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'Hole-digging' in ensembles of tunneling Molecular Magnets

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The nuclear spin-mediated quantum relaxation of ensembles of tunneling magnetic molecules causes a 'hole' to appear in the distribution of internal fields in the system. The form of this hole, and its time evolution, are studied using Monte Carlo simulations. It is shown that the line-shape of the tunneling hole in a weakly polarised sample must have a Lorentzian lineshape- the short-time half-width ξ_o in all experiments done so far should be $\sim E_o$, the half-width of the nuclear spin multiplet. After a time τ_o , the single molecule tunneling relaxation time, the hole width begins to increase rapidly. In initially polarised samples the disintegration of resonant tunneling surfaces is found to be very fast.

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In the last few years many experiments have been done on the tunneling relaxation of magnetic molecules [1, 2, 3, 4, 5, 6]. These couple to each other, via dipole and weak exchange interactions, and also to phonon [7] and nuclear [8] environments. The most complete results have appeared on the *Fe-8* system, where measurements of the relaxation [1, 3, 9, 10, 11] were interpreted using a theory in which the tunneling dynamics was controlled by dynamic hyperfine and dipolar fields [12]. A key connection between theory and experiment is the existence of 'hole-digging' in the distribution $M(\xi, t)$ of magnetisation M over longitudinal bias energy ξ in the low T regime where the molecules behave as 2-level systems and phonons are unimportant [3, 10, 12, 13]. The hole appears because a molecule can then only tunnel when in resonance. Without nuclear spins resonance only occurs if the local energy bias $|\xi| \lesssim \Delta_o$. However the nuclear spins mediate inelastic tunneling over a much larger range $|\xi| < \xi_o$; in *Fe-8* at low fields, $\xi_o/\Delta_o \sim 10^5$. Theory thus predicted an initial holewidth ξ_o , provided $\xi_o \ll$ the range of energy bias caused by the dipolar field distribution. The experimental half-width w_o of the hole at *short times*, in initially strongly annealed samples, was interpreted [3, 10] to be the total half-width E_o of the multiplet of nuclear spin states coupled to the molecule- this latter can be calculated if the hyperfine couplings are known [8]. Support for this interpretation came when isotopes were varied [11]; w_o agreed both with approximate calculations of E_o , for different sets of nuclear isotopes, and with values of ξ_o extracted from independent measurements of the sample relaxation rate τ_Q^{-1} .

It is important to understand this hole-digging, not only to evaluate the claim that it demonstrates the role of nuclear spins in controlling the molecular dynamics

(and the use of the holes as diagnostic tools), but also because the physics of the hole formation turns out to be rather interesting. There are 4 obvious questions which one may ask:

(i) Why is $\xi_o = E_o = w_o$ in the *Fe-8* experiments, when $M(0)$ is small?

(ii) The experimental hole width $w(t)$ varies in time (with $w(t) \rightarrow w_o$ at short times) - how and why?

(iii) $w(t)$ also depends very strongly on the initial polarisation $M(t=0)$ in the system ($M(t) = \int d\xi M(\xi, t)$), but w_o is apparently independent of $M(0)$ for small $M(0)/M_s$; is this expected theoretically?

(iv) Why is the experimental lineshape Lorentzian?

In fact most published experiments are on partially annealed samples, where $M(0)/M_s < 1$ (M_s being the saturated magnetisation of a fully polarised sample- henceforth we measure $M(t)$ in units of M_s). In the theory [8, 12, 13] the quantity ξ_o was not necessarily the same as E_o ; and neither the hole lineshape, nor the dependence of $w(t)$ on $M(0)$ or t , were given. Moreover the theory only deals with weakly or strongly polarised samples, whereas almost all experiments are on partially annealed samples, with intermediate polarisation- these are beyond the reach of analytic work.

To address these 4 questions, we present here numerical results for the hole lineshape, and the holewidth $w(t)$ as a function of t and initial annealing. We also calculate results for the *Fe-8* system, to provide predictions which can be compared with experiment.

1. *Short-time hole width:* The experimental interpretation, that at short times $w_o = E_o$, appears to be based on the assumption (made explicitly in ref. [14]) that the nuclear bias potential behaves as a noise, fluctuating

rapidly over the whole nuclear multiplet (halfwidth E_o). Actually this assumption is unnecessary- in many cases [15] the hole width depends on the energy exchanged between nuclear spins and the molecules during inelastic tunneling [13]. If the strength of the hyperfine interactions between the molecular spin \mathbf{S} and the k -th nuclear spin \mathbf{I}_k is ω_k^{\parallel} , then $E_o^2 = \sum_k (\omega_k^{\parallel})^2 (I_k + 1) I_k / 3$. However energy is exchanged over a range $\xi_o \sim \kappa \omega_o$, where $\omega_o = N^{-1} \sum_k \omega_k^{\parallel}$ is the mean hyperfine coupling to the N nuclear spins in the molecule. In low fields $2\kappa = \sum (\omega_k^{\perp} / \omega_k^{\parallel})^2$, where $\omega_k^{\perp} = g_k^N \mu_N H_o$ is the Zeeman coupling to a field H_o . In experiments with zero applied field, H_o is just the strength of the local dipolar field from the other molecules- its root mean square in nearly annealed Fe -8 molecules is $\sim 0.05 T$. If $\kappa \gtrsim \sqrt{N}$, then [13] $\xi_o \rightarrow E_o$.

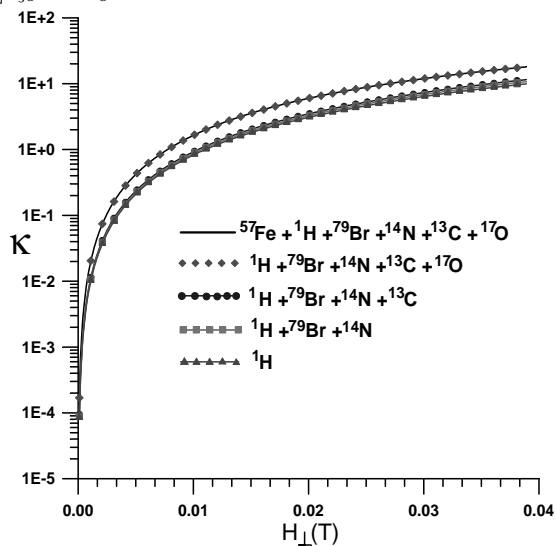


FIG. 1: The variation of $\kappa(\mathbf{H}_o^{\perp})$ with transverse field \mathbf{H}_o^{\perp} , calculated for a single Fe -8 molecule at low fields, for various isotopic mixtures. The hyperfine interactions were assumed to be dipolar, except for the core polarisation coupling to ^{57}Fe , which was taken from experiment.

Evaluation of κ at low fields is simple for Fe -8 if we assume that all hyperfine couplings are dipolar except those to ^{57}Fe nuclei [11], since all nuclear positions and moments are known [17]. The couplings $\{\omega_k^{\parallel}\}$, $\{\omega_k^{\perp}\}$ can then be computed [18]. Fig. 1 shows the results, for different isotopic concentrations in Fe -8. We see that if it were not for the strong intermolecular dipolar fields, ξ_o would be much less than E_o ; however, in fields $\sim 0.05 T$, they will be very close to each other.

2. *Time dependence of holewidth:* To find the time dependence of $w(t)$ we perform Monte Carlo simulations for the time evolution of $M(\xi, t)$ on a simple cubic lattice, averaging over several hundred random initial spin configurations consistent with the initial $M(t=0)$ (for previous MC simulations see refs. [12, 21] (polarised systems) and [14] (strongly annealed systems)). Individual spins, modelled as point dipoles oriented along

$\pm \hat{z}$, relax incoherently in a local bias field ξ at a rate $\tau_N^{-1}(\xi) = \tau_o^{-1} e^{-|\xi|/\xi_o}$, where $\tau_o^{-1} \propto \Delta_o^2 / \Lambda_N$, with Δ_o the tunneling matrix element and Λ_N a nuclear spin diffusion rate [12]. The dipolar fields at each site, calculated numerically, are updated at time intervals $\delta t \ll \tau_o$ (typically $\delta t / \tau_o \sim 10^{-3}$ at the beginning of the decay) by flipping individual spins with probability $1 - e^{-\delta t / \tau_N(\xi)}$. We define in the usual way the magnetisation distribution $M(\xi, t) = \int d^3r [P_{\uparrow}(\xi, \mathbf{r}; t) - P_{\downarrow}(\xi, \mathbf{r}; t)]$ for the sample, where $P_{\sigma}(\xi, \mathbf{r}; t)$ is the probability that a molecule at position \mathbf{r} with spin orientation $\sigma = \uparrow, \downarrow$ will be in bias field ξ at time t . A typical result is shown in Fig. 2.

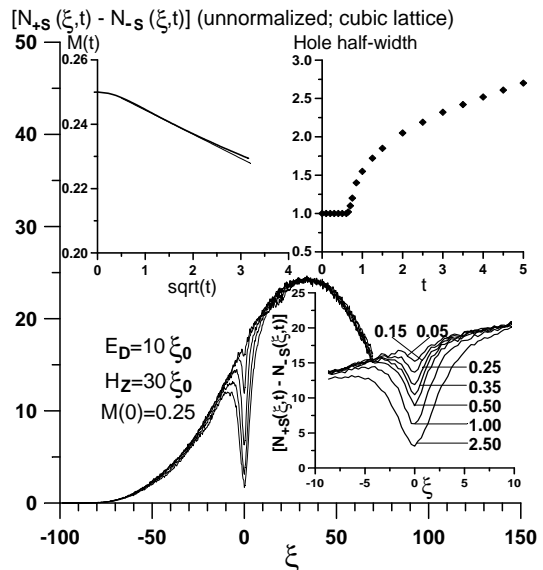


FIG. 2: The tunneling hole dynamics, obtained by Monte Carlo simulations, performed on a model cubic lattice of 40^3 point dipoles (E_D is the strength of the nearest neighbour dipolar interaction, and E_D / ξ_o here). The main graph shows the time evolution of $M(\xi, t)$, defined in the text, for a sample in external field $H_z = 30 \xi_o$ at $M(0) = 0.25$ (for which $M(\xi, 0)$ is nearly Gaussian, with a halfwidth $W_D \sim 4.4 E_D$ for this cubic lattice). The two upper insets are (i) at left, the magnetization curve $M(t)$ vs the \sqrt{t} and (ii) at right, the tunneling hole half-width $w(t)$ as a function of time. The inset at the bottom right enlarges the region around $\xi = 0$ to show the hole dynamics. Note that time t is shown in units of τ_o and bias ξ in units of ξ_o .

A number of important general features of these results are as follows. If *and only if* the Gaussian halfwidth W_D of $M(\xi, t=0)$ satisfies $W_D \gg \xi_o$, we find:

- (i) for $t < \tau_o$ the hole halfwidth $w(t) \rightarrow w_o$, and $w_o = \xi_o$ identically. Given the result above, that $\xi_o \sim E_o$, this means the short-time holewidth w_o is indeed measuring E_o , as previously assumed [10, 11, 20].
- (ii) When $t \gtrsim \tau_o$ the hole rapidly broadens. The sharp rise in $w(t)$ when $t \sim \tau_o$ appears not to be an artifact of the simulation. We have not yet been able to establish the asymptotic form of $w(t)$ for $\tau / \tau_o \gg 1$, but for $1 < t / \tau_o < 5$, $w(t)$ grows slower than $t^{0.4}$.
- (iii) For $t > \tau_o$ a square root relaxation (ie., $|M(t) - M(0)| \propto (t / \tau_o)^{1/2}$) is always found, for any $M(0)$. This

is obeyed until the fractional change in $|M(t) - M(0)| \sim 0.1 - 0.15$.

3. *Hole lineshape*: When $M(0) < 0.5$, we find the hole lineshape is Lorentzian. If $M(0) > 0.5$, deviations begin to appear; when $M(0) \sim 1$ the lineshape is not Lorentzian at all.

It is important to understand the origin of this Lorentzian lineshape. In a strongly annealed sample the dipolar field fluctuates very rapidly from one molecule to another, but on a coarse-grained scale the sample should look homogeneous. We can therefore define the average time $\tau_{de}(\xi)$ for a molecule with initial bias ξ to come to resonance. The total magnetization is then given by the homogeneous ensemble average:

$$M(t) = M_{eq} + (M(0) - M_{eq}) \int d\xi N(\xi) e^{-t/\tau_{de}(\xi)}, \quad (1)$$

where $M_{eq} = M(t \rightarrow \infty)$ and $N(\xi) = \int d^3r [P_{\uparrow}(\xi, \mathbf{r}; 0) + P_{\downarrow}(\xi, \mathbf{r}; 0)]$ is the total dipolar field distribution. The Lorentzian hole lineshape results directly from a Lorentzian form for $\tau_{de}^{-1}(\xi)$. We demonstrate this by calculating $\tau_{de}(\xi)$ using the Monte Carlo procedure.

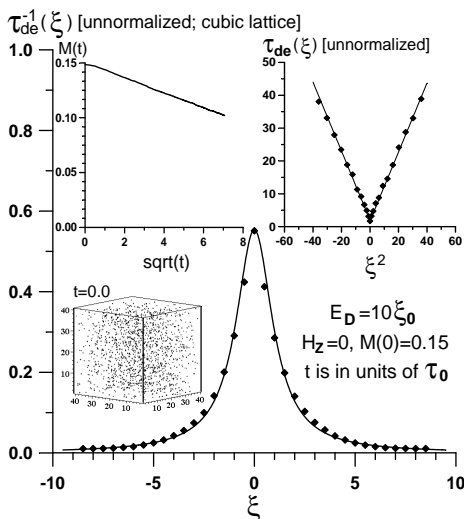


FIG. 3: The average decay rate $\tau_{de}^{-1}(\xi)$ obtained by the MC simulations in a cubic sample of 40^3 molecules (diamonds). By solid line we plot the fitting Lorentzian curve with the half width ξ_0 . Three insets are: (i) the magnetization relaxation curve $M(t)$ vs the \sqrt{t} ; (ii) the average decay time $\tau_{de}(\xi)$ vs the ξ^2 (diamonds); and (iii) the set of points in space, where for $M(0) = 0.15$ at $t = 0$ molecules are in resonance.

At $t = 0$ all molecules were split into different bias groups of width $\xi_0/2$. When some molecule flipped, the number of molecules in its group was reduced by one. The time taken for each bias group to decrease its initial number of molecules by a factor e is assumed to be the decay time τ_{de} for this group. Fig.3 shows the results for $M(0) = 0.15$; one has a Lorentzian line-shape with half-width ξ_0 .

Note one simple implication of this result: when $t/\tau_0 > 1$, the dominant contribution to the integral (1) comes

from $\xi > \xi_0$ where $\tau_{de}(\xi) \sim \xi^2$; by making the integral in (1) dimensionless, we see the magnetisation must decay like $|M(t) - M(0)| \sim \sqrt{t}$. Thus the Lorentzian lineshape of the hole in $M(\xi)$, in strongly annealed samples, is directly connected to the square root relaxation, arising from the dipolar form of the intermolecular interactions. Notice, incidentally, that the distribution of molecules in the sample found to be in resonance for these strong annealings is indeed almost homogeneous (Fig.3, inset bottom left).

4. *Application to Fe-8 system*: Instead of point dipoles we now have 8 spin-5/2 Fe^{+3} ions correctly positioned and oriented inside each molecular unit cell, arranged in a triclinic lattice array. The lattice parameters, easy and hard axis orientations, were taken from standard sources [16, 17]. As an example we show in Fig. 4 results for $M(t)$ and $\tau_{de}^{-1}(\xi)$, for an initial magnetisation $M(0) = 0.2$.

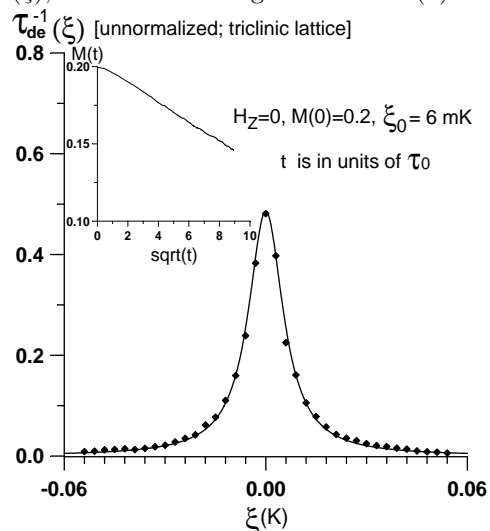


FIG. 4: Plot of τ_{de}^{-1} , as in Fig. 3, but now for a crystal of $Fe-8$ molecules (with 40^3 molecules arranged in a triclinic lattice). The inset above shows the decay of $M(t)$ with \sqrt{t} for a partially annealed sample (initial polarisation $M(0) = 0.2$). The lattice parameters for the $Fe-8$ triclinic lattice ($a=10.522(7)\text{\AA}$, $b=14.05(1)\text{\AA}$, $c=15.1(1)\text{\AA}$, with angles $\alpha = 89.90(6)$, $\beta = 109.65(5)$, $\gamma = 109.27(6)$, in degrees), and the positions of the 8 spin-5/2 ions in each unit cell, were taken from ref. [17]. The bias energy ξ is now given in Kelvin units, and the value $\xi_0 = 6\text{ mK}$ is that appropriate to natural isotopic concentration [11].

Our basic conclusion here is that none of the results found for simple cubic lattices with point dipoles is essentially altered by going to a magnetisation distributed over the 8 Fe ions, or by the change of lattice structure- one still has a Lorentzian lineshape for τ_{de}^{-1} , and the \sqrt{t}/τ_Q relaxation form for $M(t)$, for $M(0) \lesssim 0.5$, for the simulations we have done [22].

5. *Nearly polarised samples*: Finally we examine the opposite limit of strong initial polarisation, which has already been discussed both analytically and numerically [12, 21]. In a sample of generic shape, the molecules that

can tunnel inelastically (ie., those satisfying the 'resonance' condition $|\xi| < \xi_o$) form well-defined 'resonance surfaces' in space if the sample is nearly polarised, and $\xi_o \ll E_D$ [21, 23]. This is because now the dipolar field is dominated not by short-range fluctuations in space, but by the smoothly varying demagnetisation field. These resonance surfaces can be visualised by plotting those molecules satisfying the resonance condition at time t , during a Monte Carlo simulation. The spatial variation of the longitudinal component of the dipolar field can then be described by a slowly-varying demagnetisation field $E(\mathbf{r}, t)$, plus a smaller rapidly varying fluctuation $\delta\xi(\mathbf{r}, t)$, having Lorentzian distribution [12, 25] over values of $\delta\xi$, and $\langle \delta\xi(\mathbf{r}, t) \rangle = 0$.

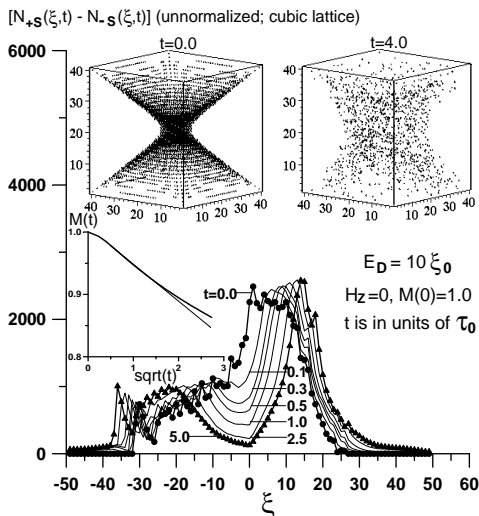


FIG. 5: The main figure shows the time evolution of the distribution $M(\xi, t)$ of magnetisation caused by dipolar fields, in an initially polarized sample ($M(t=0) = 1$); the same cubic sample of Fig. 2 was used. The 3 insets show: (i) the resonance surface at $t = 0$, showing all molecules in the sample satisfying the resonance condition in the text; (ii) the same result at $t = 4\tau_o$, where we see that the molecules satisfying the resonance condition have now spread in space (iii) the relaxation of the normalized magnetization $M(t)$ vs \sqrt{t} for the same sample (with the square root form shown as a thin line).

It then becomes interesting to ask how these surfaces evolve in time. Again we must resort to Monte Carlo simulations. Fig. 5 shows a typical example- for all sample geometries we have studied the surfaces break up rapidly once the fraction $(1 - M(t)) \sim 0.07 - 0.11$, corresponding closely with the onset of deviations from the square root scaling. This is intriguing because it indicates the deviations may be caused not only by higher correlations between the molecules, as previously assumed [12]; this result needs further investigation. Notice that the hole lineshape is now irrelevant to the square root form of the relaxation dynamics, which comes instead from the Lorentzian distribution of $\delta\xi(\mathbf{r}, t)$ [12, 25]. The hole lineshape is now controlled by the sample shape.

Our essential conclusion in this paper is that one can

use Monte Carlo methods to investigate the relaxation characteristics in regimes inaccessible to analytic theory. This allows one to understand the lineshape, width and time evolution of the hole that appears in $M(\xi, t)$.

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