Quantum thermoactivation of nanoscale magnets

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The integral relaxation time describing the thermoactivated escape of a uniaxial quantum spin system interacting with a boson bath is calculated analytically in the whole temperature range. For temperatures T much less than the barrier height ΔU, the level quantization near the top of the barrier and the strong frequency dependence of the one-boson transition probability can lead to the regularly spaced deep minima of the thermoactivation rate as a function of the magnetic field applied along the z axis. [S1063-651X(97)13203-2]

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The problem of the escape rate of a uniaxial magnetic particle has remained in the focus of attention since the work of Néel [1], who stressed the role of thermal agitation. During the last years the interest in this problem has increased in view of possible applications to the information storage and in connection with the magnetic quantum tunneling (MQT; see e.g., Ref. [2]).

For classically large particles, the thermoactivation escape rate was first calculated by Brown [3], who derived the Fokker-Planck equation for an assembly of particles and solved it perturbatively in the high-temperature case, $\Delta U \ll T$, and with the use of the Kramers transition-state method [4] for $T \ll \Delta U$. In these both limiting cases the time dependence of the average magnetization is a single exponential, and the relaxation rate of ferromagnetic particles is given by the lowest eigenvalue Λ_1 of the Fokker-Planck equation. For $T \sim \Delta U$ the latter is no longer the case, and the best measure of the relaxation rate is the integral relaxation time $\tau_{\rm int}$ determined as the area under the magnetization relaxation curve after a sudden infinitesimal change of the longitudinal magnetic field [5–8]. The quantity $\tau_{\rm int}$ can be calculated analytically in the whole range of temperatures, and $\tau_{\rm int}^{-1}$ coincides with Λ_1 in the asymptotic regions.

With the miniaturization of the magnetic particle both the thermoactivation and the MQT escape rates increase; the latter becomes dominant below the crossover temperature T_0 determined by the interactions noncommuting with the operator S_z, and hence causing the MQT. For information storage applications the most important are systems with small tunneling interactions and correspondingly low T_0. In this case the tunneling level splittings can be calculated perturbatively [9] for the arbitrary spin values S, which can be advantageous in comparison to the semiclassical instanton method (see, e.g., Ref. [2]) for nanoscale systems with *moderately* high spin values as the recently synthesized Mn clusters having $S=10$ and 12 in the ground state [10,11]. For such systems with not too large S and low T_0, the thermoactivation escape rate can be dominant down to the temperatures where it changes due to the spin level quantization.

The purpose of this paper is to calculate the thermoactivation escape rate of a quantum spin system in terms of the integral relaxation time starting from a spin-bath Hamiltonian of the type

$$\mathcal{H} = -HS_z - DS_z^2 + \mathcal{H}_b - \sum_{\mathbf{q}} V_{\mathbf{q}} (\boldsymbol{\eta}\cdot\mathbf{S})(a_{\mathbf{q}}^\dagger + a_{-\mathbf{q}}) - \sum_{\mathbf{pq}} V_{\mathbf{pq}} (\boldsymbol{\eta}\cdot\mathbf{S}) a_{\mathbf{p}}^\dagger a_{\mathbf{q}}, \quad (1)$$

where the arbitrary vector $\boldsymbol{\eta}$ is for simplicity set to be $\eta_x = \eta_y = \eta_z = 1$. If the bath excitations described by the operators $a^\dagger$ and a are phonons, then the coupling to the bath that is linear in spin variables is prohibited by the time-reversal symmetry. This means that modulations of the crystal field by phonons do not produce a *fieldlike* perturbation on a spin system, and hence $\boldsymbol{\eta} = \mathbf{0}$. Thus, in this case it would be better to write quadratic terms of the type $S_\alpha S_\beta$ instead of $(\boldsymbol{\eta}\cdot\mathbf{S})$ in Eq. (1) (see, e.g., Ref. [12]). Nevertheless, we will use Eq. (1) with $\mathcal{H}_b$ and the couplings V characteristic for phonons, since it is the most suitable for the first presentation of the method and describes the main qualitative features of the relaxation of a spin system. Moreover, Hamiltonian (1) means the direct quantum generalization of the Langevin-*field* formalism used by Brown [3] (which is subject to the same criticism), and thus provides a link to the known results for classical ferromagnetic particles.

If the spin-bath coupling is weak, the equation of motion for the density matrix of the spin system can be obtained in the second order of perturbation theory, and the diagonal part of it is the well-known system of the kinetic balance equations for the occupation numbers N_m of the spin states $|m\rangle$

$$\dot{N}_m = l_m^2 (W_{m,m+1} N_{m+1} - W_{m+1,m} N_m) + l_{m-1}^2 (W_{m,m-1} N_{m-1} - W_{m-1,m} N_m). \quad (2)$$

Here $l_m = \sqrt{S(S+1) - m(m+1)}$ are the matrix elements of the operators $S_\pm$, and the ''spin-free'' transition probabilities W are given by

$$W_{m+1,m} = W(\omega_{m+1,m}) = W^{(1)} + W^{(2)}, \quad (3)$$

where

$$\omega_{m+1,m} \equiv \varepsilon_{m+1} - \varepsilon_m = -H - D(2m+1) \quad (4)$$

are the transition frequencies, $\varepsilon_m = -Hm - Dm^2$ are the spin energy levels,

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$$W^{(1)}(\omega)=\sum_{\mathbf{q}}|V_{\mathbf{q}}|^2\{(n_q+1)\pi\delta(\omega_q+\omega)+n_q\pi\delta(\omega_q-\omega) \tag{5}$$

is the contribution of the one-phonon emission and absorption processes, and

$$W^{(2)}(\omega)=\sum_{\mathbf{pq}}|V_{\mathbf{pq}}|^2 n_p(n_q+1)\pi\delta(\omega_p-\omega_q-\omega) \tag{6}$$

is that of the two-phonon (Raman scattering) ones. One can check that the transition probabilities satisfy the detailed balance condition: $W(\omega)=W(-\omega)\exp(-\omega/T)$, which ensures the static distribution of the form

$$N_m^{(0)}=\frac{1}{Z}\exp(-\varepsilon_m/T),\quad Z=\sum_{m=-S}^{S}\exp(-\varepsilon_m/T). \tag{7}$$

The quantities $W(\omega)$, with $\omega>0$ describing transitions to upper energy levels, become exponentially small at low temperatures. For spin-phonon couplings of the type

$$V_{\mathbf{q}}\sim\theta_1\left(\frac{\omega_q}{\Omega}\right)^{1/2},\quad V_{\mathbf{pq}}\sim\theta_2\frac{(\omega_p\omega_q)^{1/2}}{\Omega}, \tag{8}$$

where $\Omega=Mc^2$, M is the unit cell mass, $\omega_q=cq$, and c is the phonon velocity, the estimation of $W(\omega)$ with $\omega<0$ with the help of Eq. (5) and (6) yields (cf. Ref. [13])

$$W^{(1)}\sim\frac{\theta_1^2|\omega|^3}{\Theta^4}(n_{|\omega|}+1)\cong\begin{cases}\theta_1^2\omega^2T/\Theta^4, & |\omega|\ll T\\ \theta_1^2|\omega|^3/\Theta^4, & T\ll|\omega|\end{cases} \tag{9}$$

and

$$W^{(2)}\sim\begin{cases}\theta_2^2\theta_D^5T^2/\Theta^8, & |\omega|\ll\theta_D\ll T\\ \theta_2^2T^7/\Theta^8, & |\omega|\ll T\ll\theta_D\\ \theta_2^2T^4|\omega|^3/\Theta^8, & T\ll|\omega|\ll\theta_D.\end{cases} \tag{10}$$

Here $\theta_D\sim\hbar\omega_{q_{\max}}$ is the Debye temperature, $\Theta^4\equiv\Omega\theta_D^3\sim\hbar^3\rho^2c^5$, and ρ is the density of the lattice.

It is convenient to introduce the reduced variables

$$\xi\equiv\frac{SH}{T},\quad\alpha\equiv\frac{S^2D}{T},\quad h\equiv\frac{\xi}{2\alpha}=\frac{H}{2SD}, \tag{11}$$

which are equivalent to those used for the description of classical single-domain magnetic particles [3,5] and should be kept constant if $S\to\infty$. In this limit the transition frequencies $\omega_{m+1,m}$ of Eq. (4) tend to zero and, accordingly, the frequency-independent two-phonon transition probabilities $W^{(2)}$ given by Eq. (10) govern the relaxation. Since the occupation numbers of the neighboring levels in Eq. (2) become close to each other, Eq. (2) goes over to the classical Fokker-Planck equation [3,5–7]. An extreme quantum case is realized for a three-level system with a barrier ($S=1$), for which the relaxation between the two lowest levels through the highest one (the so-called ''resonance fluorescence'') has at low temperatures an exponentially small rate $\Gamma\sim\exp(-\Delta/T)$ [13].

The relaxation of any initial state described by the system of the first-order differential Eqs. (2) is described in general, and particularly at intermediate temperatures, by $2S$ exponentials of the type $A_i\exp(-\Lambda_i t)$, where Λ_i are the corresponding eigenvalues. In such situations the best measure of the relaxation rate is the integral relaxation time $\tau_{\rm int}$ determined as the area under the magnetization relaxation curve after a sudden infinitesimal change of the applied field H:

$$\tau_{\rm int}\equiv\int_0^\infty dt\frac{m_z(\infty)-m_z(t)}{m_z(\infty)-m_z(0)}. \tag{12}$$

Here $m_z\equiv\langle S_z\rangle/S$ is given at equilibrium by $m_z=B(\xi,\alpha)=\partial\ \ln Z/\partial\xi$. One can calculate $\tau_{\rm int}$ analytically at arbitrary temperatures from Eqs. (2) producing the low-frequency expansion of the linear longitudinal dynamic susceptibility [5]

$$\chi_z(\omega)\cong\chi_z(1+i\omega\tau_{\rm int}+\cdots). \tag{13}$$

Here $\chi_z\equiv\partial m_z/\partial(SH)=B'/T$ is the static susceptibility, and $B'\equiv\partial B(\xi,\alpha)/\partial\xi$. Taking into account that the alternating field $\Delta H_z(t)=\Delta H_{z0}\exp(-i\omega t)$ modulates the transition frequencies (4), using the detailed balance condition and introducing $N_m\cong N_m^{(0)}(1+Q_m)$ with $Q_m=q_m(\omega)S\Delta H_z(t)/T$ one comes in the linear approximation in $\Delta H_z(t)$ to the system of equations

$$l_m^2W_{m+1,m}(q_{m+1}-q_m)+l_{m-1}^2W_{m-1,m}(q_{m-1}-q_m)+i\omega q_m=(l_m^2W_{m+1,m}-l_{m-1}^2W_{m-1,m})/S. \tag{14}$$

The susceptibility $\chi_z(\omega)$ can now be written as

$$\chi_z(\omega)=\frac{1}{TS}\sum_{m=-S}^{S}mN_m^{(0)}q_m(\omega). \tag{15}$$

The second-order finite-difference equation (14) should be solved perturbatively in ω; this can be done analytically since the first line of Eq. (14) contains only the differences of q_m, and the order of Eq. (14) can thus be lowered to 1. In the static limit, Eq. (14) reduces to $q_{m+1}^{(0)}-q_m^{(0)}=1/S$ with the solution $q_m^{(0)}=m/S-B$. In first order in ω one can introduce $p_m\equiv l_m^2W_{m+1,m}\exp(-\varepsilon_m/T)[q_{m+1}^{(1)}-q_m^{(1)}]$, satisfying $p_m-p_{m-1}=-i\omega q_m^{(0)}\exp(-\varepsilon_m/T)$. Finding p_m and then $q_m^{(1)}$, and using Eqs. (15) and (13), one obtains the final result

$$\tau_{\rm int}=\frac{1}{B'}\sum_{m=-S}^{S-1}\frac{\Phi_m^2}{N_m^{(0)}l_m^2W_{m+1,m}}, \tag{16}$$

where $N_m^{(0)}$ is given by Eq. (7) and

$$\Phi_m=\sum_{k=-S}^{m}\left(B-\frac{k}{S}\right)N_k^{(0)}. \tag{17}$$

The formulas above are valid at all temperatures, and they are a direct quantum generalization of the classical results of Ref. [5], which are recovered in the limit $S\to\infty$. At high temperatures where $\alpha,\xi\ll1$ and $W^{(1)}\ll W^{(2)}$, the calculation in Eqs. (17) and (16) yields

$$\tau_{\rm int}^{-1}\cong\Lambda_N\left[1-\frac{2\alpha}{5}\left(1-\frac{1}{2S}\right)\left(1+\frac{3}{2S}\right)\right], \qquad (18)$$

with $\Lambda_N\equiv 2W^{(2)}$ (cf. Ref. [3]). At $\alpha,\xi\sim 1$ (i.e., $T\sim\Delta U$) the sums in Eqs. (17) and (16) should be performed numerically. The recent numerical calculations of Ref. [6] for the classical model have shown that in the unbiased case, $\xi=H=0$, the difference between $\tau_{\rm int}^{-1}$ and the lowest eigenvalue of the Fokker-Planck equation Λ_1 does not exceed 1.2% in the whole range of temperatures. Λ_1 remained in the focus of interest since the work of Brown [3], but for $T\sim\Delta U$ it has no direct physical meaning and cannot be represented by a closed analytical formula. One can expect that the quantities $\tau_{\rm int}^{-1}$ and Λ_1 are even closer to each other in the unbiased *quantum* case, since the difference between them disappears for $S=1/2$.

At low temperatures $\alpha\gg 1$, the thermoactivation escape rate of the particle becomes exponentially small. Here, as was recently discovered in Ref. [7], $\tau_{\rm int}^{-1}\gg\Lambda_1$ for sufficiently strong bias ($h\gtrsim 0.2$). This effect was physically explained [8] as resulting from the depletion of the upper potential well and the competition in the integral relaxation time $\tau_{\rm int}$ of the overbarrier thermoactivation with the rate Λ_1 and the fast relaxation inside the lower well. These two relaxation mechanisms can be analytically separated for $S\gg 1$ since the summand of Eq. (16) consists for $\alpha,\xi\gg 1$ of two peaks centered at the barrier top and in the lower well ($m\sim S$). The barrier contribution $\tau_{{\rm int},B}$ can be related to Λ_1 taking into account the depletion effect [8]; in the small bias case, $h\ll 1$, which will be considered henceforth, one obtains

$$\Lambda_1^{-1}\cong\tau_{{\rm int},B}B'(\xi,\alpha)\cosh^2\xi. \qquad (19)$$

For $\xi=0$ one has $B'\cong 1$ and $\Lambda_1\cong\tau_{\rm int}^{-1}$. Since $N_k^{(0)}$ in Eq. (17) is strongly peaked at low temperatures in the wells ($k\sim\pm S$), and is small elsewhere, the function Φ_m is independent on m and given by $\Phi_m\cong 1/(2\cosh^2\xi)$ in the main part of the phase space, including the barrier region. Then Eqs. (19) and (16) can be combined to

$$\Lambda_1\cong\frac{4S(S+1)\cosh^2\xi}{Z(\xi,\alpha)}\left[\sum_{m=-\infty}^{\infty}\frac{\exp(\varepsilon_m/T)}{W_{m+1,m}}\right]^{-1}, \qquad (20)$$

where the exponential factor $\sim 1/N_k^{(0)}$ in Eq. (20) cuts the sum actually at $m\sim S\alpha^{-1/2}\ll S$ [see Eqs. (4) and (11)]. The partition function Z in Eq. (20) for $h\ll 1$ is given by

$$Z\cong\begin{cases}(S/\alpha)e^{\alpha}\cosh\xi, & SD\ll T\ll S^2D\\ 2e^{\alpha}\cosh\xi, & T\ll SD,\end{cases} \qquad (21)$$

where SD is the level spacing in the wells.

The sum in Eq. (20) depends on the relation between temperature T and the level spacing near the top of the barrier $\sim D$, as well as on the role played by the one- and two-phonon probabilities $W^{(1)}$ and $W^{(2)}$. For not too low temperatures this sum can be approximated by the integral over $x\equiv m/S$, and the quantity $W^{(1)}$ of Eq. (9) can be in this case represented in the form

$$W_{m+1,m}^{(1)}\cong\overline{W^{(1)}}\frac{\omega_{m+1,m}^2}{D^2}, \quad \overline{W^{(1)}}\sim\frac{\theta_1^2D^2T}{\Theta^4}, \qquad (22)$$

whereas $W^{(2)}\propto T^7$ is given for $T\ll\theta_D$ by the second line of Eq. (10). One can see that the integral over x in Eq. (20) can be cut either by the exponential function at $\Delta x\sim\alpha^{-1/2}$ or by the denominator $W(\omega_{m+1,m})$ at $\Delta x\sim S^{-1}\sqrt{W^{(2)}/W^{(1)}}$. Crossover between these two regimes occurs at the temperature

$$T_{12}\sim\Theta\left(\frac{D}{\Theta}\right)^{1/5}\left(\frac{\theta_1}{\theta_2}\right)^{2/5} \quad (T_{12}\ll\theta_D). \qquad (23)$$

Taking Eq. (21) into account, one obtains

$$\Lambda_1\cong A\{\exp[-\alpha(1+h)^2]+\exp[-\alpha(1-h)^2]\}, \qquad (24)$$

where $h\ll 1$, and the prefactor A is given by

$$A\cong\begin{cases}2W^{(2)}\pi^{-1/2}\alpha^{3/2}, & SD,T_{12}\ll T\\ 2S\sqrt{W^{(1)}W^{(2)}}\pi^{-1}\alpha, & SD\ll T\ll T_{12}\\ SW^{(2)}\pi^{-1/2}\alpha^{1/2}, & T_{12}\ll T\ll SD\\ S^2\sqrt{W^{(1)}W^{(2)}}\pi^{-1}, & T\ll T_{12},SD.\end{cases} \qquad (25)$$

The first of these expressions coincides with that of Brown [3] in the high-barrier limit, if one introduces $\Lambda_N\equiv 2W^{(2)}$. The temperature dependences of A read $T^{11/2}$, T^3, $T^{13/2}$, and T^4, respectively.

The continuous approximation above is only valid if $\Delta x\sim S^{-1}\sqrt{W^{(2)}/W^{(1)}}\gg S^{-1}$, or $\Delta m\gg 1$. This condition sets one more characteristic temperature

$$T_q\sim\Theta\left(\frac{D}{\Theta}\right)^{1/3}\left(\frac{\theta_1}{\theta_2}\right)^{1/3} \quad (T_q\ll\theta_D), \qquad (26)$$

below which the level quantization becomes essential. In the temperature interval $D\ll T\lesssim T_q$ the sum in Eq. (20) converges at $\Delta m\sim 1$, whereas the exponential factors can still be neglected. In this case Λ_1 shows a sinusoidal dependence on the longitudinal magnetic field in the *weak-field* region $H\sim D$, the amplitude of which is exponentially small for $W^{(2)}\gtrsim W^{(1)}$ but becomes great for $W^{(2)}\ll W^{(1)}$. In the range $D\ll T\lesssim T_q, SD$ one obtains formula (24), with the prefactor given by

$$A\cong S^2\left\{\frac{4}{\pi^2}\sin^2\left[\pi\left(\frac{H}{2D}+S+\frac{1}{2}\right)\right]\overline{W^{(1)}}+W^{(2)}\right\}. \qquad (27)$$

This result shows deep minima of the thermoactivation escape rate Λ_1 for $H/(2D)=\pm 1/2,\pm 3/2,\ldots$ for S integer and for $H/(2D)=0,\pm 1,\pm 2\ldots$ for S half-integer. At such fields two levels near the barrier top become degenerate, and the leading contribution to the transition probability between them, $W^{(1)}$, disappears.

In the extreme quantum temperature region $T\ll D$, the sum in Eq. (20) is again determined by the exponential factor. Here, however, only one or maximally two terms of the sum contribute to Eq. (20). If there is an energy level with $m=m_{\max}$ just at the top of the barrier, like for S integer and $H=0$ ($m_{\max}=0$), then equal contributions to Eq. (20) come from the terms with $m=m_{\max}$ and $m=m_{\max}-1$, which de-

scribe transitions between three upper levels with $m=m_{\max},m_{\max}\pm1$. If there are two degenerate levels to the right and left from the barrier top, like for S half-integer and $H=0$, then the leading contribution is due to the term in Eq. (20) describing transitions between these two levels. The general result is given by formula (24) with

$$A\cong S(S+1)\exp(-\Delta\varepsilon_{m_{\max}}/T)\times\left[\frac{1}{W_{m_{\max}+1,m_{\max}}}+\frac{1}{W_{m_{\max}-1,m_{\max}}}\right]^{-1}, \qquad (28)$$

where $m_{\max}=-H/(2D)+F$, $F\equiv\mathcal{F}[H/(2D)+S+1/2]-1/2$, $\Delta\varepsilon_{m_{\max}}=DF^2$ is the mismatch between $\varepsilon_{m_{\max}}$ and the barrier top, and $\mathcal{F}(X)$ is the fractional part of X. The transition probabilities W in Eq. (28) are dominated by $W^{(1)}\propto|\omega|^3$ [see Eq. (9)] with $\omega_{m_{\max}\pm1,m_{\max}}=-D(1\pm2F)$, and the escape rate Λ_1 shows qualitatively the same magnetic field dependence us that given by Eq. (27). Note that in this low-temperature limit the prefactor A is temperature independent, excluding the narrow field regions where it is determined by $W^{(2)}$ and is very small.

Summarizing, the thermoactivation escape rate of a quantum ferromagnetic particle was calculated microscopically in the whole temperature range, allowing for the frequency dependence of the transition probabilities and for the quantization of the energy levels. Even in the low-temperature range, where the escape rate is exponentially small, the situation is determined by several characteristic energies and there are rather many limiting cases for the prefactor A in Eq. (24), which can be difficult to observe if the corresponding temperature intervals are not wide enough. Not trying to give numerical estimations, since the Hamiltonian (1) is only a schematic one suitable mainly for the presentation of the method and for a qualitative analysis, we make only some general remarks about the results obtained. First, the greatest variety of different temperature intervals can be realized for particles containing a macroscopically large number N of magnetic ions and having an effective spin $S_{\rm eff}\sim N\gg1$. However, only the classical case [the first line of Eq. (25)] can be practically observed, whereas in other cases Λ_1 is unmeasurably small due to the too large values of α.

Better candidates for searching for the nonclassical thermoactivation rates predicted here are nanoscale systems such as Mn_{12} clusters with $S=10$ having a strong uniaxial anisotropy ($\Delta U=S^2D=61$ K) [10]. These clusters show a superparamagnetic behavior, and for 2 K$\leqslant T\leqslant$8 K the prefactor A in Eq. (24) is temperature independent. The latter corresponds to the extreme quantum case Eq. (28), which could, however, be expected only for $T\lesssim D\sim0.6$ K. In the main range of temperatures $T\lesssim S^2D=61$ K, one cannot expect one of the pure limiting forms of A, and should resort to using Eq. (20) because $S=10$ is not large enough. Nevertheless, one qualitative feature always remains: If the relaxation is governed by the two-phonon processes, one can expect a strong temperature dependence of A, and, if the one-phonon processes are dominant, then the temperature dependence of A is weak or absent, but there should be a strong dependence on the magnetic field of the type (27).

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