

# Molecular Magnets - Review of Quantum Tunneling

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## Abstract

The ability to consistently chemically synthesize molecules with fixed magnetic properties has allowed investigation into the quantum nature of the magnetization. Two of the most studied molecular magnets are  $\text{Mn}_{12}$  and  $\text{Fe}_8$ . The quantum nature of the magnetic moment (or spin) of these molecules is typically manifested in quantum mechanical tunneling, and interference effects due to the Berry phase of the spin state. This review comprises descriptions of two experiments on  $\text{Mn}_{12}$  which demonstrate tunneling, and two experiments on  $\text{Fe}_8$ , which demonstrate tunneling and quantum interference. The presence of tunneling is extracted from hysteretic magnetization curves, which show steps at certain applied fields. The Berry phase interference is inferred from level-crossing gaps whose size depends on the transverse applied field in an oscillatory fashion. The theoretical explanation for these measurements is described, and the theory behind the Berry phase interference is described.

## Introduction

Over the last 15 years, the ability to consistently manufacture molecular structures with fixed magnetic properties has given rise to a field known, fittingly, as molecular magnetism. There are several such molecules studied currently. Two of the more common are  $\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{OO})_{16}(\text{H}_2\text{O})_4$ , referred to as  $\text{Mn}_{12}$ , and  $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$ , known as  $\text{Fe}_8$ . Overall these are complicated molecules, but the chemical details of them need not concern us here. All that one must know for the purposes of this review is that each molecule has a ground state total spin of  $S = 10$ , which is essentially fixed (the excited state of  $S = 9$  has an energy of 30 K for  $\text{Mn}_{12}$  (1)), and has magnetocrystalline anisotropy. The anisotropy energy for reversal is 67 K and 25 K for  $\text{Mn}_{12}$  and  $\text{Fe}_8$ , respectively (2). (The fact that for  $\text{Mn}_{12}$ , the anisotropy barrier is greater than the  $S = 9$  barrier, but only  $S = 10$  is considered, will be discussed at the end.) Typically when these molecules are synthesized, they form a crystalline structure (3). The interaction between different molecules in the

crystal (dipolar interactions) are weak, and for our purposes are not important (3). So in effect one has an ensemble of individual  $S=10$  spins to manipulate at will, and can study their quantum nature. A way in which this is done is by studying the quantum mechanical tunneling characteristics of these spins. The description of this phenomena will comprise the majority of this review (and indeed comprises a large portion of the study of molecular magnets).

### Experiments with $Mn_{12}$

Since interactions between spins are unimportant, and because one can restrict one's attention to the  $S = 10$  state, the Hamiltonian of the spin can be written as a 1-body operator of the form (4):

$$H = DS_z^2 + g\mu_B \mathbf{S} \cdot \mathbf{H} \quad (1)$$

In the absence of transverse (not parallel to  $\mathbf{z}$ ) anisotropy and transverse applied field, the  $z$ -component of  $\mathbf{S}$  is a good quantum number, and the eigenvalue spectrum has the double-well structure shown below. There is a 2-fold degeneracy between  $S_z$  and  $-S_z$  for  $\mathbf{H}_{app} = 0$ .

Before going into a more detailed discussion, let me here telegraph the idea. It's revealed in the following pictures of the energy levels of the Hamiltonian (1). Essentially a term in the

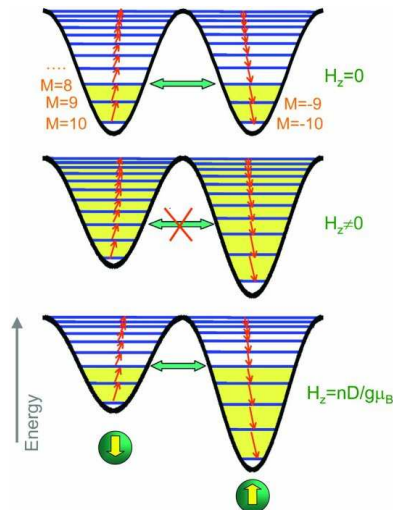


Figure 1: Energy levels for Hamiltonian eqn (1) for different applied fields. Fig. from (5)

environment which does not commute with  $S_z$  will allow for tunneling through the barrier

whenever states on either side have matching energy levels. This tunneling is the source of the discrete steps found in the hysteresis curves found experimentally.

The relevant data from the work of Friedman et al. is shown below. First is a curve of magnetization versus applied field (I'll refer to this as a hysteresis curve):

The explanation of the hysteresis curve in terms of the tunneling picture goes as follows:

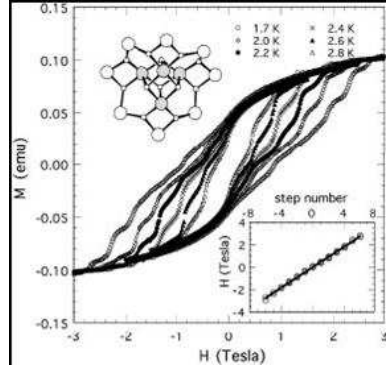


Figure 2: Magn. versus applied field. Inset shows values of field where jumps in the magn. are observed.

First, it's important to note that the steps in the curve are seen only when the field is pointing opposite to the magnetization. So, for example, the magnetization is saturated in the  $+z$  direction by a strong field, and upon sweeping the field from positive to negative, steps are seen as the field goes from 0 to negative values. The explanation follows from the picture from fig. (1): As the field hits 0 on the way down from positive values, the magnetization is in the stable minimum of the  $+S$  well. But as the field goes to negative values, the state  $-S$  becomes the global minimum. As the field is swept, levels on the two sides of the barrier will coincide. Every time this happens, quantum tunneling from the  $+S$  well to the  $-S$  well occurs. This is the reason why the magnetization is reduced at these values of the applied field. One can, from eqn (1), easily deduce the values of the field such that energy levels on either side coincide, with the result:

$$H = -Dn/g\mu_B \quad n = 0, 1, 2, \dots \quad (2)$$

It is seen from the inset of the fig (2), that for reasonable values of  $D$ , this is indeed where steps are seen. It should be noted as well that at finite temperatures, there will be a thermal

distribution of level occupation. It is proposed that levels near the top of the barrier tunnel more easily (5). That is one reason why there is not simply one tunneling event from  $+S$  to  $-S$ , and why tunneling is more efficient at slightly higher temperatures (although temperatures low enough to preclude pure thermal excitation) (3).

The following is a graph of blocking temperature versus applied field, and also indicates

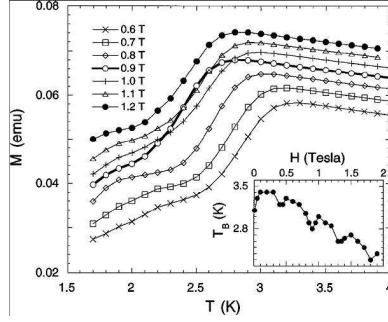


Figure 3: Magn. versus T for several applied fields. Inset is plot of  $T_B$  versus applied field.

the presence of quantum tunneling. To understand this data, one (including this author) must be reminded the meaning of the blocking temperature: typically when one has an ensemble of randomly oriented magnetic particles with uniaxial anisotropy, and one cools the ensemble in 0 magnetic field ("Zero Field Cooling" for ZFC), the particles will be frozen along their easy axes. Since they are randomly oriented, this leads to a small total magnetization. Now one applies a constant field, and heats the sample. At some point, there exists enough thermal energy to overcome the anisotropy barrier, and the particles align with the field, increasing the magnetization of the ensemble. Upon further heating, the magnetization is thermalized, and subsequently reduced. The maximum point of the  $M$  versus  $T$  curve is the blocking temperature. When heating in higher fields, it takes less thermal energy to go from anisotropy-dominated to zeeman-dominated configurations. Thus usually the blocking temperature versus field is a monotonically decreasing function.

With this in mind, the data from the inset of fig (3) is surprising. The dips in the curve indicate that at certain values of the applied field, there is an enhanced traversing of the anisotropy barrier. These points correspond to points in the applied field where levels on two sides of the barrier coincide. They are the same field values where steps in the hysteresis are found. This is therefore evidence of quantum tunneling (thermally assisted quantum

tunneling, to be more exact) through the barrier. The paper of Thomas et al.(3) came out at about the same time (1996), and arrived at similar conclusions, with similar measurements (although the steps in the hysteresis are slightly more evident in that data).

An important point of the above description is that there must be terms in the Hamiltonian which do not commute with  $S_z$  in order to have tunneling between states with different  $S_z$ . Such a term is conspicuously absent in eqn (1). One may expect some transverse anisotropy to present such a term, but  $\text{Mn}_{12}$  possesses tetragonal symmetry, and any anisotropy terms must therefore be at least of order  $S^4$ . There are without doubt neglected effects in the Hamiltonian of eqn (1). As mentioned earlier, the energy barrier for  $S = 9$  state is greater than the anisotropy energy barrier, yet the  $S = 10$  state is the only one considered. In addition, the work of Politi shows that for a Hamiltonian of the form:

$$H = S_z^2 + (S_+^2 - S_-^2) \quad (3)$$

the application of a field in the z-direction predicts tunneling at a rate significantly smaller than that seen experimentally (1). In Politi's paper, the authors argue that spin-phonon coupling should be an important contribution to the tunneling mechanism. The other important effect is the interaction with nuclear spins, this interaction is described in theoretical papers by Prokof'ev (6), and by Sinitsyn (7). This interaction causes the broadening of energy levels, which allows the width of the tunneling resonance to be large enough to be measurable. Without such significant broadening, the widths would be of the order  $10^{-8}$  and not observable (4). However I won't cover the details of these papers.

### Experiments with $\text{Fe}_8$

More recently, work done on the  $\text{Fe}_8$  has revealed some very interesting additional quantum effects in the tunneling dynamics. The  $\text{Fe}_8$  is also a stable  $S = 10$  macrospin. The Hamiltonian for it is typically written as:

$$H = -DS_z^2 + E(S_x^2 - S_y^2) + g\mu_B \mathbf{S} \cdot \mathbf{H} \quad (4)$$

One advantage of  $\text{Fe}_8$  is that there is an explicit  $S_z$  symmetry breaking term in the Hamiltonian, which is well characterized experimentally (ref. 8 and references therein). The theory

of tunneling proceeds similarly for  $\text{Fe}_8$  as for  $\text{Mn}_{12}$ . One of the first experiments done on  $\text{Fe}_8$  was by Sangregorio et al (8). In this experiment, they measure relaxation times and find that below a certain temperature (400 mK), the times no longer follow the expected thermal behavior ( $M(t) = M(0)e^{(-t/\tau)^\beta}$ ). In particular, the relaxation times are independent of T. They attribute this to tunneling. They also observe steps in hysteretic M vs. H curves, similar to those seen in  $\text{Mn}_{12}$ , as well as increased relaxation rates at the same applied fields as those which cause steps in the hysteresis curves.

The work on  $\text{Fe}_8$  was greatly extended in the work of Wernsdorfer et al (2). They again find steps in the hysteresis as the previous workers, indicating the presence of quantum tunneling of the spin. They extend the work to study the size of the energy gaps across which the tunneling occurs. The following figure taken from the paper indicates the energy spectrum as a function of the applied field. (This spectrum can easily be obtained by directly diagonalizing the 21x21 Hamiltonian matrix of (4))

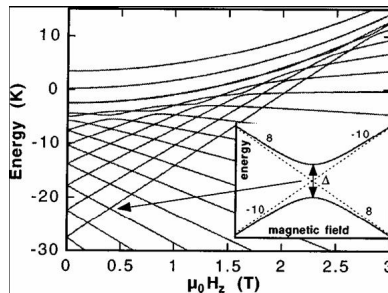


Figure 4: Energy levels versus field. Inset shows closeup of avoided crossing.

At each level crossing, there is a gap opened up by the transverse anisotropy terms, which break the  $S_z$  symmetry and cause avoided level crossings. As one sweeps the field, when a state comes upon a gap it can either jump across the gap, or remain on the same "band". The probability P to avoid crossing a gap (or to tunnel into another state) is given by the Landau Zener formula:

$$P = 1 - \exp\left(-\frac{\pi\Delta^2}{\beta}\right) \quad (5)$$

where  $\beta$  is the rate at which the external parameter is swept, in this case  $\beta = dH/dt$ , and  $\Delta$  is the size of the gap. Essentially if one sweeps the field (or any external parameter) very slowly, one will remain on the same band (adiabatic theorem).

By sweeping the field back and forth across a gap and measuring the ensuing magnetization, Wernsdorfer et al can determine the fraction of particles that change their magnetization, and the probability of crossing the gap. With this probability, they can determine the size of the gap. A very interesting effect occurs when they study the size of the gap as a function of transverse applied field. One might initially guess that a larger transverse field will more easily enable transitions between  $S_z$  states, so that the gap will be larger. However it turns out the the gap is an oscillating function of the transverse field, if the field is applied along the medium axis. The reason for this is a quantum interference effect that arises from the Berry phase (9). The result of the calculation involving the Berry phase effect is that the gap should oscillate with the transverse field with a period of (2):

$$\Delta H = \frac{2k_B}{g\mu_B} \sqrt{2E(E + D)} \quad (6)$$

Below is the data showing the oscillations. A brief explanation follows of eqn (6) follows:

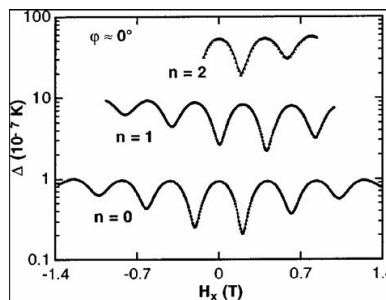


Figure 5: Energy gap at avoided crossing versus transverse applied field, for 0th, 1st, and 2nd gap.

First a physical explanation: Looking below at fig (6), one sees that when the magnetization goes from the 2 degenerate minima at points A and B, it will do so in a plane parallel to the y-z plane, in order to avoid the energetically costly x axis. (Note the presence of an external transverse field causes the energy minima to reside away from the N or S poles.) Since there are 2 equivalent paths from A to B in this case, they can destructively interfere, causing a quenching of the tunneling rate. (Note that if the minima are in the y-z plane, there is only 1 path connecting them, and there is no interference).

And now a more technical explanation: Given the Hamiltonian eqn (4) for the system,

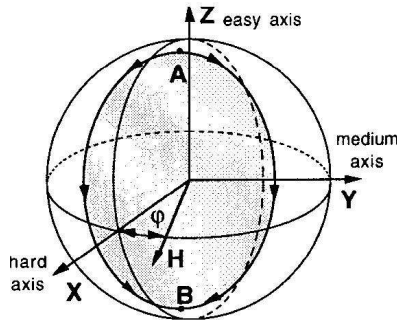


Figure 6: Depiction of 2 paths connecting degenerate energy minima points A and B.

one can construct a path integral representation connecting two states, say states A and B in fig. (6). Its physical relevance is that it contains information about the probability to go from state A at time  $t_1$  to state B at a later time  $t_2$ . We are interested in seeing how this probability depends on the value of the transverse field. When one constructs a path integral for spin states, one uses coherent spin states as a basis, and the result is the action has the form:

$$\text{action} = \int_{t_1}^{t_2} \left[ -iS(1 - \cos(\theta))\dot{\phi}(\tau) + H[\mathbf{n}(\tau)] \right] d\tau \quad (7)$$

In a semi-classical limit (in this case large-S limit), the physical path  $\theta(\tau), \phi(\tau)$  is the one that minimizes the action. The first term in the action is the Berry phase and comes from the non-orthogonality of coherent spin states. It is purely quantum mechanical. Among its important properties are that it depends only on the shape of the path (not on its dynamics), and that it is imaginary - this can cause interference effects between different paths. The other critical aspect of the Berry phase is that, for closed paths, it simply represents the area on the sphere enclosed by the loop.

If two paths start and end at the same point, and differ in phase by  $\pi$  (equivalently, sweep out an area on the sphere of  $\pi$ ), then they will constructively interfere. This occurs when the imaginary part of the action equals  $\pi$ . The energy functional for the spin has the following form:

$$E(\theta, \phi) = K_1(\cos(\theta) - \cos(\theta_0))^2 + K_2(\sin^2(\theta)\sin^2(\phi)) \quad (8)$$

Here  $\cos(\theta_0)$  is the coordinate of the energy minimum. Garg (9) evaluates the area swept out

by the trajectory indicated in the figure (or the Berry phase), and hence the imaginary part of the action. By setting this Berry phase =  $\pi$ , he determines the condition for destructive interference (or quenched tunneling, as phrased in the literature), as found in eqn (6), and experimentally seen in fig (5). There is a further detail that the location of minima depend upon which gap tunnels through (the 0th, 1st, 2nd, etc). It depends on the even-ness or odd-ness of the gap number, as seen in fig (5)). This author will leave this detail unexplained, however.

### Conclusion

The previously described experiments are a very nice demonstration of quantum effects seen in nanoscale or mesoscopic systems. In addition to their intrinsic interest, there is some possibility of using such devices as information storage devices (5). In addition to the experiments and theory on tunneling in molecular magnets, Leuenberger and Loss have recently proposed using molecular magnets as the basis for quantum computation, in particular as a system capable of implementing Grover's algorithm (10). There has also been recent work on coupled molecular magnets (dimers with exchange interactions), which show richer behavior in the hysteresis curves and quantum tunneling transitions (11). It should be noted as well that the area of tunneling with molecular magnets comprises just a portion of active research on these systems. Other fields of interest include magnetocalorics, and their use as experimental probes of 1-dimensional spin rings, which have theoretical interest (12).

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