\,|\,N',M'\rangle$ can be used to find the other nonzero matrix elements

All other cases $\langle N',M'\,|\,\mathscr{H}_N\,|\,N,M\rangle=0$

The subscripts on the ladder operators refer to the components of the doubly degenerate vibrational normal mode. The raising portion of the $\mathscr{H}_L$ term is used to generate the symmetrized zero-coupling basis functions. To illustrate this, start with the lowest $(N=0, M=0)$ θ-partner state,

$$|N=0, M=0, \theta\rangle=|n_\theta=0\rangle\,|n_\epsilon=0\rangle\,|\theta\rangle\,.$$

By using $\mathscr{H}_L^+$ on this,

$$\begin{aligned}\mathscr{H}_L^+\,|N=0, M=0, \theta\rangle&=\hbar\omega K_L(C_\theta^\dagger\mathscr{E}_\theta+C_\epsilon^\dagger\mathscr{E}_\epsilon)\,|n_\theta=0\rangle\,|n_\epsilon=0\rangle\,|\theta\rangle\\&=\hbar\omega K_L(-|n_\theta=1\rangle\,|n_\epsilon=0\rangle\,|\theta\rangle+|n_\theta=0\rangle\,|n_\epsilon=1\rangle\,|\epsilon\rangle)\\&=\sqrt{2}\hbar\omega K_L\left[\frac{1}{\sqrt{2}}(-|1\rangle\,|0\rangle\,|\theta\rangle+|0\rangle\,|1\rangle\,|\epsilon\rangle)\right].\end{aligned}$$

We associate the normalized function obtained in this way with

$$|N=1, M=0, \theta\rangle=\frac{1}{\sqrt{2}}(-|1\rangle\,|0\rangle\,|\theta\rangle+|0\rangle\,|1\rangle\,|\epsilon\rangle)\,.$$

Operating on this function again with $\mathscr{H}_L^+$ gives

$$|N=2, M=0, \theta\rangle=\frac{1}{\sqrt{2}}(|2\rangle\,|0\rangle\,|\theta\rangle+|0\rangle\,|2\rangle\,|\theta\rangle)\,.$$

TABLE IV. Matrix elements of $\mathscr{H}_A$ between zero-coupling basis functions.

For $\Delta M=0, M=1$ (Between A_1 states—with A_2 states the sign is opposite)

$$\langle N',M'\,|\,\mathscr{H}_A\,|\,N,M\rangle=\hbar\omega K_A\delta_{M,M'}[\delta_{N',N+3}\sqrt{2(I+1)(I+2)(I+3)}+3\delta_{N',N+1}\sqrt{2J(I+1)(I+2)}]$$

For $\Delta M=2, M=0$ or 2 (Between E_θ states—with E_ϵ states the sign is opposite)

$$\langle N',M'\,|\,\mathscr{H}_A\,|\,N,M\rangle=\hbar\omega K_A[\delta_{N',N+3}(\delta_{M',M+2}+\delta_{M',M-2})\sqrt{2(I+1)(I+2)(I+3)}$$
$$+3\delta_{N',N+1}(\delta_{M',M+2}+\delta_{M',M-2})\sqrt{2J(I+1)(I+2)}]$$

For $\Delta M=3$

$$\langle N',M'\,|\,\mathscr{H}_A\,|\,N,M\rangle=-\hbar\omega K_A\{\delta_{N',N+3}[\delta_{M',M+3}\sqrt{2(J+1)(J+2)(J+3)}+\delta_{M',M-3}\sqrt{2(I+1)(I+2)(I+3)}]$$
$$+3\delta_{N',N+1}[\delta_{M',M+3}\sqrt{2I(J+1)(J+2)}+\delta_{M',M-3}\sqrt{2J(I+1)(I+2)}]\}$$

Additional nonzero terms obtained by noting that $\langle\mathscr{H}_A\rangle$ is symmetric

$$\langle N',M'\,|\,\mathscr{H}_A\,|\,N,M\rangle=\langle N,M\,|\,\mathscr{H}_A\,|\,N',M'\rangle$$

All other cases

$$\langle N',M'\,|\,\mathscr{H}_A\,|\,N,M\rangle=0$$

where

For $N+M$ even $I=(N-M)/2$, $J=(N+M)/2$

For $N+M$ odd $I=(N-M-1)/2$, $J=(N+M+1)/2$

Successive operation with $\mathscr{H}_L^{\dagger}$ allows one to obtain all the higher $N=n_\theta+n_\epsilon$ functions for $M=0$. (A parallel set of functions for $M=0$ is obtained by starting with the $|N=0,M=0,\epsilon\rangle$ state.) Note that the degeneracy of each N level is $2(N+1)$.

By starting again with an $N=1$ function orthonormal to $|N=1,M=0,\theta\rangle$,

$$|N=1,M=1,A_1\rangle=\frac{1}{\sqrt{2}}(|n_\theta=0\rangle|n_\epsilon=1\rangle|\epsilon\rangle+|n_\theta=1\rangle|n_\epsilon=0\rangle|\theta\rangle)\,,$$

a set of functions for $M=1$ can be generated. For instance, the $N=2$ function is

$$\mathscr{H}_L^{\dagger}|N=1,M=1,A_1\rangle=2(\hbar\omega K_L)[\tfrac{1}{2}(-|2\rangle|0\rangle|\theta\rangle+|0\rangle|2\rangle|\theta\rangle+\sqrt{2}|1\rangle|1\rangle|\epsilon\rangle)]\,.$$

So

$$|N=2,M=1,A_1\rangle=\tfrac{1}{2}(-|2\rangle|0\rangle|\theta\rangle+|0\rangle|2\rangle|\theta\rangle+\sqrt{2}|1\rangle|1\rangle|\epsilon\rangle)\,.$$

Successive operation with $\mathscr{H}_L^{\dagger}$ on these functions would give all functions $|N,M=1,A_1\rangle$. The next step would be to generate a series of functions for $M=2$ by starting with a function orthogonal to both $|N=2,M=1,A_1\rangle$ and $|N=2,M=0,\theta\rangle$. Continuing on in this manner, one can generate all the functions $|N,M,S\rangle$ (see Table I). This is how the symmetrized zero-coupling basis functions are generated using the linear-coupling term $\mathscr{H}_L$. The result is a basis in which $\langle\mathscr{H}_L\rangle$ is tridiagonal and connects only states of the same M value:

$$\langle N',M',S|\mathscr{H}_L|N,M,S\rangle=\delta_{M,M'}\delta_{N,N'+1}\hbar\omega K_L\begin{cases}\sqrt{N+M}\,, & N+M \text{ even}\\ \sqrt{N+M+1}\,, & N+M \text{ odd}\end{cases}$$
$$+\delta_{M,M'}\delta_{N,N'-1}\hbar\omega K_L\begin{cases}\sqrt{N+M+2}\,, & N+M \text{ even}\\ \sqrt{N+M+1}\,, & N+M \text{ odd.}\end{cases}$$

Other terms in the Hamiltonian have matrix elements between these symmetrized zero-coupling (ZC) states. The harmonic term $\mathscr{H}_H$ is diagonal in this basis:

$$\langle N',M',S|\mathscr{H}_H|N,M,S\rangle=\hbar\omega(N+1)\delta_{N,N'}\delta_{M,M'}\,.$$

The nonlinear and anharmonic terms $(\mathscr{H}_N+\mathscr{H}_A)$ have more complicated matrix elements in this ZC basis. Operation with $\mathscr{H}_N$ (written in terms of ladder operators) on several of the ZC basis functions indicated a pattern of nonzero matrix elements between the ZC states. This pattern, for as many matrix elements as were calculated by hand, fits the formulas given in Table III. Similarly, a pattern for $\langle\mathscr{H}_A\rangle$ values was induced by operating on ZC functions with the $\mathscr{H}_A$ term (Table IV). These matrix elements between ZC states can be calculated on a computer following the formulas and used when solving the eigenvalue problem for the total Hamiltonian, $\mathscr{H}=\mathscr{H}_H+\mathscr{H}_L+\mathscr{H}_N+\mathscr{H}_A$.

The process used for solving the total problem is to first solve the eigenvalue problem for $\mathscr{H}_H+\mathscr{H}_L$

TABLE V. Matrix elements of orbital operators between zero-coupling states (zero-coupling reduction factors). All matrix elements are symmetric except those of $i\mathscr{A}_2$.

Orbital operator	
$\mathscr{I}$	$\langle N',M',S'\vert\mathscr{I}\vert N,M,S\rangle=\delta_{N',N}\delta_{M',M}\delta_{S',S}$
$i\mathscr{A}_2$	$\langle N',M',S'=E(\epsilon)$ or $A_2\vert(i\mathscr{A}_2)\vert N,M,S=E(\theta)$ or $A_1\rangle=(-1)^{N+M+1}\delta_{N',N}\delta_{M',M}$
	$\langle N',M',S'=E(\theta)$ or $A_1\vert(i\mathscr{A}_2)\vert N,M,S=E(\epsilon)$ or $A_2\rangle=(-1)^{N+M}\delta_{N',N}\delta_{M',M}$
$\mathscr{E}_\theta$	$M=0,N$ even $\langle N',M'=0,S'\vert\mathscr{E}_\theta\vert N,M=0,S\rangle=\delta_{N',N}(\delta_{\epsilon,\epsilon}-\delta_{\theta,\theta})$
	$N+M$ odd $\langle N',M',S'\vert\mathscr{E}_\theta\vert N,M,S\rangle=\delta_{N',N}\delta_{M',M+1}(\delta_{\theta,\theta}+\delta_{\theta,A_1}+\delta_{A_1,\theta}+\delta_{\epsilon,\epsilon}+\delta_{\epsilon,A_2}+\delta_{A_2,\epsilon})$
$\mathscr{E}_\epsilon$	$M=0,N$ even $\langle N',M'=0,S'\vert\mathscr{E}_\epsilon\vert N,M=0,S\rangle=\delta_{N',N}(\delta_{\theta,\epsilon}+\delta_{\epsilon,\theta})$
	$N+M$ odd $\langle N',M',S'\vert\mathscr{E}_\epsilon\vert N,M,S\rangle=\delta_{N',N}\delta_{M',M+1}(-\delta_{\theta,\epsilon}-\delta_{\theta,A_2}-\delta_{A_1,\epsilon}+\delta_{\epsilon,\theta}+\delta_{\epsilon,A_1}+\delta_{A_2,\theta})$
	where $S=$ symmetry of state $[A_1,A_2,E(\theta),E(\epsilon)]$ and $\delta_{\alpha,\beta}=\begin{cases}1 & \text{if } S'=\alpha \text{ and } S=\beta\\ 0 & \text{otherwise}\end{cases}$

TABLE VI. Matrix elements of polarizability operators $\mathscr{P}i$ between zero-coupling basis states. All elements in the first two columns are symmetric; all elements in the third column are antisymmetric. Otherwise, the other elements are equal to 0. (The following formulas are for A_1 and E_θ symmetry states only.)

	$\mathscr{P}_3=Q_\epsilon\mathscr{E}_\epsilon-Q_\theta\mathscr{E}_\theta$	$\mathscr{P}_4=Q_\theta\mathscr{I}$	$\mathscr{P}_5=iQ_\epsilon\mathscr{A}_2$
$M=0,1$			
	N even $\langle N+1,M=1\mid\mathscr{P}_3\mid N,M=0\rangle$ $=\sqrt{N+2}$	$\langle N+1,M=0\mid\mathscr{P}_4\mid N,M=0\rangle$ $=-\frac{1}{2}\sqrt{N+2}$	$\langle N+1,M=0\mid\mathscr{P}_5\mid N,M=0\rangle$ $=-\frac{1}{2}\sqrt{N+2}$
	N odd $\langle N,M=1\mid\mathscr{P}_3\mid N+1,M=0\rangle$ $=\sqrt{N+1}$	$\langle N+1,M=0\mid\mathscr{P}_4\mid N,M=0\rangle$ $=-\frac{1}{2}\sqrt{N+1}$	$\langle N+1,M=0\mid\mathscr{P}_5\mid N,M=0\rangle$ $=-\frac{1}{2}\sqrt{N+1}$
All M			
	$N+M$ even $\langle N',M-2\mid\mathscr{P}_3\mid N,M\rangle$ $=-\delta_{N',N+1}\sqrt{N-M+2}$ $-\delta_{N',N-1}\sqrt{N+M}$	$\langle N',M-1\mid\mathscr{P}_4\mid N,M\rangle$ $=\delta_{N',N+1}\frac{1}{2}\sqrt{N-M+2}$ $+\delta_{N',N-1}\frac{1}{2}\sqrt{N+M}$	$\langle N',M-1\mid\mathscr{P}_5\mid N,M\rangle$ $=\delta_{N',N+1}\frac{1}{2}\sqrt{N-M+2}$ $+\delta_{N',N-1}\frac{1}{2}\sqrt{N+M}$
	$N+M$ odd $\langle N',M+2\mid\mathscr{P}_3\mid N,M\rangle$ $=-\delta_{N',N+1}\sqrt{N+M+3}$ $-\delta_{N',N-1}\sqrt{N-M-1}$	$\langle N',M-1\mid\mathscr{P}_4\mid N,M\rangle$ $=\delta_{N',N+1}\frac{1}{2}\sqrt{N-M+1}$ $+\delta_{N',N-1}\frac{1}{2}\sqrt{N+M+1}$	$\langle N',M-1\mid\mathscr{P}_5\mid N,M\rangle$ $=-\delta_{N',N+1}\frac{1}{2}\sqrt{N-M+1}$ $-\delta_{N',N-1}\frac{1}{2}\sqrt{N+M+1}$

to obtain linear-coupling (LC) eigenfunctions. Then the total problem is solved with $\mathscr{H}$ expressed in terms of the LC basis. The $\langle\mathscr{H}_H+\mathscr{H}_L\rangle$ matrix elements are the eigenvalues from the first part of the solution. The $\langle\mathscr{H}_N+\mathscr{H}_A\rangle$ matrix elements are found relating back to the ZC basis:

$$\langle\Psi_{\mathrm{LC}}(l)\mid(\mathscr{H}_A+\mathscr{H}_N)\mid\Psi_{\mathrm{LC}}(m)\rangle$$
$$=\sum_{i,j}\langle\Psi_{\mathrm{ZC}}(i)\mid(\mathscr{H}_A+\mathscr{H}_N)\mid\Psi_{\mathrm{ZC}}(j)\rangle$$
$$\times\langle\Psi_{\mathrm{ZC}}(j)\mid\Psi_{\mathrm{LC}}(m)\rangle\langle\Psi_{\mathrm{LC}}(l)\mid\Psi_{\mathrm{ZC}}(i)\rangle\ ,$$

where $\mid\Psi_{\mathrm{LC}}(1)\rangle$ is a linear-coupling basis function and $\mid\Psi_{\mathrm{ZC}}(i)\rangle$ is a zero—linear-coupling basis function. The LC functions are obtained as eigenvectors in terms of the ZC functions when the linear-coupling problem $(\mathscr{H}_H+\mathscr{H}_L)$ is solved.

To obtain reduction factor and Raman polarizability operator[9] matrix elements, an approach is used similar to that for finding $\langle\mathscr{H}_N+\mathscr{H}_A\rangle$. Formulas are developed for matrix elements among ZC states (Table V); the matrix elements among LC states are then found by using the ZC values and the transformation between the ZC and LC bases. The reduction factors are easy to obtain as they are defined in the text as matrix elements of the orbital operators. The Raman polarizability tensor is slightly more complicated. The polarizability operator can be broken down into symmetrized parts and expanded in terms of orbital operators,

$$P(A_1)=a_i\mathscr{I}+b_1(\mathscr{E}_\theta Q_\theta+\mathscr{E}_\epsilon Q_\epsilon)\ ,$$
$$P(A_2)=a_2i\mathscr{A}_2+b_2(\mathscr{E}_\theta Q_\epsilon-\mathscr{E}_\epsilon Q_\theta)\ ,$$
$$P(E(\theta))=a_3\mathscr{E}_\theta+b_3(-\mathscr{E}_\theta Q_\theta+\mathscr{E}_\epsilon Q_\epsilon)$$
$$+C_3Q_\theta\mathscr{I}+d_3i\mathscr{A}_2Q_\epsilon\ ,$$
$$P(E(\epsilon))=a_3\mathscr{E}_\epsilon+b_3(\mathscr{E}_\theta Q_\epsilon+\mathscr{E}_\epsilon Q_\theta)$$
$$+C_3Q_\epsilon\mathscr{I}-d_3i\mathscr{A}_2Q_\theta\ ,$$

where a_i, b_i, c_i, and d_i are arbitrary expansion coefficients. Guha and Chase[28] show how matrix elements of these operators are used to calculate the intensities of lines in Raman spectra. Knowing the form of any of these quantities in terms of orbital and ladder operators, one can obtain formulas for the effect of the operator quantity on ZC states (Table VI). Matrix elements between the LC states can then be calculated. This is the same as the process illustrated above for $\mathscr{H}_N$ and $\mathscr{H}_A$. The final step in the solution gives the final eigenstates as vectors whose components are LC states. Since matrix elements among the LC states are known, matrix elements among the final states (FS) can easily be found. For an operator O_p:

$$\langle\Psi_{\mathrm{FS}}(l)\mid O_p\mid\Psi_{\mathrm{FS}}(m)\rangle$$
$$=\sum_{i,j}\langle\Psi_{\mathrm{FS}}(l)\mid\Psi_{\mathrm{LC}}(i)\rangle\langle\Psi_{\mathrm{LC}}(j)\mid\Psi_{\mathrm{FS}}(m)\rangle$$
$$\times\langle\Psi_{\mathrm{LC}}(i)\mid O_p\mid\Psi_{\mathrm{LC}}(j)\rangle\ .$$

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