

Geometric phases and time-odd coupling in Jahn-Teller systems

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 787

(<http://iopscience.iop.org/0953-8984/11/3/018>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.210

The article was downloaded on 14/05/2010 at 18:39

Please note that [terms and conditions apply](#).

Geometric phases and time-odd coupling in Jahn–Teller systems

Mattias T Johnsson and Geoffrey E Stedman

Department of Physics and Astronomy, University of Canterbury, Private Bag 4800, Christchurch, New Zealand

Received 12 October 1998

Abstract. Time-odd (momentum) coupling between the nuclear and electronic wavefunctions in Jahn–Teller systems, although smaller than the traditional time-even (electrostatic) coupling terms, can dramatically change the geometric phase. In the cubic $E \otimes \epsilon$ system, whose geometrical phase is a multiple of π , time-odd coupling of modes with A_2 symmetry gives a three-dimensional parameter space and arbitrary geometrical phases. We show that for equal coupling the geometric vector potential takes the form of a monopole and hence that (as in the time-even case) the nuclear angular momentum for the system is shifted from integer to half-integer values.

1. Introduction

The geometric phase has been the focus of a great deal of interest since its general topological nature was first emphasized by Berry [1]. It has been shown to arise naturally in many places in physics from classical mechanical systems (Hannay angle) [2], optical physics [3] and molecular quantum physics [4] to name but a few. Certainly it appears wherever some quantity is adiabatically evolved on a circuit around a degeneracy point in parameter space.

One useful application of adiabatic theory can be found in molecular vibrations. Here we deal with two systems differing widely in mass—the massive nuclei and the light electrons. It is thus common practice to analyse molecular systems adiabatically, i.e. break the system into two parts, and assume that the electronic subsystem can be well approximated by solving the electronic Schrödinger equation assuming the nuclei to be fixed, with no back-reaction on the electrons.

One such situation where the adiabatic approximation is employed is in the analysis of the Jahn–Teller effect [5,6]. The Jahn–Teller theorem states that a distortion along at least one of the normal lattice vibrational modes will remove an electronic degeneracy in all point groups except those of linear molecules. The origin of this effect comes from the fact that a displacement of atoms from a symmetric configuration usually produces splittings of a degenerate electronic energy level that are linear with respect to the displacement, while all elastic restoring forces are derived from potentials that are quadratic in the displacements. Equilibrium is therefore achieved for a non-zero value of the displacement creating an asymmetric molecule.

It has been shown that the geometric phase arises naturally in Jahn–Teller systems and can explain some interesting shifts in the angular momentum spectrum. The most well-studied example is that of the cubic $E \otimes \epsilon$ Jahn–Teller system where a doubly degenerate electronic state belonging to the E representation of the cubic group is coupled to a doublet lattice vibration also transforming as E (but written as ϵ to distinguish a vibration from an

electron) [7]. An isomorphic system to which the results of this paper can also be applied is the equal-coupling tetragonal system $E \otimes (b_1 \oplus b_2)$ [22]. When the adiabatic approximation is employed the geometric phase shifts the nuclear angular momentum spectrum from integer to half-integer [8]. This has been experimentally verified for the Na^+ system [9]. The theory is briefly reviewed in section 2, showing that this shift of angular momentum from a bosonic to a fermionic spectrum can be seen as arising from a geometric phase of π , or more precisely from the geometric vector potential induced by a flux tube with an associated phase of π . The restriction of this phase to a multiple of π can be attributed to the near-universal restriction to time-even couplings, in which the quasistatic effects of the electrostatic potential are assumed to induce the electron–ligand interactions (reference [10], section 2D).

Such particular values of the geometric phase are special to this situation when time-odd couplings, such as those to rotational modes of vibration, are ignored. Rotational couplings are usually discarded by an appeal to the Born–Oppenheimer approximation [11]. This approximation is not employed for, or relevant to, all of Jahn–Teller physics, e.g. when transitions are induced between the adiabatic levels. A better reason for ignoring rotational modes is that their coupling is forbidden by time-reversal selection rules when the standard quasidelectrostatic model of electron–vibration coupling is used. Even this, however, makes the approximation only as good as this model. If quasimagnetic (time-odd) effects are included, then rotational modes for example can induce couplings within a Jahn–Teller level, and then give characteristically new phenomena [12], including a generalization of the geometric phase [13], which for a system governed by a Hamiltonian that is not time-reversal symmetric can in principle take any value. Thus while the physical geometry of the coupling parameter space is actually three-dimensional, it reduces to two dimensions within a model which ignores a coupling which is inevitably present in any physical application. We demonstrate in section 3 that the inclusion of this usually ignored third dimension gives rise to a geometric vector potential which for equal coupling is equivalent to that of a monopole. The latter is known to generate arbitrary geometric phases [1], as is to be expected from the non-time-reversal-symmetric nature of the system. In section 4 we show that this monopole shifts the nuclear angular momentum spectrum from bosonic to fermionic, analogously to the situation with a flux tube.

To our knowledge the only previous inclusion of a geometric phase monopole in a Jahn–Teller system appears to be in the work of O’Brien on $T \otimes \tau_2$, who explains the geometric phases in terms of four monopoles. However, they are present only to utilize the mathematical properties of the semi-infinite Dirac string singularities attached to each monopole. In O’Brien’s work, the four monopoles are arranged such that the curl of the total field is zero, and a geometric phase is generated only if the path traced out encircles one of the singularities. This phase is always π , returning us to the simplified physics of flux tubes.

The structure of this paper is as follows. In section 2 we briefly review the adiabatic approximation and use the $E \otimes \epsilon$ system to demonstrate how the geometric phase arises within a simple Jahn–Teller system. In section 3 we examine time-odd coupling between the lattice and the electronic subsystem, and solve in detail the $E \otimes (\epsilon \oplus a_2)$ system, using a canonical transformation to obtain analytically its energy spectrum and eigenfunctions. Finally in section 4 we discuss the effect of the geometric vector potential on the nuclear angular momentum.

2. Review of the geometric phase in the adiabatic approximation

This section is largely review. The new features of our application relevant to this work are that the parameter space is ultimately three dimensional, with the result that far more complex

paths may be studied than in the two-dimensional $E \otimes \epsilon$ case, and that although in the two-dimensional case it is possible to remove the geometric vector potential by making the basis vectors double valued, this simplification is impossible in the three-dimensional case where a geometric vector potential cannot be avoided.

We take a system composed of a massive, slowly varying part (the nuclei in the molecular system) and a lighter part (the electronic subsystem) that quickly adjusts to change in the slow part. Denoting the nuclear position variables by Q and the electronic variables by q , the total Hamiltonian for the system can be written as

$$H = T_n(Q) + T_e(q) + U(q, Q) = T_n(Q) + H_e. \quad (1)$$

$T_e(q) = -(\hbar^2/2m)\nabla_q^2$ and $T_n(Q) = -(\hbar^2/2M)\nabla_Q^2$ are the electronic and nuclear kinetic energies respectively, and $U(q, Q)$ is the energy of the interaction between them. As a first step we solve the electronic Hamiltonian H_e to obtain a set of electronic basis states ψ_n for each nuclear position Q :

$$H_e \psi_n(q, Q) = \epsilon_n \psi_n(q, Q). \quad (2)$$

This basis is known as the adiabatic basis. We look for approximate solutions to the total Hamiltonian of the form

$$\Psi(q, Q) = \sum_n \psi_n(q, Q) \chi_n(Q) \quad (3)$$

where

$$H\Psi(q, Q) = E\Psi(q, Q). \quad (4)$$

Substituting equation (3) into equation (4) and integrating out the electronic wavefunctions gives

$$(T_n + \epsilon_n)\chi_n(Q) + \sum_{n'} c_{nn'}(Q)\chi_{n'}(Q) = E\chi_n(Q) \quad (5)$$

where

$$c_{nn'} = \langle \psi_n | \nabla_Q | \psi_{n'} \rangle \cdot \nabla_Q + \frac{1}{2} \langle \psi_n | \nabla_Q^2 | \psi_{n'} \rangle. \quad (6)$$

If we ignore off-diagonal terms (a reasonable assumption in view of the much larger energy difference between electronic states as compared to the nuclear states) we can rewrite equation (5) as

$$\left(\frac{1}{2M} (-i\hbar\nabla - \hbar A_n(Q))^2 + \epsilon_n \right) \chi_n = E\chi_n \quad (7)$$

where

$$A = \langle \psi | i\nabla | \psi \rangle \quad (8)$$

is the geometric vector potential of Berry. It is thus possible to consider the nuclei moving in an effective potential given by the electronic energy, with the possible complication of a vector potential.

It is not always possible to find an adiabatic basis. If this is the case, what is often done is to apply the *crude adiabatic approximation*, also known as the *Born–Oppenheimer approximation*. This approximation involves solving equation (1) with the expansion

$$\Psi^0(q, Q) = \sum_n \psi_n^0 \phi_n(Q) \quad (9)$$

where the electronic wavefunctions $\psi_n^0 = \psi_n^0(q, Q_0)$ are solutions to

$$(H(Q_0) - E_n(Q_0))\psi_n^0 = 0 \quad (10)$$

i.e. for the specialized geometry $Q = Q_0$. This is usually taken to be the point of electronic degeneracy. Using this approximation, equation (5) becomes

$$(T_n + H_{nn'} - E)\phi_n(Q) = 0 \quad (11)$$

where $H_{nn'}(Q)$ are the electronic matrix elements of the potential $V = V(Q) - V(Q_0)$ expanded in a Taylor series about Q_0 :

$$H_{nn'}(Q) = \sum_i \langle \psi_n^0 | \left(\frac{\partial V}{\partial Q_i} \right)_{Q_0} | \psi_{n'}^0 \rangle Q_i + \sum_i \sum_j \langle \psi_n^0 | \left(\frac{\partial^2 V}{\partial Q_i \partial Q_j} \right)_{Q_0} | \psi_{n'}^0 \rangle Q_i Q_j + \dots \quad (12)$$

With this background we can now briefly consider the role of the geometric phase in the $E \otimes \epsilon$ system.

In this situation we have a doubly degenerate electronic E state coupled to two possible vibrational modes, whose normal coordinates can be denoted by Q_1 and Q_2 . In this case the effective nuclear Hamiltonian in the space of crude adiabatic states ψ_1^0, ψ_2^0 is given by

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial Q_1^2} + \frac{\partial^2}{\partial Q_2^2} \right) + \frac{1}{2} m \omega^2 (Q_1^2 + Q_2^2) + \frac{1}{2} L \begin{pmatrix} -Q_2 & Q_1 \\ Q_1 & Q_2 \end{pmatrix}. \quad (13)$$

Changing to polar coordinates the effective potential becomes

$$V_{\text{eff}}(Q) = \frac{1}{2} m \omega^2 Q^2 + \frac{1}{2} L Q \begin{pmatrix} -\cos \phi & \sin \phi \\ \sin \phi & \cos \phi \end{pmatrix} \quad (14)$$

which has eigenvalues

$$\epsilon_{\pm}(Q) = \frac{1}{2} m \omega^2 Q^2 \pm \frac{1}{2} L Q. \quad (15)$$

We notice that ϵ_- has a minimum in the shape of a trough of radius $Q = L/2m\omega^2$ and consequently the low-energy motion will be around the bottom of this trough.

To obtain an adiabatic basis we diagonalize the effective potential of equation (14). The eigenvector corresponding to ϵ_- is given by $\psi_- = \cos(\phi/2)\psi_1^0 - \sin(\phi/2)\psi_2^0$. This eigenvector is double valued in ϕ ; that is, on a complete circuit of the trough the electronic wavefunction changes sign. Solving the effective nuclear Hamiltonian in this new basis yields

$$\chi_- = e^{ij\phi} f(Q). \quad (16)$$

The total wavefunction $\Psi_- = \chi_- \psi_-$ must be single valued, so we must require the quantum number j to be half an odd integer, giving the nuclear angular momentum a fermionic structure.

This structure can be explained in terms of the geometric phase [16]. To see this, notice that we chose our adiabatic basis to be real and hence double valued. Basis vectors can always be taken to be real for a time-even system. Because the basis vectors are real the geometric vector potential of equation (8) vanishes. We could, if we had wished, have chosen to rephase the basis vectors to make them single valued:

$$\tilde{\psi}_- = e^{i\phi/2}. \quad (17)$$

However, now the geometric vector potential does *not* vanish and we are left with a term in the effective nuclear Hamiltonian that looks just like a magnetic vector potential. This geometric vector potential can be calculated via equation (8); we obtain

$$\mathbf{A} = \langle \tilde{\psi}_- | i \nabla | \tilde{\psi}_- \rangle = \frac{1}{2} \nabla_Q \phi \quad (18)$$

which is the potential of a flux tube of strength π , since $\nabla \times \mathbf{A} = \pi \delta(\mathbf{r}) \hat{z}$. As in the analogous situation in electromagnetism, the Aharonov–Bohm effect, a circuit about this flux tube will induce an extra geometric phase of π in the nuclear wavefunction. More formally, the

introduction of a vector potential in the effective nuclear Hamiltonian will modify the solution to the old (in this case double-valued) nuclear Hamiltonian χ as follows:

$$\tilde{\chi}_- = \exp\left(i \int \mathbf{A} \cdot d\mathbf{x}\right) \chi_- = e^{i\pi} \chi_- \quad (19)$$

Thus j in equation (16) must still be chosen as half an odd integer.

We have now seen how a time-even Jahn–Teller-active system can shift its nuclear angular momentum by $1/2$ due to a geometric phase of π . As mentioned in section 1, a time-odd system can in principle generate a geometric phase of any value. We turn now to molecular systems which are not necessarily time-even, to investigate the new topological features which emerge when considering the geometric phase.

3. Inclusion of time-odd coupling in $E \otimes \epsilon$

Since the 1930s the Van Vleck model of electron–lattice coupling has reigned more or less supreme. This model is a quasistatic theory and considers the interactions of atoms with the static Coulomb field generated by the ligands. Consequently the interactions are governed purely by electric fields and are time-even. It has been recognized that purely electrostatic calculations of the ligand fields are inadequate for some situations such as the lanthanides, leading to the extension of the Van Vleck model [17], and modifications to dynamic ligand field theories [18]. Such modifications are at best quasistatic, however, and still ignore time-odd coupling. Review articles that even mention time-odd coupling between lattice vibrations and electronic states generally do so only to dismiss the effect as negligible [14, 19]. The very few authors who have seriously considered time-odd coupling include Fletcher [20], Fletcher and Pooler [12] and Payne and Stedman [21], all in the context of the breakdown of sum rules in Ham reduction factors in Jahn–Teller systems. More recently, the importance of time-odd lattice–electron coupling has been re-examined by Moore and Stedman, who concluded that in some instances it could contribute significantly [13], and by Riley and Furlan, who demonstrated in which point groups time-odd effects such as momentum and Barnett coupling can occur [15].

The simplest way to include time-odd terms in a vibronic system is to allow momentum coupling—that is, to allow the momentum of the nuclei to have an effect on the electronic states. This scheme fails in the crude adiabatic approximation due to the fact that the nuclear momentum matrix elements evaluated with respect to the purely position-dependent electronic states are all zero. Furthermore, not all point groups allow the possibility of momentum coupling, since in some cases a minimum complexity of the molecule is required [15]. If momentum coupling is allowed, then in addition to the electric field from the ligands there also exists a magnetic field which leads to time-odd effects via a Zeeman interaction.

As an example we take the cubic $E \otimes (\epsilon \oplus a_2)$ or equivalently the equal-coupled $E \otimes (b_1 \oplus b_2 \oplus a_2)$ system with D_4 (tetragonal) symmetry, which consists of a doubly degenerate electronic E state surrounded by four ions in a square. We label the normal coordinates by Q_{b_1} , Q_{b_2} , Q_{a_2} . In this notation the total Hamiltonian for this system is given by [22]

$$H = \frac{1}{2\mu} (P_{b_1}^2 + P_{b_2}^2 + P_{a_2}^2) + \frac{1}{2}\mu(\omega_b^2(Q_{b_1}^2 + Q_{b_2}^2) + \omega_a^2 Q_{a_2}^2) + K_b(\sigma_1 Q_{b_1} + \sigma_3 Q_{b_2}) + K_a \sigma_2 P_{a_2} \quad (20)$$

where the σ_i are the Pauli spin matrices, the ω are the vibrational frequencies of the modes, μ is the effective mass of the nuclear displacement, $P_\alpha = -i\hbar\nabla_\alpha$ and V_a , V_b are coupling constants. The crude adiabatic approximation cannot immediately be employed with this

Hamiltonian, because the matrix elements of the $\sigma_2 P_{a_2} = -i\hbar\sigma_a \nabla_{a_2}$ term will vanish in the crude adiabatic basis.

To overcome this problem we employ a canonical transformation. The quantum mechanical analogue of the classical mechanical time-independent canonical transformation is the similarity transform, of which unitary transformations are a subset [23]. We induce

$$H \rightarrow H' = U H U^{-1} \quad (21)$$

choosing

$$U = \exp \left[\frac{-i\pi}{4\hbar} \left(\frac{1}{\mu\omega_a} P_a^2 + \mu\omega_a Q_a^2 \right) \right]. \quad (22)$$

This has the effect of transforming the nuclear position and momentum operators as

$$\begin{aligned} Q_{b_1} &\rightarrow Q_{b_1} & P_{b_1} &\rightarrow P_{b_1} \\ Q_{b_2} &\rightarrow Q_{b_2} & P_{b_2} &\rightarrow P_{b_2} \\ Q_{a_2} &\rightarrow \frac{-1}{m\omega_a} P_{a_2} & P_{a_2} &\rightarrow \mu\omega_a Q_{a_2} \end{aligned} \quad (23)$$

while ensuring that the standard commutation relations still hold.

We write $Q_1 = Q_{b_1}$, $Q_2 = Q_{a_2}$, $Q_3 = Q_{b_2}$, and we introduce the *equal-coupling assumption*: $K_b = \mu\omega_a K_a \equiv K$. Under this unitary transformation the Hamiltonian of equation (20) becomes

$$H = \frac{1}{2\mu} (P_1^2 + P_2^2 + P_3^2) + \frac{1}{2}\mu(\omega_b^2(Q_1^2 + Q_3^2) + \omega_a^2 Q_2^2) + K \sum_{i=1}^3 \sigma_i Q_i. \quad (24)$$

The transformation has removed the momentum dependence in the coupling term and we can now apply an analogue to the crude adiabatic approximation.

We change to spherical polar coordinates

$$Q_1 = Q \sin \theta \cos \phi \quad Q_2 = Q \sin \theta \sin \phi \quad Q_3 = Q \cos \theta \quad (25)$$

and proceed as in section 2. The effective potential is given by

$$V_{\text{eff}} = \frac{1}{2}\mu Q^2 (\omega_b^2 (\sin^2 \theta \cos^2 \phi + \cos^2 \theta) + \omega_a^2 \sin^2 \theta \sin^2 \phi) + K Q \begin{pmatrix} \cos \theta & \sin \theta e^{-i\phi} \\ \sin \theta e^{i\phi} & -\cos \theta \end{pmatrix} \quad (26)$$

which has eigenvalues

$$\epsilon_{\pm} = \frac{1}{2}\mu Q^2 (\omega_b^2 (\sin^2 \theta \cos^2 \phi + \cos^2 \theta) + \omega_a^2 \sin^2 \theta \sin^2 \phi) \pm \frac{1}{2} K Q. \quad (27)$$

The higher-energy eigenvalue ϵ_+ is uninteresting, having a minimum at $Q = 0$, and will not lead to any Jahn–Teller activity. The lowest adiabatic potential-energy surfaces corresponding to the other energy eigenvalue ϵ_- are more complex. If $\omega_a < \omega_b$ then there exist two points that are global minima. They lie on the Q_2 -axis at $Q_2 = \pm K/2\mu\omega_a^2$, and again give rise to no interesting dynamics. If $\omega_a > \omega_b$ then the global minimum is a ring around the $Q_2 = 0$ plane, with radius $(Q_1^2 + Q_3^2)^{1/2} = K/2\mu\omega_b^2$. Thus in this case low-energy motions will be confined to a toroidal region with effectively only one degree of freedom. This situation is similar to that for the E \otimes ϵ system, where the low-energy motions were also in a ring at the bottom of the trough of a ‘Mexican hat’ potential. Following the calculations through for this case shows that this motion will give rise to phase changes of $\pm\pi$ upon circling the Q_2 -axis, as expected. The most interesting situation arises when $\omega_a = \omega_b$. In this case the lowest-energy eigenvalue has the form

$$\epsilon_- = \frac{1}{2}\mu\omega^2 Q^2 - \frac{1}{2} K Q. \quad (28)$$

Thus the lowest adiabatic potential-energy surface is a sphere of radius $Q = K/2\mu\omega^2$. A sphere allows a rich variety of paths in parameter space and consequently we choose $\omega_a = \omega_b$.

Next we change to an adiabatic basis. This is accomplished by diagonalizing the effective potential by changing to a new basis given by its eigenvectors:

$$\psi_+ = \begin{pmatrix} e^{-i\phi} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} \end{pmatrix} \quad \psi_- = \begin{pmatrix} -\sin \frac{\theta}{2} \\ e^{i\phi} \cos \frac{\theta}{2} \end{pmatrix}. \quad (29)$$

These two basis vectors are identical to those arising from a general two-level crossing, and are known to give rise to a geometric vector potential functionally equivalent to that of a monopole [24].

In this new basis the nuclear kinetic operator is no longer diagonal. After some calculation we find that its components are given by:

$$\langle \psi_+ | \nabla^2 | \psi_+ \rangle = -\frac{1}{Q^2} \left(\frac{1}{4} + \frac{1 + \cos \theta}{2 \sin^2 \theta} \right) \quad (30)$$

$$\langle \psi_+ | \nabla^2 | \psi_- \rangle = -\frac{e^{i\phi}}{2Q^2} (\cot \theta + \operatorname{cosec} \theta) \quad (31)$$

$$\langle \psi_- | \nabla^2 | \psi_+ \rangle = \frac{e^{-i\phi}}{2Q^2} (\cot \theta + \operatorname{cosec} \theta) \quad (32)$$

$$\langle \psi_- | \nabla^2 | \psi_- \rangle = -\frac{1}{Q^2} \left(\frac{1}{4} + \frac{1 + \cos \theta}{2 \sin^2 \theta} \right). \quad (33)$$

Assuming low-energy motion, corresponding to massive nuclei compared to the much lighter electrons, the nuclear motion will remain on the lowest adiabatic potential-energy surface, as given by equation (28). Writing the total vibronic wavefunction as $\Psi_{\pm} = \psi_{\pm} \chi_{\pm}$ we have

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 + \epsilon_{\pm}^{\min} \right) \Psi_{\pm} = E \Psi_{\pm}. \quad (34)$$

Denoting the matrix representation of an operator in the adiabatic basis by enclosing it in square brackets, equation (34) becomes

$$\left[-\frac{\hbar^2}{2\mu} ([\nabla^2] + 2[\nabla] \cdot \nabla + \nabla^2) + \begin{pmatrix} \epsilon_+^{\min} & 0 \\ 0 & \epsilon_-^{\min} \end{pmatrix} \right] \begin{pmatrix} \chi_+ \\ \chi_- \end{pmatrix} = E \begin{pmatrix} \chi_+ \\ \chi_- \end{pmatrix}. \quad (35)$$

We note the appearance of the geometric vector potential: $[\nabla] = -i\mathbf{A}$. In the adiabatic basis we obtain

$$\mathbf{A}_- = i \langle \psi_+ | \nabla | \psi_+ \rangle = \frac{-(1 + \cos \theta)}{2Q \sin \theta} \hat{\phi}. \quad (36)$$

This is the vector potential for a monopole of charge +1, as can be seen by noting that

$$\nabla \times \mathbf{A} = \frac{1}{Q^2} \hat{\mathbf{Q}}. \quad (37)$$

Transitions between electronic levels can be ignored in the Born–Oppenheimer approximation, enabling us to neglect the off-diagonal parts of the kinetic energy operator above. The pair of differential equations can thus be uncoupled and considered separately. Since we are considering low-energy motion, the system will remain on the spherical lowest adiabatic

potential-energy surface, in this case a sphere, and Q will remain constant. With this in mind and considering only the more interesting lower-energy surface, equation (35) becomes

$$-\frac{\hbar^2}{2\mu} \frac{1}{Q^2} \left(-\frac{1}{4} - \frac{1 + \cos \theta}{2 \sin \theta} + \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{i(1 + \cos \theta)}{\sin^2 \theta} \frac{\partial}{\partial \phi} \right) \chi_- = (E - \epsilon_-^{min}) \chi_- \quad (38)$$

The way to separate variables is to take the ϕ -dependence as $\chi_- \propto \exp(im\phi)$. Because we have included the vector potential explicitly, we must choose m to be an integer in order to preserve the single valuedness of the total vibronic wavefunction Ψ_- . Odd angular momenta will still result however, as the inclusion of the vector potential affects the form of the angular momentum operators. Separating the variables in this way yields the following equation in θ :

$$\left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} - \frac{2m^2 + (1 + 2m)(1 + \cos \theta)}{2 \sin^2 \theta} - \frac{1}{4} + \frac{2\mu Q^2}{\hbar^2} (E - \epsilon_-^{min}) \right) \chi_- = 0. \quad (39)$$

An identical equation occurs in the study by Apsel *et al* of the $\Gamma_8 \otimes (\tau_2 \oplus \epsilon)$ system [25]. The solution to equation (39) can be obtained using the following method. First, employ the change of variable

$$x = \frac{1}{2}(1 + \cos \theta) \quad (40)$$

transforming equation (39) into the form

$$\left[x(1-x) \frac{d^2}{dx^2} - (2x-1) \frac{d}{dx} - \frac{m^2 + (1+2m)x}{4x(1-x)} + E' \right] \chi_-(x) \quad (41)$$

where for simplicity we have rewritten the total energy as $E' = 2\mu Q^2(E - \epsilon_-^{min})/\hbar^2$. Equation (41) is not in the form of any standard differential equation, so in order to progress we introduce the dependent function $X(x)$ via

$$\chi_-(x) = x^{1/2}(x-1)^{(1/2)(1+m)} X(x). \quad (42)$$

This reduces (41) to

$$\left[x(1-x) \frac{d^2}{dx^2} + [(1+m) - (2m+3)x] \frac{d}{dx} - [(1+m)^2 - V] \right] X(x) = 0. \quad (43)$$

In this form it is recognizable as a specialization of the hypergeometric differential equation which is defined as [26]

$$\left[z(1-z) \frac{d^2}{dz^2} + [\gamma - (\alpha + \beta + 1)z] \frac{d}{dz} - \alpha\beta \right] w(z) = 0 \quad (44)$$

where z is complex and α, β, γ are constants. The hypergeometric differential equation has solutions based on combinations of the Gauss hypergeometric series [26]

$$F(\alpha, \beta; \gamma; z) = \frac{\Gamma(\gamma)}{\Gamma(\alpha)\Gamma(\beta)} \sum_{n=0}^{\infty} \frac{\Gamma(\alpha+n)\Gamma(\beta+n)}{\Gamma(\gamma+n)} \frac{z^n}{n!} \quad (45)$$

which has a radius of convergence $|z| < 1$. On the circle $|z| = 1$, convergence of the series is conditional, and depends on the values of the constants α, β and γ .

Comparing equations (43) and (44) we identify

$$\gamma = m + 1 \quad (46)$$

$$\alpha = m + 1 - \sqrt{E'} \quad (47)$$

$$\beta = m + 1 + \sqrt{E'}. \quad (48)$$

Returning to the first change of variable in equation (40), we see that the range of the original variable $0 \leq \theta \leq \pi$ corresponds to $0 \leq x \leq 1$. In order for the wavefunction to be finite throughout this range it is necessary that equation (45) converge at $x = 1$. This can only be accomplished if the series terminates after a finite number of terms, which requires α to be either zero or a negative integer. Setting $\alpha = -n$ and using equation (47) yields the energy condition

$$E' = (n + m + 1)^2 \quad (49)$$

which agrees with the spectrum obtained by Apsel *et al* [25].

As eigenvalues of a system are unaffected by a canonical transformation, the energy spectrum of equation (49) represents the spectrum of the untransformed Hamiltonian of equation (20).

Because equation (44) is second order, two linearly independent solutions exist. Since γ is an integer the first solution has the form [27]

$$X_1(x) = F(\alpha, \beta; \gamma; x) = F(-n, 2(m+1) + n; m+1; x) = \frac{n!m!}{(n+m)!} P_n^{(m, m+1)}(1-2x) \quad (50)$$

where we have used the identity (15.4.6) of Abramowitz and Stegun [26] to rewrite the hypergeometric series in terms of Jacobi polynomials. The second solution is of the form

$$X_2(x) = x^{-m} \frac{(n+m)!(1-n)!}{(1-m)!} P_{n+m}^{(-m, m+1)}(1-2x) \quad (51)$$

and should be discarded as unphysical because it is singular for $n, m > 1$.

The full solution thus consists only of X_1 and can be written, after some simplifications, as

$$\begin{aligned} \chi_- &= e^{i\phi} x^{m/2} (x-1)^{(1/2)(m+1)} \frac{n!m!}{(n+m)!} P_n^{(m, m+1)}(1-2x) \\ &= (-1)^{n+1} \frac{n!m!}{(n+m)!} e^{i\phi} \cos^m(\frac{1}{2}\theta) \sin^{m+1}(\frac{1}{2}\theta) P_n^{(m+1, m)}(\cos\theta). \end{aligned} \quad (52)$$

It must be remembered that the $E \otimes (\epsilon \oplus a_2)$ Hamiltonian was solved via a canonical transformation, and as such the position (Q_{a_2}) and momentum (P_{a_2}) coordinates have effectively been interchanged. Since a canonical transformation does not affect eigenvalues, the angular momentum spectrum found above applies also to the original, untransformed problem. However, when constructing excursions on the spherical minimal-energy surface to calculate geometric phases, it is important to realize that the Q_2 -coordinate is actually the momentum of the a_2 vibrational mode. Thus, for example, if one wished to consider the evolution of the system on an equatorial path in the Q_1 – Q_3 plane in order to examine the phases generated, it would have to be borne in mind that this corresponds to a zero-momentum a_2 mode, even though it need not be in its equilibrium $Q_{a_2} = 0$ position.

4. The geometric phase and angular momentum

As mentioned in section 1, the flux-tube geometric vector potential arising in the $E \otimes \epsilon$ system causes the nuclear angular momentum to become half-integral. In two dimensions there exists a simple link between the phase imparted to a charged particle by a vector potential and its angular momentum. The angular momentum is shifted from its naive value by a factor of $q\Phi/2\pi$, where q is the charge of the particle and Φ is the strength of the flux tube which is equal to the phase imparted to the particle upon it making a full circuit of the tube. The $E \otimes \epsilon$

system is effectively two dimensional. Here the flux-tube strength is $\Phi = \pi$ and the geometric ‘charge’ is unity, as in all geometric phase effects. Thus an angular momentum shift of $\frac{1}{2}$ is observed. In this section we show that the three-dimensional monopole potential also gives rise to a half-odd-integer angular momentum spectrum.

A different result might have been expected. This link between two dimensions, phase shifts and angular momenta is the basis for the existence of anyons, two-dimensional systems in which fractional statistics and non-half-integer angular momentum values are possible [28]. Anyons have been postulated in areas as diverse as the fractional quantum hall effect [29], high-temperature superconductivity [30], and P - and T -violations in field theories [31]. Their links to the geometric phase have also been noted [32]. It is an intriguing possibility that certain Jahn–Teller systems with two degrees of freedom may be able to mimic some of these properties, although, as mentioned in section 1, time-even systems such as $E \otimes \epsilon$ could not generate flux-tube strengths other than π and are restricted to non-anyonic angular momentum shifts of $\frac{1}{2}$. No such restriction exists in three dimensions.

However, in the case of the equal-coupling $E \otimes (\epsilon \oplus a_2)$ and $E \otimes (b_1 \oplus b_2 \oplus a_2)$ systems we show that an angular momentum shift of $\frac{1}{2}$ occurs, as for the two-dimensional case. This can be associated with the fact that the geometric vector potential takes the form of a monopole, whose effects on angular momentum are similarly constrained.

In a classical context it is simple to show that mechanical angular momentum is no longer conserved for a charged particle in a monopole field. To restore conservation one must add an extra term consisting of the angular momentum running between the monopole and the electric charge, with its magnitude quantized in units of the monopole charge. This extra angular momentum is of course carried by the electromagnetic field. Thus if the monopole of charge g is situated at the origin, the mechanical angular momentum of the charged particle is altered by an amount

$$\mathbf{L} \rightarrow \mathbf{L}' = \mathbf{L} - qg\hat{r}. \quad (53)$$

This argument can be carried out much more rigorously via canonical arguments and can be shown to hold quantum mechanically with the correct angular momentum operators being given by [33]

$$J_i = -i\epsilon_{ijk}r_j(\nabla_k - iA_k) - \frac{1}{2}r_i\epsilon_{lmn}r_lF_{mn} \quad (54)$$

where F_{mn} are components of the electromagnetic field tensor. Using equation (37) as the magnetic field in equation (54) and evaluating the J_z -component, we find

$$J_z = -i\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) - g \quad (55)$$

showing that the angular momentum spectrum is shifted by an amount equal to the monopole strength.

In general, the monopoles arising in geometric phase contexts have their strengths quantized in units of spin [1]. The cases considered in the earlier sections, $E \otimes (\epsilon \oplus a_2)$ and $E \otimes (b_1 \oplus b_2 \oplus a_2)$, are examples of this and have an associated monopole of strength $\frac{1}{2}$. Thus these systems exhibit a shift of vibronic angular momentum of $\frac{1}{2}$ also, as in the corresponding time-even systems. Another way of obtaining this shift is to note that it is the extended angular momentum operator

$$J_z = L_z - \frac{1}{2}\sigma_z = -i\frac{\partial}{\partial\phi} - \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (56)$$

which commutes with the effective Hamiltonian (equation (24)).

5. Conclusions

We have given a new role for the geometric monopole vector potential in Jahn–Teller physics. Although time-odd coupling terms in Jahn–Teller systems have generally been ignored, their inclusion can give rise to interesting geometric vector potentials, capable of generating arbitrary geometric phases. In the case of the $E \otimes (\epsilon \oplus a_2)$ or $E \otimes (b_1 \oplus b_2 \oplus a_2)$ systems this momentum coupling necessitates an extension from a two-dimensional to a three-dimensional parameter space, and creates a geometric vector potential in the nuclear Hamiltonian that is identical to the Dirac monopole in electromagnetism. Thus in addition to the geometric phases generated, the nuclear angular momentum spectrum is shifted from integral to half-integral.

It is also interesting to speculate on the relationship between Jahn–Teller physics and the exotic fractional angular momentum of anyonic systems. The investigation of such a link would be a worthwhile subject of future study. An indication of this is that when the equal-coupling approximation of equation (24) is not assumed, the half-integral angular momentum operator of equation (56) no longer commutes with equation (20), whose symmetry group is now axial rather than three dimensional.

References

- [1] Berry M V 1984 *Proc. R. Soc. A* **392** 45
- [2] Hannay J H 1985 *J. Phys. A: Math. Gen.* **18** 221
- [3] Bhandari R 1997 *Phys. Rep.* **281** 2
- [4] Bohm A, Kendrick B and Loewe M E 1992 *Int. J. Quantum Chem.* **41** 53
- [5] Jahn H A and Teller E 1937 *Proc. R. Soc. A* **161** 220
- [6] Blount E I 1971 *J. Math. Phys.* **12** 1890
- [7] Bersuker I B and Polinger V A 1989 *Vibronic Interactions in Molecules and Crystals* (Berlin: Springer)
- [8] Ham F S 1987 *Phys. Rev. Lett.* **58** 725
- [9] Delacrétaz G, Grant E T, Whetten R L, Wöster L and Zwanziger J W 1986 *Phys. Rev. Lett.* **56** 2598
- [10] Mead C A 1992 *Rev. Mod. Phys.* **64** 51
- [11] Judd B R 1974 *Can. J. Phys.* **52** 999
- [12] Fletcher J R and Pooler D R 1982 *J. Phys. C: Solid State Phys.* **15** 2695
- [13] Moore D J and Stedman G E 1990 *J. Phys.: Condens. Matter* **2** 2559
- [14] Gill J C 1975 *Rep. Prog. Phys.* **38** 91
- [15] Riley M J and Furlan A 1996 *Chem. Phys.* **210** 389
- [16] Aitchison I J R 1988 *Phys. Scr. T* **23** 12
- [17] Newman D J 1971 *Adv. Phys.* **20** 197
- [18] Stedman G E and Newman D J 1971 *J. Chem. Phys.* **55** 152
- [19] Stevens K W H 1967 *Rep. Prog. Phys.* **30** 189
- [20] Fletcher J R 1981 *J. Phys. C: Solid State Phys.* **14** L491
- [21] Payne S H and Stedman G E 1983 *J. Phys. C: Solid State Phys.* **16** 2679
- [22] Stedman G E 1983 *Eur. J. Phys.* **4** 156
- [23] Anderson A 1993 *Phys. Lett. B* **305** 67
- [24] Johnsson M T and Aitchison I J R 1997 *J. Phys. A: Math. Gen.* **30** 2085
- [25] Apsel S E, Chancey C C and O'Brien M C M 1992 *Phys. Rev. B* **45** 5251
- [26] Abramowitz M and Stegun I A (ed) 1970 *Handbook of Mathematical Functions* (New York: Dover)
- [27] Nikiforov A F and Uvarov V B 1988 *Special Functions of Mathematical Physics* (Basel: Birkhäuser)
- [28] Forte S 1992 *Rev. Mod. Phys.* **64** 193
- [29] Arovas D P, Schrieffer J R and Wilczek F 1984 *Phys. Rev. Lett.* **53** 722
- [30] Wilczek F 1990 *Fractional Statistics and Anyon Superconductivity* (Singapore: World Scientific)
- [31] Kitazawa Y 1990 *Phys. Rev. Lett.* **65** 1275
- [32] Kivelson S A and Rokhsar D S 1988 *Phys. Rev. Lett.* **61** 2630
- [33] Shapere A and Wilczek F 1989 *Geometric Phases in Physics* (Singapore: World Scientific)
- [34] O'Brien M C M 1989 *J. Phys. A: Math. Gen.* **22** 1779