Abrupt relaxation in high-spin molecules

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Abstract

Mean-field model suggests that the rate of resonant quantum tunneling in high-spin molecules is not only field-dependent but also time-dependent. The relaxation-assisted resonant tunneling in high-spin molecules produces an abrupt magnetization change during relaxation. When the applied field is very close to the resonant field, a time-dependent interaction field gradually shifts the energies of different collective spin states, and magnetization tunneling is observed as two energies of the spin states coincide. © 2000 Elsevier Science B.V. All rights reserved.

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Since the theoretically predicted possibility of macroscopic quantum tunneling of magnetization [1,2], it draws interests to search the coherent tunneling of a large number of spins coupled by a strong exchange interaction through an anisotropy potential barrier from one orientation to another [3–5]. Only recently a stepped hysteresis loops reported for the high-spin clusters gave a clear evidence of macroscopic quantum tunneling of magnetization below 3 K [6,7]. In contrast to the distribution of magnetic properties and activation volumes in nanoparticles, the high-spin $\text{Mn}_{12}\text{O}_{12}$ molecules consist of a large number of identical clusters [8]; therefore, a rigorous comparison between experiments and theory can be made [6–10]. One of the interesting phenomena is that an unusual large relaxation time was observed in $\text{Mn}_{12}\text{O}_{12}$ molecules in zero field [8]. For $2 \leq T \leq 6$ K, the reported experimental data are in reasonable agreement with a single relaxation time given by Arrhenius law with 6000 s waiting time [8,9], i.e., $\tau = \tau_0 \exp(T_c/T)$ with $T_c = 61$ K and a very large prefactor $\tau_0 \cong 10^{-8}$ s. At very low temperature the Arrhenius law does not satisfy the observed data, and it was interpreted as resonant tunneling. A sequence of regularly spaced maxima and minima in field-dependent relaxation rate has been

found, and the behavior was explained in terms of phonon-assisted transitions [6]. However, a spin-phonon theory [11–13] calculation shows that the relaxation time maxima occur at resonant tunneling, but this conflicts with experiments [6]. The inconsistency among the observation data the spin-phonon interaction theory was attributed to the contributions of dipolar interaction and other hyperfine fields [11–13]. Recently, a mixed quantum–thermal mechanism indicated that both dipolar fields and crystal field act jointly to produce the observed field-dependent relaxation rate [14–16].

The purpose of this paper is to study the role of the interaction field and the relaxation of magnetization in high-spin molecules. It shows that the behavior of field-dependent relaxation rate can be derived without introducing any interaction field. For an appropriate interaction field, the relaxation rate is not only field dependent but also time dependent. The high-spin molecule is embedded in a tetragonal crystal, and an effective anisotropy spin Hamiltonian in zero field [10–17] can be obtained from the second-order perturbation theory of spin–orbit interactions,

$$\mathcal{H}_{\text{an}} = -DS_z^2. \quad (1)$$

This is in qualitative agreement with EPR data [6,18]. To include the mutual interaction among the molecules, we introduce a mean field term, $-\beta \langle S_z \rangle S_z$. Indeed, $\langle S_z \rangle$ is time dependent, but the tunneling rate is usually much faster than the changing rate of the applied and the

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interaction field¹ (see, e.g., Ref. [19]); therefore, the spin Hamiltonian of the high-spin system can be treated as quasi-static,

$$\mathcal{H} = -DS_z^2 - g\mu_B H_z S_z - \beta \langle S_z \rangle S_z, \quad (2)$$

where $\langle S_z \rangle = \sum_n \langle n | S_z | n \rangle \rho_{|n\rangle}$, and $\rho_{|n\rangle}$ is the density of state $|n\rangle$. The tunneling between states $|S, m\rangle$ and $|S, n\rangle$ occurs if the spin Hamiltonian does not commute with S_z . In other words, a noncommutative perturbative field will induce the transition from $|S, m\rangle$ to $|S, n\rangle$ [9,11–13], and the lowest order of the noncommutative terms, $S_{\pm}$, may be from the uncertainty of the applied field, thermal agitation, demagnetization field, and dipolar coupling [14–16]. The transition rate from $|S, m\rangle$ to $|S, n\rangle$ can be calculated as

$$R_{m \rightarrow n} = \frac{d}{dt} |\langle m | U(t, t_0) | n \rangle|^2, \quad (3)$$

where

$$U(t, t_0) = 1 + \sum_{k=1}^{\infty} \left(\frac{-i}{\hbar} \right)^k \int_{t_0}^t dt_k \int_{t_0}^{t_k} dt_{k-1} \cdots \times \int_{t_0}^{t_2} dt_1 H'(t_k) H'(t_{k-1}) \cdots H'(t_1). \quad (4)$$

We apply the slow-turn-on perturbation [20] to calculate the transition rate from $|S, -10\rangle$ to $|S, 10\rangle$ [21]. The relaxation time is

$$\tau = f_0^{-1} \prod_{k=-9}^{10} [(E_{-10} - E_k + \beta(-10-k)\langle S_z \rangle)^2 + ((-10-k)\Gamma)^2], \quad (5)$$

where $f_0 \propto \prod_k |\langle -10 | H' | k \rangle|^2$, Γ is the energy broadening of the energy level and $E_k = -D(k)^2 - g\mu_B H_z k$. Eq. (5) gives a sequence of regularly spaced maxima and minima in the field-dependent relaxation rate. Moreover, the minima of relaxation time appear at the resonant tunneling, i.e., $E_m = E_n$, as observed in experiments [6]. For $\beta \neq 0$, interaction field gradually varies as the $\langle S_z \rangle$ relaxes and two unequal energy levels become resonant after as long enough waiting time under a fixed bias field (Fig. 1). Therefore, the tunneling rate under fixed bias field will be suddenly enhanced when the interaction field is strong enough to compensate the energy difference of two levels (Fig. 1). This abrupt relaxation is explained as the relaxation-assisted quantum tunneling in the mean field model. Indeed, the relaxation behavior can be described by a master equation, and Fig. 2 shows the relaxation of $\langle S_z \rangle$ of a $S = \frac{1}{2}$ system with the difference of two energy levels is less than the interaction energy,

Fig. 1. (a) Schematic diagram of relaxation-assisted resonant tunneling from the mean field model. The resonant tunneling at $E_m - E_n = \beta(m - n)\langle S_z \rangle$ and the tunneling rate is a maximum. The arrow indicates the variation of energy for the relaxation of $\langle S_z \rangle$. For a fixed bias field, even though it is initially not at a resonant, the mutual interaction field gradually varies as the magnetization changes and it becomes resonant after a long enough waiting time. (b) Schematic diagram of the dependence of magnetization as a function of time when the interaction field varies.

Fig. 2. The $\langle S_z(t) \rangle / \langle S_z(0) \rangle$ versus time under zero bias field. It shows the relaxation of a $S = \frac{1}{2}$ system with $|\langle 1/2 | H' | -1/2 \rangle|^2 = 10^{-7} \text{ K}^2$, $\beta = 1 \text{ K}$, $\Gamma = 0.01 \text{ K}$, and four graphs from top to bottom are $E_{-1/2} - E_{1/2} = 0.6, 0.4, 0.2$, and 0.0 K , respectively.

¹ The relaxation time for Mn_{12} system is around 10^{-8} s , while the tunneling time can be estimated as 10^{-15} s .

i.e., $E_m - E_n \leq \beta(m - n)\langle S_z \rangle$. In this interval of energy, the relaxation cannot be described by a single relaxation time and the resonant field is time dependent. For other values of $E_m - E_n$, the interaction field cannot compensate the energy discrepancy of two levels and thus the transition rate is always small and approximately a constant.

In summary, our studies do not only elucidate the origin of the field-dependent rate but also clarify the role of the interaction fields. We have reported on the possibility of an anomalous jump of relaxed magnetization with long waiting time in high-spin molecules. We attribute this unusual relaxation to the relaxation-assisted resonant tunneling of magnetization. It suggested that the interaction field is very important in the relaxation of high-spin molecules. The anomalous jump of relaxed magnetization is a strong indication of macroscopic tunneling induced from the mutual interaction in a large number of identical high-spin molecules.

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