We discuss the effect of the thermal environment on the low-temperature response of the magnetization of uniaxial magnets to a time-dependent applied magnetic field. At very low temperatures the steps-wise magnetization curves observed in molecular magnets such as Mn$_{12}$ and Fe$_8$ display little temperature dependence where the apparent thermal assisted process are suppressed. However the changes of the magnetization at each step cannot be analyzed directly in the viewpoint of a quantum mechanical nonadiabatic transition. In order to explain this deceptive apparent nonadiabatic behavior, we study the quantum dynamics of the system weakly coupled to a thermal environment and propose a relation between the observed magnetization steps and the quantum mechanical transition probability due to the nonadiabatic transition.

Magnetization processes of nanoscale molecules such as Mn$_{12}$ and Fe$_8$ have attracted much interest. For such small systems the discreteness of energy level plays an important role and staircase structures of the response of the magnetization to a sweeping magnetic field have been observed. The staircase is explained as a quantum mechanical transition at the avoided level crossing points, where levels of the Hamiltonian become almost degenerate, and form repulsive structures as shown in Fig.1, which has been called resonant tunneling. This quantum mechanical transition has been studied from the point of view of the nonadiabatic transition. There are two characteristic features of each nonadiabatic transition. One is the localization of the transition because it occurs only around avoided level crossing points. The other is the dependence of the transition probability on sweeping rate of the magnetic field, the energy gap and the gradients of the levels. Since at each avoided level crossing point only two levels play an important role, the transition probability can be described by well-known the Landau-Zener-Stückelberg (LZS) mechanism.

However the behavior of these magnetic systems can easily be affected by thermal fluctuations even at low temperatures, because the energy scales involved are rather small. At relatively high temperatures ($T \sim 1K$) the temperature dependence of the magnetization process is very significant, where excitations to higher levels provide other channels of resonance tunneling which is called thermally assisted resonant tunneling. The external noise may affect the LZS mechanism itself which has been also studied.

On the other hand, at very low temperatures ($T \sim 60$ mK), the magnetization curve shows very little change with temperatures and only quantum mechanical phenomena seem to be dominant. However, as we will show below, even at such low temperatures thermal fluctuations cause inevitable effects which prevent a direct application of mechanism of the nonadiabatic transition.

In this letter we investigate the effect of the thermal environment at very low temperatures on nonadiabatic transitions and find a relation between the observed data and the true quantum mechanical transition probability, from which the energy gap at the avoided level crossing point via the LZS formula can be deduced.

Let us consider the change of magnetization when the external field is swept from a negative value to a positive value. Initially the system is assumed to be in the ground state with the magnetization $m_0$. When the external field is swept from a negative value to a positive value, the state of the system is always in the ground state. The true quantum mechanical transition probability, $p_i$, can be deduced from the observation.

$$p_i = \frac{1}{2} \left( 1 + \sum_{j} p_j \right)$$

with $p_j$ the probability that the system remains in the same eigenstate.

We assign numbers $i (i = 1, 2, \cdots)$ for the avoided level crossing point where the state of $m_0$ crosses a state with $m_i \sim S-i+1$ ($= S, S-1, \cdots$, respectively). Let $p_i$ denote
the probability staying the same level at the ith avoided level crossing point. For pure quantum dynamical case, we have the following relation between the change of the observed magnetization at the crossing point \( i \), \( \Delta M_i \equiv M_i - M_{i-1} \) and the transition probabilities \( \{ p_i \} \):

\[
\Delta M_i = \prod_{n=1}^{i-1} (1 - p_n) \left\{ [m_0(1 - p_i) + m_i p_i] - m_0 \right\},
\]

where \( M_i \) is the observed magnetization between avoided level crossing point \( i \) and \( i+1 \). By this relation (1), all the transition probabilities \( \{ p_i \} \) are obtained from the magnetizations in pure quantum cases.

In the experiment of Perenboom et al. for Mn\(_{12}\) \( (S = 10) \) \( (T = 59\text{mK}) \) [8], shape of the magnetization process seems to saturate with the lowering of the temperature. When we analyze the data using the relation (1), we cannot find any consistent set of the transition probabilities \( \{ p_i \} \). In the experiment, the steps-wise changes of the magnetization at the points are 0, 3, 2, 1 and 0 (\( i = 7, 8, 9, \) and 10, respectively). The changes of the magnetization at the points are 0.62, 3.54, 8.00 and 6.77, respectively. The relation (1) yields \( p_7 = 0.0480, p_8 = 0.315, p_9 = 1.13, \) and \( p_{10} = -7.976, \) in contradiction to the trivial condition \( 0 \leq p_i \leq 1 \). Therefore a naive application of nonadiabatic transition theory fails to explain the saturated magnetization curve in the very low temperature.

We attribute this failure to the effect of thermal environment even at such a low temperature. In terms of the potential picture (Fig.2), the states with \( M > 0 \) belong to the right valley and we expect that these states easily relax to the bottom of the valley, i.e. to the state with \( M = S \). Thus, once a quantum mechanical transition from the metastable state of \( M = -S \) to a state of \( M > 0 \) takes place, the state is expected to relax easily to the lowest level due to some dissipation mechanism in the absence of an energy barrier. In the case of pure quantum transition, such a relaxation to the state of \( M = S \) is prohibited because the levels of the states are separated far away. If the time scale of dissipation is much shorter than that of the system and scale on which the magnetic field changes, the transfer to the lowest state takes a short time. As a result the magnetization curve will show a staircase as in the case of pure quantum dynamics, but the change of magnetization at each step is different because of the relaxation transition \( M \to S \) instead of \( S \to i + 1 \). We call this steps-wise magnetization process in a dissipative environment “a deceptive apparent nonadiabatic magnetization process”.

![Fig.2 Potential picture of the metastability.](Image)

In this scenario, we assume the following three properties: (i) First quantum mechanical transition for \( m_0(\approx -S) \to m_i \) occurs with the probability of the pure nonadiabatic (LZS) transition \( \{ p_i^{\text{LZS}} \} \), and then (ii) the relaxation from \( m_i \to m_1(\approx S) \) occurs by some dissipation mechanism. (iii) There is no relaxation directly from \( m_0 \) by the dissipation mechanism and thus the amount of magnetization change depends only on \( \{ p_i^{\text{LZS}} \} \) and does not depend on the temperature. Replacing \( m_i \) by \( m_1 \) in the relation (1), the change of the magnetization in this case is given by

\[
\Delta M_i = \prod_{n=1}^{i-1} (1 - \tilde{p}_n) \left\{ [m_0(1 - \tilde{p}_i) + m_1 \tilde{p}_i] - m_0 \right\}.
\]

Using the data of [8] now yields a reasonable solution for the \( \{ \tilde{p}_i \} \)'s: \( \tilde{p}_7 = 0.0313, \tilde{p}_8 = 0.185, \tilde{p}_9 = 0.515, \) and \( \tilde{p}_{10} = 0.898. \)

In order to demonstrate that the above three properties are really possible at very low temperatures, we simulate a relaxation phenomena of a magnetic system which very weakly couples to the external bath. Here we use a quantum master equation [3].

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

where

\[
\langle k|R|m \rangle = \zeta \left( \frac{E_k - E_m}{\hbar} \right) n_\beta(E_k - E_m) \langle k|X|m \rangle,
\]

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

Here \( \beta \) is an inverse temperature of the reservoir \( 1/T \), and we set \( \hbar = 1. \) \( |k \rangle \) and \( |m \rangle \) are the eigenstates of \( \mathcal{H} \) with the eigenenergies \( E_k \) and \( E_m \), respectively. \( I(\omega) \) is the spectral density of the boson bath. We take here the infinite number of phonons with the Ohmic dissipation \( I(\omega) = I_0 \omega^2 \) [24]. As a more realistic bath for the experimental situation at very low temperature, we may take the dipole-field from the nuclear spins [23] or other types of spectrum such as super-Ohmic type. \( X \) is an operator of the magnetic system that interacts linearly with the bosons of the reservoir. The relaxation process can
be affected by the form of interaction of the system with the thermal bath, i.e. by the choice of $X$. Here we take $X = \frac{1}{2}(S_x + S_z)$. 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 alternate choices of concrete form of thermal bath, however, do not cause any significant qualitative change because the couplings to the bath are very weak.

For Mn$_{12}$, detailed form of the Hamiltonian has been proposed $^{24}$. However the energy gap of the Mn$_{12}$ is too small to observe the phenomena within the available computation time. Thus, here, we demonstrate the qualitative features of the dynamics, i.e. the three properties (i), (ii), and (iii). We believe that the key ingredients of the general qualitative feature are the existence of the avoided level crossing points and weak coupling to the external bath. For the realistic model with much small energy gap, the features observed here should be realized in a much longer time scale. Thus we adopt a minimal model of a uniaxial $S = 10$ spin system with the two ingredients:

$$\mathcal{H} = -DS_z^2 + \Gamma S_x - H_{\text{ext}}(t)S_z, \quad (4)$$

with a linearly increasing external field, $H_{\text{ext}} = ct - H_0$, where $c$ is the sweeping velocity. The transverse field $\Gamma$ represents the terms causing quantum fluctuations. We choose $D = 0.1$, $\Gamma = 0.5$ throughout this letter.

In order to see the difference of relaxations between the case with and without the potential barrier, we compare typical two cases: (1) $H_{\text{ext}} = 0.05$ and (2) $H_{\text{ext}} = 0.15$ and set the sweep velocity $c = 0$. As the initial state we take the second level, as indicated in Fig.3.

The second level has $M \simeq -10$ in the case (1) and $M \simeq 0$ in the case 2. In the both cases, the ground state has $M \simeq 10$. The parameters are set to $T = 0.1$, $I_0 = 1.0$, and $\lambda = 1.0 \times 10^{-4}$. We study the relaxation for both cases by solving Eq.(3). These probabilities are given by a diagonal element of $\rho(t)$, i.e., $\langle 1|\rho(t)|1 \rangle$ and $\langle 2|\rho(t)|2 \rangle$, respectively. We observe almost no damping in the case (1), whereas a rather fast relaxation occurs in the case (2). Thus at a fairly low temperature, the thermal environment causes significant difference in the relaxation process depending on the presence of a potential barrier. The difference between the cases (1) and (2) can be understood analyzing the matrix elements of Eq.(3).

We now investigate time evolution of the system for a sweeping field $c = 1.0 \times 10^{-5}$ starting at $H_0 = -0.05$. We study the case of pure quantum dynamics ($\lambda = 0$)[$P$] and the case with a weak dissipation ($\lambda = 1.0 \times 10^{-4}$) [$D$]. These magnetization curves are shown in Fig.4. We show data for $H_{\text{ext}} \geq 0.45$ because almost no change is observed for $H_{\text{ext}} < 0.5$.

![Fig.3 Energy level diagram of the model (1) as a function of $H_{\text{ext}}$. The white and black diamonds correspond to the case (1) and the case (2), respectively.](image)

![Fig.4 Magnetization as a function of $H_{\text{ext}}$. The dashed line denotes the pure quantum dynamics [$P$], and the solid line denotes the dissipative quantum dynamics [$D$].](image)

For the case [$P$], we observe oscillating behavior due to spin precession, whereas in the case [$D$] this detailed structure is smoothed out by the dissipation. We find steps-wise magnetization curves in both cases. The changes of the magnetization are listed in Table I.

| Cross point $(m_0, m_1)$ | $\Delta M_P$ | $\Delta M_D$ |
|-------------------------|-------------|-------------|
| (-10, 5)                | 0.511       | 0.693       |
| (-10, 4)                | 8.32        | 13.3        |
| (-10, 3)                | 3.50        | 5.03        |

Table I The changes of magnetization. $\Delta M_P$ and $\Delta M_D$ are the changes for the case [$P$] and [$D$], respectively.

| $i$ | $(m_0, m_1)$ | $p_{P;i}$ | $p_{P;i}$ | $p_{D;i}$ | $p_{D;i}$ | $p_{D;i}$ |
|-----|-------------|-----------|-----------|-----------|-----------|-----------|
| 6   | (-10, 5)    | 0.0280    | 0.0341    | 0.0460    | 0.0346    | 0.0291    |
| 7   | (-10, 4)    | 0.730     | 0.616     | 0.995     | 0.688     | 0.716     |
| 8   | (-10, 3)    | 1.000     | 0.726     | 0.780     | 0.835     | 0.970     |

Table II The transition probabilities obtained by various ways, see the text.

From these data we estimate the transition probabilities by the relation (1) and (3) which are listed in Table II. First we obtain the transition probabilities from the data in Table I setting $m_0 = -S$ and $m_1 = S-i+1$. From
the data $\Delta M_{[D]}$, unacceptable probabilities $\{p_{[D],i}\}$ are deduced by the relation (1), while acceptable ones $\{\tilde{p}_{[D],i}\}$ are obtained by the relation (2). $\{\tilde{p}_{[D],i}\}$ agree with $\{p_{[P],i}\}$ obtained by the relation (3) from the data $\Delta M_{[P]}$. This agreement shows the three properties (i), (ii), and (iii) really realized in the present model and thus we can estimate the quantum mechanical nonadiabatic transition by the relation (4). Although the magnetization $m_i$ is almost constant: $m_0 = -S, m_i = S - i + 1 (i \geq 1)$, they show a little dependence on the magnetic field $H_{ext}$. Taking the $H_{ext}$ dependence of $m_i$ into consideration, we also calculated the transition probabilities in the case [D] with (4). They are shown as $\{\tilde{p}_{[D],i}\}$. We confirmed that $\{\tilde{p}_{[D],i}\}$ agree with the probabilities $\{p_{[R],i}\}$ directly obtained from the diagonal elements of the density matrix. The difference between $\tilde{p}_{[D],i}$ and $\tilde{p}_{[P],i}$ simply come from the large value of $\Gamma$ for the convenience of simulation. If $\Gamma$ is very small as the case of the experiment, $m_i$ is very close to $S - i + 1$ and it is expected that $\tilde{p}_{[D],i}$ and $\tilde{p}_{[P],i}$ are very close. We present the time evolution of $\langle i | \rho | i \rangle$ in Fig.5. This figure explicitly shows the three properties (i), (ii), and (iii).

![Fig.5 The time evolution of the probability of individual levels.](image)

We estimate the energy gap from the transition probabilities with the extended LZS formula $p_i^{LZS}$:

$$p_i^{LZS} = 1 - \exp\left(-\frac{\pi (\Delta E_i)^2}{2(m_i - m_0)c}\right),$$  \hspace{1cm} (5)

where $c$ is the changing rate of the Zeeman energy. Using $\{p_{[D],i}\}$, we obtain the energy gaps for the avoided level crossings as $\Delta E_0 = 1.83 \times 10^{-3}$, $\Delta E_7 = 10.1 \times 10^{-3}$. These estimates agree with the correct value $\Delta E_0 = 1.54 \times 10^{-3}$ and $\Delta E_7 = 10.0 \times 10^{-3}$ directly obtained from the energy levels (2). If we use $\tilde{p}_{[D],i}$, we have, of course, almost complete values, $\Delta E_0 = 1.57 \times 10^{-3}$, $\Delta E_7 = 9.9 \times 10^{-3}$. Thus we conclude that we can estimate the energy gap from the deceptive apparent magnetization by the relation (3).

In summary, we have considered a mechanism for deceptive apparent nonadiabatic magnetization process which is relevant when the temperature is very low and no temperature dependence is observed apparently and propose the general relation (3) between the steps in the magnetization and the energy-level splittings at very low temperature. With the relation we have estimated the quantum transition rate $\{p_i\}$ in the low temperatures (3). We demonstrated an example of deceptive apparent nonadiabatic magnetization process in a minimal model with the avoided level crossing points and weak coupling to the external bath. Elsewhere we will report on our investigation of the energy gaps $\{\Delta E_i\}$ of Mn$_{12}$ and Fe$_8$ based on the detailed information of the values of jumps and the scanning speed $c$.

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