Lie Groups and the Jahn-Teller Effect for a Color Center*

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Abstract

The F^+ center in CaO consists of an electron trapped in an oxygen vacancy. The interaction between the electron and the even normal modes of the surrounding octahedron of calcium ions can be represented by an approximate Hamiltonian possessing an oscillator term of U(5) symmetry and an interaction term of O(3) symmetry. To separate repeated angular-momentum quantum numbers L in the symmetric irreducible representations of O(5), four independent methods have been studied. A remarkable coalescence of these approaches in the case of L=6 suggests a natural way to make the separation.

*Work supported in part by the U. S. National Science Foundation

1. INTRODUCTION

The Jahn-Teller (JT) effect refers to the spontaneous distortions that symmetric molecular complexes undergo when the associated electronic state is degenerate.[1] A system of particular interest to us is the F^+ center in CaO, which consists of an electron trapped in an oxygen vacancy. The immediate environment of the electron is an octahedron of calcium ions. The two even modes, which are labelled by the appropriate irreducible representations ϵ and τ_2 of the octahedral group, possess almost exactly coincident angular frequencies ω ; moreover, the coupling of both modes to the electronic p state is approximately the same.[2,3] As a consequence of these accidents, the two components of ϵ and the three components of τ_2 can be combined to form a spherical d phonon whose five components are created by the second-rank tensor $a^\dagger$. The Hamiltonian can be written

$$H = \tfrac{1}{2}\hbar\omega\,(a^\dagger\cdot a + a\cdot a^\dagger) + T^{(2)}\cdot(a^\dagger + a),$$

where the dot means the formation of an O(3) scalar. The first term is an oscillator Hamiltonian for which the symmetry group is U(5): the second term represents phenomenologically the coupling between the phonons and the electron. Its magnitude is determined by the amplitude of the second-rank tensor $T^{(2)}$, which acts only in the space of the p electron.

To solve for the energies and eigenstates of H, we may use a basis determined by either the first or second terms in H. These choices correspond to the weak and strong JT limits respectively. The latter has been recently described in detail.[4]

For present purposes, we take the opposite point of view, and consider the group-theoretical aspects of starting from the weak JT limit. This is the approach of O'Brien,[3] who first showed that the structure of the line $s \rightarrow p$ could be accounted for by a Hamiltonian of the form of H.

2. GROUPS

If we decide to work within the basis provided by the oscillator part of H, then we are led naturally to the scheme

$$U(5) \supset O(5) \supset O(3),$$

in which the five-dimensional irreducible representation [1] of U(5) leads down to (10) of O(5), and thence to (2) of O(3), corresponding to a single d phonon. Since phonons are bosons, we have only to consider the symmetric representations [N] of U(5) and (w0) of O(5). Now, the representations (w0) possess a rather unusual property:[5] under the reduction $O(5) \rightarrow O(3)$, the sequence of L values, taken in order of increasing L, tends to a well-defined pattern as $w \rightarrow \infty$. Thus, if w is exactly divisible by 3, the low-L structure (expressed in the traditional spectroscopic labels) is S, F, G, I, I, K,.... If w is not a multiple of 3, the structure is D, G, H, I, K,.... Most of the previous theoretical work on the F^+ center has concentrated on states whose total angular momentum J is 1, and such states can only arise by coupling the p electron to either S or D. However, as soon as states of higher J are studied, multiplicity difficulties associated with the internal labelling problem arise. The earliest instance of this occurs for L=6, corresponding to the two I states in the first of the two L structures listed above. Because of the comparative

simplicity of this case, it was decided to make a detailed study of the various ways in which the two I states can be separated. The aim is not merely to formally define two distinct I states, but rather to find an approach that makes their separation a natural one. Such a result, if it could be obtained, would point the way to a general method for resolving the internal multiplicities

3. FRACTIONAL PARENTAGE COEFFICIENTS

In the weak JT limit, the oscillator part of H is diagonal with respect to the basis. Our attention is thus directed to a calculation of the matrix elements of $a^\dagger$ and a. The reduced matrix elements of $a^\dagger$ are related to the coefficients of fractional parentage (cfp) by the equation

$$(\psi \| a^\dagger \| \psi') = [(2L+1)N]^{\frac{1}{2}}(\psi\{|\psi'),$$

where ψ is a state of d^N with orbital angular momentum L. The cfp factorize:

$$(\psi\{|\psi') = ([N]W|[N-1]W' + [1](10))(W\beta L | W'\beta'L' + (10)d),$$

where W and W' are irreducible representations of O(5), and repeating values of L and L' are distinguished by β and β'. The two factors on the right-hand side of this equation are isoscalar factors; for example, the second factor is just a Clebsch-Gordan (CG) coefficient for O(5) with the CG coefficient for O(3) extracted. For simplicity, we pick the special case defined by W'=(w-1, 0), W=(w0), and N=w, for which the first isoscalar factor is 1.

Many of the cfp for which a given L and L' occur once in W and W' possess a strikingly simple form. They can be found by

applying tensorial techniques to evaluate matrix elements whose values are known from general grounds. For example, all matrix elements of $(a^{\dagger}a^{\dagger})^{(1)}$ and $(a^{\dagger}a^{\dagger})^{(3)}$ are zero, since there are no P or F states in d^2. A number of cfp have been calculated by O'Brien[7] by methods such as these. A typical example of a cfp for which no multiplicity complications arise is

$$(d^{w}(w0)K \{| d^{w-1}(w-1,\ 0)M) \quad = \quad [77(u-2)(u-13)/306u(u-1)]^{\frac{1}{2}}, \qquad (1)$$

where w is a multiple of 3, and u=2w+1. When w=6, for which a K state exists in (60) but there is no M state in (50), the cfp automatically vanishes.

The problem of distinguishing multiply-occurring L values would be ideally solved if cfp of a comparable simplicity to the one above could be introduced to define the states. It seems that this is too much to hope for. The various options open to us will now be considered with particular reference to the repeating I states

4. GODPARENTS

Perhaps the simplest way of constructing a specific I state is to pick a multiplicity-free state of (w-1, 0) and couple a creation operator to it. For example,

$$(a^{\dagger}|G\rangle)^{(6)}, \qquad (a^{\dagger}|H\rangle)^{(6)}, \qquad (a^{\dagger}|I\rangle)^{(6)}, \qquad (a^{\dagger}|K\rangle)^{(6)}$$

are I states corresponding to the godparents G, H, I, and K. When w is a multiple of 3, the (w0) parts of the four I states above is a linear combination of the two possible I states. It is easy to see that the choice of a particular godparent $|L\rangle$ for one I state, say I_1, implies $(I_2 \{| L)=0$ for the orthogonal companion I_2. This condition is enough to determine all remaining cfp for I_1 and I_2.

At first sight, there is not much to choose between the various godparents. All four lead to high primes in the denominators of the cfp. (For w=6, the primes are 251, 2113, 157, and 53 respectively.) This is not suggestive of a simple algebraic structure. However, one godparent turns out to be much more significant than the others. It is the G state, in terms of which we now separate the I_1 state from the I_2 state by means of

$$(I_2\{|G) = 0. \tag{2}$$

We can now show that

$$(I_1\{|G) = [3U/715u(u-1)]^{\frac{1}{2}},$$

$$(I_1\{|H) = 8(u-15)[(u-7)(u-2)/130u(u-1)U]^{\frac{1}{2}},$$

$$(I_2\{|H) = 10[22(u+4)(u+6)(u+11)/91(u-1)U]^{\frac{1}{2}},$$

$$(I_1\{|I) = 8(u+9)[(u+4)(u-7)/u(u-1)U]^{\frac{1}{2}},$$

$$(I_2\{|I) = -22[(u-2)(u+6)(u+11)/35(u-1)U]^{\frac{1}{2}},$$

etc., where U=61u(u+13)+1470. Although U does not break up into two linear factors with rational coefficients, its presence in the cfp does not detract too much from our ideal form.

Our definition of I_1 and I_2 coincides with the ostensibly arbitrary separation that Hecht[8] made for the special case for which w=6.

5. INTRINSIC STATES

The problem of defining the angular-momentum states of (w0) has been studied by Williams and Pursey[9] by extending the notion of intrinsic states that Elliott[10] used for SU(3). Although this approach leads to non-orthogonal components, it is of considerable

interest to us because it leads to an equivalent definition of I_2.

Consider the (unnormalized) state

$$|\Phi\rangle = (a_1^\dagger)^{2n+2}(a_{-2}^\dagger)^{n-2}|0\rangle$$

of d^w, where w=3n. The subscripts to $a^\dagger$ denote magnetic quantum numbers, the total value of which is given by

$$M_L = 2n+2 + (-2)(n-2) = 6.$$

According to the method of Williams and Pursey, $|\Phi\rangle$ is one of the two intrinsic states that separate the I terms. It is only necessary to rotate $|\Phi\rangle$ through some angle defined by the Euler triad Ω, thereby giving $|\Phi\rangle_\Omega$, and then project out an I term by forming the Hill-Wheeler integral

$$|I\rangle = \int D^{(66)}_{\cdot,-6}(\Omega)\,|\Phi\rangle_\Omega\, d\Omega, \qquad (3)$$

where the double tensor $D^{(JJ)}$ is related to the rotation matrices by the equation[11]

$$D^{(JJ)}_{M,-N}(\Omega) = (-1)^{J-N}(2J+1)^{\frac{1}{2}}\,\mathcal{D}^J_{MN}(\Omega)^*.$$

If, now, the annihilation tensor a is applied to $|I\rangle$, only those components $(D^{(22)}a^{(20)})^{(02)}_{01}$ or $(D^{(22)}a^{(20)})^{(02)}_{0,-2}$ in the rotated frame give a residue when they act on $|\Phi\rangle_\Omega$. In doing so, they introduce as coefficients $D^{(22)}_{\cdot 1}$ or $D^{(22)}_{\cdot,-2}$. When these are contracted with $D^{(66)}_{\cdot,-6}$ in the integrand, the resulting tensors are of the type $D^{(LL)}_{\cdot,-5}$ or $D^{(LL)}_{\cdot,-8}$, which implies that $L \geq 5$. Thus $\langle G|a|I\rangle = 0$, and so the I state defined by Eq.(3) is identical to I_2.

The second I state that the method of Pursey and Williams provides comes from the intrinsic state $(a_1^\dagger)^{2n+1}(a_{-2}^\dagger)^{n-1}|0\rangle$. There is no point in developing the state in detail, since it is not orthogonal to $|I_2\rangle$. However, it is worth noting that the overlap is very small: for w=6 it amounts to only $(6845/1064993)^{\frac{1}{2}}$.

6. GENERALIZED SENIORITY

For spinless bosons, seniority adds no information above that provided by the irreducible representations of O(5). However, the method of generating states of equal seniority by successive application of the scalar operator $(a^\dagger a^\dagger)^{(0)}$ suggests a possible generalization. An obvious candidate for the new scalar operator is $(a^\dagger a^\dagger a^\dagger)^{(0)}$, that is, the operator that creates the S state of d^3. For not only is it the most elementary extension of $(a^\dagger a^\dagger)^{(0)}$, but it connects states of common L in representations (w0) of O(5) for which the low-L structure is identical.

In fact, $(a^\dagger a^\dagger a^\dagger)^{(0)}$ is equivalent to one of the four operators that Sharp and Lam[12] introduced to distinguish multiply-occurring L values in the representations (w0) of O(5). The others are $a_2^\dagger$, $(a^\dagger a^\dagger)_2^{(2)}$, and $(a^\dagger a^\dagger a^\dagger)_3^{(3)}$. Sharp and Lam's idea is to form stretched products of these operators, subject to the condition that $(a^\dagger a^\dagger a^\dagger)_3^{(3)}$ occurs at most once. For example, the $M_L=6$ state of (60) can be formed in two ways, namely

$$(a^\dagger a^\dagger)_2^{(2)}(a^\dagger a^\dagger)_2^{(2)}(a^\dagger a^\dagger)_2^{(2)}|0\rangle, \tag{4}$$

$$(a^\dagger a^\dagger a^\dagger)^{(0)}a_2^\dagger\, a_2^\dagger\, a_2^\dagger\,|0\rangle, \tag{5}$$

and this indicates that an I state occurs twice. If we write (5) in the form

$$(a^\dagger a^\dagger a^\dagger)^{(0)}|d^3\ I\rangle, \tag{6}$$

we see that it represents an I state that has been constructed by precisely the method that we have in mind.

Of course, the actual states (4), (5), and (6) contain not only the stretched components, but others as well. For example,

(6) contains components of (40)I as well as those of (60)I. When the former are projected out, it is found, rather unexpectedly perhaps, that the I state of (60) is identical to I_1. To see why this should be so, the 3-particle cfp $(I_i\{|\, I_j, (30)S)$ are required (where i, j = 1, 2). They can be calculated by combining products of single-particle cfp. A detailed analysis reveals that

$$(I_2\{|\, I_1, (30)S) = 0. \tag{7}$$

There is thus no way to form an I_2 state by adding the phonon triad $(a^\dagger a^\dagger a^\dagger)^{(0)}$ to an I_1 state. This shows that a string of I_1 states can be formed by writing $[(a^\dagger a^\dagger a^\dagger)^{(0)}]^p\,|\,d^3\ I_1\rangle$ and projecting out all states that do not belong to the irreducible representation (3p+3, 0) of O(5).

If $(I_1\{|\, I_2, (30)S)$ were zero, similar statements could be made about the I_2 states. This cfp does not, however, vanish; but a number of remarkable cancellations lead to its being exceptionally small. In fact,

$$\mathrm{Lt}_{u\to\infty}\ (I_1\{|\, I_2, (30)S)/(I_2\{|\, I_2, (30)S) = 8u^{-3}(385)^{\frac{1}{2}}. \tag{8}$$

So a string of I_2 states could be formed in an analogous way in the limit of large u (or w).

7. DIAGONALIZING A SCALAR OPERATOR

A common method used by physicists to resolve multiplicity difficulties is to separate the states by requiring that they be the eigenfunctions of some convenient operator -- perhaps one of physical interest. The operator must be a scalar in O(3) so as not to mix different L values. To be effective it cannot be scalar in O(5); nor can it transform according to (22) of O(5), since an operator of this

type can be constructed from Casimir's operator for O(5) and L^2. The most elementary operator appears to be the three-body operator

$$T = (a^\dagger a^\dagger a^\dagger)^{(0)}(aaa)^{(0)}.$$

By diagonalizing this operator within the I states of (60) we obtain again the orthogonal pair I_1 and I_2; and Eqs.(7) and (8) show that the $(I_1 I_2)$ separation is also obtained when T is diagonalized within the I states of (w0) in the limit $w \to \infty$. In general, however, we must content ourselves with irrational eigenvalues.

Communications from Dr. M. C. M. O'Brien and Professor R. T. Sharp proved very helpful in the work reported here.

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