Quantum-classical crossover of the escape rate in nanomagnets with truly axial symmetry

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The quantum-classical crossover of the escape rate is studied in magnetic nanoparticles with truly axial symmetry and a large spin within the framework of the quasiclassical approach. The nonlinear perturbation method is employed to obtain the crossover diagram for first- and second-order crossovers. It is found that the regime for the first-order crossover is greatly enhanced or suppressed depending on the sign of the higher-order axial term, while it is greatly suppressed by the external magnetic field. These features can be tested experimentally in magnetic nanosystems.

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I. INTRODUCTION

Investigations of the macroscopic quantum tunneling in nanospin systems have been a topical issue of intensive theoretical and experimental studies over the past few years.[1] One good subject is a quantum-classical crossover in magnetic nanoparticles with the magnetization **M** whose direction is subject to the magnetocrystalline anisotropy. At sufficiently high temperature the direction of **M** is changed by thermal activation and its rate Γ obeys the Arrhenius law $\Gamma \sim \exp(-U/k_BT)$ with U being the height of the energy barrier, whereas at temperature close to absolute zero, pure quantum tunneling is relevant and $\Gamma \sim \exp(-S/\hbar)$, with S the action at zero temperature. Thus the crossover temperature T_c is expected to exist between the thermal activation and quantum tunneling. Whether the two regimes smoothly join or not around T_c has been a great deal of interest.

The abrupt [first-order crossover(FC)] or gradual [second-order crossover(SC)] crossover for the escape rate around T_c was raised by Chudnovsky,[2] who studied the oscillation period $\tau(E)$ of the instanton where E is the energy of the instanton. Later, Chudnovsky and Garanin[3] proposed the crossover issue in the longitudinal anisotropy system with an external transverse magnetic field. Since then, theoretical studies of the crossover in nanospin systems have been performed by many groups.[4–12] However, most of the theoretical investigations have been studied for the spin Hamiltonian without the higher-order term in anisotropy energy. In fact, such a term is of utmost importance of the quantum resonant tunneling,[13] quantum phase interference[14] and quantum-classical crossover in single-molecule magnets (SMMs).[15] Recently, Kang and Kim[16] studied the crossover for the moderate spin system ($S \sim 10$) with such a higher-order term by using a direct numerical approach, and found that such a term plays an important role in the crossover of the escape rate in SMMs. Thus the theoretical investigation of the crossover in SMMs is well understood. A lot of magnetic nanomaterials, however, have such higher-order term with a large spin value ($S \gg 10$), which might result in deviations from the previous results. Indeed, since it is not possible to perform the numerical calculation for $S \to \infty$, one has to look for alternative approach. Actually, many theoretical studies have been performed on nanospin systems with a large spin, by using a mapping of the spin problem onto a particle one and periodic instantons.[3–10] However, such methods cannot be applied to the systems higher than the second-order in the anisotropy energy, because there are no one-dimensional functional forms of the actions in such cases. Thus we make use of a theoretical method for dealing with the crossover in general nanospin systems by employing nonlinear perturbation near the top of the barrier based on the spin-coherent-state path integral method.[17] We show that the crossover boundary is greatly influenced by the higher-order term in the anisotropy energy and the regime for the first-order crossover becomes more pronounced in the limit of a large spin compared with the moderate spin such as SMMs.

The rest of the article is organized as follows. In Sec. II, we reformulate the quasiclassical theory of the spin-coherent-state path integral in terms of nonlinear perturbation method. In Sec. III, we consider the uniaxial systems with the higher-order axial term in the presence of transverse and longitudinal fields, and present the dependence of the crossover boundary on the ratio of two anisotropy constants. Also, a comparison of quasiclassical results will be made with previous numerical results. The conclusions are given in Sec. IV.

II. BASIC FORMALISM

The spin-coherent-state path integral approach to the quantum tunneling of magnetization makes use of the following expression for the partition function given by

$$Z(\beta\hbar) = \oint D[\mathbf{M}(\tau)]\exp(-S_E/\hbar), \tag{1}$$

where $\beta = 1/k_BT$, the path sum is over all periodic paths of the magnetization $\mathbf{M}(\tau) = \mathbf{M}(\tau+\beta\hbar)$, and S_E the action which includes the Euclidean version of the magnetic Lagrangian L_E as

$$S_E(\theta,\phi) = V\int d\tau\left[i\frac{M}{\gamma}(1-\cos\theta)\frac{d\phi}{d\tau} + E(\theta,\phi)\right], \tag{2}$$

where V is a volume of the particle, M the magnitude of magnetization, $\gamma = g\mu_B/\hbar$ the gyromagnetic ratio, μ_B the Bohr magneton, and θ, ϕ spherical coordinates of the magnetization. Also, $E(\theta,\phi)$ is the total energy which is composed of the anisotropy energy and the energy given by an external magnetic field. The classical trajectory of θ and ϕ is determined by

$$in\dot{\phi}\sin\theta = -E_\theta, \quad in\dot{\theta}\sin\theta = E_\phi, \tag{3}$$

where $n=M/\gamma$, $\dot{\phi}=d\phi/d\tau$, $\dot{\theta}=d\theta/d\tau$, $E_\theta=\partial E/\partial\theta$, and $E_\phi=\partial E/\partial\phi$. Employing the perturbation method for the criterion of FC or SC, the classical trajectory of θ (ϕ) is decomposed into the position of the barrier $\bar{\theta}$ ($\bar{\phi}$) and a fluctuation term $\delta\theta$ ($\delta\phi$), i.e., $\theta=\bar{\theta}+\delta\theta$ ($\phi=\bar{\phi}+\delta\phi$) for the behavior of the weakly time-dependent solutions. The solutions of the equation of motion are parametrized by the amplitude a of the oscillations, which quantifies the difference between the thermal and the time-dependent solutions near the top of the barrier. Our goal is to solve Eq. (3) for $\delta\theta(\tau)$ and $\delta\phi(\tau)$ and find the correction to the oscillation period away from the thermal saddle point. Denoting $\delta\mathbf{\Omega}(\tau)\equiv[\delta\theta(\tau),\delta\phi(\tau)]$, we have $\delta\mathbf{\Omega}(\tau+\beta\hbar)=\delta\mathbf{\Omega}(\tau)$ at finite temperature and write it as Fourier series $\delta\mathbf{\Omega}(\tau)=\Sigma_{j=-\infty}^{\infty}\delta\mathbf{\Omega}_j\exp(i\tilde{\omega}_j\tau)$ where $\tilde{\omega}_j=2\pi j/\beta\hbar$ and $\beta=1/k_BT$. Proceeding the perturbation of $\delta\mathbf{\Omega}$, we will obtain the correction $\delta\omega(\equiv\omega-\omega_0)$ at higher order where ω_0 is a small oscillation frequency in the lowest order near the top of the barrier. According to the Chudnovsky's criterion,[2] we have $\delta\omega>0$ for FC and $\delta\omega<0$ for SC. Thus we will discuss whether the corrected frequency ω is greater than the frequency ω_0 or not.

Before we get into a discussion of the specific form of the anisotropy, we consider an arbitrary anisotropy energy with a constant easy plane, e.g., $\phi=0$ which can be useful for a situation like higher-order or general symmetries. Writing $\bar{\theta}=\theta_0$, Eq. (3) is expressed in terms of $\delta\theta$ and $\delta\phi$, which results in

$$in(\delta\dot{\phi}) + A_1(\delta\theta) + A_2(\delta\theta)^2 + A_3(\delta\phi)^2 + A_4(\delta\theta)^3 + A_5(\delta\theta)(\delta\phi)^2 = 0, \tag{4}$$

$$in(\delta\dot{\theta}) + B_1(\delta\phi) + B_2(\delta\theta)(\delta\phi) + B_3(\delta\phi)^3 + B_4(\delta\theta)^2(\delta\phi) = 0, \tag{5}$$

where $\delta\dot{\phi}=d(\delta\phi)/d\tau$, $\delta\dot{\theta}=d(\delta\theta)/d\tau$, and

$$A_1 = E_{\theta\theta}\csc\theta_0, \quad A_2 = \frac{1}{2}E_{\theta\theta\theta}\csc\theta_0 - E_{\theta\theta}\cot\theta_0\csc\theta_0, \tag{6}$$

$$A_3 = \frac{1}{2}E_{\phi\phi\theta}\csc\theta_0,$$

$$A_4 = \frac{1}{6}E_{\theta\theta\theta\theta}\csc\theta_0 - \frac{1}{2}E_{\theta\theta\theta}\cot\theta_0\csc\theta_0 + E_{\theta\theta}\left(\frac{1}{2}+\cot^2\theta_0\right)\csc\theta_0, \tag{7}$$

$$A_5 = \frac{1}{2}E_{\theta\theta\phi\phi}\csc\theta_0 - \frac{1}{2}E_{\phi\phi\theta}\cot\theta_0\csc\theta_0, \tag{8}$$

$$B_1 = -E_{\phi\phi}\csc\theta_0, \tag{9}$$

$$B_2 = -E_{\theta\phi\phi}\csc\theta_0 + E_{\phi\phi}\cot\theta_0\csc\theta_0,$$

$$B_3 = -\frac{1}{6}E_{\phi\phi\phi\phi}\csc\theta_0,$$

$$B_4 = -\frac{1}{2}E_{\theta\theta\phi\phi}\csc\theta_0 + E_{\theta\phi\phi}\cot\theta_0\csc\theta_0 - E_{\phi\phi}\left(\frac{1}{2}+\cot^2\theta_0\right)\csc\theta_0. \tag{10}$$

Further, it is introduced that $E_{\theta\theta}=[\partial^2E/\partial\theta^2]_{\theta=\theta_0,\phi=0}$, $E_{\phi\phi\theta}=[\partial^3E/\partial\phi^2\partial\theta]_{\theta=\theta_0,\phi=0}$, and so on. Considering the system in which $\delta\theta$ is real and $\delta\phi$ imaginary, we can write $\delta\theta\simeq a\theta_1\cos(\omega\tau)$ and $\delta\phi\simeq ia\phi_1\sin(\omega\tau)$ to lowest order in perturbation theory. Substituting them into Eqs. (4) and (5) while neglecting terms of order higher than a, we obtain

$$\frac{\phi_1}{\theta_1} = \frac{A_1}{n\omega} = \frac{n\omega}{B_1}, \tag{11}$$

which give rise to the solution $\omega=\omega_0=\sqrt{A_1B_1}/n$.

In order to find the change of the oscillation frequency, we need to investigate Eqs. (4) and (5) by choosing $\delta\theta\simeq a\theta_1\cos(\omega\tau)+\delta\theta_2$, and $\delta\phi\simeq ia\phi_1\sin(\omega\tau)+i\delta\phi_2$, where $\delta\theta_2$ and $\delta\phi_2$ are of the order of a^2. Neglecting terms of order higher than a^2, we find $\omega=\omega_0$, and the corresponding perturbations $\delta\theta_2=a^2\theta_1^2[t_1+t_2\cos(2\omega\tau)]$ and $\delta\phi_2=a^2\theta_1^2[f_1+f_2\sin(2\omega\tau)]$ with

$$t_1 = \frac{A_1A_3 - A_2B_1}{2A_1B_1}, \tag{12}$$

$$t_2 = \frac{2A_1B_2 + A_2B_1 + A_1A_3}{6A_1B_1}, \tag{13}$$

$$f_1 = 0, \tag{14}$$

$$f_2 = \frac{A_1B_2 + 2A_2B_1 + 2A_1A_3}{6n\omega_0B_1}. \tag{15}$$

Since the oscillation frequency does not change in this order, the higher order should be taken into account by writing $\delta\theta\simeq a\theta_1\cos(\omega\tau)+\delta\theta_2+\delta\theta_3$, and $\delta\phi\simeq ia\phi_1\sin(\omega\tau)+i\delta\phi_2+i\delta\phi_3$, where $\delta\theta_2$ and $\delta\phi_2$ are of the order of a^3. Inserting them again into Eqs. (4) and (5) and retaining only terms up to $O(a^3)$, we have for the shift of the oscillation frequency

$$\omega^2 - \omega_0^2 = \left(\frac{a\theta_1}{n}\right)^2(g_1+g_2+g_3), \tag{16}$$

where

$$g_1 = 2A_2B_1\left(t_1+\frac{1}{2}t_2\right) - A_3(f_2n\omega_0), \tag{17}$$

$$g_2 = \frac{1}{2}B_2(f_2n\omega_0) + A_1B_2\left(t_1-\frac{1}{2}t_2\right), \tag{18}$$

$$g_3 = \frac{1}{4}\left(3A_4B_1 - A_1A_5 + A_1B_4 - 3\frac{A_1^2B_3}{B_1}\right). \quad (19)$$

As mentioned previously, if the oscillation period $\tau(=2\pi/\omega)$ is not a monotonic function of a where a is a function of E, the system exhibits FC. Thus the period τ in Eq. (16) should be less than $\tau_0(=2\pi/\omega_0)$, i.e., $\omega > \omega_0$ for FC and $\omega < \omega_0$ for SC. It implies that $g_1+g_2+g_3>0$ (or <0) for FC (or SC), and thereby $g_1+g_2+g_3=0$ determines the crossover boundary between FC and SC.

III. QUANTUM-CLASSICAL CROSSOVER IN MAGNETIC NANOSYSTEMS WITH AXIAL SYMMETRY

Now let us apply the formalism developed in Sec. II to the crossover for the nanospin system described by the Hamiltonian with quartic longitudinal anisotropy

$$E(\theta,\phi) = -DS_z^2 - AS_z^4 - g\mu_B H_z S_z + E_{\text{trans}}, \quad (20)$$

where S_i $(i=x,y,z)$ are three compounds of the spin operator, D is the second-order and A the fourth-order longitudinal anisotorpy constants, the third term is the Zeeman energy related with a longitudinal field H_z, and the last term (E_{trans}) describes transverse terms containing S_x or S_y spin operators. In general E_{trans} includes the transverse magnetic field and the transverse anisotropy with the second-or higher-order, which produce spin tunneling. However, in the ensuing discussion H_xS_x, which affects the spin tunneling will be considered for the sake of simplicity.[18] Hence, H_x might play the role of an effective field which includes not only an external magnetic field but also an internal magnetic field produced by the effects of the neglected even order terms in S_x and S_y of the spin Hamiltonian.

A. Unbiased case

In this case, $H_z=0$ and the total energy $E(\theta,\phi)$ of the system is given by

$$E(\theta,\phi) = -DS^2\cos^2\theta - AS^4\cos^4\theta - g\mu_B S H_x \sin\theta\cos\phi. \quad (21)$$

Introducing the dimensionless parameter $\alpha=AS^2/D$ and $h_x=g\mu_B H_x/(2DS)$, the reduced energy $\mathcal{E}(\theta,\phi)[=E(\theta,\phi)/(DS^2)]$ on the easy plane $\phi=0$ (Appendix A) is written as

$$\mathcal{E}(\theta,\phi=0) = -\cos^2\theta - \alpha\cos^4\theta - 2h_x\sin\theta, \quad (22)$$

which represents a symmetric double-well potential (Fig. 1). Noting that the position of the barrier $\theta_0=\pi/2$ in Eq. (22), we obtain from Eqs. (6)–(10)

$$A_1 = -2+2h_x, \quad A_2=A_3=0, \quad A_4 = \frac{1-12\alpha+2h_x}{3}, \quad (23)$$

$$A_5 = -h_x,$$

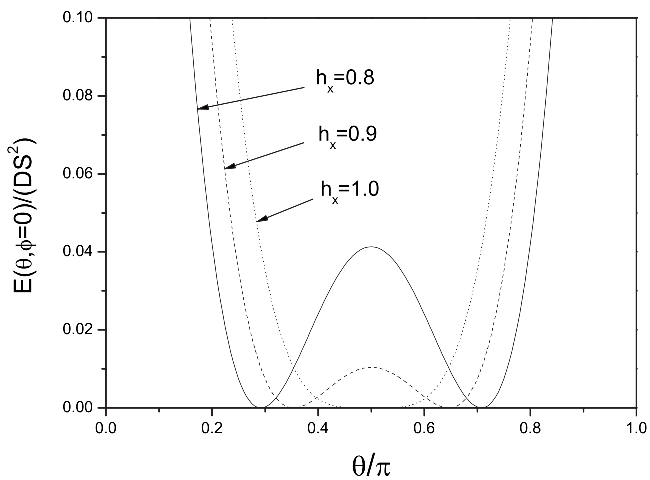

FIG. 1. Plots of the energy $\mathcal{E}(\theta,\phi=0)$ [Eq. (22)] as a function of θ/π for h_x=0.8, 0.9, and 1.0 at α=0.01. Note that the vertical scale is adjusted to make the energy zero at the minimal position θ_m for each h_x, where θ_m is a solution of a cubic equation (A1) in $\sin\theta$.

$$B_1 = -2h_x, \quad B_2=0, \quad B_3 = \frac{h_x}{3}, \quad B_4 = 0. \quad (24)$$

Substituting them into Eqs. (17)–(19), the shift of the frequency becomes from Eq. (16)

$$\omega^2 - \omega_0^2 = \frac{1}{2}\left(\frac{a\theta_1}{n}\right)^2[1-4(1-3\alpha)h_x], \quad (25)$$

where $\omega_0=2\sqrt{(1-h_x)h_x}/n$. Hence, for $\alpha<1/3$, FC occurs in the range of the transverse field

$$h_x < \frac{1}{4(1-3\alpha)}, \quad (26)$$

and the crossover boundary becomes

$$h_x = \frac{1}{4(1-3\alpha)}. \quad (27)$$

Also, in order to find the range of SC, we need to obtain the magnitude of the critical magnetic field at which the barrier height between two wells vanishes. Defining θ_c to be the angle at which the barrier vanishes by the applied magnetic field, from the relations $[d\mathcal{E}(\theta,0)/d\theta]_{\theta=\theta_c,h_x=h_{xc}} = [d^2\mathcal{E}(\theta,0)/d\theta^2]_{\theta=\theta_c,h_x=h_{xc}}=0$ we have

$$\sin(2\theta_c) + 4\alpha\cos^3\theta_c\sin\theta_c - 2h_{xc}\cos\theta_c = 0, \quad (28)$$

$$\cos(2\theta_c) + 2\alpha(-3\cos^2\theta_c\sin^2\theta_c + \cos^4\theta_c) + h_{xc}\sin\theta_c = 0, \quad (29)$$

where $h_{xc}=g\mu_B H_{xc}/(2DS)$ and H_{xc} is the critical field. After a little bit of manipulations, we get $\theta_c=\pi/2$ and $h_{xc}=1$. Actually, as discussed in Appendix B, such a critical field is valid in the range of the parameter $\alpha<1/4$, which is prevalent in magnetic nanosystems with higher-order axial term. Hence, we limit the ratio α between fourth-order and second-order anisotropies to the range of value (B2). Correspondingly, we expect SC to be in the range of field

$$\frac{1}{4(1-3\alpha)} < h_x < 1. \tag{30}$$

B. Biased case

In this section, we apply the magnetic field in the xz plane and take the $\hat{z}$ axis as the initial easy axis where there is no magnetic field. Then, we get the biased case in which the reduced Hamiltonian with $\mathbf{H}=H_x\hat{x}+H_z\hat{z}$ is written as

$$\mathcal{E}(\theta,\phi=0) = -\cos^2\theta - \alpha\cos^4\theta - 2h_x\sin\theta - 2h_z\cos\theta, \tag{31}$$

where $h_z=g\mu_B H_z/(2DS)$. In this situation the position of the barrier, θ_0 satisfies the relation given by

$$h_x = \tan\theta_0(\cos\theta_0 + h_z + 2\alpha\cos^3\theta_0), \tag{32}$$

from $[d\mathcal{E}(\theta,0)/d\theta]_{\theta=\theta_0}=0$. Since h_x depends on three quantities, θ_0, h_z, and α, it is necessary to find the range of θ determined by $0\leqslant h_x \leqslant h_{xc}$ for a given value of α and h_z. In order to do that, we first find the critical angle θ_c and the critical field $h_c[=g\mu_B H_c/(2DS)]$. In the same way as we have done in the previous section, we obtain the relations between h_c, and θ_c

$$\sin(2\theta_c) + 4\alpha\cos^3\theta_c\sin\theta_c - 2h_c\sin(\theta_c+\theta_H) = 0, \tag{33}$$

$$\cos(2\theta_c) + 2\alpha(-3\cos^2\theta_c\sin^2\theta_c + \cos^4\theta_c) - h_c\cos(\theta_c+\theta_H) = 0, \tag{34}$$

which correspond to

$$h_c = \frac{\sin(2\theta_c) + 4\alpha\cos^3\theta_c\sin\theta_c}{2\sin(\theta_c+\theta_H)} = \frac{\cos(2\theta_c) + 2\alpha(-3\cos^3\theta_c\sin^2\theta_c + \cos^4\theta_c)}{2\cos(\theta_c+\theta_H)}, \tag{35}$$

where $h_{xc}=h_c\sin\theta_H$, $h_{zc}=-h_c\cos\theta_H$, and θ_H denotes the angle between the magnetic field and $-\hat{z}$ axis. Hence, as is illustrated in Fig. 2, the range of θ_0 becomes

$$\theta_c \leqslant \theta_0 \leqslant \theta_+, \tag{36}$$

where θ_c comes from Eq. (35) for a given value of θ_H, and θ_+ from $h_x=0$ in Eq. (32) which is expressed as

$$\theta_+(\alpha,h_z) = \cos^{-1}\left[\frac{-6^{2/3} + 6^{1/3}(-9\sqrt{\alpha}h_z + \sqrt{6+81\alpha h_z^2})^{2/3}}{6\sqrt{\alpha}(-9\sqrt{\alpha}h_z + \sqrt{6+81\alpha h_z^2})^{1/3}}\right]. \tag{37}$$

In the case of $\alpha=0$ we have $\theta_c=\cos^{-1}(h_c\cos\theta_H)^{1/3}$ and $\theta_+ =\cos^{-1}(h_c\cos\theta_H)$ with the critical field h_c given by[19]

$$h_c = (\cos^{2/3}\theta_H + \sin^{2/3}\theta_H)^{-3/2}. \tag{38}$$

Continuing in the present case as in the previous one, we have the shift of the frequency

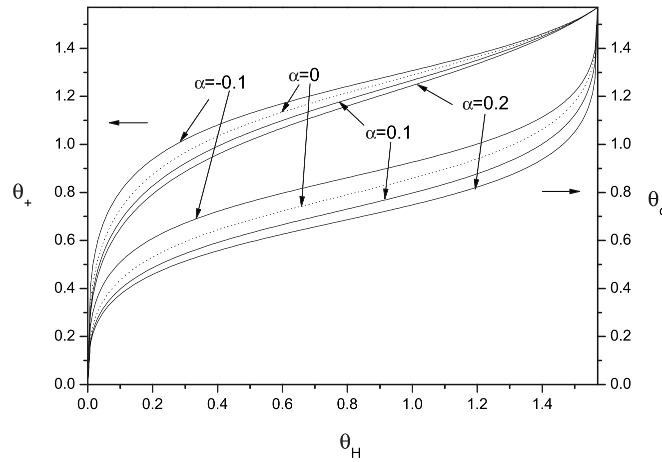

FIG. 2. θ_H dependence of θ_+ and θ_c for $\alpha=-0.1$, 0, 0,1, and 0.2, where θ_+ and θ_c correspond to $h_x=0$, and h_{xc} for a given value of θ_H, respectively. Note that the dotted line at $\alpha=0$ is for eye guidance.

$$\omega^2 - \omega_0^2 = \frac{1}{24}\left(\frac{a\theta_1}{n}\right)^2 \csc^2\theta_0\left[12p_1^2 + 4h_x\cot\theta_0 p_2 + \frac{h_x\csc\theta_0 p_3 p_4}{p_5} - 3h_x\csc\theta_0 p_6\right], \tag{39}$$

where ω_0 and the parameters p_i's $(i=1,2,\ldots,6)$ are given in Appendix C. In this situation theoretical analysis becomes cumbersome because the oscillation frequency depends on four physical quantities, α, h_x, h_z, and θ_0. However, using Eq. (32), ω is reduced to the function of three quantities. Hence, θ_0 which gives $\omega=\omega_0$ in Eq. (39) can be numerically calculated for a given value of α and h_z, and the crossover boundary between FC and SC in terms of h_x and h_z is determined by putting such θ_0 into Eq. (32). As is shown in Fig. 3,

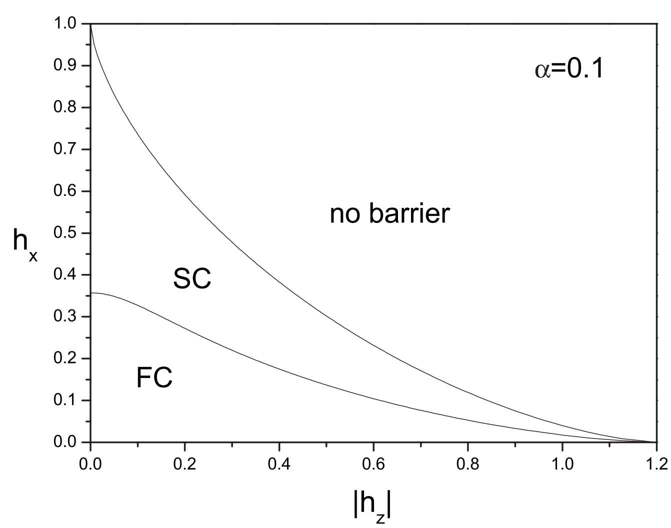

FIG. 3. Crossover diagram h_x vs $|h_z|$ at $\alpha=0.1$ obtained by the numerical calculation for the truly axial symmetry. FC and SC indicate the first- and the second-order crossover, respectively. Note that $|h_{zc}|=1+2\alpha$ at $h_{xc}=0$.

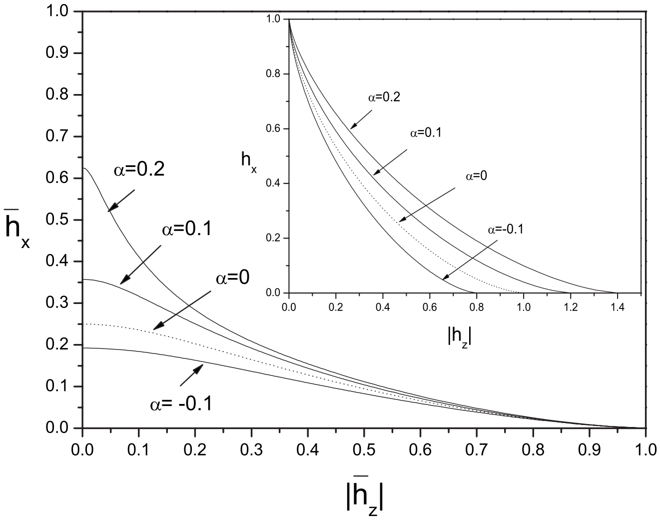

FIG. 4. Crossover diagram $\bar{h}_x(=h_x/h_{xc})$ vs $|\bar{h}_z|(=|h_z|/h_{zc})$ for $\alpha(=AS^2/D)=0.2$, 0.1, 0, and −0.1. Note that the dotted line at $\alpha=0$ is for eye guidance. Inset: Critical field h_{xc} vs $|h_{zc}|$ for a given value of α where $h_{xc}^{2/3}+h_{zc}^{2/3}=1$ at $\alpha=0$.

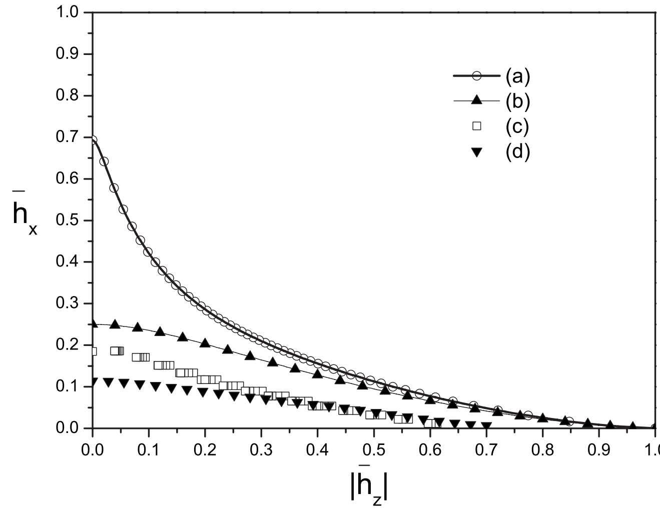

FIG. 5. Crossover boundary at (a) $\alpha=0.213$ $(S\to\infty)$, (b) $\alpha=0$ $(S\to\infty)$, (c) $\alpha=0.213$ $(S=10)$, and (d) $\alpha=0$ $(S=10)$, where the physical quantities in (c) are taken from the sample Mn_{12}-tBuAc (Ref. 20). Note that the first-order crossover is greatly enhanced with increasing S.

FC is greatly suppressed with increasing h_x and h_z. The region for the FC is enhanced with increasing α while it is suppressed for $\alpha<0$ (Fig. 4). In this respect, such a higher-order axial term plays an important role in shifting the crossover boundary.

To illustrate the above results with concrete numbers, we choose $A\simeq 10^{-6}$ K, and $D\simeq 0.1$ K, $S\simeq 100$ for typical magnetic nanomaterials, which results in $\alpha\simeq 0.1$. Thus, in the absence of the longitudinal field the crossover boundary occurs at $h_x\simeq 0.357$ from Eq. (27), which is large compared with $h_x=0.25$ in the simple uniaxial symmetry.[3] Also, in comparison with the single-molecule magnets such as Mn_{12}-tBuAc with $D=0.563$ K, $A=0.0012$ K, and $S=10$,[15] the regime for the FC becomes much larger in the limit of $S\to\infty$.(Fig. 5)

Before concluding, it will be meaningful to discuss what the effect of the fourth-order off-diagonal terms[21] such as $(C/2)(S_+^4+S_-^4)$ would be, where C is the fourth-order transverse anisotropy constant. Considering such terms in previous formulation and introducing a parameter $r(=2CS^2/D)$, we have found that the results with such terms have the same tendency to the previously obtained results with a slight increase in the crossover boundary for the typical value $(0.01 \lesssim \delta \lesssim 0.1)$, while such terms can be neglected in the limit of $\delta \ll 0.01$. Taking magnetic nanoparticle[22] with $C=2.8\times 10^{-5}$ K (i.e., $\delta\sim 0.05$), for instance, the increase of the FC regime is about 10%, and thereby the FC really becomes more robust against external magnetic fields.

IV. CONCLUSION

We have studied quantum-classical crossover in magnetic nanosystems with truly axial symmetry. We have presented the crossover boundary which determines first-or second-order crossover. The result is of interest theoretically and experimentally in two respects. First, in the presence of the higher-order axial term which is prevalent in nanomagnets, the first-order regime is greatly suppressed or enhanced depending on the sign of such a term whereas it is greatly suppressed by the external magnetic field. In fact, the regime for the first-order crossover is more reduced in the the transverse field than in the longitudinal field. Thus, in order to observe the sharp change of the escape rate around the crossover temperature, the magnitude of a transverse field should be small or moderate, and the higher-order axial term should be as large as possible. Second, since qualitative analysis shows that $\Delta T/T_c\simeq 1/S$ in the first-order crossover and $1/\sqrt{S}$ in the second-order one, we have $\Delta T/T_c\sim 0.01$ for the former and 0.1 for the latter in case of $S\sim 100$. In this respect, the larger the spin, the more likely one is to see a dramatic change of the escape rate in real experiments. These make the magnetic nanosystem with a larger spin a good candidate for the experimental study.

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APPENDIX A: BARRIER HEIGHT

The position of the minimum is determined by the equation

$$-2\alpha\sin^3\theta+(1+2\alpha)\sin\theta-h_x\cos\phi=0, \qquad \text{(A1)}$$

originated from $\partial\mathcal{E}(\theta,\phi)/\partial\theta$. Denoting the solution of Eq. (A1) to be θ_m, the barrier height U is expressed as

$$U = \mathcal{E}\left(\theta = \frac{\pi}{2}, \phi\right) - \mathcal{E}(\theta_m, \phi)$$
$$= \cos^2 \theta_m + \alpha \cos^4 \theta_m - 2h_x \cos \phi(1 - \sin \theta_m). \quad (A2)$$

Noting that $\sin \theta_m \leq 1$, the greatest reduction in the overall barrier height comes from $\phi=0$ for $h_x>0$. Also, the same argument is applied to the biased case. Hence, we keep $\phi=0$ in the whole discussion.

APPENDIX B: CRITICAL FIELD AND LIMITATION OF THE HIGHER-ORDER AXIAL TERM

In order to find the critical field h_{xc} in which the barrier vanishes, we need to investigate the behavior of the energy (22) around $\theta=\pi/2$. Plugging a new parameter η defined as $\theta=\pi/2+\eta$ into Eq. (22), we have

$$\mathcal{E}(\theta, \phi = 0) \simeq -2h_x + (-1 + h_x)\eta^2 + \left(\frac{1}{3} - \alpha - \frac{h_x}{12}\right)\eta^4 + \left(-\frac{2}{45} + \frac{2\alpha}{3} + \frac{h_x}{360}\right)\eta^6 + \cdots. \quad (B1)$$

To ensure that $\theta=\pi/2$ corresponds to the absolute minimum of energy at $h_x=1$, the coefficient of η^4 should not be negative at $h_x=1$. Accordingly, in order that $h_x=1$ is a critical field and $\theta=\pi/2$ is the absolute minimum, we have

$$\alpha < \frac{1}{4}. \quad (B2)$$

APPENDIX C: PARAMETERS IN THE BIASED CASE

The parameters for the crossover can be obtained by using Eqs. (6)–(10), and Eq. (31):

$$A_1 = 2 \csc \theta_0[h_z \cos \theta_0 + (1 + \alpha)\cos(2\theta_0) + \alpha \cos(4\theta_0) + h_x \sin \theta_0], \quad (C1)$$

$$A_2 = \frac{1}{2} \csc^2 \theta_0[-3h_z - 4(1 + \alpha)\cos \theta_0 - h_z \cos(2\theta_0) - 6\alpha \cos(3\theta_0) + 2\alpha \cos(5\theta_0) - h_x \sin(2\theta_0)], \quad (C2)$$

$$A_3 = h_x \cot \theta_0, \quad (C3)$$

$$A_4 = \frac{1}{12} \csc^3 \theta_0[13 + 13\alpha + 23h_z \cos \theta_0 + (10 + 41\alpha)\cos(2\theta_0) + h_z \cos(3\theta_0) + (1 - 13\alpha)\cos(4\theta_0) + 7\alpha \cos(6\theta_0) + 9h_x \sin \theta_0 + h_x \sin(3\theta_0)], \quad (C4)$$

$$A_5 = -h_x \csc^2 \theta_0, \quad (C5)$$

$$B_1 = -2h_x, \quad B_2 = 0, \quad B_3 = \frac{h_x}{3}, \quad B_4 = 0, \quad (C6)$$

which result in

$$\omega_0 = 2\sqrt{h_x \csc \theta_0 p_1}/n, \quad (C7)$$

$$p_1 = h_z \cos \theta_0 + (1 + \alpha)\cos(2\theta_0) + \alpha \cos(4\theta_0) + h_x \sin \theta_0, \quad (C8)$$

$$p_2 = 4h_z + 5(1 + \alpha)\cos \theta_0 + 2h_z \cos(2\theta_0) + (1 + 8\alpha)\cos(3\theta_0) - \alpha \cos(5\theta_0) + 2h_x \sin(2\theta_0), \quad (C9)$$

$$p_3 = -3h_z - 4(1 + \alpha)\cos \theta_0 - h_z \cos(2\theta_0) - 6\alpha \cos(3\theta_0) + 2\alpha \cos(5\theta_0) - h_x \sin(2\theta_0), \quad (C10)$$

$$p_4 = -8h_z - 13(1 + \alpha)\cos \theta_0 + 2h_z \cos(2\theta_0) + 7 \cos(3\theta_0) - 16\alpha \cos(3\theta_0) + 17\alpha \cos(5\theta_0) + 2h_x \sin(2\theta_0), \quad (C11)$$

$$p_5 = h_z \cos \theta_0 + (1 + \alpha)\cos(2\theta_0) + \alpha \cos(4\theta_0) + h_x \sin \theta_0, \quad (C12)$$

$$p_6 = 13 + 13\alpha + 19h_z \cos \theta_0 + (6 + 37\alpha)\cos(2\theta_0) + h_z \cos(3\theta_0) + (1 - 17\alpha)\cos(4\theta_0) + 7\alpha \cos(6\theta_0) + 5h_x \sin \theta_0 + h_x \sin(3\theta_0). \quad (C13)$$

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