Large transverse field tunnel splittings in the Fe$_8$ spin Hamiltonian

Anupam Garg

Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208

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Abstract

The spin Hamiltonian that describes the molecular magnet Fe$_8$ has biaxial symmetry with mutually perpendicular easy, medium, and hard magnetic axes. Previous calculations of the ground state tunnel splittings in the presence of a magnetic field along the hard axis are extended, and the meaning of the previously discovered oscillation of this splitting is further clarified.

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I. INTRODUCTION

The molecular magnetic cluster \([(\text{tacn}_6\text{Fe}_8\text{O}_2\text{OH})_{12}]^{8+}\) (henceforth abbreviated to \(\text{Fe}_8\)) is approximately described by a spin Hamiltonian of the type \([1–3]\)

\[\mathcal{H} = k_1 J_2^z + k_2 J_2^y - g \mu_B J \cdot H,\] (1.1)

where \(J\) is a dimensionless spin operator, \(k_1 > k_2 > 0\), and \(H\) is an externally applied magnetic field. For \(\text{Fe}_8\), \(J = 10\), \(k_1 \approx 0.33\) K, and \(k_2 \approx 0.22\) K. The zero-field Hamiltonian has biaxial symmetry with easy, medium, and hard axes along \(x\), \(y\), and \(z\) respectively \([4]\).

The magnetization dynamics of crystals of \(\text{Fe}_8\) and of a similar compound, \(\text{Mn}_{12}\)-acetate, show some remarkable phenomena \([2,5,6]\), which are not fully understood, and in this author’s view require a consideration of the spin-phonon interaction in addition to the pure spin Hamiltonian \((1.1)\) \([7,8]\). It is not the purpose of this paper to discuss these issues. It seems that at least some aspects of experimental behaviour \([9]\) can be understood on the basis of the spin Hamiltonian alone, and it is therefore worthwhile to address the simpler one-particle-quantum-mechanics problem of understanding the eigenvalue spectrum of Eq. \((1.1)\). Several authors have taken this position, and that is our motivation in this paper too.

In particular, we wish to focus on the behaviour of the two lowest energy levels when the external magnetic field \(H\) is along the hard axis, \(z\). It was predicted in Ref. \([10]\) that the tunnel splitting between these two levels would oscillate as a function of the field strength, and these oscillations appear to have been seen by Wernsdorfer and Sessoli \([9,4]\). Very briefly, for \(H < H_c = 2k_1J/g\mu_B\), the spin system has two classical ground states, in which the spin is canted away from the \(\pm x\) directions toward \(z\). The classical degeneracy of these states is lifted by quantum tunneling. The tunnel splitting, \(\Delta\), oscillates as a function of \(H\), vanishing at \(2J\) field values lying in the interval \((-H^*, H^*)\), where

\[H^* = (1 - \lambda)^{1/2}H_c,\] (1.2)

and \(\lambda = k_2/k_1\). (This quantity, along with other important parameter combinations, is tabulated in Table I.) The vanishing fields are located symmetrically around \(H = 0\); thus, in the case of half-integral \(J\), \(H = 0\) is a vanishing point, in accord with Kramers’ theorem.

The above calculation was done using instanton methods, wherein the oscillation in \(\Delta\) arises from the presence of two instantons, both of which have a complex Euclidean action. The imaginary parts of this action are equal and opposite for the two instantons (in a suitable gauge), and the vanishing of \(\Delta\) can be understood as due to superposition or destructive interference between the corresponding amplitudes \([11,12]\).

Recently, Chudnovsky and Hidalgo \([13]\) have examined this problem for \(H > H^*\), and noted that in this field range the splitting grows monotonically instead of oscillating. This is said by them to be a new topological effect or quantum interference phenomenon, arising from a new type of instanton. Indeed, their calculation of the splitting is quite intricate, and the imaginary part of the action vanishes due to a cancellation of two seemingly unrelated integrals, which they justifiably refer to as remarkable.

In fact, the monotonicity of \(\Delta\) for \(H > H^*\) is already known and, we shall argue, entirely expected on physical grounds. This is done in Sec. II. We shall also present another way of
calculating $\Delta$, which is a simple extension of that in Ref. [10], requiring nothing more than careful analytic continuation and contour integration. The imaginary part of the action vanishes in a simple and unremarkable way in this calculation. This is done in Sec. III.

II. PHYSICAL REASON FOR OSCILLATION OF TUNNEL SPLITTING

As noted in Ref. [14], there is another way to understand the vanishing of the tunnel splitting. For $H \parallel \hat{z}$, the Hamiltonian (1.1) becomes

$$H = k_1 J_z^2 + k_2 J_y^2 - g\mu_B H J_z,$$

(2.1)

which is invariant under a 180° rotation about $\hat{z}$. This symmetry is reflected in the selection rule $\langle m|H|m \pm 1 \rangle = 0$, where $|m\rangle$ is a $J_z$ eigenstate. The Hamiltonian divides into two disjoint subspaces, $V_+$, spanned by $m = J$, $J - 2$, ..., and $V_-$, spanned by $m = J - 1$, $J - 3$, .... The lowest eigenvalues (among others) from different spaces can cross as $H$ is varied. The vanishing of the tunnel splitting is no more than such a level crossing. It was shown in Ref. [14] (see also Fig. 1 there) that there are exactly $2J$ level crossings as $H$ varies from $-H_c$ to $H_c$. Since our previous instanton calculation [10] finds just as many crossings in the smaller field range ($-H^*, H^*$), it follows that there cannot be any more crossings or oscillations in $\Delta$ for $H > H^*$ (or $H < -H^*$). Chudnovsky and Hidalgo’s findings merely reflect this already known fact.

That $\Delta$ grows monotonically for large $H$ is also to be expected on physical grounds. As the field grows and approaches $H_c$, the classical ground state orientations approach closer to $\hat{z}$. The angle between them decreases, as does the energy barrier between them. The default behavior in such a case is for the splitting to grow. It is the oscillation in $\Delta$ which is surprising, not the monotonic growth.

The above argument shows that the vanishing of $\Delta$ is really not a topological effect in that it is not robust against perturbations such as a small misalignment of the magnetic field. Nevertheless, the instanton method provides an effective way of approximately calculating the splitting and the crossing points.

III. INSTANTON CALCULATION OF SPLITTING FOR $H > H^*$

We now show how to adapt the calculation of the tunnel splitting $\Delta$ in Ref. [10], where we only gave explicit results for $|H| < H^*$, to the case $H > H^*$. We refer readers to our previous paper for the calculational set-up. We also follow our previous notation, and summarize the important parameters in Table I.

In the instanton method, the splitting is given by

$$\Delta = \left| \sum_i \omega_i e^{-S_i} \right|,$$

(3.1)

where $\omega_i$ is a quantity with dimensions of frequency or energy, and $S_i$ is the Euclidean action along a semiclassical path, or instanton, connecting the two states between which one is tunneling. The sum runs over all possible instantons. In simple problems there is only
one instanton, but the converse is possible, especially in cases with high symmetry. This is
the case for our problem, where there are two instantons.

The dominant behavior of $\Delta$ is controlled by the action $S$, so we will focus on finding only
this quantity. For our problem, symmetry guarantees that the prefactors $\omega_i$ are identical
for the two instantons involved, and the vanishing or nonvanishing of $\Delta$ hinges entirely on
whether or not the actions $S_i$ are real or complex, and if the latter, what the relative phase
of the corresponding amplitudes is. Thus there is no need to find the prefactors explicitly.

The spin paths in question can be given in terms of spherical polar coordinates
$(\theta(\tau), \phi(\tau))$ where $\tau$ is an imaginary time. For a given path, the action is given by

$$ S = \int \left( iJ(1 - \cos \theta) \dot{\phi} + E(\theta, \phi) \right) d\tau, \quad (3.2) $$

where the dot denotes a $\tau$-derivative, and $E(\theta, \phi)$ is the classical energy or expectation value
of $\mathcal{H}$ in the spin coherent state that is maximally aligned along the direction $(\theta, \phi)$. For
Eq. (2.1), we get, up to an additive constant,

$$ E(\theta, \phi) = k_1 J^2 \left[ (\cos \theta - \cos \theta_0)^2 + \lambda \sin^2 \theta \sin^2 \phi \right], \quad (3.3) $$

where $\cos \theta_0 \equiv u_0 = H/H_c$, and $\lambda = k_2/k_1$. Note that $u_0$ and $\lambda$ are both less than unity.
This energy has minima at $(\theta, \phi) = (\theta_0, 0)$ and $(\theta_0, \pi)$, and the additive constant has been
adjusted to make $E = 0$ at these minima.

The instanton paths are those for which the action is stationary, and which thus obey
the Euler-Lagrange equations,

$$ iJ \dot{\theta} \sin \theta = \frac{\partial E}{\partial \phi} = 2\lambda k_1 J^2 \sin^2 \theta \sin \phi \cos \phi, \quad (3.4) $$
$$ iJ \dot{\phi} \sin \theta = -\frac{\partial E}{\partial \theta} = 2k_1 J^2 \sin \theta \left[ (\cos \theta - \cos \theta_0) - \lambda \cos \theta \sin^2 \phi \right]. \quad (3.5) $$

The boundary conditions are that the path approach the two minima as $\tau \to \pm \infty$.

Along an instanton, $E$ is conserved, so that the orbit without regard to its time depen-
dence can be found purely by using energy conservation. This point is of great utility in
calculating the instanton action, for if we arrange for $E$ to equal zero, the action is given
entirely by the first term in Eq. (3.2), which can be written as an integral over $\phi$:

$$ S_{\text{instanton}} = iJ \int (1 - \cos \theta(\phi)) d\phi. \quad (3.6) $$

In this integral, it is no longer necessary to regard $\phi$ as running over the original instanton
contour given by $\phi(\tau)$. Any deformation of this contour is allowed as long as it does not
encounter any singularities. This was the procedure followed in Ref. [10]. Setting $E = 0$ in
Eq. (3.3) we obtain

$$ \cos \theta = \frac{u_0 + i\lambda^{1/2} \sin \phi \mathcal{F}(\phi)}{1 - \lambda \sin^2 \phi}, \quad (3.7) $$

where

$$ \mathcal{F}(\phi) = (1 - u_0^2 - \lambda \sin^2 \phi)^{1/2}. \quad (3.8) $$
It is important to note that which branch of the square root is taken depends on whether the instanton starts (at \( \tau = -\infty \)) at \( \phi = 0 \) or \( \phi = \pi \). Let us consider the former case. It is obvious from symmetry that there are two instanton paths, \((\theta_{\pm}(\tau), \phi_{\pm}(\tau))\), which wind around \( \hat{z} \) in opposite senses. Examination of Eqs. (3.4) and (3.3) shows that we must take \( F(\phi) > 0 \) for both + and − instantons. The calculation is direct in the case \( u_0 < (1 - \lambda)^{1/2} \), which is equivalent to \( H < H^* \), for then, the integration contour for \( \phi \) can be taken to run from 0 to \( 0 \pm \pi \) while keeping \( F(\phi) \) real. The integration in Eq. (3.6) yields

\[
S_{\pm} = S_r \pm iS_i,
\]

where

\[
S_r = J \left[ \ln \left( \frac{\sqrt{1 - u_0^2} + \sqrt{1 - u_0^2}}{\sqrt{1 - u_0^2} - \sqrt{1 - u_0^2}} \right) - \frac{u_0}{\sqrt{1 - \lambda}} \ln \left( \frac{(1 - u_0^2)(1 - \lambda) + u_0 \sqrt{\lambda}}{(1 - u_0^2)(1 - \lambda) - u_0 \sqrt{\lambda}} \right) \right],
\]

\[
S_i = J \pi (1 - u_0/\sqrt{1 - \lambda}).
\]  

The splitting is thus proportional to \( \exp(-S_r) \cos(S_i) \), which oscillates as \( H \) is increased as discussed above. Note that \( S_i = 0 \) when \( u_0 = (1 - \lambda)^{1/2} \).

In the case when \( u_0 > (1 - \lambda)^{1/2} \), i.e., when \( H > H^* \), one may guess the answer by reasoning that it must be analytic in the magnetic field, and that there should be no imaginary part to the action, since \( \Delta \) grows with \( H \) as argued in Sec. II. And in fact, we notice that \( S_i \) is exactly what one would obtain if the denominators of the arguments of the logarithms in \( S_r \) were multiplied by \( -1 \), and the branches of the logarithm interpreted suitably. This leads us to write

\[
S_{\pm} = J \left[ \ln \left( \frac{\sqrt{\lambda} + \sqrt{1 - u_0^2}}{\sqrt{\lambda} - \sqrt{1 - u_0^2}} \right) - \frac{u_0}{\sqrt{1 - \lambda}} \ln \left( \frac{u_0 \sqrt{\lambda} + \sqrt{(1 - u_0^2)(1 - \lambda)}}{u_0 \sqrt{\lambda} - \sqrt{(1 - u_0^2)(1 - \lambda)}} \right) \right].
\]  

This expression is real when \( H > H^* \). In the other case, it can be made to agree with Eqs. (3.10) and (3.11) if we stipulate that for \( x < 0 \), \( \ln x \) is to be taken as \( \ln |x| \mp i\pi \) for \( S_{\pm} \). It turns out that Eq. (3.12) is correct.

Some readers may find the above argument too glib and reasoned after the fact. Is it possible to obtain it by honest calculation? The immediate problem is that when \( u_0 > (1 - \lambda)^{1/2} \), \( F(\phi) \) is imaginary for \( \phi \) in the real interval \( \mathcal{M} = (\phi_1, \pi - \phi_1) \), where \( \sin^2 \phi_1 = (1 - u_0^2)/\lambda \). One can proceed just as in the low field case by using Eqs. (3.6) and (3.7), keeping \( \phi \) real. \( \cos \theta \) is then purely real in the interval \( \mathcal{M} \), and the resulting imaginary contribution to the action cancels that from outside \( \mathcal{M} \). This cancellation has the same unsatisfactory and accidental character as that in Chudnovsky and Hidalgo’s calculation [13]. Further, one cannot decide which branch of \( F(\phi) \) should be used in \( \mathcal{M} \) solely from energy conservation.

Another procedure, which also entails simpler integrals, is to find the \( \tau \)-dependence of the instanton, and evaluate \( S \) as an integral over \( \tau \) via Eq. (3.2). We record the relevant formulas for the case \( H < H^* \) first. Only one instanton, say the + one, need be considered explicitly. Substituting Eq. (3.7) in Eq. (3.3) we obtain

\[
\dot{\phi} = \omega_0 \sin \phi F(\phi),
\]  

which
where \( \omega_0 = 2k_1J\lambda^{1/2} \). This equation can be integrated easily. Defining \( z = (1 - u_0^2)^{1/2}\omega_0\tau \), and

\[
G(z) = (1 - u_0^2 - \lambda \tanh^2 z)^{1/2},
\]

we obtain

\[
\cos \phi = -(1 - u_0^2 - \lambda)^{1/2} \tanh z/G(z), \quad \text{or,}
\]

\[
\tanh z = -(1 - u_0^2)^{1/2} \cos \phi/F(\phi).
\]

It is easily verified that \( \phi \to 0, \pi \), as \( \tau \to \pm \infty \).

We also obtain

\[
\frac{d\phi}{dz} = (1 - u_0^2)^{1/2}(1 - u_0^2 - \lambda)^{1/2} \text{sech} z/G^2(z),
\]

\[
1 - \cos \theta = (1 - u_0^2 - \lambda - u_0\lambda \text{sech}^2 z + i(1 + u_0)\lambda^{1/2}(1 - u_0^2 - \lambda)^{1/2} \text{sech} z)
\]

\[
(1 - u_0^2)(1 - \lambda) - u_0^2 \lambda \tanh^2 z.
\]

When \( u_0 > (1 - \lambda)^{1/2} \), it is clear that Eqs. (3.13–3.18) must continue to hold as general analytic relations since they arise from integration of the equations of motion which are unchanged. The only subtlety is in the assignment of branches to the various multivalued quantities and functions involved. Properly speaking, the integral in Eq. (3.6) should be taken over a \( \phi \) contour which is suitably indented around the branch points. It is clearly permissible to parametrize this contour in terms of any other variable, and one choice which is often convenient is to use the original time-like variable \( \tau \), but allow it to become complex. With this point in mind we first make \( F(\phi) \) analytic by using a two-sheeted \( \phi \) plane with a branch cut joining the points \( \phi = \phi_1 \) and \( \pi - \phi_1 \). We then integrate Eq. (3.13) as

\[
z = \int_{\Gamma} \frac{(1 - u_0^2)^{1/2}}{\sin \phi F(\phi)} d\phi,
\]

where the contour \( \Gamma \) is shown in Fig. 1. We leave it to the reader to verify that a consistent phase assignment can be made to \( F(\phi) \) in such a way that along this contour, we have

\[
\arg F(\phi) = \begin{cases} 
0 & \phi < \phi_1; \phi > \pi - \phi_1; \\
\pi/2 & \phi_1 < \phi < \pi - \phi_1.
\end{cases}
\]

The corresponding contour \( C \) traced out in the \( z \) plane is drawn in Fig. 2. The easiest way to see this is that for \( \phi \) outside the cut, the integrand in Eq. (3.19) is real, so the corresponding parts of \( C \) must be parallel to the real axis. Secondly, the change in \( z \) as \( \phi \) runs across the cut is given by

\[
\Delta z = e^{-i\pi/2} \int_{\phi_1}^{\pi - \phi_1} \frac{\sin \phi_1}{\sin \phi (\sin^2 \phi - \sin^2 \phi_1)^{1/2}} d\phi = -i\pi.
\]

Using the arbitrary constant of integration to adjust the overall vertical position of \( C \), we arrive at Fig. 2. We do not bother to ask how \( C \) is indented around the poles of \( \tanh z \) at
±iπ/2, because it turns out that the integrand for the action integral is analytic at these points.

The problem is now reduced to integrating the product of the factors \((1 - \cos \theta)\) and \(d\phi/dz\) over the contour \(C\). The factors are given by Eqs. (3.17) and (3.18), with the proviso that

\[
(1 - u_0^2 - \lambda)^{1/2} \to i(u_0^2 + \lambda - 1)^{1/2}. \tag{3.22}
\]

The correctness of this choice follows by noting that for \(\phi = \pi/2\), \(\dot{\phi} = \omega_0(1 - u_0^2 - \lambda)^{1/2}\), which must be positive and imaginary given our contour \(C\). Collecting together Eqs. (3.22), (3.17), (3.18), and (3.2), we obtain

\[
S_+ = J \frac{(1 - u_0^2)^{3/2}(u_0^2 + \lambda - 1)^{1/2}}{1 + u_0} \times \int_C \frac{u_0^2 + \lambda - 1 + u_0 \lambda \text{sech}^2 z - \lambda^{1/2}(u_0^2 + \lambda - 1)^{1/2}(1 + u_0) \text{sech} z}{(1 - u_0^2)(1 - \lambda) - u_0^2 \lambda \text{tanh}^2 z} (1 - u_0^2 - \lambda \text{tanh}^2 z) \text{sech} z \, dz. \tag{3.23}
\]

All square roots in this formula are regarded as positive. We now introduce the definitions

\[
\tanh^2 z_1 = \frac{(1 - u_0^2)(1 - \lambda)}{u_0^2 \lambda}, \quad \tanh^2 z_2 = \frac{1 - u_0^2}{\lambda}, \tag{3.24}
\]

and the attendant results

\[
\text{sech} z_2 = u_0 \text{sech} z_1 = \lambda^{-1/2}(u_0^2 + \lambda - 1)^{1/2}. \tag{3.25}
\]

The result for \(S_+\) simplifies greatly in terms of these quantities. The apparent singularities at \(z = \pm z_1\) and \(z = \pm z_2\) are cancelled by factors in the numerator, and we end up with

\[
S_+ = J \frac{(1 - u_0^2)^{3/2}(u_0^2 + \lambda - 1)^{1/2}}{u_0 \lambda(1 + u_0)} \int_C \frac{\text{sech} z}{(\text{sech} z + \text{sech} z_1)(\text{sech} z + \text{sech} z_2)} \, dz. \tag{3.26}
\]

The integrand now has no singularities in the strip \(-\pi < \text{Im} z < \pi\). The contour \(C\) may thus be deformed into the real line, which proves that \(S_+\) is purely real. The actual integral itself is elementary, and may be done with the help of Ref. [15]. The final result is given by Eq. (3.12). The same result is obtained for \(S_-\).

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* Electronic address: agarg@nwu.edu

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FIGURES

FIG. 1. The integration contour $\Gamma$ in the $\phi$ plane. The heavy line denotes a branch cut, and the dashed section of the contour lies on the second Riemann sheet.

FIG. 2. The contour $\mathcal{C}$ in the complex $z$ plane.
TABLES

TABLE I. Summary of important parameter combinations

| Quantity  | Formula |
|-----------|---------|
| $H_c$     | $2k_1J/g\mu_B$ |
| $u_0, \cos \theta_0$ | $H/H_c$ |
| $\lambda$ | $k_2/k_1$ |
| $H^*$     | $(1 - \lambda)^{1/2}H_c$ |
| $\omega_0$ | $2J(k_1k_2)^{1/2}$ |
| $\sin \phi_1$ | $|(1 - u_0^2)/\lambda|^{1/2}$ |
| $z$       | $(1 - u_0^2)^{1/2}\omega_0\tau$ |
Fig. 1.
Fig. 2