Berry Phase, Topology, and Degeneracies in Quantum Nanomagnets

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(Received 18 November 2005; published 22 March 2006)

A topological theory of the diabolical points (degeneracies) of quantum magnets is presented. Diabolical points are characterized by their *diabolicity index*, for which topological sum rules are derived. The paradox of the missing diabolical points for Fe_8 molecular magnets is clarified. A new method is also developed to provide a simple interpretation, in terms of destructive interferences due to the Berry phase, of the *complete* set of diabolical points found in biaxial systems such as Fe_8.

DOI: 10.1103/PhysRevLett.96.117208 PACS numbers: 75.50.Xx, 03.65.Vf, 75.45.+j

The energy levels of a quantum mechanical system generally tend to repel each other, so that degeneracies constitute exceptional events (in a sense to be specified below) [1]. Such degeneracies, called diabolical points [2], have recently attracted great attention in molecular magnets [3], where they occur as a result of destructive interference (due to the geometric Berry phase [4]) between different tunneling paths [5], and give rise to oscillations of the tunnel splitting of the ground state of quantum magnets [6]. Experiments on Fe_8 molecular magnets have not only confirmed this [7], but also revealed the existence of further series of diabolical points, which, so far, could not be understood in terms of destructive interference due to the geometric phase. Furthermore, some expected diabolical points are missing, due to higher-order anisotropies [7]. In this Letter, a general topological theory of the diabolical points of quantum magnets is presented. Diabolical points are characterized by their *diabolicity index*, for which topological sum rules are derived. The paradox of the missing diabolical points for Fe_8 molecular magnets is clarified. A new method is also developed to provide a simple interpretation, in terms of destructive interferences due to the Berry phase, of the *complete* set of diabolical points found in biaxial systems such as Fe_8.

The question of diabolical points, to be addressed in this Letter, goes back to the famous von Neumann-Wigner theorem [1] stating that, in a family of parameter-dependent Hermitian Hamiltonians, accidental degeneracies of two successive eigenvalues are found on submanifolds of codimension 3 of the parameter manifold. In other words, if a Hermitian Hamiltonian depends on 3 external real parameters, such as the 3 components of the magnetic field, degeneracies can be found only for isolated values of the magnetic field, and therefore constitute a set of measure zero. Because the double-cone shape of the eigenenergy surfaces near such degeneracies resemble the toy called *diabolo*, they have been dubbed *diabolical points* [2].

Interest in diabolical points has been renewed as Berry [4] pointed out that they behave as magnetic monopoles in parameter space, i.e., that a system that is adiabatically transported around a closed circuit in parameter space near a diabolical point acquires a phase shift (the Berry phase) proportional to the solid angle of the circuit as seen from the diabolical point. For quantum spin systems, it has been pointed out [5] that the occurrence of a diabolical point implied by Kramers's theorem [8], namely, the absence of tunneling between degenerate ground states of anisotropic quantum magnets of half-integer spin in zero field, can be understood as due to destructive interference between equivalent tunneling paths whose Berry phases differ by an odd multiple of π. Further, Garg [6] has pointed out that, as a magnetic field is applied along a hard axis, the solid angle Ω enclosed between the two equivalent tunneling paths joining the classical ground states A and B [red arrows in Fig. 1(d)] decreases from 2π to 0 with increasing magnetic field, giving rise to $2J$ equidistant diabolical point located on the hard axis [red dots at $H_z = 0$ in Fig. 1(c)]. This prediction has been confirmed in a beautiful experiment by Wernsdorfer and Sessoli [7], who observed this oscillatory behavior (with 4 diabolical points on the positive hard axis) for the spin-10 molecular magnet $[(tacn)_6Fe_8O_2(OH)_{12}]^{8+}$ (usually abbreviated as Fe_8). Furthermore, Wernsdorfer and Sessoli discovered, for nonzero values of the easy-axis field H_z [Fig. 1(b)], further series of unexpected diabolical points, displaying a characteristic parity alternation (red vs blue points, on Fig. 1(c)].

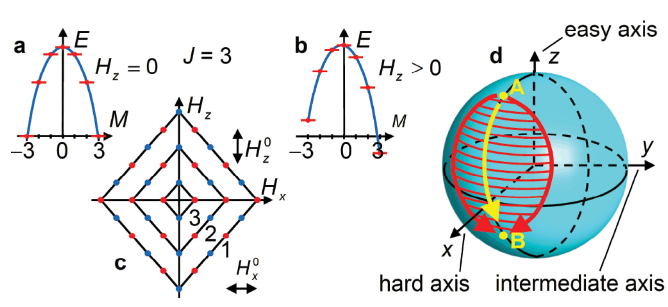

FIG. 1 (color). (a), (b) Schematic level diagram of a biaxial spin system with $J = 3$ and $0 < D \ll K$ for $H_z = 0$ (a) and $H_z > 0$ (b); (c) diabolical points for a spin $J = 3$ with biaxial anisotropy; (d) sketch of the various tunneling paths between states A and B.

Following this discovery, the complete set of diabolical points has been identified by semiclassical, perturbative, or algebraic methods [9–11]. Writing the biaxial Hamiltonian as $\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 - \mathbf{H}\cdot\hat{\mathbf{J}}$, with $\hat{\mathcal{H}}_0 = -K\hat{J}_z^2 + D(\hat{J}_x^2 - \hat{J}_y^2)$, and $0 < D < K$, the diabolical points, corresponding to degeneracies between the states M and $-M'$ (labeling as in Figs. 1(a) and 1(b)], are exactly given by [11]

$$H_z = (M - M')H_z^0, \tag{1a}$$

$$H_x = \left(\frac{M + M' - 1}{2} - n\right)H_x^0, \tag{1b}$$

with $n = 0, 1, \ldots, (M + M' - 1)$, $H_x^0 \equiv 2\sqrt{2D(K + D)}$, and $H_z^0 \equiv \sqrt{K^2 - D^2}$. The full set of diabolical points (for $J = 3$) is shown in Fig. 1(c). One should note that several diabolical points may coincide; the number of such coincident diabolical points is the same on a given diamond, as indicated on Fig. 1(c) [11]. In spite of the striking apparent similarity between the sets of diabolical points found on and off the hard axis, respectively, the latter could not be interpreted in terms of destructive interferences between tunneling paths, which is very unsatisfactory. Furthermore, only 4 diabolical points were observed on the positive hard axis, instead of the 10 predicted, which has been explained as due to a small tetragonal anisotropy term [7]. However, what happens with the missing diabolical points remains mysterious.

The general problem of diabolical points of quantum magnets may be formulated as follows. We consider a spin-J system with Hamiltonian $\hat{\mathcal{H}} = \hat{\mathcal{H}}_0(\hat{\mathbf{J}}) - \mathbf{H}\cdot\hat{\mathbf{J}}$, where the zero-field Hamiltonian $\hat{\mathcal{H}}_0(\hat{\mathbf{J}})$ is an arbitrary even function of the vector spin operator $\hat{\mathbf{J}}$. Note that the above Hamiltonian encompasses also the case of an arbitrary tensorial g factor, which can be accounted for by properly rescaling the field components along the principal axes of the g tensor. To discuss the properties of diabolical points, we take the convention to identify the $2J + 1$ eigenstates by the label μ running from $+J$ for the state of lowest energy to $-J$ for the state of highest energy, with increments of 1 (this labeling corresponds to the quantum number M of J_z for $\mathbf{H}$ in the $+\mathbf{z}$ direction, and $\mathcal{H}_0 \to 0$). We call a diabolical point of order g (or a g-diabolical point), a point in $\mathbf{H}$ space where g successive eigenstates are degenerate; the various diabolical points are labeled by an index i, running from 1 to N_d, the total number of diabolical points corresponding to a given Hamiltonian $\hat{\mathcal{H}}_0$. Note that several diabolical points involving different sets of levels may coincide in $\mathbf{H}$ space; this occurs, for instance, for the diabolical points of the biaxial case mentioned above. We also note, in passing, that the argument used by von Neumann and Wigner to discuss the occurrence of 2-diabolical points can be immediately generalized to show that the submanifolds on which we find the coincidence of n diabolical points of respective orders g_i $(1 \le i \le n)$ are of codimension $d \equiv \sum_{i=1}^n (g_i^2 - 1)$. A diabolical point where the levels μ to μ' (with $\mu' < \mu$) are degenerate will be noted $\mathbf{H}_{i(\mu)}^{(\mu')}$.

As discovered by Berry [4], a quantum system in a nondegenerate eigenstate μ adiabatically transported around a closed curve $\mathcal{C}$ in parameter space (the external magnetic field) acquires a geometric phase given by the flux through a surface Σ subtended by the circuit $\mathcal{C}$ of the Berry curvature $\mathbf{B}_{(\mu)} \equiv -\mathrm{Im}\sum'_{\mu'} \frac{\langle\mu|\hat{\mathbf{J}}|\mu'\rangle\times\langle\mu'|\hat{\mathbf{J}}|\mu\rangle}{(E_\mu - E_{\mu'})^2}$, where the sum is restricted to $\mu' \neq \mu$. The Berry curvature $\mathbf{B}_{(\mu)}$ is divergenceless, except at diabolical points involving the level μ, where monopole sources are located [4]. To each diabolical point, we can associate a closed surface Σ_i surrounding it, such that (except for coinciding diabolical points) no other diabolical point is enclosed inside Σ_i. For a diabolical point $\mathbf{H}_{i(\mu_1)}^{(\mu_2)}$, the definiteness of the wave function implies that the flux through Σ_i of $\mathbf{B}_{(\mu)}$ is topologically quantized, i.e., for $\mu_2 \le \mu \le \mu_1$, $Q_{i(\mu)} \equiv \frac{-1}{2\pi} \times \int_{\Sigma_i} \mathbf{B}_{(\mu)}\cdot d\mathbf{S} \in \mathbb{Z}$ (by convention, we define $Q_{i(\mu)} \equiv 0$ for $\mu < \mu_2$ or $\mu > \mu_1$). The *topological charge* $Q_{i(\mu)}$ is known as a Chern number, an analogous to the Euler index of a surface in differential geometry. For a given diabolical point i, one can prove the following sum rule (minor extension of a result of [4]): $\sum_\mu Q_{i(\mu)} = 0$. Further, considering a surface Σ enclosing all the diabolical points (one can show easily that such a surface exists), the flux of the Berry curvature through Σ, being a topological invariant, should remain unchanged as $\hat{\mathcal{H}}_0$ is scaled down to zero, and is therefore given by the Chern number of a spin in a Zeeman field, which yields another sum rule: $\sum_i Q_{i(\mu)} = 2\mu$.

The diabolicity index of a diabolical point i for a pair of successive levels $(\mu, \mu - 1)$ is defined as the sum of the topological charges up to level μ, i.e., $\mathcal{D}_{i(\mu)}^{(\mu-1)} \equiv \sum_{\mu'\ge\mu} Q_{i(\mu)}$. For notation convenience, for a g-diabolical point with $g > 2$, $\mathbf{H}_{i(\mu)}^{(\mu+1-g)}$, we lump the corresponding diabolicity indices into the multiplet $\mathcal{D}_{i(\mu)}^{(\mu-g+1)} \equiv (\mathcal{D}_{i(\mu)}^{(\mu-1)}; \mathcal{D}_{i(\mu-1)}^{(\mu-2)}; \ldots; \mathcal{D}_{i(\mu-g+2)}^{(\mu-g+1)})$. From the latter sum rule for the topological charges, above, we obtain the following sum rules for the diabolicity indices:

$$\mathcal{D}_{(\mu)}^{(\mu-1)} \equiv \sum_i \mathcal{D}_{i(\mu)}^{(\mu-1)} = (J + \mu)[J - (\mu - 1)], \tag{2a}$$

$$\mathcal{D} \equiv \sum_\mu \mathcal{D}_{(\mu)}^{(\mu-1)} = \frac{2J(J + 1)(2J + 1)}{3}. \tag{2b}$$

In addition to these sum rules, the set of diabolical points, for a given Hamiltonian $\hat{\mathcal{H}}_0$, must possess all symmetries of $\hat{\mathcal{H}}_0$; in particular, the time-reversal invariance of $\hat{\mathcal{H}}_0$ implies the inversion symmetry of the set of diabolical points. One observes immediately that all these rules are obeyed for the diabolical points of the biaxial system

[Eqs. (1a) and (1b)], where only 2-diabolical points with diabolicity index 1 are found. Finally, when scaling the Hamiltonian as $\hat{\mathcal{H}}_0 \to \lambda \hat{\mathcal{H}}_0$ with $\lambda > 0$ the diabolical points scale as $\mathbf{H}_{i(\mu)}^{(\mu')} \to \lambda \mathbf{H}_{i(\mu)}^{(\mu')}$ and the diabolicity indices remaining unchanged, whereas under reversing the sign of the Hamiltonian, i.e., $\hat{\mathcal{H}}_0 \to -\hat{\mathcal{H}}_0$, the diabolical points and diabolicity indices change as $\mathbf{H}_{i(\mu)}^{(\mu')} \to \mathbf{H}_{i(-\mu')}^{(-\mu)}$ and $\mathcal{D}_{i(\mu)}^{(\mu-1)} \to -\mathcal{D}_{i(1-\mu)}^{(-\mu)}$. To illustrate these rules for a case where higher-order diabolical points occur, I show in Fig. 2 the spectrum and diabolical points for spin-2 and spin-5/2 with cubic anisotropy, where a rich variety of diabolical points is obtained. The diabolicity indices characterize the energy dispersion near a diabolical point: the double-cone (diabolo) shape is obtained only for a 2-diabolical point of diabolicity index ± 1; otherwise, a different dispersion law is obtained, as seen in Fig. 2. The diabolicity index also influences the nature of the Landau-Zener tunneling taking place at a diabolical point. A systematic study of these issues will be given elsewhere.

I then address the above mentioned paradox of the missing diabolical points for Fe_8. As already indicated, it has been found that the experimental observations are well explained quantitatively by adding to the main biaxial Hamiltonian a (very small) fourth order tetragonal anisotropy term $\hat{\mathcal{H}}' \equiv C(\hat{J}_+^4 + \hat{J}_-^4)$, with $C < 0$ [7]. It has been suggested [12] that the additional anisotropy term might lead to a singular behavior; as we shall see, this explanation is both correct and incomplete. It is incomplete, because the sum rule (2a) would be violated if the diabolical had simply disappeared. Let us qualitatively discuss what happens as one continuously switches from a biaxial anisotropy ($D > 0$, $C = 0$) to a tetragonal one ($D = 0$, $C < 0$) (Fig. 3). The effect of the additional term (with $C < 0$) is to introduce a new tunneling path [yellow arrow in Fig. 1(d)]; for small values of $|C|$ and H_x, the corresponding amplitude is negligible and the effect is only to displace the diabolical points along the hard axis, reducing the distance between the last ones. At a critical value of C, beyond which the amplitude of the yellow path becomes larger than that of the red ones, the last 2 diabolical points collide and a bifurcation takes place. Beyond that point, the 2 diabolical points symmetrically diverge away from the $\mathbf{x}$ axis, towards the $\mathbf{x} + \mathbf{y}$ axis (hard axis for tetragonal anisotropy with $C < 0$); this process then repeats until all diabolical points have moved to the $\mathbf{x} + \mathbf{y}$ axis, for $D = 0$. The scenario corresponding to $C > 0$ is also shown in Fig. 3. For the case of Fe_8 ($J = 10$), this interpretation implies that 3 diabolical points should be located on each branch of the fork seen for $D > 0$ and $C < 0$ in Fig. 3. The experimental check of this prediction would allow us to confirm the present topological theory of diabolical points. Finally, I propose the following conjecture: *a spin Hamiltonian* $\hat{\mathcal{H}}_0$ *is completely determined by the set of its*

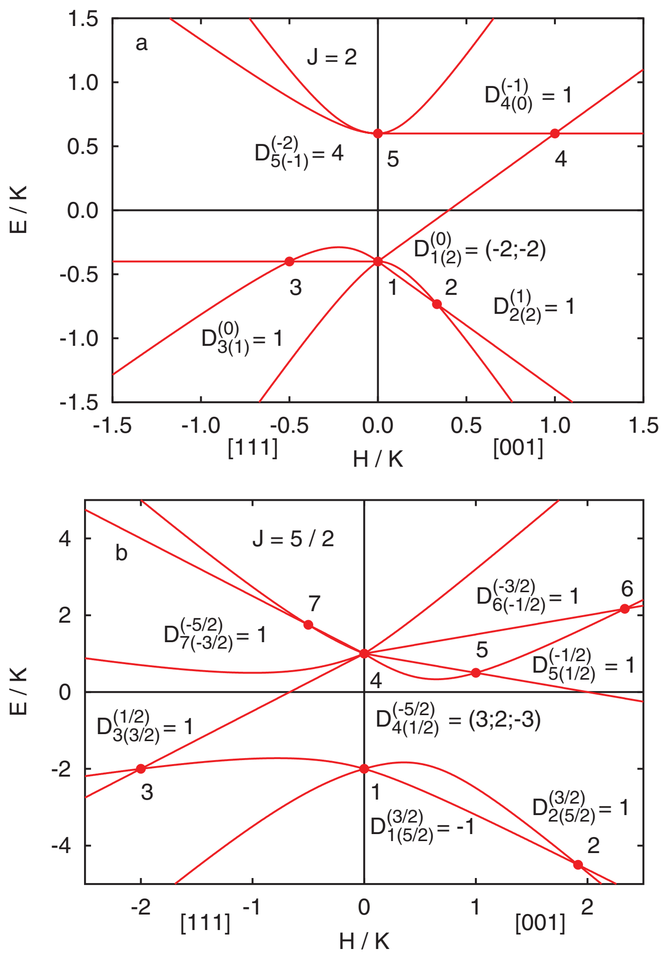

FIG. 2 (color). Spectrum and diabolical points of a spin $J = 2$ (a) and $J = 5/2$ (b) with cubic anisotropy: $\hat{\mathcal{H}}_0 \equiv E_0 + K(\hat{S}_x^4 + \hat{S}_y^4 + \hat{S}_z^4)/6$. Positive (negative) values of the field correspond to a field parallel to a fourfold (threefold) symmetry axis. The diabolical points are indicated by the solid dots. The corresponding diabolicity indices are indicated.

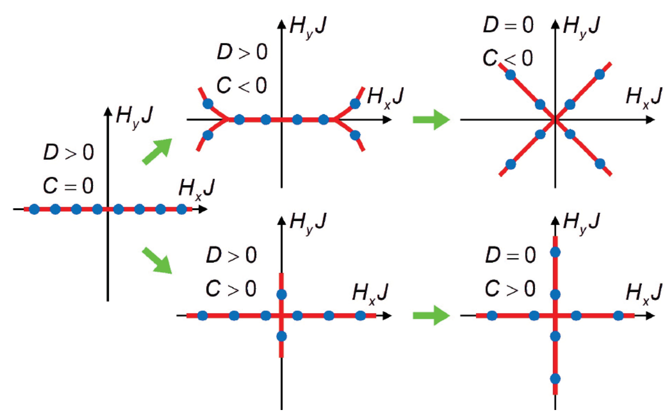

FIG. 3 (color). Schematic representation of the evolution of diabolical point distribution (for the two lowest states, $J = 4$), as the anisotropy progressively changes from biaxial to quadratic.

diabolical points and diabolicity indices (together with the value of its trace).

I now come to the last point of this Letter, namely, the Berry phase interpretation of the diabolical points found at nonzero values of H_z for the biaxial system. The difficulty lies in the fact that the initial (M) and final state ($-M'$) of the tunneling paths do not generally belong to the same set of coherent states, which makes the path integral approach of Ref. [6] impracticable. A solution to this difficulty consists in enlarging the Hilbert space to comprise all possible states of a system of $2J$ spins-1/2: $\mathbf{j}_1, \mathbf{j}_2, \ldots, \mathbf{j}_{2J}$. The Hamiltonian $\hat{\mathcal{H}}$ operates in this new Hilbert space by interpreting $\hat{\mathbf{J}}$ as $\hat{\mathbf{J}} \equiv \sum_{i=1}^{2J} \hat{\mathbf{j}}_i$. We can ensure that the physics of our problem is thereby unchanged by adding to $\hat{\mathcal{H}}$ a penalty term $\hat{\mathcal{H}}' \equiv -\alpha[\hat{\mathbf{J}}^2 - J(J+1)]$ with $\alpha \to +\infty$ and considering only the $2J+1$ lowest levels.

To study the exchange splitting between any pair of states, we need the following matrix element of the imaginary-time propagator between two coherent states: $A \equiv \langle JM\mathbf{n}|e^{-\hat{\mathcal{H}}T}|JM'\mathbf{n}'\rangle$ (we set $\hbar = 1$). The coherent states are defined as usual by rotating a state $|JM\rangle$ from the $\mathbf{z}$ axis to $\mathbf{n} \equiv (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, i.e., $|JM\mathbf{n}\rangle \equiv e^{-i\varphi\hat{\mathbf{J}}_z}e^{-i\theta\hat{\mathbf{J}}_y}e^{i\varphi\hat{\mathbf{J}}_z}|JM\rangle$. Clearly, A is unaffected by the penalty term $\hat{\mathcal{H}}'$ and we can simply omit it for our problem.

One can show that $\langle JM\mathbf{n}|[|jj\mathbf{n}\rangle \otimes |J-j, M-j, \mathbf{n}\rangle] = \sqrt{\frac{(2J-2j)!(J+M)!}{(2J)!(J+M-2j)!}} \simeq (1 - \frac{j(J-M)}{2J})$, [where the first equality is an exact result, and the second one an approximation valid for $j(J-M) \ll 2J$], so that $|JM\mathbf{n}\rangle \approx |jj\mathbf{n}\rangle \otimes |J-j, M-j, \mathbf{n}\rangle$ to relative order $\frac{j(J-M)}{2J}$. The proof of the above equality, to be detailed elsewhere, uses the fact that states of spin-J can be expressed as completely symmetrized (over all possible permutations) tensorial products of $2J$ spin-1/2 states, and exploits the group structure of permutations. By a similar argument (together with the fact that $\hat{\mathcal{H}}$, depending only on the total spin $\hat{\mathbf{J}}$, commutes with the permutation operator), one can also prove the following exact result: $A = \sqrt{\frac{(2J)!(J-M-2j)!}{(2J-2j)!(J-M)!}}[\langle jj, -\mathbf{n}| \otimes \langle J-j, M+j, \mathbf{n}|]e^{-\hat{H}T}|JM'\mathbf{n}'\rangle$. Combining those results, we obtain $A \propto [\langle jj, -\mathbf{n}| \otimes \langle \tilde{J}\tilde{M}\mathbf{n}|]e^{-\hat{H}T}[|jj\mathbf{n}'\rangle \otimes |\tilde{J}\tilde{M}\mathbf{n}'\rangle]$, with $j \equiv (M'-M)/2$ (without restriction, we assume $M' \geq M$), $\tilde{J} \equiv J - j$, and $\tilde{M} \equiv (M+M')/2$. Now, for large values of J and small values of the applied field along the hard axis, $\mathbf{n}$ and $\mathbf{n}'$ remain very close to $\mathbf{z}$ and $-\mathbf{z}$, respectively, so that we can write $|jj, -\mathbf{n}\rangle \approx e^{i\alpha}|j, -j\rangle$ and $|jj, \mathbf{n}'\rangle \approx e^{i\alpha'}|j, -j\rangle$. This finally gives $A \propto \int \mathcal{D}\mathbf{u}(\tau)e^{-\mathcal{S}[\mathbf{u}(\tau)]}$, where the path integral is for coherent states $|\tilde{J}\tilde{M}\mathbf{u}\rangle$ with $\mathbf{u}(0) \equiv \mathbf{n}$ and $\mathbf{u}(T) \equiv \mathbf{n}'$, and where the action is given, as usual, by $\mathcal{S}[\mathbf{u}(\tau)] \equiv \mathcal{S}_{\rm WZ}[\mathbf{u}(\tau)] + \mathcal{S}_H[\mathbf{u}(\tau)]$. The first term is the Wess-Zumino (or Berry phase) action, $\mathcal{S}_{\rm WZ}[\mathbf{u}(\tau)] \equiv i\tilde{M}\int(1-\cos\theta_{\mathbf{u}})d\varphi_{\mathbf{u}}$, responsible for the quantum interferences [5]; the second term is the dynamical action, $\mathcal{S}_H[\mathbf{u}(\tau)] \equiv \int_0^T d\tau E[\mathbf{u}(\tau)]$, where the energy is $E(\mathbf{u}) \equiv [\langle j, -j| \otimes \langle \tilde{J}\tilde{M}\mathbf{u}|]\hat{\mathcal{H}}[|j, -j\rangle \otimes |\tilde{J}\tilde{M}\mathbf{u}\rangle]$. In short, we have mapped our original problem onto that of the tunneling between the states $|\tilde{J}\tilde{M}\mathbf{n}\rangle$ and $|\tilde{J}\tilde{M}\mathbf{n}'\rangle$ of a fictitious spin-$\tilde{J}$ with biaxial anisotropy, which can be treated by the instanton method as in Ref. [6]. Noting that this fictitious spin is subject to the effective field $H_z^{\rm eff} \equiv H_z - 2jK$, along the easy axis, we immediately generate the *complete* set of diabolical points (1a) and (1b), with $H_z^0 \equiv K$; this agrees well with the exact result $H_z^0 \equiv \sqrt{K^2 - D^2}$ for $D \ll K$, which is actually the case for Fe_8. By mapping the original tunneling problem onto that of a fictitious spin in an effective H_z field, we obtain a simple interpretation of all the diabolical points in terms of destructive interferences due to the Berry phase for the effective spin-$\tilde{J}$. The striking parity alternation discovered by Wernsdorfer and Sessoli [7] [red vs blue points in Fig. 1(c)], is thus simply interpreted as due to $\tilde{J}$ being alternately integer and half-integer.

Note that, in principle, our approach is supposed to be valid only in the limit of large J and for small H_x and H_z; it is thus a surprise to see that it essentially yields exact results, even for small J and/or for large H_x and H_z. This puzzle has already been noticed [10,11] and is not fully understood.

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