

Level splittings in exchange-biased spin tunneling

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The level splittings in a dimer with antiferromagnetic coupling between two single-molecule magnets are calculated perturbatively for arbitrary spins. It is found that the exchange interaction between two single-molecule magnets plays an important role in the level splitting. The results are discussed in comparison with a recent experiment.

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The quantum properties of single-molecule magnets have generated considerable interest over the past decade in connection with macroscopic quantum phenomena.¹ High-spin molecules with spin-10 Mn_{12} and Fe_8 have been such good candidates because all the clusters are identical with no dispersion on the size of the clusters and the number of interaction spins, and the spin ground state and magnetic anisotropy are known with great accuracy. These molecules display particularly interesting phenomena such as quantum resonant tunneling^{2,3} and quantum phase interference.⁴ Such phenomena have received much attention, both theoretically and experimentally in view of macroscopic realization of quantum tunneling, and also because of the potential application to quantum computing.⁵ Many efforts have been made to understand their mechanisms by considering a giant spin Hamiltonian with a single-molecule magnet.^{2,3,5,6} Most of the study has neglected exchange interactions that depend on the distance and nonmagnetic atoms in the exchange pathway. Recently, however, it has been reported that a supramolecular single-molecule magnet dimer with antiferromagnetic coupling exhibits quantum behavior different from that of the individual single-molecule magnets.⁷ This result implies that exchange interaction between two single-molecule magnets can have a large influence on the quantum properties of single-molecule magnets. It is therefore important to understand the effect of the exchange interaction on magnetization tunneling.

The issue of spin tunneling with exchange interaction has been raised by several groups.⁸ In their studies exchange interaction is enhanced with magnetic anisotropy for studying tunneling of the Néel vector in antiferromagnetic particles. Using the instanton technique based on a spin coherent-state path integral, they calculated the tunneling rate of the Néel vector in uniaxial or biaxial antiferromagnetic particles. However, previous works applicable in the limit $S \gg 1$ have been confined to spin tunneling of the ground state in an antiferromagnetic particle having two collinear ferromagnetic sublattices. In this paper, we study magnetic tunneling in a system of identical, antiferromagnetically coupled dimers. By employing a perturbative approach,^{9,10} we obtain the level splitting of the states, degenerate pairwise for arbitrary spin in some typical cases, and show that even weak exchange interaction plays a crucial role in inducing spin tunneling.

The spin Hamiltonian of the dimer system can be written in the form

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + J\hat{S}_1 \cdot \hat{S}_2, \quad (1)$$

where \mathcal{H}_i ($i=1,2$) is the Hamiltonian of each single-molecule magnet which can be modeled as a giant spin of S_i . The corresponding Hamiltonian is given by

$$\mathcal{H}_i = -D\hat{S}_{zi}^2 + \mathcal{H}_i^{\text{trans}} - H_z\hat{S}_{zi}, \quad (2)$$

where D is the anisotropy constant and $\mathcal{H}_i^{\text{trans}}$ includes the transverse anisotropy or field. Also, \mathbf{H} stands for $g\mu_B\mathbf{H}$ where g is the electronic g factor and μ_B is the Bohr magneton. Henceforth, we will usually drop the combination $g\mu_B$ for better readability of the formula. Since the dimer consists of two single-molecule magnets with antiferromagnetic coupling, we take $J > 0$ to be much less than the anisotropy constant D . The system has $(2S_1+1)(2S_2+1)$ degenerate energy levels which in the absence of the transverse terms of Eq. (1) are labeled by the spin projection M_1 and M_2 on the z axis and given by $E_{M_1, M_2} = -D(M_1^2 + M_2^2) + JM_1M_2$. It can be easily checked that for the longitudinal field H_z satisfying

$$H_z = \frac{D(M_1^2 + M_2^2 - M_1'^2 - M_2'^2) + J(M_1'M_2' - M_1M_2)}{M_1' + M_2' - M_1 - M_2}, \quad (3)$$

the energy levels are degenerate:

$$E_{M_1', M_2'} = E_{M_1, M_2}. \quad (4)$$

Tunneling among the $(2S_1+1)(2S_2+1)$ energy states is allowed by the transverse terms containing \hat{S}_{xi} and \hat{S}_{yi} . In the case of small transverse terms, which are relevant for the dimer, the level splittings can be calculated in a more direct and simple way using high-order perturbation theory. In such cases, the level splitting of the degenerate level pair (M_1', M_2') and (M_1, M_2) is represented as the shortest chain of matrix elements and energy denominators connecting the states $|M_1', M_2'\rangle$ and $|M_1, M_2\rangle$ for typical situations which will be considered.

Let us consider as model I the level splitting induced by the transverse terms in the exchange interaction:

$$\mathcal{H} = -D\hat{S}_{z1}^2 - D\hat{S}_{z2}^2 + J\hat{S}_1 \cdot \hat{S}_2. \quad (5)$$

Noting that $\hat{S}_1 \cdot \hat{S}_2 = \hat{S}_{1z}\hat{S}_{2z} + \frac{1}{2}(\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+})$ and considering $\hat{S}_{1-}\hat{S}_{2+}$, the level splitting of the degenerate pair

(M'_1, M'_2) , (M_1, M_2) appears only in the chain of matrix elements when connecting the states $|M'_1+k, M'_2-k\rangle$ and $|M'_1+k+1, M'_2-k-1\rangle$ where $M'_1 = -M_1$, $M'_2 = M_1 > 0$, $M_2 = -M_1$, and k is an integer with $0 \leq k \leq M_1 - 1 - M'_1$. It corresponds to the level splitting of the degenerate pair $(-M_1, M_1) \rightarrow (M_1, -M_1)$. In this case the magnetic field does not contribute to the level splitting and thereby the longitudinal field (3) is not taken into consideration. Then, the level splitting of the degenerate pair becomes

$$\begin{aligned} \Delta E_{M'_1 M'_2, M_1 M_2} &= 2V_{M'_1 M'_2, M'_1+1, M'_2-1} \frac{1}{E_{M'_1+1, M'_2-1} - E_{M'_1 M'_2}} \\ &\times V_{M'_1+1, M'_2-1, M'_1+2, M'_2-2} \\ &\times \frac{1}{E_{M'_1+2, M'_2-2} - E_{M'_1 M'_2}} \dots \\ &\times V_{M_1-1, M_2+1, M_1 M_2}, \end{aligned} \quad (6)$$

where

$$\begin{aligned} V_{M'_1 M'_2, M'_1+1, M'_2-1} &= \langle M'_1 M'_2 | \frac{J}{2} (\hat{S}_1 + \hat{S}_2 - + \hat{S}_1 - \hat{S}_2 +) | M'_1 \\ &+ 1, M'_2 - 1 \rangle = \frac{J}{2} l_{M'_1+1, M'_2-1}, \end{aligned} \quad (7)$$

$$l_{M'_1+1, M'_2-1} = \sqrt{(S_1 + M'_1 + 1)(S_1 - M'_1)(S_2 - M'_2 + 1)(S_2 + M'_2)}$$

are the matrix elements of the operator $\hat{S}_1 - \hat{S}_2 +$, and $E_{M'_1 M'_2} = -D(M_1'^2 + M_2'^2) + JM'_1 M'_2$ are the unperturbed energy levels. Taking $S_1 = S_2$ in the ensuing discussion, we calculate the product (6) and obtain the level splitting

$$\begin{aligned} \Delta E_{-M_1, M_1, M_1, -M_1} &= (4D + 2J) \left(\frac{J}{4D + 2J} \right)^{2M_1} \left[\frac{(S_1 + M_1)!}{(S_1 - M_1)!(2M_1 - 1)!} \right]^2. \end{aligned} \quad (8)$$

In the ground state ($M_1 = S_1$) the result (8) simplifies to

$$\Delta E_{-S_1, S_1, S_1, -S_1} = (2S_1)^2 (4D + 2J) \left(\frac{J}{4D + 2J} \right)^{2S_1}. \quad (9)$$

For large value of M_1 ($S_1 - M_1, M_1 \gg 1$), Eq. (8) with the help of the Stirling formula reduces to

$$\begin{aligned} \Delta E_{-M_1, M_1, M_1, -M_1} &= \left(\frac{2D + J}{\pi} \right) \left(\frac{J}{4D + 2J} \right)^{2M_1} \\ &\times \left[\frac{(S_1 + M_1)^{2S_1 + 1 + M_1}}{(S_1 - M_1)^{2S_1 + 1 - M_1} (2M_1)^{4M_1 - 1}} \right]. \end{aligned} \quad (10)$$

Our next example, model II, corresponds to the case of transverse anisotropy in the xy plane:

$$\mathcal{H}_i^{\text{trans}} = B(\hat{S}_{xi}^2 - \hat{S}_{yi}^2). \quad (11)$$

Writing $\mathcal{H}_i^{\text{trans}} = \frac{1}{2} B(\hat{S}_{+i}^2 + \hat{S}_{-i}^2)$ and choosing $i = 2$, the level splitting of the degenerate pair exists in the matrix elements when connecting the states $|M'_1, M'_2 + 2k\rangle$ and $|M_1, M'_2 + 2k + 2\rangle$ where k is an integer with $0 \leq k \leq (M_2 - M'_2)/2 - 1$ and $M'_1 = M_1$. It corresponds to the level splitting of the degenerate pair $(M_1, M'_2) \rightarrow (M_1, M_2)$ where $M_2 > M'_2$, $M'_2 < 0$, and $M_2 - M'_2$ is even number. In the limit $B \ll D$ the level splitting of the degenerate states appears, minimally, in the $(M_2 - M'_2)/2$ th order in B/D :

$$\begin{aligned} \Delta E_{M'_1 M'_2, M_1 M_2} &= 2V_{M'_1 M'_2, M_1, M'_2+2} \frac{1}{E_{M_1, M'_2+2} - E_{M'_1 M'_2}} \\ &\times V_{M_1, M'_2+2, M_1, M'_2+4} \\ &\times \frac{1}{E_{M_1, M'_2+4} - E_{M'_1 M'_2}} \dots \\ &\times V_{M_1, M_2-2, M_1 M_2} \end{aligned} \quad (12)$$

where

$$\begin{aligned} V_{M'_1 M'_2, M_1, M'_2+2} &= \langle M'_1 M'_2 | \frac{B}{2} \hat{S}_{-2}^2 | M_1, M'_2 + 2 \rangle \\ &= \frac{B}{2} \tilde{l}_{M'_2+1} \tilde{l}_{M'_2+2}, \end{aligned} \quad (13)$$

$\tilde{l}_{M'_2} = \sqrt{(S_2 + M'_2)(S_2 - M'_2 + 1)}$ are the matrix elements of the operator \hat{S}_{-2} , and $E_{M'_1 M'_2} = -D(M_1'^2 + M_2'^2) + JM'_1 M'_2 - H_z(M'_1 + M'_2)$ are the unperturbed energy levels. Since the pair states are degenerate for the values of the longitudinal field $H_z = -D(M_2 + M'_2) + JM_1$ from Eq. (3), the elements $E_{M_1, q} - E_{M'_1 M'_2}$ in the denominators of Eq. (12) where $q = M'_2 + 2, M'_2 + 4 \dots M_2 - 2$, become independent upon M'_1 and M_1 . Also, noting that Eq. (13) is only dependent upon M'_2 , the formula for the level splittings is expected to be independent of M'_1 and M_1 and reads

TABLE I. The level splitting (ΔE) of the low-lying degenerate pair (M'_1, M'_2) , (M_1, M_2) in Mn_4 , the resonant field (H_z) from Eq. (3), and the physical origins which induce level splittings. $B \sim H_x \sim 0.1$ K is for illustration. The numbers, labeled 1–5 in the first column, indicate the transitions claimed as the strongest tunnel resonances in Ref. 7. Note that (M_1, M_2) and (M_2, M_1) are degenerate.

| Number | $(M'_1, M'_2) \rightarrow (M_1, M_2)$ | H_z (T) | ΔE (K) | Main sources of splittings |
|--------|--|-----------|-----------------------|----------------------------|
| 1 | $(-9/2, -9/2) \rightarrow (-9/2, 9/2)$ | -0.336 | 2.02×10^{-4} | B, H_x |
| | $(-9/2, -9/2) \rightarrow (9/2, 9/2)$ | 0 | 0 | |
| 2 | $(-9/2, -9/2) \rightarrow (-9/2, 7/2)$ | 0.202 | 1.76×10^{-3} | B |
| | $(-9/2, -9/2) \rightarrow (9/2, 7/2)$ | 0.233 | 0 | |
| | $(-9/2, 7/2) \rightarrow (9/2, 7/2)$ | 0.261 | 2.02×10^{-4} | B, H_x |
| 3 | $(-9/2, 9/2) \rightarrow (9/2, 9/2)$ | 0.336 | 2.02×10^{-4} | B, H_x |
| 4 | $(-9/2, -9/2) \rightarrow (-9/2, 5/2)$ | 0.739 | 1.19×10^{-3} | B, H_x |
| 5 | $(-9/2, 9/2) \rightarrow (7/2, 9/2)$ | 0.873 | 1.76×10^{-3} | B |

$$\begin{aligned} \Delta E_{M'_1, M'_2, M_1, M_2} &= 2D \left(\frac{B}{2D} \right)^{(M_2 - M'_2)/2} \sqrt{\frac{(S_2 + M_2)!(S_2 - M'_2)!}{(S_2 - M_2)!(S_2 + M'_2)!}} \\ &\times \frac{\delta_{M'_1, M_1}}{[(M_2 - M'_2 - 2)!!]^2}, \end{aligned} \quad (14)$$

which seems to be the same expression as that in the single-molecule magnet.¹¹ However, the exchange interaction between two single-molecule magnets contributes to the level splittings via the longitudinal field (3) and $\delta_{M'_1, M_1}$ in Eq. (14).

Our final example, model III, is described by

$$\mathcal{H}^{\text{trans}} = -H_x(\hat{S}_{x1} + \hat{S}_{x2}), \quad (15)$$

where H_x can be an internal or external magnetic field. Using $\hat{S}_{xi} = (\hat{S}_{+i} + \hat{S}_{-i})/2$ and considering the case at $i=2$, the level splitting of the degenerate pair appears in the matrix elements when connecting the states $|M'_1, M'_2 + k\rangle$ and $|M_1, M_2 + k + 1\rangle$ where k is an integer with $0 \leq k \leq M_2 - M'_2 - 1$ and $M'_1 = M_1$. It corresponds to the level splitting of the degenerate pair $(M_1, M'_2) \rightarrow (M_1, M_2)$ where $M_2 > M'_2$, $M'_2 < 0$, and $M'_2 - M_2$ can be any integer. Thus, the level splitting is represented as

$$\begin{aligned} \Delta E_{M'_1, M'_2, M_1, M_2} &= 2V_{M'_1, M'_2, M_1, M'_2 + 1} \\ &\times \frac{1}{E_{M_1, M'_2 + 1} - E_{M'_1, M'_2}} V_{M_1, M'_2 + 1, M_1, M'_2 + 2} \\ &\times \frac{1}{E_{M_1, M'_2 + 2} - E_{M'_1, M'_2}} \dots V_{M_1, M_2 - 1, M_1, M_2}, \end{aligned} \quad (16)$$

where

$$\begin{aligned} V_{M'_1, M'_2, M_1, M'_2 + 1} &= \langle M'_1, M'_2 | -\frac{H_x}{2} \hat{S}_{-2} | M_1, M'_2 + 1 \rangle \\ &= -\frac{H_x}{2} \tilde{T}_{M'_2 + 1}. \end{aligned} \quad (17)$$

Since the unperturbed energy levels $E_{M'_1, M'_2}$ and the resonant field H_z are the same as the ones in model II, it is also expected that the level splitting becomes independent of M'_1 and M_1 . Therefore, in the limit of small transverse field the level splitting is given by

$$\begin{aligned} \Delta E_{M'_1, M'_2, M_1, M_2} &= 2D \left(\frac{H_x}{2D} \right)^{M_2 - M'_2} \sqrt{\frac{(S_2 + M_2)!(S_2 - M'_2)!}{(S_2 - M_2)!(S_2 + M'_2)!}} \\ &\times \frac{\delta_{M'_1, M_1}}{[(M_2 - M'_2 - 1)!!]^2}, \end{aligned} \quad (18)$$

which is similar to that in the single-molecule magnet. This result shows that exchange interaction between two single magnets makes a contribution to the level splitting through the resonant field $H_z = -D(M_2 + M'_2) + JM_1$ and $\delta_{M'_1, M_1}$ in Eq. (18).

Even though we have separately considered the problems in models II and III, both the transverse field and the transverse anisotropy are present in some cases. In the presence of B , and H_x being of the same order of magnitude, the effect of the transverse field on level splitting is weaker than that of the transverse anisotropy, as is evident in Eqs. (14) and (18). Thus, we can neglect the transverse field contribution to the splittings. However, since $M_2 - M'_2$ is odd, the transverse field should be included in the level splitting through the single perturbation step along the chain connecting the degenerate states (M'_1, M'_2) and (M_1, M_2) where $M'_1 = M_1$ and $M'_2 < 0$. Hence, the corresponding level splitting becomes

$$\begin{aligned}
 \Delta E_{M'_1 M'_2, M_1, M_2} &= 2V_{M'_1 M'_2, M_1, M'_2+1}^{(H)} \frac{1}{E_{M_1, M'_2+1} - E_{M'_1 M'_2}} V_{M_1, M'_2+1, M_1, M'_2+3}^{(B)} \cdots V_{M_1, M_2-2, M_1 M_2}^{(B)} \\
 &+ 2V_{M'_1 M'_2, M_1, M'_2+2}^{(B)} \cdots V_{M_1, M_2-3, M_1 M_2-1}^{(B)} \frac{1}{E_{M_1, M_2-1} - E_{M'_1 M'_2}} V_{M_1, M_2-1, M_1 M_2}^{(H)} \\
 &+ 2 \sum_{k=M'_2+2}^{M_2-3} \left[\prod_{p_1=M'_2+2}^k V_{M_1, p_1-2, M_1, p_1}^{(B)} \right] V_{M_1, k, M_1, k+1}^{(H)} \left[\prod_{p_2=k+1}^{M_2-2} V_{M_1, p_2, M_1, p_2+2}^{(B)} \right] \\
 &\times \left(\prod_{q_1=M'_2+2}^k \frac{1}{E_{M_1, q_1} - E_{M'_1 M'_2}} \right) \left(\prod_{q_2=k+1}^{M_2-2} \frac{1}{E_{M_1, q_2} - E_{M'_1 M'_2}} \right), \quad (19)
 \end{aligned}$$

where the matrix elements $V^{(B)}$ and $V^{(H)}$ are expressed as Eqs. (13) and (17), respectively. The sum in Eq. (19) can be calculated by using the formula

$$\sum_{p=0}^r \frac{(2p-1)!!(2r-2p-1)!!}{(2p)!!(2r-2p)!!} = 1, \quad (20)$$

and the resulting splitting for the odd resonance becomes

$$\begin{aligned}
 \Delta E_{M'_1, M'_2, M_1, M_2} &= H_x \left(\frac{B}{2D} \right)^{(M_2-M'_2)/2} \sqrt{\frac{(S_2+M_2)!(S_2-M'_2)!}{(S_2-M_2)!(S_2+M'_2)!}} \\
 &\times \frac{\delta_{M'_1, M_1}}{[(M_2-M'_2-2)!!]^2}. \quad (21)
 \end{aligned}$$

To illustrate the results with a concrete example, let us consider a supramolecular dimer $\text{Mn}_4 \text{O}_3 \text{Cl}_4 (\text{O}_2 \text{CET})_3 (\text{py})_3$ (hereafter Mn_4). This compound contains three Mn^{3+} ions and one Mn^{4+} ion with the axial anisotropy constant ($D \approx 0.72$ K), and exchange coupling ($J \approx 0.1$ K) between them leads to the $[\text{Mn}_4]_2$ dimer having a ground-state spin of $S_1 = S_2 = 9/2$. At very low temperature, most of the excited states can be neglected. Thus, as is listed in Table I, the low-lying states are involved in magnetization reversal at very low temperature in the presence of the longitudinal field. At high negative field, the initial state becomes $(-9/2, -9/2)$. As the magnetic field increases, the first level crossing occurs in the degenerate pair $(-9/2, -9/2)$, $(-9/2, 9/2)$ at $H_z = -0.336$ T which corresponds to the odd resonance, i.e., $M_2 - M'_2 = \text{odd}$. In this case the main sources of the level splitting can be either the transverse anisotropy or the transverse field. Meanwhile, since the hysteresis loops in experiment⁷ display steplike features at even resonance, $H_z = 0.202$ T and 0.873 T, at least the transverse anisotropy should contribute to the level splittings. In this respect, both

the transverse anisotropy and the transverse field induce the level splittings in the odd resonance and thereby the transition between $(-9/2, -9/2)$ and $(-9/2, 9/2)$. At the next level crossing at $H_z = 0$ T, the degenerate pair is $(-9/2, -9/2)$ and $(9/2, 9/2)$. The possibility of tunneling from $(-9/2, -9/2)$ to $(9/2, 9/2)$ requires terms such as either $\hat{S}_{1+} \hat{S}_{2+}$ or $\hat{S}_{1-} \hat{S}_{2-}$ in the spin Hamiltonian. However, there is no such transverse terms in the Hamiltonian (1) which induces the level splitting between them. For this reason the steplike feature is absent in the hysteresis loop at 0 T while a strong quantum step at $H_z = 0$ is present in other single-molecule magnets.^{2,3} The situation is analogous to that in the case $(-9/2, -9/2) \rightarrow (9/2, 7/2)$. The next level crossing occurs in the degenerate pair $(-9/2, -9/2)$ and $(-9/2, 7/2)$ which corresponds to the number 2 in Table I. In this situation the level splitting is induced only by the transverse anisotropy due to the even resonance. The avoided level crossing at $H_z = 0.261$ T unclaimed in the experiment occurs from $(-9/2, 7/2)$ to $(9/2, 7/2)$. Actually, the corresponding peak position is shown in the experiment results (Fig. 4 in Ref. 7). The level crossings at $H_z = 0.336$ T and 0.739 T allow tunneling from $(-9/2, 9/2)$ to $(9/2, 9/2)$ and from $(-9/2, -9/2)$ to $(-9/2, 5/2)$, respectively, which correspond to the odd resonance. At $H_z = 0.873$ T the avoided level crossing can occur from $(-9/2, 9/2)$ to $(7/2, 9/2)$ with finite level splitting which originates from the transverse anisotropy. Finally, it is interesting to estimate the level splitting induced by the transverse exchange interaction. Inserting the value of D and J into Eq. (9), the level splitting is of the order of 10^{-11} K which is much smaller than that induced by the transverse anisotropy or the transverse field. As a result, the main sources of the steplike features in the hysteresis loops of the $[\text{Mn}_4]_2$ dimer are the transverse anisotropy and the transverse field, and each half of the dimer acts as a field bias on its neighbor via the exchange interaction within $[\text{Mn}_4]_2$.

In conclusion, we have considered the level splitting in a dimer with antiferromagnetic coupling between two single-molecule magnets. A perturbation approach allows us to obtain the level splitting of the states, degenerate pairwise for

arbitrary spin, in the presence of the exchange interaction. It is found that the level splittings are strongly affected by the exchange interaction as well as the transverse anisotropy and the transverse field. In comparison with recent experimental results, the level splitting of the low-lying degenerate pair

has been estimated for several cases and the main sources of each resonance have been clarified.

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