Quantum step heights in hysteresis loops of molecular magnets

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

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I. INTRODUCTION

Crystals of molecular magnets, such as Fe_8 and Mn_{12}, have attracted much attention for their connection to macroscopic quantum tunneling and Berry phase.[1–4] They may also have important applications in magnetic memory and quantum computing.[4,5] The earliest and most spectacular observation on such a system is the quantum steps in the hysteresis loop of magnetization at low temperatures.[1]

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 Fe_8 and Mn_{12}, $S=9/2$ for Mn_4). This has become more obvious in Refs. 6,7, where the hysteresis loop was found to converge under a very low temperature, reaching the pure quantum tunneling regime. This tunneling phenomenon is complicated by the interaction between spins and other environmental effects. Despite extensive efforts,[8] there have been no successful theories that can explain any of the step features quantitatively.

In this paper we present a successful theory on the height of the quantum steps in the hysteresis loop when the temperature is low enough that the thermal effects can be neglected. 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 of the underlying tunneling dynamics. In Fig. 1, we have adapted the experimental data on Fe_8 from Ref. 6, and show how the step height between spin states $S_z=\pm 10$ changes with the sweeping rates. The data are compared to the Landau-Zener (LZ) model,[9] which has been used to extract the tunnel splitting Δ of a single molecular spin from the step height.[4,10] 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: spin *shuffling* in the evolving distribution of dipolar fields and *jamming* among spins in the resonance window. Furthermore, our theory reveals an α/Δ^2 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 that the tunnel splitting Δ' measured with the LZ method[4,10] is not the true tunnel splitting Δ of a single molecular spin. We find that the ratio Δ'/Δ depends strongly on the sample geometry (shape and lattice structure). In our theory there are no adjustable parameters.

II. THEORY

We argue that nuclear spins do not appreciably affect the tunneling dynamics under a fast sweeping field except for a modification of the tunnel splitting. In the relaxation experiments[11] where the external field remains constant, the tunneling is strongly affected by the nuclear spins as recognized by Prokof'ev and Stamp.[12] 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. 7, 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 0.04 mT/s.

We consider spin lattices, such as crystals of Fe_8, Mn_{12}, and Mn_4, in which the spins interact with each other through the dipolar potential,

$$d(\vec{r})=\frac{E_D(1-3\cos^2\theta)\Omega_0}{r^3}, \tag{1}$$

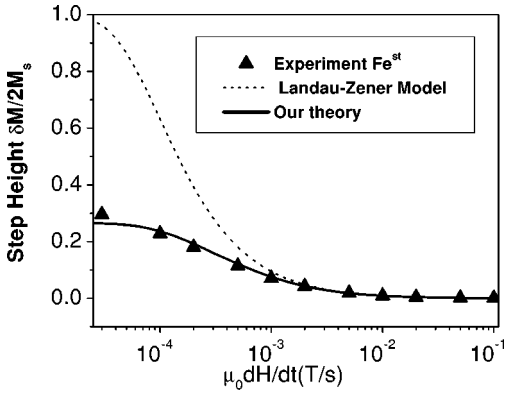

FIG. 1. Comparison between the experimental data on Fe_8,[6] the LZ model, and our theory. The normalized step height $\delta M/2M_s$ is the final fraction of up-spins F_{fin} after one sweep.

where $\vec{r}$ is the displacement vector between the spins, θ is the angle between $\vec{r}$ and the easy axis, Ω_0 is the unit-cell volume, and $E_D=(2\mu_0/4\pi)(Sg\mu_B)^2/\Omega_0$ gives the interaction strength. Our theory will be compared to the experiment, mainly on crystals of Fe_8 where the experimental data on step heights are the most abundant.[6,7] For simplicity, we focus on one step, that is, the tunneling between two spin states (for example, $S_z=\pm 10$ for Fe_8); it is rather straightforward to extend our theory to study multistep tunneling.

A. Evolution equation

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[13] $\gamma=2g\mu_B S\mu_0 H$ between the two spin states caused by the changing external field becomes very small, $|\gamma|\leqslant\Delta_{win}/2$. This tunneling time defines the resonance window, whose width Δ_{win} is the tunnel splitting Δ at the adiabatic limit and $\sqrt{2\alpha}$ ($\alpha=\hbar d\gamma/dt$) in the sudden limit.[14] Similarly for a spin interacting with other spins in a lattice, its resonance window is defined by

$$|\gamma+\xi_i|\leqslant\Delta_{win}/2, \tag{2}$$

where ξ_i is the Zeeman energy of spin i caused by the dipolar field from other spins. Since the dipolar fields felt by spins are 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

$$\frac{dF}{d\gamma}=(1-2F)D(-\gamma,F)P_{win}, \tag{3}$$

where $D(\xi,F)$ is the normalized distribution of dipolar fields 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. (3) with the initial condition $F=0$, that is, all the spins point downward at the beginning. The result $F_{fin}=F(\gamma\rightarrow\infty)$ 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 $D(\xi,F)$.

B. Flipping probability inside resonance windows

Without the dipolar interaction, the flipping probability P_{win} would be given by the LZ model, that is, $P_{win}=P_{lz}=1-\exp(-\pi\Delta^2/2\alpha)$. With the dipolar interaction, it is no longer trivial to calculate P_{win}. During the tunneling time defined by Δ_{win}/α, 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}.

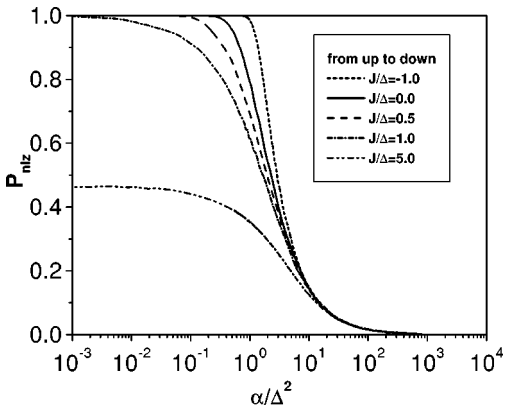

FIG. 2. The flipping probability obtained with the nonlinear LZ model. $J/\Delta=0.0$ corresponds to the linear LZ model. The flipping probability is suppressed for positive J, and enhanced for negative J.

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 a nonlinear term $\eta=(J/2)(|b|^2-|a|^2)$ into the LZ model,

$$i\frac{d}{dt}\begin{pmatrix}a\\ b\end{pmatrix}=\begin{pmatrix}\frac{\gamma}{2}+\eta & \frac{\Delta}{2}\\ \frac{\Delta}{2} & -\frac{\gamma}{2}-\eta\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix}. \tag{4}$$

This nonlinear LZ model was first proposed in the context of Bose-Einstein condensates in optical lattices.[15] The mean-field interaction constant J is proportional to the average fraction of spins in the resonant window and is calculated as

$$J/\Delta=J_0\sqrt{1+2\alpha/\Delta^2}D(-\gamma,F)(1-2F)^2, \tag{5}$$

where $J_0=\Sigma_j d(\vec{r}_j)$ is the dipolar field when all the spins point in the same direction. In the derivation of Eq. (5), we have taken advantage of the inverse cubic law of the dipolar field.

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/Δ and enhanced for negative J/Δ, 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,

$$P_{nlz}^{-1}=P_{lz}^{-1}+\frac{\sqrt{2}}{\pi}\frac{J}{\Delta}\sqrt{P_{nlz}}. \tag{6}$$

The details of these results can be found in Ref. 15.

C. Distribution of dipolar fields

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 ξ_{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 $\xi_{dm}=2CE_D(2F-1)$, 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 (see Appendix A for details)

$$D(\xi,F)=\int\frac{dk}{2\pi}\overline{D}(k,F)e^{ik(\xi-\xi_{dm})}, \tag{7}$$

where

$$\overline{D}(k,F)=\prod_{\vec{r}_j\neq 0}[(1-F)e^{-ikd(\vec{r}_j)}+Fe^{ikd(\vec{r}_j)}]. \tag{8}$$

The distribution functions calculated with Eq. (7) are compared to a Monte Carlo simulation in Fig. 4; there is an excellent agreement.

The above discussions indicate that the parameter J_0 also consists of two parts, $J_0=\Sigma_{B_r}d(\vec{r})+2CE_D$. The first part is only related to the crystal structure; for the triclinic Fe_8, centered tetragonal Mn_{12}, and hexagonal Mn_4 its value is $3.98E_D$, $1.15E_D$, and $12.63E_D$, respectively.

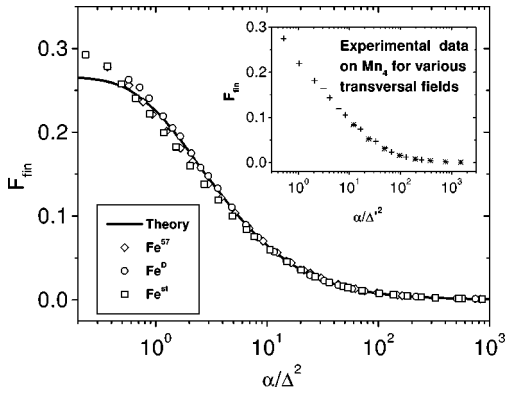

FIG. 3. Comparison between our theory and experiments. The experimental data on Fe_8 isotopes from Ref. 6, which have different tunnel splittings Δ, collapse on the same curve, demonstrating the α/Δ^2 scaling law. The inset shows the collapse of the data for Mn_4 Ref. 10, whose Δ is varied by changing the transverse field. The slight deviation in the adiabatic regime $\alpha/\Delta^2<0.5$ is likely caused by the ''hole digging'' mechanism (Ref. 17).

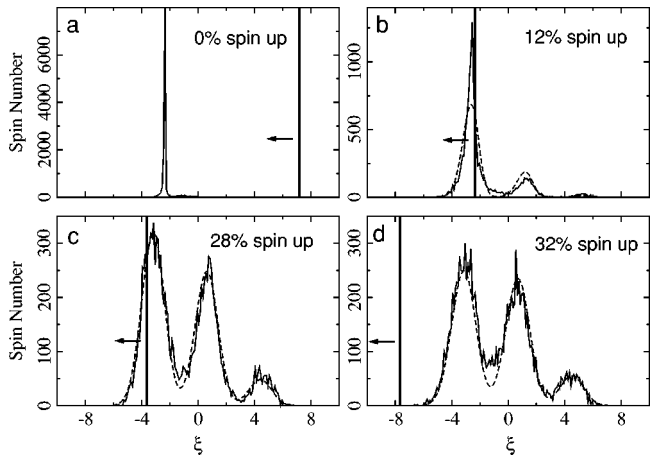

FIG. 4. Change of the internal field distribution in a sweeping field. The results are calculated from a Monte Carlo simulation, where a triclinic lattice of Fe_8 is used with 10 229 sites and a spherical shape. Other parameters are, $E_D\Omega_0=1$, $\Delta_{win}=0.1$, and $P_{win}=1$. The broadened vertical line represents the resonance window. The dashed lines are calculated from Eq. (7), showing an excellent agreement with the solid line.

III. COMPARISON WITH EXPERIMENTS

Combining Eqs. (3)–(8), we can integrate the evolution Eq. (3) 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 α/Δ^2, the experimental data for three different isotopes of Fe_8 collapse onto the curve given by our theory. This ''collapse'' is expected: Δ and α enter Eq. (3) only in the combination of α/Δ^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 modifying 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 $S=\frac{9}{2}$.[10] By changing the transversal magnetic field from 0 T to 0.085 T, the tunnel splitting of Mn_4 is varied almost by an order of magnitude. Nevertheless, these data collapse perfectly onto a single curve, as seen in the inset of Fig. 3.

IV. DISCUSSIONS AND PREDICTIONS

A. Jamming

One more important feature in Figs. 1 and 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 jamming among spins in the resonance window. Due to the sample shape[18] 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 $J>0$. As seen in Fig. 2, the flipping probability P_{nlz} is suppressed from P_{lz} for this case.

This jamming effect is 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.

Of course, it is possible to have $J<0$, which happens when the easy axis of a molecular magnet is not along the shortest lattice axis or when the sample crystal has a much smaller dimension along the easy axis than the other two dimensions. Once this is the case, we may call this effect antijamming.

B. Shuffling

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 ξ_i felt by spin i is altered and thus gets shuffled to a different part of the spectrum. In particular, many spins that 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, 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 Eq. (3).

C. Shape effect

With our theory, we can accurately determine the tunnel splitting Δ of a single molecule from the measured quantum step height. The LZ method[4,10] has been used to accomplish this, extracting an effective tunnel splitting Δ' from a step height with $F_{fin}=1-\exp(-\pi\Delta'^2/2\alpha)$. However, the effective splitting Δ' is not necessarily the true splitting Δ 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[19]

$$D(\xi,F)=\frac{\delta/\pi}{(\xi-\xi_c)^2+\delta^2}, \tag{9}$$

where $\xi_c=\Sigma_{B_r} d(\vec{r})+2CE_D(2F-1)$ and $\delta=(16\pi^2 3^{5/2})E_D F$. With the new variables $f=F/P_{lz}$, $x=\gamma/E_D P_{lz}$, one can rewrite Eq. (3) and immediately notice that the evolution equation in terms of f and x is independent of P_{lz} and E_D (see details in Appendix B). It means that, in the fast sweeping regime, the ratio $F_{fin}/P_{lz}=(\Delta'/\Delta)^2$ tends to a constant depending only 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 Δ' is not necessarily the true Δ of a single molecule.

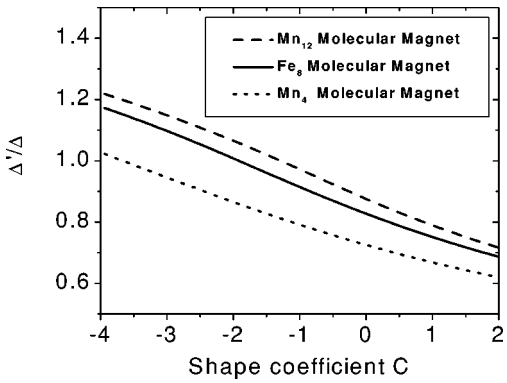

FIG. 5. The dependence of Δ'/Δ on the shape coefficient. Δ is the true tunnel splitting; Δ' is the tunnel splitting measured by the LZ method (Ref. 4).

We have calculated the ratio Δ'/Δ and its dependence on the shape coefficient C for three different molecular magnets Fe_8, Mn_{12},[1] and Mn_4 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 Fe_8 sample used in the experiments[6] the shape coefficient $C=1.4$,[18] which yields $\Delta'/\Delta\simeq 0.73$.

V. CONCLUSION

In summary, we have studied the quantum step heights in the hysteresis loop of crystals of molecular magnets. The underlying physics is the spin tunneling in such systems under sweeping fields. We have identified two physical mechanisms causing the strong suppression of step heights at low sweeping rates. They are the shuffling of spins across the spectrum of the distribution of dipolar fields and the jamming among spins inside the resonance window. With an analytical theory, we have explained an experiment, revealed a scaling law hidden in the existing experimental data, and predicted the shape effect on the measurement of the tunnel splitting with the LZ method.

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APPENDIX A: DISTRIBUTION OF DIPOLAR FIELDS

Consider a lattice of dipolar interacting Ising spins with fraction F of up-spins randomly scattered over the lattice. We want to calculate the distribution $D(\xi,F)$ of dipolar fields ξ felt by each spin in the lattice.

We proceed by noticing that when the lattice is large enough, $N\gg 100$, this is equivalent to each spin having a probability of F pointing upward. Therefore, with $s_j(=\pm 1)$ denoting the spin at site j, we can write down the distribution function as

$$D(\xi,F)=\sum_{m=0}^{N}F^m(1-F)^{N-m}\sum_{\{s_i\}_m}\delta\left(\xi-\sum_{j=1}^{N}s_jd_j\right), \tag{A1}$$

where $d_j=d(\vec{r}_j)$ is the dipolar field generated by spin j, and the second summation is over all the possible configurations that have m spins up.

The distribution function $D(\xi,F)$ can be calculated through its Fourier transform

$$\begin{aligned}\overline{D}(k,F)&=\int d\xi D(\xi,F)e^{-ik\xi}\\&=\sum_{m=0}^{N}F^m(1-F)^{N-m}\sum_{\{s_i\}_m}e^{-ik\sum_{j=1}^{N}s_jd_j}\\&=\prod_{j=1}^{N}[Fe^{-ikd_j}+(1-F)e^{ikd_j}].\end{aligned} \tag{A2}$$

Together with another Fourier transform

$$D(\xi,F)=\int\frac{dk}{2\pi}\overline{D}(k,F)e^{ik\xi}, \tag{A3}$$

we have derived Eq. (7) in the main text.

When $F\ll 1$, we have

$$\overline{D}(k,F)\approx\exp\left(-2F\sum_{j=1}^{N}\cos(kd_j)\right), \tag{A4}$$

from which one can show that $D(\xi,F)$ is a Lorentzian. Note that the distribution $D(\xi,F)$ is normalized $\int_{-\infty}^{\infty}d\xi D(\xi,F)=1$, which can be verified easily with Eq. (A1).

APPENDIX B: FAST SWEEPING REGIME

In this appendix, we solve the evolution equation

$$\frac{dF}{d\gamma}=(1-2F)D(-\gamma,F)P_{nlz}\left(\frac{\Delta^2}{\alpha},\frac{J}{\Delta}\right), \tag{B1}$$

in the fast sweeping regime $\alpha\to\infty$.

In this regime, only a very small portion of spins flip, that is, $F\ll 1$. As a result, during the whole sweeping process, the distribution function is a Lorentzian[18]

$$D(\xi,F)=\frac{\delta/\pi}{(\xi-\xi_c)^2+\delta^2}, \tag{B2}$$

where $\xi_c=\Sigma_{B_r}d(\vec{r})+2\,CE_D(2F-1)$ and $\delta=(16\pi^2/3^{5/2})E_DF$. On the other hand, in this fast sweeping regime, the nonlinear LZ flipping probability $P_{nlz}\ll 1$ is very small and is well approximated with Eq. (6).

We move on by introducing new variables,

$$f=F/P_{lz},\quad x=\frac{\gamma}{E_DP_{lz}}. \tag{B3}$$

We notice that we have the freedom to shift the center of the distribution $D(\xi,F)$ by a constant without changing the physics. It leads us to

$$D(\gamma,F)=\frac{1}{E_DP_{lz}}\tilde{D}(x,f), \tag{B4}$$

where

$$\tilde{D}(x,f)=\frac{\frac{16\pi^2}{3^{5/2}}f/\pi}{(x-4Cf)^2+\left(\frac{16\pi^2}{3^{5/2}}f\right)^2}. \tag{B5}$$

Along the other line, since $\alpha\to\infty$, we have

$$P_{lz}=1-\exp(-\pi\Delta^2/2\alpha)\approx\frac{\pi\Delta^2}{2\alpha}, \tag{B6}$$

and

$$\begin{aligned}J/\Delta&=J_0\sqrt{1+2\alpha/\Delta^2}D(-\gamma,F)(1-2F)^2\\&=\frac{J_0}{E_D}\sqrt{\pi}\frac{1}{P_{lz}^{3/2}}\tilde{D}(-x,f)(1-2P_{lz}f)^2.\end{aligned} \tag{B7}$$

Since $J_0\propto E_D$, J_0/E_D is independent of E_D. With the introduction of another scaled variable

$$j=\frac{J_0}{E_D}\sqrt{\pi}\tilde{D}(-x,f), \tag{B8}$$

we can rewrite Eq. (6) as

$$\frac{1}{P}=1+\sqrt{\frac{2j}{\pi}}\sqrt{P}, \tag{B9}$$

where we have used $P_{lz}\ll 1$ and the notation $P=P_{nlz}/P_{lz}$.

Finally, the evolution Eq. (B1) assumes the following form:

$$\frac{df}{dx}=\tilde{D}(-x,f)P. \tag{B10}$$

What is remarkable of this equation is that it does not depend on the two parameters E_D and P_{lz}. However, it does depend on the geometry of the sample: shape through C and lattice structure through J_0/E_D. Solving this equation gives us

$$f(x\to\infty)=\frac{F_{fin}}{P_{lz}}=\frac{1-\exp(-\pi\Delta'^2/2\alpha)}{1-\exp(-\pi\Delta^2/2\alpha)}\approx\left(\frac{\Delta'}{\Delta}\right)^2. \tag{B11}$$

Therefore, the ratio Δ'/Δ is independent of the sweeping rates in the fast sweeping regime; this explains the saturation of the measured tunnel splitting Δ' found in Refs. 6,7. On the other hand, the ratio does depend on the sample geometry, which can be verified by retooling the same sample to different shapes.

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

[17] For the experiment on ''hole-digging'' see, W. Wernsdorfer, T. Ohm, C. Sangragivic, R. Sessoli, D. Mailly, and C. Paulson, Phys. Rev. Lett. **82**, 3903 (1999); W. Wernsdorfer, A. Caneschi, R. Sessoli D. Gatteschi, A. Cornia, V. Villar, and C. Paulsen, *ibid.* **84**, 2965 (2000); For the Monte Carlo simulations, refer to, T. Ohm, C. Sangregorio, and C. Paulsen, Eur. Phys. J. B **6**, 195 (1998); A. Cuccoli, A. Fort, A. Rettori, E. Adam, and J. Villain, *ibid.* **12**, 39 (1999).

[18] 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 Ref. 16, we have $C = 1.4$.

[19] A. Abragam, *Principle of Nuclear Magnetism* (Oxford University Press, New York, 1961). It can also be derived from Eq. (7).