$H \otimes h$: A Jahn-Teller Coupling That Really Does Reduce the Degeneracy of the Ground State

C. P. Moate,[1] M. C. M. O'Brien,[2] J. L. Dunn,[1] C. A. Bates,[1] Y. M. Liu,[1] and V. Z. Polinger[1,3]
[1]*Physics Department, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom*
[2]*Sub-Department of Theoretical Physics, 1 Keble Road, Oxford OX1 3NP, United Kingdom*
[3]*MSC Division, BYU-Hawaii Campus, Laie, Hawaii 96762-1294*

(Received 12 July 1996)

In all linear Jahn-Teller (JT) systems studied to date, the ground state, after allowing for the vibronic interaction, has always been of the same symmetry as the original electronic state. Furthermore, the ground state remains the same symmetry for all coupling strengths. We now report results for the $H \otimes h$ JT system (as occurs in various states of the C_{60} molecule) where this is not the case. There are two possible types of JT effects in this system, depending upon whether D_{3d} or D_{5d} extrema are absolute minima. For the case of D_{3d} minima, we find that for couplings above a certain value the ground state is an A-type singlet, rather than the expected H-type quintet. [S0031-9007(96)01520-7]

PACS numbers: 61.48.+c, 71.20.Tx

In their 1937 paper [1] introducing what is now called the Jahn-Teller (JT) effect, Jahn and Teller discussed the stability of molecules with degenerate electronic states, and concluded that "*stability and degeneracy are not possible simultaneously unless the molecule is a linear one*." They pointed out that distorted configurations of a molecule can be expected to exist and be more stable than the original symmetrical configuration. Thus the electronic degeneracy is removed or reduced from that of the original degenerate electronic state. It was Van Vleck [2] in 1939, referring to a case of threefold electronic degeneracy, who pointed out explicitly that "…*when the Jahn-Teller effect "rescues" the atom from a degenerate trigonal state, it is only the instantaneous field that is of less than trigonal symmetry. …there are always three possible directions of distortion from trigonal symmetry which are on a par. Because of the "tunnel" effect there is bound to be resonance through the different equivalent configurations.*"

Over the years since then, the effect of this tunneling has been followed in many different symmetries and degeneracies. So far, the degeneracy of the ground state at strong linear coupling after tunneling has been taken into account has always turned out to be the same as that of the original electronic state [3]. It is also the case that wherever the degeneracy of the ground state has been followed through from weak to strong coupling it remains the same throughout; there is no crossover of eigenstates as the coupling strength changes. Now, however, we can report results for the $H \otimes h$ JT system where this is different.

The $H \otimes h$ JT effect can occur in a molecule whose overall symmetry is icosahedral (I_h), such as the fullerene C_{60}. The fivefold representation H is the largest irreducible representation among the molecular point groups. It is peculiar in not being simply reducible; the symmetric part of the Kroneker square $H \otimes H$ contains H twice. There are thus two independent sets of Clebsch-Gordan (CG) coefficients which describe the coupling of h-type vibrations to an H-type electronic state. However, it is not possible to define the two sets uniquely.

Earlier attempts at solving the $H \otimes h$ problem have used a particular choice of CG matrices which leads to a Hamiltonian of SO(3) symmetry [4] and thus to a minimal trough on the energy surface. When a more general choice of CG matrices is taken [5], it is found that there are minimal points of D_{3d} and D_{5d} symmetry. These points lie on the trough found in the earlier work. We will follow the choice of matrices used in Ref. [5], and label the two corresponding coupling coefficients V_1 and V_2. With this choice, the positions of the D_{5d} minima are found to be independent of V_1, and the positions of the D_{3d} minima are independent of V_2. There are also D_{2h} extrema, but they can never be absolute minima. In this Letter, we will consider the D_{3d} minima only, so we will not consider the V_2 coupling.

Only the static JT problem has been solved previously in the $H \otimes h$ system for the case of distinct minima. In this paper, the dynamic JT problem will be solved by allowing tunneling between the D_{3d} minima. We find that the ground state at strong coupling is a singlet, and not the quintet that experience leads us to expect. Along the line from weak to strong coupling, there is a crossover of the ground states.

The interaction Hamiltonian for $H \otimes h$, when coupling to the V_1 mode only is considered, can be written in terms of the CG coefficients given in Fowler and Ceulemans [6]. Their coordinate system has its z axis along a twofold axis, and is consistent with that used in Ref. [7]. The h modes, which are linear combinations of the hydrogenlike d orbitals, are labeled θ, ϵ, 4, 5, and 6. The result in matrix form is

$$H_{\text{int}} = \frac{V_1}{\sqrt{24}} \begin{bmatrix} 3Q_\theta & -3Q_\epsilon & -Q_4 & -Q_5 & 2Q_6 \\ -3Q_\epsilon & -3Q_\theta & \sqrt{3}\,Q_4 & -\sqrt{3}\,Q_5 & 0 \\ -Q_4 & \sqrt{3}\,Q_4 & -Q_\theta + \sqrt{3}\,Q_\epsilon & -2\sqrt{2}\,Q_6 & -2\sqrt{2}\,Q_5 \\ -Q_5 & -\sqrt{3}\,Q_5 & -2\sqrt{2}\,Q_6 & -Q_\theta - \sqrt{3}\,Q_\epsilon & -2\sqrt{2}\,Q_4 \\ 2Q_6 & 0 & -2\sqrt{2}\,Q_5 & -2\sqrt{2}\,Q_4 & 2Q_\theta \end{bmatrix}. \tag{1}$$

The vibrational part of the Hamiltonian is written in the usual form

$$H_{\text{vib}} = \frac{1}{2} \sum_i \left[\frac{P_i^2}{\mu} + \mu\omega^2 Q_i^2 \right], \tag{2}$$

where μ is the nuclear mass. Quadratic coupling and higher order terms in the Hamiltonian will be neglected, so that the total Hamiltonian is $H = H_{\text{int}} + H_{\text{vib}}$.

Following the method of Bates, Dunn, and Sigmund [8], a unitary transformation of the form

$$U = \exp\left[i \sum_j \alpha_j P_j \right] \tag{3}$$

can be applied to the Hamiltonian to translate the coordinates Q_j to positions $(Q_j - \alpha_j \hbar)$. The transformed Hamiltonian $\tilde{H} = U^{-1} H U$ may then be split into two parts: $\tilde{H}_1$ which depends only on the parameters α_j, and $\tilde{H}_2$ which contains the operators P_j and Q_j. As all the terms in $\tilde{H}_2$ contain phonon operators, $\tilde{H}_1$ is a good Hamiltonian for determining the ground states of the system in strong coupling. It may be obtained by replacing each Q_j by $-\alpha_j \hbar$ in the untransformed Hamiltonian and neglecting the term in P_j. The values of α_j are fixed by minimizing the energy of the system.

The easiest method of diagonalizing $\tilde{H}_1$ is that of Öpik and Pryce [9], applied in the transformed space. The resulting calculation is then very similar to that carried out previously by Ceulemans and Fowler [5]. The electronic states for the D_{3d} wells are summarized in Table I. Their energy is

$$E = -\frac{2}{9} \frac{K_1^2}{\hbar\omega} \quad \text{where } K_1^2 = \frac{V_1^2 \hbar}{\mu\omega}. \tag{4}$$

TABLE I. Electronic eigenstates for D_{3d} minima.

Label	Electronic state
a	$\frac{1}{\sqrt{3}}(0, 0, 1, 1, 1)$
b	$\frac{1}{\sqrt{3}}(0, 0, 1, -1, -1)$
c	$\frac{1}{\sqrt{3}}(0, 0, -1, 1, -1)$
d	$\frac{1}{\sqrt{3}}(0, 0, -1, -1, 1)$
e	$\frac{1}{\sqrt{6}}(1, -\sqrt{3}, \sqrt{2}, 0, 0)$
f	$\frac{1}{\sqrt{6}}(1, -\sqrt{3}, -\sqrt{2}, 0, 0)$
g	$\frac{1}{\sqrt{6}}(1, \sqrt{3}, 0, \sqrt{2}, 0)$
h	$\frac{1}{\sqrt{6}}(1, \sqrt{3}, 0, -\sqrt{2}, 0)$
i	$\frac{1}{\sqrt{3}}(-\sqrt{2}, 0, 0, 0, -1)$
j	$\frac{1}{\sqrt{3}}(-\sqrt{2}, 0, 0, 0, 1)$

The ground states of the transformed Hamiltonian may be transformed back to the original space by multiplying them by the value of U after substitution of the appropriate α_j's. These untransformed states will be denoted by x''. They are automatically vibronic as the U's contain phonon operators.

In infinite coupling, the system is localized in one of the (infinitely deep) minima so that the vibronic states so far obtained are eigenstates of the system. However, for finite coupling strengths, tunneling will occur and the correct states will be linear combinations of these states. Projection operator techniques can be used to determine the required linear combinations [10]. This results in vibronic states of *H*, *G*, and *A* symmetries. It is only necessary to know one component of each state in order to determine the energies of the vibronic mulitplets. We may use

$$|H_\theta^{3d}\rangle = \frac{1}{2\sqrt{3}} N_H^{3d} [e'' + f'' + g'' + h'' - 2i'' - 2j''],$$

$$|G_x^{3d}\rangle = \frac{1}{2\sqrt{3}} N_G^{3d} [a'' + b'' - c'' - d'' - 2e'' + 2f''],$$

and

$$|A_a^{3d}\rangle = \frac{1}{\sqrt{10}} N_A^{3d} \left[\sum_x x'' \right] (x = a \text{ to } j), \tag{5}$$

where the N_Γ^{3d} are normalization constants. The required energies can be found after the normalization factors and matrix elements of H between the untransformed states have been evaluated [11]. The matrix element of H between any well and itself is found to be

$$H_{aa} = \frac{5}{2}\hbar\omega - \frac{2}{9}\frac{K_1^2}{\hbar\omega}. \tag{6}$$

All of the matrix elements between different wells can be expressed in terms of the matrix elements between wells *a* and *b* and between wells *a* and *e*, namely,

$$\begin{aligned} H_{ab} &= S_{ab}\left(\frac{5}{2}\hbar\omega - \frac{14}{27}\frac{K_1^2}{\hbar\omega} \right), \\ H_{ae} &= S_{ae}\left(\frac{5}{2}\hbar\omega - \frac{10}{27}\frac{K_1^2}{\hbar\omega} \right), \end{aligned} \tag{7}$$

respectively, where S_{ab} and S_{ae} are the corresponding overlaps, given by

$$\begin{aligned} S_{ab} &= -\frac{1}{3} \exp\left[-\frac{8}{27} \left(\frac{K_1}{\hbar\omega} \right)^2 \right], \\ S_{ae} &= \frac{1}{3} \exp\left[-\frac{4}{27} \left(\frac{K_1}{\hbar\omega} \right)^2 \right]. \end{aligned} \tag{8}$$

These result in energies for the H, G, and A states of

$$\begin{aligned} E_H &= \frac{H_{aa} - 2H_{ab} + H_{ae}}{1 - 2S_{ab} + S_{ae}}, \\ E_G &= \frac{H_{aa} + H_{ab} - 2H_{ae}}{1 + S_{ab} - 2S_{ae}}, \\ E_A &= \frac{H_{aa} + 6H_{ab} + 3H_{ae}}{1 + 6S_{ab} + 3S_{ae}}. \end{aligned} \tag{9}$$

Figure 1 shows a plot of the two possible inversion splittings, $E_A - E_H$ and $E_G - E_H$, as a function of $K_1/\hbar\omega$. It is found that the A and H states become degenerate when $K_1/\hbar\omega = \frac{3}{2}\sqrt{-3\ln(3/\sqrt{2} - 2)} \approx 3.77$ and that the A state will be lowest in energy for all couplings stronger than this. This means that the inclusion of the JT effect has changed the ground state of the system from a quintet electronic state to a singlet vibronic state. We have also performed the above calculations including anisotropy (via a scale transformation) and obtain this same result.

It is possible to look at the appearance of a singlet ground state from another point of view. In the adiabatic approximation at strong coupling, the wave functions can be written as products of an electronic part and a vibrational part, $\Psi(\mathbf{r}, \mathbf{Q}) = \psi_{\text{el}}(\mathbf{r}, \mathbf{Q})\Phi(\mathbf{Q})$. The normal coordinates $\mathbf{Q}$ appear as parameters in the electronic states $\psi_{\text{el}}(\mathbf{r}, \mathbf{Q})$, and $\Phi(\mathbf{Q})$ carries the variation of Ψ in coordinate space. As above, the ground states in finite coupling must be linear combinations of these states. The correct symmetry adapted forms must take into account the phase changes of ψ_{el}—the Berry phase—as well as of the transformation properties of the $\Phi(\mathbf{Q})$. We will show that, in the case considered here, there is no Berry phase change, and so verify that the symmetry adapted states obtained in Eq. (5) with $S_{ae} > 0$ and $S_{ab} \approx 0$ must be valid in the strong coupling limit. The state with lowest energy is that with maximum overlap, which is then clearly the singlet state.

The phase of ψ_{el} was tracked numerically using the technique described by Cullerne and O'Brien [12]. A parametrization of the coordinate space is used that maps the minimal points onto a spherical subspace. The trigonal D_{3d} points are mapped onto the vertices of a dodecahedron and the pentagonal D_{5d} points are mapped onto the centers of the faces of the dodecahedron. We note that the mapping puts each point onto the sphere twice. The duplicated points are related by inversion. The D_{3d} points that are nearest neighbors on the sphere are also nearest neighbors in the whole configuration space. Close to the center of the edge between every pair is one of the D_{2h} saddle points.

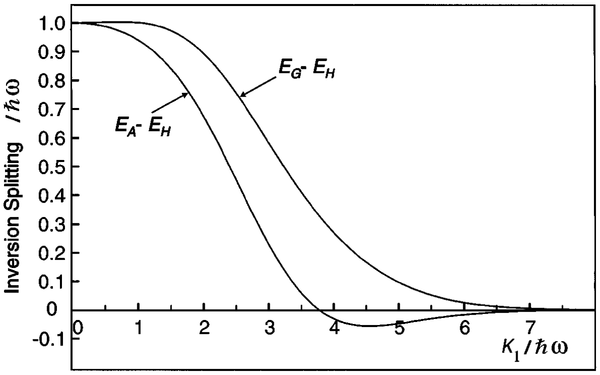

FIG. 1. Inversion splitting vs $K_1/\hbar\omega$ for D_{3d} minima.

The phase tracking was done along the lines on the surface of the sphere that join nearest neighbor wells. We found that there is no phase change around a pentagonal closed path made up of such lines. Hence there is no electronic phase change around any closed path through nearest neighbor wells made up of such lines. Consequently, the phase change between any pair of nearest neighbor wells must be zero. It is this absence of any phase change that gives rise to the singlet ground state. The absence of a phase change in this case is surprising. For convenience in discussing this apparent anomaly, we rewrite the matrix H_{int} (1) in terms of a coordinate system with the z axis along a D_{5d} direction, giving

$$H'_{\text{int}} \propto \begin{bmatrix} 0 & -\sqrt{3}\,q_2 & \sqrt{3}\,q_3 & \sqrt{3}\,q_4 & -\sqrt{3}\,q_5 \\ -\sqrt{3}\,q_2 & -\sqrt{3}\,q_1 - q_4 & -q_3 - q_5 & -q_2 + q_4 & -q_3 \\ \sqrt{3}\,q_3 & -q_3 - q_5 & \sqrt{3}\,q_1 - q_2 & -q_5 & -q_2 - q_4 \\ \sqrt{3}\,q_4 & -q_2 + q_4 & -q_5 & \sqrt{3}\,q_1 + q_2 & -q_3 + q_5 \\ -\sqrt{3}\,q_5 & -q_3 & -q_2 - q_4 & -q_3 + q_5 & -\sqrt{3}\,q_1 + q_4 \end{bmatrix}, \tag{10}$$

where the components of the h mode and the H electronic bases for H'_{int} are parametrized in terms of spherical polar coordinates using the relations

$$\begin{aligned} q_1 &= \tfrac{1}{2}(2z^2 - x^2 - y^2) = \tfrac{1}{2}(3\cos^2\theta - 1), \\ q_2 &= \sqrt{3}\,xz = \tfrac{1}{2}\sqrt{3}\sin 2\theta\cos\phi, \\ q_3 &= \sqrt{3}\,xy = \tfrac{1}{2}\sqrt{3}\sin^2\theta\sin 2\phi, \\ q_4 &= \tfrac{1}{2}\sqrt{3}(x^2 - y^2) = \tfrac{1}{2}\sqrt{3}\sin^2\theta\cos 2\phi, \\ q_5 &= \sqrt{3}\,yz = \tfrac{1}{2}\sqrt{3}\sin 2\theta\sin\phi. \end{aligned} \tag{11}$$

This also gives the values of the q_i on the spherical surface.

Berry's analysis [13] shows explicitly that for a degeneracy of the type shown in (12) there is a phase change of π as the electronic state is taken round any closed path encircling the degeneracy. Ham [14] noted the connection between this phase change and the appearance of a degeneracy in the ground state of the $E \otimes e$ JT system. We must ask why it is that a phase change is not found in the case considered here. To examine this, we look at H'_{int} (10). One D_{5d} point is at $\theta = 0$, where only q_1 is nonzero. The lowest roots near $\theta = 0$ correspond to the second and fifth electronic bases, and the linear interaction between these bases near the point can be extracted from H'_{int} in the form

$$M^{(1)} = \begin{bmatrix} -q_4 & -q_3 \\ -q_3 & -q_4 \end{bmatrix}, \qquad (12)$$

where a diagonal term $-\sqrt{3}\,q_1$ has been subtracted. This matrix is in the standard form for a conical, $E \otimes e$ type degeneracy, where the e modes are the pair $\{q_3, q_4\}$. It will induce a phase change of π on going round a circle that encloses the origin in $\{q_3, q_4\}$ space. The other pair of modes $\{q_2, q_5\}$, only appear in this interaction to second order. These second order terms can be found by perturbation within H'_{int} and this part of the interaction can be written, after subtracting $-2(q_2^2 + q_5^2)$ from the diagonal, as

$$M^{(2)} = \begin{bmatrix} -\frac{3}{2}(q_2^2 - q_5^2) & -3q_2q_5 \\ -3q_2q_5 & \frac{3}{2}(q_2^2 - q_5^2) \end{bmatrix}. \qquad (13)$$

$M^{(2)}$ is in the same form as a second order $E \otimes e^2$ JT interaction, with the e modes now represented by the $\{q_2, q_5\}$ pair.

We can understand the form of $M^{(1)}$ and $M^{(2)}$ in terms of the reduction of symmetry from I_h to D_{5d}. This reduction splits an H representation in I_h into $A_1 \oplus E_1 \oplus E_2$ representations of D_{5d}. Now in D_{5d} the product $E_1 \otimes E_1$ contains E_2 but not E_1, while $E_2 \otimes E_2$ contains E_1 but not E_2. As a result, it is possible to have $E_1 \otimes e_2$ and $E_2 \otimes e_1$ linear JT systems. Furthermore, the quadratic JT systems are $E_1 \otimes e_1^2$ and $E_2 \otimes e_2^2$. If the bases for $M^{(1)}$ and $M^{(2)}$ (i.e., the bases 2 and 5 of H'_{int}) span E_1 then $M^{(1)}$ corresponds to $E_1 \otimes e_2$ and $M^{(2)}$ to $E_1 \otimes e_1^2$. Similar results can be obtained for E_2.

The differing effects of $M^{(1)}$ and $M^{(2)}$ can be seen by following the usual treatment of the $E \otimes e$ case and putting $q_4 = q_0 \cos\alpha$, $q_3 = q_0 \sin\alpha$ so that

$$M^{(1)} = q_0 \begin{bmatrix} -\cos\alpha & -\sin\alpha \\ -\sin\alpha & +\cos\alpha \end{bmatrix}, \qquad (14)$$

which has eigenstates depending on $\alpha/2$ that produce the phase change. Putting $q_2 = q_0 \cos\alpha$, $q_5 = q_0 \sin\alpha$ gives

$$M^{(2)} = \frac{3}{2} q_0^2 \begin{bmatrix} -\cos 2\alpha & -\sin 2\alpha \\ -\sin 2\alpha & +\cos 2\alpha \end{bmatrix}, \qquad (15)$$

with eigenstates in α, and hence no phase change.

The path around the edges of the pentagon can be transformed continuously and without crossing any degeneracy into a path that goes tightly around the degeneracy at $\theta = 0$ on the spherical surface. At the $\theta = 0$ point, the spherical surface is tangential to the $\{q_2, q_5\}$ plane, and orthogonal to the $\{q_3, q_4\}$ plane. As we have seen, a path in the $\{q_2, q_5\}$ plane induces no phase change. Consequently, it is reasonable that no phase change is induced by traversing the pentagonal path.

In summary, we have found that the JT effect can change the symmetry of the ground state of the $H \otimes h$ JT system. This has never been seen before in any other JT system, and indeed it has been generally assumed (although no proof has been given) that JT effects cannot alter the symmetry of the ground state [3]. This change in symmetry has important consequences for the theory of vibronic reduction factors, which assumes no change in symmetry. Although there is no problem with reduction factors as defined for previous JT systems, a new concept must be used for the $H \otimes h$ system. This may have important consequences for the study of all icosahedral systems, including C_{60} molecules and Si_{13} clusters.

[1] H. A. Jahn and E. Teller, Proc. R. Soc. **161**, A220–A235 (1937).

[2] J. H. Van Vleck, J. Chem. Phys. **7**, 32–42 (1939).

[3] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer, Berlin, 1989), pp. 195–196.

[4] V. P. Khoplin, V. Z. Polinger, and I. B. Bersuker, Theor. Chim. Acta **48**, 87–101 (1987).

[5] A. Ceulemans and P. W. Fowler, J. Chem. Phys. **93**, 1221–1234 (1990).

[6] P. W. Fowler and A. Ceulemans, Mol. Phys. **54**, 767–785 (1985).

[7] J. L. Dunn and C. A. Bates, Phys. Rev. B **52**, 5996–6005 (1995).

[8] C. A. Bates, J. L. Dunn, and E. Sigmund, J. Phys. C **20**, 1965–83 (1987).

[9] U. Öpik and M. H. L. Pryce, Proc. R. Soc. London A **238**, 425 (1957).

[10] L. D. Hallam, C. A. Bates, and J. L. Dunn, J. Phys. Condens. Matter **4**, 6775–6796 (1992).

[11] J. L. Dunn, J. Phys. C **21**, 383–399 (1988).

[12] J. P. Cullerne and M. C. M. O'Brien, J. Phys. Condens. Matter **6**, 9017–9041 (1994).

[13] M. V. Berry, Proc. R. Soc. London A **392**, 45–57 (1984).

[14] F. S. Ham, Phys. Rev. Lett. **58**, 725–728 (1987).