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Berry's geometric quantum phase and the $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ Jahn–Teller effect

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Abstract. The ground-state wavefunctions of the linear octahedral Jahn–Teller system $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ are shown to exhibit a Berry phase for certain closed circuits in phonon coordinate space. This is shown to result from the coupling between the electronic and phonon parts of the system and from the requirement that the total wavefunction be single-valued. The associated Berry vector potential is also calculated and is interpreted in terms of a flux line.

1. Introduction

The Jahn–Teller effect has long been known to couple phonon and electronic variables in such a way that different parts of the total wavefunction change sign in a coordinated manner so as to preserve single-valuedness under rotations in phonon space (Longuet-Higgins *et al* 1958, Herzberg and Longuet-Higgins 1963, O'Brien 1964). Ham (1987) has recently shown that such behaviour in the $E \otimes \varepsilon$ Jahn–Teller system is an example of Berry's geometrical phase, a phase acquired by a quantum system moving adiabatically around a circuit in a parameter space of the system (Berry 1984). Aitchison (1988) has also discussed the Berry phase of this system in a more general context.

The linear $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ Jahn–Teller system, which couples an electronic triplet state to triply and doubly degenerate phonon modes, has a sign change phenomenon similar to that found in $E \otimes \varepsilon$ (O'Brien 1969). Both systems are, in addition, similar in that each possesses a continuous potential minimum: one dimensional for $E \otimes \varepsilon$ and two dimensional for $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$. The static Jahn–Teller distortion eigenstates, whose energies compose the potential minima, are doubly degenerate over their respective phonon coordinate spaces for both systems. We might well expect, therefore, a non-zero Berry phase in $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$, given the $E \otimes \varepsilon$ example and these similarities.

The experimental evidence for the existence of a Berry phase in the $E \otimes \varepsilon$ system is well documented, as Ham (1987) has emphasised. In particular, the recent study of the Na_3 molecular cluster by Delacrétaz *et al* (1986) has demonstrated that the $\frac{1}{2}$-odd-integral quantum number of the $E \otimes \varepsilon$ pseudorotational energy levels is a consequence of Berry's phase. For $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$, the analogous appearance of an odd-integral quantum number in the rotational energy terms serves notice of a possible Berry phase. In what follows, we hope to outline the role of Berry's phase in the $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ system, thereby providing a new physical example of this interesting quantum phenomenon.

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2. The Hamiltonian

The $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$ Jahn–Teller Hamiltonian for a complex with octahedral symmetry, assuming linear and equal couplings to the τ and ε phonon modes, takes the form (O'Brien 1969, 1971)

$$H = H_0 + H_{\mathrm{JT}} \tag{1a}$$

where

$$H_0 = \frac{-\hbar^2}{2m}\nabla^2 + \tfrac{1}{2}m\omega^2 q^2 \tag{1b}$$

and

$$H_{\mathrm{JT}} = V\begin{bmatrix} \frac{1}{2}q_\theta - \frac{1}{2}\sqrt{3}q_\varepsilon & -\frac{1}{2}\sqrt{3}q_\zeta & -\frac{1}{2}\sqrt{3}q_\eta \\ -\frac{1}{2}\sqrt{3}q_\zeta & \frac{1}{2}q_\theta + \frac{1}{2}\sqrt{3}q_\varepsilon & -\frac{1}{2}\sqrt{3}q_\xi \\ -\frac{1}{2}\sqrt{3}q_\eta & -\frac{1}{2}\sqrt{3}q_\xi & -q_\theta \end{bmatrix}. \tag{1c}$$

The q are the five normal-mode coordinates which describe the nuclear motions, with $q^2 = \Sigma_i q_i^2$, and ∇^2 is the corresponding five-dimensional cartesian Laplacian. H_{JT} thus represents a linear interaction of strength V between the phonon modes and an electronic p state spanned by the states $\{|\xi\rangle, |\eta\rangle, |\zeta\rangle\}$. We note that, because H is real (the system having time-reversal symmetry), the only non-zero Berry phases possible will be $+1$ and -1, the latter being associated with degeneracies (Berry 1984). This special situation occurs in all Jahn–Teller systems, not merely $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$ (for the $E\otimes\varepsilon$ system, see Ham (1987)).

Applying the unitary T transformation of O'Brien (1971) to H_{JT}, and expressing the result in the non-orthogonal angular coordinates $\{Q, \alpha, \varphi, \theta, \gamma\}$ (see, for example, Judd 1984, pp 284–6), we find that

$$TH_{\mathrm{JT}}T^{-1} = VQ\begin{bmatrix} \frac{1}{2}[\cos(\alpha) - \sqrt{3}\sin(\alpha)] & 0 & 0 \\ 0 & \frac{1}{2}[\cos(\alpha)+\sqrt{3}\sin(\alpha)] & 0 \\ 0 & 0 & -\cos(\alpha) \end{bmatrix}. \tag{2}$$

Expressed in these new coordinates, ∇^2 takes the form

$$\frac{1}{Q^4}\frac{\partial}{\partial Q}\left(Q^4\frac{\partial}{\partial Q}\right) + \frac{1}{Q^2\sin(3\alpha)}\frac{\partial}{\partial\alpha}\left(\sin(3\alpha)\frac{\partial}{\partial\alpha}\right)$$
$$-\frac{1}{4Q^2}\left(\frac{\lambda_\xi^2}{\sin^2(\alpha-2\pi/3)} + \frac{\lambda_\eta^2}{\sin^2(\alpha+2\pi/3)} + \frac{\lambda_\zeta^2}{\sin^2(\alpha)}\right) \tag{3}$$

where λ_ξ, λ_η and λ_ζ, the three components of a phonon angular momentum, are defined (Judd 1984) as

$$\lambda_\xi = \mathrm{i}\cos(\gamma)\left(\cot(\theta)\frac{\partial}{\partial\gamma} - \operatorname{cosec}(\theta)\frac{\partial}{\partial\varphi}\right) + \mathrm{i}\sin(\gamma)\frac{\partial}{\partial\theta}$$
$$\lambda_\eta = \mathrm{i}\sin(\gamma)\left(\cot(\theta)\frac{\partial}{\partial\gamma} - \operatorname{cosec}(\theta)\frac{\partial}{\partial\varphi}\right) + \mathrm{i}\cos(\gamma)\frac{\partial}{\partial\theta} \tag{4}$$
$$\lambda_\zeta = \mathrm{i}\frac{\partial}{\partial\gamma}.$$

3. The ground state in strong coupling

In the adiabatic approximation, solutions to (1) involve one of three potential surfaces, given by the eigenvalues of H_{JT} with the addition of the restoring term $\frac{1}{2}m\omega^2Q^2$. Using (2), we see that the lowest of these:

$$U=\tfrac{1}{2}m\omega^2Q^2 - VQ\cos\alpha$$

is a function of only two of the five phonon coordinates. The minimum on U occurs for $Q=V/m\omega^2$ and $\alpha=0$, and forms a two-dimensional equipotential surface in the full five-dimensional phonon space (see figure 1). As O'Brien (1969) has shown, this minimum energy surface can be mapped to the surface of a sphere, with the restriction that points on the sphere related to each other by inversion correspond to the same point on the two-dimensional equipotential. Specifically, the equipotential is defined by setting $Q=Q_0\equiv V/m\omega^2$, $\alpha=0$, $\gamma=0$, and by allowing both φ and θ to vary over the domain $[0, \pi)$. Interpreting θ and φ as the polar angles for a point on the surface of a sphere of radius Q_0 defines the mapping (see figure 2).

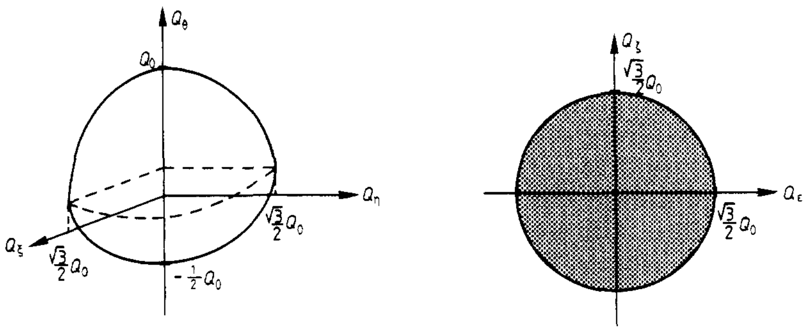

Figure 1. The equipotential minimum surface in the five-dimensional phonon space corresponding to the eigenvalue $U_0=\frac{1}{2}m\omega^2Q_0^2-VQ_0$ of $H_{JT}+\frac{1}{2}m\omega^2Q^2I$. The space is divided into two subspaces, $(Q_\xi, Q_\eta, Q_\theta)$ and (Q_ζ, Q_ε), to allow for a complete representation. In terms of the phonon coordinates, the equipotential minimum can be expressed as a parametrisation in the variables θ and φ:

$$Q_\theta = Q_0[3(\cos\theta)^2-1]/2 \qquad Q_\zeta=\sqrt{3}Q_0(\sin\theta)^2\sin(2\varphi)/2$$
$$Q_\xi=\sqrt{3}Q_0\sin(2\theta)\sin(\varphi)/2 \qquad Q_\varepsilon=\sqrt{3}Q_0(\sin\theta)^2\cos(2\varphi)/2$$
$$Q_\eta=\sqrt{3}Q_0\sin(2\theta)\cos(\varphi)/2$$

where θ and φ both vary over the domain $[0, \pi)$. The projection in $(Q_\xi, Q_\eta, Q_\theta)$ subspace is an ellipsoid centred at $(0, 0, Q_0/4)$; in the (Q_ζ, Q_ε) subspace, the equipotential projects onto a disc of radius $\sqrt{3}Q_0/2$ centred at the origin.

Given these circumstances, the ground state for this Jahn–Teller system in the strong coupling regime takes the form

$$\Psi_m=\Phi(Q,\alpha)\psi_m(\theta,\varphi)\boldsymbol{Y}^{(1)}\cdot|p\rangle \tag{5}$$

where

$$\psi_m(\theta,\varphi)=Y_m^{(1)}(\theta,\varphi) \qquad m=-1,0,+1 \tag{6}$$

and $\Phi(Q,\alpha)$ is sharply peaked at $Q=Q_0$, $\alpha=0$. $Y^{(1)}(\theta,\varphi)$, the spherical harmonic of rank one, represents motion on the equipotential energy minimum and

$$\boldsymbol{Y}^{(1)}\cdot|p\rangle=\sin(\theta)\cos(\varphi)|\xi\rangle+\sin(\theta)\sin(\varphi)|\eta\rangle+\cos(\theta)|\zeta\rangle \tag{7}$$

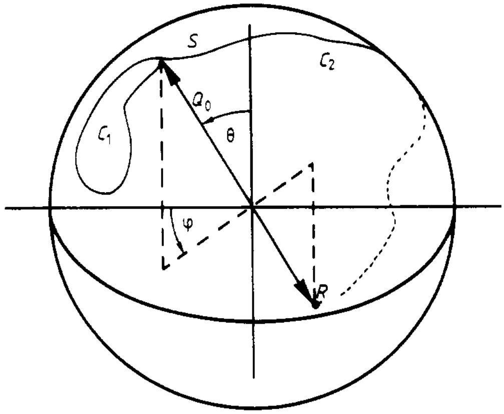

Figure 2. The Q_0 sphere. Path C_1, though closed, does not encircle the $\theta = 0$ north pole; path C_2 does enclose the $\theta = 0$ point, since $(\theta, \varphi) = (\pi - \theta, \varphi + \pi)$ by the inversion symmetry of the phonon coordinate space.

is the eigenvector corresponding to $-\cos(\alpha)$ in (2). As given in (6), $\psi_m(\theta, \varphi)$ is a solution to (3) in the limits $\alpha \to 0$, $Q \to Q_0$. The derivation of this ground-state wavefunction is given in O'Brien (1969, 1971).

Under inversion in (Q, θ, φ) space, $\boldsymbol{Y}^{(1)} \cdot |p\rangle$ changes sign while the phonon coordinates remain unaltered. This operation of inversion, which does nothing physically to the system, must not alter the total wavefunction Ψ_m, so $\psi_m(\theta, \varphi)$ must change sign under inversion. This means that the $Y_{lm}(\theta, \varphi)$, as eigenstates of (3), must be limited to odd values of l and that, in particular, the lowest energy level is a vibronic triplet corresponding to $l = 1$.

Though $\boldsymbol{Y}^{(1)} \cdot |p\rangle$ is uniquely defined on the Q_0 sphere, it is double-valued over the equipotential minimum surface. Because of its coupling to $\psi_m(\theta, \varphi)$ through the variables θ and φ, a geometric quantum phase, the so-called Berry phase, is induced in the wavefunction as the system moves through a closed circuit on the equipotential minimum surface. Aitchison (1988) has provided a general discussion on the role of Berry's phase in vibronic coupling phenomena in molecular physics, with particular reference to the $E \otimes \varepsilon$ Jahn–Teller system. In what follows, we shall show that the $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ system is likewise an example and shall calculate both the Berry phase and its associated vector potential.

In calculating the Berry phase, it would be convenient to add a phase to $\boldsymbol{Y}^{(1)} \cdot |p\rangle$ so as to make it single-valued over the equipotential surface. This can be done for every point with the exception of one, which is that point mapped to the poles $(\theta = 0, \pi)$ of the Q_0 sphere. (That one point must be excluded is due to the symmetry of the spherical harmonic $Y^{(1)}(\theta, \varphi)$ under inversion.) Additing a phase $\exp(\mathrm{i}\varphi)$ to $\boldsymbol{Y}^{(1)} \cdot |p\rangle$ and defining

$$|g(Q)\rangle = \exp(\mathrm{i}\varphi)[\sin(\theta)\cos(\varphi)|\xi\rangle + \sin(\theta)\sin(\varphi)|\eta\rangle + \cos(\theta)|\zeta\rangle] \tag{8}$$

we see that the inversion condition on the Q_0 sphere is now built in to $|g(Q)\rangle$.

4. Berry's phase

Following Berry's definition (Berry 1984), the geometric phase picked up by the eigenvector $|g(Q)\rangle$ as it follows a closed circuit C in $(Q, \alpha, \varphi, \theta, \gamma)$ space is

$$\gamma_g(C) = \mathrm{i} \oint_C \langle g(Q)|\nabla|g(Q)\rangle \cdot \mathrm{d}\boldsymbol{Q} \tag{9}$$

where

$$\nabla = \hat{Q}\frac{\partial}{\partial Q} + \hat{\alpha}\frac{1}{Q}\frac{\partial}{\partial \alpha} - \frac{\mathrm{i}}{2Q}\left(\hat{\nu}_\xi \frac{\lambda_\xi}{\sin(\alpha - 2\pi/3)} + \hat{\nu}_\eta \frac{\lambda_\eta}{\sin(\alpha + 2\pi/3)} + \hat{\nu}_\zeta \frac{\lambda_\zeta}{\sin(\alpha)}\right) \tag{10}$$

and

$$\begin{aligned}\mathrm{d}\boldsymbol{Q} = \hat{Q}\, DQ + \hat{\alpha} Q\, \mathrm{d}\alpha + \hat{\nu}_\xi 2Q \sin(\alpha - 2\pi/3)\, \mathrm{d}\nu_\xi \\ + \hat{\nu}_\eta 2Q \sin(\alpha + 2\pi/3)\, \mathrm{d}\nu_\eta + \hat{\nu}_\zeta 2Q \sin(\alpha)\, \mathrm{d}\nu_\zeta.\end{aligned} \tag{11}$$

The five-dimensional gradient operator is expressed in terms of derivatives with respect to the $(Q, \alpha, \varphi, \theta, \gamma)$ and the differential vector $\mathrm{d}\boldsymbol{Q}$ is given using the increments

$$\begin{aligned}\mathrm{d}\nu_\xi &= \sin(\gamma)\, \mathrm{d}\theta - \sin(\theta) \cos(\gamma)\, \mathrm{d}\varphi \\ \mathrm{d}\nu_\eta &= \cos(\gamma)\, \mathrm{d}\theta + \sin(\theta) \sin(\gamma)\, \mathrm{d}\varphi \\ \mathrm{d}\nu_\zeta &= \mathrm{d}\gamma + \cos(\theta)\, \mathrm{d}\varphi.\end{aligned} \tag{12}$$

We can understand the $\mathrm{d}\nu_i$ as the infinitesimal angles of rotation of the octahedral ligand complex whose principal axes are characterised by the Euler angles $(\varphi, \theta, \gamma)$ in the $(Q, \alpha, \varphi, \theta, \gamma)$ coordinate system. Following Judd (1984), we can make the identifications

$$\frac{\partial}{\partial \nu_\xi} = \mathrm{i}\lambda_\xi \qquad \frac{\partial}{\partial \nu_\eta} = \mathrm{i}\lambda_\eta \qquad \frac{\partial}{\partial \nu_\zeta} = \mathrm{i}\lambda_\zeta$$

where the λ_i are the phonon angular momentum components defined in (4). The differential vector $\mathrm{d}\boldsymbol{Q}$, as expressed in (11), has the form of one defined for an orthogonal coordinate system $\{Q, \alpha, \nu_\xi, \nu_\eta, \nu_\zeta\}$. Thus ∇^2 and ∇, though written in terms of the non-orthogonal $(Q, \alpha, \varphi, \theta, \gamma)$, have been arranged in orthogonal forms. As a consequence, the unit vectors in (10) form an orthonormal set—a great asset to calculation.

A straightforward application of the above equations allows us to evaluate and simplify (9), with the result that the Berry phase γ_g is given by

$$\gamma_g(C) = 2 \oint_C \frac{\sin(2\gamma)}{\sin(\theta)}\, \mathrm{d}\theta - \oint_C \cos(2\gamma)\, \mathrm{d}\varphi. \tag{13}$$

We shall restrict C to lie on the surface of the Q_0 sphere since only such paths involve the ground state. Under this condition, (13) reduces to

$$\gamma_g(C) = -\oint_C \mathrm{d}\varphi. \tag{14}$$

It is reassuring to note that (14) would remain unchanged had we naively replaced (10) with the two-dimensional gradient operator which acts only on the Q_0 sphere.

We can now calculate $\gamma_g(C)$ for a closed path C, arbitrary except for the requirement that C avoid the poles (referring to the Q_0 sphere). To be closed, a path must either start and finish on the same point (θ, φ) or it must finish at the inversion point $(\pi - \theta, \varphi + \pi)$. An example of the first type is labelled C_1 in figure 2; C_2 illustrates the second case in the same figure. It is clear, considering (14), that $\gamma_g(C_1)=0$ while $\gamma_g(C_2)=-\pi$. We see that only those paths which encircle the $\theta=0$ axis (the q_θ axis in the q_i coordinates) produce a non-zero Berry phase. To give a better representation of this fact, along with the necessity of excluding the Q_0 sphere poles from C, it is informative to consider the Berry vector potential.

5. The Berry vector potential

The definition of $\gamma_g(C)$, as given in (9), requires that $|g(Q)\rangle$ be single-valued (at least locally) along the path C. This was achieved for $|g(Q)\rangle$ through the addition of a phase $\exp(\mathrm{i}\varphi)$ to $\boldsymbol{Y}^{(1)}\cdot|p\rangle$. The addition of $\exp(\mathrm{i}\varphi)$ allows us not only to define the Berry phase but also forces us to include a new vector potential term in the Hamiltonian. Specifically, the momentum operator $\boldsymbol{P}\to(\boldsymbol{P}-\hbar\boldsymbol{A})$ within the kinetic term. This vector potential, $\boldsymbol{A}=\mathrm{i}\langle g(Q)|\boldsymbol{\nabla}|g(Q)\rangle$, which is tied to the appearance of $\gamma_g(C)$, can thus be given a physical interpretation within $(Q, \alpha, \varphi, \theta, \gamma)$ space. From the definition of $\boldsymbol{A}$ we see that

$$\gamma_g(C)=\oint_C \boldsymbol{A}\cdot\mathrm{d}\boldsymbol{Q}. \tag{15}$$

Evaluating $\boldsymbol{A}$ using (8) and (10) gives

$$\boldsymbol{A}=\hat{\nu}_\xi\frac{\cos(\gamma)\operatorname{cosec}(\theta)}{2Q\sin(\alpha-2\pi/3)}-\hat{\nu}_\eta\frac{\sin(\gamma)\operatorname{cosec}(\theta)}{2Q\sin(\alpha+2\pi/3)} \tag{16}$$

$$=-\boldsymbol{\nabla}\varphi. \tag{17}$$

For paths on the Q_0 sphere, $-\boldsymbol{\nabla}\varphi$ represents the vector potential of a flux tube of strength -1 along the $\theta=0$ polar axis. Evaluating $\gamma_g(C)$ using (15), we see that path C_2 produces a phase of -1; path C_1 excludes the flux tube and thus gives a null result. The appearance of a -1 phase reminds us of the special case we are considering, namely a system with a real Hamiltonian. That the phase is -1 rather than $+1$ arises from the $Q=0$ degeneracy in the adiabatic potentials common to every Jahn–Teller system.

By using this definition of $\boldsymbol{A}$, we have restricted ourselves to calculations using paths C for which $|g(Q)\rangle$ is single-valued (Berry 1984). Thus $\theta=0$ is necessarily excluded from any circuit, given our earlier definition of $|g(Q)\rangle$. The remaining singularities in $\boldsymbol{A}$ correspond to degeneracies of the adiabatic surfaces at $Q=0$ and at $\alpha=\pm2\pi/3$. The close correspondence to $E\otimes\varepsilon$ remains, for in that system which involves an electronic doublet, $\boldsymbol{A}=\frac{1}{2}\boldsymbol{\nabla}\theta$ which represents a flux tube of strength $\frac{1}{2}$ (Aitchison 1988).

6. Concluding remarks

The appearance of a Berry phase in the $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$ system has been seen to be tied to the occurrence of a ground-state triplet. Though we have not formally proved this correspondence, the double-valuedness in $\boldsymbol{Y}^{(1)}\cdot|p\rangle$ which gives rise to both the Berry phase and the $l=1$ condition makes the connection clear. Again, the analogy to $E\otimes\varepsilon$ would lead us to the same conclusion regarding $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$.

The Hamiltonian expressed in (1) is rather specialised as regards physical systems, assuming as it does equal couplings to the τ and ε modes. Yet some systems do appear to obey this so-called D-mode assumption. We mention in particular the F^+ centre in CaO studied by Hughes (1970) and Romestain and Merle d'Aubigné (1971) and the $KMgF_3$:Fe^{2+} system investigated by Ray *et al* (1973). The ground-state triplet and the higher rotational levels labelled by odd-integral quantum numbers have been observed in both systems.

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