Phase-space equilibrium distributions and their applications to spin systems with nonaxially symmetric Hamiltonians

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(Received 29 November 2007; revised manuscript received 31 January 2008; published 13 March 2008)

The Fourier series representation of the equilibrium quasiprobability density function $W_S(\vartheta,\varphi)$ or Wigner function of spin "orientations" for arbitrary spin Hamiltonians in a representation (phase) space of the polar angles (ϑ,φ) (analogous to the Wigner function for translational motion) arising from the generalized coherent state representation of the density operator is evaluated explicitly for some nonaxially symmetric problems including a uniaxial paramagnet in a transverse external field, a biaxial, and a cubic system. It is shown by generalizing transition state theory to spins [i.e., calculating the escape rate using the equilibrium density function $W_S(\vartheta,\varphi)$ only] that one may evaluate the reversal time of the magnetization. The quantum corrections to the transition state theory escape rate equation for classical magnetic dipoles appear *both* in the *prefactor* and in the *exponential part* of the escape rate and exhibit a marked dependence on the spin number. Furthermore, the phase-space representation allows us to estimate the switching field curves and/or surfaces for spin systems because quantum effects in these fields can be estimated via Thiaville's geometrical method [Phys. Rev. B **61**, 12221 (2000)] for the study of the magnetization reversal of single-domain ferromagnetic particles. The calculation is accomplished (just as the determination of the equilibrium quasiprobability distributions in the phase space of the polar angles) by calculating switching field curves and/or surfaces using the Weyl symbol (*c*-number representation) of the Hamiltonian operator for given magnetocrystalline-Zeeman energy terms. Examples of such calculations for various spin systems are presented. Moreover, the reversal time of the magnetization allows us to estimate thermal effects on the switching fields for spin systems.

DOI: 10.1103/PhysRevB.77.104418 PACS number(s): 75.45.+j, 75.40.Gb, 75.50.Tt, 75.50.Xx

I. INTRODUCTION

The interpretation of spin relaxation experiments comprises a fundamental problem of condensed phase physics and chemistry yielding a well defined means of extracting information concerning the structure and characteristics of materials as a function of spin S so providing a bridge between microscopic and macroscopic physics. For example (recalling that the number of spins in a sample roughly corresponds to the number of atoms), on an *atomic* level, nuclear magnetic and related spin resonance experiments, etc., examine the time evolution of the individual *elementary* spins[1,2] of nuclei, electrons, muons, etc., while on *mesoscales* the time evolution of magnetic *molecular clusters* (i.e., spins $15-25\mu_B$) exhibiting relatively large quantum effects is currently of interest in the fabrication of molecular magnets.[3] On *nanoscales* single-domain ferromagnetic particles (giant spins $10^4-10^5\mu_B$) with a given orientation of the particle moment and permanent magnetization exist. These have spawned very extensive magnetic recording industries, the particles commonly used being on or near the microsize scale. Finally, on the *bulk macroscopic scale* one has permanent magnets ($10^{20}\mu_B$), i.e., *multidomain* systems where magnetization reversal occurs via the *macroscopic* processes of nucleation, propagation and annihilation of domain walls. Thus a well defined size scale ranging from the bulk macroscopic down to individual atom and spins naturally exists.

On an atomic level spin relaxation experiments in nuclear magnetic or electron spin resonance are usually interpreted via the phenomenological Bloch[4] equations pertaining to the relaxation of elementary spins subjected to an external magnetic field and interacting with an environment that is assumed to be a heat reservoir at constant temperature T. On mesoscales both the behavior of the hysteresis loop and the relaxation or reversal time of the magnetization as a function of S are of extreme importance in the observation of the transition from microscopic to nanoscale physics as strong quantum effects are likely to occur as the spin decreases corresponding to the transition from a behavior reminiscent of a single-domain ferromagnetic nanoparticle to that of a molecular cluster. In this region the magnetization may reverse by resonant quantum tunneling as may be observed in the corresponding hysteresis loop.[5] In contrast on the nanoscale in single-domain ferromagnetic nanoparticles (originally encountered in paleomagnetism in the context of past reversals of Earth's magnetic field, where depending on the size of the particle, the relaxation time may vary from milliseconds to millions of years) the relaxation is treated as classical and proceeds by uniform rotation as conjectured by Néel[6] and Stoner and Wohlfarth.[7] The relaxation time epochs representing the transition from giant Langevin paramagnetic behavior (superparamagnetism) with no hysteresis involved via the magnetic after effect stage (where the relaxation time for changes in orientation of the magnetization is of the order of the time of a measurement) to stable ferromagnetism where a given ferromagnetic state corresponds to one of many possible such metastable states in which the magnetization vector is held in a preferred orientation. In the hypothesis of uniform or coherent rotation the exchange energy which is supposed constant renders all spins collinear and the magnitude of the magnetization vector is constant in space hence competition exists only between the anisotropy energy and the Zeeman energy of the applied field since the magnetization vector is perfectly aligned. This hypothesis should hold for small sample sizes, i.e., single-domain particles, where domain walls cannot form in the sample (i.e., it is energetically unfavorable to form them) and at high fields in samples of low coercivity.[8]

As far as dynamics are concerned, Néel[6] determined the magnetization relaxation time, i.e., the time of reversal of the magnetization of the particle, due to thermal agitation over its internal magnetocrystalline anisotropy barrier from the inverse escape rate over the barriers using transition state theory (TST)[9] as specialized to magnetic moments. Thus his treatment given in detail for uniaxial anisotropy only is confined to a discrete set of orientations for the magnetic moment of the particle. Moreover, the equilibrium distribution is all that is ever required since the disturbance to the Boltzmann distribution in the wells of the magnetocrystalline anisotropy potential due to the escape of the magnetization over the barrier is ignored. In addition the effect of an external applied field (Zeeman energy term) can be included which is important because[5] at low temperatures with zero applied field the energy barrier between two states of opposite magnetization is much too high for thermally agitated escape to occur. The barrier height, however, may be reduced by applying an external (biasing) field in the opposite direction to that of the magnetization of the particle. If the external field is *close* to the switching field at *zero temperature* (at which the magnetization reverses) thermal fluctuations are then strong enough to overcome the anisotropy-Zeeman energy barrier hence the magnetization is reversed.

The static magnetization currents of single-domain particles are usually calculated using the method of Stoner and Wohlfarth.[7] Their procedure simply consists in minimizing the free energy of the particle comprising the sum of Zeeman and anisotropy energies with respect to the polar and azimuthal angles specifying the orientation of the magnetization for each value of the applied field. The calculation always leads to hysteresis because in certain field ranges[10,11] two or more minima exist and thermally agitated transitions between them are neglected. The value of the applied field, at which the magnetization reverses, is as we saw above called the switching field and the angular dependence of that field with respect to the easy axis of the magnetization yields the well known Stoner–Wohlfarth astroids.[7] These were originally given for uniaxial shape anisotropy only which is the anisotropy of the magnetostatic energy of the sample induced by its nonspherical shape. The astroids represent a parametric plot of the parallel versus the perpendicular component of the switching field which in the uniaxial case is the field that destroys the bistable structure of the free energy. The astroid concept was later generalized to *arbitrary* effective anisotropy by Thiaville[8] including any given magnetocrystalline anisotropy and even surface anisotropy. He proposed a geometrical method for the calculation of the energy of a particle allowing one to determine the switching field for all values of the applied magnetic field yielding the critical switching field surface analogous to the Stoner–Wohlfarth astroids. A knowledge[5] of the switching field surface allows one to determine the effective anisotropy of the particle and all other parameters such as the frequencies of oscillations in the wells of the potential, i.e., the ferromagnetic resonance frequency, etc. We reiterate that these static calculations all ignore thermal effects on the switching field, i.e., transitions between the minima of the potential are neglected so that they are strictly only valid at zero temperature.

In the context of thermal effects giving rise to transitions between the potential minima we have mentioned that the original dynamical calculations of Néel for single-domain particles utilize classical transition state theory. In the more recent treatment formulated by Brown[10,11] (now known as the Néel–Brown model),[5] which explicitly treats the system as a gyromagnetic one and which includes nonequilibrium effects due to the loss of magnetization at the barrier, the time evolution of the magnetization of the particle $\mathbf{M}(t)$ is described by a classical Langevin equation. This is the phenomenological Landau–Lifshitz[12] or Gilbert equation[13,14] originally used to study the motion of a domain wall augmented by torques due to random white noise magnetic fields characterizing the giant spin-bath interaction. In the absence of damping and stochastic terms this equation corresponds to the Larmor equation for the motion of the giant spin so including the gyromagnetic effects. The Langevin equation of motion of the magnetization (which *inter alia* reconciles Néel's treatment of magnetization reversal with the general theory of the Brownian motion[15] and allows for a continuous distribution of the magnetic moment orientations) yields[10,11] the Fokker–Planck equation for the surface distribution of the magnetic moment orientations on the unit sphere. Moreover, the reversal time may be asymptotically calculated (in the high barrier limit as the relaxation time is of the order of the time of measurement in an experiment) by means of the Kramers escape rate theory[9,16,17] as adapted to magnetic moments by Brown.[10,11] The resulting asymptotic expressions may then be compared with the exact results for the reversal time yielded by the inverse of the smallest nonvanishing eigenvalue of the Fokker–Planck equation which may be extracted from the solution of that equation by matrix continued fraction methods as has been accomplished in Refs. 15 and 18 for many anisotropy potentials. The asymptotic expressions are valid in various dissipation regimes delineated by the ratio of the magnetization energy lost per cycle of the almost periodic motion of the magnetization at the lowest saddle point energy of the potential to the thermal energy.[17] Moreover, thermal effects on the switching field astroids due to transitions between the minima of the potential may be calculated by equating the inverse escape rate to the measuring time in a given experiment and solving the resulting implicit equation for the switching field numerically, comprising a classical treatment of the hysteresis loop at nonzero temperatures.

Now Bean and Livingston[19] have suggested that in a single-domain particle besides the overbarrier Néel process the magnetization may also reverse by *macroscopic quantum tunneling* (macroscopic since a giant spin is involved) through the magnetocrystalline-Zeeman energy potential barrier.[17] Hence the relaxation behavior as a function of spin size and the temperature and spin dependence of the associated Stoner–Wohlfarth hysteresis loops and astroids must be studied in order to distinguish tunneling reversal from reversal by thermal agitation. Thus systematic ways of introducing quantum effects into the magnetization reversal of a nanomesoscale particle (which in general may be restated as quantum effects in parameters characterizing the decay of metastable states in spin systems) are required. In general the magnetization may reverse by quantum tunneling for relatively small S or at very low temperatures for larger S which may be observed in the behavior of the Stoner–Wohlfarth asteroids. In general, so important are quantum effects in the magnetization reversal in spin systems that diverse theoretical methods, e.g., WKB formalism,[20] instantons; mapping of the spin Hamiltonian onto equivalent particle Hamiltonians;[21,22] perturbation treatment of quantum-classical escape rate transitions;[23] etc., have been developed in order to treat them. Yet another approach (that adopted here) is the extension of Wigner's phase-space representation of the density operator[24,25] (originally developed to obtain quantum corrections to the classical distributions for point particles in the phase space of positions and momenta) to the description of spin systems (see, e.g., Refs. 26–33).

The phase-space (or generalized coherent state) representation of the spin density matrix allows one to describe spin systems in terms of a *quasiprobability density function* or Wigner function $W_S(\vartheta,\varphi)$ of spin orientations in the phase (here configuration) space (ϑ,φ); ϑ and φ are the polar and azimuthal angles, respectively, constituting the canonical variables. The advantage of such a mapping of the density matrix onto a c-number quasiprobability density function $W_S(\vartheta,\varphi)$ as extensively used in quantum optics (see, e.g., Ref. 25) is that it is possible to show how $W_S(\vartheta,\varphi)$ evolves as a function of the spin size S. In the limit of large spins, $W_S(\vartheta,\varphi)$ reduces to the classical Boltzmann orientational distribution naturally linking the equilibrium quantum and classical spin regimes. The quasiprobability density $W_S(\vartheta,\varphi)$ was originally introduced by Stratonovich[31] as part of a general discussion of c-number quasiprobability distributions for quantum systems in a representation space based on the symmetry properties of the underlying group. Examples are the Heisenberg–Weyl group for particles and the SU(2) group for rotations.

Agarwal and co-workers[34,35] have explicitly given the phase-space distributions for atomic angular momentum Dicke states, coherent states, and squeezed states corresponding to a collection of two-level atoms. In the magnetic context, explicit equations for the equilibrium distributions $W_S(\vartheta,\varphi)$ have been obtained for an assembly of spins $\mathbf{S}$ in a uniform magnetic field $\mathbf{H}$ (Refs. 26 and 33) and spins in the simplest uniaxial potential of the magnetocrystalline anisotropy and Zeeman energy.[36] Moreover, the results have been used[37] to generalize Néel's classical calculation of magnetization escape rates to include spin size effects for the simplest uniaxial potential in a uniform external magnetic field applied parallel to the anisotropy axis using quantum transition state theory as adopted to spins in the manner pioneered by Wigner[38] for point particles. However, because of the limitation to axially symmetric potentials (e.g., one cannot treat surface anisotropy energy, magnetoelastic anisotropy energy, etc.) these calculations comprise a very restricted treatment of spin size effects. The first step toward a general treatment of these in the magnetic context is to calculate the equilibrium phase-space distribution function $W_S(\vartheta,\varphi)$ as a function of spin size for given *nonaxially symmetric effective anisotropy-Zeeman energy* Hamiltonians which is one purpose of this paper. Having determined the various equilibrium distributions corresponding to particular anisotropies, our second purpose is to calculate the Stoner–Wohlfarth magnetization curves represented in switching field astroid form as a function of spin size for nonaxially symmetric potentials. This calculation generalizes Thiaville's[8] geometrical method (for the construction of switching field curves for such potentials) to include quantum effects due to finite spin size permitting one to study the behavior of the astroids in the interesting magnetic cluster—single-domain particle transition region. Finally, we estimate the reversal time of the magnetization via the quantum generalization of TST (previously elaborated for the axially symmetric uniaxial potential).[37] This will allow one to estimate temperature effects in the astroids and hysteresis loops within the limitations imposed by quantum TST (moderate damping, etc.).[39]

Our calculation proceeds, by generalizing the axially symmetric results described in Ref. 36 pertaining to a spin S where the external uniform field $\mathbf{H}$ is parallel to the anisotropy axis, to show how phase-space distributions of spins can be obtained both analytically and numerically for various *nonaxially symmetric* spin systems with equilibrium states described by a canonical density matrix $\hat{\rho}$ given by

$$\hat{\rho} = e^{-\beta\hat{H}_S}/Z_S. \tag{1}$$

Here $Z_S=\mathrm{Tr}\{e^{-\beta\hat{H}_S}\}$ is the partition function for a spin system with an arbitrary nonaxially symmetric Hamiltonian $\hat{H}_S$ and $\beta=1/(kT)$ is the inverse thermal energy. We shall at first illustrate the analytical method by evaluating $W_S(\vartheta,\varphi)$ for an assembly of noninteracting spins (essentially[5] that corresponding to the quantum treatment of superparamagnetism so that in the absence of a field the spins are randomly oriented) in an external *constant* field $\mathbf{H}$ with an *arbitrary* direction in space so that the Hamiltonian of a spin is

$$\beta\hat{H}_S = -\beta\gamma\hbar\mathbf{H}\cdot\hat{\mathbf{S}} = -\xi(\gamma_X\hat{S}_X + \gamma_Y\hat{S}_Y + \gamma_Z\hat{S}_Z), \tag{2}$$

where $\gamma_X,\gamma_Y,\gamma_Z$ are the direction cosines of $\mathbf{H}$, γ is the gyromagnetic ratio, $\hbar$ is Planck's constant, and ξ is the dimensionless external field parameter. Next we consider various magnetic anisotropies establishing one or more preferred orientations of the magnetization of an assembly of spins. In particular, we shall consider a uniaxial paramagnet in a transverse external field with

$$\beta\hat{H}_S = -\xi\hat{S}_X - \sigma\hat{S}_Z^2. \tag{3}$$

In the classical limit, this Hamiltonian corresponds to the Néel–Brown model, where a uniaxial single-domain particle has two equivalent ground states of magnetization separated by a magnetocrystalline anisotropy energy barrier (the σ term) in the presence of an applied transverse field which in the quantum case will enhance the tunneling probability. Next we will consider biaxial- and cubic systems, with Hamiltonians

$$\beta \hat{H}_S = -\sigma \hat{S}_Z^2 - \delta(\hat{S}_X^2 - \hat{S}_Y^2) \tag{4}$$

and

$$\beta \hat{H}_S = -\xi \hat{S}_Z - \sigma(\hat{S}_X^4 + \hat{S}_Y^4 + \hat{S}_Z^4)/2. \tag{5}$$

Here δ and σ are dimensionless anisotropy barrier height parameters. For clarity we summarize the basic features of the Wigner–Stratonovich transformation of the density matrix. Equilibrium distribution functions for the particular Hamiltonians so determined may then be used to study the equilibrium magnetization, switching field hysteresis curves, etc., which require only a knowledge of these distributions.

II. WIGNER–STRATONOVICH TRANSFORMATION OF THE DENSITY MATRIX

The phase-space distribution function $W_S^{(s)}(\vartheta,\varphi)$ or Wigner function on the surface of the unit sphere for a spin system given by Stratonovich[31] (see also Refs. 27 and 28) is defined by the invertible map

$$W_S^{(s)}(\vartheta,\varphi) = \mathrm{Tr}\{\hat{\rho}\hat{w}_s(\vartheta,\varphi)\}, \tag{6}$$

where s parametrizes quasiprobability functions of spins belonging to the SU(2) dynamical symmetry group considered here; the Wigner–Stratonovich operator (or kernel) $\hat{w}_s(\vartheta,\varphi)$ is defined as[27,28]

$$\hat{w}_s(\vartheta,\varphi) = \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} (C_{S,S,L,0}^{S,S})^{-s} Y_{L,M}^* \hat{T}_{L,M}^{(S)}. \tag{7}$$

Here the asterisk denotes the complex conjugate, $Y_{L,M}(\vartheta,\varphi)$ are the spherical harmonics,[40] $\hat{T}_{L,M}^{(S)}$ are the irreducible tensor (polarization) operators with matrix elements[40]

$$[\hat{T}_{L,M}^{(S)}]_{m',m} = \sqrt{\frac{2L+1}{2S+1}} C_{S,m,L,M}^{S,m'}, \tag{8}$$

and $C_{S,S,L,0}^{S,S}$ and $C_{S,m,L,M}^{S,m'}$ are the Clebsch–Gordan coefficients.[40] The density matrix $\hat{\rho}$ may then be expressed using the kernel equation (7) via the inverse transformation

$$\hat{\rho} = \frac{2S+1}{4\pi} \int_{\theta,\varphi} \hat{w}_s(\vartheta,\varphi) W_S^{(-s)}(\vartheta,\varphi) \sin\vartheta d\vartheta d\varphi.$$

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 $W_S^{(-s)}(\vartheta,\varphi)$ provide the overlap relation[28]

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

where $A^{(s)}(\vartheta,\varphi) = \mathrm{Tr}\{\hat{A}\hat{w}_s(\vartheta,\varphi)\}$ is the Weyl symbol of the operator $\hat{A}$. The parameter values $s=0$ and $s=\pm 1$ correspond to the Stratonovich[31] and Berezin[32] contravariant and covariant functions, respectively (the latter are directly related to the P and Q symbols appearing naturally in the coherent state representation; see Ref. 27 for a review). Here we consider $W_S^{(-1)}(\vartheta,\varphi)$ only omitting 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 it alone satisfies the non-negativity condition required of a true probability density function, viz., $W^{(-1)}(\vartheta,\varphi) \geqslant 0$. The quasiprobability densities $W_S^{(1)}(\vartheta,\varphi)$ and $W_S^{(0)}(\vartheta,\varphi)$ violate this condition (they may take on negative values in the present problem). The relationship of the Wigner–Stratonovich operator $\hat{w}_{-1}(\vartheta,\varphi)$ from Eq. (7) to various equivalent forms[26] of the generalized coherent state representation of the density matrix is given in the Appendix.

The phase-space distribution may be presented for arbitrary S in (finite) Fourier series form (which emphasizes the relationship with the conventional infinite Fourier series representation of the associated classical Boltzmann distribution in terms of spherical harmonics), namely,

$$\frac{2S+1}{4\pi} W_S(\vartheta,\varphi) = \sum_{L=0}^{2S} \sum_{M=-L}^{L} \langle Y_{L,M}\rangle Y_{L,M}^*(\vartheta,\varphi), \tag{9}$$

where $\langle Y_{L,M}\rangle = [(2S+1)/4\pi]\int_0^{2\pi}\int_0^{\pi} Y_{L,M}(\vartheta,\varphi) W_S(\vartheta,\varphi) \times \sin\vartheta d\vartheta d\varphi$ are the equilibrium values of the spherical harmonics given explicitly by

$$\langle Y_{L,M}\rangle = \sqrt{\frac{2S+1}{4\pi}} C_{S,S,L,0}^{S,S} a_{L,M}. \tag{10}$$

Here the coefficients $a_{L,M}$ (representing expectation values of $\hat{T}_{L,M}^{(S)}$ in a state described by the density matrix $\hat{\rho}$) are[40]

$$a_{L,M} = \langle\hat{T}_{L,M}^{(S)}\rangle = \mathrm{Tr}\{\hat{\rho}\hat{T}_{L,M}^{(S)}\}. \tag{11}$$

Equation (9) is a general result valid for an *arbitrary* spin system with equilibrium states described by the canonical density matrix $\hat{\rho}$ given by Eq. (1) with an arbitrary model Hamiltonian $\hat{H}_S(\hat{S}_X,\hat{S}_Y,\hat{S}_Z)$ expressed in terms of the spin operators $\hat{S}_X$, $\hat{S}_Y$, and $\hat{S}_Z$. The spin operators can be written using the polarization operators $\hat{T}_{1,M}^{(S)}$ as[40]

$$\hat{S}_X = a[\hat{T}_{1,-1}^{(S)} - \hat{T}_{1,1}^{(S)}], \quad \hat{S}_Y = ia[\hat{T}_{1,-1}^{(S)} + \hat{T}_{1,1}^{(S)}], \quad \hat{S}_Z = \sqrt{2}a\hat{T}_{1,0}^{(S)}, \tag{12}$$

where $a=\sqrt{S(S+1)(2S+1)/6}$. Thus using Eqs. (8) and (12), we can (i) present the Hamiltonian $\hat{H}_S$ in explicit matrix form, next, (ii) evaluate numerically the density matrix $\hat{\rho}$ from Eq. (1), and then (iii) calculate the coefficients $a_{L,M}$ from Eq. (11) and so the Fourier coefficients $\langle Y_{L,M}\rangle$ from Eq. (10), having thus estimated $\langle Y_{L,M}\rangle$, we can (iv) calculate the phase-space distribution $W_S(\vartheta,\varphi)$ from the finite Fourier series equation (9) for any particular S. Moreover, the results can be presented in closed form whenever the equilibrium spin density matrix $\hat{\rho}=e^{-\beta\hat{H}_S}/Z_S$ or its elements are given explicitly.

According to the finite Fourier series equation (9), all the statistical moments $\langle Y_{L,M}\rangle$ are required (in general) to evaluate $W_S(\vartheta,\varphi)$ for given S. However, for calculation of particular observables such as the magnetization only a few moments may be necessary. For example, in the calculation of the longitudinal, $\langle\hat{S}_Z\rangle$, and transverse, $\langle\hat{S}_X\rangle$ and $\langle\hat{S}_Y\rangle$, components of the magnetization, noting the correspondence rules of operators $\hat{S}_X$, $\hat{S}_Y$, $\hat{S}_Z$ and Weyl symbols (c numbers) $S_X(\vartheta,\varphi)$, $S_Y(\vartheta,\varphi)$, $S_Z(\vartheta,\varphi)$ in the phase space (ϑ,φ),[28] namely,

$$\hat{S}_X \to S_X = \sqrt{2\pi S(S+1)/3}\sum_{L=0}^{2S}\sum_{M=-L}^{L} C^{S,S}_{S,S,L,0}Y^*_{L,M} \times \mathrm{Tr}\{(\hat{T}^{(S)}_{1,-1}-\hat{T}^{(S)}_{1,1})\hat{T}^{(S)}_{L,M}\} = \sqrt{2\pi/3}(S+1)(Y_{1,-1}+Y_{1,1}),$$

$$\hat{S}_Y \to S_Y = i\sqrt{2\pi S(S+1)/3}\sum_{L=0}^{2S}\sum_{M=-L}^{L} C^{S,S}_{S,S,L,0}Y^*_{L,M} \times \mathrm{Tr}\{(\hat{T}^{(S)}_{1,-1}+\hat{T}^{(S)}_{1,1})\hat{T}^{(S)}_{L,M}\} = i\sqrt{2\pi/3}(S+1)(Y_{1,-1}-Y_{1,1}),$$

and

$$\hat{S}_Z \to S_Z = \sqrt{4\pi S(S+1)/3}\sum_{L=0}^{2S}\sum_{M=-L}^{L} C^{S,S}_{S,S,L,0}Y^*_{L,M}\,\mathrm{Tr}\{\hat{T}^{(S)}_{1,0}\hat{T}^{(S)}_{L,M}\} = \sqrt{4\pi/3}(S+1)Y_{1,0},$$

we have

$$\langle\hat{S}_X\rangle = \sqrt{2\pi/3}(S+1)[\langle Y_{1,-1}\rangle + \langle Y_{1,1}\rangle], \quad (13)$$

$$\langle\hat{S}_Y\rangle = i\sqrt{2\pi/3}(S+1)[\langle Y_{1,-1}\rangle - \langle Y_{1,1}\rangle], \quad (14)$$

and

$$\langle\hat{S}_Z\rangle = \sqrt{4\pi/3}(S+1)\langle Y_{1,0}\rangle. \quad (15)$$

Here we have used the property of polarization operators[40]

$$\mathrm{Tr}\{\hat{T}^{(S)}_{L_1,M_1}\hat{T}^{(S)}_{L_2,M_2}\} = (-1)^{M_1}\delta_{L_1,L_2}\delta_{M_1,-M_2}. \quad (16)$$

Thus only $\langle Y_{1,0}\rangle$ and $\langle Y_{1,\pm1}\rangle$ are now required.

The results obtained so far are entirely formal. Now we shall demonstrate how the phase-space distributions for particular spin systems can be obtained for all S (integer and half-integer).

III. SPIN IN A UNIFORM EXTERNAL FIELD

As the simplest example of the Fourier series method embodied in Eqs. (9) and (10), we calculate the Wigner function of a spin in an external uniform field with Hamiltonian

$$\beta\hat{H}_S = -\xi(\gamma_X\hat{S}_X + \gamma_Y\hat{S}_Y + \gamma_Z\hat{S}_Z),$$

which yields the conventional theory of superparamagnetism. Here the matrix elements of $\hat{H}_S$ can be given in closed form, viz.,

$$[\hat{H}_S]_{m',m} = A^{(-)}\delta_{m,m'+1} + A^{(+)}\delta_{m,m'-1} - \gamma_Z\xi m\delta_{m,m'}$$

where $A^{(\pm)}=-(1/2)\xi(\gamma_X \pm i\gamma_Y)\sqrt{(S\pm m)(S\mp m+1)}$. Furthermore, for any particular S the density matrix $\hat{\rho}_S=e^{-\beta\hat{H}_S}/Z_S$ can be presented as a finite series of spin operators (using the commutation relations for spin operators).[40] For example, for $S=\frac{1}{2}$, $S=1$, etc., one has

$$\hat{\rho}_{1/2} = \frac{1}{Z_{1/2}}[\cosh(\xi/2)\hat{I} + 2\sinh(\xi/2)(\gamma_X\hat{S}_X + \gamma_Y\hat{S}_Y + \gamma_Z\hat{S}_Z)], \quad (17)$$

$$\hat{\rho}_1 = \frac{1}{Z_1}[\hat{I} + \sinh\xi(\gamma_X\hat{S}_X + \gamma_Y\hat{S}_Y + \gamma_Z\hat{S}_Z) + 2\sinh^2(\xi/2)(\gamma_X\hat{S}_X + \gamma_Y\hat{S}_Y + \gamma_Z\hat{S}_Z)^2], \quad (18)$$

etc., where $\hat{I}$ is the identity matrix. The corresponding phase-space distribution $W_S(\vartheta,\varphi)$ can then be calculated (after tedious matrix algebra best accomplished, e.g., via MATHEMATICA) from Eqs. (9)–(12) using the properties of polarization operators such as Eq. (16) and[40]

$$\mathrm{Tr}\{\hat{T}^{(S)}_{L_1,M_1}\hat{T}^{(S)}_{L_2,M_2}\hat{T}^{(S)}_{L_3,M_3}\} = (-1)^{2S+L_3+M_3}\sqrt{(2L_1+1)(2L_2+1)} \times C^{L_3,-M_3}_{L_1,M_1,L_2,M_2}\begin{Bmatrix} L_1 & L_2 & L_3 \\ S & S & S\end{Bmatrix}, \quad (19)$$

where $\begin{Bmatrix} L_1 & L_2 & L_3 \\ S & S & S\end{Bmatrix}$ is a $6j$ symbol.[40] The finite series can then be summed so that the distribution $W_S(\vartheta,\varphi)$ can be written in closed form for arbitrary spin values S as

$$W_S(\vartheta,\varphi) = [\cosh(\xi/2) + \sinh(\xi/2)F(\vartheta,\varphi)]^{2S}/Z_S, \quad (20)$$

where $F(\vartheta,\varphi)=\gamma_X\sin\vartheta\cos\varphi + \gamma_Y\sin\vartheta\sin\varphi + \gamma_Z\cos\vartheta$ and

$$Z_S = \frac{2S+1}{4\pi}\int_0^{\pi}\int_0^{2\pi}[\cosh(\xi/2) + \sinh(\xi/2)F(\vartheta,\varphi)]^{2S}\sin\vartheta\, d\vartheta\, d\varphi = \sinh[(S+1/2)\xi]/\sinh(\xi/2) \quad (21)$$

is the partition function. For three particular cases

$$\gamma_X=1,\quad \gamma_Y=0,\quad \gamma_Z=0;\quad \gamma_X=0,\quad \gamma_Y=1,\quad \gamma_Z=0;\quad \text{and}\ \gamma_X=0,\quad \gamma_Y=0,\quad \gamma_Z=1,$$

Eq. (20) reduces to the known equations of Takahashi and Shibata.[33] The average equilibrium magnetization of a spin, namely, $M_H=g\mu_B\langle\hat{\mathbf{S}}\cdot\mathbf{H}\rangle$, is

$$M_H = g\mu_B\frac{(2S+1)(S+1)}{4\pi}\times\int_0^{\pi}\int_0^{2\pi}F(\vartheta,\varphi)W_S(\vartheta,\varphi)\sin\vartheta\, d\vartheta\, d\varphi = g\mu_B SB_S(\xi S), \quad (22)$$

where μ_B is the Bohr magneton, g is the Landé factor, and $B_S(x)$ is the Brillouin function defined as[27]

$$B_S(x) = \frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S}\coth\left(\frac{x}{2S}\right). \quad (23)$$

In the classical limit, $\beta \to 0$, $S \to \infty$, and βS=const, the equilibrium distribution $W_S(\vartheta,\varphi)$ (which now becomes a conventional Fourier series) and the Brillouin function $B_S(x)$ tend, respectively, to the Boltzmann distribution $(2S+1)W_S(\vartheta,\varphi)/4\pi \to Z_{cl}^{-1}e^{S\xi F(\vartheta,\varphi)}$ and the Langevin function $B_S(x) \to L(x) = \coth(x) - 1/x$, where Z_{cl} is the classical partition function. This comprises the usual treatment of superparamagnetism, the only difference from the conventional theory of paramagnetism being that the magnetic moments of the particles are enormous. Quantum effects become important when $\beta\hbar\gamma H/S \geqslant 1$, i.e., either at small S or at very low temperatures T or for an intense field H when Eq. (23) applies.

IV. UNIAXIAL PARAMAGNET IN A TRANSVERSE FIELD

As a further example of the application of the finite Fourier series equations (9) and (10), we calculate the Wigner function of a spin in a transverse external field with Hamiltonian (i.e., the Néel–Brown model with a transverse applied field)

$$\beta\hat{H}_S = -\xi\hat{S}_X - \sigma\hat{S}_Z^2$$

(known otherwise as the Lipkin–Meshkov Hamiltonian[41]). For small S, the density matrix $\hat{\rho}_S = e^{-\beta\hat{H}_S}/Z_S$ can be given in closed form. For example, for $S=1/2$, $S=1$, etc., we have after some matrix algebra

$$\hat{\rho}_{1/2} = \frac{e^{\sigma/4}}{Z_{1/2}}[\hat{I}\cosh(\xi/2) + 2\hat{S}_X\sinh(\xi/2)], \quad (24)$$

$$\hat{\rho}_1 = \frac{1}{Z_1}[\hat{I}(e^{\sigma} - \sigma A) + A(\xi\hat{S}_X + \sigma\hat{S}_Z^2) + (e^{\sigma/2}\cosh\sqrt{\xi^2+\sigma^2/4} - e^{\sigma} + \sigma A/2)\hat{S}_X^2], \quad (25)$$

etc., where $A = e^{\sigma/2}\sinh\sqrt{\xi^2+\sigma^2/4}/\sqrt{\xi^2+\sigma^2/4}$,

$$Z_{1/2} = 2e^{\sigma/4}\cosh(\xi/2) \text{ and } Z_1 = e^{\sigma} + 2e^{\sigma/2}\cosh\sqrt{\xi^2+\sigma^2/4}.$$

The corresponding equations for the phase-space distribution $W_S(\vartheta,\varphi)$ can be obtained from Eqs. (9)–(12), (16), and (19) and are given by

$$W_{1/2}(\vartheta,\varphi) = \frac{1}{2}[1 + \tanh(\xi/2)\sin\vartheta\cos\varphi], \quad (26)$$

$$W_1(\vartheta,\varphi) = \frac{1}{2Z_1}\{e^{\sigma}(1 - \sin^2\vartheta\cos^2\varphi) + e^{\sigma/2}\cosh\sqrt{\xi^2+\sigma^2/4}(1+\sin^2\vartheta\cos^2\varphi) + (\sigma A/2) \times[\cos 2\vartheta + \sin^2\vartheta\cos^2\varphi + (4\xi/\sigma)\sin\vartheta\cos\varphi]\}, \quad (27)$$

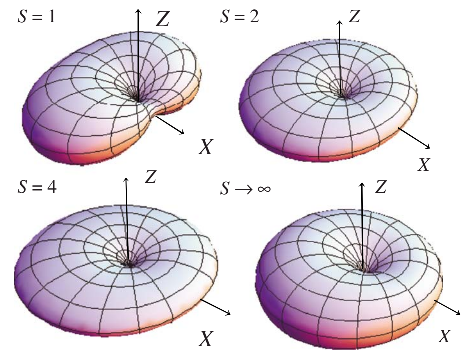

FIG. 1. (Color online) Three-dimensional (3D) plot of $\beta V(\vartheta,\varphi)$ for $\sigma'=10$, $h=0.1$, and various values of $S=1$, 2, 4, and $S\to\infty$ (classical limit).

$$W_{3/2}(\vartheta,\varphi) = \frac{e^{5\sigma/4}}{4Z_{3/2}}[e^{\xi/2}f^{+}(\vartheta,\varphi) + e^{-\xi/2}f^{-}(\vartheta,\varphi)], \quad (28)$$

etc., where

$$Z_{3/2} = 2e^{5\sigma/4}(e^{-\xi/2}\cosh\sqrt{\xi^2+\xi\sigma+\sigma^2} + e^{\xi/2}\cosh\sqrt{\xi^2-\xi\sigma+\sigma^2})$$

and

$$f^{\pm}(\vartheta,\varphi) = \frac{\sigma\sinh\sqrt{\xi^2\mp\xi\sigma+\sigma^2}}{\sqrt{\xi^2\mp\xi\sigma+\sigma^2}}\Big[2(1\pm\sin^3\vartheta\cos^3\varphi) - 3\sin^2\vartheta(1\pm\sin\vartheta\cos\varphi) \mp \frac{\xi}{\sigma}(1\pm\sin\vartheta\cos\varphi) \times(1\mp 4\sin\vartheta\cos\varphi + \sin^2\vartheta\cos^2\varphi)\Big] + 2\cosh\sqrt{\xi^2\mp\xi\sigma+\sigma^2}(1\pm\sin^3\vartheta\cos^3\varphi).$$

As S increases, the analytical equations for the Wigner function $W_S(\vartheta,\varphi)$ become more and more complicated and thus rather impractical because $W_S(\vartheta,\varphi)$ may always be calculated much faster numerically from Eq. (9).

Calculations of $\beta V(\vartheta,\varphi) = \text{const} - \ln W_S(\vartheta,\varphi)$ [$V(\vartheta,\varphi)$ has the meaning of an "effective" free energy potential] are shown in Fig. 1 for various values of S and $\sigma' = \sigma S^2 = 5$ and $h = \xi/(2\sigma S) = 0.1$. In the classical limit ($S\to\infty$, ξS=const $=\xi'$, σS^2=const=σ'), the effective potential $V(\vartheta,\varphi)$ becomes the classical free energy $V_{cl}(\vartheta,\varphi)$ given by

$$\beta V_{cl}(\vartheta,\varphi) = \text{const} - \sigma'(\cos^2\vartheta + 2h\cos\varphi\sin\vartheta),$$

which is also shown in Fig. 1 for comparison. The effective potential $V(\vartheta,\varphi)$ (just as the classical free energy $V_{cl}(\vartheta,\varphi)$] has two equivalent minima and one saddle point in the plane $\varphi=0$ at $\vartheta=\pi/2$; the potential characteristics (such as the shape and barrier heights) strongly depend on S, e.g., the smallest barrier height increases with increasing S from 0 (at $S=\frac{1}{2}$) to its classical value $\sigma'(1-h^2)$.

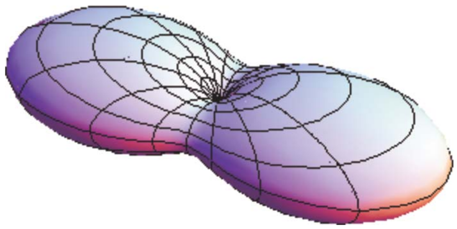

FIG. 2. (Color online) 3D plot of $\beta V(\vartheta,\varphi)$ for $S=2$, $\sigma'=5$, and $\delta'=2$.

V. BIAXIAL SYSTEM

We now calculate the Wigner function of a biaxial spin system with Hamiltonian

$$\beta\hat{H}_S = -\sigma\hat{S}_Z^2 + \delta(\hat{S}_X^2 - \hat{S}_Y^2) \tag{29}$$

commonly used to describe the magnetic properties of an octanuclear iron(III) molecular cluster Fe8.[5,42] For Fe8, $S=10$, $\sigma T=0.275$ K, and $\delta T=0.046$ K.[42] The density matrix $\hat{\rho}_S=e^{-\beta\hat{H}_S}/Z_S$ can be given in simple closed form for small S. For example, for $S=\frac{1}{2}$, $S=1$, etc., we have after matrix algebra

$$\hat{\rho}_{1/2} = \frac{e^{\sigma/4}}{Z_{1/2}}\hat{I}, \tag{30}$$

$$\hat{\rho}_1 = \frac{1}{Z_1}[\hat{I} + (e^{\sigma}\cosh\delta - 1)\hat{S}_Z^2 - e^{\sigma}\sinh\delta(\hat{S}_X^2 - \hat{S}_Y^2)], \tag{31}$$

$$\hat{\rho}_{3/2} = \frac{e^{5\sigma/4}\sinh\sqrt{3\delta^2+\sigma^2}}{Z_{3/2}\sqrt{3\delta^2+\sigma^2}}\{\sigma\hat{S}_Z^2 - \delta(\hat{S}_X^2 - \hat{S}_Y^2) + [\sqrt{3\delta^2+\sigma^2}\coth\sqrt{3\delta^2+\sigma^2} - 5\sigma/4]\hat{I}\}, \tag{32}$$

where $Z_{1/2}=2e^{\sigma/4}$, $Z_1=1+2e^{\sigma}\cosh\delta$, and $Z_{3/2}=4e^{5\sigma/4}\cosh\sqrt{3\delta^2+\sigma^2}$. The corresponding equations for $W_S(\vartheta,\varphi)$ are

$$W_{1/2}(\vartheta,\varphi) = 1/2, \tag{33}$$

$$W_1(\vartheta,\varphi) = \frac{1}{2Z_1}[\sin^2\vartheta + e^{\sigma}\cosh\delta(1+\cos^2\vartheta) - e^{\sigma}\sinh\delta\sin^2\vartheta\cos 2\varphi], \tag{34}$$

$$W_{3/2}(\vartheta,\varphi) = \frac{1}{4} + \frac{3\tanh\sqrt{3\delta^2+\sigma^2}}{8\sqrt{3\delta^2+\sigma^2}}[\sigma\cos^2\vartheta - \delta\sin^2\vartheta\cos 2\varphi - \sigma/3]. \tag{35}$$

The effective potential $\beta V(\vartheta,\varphi)=\text{const}-\ln W_S(\vartheta,\varphi)$ is shown in Fig. 2 for $S=2$, $\sigma'=\sigma S^2=5$, and $\delta'=\delta S^2=5$. In the classical limit ($S\to\infty$, $\delta'=\delta S^2=\text{const}$, and $\sigma S^2=\text{const}=\sigma'$), the effective potential $V(\vartheta,\varphi)$ again tends to the classical free energy $V_{cl}(\vartheta,\varphi)$ given by

$$\beta V_{cl}(\vartheta,\varphi) = \text{const} - (\sigma'\cos^2\vartheta - \delta'\cos 2\varphi\sin^2\vartheta).$$

The effective potential $V(\vartheta,\varphi)$ [just as $V_{cl}(\vartheta,\varphi)$] has two equivalent minima and two saddle points in the plane XZ at $\vartheta=\pi/2$; potential characteristics (such as the shape and barrier heights) again strongly depend on S. In particular, the barrier height increases with increasing S from 0 (at $S=1/2$) to its classical value σ'.

VI. CUBIC SYSTEM

Finally, we calculate the Wigner function of a cubic spin system in a longitudinal dc field with Hamiltonian

$$\beta\hat{H}_S = -\xi S_Z - \sigma(\hat{S}_X^4 + \hat{S}_Y^4 + \hat{S}_Z^4)/2,$$

where σ is the dimensionless anisotropy parameter, which may be either positive or negative. For small S, the density matrix $\hat{\rho}_S=e^{-\beta\hat{H}_S}/Z_S$ can again be given in closed form. For example, for $S=1/2$, $S=1$, etc., we have

$$\hat{\rho}_{1/2} = \frac{e^{3\sigma/32}}{Z_{1/2}}[\hat{I}\cosh(\xi/2) + 2\hat{S}_Z\sinh(\xi/2)], \tag{36}$$

$$\hat{\rho}_1 = \frac{e^{\sigma}}{Z_1}[\hat{I} + \sinh\xi\hat{S}_Z + 2\sinh^2(\xi/2)\hat{S}_Z^2], \tag{37}$$

$$\hat{\rho}_{3/2} = \frac{e^{123\sigma/32}}{Z_{3/2}}\left\{\frac{1}{8}[9\cosh(\xi/2) - \cosh(3\xi/2)]\hat{I} + \frac{1}{12}[27\sinh(\xi/2) - \sinh(3\xi/2)]\hat{S}_Z + 2\cosh(\xi/2) \times[\sinh(\xi/2)\hat{S}_Z]^2 + \frac{4}{3}[\sinh(\xi/2)\hat{S}_Z]^3\right\}, \tag{38}$$

$$\hat{\rho}_2 = \frac{1}{Z_2}\left\{\left(e^{12\sigma} - \frac{6\sigma}{\xi}R\right)\hat{I} + \frac{1}{6}(8e^{9\sigma}\sinh\xi - R)\hat{S}_Z + \frac{1}{12}\left(16e^{9\sigma}\cosh\xi - 15e^{12\sigma} - P + \frac{93\sigma}{4\xi}R\right)\hat{S}_Z^2 - \frac{1}{6}(2e^{9\sigma}\sinh\xi - R)\hat{S}_Z^3 + \frac{1}{12}\left(3e^{12\sigma} - 4e^{9\sigma}\cosh\xi + P - \frac{9\sigma}{4\xi}R\right)\times\hat{S}_Z^4 + \frac{\sigma}{4\xi}R(\hat{S}_X^4 + \hat{S}_Y^4)\right\}, \tag{39}$$

where

$$Z_{1/2} = 2\cosh(\xi/2)e^{3\sigma/32}, \quad Z_1 = (1+2\cosh\xi)e^{\sigma},$$

$$Z_{3/2} = 4\cosh(\xi/2)\cosh\xi e^{123\sigma/32},$$

$$Z_2 = e^{9\sigma}(e^{3\sigma} + 2\cosh\xi + 2e^{3\sigma/2}\cosh[2\xi\sqrt{1+(3\sigma/4\xi)^2}]),$$

$$P = e^{21\sigma/2}\cosh[2\xi\sqrt{1+(3\sigma/4\xi)^2}],$$

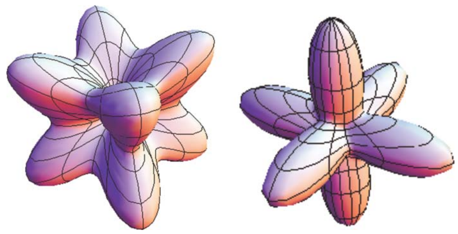

FIG. 3. (Color online) 3D plot of $\beta V(\vartheta,\varphi)$ for positive (left) and negative (right) cubic anisotropies at $S=4$ and $\xi=0$.

$$R = e^{21\sigma/2}\sinh[2\xi\sqrt{1+(3\sigma/4\xi)^2}]/\sqrt{1+(3\sigma/4\xi)^2}.$$

The corresponding equations for $W_S(\vartheta,\varphi)$ are

$$W_{1/2}(\vartheta,\varphi) = e^{3\sigma/32}[\cosh(\xi/2)+\sinh(\xi/2)\cos\vartheta]/Z_{1/2}, \tag{40}$$

$$W_1(\vartheta,\varphi) = e^{\sigma}[\cosh(\xi/2)+\sinh(\xi/2)\cos\vartheta]^2/Z_1, \tag{41}$$

$$W_{3/2}(\vartheta,\varphi) = e^{123\sigma/32}[\cosh(\xi/2)+\sinh(\xi/2)\cos\vartheta]^3/Z_{3/2}, \tag{42}$$

$$\begin{aligned} W_2(\vartheta,\varphi) = \frac{1}{8Z_2}\{&2e^{9\sigma}\sin^2\vartheta[4\sin\xi\cos\vartheta \\ &+\cosh\xi(3+\cos 2\vartheta)]+3e^{12\sigma}\sin^4\vartheta \\ &+P(8\cos^2\vartheta+\sin^4\vartheta) \\ &+4R[\cos\vartheta+\cos^3\vartheta+(3\sigma/16\xi)\cos 4\varphi\sin^4\vartheta]\}. \end{aligned} \tag{43}$$

For $\xi=0$, Eq. (43) yields

$$\begin{aligned} W_2(\vartheta,\varphi) = \frac{1}{2(3+2e^{3\sigma})}[&1+e^{3\sigma}+(e^{3\sigma}-1)(\sin^2 2\vartheta \\ &+\sin^4\vartheta\sin^2 2\varphi)/4]. \end{aligned} \tag{44}$$

The effective potential $\beta V(\vartheta,\varphi)=\text{const}-\ln W_S(\vartheta,\varphi)$ is shown in Fig. 3 for $\sigma'=\sigma S^4=\pm 8$, $\xi=0$, and $S=4$. In the classical limit ($S\to\infty$, $\sigma S^4=\text{const}=\sigma'$), the effective potential once more tends to the classical free energy $V_{cl}(\vartheta,\varphi)$ given by

$$\beta V_{cl}(\vartheta,\varphi) = \text{const} + \sigma'(\sin^2 2\vartheta + \sin^4\vartheta\sin^2 2\varphi).$$

For positive anisotropy constant $\sigma>0$, the cubic potential has 6 minima (wells), 8 maxima, and 12 saddle points. For $\sigma<0$, the maxima and minima are interchanged. The potential characteristics (such as the shape and barrier heights) again strongly depend on S. In particular, the smallest barrier height again increases with increasing S from 0 (at $S=\frac{1}{2}$) to its classical value σ'.

It is apparent from the examples chosen that the Wigner–Stratonovich transformation allows one to calculate the equilibrium phase-space distribution (Wigner function) via its finite Fourier series representation for any given anisotropy. The results may be used to estimate the reversal time of the magnetization from TST as well as to include thermal effects in the quantum generalization of Thiaville's calculation of switching field curves and/or surfaces. However, in accordance with the stated objectives of the paper we shall first demonstrate how the phase-space representation of the Hamiltonian operator for a given spin system may be used to calculate switching field curves as a function of spin at zero temperature.

VII. SWITCHING FIELD CURVES

We recall that the first calculation of the magnetization reversal of single-domain ferromagnetic particles with uniaxial anisotropy subjected to an applied field was made by Stoner and Wohlfarth[7] with the hypothesis of coherent rotation of the magnetization and zero temperature so that thermally induced switching between the potential minima is ignored. In the simplest uniaxial anisotropy as considered by them, the magnetization reversal occurs at the particular value of the applied field (switching field) which destroys the bistable nature of the potential. The parametric plot of the parallel vs the perpendicular component of the switching field then yields the famous astroids. In the general approach to the calculation of switching curves via the geometrical method of Thiaville,[8] the switching field curves or surfaces may be constructed for particles with arbitrary anisotropy at zero temperature. These calculations again, however, pertain to particles where the magnetization may be represented by a single macrospin (coherent rotation of the magnetization). In order to generalize Thiaville's geometrical method[8] to include spin size effects, we have to calculate the Weyl symbol (c number) $H_S(\vartheta,\varphi)$ corresponding to the Hamiltonian $\hat{H}_S$, which is defined as

$$\begin{aligned} H_S(\vartheta,\varphi) &= \text{Tr}[\hat{H}_S\hat{w}_{-1}(\vartheta,\varphi)] \\ &= \sqrt{\frac{4\pi}{2S+1}}\text{Tr}\left[\hat{H}_S\sum_{L=0}^{2S}\sum_{M=-L}^{L}C^{S,S}_{S,S,L,0}Y^*_{L,M}\hat{T}^{(S)}_{L,M}\right]. \end{aligned} \tag{45}$$

Then treating the c-number representation $H_S(\vartheta,\varphi)$ as an arbitrary potential energy one may in principle calculate the switching fields using Thiaville's method.[8] We illustrate this by considering the uniaxial

$$\beta\hat{H}_S^{un} = -\sigma_1\hat{S}_Z^2, \tag{46}$$

biaxial

$$\beta\hat{H}_S^{bi} = -\sigma_1 S_Z^2 + \delta(\hat{S}_X^2 - \hat{S}_Y^2), \tag{47}$$

cubic

$$\beta\hat{H}_S^{cub} = -\sigma_2(\hat{S}_X^4 + \hat{S}_Y^4 + \hat{S}_Z^4)/2, \tag{48}$$

and mixed anisotropy

$$\beta\hat{H}_S^{mix} = -\sigma_1\hat{S}_Z^2 - \sigma_2\hat{S}_Z^4 + \chi(\hat{S}_+^4 + \hat{S}_-^4) \tag{49}$$

Hamiltonians. The mixed anisotropy Hamiltonian (49) is commonly used to describe the magnetic properties of the dodecanuclear manganese molecular cluster Mn12.[42] For

Mn12, $S=10$, $\sigma_1 T=0.56$ K, $\sigma_2 T=1.1\times 10^{-3}$ K, and $\chi T = \pm 3\times 10^{-5}$ K.[42]

The Weyl symbols $H_S^{un}(\vartheta,\varphi)$, $H_S^{bi}(\vartheta,\varphi)$, $H_S^{cub}(\vartheta,\varphi)$, and $H_S^{mix}(\vartheta,\varphi)$ corresponding to the Hamiltonian operators (46)–(49) can be calculated from the general finite Fourier series representation equation (45) noting Eqs. (16) and (19). We obtain after some algebra

$$H_S^{un} = -\sigma_1 S(S-1/2)\cos^2\vartheta - \sigma_1 S/2, \quad (50)$$

$$H_S^{bi} = -\sigma_1 S[(S-1/2)(\cos^2\vartheta - \Delta\cos 2\varphi \sin^2\vartheta) + 1/2], \quad (51)$$

$$H_S^{cub} = -\sigma_2 S(2S^3+3S-1)/4 + \sigma_2 S(S-1)(S-1/2)(S-3/2) \times(\sin^2 2\vartheta + \sin^4\vartheta\sin^2 2\varphi)/4, \quad (52)$$

and

$$H_S^{mix} = -\frac{S}{4}[2\sigma_1 + \sigma_2(3S-1)] - S(S-1/2)[\sigma_1 + \sigma_2(3S-2)] \times\cos^2\vartheta - \frac{1}{2}S(S-1)(S-3/2)(S-1/2)[2\sigma_2\cos^4\vartheta - \chi\sin^4\vartheta\cos 4\varphi], \quad (53)$$

respectively, where $\Delta=\delta/\sigma_1$. If we further suppose that a uniform external magnetic field $\mathbf{H}$ is applied along the x-z plane, the Zeeman term operator $\beta\hat{H}_S = -\xi\sin\psi\hat{S}_X - \xi\cos\psi\hat{S}_Z$ transforms to the phase space as

$$\beta H_S = -\xi S\cos(\vartheta-\psi), \quad (54)$$

where ψ is the angle between the applied field $\mathbf{H}$ and the Z axis. Thus the switching fields $\mathbf{h}_{un}$, $\mathbf{h}_{bi}$, and $\mathbf{h}_{cub}$ in the x-z plane (i.e., for $\varphi=0$) can be calculated from Eqs. (50)–(52) so that

$$\mathbf{h}_{un} = Q_{un}\mathbf{h}_{un}^{cl}, \quad \mathbf{h}_{bi} = Q_{bi}\mathbf{h}_{bi}^{cl}, \quad \text{and } \mathbf{h}_{cub} = Q_{cub}\mathbf{h}_{cub}^{cl}, \quad (55)$$

where the quantum correction factors Q_{un}, Q_{bi}, and Q_{cub} and corresponding classical switching fields $\mathbf{h}_{un}^{cl}$, $\mathbf{h}_{bi}^{cl}$, and $\mathbf{h}_{cub}^{cl}$ are

$$Q_{un} = Q_{bi} = (S-1/2)/S, \quad (56)$$

$$Q_{cub} = (S-1/2)(S-1)(S-3/2)/S^3,$$

$$\mathbf{h}_{un}^{cl} = (\sin^3\psi, \cos^3\psi),$$

$$\mathbf{h}_{cub}^{cl} = [\sin^3\psi(3\cos 2\psi + 2), \cos^3\psi(3\cos 2\psi - 2)],$$

$$\mathbf{h}_{bi}^{cl} = (\sin\psi[2\Delta + f(\psi)], \cos\psi[2 - f(\psi)]), \quad (57)$$

and $f(\psi) = (1+\Delta)\sin^2\psi + |2\Delta - (1+\Delta)\sin^2\psi|$. For mixed anisotropy, the corresponding equation for the switching field $\mathbf{h}_{mix}$ is much more complicated and must be calculated numerically. The parametric plots of the parallel h_Z vs the perpendicular h_X component of the switching field yield the astroids and hypocycloids for uniaxial and cubic systems, respectively, along with the corresponding quantum correction factors [see Figs. 4(a) and 4(c)]. For biaxial and mixed anisotropies, the behavior of the switching fields is much more involved and is shown in Figs. 4(b) and 4(d). In general the figures indicate that the switching field amplitudes *increase* markedly with *increasing* S tending to their classical limiting values as $S\to\infty$ corresponding to diminishing tunneling effects as that mechanism is gradually shut off.

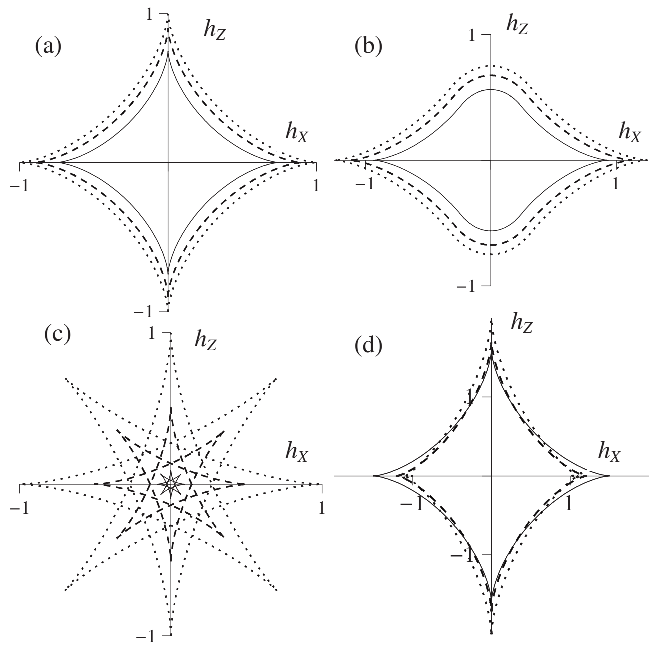

FIG. 4. Spin dependence of switching field curves for (a) uniaxial, (b) biaxial at $\sigma_1/\delta=0.25$, (c) cubic, and (d) mixed (at $\sigma_1/\sigma_2=0.5$ and $\chi=0$) anisotropies calculated at $S=2$ (solid lines), 5 (dashed lines), and $S\to\infty$ (dotted lines; classical limit).

We emphasize that the above calculations because they are entirely based on the phase-space representation of the Hamiltonian operator ignore thermal effects. To account for these it is necessary to estimate the temperature dependence of the reversal time of the magnetization which may be accomplished using transition state theory (TST). The estimation of the reversal time of magnetization in the context of TST is, probably, the most promising application of the phase-space approach. TST as we shall now see again involves only the quantum equilibrium distributions, which we have calculated in the preceding sections.

VIII. TRANSITION STATE THEORY REVERSAL TIME OF THE MAGNETIZATION

We have mentioned that TST affords the simplest possible description of quantum corrections to thermally activated decay due to thermal agitation. In applying TST to classical spins (i.e., magnetic moments $\boldsymbol{\mu}$), in order to evaluate the escape rate from a metastable orientation i to another metastable orientation j, we suppose that the free energy $V(\vartheta,\varphi)$ of a magnetic moment $\boldsymbol{\mu}$ has a multistable structure with minima at $\mathbf{n}_i$ and $\mathbf{n}_j$ separated by a potential barrier with a saddle point at $\mathbf{n}_0$. In the low temperature limit (high barrier approximation), as far as TST is concerned, the escape rate Γ_{cl} may be estimated as

$$\Gamma_{cl} \sim I_0^{cl}/Z_i^{cl}, \tag{58}$$

where $Z_i^{cl} \sim \int_{well} e^{-\beta V(\vartheta,\varphi)} \sin\vartheta d\vartheta d\varphi$ is the well partition function and I_0^{cl} is the total current of the (magnetization) representative points at the saddle point. In order to evaluate the well partition function Z_i^{cl}, we suppose[10,11] that the free energy V near the minimum $\mathbf{n}_i$ can be approximated as

$$V_{cl} = V_{cl}(\mathbf{n}_k) + \tfrac{1}{2}[c_1^{(k)}(u_1^{(k)})^2 + c_2^{(k)}(u_2^{(k)})^2], \tag{59}$$

where $(u_1^{(i)}, u_2^{(i)}, u_3^{(i)})$ denote the direction cosines of $\boldsymbol{\mu}$ near $\mathbf{n}_i$, $c_1^{(i)} = \partial^2 V_{cl}/\partial u_1^{(i)2}$, and $c_2^{(i)} = \partial^2 V_{cl}/\partial u_2^{(i)2}$. Hence

$$Z_i^{cl} \sim \int_{well} e^{-\beta V_{cl}(u_1^{(i)},u_2^{(i)})} du_1^{(i)} du_2^{(i)} \sim \frac{2\pi}{\beta\sqrt{c_1^{(i)}c_2^{(i)}}} e^{-\beta V(\mathbf{n}_i)}. \tag{60}$$

The total current I_0^{cl} may be estimated as (by supposing that the x axis of the local coordinate system at the saddle point $\mathbf{n}_0$ is in the same direction as the probability current $\mathbf{J}_0$ over the saddle and recalling that the Boltzmann distribution holds everywhere)

$$I_0^{cl} \sim \int_{saddle} \theta(u_1^{(0)})\delta(u_2^{(0)}) J_0(u_1^{(0)},u_2^{(0)}) e^{-\beta V_{cl}(u_1^{(0)},u_2^{(0)})} du_1^{(0)} du_2^{(0)}$$

$$\approx \frac{\gamma}{\mu\beta}\int_{saddle} de^{-\beta V_{cl}} \approx \frac{\gamma}{\mu\beta} e^{-\beta V_{cl}(\mathbf{n}_0)}, \tag{61}$$

where $J_0 = -(\gamma/\mu)\partial V_{cl}/\partial u_1^{(0)} = (\gamma/\beta\mu)\partial \ln(e^{-\beta V_{cl}})/\partial u_1^{(0)}$ is a divergence-free current density at the saddle point and θ is the unit step function. Hence, noting Eqs. (60) and (61), Eq. (58) yields the classical TST formula for spins

$$\Gamma_{cl} \sim (\omega_i/2\pi) e^{-\beta \Delta V^{cl}}, \tag{62}$$

where the attempt frequency

$$\omega_i = \gamma\sqrt{c_1^{(i)}c_2^{(i)}}/\mu \tag{63}$$

is the well (precession) frequency and $\Delta V_{cl} = V_{cl}(\mathbf{n}_0) - V_{cl}(\mathbf{n}_i)$ is the potential barrier height (the determination of which involves detailed knowledge of the energy landscape).

The quantum escape rate Γ_i for a spin from a metastable orientation i to another metastable orientation j as determined by quantum TST may be given by an equation similar to Eq. (58), viz.,

$$\Gamma_i \sim I_0/Z_i. \tag{64}$$

However, the well partition function Z_i and the total current over the saddle point I_0 must now be evaluated using the equilibrium phase-space distribution function $W(\vartheta,\varphi)$ instead of the Boltzmann distribution $\sim\exp[-\beta V_{cl}(\vartheta,\varphi)]$. Just as uniaxial systems,[36] the distribution W can be approximated in the vicinity of the metastable minimum $\mathbf{n}_i$ by the spin in a uniform field or Zeeman energy distribution given by Eq. (20), viz.,

$$W_S(\vartheta,\varphi) = W_S(\mathbf{n}_i) e^{-S\xi_i}[\cosh(\xi_i/2) + \sinh(\xi_i/2)F_i(\vartheta,\varphi)]^{2S}, \tag{65}$$

where $F_i(\vartheta,\varphi) = \gamma_{X_i}\sin\vartheta\cos\varphi + \gamma_{Y_i}\sin\vartheta\sin\varphi + \gamma_{Z_i}\cos\vartheta$ with $F_i(\vartheta_i,\varphi_i)=1$, γ_{X_i}, γ_{Y_i}, γ_{Z_i} are the direction cosines of the effective field $\mathbf{H}_i = -\partial V/\partial\boldsymbol{\mu}$ in the vicinity of minimum $\mathbf{n}_i$, and $\boldsymbol{\mu} = \hbar\gamma\mathbf{S}$ is the magnetic moment, $\xi_i = \beta\hbar|\boldsymbol{\omega}_i|$ is the normalized precession frequency $\boldsymbol{\omega}_i = \gamma\mathbf{H}_i$. All the foregoing results rely on the fact that the dynamics of a spin near $\mathbf{n}_i$ at low temperatures comprise steady precession in the *effective* magnetic field $\mathbf{H}_i$ in the well. The precession frequency $\boldsymbol{\omega}_i$ can be estimated from the well angular frequency (i.e., attempt frequency) Eq. (63), where the coefficients $c_1^{(i)}$ and $c_2^{(i)}$ are determined from the Taylor series expansion of the Weyl symbol $H_S(\vartheta,\varphi)$ of the Hamiltonian $\hat{H}_S$ of a spin

$$H_S = H_S(\mathbf{n}_k) + \tfrac{1}{2}[c_1^{(k)}(u_1^{(k)})^2 + c_2^{(k)}(u_2^{(k)})^2] \tag{66}$$

(ω_i can also be found experimentally by measuring the critical switching field surface and then applying Thiaville's geometrical methods). Noting Eq. (21), we can now estimate the well partition function as

$$Z_i \sim W_S(\mathbf{n}_i)e^{-S\xi_i}\int_{well}[\cosh(\xi_i/2) + \sinh(\xi_i/2)F_i(\vartheta,\varphi)]^{2S}\sin\vartheta d\vartheta d\varphi$$

$$= 4\pi W_S(\mathbf{n}_i)e^{-S\xi_i}\frac{\sinh[(S+1/2)\xi_i]}{(2S+1)\sinh(\xi_i/2)} \approx \frac{2\pi W_S(\mathbf{n}_i)}{(S+1/2)(1-e^{-\xi_i})}. \tag{67}$$

The current I_0 at the saddle point $\mathbf{n}_0$ may also be estimated just as in Eq. (61), viz.,

$$I_0 \sim \int_{top}\theta(u_1^{(0)})\delta(u_2^{(0)})J_0(u_1^{(0)},u_2^{(0)})W(u_1^{(0)},u_2^{(0)})du_1^{(0)}du_2^{(0)}$$

$$\sim \gamma W(\mathbf{n}_0)/(\mu\beta), \tag{68}$$

where $J_0 = -(\gamma/\mu)\partial V/\partial u_1^{(0)} = (\gamma/\beta\mu)\partial \ln W/\partial u_1^{(0)}$. Hence we have the TST escape rate for spins as determined from Eqs. (64), (67), and (68), viz.,

$$\Gamma_i \sim \frac{\gamma(S+1/2)(1-e^{-\xi_i})}{2\pi\mu\beta}\frac{W_S(\mathbf{n}_0)}{W_S(\mathbf{n}_i)}. \tag{69}$$

To compare this equation with the classical TST equation (62), we can write the resulting escape rate formula for spins in the canonical form

$$\Gamma \sim (\omega_i/2\pi)\Xi e^{-\beta\Delta V}, \tag{70}$$

where

$$\Xi = (S+1/2)(1-e^{-\xi_i})/S\xi_i \quad \text{and} \quad \beta\Delta V = \ln[W_S(\mathbf{n}_0)/W_S(\mathbf{n}_i)]$$

are, respectively, the *quantum correction* factor and *effective* barrier height, i.e., the argument of the exponential. Here both $\beta\Delta V$ and Ξ strongly depend on the spin number S yielding $\beta\Delta V \to \beta\Delta V_{cl}$ and $\Xi \to 1$, respectively, in the classical limit, $S\to\infty$. For example, for a uniaxial system with Hamiltonian $\beta\hat{H}_S = -\sigma\hat{S}_Z^2$, we have[37]

$$\omega_i = \sigma(2S-1)/(\hbar\beta),$$

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

$$\beta\Delta V = \sigma S^2 - \ln \frac{(2S)!}{2^{2S}} \sum_{m=-S}^{S} \frac{e^{\sigma m^2}}{(S+m)!(S-m)!}.$$

Just as the classical case, having evaluated the escape rate Γ_i for a particular anisotropy, one can calculate the reversal time at finite temperatures. In particular, by equating reversal time to measuring time this calculation allows one to estimate the switching field curves at finite temperatures just as the classical theory.[43] One should remember, however, that TST always implies that the dissipation to the bath does not affect the escape rate. Nevertheless, the results should still apply in a *wide range of dissipation* for which thermal noise is sufficiently strong to thermalize the escaping system yet insufficient to disturb the thermal equilibrium in the well, i.e., an equilibrium distribution still prevails everywhere including the saddle point. In the context of the classical Kramers escape rate theory,[16] this is the so called *intermediate damping* case.

IX. DISCUSSION

We have amply demonstrated that the phase-space method formally representing the quantum mechanics of spins as a statistical theory in the classical configuration space of polar angles (ϑ, φ) (which are now the canonical variables) may be used to construct equilibrium distribution (Wigner) functions for nonaxially symmetric model spin Hamiltonians. The Wigner function may be represented using the Wigner–Stratonovich map as a Fourier series just as the corresponding classical orientational distribution and transparently reduces to it in the classical limit. Moreover, relevant quantum mechanical averages may be calculated in a manner analogous to the corresponding classical averages using the Weyl symbol of the appropriate quantum operator. The Wigner functions can now be applied to important magnetic problems such as the equilibrium magnetization, switching, and hysteresis curves, which require only a knowledge of equilibrium distributions. Two examples given in the paper are the estimation of the reversal time of the magnetization using TST and the spin dependence of the switching fields as generalized to arbitrary magnetocrystalline anisotropy-Zeeman energy Hamiltonians by Thiaville.[8] In the latter case, it is obvious that the behavior of the switching field curves and/or surfaces as a function of spin size may be determined using the Weyl symbol of the relevant Hamiltonian and the phase-space representation generated by the Wigner–Stratonovich map just as the solution of the classical problem. This fact is important particularly from an experimental point of view as the transition between magnetic molecular cluster and single-domain ferromagnetic nanoparticle behavior is essentially demarcated via the hysteresis loops and the corresponding switching fields.[5] Yet another advantage of the phase-space representation is that via TST as corrected for spin size effects (which is readily apparent from that representation) it is possible to predict the temperature dependence of the switching fields and corresponding hysteresis loops within the limitations imposed by TST. This is likely to be of interest in experiments seeking evidence for macroscopic quantum tunneling where the temperature dependence of the loops is crucial as the loops are used[5] to demarcate tunneling behavior from thermal agitation behavior.

We have refrained in this paper from a detailed discussion of nonequilibrium phenomena involving quantum master equations in the phase-space representation which in the classical limit reduce to the Fokker–Planck equation (this will be given elsewhere). An example of such equations occurs in the treatment of the relaxation of an assembly of noninteracting spins (see, e.g., Refs. 44–47). Here a knowledge of the equilibrium phase-space distribution is important in two respects. The first is in formulating the initial conditions for their solution as the appropriate quantum equilibrium distribution must now play the role of the Boltzmann distribution in the corresponding classical problem. Secondly, the equilibrium quantum distribution plays a vital role in the determination of the diffusion coefficients in a quantum master equation because this distribution must be the stationary solution of that equation.[47–49] This fact, which is analogous to Einstein and Smoluchowski's imposition of the Maxwell–Boltzmann distribution as the stationary solution of the Fokker–Planck equation in order to determine diffusion coefficients in that equation, will allow one to calculate the diffusion coefficients in a quantum master equation in like manner. We remark, however, that calculation of the diffusion coefficients for nonaxially symmetric potentials is much more complicated than the corresponding task for axial symmetry since two canonical variables are involved rather than the single polar angle ϑ. The restriction to axial symmetry also gives rise to considerable mathematical simplifications since the quantum master equation now has essentially the same mathematical form as the classical Fokker–Planck equation in the single coordinate ϑ. Hence results already available for that equation such as formulas for the mean first passage time, integral relaxation time, etc., may be directly carried over to the quantum case.[47] This is not so for nonaxially symmetric potentials as the two variables involved give rise to a perturbation problem similar to that encountered in solving the Wigner problem for point particles in classical phase space. In the context of nonequilibrium effects in nonaxially symmetric potentials the most important quantity is the relaxation time as calculated from the appropriate quantum master equation as that allows one to determine the dependence of the quantum escape rate and so the reversal time on the dissipative coupling to the heat bath. The TST escape rate as calculated from the Wigner function is also important in this context as it constitutes the so called intermediate damping escape rate which is the limit of applicability of the intermediate to high damping quantum Kramers rate and may be obtained from that rate by letting the dissipation tend to 0. Thus the TST rate provides an important benchmark for both analytical calculations of the escape rate incorporating dissipation using quantum rate theory and numerical results obtained from the appropriate quantum master equation as well as allowing one to incorporate thermal effects in the switching fields.

ACKNOWLEDGMENTS

This publication has emanated from research conducted with the financial support of Science Foundation Ireland (Project No. 05/RFP/PHY/0070). We thank Derrick S. F. Crothers, P.-M. Déjardin, and Bernard P. J. Mulligan for helpful conversations.

APPENDIX: GENERALIZED COHERENT STATES AND WIGNER–STRATONOVICH TRANSFORMATION

As an example of a generalized coherent state representation of a spin system, one may consider the SU(2) coherent states $|S,\vartheta,\varphi\rangle$ defined as[50,51]

$$|S,\vartheta,\varphi\rangle=(1+|z|^2)^{-S}e^{z\hat{S}_-}|S,S\rangle, \quad (A1)$$

where $z=\tan(\vartheta/2)e^{i\varphi}$ and $\hat{S}_-=\hat{S}_X-i\hat{S}_Y$. The expansion of $|S,\vartheta,\varphi\rangle$ in the orthonormal basis of the eigenfunctions $|S,m\rangle$ of the spin operators $\hat{S}_Z$ and $\hat{\mathbf{S}}^2$ is given by

$$|S,\vartheta,\varphi\rangle=\cos^{2S}(\vartheta/2)\sum_{m=-S}^{S}\sqrt{\frac{(2S)!}{(S+m)!(S-m)!}}\times[\tan(\vartheta/2)e^{i\varphi}]^{S-m}|S,m\rangle, \quad (A2)$$

where the basis spin functions $|S,m\rangle$ are defined as[40]

$$|S,S\rangle=\begin{pmatrix}1\\0\\\vdots\\0\end{pmatrix},\quad |S,S-1\rangle=\begin{pmatrix}0\\1\\\vdots\\0\end{pmatrix},\ldots,\quad |S,-S\rangle=\begin{pmatrix}0\\0\\\vdots\\1\end{pmatrix}.$$

The coherent states $|S,\vartheta,\varphi\rangle$ possess the completeness properties so that an arbitrary quantum state of the spin system can be written in terms of $|S,\vartheta,\varphi\rangle$.[50,51]

The coherent state $|S,\vartheta,\varphi\rangle$ can also be presented in an equivalent form as

$$|S,\vartheta,\varphi\rangle=\chi_{S,S}(\vartheta,\varphi)e^{iS\varphi},$$

where $\chi_{S,\lambda}(\vartheta,\varphi)$ are the helicity basis functions defined as[40]

$$\chi_{S,\lambda}(\vartheta,\varphi)=\sum_{m=-S}^{S}D^S_{m,\lambda}(\varphi,\vartheta,0)|S,m\rangle.$$

Here $D^S_{m,\lambda}(\varphi,\vartheta,\psi)$ are the Wigner D functions.[40] The equivalence of both forms can be proved by noting that[40]

$$D^S_{m,\pm S}(\varphi,\vartheta,0)e^{\pm iS\varphi}=\sqrt{\frac{(2S)!}{(S+m)!(S-m)!}}\cos^{2S}(\vartheta/2)\times[\pm\tan(\vartheta/2)e^{\pm i\varphi}]^{S\mp m}.$$

Now one may introduce the transformation kernel $\hat{w}$ as[33,50,51]

$$\hat{w}=|S,\vartheta,\varphi\rangle\langle S,\vartheta,\varphi| =(2S)!\cos^{4S}(\vartheta/2)\times\sum_{m,m'=-S}^{S}\frac{e^{-i(m-m')\varphi}[\tan(\vartheta/2)]^{2S-m-m'}}{\sqrt{(S+m')!(S-m')!(S+m)!(S-m)!}}|S,m\rangle\times\langle S,m'|. \quad (A3)$$

By noting Eq. (A2) and that[40]

$$|S,m\rangle\langle S,m'|=\sum_{L=0}^{2S}\sqrt{\frac{2L+1}{2S+1}}C^{S,m}_{S,m',L,m-m'}T^{(S)}_{L,m-m'},$$

we have the kernel $\hat{w}$ in terms of the polarization operators $T^{(S)}_{L,M}$

$$\hat{w}=|S,\vartheta,\varphi\rangle\langle S,\vartheta,\varphi| =\frac{(2S)!\cos^{4S}(\vartheta/2)}{\sqrt{2S+1}}\sum_{L=0}^{2S}\sum_{M=-L}^{L}\sum_{m=-S}^{S}T^{(S)}_{L,M}\times\frac{\sqrt{2L+1}e^{-iM\varphi}[\tan(\vartheta/2)]^{2S-2m+M}C^{S,m}_{S,m-M,L,M}}{\sqrt{(S+m-M)!(S-m+M)!(S+m)!(S-m)!}}. \quad (A4)$$

Further simplification of Eq. (A4) is achieved using the known expression for the spherical harmonics, viz.,[40]

$$Y_{L,-M}=\frac{(-1)^M(2S)!\cos^{4S}(\vartheta/2)\sqrt{2L+1}}{\sqrt{4\pi}C^{S,S}_{S,S,L,0}}\times\sum_{m=-S}^{S}\frac{C^{S,m}_{S,m-M,L,M}e^{-iM\varphi}[\tan(\vartheta/2)]^{2S-2m+M}}{\sqrt{(S+m-M)!(S-m+M)!(S+m)!(S-m)!}} \quad (A5)$$

and $Y^*_{L,M}=(-1)^MY_{L,-M}$. Thus we have ultimately

$$\hat{w}=\sqrt{\frac{4\pi}{2S+1}}\sum_{L=0}^{2S}\sum_{M=-S}^{S}C^{S,S}_{S,S,L,0}Y^*_{L,M}T^{(S)}_{L,M}, \quad (A6)$$

so that the kernel $\hat{w}$ given by Eq. (A3) coincides with the operator $\hat{w}_{-1}$ defined by Eq. (7).

[1] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

[2] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1990), and references therein.

[3] D. Gatteschi, R. Sessoli, and J. Villain, *Molecular Nanomagnets* (Oxford University Press, Oxford, 2006).

[4] F. Bloch, Phys. Rev. **70**, 460 (1946).

[5] W. Wernsdorfer, Adv. Chem. Phys. **118**, 99 (2001).

[6] L. Néel, Ann. Geophys. (C.N.R.S.) **5**, 99 (1949).

[7] E. C. Stoner and E. P. Wohlfarth, Philos. Trans. R. Soc. London, Ser. A **240**, 599 (1948).

[8] A. Thiaville, Phys. Rev. B **61**, 12221 (2000).

[9] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).

[10] W. F. Brown, Jr., IEEE Trans. Magn. **15**, 1196 (1979).
[11] W. F. Brown, Jr., Phys. Rev. **130**, 1677 (1963).
[12] L. Landau and E. Lifshitz, Phys. Z. Sowjetunion **8**, 153 (1935).
[13] T. L. Gilbert, Phys. Rev. **100**, 1243 (1955) [abstract only; full report: Armor Research Foundation Project No. A059, Supplementary Report, May 1, 1956] (unpublished).
[14] R. Kubo and N. Hashitsume, Prog. Theor. Phys. **46**, 210 (1970).
[15] W. T. Coffey, Yu. P. Kalmykov, and J. T. Waldron, *The Langevin Equation*, 2nd ed. (World Scientific, Singapore, 2004).
[16] H. A. Kramers, Physica (Amsterdam) **7**, 284 (1940).
[17] W. T. Coffey, D. A. Garanin, and D. J. McCarthy, Adv. Chem. Phys. **117**, 483 (2001).
[18] W. T. Coffey, Y. P. Kalmykov, B. Ouari, and S. Titov, J. Magn. Magn. Mater. **292**, 372 (2005).
[19] C. P. Bean and J. D. Livingston, J. Appl. Phys. **30**, S120 (1959).
[20] J. L. van Hemmen and A. Sütö, Europhys. Lett. **1**, 481 (1986).
[21] E. M. Chudnovsky and L. Gunther, Phys. Rev. Lett. **60**, 661 (1988).
[22] O. B. Zaslavskii, Phys. Rev. B **42**, 992 (1990); V. V. Ulyanov and O. B. Zaslavskii, Phys. Rep. **216**, 179 (1992).
[23] D. A. Garanin and E. M. Chudnovsky, Phys. Rev. B **59**, 3671 (1999); **63**, 024418 (2000).
[24] E. P. Wigner, Phys. Rev. **40**, 749 (1932).
[25] W. P. Schleich, *Quantum Optics in Phase Space* (Wiley-VCH, Berlin, 2001).
[26] A. M. Perelomov, Usp. Fiz. Nauk **123**, 23 (1977).
[27] J. C. Várilly and J. M. Gracia-Bondía, Ann. Phys. (N.Y.) **190**, 107 (1989).
[28] A. B. Klimov, J. Math. Phys. **43**, 2202 (2002).
[29] O. Castaños, R. López-Peña, J. G. Hirsch, and E. López-Moreno, Phys. Rev. B **74**, 104118 (2006).
[30] D. Galetti, Physica A **374**, 211 (2007).
[31] R. L. Stratonovich, Zh. Eksp. Teor. Fiz. **31**, 1012 (1956) [Sov. Phys. JETP **4**, 891 (1957)].
[32] F. A. Berezin, Commun. Math. Phys. **40**, 153 (1975).
[33] Y. Takahashi and F. Shibata, J. Phys. Soc. Jpn. **38**, 656 (1975); J. Stat. Phys. **14**, 49 (1976).
[34] G. S. Agarwal, Phys. Rev. A **24**, 2889 (1981).
[35] G. S. Agarwal, Phys. Rev. A **57**, 671 (1998); J. P. Dowling, G. S. Agarwal, and W. P. Schleich, Phys. Rev. A **49**, 4101 (1994).
[36] Yu. P. Kalmykov, W. T. Coffey, and S. V. Titov, J. Phys. A: Math. Theor. **41**, 105302 (2008).
[37] Yu. P. Kalmykov and W. T. Coffey, J. Phys. A (to be published).
[38] E. P. Wigner, Z. Phys. Chem. Abt. B **19**, 203 (1932); Trans. Faraday Soc. **34**, 29 (1938).
[39] V. A. Benderskii, D. E. Makarov, and C. A. Wright, Adv. Chem. Phys. **88**, 1 (1994).
[40] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum* (World Scientific, Singapore, 1998).
[41] H. J. Lipkin, N. Meshkov, and A. J. Glick, Nucl. Phys. **62**, 188 (1965); N. Meshkov, A. J. Glick, and H. J. Lipkin, *ibid.* **62**, 199 (1965).
[42] A. Caneschi, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, A. Cornia, M. A. Novak, C. Paulsen, and W. Wernsdorfer, J. Magn. Magn. Mater. **200**, 182 (1999).
[43] P. M. Déjardin, H. Kachkachi, and Yu. P. Kalmykov, J. Phys. D (to be published).
[44] L. M. Narducci, C. M. Bowden, V. Bluemel, and G. P. Carrazana, Phys. Rev. A **11**, 280 (1975).
[45] N. Nashitsume, F. Shibata, and M. Shingu, J. Stat. Phys. **17**, 155 (1977); F. Shibata, Y. Takahashi, and N. Nashitsume, *ibid.* **17**, 171 (1977).
[46] F. Shibata, J. Phys. Soc. Jpn. **49**, 15 (1980); F. Shibata and M. Asou, *ibid.* **49**, 1234 (1980); F. Shibata and C. Ushiyama, *ibid.* **62**, 381 (1993).
[47] Yu. P. Kalmykov, W. T. Coffey, and S. V. Titov, Phys. Rev. E **76**, 051104 (2007).
[48] W. T. Coffey, Yu. P. Kalmykov, S. V. Titov, and B. P. Mulligan, Phys. Chem. Chem. Phys. **9**, 3361 (2007); J. Phys. A: Math. Theor. **40**, F91 (2007); Europhys. Lett. **77**, 20011 (2007).
[49] W. T. Coffey, Yu. P. Kalmykov, S. V. Titov, and B. P. Mulligan, Phys. Rev. E **75**, 041117 (2007); W. T. Coffey, Yu. P. Kalmykov, and S. V. Titov, J. Chem. Phys. **127**, 074502 (2007).
[50] M. Radcliffe, J. Phys. A **4**, 313 (1971).
[51] F. T. Arecchi, E. Courtens, R. Gilmore, and H. Thomas, Phys. Rev. A **6**, 2211 (1972).