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Spin tunnelling in mesoscopic systems

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Abstract. We study spin tunnelling in molecular magnets as an instance of a mesoscopic phenomenon, with special emphasis on the molecule Fe_8. We show that the tunnel splitting between various pairs of Zeeman levels in this molecule oscillates as a function of applied magnetic field, vanishing completely at special points in the space of magnetic fields, known as diabolical points. This phenomena is explained in terms of two approaches, one based on spin-coherent-state path integrals, and the other on a generalization of the phase integral (or WKB) method to difference equations. Explicit formulas for the diabolical points are obtained for a model Hamiltonian.

Keywords. Spin tunnelling; spin path integrals; discrete phase integral method; diabolical points.

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1. Introduction

The last five years or so have seen a burst of activity in the physics and chemistry of molecular magnets. This activity is fuelled to a great extent by the ability of chemists to synthesize organic molecules containing magnetic ions such as Mn, Fe, and Co, which then form molecular solids, in many cases of high crystallinity and homogeneity. More than 5000 different magnetic molecular clusters are known, and about a 100 of these show some behaviour or quirk that is of interest from the perspective of physics [1,2]. These molecules are intermediate between simple paramagnetic salts such as $CuSO_4.K_2SO_4.6H_2O$ or $Ce_2Mg_3(NO_3)_{12}.24H_2O$, in which the magnetic entities are single transition metal or rare earth ions, and superparamagnetic particles of submicrometer size. Thus, they show phenomena such as hysteresis at the molecular level [3–5], but since the magnetic entities are molecules and thus well defined with identical size, shape, and orientation, and since the interactions of the magnetic and nonmagnetic degrees of freedom are relatively well understood, there is the potential for understanding the energy relaxation process in great detail. Some of these issues are similar to those that arise in the study of magnetization reversal of small magnetic particles, and it is hoped that the molecular systems will offer insights into the latter, which has obvious implications for magnetic recording and storage technologies.

Our purpose in this article is rather different. The molecular systems have total spin of the order of 10, and magnetocrystalline anisotropies of few tens of Kelvin in energy. The quantum mechanical dynamics of the spin are then profitably viewed in terms of tunnelling in many cases, and it is of interest to look for such behavior. At present, the greatest interest

is in the molecule $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$ (henceforth abbreviated to Fe_8), which is a molecular complex in which antiferromagnetic interactions between the Fe^{3+} ions within a molecule lead to a ground state with a total spin of 10. This molecule shows clear evidence for spin tunnelling in the form of a tunnel splitting that oscillates as a function of a static external magnetic field [6]. One way to understand this effect is in terms of the spin-coherent-state path integral for spin. The kinetic term in this path integral has the properties of a Berry phase, which can allow for interference of spin trajectories [7,8]. In fact, using this property, the oscillations were found theoretically [9], without knowing of the existence of Fe_8. However, another way to understand the effect, which has the advantage of using only classical methods of analysis, is in terms of a discrete analogue of the phase integral or WKB method.

In §2 we shall give a brief discussion of the experiments on Fe_8, and in sections 3 and 4, we shall describe the instanton and discrete phase integral (DPI) methods for calculating spin tunnel splittings.

2. Summary of experimental results on Fe_8

Electron paramagnetic resonance and other measurements show that at low temperature, the Fe^{3+} spins in one molecule of Fe_8 behave as a single large spin of magnitude 10, with an anisotropy energy that is well described by the Hamiltonian,

$$\mathcal{H}_0 = k_1 J_x^2 + k_2 J_y^2, \tag{1}$$

with $J = 10$, $k_1 \approx 0.33$ K, and $k_2 \approx 0.22$ K. The g-factor of the net spin is very close to 2, with very little anisotropy in the g-tensor.

If we think of eq. (1) as a classical energy function for a classical vector $\mathbf{J}$, we see that the energy is a minimum when $\mathbf{J} \| \pm \hat{\mathbf{z}}$, and a maximum when $\mathbf{J} \| \pm \hat{\mathbf{x}}$. We refer to $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\boldsymbol{z}}$ as the hard, medium, and easy axes respectively. When the problem is treated quantum mechanically, the quantum states corresponding to the two degenerate minima at $\pm\hat{\boldsymbol{z}}$ should be able to mix together via tunnelling. This picture remains true when we add a magnetic field in the *xy* plane. The Hamiltonian is now

$$\mathcal{H} = -k_2 J_z^2 + (k_1 - k_2) J_x^2 - g\mu_B (J_x H_x + J_y H_y), \tag{2}$$

where we have subtracted out a constant $k_2 \mathbf{J} \cdot \mathbf{J}$. The minima are now moved off the $\pm\hat{\mathbf{z}}$ axes toward the equator, but they continue to be degenerate, and should mix by tunnelling. Indeed, as $H_\perp$, the magnitude of the field in the *xy* plane, increases, both the angle through which the spin must tunnel and the energy barrier decrease, and we expect that the splitting Δ will increase.

At this point, two questions arise. First, how should one think of the tunnelling of a spin? And second, how large is the splitting? One way to answer the first question is to regard the last three terms as perturbations that give rise to transitions between various Zeeman levels or eigenstates of J_z. As usual, we denote the J_z value by m. The J_x^2 term gives rise to $\Delta m = 2$ transitions, and thus mixes $m = -10$ with $m = +10$ via the -8, -6, …, $+8$ states. The H_x and H_y terms give rise to $\Delta m = 1$ transitions, and mix $m = -10$ with $+10$ via all intermediate levels -9 to $+9$ (see figure 1a). This picture allows us to think of spin tunnelling in direct analogy with a particle tunnelling through an energy barrier.

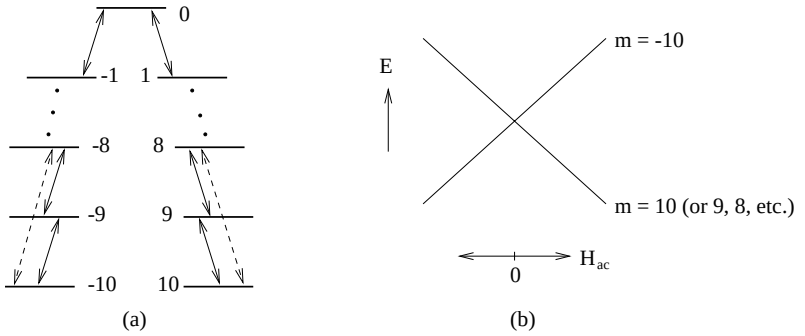

Figure 1. (**a**) Zeeman levels of Fe_8, showing $\Delta m = 1$ (solid lines) and $\Delta m = 2$ (dashed lines) transitions. (**b**) The Landau–Zener–Stückelberg process.

It is further obvious that if we also apply a field along the z direction so as to tune the energies of the -10 and $+9$ states to resonance, we can also think of tunnelling between these states. More generally, we can consider tunnelling between a state with $m = m_i$ on the negative m side and $m = m_f$ on the positive m side.

The second question is in some sense the main subject of this article. Yet it is useful to have an approximate answer before one embarks on a detailed calculation. For a massive particle tunnelling in a symmetric double well, the splitting can quite generally be written in the form

$$\Delta = c_1 \omega_0 \left(\frac{S_0}{2\pi}\right)^{1/2} \mathrm{e}^{-S_0}, \tag{3}$$

where ω_0 is the classical small oscillation frequency about the minima, S_0 is the tunnelling action or WKB exponent, and c_1 is a constant of order unity. Further, for a smooth potential, S_0 can be written as $c_2 V_0/\omega_0$, where V_0 is the energy barrier, and c_2 is another constant of order unity, generally close to 5. For the quartic potential $V(x) = V_0(x^2 - a^2)^2/a^4$, e.g., $c_1 = 4\sqrt{3}$ and $c_2 = 16/3$. To apply this approximate formula to the spin problem, we may take $V_0 = k_2 J^2$, but we still need ω_0. This, however, can be found by noting that the classical vector $\mathbf{J}$ can be given dynamics via Hamilton's equation and Poisson brackets:

$$\frac{\mathrm{d}\mathbf{J}}{\mathrm{d}t} = \{\mathbf{J}, \mathcal{H}\}_{\mathrm{PB}} = -\mathbf{J} \times \frac{\partial \mathcal{H}}{\partial \mathbf{J}}. \tag{4}$$

Then, $\dot{J}_x = 2k_2 J_y J_z$, and $\dot{J}_y = -2k_1 J_x J_z$. Linearizing around the equilibrium state $\mathbf{J} = J\hat{\boldsymbol{z}}$, we find that $\omega_0 = 2(k_1 k_2)^{1/2} J$. For Fe_8, $\omega_0 \approx 5.4$ K, and if we use the approximate formula (3) with the same c_1 and c_2 as for the quartic double well, we find that $\Delta \approx 60$ nK. This is an extraordinarily low splitting, of the order of 1 KHz in frequency units. At first sight, the question of how to experimentally detect such a low splitting would appear to be entirely moot, since each molecule experiences stray magnetic fields H' of about 200 Oe of dipolar and hyperfine origin. Consequently, the Zeeman levels $m = \pm 10$ are shifted from perfect degeneracy by an amount $\epsilon \simeq g\mu_b JH' \simeq 0.1$ K, which is enormous compared to Δ. Now to see any resonance at all between two states, the energy bias between them must be comparable to or less than the assumptive tunnelling amplitude. In Fe_8, exactly

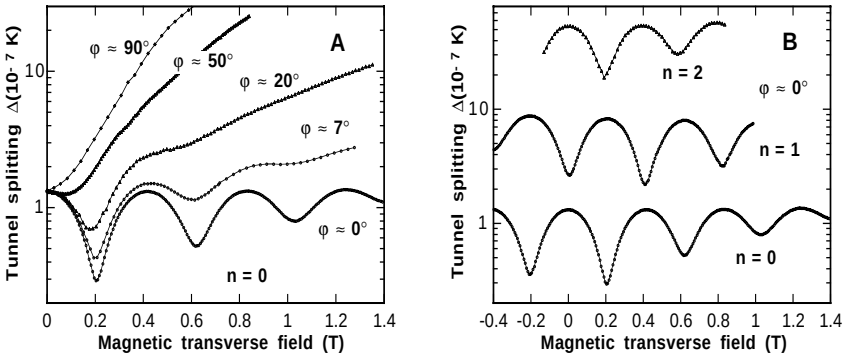

Figure 2. Measured splittings [6] for Fe_8 for (**a**) $-10 \leftrightarrow 10$ transitions for various orientations of $\mathbf{H}$ in the *xy* plane, and (**b**) for $\mathbf{H}||\hat{\mathbf{x}}$ between the states $m = -10$ and $m = 10 - n$. Figure courtesy of Dr Wernsdorfer.

the opposite is true, and it follows that left to itself, a molecule will almost never tunnel at all.

Wernsdorfer and Sessoli circumvent this problem by applying an ac magnetic field along $\hat{\mathbf{z}}$, in the shape of a triangular wave of period τ and amplitude H_0. As H_z changes with time, the energies of the $m = \pm 10$ states move in opposite directions, and cross at some point in the cycle. This induces what are known as Landau–Zener–Stückelberg (LZS) transitions [10,11]. In the limit where the crossing point is passed rapidly, the $-10 \leftrightarrow 10$ transition probability γ in each passage is very low, $\propto \Delta^2/(\mathrm{d}H/\mathrm{d}t)$. Since the stray fields are fluctuating randomly, different passages may be assumed to be independent, with no phase correlation between successive passages. The net LZS rate, or transition probability per unit time is given by

$$\Gamma_{\mathrm{LZS}} = \frac{2}{\tau}\gamma \approx \frac{\pi\Delta^2}{(g\mu_B\hbar)\Delta m H_0} \quad (\gamma \ll 1). \tag{5}$$

Wernsdorfer and Sessoli measure this rate by measuring the rate at which the magnetization, after having being initially saturated along the $-\hat{\mathbf{z}}$ direction, say, relaxes to its equilibrium direction under the influence of the ac longitudinal field, and a dc field, which may or may not have a longitudinal component.

The outcome of the experiments is shown in figure 2. (The temperature at which these data are taken is 0.36 K.) Our earlier expectation that Δ will increase monotonically as $H_\perp$ increases is seen to be false. When $\mathbf{H}||\hat{\mathbf{y}}$ ($\phi = 90°$), the behavior is monotonic, but when $\mathbf{H}||\hat{\mathbf{x}}$ ($\phi = 0°$), one finds that Δ oscillates with H_x!

3. Instanton approach to spin tunnelling

3.1 *General comments on instantons*

For massive particles, the instanton approach is an elegant and effective way to calculate tunnel splittings, especially between ground states [12,13]. Extended to spin, the basic idea

is to examine the imaginary time transition amplitude

$$U_{21} = \langle \hat{\mathbf{n}}_2 | \mathrm{e}^{-\mathcal{H}T} | \hat{\mathbf{n}}_1 \rangle, \tag{6}$$

where $\hat{\mathbf{n}}_{1,2}$ are the minima of the classical energy

$$E_{\mathrm{cl}}(\hat{\mathbf{n}}) = \langle \hat{\mathbf{n}} | \mathcal{H} | \hat{\mathbf{n}} \rangle, \tag{7}$$

and $|\hat{\mathbf{n}}\rangle$ is a maximal-projection spin coherent state, i.e., an eigenstate of $\mathbf{J} \cdot \hat{\mathbf{n}}$ with eigenvalue J.

In the $T \to \infty$ limit, only the lowest two energy eigenstates contribute in a spectral decomposition of eq. (6), and since these differ in energy by Δ, we get

$$U_{21} \sim \sinh(\Delta T), \tag{8}$$

ignoring inessential prefactors. If we can calculate U_{21} in this limit, comparison with eq. (8) will yield Δ. This calculation is done by appealing to the spin-coherent-state path integral

$$U_{21} = \int_{\hat{\mathbf{n}}_1}^{\hat{\mathbf{n}}_2} [\mathrm{d}\hat{\mathbf{n}}]\, \mathrm{e}^{-S[\hat{\mathbf{n}}(\tau)]}. \tag{9}$$

The paths $\hat{\mathbf{n}}(\tau)$ all run from $\hat{\mathbf{n}}_1$ at $-T/2$ to $\hat{\mathbf{n}}_2$ at $T/2$, and $S[\hat{\mathbf{n}}(\tau)]$ is the imaginary time or Euclidean action for the path. (This is why the exponent is $-S$ rather than $iS/\hbar$.)

Since T is tending to ∞, we can evaluate eq. (9) via the steepest descents approximation. The dominant paths, known as instantons, are just those that minimize the action, i.e. they are solutions to the classical equations of motion. The simplest such paths consist of a single transit from $\hat{\mathbf{n}}_1$ to $\hat{\mathbf{n}}_2$. If the scale over which E_{cl} varies is V, then it follows from eq. (4) that the time scale for this transit is $\tau_0 \sim J/V$. For the Hamiltonian (1), e.g., this time scale is $\omega_0^{-1} \sim J^{-1}(k_1 k_2)^{-1/2} \ll T$. Hence, the spin spends most of its time near the end points $\hat{\mathbf{n}}_{1,2}$, and the actual transit takes place in a very short time interval. (Hence the name instanton.) In the same way, we can find anti-instantons, solutions that go from $\hat{\mathbf{n}}_2$ to $\hat{\mathbf{n}}_1$. We now note that eq. (4) is autonomous, i.e., does not depend on τ explicitly. Therefore a translation of the center of the instanton yields an equally good classical path. Secondly, one can fit an arbitrary number of instantons followed by anti-instantons into the interval T. One finds that the n-instanton contribution to U_{21} is proportional to T^n, and the full series is that of a $\sinh$ [13]. The Δ which is obtained in this way can be written as

$$\Delta = D \exp(-S_{\mathrm{inst}}), \tag{10}$$

where S_{inst} is the action for a *single instanton* path, and D is a prefactor arising from doing the path-integral over small fluctuations about the instanton trajectory. If more than one instanton exists, we must add together the corresponding contributions from all of them.

In the application of this formalism to any tunnelling problem, it turns out that the calculation of S_{inst} is often very easy, while the calculation of D is quite hard. (Indeed, it turns out that the spin analogue of the van Vleck determinant for the general massive particle propagator has only recently been found in a completely logically consistent way [14–17].) Since the most interesting aspects of the Fe_8 problem can be understood at the level of the instanton action alone, and since the absolute scale of Δ can be found from the DPI method, we shall forego the calculation of D in this article.

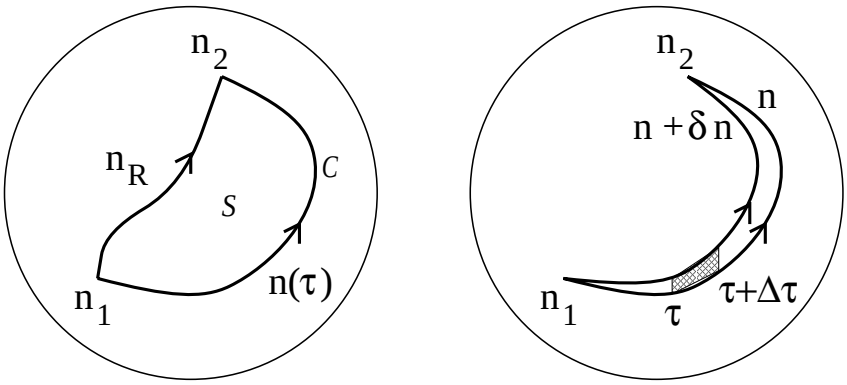

Figure 3. The kinetic term in the spin action, and its variation.

3.2 *Action for spin*

The interesting features of the spin problem lie in the form of the action,

$$S[\hat{\mathbf{n}}(\tau)] = iJ\mathcal{A}[\hat{\mathbf{n}}(\tau)] + \int_{-T/2}^{T/2} E_{\rm cl}[\hat{\mathbf{n}}(\tau)]\mathrm{d}\tau. \tag{11}$$

The term $\mathcal{A}[\hat{\mathbf{n}}(\tau)]$ is the kinetic term, and has the mathematical structure of a Berry phase. We write it as

$$\mathcal{A}[\hat{\mathbf{n}}(\tau)] = \int_{\mathcal{S}} \mathrm{d}\Omega \qquad (\mathcal{C} = \partial\mathcal{S} = \hat{\mathbf{n}}(\tau) - \hat{\mathbf{n}}_R), \tag{12}$$

by which we mean that $\mathcal{A}[\hat{\mathbf{n}}(\tau)]$ is the area of the patch $\mathcal{S}$ on the unit sphere, whose boundary $\mathcal{C}$ is the closed curve formed by the path $\hat{\mathbf{n}}(\tau)$ and a reference path $\hat{\mathbf{n}}_R$ (taken backwards) running from $\hat{\mathbf{n}}_1$ to $\hat{\mathbf{n}}_2$ (figure 3). The reference path $\hat{\mathbf{n}}_R$ is arbitrary, but must be the same for all $\hat{\mathbf{n}}(\tau)$ in the path integral. Its choice is equivalent to fixing the gauge. However, since we have defined $\mathcal{A}$ as a geometrical quantity, an area, it does not depend on how we choose coordinates on the unit sphere, and it is obviously nonsingular. Note also that on the sphere, each closed curve divides the sphere into two areas, and one cannot say which is inside or outside. (This is easily seen by thinking of the seam on a tennis ball.) The two areas differ by 4π, however, so $\mathrm{e}^{-iJ\mathcal{A}}$ is identical for the two of them for either integral or half-integral J, and hence this ambiguity does not affect the path integral.

Instead of deriving eq. (11), we shall show that it is correct by checking that its variation leads to the classical equation of motion. Suppose we vary the path $\hat{\mathbf{n}}(\tau)$ to $\hat{\mathbf{n}}(\tau) + \delta\hat{\mathbf{n}}(\tau)$. $\delta\mathcal{A}$ is given by the area of the thin sliver enclosed between the curves $\hat{\mathbf{n}}(\tau)$ and $\hat{\mathbf{n}}(\tau) + \delta\hat{\mathbf{n}}(\tau)$ (figure 3). The part of this area due to the segments between τ and $\tau + \delta\tau$ equals

$$\begin{aligned}\Delta(\delta\mathcal{A}) &= \Big[\delta\hat{\mathbf{n}}(\tau) \times [\hat{\mathbf{n}}(\tau + \Delta\tau) - \hat{\mathbf{n}}(\tau)]\Big] \cdot \hat{\mathbf{n}}(\tau) \\ &= \left(\delta\hat{\mathbf{n}}(\tau) \times \frac{\mathrm{d}\hat{\mathbf{n}}}{\mathrm{d}\tau}\right) \cdot \hat{\mathbf{n}}(\tau)\Delta\tau. \end{aligned} \tag{13}$$

Adding up the contributions from all the segments, we find the total change

$$\delta\mathcal{A} = \int \delta\hat{\mathbf{n}}(\tau) \cdot \left(\frac{\mathrm{d}\hat{\mathbf{n}}}{\mathrm{d}\tau} \times \hat{\mathbf{n}}(\tau) \right) \mathrm{d}\tau. \tag{14}$$

The variation of the second term in eq. (11) is trivial, and δS can be written as an integral of the form $\int \delta\hat{\mathbf{n}}(\tau) \cdot X$ where X depends on $\hat{\mathbf{n}}$ and E_{cl}. The extremal condition $\delta S = 0$ is thus

$$iJ \frac{\mathrm{d}\hat{\mathbf{n}}}{\mathrm{d}\tau} \times \hat{\mathbf{n}}(\tau) + \frac{\partial E_{\mathrm{cl}}}{\partial \hat{\mathbf{n}}} = 0. \tag{15}$$

Taking the cross product with $\hat{\mathbf{n}}$, and using the fact that $\hat{\mathbf{n}} \cdot (\mathrm{d}\hat{\mathbf{n}}/\mathrm{d}\tau) = 0$, we get

$$iJ \frac{\mathrm{d}\hat{\mathbf{n}}}{\mathrm{d}\tau} = -\left(\hat{\mathbf{n}} \times \frac{\partial E_{\mathrm{cl}}}{\partial \hat{\mathbf{n}}} \right). \tag{16}$$

This is exactly what we would get from eq. (4) with $\mathbf{J} = J\hat{\mathbf{n}}$ and the Wick rotation $t \to -i\tau$. In other words, it is the imaginary time equation for Larmor precession in the effective magnetic field $\partial E_{\mathrm{cl}}/\partial\hat{\mathbf{n}}$.

The actual evaluation of $\mathcal{A}$ is often more easily done by using Stokes' theorem to transform eq. (12) to a line integral. Using notation borrowed from electromagnetism, let us write $\mathrm{d}\Omega = \mathbf{B} \cdot \hat{\mathbf{n}}\, \mathrm{d}s$, where $\mathbf{B}(\hat{\mathbf{n}}) = \hat{\mathbf{n}}$, and $\mathrm{d}s$ is an area element. The line integral is $\oint_{\mathcal{C}} \mathbf{A} \cdot \mathrm{d}\hat{\mathbf{n}}$, with $\mathbf{B} = \nabla \times \mathbf{A}$. Since $\mathbf{B} = \hat{\mathbf{n}}$, it is a monopole field, which, as is known, cannot be represented in terms of a nonsingular vector potential. If this singularity is concentrated into a Dirac string at the south pole, we can write

$$\mathcal{A}[\hat{\mathbf{n}}(\tau)] = \oint_{\mathcal{C}} \left[1 - \cos\theta(\phi) \right] \mathrm{d}\phi, \tag{17}$$

where $\mathcal{C}$ is viewed as parametrized by ϕ. This formula is correct as long as $\mathcal{C}$ does not pass through the south pole, and provided one increments or decrements ϕ by 2π every time one crosses the date line.

3.3 *Application to Fe*$_8$

We now apply the above formalism to a discussion of the ground state tunnel splitting in Fe_8 when $\mathbf{H} \| \hat{\mathbf{x}}$, further limiting ourselves to finding the action, as this is sufficient to determine the field points where the splitting is quenched.

The main problem is to calculate the action for an instanton. To do this, however, we do not need to find the actual time dependence $\hat{\mathbf{n}}(\tau)$, since the energy is conserved along an instanton. To see this, note that by eq. (16)

$$\begin{aligned} \frac{\mathrm{d}E_{\mathrm{cl}}}{\mathrm{d}\tau} &= \frac{\partial E_{\mathrm{cl}}}{\partial \hat{\mathbf{n}}} \cdot \frac{\mathrm{d}\hat{\mathbf{n}}}{\mathrm{d}\tau} \\ &= \frac{i}{J} \frac{\partial E_{\mathrm{cl}}}{\partial \hat{\mathbf{n}}} \cdot \left(\hat{\mathbf{n}} \times \frac{\partial E_{\mathrm{cl}}}{\partial \hat{\mathbf{n}}} \right) \\ &= 0. \end{aligned} \tag{18}$$

Thus, using energy conservation, we can find the instanton orbit, i.e., the curve traced out on the unit sphere $\theta(\phi)$, without finding the actual time dependence. Using eq. (17), this is enough to find the action, as we can take $E_{\rm cl}$ itself to be zero by adjusting the zero of energy appropriately. One point to note is that since $\hat{\mathbf{n}}_1$ and $\hat{\mathbf{n}}_2$ are minima of $E_{\rm cl}$, there can be no real curve connecting these points on which $E_{\rm cl}$ is the same. The only way to find a solution to the instanton equations of motion is to let $\hat{\mathbf{n}}$ become complex. Correspondingly, the area $\mathcal{A}$ must also be defined on the complexified unit sphere.

The above discussion is applicable to any tunnelling problem. What is special about Fe_8 is the existence of *two* interfering instantons. If we choose the polar axis to be $\hat{\mathbf{x}}$ (not $\hat{\mathbf{z}}$), and measure the azimuthal angle in the *yz* plane from $\hat{\mathbf{y}}$, then we can write the energy as

$$E_{\rm cl}(\theta,\phi) = k_1 J^2(\cos\theta - \cos\theta_0)^2 + k_2 J^2 \sin^2\theta \sin^2\phi. \tag{19}$$

We have defined $\cos\theta_0 = H/H_c$, with $H_c = 2k_1 J/g\mu_B$, and added a constant to $E_{\rm cl}$ so that $E_{\rm cl} = 0$ along the instanton as discussed above. Writing $\cos\theta_0 = u_0$, the solution of this equation gives

$$\cos\theta = \frac{u_0 + i\lambda^{1/2}\sin\phi(1-u_0^2-\lambda\sin^2\phi)^{1/2}}{1-\lambda\sin^2\phi}. \tag{20}$$

However, it is clear that in this equation, we may take ϕ to lie in either of the two intervals $(0,\pi)$ and $(0,-\pi)$. Indeed, it is obvious from symmetry that there are two instanton paths, which wind about $\hat{\mathbf{x}}$ in opposite directions (see figure 4), and eq. (20) describes both of them. If we denote the two paths by A and B, then the imaginary parts of their actions ($= iJ\mathcal{A}$) are necessarily unequal, since by the interpretation of $\mathcal{A}$ as an area,

$$S_B - S_A = iJ \times \Omega, \tag{21}$$

where Ω [see eq. (12)] is the area enclosed between A and B (the peanut shape in figure 4). Using the line integral form (17), we obtain

$$\Omega = \int_{-\pi}^{\pi}\left(1 - \frac{u_0}{1-\lambda\sin^2\phi}\right)\mathrm{d}\phi = 2\pi\left(1 - \frac{u_0}{\sqrt{1-\lambda}}\right). \tag{22}$$

The real parts, on the other hand are equal and given by

$$\begin{aligned} S_R = \mathrm{Re}S_{\rm A,B} &= J\lambda^{1/2}\int_0^{\pm\pi}\frac{\sin\phi(1-u_0^2-\lambda\sin^2\phi)^{1/2}}{1-\lambda\sin^2\phi}\mathrm{d}\phi, \\ &= J\left[\ln\left(\frac{\sqrt{1-u_0^2}+\sqrt{\lambda}}{\sqrt{1-u_0^2}-\sqrt{\lambda}}\right)\right. \\ &\quad \left. -\frac{u_0}{\sqrt{1-\lambda}}\ln\left(\frac{\sqrt{(1-u_0^2)(1-\lambda)}+u_0\sqrt{\lambda}}{\sqrt{(1-u_0^2)(1-\lambda)}-u_0\sqrt{\lambda}}\right)\right]. \end{aligned} \tag{23}$$

The prefactors D are equal for both paths by symmetry, and so, adding together the two contributions, we get

$$\Delta = 2D\exp(-S_R)\cos(J\Omega/2), \tag{24}$$

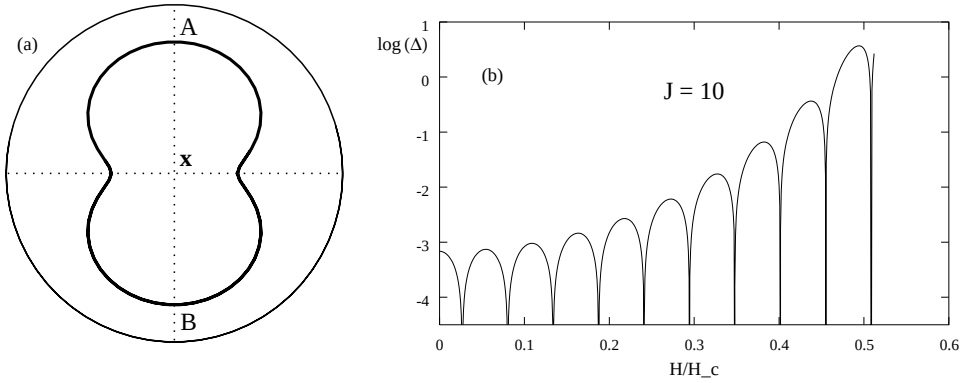

Figure 4. Interfering instanton trajectories, and numerically computed $-10 \leftrightarrow +10$ tunnel splitting for a model for Fe_8 with $\mathbf{H} \| \hat{\mathbf{x}}$.

which vanishes whenever

$$\frac{H}{H_c} = \frac{\sqrt{1-\lambda}}{J}\Big[J - n - \tfrac{1}{2}\Big], \tag{25}$$

where $n = 0, 1, \ldots, 2J-1$.

In figure 4 we also show the results of an explicit numerical diagonalization of the 21×21 Hamiltonian matrix for our model Hamiltonian for Fe_8 showing clearly that the effect is genuine. It should also be clear that the quenching phenomenon is a general one that will occur as long as $\mathcal{H}$ has the requisite symmetry, and that the detailed form will only change the locations of the quenching points. The minima in the tunnelling rate seen by Wernsdorfer and Sessoli are spaced approximately 50% further apart than implied by eq. (25). These differences are well understood in terms of higher order anisotropy corrections to the model Hamiltonian (1). These corrections do not change the centers of gravity of the levels by very much, but they affect the splittings significantly.

4. Discrete phase integral approach to spin tunnelling

It will not have escaped the reader that the Wernsdorfer and Sessoli data (figure 2b) also show an oscillation in the tunnelling amplitude for the $m = -10 \leftrightarrow +9$ and $-10 \leftrightarrow +8$ transitions. These oscillations were not predicted in ref. [9], and are nontrivial instances of a diabolical point, or conical intersection [18,19], a degeneracy obtained at isolated points in a two dimensional parameter space. In Fe_8, the parameters on which the Hamiltonian depends are H_x and H_z.

In retrospect, the new oscillations can also be understood in terms of path integrals, but it is simpler to adopt a different point of view, namely, the discrete phase integral (or WKB) method. The basic idea of this method is to directly solve Schrödinger's equation in the J_z basis as a recursion relation or difference equation, by making use of the similarity between difference and differential equations, and exploiting WKB type ideas used to solve the latter.

To see what is meant, suppose that $|\psi\rangle$ is an eigenstate of $\mathcal{H}$ with energy E. With $J_z|m\rangle = m|m\rangle$, $\langle m|\psi\rangle = C_m$, $\langle m|\mathcal{H}|m\rangle = w_m$, and $\langle m|\mathcal{H}|m'\rangle = t_{m,m'}$ ($m \neq m'$), we have

$$\sum_n{}' t_{m,n}C_n + w_m C_m = EC_m, \tag{26}$$

where the prime on the sum indicates that the term $n = m$ is to be omitted. This equation can be thought of as a tight binding model for an electron in a one-dimensional lattice with sites labelled by m, and slowly varying on-site energies (w_m), nearest-neighbor ($t_{m,m\pm1}$) hopping terms, next-nearest-neighbor ($t_{m,m\pm2}$) hopping terms, and so on. Under certain conditions (which we shall see below) we can understand the motion of the electrons in terms of wavepackets which are well localized in both quasi-momentum and real space. This is of course the approximation of semiclassical electron dynamics. As discussed in standard texts on condensed matter physics, this approximation works when the wavepacket can be assigned a real space width Δm much less than the length scale over which the properties of the electron band (in our case the w_m and $t_{m,m+\alpha}$) vary, and at the same time, a momentum space width Δq much less than the reciprocal bandwidth 2π. Since the two widths must be constrained by the uncertainty principle $\Delta q \Delta m \sim 1$, the real space width Δm must be much greater than the lattice constant (in our case 1). Formally, we need to be able to find smooth continuum approximants $w(m)$ and $t_\alpha(m)$, such that

$$w(m) = w_m, \tag{27}$$

$$t_\alpha(m) = (t_{m,m+\alpha} + t_{m,m-\alpha})/2, \quad \alpha = 1, 2, \ldots \tag{28}$$

whenever m is an eigenvalue of J_z, and that these quantities vary slowly enough that

$$\frac{\mathrm{d}w}{\mathrm{d}m} = O\left(\frac{w(m)}{J}\right), \quad \frac{\mathrm{d}t_\alpha}{\mathrm{d}m} = O\left(\frac{t_\alpha(m)}{J}\right). \tag{29}$$

These conditions are generally met when $J \gg 1$, which is also the semiclassical limit for spin that we expect intuitively.

Given the conditions (29), the basic approximation, which readers will recognize from the continuum case, is to write the wavefunction as a linear combination of the quasiclassical forms

$$C_m \sim \frac{1}{\sqrt{v(m)}} \exp\left(i \int^m q(m')\mathrm{d}m'\right), \tag{30}$$

where $q(m)$ and $v(m)$ obey the equations

$$E = w(m) + 2\sum_{\alpha\geq1} t_\alpha(m)\cos(\alpha q) \equiv \mathcal{H}_{\mathrm{sc}}(q, m), \tag{31}$$

$$v(m) = \partial\mathcal{H}_{\mathrm{sc}}/\partial q. \tag{32}$$

Equations (31) and (32) are the lattice analogues of the eikonal and transport equations. Equation (30) represents the first two terms in an expansion of $\log C_m$ in powers of $1/J$.

Previous work with the DPI method [20–24] has been limited to the case where the recursion relation has only three terms, i.e., only nearest neighbor hopping is present. Braun [23] mentions many problems in many areas (nuclear and atomic physics, to name just two) where the Schrödinger equation turns into a three-term recursion relation in a suitable basis. All the types of problems as in the continuum case can then be treated—Bohr–Sommerfeld quantization, barrier penetration, tunneling in symmetric double wells, etc. In addition, one can also use the method to give asymptotic solutions for various recursion relations of mathematical physics, such as those for the Mathieu equation, Hermite polynomials, Bessel functions, and so on. The interesting features all arise from a single fact — that the DPI approximation breaks down at the so-called *turning points*. These are points where $v(m)$ vanishes. One must relate the DPI solutions on opposite sides of the turning point by connection formulas, and the solution of all the diverse types of problems mentioned above depends on judicious use of these formulas.

For the Fe_8 Hamiltonian (1) with arbitrary **H**, the recursion relation involves five terms. The diagonal terms (w_m) arise from the J_z^2 and $J_z H_z$ parts of $\mathcal{H}$, the $t_{m,m\pm1}$ terms from the $J_x H_x$ and $J_y H_y$ parts, and the $t_{m,m\pm2}$ terms from the J_x^2 part. This seemingly minor modification is responsible for all the beautiful spectral features seen experimentally.

In the three term case, only $w(m)$ and $t_1(m)$ are present, so $\mathcal{H}_{\rm sc}(q,m) = w(m) + 2t_1(m)\cos q$, and $v(m) = -2\sin q(m) t_1(m)$. Hence, the turning points arise when $q = 0$ or $q = \pi$, corresponding to the local m-dependent band edges. This is completely analogous to the condition $V(x) = E$ that defines a turning point for a massive particle moving in a potential $V(x)$, in that a turning point is a limit of the classically allowed range of motion.

In the five term case, by contrast,

$$\mathcal{H}_{\rm sc}(q,m) = w(m) + 2t_1(m)\cos q + 2t_2(m)\cos(2q), \tag{33}$$

so that

$$v(m) = -2\sin q(m)\big(t_1(m) + 4t_2(m)\cos q(m)\big). \tag{34}$$

In addition to $q = 0$ and $q = \pi$, now the velocity can also vanish when $q = q_*(m)$, where

$$\cos q_*(m) = -t_1(m)/4t_2(m). \tag{35}$$

If we make use of the eikonal equation, we see that a turning point arises whenever

$$E = U_0(m),\ U_\pi(m),\ \text{or}\ U_*(m), \tag{36}$$

where,

$$U_0(m) = \mathcal{H}_{\rm sc}(0,m) = w(m) + 2t_1(m) + 2t_2(m), \tag{37}$$

$$U_\pi(m) = \mathcal{H}_{\rm sc}(\pi,m) = w(m) - 2t_1(m) + 2t_2(m), \tag{38}$$

$$U_*(m) = \mathcal{H}_{\rm sc}(q_*,m) = w(m) - 2t_2(m) - \frac{t_1^2(m)}{4t_2(m)}. \tag{39}$$

We call these curves *critical* curves; collectively they play the same role as the potential energy $V(x)$ in the continuum phase integral method in determining the turning points.

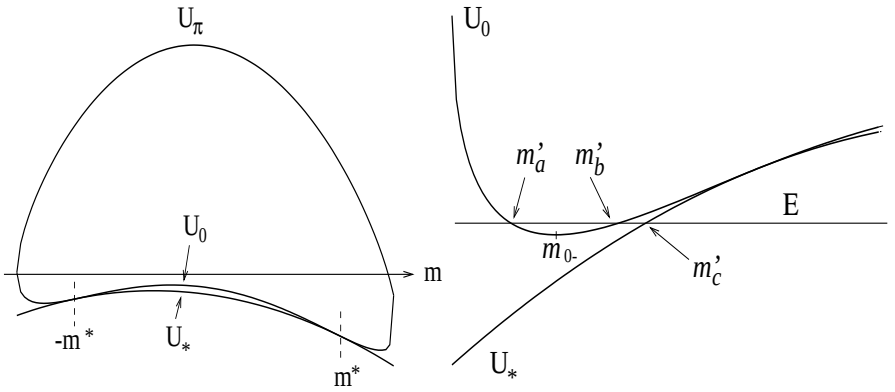

Figure 5. Critical energy curves for the Fe_8 Hamiltonian when **H** has both x and z components. In the right hand figure, the region near the left minimum of U_0 is magnified, showing the various turning points.

The new turning point $q_*(m)$ and the corresponding critical curve $U_*(m)$ have no analogue in the continuum case. This turning point need not be at the limit of the classically allowed energies for fixed m, and may lie strictly inside the band, or in the forbidden region outside it. We show the general form of the critical curves for Fe_8 when **H** has both *x* and *z* components in figure 5. The point m_c' is of this new type, and here it may be said to lie 'under the barrier.'

From this point on, the analysis of eigenfunctions and eigenvalues is conceptually straightforward, although quite lengthy, and we refer readers to already existing papers for the details [25,26]. The basic idea is simple. For an energy E such as that shown in figure 5b, the region $m_a' < m < m_b'$ is classically allowed, along with its counterpart for the right hand well. To find the eigenfunctions, one starts with a solution that is exponentially decaying to the left for $m < m_a'$, continues it through the turning points m_a', m_b', and m_c' by the use of connection formulas at each point, and matches it with a similar solution obtained by starting from the right. In general the wavefunctions will agree in the central region near $m = 0$ only if the energy E is properly chosen—this gives the eigenvalue condition. Nevertheless, as already stated, the calculation has several novel aspects. For example, referring to figure 5b, one should clearly have $\mathrm{Im}\, q(m) < 0$ in the region $m < m_a'$. In conventional WKB, there would be one solution satisfying this demand, but now there are *two*. As another example, the two solutions in the region $m_b' < m < m_c'$ which are both decaying exponentially to the right, turn into decaying solutions with an oscillatory envelope as the point m_c' is crossed. It is this oscillatory exponential solution (along with the concommitant fact that there must be two such solutions when they exist) that allows the tunnel splitting to vanish if H_x and H_z are chosen properly. Cutting short an already long tale, we give the results for the location of these points. The point where the ℓ'th level in the negative J_z well (with $\ell' = 0$ being the lowest level) and the ℓ''th level in the positive one are degenerate, is at $H_y = 0$, and

$$\frac{H_z(\ell', \ell'')}{H_c} = \frac{\sqrt{\lambda}(\ell'' - \ell')}{2J}, \tag{40}$$

$$\frac{H_x(\ell', \ell'')}{H_c} = \frac{\sqrt{1-\lambda}}{J}\left[J - n - \tfrac{1}{2}(\ell' + \ell'' + 1)\right], \tag{41}$$

with $n = 0, 1, \ldots, 2J - (\ell' + \ell'' + 1)$. Here, $\lambda = k_2/k_1$, and $H_c = 2k_1 J/g\mu_B$. Exactly as seen in the experiments, the $-10 \leftrightarrow 9$ points are shifted by half a period with respect to the $-10 \leftrightarrow 10$ points, the $-10 \leftrightarrow 8$ points are shifted by another half-period, and so on. Further, many of the degeneracies occur simultaneously, i.e., at the same values of H_x and H_z. This latter feature has only been tested indirectly in the experiments so far.

We conclude with an amusing fact about eqs (40) and (41). These are the leading $1/J$ results from a semiclassical analysis. Nevertheless, for the model (1), they are exact as written! This has been demonstrated in ref. [27], and while the exactitude is spoilt by the higher order anisotropies present in real Fe_8, the exact results may pave the way for a quantitative treatment of this and other perturbations.

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