Berry's Geometrical Phase and the Sequence of States in the Jahn-Teller Effect

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A proof is given for the Jahn-Teller problem of an orbital doublet ($E \otimes \varepsilon$) that the order of the lowest vibronic levels is fixed by the requirement that the vibrational part of the wave function change sign under 2π rotation in the vibrational coordinates. This sign change in turn is a consequence of the sign change in the electronic part of the wave function, a special case of Berry's geometrical phase. Experimental confirmation of this sign change and thus of Berry's phase is available from studies of Jahn-Teller defects in crystals that reveal the sequence of these lowest levels.

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An unusual aspect of the theory of the Jahn-Teller (JT) effect for an orbital doublet ($E \otimes \varepsilon$ problem) is the sign change[1-3] in the electronic wave functions that diagonalize the linear JT coupling, under a 2π rotation in the space of the vibrational coordinates. Correspondingly, the symmetry group of the linearly coupled JT system under rotations is isomorphic to the double group of two-dimensional rotations,[4] and eigenstates of the system are eigenstates of an effective spin[1,4,5] J corresponding to eigenvalues $J = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \ldots$. This sign change is a special case of Berry's geometrical phase,[6] which is acquired by a quantum system carried adiabatically around a circuit in an appropriate parameter space and which holds implications for topics in physics as diverse as the quantum Hall effect,[7] the optical activity of a helical optical fiber,[8] molecular dynamics,[9,10] and gauge field theories.[11]

The total wave function of a vibronic eigenstate of a JT system of course must be single valued in the space of the vibrational coordinates, and a sign change in the electronic wave function forces a compensating sign change in the vibrational part.[1,3] I show in this paper that a critical experimental test for this sign change, for a molecule or crystal defect exhibiting strong JT coupling, is the order of the lowest vibronic states of the system, specifically that the ground state is an E doublet below the A tunneling singlet. Although a vibronic doublet ground state has long been recognized as characteristic of a dynamic JT effect for an electronic E state,[3,12,13] a mathematical proof showing that this ordering is a necessary consequence of the sign-change requirement imposed on the vibrational wave function has not previously been given. Experimentally, the E state has been found to be below the A state for all those defects in crystals,[14-23] studied by electron paramagnetic resonance (EPR), optical spectroscopy, or phonon spectroscopy over the past two decades, which exhibit an $E \otimes \varepsilon$ JT effect and for which the tunneling splitting could be identified. The significance of my result is that this sequence of the lowest E and A states alone provides experimental confirmation of the sign change and thus of Berry's phase for many well-known defect systems. It is therefore not necessary in these systems to resolve higher vibronic levels in order to confirm Berry's phase, as Delacrétaz *et al.*[9] have recently done in an elegant study identifying rotational structure going as Aj^2 with half-odd-integer quantization in the two-photon ionization spectrum of the molecular cluster Na_3.

In the $E \otimes \varepsilon$ JT problem[1,12,13] we are concerned with an orbital doublet electronic state belonging to the representation E of the cubic group (or T_d), coupled to a pair of vibrational modes Q_θ, Q_ε also belonging to E (or the equivalent problem in any other symmetry with a threefold or sixfold axis). The vibronic Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}_0 \mathcal{I} + \mathcal{H}_{\mathrm{LJT}} + \mathcal{H}_{\mathrm{NL}}, \tag{1}$$

with

$$\mathcal{H}_0 = (2\mu)^{-1}(P_\theta^2 + P_\varepsilon^2) + (K/2)(Q_\theta^2 + Q_\varepsilon^2) \tag{2}$$

the Hamiltonian of an isotropic two-dimensional harmonic oscillator and

$$\mathcal{H}_{\mathrm{LJT}} = V(Q_\theta U_\theta + Q_\varepsilon U_\varepsilon) \tag{3}$$

the linear JT coupling in a conventional notation,[13,24] in which

$$\begin{aligned} U_\theta &= -\,|\theta\rangle\langle\theta| + |\varepsilon\rangle\langle\varepsilon|, \\ U_\varepsilon &= +\,|\theta\rangle\langle\varepsilon| + |\varepsilon\rangle\langle\theta|, \end{aligned} \tag{4}$$

and $\mathcal{I}$ is the identity operator, in the basis of the electronic E states $\psi_\theta \sim (3z^2 - r^2)$, $\psi_\varepsilon \sim \sqrt{3}(x^2 - y^2)$. The term $\mathcal{H}_{\mathrm{NL}}$ in Eq. (1) represents nonlinear coupling. Longuet-Higgins *et al.*[1] and Moffitt and Thorson[25] have shown that when $\mathcal{H}_{\mathrm{NL}}$ is zero the vibronic ground state for any coupling strength is an E doublet and the first excited state is a doublet comprising states A_1 and A_2. Introducing the nonlinear coupling, O'Brien[3] and others[26,27] have shown from numerical analysis of the limit of strong JT coupling that for a simple form of $\mathcal{H}_{\mathrm{NL}}$ the E state remains lowest but that the accidental degeneracy of the A_1 and A_2 states is lifted, the lower of these approaching the E ground state as the "warping" in the effective potential increases. We will give a mathematical proof for this sequence of the lowest states under the condition of strong linear JT coupling, for nonlinear coupling assumed to be much weaker but of arbitrary form.

The electronic eigenstates of $\mathcal{H}_{\rm LJT}$ for a fixed choice $Q_\theta = \rho\cos\theta$, $Q_\varepsilon = \rho\sin\theta$ of the vibrational amplitudes are[3]

$$\begin{aligned} \psi_- &= \psi_\theta\cos(\theta/2) - \psi_\varepsilon\sin(\theta/2), \\ \psi_+ &= \psi_\theta\sin(\theta/2) + \psi_\varepsilon\cos(\theta/2). \end{aligned} \tag{5}$$

If the linear coupling is strong, so that the JT energy E_{JT} is larger than the vibrational quantum $\hbar\omega$, and also strong compared to the nonlinear terms, vibronic states with energies near the minimum at $\rho = \rho_0 = |V|/K$ in the lower adiabatic potential energy surface resulting from the linear coupling may be taken as Born-Oppenheimer products involving either ψ_- or ψ_+, whichever gives the lower eigenvalue of $\mathcal{H}_{\rm LJT}$ (ψ_- if $V > 0$), and a vibrational factor ϕ which in its dependence on θ must satisfy the angular Schrödinger equation[3]

$$-\alpha(d^2\phi/d\theta^2) + V(\theta)\phi = E_n\phi, \tag{6}$$

with

$$\alpha = \hbar^2/2\mu\rho_0^2 \tag{7}$$

and $V(\theta)$ the effective angular potential energy around the trough at $\rho = \rho_0$. $V(\theta)$ depends on θ because of the nonlinear coupling but is periodic with period $2\pi/3$,

$$V(\theta + 2\pi/3) = V(\theta), \tag{8}$$

and even,

$$V(-\theta) = V(\theta), \tag{9}$$

because of the cubic symmetry. For the coupling considered by O'Brien[3] and others[26,27] $V(\theta)$ is given simply by $-\beta\cos3\theta$. Because the electronic factor ψ_- or ψ_+ in the Born-Oppenheimer wave function changes sign under a 2π rotation, ϕ must do the same,

$$\phi(\theta + 2\pi) = -\phi(\theta), \tag{10}$$

in order that the full vibronic wave function be single valued.

To determine the ordering of the solutions of Eq. (6) I make use of the theory of one-dimensional energy bands, since the effective potential $V(\theta)$ is periodic with period $2\pi/3$ according to Eq. (8). The theorem of Floquet[28] then tells us that Eq. (6) has solutions having the Bloch form[29]

$$\phi_k(\theta) = \exp(ik\theta)u(\theta), \tag{11}$$

with the parameter k real for certain ranges of the energy representing the allowed energy bands and $u(\theta)$ a periodic function with the same period $2\pi/3$ as that of $V(\theta)$. For these stable solutions the wave number k lies within the reduced zone, $-\frac{3}{2} \le k \le +\frac{3}{2}$, solutions at $k = -\frac{3}{2}$ and $k = +\frac{3}{2}$ being equivalent. Since $V(\theta)$ is real, solutions of $+k$ and $-k$ occur in pairs at the same energy and thus are independent solutions of Eq. (6) except at $k = 0$ and $\frac{3}{2}$, the only values for which $+k$ and $-k$ are not distinct.

The condition imposed by Eq. (10) requires a change of sign over three periods of the potential $V(\theta)$, so that suitable solutions of Eq. (6) are provided by the Bloch functions[30,31] of Eq. (11) with $k = \pm\frac{1}{2}$ and $k = \frac{3}{2}$. The former represent degenerate pairs of states $\phi_{+1/2}\psi_-$ and $\phi_{-1/2}\psi_-$ (or $\phi_{+1/2}\psi_+$ and $\phi_{-1/2}\psi_+$) which are easily shown[32] to belong to the representation E of the cubic group, while the latter represent nondegenerate states belonging to A_1 or A_2.

We now appeal to Haupt's theorem[28,33] from the theory of ordinary second-order differential equations with periodic coefficients. Let us denote by $E_n(k)$ the energy eigenvalues of Eq. (6) corresponding to Bloch functions of wave number k, with $n = 1,2,3,\ldots$ labeling energy bands in order of increasing energy starting with the lowest. According to Haupt's theorem the nth allowed band is bounded by $E_n(0)$ and by $E_n(\frac{3}{2})$, with $E_n(0)$ the lower bound if n is odd and the upper bound if n is even; moreover these eigenvalues must be ordered as follows:

$$\begin{aligned} E_1(0) < E_1(\tfrac{3}{2}) \le E_2(\tfrac{3}{2}) < E_2(0) \le E_3(0) < E_3(\tfrac{3}{2}) \\ \le E_4(\tfrac{3}{2}) < E_4(0) \le E_5(0) < \ldots, \end{aligned} \tag{12}$$

for any form of periodic potential $V(\theta)$ satisfying Eq. (8). Since $E_n(k)$ in a one-dimensional band is necessarily a continuous function of k with extrema only at $k = 0$ and $\frac{3}{2}$,[34] the energy $E_1(\pm\frac{1}{2})$ in the lowest band at $k = \pm\frac{1}{2}$ is necessarily below that at $k = \frac{3}{2}$, $E_1(\frac{3}{2})$. Accordingly the lowest solution of Eq. (6) subject to the condition of Eq. (10) must be an E state, with the next higher state an A_1 or A_2 state.

By contrast, solutions of Eq. (6) satisfying the alternative condition[35]

$$\phi(\theta + 2\pi) = +\phi(\theta) \tag{13}$$

occur for $k = 0$ and $k = \pm1$. By Haupt's theorem the solution $\phi_0(\theta)$ at $k = 0$ in the lowest band has the minimum energy $E_1(0)$ in this band, is nondegenerate, and transforms[32] as A_1. The pair of solutions $\phi_{\pm1}(\theta)$ with $k = \pm1$ thus lies at a higher energy $E_1(\pm1)$ and moreover transforms as E. The sequence of the lowest E and A solutions of Eq. (6) is therefore reversed when the periodicity condition, Eq. (13), is substituted for the sign-change requirement of Eq. (10). This result completes the proof that the order of these lowest states is determined by whether or not the vibrational wave function $\phi(\theta)$ is required to change sign under 2π rotation.

This requirement also fixes the sequence of states of higher energy.[36]

That the ordering of the lowest vibronic states has E below A_1 or A_2 has been recognized experimentally for many impurity ions in crystals that show an $E \otimes \varepsilon$ JT effect, and for none has the reverse order been observed. The first case of such a dynamic JT effect to be investigated by EPR was Cu^{2+} in MgO, first studied by Coffman[14] in 1965, for which a low-temperature spectrum characteristic of an orbital doublet ^2E ground state in cubic symmetry was found.[37-40] Coffman interpreted this spectrum as resulting from tunneling between JT-distorted tetragonal configurations, the singlet state $^2A_{1(2)}$ being at a higher energy given by the tunneling splitting 3Γ. This interpretation has been sustained by further EPR studies by Reynolds *et al.*[17] of the so-called "intermediate JT effect" for Cu^{2+} in MgO that show that the tunneling splitting to the lowest singlet $^2A_2$ is only a little larger than the splitting of the ^2E ground state due to random strains (a few inverse centimeters); however, a precise value for 3Γ has not been obtained. For Cu^{2+} in CaO, however, Reynolds *et al.*[17] were able to determine $3\Gamma \simeq 3$ cm^{-1} in this way, a value confirmed by Raman scattering experiments by Guha and Chase,[18] and identified the excited state as $^2A_1$. Similarly, values $3\Gamma = 3.9$ cm^{-1} ($^2A_2$) for Ag^{2+} in CaO and $3\Gamma \simeq 4.8$ cm^{-1} ($^2A_2$) for Ag^{2+} in MgO have been obtained by Boatner *et al.*[20] Other cases for which EPR spectra of the intermediate JT type have been found and the identity of the excited tunneling singlet established, but no precise value for 3Γ obtained, are listed by Setser, Barksdale, and Estle[19] and in the review of EPR studies of JT systems by Bill.[22]

Three well-established cases in which the tunneling splitting in an excited electronic state has been observed directly in the optical absorption spectrum are Eu^{2+} in SrF_2 and CaF_2[15,16] and Fe^{2+} in MgO.[21] For the first two the transition is $4f^7\,(^8S_{7/2}) \rightarrow 4f^6 5d(^2E)$, and 3Γ is given by 6.5 cm^{-1} and 15 cm^{-1}, respectively, while for the last it is $3d^6(^5T_{2g}) \rightarrow 3d^6(^5E_g)$, $3\Gamma = 14$ cm^{-1}, and the singlet is $^5A_{1g}$. Only the zero-phonon line for the transition to the doublet ground state was observed in unstrained crystals, but the presence of the higher singlet was revealed when applied stress mixed the E and A states.

Other defects which have been interpreted in terms of strong JT coupling in an electronic E state and a significant tunneling splitting with $A_{1(2)}$ above E have been investigated extensively by various techniques of phonon spectroscopy. These include Mn^{3+} and Cr^{2+} in MgO and Al_2O_3 and Ni^{3+} in Al_2O_3. This work has been reviewed by Challis and de Goër.[23]

The rotational structure going as Aj^2 with half-odd-integer quantization in the two-photon ionization spectrum of Na_3 (observed for $|j|$ as high as $\frac{11}{2}$) has been cited by Delacrétaz *et al.*[9] as the first experimental confirmation of the sign-change requirement imposed on the vibrational wave function of an $E \otimes \varepsilon$ JT system. It is clear from the present work that equally compelling experimental evidence of this sign change and thus of Berry's phase is given by the order of the lowest vibronic states and has been accumulating for twenty years in the extensive literature on the dynamic JT effect of defects in crystals.

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[28] A. H. Wilson, *The Theory of Metals* (Cambridge Univ. Press, Cambridge, 1954), 2nd ed., p. 21.

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[30] The only solutions of Eq. (6) that satisfy either Eq. (10) or Eq. (13) are those of Bloch form from the allowed bands. In the forbidden ranges of energy, solutions have the form of Eq. (11) with k pure imaginary, while at energies corresponding to nondegenerate Bloch functions at $k=0$ and $\frac{3}{2}$ which bound the allowed bands, the second solution of Eq. (6) has a more complicated behavior [see H. A. Kramers, Physica (Utrecht) **2**, 483 (1935)] under $2\pi/3$ displacement that also is not compatible with Eq. (10) or Eq. (13).

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[32] For a rotation about a threefold axis corresponding to the substitution $x \rightarrow y \rightarrow z \rightarrow x$, the transformation of Q_θ and Q_ε corresponds to the substitution $\theta \rightarrow (\theta - 2\pi/3)$. Under simultaneous transformation of the electronic functions $\psi_\theta, \psi_\varepsilon$ and of Q_θ, Q_ε we have accordingly $\psi_- \rightarrow -\psi_-$, $\psi_+ \rightarrow -\psi_+$. Similarly the twofold rotation $x \rightarrow y \rightarrow x$, $z \rightarrow -z$ and fourfold rotation $x \rightarrow y \rightarrow -x$, $z \rightarrow z$ take $\theta \rightarrow -\theta$ and $\psi_- \rightarrow +\psi_-$, $\psi_+ \rightarrow -\psi_+$. From character tables we find that the pairs $\phi_{\pm 1/2}\psi_-$ and $\phi_{\pm 1/2}\psi_+$ belong to E, while $\phi_{3/2}\psi_-$ belongs to A_1 and $\phi_{3/2}\psi_+$ to A_2 if $\phi_{3/2}(\theta)$ is an even function of θ, and $\phi_{3/2}\psi_-$ to A_2 and $\phi_{3/2}\psi_+$ to A_1 if $\phi_{3/2}(\theta)$ is odd. Similarly the pair $\phi_{\pm 1}(\theta)$ may be shown to belong to E, while $\phi_0(\theta)$ is A_1 if it is even and A_2 if it is odd. The solution $\phi_0(\theta)$ of lowest energy has no nodes according to Haupt's theorem, and so it must be even.

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[35] Equation (6) with the periodic boundary condition, Eq. (13), would be appropriate, for example, for the problem of a particle tunneling between three equivalent wells on a ring.

[36] Haupt's theorem serves to order all solutions of Eq. (6) that satisfy the sign-change condition of Eq. (10) according to the sequence $E, A_{1\,(2)}, A_{2\,(1)}, E, E, A_{1\,(2)}, A_{2\,(1)}, E, E \ldots$, as is obvious from the sequence of energy bands given by the inequalities (12) (the sequence of each pair of adjacent A_1 and A_2 states is not fixed in general). This is the sequence of rotational levels found when ordered according to increasing $|j| = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ as in the case of linear JT coupling only (see Ref. 1), and found also in the calculation of O'Brien taking account of the nonlinear terms. [It is of interest that this ordering cannot vary in the JT case and in particular that an A level can never cross an E level, no matter what the form of the nonlinear coupling, so long as we have to do with rotational levels which can be viewed as solutions of Eq. (6) for the same level of radial vibration.]

[37] Similar EPR spectra (Refs. 38–40) have been found for Sc^{2+} in CaF_2, SrF_2 BaF_2, and $SrCl_2$ and for Y^{2+} and La^{2+} in $SrCl_2$. However, for these defects the JT coupling has been shown to be too weak (Refs. 39–40), and the excitation energy of the nearest state to the ^2E ground state therefore too large, for the considerations of this paper, which require strong JT coupling, to be appropriate.

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