SU(2) Instantons with Boundary Jumps and Spin Tunneling in Magnetic Molecules

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Coherent state path integrals are shown in general to contain instantons with jumps at the boundaries, i.e., boundary points lying outside classical phase space. Inclusion of these instantons is shown to resolve the "missing quench paradox" in the magnetic molecule Fe_8, i.e., the fact that the tunneling between the ground Zeeman states of this molecule is quenched at only four magnetic field values, instead of the ten that would be expected from the topological Berry phase between interfering instantons. An approximate formula is found for the location of the four remaining quenches.

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The purpose of this paper is to discuss two problems, a specific one and a general one. The specific problem concerns quantum tunneling between Zeeman levels of certain magnetic molecules [1]. The general problem concerns the nature of tunneling paths, or instantons, in coherent state or phase space path integrals [2]. As a rule, such paths can be found only if one complexifies phase space, i.e., allows the momenta, or the coordinates, or both, to become complex. However, in all previous studies of which we are aware, the instantons always start and end in real phase space, at the points corresponding to the classical energy minima. The new instantons reported here, by contrast, do not even have end points in real phase space. We refer to these as boundary jump instantons. Such paths are a basic part of the formal structure of coherent state and phase space path integrals [3,4], but there has never been a need to include them in tunneling problems, as paths without jumps have always been available [5]. This, as we shall show, is not an accident. Boundary jump instantons are analogous to extra saddle points in the method of steepest descents for one-dimensional integrals, and like them, may or may not be relevant in any given situation. But, one cannot ignore them *a priori*. In this paper we give the rules for finding these extra paths and their contribution to tunneling, and apply them to our illustrative example.

Inclusion of the jump instantons also resolves our specific problem, namely, the "missing quench paradox" in the magnetic molecule Fe_8. Tunneling between the ground Zeeman levels of Fe_8 is quenched at certain magnetic fields. This effect is widely viewed as being due to interference between two instantons, or Feynman paths, for the spin [6,7]. The relative phase between these paths is like a Berry phase, and its topological properties imply that there have to be 10 quenching fields. But, numerical diagonalization of a realistic Hamiltonian for Fe_8 including fourth order anisotropy energy reveals (see Fig. 1) only 4 quenches [1]. The Berry phase argument still applies, so it is puzzling how a quantitative detail (the fourth order terms) can produce qualitatively new behavior.

Let us now describe the Fe_8 system in more detail. The molecular ion $[(\mathrm{tacn})_6Fe_8O_2(OH)_{12}]^{8+}$ forms a solid in which different Fe_8 groups are essentially independent, and each behaves as a single spin of magnitude $J = 10$ in its ground manifold. The degeneracy of the 21 Zeeman levels is partly lifted by spin-orbit effects. In an external magnetic field H, the system is well described by the anisotropy Hamiltonian [8]

$$\mathcal{H} = k_1 J_z^2 + k_2 J_y^2 - C[(J_z + iJ_y)^4 + \mathrm{H.c.}] - g\mu_B J_z H, \tag{1}$$

where $\mathbf{J} = (J_x, J_y, J_z)$ is a spin operator, $k_1 > k_2 > 0$, and $C \geq 0$. For future use, we define reduced variables $\lambda = k_2/k_1$, $\lambda_2 = CJ^2/k_1$, and $h = H/H_c$, with $H_c = 2k_1J/g\mu_B$. Measurements yield $g \simeq 2$, $k_1 \simeq 0.338$ K, $k_2 \simeq 0.246$ K, and $C \simeq 29$ μK [1,9].

If $H = 0$, the spin has degenerate classical minima along $\pm\hat{\mathbf{x}}$, which cant symmetrically toward $\hat{\mathbf{z}}$ for $H > 0$. The ground level tunnel splitting $\Delta(H)$ is quenched at certain H as already mentioned. The two instantons that interfere to cause this wind about $\hat{\mathbf{z}}$ in opposite directions. Their actions differ by $iJ\mathcal{A}$, where $\mathcal{A}$ is a real Berry phase equal to the area enclosed between the two paths on the complexified unit sphere. Hence, $\Delta(H) = 0$ whenever $J\mathcal{A}(H)$ is an odd multiple of π. At $H = 0$, $\mathcal{A}(H) = 2\pi$ (half the full solid angle) by symmetry, so (for $J = 10$) as

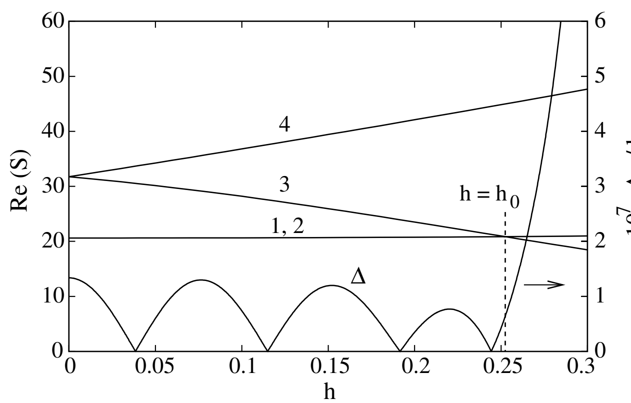

FIG. 1. ReS for the Fe_8 instantons, marked 1–4 as shown. S_3 and S_4 are purely real. Also shown is the ground pair splitting $\Delta(h)$.

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H increases, $J\mathcal{A}(H)$ has to pass through 19π, 17π, $\ldots$, π at some H, yielding 10 zeros of Δ for $H > 0$.

The number of zeros would appear to be robust against small perturbations that preserve the symmetry of $\mathcal{H}$. For $C = 0$, there is no problem: quenches occur at $H = [(2J - k)/2]\Delta H$, with $k = 1, 3, 5, \ldots, 4J - 1$, and $\Delta H = (1 - \lambda)^{1/2} H_c/J = 0.263$ T [7,10]. However, even a minute positive C has a dramatic effect. With the value for Fe_8, e.g., numerical diagonalization of $\mathcal{H}$ reveals only 4 zeros. Further, the spacing between zeros is increased by $\sim$50%. Since the C term is very small ($\lambda_2 = 8.58 \times 10^{-3}$), and it produces qualitatively new effects, it has all the hallmarks of a singular perturbation.

To analyze this problem, let us first review instantons for SU(2). In this method, one seeks a propagator such as $K_{fi} = \langle z_f | \exp[-\mathcal{H}T] | z_i \rangle$ via the path integral

$$K_{fi} = \int d[z] d[\bar{z}] e^{-S[\bar{z}(t), z(t)]} \tag{2}$$

in the limit $T \to \infty$. Here, $|z_{i,f}\rangle$ are (unnormalized) spin coherent states defined for any complex number z by $|z\rangle = e^{zJ_-}|J, J\rangle$, where $\mathbf{J}^2 |J, J\rangle = J(J+1)|J, J\rangle$ and $J_z |J, J\rangle = J|J, J\rangle$. Further, if $\hat{\mathbf{n}}$ has spherical polar coordinates (θ, ϕ), and $z = \tan(\theta/2) e^{i\phi}$, $\mathbf{J} \cdot \hat{\mathbf{n}} |z\rangle = J|z\rangle$. We will take the points z_i and z_f to be degenerate minima of the classical energy. S is the action for a path specified by $z(t)$ and $\bar{z}(t)$, and is given by (see Ref. [11], e.g.)

$$S = -\int_{-T/2}^{T/2} \left[J \frac{\dot{\bar{z}} z - \bar{z} \dot{z}}{1 + \bar{z} z} - E(\bar{z}, z) \right] dt, \tag{3}$$

where $\bar{z}$ is the formal complex conjugate of z, and

$$E(\bar{z}', z) = \langle z' | \mathcal{H} | z \rangle / \langle z' | z \rangle. \tag{4}$$

For $\mathcal{H}$'s such as (1) that are polynomial in J_i, $E(\bar{z}', z)$ is holomorphic in z and antiholomorphic in z' [12]. In Eq. (3), the first term is the Wess-Zumino or Berry phase term. We will refer to the two terms in S as the kinetic and dynamical terms, S_K and S_D.

To avoid confusion in what follows, the coordinates for a complex path must be clearly understood. In terms of θ and ϕ, this means that both θ and ϕ may be complex. Since $z = \tan(\theta/2) e^{i\phi}$ and $\bar{z} = \tan(\theta/2) e^{-i\phi}$, it follows that $\bar{z}$ need not equal z^*, the *true* complex conjugate of z. A point on the complex unit sphere (a four-dimensional manifold) is fixed by giving both z and $\bar{z}$. The real unit sphere is the submanifold with $\bar{z} = z^*$, and points on it may be specified by giving z alone (as we have done in speaking of "the points z_i and z_f" already).

Instantons are paths that start at z_i and end at z_f, and obey the Euler-Lagrange (EL) equations,

$$\dot{\bar{z}} = \frac{(1 + \bar{z} z)^2}{2J} \frac{\partial E}{\partial z}, \qquad \dot{z} = -\frac{(1 + \bar{z} z)^2}{2J} \frac{\partial E}{\partial \bar{z}}. \tag{5}$$

Along these paths energy is conserved, i.e., $dE(\bar{z}, z)/dt = 0$. Hence, and because z_i and z_f are energy minima, one cannot find a solution lying on the real unit sphere. We must complexify the path, i.e., allow $\bar{z}(t)$ to differ from $z^*(t)$. But, since $E[\bar{z}(t), z(t)] = E_{\min}$ (the minimum energy value) on the instanton, and since $E(z_i^*, z_i) = E(z_f^*, z_f) = E_{\min}$, one can always find an instanton with end points on the real sphere.

Let us illustrate this using Eq. (1) with $C = 0$. Then,

$$E(\bar{z}, z) = k_1 J^2 \left[\frac{(1 - \bar{z} z)^2 - \lambda (z - \bar{z})^2 - 2h(1 - \bar{z}^2 z^2)}{(1 + \bar{z} z)^2} \right]. \tag{6}$$

The minima are at $\bar{z} = z = \pm z_0$ where $z_0 = [(1 - h)/(1 + h)]^{1/2}$. From $E(\bar{z}, z) = E_{\min}$ $(= -k_1 J^2 h^2)$ we get

$$\bar{z} = \frac{\sqrt{\lambda}\, z \pm (1 - h)}{\sqrt{\lambda} \pm (1 + h) z}. \tag{7}$$

This relation connects $\bar{z}$ and z at every point along the instanton trajectory. For general z, $\bar{z} \neq z^*$, but if $z = \pm z_0$, $\bar{z} = z^*$. Thus the instanton end points are on the real sphere, but other points are not. From Eq. (7), we can now evaluate S, and recover previous results, along with the expected number of zeros in Δ (10 for $H > 0$) [7].

When C is turned on, the solutions (7) evolve smoothly, and continue to have classical end points, and to interfere. When we find the fields where Δ vanishes by calculating $J\mathcal{A}$ numerically, we continue to find (incorrectly) 10 zeros as per the Berry-phase argument.

The problem is that we have not formulated the principal of least action (or Hamilton principal function, to be precise) sufficiently carefully [3,4,11]. One must in fact include an explicit boundary term S_B in S:

$$S_B = J \ln \left[\frac{[1 + \bar{z}(-T/2) z_i][1 + \bar{z}_f z(T/2)]}{(1 + z_i^* z_i)(1 + \bar{z}_f \bar{z}_f^*)} \right]. \tag{8}$$

If we now vary $S = S_K + S_D + S_B$ *including the end points,* and set δS to 0, we discover of course the EL equations (5), but also that δS has no terms in $\delta \bar{z}(-T/2)$ and $\delta z(T/2)$. This implies the boundary conditions

$$z(-T/2) = z_i, \qquad \bar{z}(T/2) = \bar{z}_f, \tag{9}$$

on Eq. (5), i.e., $\bar{z}_i \equiv \bar{z}(-T/2)$ and $z_f \equiv z(T/2)$ must be left free. Otherwise, we would have four boundary conditions on a second order system of differential equations, and the problem would be overdetermined. The term S_B can also be found by careful time slicing of the propagator. Its inclusion in S has many other nice consequences: e.g., the Hamilton-Jacobi equations $\partial S^{\rm cl}/\partial \bar{z}_f = 2J/(\bar{z}_f + z_f^{-1})$, and $\partial S^{\rm cl}/\partial z_i = 2J/(z_i + \bar{z}_i^{-1})$.

Since $\bar{z}_i$ and z_f are not fixed, Eqs. (5) and (9) may have solutions with $\bar{z}_i \neq z_i^*$, $z_f \neq \bar{z}_f^*$. These are the boundary jump instantons. Their velocities $\dot{z}$ and $\dot{\bar{z}}$ do not vanish at the end points because $\partial E/\partial z$ and $\partial E/\partial \bar{z}$ are not zero.

Thus the instanton duration is finite, and although the energy $E(\bar{z}, z)$ is still a constant of motion, its value is not obvious. In fact, since $S_D = \int E(\bar{z}, z)\, dt$, we must choose $E = E_{\min}$. Otherwise, when we sum multi-instanton terms, the instantons with jumps will trivially dominate or be dominated by those without jumps. This point also emerges in Klauder's formulation. He argues that the continuum path integral is a formal construct with meaning only as a limit of its discrete version. So one may add a term to the integrand for S that is quadratic in $\dot{\bar{z}}$ and $\dot{z}$, with an infinitesimal coefficient ϵ that is sent to 0 at the end. The EL equations are then a fourth order system, and one may specify all four z_i, $\bar{z}_i$, $\bar{z}_f$, and z_f. The jump instantons then appear as solutions to the EL equations with internal boundary layers of thickness $O(\epsilon)$ since the terms in $\ddot{z}$ and $\ddot{\bar{z}}$ have coefficients ϵ. Energy is conserved in these boundary layers too, and when one takes the $\epsilon \to 0$ limit, they yield a contribution that is explicitly independent of ϵ (which makes the procedure legitimate), and is precisely equal to S_B above. Note that $S_B = 0$ for an instanton without jumps.

Hence the general procedure for finding all instantons is as follows. For any $\mathcal{H}$ with degenerate minima, we first find $E_{\min}$, and the classical minima (z_i^*, z_i), (z_f^*, z_f). We then find the allowed $\bar{z}_i$ values by solving the equation

$$E(\bar{z}, z_i) = E_{\min}\,. \tag{10}$$

This has a double root at $\bar{z} = z_i^*$, since $\partial E/\partial z$ and $\partial E/\partial \bar{z}$ both vanish at $(\bar{z}, z) = (z_i^*, z_i)$. However, it may also have extra roots at $\bar{z} \neq z_i^*$, which will then be the end points of instantons with jumps. (The procedure for z_f is analogous.) We then obtain $\bar{z}(z)$ for all instantons from energy conservation, making sure that they connect onto the appropriate end points. This is enough to compute S_K and S_B for each instanton (the time dependence is not needed), and $S_D = E_{\min}T$ for all of them. If we label the various instantons by α, we can write

$$\Delta = \sum_{\alpha} \gamma_\alpha e^{-S_\alpha}, \tag{11}$$

where γ_α is the prefactor arising from integrating over Gaussian fluctuations about each instanton. On physical grounds we expect γ_α to be of the same order for all α for smooth Hamiltonians, and it may be estimated as the small oscillation frequency about the minimum. (For instantons without boundary jumps, Ref. [13] formulates how to find γ_α.) Hence, the relative importance of various instantons is determined largely by the actions S_α.

Let us now return to our model (1). It may be verified that $E(\bar{z}, z) = P(\bar{z}, z)/(1 + \bar{z}z)^4$, where P is a polynomial of degree 4 in $\bar{z}$ and also in z. Thus Eq. (10) is a quartic in $\bar{z}$. Two of its roots are indeed z_i^*, and connect on to instantons without jumps, but two are different and distinct and connect to instantons with jumps. The equation $E(\bar{z}, z) = E_{\min}$ is also a quartic and the solution $\bar{z}(z)$ has four branches, corresponding to the different instantons.

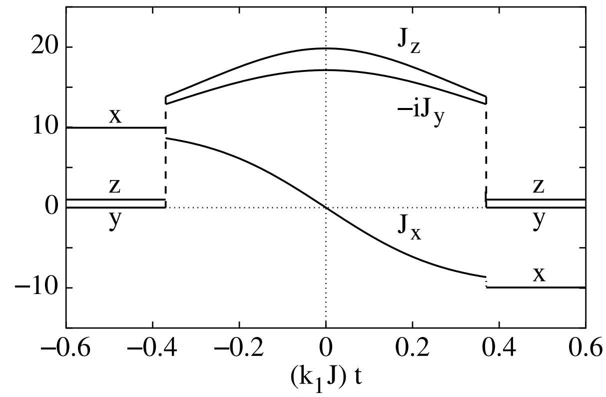

FIG. 2. Components of the spin vector $\mathbf{J}$ for jump instanton No. 3, for $H = 0.1H_c$.

We label the first two instantons, which have $\mathrm{Im}S \neq 0$, and interfere with each other, 1 and 2, and the last two, which have jumps and $\mathrm{Im}S = 0$, 3, and 4. An instanton with a jump at one end also has a jump at the other end. A 180° rotation about $\hat{\mathbf{z}}$ sends instanton 1 into 2, which guarantees $\mathrm{Re}S_1 = \mathrm{Re}S_2$, $\gamma_1 = \gamma_2$. We show instanton 3 in Fig. 2, 1 and 2 in Fig. 3 (all for $h = 0.1$), and $\mathrm{Re}S_\alpha(h)$ in Fig. 1. For any h, the dominant instanton is that with the least $\mathrm{Re}S$. Hence, except in the immediate vicinity of h_0, only instantons 1 and 2 are relevant for $h < h_0$, and only 3 is relevant for $h > h_0$. This explains why Δ does not oscillate for $h > h_0$.

We can find the quenching fields numerically, but we have also found an analytic approximation, based on the small parameter $\zeta \equiv 4\lambda_2 h^2$, which explains why they are so regularly spaced. This result may also be of wider interest, since Δ oscillations have now been seen in another system [14]. To derive this, it is better to use polar coordinates. With $u \equiv \cos\theta$, $s \equiv \sin\phi$, and

$$Z(s) \equiv 4\lambda_2(1 + 6s^2 + s^4), \tag{12}$$

$$R(s) \equiv 1 - \lambda s^2 + 12\lambda_2 s^2 + 4\lambda_2 s^4, \tag{13}$$

$$W(s) \equiv g_0 + h^2 + \lambda s^2 - 2\lambda_2 s^4, \tag{14}$$

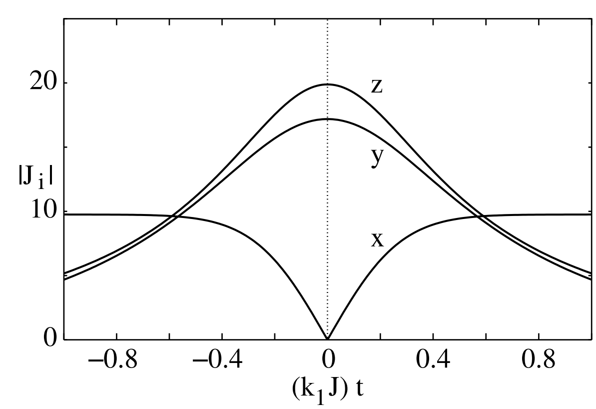

FIG. 3. A jump-free instanton for $H = 0.1H_c$. All components J_i are now complex, so their absolute values are shown. J_y slowly asymptotes to 0 as $t \to \pm\infty$.

the energy conservation condition reads

$$g(u,s) = -\tfrac{1}{2}Z(s)u^4 + R(s)u^2 - 2hu + W(s) = 0. \tag{15}$$

Here, $g_0 = -(\lambda + h^2) - E_{\min} \approx 2\lambda_2 h^4$. $g(u,s)$ has four roots $u(s)$. Regarding s as real, we are interested in the complex conjugate pair of roots which tend to the energy minima $\theta = \theta_0$, as $s \to 0$. Let the real and imaginary parts of these roots be $A(s)$ and $B(s)$, i.e., let $u(s) = A(s) \pm iB(s)$. The imaginary part of Eq. (15) gives

$$B^2 = A^2 - (R/Z) + (h/AZ), \tag{16}$$

and if we substitute this result for B into the real part, we get an equation for A alone:

$$4Z^2A^6 - 4RZA^4 + (R^2 + 2WZ)A^2 - h^2 = 0. \tag{17}$$

We now make the self-consistently verifiable assumption that $A = O(h)$. Then the terms ZA^4 and Z^2A^6 are $O(\zeta)$ and $O(\zeta^2)$ relative to the remaining terms, and may be dropped. This yields $A = h(R^2 + 2WZ)^{-1/2}$. The quantity $R^2 + 2WZ$ can be seen to be a fourth order polynomial in s, and depends on h only through the combination $\lambda_2(h^2 + g_0)$, which is $O(\zeta)$. If we neglect this weak h dependence, we get

$$A(\phi) \approx h(1 + P_2\sin^2\phi + P_4\sin^4\phi)^{-1/2}, \tag{18}$$

$$P_2 = -2\lambda + 24\lambda_2 + 8\lambda_2\lambda, \tag{19}$$

$$P_4 = \lambda^2 + 8\lambda_2 + 24\lambda\lambda_2 + 128\lambda_2^2. \tag{20}$$

Since $S_K = iJ\int(1 - \cos\theta)\dot{\phi}\,dt$ in θ, ϕ variables, $\mathcal{A} = 2\pi - \int_0^{2\pi} A(\phi)\,d\phi$. If we keep only instantons 1 and 2, $\Delta = 2\gamma_1\exp(-\mathrm{Re}S_1)\cos(J\mathcal{A}/2)$ up to a phase factor. Using Eq. (18), we see that the zeros of Δ are equally spaced with spacing $\Delta H = \pi H_c/JI(\lambda,\lambda_2)$, where

$$I(\lambda,\lambda_2) = \int_0^{\pi} \frac{d\phi}{(1 + P_2\sin^2\phi + P_4\sin^4\phi)^{1/2}}. \tag{21}$$

For the Fe_8 parameters, $I = 3.88$, implying $\Delta H = 0.409$ T. The experimental value is 0.41 T.

We conclude with some general remarks about instantons with boundary jumps (or internal boundary layers, in the Klauderian view). It is clear that they must be present in all coherent state path integrals, not just for spin, and our discussion is easily extended to these cases. It would be interesting to find other concrete instances where they occur, both in quantum mechanics, and in field theories. It would also be interesting to reexamine problems such as a particle in a one-dimensional potential well in a coherent state formulation.

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