# Quantum tunneling and classical barrier reduction for a mesoscopic spin

Jonathan R. Friedman*
*Department of Physics, The State University of New York at Stony Brook, Stony Brook, New York 11794-3800*
(Received 12 January 1998)

I show that for a large spin with uniaxial anisotropy it is, *in principle*, impossible to distinguish classical energy-barrier reduction due to a transverse magnetic field from an increase in the tunneling rate of excited levels. Given a suitable definition of the quantum energy barrier, I derive an expression for the field dependence of the barrier height that agrees with the classical result up to a constant of order unity. Numerical results show that for a mesoscopic spin ($S\sim 10$) the barrier decreases in a series of steps, which recent experiments may have revealed. [S0163-1829(98)08317-9]

Recent experiments have rekindled interest in the field of quantum tunneling of magnetization.[1] Most notable has been the discovery of resonant tunneling between spin states in a system of spin-10 molecules known as $Mn_{12}$ acetate or, simply, $Mn_{12}$. At low temperatures the magnetization in this system was found to relax significantly faster at particular values of magnetic field that correspond to resonances between spin states. First observed at just a few fields,[2,3] the phenomenon was firmly established with the discovery of multiple, regularly spaced resonances.[4] This phenomenon has been verified in other experiments on the same material[5–9] and there is now some evidence for it in other systems.[10,11]

While there have been many semiclassical treatments of tunneling in magnetic systems,[12–14] such approaches have turned out to be unnecessary for $Mn_{12}$, which with $S=10$ is easily tractable by more precise methods. The dynamics of $Mn_{12}$ have been quantitatively described[4,5,8] by a simple Hamiltonian:

$$\mathcal{H}=-DS_z^2-g\mu_B\mathbf{S}\cdot\mathbf{B}, \tag{1}$$

where $D>0$ characterizes the magnetocrystalline anisotropy that impels the spin of the molecule to lie along (or antiparallel to) the $z$ axis (the $c$ axis of the $Mn_{12}$-acetate's tetragonal lattice) and $\mathbf{B}$ is the magnetic induction. The system can be modeled as a double-well potential, as shown in Fig. 1, with the levels representing different eigenstates of $S_z$. The second term in Eq. (1) has two distinct effects. A longitudinal component of the field $B_z$ tilts the potential, as in Fig. 1, raising or lowering the energies of the states, depending on which well they are in, and bringing levels into resonance at particular values of $B_z$. On the other hand, a transverse field $B_x$ introduces a term into the Hamiltonian ($-g\mu_B B_x S_x$) that does not commute with $S_z$ and therefore allows tunneling between the otherwise unperturbed states. It has been shown[7,8,15] that the tunneling from excited levels near the top of the barrier is significantly faster than for low-lying levels. As the dynamics of $Mn_{12}$ are now understood,[7,8] the system is thermally activated to some high-lying level near the top of the barrier where the tunneling rate is high; it then tunnels across the barrier and decays down into the other well (Fig. 1).

Motivated by the notion that the tunneling is produced by some transverse (dipolar or hyperfine) field internal to the $Mn_{12}$ crystal, some experiments[5,7–9] have attempted to promote tunneling in $Mn_{12}$ by applying an external transverse field. However, it is well known that a transverse field will lower the classical relaxation barrier; so, an increase in the relaxation rate in response to an applied transverse field cannot immediately be attributed to an increase in tunneling. In this paper I show that for a large spin system the increase in the tunnel splitting of excited levels is actually responsible for the classical reduction of the energy barrier and cannot, *in principle*, be distinguished from it. Furthermore, I show that for moderately sized spins ($S\sim 10$) the discrete level structure becomes important and one should expect to find that the effective energy barrier decreases in steps, rather than continuously. I will compare these results with recent experiments.

If the field is applied along the easy ($z$) axis, the eigenstates of Eq. (1) are $|S,m\rangle$, where $S$ is the total spin and $m$ is the corresponding magnetic quantum number; the eigenenergies are $E_m=-Dm^2-g\mu_B Bm$. It is straightforward to calculate at what fields levels in opposite wells cross. The states $|S,m\rangle$ and $|S,-m+n\rangle$ (the label $S$ will remain implicit hereafter) become degenerate when[4]

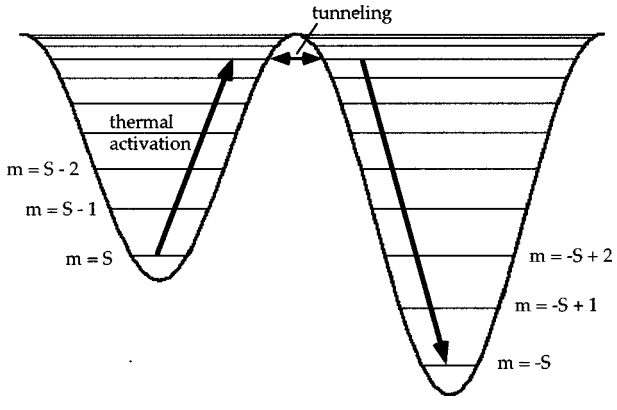


FIG. 1. Double-well potential for spin reversal. The energy barrier is due to the anisotropy and the asymmetry is produced by an applied longitudinal field. Energy levels correspond to different spin projections along the easy axis. The dynamics of thermally assisted resonant tunneling are illustrated by the arrows.

 

$$B_{m,-m+n}=-\frac{Dn}{g\mu_B}. \tag{2}$$

It is important to note that this result is independent of $m$, implying that all levels in the left well come into resonance with levels in the right well at the same values of magnetic field. Figure 1, where the field has been set such that $n=2$, illustrates this multiple resonance.

This multiple resonance can be seen as arising from a hidden symmetry in the Hamiltonian and can be made manifest by completing the square of Eq. (1) while taking $\mathbf{B}=B\mathbf{z}$:

$$\begin{aligned}\mathcal{H}&=-D\left(S_z+\frac{g\mu_B B}{2D}\right)^2+D\left(\frac{g\mu_B B}{2D}\right)^2\\&=-D\left(S_z-\frac{n}{2}\right)^2+D\left(\frac{n}{2}\right)^2,\end{aligned}$$

where the last step is an application of Eq. (2). The state $|m\rangle$ then has energy $E_m=-D(m-n/2)^2+Dn^2/4$, which is clearly invariant under the transformation $m\rightarrow -m+n$.

It is useful to relabel the states to reflect the degeneracy more clearly. If one defines $m'=m-n/2$, then for a given value of $n$ the degenerate states are $|m\rangle=|m'+n/2\rangle$ and $|-m+n\rangle=|-m'+n/2\rangle$. These can be relabeled, respectively, as $|m'\rangle$ and $|-m'\rangle$, which are now eigenstates of the operator $S_z'=S_z-n/2$. With this labeling, each degenerate pair comprises states with labels that differ only by a sign, making it clear that they are degenerate. The new label $m'$ can be thought of as a counting number, indicating how far down the state is from the top of the barrier (see Fig. 1).

It is not *prima facie* clear that the resonance condition, Eq. (2), would be unaltered if there is a component of the field perpendicular to the easy axis, $b_x=g\mu_B B_x$. When the system is tuned to resonance $n$, nondegenerate perturbation theory yields the second-order correction to the energy of $|m'\rangle$ to be

$$E_{m'}^{(2)}=-\frac{b_x^2[s(s+1)+m'^2-(n/2)^2]}{2D(4m'^2-1)}, \tag{3}$$

which is invariant under the transformation $m'\rightarrow -m'$. Hence, two states that are degenerate in the unperturbed case ($|m'\rangle$ and $|-m'\rangle$) remain degenerate when the perturbation is turned on. Note that the denominator of Eq. (3) is zero when $m'=\pm\frac{1}{2}$. This indicates that degenerate perturbation theory must be invoked. The proper treatment does not lead to a correction in the resonant condition for this pair but rather to a calculation of the tunnel splitting (see below). A similar calculation of the energy correction to fourth order in perturbation theory yields a rather cumbersome expression that is also invariant under $m'\rightarrow -m'$. Thus, the resonant condition, Eq. (2), remains unchanged to at least fourth order in perturbation theory. This apparent symmetry is not exact: numerical results show that Eq. (2) breaks down when the tunnel splitting becomes large. One may conjecture that the resonant condition for a particular pair of levels holds up to the order of perturbation theory at which tunneling arises for that pair. Several experiments[5,7,9] have confirmed that the resonance condition depends only on the longitudinal field and is apparently independent of transverse field.

A transverse component of the magnetic field breaks the rotational symmetry that Eq. (1) would otherwise have and thereby produces tunneling between degenerate states. While there are various semiclassical techniques for calculating this tunnel splitting,[12–14] in the case of Eq. (1) it can be calculated explicitly to leading order in degenerate perturbation theory. Garanin[15] has calculated the tunnel splitting for the case of zero longitudinal field ($n=0$). His formula can be generalized to the case of other resonances ($n>0$). The tunnel splitting for degenerate states $|m'\rangle$ and $|-m'\rangle$ is[16]

$$\begin{aligned}\Delta_{m'}=&\frac{2D}{[(2m'-1)!]^2}\\&\times\sqrt{\frac{(s+m'+n/2)!(s+m'-n/2)!}{(s-m'-n/2)!(s-m'+n/2)!}}\left(\frac{|b_x|}{2D}\right)^{2m'}.\end{aligned} \tag{4}$$

This equation can be used to obtain the classical reduction of the energy barrier by a transverse magnetic field. When the field is purely transverse, the energy barrier $U$ is given by the well-known result $U=U_0(1-|b_x|/b_c)^2$, where $U_0=DS^2$ is the height of the barrier in zero field and $b_c=2DS$ is the critical field at which the barrier disappears. There is no analytic expression for the energy barrier when the field has components in both the $x$ and $z$ directions. However, for $|b_x/b_c|\ll 1$ (and arbitrary $b_z$), the barrier is given by

$$U=U_0\left[\left(1-\frac{b_z}{b_c}\right)^2-2\left|\frac{b_x}{b_c}\right|\sqrt{1-\left(\frac{b_z}{b_c}\right)^2}\right]+O\left[\left(\frac{b_x}{b_c}\right)^2\right]. \tag{5}$$

This equation contains a term linear in $b_x$, which leads to an interesting paradox since the lowest-order correction to the energy of any state, Eq. (3), is quadratic in $b_x$.

In order to resolve this seeming contradiction we must carefully approach the question of the meaning of an energy barrier in the quantum picture. Naïvely, one can define it as the energy difference between the lowest-energy state ($m'=S-n/2$) and the highest-energy state ($m'=0$). But this definition leads to the paradox, as the energies of these states vary as $b_x^2$. One arrives at a better definition of the energy barrier by recognizing that the transverse field produces tunneling in the levels and that, according to Eq. (4), the tunneling is orders of magnitude faster for the highest levels than for the lower ones. One can then define the energy barrier as the energy difference between the lowest level and a level where the tunneling occurs ''sufficiently fast.'' This definition of the energy barrier corresponds to the classical result in the large-spin limit, as will be demonstrated below. That is, the term linear in $b_x$ is obtained.

In the limit of large spin ($S-n/2\gg m'\gg 1$), Eq. (4) can be simplified to

$$\Delta_{m'}=\frac{2Dm'}{\pi}\left(\frac{|b_x|e^2\sqrt{S^2-n^2/4}}{8Dm'^2}\right)^{2m'},$$

where Stirling's approximation and the identity $(1+1/x)^x \xrightarrow[x\to\infty]{} e$ have been used. The level $m_c'$ becomes the top of the barrier when the tunnel splitting is on the order of $Dm_c'$, the energy separation between neighboring levels, i.e., when $\Delta_{m_c'}/Dm_c' \approx O[1]$. The field at which this happens is then

$$|b_x| = \frac{8Dm_c'^2}{e^2\sqrt{S^2-n^2/4}}\left(\frac{\pi}{2}\,O[1]\right)^{1/2m_c'} \xrightarrow[m'\gg 1]{} \frac{8Dm_c'^2}{e^2\sqrt{S^2-n^2/4}}, \tag{6}$$

since the term in the brackets rapidly approaches 1 as $m_c'$ gets large. This indicates that the precise criterion used for a level to be tunneling ''sufficiently fast'' is irrelevant, as should be the case in the classical limit.

The definition of the barrier as the energy difference between the lowest state $|S\rangle$ and this critical tunneling state $|m_c'\rangle$ gives

$$U = D(S^2-Sn) - D(m_c'^2 - n^2/4) - \frac{b_x^2(S^2-n^2/4)}{8Dm_c'^2},$$

where the last term is the second-order correction to the energy of state $|m_c'\rangle$, Eq. (3), again in the limit $S-n/2 \gg m' \gg 1$. (The correction to the energy of state $|S\rangle$ is negligible.) Using Eq. (6) to eliminate $m_c'$ and Eq. (2) to eliminate $n$, one obtains

$$U = DS^2\left[\left(1-\frac{b_z}{b_c}\right)^2 - \frac{2|b_x|}{b_c}\sqrt{1-\left(\frac{b_z}{b_c}\right)^2}\left(\frac{e^2}{8}+\frac{1}{e^2}\right)\right]. \tag{7}$$

This reproduces the classical result, Eq. (5), except for the factor of $(e^2/8+1/e^2)=1.06$ in the second term within brackets. The discrepancy can be attributed to the fact that Eq. (4), a perturbative result, is valid when $|b_x| \ll Dm^2$; but in the above discussion it is employed for $|b_x| \approx Dm^2$, exactly where it begins to break down. This result establishes that for a macroscopically large spin the energy-barrier reduction by a transverse field is achieved via tunneling from the excited states. In a certain trivial sense, then, the obviously classical phenomenon of barrier reduction can also be viewed as a realization of macroscopic quantum tunneling. There have been some experimental reports that a transverse field promotes tunneling in $Mn_{12}$.[5,7,9] With one exception to be discussed below, these claims, while true, ironically establish nothing more than that the field suppresses the classical energy barrier.

The above model of barrier reduction can also be simulated numerically by diagonalizing the Hamiltonian and again defining the top of the barrier to be the state where the tunnel splitting is on the order of the spacing between levels. The results of such a simulation for $S=100$ and $b_z=0$ are shown in Fig. 2(a), where the critical tunneling criterion $\Delta_{m_c'}/Dm_c'$ was taken to be 0.1 or 0.001, as indicated. (Taking $\Delta_{m_c'}/Dm_c'=1$ is problematic since the tunnel splitting becomes so large that it becomes difficult to identify a particular eigenstate with an $m'$ value.) The solid curve is the classical result; the agreement is quite good. Notice that

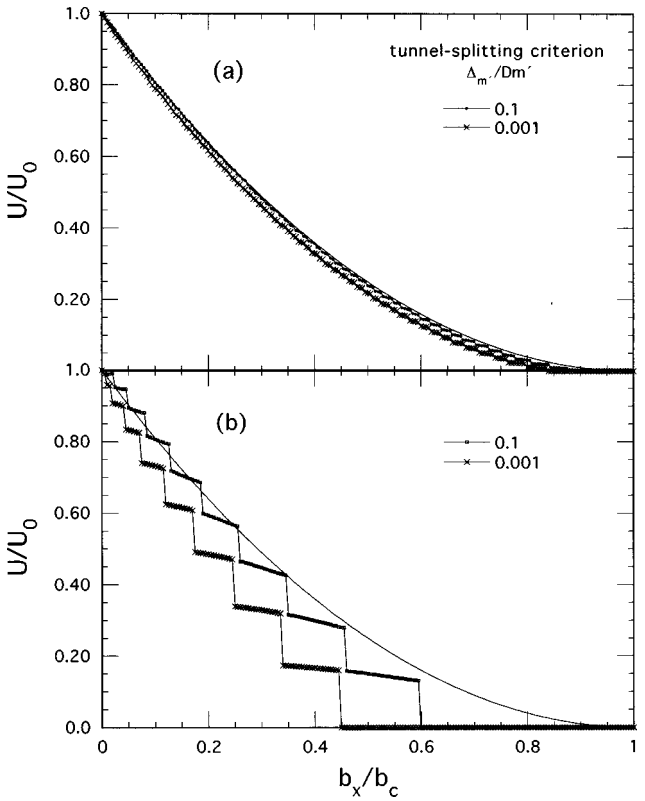


FIG. 2. Calculated barrier reduction by a transverse field for (a) $S=100$ and (b) $S=10$. The thin lines are the classical result while the points are the results of numerical diagonalization of the Hamiltonian, defining the top of the energy barrier to be the level for which the tunnel splitting is comparable to the spacing between levels, as described in the text.

changing the splitting criterion for the critical level by two orders of magnitude creates rather small deviations that are most apparent at large fields.

What happens to this picture when the magnitude of the spin is not very large so that the levels do not form a quasicontinuum? The analytical result derived above breaks down in this case, but the numerical calculations are still valid. Figure 2(b) shows the result for $S=10$ (i.e., $Mn_{12}$). The barrier no longer reduces smoothly with transverse field. Instead there is a series of jumps and plateaus. This is easy to interpret within the picture presented above: as the transverse field is raised, the ''fast-tunneling'' level abruptly changes from one level to the next lowest when the selected criterion is reached for the lower level. It should also be noted that here the result is more susceptible to the particular criterion one chooses for the critical tunnel splitting and the sharpness of the steps will depend on the dynamics. Unlike in the semiclassical limit, for $S\sim 10$ the detailed dynamics of the relaxation process are important in determining the effective barrier and what constitutes ''sufficiently fast'' tunneling. Assuming, for example, that thermally induced transitions between levels are dipole selected ($\Delta m=\pm 1$), then the critical level $m_c'$ is the lowest level for which its tunneling rate is faster than the rate of thermally populating the level above it, $m_c'-1$; i.e., $\Delta_{m_c'} > \Gamma_{m_c'\to m_c'-1} \approx \omega_{m'} \exp[(E_{m_c'} - E_{m_c'-1})/k_BT]$, where $\omega_{m'}$ is the characteristic attempt frequency for that level. It is beyond the scope of this work to

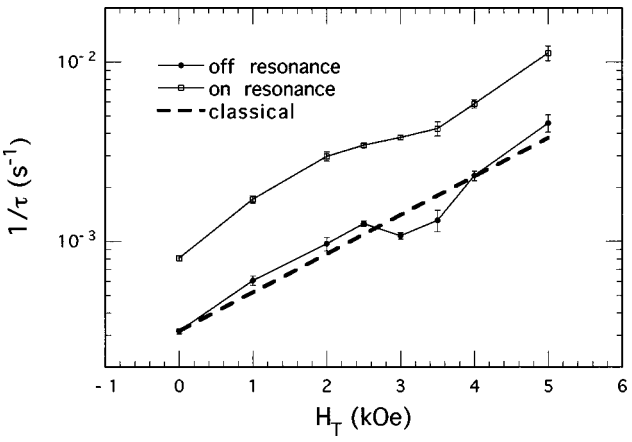


FIG. 3. Relaxation rate at 2.7 K of a single crystal of $Mn_{12}$ acetate as a function of transverse field on a semilogarithmic plot for $n=1$ (from Ref. 7). Data both on and off resonance are shown. The dashed line is the expected classical barrier reduction for the off-resonance data. A slight plateau can be seen in the data between 2 and 3.5 kOe, which may correspond to one of the plateaus in Fig. 2(b).

present a detailed dynamical theory of the relaxation that would predict the precise barrier dependence on $b_x$ for $Mn_{12}$ or related systems. Recent work[17–20] has explored the relaxation dynamics of $Mn_{12}$ with tunneling. What can be said here, without detailed knowledge of the dynamics, is that in the low-spin limit the effective barrier should depend on such experimental parameters as temperature. That is, the barrier ceases to have intrinsic significance and retains only empirical meaning. In both the low-spin and high-spin limits, however, one effect is clearly going to appear: At the lowest temperatures, tunneling from the ground state is the dominant process, the system no longer needs to reach any excited levels, and so effectively there is no barrier. This is the so-called quantum regime predicted from semiclassical analyses for large spins.[12–14]

One recent experiment[7] on $Mn_{12}$ has studied the relaxation rate as a function of transverse field in the vicinity of a resonance. The data are reproduced in Fig. 3, where the relaxation rate at 2.7 K near the $n=1$ resonance is plotted as a function of transverse field on a semilogarithmic scale. The relaxation rate (and hence barrier height) as a function of transverse field seems to roughly follow the classical expectation, shown by the straight dashed line (where the slope was determined without any fitting parameters[7]). Between $\sim 2$ and $\sim 3.5$ kOe a slight plateau in the relaxation rate was found. This plateau also appeared in another set of data taken at a different temperature, indicating that it is not spurious. This subtle deviation from classical barrier reduction may be due to the discrete level structure of this $S=10$ system. Further experimental work may uncover more plateaus and confirm the semiquantitative prediction of Fig. 2(b).

I am indebted to Eugene Chudnovsky and Myriam Sarachik for many useful and stimulating discussions. Partial support for this work was provided by the Air Force Office of Scientific Research under Grant No. F49620-92-J-0190.

*Electronic address: jrf@onnes.physics.sunysb.edu. Much of this work was done at the Physics Department of the City College of New York, New York, NY 10031.

[1] *Quantum Tunneling of Magnetization*, Vol. 301 of *NATO Advanced Studies Institute, Series E: Applied Sciences*, edited by L. Gunther and B. Barbara (Kluwer, Dordrecht, 1995).

[2] M. A. Novak and R. Sessoli, in Ref. 1, p. 171.

[3] B. Barbara, W. Wernsdorfer, L. C. Sampaio, J. G. Park, C. Paulsen, M. A. Novak, R. Ferré, D. Mailly, R. Sessoli, A. Caneschi, K. Hasselbach, A. Benoit, and L. Thomas, J. Magn. Magn. Mater. **140-144**, 1825 (1995).

[4] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996); J. R. Friedman, M. P. Sarachik, J. Tejada, J. Maciejewski, and R. Ziolo, J. Appl. Phys. **79**, 6031 (1996).

[5] J. M. Hernández, X. X. Zhang, F. Luis, J. Bartolomé, J. Tejada, and R. Ziolo, Europhys. Lett. **35**, 301 (1996); F. Luis, J. Bartolomé, J. F. Fernández, J. Tejada, J. M. Hernández, X. X. Zhang, and R. Ziolo, Phys. Rev. B **55**, 11 448 (1997).

[6] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) **383**, 145 (1996).

[7] J. R. Friedman, M. P. Sarachik, J. M. Hernández, X. X. Zhang, J. Tejada, E. Molins, and R. Ziolo, J. Appl. Phys. **81**, 3978 (1997).

[8] J. M. Hernández, X. X. Zhang, F. Luis, J. Tejada, J. R. Friedman, M. P. Sarachik, and R. Ziolo, Phys. Rev. B **55**, 5858 (1997).

[9] F. Lionti, L. Thomas, R. Ballou, B. Barbara, A. Sulpice, R. Sessoli, and D. Gatteschi, J. Appl. Phys. **81**, 4608 (1997).

[10] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. **78**, 4645 (1997).

[11] S. M. J. Aubin, S. Spagna, H. J. Eppley, R. E. Sager, K. Folting, G. Christou, and D. N. Hendrickson, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **305**, 181 (1997).

[12] E. M. Chudnovsky and L. Gunther, Phys. Rev. Lett. **60**, 661 (1988); Phys. Rev. B **37**, 9455 (1988).

[13] M. Enz and R. Schilling, J. Phys. C **19**, 1765 (1986).

[14] J. L. van Hemmen and A. Süto, Europhys. Lett. **1**, 481 (1986); Physica B & C **141**, 37 (1986).

[15] D. A. Garanin, J. Phys. A **24**, L61 (1991).

[16] J. R. Friedman and E. M. Chudnovsky (unpublished).

[17] P. Politi, A. Rettori, F. Hartmann-Boutron, and J. Villain, Phys. Rev. Lett. **75**, 537 (1995).

[18] N. V. Prokof'ev and P. C. E. Stamp, J. Low Temp. Phys. **104**, 143 (1996).

[19] J. R. Friedman, Ph.D. thesis, The City University of New York, 1996.

[20] D. A. Garanin and E. M. Chudnovsky, Phys. Rev. B **56**, 11 102 (1997).