Tunnel Window’s Imprint on Dipolar Field Distributions

Juan José Alonso and Julio F. Fernández

1Departamento de Física Aplicada I, Universidad de Málaga, 29071-Málaga, Spain
2ICMA, CSIC and Universidad de Zaragoza, 50009-Zaragoza, Spain

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We have performed Monte Carlo simulations of interacting dipoles that relax through quantum tunneling. We aim to mimic tunneling experiments on crystals of magnetic clusters, such as Fe₈, at very low temperatures. Accordingly, we allow spin flips only if the corresponding energy change is less than some $2\delta h_{hf}$. Time evolutions of the dipolar field distribution $P_i(H)$ are studied. As in experiments, a “hole” develops in $P_i(H)$. The half-width $W$ of incipient holes of weakly polarized systems are, under certain conditions, simply related to $\delta h_{hf}$. For $k_B T \approx 0.5\delta h_{hf}$ and $\delta h_{hf}$ smaller than approximately 1/10 of the half-width of the dipolar field distributions of disordered systems, $W = 0.75\delta h_{hf}$.

Quantum tunneling of single molecule magnets, such as Mn₁₂ acetate, has become a subject of considerable interest. This large molecule and others like it contain metal ion clusters, such as Mn₁₂, Fe₈, and Mn₄, which behave as sizable single spins at low temperatures $T$ [1]. They crystallize into systems of nearly isolated spins, which interact only through dipolar fields. Crystal field effects give rise to anisotropy barrier energies $U$ [2]. The first inferences that tunneling through these barriers takes place in Mn₁₂ at $T \approx 0.1U/k_B$, where $k_B$ is Boltzmann’s constant ($U = 55 \text{ K}$ in Mn₁₂), were made from anomalous magnetic relaxation [3]. Definitive experimental confirmation followed soon afterwards [4]. Relaxation rates that follow Arrhenius’ law [2,5] show that tunneling takes place from thermally excited states at these temperatures. The phenomenon is by now fairly well understood [6–8]. Quantum tunneling of the magnetization that is temperature independent has been reported for $T \approx 0.1U/k_B S$ by various groups ($U = 28 \text{ K}$ for Fe₈, and $S = 10$ both for Mn₁₂ and for Fe₈) [9–14].

Actual observation of this phenomenon had not been widely expected. It had been argued that the vast majority of spins in any given system would not meet resonant tunneling conditions. Magnetic dipolar fields would upon tunneling lead to typical Zeeman energy shifts $\delta h_Z$ which would in general exceed the ground state tunnel splitting energy $\Delta$ by many orders of magnitude. In Fe₈ spin clusters, for instance, values of $\Delta$ inferred from experiment (e.g., $\Delta = 10^{-7} \text{ K}$ in Ref. [15]) are many orders of magnitude smaller than the value $\delta h_Z = 10^{-2} \text{ K}$ [10].

The theory of Prokof’ev and Stamp (PS) [16,17] explains how tunneling can nevertheless take place. In it, hyperfine fields that are comparable to magnetic dipolar fields fluctuate rapidly in time. Hyperfine fields are thus able to repeatedly bring into resonance a significant fraction of the total number of spins in the system [18]. The PS scheme is based on Landau-Zener’s theory of nonadiabatic transitions, which is often used to estimate transfer rates between two states whose energies briefly become equal [19]. For any one given spin, the tunneling probability in the PS theory is given by the incoherent sum of probabilities for tunneling whenever the difference between the initial and final state energies becomes comparable to $\Delta$.

An experimental piece of evidence that points to the nuclear mechanism that is the centerpiece of the PS theory has been found [10,11]. Wernsdorfer et al. obtained from experiments the time evolution of the distributions $P_i(H)$ of magnetic dipolar fields $H$. For Fe₈ and for Mn₁₂, they discovered that a “hole,” that is, a sharp dip, in $P_i(H)$ develops in time, and that, at a temperature of 40 mK, it attains a seemingly “intrinsic” linewidth $W$ if initially $m \leq 0.5$, where $m$ is the magnetization and $m = 1$ is its saturation value. From here on, $W$ stands for the half-width halfway down into the hole in $P_i(H)$. $W$ turned out to have a value approximately equal to a typical hyperfine energy $\delta h_{hf}$ [20]. Reasonably, Wernsdorfer et al. related their observation to the nuclear mechanism proposed by PS.

This conjecture has, to our knowledge, thus far gone unchallenged. On the other hand, we know of no theoretical or computational evidence to support it, nor do we know of any attempt to quantify the relationship, if it indeed exists, between $\delta h_{hf}$ and $W$. This relationship can be probed by means of Monte Carlo (MC) simulations, since, in contrast with experiments, the value of $\delta h_{hf}$ can then be varied as desired. Simulations that give $P_i(H)$ have been reported [21], but not for the physical conditions (small $m$ and $T$) under which holes with intrinsic linewidths have been observed experimentally.

It is the purpose of this Letter to obtain, through Monte Carlo simulations, $P_i(H)$, and to extract from it the relation between $W$ and $\delta h_{hf}$. The model is next defined. All sites on a simple cubic (SC) lattice are occupied by $S = \pm 1$ spins which interact through dipolar fields. Let

$$H_i = \sum_j (a/r_{ij})^3 (1 - 3z_{ij}^2/r_{ij}^2) S_j,$$

where $r_{ij}$ is the distance between the $i$ and $j$ sites, $a$ is the SC lattice constant, $z_{ij}$ is the $z$ component of $r_{ij}$, and the sum is over the set of $j$ sites that we next specify. We
make use of free boundary conditions (FBC) most often. Then the sum in Eq. (1) is over all sites in the system. On the other hand, we sum over all \( j \) sites that are within an \( L \times L \times L \) cube centered on the \( i \) site in the few instances when, for comparison purposes, we make use of periodic boundary conditions (PBC). The interaction energy is given by

\[
E = \frac{1}{2} \sum_i S_i H_i, \tag{2}
\]

where the sum is over all lattice sites \( i \). Unless specified otherwise, we give all magnetic fields and energies in the units specified by Eqs. (1) and (2), respectively. Thermal contact with a heat reservoir at some temperature \( T \) is assumed. More specifically, detailed balance is enforced, that is, a spin flips if a random number \( x \) that is uniformly distributed in the \((0,1)\) interval satisfies \( x < \exp(-\Delta E/k_B T) \). Finally, a spin \( S_i \) can flip if and only if \( |H_i| \) is smaller than some given value \( \delta \hbar \omega \). This defines the energy window that in this model stands for the tunnel window that is enabled by hyperfine fields in the PS theory.

The model defined above is only a caricature of a crystalline system of tunneling magnetic clusters. Simulating tunneling of \( S = 10 \) spins through a uniaxial anisotropy barrier \( U \) by flipping \( S = \pm 1 \) spins makes sense when \( T \equiv 0.1 U/k_B S \), since only the two states \( S = \pm S \) are occupied then with a non-negligible probability [21]. On the other hand, decoherence effects that arise when tunneling spins interact with nuclear spins [22] are completely disregarded in this model. Furthermore, the thermal contact with a heat reservoir that we assume may not be there in the laboratory. Nevertheless, the model holds intrinsic interest and provides a good testing ground for the questions raised above, and it leads to time evolutions of \( P_i(t) \) that are much like the ones observed experimentally.

All initial states are set up as follows. Each spin is pointed up or down, independently of all other spins, with probabilities \( p = (1 + m)/2 \) and \( 1 - p \), respectively. The simulation then starts, using Eqs. (1) and (2) to calculate \( \Delta E \). The system never evolves with an applied magnetic field. This is intended to simulate a system that has been previously polarized, under some applied field, at infinite temperature, allowed to come to equilibrium, and then has its temperature suddenly dropped to \( T \) and the applied field removed immediately afterwards, just before experimental observation begins.

Quantity \( \Delta P \equiv P_{t=20}(H) - P_{t=0}(H) \) is shown versus \( H \) in Fig. 1 for several values of the initial magnetization \( m \). Notice in the inset how small system shape effects are for \( P_i(H) \) for weakly polarized systems [23]. On the other hand, surface effects, that one wishes to avoid, are illustrated in Fig. 1 for strongly polarized systems. The nature of the hole seems to change as \( m \) increases beyond \( m \sim 1/2 \). Indeed, the results shown below clearly show that the half-width of \( P_i(H) \) is related to \( \delta \hbar \omega \) only for \( m \leq 0.5 \).

Early time evolutions of \( P_i(H) \) are shown in Fig. 2 for cubic systems with all spins initially up or down with equal probability, are shown at times 0, 16, 64, and 160 MC steps per spin. All data points stand for averages over \( 5 \times 10^4 \) MC runs, at \( k_B T = 0.05 \), for \( \delta \hbar \omega = 0.1 \). \( \Delta P \) versus \( H \) for \( m = 0.5, 0.2, \) and 0 is also shown in the inset. In the main part of the figure, \( \bullet \) and \( \circ \) stand for spheres and cubes, respectively, both for \( m = 0.9 \) initially; \( \blacksquare \) and \( \square \) stand for spheres and cubes, respectively, both for \( m = 0.8 \) initially; the continuous line and \( \diamond \) stand for spheres and cubes, respectively, for \( m = 0 \) initially. In the inset, the continuous line and \( \bigcirc \) stand for spheres and cubes, respectively, for \( m = 0 \) initially; \( \square \) and \( \diamond \) stand for spheres and cubes, respectively, for \( m = 0 \) and \( m = 0 \) respectively; and \( \bigcirc \) and \( \square \) stand for spheres and cubes, respectively, for \( m = 0.5 \).
probability, a tunneling energy window \( \delta_{hhf} \) = 0.1, and
\( k_B T = 0.04 \). The hole in \( P_t(H) \) develops much as it does
experimentally for \( Fe_8 \) [10].

Note also that \( P_f(H) \) in Fig. 2 is nearly Gaussian at
\( t = 0 \) [24]. Data points for \( P_{t=0}(H) \) obtained for \( L = 16 \)
and \( L = 32 \) cubes, both for FBC and for PBC, as well as
for spheres of radius \( R = 8 \), show no noticeable differences [23]. A straightforward numerical calculation yields
for a SC lattice, with lattice constant \( a = 1 \), fully occup-
ied with \( S = \pm 1 \) dipoles, the rms value 3.6547 . . . for \( H \).

This gives, for a Gaussian distribution, a half width at half
maximum of 4.3031 . . . , which is in close agreement with
the value we obtain, \( h_d = 4.3 \), for the distribution shown
in Fig. 2. Experimentally, \( P_{t=0}(H) \) is “accurately Gaussian”
for a weakly polarized \( Fe_8 \) system at high temperature,
and note, for comparisons to be made below, that \( h_d \) for
\( Fe_8 \) is quoted to be 0.030 T [10,25].

In general, we obtain \( W \) by extrapolating to \textit{time} = 0
half widths at half minimum from curves, such as the ones
shown in the inset of Fig. 2, obtained for unpolarized sys-
tems. Data points thus obtained are shown in Fig. 3 versus
\( \delta_{hhf} \) for \( \delta_{hhf} = 0.1, 0.2, \) and 0.4. The differences
between data points in Fig. 3, for (i) cubes with FBC, for
(ii) cubes with PBC, and (iii) for spheres, seem insignifi-
cant. Note also that \( W \) depends rather weakly on tem-
perature for \( k_B T \approx 0.5 \delta_{hhf} \). For \( k_B T \gtrsim \delta_{hhf} \), holes in
\( P_t(H) \) grow in more slowly.

In order to obtain the desired relation between \( W \) and
\( \delta_{hhf} \), we have obtained data for \( W \) at \( T = 0 \) for several
values of \( \delta_{hhf} \) for unpolarized systems. The results are
displayed in Fig. 4. Data points for \( W \) obtained for ini-
itially polarized spheres with \( m = 0.8 \) and \( m = 0.9 \) are
also shown. Note the strikingly different behavior of polari-
zated and unpolarized systems exhibited in Figs. 1 and
4. Whereas the former exhibit surface effects and seem to
bear little relation to the tunnel energy window \( \delta_{hhf} \), the
latter seem not to suffer from surface effects and to depend
only on \( \delta_{hhf} \). More precisely, the half-width \( W \) of incipient
holes seems to be boundary independent for unpolarized
systems if \( \delta_{hhf} \approx 0.5 \), i.e., \( \delta_{hhf} \leq 0.1 h_d \). Then, if
\( k_B T \approx 0.5 \delta_{hhf} \),

\[
W \approx 0.75 \delta_{hhf}.
\]  

Comments about the applicability of Eq. (3) to the holes
that have been observed in \( P_t(H) \) of tunneling \( Fe_8 \) and
\( Mn_{12} \) clusters follow. Straightforward numerical calcula-
tions of the rms dipolar fields yield, assuming Gaussian
distributions [24], 33 mT for \( Fe_8 \). This is in rough agree-
ment with the number 30 mT that has been inferred from exper-
iment [10], which gives a magnetic energy of 0.4 K
[25]. On the other hand, \( \delta_{hhf} = 5 \) mK has been esti-
ated, from EPR data, for \( Fe_8 \) [12]. It follows then for
\( Fe_8 \) that \( \delta_{hhf}/h_d = 0.01 \), which is well within the region of
validity of Eq. (3). Thus, the conjecture of Wernsdor-
fer et al. that \( W \) and \( \delta_{hhf} \) are related is justified for \( Fe_8 \)
[10]. On the other hand, the experiments of Ref. [10] were
performed at 40 mK, which is several times larger than
\( \delta_{hhf}/k_B \) and is therefore outside the domain of validity
of Eq. (3). For \( Mn_{12} \) clusters, the situation is quite dif-
ferent. Holes have been observed [11] in the dipolar field
distributions of a small \textit{minority} “species” of \( Mn_{12} \) clusters
that tunnel while the majority species does not [26]. Our
model, in which all spins can tunnel and feel the changing
dipolar fields from other tunneling spins, is then clearly in-
applicable. We have nevertheless simulated (not reported
here) a two species \( Mn_{12} \)-like system. It then turns out that
a relation between \( W \) and \( \delta_{hhf} \) exists even if inequality
\( \delta_{hhf} \approx 0.1 h_d \) is not fulfilled. This is fortunate because
the holes observed in the \( Mn_{12} \) experiments are quite wide

![FIG. 3. Incipient holes’ half-width W versus \( k_B T/\delta_{hhf} \) for \( \delta_{hhf} = 0.1, 0.2, \) and 0.4. \( \bigcirc, \bigodot, \) and \( \square \) stand for unpolarized systems of \( 16 \times 16 \times 16 \) cubes with PBC, with FBC, and \( R = 8 \) spheres, respectively.](image-url)

![FIG. 4. Data points for the half-width \( W \) at \( T = 0 \) versus \( \delta_{hhf} \). •, x, and □ stand for \( 16 \times 16 \times 16 \) cubes with PBC, with FBC, and \( R = 8 \) spheres, respectively.](image-url)
Further discussion of this system is beyond the scope of this paper.

In summary, we have given convincing numerical evidence that: (i) tunnel windows of interacting dipoles lead to holes in their dipolar field distributions; (ii) the holes' half-widths \( W \) depend on the system's surface if either the half-widths \( \delta h_{hf} \) of the tunnel windows fulfill \( \delta h_{hf} \geq 0.1h_d \) or the system is strongly polarized; (iii) if conditions for its validity are fulfilled, then Eq. (3) gives the relation between \( W \) and \( \delta h_{hf} \).

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*Email address: JFF@Pipe.Unizar.Es


[23] This is because long range effects vanish for random configurations of unpolarized dipolar systems but not if they are polarized. All \( 4\pi r^2 dr/a^3 \) dipoles within a spherical shell of radius \( r \) contribute a random field \( H \sim r^{-2} \) at the origin in the former case, but \( H \sim r^{-1} \) for nonvanishing polarizations. There are clearly no cancellations from different spherical shells in the latter case. It is therefore not surprising to find that early hole development starting from completely random spin configurations seems to be boundary independent, but not for polarized systems.

[24] This is in contrast with the Lorentzian behavior predicted by P. W. Anderson, Phys. Rev. 82, 342 (1951), for dilute spin systems, but is expected for a fully occupied lattice. Nearly Gaussian dipolar field distributions are also exhibited by dipoles that are densely packed in an otherwise spatially random distribution [see D. V. Berkov, Phys. Rev. B 53, 731 (1996)].

[25] The magnetic energy \( g\mu_B H_d \) for \( h_d = 0.030 \) T is 0.40 K for Fe\(_3\), since \( g\mu_B S = 13.4 \) K/T then.