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Transition state theory for spins: phase-space formulation

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Abstract

The quasi-probability distribution function for spins in the representation (phase) space of the polar and azimuthal angles (ϑ, φ) (analogous to the Wigner distribution for translational motion of a particle) is used to calculate the escape rate for a uniaxial spin system via quantum transition state theory (TST). The quantum corrections to the TST escape rate equation for classical magnetic dipoles appear *both* in the *prefactor* and in the *exponential part* of the escape rate unlike in the corresponding Wigner TST formula for particles and exhibit a marked dependence on the spin number.

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(Some figures in this article are in colour only in the electronic version)

An understanding of quantum effects in the decay of metastable states of Brownian particles and spins is essential in various relaxation problems in physics and chemistry, e.g. chemical reaction rates, dynamics of a superconducting tunnelling junction, the reversal of the magnetization of magnetic nanoparticles and molecular magnets, etc. The simplest description of quantum corrections to thermally activated decay, via escape of particles over a potential barrier due to thermal agitation, is afforded by transition state theory (TST) [1–4]. We remark that in the rudimentary form of *classical* TST pertaining to a system with one degree of freedom, the escape rate of a particle from an isolated potential well with normalized barrier height $\beta\Delta V$ is

$$\Gamma_{\mathrm{cl}} \sim \frac{\omega_a}{2\pi} \mathrm{e}^{-\beta\Delta V}, \tag{1}$$

where ω_a is the well angular (attempt) frequency, $\beta = (k_B T)^{-1}$, and $k_B T$ is the thermal energy. In the present context, the first guess at a quantum transition state theory appears to have been made by Wigner [5]. He proposed a quantum generalization of the classical TST by introducing a phase-space (x, p) *quasiprobability* distribution function $W(x, p, t)$, exhibiting most of the properties of a classical phase-space distribution (see [6–9] for review). Wigner [5] showed that the quantum correction represents an effective lowering of the potential barrier so enhancing the escape rate due to quantum tunnelling effects. Now TST always implies that the dissipation to the bath does not affect the escape rate. Nevertheless, the results of TST should still apply in a *wide range of dissipation* for which thermal noise is sufficiently strong to thermalize the escaping particles yet not strong enough to disturb thermal equilibrium in the well, i.e., a Maxwell–Boltzmann distribution still prevails everywhere including the top of the barrier. In the context of the Kramers escape rate theory [10] model this is the so-called intermediate damping case. Comprehensive reviews of applications and developments of TST have been given by Hänggi *et al* [2], Benderskii *et al* [3] and Pollak and Talkner [4].

The quantum TST may also be used to study thermally assisted tunnelling of the magnetization in spin systems. Mindful of the original classical calculation of the magnetization relaxation time by Néel [11] using transition state theory (TST) such effects will be important in quantum tunnelling phenomena in ferromagnetic nanoparticles [12] (particularly in the crossover region between reversal of their magnetization by thermal agitation over a potential barrier and reversal by macroscopic quantum tunnelling [12]) and also in the spin dynamics of molecular magnets [13] as a function of (spin) size. Indeed such is the importance of quantum effects in parameters characterizing the decay of metastable states in spin systems that diverse theoretical methods, e.g., instantons, mapping of the spin Hamiltonian onto equivalent particle Hamiltonians [14, 15], perturbation treatment of quantum-classical escape rate transitions [16] have been developed in order to evaluate them. Yet another approach to the foregoing problem essentially involves the extension of Wigner's methods to the phase-space description of spin systems. Thus quasiprobability density functions $W(\vartheta, \varphi)$ in the representation space of polar and azimuthal angles (ϑ, φ) (the relevant canonical variables) for spin systems at equilibrium have been determined using the Wigner–Stratonovich phase-space formalism (see, e.g., [17–25]). The function $W(\vartheta, \varphi)$ for spins was originally introduced by Stratonovich [17] and further developed by others (e.g., [18–25]). It is entirely analogous to the translational Wigner distribution $W(x, p)$ in phase space (x, p) [5] which is the quasiprobability representation of the density operator except that certain differences arise because of the angular momentum commutation relations. The phase-space formalism allows quantum-mechanical averages involving the density matrix to be calculated just as classical ones and so is eminently suited to the calculation of quantum corrections because it formally represents quantum mechanics as a statistical theory on classical phase space [25].

Again recalling Néel's classical TST calculation [11], the simplest description of quantum effects in the magnetization reversal time of a nanoparticle should be provided by the inverse escape rate from the wells of the magnetocrystalline and the external field potential as determined by the quantum TST [3]. We reiterate that all forms of TST *ignore* the disturbance to the equilibrium distribution in the wells created by the loss of representative points (in this case the magnetization) due to escape over a barrier. Thus *only* the equilibrium distribution is involved hence a quantum master equation describing the time evolution of the quasiprobability density is unnecessary. Such an equation would be required, for example, to generalize the classical escape rate theory of Kramers [10] for point particles and that of Brown [26, 27] for single domain ferromagnetic particles using the Fokker–Planck equation (i.e., the bath–particle interaction is characterized by the *ansatz* of frequent but weak collisions). In the classical theory, the drift and diffusion coefficients may be determined using Einstein's imposition [28] of the Maxwell–Boltzmann distribution as the equilibrium solution of the Fokker–Planck equation. In like manner, postulating [28–30] a Kramers–Moyal-like expansion truncated at the second term (leading of course in the classical limit to the Fokker–Planck equation) as the phase-space representation of the collision operator, the drift and diffusion coefficients in the resulting quantum master equation may be determined by requiring that the equilibrium quasiprobability distribution in the representation space renders the collision term zero. This has been illustrated for a spin in a uniform field in [31] and indicates clearly how all the methods of solution of the Fokker–Planck equation extend to the master equation for quantum spin relaxation just as for particles [28–30] leading in general, however, to involved analytical and numerical calculations.

Now in view of the mathematical simplifications offered by the TST treatment of escape rates, the object of this paper is to describe a phase-space formulation of TST for spins. Moreover, because the uniaxial anisotropy potential is important in physical applications (see, e.g., [24, 32–34] (in general giving rise to a multi-stable potential), we shall illustrate the method by evaluating the TST escape rate for a uniaxial paramagnet of arbitrary spin value S with Hamiltonian

$$\beta \hat{H}_S = -\sigma \hat{S}_Z^2, \tag{2}$$

where $\hat{S}_Z$ is the Z-component of the spin operator $\hat{\mathbf{S}}$, σ is the dimensionless internal field parameter. In the classical limit, $S \to \infty$, $\sigma \to 0$ and $\sigma S^2 = \sigma' = \text{const}$, taking a single domain ferromagnetic particle as example, equation (2) corresponds to the uniaxial anisotropy potential

$$\beta \hat{H}_S \to -\sigma' \cos^2 \vartheta, \tag{3}$$

where σ' is the dimensionless anisotropy parameter.

In order to outline the calculation of the escape rate for spins as determined by the quantum TST, we must first briefly recall Wigner's [5] quantum generalization of the classical TST for particles. Here the over-barrier escape rate Γ for a particle moving in a potential $V(x)$ is defined by

$$\Gamma \sim I_{\text{top}}/Z_{\text{well}}, \tag{4}$$

where $I_{\text{top}} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} J(x,p)\delta(x-x_c)\,\mathrm{d}p\,\mathrm{d}x$ is the current of particles over the barrier with the current density $J(x,p) = \theta(p)(p/m)W_{\text{st}}(x,p)$, $W_{\text{st}}(x,p)$ is the un-normalized Wigner distribution function, θ is the unit step function and $Z_{\text{well}} = \int\int_{\text{well}} W_{\text{st}}(x,p)\,\mathrm{d}p\,\mathrm{d}x$ is the partition function of the well region. The point c is the top of the barrier and point a is the bottom of the well. Near the bottom of the well, Z_{well} may be approximated by that of a harmonic oscillator with the characteristic well frequency $\omega_0 = \omega_a$ so that using the explicit form of the Wigner function for a quantum oscillator, namely,

$$W_a(x,p) = \mathrm{e}^{-\beta V(x_a) - (x^2/\langle x^2\rangle + p^2/\langle p^2\rangle)/2},$$

where $\langle p^2\rangle = m^2\omega_a^2\langle x^2\rangle = (m\hbar\omega_a/2)\coth(\beta\hbar\omega_a/2)$, we have

$$Z_{\text{well}} \approx \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_a(x,p)\,\mathrm{d}x\,\mathrm{d}p = \pi\hbar\,\mathrm{csch}(\beta\hbar\omega_a/2)\,\mathrm{e}^{-\beta V(x_a)}. \tag{5}$$

Near the top of the barrier, the Wigner function $W_{\text{st}}(x,p)$ approximately corresponds to that of an inverted harmonic oscillator with the top frequency $\omega_0 = \mathrm{i}\omega_c$ so that

$$W_{\text{st}}(x_c,p) \approx \mathrm{e}^{-\beta V(x_c)}\sec(\hbar\omega_c\beta/2)\,\mathrm{e}^{-p^2\tan(\beta\hbar\omega_c/2)/(m\hbar\omega_c)},$$

whence

$$I_{\text{top}} \approx m^{-1}\int_0^{\infty} pW_{\text{st}}(x_c,p)\,\mathrm{d}p = \hbar\omega_c\csc(\beta\hbar\omega_c/2)\,\mathrm{e}^{-\beta V(x_c)}/2. \tag{6}$$

Substituting equations (5) and (6) into equation (4), we have Wigner's result

$$\Gamma \approx (\omega_a/2\pi)\,\Xi\,\mathrm{e}^{-\beta\Delta V}, \tag{7}$$

where $\Delta V = V(x_c) - V(x_a)$ is the barrier height and

$$\Xi = \frac{\omega_c\sinh(\beta\hbar\omega_a/2)}{\omega_a\sin(\beta\hbar\omega_c/2)} = 1 + \frac{\beta^2\hbar^2}{24}\left(\omega_c^2 + \omega_a^2\right) + \cdots$$

is the quantum correction factor merely appearing as a *change in the prefactor* of the classical TST escape rate equation (1).

Now in applying TST to classical spins (i.e., magnetic moments $\boldsymbol{\mu}$) and axially symmetric problems (such as uniaxial anisotropy) the equation of motion of the magnetic moment $\boldsymbol{\mu}$ in the effective field $\mathbf{H} = -\partial V/\partial\boldsymbol{\mu}$ is

$$\dot{\boldsymbol{\mu}} = \boldsymbol{\omega}_0 \times \boldsymbol{\mu}, \tag{8}$$

where $\boldsymbol{\omega}_0 = \gamma\mathbf{H}$ is the precession frequency, γ is the gyromagnetic ratio, and

$$V(\vartheta) = -kT\sigma'\cos^2\vartheta \tag{9}$$

is the (Helmholtz) free energy. In the low temperature limit (high barrier approximation), as far as TST is concerned, we have

$$\Gamma_{\mathrm{cl}} \sim I_{\mathrm{top}}^{\mathrm{cl}}/Z_{\mathrm{well}}^{\mathrm{cl}}, \tag{10}$$

where $Z_{\mathrm{well}}^{\mathrm{cl}} \sim \int_{\mathrm{well}} \mathrm{e}^{-\beta V(\vartheta)}\sin\vartheta\,\mathrm{d}\vartheta$ is the well partition function and $I_{\mathrm{top}}^{\mathrm{cl}}$ is the total current of the (magnetization) representative points over the barrier. Now for the uniaxial anisotropy given by equation (9), the top of the barrier is situated at $\vartheta_c = \pi/2$ and the bottom of the well at $\vartheta_a = 0$. The well partition function and total current may be estimated as

$$Z_{\mathrm{well}}^{\mathrm{cl}} \sim \mathrm{e}^{-\beta V(\vartheta_a)}/(2\sigma'), \tag{11}$$

$$I_{\mathrm{top}}^{\mathrm{cl}} \sim \frac{1}{2\pi}\int_{\mathrm{top}} J_\vartheta\,\mathrm{e}^{-\beta V(\vartheta)}\,\mathrm{d}\vartheta \approx \frac{\gamma}{2\pi\mu\beta}\,\mathrm{e}^{-\beta V(\vartheta_c)}. \tag{12}$$

Here $\beta V(\vartheta_a) = -\sigma'$, $\beta V(\vartheta_c) = 0$ and $J_\vartheta = |\dot{\boldsymbol{\mu}}|/\mu = (\gamma/\mu)\partial_\vartheta V(\vartheta) = \omega_c\cos\vartheta\sin\vartheta$ is a divergence-free current density [26], where $\omega_c = 2\gamma\sigma'/(\beta\mu)$ is the barrier frequency. Hence equation (10) yields the Néel formula [11]

$$\Gamma_{\mathrm{cl}} \sim (\omega_0/2\pi)\,\mathrm{e}^{-\beta\Delta V}, \tag{13}$$

where $\Delta V = V(\vartheta_c) - V(\vartheta_a)$ is the barrier height and $\omega_0 = 2\gamma\sigma'/(\mu\beta)$ is the well (precession) frequency.

In order to calculate the quantum correction factor to the escape rate for a spin system using the phase-space method, the equilibrium quasiprobability density function of spin orientations on the surface of the unit sphere is required. The phase-space distribution $W_S^{(s)}(\vartheta,\varphi)$ for a spin system given by Stratonovich [17] is defined by the invertible map

$$W_S^{(s)}(\vartheta,\varphi) = \mathrm{Tr}\{\hat{\rho}\hat{w}_s(\vartheta,\varphi)\}, \tag{14}$$

where s parameterizes quasiprobability functions of spins belonging to the $SU(2)$ dynamical symmetry group such as considered here, $\hat{w}_s(\vartheta,\varphi)$ is the Wigner–Stratonovich operator or kernel of the (bijective) transformation given by equation (14) defined as [24]

$$\hat{w}_s(\vartheta,\varphi) = \sqrt{\frac{4\pi}{2S+1}}\sum_{L=0}^{2S}\sum_{M=-L}^{L}\left(C_{S,S,L,0}^{S,S}\right)^{-s} Y_{L,M}^{*}\hat{T}_{L,M}^{(S)}. \tag{15}$$

Here the asterisk denotes the complex conjugate, $Y_{L,M}(\vartheta,\varphi)$ are the spherical harmonics [35], $\hat{T}_{L,M}^{(S)}$ are the irreducible tensor (polarization) operators with matrix elements given by [35]

$$[\hat{T}_{L,M}^{(S)}]_{m',m} = \sqrt{\frac{2L+1}{2S+1}}C_{S,M,L,m}^{S,m'}, \tag{16}$$

and $C^{S,S}_{S,S,L,0}$ and $C^{S,m\prime}_{S,M,L,m}$ are the Clebsch–Gordan coefficients [35]. The function $W_S^{(-s)}(\vartheta,\varphi)$ now allows us to calculate the *average* value $\langle\hat{A}\rangle = \mathrm{Tr}\{\hat{\rho}\hat{A}\}$ of an arbitrary spin operator $\hat{A}$ because the $W_S^{(-s)}(\vartheta,\varphi)$ provides the overlap relation [17]

$$\langle\hat{A}\rangle = \frac{2S+1}{4\pi}\int_{\theta,\varphi} A_s(\vartheta,\varphi)W_S^{(-s)}(\vartheta,\varphi)\sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi, \tag{17}$$

where $A_s(\vartheta,\varphi) = \mathrm{Tr}\{\hat{A}\hat{w}_s(\vartheta,\varphi)\}$ is the Weyl symbol of the operator $\hat{A}$ (see, e.g., [25]). The parameter values $s = 0$ and $s = \pm 1$ correspond to the Stratonovich [17] and Berezin [20] contravariant and covariant functions, respectively (the latter are directly related to the *P*- and *Q*-symbols which appear naturally in the coherent state representation; see [22] for a review). Here we consider $W_S^{(-1)}(\vartheta,\varphi)$ only; thus we omit everywhere the superscript -1 in $W_S^{(-1)}(\vartheta,\varphi)$ ($W_S^{(1)}(\vartheta,\varphi)$ and $W_S^{(0)}(\vartheta,\varphi)$ can be treated in like manner). We have chosen $W_S^{(-1)}(\vartheta,\varphi)$ because only this distribution satisfies the non-negativity condition required of a true probability density function, namely $W_S^{(-1)}(\vartheta,\varphi) \geqslant 0$. The quasiprobability densities $W_S^{(1)}(\vartheta,\varphi)$ and $W_S^{(0)}(\vartheta,\varphi)$ do not satisfy this condition [36].

The equilibrium phase-space distribution for a spin system with Hamiltonian $\beta\hat{H}_S = -\xi\hat{S}_Z - \sigma\hat{S}_Z^2$ has been obtained and discussed in detail in [36]. Here we only need the particular case $\xi = 0$, so that $W_S(\vartheta)$ is given by [36]

$$W_S(\vartheta) = \sum_{\substack{L=0\\ \Delta L=2}}^{2S}\frac{(2L+1)}{(2S+1)}P_L(\cos\vartheta)C^{S,S}_{S,S,L,0}\sum_{m=-S}^{S}C^{S,m}_{S,m,L,0}\,\mathrm{e}^{\sigma m^2}, \tag{18}$$

where $P_L(\cos\vartheta)$ are the Legendre polynomials [35] and the explicit equations for the Clebsch–Gordan coefficients $C^{S,m}_{S,m,L,m}$ and $C^{S,m}_{S,m;L,0}$ are

$$C^{S,S}_{S,S,L,0} = (2S)!\sqrt{\frac{2S+1}{(2S-L)!(2S+L+1)!}},$$

$$C^{S,m}_{S,m,L,0} = (S+m)!(S-m)!(L!)^2\sqrt{\frac{(2S+1)(2S-L)!}{(2S+L+1)!}}$$
$$\times\sum_{n=0}^{L}\frac{(-1)^n}{[(L-n)!]^2(n!)^2(S-m-n)!(m+S+n-L)!}.$$

The distribution W from equation (18) corresponds to the equilibrium spin density matrix $\hat{\rho}_{\mathrm{eq}} = \mathrm{e}^{-\beta\hat{H}_S}/Z_S$, where $Z_S = \mathrm{Tr}\{\mathrm{e}^{-\beta\hat{H}_S}\} = \sum_{m=-S}^{S}\mathrm{e}^{\sigma m^2}$ is the partition function. For *arbitrary* S, the leading terms of the series in $\sin^2\vartheta$ and $\cos^2\vartheta$ for the equilibrium distribution $W(\vartheta)$ from equation (18) are

$$W_S(\vartheta) = W_S(0)\{1 + (S/2)[\mathrm{e}^{-(2S-1)\sigma} - 1]\sin^2\vartheta + \cdots\}, \tag{19}$$

$$W_S(\vartheta) = W_S(\pi/2)[1 + A\cos^2\vartheta + \cdots], \tag{20}$$

respectively, where

$$W_S(0) = \mathrm{e}^{S^2\sigma}, \tag{21}$$

$$W_S(\pi/2) = \frac{(2S)!}{2^{2S}}\sum_{m=-S}^{S}\frac{\mathrm{e}^{\sigma m^2}}{(S+m)!(S-m)!}, \tag{22}$$

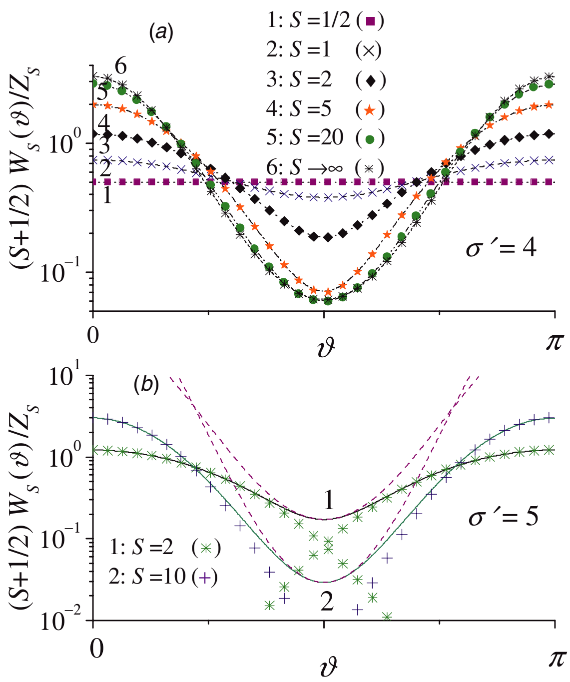

Figure 1. (*a*) The distribution $(S + 1/2)W_S(\vartheta)/Z_S$ for $\sigma' = 4$ and various values of S. (*b*) The distribution $(S + 1/2)W_S(\vartheta)/Z_S$ (solid lines) for $\sigma' = 5$ and $S = 2$ and 10. Crosses (+) and stars: equation (23). Dashed lines: equation (24).

$$A = \frac{\sum_{m=-S+1}^{S-1} \frac{e^{(m-1)^2\sigma} + e^{(m+1)^2\sigma} - 2e^{m^2\sigma}}{(S-1+m)!(S-1-m)!}}{2\sum_{m=-S}^{S} \frac{e^{m^2\sigma}}{(S+m)!(S-m)!}}.$$

In the classical limit ($S \to \infty, \sigma \to 0, \sigma S^2 = \text{const} = \sigma'$), the equilibrium distribution $W_S(\vartheta)$ tends to the Boltzmann distribution, i.e.,

$$(S + 1/2)W_S(\vartheta)/Z_S \to e^{\sigma' \cos^2\vartheta}/Z_{\text{cl}},$$

where $Z_S = (S + 1/2)\int_0^\pi W_S(\vartheta)\sin\vartheta\,d\vartheta$ and $Z_{\text{cl}} = \sqrt{\pi/\sigma'}\,\text{erf}\,i(\sqrt{\sigma'})$ are the quantum and classical partition functions, respectively, and $\text{erf}\,i(x) = (2/\sqrt{\pi})\int_0^x e^{t^2}\,dt$ is the error function of imaginary argument. The distribution $(S + 1/2)W_S(\vartheta)/Z_S$ is shown in figure 1(*a*) for various values of S.

In the low temperature limit ($2\sigma' \gg 1$), the series $W(\vartheta)$ in equation (18) can be approximated to a very high degree of accuracy in the vicinity of the maxima at $\vartheta = 0$ and $\vartheta = \pi$ as

$$W_S(\vartheta) \approx e^{-\sigma S(S-1)} \begin{cases} f_{(2S-1)\sigma}^{2S}(\vartheta), & \vartheta \leqslant 1, \\ f_{-(2S-1)\sigma}^{2S}(\vartheta), & \pi - \vartheta \leqslant 1, \end{cases} \tag{23}$$

where the function $f_\xi(\vartheta)$ is defined as $f_\xi(\vartheta) = \cosh(\xi/2) + \sinh(\xi/2)\cos\vartheta$. The interpretation of equation (23) is that the dynamics of the spin at low temperatures comprise precession in the effective magnetic field $H = (\beta\gamma\hbar)^{-1}(2S - 1)\sigma$. Next according to equation (20), $W_S(\vartheta)$ can be approximated in the vicinity of the barrier top by the

Boltzmann-like distribution

$$W_S(\vartheta) \approx W_S(\pi/2)\,\mathrm{e}^{A\cos^2\vartheta} \tag{24}$$

(see figure 1(*b*)).

Now for a system of noninteracting spins (so that exchange interactions are ignored), the quantum dynamics of a spin in an external magnetic field $\mathbf{H}$, with Hamiltonian $\hat{H}_S = -\gamma\hbar\hat{\mathbf{S}}\cdot\mathbf{H}$ obey [37] the equation (cf equation (8))

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\mathbf{S}} = \frac{\mathrm{i}}{\hbar}[\hat{H}_S, \hat{\mathbf{S}}] = \boldsymbol{\omega}\times\hat{\mathbf{S}}, \tag{25}$$

where $\boldsymbol{\omega} = \gamma\mathbf{H}$. Noting that the appropriate correspondence rules (equation (17)) of spin operators and Weyl symbols (*c*-numbers) in the phase space (ϑ, φ) are [24]

$$\hat{S}_X \to (S+1)\sin\vartheta\cos\varphi, \qquad \hat{S}_Y \to (S+1)\sin\vartheta\sin\varphi, \qquad \hat{S}_Z \to (S+1)\cos\vartheta,$$

we have $|\dot{\mathbf{S}}| \to \omega\,(S+1)\sin\vartheta$. Furthermore, equation (25) may also be used as an approximate equation of motion for a spin in the effective anisotropy field $\mathbf{H}$. Hence, we may evaluate the semiclassical TST escape rate Γ for a uniaxial paramagnet of arbitrary spin value S in the low temperature limit from the flux over barrier, equation (4), where I_{top} and Z_{well} denote the total current of representative points over the barrier ($\vartheta_c = \pi/2$) and the well partition function, respectively,

$$I_{\mathrm{top}} \sim \frac{1}{2\pi(S+1)}\int_{\mathrm{top}} |\dot{\mathbf{S}}|\, W_S(\vartheta)\,\mathrm{d}\vartheta, \tag{26}$$

$$Z_{\mathrm{well}} \sim \int_{\mathrm{well}} W_S(\vartheta)\sin\vartheta\,\mathrm{d}\vartheta, \tag{27}$$

First by noting that

$$\left(S+\frac{1}{2}\right)\int_0^{\pi} f_\xi^{2S}(\vartheta)\sin\vartheta\,\mathrm{d}\vartheta = \sinh\left[\left(S+\frac{1}{2}\right)\xi\right]\Big/\sinh\frac{1}{2}\xi,$$

equations (23) and (27) yield

$$Z_{\mathrm{well}}^{-1} \approx \left(S+\frac{1}{2}\right)[1-\mathrm{e}^{-\sigma(2S-1)}]\,\mathrm{e}^{-\sigma S^2}. \tag{28}$$

Next in view of equation (24), the barrier angular frequency ω_c for the uniaxial potential $-A\cos^2\vartheta$, is $\omega_c = 2\gamma A/(\mu\beta)$, where $\mu = \hbar\gamma S$. Hence using $J_\vartheta = |\dot{\mathbf{S}}|/(S+1) \sim \omega_c\cos\vartheta\sin\vartheta$, the current I_{top} may be estimated as

$$I_{\mathrm{top}} \approx \gamma W_S(\pi/2)/(2\pi\mu\beta). \tag{29}$$

For the purpose of comparison with the TST equations (7) and (13) for particles and classical magnetic dipoles, we can write the resulting TST escape rate formula for spins in canonical form, namely,

$$\Gamma \sim (\omega_0/2\pi)\,\Xi\,\mathrm{e}^{-\beta\Delta V}, \tag{30}$$

where $\omega_0 = \sigma(2S-1)/(\hbar\beta)$, Ξ and $\beta\Delta V = \ln[W_S(0)/W_S(\pi/2)]$ are, respectively, the *quantum correction* factor (analogous to that for particles equation (7)) and '*effective*' barrier height given by

$$\Xi = \frac{2S+1}{2\sigma S(2S-1)}[1-\mathrm{e}^{-\sigma(2S-1)}], \tag{31}$$

$$\beta\Delta V = \sigma S^2 - \ln W_S(\pi/2). \tag{32}$$

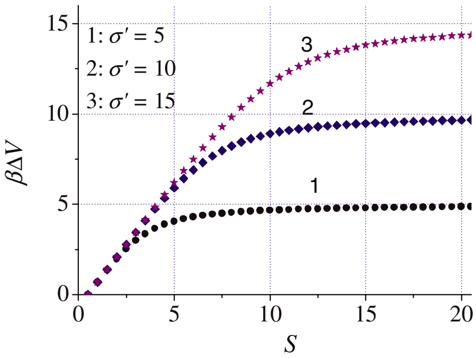

Figure 2. The barrier height $\beta\Delta V$ versus S for $\sigma' = 5$, 10 and 15. Symbols: equation (32).

The TST spin escape rate so written displays, however, a vital difference with the corresponding result for particles equation (7) because now *both* the effective barrier height $\beta\Delta V$, i.e., the argument of the exponential *and* the quantum correction factor Ξ which is associated with the prefactor strongly depend on the spin number S yielding $\beta\Delta V \to \beta\Delta V^{\mathrm{cl}} = \sigma'$ and $\Xi \to 1$, respectively in the classical limit unlike in equation (7) where the exponential is simply the classical Boltzmann factor. This may be explained as follows. For particles, a harmonic oscillator approximation may be used in calculating the Wigner distribution at *both* the well and saddle point which is effectively a Maxwell–Boltzmann distribution at these points consequently leading to equation (7) so that the Boltzmann factor is preserved (a result which is entirely in accord with the fact that [38] the Wigner evolution equation for a harmonic oscillator is the same as the Liouville equation). This is obviously not true of the Wigner function for spins which never has the form of such a distribution with the sole exception of the classical limit. We remark, however, that the effective barrier $\beta\Delta V$ is still smaller than its classical value σ' (see figure 2) in accordance with Wigner's prediction for particles.

In this note we have illustrated how the Wigner–Stratonovich phase-space approach for spins may be used to *directly* calculate TST escape rates. Hitherto these have usually been calculated *indirectly* by mapping the spin Hamiltonian onto an equivalent particle Hamiltonian and then using TST for particles [15, 16, 39]. Thus one may determine the greatest relaxation time of the magnetization as a function of spin size as we have illustrated for the simple uniaxial potential of the magnetocrystalline anisotropy in a manner essentially very similar to the classical case. The result epitomises the difference between the quantum corrections for particles and those for spins, e.g., the correction to *both* the effective barrier height and prefactor already alluded to. The method we have outlined may also be extended to non-axially symmetric systems [40] as the equilibrium distribution $W(\vartheta, \varphi)$ can be evaluated for an arbitrary spin Hamiltonian $\hat{H}_S$ [36, 40].

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