Quantum dynamics of the molecular magnet driven by external magnetic fields

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The quantum dynamics of the mesoscopic molecular magnet under the influence of external magnetic fields is studied. We show that when the frequency and the reduced amplitude of the longitudinal magnetic field are related in a specific manner, the magnetization tunneling will be dynamically suppressed during time evolution. The effects of external noise and anisotropy on this dynamic spin localization are studied. In particular, we show that the anisotropy interaction may enhance the spin localization phenomenon.

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Study of the quantum properties of the magnetic particles, especially molecular magnets such as Fe_8, Mn_{12}, and V_{15}, has been an active research focus for the past decade.[1] These molecular magnetic clusters possess several advantages that make them ideal candidates to study quantum phenomena at the mesoscopic level. Quantum tunneling,[2–7] quantum interference,[8,9] and quantum coherence[10–12] had been observed in these nanoscale molecular magnet systems. Quantum resonance tunneling is characterized by the observation of discrete steps in the magnetic hysteresis loops at low temperatures, whereas quantum interference is featured by the tunneling splitting that oscillates as a function of the static external magnetic field. Study of these mesoscopic quantum phenomena is not only for academic interest but also for the future applications, e.g., in quantum computation.[13,14]

In this paper we investigate quantum tunneling dynamics of the molecular magnet in the presence of external magnetic fields with longitudinal and transverse field strengths $H_z(t)$ and H_x, respectively. Here the longitudinal magnetic field lifts the energy degeneracy of the spin states through Zeeman effect, while the transverse field appears as a coupling between different spin components. We assume the longitudinal field to be time-dependent and that the transverse field is static. Using perturbation theory, a general formula for the oscillation period to describe the passing across the initial spin state is obtained. Another aspect we are interested is the effects of the external noise and anisotropy on the quantum coherent behavior of the molecular magnet.

The molecular structure of Mn_{12} contains four Mn^{4+} ions in a central tetrahedron surrounded by eight Mn^{3+} ions. The Mn^{3+} and Mn^{4+} ions are antiferromagnetically coupled, so that these molecules possess a high-spin ground state of $S=10$.[15] The coupling between the eight Fe^{2+} ions in Fe_8 results, like in Mn_{12}, in a net total spin $S=10$. Both compounds can be well described by a single-spin Hamiltonian,

$$H(t) = -b_z(t)\hat{S}_z - b_x\hat{S}_x - D\hat{S}_z^2, \tag{1}$$

where $b_z(t)=\mu_B g H_z(t)$, $b_x=\mu_B g H_x$, $g\simeq 2$ and μ_B is Bohr magneton; $\hat{S}_i(i=x,y,z)$ are the components of spin spin operators; D is the anisotropy constant defining an Ising-type anisotropy. In the absence of a magnetic field, the anisotropy stabilizes the degenerate spin states of $m=\pm 10$.[16] These states correspond to opposite directions of the magnetization in the classical sense. Given the initial state condition $\psi(0)=\sum_{m=-S}^{S}c_m(0)|S,m\rangle$, the subsequent evolution of the state is determined by the time-dependent Schrödinger equation ($\hbar=1$)

$$i\frac{d}{dt}\psi(t) = H(t)\psi(t). \tag{2}$$

A quantity tailored to the dynamics of the system is the longitudinal magnetization given by

$$M_z(t) = \langle \psi(t)|\hat{S}_z|\psi(t)\rangle. \tag{3}$$

Throughout this paper the initial state is assumed to be one of the ground states $|S,S\rangle$ in the absence of magnetic fields.

Rabi oscillations and dynamic spin localization with no anisotropy. In this section, we analyze time evolution of the magnetization in the absence of anisotropy ($D=0$). The effect of anisotropy will be discussed afterwards. Assuming that $\psi(t)=e^{i\int_0^t d\tau\, b_z(\tau)\hat{S}_z}\varphi(t)$, we obtain

$$i\frac{d}{dt}\varphi(t) = H_I(t)\varphi(t), \tag{4}$$

where $H_I(t)=-b_x \exp\big(-i\int_0^t d\tau\, b_z(\tau)\hat{S}_z\big)\hat{S}_x \exp\big(i\int_0^t d\tau\, b_z(\tau)\hat{S}_z\big)$. Making use of the identity

$$\exp(i\lambda\hat{S}_z)\hat{S}_x\exp(-i\lambda\hat{S}_z) = \hat{S}_x\cos\lambda - \hat{S}_y\sin\lambda,$$

the formal solution of Eq. (4) is obtained,

$$\varphi(t) = \hat{T}e^{i\int_0^t d\tau[X(\tau)\hat{S}_x + Y(\tau)\hat{S}_y]}\varphi(0), \tag{5}$$

where $X(t)=b_x\cos[\int_0^t d\tau\, b_z(\tau)]$, $Y(t)=b_x\sin[\int_0^t d\tau\, b_z(\tau)]$, and $\hat{T}$ denotes time ordering. Considering the situation in which the transverse magnetic field b_x is weak, we may approximate Eq. (5) by the following solution:

$$\varphi(t) = e^{i\int_0^t d\tau[X(\tau)\hat{S}_x + Y(\tau)\hat{S}_y]}\varphi(0). \quad (6)$$

This solution is valid to the first order in b_x and preserves unitarity. After a straightforward calculation, we obtain the time evolution of the population of the spin-m state as

$$P_m(t) = |c_m(t)|^2 = \left| \sum_{n=-S}^{S} d^S_{m,n}(\pi/2) d^S_{S,n}(\pi/2) e^{-i\alpha\int_0^t d\tau\, b_z(\tau)} e^{in\lambda} \right|^2, \quad (7)$$

where $\lambda = \sqrt{(\int_0^t d\tau X(\tau))^2 + (\int_0^t d\tau Y(\tau))^2}$, and the matrix element is defined as

$$d^S_{m.n}(\theta) = \langle S,m|e^{-i\theta\hat{S}_y}|S,n\rangle, \ (m,n = S, \ldots, -S).$$

From Eq. (7), we obtain the population of the initial spin-S state at time t as follows:

$$P_S(t) = |c_S(t)|^2 = \cos^2 \left| \int_0^t d\tau_1\, b_x e^{i\int_0^{\tau_1} d\tau_2\, b_z(\tau_2)} \right|. \quad (8)$$

Thus to the first-order approximation in b_x we obtain the analytical expression of the evolution probability for the molecular magnet remaining in the initial spin state. Expression (8) is valid for arbitrary time-dependent external magnetic fields. Obviously, $e^{i\int_0^t d\tau\, b_z(\tau)}$ can be expanded as a discrete Fourier series, and the time integral is either bounded or increases linearly in time (on top of an oscillatory piece). In the former case, P_S remains close to unity at all times because of the smallness of b_x. This high population of the initial spin state is just the spin localization. In the latter case, P_S oscillates between 0 and 1, implying population transfer between initial state $|S,S\rangle$ and other spin states. Hence we have the spin delocalization, i.e., Rabi oscillation. The oscillation period T is given by

$$T = \frac{\pi}{\lim_{t\to\infty}\left| \frac{1}{t}\int_0^t d\tau_1\, b_x e^{i}\int_0^{\tau_1} d\tau_2\, b_z(\tau_2)\right|} \quad (9)$$

Below we give two examples of special time-dependent external magnetic fields.

(a) Sinusoidal field $b_z(t) = b\cos(\omega t)$. According to Eq. (9), the oscillation period is

$$T = \frac{\pi}{b_x J_0(b/\omega)}, \quad (10)$$

where J_0 is the zeroth-order Bessel function of the first kind. From this result, it can be seen that when $J_0(b/\omega) \neq 0$, there exists a finite oscillation period, indicating that the population weight can transit from an initial spin-ground state to other spin states within the driving process. When $b=0$, the longitudinal field-free oscillation has period $T_0 = \pi/b_x$. The fact $|J_0(b/\omega)| \leqslant 1$ implies that $T \geqslant T_0$. This shows that the invasion of the longitudinal magnetic field will suppress the coherent spin tunneling. The extreme case occurs when b/ω is a root of J_0. In this case, we have $T \to \infty$, which implies that the spin tunneling is totally suppressed. Hence the system will mostly stay in the initial spin-minimum state during the whole driving process. This is just the phenomenon of spin localization.

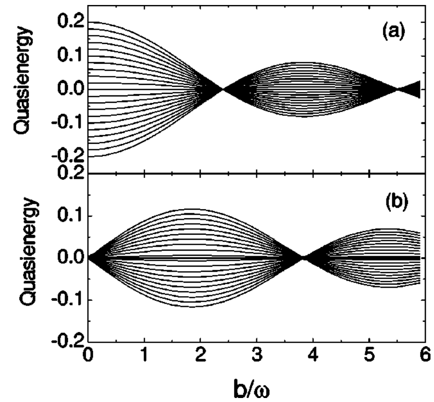

FIG. 1. Anisotropy-free quasienergies as a function of b/ω for the value of (a) $b_0=0$ and (b) $b_0=\omega$.

(b) A combination of static and sinusoidal magnetic fields $b_z(t) = b_0 + b\cos(\omega t)$. In this case, the oscillation period is

$$T = \frac{\pi}{\left| b_x \lim_{N\to\infty} \frac{\sin(b_0\pi N/\omega)}{N\sin(b_0\pi/\omega)} \tilde{J}_{b_0/\omega}(b/\omega)\right|}, \quad (11)$$

where $\overline{J}$ is the Anger function[17] defined by

$$\overline{J}_a(b) = \frac{1}{\pi}\int_0^\pi dx\cos(ax - b\sin x).$$

When $b_0/\omega \neq k$ (k is an integer), T tends to be infinite. When $b_0/\omega = k$, the oscillation period becomes

$$T = \frac{\pi}{b_x J_k(b/\omega)}, \quad (12)$$

where J_k are k-th-order Bessel functions. When b/ω becomes a root of J_k, again, the oscillation period approaches infinity, and we have the spin localization.

The phenomenon of dynamic spin localization closely related to the property of the dressed energy spectrum of the system. In the presence of an oscillating magnetic field, the time periodicity of the Hamiltonian (1) enables us to describe quantum evolution of the system in terms of Floquet formalism. Suppose $b_z(t) = b_0 + b\cos(\omega t)$; we plot the quasienergy spectrum versus rescaled oscillating amplitude b/ω for two values of b_0. The results are shown in Fig. 1(a) ($b_0=0$) and Fig. 1(b) ($b_0=\omega$), respectively. In Fig. 1(a) one can see that the quasienergies collaspes to a point at $b/\omega=2.4$, which is a root of the zeroth order Bessel function J_0. This energy collapse completely suppresses quantum coherent tunneling, consistent with the prediction from Eq. (10). If the longitudinal magnetic field consists of both static and oscillating components, then when static-component strength b_0 is related to the frequency ω of the oscillating component via the relation $b_0 = k\omega$ (k is an integer), the quasienergies will collapses into a point at the values of oscillating-component amplitude b satisfying $J_k(b/\omega)=0$, which is shown in Fig. 1(b).

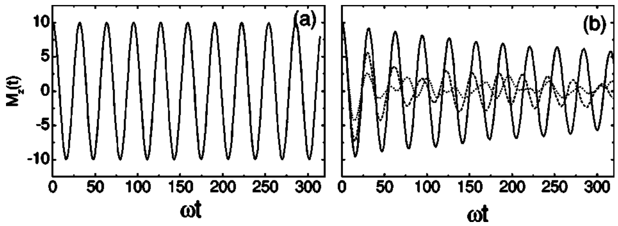

FIG. 2. Time evolution of the magnetization with and without external noise in the sinusoidal magnetic field, $b=0.2\omega$, $b_x=0.1\omega$. (a) The case without the noise; (b) the case with the noise $\Delta=0.02\omega$ (solid line), $\Delta=0.04\omega$ (dashed line), and $\Delta=0.1\omega$ (dotted line). $b_x\tau_c$ is fixed to be 1.0 for the case with the noise.

We emphasize that this spin localization effect is purely a consequence of the collapse of quasienergies, which fully suppresses interference among Floquet states. So it does not depend on whether the initially populated level feels the "ends" of the spin ladder or not.[18]

Effect of the external noise. In practice, since the external magnetic field may have a fluctuation component, the effect of external noise has to be considered. Another motivation for the introduction of an external noise is to provide the fluctuations required to destroy the coherence of the quantum tunneling process and, in suitable cases, leads to a rate process for the decay of the population. Leuenberger *et al.*[19] have generalized the Landau-Zener theory[20] of coherent tunneling transitions to an incoherent region by taking into account the thermal relaxation effect. Remarkably, this incohent transition has been detected by Wernsdorfer *et al.*[21] in Fe_8 molecular nanomagnets. In this section, we study the dynamics of the magnetization when the external magnetic field has a fluctuating component. Compared to the previous thermal relaxation studies,[19,21] the introduction of external fluctuation permits the investigation of the role of the strength and size of the noise on the time evolution of the molecular magnets. As a versatile choice for the noise, an Ornstein-Uhlenbeck (OU) process[22] is used: the longitudinal magnetic field $b_z(t)$ is assumed to contain two components, a stochastic part $f(t)$ and a systematic part $b_0+b\cos(\omega t)$, i.e.,

$$b_z(t) = b_0 + b\cos(\omega t) + f(t) \tag{13}$$

The noise $f(t)$ is assumed to be characterized by an OU process whereby it has a zero average value and correlation function,

$$\langle f(t)f(s)\rangle = \Delta^2 \exp(-|t-s|/\tau_c) \tag{14}$$

Here the quantities Δ and τ_c are the strength and decay constant of the noise, respectively. When the noise is external to the system, and therefore not necessarily thermal in character, Δ and τ_c can be varied in a controlled manner, and are not restricted by the physical properties of the system. The population distribution in the $(2S+1)$ spin components with the external noise are solved numerically by generating trajectories[23] for the different realization of the noise.

Figure 2 shows the time dependence of the magnetization $M_z(t)$ in the longitudinal magnetic field with the systematic part $b_z=b\cos(\omega t)$. The field parameters are chosen as $b=0.2\omega$ and $b_x=0.1\omega$, corresponding to the Rabi oscillation with period $T=T_0/J_0(0.2)$, as shown in Fig. 2(a). In the case of a weak noise $\Delta/b_x=0.2$ [the solid curve in Fig. 2(b)], the magnetization is still oscillatory in our scope of time, but its oscillation amplitude decreases with time. When the strength of the noise increases to $\Delta/b_x=1.0$ (dotted curve), the Rabi oscillation breaks down completely and the system decays fast towards equilibrium. This suggests that the coherent Rabi oscillation for a molecular magnet is sensitive to the external noise and is destroyed even in a weak coupling regime. Figure 3 plots the time evolution of $M_z(t)$ for the value of $b/\omega=2.4$, corresponding to the dynamic localization condition in the absence of noise, as shown in Fig. 3(a). In Fig. 3(b), we can see that in the case of intermediate $(\Delta\tau_c\sim 1)$ noise modulation (solid curve), the magnetization still remains its initial value for an extremely long time. This insensitivity to the presence of weak noise reflects the strength of the systematic field. When the strength of noise increases to a strong coupling regime, a more rapid and less oscillatory decay is observed in the population evolution, as shown in Fig. 3(b) (dotted curve).

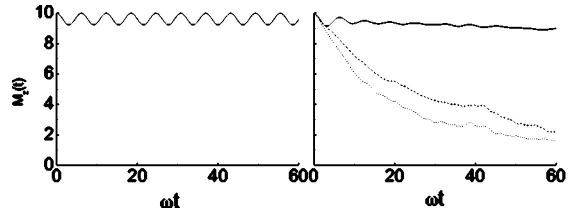

FIG. 3. The time evolution of the magnetization with and without external noise in the sinusoidal magnetic field, $b=2.4\omega$, $b_x=0.1\omega$. (a) The case without the noise; (b) the case with the noise $\Delta=0.1\omega$ (solid line), $\Delta=0.5\omega$ (dashed line), and $\Delta=\omega$ (dotted line).

Anisotropy effect. In the above discussions we have not taken the spin anisotropy effect into account. In this case, the dynamics of the magnet system is nothing but the equivalent of a driving charge moving in a finite lattice with a tight-binding description. Thus the dynamic spin localization is simply reminiscent of the charge localization reported by Dunlap and Kenkre.[24] However, this similarity is broken by the presence of the anisotropy term in Eq. (1), which shuffles the equally-spaced spin ladders. How this nonlinear spin interaction influences the driving dynamics is what we concern in the following.

Figure 4 shows the quasienergies in the presence of a weak anisotropy. The other system parameters are the same as used in Fig. 1(a). Compared to Fig. 1(a), two prominent

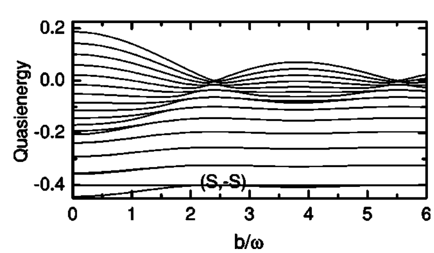

FIG. 4. Quasienergy spectrum in the presence of weak anisotropy $D=0.004\omega$. Other parameters are the same as in Fig. 1(a).

features can be seen from Fig. 4: (i) The anisotropy removes the exact level crossing among $(2S+1)$ spin states and thus induces avoided crossings. This breakdown of the exact crossing is due to the fact that the quadratic anisotropy disarranges the spin levels which are equally spaced without anisotropy; (ii) with increasing the value of the amplitude of the driving field, the quasienergies evolve into many doublets and every doublet has an exact degeneracy in the field parameter space. To label these doublets, we note that in the absence of longitudinal magnetic field, the spin states $|S,m\rangle$ and $|S,-m\rangle$ are nearly degenerate, with mixed by weak transverse magnetic field. Therefore, we can label the doublet formed by these two states with a notation $(m,-m)$. In the presence of a time-dependent longitudinal magnetic field, the corresponding Floquet states developed from the doublet $(m,-m)$ will evolve into an exact crossing with increasing driving amplitude b, as shown in Fig. 4. Note that the different doublets feel different coupling strength induced by the transverse magnetic field, so every doublet crossing occurs in the parameter space with different parameter values. In particular, the crossing of doublet $(S,-S)$ is indicated explicitly in Fig. 4

Due to the fact shown in Fig. 4 that the quasienergies are scattered by the anisotropy, the spin localization phenomenon cannot persist at parameter points that correspond to otherwise level crossings. As a result, the magnetization will oscillate during its time evolution. However, we find that if the system parameters are chosen at the exact degeneracy of the doublet $(m,-m)$, then the dynamic spin localization revives again. As an example, we show in Fig. 5 time evolution of $M_z(t)$ for the value of $b/\omega=2.52$, and $D/\omega=0.004$, corresponding to the degeneracy of the doublet $(S,-S)$ in Fig. 4. The initial state is chosen to be $|S,S\rangle$. As a comparison, we also show the case without anisotropy [dashed line in Fig. 5]. Interestingly and surprisingly, compared to the case without anisotropy, the localization effect is enhanced by the presence of anisotropy. To make the mechanism of this enhancement of the localization more clear, by projection to the spin-state space, we find the two Floquet states which compose the doublet $(S,-S)$ are dominated by the spin states $|S,S\rangle$ and $|S,-S\rangle$, respectively. Thus in contrast to the anisotropy-free case, the initial spin state $|S,S\rangle$ can be approximated by one Floquet state of the doublet $(S,-S)$, subsequent time evolution. This is different from the case for a double-well trap,[25] wherein an initial localized state always can be described by a superposition of two delocalized and degenerate Floquet states. In the present case, both of two Floquet states in doublet $(S,-S)$ is spin localized at the level crossing. Therefore, we arrive at a conclusion that the anisotropy may enhance the localization, as shown in Fig. 5.

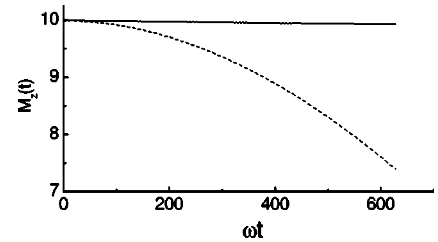

FIG. 5. Time evolution of the magnetization with (solid line) and without (dashed line) an anisotropy interaction. Parameters are chosen to correspond to level crossing of the doublet $(S,-S)$ shown in Fig. 4.

In summary, by application of the external magnetic fields which may contain a random component, we have shown magnetization dynamics of the molecular magnet. A general formula is obtained for the oscillation period to describe the quantum transition from the initial spin state $|S,S\rangle$ to other spin states. In particular, when the frequency and reduced amplitude of the longitudinal magnetic field are related in a specific manner, the magnetization tunneling is dynamically suppressed during time evolution. In addition, the effects of external noise and nonlinear anisotropy are studied. It has been shown that while the Rabi oscillation is sensitive to the external noise, the dynamic spin localization may remain for experimentally relevant times in the presence of a weak noise field. We have also found that the dynamic spin localization may be enhanced by the spin anisotropy interaction.

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