Quantum Step Heights in Hysteresis Loops of Molecular Magnets

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(Dated: Nov. 15th, 2001)

We present an analytical theory on the heights of the quantum steps observed in the hysteresis loops of molecular magnets. By considering the dipolar interaction between molecular spins, our theory successfully yields the step heights measured in experiments, and reveals a scaling law for the dependence of the heights on the sweeping rates hidden in the experiment data on Fe₈ and Mn₄.

With this theory, we show how to accurately determine the tunnel splitting of a single molecular spin from the step heights.

PACS numbers: 75.45.+j, 75.60.Ej

Crystals of molecular magnets, such as Fe₈ and Mn₁₂, have attracted much attention for their connection to macroscopic quantum tunneling and Berry phases. They may also have important applications in magnetic memory and quantum computing. The earliest and most spectacular observation on such a system is the quantum steps in the hysteresis loop of magnetization at low temperatures.

These quantum steps are a manifestation of macroscopic quantum tunneling, resulting from the tunneling between different spin states of large molecular spins (S = 10 for both Fe₈ and Mn₁₂, S = 9/2 for Mn₄). As in any many-spin system, this tunneling phenomenon is naturally complicated by the interaction between spins and other environmental effects. A full understanding of this phenomenon demands a successful theory on the quantum steps, describing their widths, shapes, and heights. So far, besides speculations, no serious attempt has been made to develop quantitative theories on any of the step features.

In this letter we present a successful theory on the step height as the first step towards a complete theory on the quantum steps in the hysteresis loop. Since the height measures the tunneling probability between different spin states, it is the most prominent feature of the quantum step, and holds the key to understanding the underlying tunneling dynamics. In Fig. 1, we have adapted the experimental data on Fe₈ from Ref. [6], and show how the step height between spin states Sᵢ = ±10 changes with the sweeping rates. The data are compared to the Landau-Zener (LZ) model, which has been used to extract the tunnel splitting Δ of a single molecular spin from the step heights. When we fit the LZ model with the data at the fast sweeping regime there is a dramatic difference at slow sweepings: a two-third suppression.

By taking into account the dipolar interaction between molecular spins, our theory successfully gives the step heights measured in the experiment, as shown in Fig. 1. Two physical mechanisms influencing step heights are identified: the spin shuffling in the evolving distribution of dipolar fields and the dipolar interaction between spins in the resonance window. Furthermore, our theory reveals an α/Δ² scaling law for the dependence of the heights on the sweeping rate α of the external field. This law is confirmed by the collapse of the experimental data in terms of the scaled sweeping rates (see Fig. 3). As a direct application of our theory, we show how to accurately extract the tunnel splitting Δ of a single molecular spin from the step heights and the sample geometry. In our theory there are no adjustable parameters.

We argue that nuclear spins do not appreciably affect the tunneling dynamics under a fast sweeping field except for a renormalization of the tunnel splitting. In the relaxation experiments where the external field remains constant, the tunneling is strongly affected by the nuclear spins as recognized by Prokof’ev and Stamp. However, in the sweeping field experiments, the role of nuclear spins is marginalized by the sweeping fields. This
can be clearly seen in Fig. 6 of Ref. [1], where the relaxation with a constant external field is shown to be much slower than the one with a sweeping field of the slowest rate applied 0.04mT/s.

We consider spin lattices, such as crystals of Fe₈, Mn₁₂, and Mn₄, in which the spins interact with each other through the dipolar potential, \( d(\vec{r}) = E_D(1 - 3 \cos^2 \theta)\Omega_0/r^3 \), where \( \vec{r} \) is the displacement vector between the spins, \( \theta \) is the angle between \( \vec{r} \) and the easy axis, \( \Omega_0 \) is the unit cell volume, and \( E_D = \frac{2\mu_0}{3\pi}(Sg\mu_B)^2/\Omega_0 \) gives the interaction strength. Our theory will be compared to the experiment, mainly on crystals of Fe₈ where the experimental data on step heights are the most abundant [3, 1].

For simplicity, we focus on one step, that is, the tunneling between two spin states (for example, \( S_z = \pm 10 \) for Fe₈); it is rather straightforward to extend our theory to study multi-step tunneling.

We now have a system of Ising spins sitting at each site of a lattice. In a sweeping magnetic field along the easy axis, the spins will flip from one state to the other back and forth as a result of the tunneling driven by the sweeping. However, at any given moment, only a small fraction of spins are flipping by being in the resonance window while the others remain static. This can be understood by first considering an isolated spin in a sweeping field, which can be described exactly with the LZ model. In the LZ model the flipping occurs mainly in a tunneling time interval, when the Zeeman energy bias \( \gamma = 2g\mu_BS\mu_0H \) [12] between the two spin states caused by the changing external field becomes very small, \( |\gamma| \leq \Delta_{win}/2 \). This tunneling time defines the resonance window, whose width \( \Delta_{win} \) is the tunnel splitting \( \Delta \) at the adiabatic limit and \( \sqrt{2\alpha} = \hbar d\alpha/dt \) in the sudden limit [13]. Similarly for a spin interacting with other spins in a lattice, its resonance window is defined by \( |\gamma + \xi| \leq \Delta_{win}/2 \) for spin \( i \), where \( \xi_i \) is the Zeeman energy of spin \( i \) caused by the dipolar field from other spins. Since the dipolar field felt by spins is a distribution, only a small fraction of spins are in the resonance window at any given moment.

With this physical picture in mind, we can write down the evolution equation for the fraction \( F \) of up-spins. If spins in the resonant window flip with probability \( P_{win} \), we have

\[
\frac{dF}{d\gamma} = (1 - 2F)D(-\gamma, F)P_{win},
\]

where \( D(\xi, F) \) is the normalized distribution of dipolar field with the fraction \( F \) of up-spins randomly located throughout the lattice, and \( \gamma = \alpha t \) represents the sweeping field. The combination \( (1 - 2F)D(-\gamma, F) \) is the difference between the fractions of up-spins and down-spins in the resonance window. We want to solve Eq. (1) with the initial condition \( F = 0 \), that is, all the spins point downwards at the beginning. The result \( F_{win} = F(t \to \infty) \) is the fraction of up-spins at the end of the sweep, or the normalized height \( \delta M/2M_s \) of the quantum step between the two spin states. However, we need to first find what \( P_{win} \) is, and how to calculate the distribution function \( D(\xi, F) \).

![Fig. 2: The flipping probability obtained with the nonlinear LZ model. \( J/\Delta = 0.0 \) corresponds to the linear LZ model. The flipping probability is suppressed for positive \( J \), and enhanced for negative \( J \).](image)

Without the dipolar interaction, the flipping probability \( P_{win} \) would be given by the LZ model, that is, \( P_{win} = P_{fin} = 1 - \exp(-\frac{\Delta_{win}}{\hbar}) \). With the dipolar interaction, it is no longer trivial to calculate \( P_{win} \). During the tunneling time defined by \( \Delta_{win}/\alpha \), a spin inside the resonance window feels two kinds of dipolar fields: one from spins outside the window, the other from spins inside the window and trying to flip together. The former remains static during the short-time flipping process; it merely defines the position of the resonance window and does not affect the flipping probability. In contrast, the latter is changing with time, and will strongly affect \( P_{win} \).

To account for this effect, we use a mean-field theory, treating each spin inside the resonance window equally. The interaction is described by adding into the LZ model a nonlinear term, \( J\vec{s}\vec{s} \), where \( J \) is the average coupling constant between spins and \( \vec{s} \) is the average spin. This nonlinear LZ model was first proposed in the context of Bose-Einstein condensation[4]. The coupling constant \( J \) is proportional to the average fraction of spins in the resonant window and is calculated as \( J/\Delta = J_0\sqrt{1 + 2\alpha/\Delta^2}D(-\gamma, F)(1 - 2F)^2 \), where \( J_0 = \sum_j d(r_j) \) is the dipolar field when all the spins point in the same direction.

The probability \( P_{win} \) is then given by the flipping probability \( P_{nlz} \) obtained with this nonlinear model, which has been solved numerically and plotted in Fig. 2. The flipping probability is suppressed for positive \( J/\Delta \) and increased for negative \( J/\Delta \), compared with the linear LZ
probability. Furthermore, we have found that the nonlinear LZ flipping probability depends on only two parameters, \( P_{nlz} = P_{nlz}(\alpha/\Delta^2, J/\Delta) \), and it has an approximate expression

\[
P_{nlz}^{-1} = P_z^{-1} + \frac{\sqrt{J}}{\pi} \sqrt{P_{nlz}}.
\]

The remaining task is to calculate the distribution of local fields. The dipolar field felt by a spin in the lattice, consists of two parts: one is the demagnetization field from the spins very far away; the other from the neighboring spins inside a ball \( B_r \) of radius \( r \sim (E_D/\Delta)^{1/3} \). Since the demagnetization \( \xi_{dm} \) is contributed by the distant spins, it is independent of the lattice structure and only depends on the sample shape and the fraction of up-spins. Our calculation shows that \( \xi_{dm} = 2C E_D (2F - 1) \), where the constant \( C \) is called the shape coefficient and can be calculated theoretically\(^{[16]}\). On the other hand, the dipolar field from the neighboring spins is a distribution depending on the lattice structure. With its center shifted by the demagnetization field, the overall distribution function is

\[
D(\xi, F) = \int \frac{dk}{2\pi} \tilde{D}(k, F) e^{ik(\xi - \xi_{dm})},
\]

where \( \tilde{D}(k, F) = \Pi_{r \neq 0} \left[ (1 - F) e^{-ikd(\bar{r})} + F e^{ikd(\bar{r})} \right] \). The distribution functions calculated with Eq. (3) are compared to a Monte-Carlo simulation in Fig. 4, there is an excellent agreement.

![Experiment data on Fe\((\alpha)\) isotopes from Ref.\(^{[4]}\), which have different tunnel splittings \( \Delta \), collapse on the same curve, demonstrating the \( \alpha/\Delta^2 \) scaling law. The inset shows the collapse of the data for Mn\(4\) Ref.\(^{[3]}\), whose \( \Delta \) is varied by changing the transverse field. The slight deviation in the adiabatic regime \( \alpha/\Delta^2 \ll 0.5 \) is likely caused by the “hole digging” mechanism\(^{[15]}\).](image)

The above discussions indicate that the parameter \( J_0 \) also consists of two parts, \( J_0 = \sum_{\alpha} d(\bar{r}) + 2C E_D \). The first part only relates to the crystal structure; for the triclinic Fe\(8\), centered tetragonal Mn\(12\), and hexagonal Mn\(4\) its value is 3.98\(E_D\), 1.15\(E_D\) and 12.63\(E_D\), respectively.

Combining Eqs.(1-3), we can integrate the evolution equation (1) with the initial condition \( F = 0 \). The results for the tunneling between the two spin states \( S = \pm 10 \) of Fe\(8\) are plotted in Fig. 3. With the horizontal axis taken as \( \alpha/\Delta^2 \), the experimental data for three different isotopes of Fe\(8\) collapse onto the curve given by our theory. This “collapse” is expected: \( \Delta \) and \( \alpha \) enter Eq. (1) only in the combination of \( \alpha/\Delta^2 \) through \( P_{nlz} \). This remarkable scaling law, along with the excellent agreement of our theory with the experiments, strongly supports our previous argument that nuclear spins do not appreciably affect the flipping dynamics of the molecular spins, except for renormalizing the tunnel splitting through hyperfine coupling. This scaling law is further confirmed by a set of new experimental data on a different system, Mn\(4\) with \( S = \frac{9}{2} \). By changing the transversal magnetic field from 0T to 0.085T, the tunnel splitting of Mn\(4\) is varied almost by an order of magnitude. Nevertheless, these data collapse perfectly onto a single curve (inset of Fig. 3).

One more important feature in Figs. 1&3 is the strong suppression of the quantum step height, compared with the predictions of the LZ model. Two physical mechanisms are behind the suppression. One is the ferromagnetic blocking between spins in the resonance window. Due to the sample shape\(^{[19]}\) and with the shortest lattice vector being along the easy axis, the dipolar interaction between spins in Fe\(8\) is very much ferromagnetic, yielding a positive coupling constant \( J \). As seen in Fig. 2, the flipping probability \( P_{nlz} \) is suppressed from \( P_z \) for this case. This effect is relatively more significant in the fast sweeping regime, where there are more spins in the resonance window due to the broadened window width and narrow dipolar field distribution. Our calculation finds suppression of up to 13% due to this mechanism. However, this does not account for all the suppression, especially for the slow sweeping limit where the resonant window is narrower and the distribution function is wider.

The other mechanism is the shuffling of spins across the spectrum of the dipolar distribution \( D(\xi, F) \). As other spins flip, the dipolar field \( \xi_i \) felt by spin \( i \) is altered and thus gets shuffled to a different part of the spectrum. In particular, many spins which are yet to be brought into resonance can get shuffled into the swept part of the spectrum, losing their chances of flipping. This is confirmed by our Monte-Carlo simulation\(^{[13]}\), where the position of the resonance window is updated after the spins in the window are flipped with probability \( P_{win} \). In Fig. 4 we show how the dipolar distribution function changes with the sweeping field in one simulation with \( P_{win} = 1 \). Many spins in the main peak are shuffled into the two right peaks. This dominant shuffling to the right is related to the largely ferromagnetic character of
the dipolar interaction between spins. A careful tracking in our simulation shows that about 50% of the spins are never brought into resonance and flip zero times, 28% flip once, and 12% flip twice. This shuffling mechanism gives an intuitive picture of the physics hidden in the evolution equation (3).

$$\Delta'$$ is the true tunnel splitting; $$\Delta$$ is the true splitting as the LZ model is inadequate to give the correct step height.

Let us consider the fast sweeping limit, where the magnetization is very small. In this case, the dipolar field distribution Eq.(3) is a Lorentzian centered at $$\left(\sum_{\beta} d(\beta) + 2CE_D\right)\left(2F - 1\right)$$ with width $$\gamma / E_D$$ (3). Then, using the new variables $$f = F/P_z$$, we can rewrite Eq.(1) and immediately notice that the evolution equation in terms of $$f$$ and $$\alpha$$ is independent of $$P_z$$ and $$E_D$$. It means that, in the regime $$\alpha \to \infty$$, the ratio $$F_{min}/P_z = \left(\Delta' / \Delta\right)^2$$ tends to a constant depending on $$C$$ and $$J_0/E_D$$, which describe the geometry of the sample: its shape and lattice structure. This asymptotic relation explains why the $$\Delta'$$ is not necessarily the true $$\Delta$$ of a single molecule. We have calculated the ratio $$\Delta' / \Delta$$ and its dependence on the shape coefficient $$C$$ for three different molecular magnets Fe₈, Mn₁₂, and Mn₄ as shown in Fig. 5. With this, one can obtain the real tunnel splitting from the corresponding step height given the shape of the sample. For the Fe₈ sample used in the experiments, the shape coefficient $$C = 1.4$$, which yields $$\Delta' / \Delta \approx 0.73$$.

We thank Wolfgang Wernsdorfer for stimulating discussion. This project is supported by the NSF of US, the Welch Foundation in Texas, and the NNSF of China.

FIG. 4: Change of the internal field distribution in a sweeping field. $$E_D\Omega_0 = 1$$, $$\Delta_{win} = 0.1$$, $$P_{win} = 1$$. The broadened vertical line represents the resonance window. The dashed lines are calculated from Eq.(3), showing an excellent agreement with the solid line.

FIG. 5: The dependence of $$\Delta' / \Delta$$ on the shape coefficient. $$\Delta$$ is the tunnel splitting; $$\Delta'$$ is the tunnel splitting measured by the LZ method [10].

With our theory, we can accurately determine the tunnel splitting $$\Delta$$ of a single molecule from the measured quantum step height. The LZ method [4, 8] has been used to accomplish this, extracting an effective tunnel splitting $$\Delta'$$ from a step height with $$F_{fin} = 1 - \exp(-\pi \Delta'^2/2\alpha)$$. However, the effective splitting $$\Delta'$$ is not necessarily the true splitting $$\Delta$$ as the LZ model is inadequate to give the correct step height.

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In this letter, we interpolate these two limits by $\Delta_{\text{win}} = \sqrt{\Delta^2 + 2\alpha}$.

For an ellipsoid with three axes $a, b$ and $c$, the shape coefficient $C = 2\pi(1/3 - R_g)$. Here the demagnetization factor $R_g = 0.5abc \int_0^\infty \frac{dx}{(x+a^2)(x+b^2)(x+c^2)}$.

For the experiment on the "hole-digging" see, W. Wernsdorfer et al., Phys. Rev. Lett. 82, 3903 (1999); W. Wernsdorfer et al., ibid. 84, 2965 (2000). For the Monte-Carlo simulations, refer to, T. Ohm et al., Euro. Phys. J. B 6, 195 (1998); A. Cuccoli et al., Euro. Phys. J. B 12, 39 (1999); J.J. Alonso and Julio F. Fernandez, Phys. Rev. Lett. 87, 097205 (2001).

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From private communication with Wernsdorfer, in the experiment of Fe$_8$ isotopes, the sample shape is $a = 1$ (easy axis direction), $b = 0.7$ and $c = 0.2$. Using the formula in (16), we have $C = 1.4$.

Here we only consider a perfect crystal, ignoring effects induced by the dislocation (see cond-mat/0105518).