Coherent states and the Jahn-Teller effect*

B. R. Judd and E. E. Vogel†
Department of Physics, The Johns Hopkins University, Baltimore, Maryland 21218
(Received 8 July 1974)

The two Jahn-Teller systems $T_1 \otimes (\epsilon + \tau_2)$ and $E \otimes \epsilon$ are studied in the strong-coupling limit. Two methods are used: the first depends on Glauber states to represent the displaced oscillators, the second involves a separation of the vibrational coordinates from the rotational coordinates that are associated with the spatial degeneracies of the systems. The analysis for $T_1 \otimes (\epsilon + \tau_2)$ is described in detail; that for $E \otimes \epsilon$ is summarized. The distribution of the angular momentum states among the oscillator levels of the $T_1 \otimes (\epsilon + \tau_2)$ system is specified. Analytical expressions are given for Ham factors, for relative absorption intensities, and for the energies of the levels in the region near the strong-coupling limit.

I. INTRODUCTION

For many symmetric molecular complexes, the interaction between a vibrational mode and a degenerate electronic state leads to a distortion of the complex and a corresponding reduction in its symmetry. This is the Jahn-Teller (JT) effect.[1] We are concerned in this article with two cases for which an infinity of distortions are energetically equivalent. They correspond to octahedral complexes, and are commonly written[2] $E \otimes \epsilon$ and $T_1 \otimes (\epsilon + \tau_2)$. The letters refer to the irreducible representations of the octahedral group: italics are used for the electronic state and greek for the vibrational mode. Although both cases share many common features, the complexity of $T_1 \otimes (\epsilon + \tau_2)$, which derives mainly from the high degeneracies of the representations, makes it essential to give it special attention. We shall therefore use this case to exemplify our general approach. The much more elementary case of $E \otimes \epsilon$ can then be treated by describing the simplifications and summarizing the principal results.

II. F^+ CENTER IN CaO

In second quantization, the Hamiltonian for $T_1 \otimes (\epsilon + \tau_2)$ is given by $H = H_o + V$, where

$$H_o = \tfrac{1}{2}\hbar\omega(a^\dagger \circ a + a \cdot a^\dagger), \quad V = T^{(2)} \cdot (a^\dagger + a). \qquad (1)$$

The creation and annihilation operators, $a^\dagger$ and a, are spherical tensors of rank 2. Their five components correspond to the five components of the modes ϵ and τ_2. The assumption of equal frequencies ω for both modes has been shown to be well obeyed for the F^+ center in CaO.[3] The tensor $T^{(2)}$ acts only in the space of the electronic T_1 states. For the F^+ center, these states correspond to a single p electron trapped in an oxygen vacancy. By forming the scalar between $T^{(2)}$ and $a^\dagger + a$, we follow the well-established[4,5] assumption that the coupling between T_1 and both modes ϵ and τ_2 is approximately the same. We also suppose that a reasonably good representation of the physical situation in the solid can be obtained by using just one effective frequency ω rather than an extended spectrum, an assumption for which some justification has been provided.[6]

The most complete analysis of the Hamiltonian H so far reported is that of O'Brien.[4] This was done in a basis provided by a limited set of the eigenfunctions of the oscillator Hamiltonian H_o. Although $|V| \gg |H_o|$, O'Brien was able to obtain an adequate representation of the low experimental levels by taking large enough matrices of H and by introducing a parameter W with respect to which the energy of the lowest level was minimized. This variational procedure is equivalent to taking basis functions characterized by a different frequency ω to that appearing in H_o. This approach was successfully introduced by Englman, Caner, and Toaff[7] in their analysis of $T_1 \otimes \tau_2$. It is the purpose of much of the present article to describe calculations in the alternative basis corresponding to the strong JT limit for which $|V| \gg |H_o|$. In this way we obtain analytic expressions for quantities of interest, such as Ham factors and the energies of the levels. We can explore the region near the limit by using perturbation theory, thereby obtaining a complete and precise picture of the approach to the limit itself.

III. GLAUBER STATES

Two independent methods will be used in the analysis. Apart from a safeguard against error, their complementary character provides added insight into the physics of the situation. The first method is conceptually the more elementary. To calculate the eigenvalues of H in the strong JT limit, we should evidently seek eigenfunctions of $T^{(2)} \circ (a^\dagger + a)$. Following the work of Glauber,[8] we may readily verify that

$$(T^{(2)} \circ a)\exp(k a^\dagger \circ C^{(2)})\,|\,0\rangle = k(T^{(2)} \cdot C^{(2)}) \times \exp(k a^\dagger \circ C^{(2)})\,|\,0\rangle \tag{2}$$

for all polar angles of the spherical tensor $C^{(2)}(\theta,\phi)$.[9] The normalization of $C^{(2)}$ is not important here, though in general it is convenient to follow Edmonds's definition[10]

$$C_q^{(t)}(\theta,\phi) = [4\pi/(2t+1)]^{1/2} Y_{tq}(\theta,\phi)\ .$$

Equation (2) provides a generalized Glauber state as an eigenfunction of $T^{(2)} \cdot a$. Since the adjoints of the Glauber states are eigenbras of $T^{(2)} \cdot a^\dagger$, the matrix elements of V can be calculated by allowing the two terms making up V to act in opposite senses, $T^{(2)} \cdot a$ to the right, and $T^{(2)} \cdot a^\dagger$ to the left.

However, the state

$$\exp(k a^\dagger \cdot C^{(2)})\,|\,0\rangle$$

does not include the electronic part. It is convenient to denote the three orbital states of the p electron by the vectorial ket $|\,p\rangle$, for then the linear combinations of p-electron states appropriate to the lower (stable) branch, as found by O'Brien,[11] can be concisely expressed as $C^{(1)} \cdot |\,p\rangle$. Two orthogonal linear combinations are required for the upper branch. At this point, we introduce the double tensors $D^{(tt)}$, which are derived from the rotation matrices $\mathfrak{D}^t_{uv}(\Omega)$, where Ω stands for the Euler angles $(\phi\theta\gamma)$, by the equation[12]

$$D^{(tt)}_{u,-v} = (-1)^{t-v}(2t+1)^{1/2}\mathfrak{D}^t_{uv}(\Omega)^*.$$

The two angular momentum vectors $\vec{l}$ and $\vec{\lambda}$ with respect to which the ranks and their components are defined[13] are specified by[14]

$$l_x \pm i l_y = i e^{\pm i\phi}(\cot\theta\,\partial_\phi \mp i\partial_\theta - \csc\theta\,\partial_\gamma), \tag{3}$$

$$l_z = -i\partial_\phi \tag{4}$$

for the first rank t and its component u, and

$$\lambda_\xi \pm i\lambda_\eta = i e^{\mp i\gamma}(\cot\theta\,\partial_\gamma \pm i\partial_\theta - \csc\theta\,\partial_\phi), \tag{5}$$

$$\lambda_\xi = i\partial_\gamma \tag{6}$$

for the second rank t and its component $-v$. In the above equations, we have used the abbreviation $\partial_\phi \equiv \partial/\partial\phi$, etc. If we regard the subscripts x, y, z as referring to components of $\vec{l}$ in the laboratory frame F, then the components ξ, η, or ζ of $\vec{\lambda}$ refer to a frame F' that is obtained by subjecting F to a rotation of γ about its z axis, then θ about its (old) y axis, and finally by ϕ about the original z axis.[14]

It is straightforward to prove that

$$C_u^{(t)}(\theta,\phi) = (-1)^t(2t+1)^{-1/2} D^{(tt)}_{u0},$$

so that the electronic eigenfunction obtained above can be written (with a trivial change of normalization) as $D^{(11)}_{\cdot 0} \cdot |\,p\rangle$. The subscripted dot merely indicates a blank space for the unspecified components of the first rank 1 that are to be combined with the appropriate components of $|\,p\rangle$ to form a scalar product. We can now immediately write down the two orthogonal states belonging to the upper branch as $D^{(11)}_{\cdot\pm1} \cdot |\,p\rangle$.

Before combining the electronic states and the Glauber states to form the total eigenfunction, we note that states of definite angular momentum J (and component M) can be projected out by including $D^{(JJ)}_{MN}$ in the product and integrating over Ω. Such a state is

$$\int D^{(11)}_{\cdot r} \cdot |\,p\rangle D^{(JJ)}_{MN} \exp(k a^\dagger \cdot C^{(2)})\,|\,0\rangle\, d\Omega. \tag{7}$$

For it not to vanish, $r+N=0$. The ground state of the system in the strong JT limit corresponds to taking $r=0$. For an integrand of even parity, we must have odd J, in agreement with O'Brien.[11] An equivalent form of (7) has already been given[9] in a notation that is less suited to the generalizations that we now embark upon.

IV. EXCITED STATES

Since Glauber states are displaced forms for zero-point motions, that state (7) is a coherent superposition of ligand displacements. This idea will be viewed from a different standpoint in Sec. VII; for the moment, we need only note that the orientation of the coherent structure is specified by the Euler angles Ω. We can evidently superimpose vibrational effects on this structure by including creation operators in the integrand; but, to be sure that the new vibrations are referred to the rotated frame, we need the rotated forms

$$b^\dagger_m = (D^{(22)}_{\cdot m} \circ a^\dagger) - k\delta(m,0) \tag{8}$$

rather than the simple expressions $a^\dagger_m$. We now introduce the generalized states

$$|\,r,\lambda\mu\nu,JM\rangle = \int D^{(11)}_{\cdot r} \cdot |\,p\rangle D^{(JJ)}_{MN}(b^\dagger_0)^\lambda (b^\dagger_2)^\mu (b^\dagger_{-2})^\nu \exp(k a^\dagger \cdot C^{(2)})\,|\,0\rangle\, d\Omega\ . \tag{9}$$

These provide bases for all our calculations. For them not to vanish, $r+N+2\mu-2\nu=0$.

Two subsidiary points need comment: the limitation of m to 0 and ± 2, and the δ-function term in $b^\dagger_m$. If we replace Ω in the integrand of (9) by some augmented Euler triad Ω', the integral itself cannot change. This means that a rotation operator of the type $(1+\vec{v}\circ\vec{l})$, where $\vec{v}$ is an arbi-

trary infinitesimal vector, cannot affect $|0,000, JM\rangle$ if it is allowed to act on the terms of the integrand. By so doing, we obtain superpositions of states of the type (9) and, in addition, a state of the type (7) in which $b^\dagger_{\pm 1}$ is included in the integrand. This means that the components ± 1 for m correspond to rotations of the coherent structure and are not required for the vibrational superstructure. A precisely similar effect occurs for the vibrations of deformed nuclei.[15,16]

The δ-function term in (8) is needed to ensure that, for the normalized states,

$$\langle r, \lambda\,\mu\,\nu,\ JM |\ r, \lambda'\mu\nu,\ JM\rangle \to 0$$

when $k \to \infty$ and $\lambda \neq \lambda'$. This can be rapidly verified by picking $(\lambda\mu\nu) = (100)$ and $(\lambda'\mu\nu) = (000)$, for example. The parameter k can be related to the relative strengths of V and H_0 as follows. For the lower branch (corresponding to $r = 0$), the electronic integrations can be performed by abstracting, from a general matrix element, $C_2^{(1)} \cdot |p\rangle$ from the ket and $\langle p| \cdot C_1^{(1)}$ from the bra, where $C_i^{(1)}$ is an abbreviation for $C^{(1)}(\theta_i, \phi_i)$. The Hamiltonian H can now be replaced by an effective Hamiltonian H', which acts solely between vibrational states. It is easy to show that

$$H' = \tfrac{1}{2}\hbar\omega(a^\dagger \circ a + a \circ a^\dagger)(C_1^{(1)} \cdot C_2^{(1)}) + K(a^\dagger + a) \circ (C_1^{(1)} C_2^{(1)})^{(2)},$$

where

$$K = (5)^{-1/2}(p\,||\,T^{(2)}\,||\,p). \tag{10}$$

A straightforward calculation yields

$$[H', b^\dagger_m] = \hbar\omega(C_1^{(1)} \cdot C_2^{(1)})b^\dagger_m, \tag{11}$$

provided

$$\hbar\omega k = -K(\tfrac{2}{3})^{1/2}. \tag{12}$$

The ultimate integration over Ω_1 and Ω_2 (that must be carried out to evaluate a matrix element) is weighted heavily near $\Omega_1 = \Omega_2$, owing to the exponentials in the states (9). So Eq. (11) can be written

$$[H', b^\dagger_m] \approx \hbar\omega b^\dagger_m\ ,$$

which is what we expect for the Hamiltonian of a vibrational spectrum. Combining Eqs. (10) and (12), we find

$$k = -(\tfrac{2}{15})^{1/2}(p\,||\,T^{(2)}\,||\,p)/\hbar\omega\ . \tag{13}$$

As such, k is directly related to the ratio of the magnitudes of V and H_0. The strong and weak JT limits correspond to $k \to \infty$ and $k \to 0$, respectively.

V. ENUMERATING THE STATES

Before we put H between the states (9) to set up the energy matrix, the frequency of occurrence of states of various kinds needs to be studied. To find the number $Z_r(nJ)$ of states with angular momentum J in the vibrational level n $(= \lambda + \mu + \nu)$ in the strong JT limit, we apply the inequality $J \geq N$ together with the condition that the integrand appearing in the construction of $|r, \lambda\mu\nu, JM\rangle$ has even parity. As an example, take $r = 0$, $n = 2$, and $J = 1$. The acceptable values of $(\lambda\mu\nu)$ are (200) and (011) only. Under the inversion operations

$$\phi \to \pi + \phi,\ \theta \to \pi - \theta,\ \gamma \to \pi - \gamma,$$

we find

$$D^{(tt)}_{uv} \to (-1)^{t-v} D^{(tt)}_{u,-v}\ .$$

So $b^\dagger_m \to (-1)^m b^\dagger_{-m} = b^\dagger_{-m}$, since m is even. Thus both $(b^\dagger_0)^2$ and $b^\dagger_2 b^\dagger_{-2}$ possess even parity and give rise to two distinct states. On the other hand, there is only one state for which $J = 2$, since the products $b^\dagger_0 b^\dagger_2$ and $b^\dagger_0 b^\dagger_{-2}$ can be combined to give $b^\dagger_0(b^\dagger_2 - b^\dagger_{-2})$, which possesses odd parity. A brief listing of the acceptable J values is given in Table I. Spectroscopic symbols are used for J; their multiplicities are indicated by superscripts.

The situation in the weak JT limit is well understood.[4,9] The five-dimensional oscillator Hamiltonian H_0 gives a sequence of equally spaced levels for which the labels [0], [1], [2], ..., [n] are available, where [n] denotes an irreducible representation of the unitary group U_5. The reduction $U_5 \to R_3$ yields the angular momenta L of the oscillator quanta. We have only to couple each L to the p electron to obtain the total angular momenta J. A listing is made of the structure of some of the lowest levels in Table II. In analogy with Table I, the number of times $Z'(nJ)$ that a given J level occurs is indicated by a superscript to the appropriate spectroscopic symbol.

Comparison of Tables I and II reveals the correspondence

$$Z_0(nJ) = Z'(n + \tfrac{1}{2}J - x, J),$$

where $x = \frac{1}{2}$ if J is odd and $x = 1$ if J is even. This strongly suggests that the infinite sequence of

TABLE I. Angular momentum states for $T_1 \otimes (\epsilon + \tau_2)$ in the strong JT limit.

r	n	J
0	0	$PFHKMO\cdots$
	1	$PDF^2GH^2IK^2LM^2\cdots$
	2	$P^2DF^3G^2H^4I^2K^4L^2M^4\cdots$
	3	$P^2D^2F^4G^3H^5I^4K^6L^4M^6\cdots$
± 1	0	$PDFGHI\cdots$
	1	$P^2D^2F^3G^3H^3I^3\cdots$
	2	$P^3D^3F^5G^5H^6I^6K^6L^6\cdots$
	3	$P^4D^4F^7G^7H^9I^9K^{10}L^{10}M^{10}\cdots$

TABLE II. Angular momentum states for $T_1 \otimes (\epsilon + \tau_2)$ in the weak JT limit.

n	J
0	P
1	PDF
2	P^2DF^2GH
3	$P^2D^2F^3G^2H^2IK$
4	$P^3D^2F^4G^3H^4I^2K^2LM$
5	$P^3D^3F^5G^4H^5I^4K^4L^2M^2NO$
6	$P^4D^3F^6G^5H^7I^5K^6L^4M^4N^2O^2QR$

terms of a given J provides a basis for a representation of a noncompact group. Speculation on this question would take us too far afield.

An interesting regularity appears in the decomposition $U_5 \to R_3$ as $n \to \infty$. With the aid of Table I of Le Tourneux,[17] we find

$$\lim_{n\to\infty}[n] \otimes p = P^{n/2}D^{n/2}F^nG^nH^{3n/2}I^{3n/2}K^{2n}\cdots .$$

This determines the relative frequency of states of different J in the total energy-level structure. Although every J state (except $J=0$) occurs an infinite number of times, we see, for example, that there are twice as many levels for which $J=4$ as there are levels for which $J=1$.

VI. MATRIX ELEMENTS

Having enumerated the states, it remains to calculate the matrix elements

$$\langle r, \lambda\mu\nu, JM \mid H \mid r', \lambda'\mu'\nu', JM\rangle$$

and the associated overlap integrals

$$\langle r, \lambda\mu\nu, JM \mid r', \lambda'\mu'\nu', JM\rangle .$$

This can be done by using the commutation relations satisfied by the boson operators $a_m^\dagger$ and a_m in order to transfer the creation operators to the left and the annihilation operators to the right. We then use

$$a_m \exp(ka^\dagger \circ C_2^{(2)}) \mid 0\rangle = (-1)^m k(C_2^{(2)})_{-m} \times \exp(ka^\dagger \cdot C_2^{(2)}) \mid 0\rangle$$

and its adjoint to remove all annihilation and creation operators except those in the exponentials, for which

$$\langle 0 \mid \exp(ka \circ C_1^{(2)}) \exp(ka^\dagger \cdot C_2^{(2)}) \mid 0\rangle = \exp(SC_1^{(2)} \circ C_2^{(2)}) ,$$

where $S = k^2$. (It is convenient to introduce the symbol S here because it turns out to be identical to that used by O'Brien.[4]) To complete the calculation, we need to perform the integration over Ω_1 and Ω_2. Recouplings of the type

$$(C_1^{(g)} \circ C_2^{(g)})(C_1^{(h)} \cdot C_2^{(h)}) = \sum_t (2t+1) \begin{pmatrix} t & g & h \\ 0 & 0 & 0 \end{pmatrix}^2 \times (C_1^{(t)} \cdot C_2^{(t)})$$

can be used to reduce all integrals to the standard form (for even t)

$$\iint (C_1^{(t)} \circ C_2^{(t)}) \exp(SC_1^{(2)} \circ C_2^{(2)})\, d\Omega_1\, d\Omega_2 = (64\pi^4 e^S/3S)[1 - (T-2)/6S + (T-2)(T-12)/2!(6S)^2 - (T-2)(T-12)(T-30)/3!(6S)^3 + \cdots] , \quad (14)$$

where $T = t(t+1)$. To obtain Eq. (14), the exponential is expanded in a series of Whittaker functions, and these are then expanded in turn by means of the equations of Sec. 16.3 of Whittaker and Watson.[18]

Normalization removes the term e^S from the integrals (14), and so all matrix elements of the total Hamiltonian can be expanded in inverse powers of S. This is the appropriate form for the strong JT limit, for which $k \to \infty$. The energy levels and other properties of interest, such as the Ham factors, can be calculated by a straightforward application of perturbation theory. Before describing the results, we outline an alternative approach to the problem.

VII. NORMAL COORDINATES

The properties of the lowest level have been explored in the strong JT limit by O'Brien.[4,11] In her approach, the five normal coordinates q_m $(-2 \le m \le 2)$ are parametrized by introducing a new set of coordinates $(q\,\alpha\,\beta\,\theta\,\phi)$. Those representing rotations (namely θ and ϕ) are separated from the vibrational coordinates $(q\,\alpha\,\beta)$ before the quantization of the oscillations is carried out. A formal definition of O'Brien's coordinates is succinctly provided by the tensorial equation

$$q_m^{(2)} = qD_{m*}^{(22)}(\phi, \theta, \tfrac{1}{2}\beta) \circ X^{(2)} , \quad (15)$$

where the pseudotensor $X^{(2)}$ is defined through its components:

$$X_{\pm 2}^{(2)} = (10)^{-1/2} \sin\alpha ,$$
$$X_0^{(2)} = (5)^{-1/2} \cos\alpha ,$$
$$X_{\pm 1}^{(2)} = 0 .$$

To parallel our previous notation, we take $\beta = 2\gamma$.

The first step in the analysis is to express the kinetic energy in terms of $(q\,\alpha\,\gamma\,\theta\,\phi)$. This entails

the construction of the five-dimensional Laplacian ∇^2, only part of which has been given in the literature.[4] The resulting second-order differential form can be greatly simplified if the components of $\vec{\lambda}$, as given in Eqs. (5) and (6), are used. We find

$$\nabla^2 = q^{-4}\partial_q(q^4\partial_q) + q^{-2}\csc 3\alpha\,\partial_\alpha(\sin 3\alpha\,\partial_\alpha) + (\sin 3\alpha/12q^2\sin^3\alpha)\partial_\gamma^2 - (\sin\alpha/q\sin 3\alpha)^2(\sin^2\alpha + 3\cos^2\alpha)\vec{\lambda}^2$$
$$+ 3^{1/2}(\sin\alpha/\sin 3\alpha)^2(1/2q^2)\sin 2\alpha\,(\lambda_+^2 + \lambda_-^2)\ , \tag{16}$$

where $\lambda_\pm = \lambda_\xi \pm i\lambda_\eta$. In terms of an effective mass μ, the oscillator Hamiltonian is given by

$$H_o = -(\hbar^2/2\mu)\nabla^2 + \tfrac{1}{2}\mu\omega^2 q^2.$$

We begin the analysis of V by noting that

$$V = (2\mu\omega/\hbar)^{1/2}\, T^{(2)}\cdot q^{(2)}\ .$$

By using Eqs. (13) and (15), it can be shown that, for the lower branch, the following equivalence is valid:

$$V \equiv -(2\mu\omega/\hbar)^{1/2}\hbar\omega kq\cos\alpha\ .$$

We introduce O'Brien's parameter q_0 by writing

$$S^{1/2} = k = q_0(\mu\omega/2\hbar)^{1/2}$$

so that

$$H_o + V = -(\hbar^2/2\mu)\nabla^2 + \tfrac{1}{2}\mu\omega^2 q^2 - \mu\omega^2 q_0 q\cos\alpha$$
$$= -(\hbar^2/2\mu)\nabla^2 + \tfrac{1}{2}\mu\omega^2[(q\cos\alpha - q_0)^2 + (q\sin\alpha)^2] - \hbar\omega S\ .$$

If, now, we make the transformation

$$H' = U^{-1}(H_o + V)U,$$

where

$$U = q^{-1}(\sin\alpha/\sin 3\alpha)^{1/2}\ ,$$

it is found that

$$H' = H_o' + V'\ ,$$

where

$$H_o' = -(\hbar^2/2\mu)[q^{-2}\partial_q(q^2\partial_q) + q^{-2}\csc\alpha\,\partial_\alpha(\sin\alpha\,\partial_\alpha) + \tfrac{1}{4}q^{-2}\csc^2\alpha\,\partial_\gamma^2] + \tfrac{1}{2}\mu\omega^2[(q\cos\alpha - q_0)^2 + (q\sin\alpha)^2] - \hbar\omega S \tag{17}$$

and

$$V' = (\hbar^2/2\mu)(\sin\alpha/\sin 3\alpha)^2 q^{-2}[(\sin^2\alpha + 3\cos^2\alpha)(\vec{\lambda}^2 - 2) - \tfrac{1}{2}(3)^{1/2}\sin 2\alpha(\lambda_+^2 + \lambda_-^2)] + (\hbar^2/6\mu)q^{-2}\lambda_\xi^2\ . \tag{18}$$

By means of these equations we have expressed the total Hamiltonian in terms of the coordinates $(q\,\alpha\,\gamma\,\theta\,\phi)$ and the differential operators formed from them. Of course, H' is appropriate only for the lower branch, owing to the equivalence used for V. The original form for V must be used to study the upper branch.

VIII. EIGENFUNCTIONS

The separation of H' into H_o' and V' prepares the ground for an application of perturbation theory in which H_o' determines the zeroth-order eigenfunctions and V' is the perturbation. The leading term, H_o', corresponds to an isotropic three-dimensional harmonic oscillator centered on the point whose z coordinate is q_0. We thus obtain a sequence of levels separated by $\hbar\omega$ for the spectrum of H_o'. The factor $\frac{1}{4}$ preceding ∂_γ^2 in Eq. (17) can be eliminated by using $\frac{1}{2}\beta$ in place of γ. The usual boundary conditions for a harmonic oscillator are satisfied, since the normal coordinates q_m go into themselves (i.e., $q_m \to q_m$) when β is advanced by 2π. Thus the factor $e^{iM'\beta}$ appears in the eigenfunctions, where $M' = 0, \pm 1, \pm 2, \ldots$. However, we cannot interpret M' as the quantum number for a projected angular momentum vector. This is because $i\partial_\gamma$ is the component of such a vector, not $i\,\partial_\beta$. We therefore replace $e^{iM'\beta}$ by $e^{iN\gamma}$, where $N = 0, \pm 2, \pm 4, \ldots$. This is consistent with

the single-boson condition $m = 0, \pm 2$ obtained in Sec. IV.

As an example, consider the first excited level of the harmonic oscillator. The eigenfunctions for which $M' = \pm 1$ become converted to $e^{\pm 2i\tau}$, which correspond to those of a Δ state of a diatomic molecule. The acceptable angular momenta of the associated rotational band are 2, 3, 4, etc. The eigenfunction corresponding to $M' = N = 0$ yields the J sequence 1, 3, 5, ... just as the ground state does. The combined sequence is 1, 2, 3^2, 4, 5^2, ..., in agreement with the entry in Table I for which $(rn) \equiv (01)$.

Since H_o' does not involve θ or ϕ, we could multiply the eigenfunctions $\psi(q\,\alpha\,\gamma)$ of H_o' by any convenient function of θ and ϕ to form the total eigenfunction. The best plan appears to be to extract $e^{iN\tau}$ from ψ to form $D^{(JJ)}_{M',-N}(\phi\,\theta\,\gamma)$, for then the components of $\vec{\lambda}$ that appear in V' act directly on the subscript $-N$. At the same time, we obtain states of well-defined angular momentum J. After a reversal of the sign of N and a transference of origin according to the scheme

$$r\sin\tau = q\sin\alpha, \quad r\cos\tau = q\cos\alpha - q_0, \tag{19}$$

we can conveniently write the eigenfunctions of H_0 for the lower branch as

$$f_{nL}(r)P_L^{N/2}(\cos\tau)D^{(JJ)}_{MN}(\phi\,\theta\,\gamma)C^{(1)}(\theta\,\phi)\circ|p\rangle\,. \tag{20}$$

The corresponding eigenvalue is

$$-\hbar\omega\,S + (n+\tfrac{3}{2})\hbar\omega. \tag{21}$$

In (20), L is, from a formal point of view, an angular momentum quantum number for a state of the nth excited level of a three-dimensional harmonic oscillator; f_{nL} is the corresponding radial eigenfunction, and $P_L^{N/2}$ is an associated Legendre polynomial. If (17) is treated in Cartesian coordinates rather than the spherical polars $(r\,\tau\,\gamma)$, then the three quantum numbers $(n\,L\,N)$ are replaced by the set $(\lambda\,\mu\,\nu)$. To parallel the analysis of Sec. IV, we can order the integers λ, μ, and ν to count the number of oscillator quanta for which $m = 0$, 2, and -2, respectively. As before, we have

$$\lambda + \mu + \nu = n, \quad 2\mu - 2\nu + N = 0.$$

A given L will, of course, involve a superposition of the states defined by $(\lambda\,\mu\,\nu)$. For example, when $n = 3$, we can have $L = 1$ or 3. A state defined by $(n\,L\,N) = (312)$ is equivalent to a superposition of the two states for which $(\lambda\,\mu\,\nu) \equiv (201)$ and (012).

IX. ENERGY LEVELS

To conclude the analysis of the alternative method begun in Sec. VII, we have to calculate the effect of the perturbation V' of Eq. (18) within the basis (20). (For low orders of perturbation theory, the states of the excited branch are not required.) Although this is reasonably straightforward, two points should perhaps be made. First, the components of $\vec{\lambda}$ act not only on the $D^{(JJ)}$ tensor of (20), but also on the part $C^{(1)}\circ|p\rangle$. On recoupling $D^{(JJ)}$ and $C^{(1)}$, we find

$$(\vec{\lambda}^2 - 2)D^{(JJ)}C^{(1)}\circ|p\rangle = J(J+1)D^{(JJ)}C^{(1)}\circ|p\rangle\,,$$

so the eigenvalue of $\vec{\lambda}^2 - 2$ is $J(J+1)$.

Secondly, the transformation (19), when applied to V', gives an expression that can be simplified by expanding it in a power series in r/q_0. This is an appropriate expansion for the strong JT limit, since it is easy to show that $r/q_0 \sim k^{-1}$. For example, we find

$$(\hbar^2/2\mu)(\sin\alpha/\sin3\alpha)^2 q^{-2}(\sin^2\alpha + 3\cos^2\alpha) = (\hbar\omega/12S)[1 - 2(r/q_0)\cos\tau + (r/q_0)^2(3\cos^2\tau + \sin^2\tau) + \cdots]\,. \tag{22}$$

Since the eigenvalue of λ_ζ is N, and since λ_+ and λ_- cannot contribute to diagonal matrix elements, we see that the first-order effect of V' is to add to (21) the energy

$$(\hbar\omega/12S)[J(J+1) - N^2]. \tag{23}$$

A term of this type appears in the energy spectrum of a symmetric top whose two common moments of inertia I are given by $I = 3\mu\,q_0^2$. A special case of (23) has been given by O'Brien[4,11] for $N = n = 0$.

An identical term to (23) can be derived using the Glauber-state analysis of Secs. III–VI. However, the source is different. Unlike the treatment above, the excited branch (corresponding to $r = \pm 1$) plays a role. This is characteristic of the approach using Glauber states: although the analysis is conceptually simpler, it often turns out that perturbation theory has to be carried to a higher order to obtain comparable effects.

We have carried the analysis to $O(S^{-2})$ for the $J = 1$ levels. These are the only ones that can be reached by electric dipole radiation from the ground level (for which $J = 0$), and hence are the only ones directly observable. They all correspond to $N = 0$. For the lower branch, we find that the energies $E(r, \lambda\,\mu\,\nu, JM)$, in units of $\hbar\omega$, are given by

$$E(0, \lambda\,\mu\,\nu, 1M) = -S + (\lambda + \mu + \nu + \tfrac{3}{2}) + 1/6S + (6\lambda + 2\mu + 2\nu + 5)/24S^2 + O(S^{-3}). \tag{24}$$

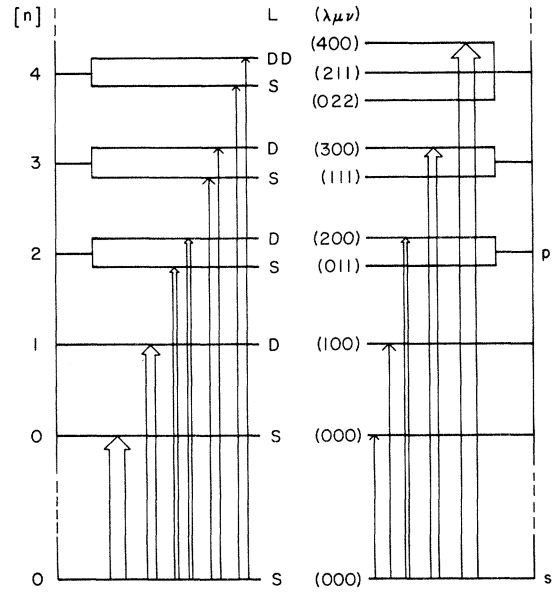

FIG. 1. Schematic representation of $s \rightarrow p$ transitions and the $J=1$ levels of $T_1 \otimes (\epsilon + \tau_2)$ for weak JT coupling (on the left) and strong JT coupling (on the right). The pairs of levels deriving from a common $[n]$ are separated by an energy $9\hbar\omega S/4$ on the left. In the strong JT limit, the energies between adjacent levels possessing a common $\lambda+\mu+\nu$ are all $\hbar\omega/3S^2$.

The origin of the S^{-2} term here can be most directly seen by replacing the relevant terms of Eq. (22) by their second-quantized forms, namely,

$$(r/q_0)^2 \cos^2\tau \rightarrow (1/4S)(b_0^\dagger + b_0)^2,$$

$$(r/q_0)^2 \sin^2\tau \rightarrow (1/4S)[(b_2^\dagger + b_2)^2 + (b_{-2}^\dagger + b_{-2})^2],$$

and then using the fact that the eigenvalues of $b_0^\dagger b_0$, $b_2^\dagger b_2$, and $b_{-2}^\dagger b_{-2}$ are λ, μ, and ν, respectively. A schematic representation of the levels is given in Fig. 1.

In a private communication, O'Brien has shown that a similar arrangement of at least the levels for which $n \leq 4$ can be obtained by taking the lowest 90 states corresponding to the weak JT limit and diagonalizing the Hamiltonian H within this limited set. It appears essential, however, to include the parameter W (mentioned in Sec. II) in the analysis. For $S=21.85$, it turns out that W should be roughly 0.4.

X. HAM FACTORS

Tensors $Z^{(t)}$ of a specified rank t, acting solely in the electronic space, are reduced when the full vibronic eigenfunctions are used. The reduction factor, $K(t)$, is called a Ham factor.[19] We have two methods for finding $K(t)$ near the strong JT limit. Both employ perturbation theory. Taking the method of Secs. VII–IX first, we calculate the coupling of $Z^{(t)}$ and also of V' between the upper and lower branches. The cross term coming from these two operators yields, for the lowest level for which $J=1$, the results

$$K(0)=1,\ K(1)=1/9S^2,\ K(2)=\tfrac{2}{5}+1/15S^2,$$
$$K(t)=0 \quad (t>2) \tag{25}$$

to $O(S^{-2})$. O'Brien has calculated $K(1)$ (for the lowest $J=1$ level) with a truncated oscillator basis subject to her special variational procedure.[4] She finds $K(1)=0.0007732$ and 0.0002608 for $S=13.33$ and 21.85, respectively. The corresponding values of $1/9S^2$ are 0.000625 and 0.0002328. As might be expected, the analytic forms are slightly smaller than the others, but the agreement is remarkably good.

The approach using Glauber states gives the same expressions for $K(t)$ as those in Eqs. (25). However, it is now necessary to go to fourth order in perturbation theory. The way that the various contributions combine to produce $1/9S^2$ for $K(1)$ is shown in Table III. All listed states correspond to $J=1$. The agreement between such different methods gives one considerable confidence in the calculations.

XI. INTENSITIES

Intensities of the transition $s \rightarrow p$ can be readily calculated from the Glauber states. The ground

TABLE III. Sources for $K(1)$ using Glauber states.

Perturbation order	States $(r;\ \lambda\mu\nu)$ linked by perturbation	Contribution to $K(1)$
1	$(0;000)(0;000)$	$1/3S+1/3S^2$
2	$(0;000)(\pm1;000)(0;000)$	$-1/3S-1/9S^2$
2	$(0;000)(\pm1;100)(0;000)$	$-1/3S^2$
3	$(0;000)(\pm1;000)(\pm1;000)(0;000)$	$1/36S^2$
3	$(0;000)(\pm1;000)(\pm1;100)(0;000)$	$1/3S^2$
4	$(0;000)(\pm1;000)(\pm1;100)(\pm1;000)(0;000)$	$-1/12S^2$
4	$(0;000)(\pm1;000)(\pm1;010)(\pm1;100)(0;000)$	$-1/36S^2$
4	$(0;000)(\pm1;000)(\pm1;001)(\pm1;100)(0;000)$	$-1/36S^2$
	Total:	$1/9S^2$

state is simply $|s\rangle|0\rangle$, and the electric dipole operator acts only in the electronic space. We note that the equation $\langle 0|a^\dagger = 0$ implies

$$\langle 0|(b_0^\dagger)^\lambda (b_2^\dagger)^\mu (b_{-2}^\dagger)^\nu \exp(ka^\dagger \circ C^{(2)})|0\rangle = (-k)^\lambda \delta(\mu,0)\delta(\nu,0), \quad (26)$$

since the creation operators can all be allowed to act directly on the bra, and only $b_0^\dagger$ contains a part (namely $-k$) that does not involve $a^\dagger$. In performing the integration over the Euler angles, the product $D_{\cdot 0}^{(11)} D_{MN}^{(JJ)}$ necessarily introduces the factor $\delta(J,1)$. Transitions from the s state can therefore only be made to $J=1$ levels corresponding to $\mu=\nu=0$; and their strength is proportional to S^λ [the square of the right-hand side of Eq. (26)] divided by the normalization integral I for $|0,\lambda 00, 1M\rangle$. We find

$$I = 64\pi^4 e^S \lambda!/9S,$$

so the intensity (for $S \gg \lambda$) exhibits a dependence on on λ and S given by $S^{\lambda+1}e^{-S}/\lambda!$. This agrees with O'Brien's formula for the special case $\mu=\nu=\lambda=0$. It can also be checked, in a rough way, by referring to the intensity diagrams given by Le Tourneux for the components of the giant dipole resonance of spherical nuclei.[17] As has been mentioned elsewhere,[9] this is an equivalent physical system to the one under study.

XII. THE $E \otimes \epsilon$ CASE

We have used similar methods to those described in Secs. III–X to investigate the $E \otimes \epsilon$ case in the strong JT limit. Instead of five degenerate modes, we now have only two. The decomposition of the former into two rotational and three vibrational modes is replaced, for the $E \otimes \epsilon$ case, by a simple separation into one rotational mode (characterized by an angle ϕ) and one vibrational mode. We again performed calculations using two methods: that using Glauber states and that based on a separation of the rotational and vibrational motions before quantization. As before, it is advantageous to use the second method when high orders of perturbation theory are required.

Following the traditional notation,[2] the two electronic states spanning E are designated $|\theta\rangle$ and $|\epsilon\rangle$. The corresponding oscillator creation operators that span ϵ are $a_\theta^\dagger$ and $a_\epsilon^\dagger$. The Glauber state that is the analog of the right-hand side of Eq. (9) is

$$|r,\lambda,m\rangle = \int |r\rangle e^{im\phi}(b^\dagger)^\lambda \times \exp[\kappa(a_\theta^\dagger \cos\phi + a_\epsilon^\dagger \sin\phi)]|0\rangle d\phi, \quad (27)$$

where r refers either to the lower branch ($r \equiv l$) or to the upper branch ($r \equiv u$), for which

$$|l\rangle = \cos\tfrac{1}{2}\phi\,|\theta\rangle - \sin\tfrac{1}{2}\phi\,|\epsilon\rangle,$$
$$|u\rangle = \sin\tfrac{1}{2}\phi\,|\theta\rangle + \cos\tfrac{1}{2}\phi\,|\epsilon\rangle.$$

The creation operator $b^\dagger$ is the analog of $b_0^\dagger$:

$$b^\dagger = a_\theta^\dagger \cos\phi + a_\epsilon^\dagger \sin\phi - \kappa.$$

The strong JT limit corresponds to $\kappa \to \infty$. The Hamiltonian H is the analog of Eqs. (1):

$$H = \hbar\omega(a_\theta^\dagger a_\theta + a_\epsilon^\dagger a_\epsilon + 1) + T_\theta(a_\theta^\dagger + a_\theta) + T_\epsilon(a_\epsilon^\dagger + a_\epsilon),$$

where T_θ and T_ϵ are electronic operators whose transformation properties under the octahedral group O are defined by the subscripts. To find the energy levels of the system, we calculate the matrix elements of the Hamiltonian H with respect to the states (27) and use standard perturbation theory.

Alternatively, we may separate the rotational and vibrational motions by introducing the following change of variables for the normal coordinates:

$$q_\theta = q\cos\phi, \quad q_\epsilon = q\sin\phi.$$

The Hamiltonian is given in terms of the coordinates $(q\phi)$ by

$$H = -(\hbar^2/2\mu)(\partial_q^2 + q^{-1}\partial_q + q^{-2}\partial_\phi^2) + \tfrac{1}{2}\mu\omega^2 q^2 + q(2\omega\mu/\hbar)^{1/2}(T_\theta\cos\phi + T_\epsilon\sin\phi).$$

In analogy to Eqs. (19), we write $q - q_0 = x$, where q_0 is now the radius of that circle in the plane defined by q_θ and q_ϵ for which the effective potential energy of the lower branch is a minimum. It turns out that

$$\kappa^2 = \mu\omega q_0^2/2\hbar.$$

To parallel the relation $k^2 = S$ for $T_1 \otimes (\epsilon + \tau_2)$, we write $\kappa^2 = s$. The ratio x/q_0 can be used as an expansion parameter and the perturbative methods of Sec. IX adjusted to calculate the vibronic levels and the Ham factors. To perform the analysis, the eigenfunctions specified by the equation

$$|r,n,m\rangle = (2\pi q)^{-1/2}|r\rangle e^{im\phi}|n\rangle$$

are used, where $|n\rangle$ is the nth harmonic-oscillator eigenfunction associated with the variable x.

For the lower branch, we find that the energies $E(l,n,m)$, in units of $\hbar\omega$, are given by

$$E = -s + f + (m^2/4s)\{1 + 3f/2s + [15(2f^2+\tfrac{1}{2}) - 1]/16s^2 + [35(4f^3+5f) - 8f]/64s^3\} - (m^4/16s^3)(1 + 9f/8s) + O(s^{-5}), \quad (28)$$

where f is related to the vibrational quantum number n by $f = n + \frac{1}{2}$. The half-integral quantum number l of Longuet-Higgins *et al.*[20] is identical to our m.

The two Ham factors p and q, corresponding to operators belonging to the respective irreducible representations A_2 and E of the octahedral group, are found to be

$$p = (4s)^{-2} - (4s)^{-4},$$

$$q = \tfrac{1}{2}[1 + (4s)^{-2} - (4s)^{-4}]$$

to $O(s^{-4})$ for the lowest level. These expressions for E, p, and q agree with the lower-order results previously reported[20,21] [including an unpublished calculation of E to $O(s^{-3})$ by O'Brien].

XIII. CONCLUDING REMARKS

The energies and Ham factors that we have obtained for $E \otimes \epsilon$ and $T_1 \otimes (\epsilon + \tau_2)$ can be carried to higher orders of perturbation theory by extending the analysis in a straightforward way. However, the simplifications that have been made, particularly the assumption of a single frequency ω for both cases, would severely limit the usefulness of such extensions. As it is, the contribution of the analysis presented above lies principally in the description of two complementary methods for studying degenerate systems near the strong JT limit.

We thank Dr. M. C. M. O'Brien for extremely useful letters and conversations.

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*Work supported in part by the National Science Foundation.

†On leave from Instituto de Física, Universidad de Concepción, Concepción, Chile.

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