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Quantum Dynamics in Nanoscale Magnets in Dissipative Environments

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In discrete energy structure of nanoscale magnets, nonadiabatic transitions at avoided level crossings lead to fundamental processes of dynamics of systems. The thermal environment causes dissipative effects on these processes. In this paper we review the features of the nonadiabatic transition and the influence of the thermal environment. In particular we discuss the temperature independent stepwise structure of magnetization at very low temperatures (deceptive nonadiabatic transition), the alternate enhancement of relaxation in the sequence of resonant tunneling points (parity effects), and processes caused by combinations of nonadiabatic transitions and disturbance of external noises.

KEYWORDS: Nanoscale magnets,nonadiabatic transitions, Landau-Zener-Stückelberg transitions,dissipative environments

§1. Introduction

Hysteresis phenomena of ferromagnets have been one of the most interesting problems in magnetization and statistical physics. Mechanism of the coercive force has been investigated by studying the processes that lead to the critical nucleation and motion of the domain wall.[1)] From the point of view of free energy of the system, the hysteresis phenomena have been discussed in terms of the relaxation process of the metastable state to the true equilibrium state in the picture shown in Fig. 1 (a). Usually the end point of hysteresis is related to the so-called spinodal point where the metastability disappears (see Fig. 1 (b)).

However there is some probability of relaxation from the metastable state B to the equilibrium state A. For example at finite temperatures the probability of thermal excitation to the top of barrier C is proportional to $\exp(-\Delta E_{\rm B}/k_{\rm B}T)$ and thus the relaxation rate $p_{\rm th}$ of the metastable state is given by

$$p_{\rm th} = \frac{1}{\tau_0} e^{\frac{-\Delta E_{\rm B}}{k_{\rm B}T}}, \tag{1.1}$$

i.e., the Arrhenius law. At low temperatures the relaxation time $\tau = 1/p_{\rm th}$ of this process diverges exponentially.

The shapes of the free energy in Fig. 1 are given by the mean field theory, which gives a good intuitive picture of the metastability. Here it should be noted that $\Delta E_{\rm B}$ should be a microscopic quantity. Otherwise for a bulk system $\Delta E_{\rm B}$ is of order the system size and then $p_{\rm th} = 0$. For a more quantitative understanding, we must look at the system microscopically. There the system is not uniform and a microscopic break through of the metastable state yields the critical nuclei. In this case we have to consider the process of creating such critical nuclei.[2)] There Figs. 1(a)-(b) represent the effective potential of the size of the nuclei. The relaxation time of metastable states has been classified according to

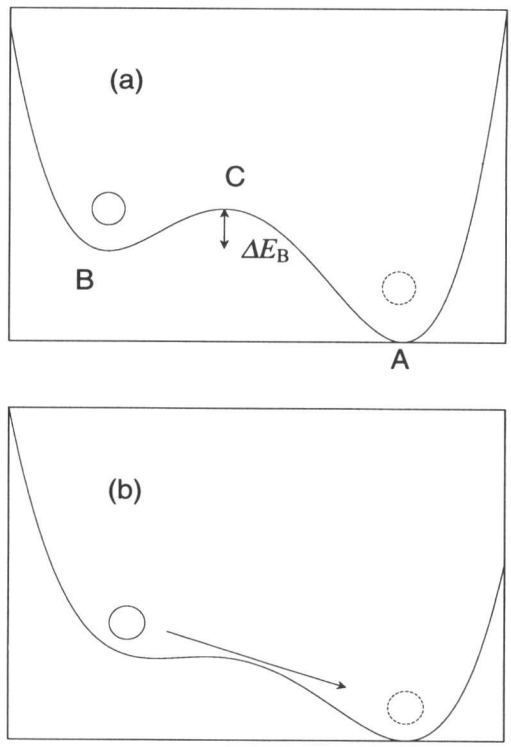

Fig. 1. Potential pictures of relaxation: (a) metastable (b) spinodal.

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the size of system and the generating rate of the critical nuclei. There are two regions, i.e., a single nucleation region (stochastic region) and a multi nucleation region (Avrami region).[3]

When the size of the magnets becomes smaller than the width of the domain wall, the nucleus can not be defined. In such cases, the magnetization of the system changes uniformly and this process of breakdown of the metastable state is called "coherent process". Relaxations in this situation also have been studied extensively.[4]

It has been pointed out that quantum fluctuation may play an important role in such small systems. In order to detect such quantum processes, several experiments have been conceived out.[5] However due to the distribution of particle sizes, it is difficult to analyze their processes.[6] Studies on single magnetic particles have been also performed but clear evidence of quantum processes has not yet been found.[7]

In this respect, nanoscale molecular magnets such as Mn_{12},[8–13] Fe_8,[14–16] and V_{15}[17] etc. are more promising. These molecules Mn_{12} and Fe_8 consist of small number of atoms forming an effective $S = 10$ spin and interactions among molecules are very small. Thus each atoms can be regarded as a $S = 10$ single spin. The Hamiltonian of such model is generally given by

$$\mathcal{H} = -DS_z^2 - HS_z + Q, \tag{1.2}$$

where $S_z = -10, -9, \cdots 10$ and Q denotes a term which causes the quantum fluctuation, such as $S_x, S_x^2 - S_y^2$, or $(S^+)^4 + (S^-)^4$. In these systems the energy levels as a function of the field have a discrete structure (Fig.2(a)) such that very explicit quantum mechanical dynamics can be expected.

At each crossing point, a small energy gap is formed due to Q (Fig.2(b)). This local structure is called avoided level crossing. When the field is swept through such an avoided level crossing point, so called nonadiabatic transition occurs. Nonadiabatic transition plays important roles in microscopic quantum dynamics such as level dynamics of semiconductor, chemical reaction and optics. The transition probability in various cases of nonadiabatic transitions has been reviewed by Nakamura.[18]

In the present case of uniaxial magnets, the nonadiabatic transition between two crossing levels as shown in Fig.2(b) will be concerned. The population coming in from the channel A is scattered to B and C with a probability p and $1-p$, respectively. Here p is a probability to stay in the same level, i.e. to behave adiabatically. This process corresponds to tunnel. On the other hand, $1-p$ is a probability to jump up to the channel C. The states of the channel A and C are the same state when there is no quantum fluctuation i.e., $Q = 0$. This unperturbed state is called diabatic state. The these channels A and C have similar states even in the presence of Q. This process corresponds to un-tunnel. The probability p was studied by Landau,[19] Zener[20] and Stückelberg[21] and is given by

$$p = 1 - \exp\left(-\frac{\pi(\Delta E)^2}{2c\hbar g\mu_{\mathrm{B}}\Delta m}\right), \tag{1.3}$$

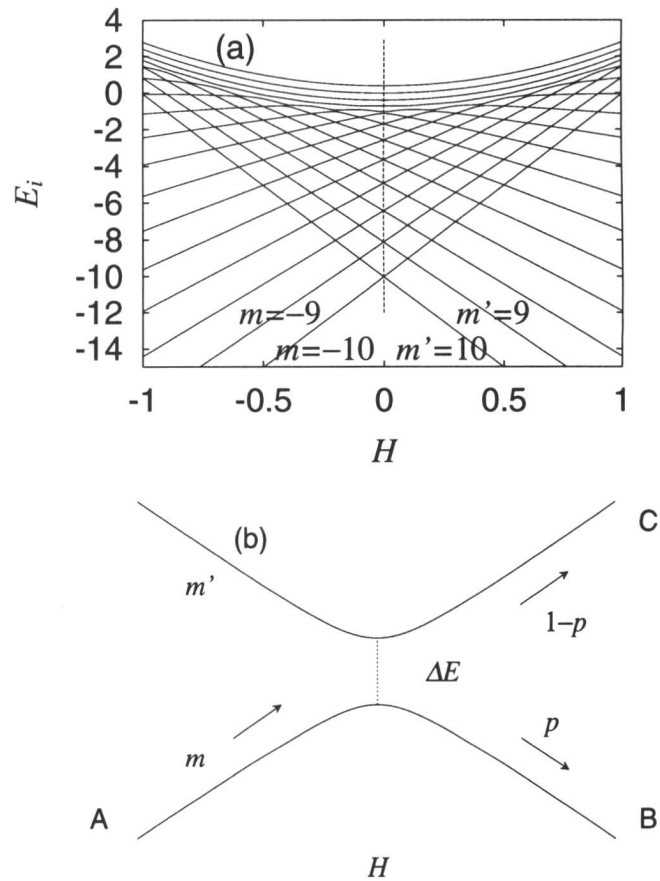

Fig. 2. Energy structure of $S = 10$ Uniaxial magnet as functions of the external field H. (a) global structure and (b) avoided level crossing.

where ΔE is a gap at the avoided level crossing and Δm is the difference of magnetization of the levels. c is the speed of the sweeping field, $c = dH/dt$. Thus $g\mu_{\mathrm{B}}\Delta mc$ is the changing rate of the Zeeman energy.[22–24] The probability p plays an important role in quantum mechanical relaxation of the present system.

This LZS type nonadiabatic transition has two characteristics. One is the localization of transition. That is, the transition occurs only in the vicinity of the crossing points. The other is the sweeping rate dependence. The first property is essential ingredient for the relaxation at discrete points of magnetic field found in molecular magnets.[24] Making use of this dependence we can estimate ΔE from change of magnetization ΔM . Let the crossing levels have magnetizations m and m' at off-resonant region. The change of magnetization is given by

$$\Delta M = pm' + (1-p)m - m = p(m' - m). \tag{1.4}$$

In the cases where ΔE is observed by other methods such as AC-susceptibility, this sweeping dependence of ΔM would give a method to confirm that ΔE is really comes from the tunneling gap.[23] However such confirmation has not yet observed in small magnetic particles such as magnetic dots and ferritin. On the other hand the two characteristics have been observed in molecular magnets at least qualitatively. It has been also pointed out that

the application of an alternate field at the resonant points will cause a nontrivial oscillation of magnetization due to phase interference.[25)]

For quantitative analysis we need to incorporate the effects of environments. Effects of noise on the LZS transition has been studied by Kayanuma.[26)] A thermal bath causes enhancement of the relaxation, e.g. the thermally assisted resonant tunneling, where resonant tunnelings of excited states play an important role. Furthermore contact with the bath causes relaxation between levels which have magnetizations of the same sign, because an energy barrier does not exist. In the potential picture of Fig. 1(a), both states belong to the same valley and the energy barrier does not exist between them. In pure quantum mechanical motion, transitions between these levels are very rare except near the avoided level crossing points.

In this paper we study the characteristics of the resonant tunneling affected by thermal disturbance. In particular, we study the effect of environment at very low temperatures such that relaxation process does not depend on the temperature. But the magnetization curve is different from the one of a pure quantum case. We call such process "deceptive nonadiabatic transition".[27)] At higher temperatures, excitation levels begin to contribute to the relaxation phenomena. At higher temperatures, alternate enhancements of relaxation at resonant points are observed, which is called 'parity effect' reflecting the structure of energy levels. we consider the mechanism of such alternate in a view point of nonadiabatic transition of excited state and find it as a general property of resonant tunneling of excited states.[28)] We also discuss the $\sqrt{t}$-dependence of initial decay at resonant points. Furthermore we study various cases of the LZS process in fluctuating random environments.

§2. Numerical Method

In order to investigate quantum dynamics in dissipative environments, we have used two kinds of numerical method. The most standard method to study quantum dynamics in dissipative environments is the quantum master equation which describes the equation of the motion of the reduced density matrix of the system $\rho(t)$.[29)] The equation is derived by tracing out the degree of the freedom of the environment from the density matrix of the total system which consists of the system $\mathcal{H}_{\rm S}$, the thermal bath $\mathcal{H}_{\rm B}$ and interaction between them $\mathcal{H}_{\rm I}$:

$$\mathcal{H} = \mathcal{H}_{\rm S} + \mathcal{H}_{\rm I} + \mathcal{H}_{\rm B}, \tag{2.1}$$

and

$$\rho(t) = {\rm Tr}_{\rm B} e^{-\beta\mathcal{H}}. \tag{2.2}$$

In the limit of weak coupling, assuming that the correlation time of the bath variable is very short (Markovian approximation), we have an equation in the following form

$$\frac{d}{dt}\rho(t) = \frac{1}{i\hbar}[\mathcal{H}, \rho(t)] + \Gamma\rho(t), \tag{2.3}$$

where Γ is a linear operator acting on $\rho(t)$. This equation has been used to study quantum dynamics of optical process, etc. In most cases $\Gamma\rho$ has the so-called Lindblad form[30)]

$$\Gamma\rho = A^\dagger A\rho + \rho A^\dagger A + A^\dagger\rho A + A\rho A^\dagger, \tag{2.4}$$

where A is an operator of the system. However in multileveled phenomena $\Gamma\rho$ has more general form.

In the cases where the bath consists of infinite number of bosons, a general expression can be derived.[31)]

$$\frac{\partial\rho(t)}{\partial t} = -{\rm i}\,[\mathcal{H}, \rho(t)] - \lambda\left([X, R\rho(t)] + [X, R\rho(t)]^\dagger\right), \tag{2.5}$$

where

$$\langle\bar{k}|R|\bar{m}\rangle = \zeta(\frac{E_{\bar{k}} - E_{\bar{m}}}{\hbar})n_\beta(E_{\bar{k}} - E_{\bar{m}})\langle\bar{k}|X|\bar{m}\rangle,$$

$$\zeta(\omega) = I(\omega) - I(-\omega), \quad \text{and} \quad n_\beta(\omega) = \frac{1}{e^{\beta\omega} - 1}.$$

Here β is an inverse temperature of the reservoir $1/T$, and we set $\hbar$ to be unity. $|\bar{k}\rangle$ and $|\bar{m}\rangle$ are the eigenstates of $\mathcal{H}$ with the eigenenergies $E_{\bar{k}}$ and $E_{\bar{m}}$, respectively. $I(\omega)$ is the spectral density of the boson bath. Here we adopt the form $I(\omega) = I_0\omega^\alpha$. When $\alpha = 1$, it corresponds to the so called Ohmic bath[32)] and when $\alpha = 2$, it corresponds to the phonon bath (super-Ohmic). As a more realistic bath for the experimental situation at very low temperature, we may take the dipole-field from the nuclear spins.[33)] X is an operator of system which is attached to bosons of the reservoir linearly representing the interaction between the system and the thermal bath. Here we take $X = \frac{1}{2}(S_x + S_z)$. The relaxation process can be affected by the form of X. Generally $X = S_x$ is more efficient than $X = S_z$ for the relaxation. A detailed comparison with other choices will be presented elsewhere. The concrete form of $\Gamma\rho$ depends on the way of coupling between the system and the thermal bath, and also on the nature of the thermal bath, e.g., the spectrum density, etc. However, here we discuss only natures which does not depend on the detail of the model.[34)]

For strong noise caused by fluctuating forces we can also simulate quantum dynamics in random fields by solving the Schrödinger equation.

§3. Quantum Dynamics in Dissipative Environment

3.1 Deceptive nonadiabatic transition

In the lowest avoided level crossing point $(-S, S)$ the change of magnetization ΔM is given by (1.4) . However at higher crossing points (m, m') with $m' < S$, the population that is scattered from m to m' is found to decay easily to the ground state, i.e., $m' \to S$, even when the dissipative effect is so small that the population at the metastable level of m hardly decays. This difference can be easily understood from the intuitive picture of Fig. 1(a). That is, the relaxation in the same valley, i.e., $m' \to S$, is easy while the relaxation over the barrier $m \to S$ is hard. In this situation, we can not apply the relaxation (1.4) directly to estimate the LZS probability p. However we can still estimate p using ΔM because

the relaxation from the level of m occurs with the LZS probability and the relaxing population decays to the ground state in a rather short time. Taking these points into account, we modify the relation (1.4) by replacing the final magnetization m' by S:

$$\Delta M = pS - (1-p)m - m = p(S-m). \tag{3.1}$$

In order to confirm these processes we performed simulations using the QME. First we confirmed that relaxation from the metastable point is unlikely to occur when the coupling between the bath and system is weak and the temperature is low. On the other hand, a fast relaxation is observed between levels with magnetizations of the same sign, which are in the same valley in Fig. 1(a). Furthermore when we sweep the field we find a step-wise magnetization curve whose step heights do not depend on the temperature but are definitely different from the pure quantum case. In Fig. 3, we show an example of magnetization process for $T = 0.1, \Gamma = 0.5$ with very small effects of environment ($\lambda = 0.00001$: a solid line) and that of pure quantum system ($\lambda = 0$: dashed line). Both of them are not temperature dependent within this temperature range. We call this stepwise structure in dissipative environments 'deceptive nonadiabatic transition'. We find that we can correctly estimate the pure quantum transition probabilities using the relation (3.1). Thus even at very low temperatures the effect the environment can not be excluded, but quantum mechanical processes and dissipative effects due to environments can be disentangled, and the information of the LZS probabilities can be extracted.

For the phenomena described above, the existence of the environment is important but the detailed nature is not important as long as it leads to fast relaxation to the ground state. If the environment causes a change of LZS probability, which would be possible when the sweeping rate is very slow,[26] further consideration is necessary, this will be discussed later.

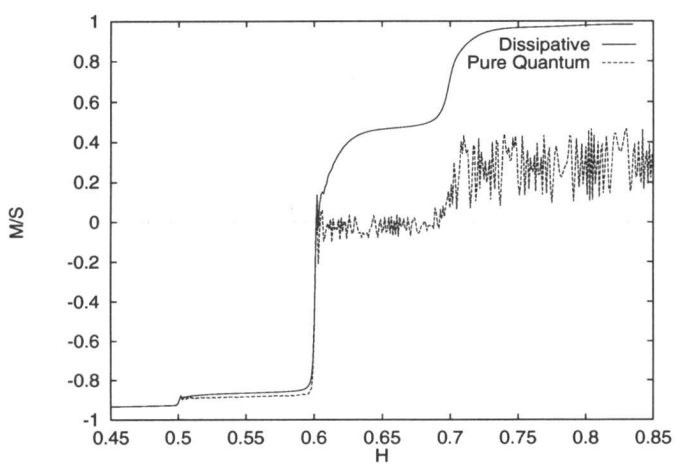

Fig. 3. Magnetization processes in pure quantum dynamics and a weak dissipative environment.

3.2 *Parity effect*

At higher temperatures, excitation levels begin to contribute to the relaxation leading to temperature dependent phenomena. These processes would depend on the detailed characteristics of the bath and the ways of the coupling between the system and the bath. Therefore general description is difficult. However here we point out a general property of relaxation under these conditions.

Experimentally it has been observed that the amount of relaxation at the resonant points change alternatively. The transition probabilities at the resonant points increase monotonically as the difference of magnetizations $|m - m'|$ of levels decreases. In fact, in perturbation the energy gap depends on the difference as[35]

$$\Delta E \propto \left(\frac{\Gamma}{D}\right)^{|m-m'|} \tag{3.2}$$

Thus we expect that the transition probabilities at resonant points with the same value of $|m - m'|$ are nearly the same. Those points are located at the same horizontal level in Fig. 2. For example the values of p given by (1.3) for the case of $\Gamma = 0.45$ with the sweeping speed $c = 0.0001$ at the points, (-8,5), (-9,4), and (-10,3) are 0.91, 0.64 and 0.99, respectively. On the other hand, those at (-8,6), (-9,5) and (-10,4) are 0.72, 0.037 and 0.01, which are very small. Thus most of the population at the levels $m = -8, -9$ and -10 decays at the former points. These decays cause enhancements of relaxation at $H = 0.3, 0.5$ and 0.7, which gives the parity effect. In Fig. 4, we show the magnetization of this case with its time derivative.

Because the energy structure shown in Fig. 2 is general for uniaxial magnets, we expect that the alternate enhancement of relaxation, i.e., the parity effect, is a general property of resonant tunneling in the thermal environment. We have also pointed out that if we change the sweeping rate the enhanced sequence is shifted. For example if we sweep much slower, the probabilities at (-8,6), (-9,5) and (-10,4) become large and populations on the lines decay there, which causes the shift of the enhanced sequence at $H = 0.2, 0.4$ and 0.6.

3.3 *Non exponential decay at the resonant point*

The magnetization which is initially polarized upward decays rather fast at a resonant point. Here the field is set at this point and is not swept. There are several paths for the magnetization to relax at this point. First let us consider relaxation by the nonadiabatic transitions at lowest resonant point. Because at the resonant point the energy gap is very narrow, the field fluctuates around the point as shown in Fig. 5(a). If we regard the motion of the field as Brownian motion, it is known that the number of the times the field crosses the resonant point is proportional to $\sqrt{t}$, i.e., the recurrence time of one-dimensional Brownian motion.[36]

At each crossing, the population moves to the other

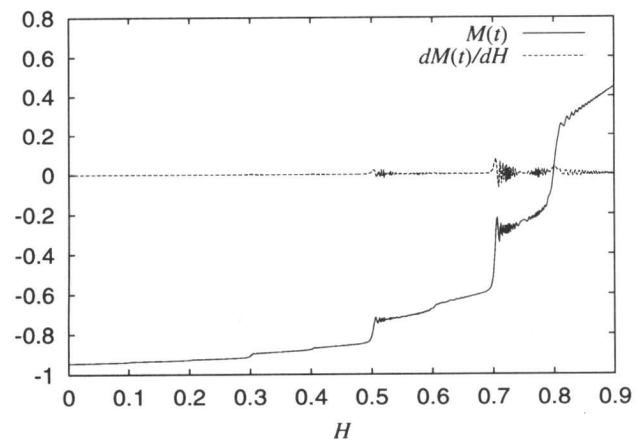

Fig. 4. Magnetization process and its time derivative.

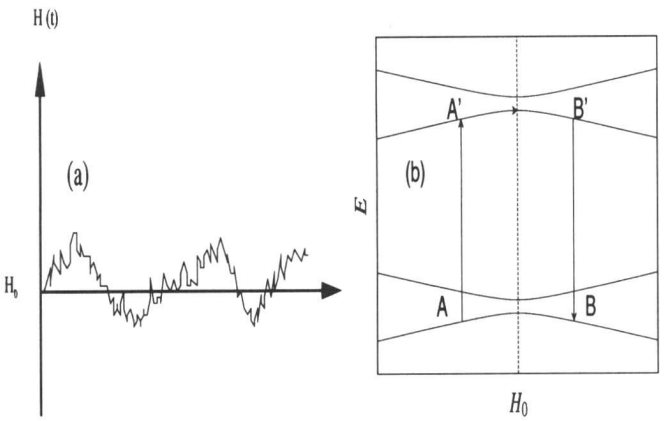

Fig. 5. (a) Random field near the resonant point and (b) Relaxation process through the excited state.

branch by the LZS transition probability

$$p_i = 1 - \exp(-\frac{\pi(\Delta E)^2}{4c_i}) \simeq \frac{\pi(\Delta E)^2}{4c_i}. \tag{3.3}$$

In a pure quantum mechanical process, quantum mechanical interference occurs among the transitions.[25] But assuming a fast decoherence, the total transition probability is expected to be given by

$$p_{\text{total}}(t) \simeq \sum_i p_i \simeq \sqrt{t}\left\langle \frac{1}{c_i} \right\rangle \frac{\pi(\Delta E)^2}{4} \equiv \alpha\sqrt{t}. \tag{3.4}$$

Thus we naturally expect that the magnetization decays as

$$\Delta M = M_0(1 - 2\alpha\sqrt{t}) \tag{3.5}$$

at the initial stage.

For a longer time scale, the field does not fluctuate freely but is confined near the resonant point. Thus p_{total} for long time is proportional to t. Therefore the magnetization decays in exponentially

$$M(t) \simeq e^{-t/\tau}, \quad \tau = \frac{p_{\text{total}}(t)}{t}. \tag{3.6}$$

This mechanism described above may give the simplest explanation of the $\sqrt{t}$ behavior. A more detail analysis has been given by the reference,[33] taking into account the explicit nature of the fluctuation of the external field.

3.4 Modification of the transition rate

When the amplitude of the external disturbance is strong we have to use another estimation of the transition probability. Kayamura and Nakayama have investigated LZS transition in fluctuating field and obtained expression of the transition probability.[26] In the case where the sweeping rate is slow and the transient time through the resonant point is much larger than the phase coherence time, then they obtained the transition probability as

$$p = p_{\text{SD}} = \frac{1}{2}(1 - \exp(-\pi(\Delta E)^2/2c)). \tag{3.7}$$

On the other hand, when the transient time is very short, transition probability does not change from that of the pure LZS transition

$$p = p_{\text{LZS}} = 1 - \exp(-\pi(\Delta E)^2/4c). \tag{3.8}$$

They confirmed such dependences by numerical simulation.

Next, let us consider a case where excited levels contribute to the relaxation. If the frequency of contacts between the system and the bath is high, a tunneling through the excited state would enhance the relaxation rate even the population at the excited state is very little.[37]

Let us consider the case where the LZS transition probability at the lowest level p_0 is very small and the one at the excited level p_1 is of the order 1. Let us consider a case where an state is excited to the exited level. In the off-resonant region this excited state decays to the original state very rapidly. The population at the excited state n_{E} is determined by the balance equation

$$n_{\text{E}} R_{\text{E}\to\text{G}} = n_G R_{\text{G}\to\text{E}}, \tag{3.9}$$

where n_{G} is the population in the ground state and $R_{\text{E}\to\text{G}}$ and $R_{\text{G}\to\text{E}}$ are transition rate from the excited state to the ground state and vise versa. Although $n_{\text{E}} = R_{\text{G}\to\text{E}}/R_{\text{E}\to\text{G}} n_G$ is very small, $R_{\text{E}\to\text{G}}$ and $R_{\text{G}\to\text{E}}$ themselves can be very large.

At the resonant point, small fluctuations of the field would cause the crossing the point. Thus the population pumped to the excited state can be transferred to the state B' and then it decays to B instead of A. (Fig.5(b)) This path (A→ A'→ B'→ B) becomes dominant path when $p_1 \gg p_0$ and fluctuation of the field is rather fast. The opposite path (B→ B'→ A'→ A) is also large, but at least in the initial stage where most of the population is at A. Thus the population moves along the former path. Thus the effective transition rate A → B is enhanced very much.

$$p_{\text{eff}} \simeq R_{\text{G}\to\text{E}} \nu p_1, \tag{3.10}$$

where ν is the frequency of the crossing. For short time ν is proportional to $\sqrt{t}$ and for long time it is proportional to t as we saw above.

To study the transition probability in such case, correct informations for $R_{G\to E}$ and ν are necessary, but it is generally difficult. However, if we could estimate these quantities from the enhancement, which would yield detailed knowledge of the bath. In nanoscale molecular magnets, it would be possible to study such detailed property, which is a very interesting research area in the future.

§4. Summary and Discussion

In nanoscale molecular magnets display several phenomena which originate from explicit quantum mechanical transitions between discrete levels. In this paper we studied effects of dissipative environment which smears the pure quantum processes. So far the relaxation processes have been a kind of black-box and has been treated only phenomenologically. But it would be possible to begin to study explicit processes of relation in nanoscale magnets because of the simple form.

So far we studied the $S = 10$ spin representing the low energy structure of magnetic energy levels. Let us consider structure of the full energy level. The molecular magnets have complicated structures. For example Mn_{12} includes 12 Mn molecules with many other atoms which have nuclear spins. Thus the dimension of total hamiltonian is $4^8 \cdot 5^4 \times I$ where I comes from the degree of freedom of nuclear spins. This degree of nuclear spins causes random effects on each Mn atom. It would be an interesting problem to study how this random field on individual atoms causes changes of the energy levels at low temperatures.

Even without the effects of nuclear spins, there are dipole-dipole couplings among the molecules which cause random noise on the whole molecule. Thus it should be taken into account even in the view point of $S = 10$ spin. Effects of this field are studying as 'Feedback-effect' on the LZS process of magnetization.[38] It would be interesting to study natures of noises explicitly in nanoscale molecular magnets.

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