First- and Second-Order Transitions between Quantum and Classical Regimes for the Escape Rate of a Spin System

E. M. Chudnovsky* and D. A. Garanin†

Department of Physics and Astronomy, City University of New York-Lehman College, Bedford Park Boulevard West, Bronx, New York 10468-1589

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We have found a novel feature of the bistable large-spin model described by the Hamiltonian $\mathcal{H} = -DS_z^2 - H_x S_x$. The crossover from thermal to quantum regime for the escape rate can be either first ($H_x < SD/2$) or second ($SD/2 < H_x < 2SD$) order, that is, sharp or smooth, depending on the strength of the transverse field. This prediction can be tested experimentally in molecular magnets like $Mn_{12}Ac$. [S0031-9007(97)04645-0]

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Transitions between two states in a bistable system can occur either due to the classical thermal activation or via quantum tunneling. A rigorous study of that problem was begun by Kramers [1] and WKB [2–4], and a review of the progress that followed can be found in Ref. [5]. At high temperature the transition rate follows the Arrhenius law, $\Gamma \sim \exp(-\Delta U/T)$, with ΔU being the height of the energy barrier between the two states. In the limit of $T \to 0$, the transitions are purely quantum, $\Gamma \sim \exp(-B)$, with B independent on temperature. Because of the exponential dependence of the thermal rate on T, the temperature T_0 of the crossover from quantum to thermal regime can be estimated as $T_0^{(0)} = \Delta U/B$. For a quasiclassical particle in a potential $U(x)$, Goldanskii [6] noticed the possibility of a more accurate definition, $T_0^{(2)} = \hbar/\tau_0$, where τ_0 is the period of small oscillations near the bottom of the inverted potential, $-U(x)$. Below $T_0^{(2)}$, thermally assisted tunneling occurs from the excited levels, that reduces to the tunneling from the ground-state level at $T = 0$. Above $T_0^{(2)}$ quantum effects are small and the transitions occur due to the thermal activation to the top of the barrier. Affleck [7] demonstrated that the two regimes smoothly join at $T = T_0^{(2)}$. Larkin and Ovchinnikov [8] called this situation the second-order phase transition from classical to quantum behavior. This means that for Γ written as $\Gamma \sim \exp(-\Delta U/T_{\rm eff})$, the dependence of both $T_{\rm eff}$ and its first derivative on T are continuous at $T = T_0^{(2)}$. This situation is not generic, however. The transition between the two regimes can also be of the first order [8,9], i.e., more abrupt, with $dT_{\rm eff}/dT$ discontinuous at a certain temperature $T_0^{(1)} > T_0^{(2)}$. Chudnovsky derived the criterion allowing one to establish whether first- or second-order transition takes place, based on the shape of the potential $U(x)$. Commonly studied potentials $U = -x^2 + x^4$ and $U = -x^2 + x^3$ yield the second-order transition. Physically relevant potentials which would exhibit the first-order transitions were not known. In this Letter we show that spin systems readily accessible in the experiment possess both first- and second-order transitions between the classical and quantum behavior of the escape rate. The order of the transition in these systems can be controlled by external magnetic field.

Consider a spin system described by the Hamiltonian

$$\mathcal{H} = -DS_z^2 - H_x S_x\,, \tag{1}$$

where $S \gg 1$. This model is generic for problems of spin tunneling studied by different methods [10–15]. It is believed to be a good approximation for the molecular magnet $Mn_{12}Ac$ of spin $S = 10$, intensively studied in the last few years (see, e.g., Ref. [16]). In the quasiclassical approximation the transition rate is given by

$$\Gamma \sim \int dE\, W(E) e^{-(E-E_{\rm min})/T}, \tag{2}$$

where $W(E)$ is the probability of tunneling at an energy E and $E_{\rm min}$ corresponds to the bottom of the potential. This probability is defined via the imaginary-time action

$$W(E) \sim e^{-S(E)}. \tag{3}$$

With the accuracy to the exponent,

$$\Gamma \sim e^{-F_{\rm min}/T}, \tag{4}$$

where $F_{\rm min}$ is the minimum of the effective "free energy"

$$F \equiv E + TS(E) - E_{\rm min} \tag{5}$$

with respect to E.

In order to obtain $S(E)$ for the Hamiltonian (1) we will use the method of mapping the spin problem onto a particle problem [12,14,17,18]. The equivalent particle Hamiltonian is

$$\mathcal{H} = -\frac{\nabla^2}{2m} + U(x)\,, \tag{6}$$

where

$$U(x) = \left(S + \frac{1}{2}\right)^2 D(h_x^2 \sinh^2 x - 2h_x \cosh x)\,, \tag{7}$$

and

$$m \equiv \frac{1}{2D}, \qquad h_x \equiv \frac{H_x}{(2S+1)D}\,. \tag{8}$$

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In the future we shall neglect $1/2$ in comparison to $S \gg 1$.

The imaginary-time action is then given by the WKB expression

$$S(E) = 2(2m)^{1/2} \int_{-x(E)}^{x(E)} dx \sqrt{U(x) - E}, \qquad (9)$$

where $\pm x(E)$ are the turning points for the particle oscillating inside the inverted potential $-U(x)$. The period of these oscillations, $\tau_p(E) = -dS(E)/dE$, depends on energy. Minimization of (5) gives

$$\tau_p(E) = \frac{1}{T}, \qquad (10)$$

the condition familiar from the quantum statistics [7,8,19]. It determines the instanton trajectory that dominates the transition rate at a temperature T.

The dependence of $\tau_p(E)$ on E determines the kind of crossover from quantum tunneling to thermal activation [9]. If τ_p monotonically increases with the amplitude of oscillations, i.e., with decreasing energy E, the transition is of second order. This kind of crossover has been intensively studied, including the case of tunneling with dissipation [20–24]. If, however, the dependence of $\tau_p(E)$ is nonmonotonic, the first-order crossover takes place. Let us demonstrate that both kinds of the crossover exist for our spin model, depending on the strength of the transverse field. Expanding (7) near $x = 0$, one obtains

$$U(x) \cong U(0) + S^2 D\Big[-h_x(1 - h_x)x^2 + \frac{h_x}{3}\Big(h_x - \frac{1}{4}\Big)x^4 + O(x^6)\Big]. \qquad (11)$$

The second-order term in (11) is negative for $h_x < 1$, which corresponds to the existence of the energy barrier

$$U_{\max} - U_{\min} = S^2 D(1 - h_x)^2. \qquad (12)$$

For $h_x > 1/4$ the fourth-order term in (11) is positive; i.e., $U(x)$ is of the form $-x^2 + x^4$. The inverted potential $-U(x)$ is hence of the type $x^2 - x^4$, which results in the increase of τ_p with the oscillation amplitude (i.e., with lowering the energy E) and to the second-order transition [9]. At $h_x < 1/4$ the anharmonicity of $-U(x)$ has the opposite sign, $-U(x) \sim x^2 + x^4$, which leads to the decrease of τ_p when lowering E for energies below the top of the barrier. However, with further lowering of E the period τ_p begins to increase and diverges logarithmically for E approaching the bottom of the potential. This nonmonotonic behavior of $\tau_p(E)$ leads to the first-order transition from the thermally activated escape to the quantum escape [9].

In the case of the second-order transition the crossover occurs at temperature

$$T_0^{(2)} = \frac{\tilde{\omega}_0}{2\pi} = \frac{SD}{\pi}\sqrt{h_x(1 - h_x)}, \qquad (13)$$

where $\tilde{\omega}_0 = \sqrt{|U''(0)|/m}$ is the instanton frequency [6,7]. It is convenient to introduce dimensionless temperature and energy variables

$$\theta \equiv \frac{T}{T_0^{(2)}}, \qquad P \equiv \frac{U_{\max} - E}{U_{\max} - U_{\min}}. \qquad (14)$$

The effective free energy (5) near the top of the barrier ($P \ll 1$) can be calculated with the use of Eqs. (9) and (11) and reads

$$\frac{F(P)}{U_{\max} - U_{\min}} \cong 1 + (\theta - 1)P + \frac{\theta}{8}\Big(1 - \frac{1}{4h_x}\Big)P^2 + \frac{3\theta}{64}\Big(1 - \frac{1}{3h_x} + \frac{1}{16h_x^2}\Big)P^3 + O(P^4). \qquad (15)$$

The analogy with the Landau theory of phase transitions, described by $F = a\psi^2 + b\psi^4 + c\psi^6$, now becomes apparent. The factor in front of P (the Landau coefficient a) changes the sign at the phase transition temperature $T = T_0^{(2)}$. The factor in front of P^2 (the Landau coefficient b) changes the sign at the field value $h_x = 1/4$ determining the phase boundary between the first- and the second-order transitions, as has been already noticed from Eq. (11). The factor in front of P^3 (the Landau coefficient c) remains always positive. The numerically computed dependence of F on P for the entire range of energy is plotted in Fig. 1.

At $h_x = 0.3$ [Fig. 1(a)] the minimum of F remains $U_{\max} - U_{\min}$ for all $T > T_0^{(2)}$. Below $T_0^{(2)}$ it continuously shifts from the top to the bottom of the potential as temperature is lowered. This corresponds to the second-order transition from thermal activation to thermally assisted tunneling. At $h_x = 0.1$ [Fig. 2(b)], however, there can be one or two minima of F, depending on temperature. The crossover between classical and quantum regimes occurs when the two minima have the same free energy, which for $h_x = 0.1$ takes place at $T_0^{(1)} = 1.078 T_0^{(2)}$.

The crossover temperature for the escape rate is frequently estimated by equating the ground-state tunneling exponent to that of thermal activation:

$$S(E_{\text{bottom}}) \equiv B = \frac{U_{\max} - U_{\min}}{T_0^{(0)}}. \qquad (16)$$

The ground-state tunneling exponent B given by Eq. (9) can be analytically calculated [10], which together with Eq. (12) yields

$$T_0^{(0)} = \frac{SD}{4}\frac{(1 - h_x)^2}{\ln\Big(\dfrac{1 + \sqrt{1 - h_x^2}}{h_x}\Big) - \sqrt{1 - h_x^2}} \cong \frac{SD}{4}\begin{cases} \dfrac{1}{\ln[2/(eh_x)]}, & h_x \ll 1, \\ \dfrac{3}{8^{1/2}}(1 - h_x)^{1/2}, & 1 - h_x \ll 1. \end{cases} \qquad (17)$$

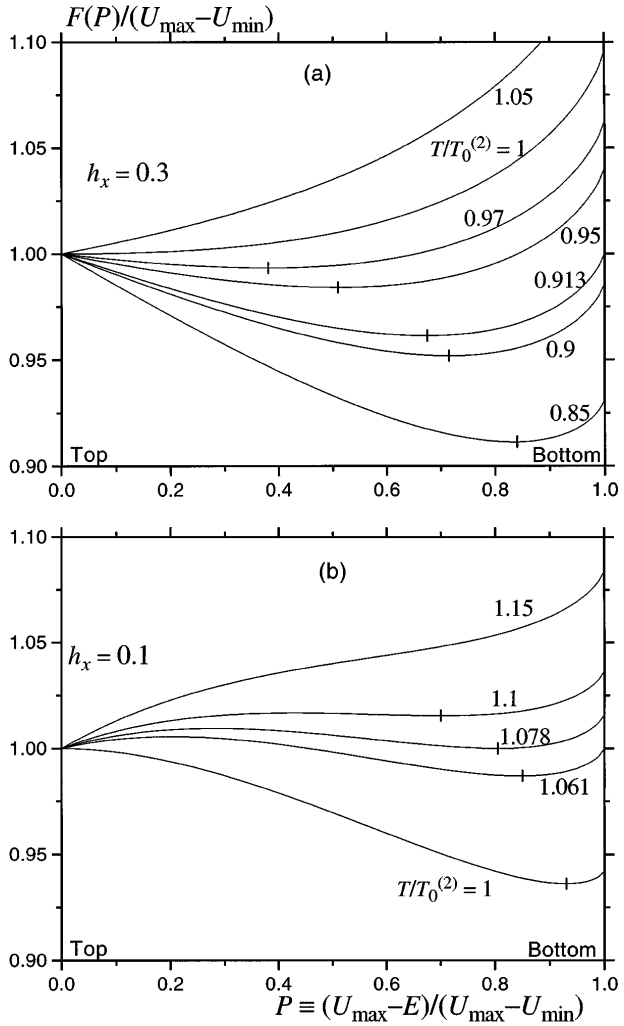

FIG. 1. Effective free energy for the escape rate: (a) $h_x \equiv H_x/2SD = 0.3$, second-order transition; (b) $h_x = 0.1$, first-order transition.

One can see from Fig. 1(b) that $T_0^{(0)}$ somewhat underestimates the crossover temperature. For $h_x = 0.1$ one has $T_0^{(0)} = 1.061 T_0^{(2)} < T_0^{(1)}$. The estimation $T_0^{(0)}$ becomes, however, accurate in the limit of small h_x. The dependence of the crossover temperature T_0 on the transverse field in the whole range, $0 < h_x < 1$, is presented in Fig. 2. The temperature dependence of the escape rate can be conveniently written in the form $\Gamma \sim \exp[-(U_{\max} - U_{\min})/T_{\text{eff}}(T)]$, where the dependence of the effective temperature on T is presented in Fig. 3 for different h_x. It can be seen from Fig. 3 that the most significant difference between the crossover temperature $T_0^{(0)}$ of Eq. (16) and the actual crossover temperature T_0 arises in the limit of a small barrier, that is, at $h_x \to 1$. The former is described by the intersection of the dotted Arrhenius line with the horizontal line corresponding to $T_{\text{eff}}(T)/T_0$ at zero temperature. From Eqs. (13) and (17) for $h_x \to 1$ one obtains $T_0^{(0)}/T_0^{(2)} = 3\pi/(8\sqrt{2}) \approx 0.833$.

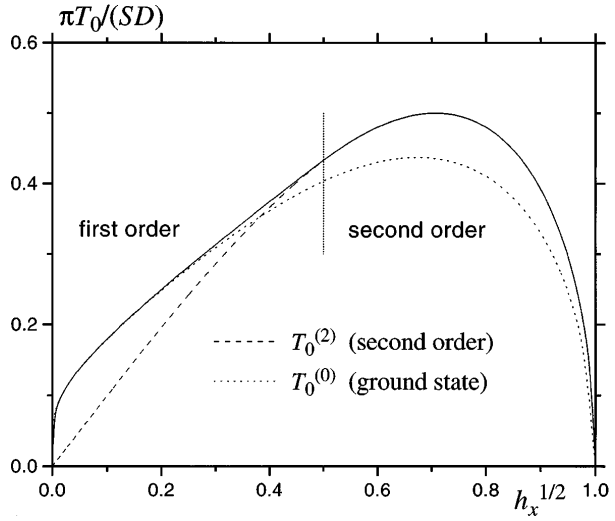

FIG. 2. Dependence of the crossover temperature T_0 on the transverse field.

As follows from Fig. 3, the difference between the curves $T_{\text{eff}}(T)$ describing the first- and second-order crossover is quite dramatic. It must be easily observed in experiment if the appropriate system is found. Very recently experiments on individual small magnetic particles with $S \sim 10^5$–10^6 have become possible [25]. In these experiments the barrier is lowered by tuning the magnetic field to the critical value. In our model this is the case of the second-order transition. In order to get the first-order transition, H_x must be lower than $H_A/4$, where $H_A \equiv 2SD/g\mu_B$ is the anisotropy field. This case requires a moderate spin S in order to provide a significant escape rate. The Hamiltonian (1) has been found to be a good model for $Mn_{12}Ac$ [16], $S = 10$. In this case the quantization of spin levels becomes important.

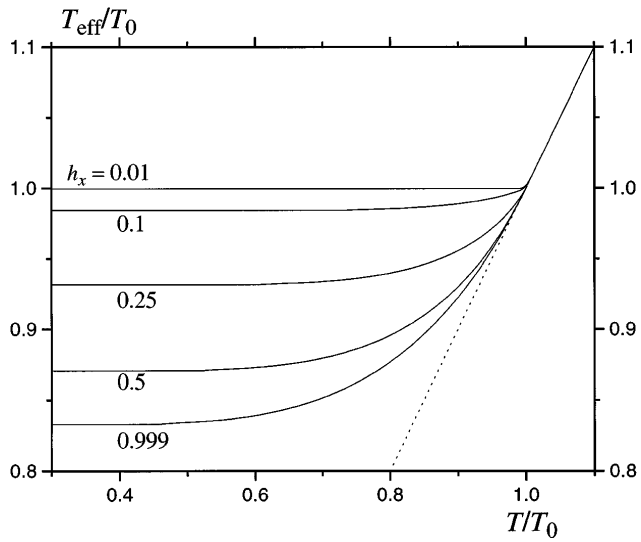

FIG. 3. Dependences of the effective temperature T_{eff} on T for the different values of the transverse field.

However, our statement regarding the possibility of first- and second-order transitions remains valid [26].

The analogy with phase transitions in the temperature dependence of the escape rate formally exists only in the limit of $S \to \infty$. For a finite S, the transition from (2) to (4) has the accuracy of $1/S$. Quantum corrections to the escape rate above T_0 [5] are of the same order. Thermal and quantum corrections will smoothen the first-order transition in the narrow temperature region close to T_0. Nevertheless, even for $S = 10$, the difference between the crossover at small and large H_x must be easily observable. The sharpness of the crossover between thermal and quantum regimes also depends on the strength of the dissipation. In the case of the low dissipation which is common for the magnetic systems, its effect on the crossover is small [5].

For $Mn_{12}Ac$ the anisotropy field is about 10 T. The crossover from thermal to quantum regime should, therefore, switch from first to second order at $H_x \simeq 2.5$ T. The crossover temperature is about 1 K [26]. These ranges of field and temperature are easily accessible in experiment. Note that similar effects may exist in the Fe_8 molecular magnet where the crossover from thermal to quantum regime has been already observed [27]. This system, however, is described by the spin Hamiltonian with the transverse anisotropy which requires separate theoretical investigation. We believe that the statement made in this paper, regarding the possibility of first- and second-order crossover from thermal to quantum regime, must be very general for spin systems.

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*Electronic address: chudnov@lcvax.lehman.cuny.edu
†Permanent address: I. Institut für Theoretische Physik, Universität Hamburg, Jungiusstrasse 9, D-20355 Hamburg, Germany.
Electronic address: garanin@physnet.uni-hamburg.de

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