Lost and found: The missing diabolical points in the Fe_8 molecular magnet

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Certain diabolical points in the tunneling spectrum of the single-molecule magnet Fe_8 were previously believed to be have been eliminated as a result of a weak fourth-order anisotropy. As shown by Bruno, this is not so, and the points are only displaced in the magnetic field space along the medium anisotropy direction. The previously missing points are numerically located by following the lines of the Berry curvature. The importance of an experimental search for these rediscovered points is discussed.

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The purpose of this note is to report on a numerical search of certain diabolical points (DP's) in the energy spectrum of Fe_8 that were earlier believed to be missing, but are in fact not so [1]. Several other DP's *have* been seen experimentally in Fe_8 [2], and their observation provides the best evidence of spin orientation tunneling between deep levels in all molecular magnets studied to date. Observation of even some of the missing DP's would advance our understanding of Fe_8 substantially.

For a system whose Hamiltonian depends on some parameter, a DP is a point in parameter space where two (or more) energy levels are degenerate. In Fe_8, the parameter is the static applied magnetic field, and the locations of the DP's so far observed (as well as many other experimental measurements) are well described by the following anisotropy Hamiltonian:

$$\mathcal{H} = k_1 J_x^2 + k_2 J_y^2 - C(J_+^4 + J_-^4) - g\mu_B \mathbf{J}\cdot\mathbf{H}. \qquad (1)$$

Here $\mathbf{J} = (J_x, J_y, J_z)$ is the spin of magnitude 10, $\mathbf{H}$ is an external magnetic field, $k_1 \simeq 0.338$ K, $k_2 \simeq 0.246$ K, $C \simeq 29\,\mu$K, and $g \simeq 2$. The DP's can be understood as arising when tunneling between two states with (nearly) oppositely oriented magnetic moment is quenched because of destructive interference between instantons (spin tunneling trajectories) [3, 4].

The model Hamiltonian (1) was first analyzed in 1993 [3] with $C = 0$, and it was found that for ground state tunneling it had 10 DP's along the positive H_x axis, corresponding to $J = 10$. In reality only 4 DP's are seen [2], which was explained in Ref. [5] as follows. When $C \neq 0$, we get two new (but noninterfering) instantons, which are discontinuous at the end points. One of these instantons has the least action for $H_x \gtrsim H^*$, where H^* is just beyond the location of the fourth DP, and since it has no interfering partner, there are no more DP's for $H_x > H^*$.

However, as shown by Bruno [1], the above picture, though correct, is incomplete. For any energy level, the sum of the Chern numbers for all DPs involving that level is a topological invariant as parameters like k_1, k_2, or C are varied. Since DP's in any system are generically simple, we expect this to be so in Fe_8 also, and the Chern number for any one DP should be ± 1 whether $C = 0$ or $C \neq 0$. Hence the six missing DP's must be present elsewhere in magnetic field space. For tunneling between the ground states, they merely move off the x axis into the xy plane. For the higher energy levels, they move off the xz plane into the full three dimensional $\mathbf{H}$ space. This point can also be understood by noting that for a system with purely four-fold symmetry ($k_2 = k_1$, $C \neq 0$), the ground state DP's lie on the $\pm\hat{\mathbf{x}} \pm \hat{\mathbf{y}}$ axes, while for the excited states they lie in the planes formed by these axes and the $\hat{\mathbf{z}}$ axis [6]. When both two-fold and four-fold anisotropies are present ($k_2 \neq k_1$, $C \neq 0$), it is then not surprising that the location of some of the DP's is also intermediate [1].

Observation of these rediscovered DPs would be interesting in itself, and also provide an important test of the validity of the model (1) vs. other models [7] that add extra 6th and 8th order anisotropies because the location of the DPs is very sensitive to the higher order anisotropies. With this motivation, we have undertaken a search for the DP's for the ground state and some of the excited states. We stress that the key insight that these points should exist in the first place is due to Bruno, and our contribution is only to find their specific locations. Neverthless, finding them is not without challenge as we discuss next.

A direct search for the DPs by numerical minimization of the energy differences fails because the energy surface is like a golf course with rolling hills on which the DPs are the holes. Because the holes are so localized, unless one starts close to one of them by luck, any numerical algorithm will simply head for the valleys of the course and miss the holes entirely. Because $\mathcal{H}$ is not real for general $\mathbf{H}$, we cannot also corral the DPs by using the Longuet-Higgins theorem to find and successively bisect a sign-reversing circuit [6]. We therefore proceed as follows. Let us denote the eigenstates and eigenvalues of Eq. (1) for fixed $\mathbf{H}$ by $|n(\mathbf{H})\rangle$ and $E_n(\mathbf{H})$, $n = 1,\ 2, \ldots, 21$, and order them so that $E_n \geq E_{n-1}$ for every $\mathbf{H}$. Except at degeneracies (the DPs), the Berry curvature for the nth

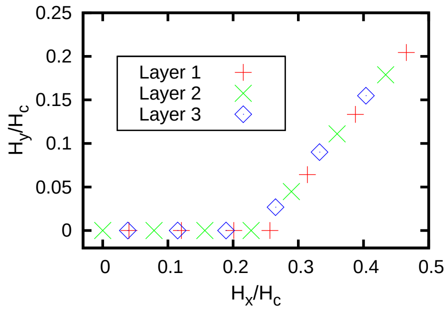

FIG. 1: Diabolic points of Fe_8 in the first three layers projected onto the xy plane. $H_c = 2k_1J/g\mu_B$.

level is defined by [8]

$$\mathbf{B}_n = -\mathrm{Im} \sum_{n' \neq n} \frac{\langle n|\boldsymbol{\nabla}_{\mathbf{H}}\mathcal{H}|n'\rangle \times \langle n'|\boldsymbol{\nabla}_{\mathbf{H}}\mathcal{H}|n\rangle}{(E_{n'} - E_n)^2}, \tag{2}$$

Near a DP, $\mathbf{B}_n$ has the form of a monopole field with flux equal to $\pm 2\pi$ (see below). Hence, to find the DPs, we numerically evaluate $\mathbf{B}_n$ for an initial $\mathbf{H}$, and follow the lines of $\mathbf{B}_n$ in the direction of increasing strength until we hit a monopole. Since the number of DPs where levels n and $n+1$ are degenerate is topologically fixed and known, all the DPs can be found by taking sufficiently many initial values of $\mathbf{H}$. The DPs for successive pairs of levels occur in layers, with H_z essentially constant in a layer. With $\mathbf{h} \equiv g\mu_B \mathbf{H}/2k_1 J$, the first three layers are at $h_z = 0$ (exactly), 0.0427, and 0.0854, and their projections onto the xy plane are shown in Fig. 1. For the lowest two levels (first layer), the DPs are at $(h_x, h_y) = (0.0404, 0)$, $(0.121, 0)$, $(0.201, 0)$, $(0.257, 0)$, $(0.314, \pm 0.0642)$, $(0.388, \pm 0.133)$, $(0.466, \pm 0.204)$.

In the rest of this note, we discuss the form of the Berry curvature near a DP in more detail. For simplicity, we will divide $\mathcal{H}$ by $k_1 J^2$. Since $\boldsymbol{\nabla}_{\mathbf{H}}\mathcal{H}$ and E_n are both divided by this factor, it follows from Eq. (2) that $\mathbf{B}_n$ is unchanged. With this preliminary remark, let us suppose that $E_n = E_{n-1} \equiv E_{n,n-1}$ at $\mathbf{h} = \mathbf{h}_{n,n-1}$, and denote

$$\mathbf{r} = \mathbf{h} - \mathbf{h}_{n,n-1}. \tag{3}$$

Further, let us make a particular choice of the two degenerate states at $\mathbf{r} = 0$, and denote them by $|a\rangle$ and $|b\rangle$, with $\langle b|a\rangle = 0$. (Any orthogonal linear combination of $|a\rangle$ and $|b\rangle$ would also work.) It suffices to truncate the Hamiltonian to this two dimensional subspace since the sum in Eq. (2) is dominated by degenerate states. Hence, at $\mathbf{r} = 0$, we have

$$\mathcal{H} = E_{n,n-1} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{4}$$

For small enough $\mathbf{r}$, we can take $|a\rangle$ and $|b\rangle$ to be unchanged, so

$$\boldsymbol{\nabla}_{\mathbf{h}}\mathcal{H} = -\frac{2}{J} \begin{pmatrix} \mathbf{J}_{aa} & \mathbf{J}_{ab} \\ \mathbf{J}_{ba} & \mathbf{J}_{bb} \end{pmatrix}, \tag{5}$$

where $\mathbf{J}_{aa} = \langle a|\mathbf{J}|a\rangle$ etc. Next, let us define $\mathbf{J}_{aa} + \mathbf{J}_{bb} = J\mathbf{s}$, $\mathbf{J}_{aa} - \mathbf{J}_{bb} = J\mathbf{u}$, $\mathbf{J}_{ab} = J(\mathbf{v} + i\mathbf{w})/2$, where $\mathbf{s}$, $\mathbf{u}$, $\mathbf{v}$, and $\mathbf{w}$ are real vectors. In terms of these vectors, we have

$$\mathcal{H} = -\frac{\mathbf{s}\cdot\mathbf{r}}{J} - \begin{pmatrix} \mathbf{u}\cdot\mathbf{r} & (\mathbf{v}+i\mathbf{w})\cdot\mathbf{r} \\ (\mathbf{v}-i\mathbf{w})\cdot\mathbf{r} & \mathbf{u}\cdot\mathbf{r} \end{pmatrix}. \tag{6}$$

Ignoring the constant $-\mathbf{s}\cdot\mathbf{r}/J$, the eigenvalues of this matrix are $\pm\epsilon(\mathbf{r})$, with

$$\epsilon(\mathbf{r}) = [(\mathbf{u}\cdot\mathbf{r})^2 + (\mathbf{v}\cdot\mathbf{r})^2 + (\mathbf{w}\cdot\mathbf{r})^2]^{1/2}. \tag{7}$$

To write the eigenvectors compactly, we define

$$\begin{aligned} \cos\theta(\mathbf{r}) &= \mathbf{u}\cdot\mathbf{r}/\epsilon(\mathbf{r}), && (8) \\ \sin\theta(\mathbf{r})e^{i\varphi(\mathbf{r})} &= (\mathbf{v}+i\mathbf{w})\cdot\mathbf{h}/\epsilon(\mathbf{r}). && (9) \end{aligned}$$

The eigenvectors are then

$$|-\rangle = \begin{pmatrix} \cos\frac{1}{2}\theta \\ \sin\frac{1}{2}\theta e^{-i\varphi} \end{pmatrix}, \quad |+\rangle = \begin{pmatrix} \sin\frac{1}{2}\theta \\ -\cos\frac{1}{2}\theta e^{-i\varphi} \end{pmatrix}. \tag{10}$$

Further abbreviating $c = \cos\frac{1}{2}\theta$ and $s = \sin\frac{1}{2}\theta$, and $\mathbf{g} = \langle +|\boldsymbol{\nabla}_{\mathbf{h}}\mathcal{H}|-\rangle$, we have

$$\mathbf{g} = -2cs\mathbf{u} - s^2 e^{-i\varphi}(\mathbf{v}+i\mathbf{w}) + c^2 e^{i\varphi}(\mathbf{v}-i\mathbf{w}). \tag{11}$$

It then follows that

$$\mathbf{g}\times\mathbf{g}^* = 2i[\cos\theta(\mathbf{v}\times\mathbf{w}) + \sin\theta\cos\varphi(\mathbf{w}\times\mathbf{u}) + \sin\theta\sin\varphi(\mathbf{u}\times\mathbf{v})], \tag{12}$$

so that

$$\mathbf{B}_+ = \frac{-1}{2\epsilon^3(\mathbf{r})}\left[(\mathbf{u}\cdot\mathbf{r})(\mathbf{v}\times\mathbf{w}) + (\mathbf{v}\cdot\mathbf{r})(\mathbf{w}\times\mathbf{u}) + (\mathbf{w}\cdot\mathbf{r})(\mathbf{u}\times\mathbf{v})\right]. \tag{13}$$

This is clearly of monopole form with appropriately scaled and sheared axes.

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