

Quantum tunneling of two coupled single-molecular magnets

Jian-Ming Hu¹, Zhi-De Chen^{1,2} and Shun-Qing Shen¹

¹*Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, China*

²*Department of Physics and Institute of Modern Condensed Matter Physics, Guangzhou University, Guangzhou 510405, China*

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Two single-molecule magnets are coupled antiferromagnetically to form a supramolecule dimer. We study the coupling effect and tunneling process by means of the numerical exact diagonalization method, and apply them to the recently synthesized supramolecular dimer $[\text{Mn}_4]_2$. The model parameters are calculated for the dimer based on the tunneling process. The absence of tunneling at zero field and sweeping rate effect on the step height in the hysteresis loops are understood very well in this theory.

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Nanometer-sized magnetic particles and clusters have generated continuous interests as study of their properties has proved to be scientifically and technologically very challenging.^{1,2,3,4,5,6} Up to now magnetic molecular clusters have been the most promising candidates for observing quantum phenomena since they have a well defined structure with well characterized spin ground state and anisotropy.⁷ One of the well studied systems is single-molecule magnet (SMM) $[\text{Mn}_4\text{O}_3\text{Cl}(\text{O}_2\text{CCH}_3)_3(\text{dbm})_3]$ (short for Mn_4).^{8,9,10,11} The molecule has well isolated ground state with a half integer spin $S = 9/2$, and magnetization tunneling is observed at zero magnetic field. Very recently a supramolecular dimer of two SMMs $[\text{Mn}_4]_2$ was reported to be synthesized successfully.¹² The antiferromagnetic coupling between two SMMs leads to this dimer with a spin singlet ground state and makes the quantum tunneling quite different from SMMs Mn_4 . The coupling also makes this dimer an excellent candidate for studying quantum tunneling in a system of two truly and coupled identical particles. Quantum tunneling of magnetization can be advantage for some applications of SMMs in providing quantum superpositions of states required for quantum computing.^{13,14} So the coupling effect in quantum tunneling between SMMs is a very important issue in application of integrated molecular magnets. In this paper we first study the tunneling process in one SMM Mn_4 with spin $S = 9/2$. A local stray field has to be introduced to explain the tunneling of the ground state at zero field.¹¹ Then we study the coupling effect of two SMMs and observe a novel triangle tunneling process. We apply our observation to the newly synthesized supramolecular dimer of two SMM $[\text{Mn}_4]_2$ and make use of the two triangle tunneling processes to deduce the the model parameters from the experimental data, and, furthermore, explain the sweeping rate effect in the derivatives of hysteresis loops.

We first start with a biaxial model for a SMM Mn_4 with spin $S = 9/2$,

$$H_i = -DS_{zi}^2 + E(S_{xi}^2 - S_{yi}^2) + g\mu_B\mu_0\mathbf{S}_i \cdot (\mathbf{B} + \mathbf{h}) \quad (1)$$

where $i = 1$ or 2 referring to the two SMMs in the dimer, D and E are the axial anisotropic constants,

$\mathbf{B} = B\mathbf{e}_z$ is the external magnetic field along the z axis. The term $g\mu_B\mu_0\mathbf{S}_i \cdot \mathbf{h}$ is the local stray field interaction between the SMMs and the environment. For simplicity we denote the energy eigenstate of the biaxial model $|m\rangle$ by its dominant $S_z = m$ component, and $m = -S, -S + 1, \dots, S$. The E term and the stray field may lead to some minor correction to these states. If the stray field is not included, it is well known that for a half integer spin the tunneling between the state $| -S \rangle$ and $| S \rangle$ is quenched due to the parity symmetry.^{15,16,17} It can be proved simply that, for any integer n , we always have $\langle -S | (H_i)^n | M \rangle = 0$ with $M = -S + 1, -S + 3, \dots, S$. The equality indicates that there is no connection or no tunneling occurs between these states $| -S \rangle$ and $| M \rangle$. Experimentally quantum tunneling was observed in a SMM Mn_4 between the states $| -S \rangle$ and $| S \rangle$.⁹ So there must be a small internal magnetic field by the nuclear spins of the Mn ions and/or the dipole-dipole interaction between different molecules. We model the interaction as a local stray field \mathbf{h} with a random Gaussian distribution with the equal width σ in three directions as we did for the molecular magnets Fe_8 ,¹⁸

$$P(\mathbf{h}) = \frac{1}{(2\pi\sigma^2)^{3/2}} \exp[-\mathbf{h}^2/2\sigma^2]. \quad (2)$$

A transverse component of such a field may lead to a tunneling splitting at zero field as observed in Ref.⁹. In this paper we take the parameters for a SMM Mn_4 $D = 0.762\text{K}$, $E = 0.0317\text{K}$,^{9,10} and $\sigma = 0.035\text{T}$.¹¹ The resulting tunneling splitting for the ground states $| -9/2 \rangle$ and $| 9/2 \rangle$ at zero field is $\sqrt{\langle \Delta_0^2 \rangle} = 3.280 \times 10^{-7}\text{K}$, and that for the states $| -9/2 \rangle$ and $| 7/2 \rangle$ is $\sqrt{\langle \Delta_1^2 \rangle} = 1.52627 \times 10^{-5}\text{K}$ by using the exact diagonalization method where $\langle \dots \rangle$ stands for the averaging over the stray field.¹⁹ Thus the local stray field may cause a tunneling splitting between the ground states.

Following Wernsdorfer et al., the two SMM Mn_4 s in the dimer $[\text{Mn}_4]_2$ are coupled via a weak antiferromagnetic superexchange coupling J . Thus the model Hamiltonian for the dimer is

$$H = H_1 + H_2 + JS_1 \cdot S_2 \quad (3)$$

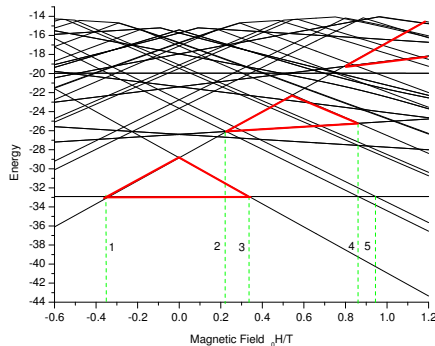


FIG. 1: Spin state energy of the model Hamiltonian (Eq. (3)) for $[\text{Mn}_4]_2$ without local stray fields as a function of applied magnetic field by taking $D = 0.762\text{K}$, $E = 0.0317\text{K}$, and $J = 0.1\text{K}$. The two triangles are related to the tunneling (1) from $|-9/2, -9/2\rangle_+$ to $|-9/2, 9/2\rangle_+$ at point 1, then to $|9/2, 9/2\rangle_+$ at point 3, and (2) from $|-9/2, -9/2\rangle_+$ to $|-9/2, 7/2\rangle_+$ at point 2, then to $|7/2, 7/2\rangle_+$ at point 4. The Point 5 is from $|-9/2, 9/2\rangle_+$ to $|9/2, 7/2\rangle_+$. The resonance fields for the five points are -0.335T , 0.233T , 0.335T , 0.861T , and 0.943T , respectively.

where $S_1 = S_2 = 9/2$. For each dimer there are $(2S_1 + 1)(2S_2 + 1) = 100$ energy eigenstates. Like in a SMM Mn_4 , each state can be labelled approximately by two predominant quantum numbers $|m_1, m_2\rangle$ for two SMMs with $m_{1,2} = -9/2, -7/2, \dots, 9/2$. Without the coupling J the states $|m_1, m_2\rangle$ and $|m_2, m_1\rangle$ are degenerated. As the two SMMs can be regarded as truly identical particles there exists the permutation symmetry between particle 1 and 2 and the eigenstates may possess parity symmetry. Thus the eigenstates for the system are denoted by $|m_1, m_2\rangle_+$ for even parity and $|m_1, m_2\rangle_-$ for odd parity. The antiferromagnetic coupling J may remove the degeneracy of these two states, but the parity in the states remain unchanged. Even when we take into account the the coupling J and the transverse terms the states become the linear combination of all possible states, for simplicity, we still use the two dominant quantum numbers to represent the states. All the energy eigenvalues by neglecting the local stray fields are plotted in Fig. 1. The average over the local stray field does not move the position of energy level crossing.

Before explaining the experimental observation from the dimer we first consider the effect caused by the coupling J between the two particles. Assume the tunneling between the states $|m_1\rangle$ and $|m_{1'}\rangle$ under a sweeping field $\mathbf{B} (= -c_b t)$ and the tunneling splitting between the two states is Δ , the pair of the splitting energy eigenvalues near the resonant point can be written as

$$\varepsilon_{\pm} = \frac{1}{2} \left[(m_1 + m_{1'})c_b t \pm \sqrt{[(m_1 - m_{1'})c_b t]^2 + \Delta^2} \right] \quad (4)$$

with $c_b = g\mu_B\mu_0\hbar dB/dt$, and the two states are given by

$$\phi_{\pm}^1(t) = (\pm c_{\pm} |m_1\rangle + c_{\mp} |m_{1'}\rangle) / \sqrt{2} \quad (5)$$

with $c_{\pm} = \sqrt{1 \pm (m_1 - m_{1'})c_b t / \sqrt{[(m_1 - m_{1'})c_b t]^2 + \Delta^2}}$. Before the resonant tunneling, the initial state is at $|m_1\rangle$, i.e., at $t = -\infty$, $\phi_+(t) \rightarrow |m_{1'}\rangle$ and $\phi_-(t) \rightarrow |m_1\rangle$; after the tunneling, at $t = +\infty$, $\phi_+(t) \rightarrow |m_1\rangle$ and $\phi_-(t) \rightarrow -|m_{1'}\rangle$. When two identical particles are put together there are four possible states: $|+, +\rangle_+ = \phi_+^1 \otimes \phi_+^2$ with the energy $2\varepsilon_+$, $|+, -\rangle_{\pm} = (\phi_+^1 \otimes \phi_-^2 \pm \phi_-^1 \otimes \phi_+^2) / \sqrt{2}$ with the energy $\varepsilon_+ + \varepsilon_-$, and $|-, -\rangle_+ = \phi_-^1 \otimes \phi_-^2$ with the energy $2\varepsilon_-$. We denote the even and odd parity of the states by the subscripts \pm , respectively. The energies vary with time t , and are plotted in Fig. 2, for an illustration, by choosing $m_1 = m_2 = -9/2$ and $m_{1'} = m_{2'} = 7/2$ for the model in Eq.(3). The tunneling splitting between the two states $|+, +\rangle_+$ and $|-, -\rangle_+$ is 2Δ , the double of a single particle as expected. To see the coupling effect of two particles, we plot the energy eigenvalues for several different couplings in Fig. 2. It is obtained by the exact diagonalization of 100×100 matrix for the Hamiltonian. The two states $|+, -\rangle_{\pm}$ are degenerated for $J = 0.0$. A very little coupling J may remove the degeneracy of the two states. The state $|+, -\rangle_-$ has odd parity and does not take part in the tunneling process as other three states have even parity. It is shown that the coupling J leads to two consequences: (1) The tunneling splitting from $|-, -\rangle_+$ and $|+, +\rangle_+$ decreases very quickly with increasing J , and almost closes for $J > 0.3 \times 10^{-5}\text{K}$. In the dimer of $[\text{Mn}_4]_2$ the coupling $J \approx 0.1\text{K}$ and tends to suppress the tunneling at this point completely. (2) The tunneling splitting from $|-, -\rangle_+$ to $|+, +\rangle_+$ occurs at two separated points via a intermediate state $|+, -\rangle_+$. The coupling J provides an inner bias field to expel the two resonant points away from the original ones of $|+, +\rangle_+$ and $|+, -\rangle_+$. This triangle process reflects the structure of the tunneling of the two identical particles. In the language of m_1 and m_2 , the process from $|m_1, m_1\rangle_+$ to $|m_{1'}, m_{1'}\rangle_+$ is described as follows: *the first resonant tunneling occurs from $|m_1, m_1\rangle_+$ to $|m_1, m_{1'}\rangle_+$, and the second one follows from $|m_1, m_{1'}\rangle_+$ to $|m_{1'}, m_{1'}\rangle_+$. The explicit tunneling from $|m_1, m_1\rangle_+$ to $|m_{1'}, m_{1'}\rangle_+$ is suppressed completely by the coupling J .*

Now we are ready to analyze the quantum tunneling in the dimer. Typical hysteresis loops in magnetization versus sweeping external field applied along the easy axis are observed. These loops display step-like features separated by plateaus. The step heights become temperature-independent below 0.3K , but depend on the sweeping rate of magnetic field $c = dB/dt$. Derivatives of the loops at different sweeping rate reflect that quantum tunneling occurs at several points, but is absent at zero field. At high field the initial state is $|-9/2, -9/2\rangle_+$, which has even parity. Due to the permutation symmetry of identical particles all the tunneling to the states $|m_1, m_2\rangle_-$

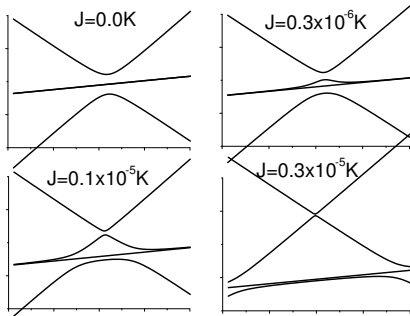


FIG. 2: Energy levels of the states $|-9/2, -9/2\rangle_+$, $|7/2, 7/2\rangle_+$ and $|-9/2, 7/2\rangle_\pm$ versus sweeping field at different coupling J of two coupled identical particles as an example to illustrate the tunneling process from $|m_1, m_1\rangle_+$ to $|m_1', m_1'\rangle_+$ via $|m_1, m_1'\rangle_+$. (x-axis: Energy/ 10^{-4} K, y-axis: Magnetic Field/ 5×10^{-6} T)

with odd parity in this system are prohibited. The tunneling process in the dimer can be understood essentially by two triangle processes as shown in Fig. 1. Starting from the initial state $|-9/2, -9/2\rangle_+$, the first level crossing happens at magnetic field $b_1 = -0.33$ K, which is from $|-9/2, -9/2\rangle_+$ to $|-9/2, 9/2\rangle_+$ at point 1, and the dual resonant point is from $|-9/2, 9/2\rangle_+$ to $|9/2, 9/2\rangle_+$ at point 3 $b_3 = +0.33$ K in the first triangle process. The energy of the intermediate state $|-9/2, 9/2\rangle_+$ is independent of the external field. The resonant field for the points 1 and 3 are $b_{1,3} = \pm 0.9J/2g\mu_B\mu_0$ from the model (Eq.(3)). Thus J is calculated to be 0.1K as Wernsdorfer et al. did. The finite coupling does not lead to a tunneling splitting at this point, which can be proved explicitly: for an integer n we have

$$+ \langle -9/2, -9/2 | H^n | -9/2, 9/2 \rangle_+ = 0 \quad (6)$$

when the stray field is absent. The tunneling splitting at points 1 and 3 are caused by the local stray field. These two points were consistent with Ref.¹². The second process is from $|-9/2, -9/2\rangle_+$ to $|7/2, 7/2\rangle_+$ via an intermediate state $|-9/2, 7/2\rangle_+$. The two energy level crossings are from $|-9/2, -9/2\rangle_+$ to $|-9/2, 7/2\rangle_+$ at point 2, and from $|-9/2, 7/2\rangle_+$ to $|7/2, 7/2\rangle_+$ at point 4. We take the parameters for D and E for a SMM Mn_4 , and find that the calculated resonant fields are $b_2 = 0.233$ T and $b_4 = 0.861$ T, which is very closed to the experimental data 0.87T.²⁰ As the points 2 and 3 are very close such that the resonant peaks are smeared to a broaden one. In Wernsdorfer et al's paper they neglect the transition from $|-9/2, 7/2\rangle_+$ to $|7/2, 7/2\rangle_+$ and thought that the third peak in the Fig. 4 of Ref.¹² are caused by those from $|-9/2, -9/2\rangle_+$ to $|-9/2, 5/2\rangle_+$ and from $|-9/2, 9/2\rangle_+$ to $|7/2, 9/2\rangle_+$ (i.e. the point 5 in Fig. 1). D was calculated to be 0.72T by neglecting the transverse component E . After a detailed analysis we found that the transverse component E remove the degeneracy of $|-9/2, 9/2\rangle_+$ and

$|-9/2, 9/2\rangle_-$. Even if we take $D = 0.72$ T we find that $b_2 = 0.20$ T, $b_4 = 0.833$ T and $b_5 = 0.9138$ T which is larger than 0.87T. If we fix the point 5 at 0.87T, D is calculated to be 0.664T smaller than 0.72T. The tunneling from $|-9/2, -9/2\rangle_+$ to $|-9/2, 5/2\rangle_+$ belongs to another the triangle process and the splitting which is caused by the stray field is much smaller than those at points 2 and 4. On the other hand we anticipate that the weak coupling between two SMMs does not affect the intrinsic properties of a SSM in the dimer too much. Our calculation shows that it is reasonable to take the parameters D and E from the SMM Mn_4 for the model of the dimer of the two SMMs with a weak coupling. It is worth pointing out that the coupling J can also drive the tunneling splitting between some states such as $|-9/2, +7/2\rangle_+$ and $|9/2, 7/2\rangle_+$. However these tunnelings do not contribute significantly to what observed in Ref.¹² We do not discuss them here.

After determining the positions of the resonant points and model parameters we are in a position to calculate the tunneling splitting, which determines the transition rate in the Landau-Zener model. The exact diagonalization method is applied to calculate the energy eigenvalues at different external field. The sampling average is taken for the local stray field. For each sampling we calculate the energy levels as in Fig. 1 and find the energy splitting Δ_n at each resonant point. More than 1000 sampling are taken to calculate the averaging tunneling splitting $\sqrt{\langle \Delta_n^2 \rangle}$ for each distribution width σ . The calculated tunneling splittings are listed in Table I.

Table I: The calculated tunneling splitting $\sqrt{\langle \Delta^2 \rangle}$ in unit 10^{-5} K at different resonant points with different distribution width σ of the stray field \mathbf{h} by using the exact diagonalization method. ($D = 0.762$ K, $E = 0.0317$ K.)

σ/T	1	2	3	4	5
0.000	$<10^{-7}$	2.21907	$<10^{-7}$	2.81552	1.52671
0.010	0.01960	2.19227	0.01960	2.83557	1.59807
0.020	0.03207	2.19487	0.03207	2.84268	1.59723
0.035	0.04687	2.20155	0.04687	2.87249	1.61907
0.050	0.06264	2.78338	0.06264	2.98306	1.68816

The derivatives of the hysteresis loops at different sweeping rates in Fig. 4 of Ref.¹² indicate that the peak heights in the derivatives depend on the sweeping rate. The height of the first peak decreases with the increasing rate while oppositely the second peak increases. This phenomenon can be understood qualitatively in the modified Landau-Zener model. In principle the time-evolution of the spin system can be reached by solving the $100(= (2S+1)(2S+1))$ coupled time-dependent Schrödinger equation. As the tunneling splitting is very small, the coupled equations near the two resonant states can be reduced to an effective two-level system with the Hamiltonian

$$H_{eff} = \begin{pmatrix} (m_1' + m_2')(c_b t + h_z) & \Delta(\mathbf{h})/2 \\ \Delta(\mathbf{h})/2 & (m_1 + m_2)(c_b t + h_z) \end{pmatrix}.$$

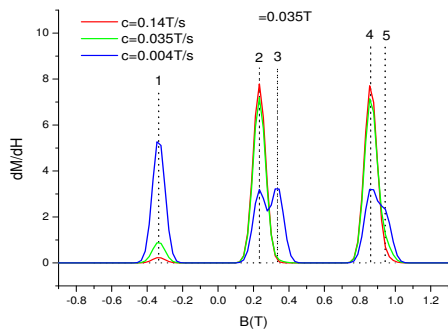


FIG. 3: Calculated derivative of the hysteresis loop at different sweeping fields based on the modified Landau-Zener model.

The tunneling splitting $\Delta(\mathbf{h})$ between two states $|m_1, m_2\rangle_+$ and $|m_{1'}, m_{2'}\rangle_+$ can be obtained by diagonalizing the Hamiltonian with a specific field \mathbf{h} . The state evolves with time,

$$\Phi_{eff}(t) = \exp\left[-\frac{i}{\hbar} \int_{-\infty}^t H_{eff}(t) dt\right] \Phi_{eff}(t = -\infty),$$

and the magnetization varying with time is given by $M(t) = \langle \Phi_{eff} | \mathbf{S}_1^z + \mathbf{S}_2^z | \Phi_{eff} \rangle$. The average over the stray field \mathbf{h} is taken for $\langle dM(t)/dt \rangle = \int d\mathbf{h} P(\mathbf{h}) dM(t)/dt$. Physically, with the local stray field, the Landau-Zener transition formula is given by

$$P_{LZ} = 1 - \langle \exp[-\pi \Delta_{mm'}^2 / \nu_{mm'}] \rangle \approx \pi \langle \Delta_{mm'}^2 \rangle / \nu_{mm'},$$

where $\nu_{mm'} = 2g\mu_B \hbar \left| \sum_{i=1,2} (m_{i'} - m_i) \right| dB/dt$. The

rate is proportional to the reverse of the sweeping rate $c = dB/dt$, approximately. The larger the sweeping rate is, the less particles tunnel to the new state. The step height is related to the transition rate by $\Delta M = P_{LZ} \sum_i (m_i - m_{i'})$. The presence of the local stray field will smear the “jump” of the magnetization around the resonant point.¹⁸ At a field b around the resonant point, the variation of the magnetization due to quantum tunneling can be approximately given by $M(b) \simeq \Delta M \int_{-\infty}^b d\mathbf{h}_z P(\mathbf{h}_z)$, which leads to the derivative of the hysteresis loop around the resonant point, $dM/db \simeq \Delta M P(b)$. The calculated results are plotted in Fig. 3. Comparing with Fig. 4 in Ref.¹², we find that the numerical results based a Landau-Zener model are consistent with the experimental observation, and essentially reflect the sweeping rate effect on the peak height of derivatives of hysteresis loops.

In conclusion, we study the coupling effect of two truly identical particles, and analyze the quantum tunneling of magnetization in the supramolecular dimer of two Mn_4 s. The exchange coupling between two SMMs provides a biased field to expel the tunneling to two new resonant points via an intermediate state, and direct tunneling is prohibited. Based on the analysis we deduce the model parameters from the experimental data, and find out that the coupling does not change the model parameters for a SMM too much. Finally we point out that the sweeping rate effect in the derivatives of hysteresis loops can be explained quantitatively in the modified Landau-Zener model.

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¹⁹ As there exists higher order unknown transverse terms in the model Hamiltonian, the tunnel splitting calculated in this paper is comparable with the experimental data qualitatively.
²⁰ If we take $b_4 = 0.87$ T exactly, D is deduced as 0.775K, which is slightly larger than 0.762K for the value of a SMM.

