SPIN RELAXATION IN PHASE SPACE

YURI P. KALMYKOV[1], WILLIAM T. COFFEY[2], and SERGUEY V. TITOV[3]

[1]*Laboratoire de Mathématiques et Physique (LAMPS, EA 4217),
Université de Perpignan Via Domitia, Perpignan, France*
[2]*Department of Electronic and Electrical Engineering, Trinity College,
Dublin, Ireland*
[3]*Kotel'nikov Institute of Radio Engineering and Electronics of the Russian
Academy of Sciences, Moscow, Russian Federation*

CONTENTS

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 spin dynamics in gases, liquids, and solids, so providing a bridge between microscopic and macroscopic physics. For example, since 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, and so on, examine the time evolution of the individual *elementary* spins [1, 2] of nuclei, electrons, muons, and so on, while on *mesoscales* the time evolution of magnetic *molecular clusters* (i.e., spins 15–25 μ_B) exhibiting relatively large quantum effects is relevant to the fabrication of molecular magnets [3]. On *nanoscales* single domain ferromagnetic particles (giant spins 10^4–10^5 μ_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. Also on a *nanoscale* level, we have magnetic fluids composed of single domain ferromagnetic particles in a

colloidal suspension. Here, relaxation experiments detect [4, 5] both the Arrhenius or solid-state-like (Néel) mechanism [6] of relaxation of the magnetization, which may be overcome via thermal agitation anisotropy potential barriers inside the particle and the Debye orientational relaxation [7, 8] due to physical Brownian rotation of the suspended particles in the presence of thermal agitation. Here, quantum effects are expected to be much smaller. Finally, on the *bulk macroscopic scale*, permanent magnets (10^{20} μ_B) exist, that is, *multi-domain* systems, where magnetization reversal occurs via the *macroscopic* processes of nucleation, propagation, and annihilation of domain walls. Thus, a *well-defined spin number scale* ranging from the bulk macroscopic down to individual atom and spins naturally occurs [9] (see Fig. 1).

On an atomic-level, spin relaxation experiments in nuclear magnetic or electron spin resonance are usually interpreted via the phenomenological Bloch [10] equations and their later modifications [1, 2] pertaining to the relaxation of elementary spins subjected to an external magnetic field and interacting with an environment constituting a heat reservoir at constant temperature T. These simple linear equations of motion for the nuclear magnetization were originally proposed on phenomenological grounds. The main assumption is that the effects of the heat bath can be described two different time constants: the so-called T1 and T2 relaxation times. They provide a substantially correct quantitative description
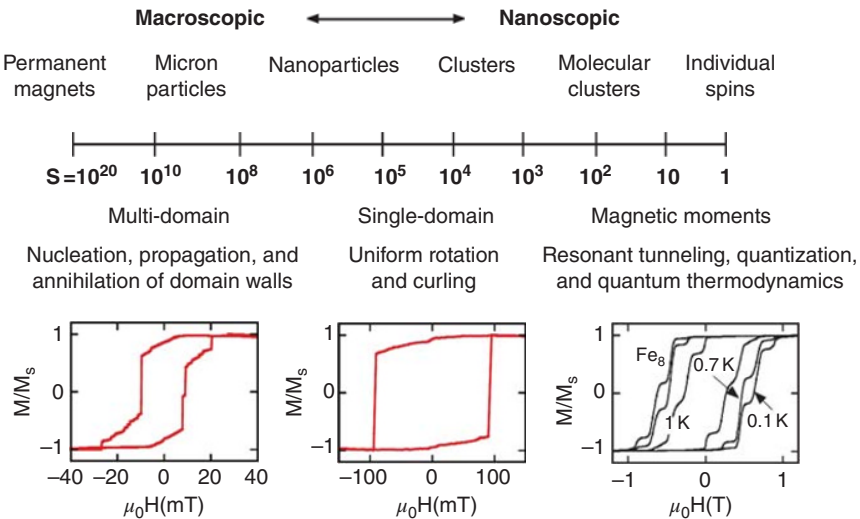
Figure 1. The transition from macroscopic to nanoscopic magnets. The hysteresis loops are typical examples of magnetization reversal via nucleation, propagation, and annihilation of domain walls (left), via uniform rotation (middle), and via quantum tunneling (right). Wernsdorfer [9], Reproduced with permission of John Wiley & Sons, Inc. (Color on line).

for liquid samples [1]. Microscopic theories of the relaxation in quantum spin systems have been developed by Bloch [11], Bloembergen, et al. [12], and other authors (see, e.g., Refs. 13–15). These microscopic theories have provided general evolution equations for the density matrix operator of the spin system allowing one, in principle, to evaluate all desired observables such as relaxation times, and so on.

On meso- and nanoscales, both the behavior of the hysteresis loop and the reversal time of the magnetization of molecular clusters and nanomagnets are essential for observation of the transition from the macroscopic to the nanoscale level as quantum effects are likely to occur as the spin number decreases (see Fig. 1). In this region, the magnetization in molecular nanomagnets may reverse both due to thermal agitation and quantum tunneling as may be observed in the corresponding hysteresis loop [9]. In contrast, in single, domain ferromagnetic nanoparticles (originally encountered in paleomagnetism in the context of past reversals of the Earth's magnetic field, where depending on the volume of the particle, the relaxation time may vary from nanoseconds to millions of years), the magnetization reversal is treated classically by assuming *uniform* rotation of the magnetization vector as conjectured by Néel [16] and Stoner and Wohlfarth [17]. The relaxation time epochs represent the transition from Langevin paramagnetic behavior of nanoparticles (superparamagnetism) with no hysteresis involved via the magnetic after-effect stage, where the magnetization reversal time is of the order of the time of a measurement, to stable ferromagnetism. There a given ferromagnetic state that 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 interactions render all atomic spins collinear and the magnitude of the magnetization vector is constant in space. This hypothesis should hold for fine (nanometric) magnetic particles, where domain walls cannot form in the sample because it is energetically unfavorable.

The *static* magnetization properties of single, domain particles are usually treated via the method given by Stoner and Wohlfarth [17]. Their procedure simply consists in *minimizing the free energy of the particle*, that is, the sum of the 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, 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 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 [17, 18]. 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 [19], including any given magnetocrystalline and 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 [9] of the switching field surface permits 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, that is, the ferromagnetic resonance frequency, and so on. We reiterate that these *static* calculations all ignore thermal effects on the switching field, that is, transitions between the minima of the potential are neglected so that they are strictly only valid at zero temperature.

As far as the magnetization dynamics of fine particles at finite temperatures are concerned, Néel [16] determined the magnetization relaxation time, that is, 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) [20] as specialized to magnetic moments, namely,

$$\tau \sim f_0^{-1} e^{\beta \Delta V}. \tag{1}$$

Here, ΔV is the barrier height, $\beta = (kT)^{-1}$, k is Boltzmann's constant, T is the absolute temperature, and f_0 is the so-called attempt frequency associated with the frequency of the *gyromagnetic precession* of the magnetization in the effective field of the magnetocrystalline anisotropy. It follows that, by varying the volume or the temperature of the particles, τ can be made to vary from 10^{-9}s to *millions of years* (f_0^{-1} is often taken as small as 10^{-10}–10^{-11} s in practice). The presence of the exponential factor in Eq. (1) indicates that, in order to approach the zero remanence (corresponding to thermal equilibrium), a sufficient number of particles (magnetic moments) must be reversed by thermal activation over the energy barrier. 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. Besides the overbarrier relaxation process, Bean and Livingston [21] have suggested that in a single-domain particle, the magnetization may also reverse by *macroscopic quantum tunneling* (macroscopic since a giant spin is involved) through the magnetocrystalline–Zeeman energy potential barrier. In general, the magnetization may reverse by quantum tunneling at *very low temperatures* [22], which may be observed in the behavior of the Stoner–Wohlfarth asteroids and associated hysteresis loops. Hence, in order to distinguish tunneling reversal from reversal by thermal agitation, systematic ways of introducing quantum effects into the magnetization reversal of nano-mesoscale magnets, which in general may be

restated as quantum effects in parameters characterizing the decay of metastable states in spin systems, are required.

In the context of thermal effects in the magnetization reversal of classical spins, we have mentioned that the original dynamical calculations of Néel for single-domain particles utilize classical TST. In the more recent treatment formulated by Brown [23, 24] (now known as the Néel–Brown model [6, 9]), 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 (magnetic) Langevin equation. This is the phenomenological Landau–Lifshitz [25] or Gilbert equation [26, 27] augmented by torques due to random white noise magnetic fields $\mathbf{h}(t)$ characterizing the giant spin–bath interaction, namely,

$$\dot{\mathbf{u}} = \gamma \left[\mathbf{u} \times \left(\mathbf{H}_{ef} + \mathbf{h} \right) \right] - \alpha \left[\mathbf{u} \times \dot{\mathbf{u}} \right]. \tag{2}$$

Here $\mathbf{u} = \mathbf{M}/M_S$ is a unit vector in the direction of $\mathbf{M}$, M_S is the saturation magnetization, assumed constant, γ is the gyromagnetic-type constant, α is the dimensionless damping constant, $\mathbf{H}_{ef} = -\mu_0^{-1} \partial V / \partial \mathbf{M}$ is the effective magnetic field, $\mu_0 = 4\pi \cdot 10^{-7} \mathrm{JA}^{-2} \mathrm{m}^{-1}$ is the permeability of free space in SI units, and V is the free energy per unit volume comprising the *non-separable* Hamiltonian of the magnetic anisotropy and Zeeman energy densities. Thus, the only variable is the orientation of $\mathbf{M} = M_S \mathbf{u}$, which is specified by the polar and azimuthal angles ϑ and φ of the spherical polar coordinate system (see Fig. D.1). The stochastic differential equation (2) for the isotropic Brownian motion of the classical spin containing both precessional and alignment terms is then used to derive the Fokker–Planck equation accompanying Eq. (2), governing the time evolution of the distribution function $W(\vartheta, \varphi, t)$ of magnetization orientations on the surface of a sphere of constant radius M_S. The relevant Fokker–Planck equation is [5, 6]

$$\frac{\partial W}{\partial t} = L_{FP} W, \tag{3}$$

where the Fokker–Planck operator L_{FP} again comprising both precessional and alignment terms is defined as follows:

$$L_{FP} W = \frac{1}{2\tau_N} \left\{ \frac{\beta v}{\alpha} \left(\mathbf{u} \cdot \left[\frac{\partial V}{\partial \mathbf{u}} \times \frac{\partial W}{\partial \mathbf{u}} \right] \right) + \beta v \left(\frac{\partial}{\partial \mathbf{u}} \cdot W \frac{\partial V}{\partial \mathbf{u}} \right) + \Delta W \right\}. \tag{4}$$

Here, Δ is the Laplacian operator on the surface of the unit sphere, $\tau_N = (\alpha + \alpha^{-1}) v \beta \mu_0 M_S / (2\gamma)$ is the characteristic free-diffusion time of $\mathbf{M}(t)$, and v is the volume of a typical particle. A detailed discussion of the assumptions made in deriving the Fokker–Planck and Gilbert equations is given elsewhere (see e.g., Refs. 5 and 6; see also Appendix D). Now Brown's model [23, 24], rooted in a magnetic Langevin equation, allows one to treat the relaxation processes in classical spin systems (single-domain particles, etc.) using powerful computational techniques that have been developed in the theory of the Brownian

motion. These include continued fractions, mean first passage times, escape rate theory, and so on [5, 6]. For example, by using the Kramers' escape rate method [28, 29], as ingeniously adapted to magnetic relaxation by Brown [23, 24], we can evaluate the reversal time of the magnetization over wide ranges of temperature and damping [6]. Thus, we can compare theoretical predictions with experimental data on superparamagnetic relaxation, which we saw plays a fundamental role in information storage, paleomagnetism, biotechnology, and so on.

Many quantum, semiclassical, and classical methods for the description of spin relaxation and resonance already exist. These include the reduced density matrix evolution equation [2, 30, 31], the stochastic Liouville equation [32, 33], and the Langevin equation [5, 6], besides the phase space (generalized coherent-state) [34–40] treatment. The latter comprises the extension of Wigner's phase space representation of the density operator [41–48] (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. [35–40] and [49–51]). Furthermore, phase space representations of quantum mechanical evolution equations provide a formal means of treating quantum effects in dynamical systems transparently linking to the classical representations, facilitating the calculation of quantum corrections to classical distribution functions. These representations generally based on the coherent-state representation of the density matrix introduced by Glauber and Sudarshan and widely used in quantum optics [45, 46] when applied to spin systems (see e.g., Refs. 35–40 and 52–69) allow one to analyze quantum spin relaxation using [70] a master equation for a *quasiprobability distribution function* $W_S(\vartheta, \varphi, t)$ of spin orientations in a phase (here configuration) space (ϑ, φ). The mapping of the quantum spin dynamics onto *c*-number quasiprobability density evolution equations clearly shows how these equations reduce to the Fokker–Planck equation in the classical limit [40, 62]. The phase space distribution function for spins was originally introduced by Stratonovich [49] for closed systems, and it was further developed both for closed and open spin systems see Refs. 35–40 and 52–69. It is entirely analogous to the Wigner distribution $W(q, p, t)$ in the phase space of positions and momenta (q, p) of a particle [41–47], which is a certain (overlap) Fourier transform corresponding to a quasiprobability representation of the density matrix operator $\hat{\rho}(t)$. However, particular differences arise because of the angular momentum commutation relations. The phase space distribution function $W_S(\vartheta, \varphi, t)$ of spin orientations in a configuration space, just as the Wigner function $W(q, p, t)$ for the translational motion of a particle, enables one to calculate the expected value of a spin operator $\hat{A}$ in Hilbert space via the *corresponding c-number* (or Weyl) symbol $A(\vartheta, \varphi)$. Hence, quantum mechanical averages may be determined in a classical-like manner. The Wigner representation contains only such features as are common to both quantum and classical statistical mechanics, and it formally represents quantum mechanics as a statistical theory on classical phase space [42, 47]. Therefore, it is especially suitable for the development of semiclassical

methods of solution, for example, for the purpose of analysis of two interacting systems: where one is treated quantum mechanically, while the other is treated by using classical theory. Here, the Wigner representation allows one to easily obtain quantum corrections to the classical results, which is naturally suited to the calculation of quantum corrections to the latter. The formalism is relatively easy to implement because master equations governing the time evolution of phase space distributions enable powerful computational techniques originally developed for the solution of classical Fokker–Planck equations for the rotational Brownian motion of classical magnetic dipoles (e.g., continued fractions, and mean first passage times. [5, 71]) to be seamlessly carried over into the quantum domain [62, 65, 72, 73].

Despite the undoubted merits of the phase space description of spin relaxation [35–40], it appears that the formulation has been relatively underexploited outside the realm of quantum optics [45, 46]. Thus, applications to other spin systems are few including spin relaxation problems, and so on. This may, in part, be due to the relatively complex mathematical manipulations, which are involved in comparison with the phase space formulation for particles with separable and additive Hamiltonians. Therefore, it is now our purpose to provide in the spirit of the *Advances in Chemical Physics*: a reasonably comprehensive and didactic account of the phase space description of spin relaxation and other allied topics. It is also our purpose to show, by using Wigner's quasiprobability distribution function formalism, how the existing methods of analysis of the Brownian motion of classical spins may be extended to include quantum effects. Thus, a semiclassical theory of spin relaxation will ensue. Moreover, we shall demonstrate how the results of calculations of relaxation times, dynamic susceptibilities, and so on, for various model systems via the phase space formalism are in complete agreement with those obtained from the solution of quantum master equations for the density matrix. The results are significant, particularly because they will elucidate the role played by quantum effects in the various spin relaxation processes in nanomagnets as well as providing a basis for a theory of macroscopic quantum tunneling for which the semiclassical approach is ideally suited.

The remaining contents can be summarized as follows. In Section II, we recall the principal features of both the density matrix in Hilbert space and the phase space formalisms as applied to spin relaxation phenomena. In particular, we present a detailed derivation of the evolution equation for the density matrix and the corresponding differential recurrence equation for the statistical moments (average polarization operators) in the Markovian approximation. Furthermore, we introduce the Wigner quasiprobability distribution function for particles and illustrate its application to both TST and Brownian motion. Then we describe the basic aspects of the phase space formalism for spins and derive the master equation for the spin phase space quasiprobability distributions and the differential recurrence equation for the statistical moments (average spherical harmonics). Finally, we treat in detail the stationary solutions of phase space master equations

for various model spin systems with arbitrary spin number S (e.g., spins in a uniform external field, uniaxial nanomagnets in longitudinal and transverse fields, and biaxial and cubic systems), and we calculate quantum corrections to both switching field curves and to the spin TST reversal time. Section III is devoted to both the derivation of and the solution of phase space master equations for axially symmetric problems concerning both noninteracting spins in a dc magnetic field and uniaxial nanomagnets subjected to a dc magnetic field. We evaluate characteristic relaxation times and dynamic susceptibility for these spin systems besides treating nonlinear longitudinal relaxation of spins in superimposed ac and dc magnetic fields and investigating quantum effects in dynamic magnetic hysteresis and stochastic resonance. In Section IV, we derive and solve the statistical moment equations for average spherical harmonics for an arbitrary spin Hamiltonian. As a particular example, we calculate the characteristic relaxation times and dynamic susceptibility of a uniaxial nanomagnet subjected to a dc bias field of *arbitrary* orientation with respect to the easy axis. Throughout, we shall compare the results obtained via the phase space formalism with the corresponding classical limit, $S \rightarrow \infty$. In order to facilitate a better understanding of the spin phase space formalism and its connection to the theory of relaxation of classical spins, the appendixes contain a detailed account of the properties of spin and polarization operators (Appendix A) and spherical harmonics (Appendix B). Appendix C describes in detail the intricate calculations involved in transforming the reduced density matrix evolution equation into a master equation in phase space for a uniaxial nanomagnet. The principal results of the classical theory of the Brownian motion of magnetic moments are summarized in Appendix D, while definitions and derivations of characteristic relaxation times and correlation functions are given in Appendix E.

II.   DENSITY MATRIX AND PHASE SPACE FORMULATIONS OF RELAXATION PHENOMENA IN SPIN SYSTEMS

A.   Density Matrix Formulation of Spin Relaxation and Resonance

1.   *General Equations*

In classical mechanics, we consider the behavior of any given mechanical system of interest as it changes in time from one precisely defined state to another. In statistical mechanics, we have some knowledge of the system, but that is not enough for a complete specification of the precise state. For this purpose, we consider the average behavior of a collection of systems of the same structure as the one of actual interest, but distributed over a range of different possible states. We speak of such a collection as an *ensemble* of systems. Thus, we represent the instantaneous state of a dynamical system of N degrees of freedom by a phase point $(\mathbf{q}, \mathbf{p})$ in a $2N$-dimensional phase space Γ of all the coordinates $\mathbf{q} = (q_1, \ldots, q_N)$

and momenta $\mathbf{p} = (p_1, \ldots, p_N)$ of the system. The instantaneous state of any system in an ensemble can then be regarded as being specified by the position of a *representative point* in the phase space, and the condition of the ensemble as a whole can be described by a "cloud" of density $f(\mathbf{q}, \mathbf{p}, t)$ of such representative points, one for each system in the ensemble. The behavior of the ensemble over time can then be associated with the "streaming" motion of the representative points as they describe trajectories in the phase space, in accordance with the laws of classical mechanics. The probability density function $f(\mathbf{q}, \mathbf{p}, t)$ defined such that $f(\mathbf{q}, \mathbf{p}, t)d\mathbf{q}d\mathbf{p}$ is the probability at time t that the phase point will be inside a volume element $d\mathbf{q}d\mathbf{p}$ in phase space obeys the classical Liouville equation, namely [74–76],

$$\frac{\partial f}{\partial t} = -\{H, f\} = -i\mathrm{L}f, \tag{5}$$

where $H = K + U$ is the Hamiltonian (total energy of the system); K and U are kinetic and potential energies, respectively; $\{H, f\}$ defines the classical Poisson bracket, namely,

$$\{H, f\} = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial H}{\partial q_i} \right);$$

and $\mathrm{L} = -i\{H, \ \}$ is the classical Liouville operator. From the principle of the *conservation of density in phase space*, it follows [74] that when we consider the rate of change of density in the neighborhood of any selected moving phase point instead of in the neighborhood of a fixed point that the hydrodynamical derivative

$$\frac{df}{dt} = 0, \tag{6}$$

that is, the density of the phase points is a constant along a phase space trajectory at all times, namely,

$$f(\mathbf{q}(0), \mathbf{p}(0), t = 0) = f(\mathbf{q}(t), \mathbf{p}(t), t). \tag{7}$$

Now, the evolution equation for a dynamical variable $A(\mathbf{q}, \mathbf{p})$ is given by

$$\frac{dA}{dt} = \sum_{i=1}^{N} \left(\frac{\partial A}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = \{H, A\} = i\mathrm{L}A. \tag{8}$$

The expectation value of $A(\mathbf{q}, \mathbf{p})$ at time t is then defined as

$$\langle A \rangle (t) = \int A(\mathbf{q}, \mathbf{p}) f(\mathbf{q}, \mathbf{p}, t) d\mathbf{q}d\mathbf{p} \tag{9}$$

with the normalization

$$\int f(\mathbf{q}, \mathbf{p}, t) d\mathbf{q} d\mathbf{p} = 1. \tag{10}$$

In the quantum mechanics, on the other hand, such a probability density function is replaced by a density matrix $\hat{\rho}$ in Hilbert space to play a role somewhat similar to the density f in the classical statistical mechanics [74, 77]. For convenience, we briefly recall the basic equations of the density matrix formalism [30, 76].

The *state* of a quantum many-particle system characterized by the Hamiltonian operator $\hat{H}$ is represented by a wave function Ψ and the corresponding state vector $|\Psi\rangle$ in Hilbert space. The wave function Ψ satisfies the Schrödinger equation

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} \hat{H} \Psi, \tag{11}$$

where $\hbar = h/(2\pi)$ and h is Planck's constant. Now, in the quantum mechanics, a dynamical variable A always corresponds to a Hermitian operator $\hat{A}$ and the expectation value of $\hat{A}$ is formally defined as the scalar (inner) product

$$\left\langle \hat{A} \right\rangle (t) = \langle \Psi(t) | \hat{A} | \Psi(t) \rangle, \tag{12}$$

where $\langle \Psi(t)| = |\Psi(t)\rangle^{\dagger}$ and the symbol $\dagger$ denotes the Hermitian conjugate. Equation (12) implies that the wave function $\Psi(t)$ must be normalized to unity, that is, $\langle \Psi(t) | \Psi(t) \rangle = 1$. Furthermore, the wave function may be expanded in the complete orthonormal basis of eigenstates $\{\phi_n\}$ of the Hamiltonian operator $\hat{H}$ as

$$\Psi(t) = \sum_n c_n(t) \phi_n, \tag{13}$$

where $c_n(t)$ is given by the scalar product $c_n(t) = \langle \phi_n | \Psi(t) \rangle$ with the normalization $\sum_n |c_n(t)|^2 = 1$, which follows from normalization of $\Psi(t)$. In this case, one says that the system is in the *pure* state. Now, the expectation value $\left\langle \hat{A} \right\rangle (t) = \langle \Psi(t) | \hat{A} | \Psi(t) \rangle$ of a dynamical variable A represented by an operator $\hat{A}$ is given by [76]

$$\left\langle \hat{A} \right\rangle (t) = \sum_{n,n'} c_{n'}(t) c_n^*(t) A_{nn'} \equiv \sum_{n,n'} \rho_{n'n}(t) A_{nn'}, \tag{14}$$

where the coefficients $A_{nn'} = \langle \phi_n | \hat{A} | \phi_{n'} \rangle$ and $\rho_{n'n}(t) = c_{n'}(t) c_n^*(t)$ are the matrix elements of the operators $\hat{A}$ and the density operator $\hat{\rho}$, respectively, in the orthonormal basis of the eigenstates $\{\phi_n\}$ and the asterisks denote the complex conjugate. For a pure state, the density operator $\hat{\rho}$ can be written as the outer product as follows: [76]

$$\hat{\rho}(t) = |\Psi(t)\rangle \langle \Psi(t)| = \sum_{n,n'} c_{n'}(t) c_n^*(t) |\phi_{n'}\rangle \langle \phi_n|. \tag{15}$$

The density matrix operator defined by Eq. (15) is Hermitian, that is, $\hat{\rho}^{\dagger}(t) = \hat{\rho}(t)$, and idempotent, that is, it satisfies the condition $\hat{\rho}^2(t) = \hat{\rho}(t)$.

The density matrix operator defined in Eq. (15) for a quantum system in a *pure* state can also be applied with some modifications to a quantum system in a *mixed* state, that is, to a system, whose actual state $\psi(t) = \sum_n c_n(t)\phi_n$ is not known completely, and only the probabilities $P_n = |c_n(t)|^2$ to be in any of the different states n can be evaluated [76]. An example is a system in thermal equilibrium, whose eigenfunctions constitute the orthonormal basis $\{\phi_n\}$ with probabilities P_n to be found in the different states n given by the Boltzmann distribution, and all microscopic states compatible with these probabilities are assumed to be equally probable; here, $\rho_{n'n} = P_n\delta_{n'n}$. The most obvious difference between pure and mixed states is encountered in their diagonal representation, where the pure-state density matrix must, on the one hand, have only one nonzero element on its diagonal (equal to 1), while the mixed-state density matrix must, on the other hand, have at least two nonzero elements (whose sum is 1) [76].

For our purposes, the most relevant properties of the density matrix operator $\hat{\rho}$, which are valid both for pure and mixed states are the following: (i) $\hat{\rho}$ is a *positive definite operator*, that is, $\langle\psi(t)|\hat{\rho}|\psi(t)\rangle \geq 0$, yielding the average probability to find the system in the state $|\psi(t)\rangle$; (ii) $\hat{\rho}$ is *Hermitian* and its diagonal elements ρ_{nn} are real, positive, and represent the *average* probability that a system chosen at random from the ensemble would be found in the state specified by n. Moreover, $\hat{\rho}$ satisfies the normalization condition [74]

$$\text{Tr}\left(\hat{\rho}\right) = 1, \tag{16}$$

where $\text{Tr}\left(\hat{\rho}\right)$ denotes its trace. Furthermore, the quantum mechanical analog of the classical expression (Eq. 9) for the mean value of a dynamical variable A is as follows:

$$\left\langle\hat{A}\right\rangle = \text{Tr}\left(\hat{\rho}\hat{A}\right). \tag{17}$$

Thus, the integrals over all phase space Γ in the classical equations (9 and 10) are replaced by the traces in the quantum equations (16 and 17). Now, the time evolution of the density operator $\hat{\rho}$ is described by the quantum Liouville equation [74, 76]

$$\frac{\partial\hat{\rho}}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}\right] = -i\text{L}\hat{\rho}, \tag{18}$$

where $\hat{H}$ is the Hamiltonian operator, the brackets denote the commutator, namely,

$$\left[\hat{H}, \hat{\rho}\right] = \hat{H}\hat{\rho} - \hat{\rho}\hat{H},$$

and $L = \hbar^{-1}\left[\hat{H}, \right]$ is the quantum Liouville operator. The formal solution of the operator equation (18) is as follows: [76, 78]

$$\hat{\rho}(t) = e^{-\frac{i}{\hbar}\hat{H}t}\hat{\rho}(0)e^{\frac{i}{\hbar}\hat{H}t}. \qquad (19)$$

Finally, the quantum evolution equation for an operator $\hat{A}$ is given by

$$\frac{d\hat{A}}{dt} = \frac{i}{\hbar}\left[\hat{H},\hat{A}\right] = i L\hat{A}. \qquad (20)$$

Equations (18) and (20) are quantum analogs of Eqs. (5) and (8), respectively. We emphasize [74] that the quantum Liouville equation (18) for the density matrix $\hat{\rho}$ has the same mathematical form as the classical Liouville equation (5) for the distribution function f.

Now the object of our interest is the dynamics of a spin characterized by the spin number S in contact with a thermal bath or environment, which is only of relevance to us insofar as it influences the spin dynamics (a detailed account of properties of relevant spin operators is given in Appendix A). Moreover, it is impossible to follow every variable of the composite spin environment taken as a whole [79]. Hence, we desire a closed evolution equation for a *reduced density matrix*, where only *relevant* variables, that is, those belonging to the subspace comprising the spin, appear explicitly. Then by tracing Eq. (18) over the bath variables, we shall ultimately have a master or reduced density matrix evolution equation [76]. In other words, we can average out the environment of the spin, so yielding a *statistical* description of the spin alone [69]. The ideas being entirely analogous to those used to derive an evolution equation for the single-particle distribution function in the classical statistical mechanics.

In order to treat the spin dynamics in a dissipative environment via the density matrix formalism, we loosely follow arguments advanced by Nitzan [76]. Thus, it is supposed that the overall Hamiltonian $\hat{H}$ may be decomposed into

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB}, \qquad (21)$$

where the operators $\hat{H}_S$, $\hat{H}_{SB}$, and $\hat{H}_B$ are the Hamiltonians of the spin alone, the spin–bath interactions, and the bath, respectively. The time evolution equation for the *overall* system–bath density matrix $\hat{\rho}_{SB}(t)$ of a spin system (S) in contact with a heat bath (B) may now be written taking account of the Liouville equation (18) as follows:

$$\frac{\partial\hat{\rho}_{SB}}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_S, \hat{\rho}_{SB}\right] - \frac{i}{\hbar}\left[\hat{H}_B, \hat{\rho}_{SB}\right] - \frac{i}{\hbar}\left[\hat{H}_{SB}, \hat{\rho}_{SB}\right]. \qquad (22)$$

Now our ultimate objective is to obtain an evolution equation for a *reduced* density matrix, describing the spin relaxation in contact with the thermal bath. Therefore, it

is natural to first simplify Eq. (22) by considering the time evolution of the overall density matrix in the *interaction* representation, which is defined for an arbitrary operator $\hat{A}(t)$ as follows [76]:

$$\hat{A}^I(t) = e^{i\hat{H}_0 t/\hbar} \hat{A}(t) e^{-i\hat{H}_0 t/\hbar}. \tag{23}$$

Here $\hat{H}_0 = \hat{H}_S + \hat{H}_B$. Next taking the time derivative of $\hat{\rho}^I_{SB}(t)$ yields

$$\frac{\partial \hat{\rho}^I_{SB}}{\partial t} = \frac{i}{\hbar} \left[\hat{H}_0, \hat{\rho}^I_{SB} \right] + e^{i\hat{H}_0 t/\hbar} \frac{\partial \hat{\rho}_{SB}}{\partial t} e^{-i\hat{H}_0 t/\hbar}. \tag{24}$$

Therefore, substituting Eq. (22) into Eq. (24), we obtain the evolution equation for $\hat{\rho}^I_{SB}(t)$ in the interaction representation as follows [76]:

$$\frac{\partial \hat{\rho}^I_{SB}}{\partial t} = -\frac{i}{\hbar} \left[\hat{H}^I_{SB}, \hat{\rho}^I_{SB} \right]. \tag{25}$$

Now recall that we desire the effect of the thermal environment on the dynamical behavior of a given spin and that the dynamics of the spin alone is given by $\hat{H}_S$. Therefore, a quite natural viewpoint is to consider the spin–bath interaction Hamiltonian $\hat{H}_{SB}$ as a perturbation of the *bare* dynamics of the spin. In order to formulate this idea, projection operators are used [75, 76]. In particular, for problems involving a system interacting with its equilibrium thermal environment, a projection operator $\hat{P}$ is a particular operator projecting the overall system–bath density operator $\hat{\rho}_{SB}$ onto a product of the reduced density operator of the system $\hat{\rho}_S$ and the equilibrium density operator of the bath $\hat{\rho}_B^{eq}$, namely,

$$\hat{P}\hat{\rho}_{SB} = \hat{\rho}_B^{eq} \text{Tr}_B\left(\hat{\rho}_{SB}\right) = \hat{\rho}_B^{eq} \hat{\rho}_S. \tag{26}$$

Here, the operator $\hat{\rho}_S = \text{Tr}_B\left(\hat{\rho}_{SB}\right)$ resulting from tracing over the bath variables designates a *reduced density operator* in contrast to the *overall* system-bath density operator $\hat{\rho}_{SB}(t)$, and our task is to then find an evolution equation for $\hat{\rho}_S$. In order to achieve this because by definition $\text{Tr}_B(\hat{\rho}_B^{eq}) = 1$, we will have $\hat{P}^2 = \hat{P}$, that is, $\hat{P}$ is idempotent, while the complementary projector is just $\hat{Q} = 1 - \hat{P}$. Moreover, we have the commutation relations

$$\hat{P}\left[\hat{H}_S, \hat{\rho}_{SB}\right] = \left[\hat{H}_S, \hat{P}\hat{\rho}_{SB}\right] = \hat{\rho}_B^{eq}\left[\hat{H}_S, \hat{\rho}_S\right] \tag{27}$$

and

$$\hat{P}\left[\hat{H}_B, \hat{\rho}_{SB}\right] = 0. \tag{28}$$

Now Eqs. (26)–(28) are also valid in the interaction representation implying that we can rewrite Eq. (25) as the two projected equations as follows [76]:

$$\frac{\partial}{\partial t}\hat{P}\hat{\rho}_{SB}^I = -\frac{i}{\hbar}\hat{P}\left[\hat{H}_{SB}^I, (\hat{P}+\hat{Q})\hat{\rho}_{SB}^I\right], \tag{29}$$

$$\frac{\partial}{\partial t}\hat{Q}\hat{\rho}_{SB}^I = -\frac{i}{\hbar}\hat{Q}\left[\hat{H}_{SB}^I, (\hat{P}+\hat{Q})\hat{\rho}_{SB}^I\right]. \tag{30}$$

Next, we use the projection equation (26) to further rewrite these equations as follows:

$$\frac{\partial}{\partial t}\hat{\rho}_S^I = -\frac{i}{\hbar}\mathrm{Tr}_B\left(\left[\hat{H}_{SB}^I, \hat{\rho}_B^{eq}\hat{\rho}_S^I\right]\right) - \frac{i}{\hbar}\mathrm{Tr}_B\left(\left[\hat{H}_{SB}^I, \hat{Q}\hat{\rho}_{SB}^I\right]\right), \tag{31}$$

$$\frac{\partial}{\partial t}\hat{Q}\hat{\rho}_{SB}^I = -\frac{i}{\hbar}\hat{Q}\left[\hat{H}_{SB}^I, \hat{\rho}_B^{eq}\hat{\rho}_S^I\right] - \frac{i}{\hbar}\hat{Q}\left[\hat{H}_{SB}^I, \hat{Q}\hat{\rho}_{SB}^I\right]. \tag{32}$$

Formal integration of the complementary projection equation (32) then yields

$$\hat{Q}\hat{\rho}_{SB}^I(t) = \hat{Q}\hat{\rho}_{SB}^I(0) - \frac{i}{\hbar}\int_0^t \hat{Q}\left[\hat{H}_{SB}^I, \hat{\rho}_B^{eq}\hat{\rho}_S^I(t')\right]dt' - \frac{i}{\hbar}\int_0^t \hat{Q}\left[\hat{H}_{SB}^I, \hat{Q}\hat{\rho}_{SB}^I(t')\right]dt'. \tag{33}$$

This integral equation can be solved in iterative fashion by successively inserting $\hat{Q}\hat{\rho}_{SB}^I(t)$ into the integrand in the third term on the right-hand side. Thus, we have a perturbation expansion for that quantity as increasing powers of the system–bath Hamiltonian in the interaction representation $\hat{H}_{SB}^I$ by continuing this procedure repeatedly in the usual manner of perturbation theory. Now if we neglect all the highest orders of $\hat{H}_{SB}^I$, we can use a simplified version of Eq. (33), namely,

$$\hat{Q}\hat{\rho}_{SB}^I(t) = -\frac{i}{\hbar}\int_0^t \hat{Q}\left[\hat{H}_{SB}^I, \hat{\rho}_B^{eq}\hat{\rho}_S^I(t')\right]dt'. \tag{34}$$

In so doing, we have disregarded the initial correlation term $\hat{Q}\hat{\rho}_I(0)$ in Eq. (33). The latter approximation is tantamount to assuming that $\hat{\rho}_{SB}^I(0)$ is in P space, that is, *initially the system and the bath are uncorrelated* and also that the bath is in thermal equilibrium, or at least that the effect of initial correlations decays rapidly relative to the time scale on which the system is observed [76]. Inserting the (truncation) *Ansatz* equation (34) into Eq. (31) then leads to the *closed* equation in the interaction representation as follows:

$$\frac{\partial\hat{\rho}_S^I(t)}{\partial t} = -\frac{i}{\hbar}\mathrm{Tr}_B\left(\left[\hat{H}_{SB}^I, \hat{\rho}_B^{eq}\hat{\rho}_S^I(t)\right]\right) - \frac{1}{\hbar^2}\int_0^t \mathrm{Tr}_B\left(\left[\hat{H}_{SB}^I, \hat{Q}\left[\hat{H}_{SB}^I, \hat{\rho}_B^{eq}\hat{\rho}_S^I(t')\right]\right]\right)dt'. \tag{35}$$

Now returning to the Schrödinger representation, Eq. (35) can be rewritten in that representation as the *reduced* equation

$$\frac{\partial \hat{\rho}_S}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_S + \hat{\bar{V}}, \hat{\rho}_S\right] + \text{St}\left(\hat{\rho}_S\right), \tag{36}$$

where

$$\hat{\bar{V}} = \text{Tr}_B\left(\hat{H}_{SB}\hat{\rho}_B^{eq}\right), \tag{37}$$

$$\text{St}\left(\hat{\rho}_S\right) = -\frac{1}{\hbar^2}e^{-i\hat{H}_0 t/\hbar}\text{Tr}_B\left(\left[\hat{H}_{SB}^I, \int_0^t \left(1-\hat{P}\right)\left[\hat{H}_{SB}^I, \hat{\rho}_B^{eq}\hat{\rho}_S^I(t')\right]dt'\right]\right)e^{i\hat{H}_0 t/\hbar}. \tag{38}$$

By inspection of Eq. (36), it is apparent that the operator $\hat{\bar{V}}$ now has a simple interpretation. It is just a mean potential that corrects the spin Hamiltonian $\hat{H}_S$ for the *average* effect of the bath. Such corrections are very important in chemical physics, for example, in determining solvent shifts of spectral lines. The shifts occur because the average solvent interaction may influence in a different way the energies of the ground and excited states of a solvent molecule. However, it is also clear that such *average* interactions can only affect the system eigenstates and energy levels, and therefore cannot cause relaxation [76]. Thus, relaxation phenomena are solely associated with the collision (relaxation) operator kernel $\text{St}\left(\hat{\rho}_S\right)$ in Eq. (36). Hence, in addressing spin relaxation, we shall disregard the operator $\hat{\bar{V}}$, or else if unconvinced, one could consider a renormalized system Hamiltonian $\hat{H}_S$, which includes the energy shifts associated with the average effect of the bath.

Next we consider the term containing the projection operator $\hat{P}$ involved in the integrand of Eq. (38). Investigation of this term may be simplified if we assume that the interaction $\hat{H}_{SB}^I$ is merely the *product* of system and bath operators, that is, $\hat{H}_{SB}^I = \hat{V}_S^I\hat{V}_B^I$. Considering the relevant term in Eq. (38), we then have [76]

$$\text{Tr}_B\left(\left[\hat{H}_{SB}^I, \hat{P}\left[\hat{H}_{SB}^I, \hat{\rho}_B^{eq}\hat{\rho}_S^I(t')\right]\right]\right) = \text{Tr}_B\left(\hat{V}_B^I\hat{\rho}_B^{eq}\right)\text{Tr}_B\left(\hat{V}_B^I\hat{\rho}_B^{eq}\right)\left[\hat{V}_S^I, \left[\hat{V}_S^I, \hat{\rho}_S^I(t')\right]\right] \tag{39}$$

$$= \left(\hat{\bar{V}}^B\right)^2\left[\hat{V}_S^I, \left[\hat{V}_S^I, \hat{\rho}^I(t')\right]\right],$$

where $\hat{\bar{V}}^B = \text{Tr}_B\left(\hat{V}_B^I\hat{\rho}_B^{eq}\right)$. Now the mean value of the bath operator $\hat{\bar{V}}^B$ is zero for isotropic bath operators (however, it gives rise to corrections to bath correlation functions for *anisotropic* baths). Therefore, assuming for simplicity that the bath is isotropic and neglecting this term in Eq. (38), we have the desired reduced density

matrix evolution equation describing the spin relaxation in contact with a thermal bath, namely,

$$\frac{\partial \hat{\rho}_S}{\partial t} + \frac{i}{\hbar} \left[\hat{H}_S, \hat{\rho}_S \right] = \text{St} \left(\hat{\rho}_S \right), \tag{40}$$

where $\text{St} \left(\hat{\rho}_S \right)$ is given by with an obvious change of variable in Eq. (38) [76]

$$\text{St} \left(\hat{\rho}_S \right) = -\frac{1}{\hbar^2} \int\limits_0^t \text{Tr}_B \left(\left[\hat{H}_{SB}, e^{-i\hat{H}_0\tau/\hbar} \left[\hat{H}_{SB}, \hat{\rho}_B^{eq} \hat{\rho}_S(t-\tau) \right] e^{i\hat{H}_0\tau/\hbar} \right] \right) d\tau. \tag{41}$$

The reduced nature of the evolution equation (40) manifests itself in the *appearance of memory* meaning that the time evolution of $\hat{\rho}_S(t)$ at time t is determined not only by $\hat{\rho}_S(t)$ but also by its past history, namely, $\hat{\rho}_S(t - \tau)$. The nonlocal temporal (or non-Markovian) behavior appears because the system evolves at time t in response to the state of the bath at that time which in turn is determined by the history of the system–bath interaction. Now we saw that the closed equation (40) ultimately results from a *low-order* perturbation expansion of the system–bath interaction (cf. Eq. (34)), so its validity is expected to be limited to *weak system–bath coupling*. Furthermore, the neglect of initial spin–bath correlations, as expressed by dropping the term $\hat{Q}\hat{\rho}_{SB}^I(0)$ in Eq. (33) constitutes yet another approximation, or, more precisely, a *restriction on the choice of the initial nonequilibrium state*.

2. Collision Kernel in the Markovian Approximation

The collision kernel $\text{St}(\hat{\rho})$ in Eq. (41) can be further considerably simplified in the limit, where *the thermal bath dynamics are much faster than those of the spin* [76]. However, in order to implement this condition in the evolution equation (40), we require an *explicit* form for the spin–bath interaction Hamiltonian $\hat{H}_{SB}$. Various models for spin–bath interactions have been discussed in detail, for example, in Refs. 12–15, 76 and 80–82. Here, we suppose for simplicity that the spin–bath interaction Hamiltonian operator $\hat{H}_{SB}$ has the rudimentary Zeeman form (see, e.g., Refs. 35–37; in our notation)

$$\hat{H}_{SB} = -\gamma \hbar \left(\hat{\mathbf{S}} \cdot \hat{\mathbf{h}} \right) = -\gamma \hbar \sum_{\mu=-1}^{1} \hat{h}^\mu \hat{S}_\mu, \tag{42}$$

where the operator $\hat{\mathbf{h}} = (\hat{h}_X, \hat{h}_Y, \hat{h}_Z)$ represents the random noise field characterizing collisional damping due to the bath,

$$\hat{S}_0 = \hat{S}_Z, \quad \hat{S}_{\pm 1} = \mp \frac{1}{\sqrt{2}} \left(\hat{S}_X \pm i\hat{S}_Y \right) \tag{43}$$

and

$$\hat{h}^0 = \hat{h}_Z, \quad \hat{h}^{\pm 1} = \mp \frac{1}{\sqrt{2}} \left(\hat{h}_X \mp i\hat{h}_Y \right) \tag{44}$$

are, respectively, the covariant and contravariant spherical components of the spin operator $\hat{\mathbf{S}}$ and field operator $\hat{\mathbf{h}}$ (the properties of $\hat{\mathbf{S}}$ and $\hat{S}_\mu$ are explained in detail in Appendix A). We select the interaction operator $\hat{H}_{SB}$ in the form of Eq. (42) merely because that particular choice renders Eqs. (40) and (41) as a direct quantum analog of the Brownian rotation of a magnetic dipole [5] (cf. Eq. (2)). Alternative forms of the Hamiltonian $\hat{H}_{SB}$ are discussed, for example, in Refs. 76 and 80–82. Then using the properties of the bath correlation functions, namely,

$$\left\langle \hat{h}^\mu(t_1)\hat{h}^{-\nu}(t_2) \right\rangle = \delta_{\mu\nu} \mathrm{Tr}_B \left(\hat{h}^\mu(t_1)\hat{h}^{-\nu}(t_2)\rho_B^{eq} \right)$$

($\delta_{\mu\nu}$ is Kronecker's delta), the collision kernel equation (41) further simplifies to

$$\mathrm{St}\left(\hat{\rho}_S\right) = \gamma^2 \sum_{\mu=-1}^{1} \int_0^t \left\{ \left\langle \hat{h}^\mu \hat{h}^{-\mu}(\tau) \right\rangle \left[e^{-\frac{i}{\hbar}\hat{H}_S\tau} \hat{S}_{-\mu}\hat{\rho}_S(t-\tau)e^{\frac{i}{\hbar}\hat{H}_S\tau}, \hat{S}_\mu \right] \right.$$
$$\left. + \left\langle \hat{h}^\mu(\tau)\hat{h}^{-\mu} \right\rangle \left[\hat{S}_{-\mu}, e^{-\frac{i}{\hbar}\hat{H}_S\tau} \hat{\rho}_S(t-\tau)\hat{S}_\mu e^{\frac{i}{\hbar}\hat{H}_S\tau} \right] \right\} d\tau. \tag{45}$$

Now, in general, the elementary collision kernel equation (45) although now vastly simplified still describes the *non-Markovian* behavior of the spin as coupled to the bath, which is determined by the history of the spin–bath interaction. In order to avoid these memory effects, we may use the so-called Markovian limit [76], whereby the bath dynamics are supposed *much faster* than those of the spin. A similar *Ansatz* is essentially made in the classical theory of the Brownian motion [5]. Moreover, because the correlation functions $C_{\mu,-\mu}(\pm\tau)$ characterizing the properties of the equilibrium bath, namely,

$$C_{\mu,-\mu}(\tau) = (-1)^\mu \gamma^2 \left\langle \hat{h}^\mu(0)\hat{h}^{-\mu}(\tau) \right\rangle \tag{46}$$

and

$$C_{\mu,-\mu}(-\tau) = (-1)^\mu \gamma^2 \left\langle \hat{h}^\mu(\tau)\hat{h}^{-\mu}(0) \right\rangle \tag{47}$$

decay to zero much faster than any characteristic system time scale of the system [76], we can extend the upper limit of integration in Eq. (45) to infinity, yielding the collision kernel in the more appealing form

$$\mathrm{St}\left(\hat{\rho}_S\right) = \sum_{\mu=-1}^{1} (-1)^\mu \int_0^\infty \left\{ C_{\mu,-\mu}(\tau) \left[e^{-\frac{i}{\hbar}\hat{H}_S\tau} \hat{S}_{-\mu}e^{\frac{i}{\hbar}\hat{H}_S\tau} \hat{\rho}_S(t-\tau), \hat{S}_\mu \right] \right.$$
$$\left. + C_{\mu,-\mu}(-\tau) \left[\hat{S}_{-\mu}, \hat{\rho}_S(t-\tau)e^{-\frac{i}{\hbar}\hat{H}_S\tau} \hat{S}_\mu e^{\frac{i}{\hbar}\hat{H}_S\tau} \right] \right\} d\tau, \tag{48}$$

which is amenable to further simplification. However, tempting as it may seem, the rapidly decaying noise correlation functions $C_{\mu,-\mu}(\tau)$ and $C_{\mu,-\mu}(-\tau)$ in the collision kernel equation (48) cannot simply be replaced by Dirac delta functions $\sim\delta(\tau)$ in order to avoid memory effects, because in the quantum case *the bath dynamics may be slower than the phase oscillations in the system* [76]. For example, in the free or bare system, that is, without coupling to the reservoir, so that St $\left(\hat{\rho}_S\right) = 0$, the solution of the evolution equation (40) is as follows:

$$\hat{\rho}_S(t) = e^{-\frac{i}{\hbar}\hat{H}_St}\hat{\rho}_S(0)e^{\frac{i}{\hbar}\hat{H}_St}. \tag{49}$$

Hence, quantities involving fast phase oscillations of $\hat{\rho}_S(t)$ due to the phase factors $e^{\pm i\hat{H}_St/\hbar}$ embodied in Eq. (49), or its remaining signature in the presence of system–bath coupling (i.e., when St $\left(\hat{\rho}_S\right) \neq 0$), cannot simply be taken outside the integrals in the collision kernel equation (45). Therefore, to circumvent this problem, we again use the interaction representation of $\hat{\rho}_S(t)$, namely,

$$\hat{\rho}_S(t) = e^{-\frac{i}{\hbar}\hat{H}_St}\hat{\rho}_S^I(t)e^{\frac{i}{\hbar}\hat{H}_St}.$$

Thus, the collision operator St $\left(\hat{\rho}\right)$ becomes in that representation

$$\text{St}\left(\hat{\rho}_S\right) = \sum_{\mu=-1}^{1} (-1)^{\mu}$$

$$\times \int_0^{\infty} \left\{ C_{\mu,-\mu}(\tau) \left[e^{-\frac{i}{\hbar}\hat{H}_S\tau}\hat{S}_{-\mu}e^{-\frac{i}{\hbar}\hat{H}_S(t-\tau)}\hat{\rho}_S^I(t-\tau)e^{\frac{i}{\hbar}\hat{H}_S(t-\tau)}e^{\frac{i}{\hbar}\hat{H}_S\tau}, \hat{S}_{\mu} \right] \right.$$

$$+ C_{\mu,-\mu}(-\tau) \left[\hat{S}_{-\mu}, e^{-\frac{i}{\hbar}\hat{H}_S\tau}e^{-\frac{i}{\hbar}\hat{H}_S(t-\tau)}\hat{\rho}_S^I(t-\tau)e^{\frac{i}{\hbar}\hat{H}_S(t-\tau)}\hat{S}_{\mu}e^{\frac{i}{\hbar}\hat{H}_S\tau} \right] \right\}$$

$$\times d\tau. \tag{50}$$

In order to further simplify Eq. (50), we next assume that the relaxation of the noise correlation functions $C_{\mu,-\mu}(\tau)$ and $C_{\mu,-\mu}(-\tau)$ to zero as $\tau \rightarrow \infty$ is *fast* relative to the time scale on which the time shifted density matrix $\hat{\rho}_S^I(t-\tau)$ in the interaction representation changes. We then make the approximation $\hat{\rho}_S^I(t-\tau) \approx \hat{\rho}_S^I(t)$ and then finally return to $\hat{\rho}_S(t)$. Thus, we have our final simplified expression for the collision kernel

$$\text{St}\left(\hat{\rho}_S\right) = \sum_{\mu=-1}^{1} (-1)^{\mu} \int_0^{\infty} \left\{ C_{\mu,-\mu}(\tau) \left[e^{-\frac{i}{\hbar}\hat{H}_S\tau}\hat{S}_{-\mu}e^{\frac{i}{\hbar}\hat{H}_S\tau}\hat{\rho}_S(t), \hat{S}_{\mu} \right] \right.$$

$$\left. + C_{\mu,-\mu}(-\tau) \left[\hat{S}_{-\mu}, \hat{\rho}_S(t)e^{-\frac{i}{\hbar}\hat{H}_S\tau}\hat{S}_{\mu}e^{\frac{i}{\hbar}\hat{H}_S\tau} \right] \right\} d\tau, \tag{51}$$

which we note now involves only $\hat{\rho}_S(t)$ and not the shifted expression $\hat{\rho}_S(t-\tau)$.

The approximate equation (51) for the collision kernel corresponds to the traditional Redfield equation derived in Ref. 14. This can be proved as follows. We first express $\text{St}\left(\hat{\rho}_S\right)$ in the representation defined by the eigenstates $|\alpha\rangle$ of the system Hamiltonian $\hat{H}_S$ and then use the various commutation relations in Eq. (51) as written in terms of their matrix elements, namely,

$$\left[e^{-\frac{i}{\hbar}\hat{H}_S\tau}\hat{S}_{-\mu}e^{\frac{i}{\hbar}\hat{H}_S\tau}\hat{\rho}_S(t),\hat{S}_\mu\right]_{\alpha\alpha'} = \sum_{\varepsilon,\varepsilon'}\left[\hat{S}_{-\mu}\right]_{\alpha\varepsilon}\left[\hat{S}_\mu\right]_{\varepsilon'\alpha'}\rho_{\varepsilon\varepsilon'}(t)e^{-\frac{i}{\hbar}(E_\alpha-E_\varepsilon)\tau}$$

$$-\sum_{\varepsilon',\varepsilon}\left[\hat{S}_\mu\right]_{\alpha\varepsilon'}\left[\hat{S}_{-\mu}\right]_{\varepsilon'\varepsilon}\rho_{\varepsilon\alpha'}(t)e^{-\frac{i}{\hbar}(E_{\varepsilon'}-E_\varepsilon)\tau},$$

(52)

$$\left[\hat{S}_{-\mu},\hat{\rho}_S(t)e^{-\frac{i}{\hbar}\hat{H}_S\tau}\hat{S}_\mu e^{\frac{i}{\hbar}\hat{H}_S\tau}\right]_{\alpha\alpha'} = \sum_{\varepsilon,\varepsilon'}\left[\hat{S}_{-\mu}\right]_{\alpha\varepsilon}\left[\hat{S}_\mu\right]_{\varepsilon'\alpha'}\rho_{\varepsilon\varepsilon'}(t)e^{\frac{i}{\hbar}(E_{\alpha'}-E_{\varepsilon'})\tau}$$

$$-\sum_{\varepsilon',\varepsilon}\left[\hat{S}_\mu\right]_{\varepsilon'\varepsilon}\left[\hat{S}_{-\mu}\right]_{\varepsilon\alpha'}\rho_{\alpha\varepsilon'}(t)e^{\frac{i}{\hbar}(E_\varepsilon-E_{\varepsilon'})\tau}.$$

(53)

Next by introducing the matrix elements $R_{\alpha\alpha'\varepsilon\varepsilon'}$ of the relaxation operator $\text{St}(\hat{\rho}_S)$ via

$$\left[\text{St}\left(\hat{\rho}_S\right)\right]_{\alpha\alpha'} = \sum_{\varepsilon\varepsilon'}R_{\alpha\alpha'\varepsilon\varepsilon'}\rho_{\varepsilon\varepsilon'},$$

then from Eq. (51) we have $R_{\alpha\alpha'\varepsilon\varepsilon'}$ in the eigenvector representation of the Hamiltonian $\hat{H}_S$, rendered as the Redfield form

$$R_{\alpha\alpha'\varepsilon\varepsilon'} = \sum_{\mu=-1}^{1}(-1)^\mu\left\{\left(\tilde{C}_{\mu,-\mu}(\omega_{\alpha\varepsilon})+\tilde{C}^*_{-\mu,\mu}(\omega_{\alpha'\varepsilon'})\right)\left[\hat{S}_{-\mu}\right]_{\alpha\varepsilon}\left[\hat{S}_\mu\right]_{\varepsilon'\alpha'}\right.$$

$$-\delta_{\varepsilon'\alpha'}\sum_\lambda e^{\beta\hbar\omega_{\varepsilon\lambda}}\tilde{C}^*_{\mu,-\mu}(\omega_{\varepsilon\lambda})\left[\hat{S}_\mu\right]_{\alpha\lambda}\left[\hat{S}_{-\mu}\right]_{\lambda\varepsilon}$$

$$\left.-\delta_{\alpha\varepsilon}\sum_\lambda e^{\beta\hbar\omega_{\varepsilon'\lambda}}\tilde{C}_{-\mu,\mu}(\omega_{\varepsilon'\lambda})\left[\hat{S}_\mu\right]_{\varepsilon'\lambda}\left[\hat{S}_{-\mu}\right]_{\lambda\alpha'}\right\}.$$

(54)

Here

$$\omega_{\alpha\beta} = \frac{E_\alpha-E_\beta}{\hbar}$$

are the transition frequencies; E_α, and E_ε are the energy eigenvalues; and the Fourier transforms $\tilde{C}_{\nu,\mu}(\omega)$ of the noise correlation functions (spectral density) are

$$\tilde{C}_{\nu,\mu}(\omega) = \int_0^\infty C_{\nu,\mu}(\tau) e^{-i\omega\tau} d\tau$$

with

$$C_{-\mu,\mu}(-\tau) = C^*_{\mu,-\mu}(\tau) \text{ and } \tilde{C}^*_{\mu,-\mu}(\omega) = e^{-\beta\hbar\omega}\tilde{C}_{\mu,-\mu}(-\omega).$$

The latter relation between the spectral densities can be proved as follows (with $\hbar\omega + E_l = E_k$). We have

$$e^{-\beta\hbar\omega}\tilde{C}_{\mu,-\mu}(-\omega) = Z_B^{-1} e^{-\beta\hbar\omega} \int_0^\infty \sum_{k,l} e^{iE_l\tau/\hbar} h_{lk}^\mu e^{-iE_k\tau/\hbar} h_{kl}^{-\mu} e^{-\beta E_l} e^{i\omega\tau} d\tau$$

$$= Z_B^{-1} \int_0^\infty \sum_{k,l} e^{iE_l\tau/\hbar} \left(h_{lk}^{-\mu}\right)^* e^{-iE_k\tau/\hbar} \left(h_{kl}^\mu\right)^* e^{-\beta E_k} e^{i\omega\tau} d\tau$$

$$= \tilde{C}^*_{\mu,-\mu}(\omega). \tag{55}$$

The Redfield equation (54) describes the time evolution of the reduced density matrix of a system coupled to an equilibrium bath. The effect of the bath enters via the matrix elements of the "relaxation operator" $R_{\alpha\alpha'\varepsilon\varepsilon'}$. Equation (54) for this relaxation operator is written on the basis of eigenstates of the Hamiltonian $\hat{H}_S$. That equation has been obtained using the following three approximations: (i) the neglect of initial correlations; (ii) the assumption of weak coupling, and (iii) the assumption of a distinct time scale separation between the (fast) bath variables and the (slow) system (spin) variables, which have been used to get the final Markovian form. The dynamics of the bath or environment merely enters through the bath correlation functions (Eqs. 46 and 47). These functions are properties of the *equilibrium* bath only, regardless of whatever system it may be coupled to. We reiterate that although we have assumed that the bath dynamics are *fast on the time scale of the system dynamics*, the details of its dynamics do indeed matter, that is, we could not have simply assumed that the correlation functions are $C_{\mu,-\mu}(\tau) = 2D_\mu\delta(\tau)$ as in the classical case in the white noise approximation for random fields. The reason again is the fact that the *bath dynamics are usually slow relative to the phase oscillations* (which are obviously related to the inverse spacing between energy levels) in the system. We emphasize that solutions of Redfield-like equations for the density matrix even for simple systems (i.e., harmonic oscillators) do not necessarily satisfy the positivity property [76, 83] (for some extreme, nevertheless physically acceptable initial conditions, this *breakdown of positivity* arises from the *omission of memory effects*

in the early time evolution [76]). However, in regard to relaxation of spin systems *close to thermal equilibrium*, the Redfield form is always positively defined; moreover, it also has a well-defined classical limit (likewise invariably positively defined). Furthermore, for a wide range of initial distributions (in particular, for those considered here), the solutions of Redfield-like equations *invariably preserve positivity*; hence, under these conditions their use appears justifiable on physical grounds alone [76, 84].

Now the collision kernel also satisfies the equilibrium condition [14]

$$\sum_{\alpha} \left[\mathrm{St}\left(\hat{\rho}_{eq} \right) \right]_{\alpha\alpha} = \sum_{\alpha,\varepsilon} R_{\alpha\alpha\varepsilon\varepsilon}\, \rho_{\varepsilon\varepsilon}^{eq} = 0, \tag{56}$$

where $\rho_{\varepsilon\varepsilon'}^{eq} = \rho_{\varepsilon\varepsilon}^{eq}\delta_{\varepsilon\varepsilon'}$. In order to demonstrate this, we use Eqs. (52) and (53). We have

$$
\begin{aligned}
\sum_{\alpha} \left[\mathrm{St}\left(\hat{\rho}_{eq} \right) \right]_{\alpha\alpha} = & \sum_{\alpha,\varepsilon} \sum_{\mu=-1}^{1} (-1)^{\mu} \\
& \times \int_{0}^{\infty} \Big\{ C_{\mu,-\mu}(\tau) \left(\left[\hat{S}_{-\mu} \right]_{\alpha\varepsilon} \left[\hat{S}_{\mu} \right]_{\varepsilon\alpha} \rho_{\varepsilon\varepsilon}^{eq}(t) e^{-i(E_{\alpha}-E_{\varepsilon})\tau/\hbar} \right. \\
& \left. - \left[\hat{S}_{\mu} \right]_{\alpha\varepsilon} \left[\hat{S}_{-\mu} \right]_{\varepsilon\alpha} \rho_{\alpha\alpha}^{eq}(t) e^{-i(E_{\varepsilon}-E_{\alpha})\tau/\hbar} \right) + C_{\mu,-\mu}(-\tau) \\
& \times \left(\left[\hat{S}_{-\mu} \right]_{\alpha\varepsilon} \left[\hat{S}_{\mu} \right]_{\varepsilon\alpha} \rho_{\varepsilon\varepsilon}^{eq}(t) e^{i(E_{\alpha}-E_{\varepsilon})\tau/\hbar} \right. \\
& \left. - \left[\hat{S}_{\mu} \right]_{\alpha\varepsilon} \left[\hat{S}_{-\mu} \right]_{\varepsilon\alpha} \rho_{\alpha\alpha}^{eq}(t) e^{i(E_{\varepsilon}-E_{\alpha})\tau/\hbar} \right) \Big\}\, d\tau.
\end{aligned}
$$

Then by interchanging indices $\alpha \leftrightarrow \varepsilon$ in the second and fourth sums, we have Eq. (56). Next, we can formally define diffusion matrix coefficients D_{μ} as

$$D_{\mu} = \tilde{C}_{\mu}^{sym}(\omega)\, \mathrm{sech}\left(\frac{\beta\hbar\omega}{2} \right), \tag{57}$$

where the symmetrized spectral density

$$\tilde{C}_{\mu}^{sym}(\omega) = \frac{1}{2} \left[\tilde{C}_{\mu,-\mu}(-\omega) + \tilde{C}_{\mu,-\mu}^{*}(\omega) \right]$$

determines the spectrum of the *symmetrized* bath correlation functions [85] which are

$$C_{\mu}^{sym}(\tau) = \frac{(-1)^{\mu}}{2}\gamma^{2} \left(\left\langle \hat{h}^{\mu}\hat{h}^{-\mu}(\tau) \right\rangle + \left\langle \hat{h}^{-\mu}(\tau)\hat{h}^{\mu} \right\rangle \right). \tag{58}$$

Thus, with this definition, we have for the matrix elements $R_{\alpha\alpha'\varepsilon\varepsilon'}$ in the eigen-vector representation

$$
\begin{aligned}
R_{\alpha\alpha'\varepsilon\varepsilon'} \approx \sum_{\mu=-1}^{1} (-1)^{\mu} D_{\mu} \Big\{ & e^{\beta\hbar\omega_{\varepsilon\alpha}/2} \left[\hat{S}_{-\mu}\right]_{\alpha\varepsilon} \left[\hat{S}_{\mu}\right]_{\varepsilon'\alpha'} \\
& + e^{\beta\hbar\omega_{\varepsilon'\alpha'}/2} \left[\hat{S}_{-\mu}\right]_{\alpha\varepsilon} \left[\hat{S}_{\mu}\right]_{\varepsilon'\alpha'} \\
& - \sum_{\lambda} \Big(\delta_{\varepsilon'\alpha'} e^{\beta\hbar\omega_{\varepsilon\lambda}/2} \left[\hat{S}_{-\mu}\right]_{\alpha\lambda} \left[\hat{S}_{\mu}\right]_{\lambda\varepsilon} \\
& - \delta_{\alpha\varepsilon} e^{\beta\hbar\omega_{\varepsilon'\lambda}/2} \left[\hat{S}_{-\mu}\right]_{\varepsilon'\lambda} \left[\hat{S}_{\mu}\right]_{\lambda\alpha'} \Big) \Big\}.
\end{aligned}
\tag{59}
$$

In the operator notation, Eq. (59) then yields the collision kernel operator in the *symmetrized* form as follows [86]:

$$
\begin{aligned}
\text{St}\left(\hat{\rho}_S\right) = \sum_{\mu=-1}^{1} (-1)^{\mu} D_{\mu} \Big(& \left[\hat{S}_{\mu}, \hat{\rho}_S e^{\beta\hat{H}_S/2} \hat{S}_{-\mu} e^{-\beta\hat{H}_S/2}\right] \\
& + \left[e^{-\beta\hat{H}_S/2} \hat{S}_{-\mu} e^{\beta\hat{H}_S/2} \hat{\rho}_S, \hat{S}_{\mu}\right] \Big).
\end{aligned}
\tag{60}
$$

The vital difference between Eqs. (59) and Eq. (60) is that the latter is valid for an *arbitrary-state* representation, whereas Eq. (59) originates in contrast in the *energy-state* representation [76].

Now the collision kernel $\text{St}\left(\hat{\rho}_S\right)$ in the operator form equation (60) satisfies certain basic requirements constituting important consistency checks. These are as follows:

1. $\text{St}\left(\hat{\rho}_S\right)$ is also Hermitian if $\hat{\rho}_S(t)$ and $\hat{H}_S$ are Hermitian.
2. The equilibrium density matrix $\hat{\rho}_{eq} = e^{-\beta\hat{H}_S}/\text{Tr}\left(e^{-\beta\hat{H}_S}\right)$ renders $\text{St}\left(\hat{\rho}_{eq}\right) = 0$ ensuring that the spin system reaches a Boltzmann distribution at equilibrium.
3. While the matrix exponents $e^{\pm\beta\hat{H}_S/2}$ in the collision kernel operator equation (60) ensure detailed balance.
4. $\text{St}\left(\hat{\rho}_S\right)$ in Eq. (60) is invariant under rotations of the coordinate system.
5. The Hubbard model [86] embodied in Eq. (60) can be generalized to time-dependent Hamiltonians (see Section II.A.3); finally,
6. Spin density matrix evolution equation (40) with $\text{St}\left(\hat{\rho}_S\right)$ in the form of Eq. (60) effectively constitutes the direct analog of the classical Fokker–Planck equation (3) for rotational diffusion of a classical magnetic dipole.

The relaxation operator in the form of Eq. (60) is a reasonable approximation in the high-temperature limit [35, 36]. Essentially, it follows from the equation of

motion of the reduced density matrix in the rotating-wave approximation (familiar in quantum optics, where counter rotating, rapidly oscillating terms, are averaged out [27]) provided the spin–bath interactions are taken in the weak coupling limit and for Ohmic damping. In which case, the correlation time τ_c characterizing the bath may be regarded as very short so that the stochastic process originating in the bath is Markovian ($\gamma H \tau_c \ll 1$, where H is the averaged amplitude of the random magnetic field). If the approximation rendered by Eq. (60) is invalid (e.g., throughout the very-low-temperature region), alternative models for the spin–bath interactions should be used [76, 80–82, 85–89]. Nevertheless, we shall persevere with the model as just described because despite its drawbacks our objective is merely to understand in a semiclassical fashion how quantum effects alter the rotational Brownian motion and longitudinal relaxation of a classical giant spin at finite S. Moreover, that model as well as providing a qualitative description of the spin relaxation of a variety of systems can also be regarded as the direct analog of the Fokker–Planck equation formalism used by Brown [23, 24] and others (e.g., see Refs. 5, 6, 27 and 90–94) to treat relaxation of classical macrospins (see Appendix D).

We remark that the collision kernel equation (60) can be further simplified in the high-temperature limit, $\beta \hbar \omega_{\varepsilon \alpha} \ll 1$, by supposing that the diffusion matrix coefficients D_μ are *frequency-independent*, that is,

$$D_\mu = D_{-\mu} \approx \tilde{C}_\mu^{sym}(0). \tag{61}$$

In the time domain, this approximation corresponds to the representation of the bath correlation functions $C_\mu^{sym}(\tau)$ equation (58) as the sum of two delta function, namely,

$$C_\mu^{sym}(\tau) \approx D_\mu \left[\delta \left(\tau + \frac{i\beta\hbar}{2} \right) + \delta \left(\tau - \frac{i\beta\hbar}{2} \right) \right]. \tag{62}$$

In the classical limit $\hbar \to 0$, Eq. (62) reduces to the familiar result for the classical bath correlation functions in the white noise approximation for random fields, namely, $C_\mu^{cl}(\tau) = 2D_\mu \delta(\tau)$.

3. *Time-dependent Hamiltonian*

The derivation given before assumes that the spin Hamiltonian does not depend explicitly on the time [14]. However, Hubbard [86] also considered the more general case, namely, the time-dependent operator $\hat{H}_S = \hat{H}_S(t)$ and in so doing proposed the corresponding form for the collision kernel (in our notation)

$$\mathrm{St}\left(\hat{\rho}_S\right) = \sum_{\mu=-1}^{1} \sum_r (-1)^\mu e^{i\omega_r^{-\mu} t} D_\mu(\omega_r^{-\mu}) \left\{ e^{\beta\hbar\omega_r^{-\mu}/2} \left[\hat{S}_\mu, \hat{\rho}_S \hat{U}^{-1}(t) \hat{S}_{-\mu}^r \hat{U}(t) \right] \right.$$

$$\left. + e^{-\beta\hbar\omega_r^{-\mu}/2} \left[\hat{U}^{-1}(t) \hat{S}_{-\mu}^r \hat{U}(t) \hat{\rho}_S, \hat{S}_\mu \right] \right\}, \tag{63}$$

where the $\hat{S}^r_{\mu'}$ are the coefficients in the series expansion of the time-dependent spin operators $\hat{S}_{\mu'}(t) = \hat{U}(t)\hat{S}_{\mu'}\hat{U}^{-1}(t)$, namely,

$$\hat{S}_{\mu'}(t) = \sum_r \hat{S}^r_{\mu'} e^{i\omega^{\mu'}_r t}, \tag{64}$$

where $\omega^{\mu'}_r$ represents a parameter, the operator $\hat{U}(t)$ is defined as

$$\hat{U}(t) = e^{\frac{i}{\hbar}\int_0^t \hat{H}_S(t')dt'}, \tag{65}$$

and $D_\mu(\omega)$ is the correlation function of the bath given by Eq. (57). Then reconverting the result to operator form (see Eq. (64)), we have for the collision kernel

$$\begin{aligned}
\text{St}\left(\hat{\rho}_S\right) = {} & \sum_{\mu=-1}^{1} \sum_r (-1)^\mu D_\mu e^{i\omega^{-\mu}_r t} \\
& \times \left(e^{\beta\hbar\omega^{-\mu}_r/2}\left[\hat{S}_\mu, \hat{\rho}_S \hat{U}^{-1}(t)\hat{S}^r_{-\mu} U(t)\right]\right. \\
& \left. + e^{-\beta\hbar\omega^{-\mu}_r/2}\left[\hat{U}^{-1}(t)\hat{S}^r_{-\mu}\hat{U}(t)\hat{\rho}_S, \hat{S}_\mu\right]\right) \\
= {} & \sum_{\mu=-1}^{1} (-1)^\mu D_\mu \left(\left[\hat{S}_\mu, \hat{\rho}_S \hat{U}^{-1}(t)\hat{U}(t-i\beta\hbar/2)\hat{S}_{-\mu}\hat{U}^{-1}(t-i\beta\hbar/2)\hat{U}(t)\right]\right. \\
& \left. + \left[\hat{U}^{-1}(t)\hat{U}(t+i\beta\hbar/2)\hat{S}_{-\mu}\hat{U}^{-1}(t+i\beta\hbar/2)\hat{U}(t)\hat{\rho}_S, \hat{S}_\mu\right]\right). \tag{66}
\end{aligned}$$

Next we consider typical products like $\hat{U}^{-1}(t)\hat{U}(t \pm i\beta\hbar/2)$ given by

$$\hat{U}^{-1}(t)\hat{U}\left(t \pm \frac{i\beta\hbar}{2}\right) = e^{\frac{i}{\hbar}\int_t^{t\pm i\beta\hbar/2} \hat{H}_S(t')dt'}. \tag{67}$$

In the high-temperature limit, we have for the integral

$$\frac{i}{\hbar}\int_t^{t\pm i\beta\hbar/2} \hat{H}_S(t')dt' \approx \mp\frac{\beta}{2}\hat{H}_S(t). \tag{68}$$

Here, we have supposed that the operator $\hat{H}_S(t)$ does not alter significantly during the small time increments $\Delta t \sim \beta\hbar/2 \ll 1$ in Eq. (68). Thus, we can simply take the value of that operator at time t and, consequently, may place it outside the integral. By treating, in a like manner, all other such time-dependent functions in Eq. (66), we have an equation similar to Eq. (60). Thus, the Hubbard form

of the collision kernel equation (66) with time-dependent Hamiltonian $\hat{H}_S(t)$ simplifies to

$$
\begin{aligned}
\mathrm{St}\left(\hat{\rho}_S\right) = \sum_{\mu=-1}^{1} (-1)^\mu D_\mu &\left(\left[\hat{S}_\mu, \hat{\rho}_S e^{\beta\hat{H}_S(t)/2}\hat{S}_{-\mu}e^{-\beta\hat{H}_S(t)/2}\right]\right. \\
&\left.+ \left[e^{-\beta\hat{H}_S(t)/2}\hat{S}_{-\mu}e^{\beta\hat{H}_S(t)/2}\hat{\rho}_S, \hat{S}_\mu\right]\right).
\end{aligned}
\tag{69}
$$

As discussed before, the form of the collision kernel given by Eq. (69) corresponds to the high-temperature limit and short correlation time of the Markovian approximation.

4.   Method of Statistical Moments

One of the most powerful techniques for the solution of the evolution equations governing the relaxation dynamics of classical and quantum spins ultimately is the method of statistical moments [5, 30, 71, 95]. In order to summarize the principal equations of that method for quantum spins (the corresponding classical results are presented in Appendix D), we first recall that the density matrix $\hat{\rho}_S$ of the particles of spin S is represented by a $(2S + 1) \times (2S + 1)$ square matrix [95]. We also recall that in order to describe spin states of a particle, the so-called polarization operators $\hat{T}_{LM}^{(S)}$ are widely used [30, 95] (the main properties of $\hat{T}_{LM}^{(S)}$ are explained in Appendix A). Because the polarization operators constitute an orthonormal basis in the space of $(2S + 1) \times (2S + 1)$ square matrices, the density matrix $\hat{\rho}_S$ may be expanded into a finite sum of the polarization operator $\hat{T}_{LM}^{(S)}$ as [30, 95]

$$
\hat{\rho}_S(t) = \sum_{L=0}^{2S} \sum_{M=-L}^{L} a_{L,M}(t)\hat{T}_{LM}^{(S)},
\tag{70}
$$

where the expansion coefficients $a_{L,M}(t)$ defined as

$$
a_{L,M}(t) = \left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle(t) = \mathrm{Tr}\left(\hat{\rho}_S(t)\hat{T}_{LM}^{\dagger(S)}\right)
\tag{71}
$$

are simply the *statistical moments* representing expectation values of the operators $\hat{T}_{LM}^{\dagger(S)}$ in a state described by the density matrix $\hat{\rho}_S$. Equation (71) follows immediately from the orthogonality properties of the operators $\left\{\hat{T}_{LM}^{(S)}\right\}$ given by Eq. (A.34).

Now, the *formal* solution of the spin density matrix evolution equation (40) with an arbitrary collision kernel $\mathrm{St}(\hat{\rho}_S)$ can be written as the operator series equation (70). Therefore to find the statistical moments $\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle(t)$, we simply substitute Eq. (70) into Eq. (40). We have

$$\sum_{L=0}^{2S} \sum_{M=-L}^{L} \hat{T}_{LM}^{(S)} \frac{d}{dt} a_{L,M}(t) = \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(-\frac{i}{\hbar} \left[\hat{H}_S, \hat{T}_{LM}^{(S)} \right] + \mathrm{St}\left(\hat{T}_{LM}^{(S)} \right) \right) a_{L,M}(t),$$

(72)

where the collision operator is

$$\mathrm{St}\left(\hat{T}_{LM}^{(S)} \right) = \sum_{\mu=-1}^{1} (-1)^\mu D_\mu \left(\left[\hat{S}_\mu, \hat{T}_{LM}^{(S)} e^{\frac{\beta}{2} \hat{H}_S} \hat{S}_{-\mu} e^{-\frac{\beta}{2} \hat{H}_S} \right] \right.$$
$$\left. + \left[e^{-\frac{\beta}{2} \hat{H}_S} \hat{S}_{-\mu} e^{\frac{\beta}{2} \hat{H}_S} \hat{T}_{LM}^{(S)}, \hat{S}_\mu \right] \right).$$

Now the term

$$-\frac{i}{\hbar} \left[\hat{H}_S, \hat{T}_{LM}^{(S)} \right] + \mathrm{St}\left(\hat{T}_{LM}^{(S)} \right)$$

in Eq. (72) is itself just a matrix operator and can also be formally expanded in terms of the polarization operator series (see Appendix A), yielding (the expansion coefficients that are as usual defined by the trace of that operator)

$$-\frac{i}{\hbar} \left[\hat{H}_S, \hat{T}_{LM}^{(S)} \right] + \mathrm{St}\left(\hat{T}_{LM}^{(S)} \right)$$
$$= \sum_{L'=0}^{2S} \sum_{M'=-L}^{L} \mathrm{Tr} \left\{ \left(-\frac{i}{\hbar} \left[\hat{H}_S, \hat{T}_{LM}^{(S)} \right] + \mathrm{St}\left(\hat{T}_{LM}^{(S)} \right) \right) \hat{T}_{L'M'}^{\dagger(S)} \right\} \hat{T}_{L'M'}^{(S)}.$$

(73)

Consequently, by substituting the polarization operator expansion equation (73) into Eq. (72) and equating (by orthogonality) terms with the same $\hat{T}_{LM}^{(S)}$, we have the formal evolution equations for the statistical moments $a_{L,M}(t)$, namely,

$$\frac{d}{dt} a_{L,M}(t) = \sum_{L'=0}^{2S} \sum_{M'=-L}^{L} g_{L'M';LM} a_{L',M'}(t),$$

(74)

where the $g_{LM;L'M'}$ are formally defined as follows:

$$g_{LM;L'M'} = \mathrm{Tr} \left\{ -\frac{i}{\hbar} \left[\hat{H}_S, \hat{T}_{LM}^{(S)} \right] \hat{T}_{L'M'}^{\dagger(S)} + \mathrm{St}\left(\hat{T}_{LM}^{(S)} \right) \hat{T}_{L'M'}^{\dagger(S)} \right\}.$$

(75)

The coefficients $g_{L'M';LM}$ used in Eq. (74) can be obtained from the coefficients $g_{LM;L'M'}$ defined in Eq. (75) by the replacements $L \leftrightarrow L'$ and $M \leftrightarrow M'$. Now Eqs. (74) and (75) are valid for an *arbitrary* collision kernel operator $\mathrm{St}\left(\hat{\rho}_S \right)$.

In particular cases, for example, for $St(\hat{\rho}_S)$ given by the symmetrized Hubbard form of equation (60), Eq. (75) becomes

$$
\begin{aligned}
g_{L,M;L',M'} = \text{Tr}\Bigg\{ & \left(-\frac{i}{\hbar}\left[\hat{H}_S, \hat{T}_{LM}^{(S)}\right] + \sum_{\mu=-1}^{1} (-1)^{\mu} D_{\mu} \right. \\
& \left. \times \left(\left[\hat{S}_{\mu}, \hat{T}_{LM}^{(S)} e^{\frac{\beta}{2}\hat{H}_S}\hat{S}_{-\mu} e^{-\frac{\beta}{2}\hat{H}_S}\right] + \left[e^{-\frac{\beta}{2}\hat{H}_S}\hat{S}_{-\mu} e^{\frac{\beta}{2}\hat{H}_S}\hat{T}_{LM}^{(S)}, \hat{S}_{\mu}\right] \right) \right) \hat{T}_{L'M'}^{\dagger(S)} \Bigg\}.
\end{aligned}
$$
(76)

Nowadays, the explicit calculation of the coefficients $g_{LM;L'M'}$ for a particular collision operator is best accomplished using MATHEMATICA. In general, we will always have a *finite* set of differential recurrence equations for the averages $\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle (t)$ defined by Eq. (71), namely,

$$
\frac{d}{dt}\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle (t) = \sum_{L'=0}^{2S} \sum_{M'=-L}^{L} g_{LM;L'M'} \left\langle \hat{T}_{L'M'}^{\dagger(S)} \right\rangle (t),
$$
(77)

or because $\hat{T}_{LM}^{\dagger(S)} = (-1)^M \hat{T}_{L-M}^{(S)}$ we also have

$$
\frac{d}{dt}\left\langle \hat{T}_{LM}^{(S)} \right\rangle (t) = \sum_{L',M'} (-1)^{M'-M} g_{L'-M';L-M} \left\langle \hat{T}_{L'M'}^{(S)} \right\rangle (t).
$$
(78)

The differential recurrence equations (77 and 78) constitute the *general* solution of the problem in the operator representation for *arbitrary spin* Hamiltonians. Explicit forms of the coefficients $g_{LM;L'M'}$ resulting from the polarization operator expansion of the Liouville and collision terms in the density matrix evolution equation, for example, Eq. (76), for specific cases of the Hamiltonian $\hat{H}_S$ and particular examples of solutions of the differential recurrence equations (Eqs. 77 and 78) will be given later. Moreover, Eqs. (77) and (78) are very useful for the purpose of obtaining differential recurrence relations for phase space observables as we demonstrate in Sections II.C and III.A.

Equation (77) may be formally solved using standard matrix-inversion techniques. This is accomplished by first noting that according to Eq. (77), the behavior of any selected average of the polarization operators $a_{L',M'}(t) = \left\langle \hat{T}_{L'M'}^{\dagger(S)} \right\rangle (t)$ say is coupled to that of all the others so forming a *finite* hierarchy of differential recurrence equations because the index L ranges only between 0 and $2S$. Now the solution of such a multi-term recurrence relation may always be obtained [5] by rewriting it as a first-order linear matrix differential equation with constant coefficients. This is accomplished by first defining a supercolumn vector $\mathbf{C}(t)$ such that

$$\mathbf{C}(t) = \begin{pmatrix} \mathbf{c}_1(t) \\ \mathbf{c}_2(t) \\ \vdots \\ \mathbf{c}_{2S}(t) \end{pmatrix}, \quad \mathbf{c}_L(t) = \begin{pmatrix} a_{L,-L}(t) \\ a_{L,-L+1}(t) \\ \vdots \\ a_{L,L}(t) \end{pmatrix}, \tag{79}$$

whereupon the evolution equation (77) of the average polarization operators becomes the linear homogeneous matrix differential equation

$$\frac{d}{dt}\mathbf{C}(t) + \mathbf{X}\mathbf{C}(t) = 0, \tag{80}$$

where $\mathbf{X}$ is the $4S(S+1)\times4S(S+1)$ transition supermatrix with matrix elements

$$(\mathbf{X})_{L,L'} = \mathbf{G}^S_{L,L'}, \tag{81}$$

and

$$\left[\mathbf{G}^S_{L,L'}\right]_{M,M'} = -g_{L'M';LM}. \tag{82}$$

Here, we have utilized the evolution equation for $a_{0,0}(t)$, namely, $\partial_t a_{0,0}(t) = 0$ with the trivial solution $a_{0,0}(t) = const$. The formal solution of Eq. (80) for the desired column vector is [96]

$$\mathbf{C}(t) = e^{-\mathbf{X}t}\mathbf{C}(0) = \mathbf{U}e^{-\Lambda t}\mathbf{U}^{-1}\mathbf{C}(0), \tag{83}$$

where $\Lambda = \mathbf{U}^{-1}\mathbf{X}\mathbf{U}$ is a diagonal matrix with elements composed of all the eigenvalues λ_k of the transition matrix $\mathbf{X}$ and $\mathbf{U}$ is a right eigenvector matrix composed of all the eigenvectors of $\mathbf{X}$. Now having calculated $\mathbf{C}(t)$ from the matrix Eq. (83), we have all the statistical moments

$$a_{L,M}(t) = \left\langle \hat{T}^{\dagger(S)}_{LM} \right\rangle(t) = (-1)^M \left\langle \hat{T}^{(S)}_{L-M} \right\rangle(t).$$

Next, recalling that the spin operators $\hat{S}_X$, $\hat{S}_Y$, and $\hat{S}_Z$ may always be expressed in terms of the $\hat{T}^{(S)}_{10}$ and $\hat{T}^{(S)}_{1\pm1}$ via Eq. (A.21), we can evaluate the average components of the spin operators in terms of the average polarization operators, namely,

$$\left\langle \hat{S}_X \right\rangle(t) = a\left[\left\langle \hat{T}^{(S)}_{1-1} \right\rangle(t) - \left\langle \hat{T}^{(S)}_{11} \right\rangle(t)\right], \tag{84}$$

$$\left\langle \hat{S}_Y \right\rangle(t) = ia\left[\left\langle \hat{T}^{(S)}_{1-1} \right\rangle(t) + \left\langle \hat{T}^{(S)}_{11} \right\rangle(t)\right], \tag{85}$$

$$\left\langle \hat{S}_Z \right\rangle(t) = \sqrt{2}a\left\langle \hat{T}^{(S)}_{10} \right\rangle(t), \tag{86}$$

where

$$a = \sqrt{\frac{S(S+1)(2S+1)}{6}}.$$

We remark that the differential recurrence equation (77) can also be solved by the matrix continued fraction method [5, 71] (see also Appendix D).

The density matrix method that we have illustrated via the evolution equation for the polarization operators has hitherto constituted the usual approach to the treatment of spin relaxation and resonance phenomena. However, relaxation and resonance of spins interacting with a bath can also be treated in classical-like fashion via the relevant quasiprobability distribution function $W_S(\vartheta, \varphi, t)$ of spin orientations in a phase space (here configuration space) (ϑ, φ); ϑ and φ are the polar and azimuthal angles (see, e.g., Refs. 35–40 and 52–70). The quasiprobability distribution function $W_S(\vartheta, \varphi, t)$ is considered in the following sections.

B.   Quasiprobability Distribution Functions for Particles

In order to introduce the concept of a quasiprobability distribution function, we recall that, in general, a classical dynamical system of one degree of freedom may be described by a phase space probability distribution function $W(q, p, t)$ yielding the probability $W(q, p, t)dpdq$ that the system is in a volume element $dqdp$ centered around the phase space point (q, p) of coordinate q and momentum p. However, in the quantum mechanical description of a dynamical system (because of the uncertainty principle) the phase space coordinates (q, p) cannot take definite values simultaneously. Therefore, the concept of such a function does not exist for a quantum system because the idea of a *sharp* phase point, and a collection or ensemble of such sharp points has of itself no meaning. Nevertheless, it is still possible to utilize certain mathematical constructs called *quasiprobability distributions*, closely resembling the classical phase space distribution functions. Such quasiprobability distributions have proven [41–47] to be very useful in various physical applications as they provide fruitful insights into the connection between classical and quantum mechanics allowing one to express quantum mechanical averages in a form very similar to that of classical averages. Thus, they are ideally suited to the study of the quantum classical correspondence. Furthermore, they provide a useful tool for introducing quantum corrections to classical models of dissipation such as many-body collisions, Brownian motion, escape-rate theory, and so on. (see, e.g., Refs. 47, 87 and 97–100) as well as the connection between decoherence and the quantum to classical transition [101]. The first of these quasiprobability distributions was introduced by Wigner [41] in 1932 in order to study in a semiclassical fashion quantum corrections to the Maxwell–Boltzmann distribution of classical statistical mechanics, which *inter alia* elucidated the role played by tunneling effects at high temperatures in reaction-rate theory [97–100]. In principle, the Wigner distribution function was meant to be a reformulation, using the concept of a quasiprobability distribution in *phase space*, of Schrödinger's wave mechanics, which describes quantum states in *configuration space*.

Before proceeding, we recall the properties of the coordinate and momentum operators $\hat{q}$ and $\hat{p} = -i\hbar\partial/\partial q$, which are used to describe a quantum mechanical system in Hilbert space with one degree of freedom [78] as follows:

1. The operators $\hat{q}$ and $\hat{p}$ are *non-commutative*, that is,

$$[\hat{q}, \hat{p}] = \hat{q}\hat{p} - \hat{p}\hat{q} = i\hbar. \tag{87}$$

2. The *eigenvectors* $|q\rangle$ and $|p\rangle$ of the operators $\hat{q}$ and $\hat{p}$ obey the following conditions:

$$\hat{q}\,|q\rangle = q\,|q\rangle, \tag{88}$$

$$\hat{p}\,|p\rangle = p\,|p\rangle, \tag{89}$$

$$\langle q'\,|q''\rangle = \delta(q' - q''), \tag{90}$$

$$\langle p'\,|p''\rangle = \delta(p' - p''), \tag{91}$$

$$\langle q\,|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{iqp/\hbar}, \tag{92}$$

$$\langle p\,|q\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{-iqp/\hbar}, \tag{93}$$

$$\int |q\rangle\,\langle q|\,dq = \hat{I}, \tag{94}$$

$$\int |p\rangle\,\langle p|\,dp = \hat{I}, \tag{95}$$

where $\hat{I}$ is the unity operator and δ is the Dirac delta function.

3. The wave functions in the *coordinate* and *momentum* representations are defined via a *state vector* $|\psi(t)\rangle$ in Hilbert space as follows:

$$\psi(q, t) = \langle q|\,\psi(t)\rangle, \tag{96}$$

$$\psi(p, t) = \langle p|\,\psi(t)\rangle. \tag{97}$$

4. And, finally, the probability densities of the coordinate and momentum are given by

$$W(q, t) = |\langle q|\,\psi(t)\rangle|^2, \tag{98}$$

$$W(p, t) = |\langle p|\,\psi(t)\rangle|^2. \tag{99}$$

Now for purposes of exposition, we consider following Puri [51], a one-dimensional dynamical system described classically by a phase space distribution function $W(q, p, t)$. Then the classical statistical average of any function $A(q, p)$ is by definition

$$\langle A(q, p)\rangle_{cl} = \int W(q, p, t)A(q, p)dqdp. \tag{100}$$

By analogy, the quantum mechanical description of a system is contained in its Hilbert space density operator $\hat{\rho}(t)$, which determines the quantum statistical average of any function $A(\hat{q}, \hat{p})$ of the coordinate and momentum operators $\hat{q}$ and $\hat{p}$ by the following relation:

$$\langle A(\hat{q}, \hat{p}) \rangle = \text{Tr} \left[\hat{\rho}(t) A(\hat{q}, \hat{p}) \right]. \tag{101}$$

Now the classical distribution function $W(q, p, t)$ may always be expressed in terms of the averages of a *complete* set of functions of q and p. This fact suggests that we may be able to construct a quantum analog of the classical distribution function by expressing the latter distribution in terms of the average of a suitably chosen complete set of functions and then relabeling those classical averages as quantum mechanical ones. In order to explore this possibility, we rewrite a typical classical distribution in integral form as follows [51]:

$$W(q, p, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \delta(p - p') \delta(q - q') W(q', p', t) dq' dp'$$

$$= \frac{1}{4\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{ik(q-q')} e^{il(p-p')} W(q', p', t) dq' dp' dk dl, \tag{102}$$

which by definition is

$$W(q, p, t) = \frac{1}{4\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{ikq} e^{ilp} \left\langle e^{-ikq} e^{-ilp} \right\rangle_{cl} dk dl. \tag{103}$$

Thus, we have expressed the classical distribution function $W(q, p, t)$ in terms of the *average* of a complete set of functions of e^{-ikq} and e^{-ilp} or in statistical terminology as the inverse Fourier transform of the characteristic function $\left\langle e^{-ikq} e^{-ilp} \right\rangle_{cl}$. To construct the quantum analog of $W(q, p, t)$, we must first replace the *classical dynamical variables* (q, p) by the Hilbert space *quantum operators* $(\hat{q}, \hat{p})$ and then replace the classical average $\left\langle e^{-ikq} e^{-ilp} \right\rangle_{cl}$ or characteristic function in the integrand of Eq. (103) by the quantum average as defined by Eq. (101). Thus, we have a quantum analog of the classical phase space distribution function

$$W^{\text{T}}(q, p, t) = \frac{1}{4\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{ikq} e^{ilp} \left\langle \text{T}(e^{-ik\hat{q}}, e^{-il\hat{p}}) \right\rangle_{qm} dk dl \tag{104}$$

called a *quasiprobability distribution*. In writing Eq. (104), we formally wrote the product $e^{-ikq} e^{-ilp}$ as an ordering operator $\text{T}(e^{-ik\hat{q}}, e^{-il\hat{p}})$ because owing to the *non-commutativity* of the Hilbert space operators $\hat{q}$ and $\hat{p}$ several *different* quantum operator forms exist, which all may be considered as *quantum analogs* of the

unique classical product $e^{-ikq}e^{-ilp}$. The different operator forms must then be formally described by an ordering operator $T(e^{-ik\hat{q}}, e^{-il\hat{p}})$. Hence, *different choices* of $T(e^{-ik\hat{q}}, e^{-il\hat{p}})$ ultimately lead to *different quantum phase space distribution functions* $W^T(q, p, t)$ [47].

The name *quasiprobability* is used to emphasize that such a distribution represents a merely mathematical construct and is not in itself a true phase space distribution function as no such joint distribution function can exist for a quantum system [47]. Now in order to systematically investigate various operator orderings $T(e^{-ik\hat{q}}, e^{-il\hat{p}})$, it is convenient to express the quantum operators $\hat{q}, \hat{p}$ in terms of the creation and annihilation operators $\hat{a}$ and $\hat{a}^{\dagger}$ defined as [40]

$$\hat{a} = \frac{1}{\sqrt{2\hbar}}(\hat{q} + i\hat{p}), \quad \hat{a}^{\dagger} = \frac{1}{\sqrt{2\hbar}}(\hat{q} - i\hat{p}) \qquad (105)$$

so that

$$\hat{q} = \sqrt{\frac{\hbar}{2}}(\hat{a} + \hat{a}^{\dagger}), \quad \hat{p} = i\sqrt{\frac{\hbar}{2}}(\hat{a}^{\dagger} - \hat{a}) \qquad (106)$$

and then consider the operator $T(e^{i\xi\hat{a}}, e^{i\xi^*\hat{a}^{\dagger}})$ which may be rewritten as [51]

$$T(e^{i\xi\hat{a}}, e^{i\xi^*\hat{a}^{\dagger}}) = e^{s|\xi|^2/2}e^{i\xi\hat{a}+i\xi^*\hat{a}^{\dagger}}. \qquad (107)$$

Here, s is a complex number. The ordering for $s = 0$, usually called the *Weyl ordering* or the *symmetric ordering* corresponds to the *Wigner function*. The quasiprobability distribution function for $s = 1$ is known as the *P-function* $W^P(q, p, t)$, while that for $s = -1$ is known as the *Q-function* $W^Q(q, p, t)$ [40, 51, 54]. The *Q*- and *P*-representations, and the Wigner function representation, arise from three different aims. On the one hand, in the *Q*-representation, it is desired to create a quasiprobability density for the quantum system by using the *diagonal matrix elements of the density operator* for this purpose. On the other hand, the *P*-representation arises from the desire to represent the density operator as an *ensemble of coherent states* [78]. Finally, the Wigner function yields a *joint* quasi-distribution for *canonically conjugate* variables p and q, which in many respects resembles a classical probability distribution. All of these phase space representations have their particular advantages and disadvantages [102]. At first, we restrict ourselves to the Wigner function for particles. For spins, the *Q*- and *P*-representations as well as the Wigner function representation will be considered in detail in Section II.B.1.

1. The Wigner Distribution Function for Particles

By directly proceeding from a statistical viewpoint, Moyal [103] has shown how the Wigner function follows naturally from the inversion of a characteristic function $M(\mu, \nu)$ for canonically conjugate variables such as position and momentum

in a state described by a state vector $|\psi(t)\rangle$ in the Hilbert space. Moyal [103], in view of his strong background in statistics, starts by defining a *characteristic function operator* (cf. Eq. (103) et seq; coordinates and momenta are once more used instead of the creation and annihilation operators), namely,

$$\mathbf{M}_{\hat{q},\hat{p}}(\mu, v) = e^{i\mu\hat{q}+iv\hat{p}}. \tag{108}$$

The characteristic function $M(\mu, v)$ in a state $|\psi(t)\rangle$ in Hilbert space is then given by definition as the scalar product

$$M(\mu, v) = \left\langle e^{i\mu\hat{q}+iv\hat{p}} \right\rangle = \mathrm{Tr}\left(\hat{\rho} e^{i\mu\hat{q}+iv\hat{p}} \right)$$

$$= \langle \psi(t)| \, e^{i\mu\hat{q}+iv\hat{p}} \, |\psi(t)\rangle = \int_{-\infty}^{\infty} \psi^*(q,t) e^{i\mu\hat{q}+iv\hat{p}} \psi(q,t)dq, \tag{109}$$

where $\psi(q,t) = \langle q| \, \psi(t)\rangle$ is the wave function in the coordinate representation and $\hat{q}$ and $\hat{p} = -i\hbar\partial/\partial q$ are the canonically conjugate coordinate and momentum operators. Because the non-commuting operators $\hat{p}$ and $\hat{q}$ satisfy the Baker–Campbell–Hausdorff identity [43]

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}e^{-[\hat{A},\hat{B}]/2}, \tag{110}$$

the characteristic function operator $\mathbf{M}_{\hat{q},\hat{p}}(\mu, v)$ then becomes

$$\mathbf{M}_{\hat{q},\hat{p}}(\mu, v) = e^{i\hbar\mu v/2}e^{i\mu\hat{q}}e^{iv\hat{p}} = e^{-i\hbar\mu v/2}e^{iv\hat{p}}e^{i\mu\hat{q}} \tag{111}$$

since we have Eq. (87) for the commutator of the operators $\hat{q}$ and $\hat{p}$. Next, since we may eliminate $\hat{p}$ via [78]

$$e^{iv\hat{p}}\psi(q) = \psi(q) + \hbar v\frac{\partial}{\partial q}\psi(q) + \cdots = \psi(q + v\hbar), \tag{112}$$

we have the simplified expression

$$M(\mu, v) = \int_{-\infty}^{\infty} \psi^*(q,t) e^{i\mu(q+v\hbar/2)}\psi(q + v\hbar, t)dq, \tag{113}$$

which with the replacement $q \to q - v\hbar/2$ yields the characteristic function as the overlap integral

$$M(\mu, v) = \int_{-\infty}^{\infty} \psi^*(q - u, t) e^{i\mu q}\psi(q + u, t)dq, \tag{114}$$

where $u = v\hbar/2$. The phase space quasi-distribution $W(q, p, t)$ is thus by Fourier inversion

$$
\begin{aligned}
W(q, p, t) &= \frac{1}{4\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} M(\mu, v) e^{-i\mu q - ivp} \, d\mu \, dv \\
&= \frac{1}{2\hbar\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\mu(q-x)} \psi^*(x - u, t) e^{-2iup/\hbar} \psi(x + u, t) \, du \, dx \, d\mu \\
&= \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \psi^*(q - u, t) e^{-2iup/\hbar} \psi(q + u, t) \, du,
\end{aligned}
\tag{115}
$$

which is real but not *everywhere positive* so that it is indeed a quasiprobability distribution. Here, we have used the definition

$$
\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\mu(q-x)} d\mu = \delta(q - x).
\tag{116}
$$

Equation (115) defining the Wigner function $W(q, p, t)$ (which represents the Fourier transform of the overlap function, namely, a type of spatial autocorrelation function of the wave function ψ in coordinate space [77]) holds if ψ evolves according to the Schrödinger equation

$$
i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial q^2} + V(q)\psi
\tag{117}
$$

for a particle of mass m moving in a potential $V(q)$. Now integration of $W(q, p, t)$ with respect to the momentum p yields

$$
\int_{-\infty}^{\infty} W(q, p, t) dp = |\psi(q, t)|^2,
\tag{118}
$$

that is, the correct quantum mechanical probability for the coordinate q. Conversely, integration of W with respect to q, yields the correct quantum mechanical probability for the momentum p, viz.,

$$
\int_{-\infty}^{\infty} W(q, p, t) dq = |\Phi(p)|^2,
\tag{119}
$$

where $\Phi(p)$ is the wave function of the momentum given by

$$\Phi(p) = \int_{-\infty}^{\infty} \psi(q,t)e^{-ipq}dq.$$

It follows from Eq. (118) that if the wave function $\psi(q,t)$ is normalized to unity then

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W(q,p,t)dqdp = 1. \tag{120}$$

Now by recalling Ref. 77, the definition of the density matrix operator $\hat{\rho}$ for a pure state, namely,

$$\hat{\rho}(q_1,q_2,t) = \langle q_1 | \psi(t)\rangle \langle \psi(t)| q_2\rangle = \psi(q_1,t)\psi^*(q_2,t),$$

and introducing the replacements $q = (q_1 + q_2)/2$ and $y/2 = u = (q_1 - q_2)/2$, one can finally write Eq. (115) as follows [77]:

$$W(q,p,t) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} \hat{\rho}(q+y/2,q-y/2,t)e^{-ipy/\hbar}dy$$

$$= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} \hat{\rho}(q-y/2,q+y/2,t)\,e^{ipy/\hbar}dy. \tag{121}$$

Moreover, the inverse transformation is given by the Weyl transform yielding the mapping from the phase space back to operators in Hilbert space [47], namely,

$$\hat{\rho}(t) = \frac{\hbar}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W(q,p,t)\,e^{ix(\hat{q}-q)+iy(\hat{p}-p)}dqdpdxdy. \tag{122}$$

We remark in passing that in contrast to Eq. (115), the definition of the Wigner function $W(q,p,t)$ via the density operator $\hat{\rho}(t)$, Eq. (121), is valid both for *pure* and mixed states. The only difference is in the definition of $\hat{\rho}(t)$. For a pure state $|\psi(t)\rangle$, the density operator is given by $\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|$, while for a mixed state, the density operator is defined as follows [76]:

$$\hat{\rho}(t) = \sum_n P_n |\psi_n(t)\rangle \langle\psi_n(t)|, \tag{123}$$

where P_n is the probability of each state $|\psi_n(t)\rangle$. The Wigner function of a *mixed* state $W(q,p,t)$ is then given by the following relation [76]:

$$W(q,p,t) = \sum_n P_n W_n(q,p,t). \tag{124}$$

Here $W_n(q,p,t)$ is the Wigner function for the state $|\psi_n(t)\rangle$. In particular, the definition, Eq. (124), applies to a canonical ensemble of particles at temperature T, where $P_n = e^{-\beta E_n}/Z$ is the probability to find the particle in an energy state E_n, and Z is the partition function.

The Wigner function $W(q,p,t)$ exhibits most of the properties of a classical phase space distribution, including the fact that the expectation value $\left\langle \hat{A} \right\rangle (t) =$ Tr $\left(\hat{\rho}\hat{A} \right)$ of a quantum operator $\hat{A}$ may be calculated in *classical fashion via the corresponding Weyl symbol* $A(q,p)$ as [47]

$$\left\langle \hat{A} \right\rangle (t) = \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} W(q,p,t)A(q,p)dq\,dp, \tag{125}$$

where

$$A(q,p) = \int\limits_{-\infty}^{\infty} e^{-ipy/\hbar} \langle q + y/2|\,\hat{A}\,|q - y/2\rangle \, dy \tag{126}$$

is the Weyl transform of the operator $\hat{A}$ expressed in the position q basis. Equivalently, the Weyl transform can be expressed in terms of matrix elements of the operator $\hat{A}$ in the momentum p basis as

$$A(q,p) = \int\limits_{-\infty}^{\infty} e^{-iqy/\hbar} \langle p + y/2|\,\hat{A}\,|p - y/2\rangle \, dy. \tag{127}$$

The Weyl transform implies that the trace of the product of two operators $\hat{A}$ and $\hat{B}$ is given by the integral over the phase space (q,p) of the product of their Weyl transforms $A(q,p)$ and $B(q,p)$, namely, [47]

$$\mathrm{Tr}\left\langle \hat{B}\hat{A} \right\rangle = \frac{1}{2\pi\hbar} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} B(q,p)A(q,p)dq\,dp. \tag{128}$$

Equations (121) and (128) (for $\hat{B} \equiv \hat{\rho}$) yield immediately Eq. (125).

We may now determine from the overlap Fourier transform equation (115) the partial differential equation governing the time evolution of the Wigner function. Taking the derivative of Eq. (115), we obtain the following equation:

$$\frac{\partial W}{\partial t} = \frac{1}{\pi\hbar} \int\limits_{-\infty}^{\infty} \left[\psi^*(q+u,t) \frac{\partial \psi\,(q-u,t)}{\partial t} + \frac{\partial \psi^*(q+u,t)}{\partial t} \psi\,(q-u,t) \right]$$
$$\times e^{2ipu/\hbar}du. \tag{129}$$

Now since the wave function ψ in coordinate space evolves according to the Schrödinger equation (117), substitution of that equation into Eq. (129) gives

$$
\begin{aligned}
\frac{\partial W}{\partial t} &= -\frac{i}{2m\pi} \int_{-\infty}^{\infty} \left\{ \psi\,(q-u)\, \frac{\partial^2 \psi^*(q+u)}{\partial u^2} - \psi^*\,(q+u)\, \frac{\partial^2 \psi\,(q-u)}{\partial u^2} \right. \\
&\quad \left. - \frac{2m}{\hbar^2} \psi\,(q-u)\,\psi^*\,(q+u)\left[V(q+u) - V(q-u)\right] \right\} e^{2ipu/\hbar} du \quad (130) \\
&= -\frac{p}{m}\frac{\partial W}{\partial q} + \frac{i}{\pi\hbar^2} \int_{-\infty}^{\infty} \psi\,(q-u)\,\psi^*\,(q+u)\left[V(q+u) - V(q-u)\right] \\
&\quad \times e^{2ipu/\hbar} du.
\end{aligned}
$$

Here, we have utilized the derivative property

$$
\frac{\partial^2 \psi\,(q\pm u)}{\partial q^2} = \frac{\partial^2 \psi\,(q\pm u)}{\partial u^2}
$$

and have performed one partial integration with respect to u in the terms that do not involve the potential functions $V(q \pm u)$. Equation (130) is identical to the classical Liouville equation in the force-free case $V(q) = 0$ and concurs with that given by Hillery et al. [44]. We now expand $V(q + u) - V(q - u)$ in Eq. (130) in a Taylor series about the point q yielding

$$
V(q+u) - V(q-u) = 2\sum_{n=1}^{\infty} \frac{u^{2n-1}}{(2n-1)!} \frac{\partial^{2n-1}V}{\partial q^{2n-1}}. \quad (131)
$$

Substituting Eq. (131) into Eq. (130), we have

$$
\frac{\partial W}{\partial t} + \frac{p}{m}\frac{\partial W}{\partial q} = \frac{2i}{\pi\hbar} \int_{-\infty}^{\infty} \sum_{n=1}^{\infty} \frac{u^{2n-1}}{(2n-1)!} \frac{\partial^{2n-1}V}{\partial q^{2n-1}} \psi^*\,(q+u)\,\psi\,(q-u)\, e^{2ipu/\hbar} du.
$$
$$
(132)
$$

Next, because of the relation

$$
u^{2n-1}e^{2ipu/\hbar} = \left(\frac{\hbar}{2i}\right)^{2n-1} \frac{\partial^{2n-1}}{\partial p^{2n-1}} e^{2ipu/\hbar}, \quad (133)
$$

we have

$$
\frac{2i}{\pi\hbar}\sum_{n=1}^{\infty}\frac{1}{(2n-1)!}\left(\frac{\hbar}{2i}\right)^{2n-1}\frac{\partial^{2n-1}V}{\partial q^{2n-1}}\frac{\partial^{2n-1}}{\partial p^{2n-1}}\int_{-\infty}^{\infty}\psi^*\left(q+u\right)\psi\left(q-u\right)e^{2ipu/\hbar}du
$$

$$
=\sum_{n=1}^{\infty}\frac{1}{(2n-1)!}\left(\frac{\hbar}{2i}\right)^{2n-2}\frac{\partial^{2n-1}V}{\partial q^{2n-1}}\frac{\partial^{2n-1}W}{\partial p^{2n-1}}
$$

$$
=-\frac{\partial V}{\partial q}\frac{\partial W}{\partial p}-\sum_{r=1}^{\infty}\frac{(i\hbar/2)^{2r}}{(2r+1)!}\frac{\partial^{2r+1}V}{\partial q^{2r+1}}\frac{\partial^{2r+1}W}{\partial p^{2r+1}}. \tag{134}
$$

Thus, we have the time evolution equation for the Wigner distribution function $W(q,p,t)$, namely,

$$
\frac{\partial W}{\partial t}+\hat{M}_W W=0, \tag{135}
$$

where the operator $\hat{M}_W$ is defined as follows:

$$
\hat{M}_W W=\frac{p}{m}\frac{\partial W}{\partial q}-\frac{\partial V}{\partial q}\frac{\partial W}{\partial p}-\sum_{r=1}^{\infty}\frac{(i\hbar/2)^{2r}}{(2r+1)!}\frac{\partial^{2r+1}V}{\partial q^{2r+1}}\frac{\partial^{2r+1}W}{\partial p^{2r+1}}. \tag{136}
$$

Equation (135) often known as the Wigner–Moyal equation [77] is a quantum analog of the classical Liouville equation. Equations (135) and (136) also hold if the system is in a mixed state represented by a density matrix $\hat{\rho}$.

Now Wigner [41] originally calculated quantum correction terms to the classical stationary distribution functions for a system with n degrees of freedom. However, for illustrative purposes, we only consider a system with $n = 1$. As an example, we determine the stationary (equilibrium) solution of Eq. (135) for an assembly of noninteracting particles each of mass m moving in a potential $V(q)$ at temperature T. Each particle is characterized by the energy

$$
\varepsilon(q,p)=\frac{p^2}{2m}+V(q). \tag{137}
$$

Following Wigner [41], we develop the stationary distribution function $W_{eq}(q,p)$ in a power series

$$
W_{eq}(q,p)=W_0(q,p)+\hbar^2 W_2(q,p)+\hbar^4 W_4(q,p)+\cdots, \tag{138}
$$

where $W_0(q,p)=e^{-\beta\varepsilon(q,p)}$ is the (unnormalized) Maxwell–Boltzmann distribution. By substituting Eq. (138) into Eq. (135), the function $W_2(q,p)$ and $W_4(q,p)$ are easily evaluated. Thus, we have [48]

$$W_{eq}(q,p) = e^{-\beta\varepsilon(q,p)} \left\{ 1 + \Lambda \left(\frac{\beta p^2}{m} V^{(2)} - 3V^{(2)} + \beta \left(V^{(1)} \right)^2 \right) \right.$$

$$+ 3\Lambda^2 \left[\frac{\beta^2}{6} \left(V^{(1)} \right)^4 + \frac{5}{2} \left(V^{(2)} \right)^2 - \frac{9\beta}{5} V^{(2)} \left(V^{(1)} \right)^2 \right.$$

$$+ 2V^{(3)} V^{(1)} - \frac{3}{2\beta} V^{(4)} + \frac{p^2}{m} \left(V^{(4)} - \frac{2\beta}{5} V^{(3)} V^{(1)} \right) \qquad (139)$$

$$+ \frac{1}{3} V^{(2)} \left(\beta V^{(1)} \right)^2 - \frac{9\beta}{5} \left(V^{(2)} \right)^2 \right)$$

$$+ \left. \left. \frac{p^4}{m^2} \left(\frac{1}{6} \left(\beta V^{(2)} \right)^2 - \frac{\beta V^{(4)}}{10} \right) \right] \right\} + \cdots ,$$

where $\Lambda = \hbar^2 \beta^2 / (24m)$ is a characteristic quantum parameter and $V^{(m)} \equiv d^m V / dq^m$. These equations are written explicitly to $o(\hbar^4)$. In a like manner, higher order quantum correction terms to the Wigner stationary distribution $W_{eq}(q,p)$ may be calculated. Thus, $W_{eq}(q,p)$ can be given, in principle, to any desired degree r of $\hbar^{2r}$. In general, quantum effects give rise to *non-Gaussian behavior* of the equilibrium phase space distribution function $W_{eq}(q,p)$, and it is no longer separable in the position and momentum variables.

Obviously, the calculation of the equilibrium Wigner distribution $W_{eq}(q,p)$ is a tedious task for an arbitrary potential $V(q)$. However, in some cases, $W_{eq}(q,p)$ can be found in closed form (various methods for the calculation of Wigner functions are described, for example, in Refs. 43, 44, 46, and 47). A famous example is the quantum harmonic oscillator, where the potential is

$$V(q) = \frac{1}{2} m\omega_0^2 q^2 \qquad (140)$$

(ω_0 is the angular frequency of the oscillator). Here, perturbation theory may be avoided because the evolution equation for the Wigner function equation (135) for the potential (140) now coincides with the corresponding classical Liouville equation and the unnormalized equilibrium Wigner function $W_{eq}(q,p)$ can be written in the exact Gaussian form [43, 44, 48, 104]

$$W_{eq}(q,p) = \frac{\mathrm{sech}\,(\beta\hbar\omega_0/2)}{2\pi\hbar} e^{-\frac{q^2}{2\langle q^2\rangle_{eq}} - \frac{p^2}{2\langle p^2\rangle_{eq}}}, \qquad (141)$$

where

$$\langle q^2 \rangle_{eq} = \frac{\hbar}{2m\omega_0} \coth \frac{\beta\hbar\omega_0}{2} \qquad (142)$$

and

$$\left\langle p^2 \right\rangle_{eq} = \frac{m\hbar\omega_0}{2} \coth \frac{\beta\hbar\omega_0}{2}. \tag{143}$$

The Wigner function $W_{eq}(q,p)$ from Eq. (141) is in fact a *superposition* of the Wigner functions $W_n(q,p)$ for the pure states of a harmonic oscillator, namely, [43, 44, 48]

$$W_{eq}(q,p) = \sum_{n=0}^{\infty} W_n(q,p) e^{-\beta\hbar\omega_0(n+1/2)}. \tag{144}$$

Here, $W_n(q,p)$ and the corresponding eigenfunctions of the harmonic oscillator $\psi_n(q)$ are given by the well-known analytic equations [46]

$$W_n(q,p) = \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \psi_n(q+u)\psi_n^*(q-u)e^{-2ipu/\hbar} du$$

$$= \frac{(-1)^n}{\pi\hbar} e^{-\frac{p^2+m^2\omega_0^2 q^2}{m\hbar\omega_0}} L_n \left[\frac{2(p^2 + m^2\omega_0^2 q^2)}{m\hbar\omega_0} \right], \tag{145}$$

$$\psi_n(q) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega_0}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega_0 q^2}{2\hbar}} H_n \left(q\sqrt{\frac{m\omega_0}{\hbar}} \right), \tag{146}$$

where $H_n(z)$ and $L_n(z)$ are the Hermite and Laguerre polynomials, respectively [105]. For illustration, the Wigner functions W_n of a harmonic oscillator for the pure states $n = 1, 2, 3$, and 4, Eq. (145), are shown in Fig. 2. In contrast to the behavior of the equilibrium Wigner function $W_{eq}(q,p)$, Eq. (141), the Wigner functions $W_n(q,p)$ of the pure states can take on *negative* values so that it is impossible to interpret the Wigner function W_n as a true probability distribution.

Equilibrium Wigner functions have also been calculated for various simple quantum systems such as a particle in an infinite square well [104], the Morse oscillator [106, 107], the anharmonic quartic oscillator [108, 109], and the inverted harmonic oscillator [110].

2. *Application to Transition-State Theory*

The simplest description of thermally activated escape of a particle with the total energy $\varepsilon(q,p)$ given by Eq. (137) over a potential barrier may be given in terms of TST. In the simplest form of TST, two assumptions are made [5, 20]. First, thermal equilibrium prevails in the well (e.g., through the action of Maxwell's demon who keeps replenishing the particles at the source) so that the metastable state is represented by a canonical equilibrium distribution (unlike in the Kramers [28] treatment of the escape rate, where nonequilibrium effects due to the loss of particles from the well are accounted for using the theory of Brownian motion, automatically leading to friction dependence of the transmission coefficient).
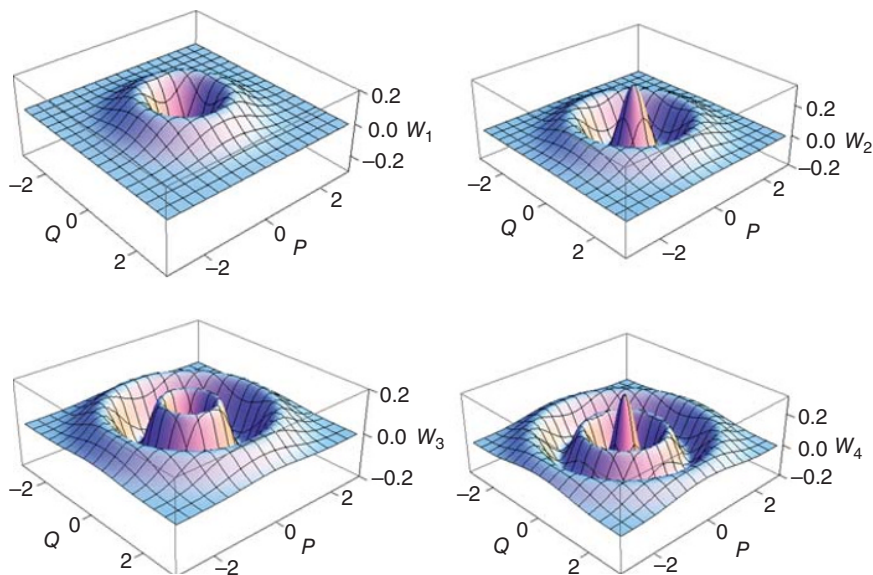
Figure 2.   3D plots of the Wigner functions W_n of a harmonic oscillator versus. the normalized coordinate $Q = q\sqrt{m\omega_0/\hbar}$ and momentum $P = p/\sqrt{m\hbar\omega_0}$ for the pure states $n = 1, 2, 3,$ and 4. (Color on line).

Second, a particle is never supposed to return to the well once it has crossed the potential barrier. The first assumption means that friction, that is, dissipation to the bath does not affect the escape rate. Thus, the system in effect is a closed classical one. Nevertheless, according to Mel'nikov [111], the results of classical TST should also be applicable in a *wide range of dissipation* for which thermal noise is sufficiently strong to thermalize the escaping particles yet not so strong as to affect particle motion across the top of the potential barrier, that is, a Maxwell–Boltzmann distribution still holds there. In the context of the Kramers model, this is the so-called intermediate damping case (cf. Fig. 1.13.2 of Ref. 5). In the treatment of Kramers, however, which explicitly involves an *open* classical system with fluctuation-dissipation due to the bath described by the Brownian motion *Stosszahlansatz*, he shows that for sufficiently weak friction the escape rate is suppressed because of the *depletion of the well population* while for strong friction the escape rate is also suppressed due to the *slowing down of the particle motion at the barrier top*.

The suggestion that quantum mechanical tunneling might play a significant role in some chemical reactions was first made in 1927 by Hund [99], almost at the inception of quantum mechanics. The first guess at a quantum

transition-state theory appears to have been made by Wigner who proposed a quantum generalization of the classical TST [97–99], where the reaction rate Γ is given via the flux-over-population method [20]

$$\Gamma \sim \frac{I_C}{Z_A}, \tag{147}$$

where

$$Z_A = \iint_{well} W_{eq}(q,p)\,dpdq \tag{148}$$

and

$$I_C = \iint_{barrier} J_C(q,p)\,dpdq \tag{149}$$

are, respectively, the well partition function and the total current of the particles at the top of the barrier point C (see Fig. 3). Here the current density at the barrier point J_C is given by

$$J_C(q,p) = \theta(p)\delta(q - q_C)\dot{q}W_{eq}(q,p), \tag{150}$$

where $\theta(x)$ and $\delta(x)$ are the unit step and Dirac delta functions, respectively, and $\dot{q} = \partial\varepsilon/\partial p = p/m$ is the particle velocity. Now we assume that near the
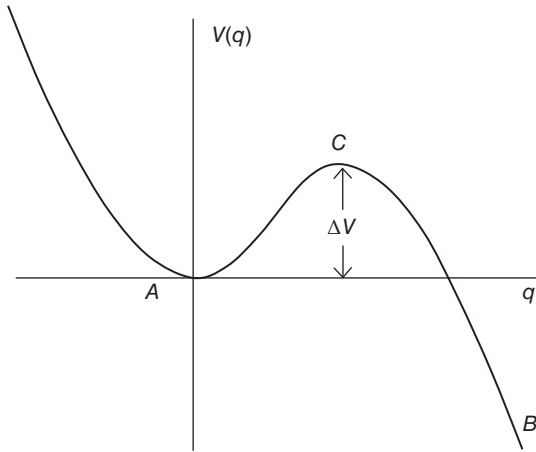
Figure 3. Single-well potential function as the simplest example of escape over a barrier. Particles are initially trapped in the well near point A by a high potential barrier at point C. They very rapidly thermalize in the well. Due to thermal agitation, however, very few may attain enough energy to escape over the barrier into region B whence they never return. The height of the barrier $\Delta V = V(q_C) - V(q_A)$ is supposed to be large compared with the thermal energy kT.

summit point C and near the bottom point A of the well, the potential $V(q)$ may be described by inverted harmonic oscillator and harmonic oscillator potentials, respectively, namely,

$$V(q) \approx \begin{cases} V(q_C) - \frac{m\omega_C^2}{2} (q - q_C)^2 \\ V(q_A) + \frac{m\omega_A^2}{2} (q - q_A)^2, \end{cases} \tag{151}$$

where

$$\omega_C = \sqrt{|V''(q_C)|/m} \quad \text{and} \quad \omega_A = \sqrt{V''(q_A)/m}.$$

Thus, near the bottom of the well, $W_{eq}(q,p)$ is approximated by that of a harmonic oscillator with $\omega_0 = \omega_A$ (see Eq. (141)), meaning that the well partition function Z_A can be evaluated as follows [48]:

$$Z_A \approx \frac{e^{-\beta V(q_A)}}{2\pi\hbar \cosh(\beta\hbar\omega_A/2)} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} e^{-\frac{2}{\hbar\omega_A}\left(\frac{m}{2}\omega_A^2 q^2 + \frac{1}{2m}p^2\right)\tanh\left(\frac{\beta\hbar\omega_A}{2}\right)} dqdp$$

$$= \frac{e^{-\beta V(q_A)}}{2\sinh(\hbar\omega_A\beta/2)}. \tag{152}$$

Here, the limits of integration with respect to q may be formally extended to $\pm$ infinity without significant error since the particles are almost all at A. Near the top of the barrier, the Wigner function $W_{eq}(q,p)$ is approximated by that of an *inverted* harmonic oscillator with $\omega_0 = i\omega_C$ in Eq. (141) so that at C, it is given by [48]

$$W_{eq}^C(q_C,p) \approx \frac{e^{-\beta V(q_C) - \frac{p^2 \tan(\beta\hbar\omega_C/2)}{m\hbar\omega_C}}}{2\pi\hbar \cos(\beta\hbar\omega_C/2)}. \tag{153}$$

Thus, we have from Eqs. (149) and (153)

$$I_C \approx \frac{e^{-\beta V(q_C)}}{2\pi\hbar m \cos(\beta\hbar\omega_C/2)} \int\limits_0^\infty p e^{-\frac{p^2 \tan(\beta\hbar\omega_C/2)}{m\hbar\omega_C}} dp$$

$$= \frac{\omega_C e^{-\beta V(q_C)}}{4\pi \sin(\beta\hbar\omega_C/2)}. \tag{154}$$

Finally, substituting Eqs. (152) and (154) into Eq. (147), we obtain [48]

$$\Gamma \approx \frac{\omega_A}{2\pi} \Xi e^{-\beta\Delta V}, \tag{155}$$

where $\Delta V = V(q_C) - V(q_A)$ is the barrier height and

$$\Xi = \frac{\omega_C}{\omega_A} \frac{\sinh(\hbar\beta\omega_A/2)}{\sin(\hbar\beta\omega_C/2)} = 1 + \frac{\beta^2\hbar^2}{24}\left(\omega_C^2 + \omega_A^2\right) + \cdots \qquad (156)$$

is the quantum correction to the classical TST result. The lowest order quantum correction to this pre-exponential factor was first obtained by Wigner [97] (see also Ref. 98). He emphasized that the quantum factor Ξ represents an *effective lowering* of the potential barrier, so enhancing the escape rate. According to Wigner [97], Eq. (155) constitutes the quantum correction to classical TST at high temperatures. In the context of quantum dissipation, one may infer that Eq. (155) also represents the extension of the intermediate damping Kramers escape rate (for which classical TST provides a reasonably accurate approximation) to include quantum effects. An important feature of Eq. (155) not appearing in the first order in h^2 approximation is that the prefactor Ξ *diverges* at a crossover temperature T_c given by

$$T_c = \frac{\hbar\omega_C}{2\pi k}.$$

The divergence occurs because the parabolic (or inverted oscillator) approximation for the potential is only valid near the top of the barrier. However, at very low temperatures $T \ll T_c$, where the particle is near the bottom of the well, the parabolic approximation to the barrier shape is no longer sufficient [111]. In contrast for $T > T_c$, transitions near the barrier top dominate so that the parabolic approximation is accurate [111]. Moreover, the simple approximation appearing on the right-hand side of Eq. (156) should hold with a reasonable degree of accuracy. This approximation also appears to be in substantial agreement with the experimental results of Bouchaud *et al.* [112].

We have demonstrated how the quantum escape rate in the absence of dissipation, namely Eq. (155), may be obtained by Wigner's perturbation method. However, that result may be obtained in a more succinct fashion without using perturbation theory by recalling that the rate constant may be written as [99, 113]

$$\Gamma = \frac{1}{Z_A} \int_{-\infty}^{\infty} w(\varepsilon)e^{-\beta\varepsilon}d\varepsilon, \qquad (157)$$

where the quantity

$$w(\varepsilon) = \frac{1}{1 + e^{-2\pi(\varepsilon - V_C)/(\hbar\omega_C)}} \qquad (158)$$

is the quantum transmission coefficient (ignoring dissipation) of a parabolic barrier [78]. We again approximate the potential near the top of the barrier by that of an inverted harmonic oscillator, which holds good at the barrier as well as at a small distance below it. Hence, one can regard the integral in Eq. (157) as having infinite

limits. Thus, one finds on evaluating that integral with these limits that the escape rate is given by

$$\Gamma = \frac{\hbar\omega_C}{2Z_A \sin(\beta\hbar\omega_C/2)} e^{-\beta V_C}. \tag{159}$$

Then using Eq. (152), we have the quantum TST escape rate Eq. (155) from Eq. (159).

Quantum TST as formulated for particles with separable and additive Hamiltonians in the manner just described has also been applied [114] in the context of magnetization reversal to the escape rate of the giant spin model of single-domain ferromagnetic particles. This model describes a ferromagnetic particle with uniaxial anisotropy with external fields applied parallel and perpendicular to the anisotropy axis. Tunneling in such a model will be caused by the transverse field [114]. Now, the Hamiltonian of the model (which is not separable and additive as the canonical variables are now the polar angles ϑ and φ specifying the orientation of the magnetization vector) may be mapped [114] onto that of a mechanical particle moving in a double-well potential. Hence, the quantum TST rate described earlier which is a close approximation to the exact escape rate in the intermediate damping region may also be used to study thermally assisted tunneling of the magnetization of a single-domain ferromagnetic particle. Nevertheless, the complete solution of the foregoing problem [64] will involve the extension of Wigner's phase space formalism to spin systems, and will be given in Section II.D.6.

3.   Application to Quantum Brownian Motion

The classical theory of the Brownian motion in a potential is ubiquitous in many areas of physics and chemistry, particularly those dealing with the nature of metastable states and the rates at which these states decay. Typical examples are current–voltage characteristics of Josephson junctions, the rate of condensation of a supersaturated vapor, dielectric and Kerr effect relaxation in liquids and nematic liquid crystals, dynamic light scattering, chemical reaction-rate theory in condensed phases, superparamagnetic relaxation, polymer dynamics, nuclear fission etc. [5, 20, 115, 116]. All these phenomena in one way or the other depend on the nucleation and growth of some characteristic disturbance within a metastable system, for example, condensation of a saturated vapor is initiated by the formation of a sufficiently large droplet of the liquid. If this droplet is big enough, it will be more likely to grow than to dissipate and will bring about condensation of the entire sample [115]. In many cases, particularly at low temperatures, a theory of dissipation based on the classical Brownian motion may be inadequate because it ignores quantum effects. Quantum noise arising from quantum fluctuations is also important in nanoscale and biological systems.

We mention [116] the noise-assisted tunneling and transfer of electrons and quasiparticles. The characteristics of such quantum noise vary strongly with temperature, and at high temperatures a crossover to Johnson-Nyquist noise that is essentially governed by the classical Brownian motion takes place. Yet another aspect of the subject, which has come to the fore in recent years, is the quantum mechanics of macroscopic quantum variables such as the decay of a zero-voltage state in a biased Josephson junction, flux quantum transitions in a SQUID [116], and the possible reversal by quantum tunneling of the magnetization of a single-domain ferromagnetic particle. It has been conjectured by Bean and Livingston [21] that the magnetization may reverse by quantum tunneling through the internal magnetocrystalline anisotropy barrier of the particle instead of by the conventional mechanism of thermally agitated jumping over the barrier, namely, Néel relaxation [16].

All these considerations necessitate the development of a theory of quantum Brownian motion particularly a theory, which directly addresses the issue of the quantum classical correspondence [117] in terms of a quantum analog of the classical Fokker–Planck equation. Such an evolution equation will allow dynamical parameters such as escape rates, correlation times, and susceptibilities to be calculated in terms of the eigensolutions of that equation in a manner analogous to those of the Fokker–Planck equation. Moreover, it would be possible to compare asymptotic solutions for parameters such as escape rates yielded by reaction rate theory with the corresponding quantities calculated from the quantum master equation. The description of quantum mechanics in terms of phase space distributions as advanced by Wigner is also an ideal starting point for the formulation of semiclassical quantum master equations of *open* quantum systems [102]. In particular, for quantum Brownian motion, the evolution equation for $W(q, p, t)$, which we shall call the *Wigner–Fokker–Planck* equation for the translational Brownian motion of a particle in a potential $V(q)$, can be derived by proceeding to the high-temperature limit. This procedure is equivalent to treating the system as a quantum mechanical particle embedded in a classical bath [118] and is effected by regarding the Brownian particle as bilinearly coupled to a bath of harmonic oscillators in thermal equilibrium at temperature T [119]. The most convenient way of characterizing the influence of the bath is by means of the *spectral density* characterizing the coupling to the bath of oscillators. The oscillators constituting the string or transmission line then represent the normal modes of the bath. We remark that the effect of friction is regarded as entirely equivalent to the bilinear coupling to these normal modes. Quantization of the bath of oscillators [119] then yields the following semiclassical master equation for the Wigner distribution function $W(q, p, t)$, which has intuitive appeal [120–128]:

$$\frac{\partial W}{\partial t} + \hat{M}_W W = \text{St}(W). \tag{160}$$

In this equation, the operator $\widehat{M}_W$ is given by Eq. (136) and the collision kernel operator $\text{St}(W)$ is

$$\text{St}(W) = \frac{\partial}{\partial p}\left(D_p p W + D_{pp}\frac{\partial W}{\partial p} + D_{qp}\frac{\partial W}{\partial q}\right) + \frac{\partial}{\partial q}\left(D_{qq}\frac{\partial W}{\partial q}\right). \qquad (161)$$

Here, $D_p, D_{pp}, D_{qp}, D_{qq}$ are coordinate, momentum, and time-dependent parameters (diffusion coefficients). The left-hand side of Eq. (160) again comprising the Wigner–Moyal operator is of course the quantum analog of the Liouville equation, while $\text{St}(W)$ characterizes the interaction of the Brownian particle with the thermal bath at temperature T, the collision kernel $\text{St}(W)$ being the analog of the collision kernel (*Stosszahlansatz*) in the classical kinetic theory. Conditions for the validity of the master equation (160) are discussed elsewhere (see e.g., Refs. 104 and 129). In the classical limit, $\hbar \to 0$, Eq. (160) reduces to the Klein–Kramers (Fokker–Planck) equation for the translational Brownian motion of a particle in a potential $V(q)$, namely,

$$\frac{\partial W}{\partial t} + \frac{p}{m}\frac{\partial W}{\partial q} - \frac{\partial V}{\partial q}\frac{\partial W}{\partial p} = \frac{\zeta}{m}\frac{\partial}{\partial p}\left(pW + \frac{m}{\beta}\frac{\partial W}{\partial p}\right) \qquad (162)$$

and the coefficients $D_p, D_{pp}, D_{qp}, D_{qq}$ become

$$D_p = \frac{\zeta}{m}, \quad D_{pp} = \frac{\zeta}{\beta}, \quad D_{qp} = D_{qq} = 0, \qquad (163)$$

where ζ is the drag coefficient of a Brownian particle.

Now being in possession of the functional form of the master equation (160) for a Brownian particle, the next crucial step is to determine $D_p, D_{pp}, D_{qp}, D_{qq}$. With this end in mind, we shall select the extension to the semiclassical case of a simple heuristic idea originally used by Einstein, Smoluchowski, Langevin, and Kramers to determine diffusion coefficients in the classical theory of the Brownian motion [5, 71]. Thus in order to obtain the explicit form of $D_p, D_{pp}, D_{qp}, D_{qq}$ in Eq. (161), we first recall Wigner's results for the unnormalized equilibrium distribution $W_{eq}(q,p)$ developed in a power series in $\hbar^2$ Eq. (139). This equilibrium distribution, being a stationary solution of the Wigner–Moyal equation (135), must be the equilibrium solution of the generic master equation (160), that is, it must also satisfy $\text{St}(W_{eq}) = 0$. Hence, if $W_{eq}(q,p)$ from Eq. (139) is to satisfy $\text{St}(W_{eq}) = 0$, the coefficients D_p, D_{qp}, and D_{qq} should remain as in Eq. (163) and only D_{pp} must be altered to read [48, 130] (for simplicity, we retain only the leading quantum correction terms)

$$D_{pp} = \frac{\zeta}{\beta} + \frac{\zeta\beta\hbar^2}{12m}\frac{\partial^2 V}{\partial q^2} + \cdots. \qquad (164)$$

Thus, the explicit form of the Wigner–Fokker–Planck equation up to $o\left(\hbar^2\right)$ is [48, 130]

$$\frac{\partial W}{\partial t} + \frac{p}{m}\frac{\partial W}{\partial q} - \frac{\partial V}{\partial q}\frac{\partial W}{\partial p} + \frac{\hbar^2}{24}\frac{\partial^3 V}{\partial q^3}\frac{\partial^3 W}{\partial p^3} + \cdots$$
$$= \frac{\zeta}{m}\frac{\partial}{\partial p}\left[pW + \left(\frac{m}{\beta} + \frac{\beta\hbar^2}{12}\frac{\partial^2 V}{\partial q^2} + \cdots\right)\frac{\partial W}{\partial p}\right]. \qquad (165)$$

The phase space master equation (165) has been derived in Refs. 48 and 130 assuming that $D_p, D_{pp}, D_{qp}, D_{qq}$ in Eq. (161) are time-independent. We observe that in the high-temperature limit, $\beta \to 0$, Eq. (165) obviously reduces to the Caldeira–Leggett master equation [119], where the collision kernel St(W) has the same form as in the classical Fokker–Planck equation (162). The evolution equation for the density matrix $\hat{\rho}$ in Hilbert space corresponding to Eq. (165) is again to order $\hbar^2$ [131]

$$\frac{\partial\hat{\rho}}{\partial t} + \frac{i}{\hbar}\left[\hat{H},\hat{\rho}\right] = -\frac{\zeta}{m}\left(\frac{i}{2\hbar}\left[\hat{q},\hat{p}\hat{\rho} + \hat{\rho}\hat{p}\right] + \frac{m}{\beta\hbar^2}\left[\hat{q},\left[\hat{q},\hat{\rho}\right]\right] + \frac{\beta}{6}\left[\hat{q},\left[\partial_q\hat{V},\hat{\rho}\right]\right]\right). \qquad (166)$$

We also observe that the imposition of the Wigner phase space distribution $W_{eq}(q,p)$ as the equilibrium solution of Eq. (160) so yielding a diffusion coefficient D_{pp}, which depends on the derivatives of the potential, appears to be the quantum analog of the *Ansatz* of a Maxwell–Boltzmann stationary distribution for the classical Klein–Kramers equation, Eq. (162). Furthermore, the condition St$\left(W_{eq}\right) = 0$ is equivalent to the property of the collision kernel St(W) in the classical kinetic theory, whereby the reduced or single-particle phase space distribution function $W(q,p,t)$ obeys the kinetic equation,

$$\frac{\partial W}{\partial t} + \frac{p}{m}\frac{\partial W}{\partial q} - \frac{\partial V}{\partial q}\frac{\partial W}{\partial p} = \text{St}(W). \qquad (167)$$

Here, the equilibrium Maxwell–Boltzmann distribution function $W_{eq}(q,p) \sim e^{-\beta\varepsilon(q,p)}$ always satisfies the condition St$\left(W_{eq}\right) = 0$. In particular, this is so for the Fokker–Planck equation (162). In the quantum case, this idea has been used before, for example, by Gross and Lebowitz [132] in formulating quantum kinetic models of impulsive collisions. According to Ref. 132, for a system with a Hamiltonian $\hat{H}$, the equation governing the time behavior of the density matrix $\hat{\rho}$ is given by the (reduced) equation (40), where the collision kernel operator St$\left(\hat{\rho}\right)$ satisfies the condition St$\left(\hat{\rho}_{eq}\right) = 0$, where $\hat{\rho}_{eq}$ is the equilibrium density matrix. The condition St$\left(\hat{\rho}_{eq}\right) = 0$ has also been used by Redfield [14] (see Eq. 56) in calculating the matrix elements of the relaxation operator St$\left(\hat{\rho}\right)$. Now we have evaluated $D_p, D_{pp}, D_{qp}, D_{qq}$ for frequency-independent damping, meaning that in

Eq. (160) they are *independent* of the time [123, 126]. In the high-temperature limit, this approximation may be used in a wide range of the model parameters both in the limits of weak and strong damping (a detailed discussion of the validity of this approximation is given by Grabert [133]). However, for the parameter range, where it is invalid, for example, throughout the very-low-temperature region, other methods should be used.

The evolution equation (165) obtained for an arbitrary potential $V(q)$ simplifies substantially for the harmonic potential, Eq. (140), that is, the quantum Brownian oscillator model, namely, [48]

$$\frac{\partial W}{\partial t} + \frac{p}{m}\frac{\partial W}{\partial q} - m\omega_0^2 q\frac{\partial W}{\partial p} = \frac{\zeta}{m}\frac{\partial}{\partial p}\left(pW + D_{pp}\frac{\partial W}{\partial p}\right), \qquad (168)$$

where our heuristic generalization of the Einstein procedure yields D_{pp} in closed form as follows:

$$D_{pp} = \left\langle p^2\right\rangle_{eq} = \frac{m\hbar\omega_0}{2}\coth\frac{\beta\hbar\omega_0}{2}.$$

The master equation (168) coincides in all respects with that of Agarwal [120], who first developed a detailed theory of the Brownian motion of a quantum oscillator for the *weak-coupling* case (see his equation (2.11) with $\lambda = 0$). Furthermore, Eq. (168) is the same as the Fokker–Planck equation (here the Klein–Kramers equation) for a classical Brownian oscillator [48] except that the diffusion coefficient D_{pp} is altered to include the quantum effects. It is known, however, that according to the theory of quantum dissipation for a quantum Brownian oscillator, both the stationary distribution and the corresponding averages $\langle q^2\rangle$ and $\langle p^2\rangle$ *depend on damping* (appropriate equations are given in chapter 6 of Ref. 134). In the approximation of Ohmic damping with Drude's regularization, these equations read as [134]

$$\left\langle q^2\right\rangle = \frac{1}{m\beta}\sum_{n=-\infty}^{\infty}\frac{1}{\omega_0^2 + v_n^2 + \frac{\omega_D\zeta/m}{1+\omega_D/v_n}} \qquad (169)$$

and

$$\left\langle p^2\right\rangle = \frac{m}{\beta}\sum_{n=-\infty}^{\infty}\frac{\omega_0^2 + \frac{\omega_D\zeta/m}{1+\omega_D/v_n}}{\omega_0^2 + v_n^2 + \frac{\omega_D\zeta/m}{1+\omega_D/v_n}}, \qquad (170)$$

where $v_n = 2\pi\,|n|\,/(\hbar\beta)$ and ω_D is a cutoff frequency (a Drude regularization is necessary as in pure Ohmic damping $\langle p^2\rangle$ diverges [134]). However, both of these equations reduce to Eqs. (142) and (143) either for vanishing damping ($\zeta/m \to 0$) or in the high-temperature limit ($\beta\hbar\omega_0 \to 0$). Moreover, the difference between the damping-dependent and damping-independent equations is negligible

for $\zeta/(m\omega_0) < 0.1$ (which is simply the condition for the existence of damped oscillations and/or narrow spectral lines). Furthermore, for $\beta\hbar\zeta/m \leq 1$, Eq. (168) (i.e., the Agarwal model) may be used as an approximate description of the kinetics of a quantum oscillator.

To summarize the merit of the phase space formalism for the quantum Brownian motion in a potential is that it originates in the master equation (160). This equation is a partial differential equation in phase space akin to the Fokker–Planck equation, and so operators are not involved. Moreover, the main advantage of the phase space approach now becomes apparent, namely it provides a master equation that may be solved using the methods [6, 71] associated with the classical theory of the Brownian motion in a potential, allowing one to study the quantum classical correspondence for dissipative systems (see, e.g., Refs. 73, 130, 131, 135–140). Many other examples of the use of the Wigner function representation of the density matrix in various applications in physics and chemistry may be found in Refs. 42, 46, 47, and 77 and references cited therein.

We now turn our attention to phase space representations for spins demonstrating how the Wigner–Moyal formulation of quantum mechanics as a statistical theory on classical phase space can be applied successfully to spinning particles.

C.   Quasiprobability Distribution Functions for Spins

By way of background to the discussion which follows, we recall that in providing a phase space description of spin systems, Stratonovich in 1956 [49] introduced the quasiprobability (Wigner) distribution function $W_S(\vartheta, \varphi, t)$ for the spin orientations in the configuration space of the polar and the azimuthal angles (ϑ, φ). This idea formed 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. The c-number representation for spins is especially important in treating spin relaxation phenomena. There *the spin orientation distribution is defined as the linear invertible bijective map onto the representation space comprising the trace of the product of the system density matrix and the irreducible tensor operators with matrix elements in the spherical basis representation given via the Clebsch–Gordan coefficients*. Alternative quasiprobability distribution functions for spins have also been proposed using the spin coherent-state representation of the density matrix [40, 50–54, 57–60] introduced by Glauber and Sudarshan and commonly used in quantum optics (see, e.g., Refs. 45, 46, and 51). Moreover, Várilly and Gracia-Bondía [50] have shown that the spin coherent-state representation approach is equivalent to the Stratonovich formalism.

In view of the importance of and the generality of Stratonovich's study of representation distributions for quantum systems, we shall summarize the general principles underlying such representations as given by him. Then, we shall apply

them to derive the Wigner and other representation distributions for systems with symmetries described by the SU(2) rotation group.

Stratonovich [49] defines the "representation distribution" in the representation space M by the following requirements:

1. The space, in which the "representation distribution" is defined, has a *classical* meaning, for example, phase space (q, p) or the space of orientations (ϑ, φ).

2. The representation distribution can be expressed *linearly* in terms of the density matrix $\hat{\rho}$. This requirement is directly related to the linearity of the whole apparatus of quantum theory, that is, it is connected with the statistical interpretation of the theory. The density matrix $\hat{\rho}$ like any other quantum operator $\hat{A}$, has associated with it a (*c*-number) function in the representation space, namely,

$$\rho(M, t) = \mathrm{Tr}\left\{\hat{\rho}(t)\hat{w}(M)\right\}, \qquad (171)$$

and, in general,

$$A(M) = \mathrm{Tr}\left\{\hat{A}\hat{w}(M)\right\}, \qquad (172)$$

comprising the *direct* mapping of the quantum operator $\hat{A}$ onto the representation space via the kernel $\hat{w}$, which is an operator depending on the point M as a parameter. For example, the point of the representation space could be a point on the unit sphere (ϑ, φ).

3. The representation distribution must be real, that is, in general, to a Hermitian operator $\hat{A}$ there must correspond a real *c*-number (Weyl symbol) $A(\vartheta, \varphi)$. This requirement amounts to the condition that the bijective operator $\hat{w}(M)$ must be Hermitian for all points M.

4. Statistical averaging of the *c*-number $A(M)$ over the representation distribution *must* give the same results as the rule for averaging of Hilbert space operators, namely,

$$\left\langle \hat{A} \right\rangle (t) = \mathrm{Tr}\left(\hat{\rho}(t)\hat{A}\right) = \int A(M)\rho(M, t)dM. \qquad (173)$$

Moreover, we have as a representation of a Hilbert space operator $\hat{A}$ the *inverse* map

$$\hat{A} = \int A(M)\hat{w}(M)dM \qquad (174)$$

as can be easily verified by forming $\mathrm{Tr}\left(\hat{\rho}\hat{A}\right)$ via Eq. (174) and then using Eq. (171), thereby yielding Eq. (173).

These transformation rules tell one how to get the operator relation from the c-number representation and vice versa. Thus condition 4 is equivalent to the requirement that the *direct* Eq. (172), and *inverse* maps, Eq. (174), are accomplished via the *same kernel* $\hat{w}(M)$, that is, the mapping given by Eq. (172) is *bijective* (one-to-one onto).

By regarding the given operators say $\hat{A}, \hat{B}, \ldots$ as elements of a complex Euclidean space with a scalar product given by the trace

$$\left(\hat{A}, \hat{B}\right) = \mathrm{Tr}\left(\hat{A}\hat{B}^{\dagger}\right),$$

we can then introduce an orthonormal basis of operators $\{\hat{A}_1, \hat{A}_2, \ldots\}$ with orthogonality relation

$$\mathrm{Tr}\left(\hat{A}_i \hat{A}_j^{\dagger}\right) = \delta_{ij}. \tag{175}$$

Thus, the kernel operator $\hat{w}(M)$ may be represented by its expansion in the orthonormal basis of operators as

$$\hat{w}(M) = \sum_i \hat{A}_i^{\dagger} A_i(M), \tag{176}$$

where by definition the c-number expansion coefficients $A_i(M)$ are given by the direct map (cf. Eq. 172)

$$A_i(M) = \mathrm{Tr}\left\{\hat{A}_i \hat{w}(M)\right\}. \tag{177}$$

The requirement given by Eq. (175) is entirely equivalent to the c-number orthogonality relation

$$\int A_i(M) A_j^*(M)\, dM = \delta_{ij}. \tag{178}$$

According to Eq. (173), the normalization condition for the density matrix $\hat{\rho}$, viz. $\mathrm{Tr}(\hat{\rho}) = 1$, must become

$$\int \rho(M, t) \mathrm{Tr}\left\{\hat{w}(M)\right\} dM = 1. \tag{179}$$

Thus, as the normalized distribution we must take a c-number function $W(M, t)$ given by

$$W(M, t) = \mathrm{Tr}\left\{\hat{w}(M)\right\} \rho(M, t) \tag{180}$$

and the averaging rule, Eq. (173), becomes

$$\left\langle \hat{A} \right\rangle(t) = \int W(M, t) A(M) \left[\mathrm{Tr}\left\{\hat{w}(M)\right\}\right]^{-1} dM. \tag{181}$$

Stratonovich's abstract treatment presented before may be used to derive specific distributions. The Wigner distribution function $W(q, p, t)$ defined by Eq. (121) is an important explicit example. In this instance, Eq. (121) can also be rewritten in terms of a bijective map $\hat{w}$ using the density matrix $\hat{\rho}(q_1, q_2, t)$ in the (q_1, q_2) notation [77] as

$$W(q, p, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \hat{\rho}(q_1, q_2, t) \, \hat{w}(q, p, q_1, q_2) dq_1 dq_2, \qquad (182)$$

where the kernel $\hat{w}(q, p, q_1, q_2)$ is now given by the following equation [49]:

$$\hat{w}(q, p, q_1, q_2) = \frac{1}{\pi \hbar} e^{i(q_1 - q_2)p/\hbar} \delta\left(q - \frac{q_1 + q_2}{2}\right). \qquad (183)$$

Thus, the Wigner distribution function $W(q, p, t)$ is derived merely by applying the principles of homogeneity and equivalence of directions embodied in the symmetries of the Heisenberg–Weyl group combined with the notion of a classical phase space. This group theoretic argument should be compared with the intuitive method of Wigner who appears to have arrived at his distribution by *ad hoc* reasoning insofar as that distribution yields the correct marginal probabilities for either the positions or the momentum.

1. Spin Phase-Space Distribution Functions

Now Stratonovich [49] originally introduced the spin phase space distribution function for zero dissipation, that is, for closed systems. This function was further developed both for closed and open spin systems (see e.g., Refs. 35–39 and 50–60) and is entirely analogous to the translational Wigner distribution $W(q, p, t)$ in phase space (q, p), which is the quasiprobability representation of the density operator except that certain differences arise because of the angular momentum commutation relations. The basic ideas may be summarized as follows [51]. First, we recall that the classical distribution function $W(\vartheta, \varphi, t)$ of magnetic moment orientations on the surface of a unit sphere can be expanded in an *infinite* series of the spherical harmonics $Y_{LM}(\vartheta, \varphi)$ (see Ref. 5; cf. Eq. B.12) as follows:

$$W(\vartheta, \varphi, t) = \sum_{L=0}^{\infty} \sum_{M=-L}^{L} Y_{LM}(\vartheta, \varphi) \langle Y_{LM}^* \rangle (t). \qquad (184)$$

Here the expansion coefficients (statistical moments) $\langle Y_{LM}^* \rangle (t)$ are defined by

$$\langle Y_{LM}^* \rangle (t) = \int_0^{\pi} \int_0^{2\pi} Y_{LM}^*(\vartheta, \varphi) W(\vartheta, \varphi, t) \sin \vartheta \, d\vartheta \, d\varphi \qquad (185)$$

(the asterisk denotes the complex conjugate) because $Y_{LM}(\vartheta, \varphi)$ are orthogonal and constitute a complete set in configuration space (ϑ, φ). Various definitions and properties of the spherical harmonics $Y_{LM}(\vartheta, \varphi)$ are discussed in detail in Appendix B. In particular, the spherical harmonics $Y_{LM}(\vartheta, \varphi)$, which are components of some irreducible tensor of rank L, may formally be defined by the commutation relations [95]

$$\left[\hat{L}_\mu, Y_{LM}(\vartheta, \varphi)\right] = \sqrt{l(l+1)}C_{LM1\mu}^{LM+\mu}Y_{LM+\mu}(\vartheta, \varphi), \qquad (186)$$

yielding three relations ($\mu = 0, \pm 1$), namely, [95]

$$\hat{L}_0 Y_{LM}(\vartheta, \varphi) = MY_{LM}(\vartheta, \varphi), \qquad (187)$$

$$\hat{L}_{\pm 1} Y_{LM}(\vartheta, \varphi) = \mp\sqrt{\frac{L(L+1) - M(M \pm 1)}{2}}Y_{LM \pm 1}(\vartheta, \varphi), \qquad (188)$$

where $\hat{L}_\mu$ are the components of the orbital angular momentum operator $\hat{\mathbf{L}}$ in the spherical basis given by the differential operators [95]

$$\hat{L}_0 = -i\frac{\partial}{\partial\varphi}, \qquad (189)$$

$$\hat{L}_{\pm 1} = -\frac{e^{\pm i\varphi}}{\sqrt{2}}\left(\frac{\partial}{\partial\vartheta} \pm i\cot\vartheta\frac{\partial}{\partial\varphi}\right). \qquad (190)$$

The angular momentum operators $\hat{L}_\mu$ satisfy the same commutation relations as the spherical components $\hat{S}_\mu$ of the spin operator $\hat{\mathbf{S}}$ given by Eq. (A.8). Now the quantum quasiprobability distribution function for spins $W_S(\vartheta, \varphi, t)$ may be obtained in the manner of Eqs. (100) *et seq.* merely by replacing the *classical* average $\langle Y_{LM}^* \rangle(t)$ in Eq. (184) by the *quantum mechanical expectation values* of appropriate operators, which must transform under rotation of the coordinate system in exactly the same way as the spherical harmonics $Y_{LM}(\vartheta, \varphi)$. Therefore, we must seek *specific* operators in Hilbert space corresponding to the spherical harmonics $Y_{LM}(\vartheta, \varphi)$ such that they have commutation relations with the spin spherical component operators $\hat{S}_\mu$ which are the same as those, Eq. (186), between the spherical harmonics $Y_{LM}(\vartheta, \varphi)$ and the spherical component operators $\hat{L}_\mu$ of the angular momentum operator $\hat{\mathbf{L}}$ [51]. The particular operators with these commutation properties are the polarization operators $\hat{T}_{LM}^{(S)}$ [51, 95]; see Eq. (A.30). This correspondence becomes obvious by comparing Eqs. (187) and (188) for the spherical harmonics with the commutation equation (A.30) for the polarization and spin operators yielding [95]

$$[\hat{S}_0, \hat{T}_{LM}^{(S)}] = M\hat{T}_{LM}^{(S)} \qquad (191)$$

and

$$[\hat{S}_{\pm 1}, \hat{T}_{LM}^{(S)}] = \mp \sqrt{\frac{L(L+1) - M(M \pm 1)}{2}} \hat{T}_{LM\pm 1}^{(S)}. \qquad (192)$$

We may go into more details in the following manner. We have seen earlier that the density matrix $\hat{\rho}_S$ of the spin characterized by the spin number S may be expanded as a finite series of the polarization operators $\hat{T}_{LM}^{(S)}$, Eq. (70), namely,

$$\hat{\rho}_S(t) = \sum_{L=0}^{2S} \sum_{M=-L}^{L} \hat{T}_{LM}^{(S)} \left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle(t). \qquad (193)$$

Therefore, in order to construct the quasiprobability distribution function $W_S(\vartheta, \varphi, t)$ of the polar and the azimuthal angles (ϑ, φ) corresponding to the density matrix $\hat{\rho}_S$ from Eq. (193), we first, in light of the previous paragraph, formally express $W_S(\vartheta, \varphi, t)$ as a *finite* series of spherical harmonics $Y_{LM}(\vartheta, \varphi)$ in the representation space, namely,

$$\frac{2S+1}{4\pi} W_S(\vartheta, \varphi, t) = \sum_{L=0}^{2S} \sum_{M=-L}^{L} Y_{LM}(\vartheta, \varphi) \left\langle Y_{LM}^* \right\rangle(t), \qquad (194)$$

where the expansion coefficients $\left\langle Y_{LM}^* \right\rangle(t)$ are given by

$$\left\langle Y_{LM}^* \right\rangle(t) = \frac{2S+1}{4\pi} \int_0^\pi \int_0^{2\pi} Y_{LM}^*(\vartheta, \varphi) W_S(\vartheta, \varphi, t) \sin \vartheta \, d\vartheta \, d\varphi \qquad (195)$$

due to the orthogonality property of the $Y_{LM}(\vartheta, \varphi)$ given by Eq. (B.11). Equation (194) represents a quantum analog of the expansion, Eq. (184), of the *classical* distribution function $W(\vartheta, \varphi, t)$ of spin orientations in configuration space in terms of spherical harmonics. Thus, following this argument, it appears that both the quasiprobability (Wigner) distribution function on the sphere $W_S(\vartheta, \varphi, t)$ and the corresponding kernel operator $\hat{w}(\vartheta, \varphi)$ of the Wigner–Stratonovich bijective map onto phase space defined by Eq. (171), namely,

$$W_S(\vartheta, \varphi, t) = \mathrm{Tr}\left\{ \hat{\rho}_S(t) \hat{w}(\vartheta, \varphi) \right\}, \qquad (196)$$

can be obtained by merely replacing the averages of spherical harmonics $\left\langle Y_{LM}^* \right\rangle(t)$ over the representation space (ϑ, φ) in Eq. (194) by the quantum mechanical expectation values of the polarization operators $\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle(t)$. However, the replacement

must be achieved in order to preserve commutation relations according to the prescription indicated by Eq. (195), that is, we must have

$$\left\langle Y_{LM}^*(\vartheta,\varphi)\right\rangle(t) = \frac{2S+1}{4\pi}\Omega_{L,M}^S\left\langle\hat{T}_{LM}^{\dagger(S)}\right\rangle(t), \tag{197}$$

where $\Omega_{L,M}^S$ is a constant to be determined. Substitution of Eq. (197) into Eq. (194) immediately yields the desired equation (194) in representation space in the finite series form as follows:

$$W_S(\vartheta,\varphi,t) = \text{Tr}\left\{\hat{\rho}_S\hat{w}(\vartheta,\varphi)\right\} = \sum_{L=0}^{2S}\sum_{M=-L}^{L}\Omega_{L,M}^S Y_{LM}(\vartheta,\varphi)\left\langle\hat{T}_{LM}^{\dagger(S)}\right\rangle(t). \tag{198}$$

Equation (198) implies that *different* forms of the quasiprobability distribution function $W_S(\vartheta,\varphi,t)$ exist corresponding to different choices of the constant $\Omega_{L,M}^S$ in Eq. (197) analogous to Eq. (107) for the translational case. Thus, we have obtained quasiprobability distribution functions of spins *by identifying the average of the spherical harmonic $Y_{LM}(\vartheta,\varphi)$ over (ϑ,φ) as an average of the polarization operator $\hat{T}_{LM}^{(S)}$ via the spin density matrix $\hat{\rho}_S$* [51].

Now in order to find explicit equations for the prefactor $\Omega_{L,M}^S$ with the ultimate aim of introducing three different quasiprobability distribution functions analogous to those already described for particles (cf. Eq. 107), we first consider the SU(2) coherent (or minimum uncertainty) states. Many spin relaxation problems can be dealt with in terms of the interaction of an assembly of spins with electromagnetic fields or with those arising from internal anisotropy potentials. In these problems, a particular set of spin states has to be selected. The choice of a particular representation is motivated rather by convenience than by necessity. In this section, we define the coherent spin states and discuss their properties following Ref. 52. The coherent-state representation of the density matrix when applied to spin systems allows one to analyze spin relaxation phenomena using a quasiprobability distribution function $W_S(\vartheta,\varphi,t)$ of spin orientations in a phase (here configuration) space of the polar and the azimuthal angles (ϑ,φ).

In quantum mechanics, the spin operator $\hat{\mathbf{S}}$ is usually represented by a set of three square $(2S+1)\times(2S+1)$ matrices $\hat{S}_X$, $\hat{S}_Y$, and $\hat{S}_Z$ with S being the spin number, while the basis spin functions $\chi_{Sm} = |S,m\rangle$, which describe the states with definite spin S and spin projection m onto the Z-axis, are eigenfunctions of the spin operators $\hat{\mathbf{S}}^2$ and $\hat{S}_Z$ [95] (the properties of the spin operators $\hat{\mathbf{S}}$, $\hat{S}_Z$, etc., and the spin functions χ_{Sm} are described in Appendix A). Now, the spin coherent states $|\psi_\kappa\rangle$ for a single particle of spin S can be defined as [52] (in our notation)

$$|\psi_\kappa\rangle = \frac{1}{\sqrt{N}}e^{\kappa\hat{S}_{-1}}\chi_{SS}. \tag{199}$$

Here, κ is complex valued, N is a normalization factor, $\hat{S}_{-1} = (\hat{S}_X - i\hat{S}_Y)/\sqrt{2}$ is the spin spherical component operator, and χ_{SS} is the spin ground state such that

$$\hat{S}_Z \chi_{SS} = S \chi_{SS}.$$

Expanding the exponential operator $e^{\kappa \hat{S}_{-1}}$ in Eq. (199) yields in turn the expansion of the state $|\psi_\kappa\rangle$ in the orthonormal basis of the spin eigenstates χ_{Sm}, namely [52],

$$|\psi_\kappa\rangle = \frac{1}{\sqrt{N}} \sum_{p=0}^{\infty} \left(\kappa \hat{S}_{-1}\right)^p \chi_{SS} = \frac{1}{\sqrt{N}} \sum_{p=0}^{2S} \kappa^p \sqrt{\frac{p!(2S)!}{2^p (2S-p)!}} \chi_{SS-p}. \qquad (200)$$

Here, we have utilized the fact that the operator $\hat{S}_{-1}$ acting on the ground state χ_{SS} creates spin deviations of the following form: [52]

$$\left(\hat{S}_{-1}\right)^p \chi_{SS} = \sqrt{\frac{p!(2S)!}{2^p (2S-p)!}} \chi_{SS-p}, \quad 0 \le p \le 2S. \qquad (201)$$

Now the normalization factor N is determined by the equality

$$\langle \psi_\kappa | \psi_\kappa \rangle = N^{-1} \sum_{p=0}^{2S} \frac{(2S)! |\kappa|^{2p}}{2^p p!(2S-p)!}$$

$$= N^{-1} \left(1 + |\kappa|^2/2\right)^{2S} = 1, \qquad (202)$$

so that the normalized state $|\psi_\kappa\rangle$ is then given by

$$|\psi_\kappa\rangle = \left(1 + |\kappa|^2/2\right)^{-S} \sum_{p=0}^{2S} \kappa^p \sqrt{\frac{p!(2S)!}{2^p (2S-p)!}} \chi_{SS-p}. \qquad (203)$$

However, the coherent spin states are *not orthogonal* so that the scalar product of two states $|\psi_\kappa\rangle$ and $|\psi_\lambda\rangle$ is

$$\langle \psi_\lambda | \psi_\kappa \rangle = \left(1 + |\lambda|^2/2\right)^{-S} \left(1 + |\kappa|^2/2\right)^{-S} \sum_{p=0}^{2S} \frac{(2S)! \lambda^{*p} \kappa^p}{2^p p!(2S-p)!}$$

$$= \frac{(2 + \lambda^*\kappa)^{2S}}{\left(2 + |\lambda|^2\right)^S \left(2 + |\kappa|^2\right)^S} \qquad (204)$$

and so

$$|\langle \psi_\lambda | \psi_\kappa \rangle|^2 = \left(1 - \frac{2|\lambda - \kappa|^2}{\left(2 + |\lambda|^2\right)\left(2 + |\kappa|^2\right)}\right)^{2S}. \qquad (205)$$

Now, if we write in Eq. (203) that

$$\kappa = \sqrt{2}e^{i\varphi}\tan\left(\frac{\vartheta}{2}\right), \quad 0 \le \vartheta < \pi,\ 0 \le \varphi < 2\pi, \tag{206}$$

then the normalized states $|\psi_\kappa\rangle = |S, \vartheta, \varphi\rangle$ can be written as (with $m = S - p$) follows:

$$
\begin{aligned}
|S, \vartheta, \varphi\rangle &= \cos^{2S}\frac{\vartheta}{2}e^{\sqrt{2}e^{i\varphi}\tan(\vartheta/2)\hat{S}_{-1}}\chi_{SS} \\
&= \cos^{2S}\frac{\vartheta}{2}\sum_{m=-S}^{S}\sqrt{\frac{(2S)!}{(S+m)!(S-m)!}}\left(e^{i\varphi}\tan\frac{\vartheta}{2}\right)^{S-m}\chi_{Sm}. \tag{207}
\end{aligned}
$$

Now the spin coherent-state vector $|S, \vartheta, \varphi\rangle$ defined by Eq. (207) can also be written in the *equivalent* form

$$|S, \vartheta, \varphi\rangle = \tilde{\chi}_{SS}(\vartheta, \varphi)e^{iS\varphi},$$

where the $\tilde{\chi}_{S\lambda}(\vartheta, \varphi)$ constitute the helicity basis functions defined as [95]

$$\tilde{\chi}_{S\lambda}(\vartheta, \varphi) = \sum_{m=-S}^{S}D_{m\lambda}^{S}(\varphi, \vartheta, 0)\chi_{Sm},$$

and $D_{m\lambda}^{S}(\varphi, \vartheta, \psi)$ are the Wigner D functions [95]. Both forms of the state vector $|S, \vartheta, \varphi\rangle$ are equivalent due to the trigonometric identity [95]

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

The states $|S, \vartheta, \varphi\rangle$ so defined form *a complete set* with the completeness relation given by

$$
\begin{aligned}
\frac{2S+1}{4\pi}&\int_0^\pi\int_0^{2\pi}|S, \vartheta, \varphi\rangle\langle S, \vartheta, \varphi|\sin\vartheta\,d\vartheta\,d\varphi \\
&= \frac{2S+1}{2}\sum_{m=-S}^{S}\frac{(2S)!\chi_{Sm}\chi_{Sm}^{\dagger}}{(S+m)!(S-m)!}\int_0^\pi\cos^{4S}\frac{\vartheta}{2}\tan^{2(S-m)}\frac{\vartheta}{2}\sin\vartheta\,d\vartheta \tag{208} \\
&= \sum_{m=-S}^{S}\chi_{Sm}\chi_{Sm}^{\dagger} = \hat{I},
\end{aligned}
$$

where $\hat{I}$ is the $(2S+1) \times (2S+1)$ identity matrix. Furthermore, the overlap of two states $|S, \vartheta, \varphi\rangle$ and $\left|S, \vartheta', \varphi'\right\rangle$ is [52]

$$\langle S, \vartheta', \varphi' | S, \vartheta, \varphi\rangle = \left[\cos \frac{\vartheta}{2} \cos \frac{\vartheta'}{2} + e^{i(\varphi - \varphi')} \sin \frac{\vartheta}{2} \sin \frac{\vartheta'}{2} \right]^{2S}, \tag{209}$$

and so

$$\left|\langle S, \vartheta', \varphi' | S, \vartheta, \varphi\rangle\right| = 2^{-S} \left[1 + (\mathbf{u} \cdot \mathbf{u}') \right]^{S}, \tag{210}$$

where $\mathbf{u}$ and $\mathbf{u}'$ are unit vectors in the directions specified by spherical polar coordinates (ϑ, φ) and (ϑ', φ'), respectively.

Now, the matrix elements $\langle S, \vartheta, \varphi | \hat{T}_{LM}^{(S)} | S, \vartheta, \varphi\rangle$ of the polarization operator $\hat{T}_{LM}^{(S)}$ in the coherent-state representation may be expressed via the spherical harmonics $Y_{LM}(\vartheta, \varphi)$ by using the trigonometric expansion of the latter equation (B.18) and Eq. (A.17) yielding the matrix elements in the following compact closed form:

$$\langle S, \vartheta, \varphi | \hat{T}_{LM}^{(S)} | S, \vartheta, \varphi\rangle$$
$$= (2S)! \cos^{4S} \frac{\vartheta}{2} \sum_{m,m'=-S}^{S} \frac{e^{-i(m-m')\varphi} \left(\tan \frac{\vartheta}{2} \right)^{2S-m-m'} \left(\chi_{Sm'}^{\dagger} \hat{T}_{LM}^{(S)} \chi_{Sm} \right)}{\sqrt{(S+m')!(S-m')!(S+m)!(S-m)!}} \tag{211}$$
$$= \sqrt{\frac{4\pi}{2S+1}} C_{SSL0}^{SS} Y_{LM}(\vartheta, \varphi).$$

Here C_{SSL0}^{SS} is the Clebsch–Gordan coefficient [95] given by

$$C_{SSL0}^{SS} = \frac{(2S)!\sqrt{2S+1}}{\sqrt{(2S-L)!(2S+L+1)!}}. \tag{212}$$

Thus, taking into account Eqs. (211) and (212), the definitions of the operators of the Cartesian components of the spin $\hat{S}_X$, $\hat{S}_Y$, and $\hat{S}_Z$ via the polarization operators $\hat{T}_{10}^{(S)}$ and $\hat{T}_{1\pm1}^{(S)}$, Eq. (A.21), and the definitions of the spherical harmonics $Y_{10}(\vartheta, \varphi)$ and $Y_{1\pm1}(\vartheta, \varphi)$, Eq. (B.5), we have the matrix elements of $\hat{S}_X$, $\hat{S}_Y$, and $\hat{S}_Z$ in the coherent-state representation as

$$\langle S, \vartheta, \varphi | \hat{S}_Z | S, \vartheta, \varphi\rangle = S \cos \vartheta, \tag{213}$$

$$\langle S, \vartheta, \varphi | \hat{S}_X | S, \vartheta, \varphi\rangle = S \sin \vartheta \cos \varphi, \tag{214}$$

$$\langle S, \vartheta, \varphi | \hat{S}_Y | S, \vartheta, \varphi\rangle = S \sin \vartheta \sin \varphi, \tag{215}$$

in turn, yielding the matrix elements of the spin operator $\hat{\mathbf{S}}$ as follows:

$$\langle S, \vartheta, \varphi | \hat{\mathbf{S}} | S, \vartheta, \varphi\rangle = S\mathbf{u}. \tag{216}$$

Hence, the spin operator $\hat{\mathbf{S}}$ in the coherent-state representation is the direct quantum analogue of the classical magnetic dipole vector $\boldsymbol{\mu} = \mu\mathbf{u}$.

Now, we shall use the coherent spin-state representation of the spin density matrix to derive transformation kernels for the spin Q-, P-, and Wigner quasiprobability distributions. Proceeding, we first consider the so-called Q-function representation. The Q-function representation distribution corresponding to a spin density matrix $\hat{\rho}_S$ in Hilbert space may be defined in a manner analogous to that for particles (cf. Eq. (107) with $s = -1$) via the *diagonal* matrix elements of the density matrix in the spin coherent-state representation [51]. Thus, we may then form the matrix elements $\langle S, \vartheta, \varphi| \hat{\rho}_S |S, \vartheta, \varphi\rangle$ of the density matrix $\hat{\rho}_S$ as defined by the polarization operator expansion equation (70) in the spin coherent-state representation $|S, \vartheta, \varphi\rangle$ as the linear combination (mindful that in Eq. (70) $a_{L,M}(t) = \left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle (t)$)

$$\langle S, \vartheta, \varphi| \hat{\rho}_S |S, \vartheta, \varphi\rangle = \sum_{L=0}^{2S} \sum_{M=-L}^{L} \langle S, \vartheta, \varphi| \hat{T}_{LM}^{(S)} |S, \vartheta, \varphi\rangle \left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle (t), \qquad (217)$$

where the $\langle S, \vartheta, \varphi| \hat{T}_{LM}^{(S)} |S, \vartheta, \varphi\rangle$ are given by Eq. (211). Then taking account of the replacement prescription for averages of polarization operators of the density matrix $\hat{\rho}_S$ embodied in Eq. (197) and using (211), we have from Eq. (217) the matrix elements $\langle S, \vartheta, \varphi| \hat{\rho}_S |S, \vartheta, \varphi\rangle$ of $\hat{\rho}_S$ rendered as the finite sum of spherical harmonics

$$\langle S, \vartheta, \varphi| \hat{\rho}_S |S, \vartheta, \varphi\rangle = \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(\Omega_{L,M}^S\right)^{-1} C_{SSL0}^{SS} Y_{LM}(\vartheta, \varphi) \left\langle Y_{LM}^* \right\rangle (t). \qquad (218)$$

Now, if we let the prefactor

$$\Omega_{L,M}^S = \sqrt{\frac{4\pi}{2S+1}} C_{SSL0}^{SS}, \qquad (219)$$

then in accordance with the representation distribution equation (194), we have the final form of the matrix elements of the density operator in the spin coherent-state representation

$$\langle S, \vartheta, \varphi| \hat{\rho}_S |S, \vartheta, \varphi\rangle = \sum_{L=0}^{2S} \sum_{M=-L}^{L} Y_{LM}(\vartheta, \varphi) \left\langle Y_{LM}^* \right\rangle (t), \qquad (220)$$

that is, we have with the formal Eq. (194) the phase space representation distribution $W_S^Q(\vartheta, \varphi, t)$ defined as follows:

$$W_S^Q(\vartheta, \varphi, t) = \frac{4\pi}{2S+1} \langle S, \vartheta, \varphi| \hat{\rho}_S |S, \vartheta, \varphi\rangle.$$

This quasiprobability distribution function $W_S^Q(\vartheta, \varphi, t)$ (called the Q-function) thus comprises the *diagonal* matrix elements of the density operator $\hat{\rho}_S$ in the *spin coherent-state representation* and is finally given explicitly (returning to averages of the polarization operators) by

$$W_S^Q(\vartheta, \varphi, t) = \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} C_{SSL0}^{SS} Y_{LM}(\vartheta, \varphi) \left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle(t). \tag{221}$$

The normalization of $W_S^Q(\vartheta, \varphi, t)$ in Eq. (221) can be found because by orthogonality, we have

$$\int_0^\pi \int_0^{2\pi} W_S^Q(\vartheta, \varphi, t) \sin \vartheta \, d\vartheta \, d\varphi = \frac{4\pi}{2S+1}. \tag{222}$$

Next, we consider the *P-function* $W_S^P(\vartheta, \varphi, t)$, which is defined in terms of the density matrix $\hat{\rho}_S$ in the coherent state representation via the inverse Wigner–Stratonovich map [51]

$$\hat{\rho}_S(t) = \frac{2S+1}{4\pi} \int_0^\pi \int_0^{2\pi} W_S^P(\vartheta, \varphi, t) \, |S, \vartheta, \varphi\rangle \, \langle S, \vartheta, \varphi| \sin \vartheta \, d\vartheta \, d\varphi. \tag{223}$$

However, the definition equation (223) implies that the average polarization operator

$$\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle(t) = \mathrm{Tr}\left(\hat{\rho}_S(t) \hat{T}_{LM}^{\dagger(S)} \right)$$

is given by

$$
\begin{aligned}
\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle(t) &= \frac{2S+1}{4\pi} \int_0^\pi \int_0^{2\pi} W_S^P(\vartheta, \varphi, t) \mathrm{Tr}\left(|S, \vartheta, \varphi\rangle \langle S, \vartheta, \varphi| \hat{T}_{LM}^{\dagger(S)} \right) \sin \vartheta \, d\vartheta \, d\varphi \\
&= \frac{2S+1}{4\pi} \int_0^\pi \int_0^{2\pi} W_S^P(\vartheta, \varphi, t) \langle S, \vartheta, \varphi| \hat{T}_{LM}^{\dagger(S)} |S, \vartheta, \varphi\rangle \sin \vartheta \, d\vartheta \, d\varphi \\
&= \sqrt{\frac{2S+1}{4\pi}} C_{SSL0}^{SS} \int_0^\pi \int_0^{2\pi} W_S^P(\vartheta, \varphi, t) Y_{LM}^*(\vartheta, \varphi) \sin \vartheta \, d\vartheta \, d\varphi \\
&= \sqrt{\frac{4\pi}{2S+1}} C_{SSL0}^{SS} \left\langle Y_{LM}^* \right\rangle(t).
\end{aligned} \tag{224}
$$

Here, we have used the fact that

$$\mathrm{Tr}\left(|S,\vartheta,\varphi\rangle\,\langle S,\vartheta,\varphi|\,\hat{T}_{LM}^{\dagger(S)}\right) = \langle S,\vartheta,\varphi|\,\hat{T}_{LM}^{\dagger(S)}\,|S,\vartheta,\varphi\rangle,$$

which in turn based on Eqs. (A.17), (A.27), and (A.34) and the identity equation (211). Comparing Eq. (224) and the general prescription given by Eq. (197) then yields in this case the following:

$$\Omega_{L,M}^{S} = \left(\sqrt{\frac{4\pi}{2S+1}}\,C_{SSL0}^{SS}\right)^{-1}. \tag{225}$$

For purposes of symmetry and in order to satisfy the normalization condition, Eq. (222), we define the P-function $W_S^P(\vartheta,\varphi,t)$ in a form like Eq. (221)

$$W_S^P(\vartheta,\varphi,t) = \sqrt{\frac{4\pi}{2S+1}}\sum_{L=0}^{2S}\sum_{M=-L}^{L}\left(C_{SSL0}^{SS}\right)^{-1}Y_{LM}(\vartheta,\varphi)\left\langle\hat{T}_{LM}^{\dagger(S)}\right\rangle(t) \tag{226}$$

which differs from Eq. (221) only because of the reciprocal of the Clebsch–Gordan coefficients involved in the summand.

Finally, the *Wigner function for spins* is defined as the function, which is its *own conjugate*, that is, the function obtained by setting [51]

$$\Omega_{L,M}^{S} = 1. \tag{227}$$

Again for purposes of symmetry and in order to satisfy the normalization relation, Eq. (222), we define the Wigner function $W_S^W(\vartheta,\varphi,t)$ as follows:

$$W_S^W(\vartheta,\varphi,t) = \sqrt{\frac{4\pi}{2S+1}}\sum_{L=0}^{2S}\sum_{M=-L}^{L}Y_{LM}(\vartheta,\varphi)\left\langle\hat{T}_{LM}^{\dagger(S)}\right\rangle(t). \tag{228}$$

Now, by introducing the parameter s, which takes the values $s = -1, 0, +1$ for Q-, Wigner-, and P-functions, respectively, we can finally rewrite Eqs. (221), (226), and (228) as the single mapping [59]

$$\begin{aligned}
W_S^{(s)}(\vartheta,\varphi,t) &= \mathrm{Tr}\left\{\hat{\rho}_S(t)\hat{w}_s(\vartheta,\varphi)\right\} \\
&= \sqrt{\frac{4\pi}{2S+1}}\sum_{L=0}^{2S}\sum_{M=-L}^{L}\left(C_{SSL0}^{SS}\right)^{-s}Y_{LM}(\vartheta,\varphi)\left\langle\hat{T}_{LM}^{\dagger(S)}\right\rangle(t),
\end{aligned} \tag{229}$$

where $\hat{w}_s(\vartheta, \varphi)$ is the Wigner–Stratonovich kernel of the bijective transformation given by

$$\hat{w}_s(\vartheta, \varphi) = \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{SSL0}^{SS}\right)^{-s} Y_{LM}^*(\vartheta, \varphi) \hat{T}_{LM}^{(S)} \qquad (230)$$

such that (cf. Eqs. 175–180) $\hat{w}_s(\vartheta, \varphi) = \hat{w}_s^\dagger(\vartheta, \varphi)$, $\mathrm{Tr}(\hat{w}_s) = 1$, and

$$\frac{2S+1}{4\pi} \int_0^\pi \int_0^{2\pi} \hat{w}_s(\vartheta, \varphi) \sin\vartheta \, d\vartheta \, d\varphi = \hat{I}.$$

Now, due to the orthogonality properties of the spherical harmonics equation (B.11), all the phase space distributions embodied in Eq. (229) can also be written in a compact form as the finite series

$$\frac{2S+1}{4\pi} W_S^{(s)}(\vartheta, \varphi, t) = \sum_{L=0}^{2S} \sum_{M=-L}^{L} Y_{LM}(\vartheta, \varphi) \left\langle Y_{LM}^* \right\rangle^{(s)}(t), \qquad (231)$$

where

$$\left\langle Y_{LM}^* \right\rangle^{(s)}(t) = \frac{2S+1}{4\pi} \int_0^\pi \int_0^{2\pi} Y_{LM}^*(\vartheta, \varphi) W_S^{(s)}(\vartheta, \varphi, t) \sin\vartheta \, d\vartheta \, d\varphi$$

$$= \sqrt{\frac{4\pi}{2S+1}} \left(C_{SSL0}^{SS}\right)^{-s} \left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle(t). \qquad (232)$$

The quantum distribution function $(2S+1)W_S^{(s)}(\vartheta, \varphi, t)/4\pi$ given by the general finite series of Eq. (231) clearly has a similar form to the Fourier expansion of the classical orientational distribution $W(\vartheta, \varphi, t)$, Eq. (184), and reduces to it in the classical limit, $S \to \infty$. Furthermore, the quantum distribution equation (231) in representation space is a general result valid for an *arbitrary* spin system described by a spin density matrix $\hat{\rho}_S(t)$. Therefore, the phase space representation allows one (as already discussed for particles) to describe spin systems via a *quasiprobability density function* $W_S^{(s)}(\vartheta, \varphi, t)$ of spin orientations in the phase (here configuration) space (ϑ, φ). The advantage of such a mapping of the density matrix onto a c-number quasiprobability density function $W_S^{(s)}(\vartheta, \varphi, t)$ as extensively used in quantum optics (see, e.g., Refs. [45] and [46]) is that it is possible to learn *how* $W_S^{(s)}(\vartheta, \varphi, t)$ *evolves as a function of S*. In addition for large spins, $(2S+1)W_S^{(s)}(\vartheta, \varphi, t)/4\pi$ as defined by Eq. (231) reduces to the classical distribution $W(\vartheta, \varphi, t)$, Eq. (184), thereby naturally linking the quantum and classical regimes.

Now, knowing the Wigner–Stratonovich kernel $\hat{w}_s(\vartheta, \varphi)$ of the bijective map, we can calculate the Weyl symbol $A^{(s)}(\vartheta, \varphi)$ of any spin operator $\hat{A}$ as follows:

$$A^{(s)}(\vartheta, \varphi) = \text{Tr}\left(\hat{A}\hat{w}_s(\vartheta, \varphi)\right). \tag{233}$$

Conversely, as we shall immediately justify via Eqs. (236)–(238), the operator $\hat{A}$ can be reconstructed from its Weyl symbol $A^{(s)}(\vartheta, \varphi)$ via the inverse Wigner–Stratonovich map,

$$\hat{A} = \frac{2S+1}{4\pi} \int_0^\pi \int_0^{2\pi} A^{(-s)}(\vartheta, \varphi)\hat{w}_s(\vartheta, \varphi) \sin\vartheta \, d\vartheta \, d\varphi. \tag{234}$$

In particular, via the inverse equation (234), the density matrix $\hat{\rho}_S(t)$ (like any other quantum operator) may then be neatly expressed as follows:

$$\hat{\rho}_S(t) = \frac{2S+1}{4\pi} \int_0^\pi \int_0^{2\pi} W_S^{(-s)}(\vartheta, \varphi, t)\hat{w}_s(\vartheta, \varphi) \sin\vartheta \, d\vartheta \, d\varphi. \tag{235}$$

Thus knowing the phase space distribution $W_S^{(s)}(\vartheta, \varphi, t)$, the density matrix $\hat{\rho}_S(t)$ in Hilbert space can then be directly reconstructed via the particular inverse Wigner–Stratonovich map, Eq. (235). This procedure may be justified, as we shall now prove, because the Weyl symbols of any two spin operators $\hat{A}$ and $\hat{B}$ will provide the overlap relation (cf. Eq. 128)

$$\frac{2S+1}{4\pi} \int_0^\pi \int_0^{2\pi} A^{(s)}(\vartheta, \varphi)B^{(-s)}(\vartheta, \varphi) \sin\vartheta \, d\vartheta \, d\varphi = \text{Tr}\left(\hat{A}\hat{B}\right), \tag{236}$$

leading to Eqs. (234) and (235). To justify Eq. (236), we substitute the Weyl symbols of the operators $\hat{A}$ and $\hat{B}$ defined by Eq. (233) into Eq. (236), and we then use the series expression for the kernel equation (230) of the bijective map and the orthogonality property of spherical harmonics equation (B.11). Thus, we have from Eq. (233) and (236),

$$\frac{2S+1}{4\pi} \int_0^\pi \int_0^{2\pi} A^{(s)}(\vartheta, \varphi)B^{(-s)}(\vartheta, \varphi) \sin\vartheta \, d\vartheta \, d\varphi$$

$$= \sum_{L,L'=0}^{2S} \sum_{M,M'=-L}^{L} \left(\frac{C_{SSL'0}^{SS}}{C_{SSL0}^{SS}}\right)^s \text{Tr}\left(\hat{A}\hat{T}_{LM}^{(S)}\right) \text{Tr}\left(\hat{B}\hat{T}_{L'M'}^{\dagger(S)}\right)$$

$$\times \int_0^\pi \int_0^{2\pi} Y_{LM}^*(\vartheta, \varphi)Y_{L'M'}(\vartheta, \varphi) \sin\vartheta \, d\vartheta \, d\varphi$$

$$= \sum_{L=0}^{2S} \sum_{M=-L}^{L} \mathrm{Tr}\left(\hat{A}\hat{T}_{LM}^{(S)}\right) \mathrm{Tr}\left(\hat{B}\hat{T}_{LM}^{\dagger(S)}\right) \tag{237}$$

$$= \sum_{L=0}^{2S} \sum_{M=-L}^{L} \sum_{m,n,i,j=-S}^{S} A_{mi}B_{nj}\left[\hat{T}_{LM}^{(S)}\right]_{im}\left[\hat{T}_{LM}^{\dagger(S)}\right]_{jn}$$

$$= \sum_{m,n,i,j=-S}^{S} A_{mi}B_{nj}\sum_{L=0}^{2S}\sum_{M=-L}^{L}(-1)^M \frac{2L+1}{2S+1} C_{SnL-M}^{Sj} C_{SmLM}^{Si}$$

$$= \sum_{m,n=-S}^{S} A_{mn}B_{nm} = \mathrm{Tr}\left(\hat{A}\hat{B}\right).$$

Here, we have used Eq. (A.17) for the matrix elements of the polarization operators $\left[\hat{T}_{LM}^{(S)}\right]_{im}$ and $\left[\hat{T}_{LM}^{\dagger(S)}\right]_{jn}$ as well as a property of Clebsch–Gordan coefficients [95], namely,

$$\sum_{L=0}^{2S}\sum_{M=-L}^{L}(-1)^M \frac{2L+1}{2S+1} C_{SnL-M}^{Sj} C_{SmLM}^{Si}$$

$$= \sum_{L=0}^{2S}\sum_{M=-L}^{L} C_{S-jSn}^{LM} C_{S-mSi}^{LM} = \delta_{in}\delta_{mj}.$$

Thus, according to Eq. (236), with obvious replacements, the *average* value $\langle\hat{A}\rangle = \mathrm{Tr}\left(\hat{\rho}_S\hat{A}\right)$ of a spin operator $\hat{A}$ is given by the integral

$$\langle\hat{A}\rangle = \frac{2S+1}{4\pi} \int_0^\pi \int_0^{2\pi} A^{(-s)}(\vartheta,\varphi) W_S^{(s)}(\vartheta,\varphi,t)\sin\vartheta\, d\vartheta\, d\varphi, \tag{238}$$

thereby transparently leading to Eqs. (234) and (235). By definition, the observable $\langle\hat{A}\rangle$ calculated from Eq. (238) is *independent* of the value of the parameter s chosen, that is, the Q-, Wigner-, and P-functions will all yield identical results for $\langle\hat{A}\rangle$ as they must do.

   In summary, the one-to-one correspondence between the quantum state in the Hilbert space and a real representation space function first envisaged for the closed system in the spin context by Stratonovich [49], formally represents the quantum mechanics of a spin as a statistical theory in the representation space of polar

angles (ϑ, ϕ). This is accomplished essentially in the manner of Wigner [41] who we recall formally represented the quantum mechanics of a particle with Hamiltonian

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + V(\hat{q})$$

as a statistical theory in phase space with the canonical variables (p, q). Clearly, the average value of a quantum spin operator may be calculated from Eq. (238) like in classical mechanics. Thus, the Stratonovich representation for spins [49] just as the Wigner representation for particles is well suited to the development of semiclassical methods of solution allowing one to obtain quantum corrections for finite S in a manner closely analogous to the classical case, $S \to \infty$ (see, e.g., Ref. 5). We emphasize that besides spin relaxation of assemblies of noninteracting spins in contact with the thermal bath, the phase space formalism can also be applied to related problems such as spin waves, interacting spins with Heisenberg coupling, and so on. (see, e.g., Refs. 51, 52, and 140).

2. Weyl Symbols of Some Spin Operators

Any spin operator $\hat{A}$ is associated via Eq. (238) with its Weyl symbol (c−number function) $A^{(s)}(\vartheta, \varphi)$ in the representation space. In this section, we evaluate the Weyl symbols of the spin operators $\hat{S}_X, \hat{S}_Y, \hat{S}_Z$, and $\hat{\mathbf{S}}$ and also those of some other model spin Hamiltonians $\hat{H}_S$. Using the definition of the spin operators in terms of the polarization operators given by Eq. (A.21), the Weyl symbols $S_X^{(s)}(\vartheta, \varphi), S_Y^{(s)}(\vartheta, \varphi), S_Z^{(s)}(\vartheta, \varphi)$, and $\mathbf{S}^{(s)}(\vartheta, \varphi)$ of the corresponding spin operators $\hat{S}_X, \hat{S}_Y, \hat{S}_Z$, and $\hat{\mathbf{S}}$ can be calculated from the mapping equation (233) for $s = 0, \pm 1$ via the orthogonality property of the polarization operators defined by Eq. (A.34). Thus, we have the simple maps from Hilbert space onto phase space [59] (cf. Eqs. 213–215)

$$\begin{aligned}
\hat{S}_X \to S_X^{(s)}(\vartheta, \varphi) &= \sqrt{\frac{2\pi S(S+1)}{3}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{SSL0}^{SS} \right)^{-s} Y_{LM}^*(\vartheta, \varphi) \\
&\quad \times \mathrm{Tr}\left\{ (\hat{T}_{1-1}^{(S)} - \hat{T}_{11}^{(S)}) \hat{T}_{LM}^{(S)} \right\} \\
&= \sqrt{\frac{2\pi}{3}} S \left(\frac{S+1}{S} \right)^{(s+1)/2} [Y_{1-1}(\vartheta, \varphi) - Y_{11}(\vartheta, \varphi)] \\
&= S \left(\frac{S+1}{S} \right)^{(s+1)/2} \sin\vartheta \cos\varphi,
\end{aligned} \tag{239}$$

$$\hat{S}_Y \to S_Y^{(s)}(\vartheta, \varphi) = i\sqrt{\frac{2\pi S(S+1)}{3}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{SSL0}^{SS}\right)^{-s} Y_{LM}^*(\vartheta, \varphi)$$

$$\times \mathrm{Tr}\left\{(\hat{T}_{1-1}^{(S)} + \hat{T}_{11}^{(S)})\hat{T}_{LM}^{(S)}\right\}$$

$$= i\sqrt{\frac{2\pi}{3}} S \left(\frac{S+1}{S}\right)^{(s+1)/2} [Y_{1-1}(\vartheta, \varphi) + Y_{11}(\vartheta, \varphi)] \qquad (240)$$

$$= S\left(\frac{S+1}{S}\right)^{(s+1)/2} \sin\vartheta \sin\varphi,$$

$$\hat{S}_Z \to S_Z^{(s)}(\vartheta, \varphi) = \sqrt{\frac{4\pi S(S+1)}{3}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{SSL0}^{SS}\right)^{-s} Y_{LM}^*(\vartheta, \varphi)\mathrm{Tr}\left\{\hat{T}_{10}^{(S)}\hat{T}_{LM}^{(S)}\right\}$$

$$= \sqrt{\frac{4\pi}{3}} S \left(\frac{S+1}{S}\right)^{(s+1)/2} Y_{10}(\vartheta, \varphi) \qquad (241)$$

$$= S\left(\frac{S+1}{S}\right)^{(s+1)/2} \cos\vartheta.$$

Clearly, these phase space mappings bear a close resemblance to the corresponding classical quantities. Moreover, we have the overall compact form of the phase space mapping of the spin operator $\hat{\mathbf{S}}$, namely,

$$\hat{\mathbf{S}} \to \mathbf{S}^{(s)}(\vartheta, \varphi) = S\left(\frac{S+1}{S}\right)^{(s+1)/2} \begin{pmatrix} \sin\vartheta \cos\varphi \\ \sin\vartheta \sin\varphi \\ \cos\vartheta \end{pmatrix}$$

$$= S\left(\frac{S+1}{S}\right)^{(s+1)/2} \mathbf{u}. \qquad (242)$$

Next, since the magnetic moment operator $\hat{\boldsymbol{\mu}}$ is defined via the spin operator $\hat{\mathbf{S}}$ as $\hat{\boldsymbol{\mu}} = \gamma\hbar\hat{\mathbf{S}}$, it then follows that the *Weyl symbol* $\boldsymbol{\mu}^{(s)} = \mu^{(s)}\mathbf{u}$ *of* $\hat{\boldsymbol{\mu}}$ *has essentially the form of the magnetic moment vector* $\boldsymbol{\mu}$ *for a classical spin* [$\mu^{(s)} = \gamma\hbar S(1 + S^{-1})^{(s+1)/2}$].

As further examples of the mapping procedure onto phase space, we evaluate the Weyl symbols for the uniaxial, biaxial, cubic, and mixed anisotropy Hamiltonians defined, respectively, as follows:

$$\beta\hat{H}_S^{un} = -\frac{\sigma}{S^2}\hat{S}_Z^2, \qquad (243)$$

$$\beta\hat{H}_S^{bi} = -\frac{\sigma}{S^2}\hat{S}_Z^2 + \frac{\delta}{S^2}\left(\hat{S}_X^2 - \hat{S}_Y^2\right), \qquad (244)$$

$$\beta\hat{H}_S^{cub} = -\frac{\sigma_c}{2S^4}\left(\hat{S}_X^4 + \hat{S}_Y^4 + \hat{S}_Z^4\right), \qquad (245)$$

$$\beta\hat{H}_S^{mix} = -\frac{\sigma_1}{S^2}\hat{S}_Z^2 - \frac{\sigma_2}{S^4}\hat{S}_Z^4 + \frac{\chi}{S^4}\left(\hat{S}_{+1}^4 + \hat{S}_{-1}^4\right), \qquad (246)$$

where σ, δ, σ_c, σ_1, σ_2, and χ are dimensionless anisotropy parameters. The uniaxial Hamiltonian Eq. (243) is commonly used, for example, to describe the magnetic properties of the dodecanuclear manganese molecular cluster Mn12 with $S = 10$, $\sigma_1 T/S^2 = 0.6 \div 0.7\,\mathrm{K}$ [142]. The biaxial anisotropy Hamiltonian $\hat{H}_S^{bi}$, Eq. (244), is commonly used to describe the magnetic properties of an octanuclear iron(III) molecular cluster Fe8 [9, 143] with $S = 10$, $\sigma T/S^2 = 0.275\,\mathrm{K}$ and $\delta T/(S^2) = 0.046\,\mathrm{K}$. The cubic anisotropy Hamiltonian equation (245) contributes to the mixed anisotropy Hamiltonian equation (246), which is commonly used, for example, to describe more accurately the magnetic properties of the dodecanuclear manganese molecular cluster Mn12 with $S = 10$, $\sigma_1/(\beta S^2) = 0.56\,K$, $\sigma_2/(\beta S^4) = 1.1 \cdot 10^{-3}\,\mathrm{K}$, and $\chi/(\beta S^4) = \pm 3 \cdot 10^{-5}\,\mathrm{K}$ [143].

Here for simplicity, we only evaluate the Weyl symbols for the Hamiltonians equation (243–246) for the Q-function corresponding to $s = -1$ (for $s = 0$ and $s = +1$ the calculations can be accomplished in like manner). Thus, 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 Hamiltonians, Eqs. (243)–(246), can now be calculated from the general finite series representation of the kernel $\hat{w}_s$ (cf. Eq. 230)

$$
\begin{aligned}
H_S^{(-1)}(\vartheta, \varphi) &= \mathrm{Tr}\left\{ \hat{H}_S \hat{w}_{-1}(\vartheta, \varphi) \right\} \\
&= \sqrt{\frac{4\pi}{2S+1}} \mathrm{Tr}\left\{ \hat{H}_S \sum_{L=0}^{2S} \sum_{M=-L}^{L} C_{SSL0}^{SS} Y_{LM}^*(\vartheta, \varphi) \hat{T}_{LM}^{(S)} \right\}
\end{aligned}
\tag{247}
$$

(cf. the mapping equation (233) for the phase space representation of an arbitrary spin operator $\hat{A}$). Hence, we obtain from the Hamiltonians given by Eqs. (243)–(246) and the general mapping equation (247) after some algebra involving both products of the polarization operators and their orthogonality relations as described in Appendix A the following explicit maps onto phase space

$$
\beta \hat{H}_S^{un} \underset{s=-1}{\to} \beta H_S^{un}(\vartheta, \varphi) = -\sigma \frac{S - 1/2}{S} \cos^2 \vartheta - \frac{\sigma}{2S},
\tag{248}
$$

$$
\beta \hat{H}_S^{bi} \underset{s=-1}{\to} \beta H_S^{bi}(\vartheta, \varphi) = -\frac{S - 1/2}{S}\left(\sigma \cos^2 \vartheta - \delta \cos 2\varphi \sin^2 \vartheta \right) - \frac{\sigma}{2S},
\tag{249}
$$

$$
\begin{aligned}
\beta \hat{H}_S^{cub} \underset{s=-1}{\to} \beta H_S^{cub}(\vartheta, \varphi) = &-\sigma_c \frac{2S^3 + 3S - 1}{4S^3} \\
&+ \sigma_c \frac{(S - 1/2)(S - 1)(S - 3/2)}{4S^3} \\
&\times \left(\sin^2 2\vartheta + \sin^4 \vartheta \sin^2 2\varphi \right),
\end{aligned}
\tag{250}
$$

$$
\begin{aligned}
\beta\hat{H}_S^{mix} \underset{s=-1}{\to} \beta H_S^{mix}(\vartheta, \varphi) = &-\frac{1}{4S}\left(2\sigma_1 + \sigma_2\frac{3S-1}{S^2}\right) \\
&-\frac{S-1/2}{S}\left(\sigma_1 + \sigma_2\frac{3S-2}{S^2}\right)\cos^2\vartheta \\
&-\frac{(S-1/2)(S-1)(S-3/2)}{2S^3} \\
&\times\left[2\sigma_2\cos^4\vartheta - \chi\sin^4\vartheta\cos 4\varphi\right].
\end{aligned}
\tag{251}
$$

Again, the Weyl symbols of these quantum Hamiltonians bear a close resemblance to the classical free energies of the corresponding magnetocrystalline anisotropies (see, e.g., Ref. 6). All these Weyl symbols will be used later.

3. Master Equation and Statistical Moment Equations for Spin Relaxation in Phase Space

By transforming the reduced density operator evolution equation (40) into phase space via the Wigner–Stratonovich map Eqs. (229 and 235), the phase space evolution (master) equation for $W_S^{(s)}(\vartheta, \varphi, t)$ may be formally written as follows:

$$
\frac{\partial W_S^{(s)}}{\partial t} = L_S W_S^{(s)},
\tag{252}
$$

where L_S is the phase space differential operator *corresponding* to the operator in Hilbert space

$$
-\frac{i}{\hbar}[\hat{H}_S, \hat{\rho}_S] + \text{St}\left(\hat{\rho}_S\right)
$$

in the density matrix evolution equation (40). Although the operator L_S will have, in general, a very complicated form even for axial symmetry, nevertheless the phase space master equation (252) still has some obvious advantages over the density matrix evolution equation (40) because it is now possible to treat the spin relaxation for arbitrary S like that of classical spins (e.g., Eqs. 239–242) (see Appendix C for a specific nontrivial example). Indeed, in the classical limit, the phase space evolution equation (252) reduces to the Fokker-Planck equation (3) for the distribution function $W_{cl}(\vartheta, \varphi, t)$ of the orientations of classical spins thereby naturally linking the quantum and classical regimes. We reiterate that the analogy between the quantum and classical formulations for spins again enables powerful methods of solution of classical Fokker-Planck equations for the rotational Brownian motion of classical magnetic dipoles (e.g., continued fractions and, mean first passage times. [5]) to be used in the quantum domain [62–70].

As shown in Section II.A.4, the formal solution of the evolution equation (40) for the reduced density matrix can be written using the polarization operators

$\hat{T}_{LM}^{(S)}$ and the statistical moments $\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle (t)$ as the finite linear combination given by Eq. (70) [30, 95]. The statistical moments $\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle (t)$ can then be evaluated (usually after lengthy operator algebra) from the differential recurrence equation (77). Now the statistical moment method can also be applied in analogous fashion to the phase space master equation (252) because the phase space distribution $W_S^{(s)}(\vartheta, \varphi, t)$ may be written for arbitrary S in terms of a finite linear combination of the spherical harmonics, Eq. (231). Then by using Eq. (232) relating the average spherical harmonics $\left\langle Y_{LM}^* \right\rangle^{(s)} (t)$ and the average polarization operators $\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle (t)$, the differential recurrence equations for $\left\langle Y_{LM}^* \right\rangle^{(s)} (t)$ can be obtained by simple algebraic transformation from the differential recurrence equation (77) so that the latter becomes

$$\frac{d}{dt} \left\langle Y_{LM}^* \right\rangle^{(s)} (t) = \sum_{L',M'} p_{L'M';LM} \left\langle Y_{L'M'}^* \right\rangle^{(s)} (t). \tag{253}$$

Here, the coefficients

$$p_{L'M';LM} = \int_0^\pi \int_0^{2\pi} Y_{LM}(\vartheta, \varphi) L_S Y_{L'M'}^*(\vartheta, \varphi) \sin \vartheta \, d\vartheta \, d\varphi \tag{254}$$

by definition constitute the matrix elements of the phase space operator L_S given by

$$p_{L'M';LM} = \left(\frac{C_{SSL0}^{SS}}{C_{SSL'0}^{SS}} \right)^{-s} g_{L'M';LM}, \tag{255}$$

where the coefficients $g_{L'M';LM}$ which depend upon the precise form of the Hamiltonian $\hat{H}_S$ are defined by the averages indicated by Eq. (75). For classical spins, $S \to \infty$, the explicit equation for $p_{L'M';LM}$ for an arbitrary free energy has been derived in Ref. [143] (see Appendix D). Equation (253) is just a phase space correspondent of Eq. (77), which governs the evolution of the average polarization operators $\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle (t)$. Now Eq. (253) written as a matrix differential equation can be solved either by direct matrix diagonalization, involving the calculation of the eigenvalues and eigenvectors of the system matrix, or by the computationally efficient (matrix) continued fraction method [5, 71]. We remark that due to the identity $Y_{lm}^* = (-1)^m Y_{l-m}$ [95], the conjugate equation (253) can also be rewritten as an evolution equation for the statistical moments $\left\langle Y_{LM} \right\rangle^{(s)} (t)$, namely,

$$\frac{d}{dt} \left\langle Y_{LM} \right\rangle^{(s)} (t) = \sum_{L',M'} (-1)^{M'-M} p_{L'-M';L-M} \left\langle Y_{L'M'} \right\rangle^{(s)} (t). \tag{256}$$

Now the phase space evolution equation (253) for the average spherical harmonics $\langle Y^*_{LM} \rangle^{(s)}(t)$ and its corresponding equation (77) for the average polarization operators $\langle \hat{T}^{\dagger(S)}_{LM} \rangle(t)$ are equivalent. Thus having determined $\langle Y^*_{LM} \rangle^{(s)}(t)$ from the phase space equations (231 and 252), we can also evaluate the density matrix $\hat{\rho}$ from the polarization operator expansion equations (70 and 71) without formally solving its evolution equation (40). Vice versa, having calculated $\langle \hat{T}^{\dagger(S)}_{LM} \rangle(t)$ from the density matrix equations (40 and 70), we also have the phase space distribution $W^{(s)}_S(\vartheta, \varphi, t)$ from Eqs. (231) and (232) without solving the phase space evolution equation (252).

According to the finite series phase space representation equation (231), all the statistical moments $\langle Y_{LM} \rangle^{(s)}(t)$ are required (in general) to evaluate the phase space distribution $W^{(s)}_S(\vartheta, \varphi, t)$ for given S. However, for the calculation of *particular* observables only a *few* moments may in practice be necessary. For example, in evaluating the *average* spin operators $\langle \hat{S}_X \rangle(t)$, $\langle \hat{S}_Y \rangle(t)$, and $\langle \hat{S}_Z \rangle(t)$, only the spherical harmonic averages $\langle Y_{10} \rangle^{(s)}(t)$ and $\langle Y_{1\pm1} \rangle^{(s)}(t)$ are required according to the Weyl symbols, given by Eqs. (239)–(241), namely, (cf. Eqs. (84)–(86) for these averages in terms of polarization operators)

$$\left\langle \hat{S}_X \right\rangle(t) = \sqrt{\frac{2\pi}{3}} S \left(\frac{S+1}{S} \right)^{(s+1)/2} \left[\langle Y_{1-1} \rangle^{(s)}(t) - \langle Y_{11} \rangle^{(s)}(t) \right], \qquad (257)$$

$$\left\langle \hat{S}_Y \right\rangle(t) = i\sqrt{\frac{2\pi}{3}} S \left(\frac{S+1}{S} \right)^{(s+1)/2} \left[\langle Y_{1-1} \rangle^{(s)}(t) + \langle Y_{11} \rangle^{(s)}(t) \right], \qquad (258)$$

$$\left\langle \hat{S}_Z \right\rangle(t) = \sqrt{\frac{4\pi}{3}} S \left(\frac{S+1}{S} \right)^{(s+1)/2} \langle Y_{10} \rangle^{(s)}(t). \qquad (259)$$

These results are formal and general. Specific applications of Eqs. (252)–(256) are given in Sections III.A.2 and IV. Next, we shall demonstrate how the phase space distributions for *particular* spin systems can be determined. Note that the representation space analysis for spins is intrinsically more complicated than that for particles because spin and polarization operators are involved. Hence, the Wigner correspondents must be evaluated from first principles for a given Hamiltonian as we shall now illustrate.

D.   Equilibrium Phase Space Distribution Functions for Spins

Here, we shall demonstrate how to obtain both analytically and numerically *equilibrium* time-independent quasiprobability distribution functions for spin systems with various time-independent Hamiltonians $\hat{H}_S$, where the equilibrium density matrix $\hat{\rho}_S$ is given by

$$\hat{\rho}_S = \frac{1}{Z_S} e^{-\beta \hat{H}_S} \tag{260}$$

with the partition function $Z_S = \text{Tr}\left(e^{-\beta \hat{H}_S}\right)$. We recall that according to Eq. (70), the density matrix $\hat{\rho}_S$ for an arbitrary Hamiltonian $\hat{H}_S$ can be written as a finite series of polarization operators, namely,

$$\hat{\rho}_S = \sum_{L=0}^{2S} \sum_{M=-L}^{L} \hat{T}_{LM}^{(S)} \left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle_{eq}, \tag{261}$$

while the general equation (231) yields the corresponding equilibrium phase space distributions $W_S^{(s)}(\vartheta, \varphi)$ as a finite series of spherical harmonics, namely,

$$\frac{2S+1}{4\pi} W_S^{(s)}(\vartheta, \varphi) = \sum_{L=0}^{2S} \sum_{M=-L}^{L} Y_{LM}(\vartheta, \varphi) \left\langle Y_{LM}^* \right\rangle_{eq}^{(s)}, \tag{262}$$

where averaged spherical harmonics are related to averaged polarization operators via

$$\left\langle Y_{LM}^* \right\rangle_{eq}^{(s)} = \sqrt{\frac{4\pi}{2S+1}} \left(C_{SSL0}^{SS}\right)^{-s} \left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle_{eq}. \tag{263}$$

Hence, $W_S^{(s)}(\vartheta, \varphi)$ can also be written as a finite series of the averaged polarization operators thus it can always be determined (analytically or numerically) for a given Hamiltonian $\hat{H}_S$.

Following Ref. 65 and 66, we shall evaluate analytically (for small S) or numerically (for large S) from Eqs. (262) and (263) the equilibrium phase space distributions $W_S^{(s)}(\vartheta, \varphi)$. In order to implement this procedure for a particular Hamiltonian,

1. First, we write the density matrix operator $\hat{\rho}_S$ from Eqs. (260) and (261) for the given *effective anisotropy–Zeeman energy* Hamiltonian expressed either in terms of polarization operators $\hat{T}_{L,M}^{(S)}$ (as will be needed to implement the following step (ii)) or, using Eqs. (A.21) and (A.28), in terms of the spin operators $\hat{S}_i$ ($i = X, Y, Z$).
2. Next, we calculate for the given Hamiltonian the averaged polarization operator $\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle_{eq} = \text{Tr}\left(\hat{\rho}_S \hat{T}_{LM}^{\dagger(S)}\right)$ using the operator expansion method described in Appendix A (Eq. (A.20) *et seq.*).
3. Then, we can write from Eq. (263) the Fourier coefficients $\left\langle Y_{LM}^* \right\rangle_{eq}^{(s)}$ connecting the average of a spherical harmonic to that of a polarization operator.
4. Thus, we obtain the phase space distribution $W_S^{(s)}(\vartheta, \varphi)$ for the chosen Hamiltonian from the formal finite series equation (262) for any particular S.

All the calculations for a given Hamiltonian $\hat{H}_S$, which are tedious, can be accomplished using MATHEMATICA.

Initially, we evaluate the equilibrium Wigner ($s = 0$), Q- ($s = -1$) and P- ($s = 1$) phase space distributions $W_S^{(s)}(\vartheta, \varphi)$ for the very simple case of a spin with spin number S and magnetic moment $\mu = \gamma \hbar S / \mu_0$ in an external *constant* field **H** applied along the Z-axis (essentially these distributions correspond to the usual treatment of quantum paramagnetism). Consequently, the spin Hamiltonian $\hat{H}_S$ is just

$$\beta \hat{H}_S = -\frac{\xi}{S} \hat{S}_Z, \tag{264}$$

where $\xi = \beta \mu_0 \mu H$ is the dimensionless external field parameter. Hence we shall see that the Q-function $W_S^{(-1)}(\vartheta, \varphi)$ alone satisfies the *nonnegativity* condition, namely, $W_S^{(-1)} \geq 0$, required of a true probability density function. The quasiprobability densities $W_S^{(1)}$ and $W_S^{(0)}$ do not satisfy this condition (because they may take on negative values). Thus in future determinations of a phase space representation, we shall usually restrict ourselves to the (Q-) function $W_S^{(-1)}(\vartheta, \varphi)$ as all other functions can be treated in like manner. First, we shall determine the equilibrium Q- ($s = -1$) phase space distributions for an assembly of noninteracting spins in an external *constant* field **H** applied in an *arbitrary* direction in space. Here, the Hamiltonian of a spin is

$$\beta \hat{H}_S = -\frac{\xi}{S} \left(\gamma_X \hat{S}_X + \gamma_Y \hat{S}_Y + \gamma_Z \hat{S}_Z \right), \tag{265}$$

where γ_X, γ_Y, and γ_Z are the direction cosines of the field **H**. Next, we shall treat various magnetic anisotropies, so establishing one or more preferred orientations of the magnetization of an assembly of spins. In particular, we shall consider a uniaxial paramagnet in an external magnetic field with *arbitrary* orientation so that

$$\beta \hat{H}_S = -\frac{\xi}{S} \left(\gamma_X \hat{S}_X + \gamma_Y \hat{S}_Y + \gamma_Z \hat{S}_Z \right) - \frac{\sigma}{S^2} \hat{S}_Z^2 \tag{266}$$

as well as two particular cases of Eq. (266), namely, a uniaxial nanomagnet in both a longitudinal and a transverse external field with

$$\beta \hat{H}_S = -\frac{\xi}{S} \hat{S}_Z - \frac{\sigma}{S^2} \hat{S}_Z^2 \tag{267}$$

and

$$\beta \hat{H}_S = -\frac{\xi}{S} \hat{S}_X - \frac{\sigma}{S^2} \hat{S}_Z^2, \tag{268}$$

respectively, where σ is the dimensionless anisotropy parameter. In the classical limit, $S \to \infty$, the latter Hamiltonian corresponds to the nonaxially symmetric

problem of a uniaxial nanomagnet with two equivalent ground states of magne-
tization separated by a magnetocrystalline anisotropy energy barrier (the σ term)
in the presence of an applied transverse field. The transverse field in the quantum
case will *enhance* the tunneling probability. Finally, we shall consider biaxial and
cubic-like systems with Hamiltonians

$$\beta\hat{H}_S = -\frac{\sigma}{S^2}\hat{S}_Z^2 - \frac{\delta}{S^2}(\hat{S}_X^2 - \hat{S}_Y^2), \tag{269}$$

(δ is a dimensionless biaxiality parameter) and

$$\beta\hat{H}_S = -\frac{\xi}{S}\hat{S}_Z - \frac{\sigma_c}{2S^4}\left(\hat{S}_X^4 + \hat{S}_Y^4 + \hat{S}_Z^4\right), \tag{270}$$

where σ_c is the dimensionless cubic anisotropy parameter, which may be either
positive or negative.

Having determined the equilibrium quasiprobability distributions $W_S^{(s)}(\vartheta, \varphi)$
corresponding to these Hamiltonians $\hat{H}_S$, our second purpose is to calculate the
magnetization reversal time via the quantum generalization of TST (previously
treated for classical spins by Néel [16]), permitting one to estimate temperature
effects in the astroids and hysteresis loops within the limitations imposed by
quantum TST (moderate damping, and so on.) [5, 6]. Finally, we shall calculate
the Stoner–Wohlfarth magnetization curves (represented in switching field astroid
form) as a function of spin number S for nonaxially symmetric potentials. This
calculation will generalize Thiaville's geometrical method [19] (for the construc-
tion of switching field curves for such potentials) to include quantum effects due
to *finite* spin number. Thus, one may study the behavior of the astroids in the
interesting magnetic cluster — single-domain nanoparticle transition region. In the
magnetic context, explicit equations for the equilibrium phase space distributions
have already been obtained for an assembly of noninteracting spins in a uniform
magnetic field [35, 36] and for spins in the simplest uniaxial potential of the
magnetocrystalline anisotropy and Zeeman energy [65].

1. Spins in a Uniform External Field

First, we evaluate the equilibrium phase space distributions for the axially sym-
metric situation pertaining to a spin with spin number S (integer or half-integer) in
an external dc field **H** applied along the Z-axis. The spin Hamiltonian $\hat{H}_S$ is then
given by Eq. (264), namely [2],

$$\hat{H}_S = -\gamma\hbar H\hat{S}_Z \tag{271}$$

with the eigenenergies

$$E_m = -\gamma\hbar Hm \text{ with } m = -S, -S+1, \ldots, S,$$

the distance between adjacent energy levels being $\gamma \hbar H$. Now in equilibrium, the phase space distributions $W_S^{(s)}(\vartheta)$ are independent of the azimuthal angle φ and, according to Eq. (262), can be expressed by the series [65]

$$
\begin{aligned}
W_S^{(s)}(\vartheta) &= \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \left(C_{SSL0}^{SS}\right)^{-s} Y_{L0}(\vartheta,\varphi) \left\langle \hat{T}_{L0}^{\dagger(S)} \right\rangle_{eq} \\
&= \frac{1}{Z_S(2S+1)} \sum_{L=0}^{2S} (2L+1) \left(C_{SSL0}^{SS}\right)^{-s} P_L(\cos\vartheta) \sum_{m=-S}^{S} C_{SmL0}^{Sm} e^{\xi m/S},
\end{aligned}
$$

$$(272)$$

where $P_L(z)$ are the Legendre polynomials [105], $\xi = \beta\gamma\hbar HS$ is the dimensionless field parameter, and the partition function Z_S is given by

$$
Z_S = \sum_{m=-S}^{S} e^{\xi m/S} = \frac{\sinh\left[\left(S+\frac{1}{2}\right)\xi/S\right]}{\sinh\left(\frac{1}{2}\xi/S\right)}. \tag{273}
$$

In writing Eq. (272), we have noted Eq. (B.4) and have utilized the explicit expression for the matrix elements $\rho_{m'm}$ of the density matrix $\hat{\rho}_S$, namely,

$$
\rho_{m'm} = \frac{\delta_{mm'}}{Z_S} e^{\xi m/S}, \tag{274}
$$

and Eq. (A.17) for $\hat{T}_{LM}^{\dagger(S)}$ so yielding the closed-form expression for the average polarization operators in Eq. (272), namely,

$$
\left\langle \hat{T}_{L0}^{\dagger(S)} \right\rangle_{eq} = \frac{1}{Z_S} \sqrt{\frac{2L+1}{2S+1}} \sum_{m=-S}^{S} C_{SmLM}^{Sm} e^{\xi m/S}. \tag{275}
$$

Furthermore, the finite series in Eq. (272) for $s = -1$ can be summed (after some algebra, which is best accomplished via MATHEMATICA). Thus, the Q-function $W_S^{(-1)}(\vartheta)$ can finally be written for arbitrary S in the (known) concise closed form [36], namely,

$$
W_S^{(-1)}(\vartheta) = \frac{1}{Z_S} \left[\cosh\frac{\xi}{2S} + \cos\vartheta \sinh\frac{\xi}{2S}\right]^{2S}. \tag{276}
$$

Moreover, using the general rule for the calculation of the expected value of the spin operator $\hat{S}_Z$ via the corresponding (c-number) function, Eq. (241), the average longitudinal component of the spin at equilibrium is (because the integral over φ is 2π)

$$\left\langle \hat{S}_Z \right\rangle_{eq} = \left(S + \tfrac{1}{2}\right) S \left(\frac{S+1}{S}\right)^{(s+1)/2} \int\limits_0^\pi \cos \vartheta \, W_S^{(-s)}(\vartheta) \sin \vartheta \, d\vartheta$$

$$= \frac{S}{Z_S} \left(\frac{S+1}{S}\right)^{(s+1)/2} \left(\frac{(2S)!\sqrt{2S+1}}{\sqrt{(2S-1)!(2S+2)!}}\right)^s \sum_{m=-S}^S C_{Sm10}^{Sm} e^{\xi m/S}$$

$$= \frac{1}{Z_S} \sum_{m=-S}^S m e^{\xi m/S} = S B_S(\xi), \qquad (277)$$

where $B_S(x)$ is the Brillouin function defined as [2]

$$B_S(x) = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S} \coth\left(\frac{x}{2S}\right), \qquad (278)$$

and we have utilized the Clebsch–Gordan identity [95]

$$C_{Sm10}^{Sm} = \frac{m}{\sqrt{S(S+1)}}.$$

Obviously, $\left\langle \hat{S}_Z \right\rangle_{eq}$ from Eq. (277) has the all-important feature that it is independent of the parameter s. Note for future reference that setting $s = 1$ unlike in the Weyl symbol equation (241) means that we are utilizing the Q-distribution, where $s = -1$. Moreover, Eq. (277) is in complete agreement with the established result for the equilibrium magnetization of an assembly of noninteracting spins in a uniform magnetic field [1, 2]. Furthermore, in the classical limit,

$$S \to \infty \quad \text{and} \quad \mu = \gamma \hbar S / \mu_0 = \text{const}, \qquad (279)$$

the distribution $W_S^{(s)}(\vartheta)$ tends to the Boltzmann distribution for classical magnetic dipoles

$$(S + 1/2) \, W_S^{(s)}(\vartheta) \to Z_{cl}^{-1} e^{\xi \cos \vartheta}, \qquad (280)$$

while the Brillouin function $B_S(\xi)$ tends to the Langevin function $L(\xi) = \coth \xi - 1/\xi$, namely,

$$B_S(\xi) \to \frac{1}{Z_{cl}} \int\limits_0^\pi \cos \vartheta \, e^{\xi \cos \vartheta} \sin \vartheta \, d\vartheta = L(\xi). \qquad (281)$$

Here, Z_{cl} is the classical partition function given by

$$Z_{cl} = \int\limits_0^\pi e^{\xi \cos \vartheta} \sin \vartheta \, d\vartheta = 2 \frac{\sinh \xi}{\xi}. \qquad (282)$$

Experimental studies of the magnetization of various paramagnetic atoms and molecules indicate that they agree closely with the Brillouin function equation (278) (see, e.g., Refs. 145 and 146). In Fig. 4, the magnetization $M = \mu B_S(\xi)$ per molecule in units of μ_B as a function of applied field H at $T = 2$ K is shown for the three isotropic high-spin molecules [Cr{(CN)Cu(tren)}$_6$](ClO$_4$)$_{21}$ ($S = 9/2$), [Cr{(CN)Ni(tetren)}$_6$](ClO$_4$)$_9$ ($S = 15/2$), [Cr{(CN)Mn(tren)}$_6$](ClO$_4$)$_{21}$ ($S = 27/2$), which are labeled as CrCu$_6$, CrNi$_6$, and CrMn$_6$, respectively. These consist of clusters of metal ions ordered in a crystal lattice and coupled only via Heisenberg ferromagnetic or antiferromagnetic interactions between spins inside the molecule. In all cases, M increases with the applied field reaching a saturation value of $(9/2)g\mu_B$, $(15/2)g\mu_B$, and $(27/2)g\mu_B$ in CrCu$_6$, CrNi$_6$, and CrMn$_6$, respectively ($g \simeq 2$ is Landé's factor).

The three phase space equilibrium distributions $W_S^{(s)}(\vartheta)$ embodied in the finite series representation equation (272) are shown for comparison purposes in Fig. 5 for $s = 0, \pm 1$. The foregoing example then amply demonstrates that the Q-function $W_S^{(-1)}(\vartheta, \varphi)$ alone satisfies the *nonnegativity* condition, namely, $W_S^{(-1)} \geq 0$, required of a true probability density function. The other quasiprobability distribution functions $W_S^{(1)}$ and $W_S^{(0)}$ violate this condition (because they may take on negative values). From now on for purposes of convenience, we shall consider $W_S^{(-1)}(\vartheta, \varphi, t)$ only omitting everywhere the superscript (-1) in
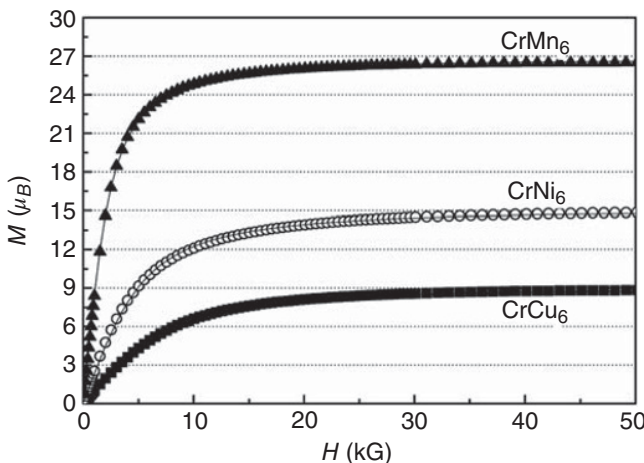
Figure 4. The magnetization $M = g\mu_B S B_S(\beta\mu_0 g\mu_B S H)$ per molecule in units of Bohr magnetons μ_B of CrCu$_6$, CrNi$_6$, and CrMn$_6$ vs. the external applied field H at $T = 2$ K. The experimental data (symbols) are accurately described by the Brillouin functions (solid lines). Reproduced with permission of American Physical Society Salman et al. [147].
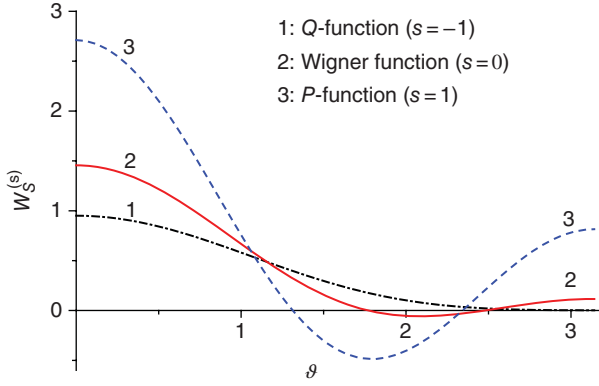
Figure 5. $W_S^{(s)}(\vartheta)$ versus the polar angle ϑ for $s = 0, \pm 1$, $\xi = 3$, and $S = 1$, (Color on line).

$W_S^{(-1)}(\vartheta, \varphi, t)$ (nevertheless all results may be easily generalized for $W_S^{(1)}(\vartheta, \varphi, t)$ and $W_S^{(0)}(\vartheta, \varphi, t)$, which can be treated in a like manner).

Next, we calculate the phase space Q-function distribution (henceforth, this will be given the generic title "Wigner function") for spins in an external uniform field **H** of an *arbitrary* orientation rather than just applied along the Z-axis so that the Hamiltonian is given by Eq. (265). This operator that now pertains to a *nonaxially symmetric* problem can be rewritten in terms of the spherical spin operators $\hat{S}_\mu$ (see Appendix A) as

$$\beta \hat{H}_S = -\frac{\xi}{S} \sum_{\mu=-1}^{1} \gamma^\mu \hat{S}_\mu,$$

where in terms of direction cosines $\gamma^{\pm 1} = \mp 2^{-1/2}(\gamma_X \mp i\gamma_Y)$, $\gamma^0 = \gamma_Z$, and the matrix elements of the Hamiltonian operator $\hat{H}_S$ can again be given in closed form, namely,

$$\left[\beta \hat{H}_S\right]_{m'm} = -\frac{\xi}{S}\left(\gamma^{-1}\left[\hat{S}_{-1}\right]_{m-1m'}\delta_{m-1m} + \gamma^0 m\delta_{mm'} + \gamma^1\left[\hat{S}_1\right]_{m+1m}\delta_{m+1m'}\right), \tag{283}$$

where the matrix elements of the spherical spin operator $\hat{S}_{\pm 1}$ are given by Eq. (A11), namely,

$$\left[\hat{S}_{\pm 1}\right]_{m\pm 1m} = \mp\sqrt{(S \mp m)(S \pm m + 1)/2}. \tag{284}$$

Furthermore, for small S, the equilibrium density matrix $\hat{\rho}_S = e^{-\beta \hat{H}_S}/Z_S$ can be written in closed form as a finite series of the spin operators. For example, for $S = 1/2$, $S = 1$, and so on, one has

$$\hat{\rho}_{1/2} = \frac{1}{Z_{1/2}} \left(\hat{I} \cosh \xi + 2 \sum_{\mu=-1}^{1} \gamma^\mu \hat{S}_\mu \sinh \xi \right), \qquad (285)$$

$$\hat{\rho}_1 = \frac{1}{Z_1} \left[\hat{I} + \sum_{\mu=-1}^{1} \gamma^\mu \hat{S}_\mu \sinh \xi + 2 \left(\sum_{\mu=-1}^{1} \gamma^\mu \hat{S}_\mu \right)^2 \sinh^2 \frac{\xi}{2} \right], \qquad (286)$$

and so on, where $\hat{I}$ is the identity matrix.

The corresponding Q-distribution $W_S(\vartheta, \varphi)$ can then be calculated in the finite series form given by Eq. (262). In turn, this finite series can then be summed (after tedious algebra, which is again best accomplished via MATHEMATICA) so that the distribution $W_S(\vartheta, \varphi)$ can ultimately be written for arbitrary spin S in concise closed form [66], namely, (cf. Eq. 276)

$$W_S(\vartheta, \varphi) = \frac{1}{Z_S} \left[\cosh \frac{\xi}{2S} + F(\vartheta, \varphi) \sinh \frac{\xi}{2S} \right]^{2S}, \qquad (287)$$

where

$$F(\vartheta, \varphi) = \gamma_X \sin \vartheta \cos \varphi + \gamma_Y \sin \vartheta \sin \varphi + \gamma_Z \cos \vartheta \qquad (288)$$

and

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

$$= \frac{\sinh \left[\left(S + \frac{1}{2} \right) \xi/S \right]}{\sinh \left(\frac{1}{2} \xi/S \right)} \qquad (289)$$

is the partition function [Eq. (289) concurs with Eq. (273)]. Moreover, for the three specific cases represented by the following direction cosines

$$\gamma_X = 1, \quad \gamma_Y = 0, \quad \gamma_Z = 0,$$
$$\gamma_X = 0, \quad \gamma_Y = 1, \quad \gamma_Z = 0,$$

and

$$\gamma_X = 0, \quad \gamma_Y = 0, \quad \gamma_Z = 1,$$

the phase space distribution equation (287) reduces to the equations already given by Takahashi and Shibata [35, 36] and reproduces Eq. (276). Now, the equilibrium average $\left\langle(\hat{\boldsymbol{\mu}} \cdot \mathbf{H})\right\rangle_{eq}$ is then from Eqs. (287) and (288) (cf. Eq. 277)

$$
\begin{aligned}
\left\langle(\hat{\boldsymbol{\mu}} \cdot \mathbf{H})\right\rangle_{eq} &= \mu H \frac{(2S+1)(S+1)}{4\pi} \int_0^\pi \int_0^{2\pi} F(\vartheta, \varphi) W_S(\vartheta, \varphi) \sin \vartheta \, d\vartheta \, d\varphi \\
&= \mu H B_S(\xi),
\end{aligned} \tag{290}
$$

where $B_S(x)$ is the Brillouin function defined by Eq. (278). In the classical limit $S \to \infty$, the equilibrium distribution $W_S(\vartheta, \varphi)$ given by Eq. (287) tends to the Boltzmann distribution

$$
\frac{2S+1}{4\pi} W_S(\vartheta, \varphi) \to \frac{1}{Z_{cl}} e^{\xi F(\vartheta, \varphi)}, \tag{291}
$$

while the the equilibrium average $\left\langle(\hat{\boldsymbol{\mu}} \cdot \mathbf{H})\right\rangle_{eq}$ tends to the Langevin function

$$
\begin{aligned}
\left\langle(\hat{\boldsymbol{\mu}} \cdot \mathbf{H})\right\rangle_{eq} &\to \frac{\mu H}{Z_{cl}} \int_0^\pi \int_0^{2\pi} \cos \vartheta \, e^{\xi F(\vartheta, \varphi)} \sin \vartheta \, d\vartheta \, d\varphi \\
&= \mu H L(\xi) = \mu H \left(\coth \xi - \frac{1}{\xi} \right),
\end{aligned} \tag{292}
$$

where Z_{cl} is the classical partition function given by

$$
Z_{cl} = \int_0^\pi \int_0^{2\pi} e^{\xi F(\vartheta, \varphi)} \sin \vartheta \, d\vartheta \, d\varphi = 4\pi \frac{\sinh \xi}{\xi}. \tag{293}
$$

Clearly, these calculations represent quantum and classical treatments of paramagnetism [2]. Here, quantum effects as identified via the Brillouin function equation (278) become important at small S when that function must be used instead of the Langevin function given by Eq. (291), which is valid in the classical limit.
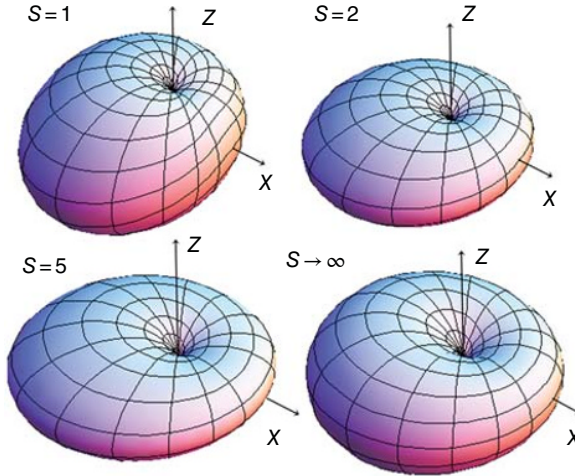
2. *Uniaxial Nanomagnet in an External Field*

Now we calculate the equilibrium Wigner function $W_S(\vartheta, \varphi)$ for a *uniaxial* nanomagnet of arbitrary spin number S in an external magnetic field of an *arbitrary* orientation. First, we briefly consider the more general nonaxially symmetric case of a spin in an external *constant* field $\mathbf{H}$ with the Hamiltonian operator $\hat{H}_S$ given by Eq. (266); then we specialize it to a longitudinal field. In the general case, the matrix elements of $\hat{H}_S$ can again be given via the matrix elements of the spherical

spin operators $\hat{S}_\mu(\mu = 0, \pm 1)$ and $\hat{S}_0^2$, namely (cf. Eq. (283) with superimposed anisotropy term),

$$
\begin{aligned}
\left[\beta \hat{H}_S\right]_{m'm} &= \left[-\frac{\xi}{S} \sum_{\mu=-1}^{1} \gamma^\mu \hat{S}_\mu - \frac{\sigma}{S^2} \hat{S}_0^2 \right]_{m'm} \\
&= -\frac{\xi}{S} \left(\gamma^{-1} \left[\hat{S}_{-1}\right]_{m-1m'} \delta_{m-1m'} + \gamma^1 \left[\hat{S}_1\right]_{m+1m'} \delta_{m+1m} \right) \\
&\quad - \left(m^2 \frac{\sigma}{S^2} + \gamma^0 m \frac{\xi}{S} \right) \delta_{mm'},
\end{aligned}
\tag{294}
$$

where the matrix elements $\left[\hat{S}_{\pm1}\right]_{m\pm1m}$ are defined by Eq. (284). The corresponding phase space distribution $W_S(\vartheta, \varphi)$ can then be calculated in the finite series form given Eqs. (262) and (263). Now motivated by the form of the classical potential, the results of the calculation of an "effective" free energy potential defined by $\beta V(\vartheta, \varphi) = -\ln W_S(\vartheta, \varphi)$ are shown in Fig. 6 for various values of S. The effective potential $V(\vartheta, \varphi)$ has two nonequivalent minima (the minimum at $\vartheta = \pi$ is masked in these plots) and one saddle point in the plane $\varphi = 0$; the potential shape and barrier heights strongly depend on the spin number S. Moreover, in the classical limit, $S \to \infty$, $V(\vartheta, \varphi)$ tends to the normalized classical free energy $V_{cl}(\vartheta, \varphi)$ given by

Figure 6. 3D plot of the "effective" free energy potential $\beta V(\vartheta, \varphi)$ for a uniaxial nanomagnet in an external field for various values of $S = 1, 2, 5$, and $S \to \infty$ [classical limit; Eq. (295)] and the parameters $\sigma = 5$, $h = \xi/2\sigma = 0.2$, $\gamma_Z = 1/2$, $\gamma_Y = 0$, and $\gamma_X = \sqrt{3}/2$ (i.e., the field **H** is in the XZ-plane and directed at an angle $\pi/3$ to the Z-axis) (Color on line).

$$\beta V_{cl}(\vartheta, \varphi) = -\sigma \left\{ \cos^2 \vartheta + 2h \left[(\gamma_X \cos \varphi + \gamma_Y \sin \varphi) \sin \vartheta + \gamma_Z \cos \vartheta \right] \right\}, \tag{295}$$

which is also shown in Fig. 6 for the purpose of comparison.

However, this general treatment considerably simplifies for a longitudinal field (ubiquitous in magnetic applications) so that $\gamma_X = 0$, $\gamma_Y = 0$ and $\gamma_Z = 1$ (see Eq. 267), and so the problem becomes axially symmetric. Here, the density matrix $\hat{\rho}_S$ is diagonal with matrix elements $\rho_{mm'}$ given explicitly by [142, 147]

$$\rho_{mm'} = \frac{\delta_{mm'}}{Z_S} e^{\frac{\sigma m^2}{S^2} + \frac{\xi m}{S}}, \tag{296}$$

where the partition function Z_S is

$$Z_S = \sum_{m=-S}^{S} e^{\frac{\sigma m^2}{S^2} + \frac{\xi m}{S}}. \tag{297}$$

The explicit matrix elements $\rho_{mm'}$ from Eq. (296) can then be used to evaluate the averages $\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle_{eq}$ in Eq. (263) as (cf. Eq. 275)

$$\left\langle \hat{T}_{LM}^{\dagger(S)} \right\rangle_{eq} = \frac{\delta_{M0}}{Z_S} \sqrt{\frac{2L+1}{2S+1}} \sum_{m=-S}^{S} C_{SmLM}^{Sm} e^{\frac{\sigma m^2}{S^2} + \frac{\xi m}{S}}. \tag{298}$$

Furthermore, due to the symmetry about the Z-axis, the phase space distribution function $W_S(\vartheta, \varphi) \equiv W_S(\vartheta)$ is independent of the azimuthal angle φ so that the Wigner function equation (262) for this important problem simplifies to the series of Legendre polynomials [65]

$$W_S(\vartheta) = \sum_{L=0}^{2S} \frac{L + 1/2}{S + 1/2} \langle P_L \rangle_{eq} P_L(\cos \vartheta). \tag{299}$$

Here, $\langle P_L \rangle_{eq}$ are the equilibrium averages of the Legendre polynomials $P_L(\cos \vartheta)$ given by

$$\langle P_L \rangle_{eq} = (S + 1/2) \int_0^\pi P_L(\cos \vartheta) W_S(\vartheta) \sin \vartheta \, d\vartheta$$

$$= \frac{(2S)! \sqrt{2S+1}}{Z_S \sqrt{(2S-L)!(2S+L+1)!}} \sum_{m=-S}^{S} C_{SmL0}^{Sm} e^{\frac{\sigma m^2}{S^2} + \frac{\xi m}{S}} \tag{300}$$

and we have used Eqs. (298) and Eq. (B4). The equilibrium statistical moment $\langle P_1 \rangle_{eq}$ then yields the average longitudinal component of the spin as

$$
\left\langle \hat{S}_Z \right\rangle_{eq} = (S+1) \langle P_1 \rangle_{eq} = (S+1) \langle \cos \vartheta \rangle_{eq}
$$

$$
= \frac{1}{Z_S} \sum_{m=-S}^{S} m \, e^{\frac{\sigma m^2}{S^2} + \frac{\xi m}{S}}, \tag{301}
$$

which concurs with the well-known result for the equilibrium magnetization for arbitrary S [142, 147]. Here, we have used the Weyl symbol of the operator $\hat{S}_Z$ given by Eq. (241) with $s = 1$. From the explicit expressions for the $P_L(\cos \vartheta)$ [105] in Eq. (299), we then have explicit trigonometric forms for the distribution functions, for example, for $S = 1/2, 1, 3/2, 2, \cdots$. [65]

$$
W_{1/2}(\vartheta) = \frac{e^{\sigma}}{Z_{1/2}} f_{\xi}(\vartheta),
$$

$$
W_1(\vartheta) = \frac{e^{\sigma}}{Z_1} \left[\left(f_{\xi}^{(1)}(\vartheta) \right)^2 + \frac{1}{2} \left(e^{-\sigma} - 1 \right) \sin^2 \vartheta \right],
$$

$$
W_{3/2}(\vartheta) = \frac{e^{9\sigma/4}}{Z_{3/2}} \left[\left(f_{\xi}^{(3/2)}(\vartheta) \right)^3 + \frac{3}{4} \left(e^{-8\sigma/9} - 1 \right) f_{\xi}^{(3/2)}(\vartheta) \sin^2 \vartheta \right],
$$

$$
W_2(\vartheta) = \frac{e^{\sigma}}{Z_2} \left[\left(f_{\xi}^{(2)}(\vartheta) \right)^4 + \left(e^{-3\sigma/4} - 1 \right) \left(f_{\xi}^{(2)}(\vartheta) \right)^2 \sin^2 \vartheta \right.
$$

$$
\left. + \frac{1}{8} \left(3e^{-\sigma} - 4e^{-3\sigma/4} + 1 \right) \sin^4 \vartheta \right],
$$

and so on, where the function

$$
f_{\xi}^{(S)}(\vartheta) = \cosh \frac{\xi}{2S} + \cos \vartheta \sinh \frac{\xi}{2S}. \tag{302}
$$

For *arbitrary* S, the trigonometric series in $\left(f_{\xi}^{(S)}(\vartheta) \right)^{2(S-m)} \sin^{2m} \vartheta$ for the distribution $W_S(\vartheta)$ can be rewritten in general form as
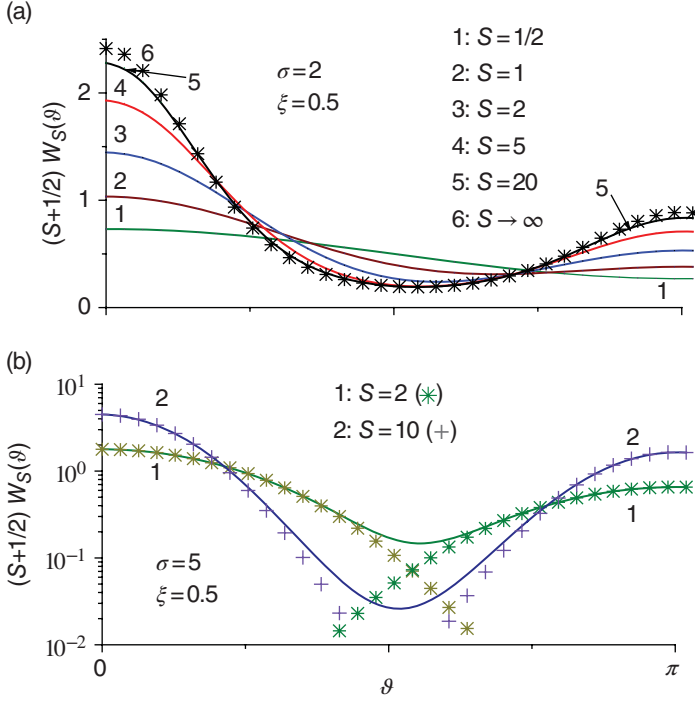
$$
W_S(\vartheta) = \frac{e^{\sigma}}{Z_S} \sum_{n=0}^{[S]} b_n \left(f_{\xi}^{(S)}(\vartheta) \right)^{2(S-n)} \sin^{2n} \vartheta, \tag{303}
$$

where $[S]$ means the whole part of S and the leading coefficients b_n are

$$
b_0 = 1,
$$

$$
b_1 = \frac{S}{2} \left[e^{-(2S-1)\sigma/S^2} - 1 \right],
$$

$$
b_2 = \frac{S}{16} \left[(2S-1)e^{-4(S-1)\sigma/S^2} - 4(S-1)e^{-(2S-1)\sigma/S^2} + 2S - 3 \right],
$$

and so on.

Figure 7. (a) $(S + 1/2) W_S(\vartheta)$ versus ϑ for $\sigma = 2$, $\xi = 0.5$, and various values of S including the classical limit, $S \to \infty$ (asterisks), Eq. (305). (b) The distribution $(S + 1/2) W_S(\vartheta)$ (solid lines) for $\sigma = 5$, $\xi = 0.5$, and $S = 2$ and 10. Crosses ($\times$) and stars ($*$): Eq. (306) (Color on line).

The distribution $W_S(\vartheta)$ given by Eq. (299) is shown in Fig. 7 as a function of the polar angle ϑ. The maxima of $W_S(\vartheta)$ occur at $\vartheta = 0$ and $\vartheta = \pi$, where

$$W_S(0) = \frac{1}{Z_S} e^{\xi + \sigma} \quad \text{and} \quad W_S(\pi) = \frac{1}{Z_S} e^{-\xi + \sigma}, \tag{304}$$

respectively, meaning classically speaking that the spins are concentrated at the bottom of the wells, where the minima of the potential energy occur. In the classical limit, $S \to \infty$, $W_S(\vartheta)$ from Eq. (299) tends to the usual Boltzmann distribution for a uniaxial nanomagnet in a longitudinal field, that is,

$$(S + 1/2) W_S(\vartheta) \to \frac{1}{Z_{cl}} e^{\xi \cos \vartheta + \sigma \cos^2 \vartheta}, \tag{305}$$

where

$$Z_{cl} = \int\limits_0^\pi e^{\xi \cos \vartheta + \sigma \cos^2 \vartheta} \sin \vartheta \, d\vartheta$$

is the classical partition function. Clearly from Fig. 7(a), the deviations of the quantum distribution $(S + 1/2) W_S(\vartheta)$ from the classical Boltzmann distribution equation (305) become pronounced only for *small* spin numbers $S < 10$ while as S increases, the distribution $(S + 1/2) W_S(\vartheta)$ tends to the classical expression (Eq. 305) (e.g., for $S = 20$, the differences between the two distributions Eqs. (303) and (305) do not exceed 10%; see the curve 5 in Fig. 7(a)). Due to the biasing effect of the external field, the maxima are unequal in height. Moreover, in the low temperature limit, the dynamics of the spin in the vicinity of the maxima $\vartheta = 0$ and $\vartheta = \pi$ represent precession in the effective magnetic field with characteristic angular frequencies ω^+ and ω^-, respectively,

$$\omega^\pm = \frac{1}{\beta\hbar} \left[\pm\frac{\xi}{S} + (2S - 1)\frac{\sigma}{S^2} \right],$$

so that the distribution $W_S(\vartheta)$ can be approximated by

$$W_S(\vartheta) \approx \begin{cases} Z_S^{-1} e^{-\sigma(1-S^{-1})} \left(f_{\beta\hbar\omega^+}^{(S)}(\vartheta) \right)^{2S}, & (\vartheta \leq 1) \\ Z_S^{-1} e^{-\sigma(1-S^{-1})} \left(f_{\beta\hbar\omega^-}^{(S)}(\vartheta) \right)^{2S}, & (\pi - \vartheta \leq 1) \end{cases}$$

$$= \begin{cases} W_S(0) e^{-\xi/S - \sigma(1-S^{-1})} \left(f_{\beta\hbar\omega^+}^{(S)}(\vartheta) \right)^{2S}, & (\vartheta \leq 1) \\ W_S(\pi) e^{\xi/S - \sigma(1-S^{-1})} \left(f_{\beta\hbar\omega^-}^{(S)}(\vartheta) \right)^{2S}, & (\pi - \vartheta \leq 1) \end{cases} \tag{306}$$

For $\sigma = 0$, that is, for *a spin in a uniform external magnetic field*, when the Hamiltonian becomes simply $\beta\hat{H}_S = -\xi\hat{S}_Z/S$, Eq. (299) reduces to our previous result given by Eq. (276) [35, 36], viz.,

$$W_S(\vartheta) = \frac{1}{Z_S} \left(f_\xi^{(S)}(\vartheta) \right)^{2S}, \tag{307}$$

where Z_S is defined by Eq. (273). As may be seen in Fig. 7(b), the "oscillator" function f from Eq. (307) describes with a very high degree of accuracy the behavior of $W_S(\vartheta)$ near $\vartheta = 0$ and $\vartheta = \pi$ as expected from intuitive reasoning. Equation (307) represents a quantum analog of the Boltzmann distribution equation (280) for classical magnetic dipoles $\boldsymbol{\mu}$ precessing in the uniform magnetic field $\mathbf{H}$ with the precession angular frequency $\omega_0 = \gamma H$.

For another particular case, namely, $\xi = 0$, that is, for a uniaxial spin system alone with Hamiltonian $\beta\hat{H}_S = -\sigma\hat{S}_Z^2/S^2$, the equilibrium phase space distribution $W_S(\vartheta)$ from Eq. (299) simplifies to

$$W_S(\vartheta) = \frac{1}{Z_S} \sum_{L=0}^{2S} \frac{(2S)!(2L + 1)P_L(\cos\vartheta)}{\sqrt{(2S + 1)(2S - L)!(2S + L + 1)!}} \sum_{m=-S}^{S} C_{SmL0}^{Sm} e^{\sigma m^2/S^2}, \tag{308}$$

where the partition function

$$Z_S = \sum_{m=-S}^{S} e^{\sigma m^2/S^2}.$$ (309)

Near $\vartheta = 0$ and $\vartheta = \pi/2$, the leading terms of the series expansion of the equilibrium distribution $W(\vartheta)$ from Eq. (308) (i.e., in $\sin^2 \vartheta$ and $\cos^2 \vartheta$, respectively) are [65]

$$W_S(\vartheta) = W_S(0) \left\{ 1 + \frac{S}{2} \left[e^{-(2S-1)\sigma/S^2} - 1 \right] \sin^2 \vartheta + \dots \right\},$$ (310)

$$W_S(\vartheta) = W_S(\pi/2) \left[1 + A \cos^2 \vartheta + \dots \right],$$ (311)

where

$$W_S(0) = \frac{e^{\sigma}}{Z_S},$$ (312)

$$W_S(\pi/2) = \frac{(2S)!}{2^{2S} Z_S} \sum_{m=-S}^{S} \frac{e^{\sigma m^2/S^2}}{(S+m)!(S-m)!},$$ (313)

$$A = \frac{\displaystyle\sum_{m=-S+1}^{S-1} e^{m^2\sigma/S^2} \frac{e^{(1-2m)\sigma/S^2} + e^{(1+2m)\sigma/S^2} - 2}{(S-1+m)!(S-1-m)!}}{2 \displaystyle\sum_{m=-S}^{S} \frac{e^{m^2\sigma/S^2}}{(S+m)!(S-m)!}}.$$ (314)

3. *Uniaxial Nanomagnet in a Transverse Field*

As a further example, we calculate the Wigner function of a uniaxial nanomagnet in a *transverse* external field with the *nonaxially symmetric* Hamiltonian $\hat{H}_S$ given by Eq. (268) otherwise known as the Lipkin–Meshkov Hamiltonian [148]. For small S, the density matrix $\hat{\rho}_S = e^{-\beta \hat{H}_S}/Z_S$ can again be calculated in closed form using MATHEMATICA. For example, for $S = 1/2$, $S = 1$, and so on, we have in terms of the spin operators [66]

$$\hat{\rho}_{1/2} = \frac{e^{\sigma}}{Z_{1/2}} \left[\hat{I} \cosh \xi + 2 \hat{S}_X \sinh \xi \right],$$ (315)

$$\begin{aligned} \hat{\rho}_1 = \frac{1}{Z_1} \bigg[& \left(e^{\sigma} - \sigma A \right) \hat{I} + A \left(\xi \hat{S}_X + \sigma \hat{S}_Z^2 \right) \\ & + \left(e^{\sigma/2} \cosh \sqrt{\xi^2 + \frac{\sigma^2}{4}} - e^{\sigma} + \frac{\sigma A}{2} \right) \hat{S}_X^2 \bigg], \end{aligned}$$ (316)

and so on, where

$$Z_{1/2} = 2e^{\sigma} \cosh(\xi),$$

$$Z_1 = e^{\sigma} + 2e^{\sigma/2} \cosh\sqrt{\xi^2 + \sigma^2/4},$$

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

The corresponding equations for the phase space distribution $W_S(\vartheta, \varphi)$ which can be obtained from the general expressions of Eqs. (262) and (263) are given by [66]

$$W_{1/2}(\vartheta, \varphi) = \frac{e^{\sigma}}{Z_{1/2}} \left[\cosh\xi + \sinh\xi \sin\vartheta \cos\varphi \right], \tag{317}$$

$$W_1(\vartheta, \varphi) = \frac{1}{2Z_1} \left\{ e^{\sigma} \left(1 - \sin^2\vartheta \cos^2\varphi \right) \right.$$

$$+ e^{\sigma/2} \cosh\sqrt{\xi^2 + \frac{\sigma^2}{4}} \left(1 + \sin^2\vartheta \cos^2\varphi \right)$$

$$\left. + \frac{\sigma A}{2} \left[\cos 2\vartheta + \sin^2\vartheta \cos^2\varphi + \frac{4\xi}{\sigma} \sin\vartheta \cos\varphi \right] \right\}, \tag{318}$$

and so on. However, once again as the spin number S increases, the analytical equations for the Wigner function $W_S(\vartheta, \varphi)$ rapidly become more and more complicated and thus rather impractical to use because $W_S(\vartheta, \varphi)$ for given spin may always be calculated much faster numerically from the general series expression (Eq. 262).

Calculations of the "effective" free energy $\beta V(\vartheta, \varphi) = -\ln W_S(\vartheta, \varphi)$ are shown in Fig. 8 for various values of S and $\sigma = 5$ and $h = \xi/(2\sigma) = 0.1$. In the classical limit, $S \to \infty$, the effective free energy function $V(\vartheta, \varphi)$ becomes the classical free energy $V_{cl}(\vartheta, \varphi)$ given by

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

which is also shown in Fig. 8 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 (i.e., the shape and barrier heights) strongly depend on S, for example, the smallest barrier height increases with increasing S from 0 (at $S = 1/2$) to its classical value $\sigma(1 - h^2)$.

4. Biaxial Anisotropy

We now calculate the Wigner function of a *biaxial* Hamiltonian $\hat{H}_S$ given by Eq. (269). Here, the density matrix $\hat{\rho}_S = e^{-\beta\hat{H}_S}/Z_S$ can again be calculated in simple
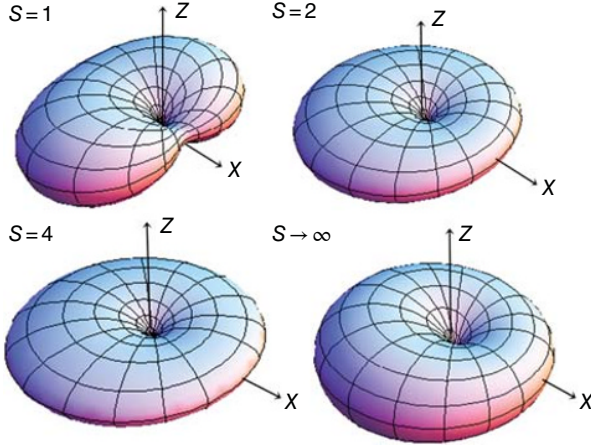
Figure 8. 3D plot of $\beta V(\vartheta, \varphi)$ for $\sigma = 10$, $h = 0.1$ and various values of $S = 1, 2, 4$, and $S \to \infty$ (classical limit) (Color on line).

closed form for small S using MATHEMATICA. For example, for $S = 1/2$, $S = 1$, etc., we have in terms of the spin operators [66]

$$\hat{\rho}_{1/2} = \frac{e^{\sigma}}{Z_{1/2}} \hat{I}, \tag{319}$$

$$\hat{\rho}_1 = \frac{1}{Z_1} \left[\hat{I} + \left(e^{\sigma} \cosh \delta - 1 \right) \hat{S}_Z^2 - e^{\sigma} \sinh \delta \left(\hat{S}_X^2 - \hat{S}_Y^2 \right) \right], \tag{320}$$

and so on, where $Z_{1/2} = 2e^{\sigma}$ and $Z_1 = 1 + 2e^{\sigma} \cosh \delta$. The corresponding equations for the phase space distribution $W_S(\vartheta, \varphi)$ are [66]

$$W_{1/2}(\vartheta, \varphi) = \frac{1}{2}, \tag{321}$$

$$W_1(\vartheta, \varphi) = \frac{1}{2Z_1} \left[\sin^2 \vartheta + e^{\sigma} \cosh \delta \left(1 + \cos^2 \vartheta \right) - e^{\sigma} \sinh \delta \sin^2 \vartheta \cos 2\varphi \right], \tag{322}$$

and so on. As before with increasing S, $W_S(\vartheta, \varphi)$ may always be calculated numerically from the general expression given by Eq. (262).

The "effective" potential $\beta V(\vartheta, \varphi) = -\ln W_S(\vartheta, \varphi)$ is shown in Fig. 9 for $S = 2$, $\sigma = 5$, and $\delta = 5$. In the classical limit, $S \to \infty$, $V(\vartheta, \varphi)$ again tends to the classical free energy $V_{cl}(\vartheta, \varphi)$ given by

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

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
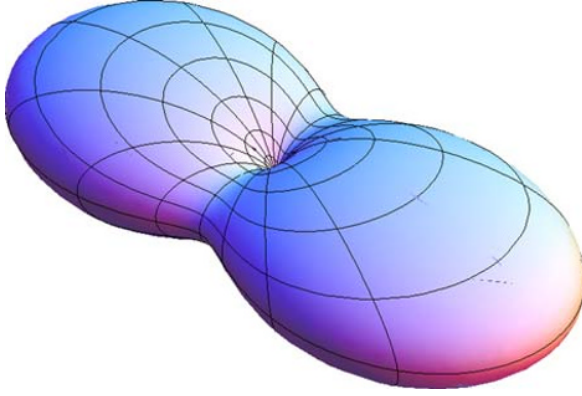
Figure 9.   3D plot of $\beta V(\vartheta, \varphi)$ for $S = 2$ and $\sigma = 5$ and $\delta = 2$ (Color on line).

(i.e., 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.

5. Cubic Anisotropy

Finally, we calculate the Wigner function of a cubic anisotropy free energy in the presence of a dc field with Hamiltonian $\hat{H}_S$ given by Eq. (270). For small S, the density matrix $\hat{\rho}_S = e^{-\beta \hat{H}_S}/Z_S$ can again be evaluated in closed form using MATHEMATICA. For example, for $S = 1/2$, $S = 1$, 3/2, and 2, we have [66]

$$\hat{\rho}_{1/2} = \frac{e^{3\sigma_c/2}}{Z_{1/2}} \left(\hat{I} \cosh \xi + 2 \hat{S}_Z \sinh \xi \right), \tag{323}$$

$$\hat{\rho}_1 = \frac{e^{\sigma_c}}{Z_1} \left[\hat{I} + \sinh \xi \hat{S}_Z + 2 \sinh^2 \frac{\xi}{2} \hat{S}_Z^2 \right], \tag{324}$$

$$\hat{\rho}_{3/2} = \frac{e^{41\sigma_c/54}}{Z_{3/2}} \left\{ \frac{1}{8} \left(9 \cosh \frac{\xi}{3} - \cosh \xi \right) \hat{I} + \frac{1}{12} \left(27 \sinh \frac{\xi}{3} - \sinh \xi \right) \hat{S}_Z \right.$$
$$\left. + 2 \cosh \frac{\xi}{3} \sinh^2 \frac{\xi}{3} \hat{S}_Z^2 + \frac{4}{3} \sinh^3 \frac{\xi}{3} \hat{S}_Z^3 \right\}, \tag{325}$$

$$\hat{\rho}_2 = \frac{1}{Z_2} \left\{ \left(e^{3\sigma_c/4} - \frac{3\sigma_c}{4\xi} R \right) \hat{I} + \frac{1}{6} \left(8 e^{9\sigma_c/16} \sinh \frac{\xi}{2} - R \right) \hat{S}_Z \right.$$
$$\times \frac{1}{12} \left(16 e^{9\sigma_c/16} \cosh \frac{\xi}{2} - 15 e^{3\sigma_c/4} - P - \frac{93\sigma_c}{32\xi} R \right) \hat{S}_Z^2$$
$$- \frac{1}{6} \left(2 e^{9\sigma_c/16} \sinh \frac{\xi}{2} - R \right) \hat{S}_Z^3 \tag{326}$$
$$\left. + \frac{1}{12} \left(3 e^{3\sigma_c/4} - 4 e^{9\sigma_c/16} \cosh \frac{\xi}{2} + P - \frac{9\sigma_c}{32\xi} R \right) \hat{S}_Z^4 + \frac{\sigma_c}{32\xi} R \left(\hat{S}_X^4 + \hat{S}_Y^4 \right) \right\},$$

where

$$Z_{1/2} = 2e^{3\sigma_c/2} \cosh \xi,$$

$$Z_1 = e^{\sigma_c}(1 + 2\cosh\xi),$$

$$Z_{3/2} = 4e^{41\sigma_c/54} \cosh\frac{\xi}{3} \cosh\frac{2\xi}{3},$$

$$Z_2 = e^{3\sigma_c/4} + 2e^{9\sigma_c/16}\cosh\frac{\xi}{2} + 2e^{21\sigma_c/32}\cosh\left[\sqrt{\xi^2 + (3\sigma_c/32)^2}\right],$$

$$P = e^{21\sigma_c/32}\cosh\left[\sqrt{\xi^2 + (3\sigma_c/32)^2}\right],$$

$$R = \frac{\xi e^{21\sigma_c/32}}{\sqrt{\xi^2 + (3\sigma_c/32)^2}}\sinh\left[\sqrt{\xi^2 + (3\sigma_c/32)^2}\right].$$

The corresponding equations for $W_S(\vartheta, \varphi)$ are as follows [66]:

$$W_{1/2}(\vartheta, \varphi) = \frac{e^{3\sigma_c/2}}{Z_{1/2}}\left(\cosh\frac{\xi}{2} + \sinh\frac{\xi}{2}\cos\vartheta\right), \tag{327}$$

$$W_1(\vartheta, \varphi) = \frac{e^{\sigma_c}}{Z_1}\left(\cosh\frac{\xi}{2} + \sinh\frac{\xi}{2}\cos\vartheta\right)^2, \tag{328}$$

$$W_{3/2}(\vartheta, \varphi) = \frac{e^{41\sigma_c/54}}{Z_{3/2}}\left(\cosh\frac{\xi}{2} + \sinh\frac{\xi}{2}\cos\vartheta\right)^3, \tag{329}$$

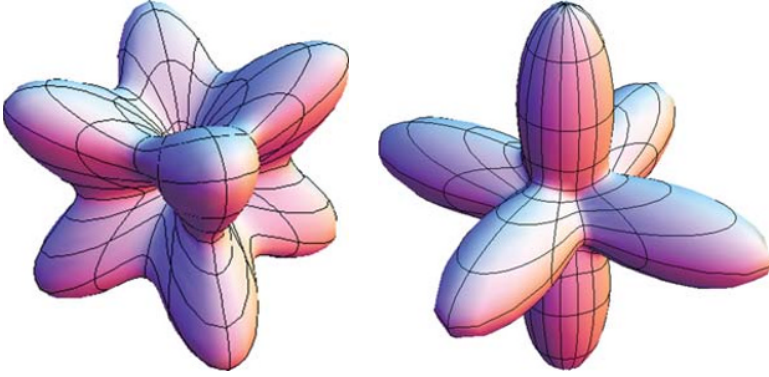$$W_2(\vartheta, \varphi) = \frac{1}{8Z_2}\left\{2e^{9\sigma_c/16}\sin^2\vartheta\left[4\cos\vartheta\sin\frac{\xi}{2} + (3 + \cos 2\vartheta)\cosh\frac{\xi}{2}\right]\right.$$
$$+ 3e^{3\sigma_c/4}\sin^4\vartheta + P(8\cos^2\vartheta + \sin^4\vartheta) \tag{330}$$
$$\left. + 4R\left(\cos\vartheta + \cos^3\vartheta + \frac{3\sigma}{128\xi}\cos 4\varphi\sin^4\vartheta\right)\right\}.$$

For $\xi = 0$, Eq. (330) yields

$$W_2(\vartheta, \varphi) = \frac{1}{2\left(3 + 2e^{3\sigma_c/16}\right)}$$
$$\times\left[1 + e^{3\sigma_c/16} + \frac{1}{4}\left(1 - e^{3\sigma_c/16}\right)\left(\sin^2 2\vartheta + \sin^4\vartheta\sin^2 2\varphi\right)\right]. \tag{331}$$

For large S, $W_S(\vartheta, \varphi)$ may always be calculated numerically from the general equation (262).

The normalized "effective" potential $\beta V(\vartheta, \varphi) = -\ln W_S(\vartheta, \varphi)$ is shown in Fig. 10 for $\sigma_c = \pm 8, \xi = 0$, and $S = 4$. The potential characteristics (i.e., the shape

Figure 10. 3D plot of $\beta V(\vartheta, \varphi)$ for positive (left) and negative (right) cubic anisotropies for $S = 4$ and $\xi = 0$ (Color on line).

and barrier heights) again strongly depend on S. In the classical limit, $S \to \infty$, that potential once more tends to the classical free energy $\beta V_{cl}(\vartheta, \varphi)$ given by

$$\beta V_{cl}(\vartheta, \varphi) = \frac{\sigma_c}{4} \left(\sin^2 2\vartheta + \sin^4 \vartheta \sin^2 2\varphi \right).$$

For positive anisotropy constant $\sigma_c > 0$, the cubic potential has 6 minima (wells), 8 maxima, and 12 saddle points. For $\sigma_c < 0$, the maxima and minima are interchanged.

Clearly the Wigner–Stratonovich transformation yields, in principle, the equilibrium phase space distribution via its finite series representation for any given anisotropy free energy. In particular, these results may be used to estimate the spin reversal time from TST just as for particles in Section II.B.2.

6. TST Reversal Time

As we have seen in Section II.B.2, TST because it is based on *equilibrium distributions* affords the simplest possible description of quantum corrections to the thermally activated escape rate. Now in applying TST to classical spins (i.e., classical magnetic moments $\boldsymbol{\mu}$) to determine the escape rate due to thermal agitation from one metastable orientation say A to another metastable orientation say B, we suppose that the free energy $V_{cl}(\vartheta, \varphi)$ has a multistable structure. Such a structure has minima at $\mathbf{n}_A$ and $\mathbf{n}_B$ separated by a potential barrier with a saddle point at $\mathbf{n}_C$. In the high barrier approximation, as far as TST is concerned, the classical escape rate Γ_{cl} may be estimated via the flux over the barrier [20]

$$\Gamma_{cl} \sim \frac{I_C^{cl}}{Z_A^{cl}}, \tag{332}$$

where the well partition function Z_A^{cl} and the total current I_C^{cl} of the (spin) representative points at the saddle point C are, respectively,

$$Z_A^{cl} \sim \iint\limits_{well} e^{-\beta V_{cl}(\vartheta,\varphi)} \sin\vartheta\, d\vartheta\, d\varphi \tag{333}$$

and

$$I_C^{cl} \sim \iint\limits_{saddle} J_C(\vartheta,\varphi) \sin\vartheta\, d\vartheta\, d\varphi \tag{334}$$

($J_C(\vartheta,\varphi)$ is the current density near the saddle point C).

Near the metastable minimum $\mathbf{n}_A$, the spin precesses about a uniform "effective" field, which may be represented as the gradient of a potential, namely,

$$\mathbf{H}_A = -\mu_0^{-1} \frac{\partial V_{cl}}{\partial \boldsymbol{\mu}}, \tag{335}$$

so that the equation of motion of the magnetic moment $\boldsymbol{\mu}$ is

$$\frac{d\boldsymbol{\mu}}{dt} = \gamma\left[\boldsymbol{\mu} \times \mathbf{H}_A\right]. \tag{336}$$

Then to evaluate the classical partition function Z_A^{cl} and the total current I_C^{cl}, we simply suppose [5,6,24] that the free energy V_{cl} near the minimum $\mathbf{n}_A$ and the saddle point $\mathbf{n}_C$ can be approximated by the first two terms of its Taylor expansion, namely,

$$V_{cl}(u_1^{(A)}, u_2^{(A)}) = V_{cl}(\mathbf{n}_A) + \frac{1}{2}\left[c_1^{(A)}\left(u_1^{(A)}\right)^2 + c_2^{(A)}\left(u_2^{(A)}\right)^2\right], \tag{337}$$

and

$$V_{cl}(u_1^{(C)}, u_2^{(C)}) = V_{cl}(\mathbf{n}_C) + \frac{1}{2}\left[c_1^{(C)}\left(u_1^{(C)}\right)^2 + c_2^{(C)}\left(u_2^{(C)}\right)^2\right], \tag{338}$$

where $(u_1^{(A)}, u_2^{(A)}, u_3^{(A)})$ and $(u_1^{(C)}, u_2^{(C)}, u_3^{(C)})$ denote the direction cosines of a magnetic moment $\boldsymbol{\mu}$ near $\mathbf{n}_A$ and $\mathbf{n}_C$, respectively, $c_1^{(A)} = \partial^2 V_{cl}/\partial u_1^{(A)2} > 0$ and $c_2^{(A)} = \partial^2 V_{cl}/\partial u_2^{(A)2} > 0$, that is, the well has the form of an elliptic paraboloid, while $c_1^{(C)} = \partial^2 V_{cl}/\partial u_1^{(C)2} < 0$ and $c_2^{(C)} = \partial^2 V_{cl}/\partial u_2^{(C)2} > 0$, that is, the saddle has the form of an hyperbolic paraboloid. Hence, in order to estimate Z_A^{cl} from Eq. (333) in the high barrier limit, we have via Gaussian integrals using the Taylor expansion given by Eq. (337) the well partition function

$$Z_A^{cl} \sim \iint_{well} e^{-\beta V_{cl}(u_1^{(A)}, u_2^{(A)})} du_1^{(A)} du_2^{(A)}$$

$$\approx \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\beta V_{cl}(u_1^{(A)}, u_2^{(A)})} du_1^{(A)} du_2^{(A)} \qquad (339)$$

$$= \frac{2\pi e^{-\beta V_{cl}(\mathbf{n}_A)}}{\beta \sqrt{c_1^{(A)} c_2^{(A)}}} = \frac{2\pi \gamma e^{-\beta V_{cl}(\mathbf{n}_A)}}{\beta \mu \mu_0 \omega_A},$$

where

$$\omega_A = \frac{\gamma}{\mu_0 \mu} \sqrt{c_1^{(A)} c_2^{(A)}} \qquad (340)$$

is the well (precession) frequency playing the role of the attempt angular frequency in TST [20]. Here, the limits of integration may be formally extended to $\pm$ infinity without significant error since the spins are almost all at $\mathbf{n}_A$. The total current I_C^{cl} of representative points at the saddle point $\mathbf{n}_C$ may then be estimated as follows. We initially suppose that the saddle region has the shape of a hyperbolic paraboloid and the u_1-axis of the local coordinate system at the saddle point $\mathbf{n}_C$ lies in the *same direction as the current density* $\mathbf{J}_C$ *over the saddle*. Next, recall that in TST, the Boltzmann distribution $\sim e^{-\beta V_{cl}}$ holds *everywhere* and that the current density J_C is given by at the saddle point C [24]

$$J_C(u_1^{(C)}, u_2^{(C)}) = -\frac{\gamma}{\mu_0 \mu} \delta\left(\partial u_1^{(C)}\right) \frac{\partial V_{cl}}{\partial u_2^{(C)}} e^{-\beta V_{cl}\left(u_1^{(C)}, u_2^{(C)}\right)}$$

$$= \frac{\gamma}{\beta \mu_0 \mu} \delta\left(\partial u_1^{(C)}\right) \frac{\partial}{\partial u_2^{(C)}} e^{-\beta V_{cl}\left(u_1^{(C)}, u_2^{(C)}\right)}. \qquad (341)$$

Thus, we must have for the current at the saddle point

$$I_C^{cl} \sim \iint_{saddle} J_C(u_1^{(C)}, u_2^{(C)}) du_1^{(C)} du_2^{(C)} \approx \frac{\gamma}{\mu \mu_0 \beta} e^{-\beta V_{cl}(\mathbf{n}_C)}. \qquad (342)$$

Hence, using Eqs. (339) and (342), the flux over barrier given by Eq. (332) yields the *classical* TST formula for spins

$$\Gamma_{cl} \sim \frac{\omega_A}{2\pi} e^{-\beta \Delta V_{cl}}, \qquad (343)$$

where

$$\Delta V_{cl} = V_{cl}(\mathbf{n}_C) - V_{cl}(\mathbf{n}_A) \qquad (344)$$

is the potential barrier height the determination of which always involves a detailed knowledge of the energy landscape.

In a like manner, the *quantum* escape rate Γ for a spin from a metastable orientation A to another metastable orientation B via the saddle point C as determined by quantum TST may be given by an equation similar to the classical equation (332), namely,

$$\Gamma \sim \frac{I_C}{Z_A}. \tag{345}$$

However, the well quantum partition function Z_A and the total current over the saddle point I_C must now be evaluated using the equilibrium phase space distribution function $W_S(\vartheta, \varphi)$ of the spin system with the quantum spin Hamiltonian $\hat{H}_S$ instead of the classical Boltzmann distribution $\sim e^{-\beta V_{cl}(\vartheta,\varphi)}$. Nevertheless, the dynamics of a spin $\hat{\mathbf{S}}$ still comprise steady precession with the angular frequency $\boldsymbol{\omega}_A^S = \gamma \mathbf{H}_A^S$ in the *effective* magnetic field $\mathbf{H}_A^S$ in the well near the metastable minimum $\mathbf{n}_A$ so that the spin Hamiltonian $\hat{H}_S$ may be approximated by the simple equation $\hat{H}_S \approx -\hbar(\boldsymbol{\omega}_A^S \cdot \hat{\mathbf{S}})$. Thus, the quantum dynamics of the spin $\hat{\mathbf{S}}$ obeys the Larmor equation [2, 37] (cf. Eq. 336)

$$\frac{d\hat{\mathbf{S}}}{dt} = \frac{i}{\hbar}\left[\hat{H}_S, \hat{\mathbf{S}}\right] = \gamma \left[\hat{\mathbf{S}} \times \mathbf{H}_A^S\right]. \tag{346}$$

However, near the metastable minimum $\mathbf{n}_A$, the distribution W_S can be approximated simply by the Zeeman energy distribution for a spin in a uniform "effective" field $\mathbf{H}_A^S$ given by Eq. (287), namely, (cf. Eq. (306) for the uniaxial nanomagnet)

$$W_S(\vartheta, \varphi) \approx W_S(\mathbf{n}_A)e^{-S\xi_A}\left[\cosh\frac{\xi_A}{2} + F_A(\vartheta, \varphi)\sinh\frac{\xi_A}{2}\right]^{2S}, \tag{347}$$

where $\xi_A = \beta\hbar\left|\boldsymbol{\omega}_A^S\right|$ in accordance with Eq. (287),

$$F_A(\vartheta, \varphi) = \gamma_{X_A}\sin\vartheta\cos\varphi + \gamma_{Y_A}\sin\vartheta\sin\varphi + \gamma_{Z_A}\cos\vartheta,$$

and $\gamma_{X_A}, \gamma_{Y_A}$, and γ_{Z_A} are the direction cosines of the "effective" field $\mathbf{H}_A^S$ at the minimum $\mathbf{n}_A$. This effective field distribution approximation given by Eq. (347) is just the rotational analog of the harmonic oscillator distribution approximation for the well dynamics in the particle case (see Section II.B.2). Just as with the classical case, the precession frequency $\boldsymbol{\omega}_A^S$ can be estimated from the well angular frequency given by Eq. (340); however, the coefficients $c_1^{(A)}$ and $c_2^{(A)}$ are now determined from the truncated Taylor series expansion of the Weyl symbol H_S of the Hamiltonian $\hat{H}_S$ of the spin, namely,

$$\beta H_S = \beta H_S(\mathbf{n}_A) + \frac{1}{2}\left[c_1^{(A)}\left(u_1^{(A)}\right)^2 + c_2^{(A)}\left(u_2^{(A)}\right)^2\right]. \tag{348}$$

Now by using the partition function defined by the left-hand side of Eq. (289), we can approximate the well partition function in the context of quantum TST as follows:

$$Z_A \sim W_S(\mathbf{n}_A)e^{-S\xi_A} \int\limits_{well} [\cosh(\xi_A/2) + \sinh(\xi_A/2)F_A(\vartheta,\varphi)]^{2S} \sin\vartheta\, d\vartheta\, d\varphi$$

$$\approx 4\pi\, W_S(\mathbf{n}_A)e^{-S\xi_A} \frac{\sinh\left[(S+1/2)\,\xi_A\right]}{(2S+1)\sinh\left(\xi_A/2\right)} \tag{349}$$

$$= \frac{2\pi\left[1 - e^{-(2S+1)\xi_A}\right]}{(S+1/2)(1 - e^{-\xi_A})} W_S(\mathbf{n}_A).$$

Finally, the total spin current I_C from the well may also be estimated just as with the classical equation (342) by defining the current density J_C at the vicinity of the saddle point $\mathbf{n}_C$ of the "effective" potential $V_{ef}(u_1^{(C)}, u_2^{(C)}) = -\ln W_S(u_1^{(C)}, u_2^{(C)})$. Thus, we have (cf. Eq. 341)

$$I_C \sim \frac{1}{\beta\hbar S}W_S(\mathbf{n}_C), \tag{350}$$

since the magnetic moment is now given by $\mu = \gamma\hbar S/\mu_0$. Hence, we obtain the TST escape rate as determined from Eqs. (345), (349), and (350), namely,

$$\Gamma \sim \frac{(S+1/2)\left(1 - e^{-\xi_A}\right)}{2\pi\beta\hbar S\left[1 - e^{-(2S+1)\xi_A}\right]} \frac{W_S(\mathbf{n}_C)}{W_S(\mathbf{n}_A)}. \tag{351}$$

To compare this equation with the classical TST equation (343), we rewrite it in the form of the quantum TST equation (155) for particles, namely,

$$\Gamma \sim \frac{\omega_A}{2\pi}\Xi_S e^{-\beta\Delta V_{cl}} = \Xi_S\Gamma_{cl}, \tag{352}$$

where

$$\Xi_S = \frac{\omega_A^S(S+1/2)\left(1 - e^{-\xi_A}\right)}{\omega_A\xi_A S\left[1 - e^{-(2S+1)\xi_A}\right]} \frac{W_S(\mathbf{n}_C)}{W_S(\mathbf{n}_A)}e^{\beta\Delta V_{cl}}, \tag{353}$$

represents the *quantum correction* factor strongly depending on the spin number S and yielding $\Xi_S \to 1$ and $\Gamma \to \Gamma_{cl}$ in the classical limit, $S \to \infty$.

For example, for a uniaxial nanomagnet with the Hamiltonian $\beta\hat{H}_S = -\sigma\hat{S}_Z^2/S^2$, the Weyl symbol $\beta H_S(\vartheta)$ and equilibrium phase space distribution $W_S(\vartheta)$ are given by Eqs. (248) and (299), respectively. Furthermore, $W_S(\mathbf{n}_A) = W_S(\vartheta = 0)$ and $W_S(\mathbf{n}_C) = W_S(\vartheta = \pi/2)$ are given by Eqs. (312) and (313). Thus, noting that in the classical limit

$$\omega_A = \frac{2\sigma\gamma}{\mu_0\mu\beta}, \tag{354}$$

$$\beta\Delta V_{cl} = \sigma \tag{355}$$

while

$$\omega_A^S = \omega_A \left(1 - \frac{1}{2S}\right),\qquad(356)$$

the quantum correction factor Ξ_S is given by

$$\Xi_S = \frac{(S+1/2)\left[1 - e^{-\sigma(2S-1)/S^2}\right]}{\sigma\,2^{2S+1}\left[1 - e^{-\sigma(4S^2-1)/S^2}\right]} \sum_{m=-S}^{S} \frac{(2S)!\,e^{\sigma m^2/S^2}}{(S+m)!(S-m)!}.\qquad(357)$$

In the limit $S \to \infty$, Eq. (352) reduces to the well-known classical TST (Néel) formula for a uniaxial nanomagnet, namely,

$$\Gamma_{cl} \sim \frac{1}{2\pi\tau_0} e^{-\sigma},\qquad(358)$$

where $\tau_0 = 1/\omega_A$ is a normalizing time. The normalized inverse escape rate $(\tau_0\Gamma)^{-1}$ as a function of the inverse temperature parameter $\sigma \sim 1/T$ is shown in Fig. 11 for various values of S. Clearly, the qualitative behavior of the quantum escape rates Γ for finite S strongly deviates from the Arrhenius behavior of the classical escape rates Γ_{cl} at low temperatures. This difference is due to the tunneling effect.
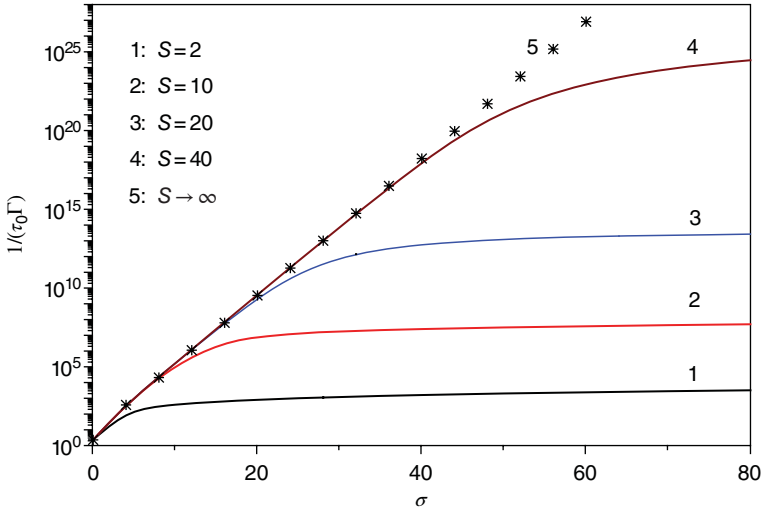
Figure 11. Normalized inverse escape rate $(\tau_0\Gamma)^{-1}$ as a function of the inverse temperature parameter $\sigma \sim 1/T$ for various values of $S = 2, 10, 20, 40$, and $S \to \infty$ (classical limit) (Color on line).

Like the classical case, having evaluated the escape rate Γ for a particular anisotropy, we have the reversal time at finite temperatures. In particular, by *equating the reversal time to the measuring time of a switching time experiment* one may estimate the switching field curves at *finite* temperatures just as with the classical theory [5]. Although 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*. The latter may be defined as wide enough to ensure that thermal noise is sufficiently strong to thermalize the escaping system yet not so wide as to disturb the thermal equilibrium in the well, that is, an equilibrium distribution still prevails everywhere including the saddle point. In classical Kramers escape rate theory [6], this represents the so-called intermediate damping case.

We shall now demonstrate how the phase space representation for a given spin Hamiltonian may be used to calculate switching field curves and/or surfaces as a function of spin number S at zero temperature.

7.   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 [17], 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 consequently occurs at that particular value of the applied field (called the switching field), which destroys the bistable nature of the potential. The parametric plot of the parallel versus the perpendicular component of the switching field then yields the famous astroids. As mentioned in Section I, Thiaville [19] later developed 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. This surface, as it generalizes the critical curves of the 2D problem of Stoner and Wohlfarth [17], is called the *limit of metastability surface*. In the general approach to the calculation of switching curves via the geometrical method of Thiaville [19], these curves or surfaces may be constructed for particles with *arbitrary* anisotropy at zero temperature. By fitting experimental switching field curves and surfaces, one can in particular determine the free energy of a nanomagnet and the corresponding anisotropy constants (see Fig. 12).

In order to generalize Thiaville's geometrical method [19] to include quantum effects in switching field curves and surfaces of a spin system with a model spin Hamiltonian $\hat{H}_S$, we must first determine the *Weyl symbol* $H_S(\vartheta, \varphi)$ corresponding to $\hat{H}_S$, which is defined by the map onto phase space given by Eq. (247). Then one may, in principle, again calculate the switching fields using Thiaville's
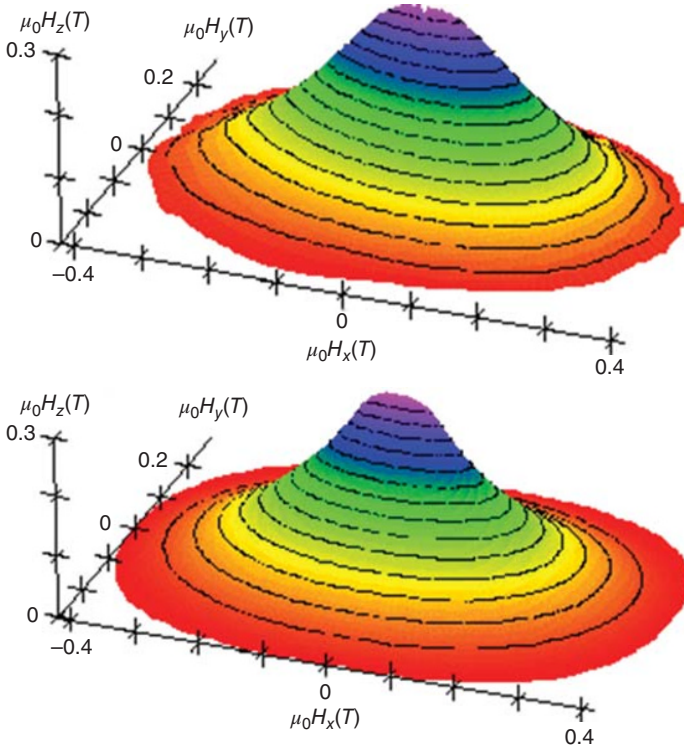
Figure 12. 3D theoretical and experimental (measured at $T = 35$ mK with the microSQUID; upper figure) switching field surfaces of a 3 nm cobalt cluster. These surfaces are symmetrical with respect to the H_x–H_y plane, and only the upper part ($\mu_0 H_z > 0$) is shown. Continuous lines on the surface are contour lines on which $\mu_0 H_z$ is constant. The theoretical switching field surface is calculated via Thiaville's method [19], the free energy $V = -K_1 \cos^2 \vartheta + K_2 \sin^2 \vartheta \sin^2 \varphi - (K_4/4)\left(\sin^2 2\vartheta + \sin^4 \vartheta \cos^2 2\varphi\right)$ with the anisotropy constants $K_1 = 2.2 \cdot 10^5$ J/m^3, $K_2 = 0.9 \cdot 10^5$ J/m^3, $K_4 = 0.1 \cdot 10^5$ J/m^3. Jamet et al. [150]. Reproduced with permission of the American Physical Society. (*See insert for color representation of the figure.*)

method [19]. The starting point of this calculation is the normalized energy of the spin $\bar{V}(\mathbf{u})$ in the presence of a dc magnetic field $\mathbf{H}$ defined as

$$\bar{V}(\mathbf{u}) = G(\mathbf{u}) - 2(\mathbf{u} \cdot \mathbf{h}), \tag{359}$$

where $\mathbf{u} = (\sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi, \cos \vartheta)$ is the unit vector specifying the representative point (ϑ, φ) in phase space (see Fig. D.1), $\mathbf{h}$ is the normalized external field $\mathbf{H}/H_A$ (H_A is a normalizing constant which has the meaning of the effective anisotropy field), and $G(\mathbf{u}) = H_S(\vartheta, \varphi)/H_A$ is the normalized Hamiltonian in the absence of the external field $\mathbf{H}$. The switching field is characterized by the

requirement that both the first and second derivatives of the normalized energy $\bar{V}$ with respect to ϑ and ϕ must vanish, indicating that one metastable minimum and one saddle point in the potential $\bar{V}$ *merge*, giving rise to a point of inflexion. These conditions correspond to a *switching field surface* in 3D space. At any point of that surface, $\bar{V}$ must satisfy the stationary conditions

$$\frac{\partial \bar{V}}{\partial \vartheta} = \frac{\partial G}{\partial \vartheta} - 2 (\mathbf{h} \cdot \mathbf{e}_\vartheta) = 0,$$

$$\frac{\partial \bar{V}}{\partial \varphi} = \frac{\partial G}{\partial \varphi} - 2 (\mathbf{h} \cdot \mathbf{e}_\varphi) \sin \vartheta = 0,$$

so that the field vector $\mathbf{h}$ can be described by a parameter λ, namely,

$$\mathbf{h} = \lambda \mathbf{e}_r + \frac{1}{2} \frac{\partial G}{\partial \vartheta} \mathbf{e}_\vartheta + \frac{1}{2 \sin \vartheta} \frac{\partial G}{\partial \varphi} \mathbf{e}_\varphi, \tag{360}$$

where the unit vectors $\mathbf{e}_r, \mathbf{e}_\vartheta$, and $\mathbf{e}_\varphi$ forming the orthonormal direct basis are defined as follows:

$$\mathbf{e}_r = \begin{pmatrix} \sin \vartheta \cos \varphi \\ \sin \vartheta \sin \varphi \\ \cos \vartheta \end{pmatrix}, \mathbf{e}_\vartheta = \begin{pmatrix} \cos \vartheta \cos \varphi \\ \cos \vartheta \sin \varphi \\ -\sin \vartheta \end{pmatrix}, \mathbf{e}_\varphi = \begin{pmatrix} -\sin \varphi \\ \cos \varphi \\ 0 \end{pmatrix}. \tag{361}$$

The switching conditions are now determined by the following equation

$$\frac{\partial^2 \bar{V}}{\partial \vartheta^2} \frac{\partial^2 \bar{V}}{\partial \varphi^2} - \left[\frac{\partial^2 \bar{V}}{\partial \vartheta \, \partial \varphi} \right]^2 = 0. \tag{362}$$

Because the second derivatives of $\bar{V}$ are given by

$$\frac{\partial^2 \bar{V}}{\partial \vartheta^2} = \frac{\partial^2 G}{\partial \vartheta^2} + 2\lambda,$$

$$\frac{\partial^2 \bar{V}}{\partial \varphi^2} = \frac{\partial^2 G}{\partial \varphi^2} + \left(\cot \vartheta \frac{\partial G}{\partial \vartheta} + 2\lambda \right) \sin^2 \vartheta,$$

$$\frac{\partial^2 \bar{V}}{\partial \vartheta \, \partial \varphi} = \frac{\partial^2 \bar{V}}{\partial \varphi \, \partial \vartheta} = \sin \vartheta \frac{\partial}{\partial \vartheta} \left(\frac{1}{\sin \vartheta} \frac{\partial G}{\partial \varphi} \right),$$

equation (362) reduces to a quadratic equation in λ, namely,

$$4\lambda^2 + 2\lambda \left[\frac{1}{\sin^2 \vartheta} \frac{\partial^2 G}{\partial \varphi^2} + \cot \vartheta \frac{\partial G}{\partial \vartheta} + \frac{\partial^2 G}{\partial \vartheta^2} \right]$$

$$+ \left[\frac{1}{\sin^2 \vartheta} \frac{\partial^2 G}{\partial \varphi^2} + \cot \vartheta \frac{\partial G}{\partial \vartheta} \right] \frac{\partial^2 G}{\partial \vartheta^2} - \left[\frac{\partial}{\partial \vartheta} \left(\frac{1}{\sin \vartheta} \frac{\partial G}{\partial \varphi} \right) \right]^2 = 0,$$

which has two roots $\lambda^+(\vartheta,\varphi)$ and $\lambda^-(\vartheta,\varphi)$ given by

$$\lambda^{\pm} = -\frac{1}{4}\left(\frac{1}{\sin^2\vartheta}\frac{\partial^2 G}{\partial\varphi^2} + \cot\vartheta\frac{\partial G}{\partial\vartheta} + \frac{\partial^2 G}{\partial\vartheta^2}\right)$$
$$\pm\frac{1}{4}\sqrt{\left[\frac{1}{\sin^2\vartheta}\frac{\partial^2 G}{\partial\varphi^2} + \cot\vartheta\frac{\partial G}{\partial\vartheta} - \frac{\partial^2 G}{\partial\vartheta^2}\right]^2 + 4\left[\frac{\partial}{\partial\vartheta}\left(\frac{1}{\sin\vartheta}\frac{\partial G}{\partial\varphi}\right)\right]^2}.$$
$$(363)$$

Now the semi-axis, Eq. (360), described by $\lambda > \lambda^+$ is the locus of the fields for which the magnetization is stable. Moreover, when $\lambda = \lambda^+$ the metastable minimum in the potential $\bar{V}$ disappears so that the spin vector $\mathbf{S}$ can then escape from the potential well. Thus, the switching field surface may be obtained from the vector $\mathbf{h}_S$ defined as follows [19]:

$$\mathbf{h}_S = \lambda^+\mathbf{e}_r + \frac{1}{2}\frac{\partial G}{\partial\vartheta}\mathbf{e}_\vartheta + \frac{1}{2\sin\vartheta}\frac{\partial G}{\partial\varphi}\mathbf{e}_\varphi. \qquad (364)$$

Numerous examples of the calculation of switching field surfaces in 3D space and the 2D critical curves for various *classical* free energy densities have been given, for example, in Refs. 5, 6, 18 and 19. Here, following Ref. 66, we calculate 2D critical curves for the uniaxial, biaxial, cubic, and mixed Hamiltonians defined by Eqs. (243)–(246). The Weyl symbols $H_S^{un}(\vartheta,\varphi)$, $H_S^{bi}(\vartheta,\varphi)$, $H_S^{cub}(\vartheta,\varphi)$, and $H_S^{mix}(\vartheta,\varphi)$ of these four model Hamiltonians are given by Eqs. (248)–(251), which bear an obvious resemblance to the corresponding classical free energy densities (see Sections II.D.1–II.D.5). If we further suppose that a uniform external magnetic field $\mathbf{H}$ is applied in the $x-z$ plane, the Zeeman term operator $-(\xi/S)\left(\sin\psi\hat{S}_X - \cos\psi\hat{S}_Z\right)$ just transforms to the simple phase space expression $-\xi\cos(\vartheta-\psi)$, 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 the Weyl symbols given by Eqs. (248)–(250) and Eq. (364), yielding

$$\mathbf{h}_{un} = Q_{un}\mathbf{h}_{un}^{cl}, \qquad (365)$$

$$\mathbf{h}_{bi} = Q_{bi}\mathbf{h}_{bi}^{cl}, \qquad (366)$$

$$\mathbf{h}_{cub} = Q_{cub}\mathbf{h}_{cub}^{cl}, \qquad (367)$$

where

$$Q_{un} = Q_{bi} = 1 - \frac{1}{2S}, \qquad (368)$$

$$Q_{cub} = \frac{(S-1/2)(S-1)(S-3/2)}{S^3} \qquad (369)$$

are the quantum correction factors to the corresponding classical switching fields $\mathbf{h}_{un}^{cl}$, $\mathbf{h}_{bi}^{cl}$, and $\mathbf{h}_{cub}^{cl}$ in the $x - z$ plane given by the known equations [5, 6]

$$\mathbf{h}_{un}^{cl} = \left(\sin^3 \vartheta, - \cos^3 \vartheta \right),$$

$$\mathbf{h}_{cub}^{cl} = \left(\sin^3 \vartheta \, (3 \cos 2\vartheta + 2), \cos^3 \vartheta \, (3 \cos 2\vartheta - 2) \right),$$

$$\mathbf{h}_{bi}^{cl} = \left(\sin \vartheta \, [2\Delta + f(\vartheta)] , \cos \vartheta \, [2 - f(\vartheta)] \right),$$

where $\Delta = \delta/\sigma$ and

$$f(\vartheta) = (1 + \Delta) \sin^2 \vartheta + \left| 2\Delta - (1 + \Delta) \sin^2 \vartheta \right|.$$

For *mixed* anisotropy, however, the corresponding, equation for the switching field $\mathbf{h}_{mix}$ is much more complicated, and therefore must be calculated numerically. The parametric plots of the parallel h_Z versus the perpendicular h_X component of the switching field for the given spin systems are shown in Fig. 13. In general, the figure indicates that the switching field amplitudes *increase* markedly with *increasing S* all the while tending to their classical limiting values as $S \to \infty$ corresponding to diminishing tunneling effects as that mechanism is gradually shut off.

We emphasize that these calculations because they are entirely based on the phase space representation of the Hamiltonian operator *ignore thermal effects* as in the original Stoner–Wohlfarth and Thiaville calculations. In order to account for these, it is necessary to estimate the temperature dependence of the spin reversal time, which may be accomplished, for example, using the quantum TST, which we have described in Section II.D.6. This will again only involve the quantum equilibrium phase space distributions, which we have calculated in the preceding sections.

8. *Discussion*

We have just shown how the phase space method may be used to construct equilibrium distribution functions in the configuration space of polar angles (ϑ, φ) for spin systems in the equilibrium state described by the equilibrium distribution $\hat{\rho}_S = e^{-\beta \hat{H}_S}/Z_S$. The Wigner function may be represented in all cases as a finite series of spherical harmonics like the corresponding classical orientational distribution and transparently reduces to the usual Fourier series equation (184) in the classical limit, $S \to \infty$. Moreover, relevant quantum mechanical averages (i.e., the magnetization) may be calculated in a manner analogous to the corresponding classical averages using the Weyl symbol of the appropriate quantum operator (see Eq. 238). The resulting Wigner functions can now be used to determine the spin dependence of the switching fields and hysteresis curves and may also be applied to other problems requiring only a knowledge of equilibrium distributions. This conclusion is significant particularly from an experimental point of view as the
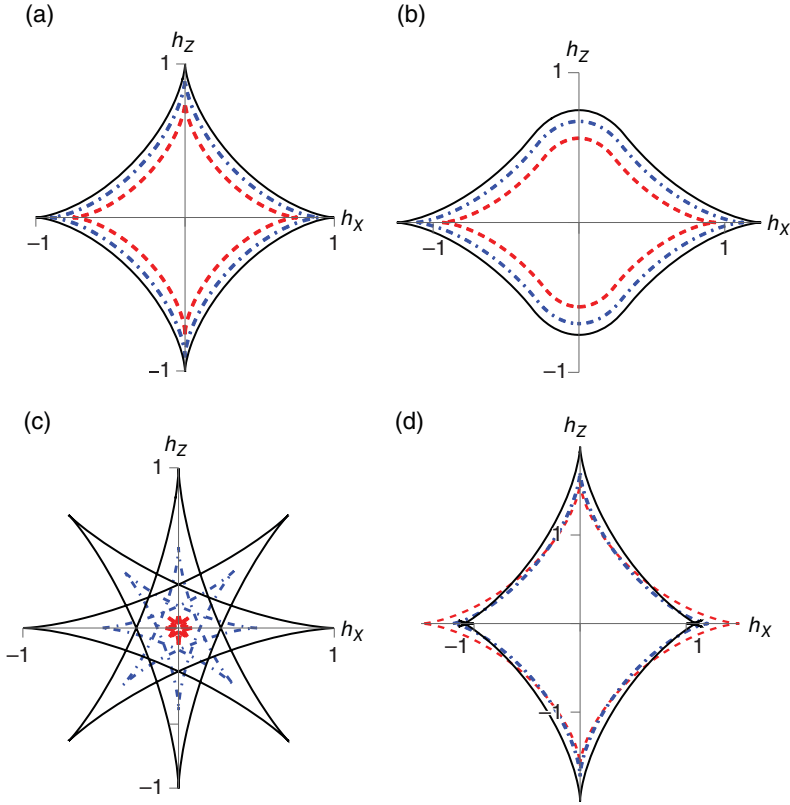
Figure 13. Spin dependence of switching field curves for uniaxial (a), biaxial at $\sigma/\delta = 0.25$ (b), cubic (c), and mixed at $\sigma_1/\sigma_2 = 0.5$ and $\chi = 0$ (d) anisotropies for $S = 2$ (red dashed lines), 5 (blue dash-dotted lines), and $S \rightarrow \infty$ (black solid lines; classical limit) (Color on line).

transition between magnetic molecular cluster and single-domain ferromagnetic nanoparticle behavior is essentially demarcated via the hysteresis loops and the corresponding switching field curves [9]. Furthermore, such Wigner functions are important, in the interpretation of quantum tunneling phenomena in ferromagnetic nanoparticles and molecular magnets (see, e.g., Ref. [9]) and also in the investigation of the crossover region between reversal of the magnetization of these particles by thermal agitation and reversal by macroscopic quantum tunneling. For instance, by analogy with Néel's classical calculation [16], the simplest description of quantum effects in the magnetization reversal time of a nanoparticle is provided by the inverse escape rate from the wells of the magnetocrystalline and external field potential as rendered by quantum TST. Thus, the TST rate provides an important benchmark for both analytical calculations of the escape rate, which account for dissipation using quantum rate theory and for the numerical

results obtained from the appropriate quantum master equation as well as allowing one to incorporate thermal effects in the switching fields. Now TST ignores the disturbance to the equilibrium distribution in the wells created by the loss of the magnetization due to escape over the barrier, and so involves the equilibrium distribution only as that is assumed to prevail everywhere. Nevertheless, via TST as corrected for quantum effects (e.g., Eq. 351), which stems from the phase space representation, it is possible to predict the temperature dependence of the switching fields and corresponding hysteresis loops within the limitations imposed by that theory. Therefore, the results should be relevant to experiments seeking evidence for macroscopic quantum tunneling where the temperature dependence of the loops is crucial as they are used [9] to differentiate tunneling from thermal agitation behavior. The equilibrium quantum distribution is also essential in the inclusion of *nonequilibrium* effects in the quantum escape rate. For example, a master equation describing the time evolution of the quasiprobability density in the representation space is required in generalizing the classical escape rate calculations pioneered by Kramers [28] for point particles and by Brown [23, 24] for single-domain ferromagnetic particles using the Fokker–Planck equation.

In Section III, we shall show that a knowledge of the equilibrium phase space distribution is also important in two other fundamental aspects of nonequilibrium phenomena involving master equations in the phase space representation. The first is in formulating the initial conditions for their solution as the appropriate quantum equilibrium distribution, which must now play the role of the Boltzmann distribution in the corresponding classical problem. Second, the quantum equilibrium 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. This fact, 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 drift and diffusion coefficients, will also allow one to calculate these coefficients in the quantum case. This is illustrated for the particular case of a spin in a uniform field in Section III.B.3 below (see also [62]), indicating clearly how all the solution methods developed for the classical Fokker–Planck equation apply to the quantum case just as the corresponding solutions for particles [48] (see Section II.B.3). We remark, however, that the calculation of the drift and diffusion coefficients for axially symmetric potentials is much simpler than that for nonaxial symmetry since only the single polar angle ϑ is involved rather than the two angles ϑ and φ. The restriction to axial symmetry also gives rise to further mathematical simplifications, since the quantum master equation now has essentially the same form as the classical Fokker–Planck equation in the single coordinate ϑ, implying that formulas for the mean first passage time, integral relaxation time, and so on, may be directly carried over to the quantum case. 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 particles in a classical phase space.

III.   MASTER EQUATION IN PHASE SPACE FOR AXIALLY SYMMETRIC SYSTEMS

A.   Master Equation for a Uniaxial Nanomagnet Subjected to a dc Magnetic Field

We shall now apply, as an illustrative example, the phase space method to a uniaxial nanomagnet of arbitrary spin number S in an external *constant* magnetic field **H** applied along the Z-axis, that is, the easy axis, where the Hamiltonian operator $\hat{H}_S$ has the axially symmetric form given by Eq. (267), namely,

$$\beta\hat{H}_S = -\frac{\sigma}{S^2}\hat{S}_Z^2 - \frac{\xi}{S}\hat{S}_Z. \tag{370}$$

This Hamiltonian comprises a uniaxial anisotropy term $-\sigma\hat{S}_Z^2/S^2$ plus the Zeeman coupling to the external field $-\xi\hat{S}_Z/S$, constituting a generic model for relaxation phenomena in uniaxial spin systems such as molecular magnets, nanoclusters, and so on (see, e.g., Refs. 3, 80, and references cited therein). In the standard basis of spin functions $|S, m\rangle$ (see Appendix A), which describe the states with definite spin S and spin projection m onto the Z-axis, that is, $\hat{S}_Z|S, m\rangle = m|S, m\rangle$, the Hamiltonian $\hat{H}_S$, Eq. (370), has an energy spectrum with a double-well structure and two minima at $m = \pm S$ separated by a potential barrier. Note that in strong bias fields, $\xi_0 > \sigma(2S - 1)/S$, the barrier disappears. Now generally speaking, spin reversal can take place either by thermal activation or by tunneling or a combination of both. The tunneling may occur from one side of the barrier to the other between resonant, equal-energy states coupled by transverse fields or high-order anisotropy terms [80–82]. Now Garanin [80] and García-Palacios and Zueco [81, 82] by using the spin density matrix in the second order of perturbation theory in the spin–bath coupling have studied the longitudinal relaxation of quantum uniaxial nanomagnets with the Hamiltonian equation (370). In other words, they gave a concise treatment of the spin dynamics by directly proceeding from the quantum Hubbard operator representation of the evolution equation for the spin density matrix. This axially symmetric problem has also been treated via the phase space method in Ref. 64 and may be summarized as follows.

1.   Explicit Form of the Master Equation

Using the collision operator in the symmetrized Hubbard form (60) as written for the particular Hamiltonian given by Eq. (370), we have from the general reduced density matrix evolution given by Eq. (40) the evolution equation for the reduced density matrix of a uniaxial nanomagnet [64]

$$\frac{\partial\hat{\rho}_S}{\partial t} - \frac{i}{\hbar\beta}\left\{\frac{\sigma}{S^2}\left[\hat{S}_0^2, \hat{\rho}_S\right] + \frac{\xi}{S}\left[\hat{S}_0, \hat{\rho}_S\right]\right\} = \mathrm{St}\left(\hat{\rho}_S\right). \tag{371}$$

Thus, written explicitly the collision kernel operator $\text{St}\left(\hat{\rho}_S\right)$, characterizing the spin–bath interaction, is given by

$$
\begin{aligned}
\text{St}\left(\hat{\rho}_S\right) = D_0 &\left(\left[\hat{S}_0, \hat{\rho}_S\hat{S}_0\right] + \left[\hat{S}_0\hat{\rho}_S, \hat{S}_0\right]\right) \\
- D_{-1} &\left(\left[\hat{S}_{-1}, \hat{\rho}_S e^{-\frac{\sigma}{2s^2}\hat{S}_0^2 - \frac{\xi}{2s}\hat{S}_0}\hat{S}_1 e^{\frac{\sigma}{2s^2}\hat{S}_0^2 + \frac{\xi}{2s}\hat{S}_0}\right]\right. \\
&\left. + \left[e^{\frac{\sigma}{2s^2}\hat{S}_0^2 + \frac{\xi}{2s}\hat{S}_0}\hat{S}_1 e^{-\frac{\sigma}{2s^2}\hat{S}_0^2 - \frac{\xi}{2s}\hat{S}_0}\hat{\rho}_S, \hat{S}_{-1}\right]\right) \\
- D_1 &\left(\left[\hat{S}_1, \hat{\rho}_S e^{-\frac{\sigma}{2s^2}\hat{S}_0^2 - \frac{\xi}{2s}\hat{S}_0}\hat{S}_{-1} e^{\frac{\sigma}{2s^2}\hat{S}_0^2 + \frac{\xi}{2s}\hat{S}_0}\right]\right. \\
&\left. + \left[e^{\frac{\sigma}{2s^2}\hat{S}_0^2 + \frac{\xi}{2s}\hat{S}_0}\hat{S}_{-1} e^{-\frac{\sigma}{2s^2}\hat{S}_0^2 - \frac{\xi}{2s}\hat{S}_0}\hat{\rho}_S, \hat{S}_1\right]\right).
\end{aligned}
\tag{372}
$$

Because of the operator relations

$$
e^{\frac{\sigma}{2s^2}\hat{S}_0^2 + \frac{\xi}{2s}\hat{S}_0}\hat{S}_{\pm 1} e^{-\frac{\sigma}{2s^2}\hat{S}_0^2 - \frac{\xi}{2s}\hat{S}_0} = e^{-\frac{\sigma}{2s^2} \pm \frac{\xi}{s^2}} e^{\pm \frac{\sigma}{s^2}\hat{S}_0}\hat{S}_{\pm 1},
\tag{373}
$$

$$
\hat{S}_{\pm 1} e^{\mp \frac{\sigma}{s^2}\hat{S}_0} = e^{\frac{\sigma}{s^2}} e^{\mp \frac{\sigma}{s^2}\hat{S}_0}\hat{S}_{\pm 1},
\tag{374}
$$

we have from Eq. (372) a simplified form of $\text{St}\left(\hat{\rho}_S\right)$, namely,

$$
\begin{aligned}
\text{St}\left(\hat{\rho}_S\right) = D_{\parallel} &\left(\left[\hat{S}_0, \hat{\rho}_S\hat{S}_0\right] + \left[\hat{S}_0\hat{\rho}_S, \hat{S}_0\right]\right) \\
- 2D_{\perp} &\left\{e^{\frac{\sigma}{2s^2} + \frac{\xi}{2s}}\left(\left[\hat{S}_1 e^{\frac{\sigma}{s^2}\hat{S}_0}\hat{\rho}_S, \hat{S}_{-1}\right] + \left[\hat{S}_1, \hat{\rho}_S e^{\frac{\sigma}{s^2}\hat{S}_0}\hat{S}_{-1}\right]\right)\right. \\
&\left. + e^{\frac{\sigma}{2s^2} - \frac{\xi}{2s}}\left(\left[\hat{S}_{-1}, \hat{\rho}_S e^{-\frac{\sigma}{s^2}\hat{S}_0}\hat{S}_1\right] + \left[\hat{S}_{-1} e^{-\frac{\sigma}{s^2}\hat{S}_0}\hat{\rho}_S, \hat{S}_1\right]\right)\right\},
\end{aligned}
\tag{375}
$$

where we have introduced the notation $D_{\perp} = D_{\pm 1}/2$ and $D_{\parallel} = D_0$ for the diffusion coefficients. Now Eq. (371) describes the evolution of the spin system in contact with the thermal bath at temperature T. Thus, one important property of the collision kernel operator, namely, Eq. (56), is satisfied by the $\text{St}\left(\hat{\rho}_S\right)$ given by Eq. (375), namely, that the equilibrium spin density matrix $\hat{\rho}_{eq} = e^{-\beta\hat{H}_S}/\text{Tr}\{e^{-\beta\hat{H}_S}\}$ renders the collision kernel equal to zero, that is, $\text{St}\left(\hat{\rho}_{eq}\right) = 0$. Conditions for the validity of the reduced density matrix evolution given by Eq. (371) have been discussed in detail in Section II.A.2.

We now proceed to the phase space representation of Eq. (371), which is accomplished by writing that equation as the inverse map of a Weyl symbol (see also [76]). By substituting the density matrix $\hat{\rho}_S$ so rendered into the reduced

density matrix evolution given by Eq. (371), we have the inverse map (dropping the parameter s)

$$\int \left(\hat{w} \frac{\partial}{\partial t} W_S - W_S \left\{ \frac{i}{\hbar\beta} \left(\frac{\sigma}{S^2} \left[\hat{S}_0^2, \hat{w} \right] + \frac{\xi}{S} \left[\hat{S}_0, \hat{w} \right] \right) + \mathrm{St}\left(\hat{w} \right) \right\} \right) d\Omega = 0, \quad (376)$$

where $d\Omega = \sin\vartheta\, d\vartheta\, d\varphi$. Now as it stands the formal inverse map given by Eq. (376) does not have the standard form, Eq. (235), of the usual inverse Wigner–Stratonovich map with kernel $\hat{w}(\vartheta, \varphi)$. Therefore, in order to facilitate this objective, we must first transform the various commutators occurring in the integrand of Eq. (376) into the phase space representation. These will then appear as configuration space differential operators acting on the Wigner–Stratonovich kernel $\hat{w}(\vartheta, \varphi)$ [cf. Eq. (C11) *et seq.*]. This procedure, which involves lengthy operator manipulations for each commutator occurring in Eq. (376) as fully described in Appendix C, will then allow one to express the earlier integrand in the standard phase space form demanded by Eq. (235). In this way, we will ultimately have the master equation for the phase space distribution $W_S(\vartheta, \varphi, t)$, namely,

$$\frac{\partial}{\partial t} W_S - \frac{\sigma}{\hbar\beta S^2} \left(2S\cos\vartheta - \sin\vartheta \frac{\partial}{\partial\vartheta} + \frac{S\xi}{\sigma} \right) \frac{\partial}{\partial\varphi} W_S$$

$$= D_\parallel \frac{\partial^2}{\partial^2\varphi} W_S + D_\perp \frac{\cot\vartheta}{\sin\vartheta} \left[\cos\vartheta \frac{\partial^2}{\partial^2\varphi} R_+^{\prime(S)} W_S + \frac{\partial^2}{\partial^2\varphi} R_-^{\prime(S)} W_S \right] \qquad (377)$$

$$+ \frac{D_\perp}{\sin\vartheta} \left[\frac{\partial}{\partial\vartheta} \sin\vartheta \left(\frac{\partial}{\partial\vartheta} R_+^{\prime(S)} W_S + \cos\vartheta \frac{\partial}{\partial\vartheta} R_-^{\prime(S)} W_S + 2S\sin\vartheta R_-^{\prime(S)} W_S \right) \right]$$

$$+ D_\perp \left[\left(\sin\vartheta \frac{\partial}{\partial\vartheta} - 2S\cos\vartheta \right) \frac{\partial}{\partial\varphi} R_+^{\prime\prime(S)} W_S - \frac{\partial}{\partial\varphi} R_-^{\prime\prime(S)} W_S \right],$$

where the phase space differential operators $R_\pm^{(S)} = R_\pm^{\prime(S)} + iR_\pm^{\prime\prime(S)}$ are defined in Appendix C. The left-hand side of Eq. (377) is just the quantum analog of the classical Liouville equation for a uniaxial nanomagnet, while the collision operator given by the right-hand side of Eq. (377) is the quantum analog of the Fokker–Planck operator for classical spins given by Eq. (4). In summary, the master equation (377) follows from the equation of motion of the reduced density matrix given by Eq. (371) written as the standard form, Eq. (235), of the inverse Wigner–Stratonovich map of a Weyl symbol (see Appendix C). Everywhere, the interactions between the spin and the heat bath are taken small enough to use the weak coupling limit and the correlation time characterizing the bath is taken short enough to regard the stochastic process originating in the bath as Markovian.

In purely longitudinal relaxation, when the azimuthal angle dependence of W_S may be ignored, the Liouville term vanishes in Eq. (377), and the corresponding phase space evolution equation for $W_S(z = \cos\vartheta, t)$ then simplifies to the axially symmetric form

$$\frac{\partial W_S}{\partial t} = \frac{\partial}{\partial z} \left(D^{(2)} W_S + D^{(1)} W_S \right), \qquad (378)$$

where

$$D^{(1)} = 2D_\perp S(1 - z^2)R_-'^{(S)} \tag{379}$$

and

$$D^{(2)} = D_\perp (1 - z^2) \left(\frac{\partial}{\partial z} R_+'^{(S)} + z \frac{\partial}{\partial z} R_-'^{(S)} \right). \tag{380}$$

The phase space master equation (378) is then *formally* similar to the single spatial variable Fokker–Planck equation for the orientation distribution function $W(z, t)$

$$\frac{\partial W}{\partial t} = D_\perp \frac{\partial}{\partial z} \left[(1 - z^2) \left(\frac{\partial W}{\partial z} + \beta W \frac{\partial V}{\partial z} \right) \right], \tag{381}$$

describing rotational diffusion of a classical spin in an axially symmetric potential [5]

$$\beta V = -\sigma \cos^2 \vartheta - \xi \cos \vartheta \tag{382}$$

and in the classical limit, Eq. (378) reduces after lengthy manipulations to it as we shall demonstrate in Appendix C.

One of the major computational difficulties associated with the phase space master equation (377) now appears. By inspection of that equation even for axial symmetry high order spin number-dependent differential operators occur apart from two notable exceptions. The first of these comprises noninteracting spins in a uniform field where all the higher order derivatives in the operators $R_\pm^{(S)}$ vanish. Thus, they become closed transcendental functions (see e.g., Eq. (411) et. seq.). In this case, we will have differential recurrence relations (see Eq. (418) et. seq.), which are essentially similar to those occurring in the corresponding classical problem (see e.g., Eq. (434) et. seq.). The other exception is that in the absence of any potential whatsoever, that is, when $\sigma = 0$ and $\xi = 0$, the differential operators merely reduce to $R_+^{(S)} = 1$ and $R_-^{(S)} = 0$, respectively (see Appendix C), so that Eq. (377) becomes (setting $D_\parallel = D_\perp$)

$$\frac{\partial W_S}{\partial t} = D_\perp \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial W_S}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 W_S}{\partial \varphi^2} \right]. \tag{383}$$

Equation (383) corresponds to the classical Fokker–Planck equation [5] in the single coordinate ϑ for the orientational distribution function of free magnetic dipole moments on the unit sphere. Hence, like the free quantum translational Brownian motion (see Section II.B.3), the phase space distribution W_S of free quantum spins obeys the classical Fokker–Planck equation (383) for the rotational diffusion of free classical spins [5].

Thus, it would appear that the phase space master equation (377) is in general of limited practical use. However, this does not preclude one from deriving

differential recurrence relations for observables via the density matrix evolution equation by using the one-to-one correspondence between the averages of the polarization operators in Hilbert space and the averages of the spherical harmonics (see Section II.C) as we now describe. This will automatically yield the recurrence relations, Eq. (389), for the averages of the polarization operators that may be mapped onto averages of the spherical harmonics via Eq. (392). This procedure is of course just a special case of the formal one outlined in Section II.C.3 [Eq. (252) *et seq.*]

2. *Differential Recurrence Relations for the Statistical Moments*

Recalling the previous paragraph of the previous section, the formal solutions of the axially symmetric density matrix evolution given by Eq. (371) corresponding to the Hamiltonian equation (370) and the corresponding phase space equation (377) for *arbitrary S* may be written as

$$\hat{\rho}_S(t) = \hat{\rho}_{eq} + \sum_{L=0}^{2S} c_L(t)\hat{T}_{L0}^{(S)} \tag{384}$$

and

$$W_S(\vartheta, \varphi, t) = W_S^{eq}(\vartheta) + \sum_{L=0}^{2S} b_L(t)Y_{L0}(\vartheta, \varphi), \tag{385}$$

respectively. The equilibrium phase space distribution $W_S^{eq}(\vartheta)$ is the stationary solution of both of the phase space equation (377 and 378). We emphasize that $W_S^{eq}(\vartheta)$ corresponds to the equilibrium spin density matrix $\hat{\rho}_{eq}$ and is defined by Eq. (229), that is

$$W_S^{eq}(\vartheta) = \text{Tr}\left\{\hat{\rho}_{eq}\hat{w}(\vartheta)\right\}. \tag{386}$$

The distribution $W_S^{eq}(\vartheta)$ defined by the map, Eq. (386), has already been calculated in Section II.D.2 and is given by the finite series of Legendre polynomials given by Eq. (299), while the collision kernel of Eq. (377) satisfies $\text{St}(W_S^{eq}) = 0$, that is, the distribution W_S^{eq} defined by Eq. (299) is indeed the stationary solution of the phase space master equation (377) and (378). The coefficients $c_L(t)$ and $b_L(t)$ (corresponding to the statistical moments) are, in turn, the averages of the polarization operators $\hat{T}_{L0}^{(S)}$ and the spherical harmonics Y_{L0}, respectively, namely,

$$c_L(t) = \left\langle\hat{T}_{L0}^{(S)}\right\rangle(t) - \left\langle\hat{T}_{L0}^{(S)}\right\rangle_{eq}, \tag{387}$$

$$b_L(t) = \langle Y_{L0}\rangle(t) - \langle Y_{L0}\rangle_{eq}. \tag{388}$$

By substituting the operator expansion equation (384) and the spherical harmonic expansion equation (385) into the density matrix evolution equation (371) and the phase space equation (377), respectively, we have in each case a *finite* hierarchy of differential recurrence equations for the statistical moments (in contrast to the classical case, where the corresponding hierarchy is *infinite*).

Since either of the equations (384 and 385) will yield similar hierarchies for the statistical moments (see Section II.C.3), we shall describe the derivation of their recurrence relations using the density matrix. This is accomplished by first substituting the operator expansion equation (384) into the explicit evolution equation (371). Next, we use Eq. (C19) for the expansion of the matrix exponents $e^{\frac{\sigma}{2S^2} \pm \frac{\xi}{2S}} e^{\pm \frac{\sigma}{S^2} \hat{S}_0}$ in terms of the polarization operators $\hat{T}_{l0}^{(S)}$ and the product formula given by Eq. (A.28) for the operators $\hat{T}_{LM}^{(S)}$, which allows products of these to be expressed as a sum. In this way, we ultimately have a hierarchy of multi-term differential recurrence equations for the relaxation functions $c_L(t)$ in Eq. (384), namely,

$$\tau_N \frac{d}{dt} c_L(t) = \sum_{L'=0}^{2S} g_{L,L'}^{(S)} c_{L'}(t). \tag{389}$$

Here, $\tau_N = (2D_\perp)^{-1}$ is the characteristic (free diffusion) time, and we have for the expansion coefficients that are defined in the usual way by the average

$$
\begin{aligned}
g_{L,L'}^{(S)} = -\frac{1}{2} e^{\frac{\sigma}{2S^2}} L(L+1) \mathrm{Tr} \Bigg\{ \hat{T}_{L'0}^{(S)} \Bigg[&\cosh\left(\frac{\sigma}{S^2} \hat{S}_0 + \frac{\xi}{2S} \right) \hat{T}_{L0}^{(S)} + \sinh\left(\frac{\sigma}{S^2} \hat{S}_0 + \frac{\xi}{2S} \right) \\
\times \Bigg(&\frac{\sqrt{(2S-L)(2S+L+2)}}{\sqrt{(2L+3)(2L+1)}} \hat{T}_{L+10}^{(S)} \\
&- \frac{\sqrt{(2S-L+1)(2S+L+1)}}{\sqrt{(2L-1)(2L+1)}} \hat{T}_{L-10}^{(S)} \Bigg) \Bigg] \Bigg\},
\end{aligned}
\tag{390}
$$

where $\cosh(\hat{A})$ and $\sinh(\hat{A})$ appearing in Eq. (390) are matrix functions. Likewise, in the phase space representation, we formally have the relevant system of differential recurrence equations for the relaxation functions $b_L(t)$ from the general recurrence relation given by Eq. (253), the matrix elements of Eq. (255), and the particular equation (389), namely,

$$\tau_N \frac{d}{dt} b_L(t) = \sum_{L'} p_{L',L}^{(S)} b_{L'}(t), \tag{391}$$

where

$$p_{L',L}^{(S)} = \sqrt{\frac{(2S-L')!(2S+L'+1)!}{(2S-L)!(2S+L+1)!}} \, g_{L',L}^{(S)}. \tag{392}$$

Alternatively, using the phase space method the recurrence relation given by Eqs. (391) could be derived by directly substituting the spherical harmonic expansion equation (385) into the phase space evolution equation (377) and then using the recurrence relations of the spherical harmonics, namely, Eqs. (B15)–(B17). However, in general, very detailed manipulations would be involved for the reasons we have outlined. It should be mentioned that the equilibrium averages $\left\langle \hat{T}_{L0}^{(S)} \right\rangle_{eq}$ and $\langle Y_{L0} \rangle_{eq}$ satisfy similar, however, time-independent recurrence relations, namely,

$$\sum_{L'=0}^{2S} g_{L,L'}^{(S)} \left\langle \hat{T}_{L'0}^{(S)} \right\rangle_{eq} = 0 \tag{393}$$

and

$$\sum_{L'} p_{L',L}^{(S)} \langle Y_{L'0} \rangle_{eq} = 0. \tag{394}$$

The resulting system of Eq. (390) and/or (391), which we have just derived, can be solved by either direct matrix diagonalization, which involves calculating the eigenvalues and eigenvectors of the system matrix (see Section II.A.4) or by the computationally efficient (matrix) continued fraction method [5, 71]. As shown in the following text, the solutions can be obtained both for the transient and ac stationary (linear and nonlinear) responses of spins in magnetic fields.

In the limiting case of zero anisotropy $\sigma = 0$, Eq. (390) can be further simplified by once again using the general formula for the product of polarization operators in terms of the Clebsch–Gordan series, that is, Eq. (A.28), thereby yielding

$$g_{L,L'}^{(S)} = -\frac{1}{2} L(L+1) \left[\delta_{L'L} \cosh \frac{\xi}{2S} + \sinh \frac{\xi}{2S} \left(\delta_{L'L+1} \sqrt{\frac{(2S-L)(2S+L+2)}{(2L+3)(2L+1)}} \right. \right.$$
$$\left. \left. -\delta_{L'L-1} \sqrt{\frac{(2S-L+1)(2S+L+1)}{(2L-1)(2L+1)}} \right) \right]$$

so that with the replacement

$$c_L(t) \rightarrow (-1)^L \frac{\sqrt{(2S-L)!(2S+L+1)!(2L+1)}}{4\pi (2S)!} f_L(t), \tag{395}$$

we have from Eq. (389) the simple three-term differential recurrence relation

$$\tau_N \frac{d}{dt} f_L(t) = q_L f_L(t) + q_L^- f_{L-1}(t) + q_L^+ f_{L+1}(t), \tag{396}$$

with

$$q_L = -\frac{L(L+1)}{2}\cosh\frac{\xi}{2S}, \tag{397}$$

$$q_L^{\pm} = \pm\frac{L(L+1)(2S\pm L+3/2\pm 1/2)}{2(2L+1)}\sinh\frac{\xi}{2S}, \tag{398}$$

The quantum relaxation function $f_L(t)$ defined by Eq. (395) for a given S corresponds to

$$f_L(t) = \langle P_L\rangle(t) - \langle P_L\rangle_{eq}$$

where the $P_L(z)$ are the Legendre polynomials [105]. This limiting case exactly corresponds to the spin relaxation in a uniform field treated comprehensively in Section III.B.

Returning to the general case, in the classical limit, $S \to \infty$, the Hamiltonian equation (370) corresponds to the classical free energy equation (382), while the quantum differential recurrence relation given by Eq. (389) reduces to the usual five-term differential recurrence relation for a classical uniaxial nanomagnet subjected to a uniform longitudinal field, namely,

$$\tau_N\frac{d}{dt}f_L(t) = q_Lf_L(t) + q_L^-f_{L-1}(t) + q_L^+f_{L+1}(t) + q_L^{--}f_{L-2}(t) + q_L^{++}f_{L+2}(t), \tag{399}$$

where

$$f_L(t) = \langle P_L(\cos\vartheta)\rangle(t) - \langle P_L(\cos\vartheta)\rangle_{eq} \tag{400}$$

is now the *classical* relaxation function with

$$q_L = -\frac{L(L+1)}{2}\left(1 - \frac{2\sigma}{(2L-1)(2L+3)}\right),$$

$$q_L^{\pm} = \mp\xi\frac{L(L+1)}{2(2L+1)},$$

and

$$q_L^{--} = -q_{L-1}^{++} = \frac{\sigma L(L+1)(L-1)}{(2L-1)(2L+1)}.$$

This classical problem has been treated in detail in Refs. 5, 6, 23 and 150–155. In particular, the exact solution of Eq. (399) is given in Ref. 5, ch. 7. For zero anisotropy, that is, $\sigma = 0$, we have from Eq. (399) the known result for relaxation of a classical spin in a uniform field [5, 156–159]

$$\tau_N\frac{d}{dt}f_L(t) + \frac{L(L+1)}{2}f_L(t) = \frac{\xi L(L+1)}{2(2L+1)}\left[f_{L-1}(t) - f_{L+1}(t)\right], \tag{401}$$

which exact solution has been also given in Ref. 5, ch. 7.

We have indicated (see Appendix C for details) how one may derive a master equation for the evolution of the phase space quasiprobability distribution for a uniaxial nanomagnet in contact with a heat bath at temperature T. This is accomplished by first expressing the reduced density matrix master equation in Hilbert space in terms of an inverse Wigner–Stratonovich transformation according to Eq. (376). The various commutators in the integrand of Eq. (376) involving the spin operators may then be converted into phase space differential operators using the orthogonality and recurrence properties of the polarization operators and the corresponding spherical harmonics to ultimately yield via the standard form of the inverse transformation equations (234 and 235) the desired master equation for the distribution function in the phase space of the polar angles. Despite the superficial resemblance of the quantum diffusion equation (377 and 378) (governing the behavior of the phase space distribution) to the Fokker–Planck equations for classical spins, the problem is actually much more complicated. The difficulty lies in the collision kernel, which involves powers of differential operators up to the spin number S considered, only simplifying for large spin numbers ($S \rightarrow \infty$) when the high-order derivatives occurring in the operators may be ignored.

We have illustrated the phase space representation of spin relaxation by treating a uniaxial nanomagnet in a uniform magnetic field of arbitrary strength directed along the easy axis, thereby realizing that only a master equation in configuration space akin to the Fokker–Planck equation for classical spins is involved. Hence, for spins (just as particles), the existing classical solution methods [5, 71] also apply in the quantum case indeed suggesting new closed form quantum results via classical ones. The magnetization, dynamic susceptibility, characteristic relaxation times, and so on, for the uniaxial system may now be evaluated. Note that the spin relaxation of this uniaxial system has already been treated using the quantum Hubbard operator representation of the evolution equation for the spin density matrix [80–82], and as shown in Ref. [62] for spins in an external field alone both the phase space and density matrix methods yield results in outwardly very different forms. Nevertheless, the numerical values from both methods for the same physical quantities (i.e., relaxation times and susceptibility) coincide, thereby establishing a vital corollary between the phase space and the density matrix methods. Thus, the phase space representation, because it is closely allied to the classical representation, besides being complementary to the operator one, transparently illustrates how quantum distributions reduce to the classical ones. The analysis is carried out via the finite Fourier series representation embodied in the Wigner–Stratonovich map as we have illustrated for axially symmetric potentials. It may be extended in the appropriate limits to nonaxially symmetric systems such as biaxial, cubic, and so on. However, the difficulties (e.g., the operator form of the diffusion coefficients in the master equation) encountered in our treatment of axially symmetric potentials are indicative of the even greater

ones, which would be faced when generalizing the phase space representation to such potentials, where the Liouville term never vanishes.

In the Section III.B, we first consider the linear and nonlinear longitudinal relaxation for the particular case of the model parameters $\sigma = 0$ and $\xi \neq 0$ corresponding to a spin in an external dc magnetic field $\mathbf{H}$ directed along the Z−axis. Then, we shall consider in Section III.C the general case $\sigma \neq 0$ and $\xi \neq 0$, that is, a uniaxial nanomagnet in an external magnetic field.

B.   Spin Relaxation in a dc Magnetic Field

For noninteracting spins in an external dc magnetic field $\mathbf{H}$ directed along the Z-axis, the Hamiltonian $\hat{H}_S$ is simply Eq. (370) with $\sigma = 0$

$$\hat{H}_S = -\hbar\omega_0\hat{S}_Z, \tag{402}$$

where $\omega_0 = \xi/(\beta\hbar S)$ is the precession (Larmor) frequency. We shall determine both the *exact* and approximate solutions yielding the averaged longitudinal component of a spin $\left\langle\hat{S}_Z\right\rangle(t)$ for arbitrary S. Furthermore, we shall show how the solution of the corresponding classical problem [5, 159] carries over into the quantum domain and how the *exact* solution for the integral relaxation time due to an *arbitrarily strong* sudden change in the uniform field may be obtained. We remark that the original treatment of this transient-response problem via the master equation in phase space was first given by Shibata *et al.* [35–37] and was further developed by Kalmykov *et al.* [62]. In the *linear-response approximation,* the solution reduces to that previously given by Garanin [80] using the spin density matrix in the second order of perturbation theory in the spin-bath coupling. That result was later re-derived by García-Palacios and Zueco [81] who (again using the density matrix solution) considered the linear response of the longitudinal relaxation of a spin for arbitrary S

1.   Basic Equations

Expanding on the introductory paragraph following [62], we analyze the transient relaxation dynamics of a spin $\hat{\mathbf{S}}$ in an external dc magnetic field $\mathbf{H}$ directed along the Z-*axis* and a random field $\mathbf{h}(t)$ characterizing the collision damping (due to the heat bath) incurred by the precessional motion of the spin. For the Hamiltonian given by Eq. (402), the evolution equation for the reduced density matrix is simply

$$\frac{\partial\hat{\rho}_S}{\partial t} - i\omega_0\left[\hat{S}_0, \hat{\rho}_S\right] = \text{St}\left(\hat{\rho}_S\right). \tag{403}$$

Equation (403) merely represents the *particular* case $\sigma = 0$ of the more general equation (371) for a uniaxial nanomagnet subjected to a uniform dc magnetic

field treated in the Section III.B. For the Hamiltonian $\hat{H}_S$ given by Eq. (402), the collision kernel operator $\mathrm{St}\left(\hat{\rho}_S\right)$ (Eq. (375) with $\sigma = 0$) becomes

$$
\begin{aligned}
\mathrm{St}\left(\hat{\rho}_S\right) = {} & D_{\parallel}\left(\left[\hat{S}_0, \hat{\rho}_S\hat{S}_0\right] + \left[\hat{S}_0\hat{\rho}_S, \hat{S}_0\right]\right) \\
& - 2D_{\perp}\left\{e^{-\beta\hbar\omega_0/2}\left(\left[\hat{S}_{-1}, \hat{\rho}_S\hat{S}_1\right] + \left[\hat{S}_{-1}\hat{\rho}_S, \hat{S}_1\right]\right)\right. \\
& \left. + e^{\beta\hbar\omega_0/2}\left(\left[\hat{S}_1\hat{\rho}_S, \hat{S}_{-1}\right] + \left[\hat{S}_1, \hat{\rho}_S\hat{S}_{-1}\right]\right)\right\}.
\end{aligned}
\tag{404}
$$

Now, in the master equation (377) for the *particular* case $\sigma = 0$ *corresponding to a spin in a uniform field*, all the higher order derivatives will disappear so that the operators $R_{\pm}^{(S)}$ just become the closed transcendental expressions

$$
R_+^{(S)} = \cosh\frac{\beta\hbar\omega_0}{2} \quad \text{and} \quad R_-^{(S)} = \sinh\frac{\beta\hbar\omega_0}{2}.
$$

Then the master equation (377) takes on a much simpler form, namely,

$$
\begin{aligned}
\frac{\partial W_S}{\partial t} = {} & \omega_0\frac{\partial W_S}{\partial\varphi} + \frac{D_{\perp}\sinh\left(\frac{1}{2}\beta\hbar\omega_0\right)}{\sin\vartheta}\left\{\cot\vartheta\left[\cos\vartheta\coth\frac{\beta\hbar\omega_0}{2} + 1\right]\frac{\partial^2 W_S}{\partial^2\varphi}\right. \\
& + \frac{\partial}{\partial\vartheta}\left[\sin\vartheta\left(\coth\frac{\beta\hbar\omega_0}{2} + \cos\vartheta\right)\frac{\partial W_S}{\partial\vartheta} + 2S\sin^2\vartheta\, W_S\right]\right\} + D_{\parallel}\frac{\partial^2 W_S}{\partial^2\varphi}.
\end{aligned}
\tag{405}
$$

By introducing the renormalization of the diffusion coefficients $D_{\perp}e^{-\beta\hbar\omega_0/2} \to D_{\perp}$, Eqs. (404) and (405) yield the result previously obtained for a nonsymmetrized form of the collision kernel operator [35–37]. This master equation describing the time evolution of $W_S(\vartheta, \varphi, t)$ again has essentially the same form as the corresponding Fokker–Planck equation for the distribution function $W(\vartheta, \varphi, t)$ of classical spin orientations in the configuration space [35]

$$
\begin{aligned}
\frac{\partial W}{\partial t} = {} & \omega_0\frac{\partial W}{\partial\varphi} \\
& + D_{\perp}\left\{\frac{\xi}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin^2\vartheta\, W\right) + \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial W}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2 W}{\partial\varphi^2}\right\}
\end{aligned}
\tag{406}
$$

($\xi = \beta\hbar\omega_0 S$). Equation (405) serves as the simplest example of the phase space method for open spin systems. In fact, it is just the rotational analog of the quantum translational harmonic oscillator treated using the Wigner function by Agarwal [120]. In this instance, the evolution equation (168) for the Wigner distribution $W(q, p, t)$ in the phase space of positions and momenta has the same mathematical form as the Fokker–Planck equation for the classical oscillator (see Section II.B.3).

For longitudinal relaxation, where the distribution function W_S is independent of the azimuth, the Liouville term in the evolution equation vanishes, and Eq. (405) reduces to an equation very similar to that governing a classical spin in a uniform magnetic field [5]

$$\frac{\partial W_S}{\partial t} = \frac{D_\perp \sinh(\beta\hbar\omega_0/2)}{\sin\vartheta}$$
$$\times \frac{\partial}{\partial\vartheta}\left\{\left[\sin\vartheta\left(\cos\vartheta + \coth\frac{\beta\hbar\omega_0}{2}\right)\right]\frac{\partial W_S}{\partial\vartheta} + 2S\sin^2\vartheta\, W_S\right\}. \quad (407)$$

This simplification arises naturally and is to be expected on intuitive grounds because precession of a spin in a uniform field is effectively the rotational analog of the translational harmonic oscillator.

Equation (405) applies in the *narrowing limit case* in which the correlation time τ_c of the random field $\mathbf{h}(t)$ acting on the spin satisfies the condition $\gamma H \tau_c << 1$, where H is the averaged amplitude of the random magnetic field. The left-hand side of Eq. (405) is the quantum analog of the Liouville equation for a spin, which is now the same as the classical case for particles with quadratic Hamiltonians, while the right-hand side (collision kernel) characterizes the interaction of the spin with the thermal bath at temperature T. The remaining conditions for the validity of Eq. (405) have already been discussed. We remark that for longitudinal relaxation, Eq. (405) may be plausibly derived by postulating (like in the phase space treatment of the quantum translational Brownian motion, see Section II.B.3) a master equation for the Wigner function W_S with collision terms given by a Kramers–Moyal expansion truncated at the second term. The various drift and diffusion coefficients in the truncated expansion may then be calculated by requiring that the equilibrium Wigner distribution W_{eq}, corresponding to the equilibrium spin density matrix $\hat{\rho}_{eq} = e^{-\beta\hat{H}_S}/\text{Tr}\left(e^{-\beta\hat{H}_S}\right)$, renders the collision kernel equal to zero (see Section III.B.3).

2. *Quantum Analog of the Magnetic Langevin Equation*

The spin relaxation described by the master equation (405) may also be equivalently described using a quantum analog of the magnetic Langevin equation with multiplicative noise. For this, we use the Stratonovich definition [160] of such equations constituting the mathematical idealization of the spin relaxation process [161]. Thus, it is unnecessary to transform them to Itô stochastic differential equations (see e.g., Ref. [161]). Moreover, one can then use conventional calculus [5, 161]. The Langevin equations governing the two stochastic equations of motion for the variables ϑ and φ corresponding to the phase space master equation (405) are in the Stratonovich interpretation [5, 67]

$$\dot{\vartheta}(t) = D_\perp \cot \vartheta(t) \left(Q_1^S[\vartheta(t)] - \sqrt{Q_1^S[\vartheta(t)] Q_2^S[\vartheta(t)]} \right)$$

$$- 2D_\perp(S + 1/4) \sin \vartheta(t) \sinh \frac{\beta \hbar \omega_0}{2} + \sqrt{Q_1^S[\vartheta(t)]} \left[h_\vartheta(t) - \alpha^{-1} h_\varphi(t) \right], \tag{408}$$

$$\dot{\varphi}(t) = -\omega_0 + \sqrt{Q_2^S[\vartheta(t)]} \csc \vartheta(t) \left[h_\varphi(t) + \alpha^{-1} h_\vartheta(t) \right], \tag{409}$$

where

$$Q_1^S[\vartheta(t)] = \frac{D_\perp \beta}{\eta(1+\alpha^{-2})} \left(\cosh \frac{\beta \hbar \omega_0}{2} + \cos \vartheta(t) \sinh \frac{\beta \hbar \omega_0}{2} \right), \tag{410}$$

$$Q_2^S[\vartheta(t)] = \frac{D_\perp \beta}{\eta(1+\alpha^{-2})}$$

$$\times \left\{ \cos^2 \vartheta(t) \cosh \frac{\beta \hbar \omega_0}{2} + \cos \vartheta(t) \sinh \frac{\beta \hbar \omega_0}{2} + \frac{D_\parallel}{D_\perp} \sin^2 \vartheta(t) \right\}, \tag{411}$$

and the components $h_\vartheta(t)$, $h_\varphi(t)$ of the random field $\mathbf{h}(t)$ in the spherical coordinate system or basis are expressed in terms of the components $h_X(t), h_Y(t), h_Z(t)$, in the Cartesian basis as [5]

$$h_\vartheta(t) = h_X(t) \cos \vartheta(t) \cos \varphi(t) + h_Y(t) \cos \vartheta(t) \sin \varphi(t) - h_Z(t) \sin \vartheta,$$

$$h_\varphi(t) = -h_X(t) \sin \varphi(t) + h_Y(t) \cos \varphi(t),$$

with

$$\overline{h_i(t)} = 0, \quad \overline{h_i(t)h_j(t')} = \frac{2\eta}{\beta} \delta_{ij} \delta(t - t'). \tag{412}$$

Here the indices $i, j = 1, 2, 3$ in Kronecker's delta δ_{ij} correspond to the Cartesian axes X, Y, Z of the laboratory coordinate system $OXYZ$, and $\alpha = \gamma \eta \mu$ is a dimensionless dissipation (damping) parameter, η is a "friction" coefficient, and the overbar means the statistical average over the realizations of the random field. In the isotropic diffusion ($D_\perp = D_\parallel$) and classical ($S \to \infty$) limit, the Langevin equation (408 and 409) reduce to those for isotropic diffusion of a classical spin in spherical coordinates [5], namely,

$$\dot{\vartheta}(t) = D_\perp \left\{ -\xi \sin \vartheta(t) + \sqrt{\frac{D_\perp \beta}{\eta(1+\alpha^{-2})}} \left[h_\vartheta(t) - \alpha^{-1} h_\varphi(t) \right] \right\}, \tag{413}$$

$$\dot{\varphi}(t) = -\omega_0 + \sqrt{\frac{D_\perp \beta}{\eta(1+\alpha^{-2})}} \csc \vartheta(t) \left[h_\varphi(t) + \alpha^{-1} h_\vartheta(t) \right]. \tag{414}$$

To show that the Langevin equations (408 and 409) are equivalent to the master equation (405), we recall that by choosing Langevin equations for a set of two stochastic variables $\{\xi_1(t) = \vartheta(t), \xi_2(t) = \varphi(t)\}$ as

$$\dot{\xi}_i(t') = H_i[\xi_1(t'), \xi_2(t')] + \sum_{j=1}^{3} G_{ij}[\xi_1(t'), \xi_2(t')]h_j(t'),$$

($i = 1, 2, j = 1, 2, 3$) and subsequently interpreting them as Stratonovich stochastic differential equations, then the averaged equations for the drift, D_i, and diffusion, D_{ij}, coefficients time t are [5, 71]

$$D_i = \overline{\dot{\xi}_i} = \lim_{\tau \to 0} \frac{1}{\tau} \overline{[\xi_i(t + \tau) - \xi_i(t)]}$$

$$= H_i(x_1, x_2, t) + \frac{\eta}{\beta} \sum_{k=1}^{2} \sum_{j=1}^{3} G_{kj}(x_1, x_2) \frac{\partial}{\partial x_k} G_{ij}(x_1, x_2), \qquad (415)$$

$$D_{ij} = \lim_{\tau \to 0} \frac{1}{2\tau} \overline{[\xi_i(t + \tau) - \xi_i(t)] [\xi_j(t + \tau) - \xi_j(t)]}$$

$$= \frac{\eta}{\beta} \sum_{k=1}^{3} G_{ik}(x_1, x_2) G_{jk}(x_1, x_2). \qquad (416)$$

Moreover due to Eqs. (415) and (416), we have from Eqs. (408) and (409) the drift and diffusion coefficients

$$D_1 = -D_\perp \left[(2S + 1) \sin \vartheta \sinh \frac{\beta \hbar \omega_0}{2} \right.$$
$$\left. - \cot \vartheta \left(\cosh \frac{\beta \hbar \omega_0}{2} + \cos \vartheta \sinh \frac{\beta \hbar \omega_0}{2} \right) \right],$$

$$D_2 = -\omega_0,$$

$$D_{11} = D_\perp \left(\cosh \frac{\beta \hbar \omega_0}{2} + \cos \vartheta \sinh \frac{\beta \hbar \omega_0}{2} \right),$$

$$D_{22} = D_\| + \frac{D_\perp}{\sin^2 \vartheta} \left(\cos^2 \vartheta \cosh \frac{\beta \hbar \omega_0}{2} + \cos \vartheta \frac{\beta \hbar \omega_0}{2} \right).$$

The Fokker–Planck equation for the probability density function $P(\vartheta, \varphi, t) = \sin \vartheta \, W_S(\vartheta, \varphi, t)$ corresponding to Eqs. (408) and (409) is

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial \vartheta} (D_1 P) - \frac{\partial}{\partial \varphi} (D_2 P) + \frac{\partial^2}{\partial \vartheta^2} (D_{11} P) + \frac{\partial^2}{\partial \varphi^2} (D_{22} P). \qquad (417)$$

Equation (417) ultimately reduces to the master equation (405) for the phase space distribution function $W_S(\vartheta, \varphi, t)$.

Moreover via the Langevin equations (408 and 409) for the stochastic variables $\vartheta(t)$ and $\varphi(t)$, we also have the Langevin equation for the evolution of the spherical harmonics $Y_{lm}(\vartheta, \varphi)$ rendered as [5]

$$\dot{Y}_{lm}[\vartheta(t), \varphi(t)] = \dot{\vartheta}(t)\frac{\partial}{\partial \vartheta}Y_{lm}[\vartheta(t), \varphi(t)] + \dot{\varphi}(t)\frac{\partial}{\partial \varphi}Y_{lm}[\vartheta(t), \varphi(t)],$$

where $\dot{\vartheta}(t)$ and $\dot{\varphi}(t)$ are given by Eqs. (408) and (409), respectively. Then by averaging the Langevin equation for $Y_{lm}(\vartheta, \varphi)$ over its realizations as described in Ref. [5], and using the recursion relations for the spherical harmonics (see Appendix B), we ultimately have a *closed* system of differential recurrence equations for the statistical moments (averaged spherical harmonics), namely,

$$\frac{d}{dt}\langle Y_{lm}\rangle(t) = q_{l,m}^{-}\langle Y_{l-1m}\rangle(t) + q_{l,m}\langle Y_{lm}\rangle(t) + q_{l,m}^{+}\langle Y_{l+1m}\rangle(t), \qquad (418)$$

where $0 \le l \le 2S$,

$$q_{l,m} = -D_{\parallel}m^2 + im\omega_0 - D_{\perp}\left[l(l+1) - m^2\right]\cosh\frac{\beta\hbar\omega_0}{2},$$

$$q_{l,m}^{-} = D_{\perp}(l - 2S - 1)\sqrt{\frac{l^2 - m^2}{4l^2 - 1}}\sinh\frac{\beta\hbar\omega_0}{2},$$

$$q_{l,m}^{+} = D_{\perp}(l + 2S + 2)\sqrt{\frac{(l+1)^2 - m^2}{(2l+1)(2l+3)}}\sinh\frac{\beta\hbar\omega_0}{2}.$$

Here, the number of recurrent equations is *finite* namely $2S + 1$ because $\langle Y_{Lm}\rangle(t) = 0$ for $L > 2S$, which is the main difference from the corresponding classical hierarchy of differential recurrence equations for the moments, where the number of equations is infinite. Thus, the Langevin and master equation treatments are now equivalent and yield the same results.

Here, we have illustrated how a phase space Langevin equation may be written by considering the simplest possible yet meaningful problem, namely, the relaxation of a spin of arbitrary number S in a uniform magnetic field of arbitrary strength directed along the Z-axis. We emphasize that the Langevin equations are written down from *a priori* knowledge of the master equation *unlike the classical case* where they are written down independently of the Fokker–Planck equation. Consequently, the results of each method in the classical case only coincide due to the Gaussian white noise properties of the random field, particularly Isserlis's (or Wick's) theorem [5] is satisfied. This theorem allows multiple time correlations of Gaussian random variables to be expressed as two time ones, thereby leading directly to the correspondence between the Langevin and Fokker–Planck equations in the classical case.

### 3.   Exact Solution of the Master Equation for Longitudinal Relaxation

Having formulated the relevant evolution equations, we shall now explicitly treat transient *nonlinear* spin relaxation by direct using the phase space master equation because in this particular case it takes the Fokker–Planck form (see Eq. 419). In order to accomplish this, we suppose that the magnitude of an externally uniform dc magnetic field is suddenly altered at time $t = 0$ from $\mathbf{H_I}$ to a new value $\mathbf{H_{II}}$ (the fields $\mathbf{H_I}$ and $\mathbf{H_{II}}$ are assumed to be applied parallel to the Z-axis of the laboratory coordinate system). Thus, we study as in the classical case [5], the transient longitudinal relaxation of a system of noninteracting spins starting from an equilibrium state I, say with the initial distribution function $W_{eq}^{H_I}$ ($t \leq 0$), to a new equilibrium state II, say with the final distribution function $W_{eq}^{H_{II}}$ ($t \to \infty$). Here, the longitudinal component of the spin operator relaxes from the initial equilibrium value $\left\langle \hat{S}_Z \right\rangle_I$ to the final equilibrium value $\left\langle \hat{S}_Z \right\rangle_{II}$, the intervening transient being described by an appropriate relaxation function $\left\langle \hat{S}_Z \right\rangle(t) - \left\langle \hat{S}_Z \right\rangle_{II}$ (see Fig. 14). The transient response so formulated is truly *nonlinear* because the change in amplitude $H_I - H_{II}$ of the external dc magnetic field is *arbitrary* (the linear response can be regarded as the particular case $|H_I - H_{II}| \to 0$). Here, the azimuthal angle dependence of the distribution function W_S may be ignored. Thus, the master equation (407) becomes the single-variable Fokker–Planck equation

$$\frac{\partial W_S}{\partial t} = \frac{\partial}{\partial z}\left(D_2(z)\frac{\partial W_S}{\partial z} + D_1(z)W_S \right), \tag{419}$$

where $z = \cos \vartheta$,

$$D_1(z) = \frac{S(1 - z^2)}{\tau_N} \sinh \frac{\xi}{2S}, \tag{420}$$

$$D_2(z) = \frac{(1 - z^2)}{2\tau_N}\left(\cosh \frac{\xi}{2S} + z\sinh \frac{\xi}{2S} \right), \tag{421}$$
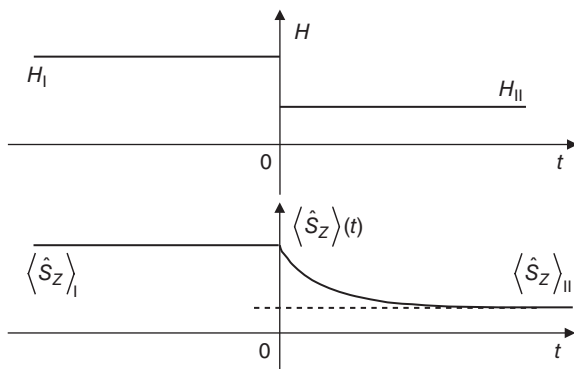
Figure 14.   Schematic representation of the nonlinear transient response.

$\tau_N = 1/(2D_\perp)$ is the characteristic time of the free rotational "diffusion" of the spin, and the dimensionless field parameter ξ is defined as follows:

$$\xi = \beta\mu_0\mu H_{\mathrm{II}}. \tag{422}$$

Hitherto, the explicit expressions (Eqs. 420 and 421) for $D_1(z)$ and $D_2(z)$ for spins subjected to a dc magnetic field $\mathbf{H}_0$ have been obtained (as we have just seen) by starting from the evolution equation for the density matrix $\hat{\rho}_S$ giving rise to lengthy calculations. However, these equations can also be obtained in far simpler fashion merely by knowing the functional form of the master equation (419) and the equilibrium phase space distribution $W_{eq}^{\xi}(z)$ for spins. To illustrate this, we shall again select the extension to the semiclassical case of the *Ansatz* of the imposition of a Boltzmann distribution originally used by Einstein, Smoluchowski, Langevin, and Kramers to determine drift and diffusion coefficients in the classical Brownian motion. We have already used this idea for the quantum translational Brownian motion in Section II and in Ref. 48.

Thus, to determine $D_1(z)$ and $D_2(z)$ in Eq. (419) explicitly, we first recall that the equilibrium distribution $W_{eq}^{\xi}(z)$ given by Eq. (287) with $\gamma_X = \gamma_Y = 0$, namely,

$$W_{eq}^{\xi}(z) = \frac{\sinh\left(\frac{1}{2}\xi/S\right)}{\sinh\left[\left(S+\frac{1}{2}\right)\xi/S\right]}\left(\cosh\frac{\xi}{2S} + z\sinh\frac{\xi}{2S}\right)^{2S} \tag{423}$$

must also be the equilibrium solution of the generic master equation (419), that is, it must satisfy

$$\frac{\partial}{\partial z}\left(D_2(z)\frac{\partial}{\partial z}W_{eq}^{\xi}(z) + D_1(z)W_{eq}^{\xi}(z)\right) = 0. \tag{424}$$

Now one is at liberty to seek $D_1(z)$ and $D_2(z)$ in series form as

$$D_1(z) = \left(1 - z^2\right)\left(a_0^S + a_1^S z + a_2^S z^2 + \ldots\right), \tag{425}$$

$$D_2(z) = \left(1 - z^2\right)\left(b_0^S + b_1^S z + b_2^S z^2 + \ldots\right). \tag{426}$$

By substituting Eqs. (425) and (426) into Eq. (424), then if $W_{eq}^{\xi}(z)$ from Eq. (423) is to satisfy Eq. (424), only the coefficients a_0^S, b_0^S, and b_1^S can be nonzero so that $D_1(z)$ and $D_2(z)$ are, respectively,

$$D_1(z) = 2Sb_0^S\left(1 - z^2\right)\tanh\frac{\xi}{2S}$$

and

$$D_2(z) = b_0^S\left(1 - z^2\right)\left(1 + z\tanh\frac{\xi}{2S}\right).$$

In order to determine the normalizing coefficient b_0^S, we use the fluctuation–dissipation theorem [75] along with the additional requirements that in the classical limit $S \to \infty$, $D_1(z)$ and $D_2(z)$ must reduce to their classical counterparts for the rotational Brownian motion of a classical spin [5], namely,

$$D_1(z) \to \frac{\xi}{2\tau_N}\left(1 - z^2\right)$$

and

$$D_2(z) \to \frac{1}{2\tau_N}\left(1 - z^2\right).$$

Thus, we obtain

$$b_0^S = \frac{1}{2\tau_N} \cosh \frac{\xi}{2S}$$

so that $D_1(z)$ and $D_2(z)$ are given by the closed form equations (420 and 421). Now in the derivation of $D_1(z)$ and $D_2(z)$, we have imposed the stationary solution of the master equation as the equilibrium phase space distribution equation (423) corresponding to the equilibrium density matrix $\hat{\rho}_{eq}$ given by Eq. (274) describing the system in *thermal equilibrium without coupling* to the thermal bath. However, from the theory of open quantum systems [134], the equilibrium state, in general may deviate from the equilibrium density matrix $\hat{\rho}_{eq}$; the latter describes the thermal equilibrium of the system in the weak coupling and high-temperature limits only. A detailed discussion is given, for example, by Geva *et al.* [162]. Nevertheless, the imposition of the phase space distribution equation (423) as the equilibrium solution of Eq. (424), so yielding $D_1(z)$ and $D_2(z)$, appears to be the exact analog of the *Ansatz* used by Gross and Lebowitz [132] in their formulation of quantum kinetic models of impulsive collisions. According to Ref. [132], for a system with a Hamiltonian $\hat{H}$, the equation governing the time behavior of the density matrix $\hat{\rho}_S$ is Eq. (40), where the collision kernel operator $\mathrm{St}(\hat{\rho}_S)$ satisfies the condition $\mathrm{St}(\hat{\rho}_{eq}) = 0$. Equation (424) is entirely analogous to this condition. Moreover, as we have seen in Section II.A.2, the condition $\mathrm{St}(\hat{\rho}_{eq}) = 0$ was also used by Redfield [14] to determine the matrix elements of the relaxation operator in his theory of quantum relaxation processes.

The time-dependent solution of the axially symmetric evolution given by Eq. (419) is obtained as usual by expanding the distribution function $W_S(z, t)$ in Legendre polynomials $P_n(z)$

$$W_S(z, t) = W_{eq}^{\xi}(z) + \sum_{n=0}^{2S} (n + 1/2)P_n(z)f_n(t), \tag{427}$$

where

$$f_n(t) = \langle P_n \rangle (t) - \langle P_n \rangle_{eq}^{\xi}$$

are the relaxation functions, the angular brackets $\langle \rangle$ (t) and $\langle \rangle^{\xi}_{eq}$ designate statistical averaging defined as

$$\langle P_n \rangle (t) = \left(S + \tfrac{1}{2} \right) \int_{-1}^{1} P_n(z) \, W_S(z, t) dz \tag{428}$$

and

$$\langle P_n \rangle^{\xi}_{eq} = \left(S + \tfrac{1}{2} \right) \int_{-1}^{1} P_n(z) W^{\xi}_{eq}(z) dz. \tag{429}$$

In particular, Eqs. (429) and (431) yield the *equilibrium* average of $P_1(z)$, namely,

$$\langle P_1 \rangle^{\xi}_{eq} = \left(S + \tfrac{1}{2} \right) \int_{-1}^{1} z W^{\xi}_{eq}(z) dz = \frac{S}{S + 1} B_S(\xi), \tag{430}$$

where $B_S(\xi)$ is the Brillouin function defined by Eq. (278). The equilibrium distribution $W^{\xi}_{eq}(z)$ can be equivalently defined as (cf. Eq. 307)

$$W^{\xi}_{eq}(z) = \sum_{n=0}^{2S} \left(n + \frac{1}{2} \right) P_n(z) \langle P_n \rangle^{\xi}_{eq}. \tag{431}$$

Substituting Eq. (427) into Eq. (421) and using the orthogonality and recurrence properties of Legendre polynomials $P_n(z)$, we have as in the classical case [5] a differential recurrence relation for the relaxation functions $f_n(t)$, namely, (cf. the three-term recurrence relation given by Eq. 396)

$$\tau_n \dot{f}_n(t) = q_n^- f_{n-1}(t) + q_n f_n(t) + q_n^+ f_{n+1}(t), \tag{432}$$

where $1 \leq n \leq 2S$,

$$f_0(t) = f_{2S+1}(t) = 0,$$
$$\tau_n = \frac{2\tau_N}{n(n+1)},$$
$$q_n = -\cosh \frac{\xi}{2S},$$
$$q_n^{\pm} = \mp \frac{2S \pm n + (3 \pm 1)/2}{(2n+1)} \sinh \frac{\xi}{2S}.$$

Since the initial value of the distribution function is $W_S(z, 0) = W^{\xi+\delta}_{eq}(z)$, where the transient parameter $\delta = \beta \mu_0 \mu \left(H_{\mathrm{II}} - H_{\mathrm{I}} \right)$, the initial values of the relaxation function $f_n(t)$ are

$$f_n(0) = \langle P_n \rangle^{\xi+\delta}_{eq} - \langle P_n \rangle^{\xi}_{eq}. \tag{433}$$

Equation (432) is a quantum counterpart of the recurrence relation given by Eq. (401) for a classical spin and has been solved in Refs. 38 and 39 for the *particular* spin numbers $S = 1/2, 1$, and $3/2$. Now, we give the exact solution for the transient quantum nonlinear longitudinal relaxation governed by Eq. (432) for *arbitrary S*.

Using the one-sided Fourier transform, we have from Eq. (432)

$$(i\omega\tau_n - q_n)\tilde{f}_n(\omega) - q_n^+\tilde{f}_{n-1}(\omega) - q_n^+\tilde{f}_{n+1}(\omega) = \tau_n f_n(0), \qquad (434)$$

where

$$\tilde{f}_n(\omega) = \int_0^\infty e^{-i\omega t} f_n(t) dt.$$

The inhomogeneous algebraic three-term recurrence equation (434) can be solved exactly for the one-sided Fourier transform of the relaxation function $\tilde{f}_1(\omega)$ using continued fractions like the corresponding classical problem (see for details the general solution of three-term recurrence relations given in Ref. [5], ch. 2), yielding

$$
\begin{aligned}
\tilde{f}_1(\omega) &= \tau_N \operatorname{csch}\frac{\xi}{2S} \sum_{n=1}^{2S} \frac{f_n(0)}{n(n+1)(S+1)} \prod_{k=1}^{n} \frac{q_{k-1}^+}{q_k^-} \Delta_k(\omega,\xi) \\
&= \tau_N \operatorname{csch}\frac{\xi}{2S} \sum_{n=1}^{2S} (-1)^{n+1} \frac{(2n+1)(2S+n+1)!(2S-n)!}{n(n+1)\,(S+1)\,(2S+1)!(2S)!} \\
&\quad \times f_n(0) \prod_{k=1}^{n} \Delta_k(\omega,\xi).
\end{aligned}
\qquad (435)
$$

Here, the *finite* continued fraction $\Delta_n(\omega,\xi)$ is defined by the two-term recurrence relation

$$\Delta_n(\omega,\xi) = \frac{q_n^-}{i\omega\tau_n - q_n - q_n^+\Delta_{n+1}(\omega,\xi)}$$

with $\Delta_{2S+1}(\omega,\xi) = 0$, moreover, we have the product

$$\prod_{k=1}^{n} \frac{q_{k-1}^+}{q_k^-} = (-1)^{n+1} \frac{(2n+1)(2S+n+1)!(2S-n)!}{(2S+1)!(2S)!}.$$

The equilibrium averages $\langle P_n\rangle_{eq}^\xi$, Eq. (429), can also be evaluated in terms of the continued fraction $\Delta_n(0,\xi)$ since $\langle P_n\rangle_{eq}^\xi$ satisfies the three-term recurrence relation

$$q_n^- \langle P_{n-1}\rangle_{eq}^\xi + q_n \langle P_n\rangle_{eq}^\xi + q_n^+ \langle P_{n+1}\rangle_{eq}^\xi = 0, \qquad (436)$$

so that

$$\Delta_n(0, \xi) = \frac{\langle P_n \rangle_{eq}^{\xi}}{\langle P_{n-1} \rangle_{eq}^{\xi}}.$$

Consequently, we have

$$\langle P_n \rangle_{eq}^{\xi} = \prod_{k=1}^{n} \Delta_k(0, \xi). \tag{437}$$

Equation (435) is the exact solution for the one-sided Fourier transform of the non-linear relaxation function $f_1(t)$ in terms of continued fractions. Having determined $f_1(t)$, various transient nonlinear responses of the longitudinal component of the magnetic moment may always be evaluated because in terms of averages of spin operators

$$\left\langle \hat{S}_Z \right\rangle(t) - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}} = (S+1) f_1(t), \tag{438}$$

where in terms of the Brillouin function the final equilibrium value is

$$\left\langle \hat{S}_Z \right\rangle_{\mathrm{II}} = (S+1) \langle P_1 \rangle_{eq}^{\xi} = S B_S(\xi).$$

In particular, we mention the rise, decay, and rapidly reversing field transient responses. The general relaxation equation (435) can often be simplified. For example, to treat the rise transient we suppose that a *strong* constant field $\mathbf{H}_{\mathrm{II}}$ is suddenly switched on at time $t = 0$ (so that $\mathbf{H}_{\mathrm{I}} = 0$). Thus, we require the nonlinear relaxation behavior of a system of spins starting from an equilibrium state I with the *isotropic* distribution function $W_{eq}^0 = 1/(2S+1)$ ($t \le 0$) to another equilibrium state II with the *final* distribution function $W_{eq}^{H_{\mathrm{II}}} = W_{eq}^{\xi}(z)$ ($t \to \infty$). Using Eq. (437), Eq. (435) simplifies to

$$\tilde{f}_1(\omega) = \frac{i}{\omega} [\Delta_1(0, \xi) - \Delta_1(\omega, \xi)]$$

$$= \frac{i}{\omega} \left[\langle P_1 \rangle_{eq}^{\xi} - \Delta_1(\omega, \xi) \right], \tag{439}$$

yielding the spectrum of the relaxation function $\tilde{f}_1(\omega)$ for the rise transient.

4. *Nonlinear Longitudinal Relaxation Time*

The overall transient behavior of the relaxation function $f_1(t)$ is characterized by the integral relaxation time [5] (see Appendix E)

$$\tau_{int} = \frac{1}{f_1(0)} \int_0^{\infty} f_1(t) dt = \frac{\tilde{f}_1(0)}{f_1(0)} \tag{440}$$

(i.e., the area under the normalized relaxation function $f_1(t)/f_1(0)$), which can be evaluated in series form from the zero frequency limit [5] of Eqs. (435) and (437) is

$$\tau_{int} = \tau_N \operatorname{csch} \frac{\xi}{2S} \sum_{n=1}^{2S} \frac{(-1)^{n+1}(2n+1)(2S+n+1)!(2S-n)! f_n(0) \langle P_n \rangle_{eq}^{\xi}}{n(n+1)(S+1)(2S+1)!(2S)! f_1(0)}. \tag{441}$$

Moreover, the latter result can also be written in an equivalent integral form because the master equation (419) is actually just a single-variable Fokker–Planck equation, which may be integrated by quadratures. Now for any system with dynamics governed by a single-variable Fokker–Planck equation, for example, Eq. (419), the integral relaxation time τ_{int}, characterizing the nonlinear relaxation behavior of $f_1(t)$, can be obtained in integral form in terms of the equilibrium distribution and the diffusion coefficient $D_2(z)$ only (see Appendix E for details) [5]. Hence, with Eqs. (419) and (E.22), we have like the classical case [5] an exact integral expression for τ_{int}, namely,

$$\tau_{int} = \frac{1}{\left(S+\frac{1}{2}\right) f_1(0)} \int_{-1}^{1} \frac{\Phi(z)\Psi(z)}{D_2(z) W_{eq}^{\xi}(z)} dz, \tag{442}$$

where

$$\Psi(z) = \left(S+\frac{1}{2}\right) \int_{-1}^{z} \left(x - \langle P_1 \rangle_{eq}^{\xi}\right) W_{eq}^{\xi}(x) dx,$$

$$\Phi(z) = \left(S+\frac{1}{2}\right) \int_{-1}^{z} \left[W_{eq}^{\xi+\delta}(x) - W_{eq}^{\xi}(x)\right] dx,$$

$$f_1(0) = \langle P_1 \rangle_{eq}^{\xi+\delta} - \langle P_1 \rangle_{eq}^{\xi}$$

$$= \frac{S}{S+1} \left[B_S(\xi+\delta) - B_S(\xi)\right].$$

For the limiting case $S = 1/2$, τ_{int} is independent of the parameter δ and is given by

$$\tau_{int} = \frac{\tau_N}{\cosh \xi}, \tag{443}$$

while in the classical limit $S \to \infty$, one has

$$\tau_{int} = \frac{\tau_N \xi \operatorname{csch} \xi}{\langle P_1 \rangle^{\xi} - \langle P_1 \rangle^{\xi+\delta}} \int_{-1}^{1} \frac{\phi(z)\psi(z) e^{-\xi z}}{1 - z^2} dz, \tag{444}$$

where

$$\langle P_1 \rangle^\xi = \coth \xi - \frac{1}{\xi},$$

$$\phi(z) = \int_{-1}^{z} \left[e^{\xi z'} - e^{(\xi+\delta)z'} \right] dz',$$

$$\psi(z) = \int_{-1}^{z} \left(\cos z' - \langle P_1 \rangle^\xi \right) e^{\xi z'} dz'$$

agreeing entirely with the established classical result (5, ch. 7).

Numerical calculations show that both the series expression equation (441) and the integral equation (442) yield identical results. Thus, τ_{int} for various nonlinear transient responses (i.e., the rise, decay, and rapidly reversing field transients) may be easily evaluated from Eq. (442). The normalized relaxation time τ_{int}/τ_N from Eq. (442) is plotted in Fig. 15 for various values of the transient strength δ, the field strength parameter ξ, and spin number S. The figure indicates that the relaxation time decreases with increasing field strength ξ with a strong dependence on *both S* and the transient strength δ. The nonlinear effect *comprising accelerated*
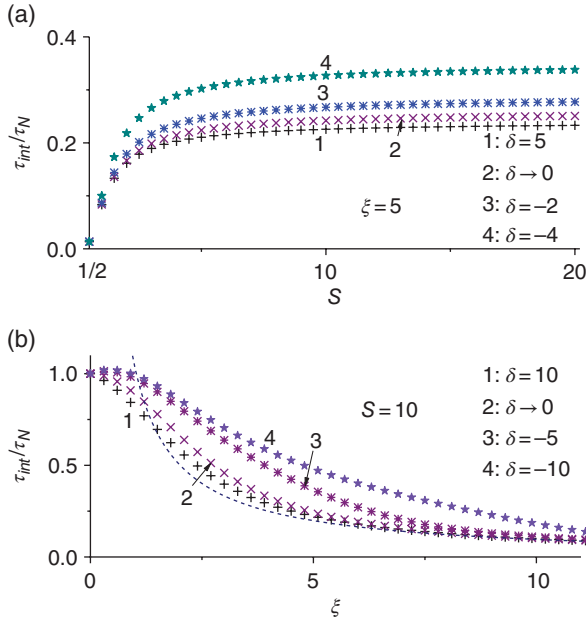
Figure 15. (Color on line) Normalized relaxation time τ_{int}/τ_N from Eq. (442) as a function of S (a) and ξ (b) for various values of δ (symbols). Dashed line: Eq. (447).

relaxation in the external field also exists for classical dipoles [5]. An explanation may be given as follows. In the absence of the field ($\xi = 0$), the relaxation time of the spin is just the *free-diffusion relaxation time* τ_N so that $\tau_{int} = \tau_N$. However, in a *strong* field ($\xi >> 1$) and $S >> 1$, the relaxation time of the spin is determined by the *damped diffusion* of the spin in the field $\mathbf{H}_{\text{II}}$, and the characteristic frequency is now the frequency of the spin oscillation about $\mathbf{H}_{\text{II}}$ (in the vicinity of $z = 0$). Thus, τ_{int} is of the order of $\sim 1/[2D_1(0)] = \tau_N/\xi$ so that

$$\tau_{int} \sim \frac{\tau_N}{\xi}. \tag{445}$$

This asymptotic formula may be used to estimate τ_{int} for $\xi >> 1$ and $\delta > 0$ and $|\delta| << \xi$. However, for $\delta \sim -\xi$, a more accurate formula is

$$\tau_{int} \sim \frac{\tau_N}{\xi - 1 - \xi(\xi + \delta)}. \tag{446}$$

The influence of the transient parameter δ entering into the relaxation time owing to the initial distribution function $W_{eq}^{\xi+\delta}$ is more pronounced for field strengths $\xi \sim 2 \div 7$ (see Fig. 15). The enhanced dependence of τ_{int} on δ for negative values of δ can be understood because these situations correspond to the situation of rise and rapidly reversing transients, where the initial and final distributions differ considerably. As far as the *spin dependence* of τ_{int} for $\xi >> 1$ and $\delta > 0$ and $|\delta| << \xi$ is concerned, a simple asymptotic formula for τ_{int} is (see Fig. 14)

$$\tau_{int} \sim \frac{1}{2D_1(0)} = \frac{\tau_N}{2S} \operatorname{csch} \frac{\xi}{2S}. \tag{447}$$

5. *Linear Response*

Now using these results, we may also evaluate the *linear response* of a spin system to *infinitesimally small* changes in the magnitude of the dc field $\mathbf{H}_{\text{II}}$. This is of particular interest as the corresponding integral relaxation time now becomes the correlation time, which has been previously evaluated [80–82] from the spin density matrix. Thus, we again suppose that the uniform dc field $\mathbf{H}_{\text{II}}$ is directed along the Z-axis of the laboratory coordinate system and that a *small* probing field $\mathbf{H}_1$, having been applied to the assembly of noninteracting spins in the distant past ($t = -\infty$) so that equilibrium conditions obtain at time $t = 0$, is suddenly switched off at $t = 0$. Here, the normalized relaxation function $f_1(t)/f_1(0)$ reduces to the longitudinal equilibrium correlation function $C(t)$, that is [33, 75],

$$C(t) = \lim_{\delta \to 0} \frac{f_1(t)}{f_1(0)} = \frac{1}{\beta \chi} \left\langle \int_0^\beta \left[\hat{S}_Z(-i\lambda\hbar) - \left\langle \hat{S}_Z \right\rangle_{\text{II}} \right] \left[\hat{S}_Z(t) - \left\langle \hat{S}_Z \right\rangle_{\text{II}} \right] d\lambda \right\rangle_{\Big/ \text{II}}, \tag{448}$$

where χ is the static susceptibility defined in terms of the Brillouin function given by Eq. (278) as follows:

$$\chi = S^2 \frac{\partial}{\partial \xi} B_S(\xi) = \frac{1}{4}\left[\operatorname{csch}^2\left(\frac{\xi}{2S}\right) - (2S+1)^2 \operatorname{csch}^2\left(\frac{2S+1}{2S}\xi\right)\right]. \quad (449)$$

According to linear-response theory (see, e.g., Ref. 75 and Appendix D), the dynamic susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ is defined as [75]

$$\frac{\chi(\omega)}{\chi} = 1 - i\omega\tilde{C}(\omega), \quad (450)$$

where $\tilde{C}(\omega)$ is the one-sided Fourier transform of $C(t)$, namely,

$$\tilde{C}(\omega) = \int_0^\infty C(t)e^{-i\omega t}dt. \quad (451)$$

In linear response, the integral relaxation time, that is, the correlation time $\tau_{int}|_{\delta\to 0} = \tau_{cor} = \tilde{C}(0)$ of $C(t)$, follows from the general nonlinear equation (442) in the limit of a very small transient strength parameter $\delta \to 0$ and is given by

$$\tau_{cor} = \frac{S(S+1)\left(S+\frac{1}{2}\right)}{\chi} \int_{-1}^{1} \frac{\int_{-1}^{z} \frac{\partial}{\partial \xi} W_{eq}^\xi(x)dx \int_{-1}^{z}\left(y - \frac{SB_S(\xi)}{S+1}\right)W_{eq}^\xi(y)dy}{D_2(z)W_{eq}^\xi(z)}dz, \quad (452)$$

where

$$\frac{\partial}{\partial \xi}W_{eq}^\xi(z) = \frac{\operatorname{csch}(\xi/2S) - (2S+1)\operatorname{csch}(\xi+\xi/2S)(\cosh\xi - z\sinh\xi)}{2S[\cosh(\xi/2S) + z\sinh(\xi/2S)]}W_{eq}^\xi(z).$$

For the limiting case $S = 1/2$, τ_{cor} is equal to τ_{int} as yielded by the closed expression equation (443), while in the classical limit $S \to \infty$, Eq. (452) becomes

$$\tau_{cor} = \frac{\tau_N \xi \operatorname{csch}\xi}{1 + \xi^{-2} - \coth^2\xi}\int_{-1}^{1}\left[z - \coth\xi + e^{-\xi(1+z)}(1 + \coth\xi)\right]^2\frac{e^{\xi z}dz}{1 - z^2} \quad (453)$$

concurring with the result for classical spins [5, ch. 7]. As far as the spin number dependence of τ_{cor} for $\xi \gg 1$ is concerned, an asymptotic formula for $\tau_{cor} = \tau_{int}|_{\delta\to 0}$ is given by Eq. (447). Generally, τ_{cor} varies smoothly from power law-like behavior ($\tau_{cor} \sim \tau_N/\xi$) as $S \to \infty$ to exponential decrease $\tau_{cor} \sim \tau_N \operatorname{csch}\xi$ for $S = 1/2$ and is plotted from the exact equation (452) in Fig. 16 as a function of ξ for various S; the asymptotic equation (447) is also shown for comparison.

We remarked before that the linear response has been studied previously by Garcia-Palacios and Zueco [81] using the spin density matrix. They also gave an explicit expression for the linear-response integral relaxation time, which was
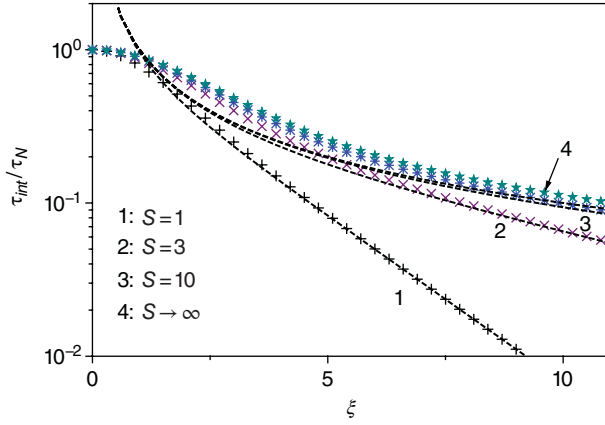
Figure 16. Normalized correlation time τ_{cor}/τ_N of $C_\parallel(t)$ from Eq. (452) as a function of ξ for various S (symbols). Dashed lines: Eq. (447) (Color on line).

first derived by Garanin [80]. He derived his formula pertaining to a *uniaxial nanomagnet in a uniform field* with the Hamiltonian $\hat{H}_S = -\hbar\omega_0\hat{S}_Z - D\hat{S}_Z^2$, which is also valid in the limit $D \to 0$, corresponding to our case. By applying his method [80] to the symmetrized form of the collision kernel given by Eq. (558), the corresponding equations are (see for details Section III.C.3, Eq. (521))

$$\tau_{int} = \frac{2\tau_N}{\left\langle \hat{S}_Z \right\rangle_{\mathrm{I}} - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}}} \sum_{k=1-S}^{S} \frac{\sum\limits_{m=k}^{S} \left(\rho_m^{\mathrm{I}} - \rho_m^{\mathrm{II}} \right) \sum\limits_{m'=k}^{S} \left(m' - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}} \right) \rho_{m'}^{\mathrm{II}}}{[S(S+1) - k(k-1)]\sqrt{\rho_k^{\mathrm{II}}\rho_{k-1}^{\mathrm{II}}}}, \qquad (454)$$

$$\tau_{cor} = \frac{2\tau_N}{\chi} \sum_{k=1-S}^{S} \frac{\left(\sum\limits_{m=k}^{S} \left(m - \left\langle \hat{S}_Z \right\rangle_0 \right) \rho_m^{\mathrm{II}} \right)^2}{[S(S+1) - k(k-1)]\sqrt{\rho_k^{\mathrm{II}}\rho_{k-1}^{\mathrm{II}}}}. \qquad (455)$$

where

$$\rho_n^i = \frac{e^{\xi_i n/S}}{\sum\limits_{m=-S}^{S} e^{\xi_i m/S}}, \quad \left\langle \hat{S}_Z \right\rangle_i = \sum_{m=-S}^{S} m\rho_m^i, \quad \chi = \sum_{m=-S}^{S} m^2\rho_m - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}}^2.$$

Although the integral and series expressions given by Eqs. (442), (452), (454), and (455), respectively, have outwardly very different forms, nevertheless numerical calculation shows that both yield *identical* results establishing an essential corollary between the phase space and density matrix methods.

6. *Single-Mode Approximation*

Although the continued fraction solution given before is effective in numerical calculations, it has one significant drawback, namely, the qualitative behavior of the system is not at all obvious in a physical sense. Thus, to gain a physical understanding of the relaxation process, we shall use the single-mode approximation suggested by Shibata *et al.* [38, 39] and Kalmykov *et al.* [62] for the relaxation of quantum and classical spins. We first recall that the spectrum $\tilde{f}_1(\omega)$ from Eq. (435) on Fourier inversion indicates that the time behavior of the relaxation function $f_1(t)$ in general comprises $2S$ exponentials

$$f_1(t) = f_1(0) \sum_{k=1}^{2S} c_k e^{-\lambda_k t}, \tag{456}$$

where the λ_k are the eigenvalues of the tridiagonal system matrix $\mathbf{X}$ with the matrix elements

$$(\mathbf{X})_{qp} = \delta_{pq+1} q_p^- + \delta_{pq} q_p + \delta_{pq-1} q_p^+.$$

In the frequency domain, the corresponding spectrum $\tilde{f}_1(\omega)$ is thus the series of $2S$ Lorentzians

$$\tilde{f}_1(\omega) = f_1(0) \sum_{k=1}^{2S} \frac{c_k}{\lambda_k + i\omega}. \tag{457}$$

According to Eq. (457), the finite number of relaxation modes (corresponding to the eigenvalues λ_k) each contribute to the spectrum $\tilde{f}_1(\omega)$. However, as we shall see later, these *near-degenerate* individual modes are indistinguishable in the spectrum $\tilde{f}_1(\omega)$ appearing merely as a single band suggesting that $\tilde{f}_1(\omega)$ may be approximated by the *single* Lorentzian

$$\frac{\tilde{f}_1(\omega)}{f_1(0)} \approx \frac{\tau_{int}}{1 + i\omega\tau_{int}}, \tag{458}$$

where τ_{int} is given by Eq. (442). In the time domain, the single-mode approximation given by Eq. (458) amounts to the *Ansatz* that the relaxation function $f_1(t)$ as determined by Eq. (456) (comprising $2S$ exponentials) may be approximated by a *single* exponential, namely,

$$f_1(t) \approx f_1(0) e^{-t/\tau_{int}}. \tag{459}$$

Now, García-Palacios and Zueco [81, 82] have also used the single-mode approximation to evaluate the *linear* response of an isotropic spin system. In linear response, Eqs. (458) and (459) can be reformulated for the susceptibility $\chi(\omega)$ and correlation function $C(t)$ as

$$C(t) \approx e^{-t/\tau_{cor}} \tag{460}$$

and

$$\chi(\omega) \approx \frac{\chi}{1 + i\omega\tau_{cor}},\tag{461}$$

where τ_{cor} is given by Eq. (455).

In order to test the single-mode approximation, we plot in Fig. 17 the real parts of the normalized spectra $\tilde{f}_1(\omega)/f_1(0)$ as calculated both from the exact continued fraction solution (Eq. (435): solid lines) and from that approximation equation (458). Clearly, no practical difference exists between the exact continued fraction solution and the single-mode one (the maximum deviation between the corresponding curves does not exceed a few percent). Like the classical case (see 5, ch. 7), the single-mode approximation is accurate because the finite number (2S) of relaxation modes are *near degenerate* again appearing merely as a *single* high-frequency band in the spectrum. Thus, they may be effectively approximated
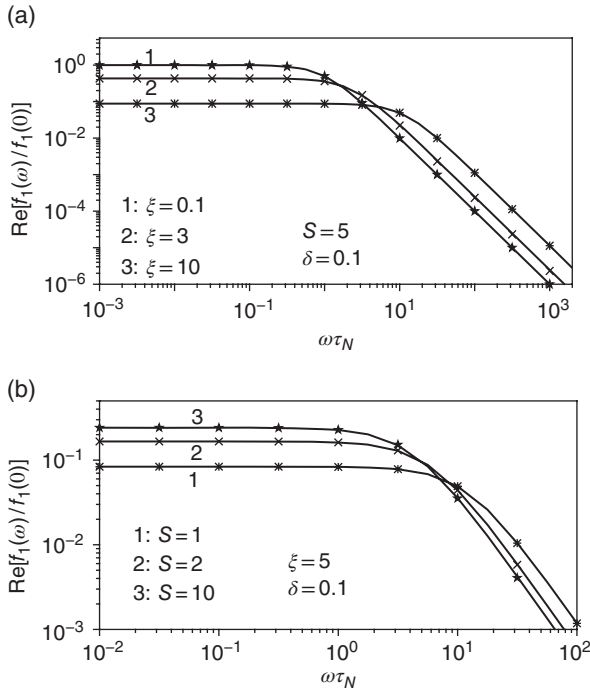
Figure 17. The real parts of the normalized spectra $\tilde{f}_1(\omega)/f_1(0)$ versus the normalized frequency $\omega\tau_N$ evaluated from the exact continued fraction solution (Eq. (435): solid lines) for (a) $S = 5, \delta = 0.1$, and various ξ and for (b) $\xi = 3, \delta = 0.1$ and various S compared with those calculated from the single Lorentzian approximation equation (458) (symbols).

by a single mode, that is, both the linear and nonlinear longitudinal relaxation for all S is accurately described by the Bloch equation

$$\frac{d}{dt} \left\langle \hat{S}_Z \right\rangle (t) + \frac{1}{T_\parallel} \left(\left\langle \hat{S}_Z \right\rangle (t) - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}} \right) = 0, \tag{462}$$

where $T_\parallel = \tau_{int}$ is the longitudinal relaxation time, $\left\langle \hat{S}_Z \right\rangle_{\mathrm{II}} = SB_S(\xi)$ is the equilibrium average of the operator $\hat{S}_Z$, and $B_S(x)$ is the Brillouin function given by Eq. (278).

We have treated nonlinear spin relaxation of noninteracting spins using phase space quasiprobability density evolution equations in configuration space via the extension of Wigner's phase space formulation of quantum mechanics to *open* systems. The calculations show that in particular limiting cases (e.g., the correlation time given by Eq. (452)), the results reduce to established ones obtained using the evolution equation for the density matrix in the second order of perturbation theory in the spin–bath coupling. Thus, we have an important check on the validity of our approach by demonstrating the equivalence of the two methods. Both exact (continued fraction) and approximate (single-mode) solutions are given. The continued fraction solution yields the dependence of the longitudinal spin relaxation on the spin number S in closed form. This solution is dominated by a single exponential having as time constant the integral relaxation time τ_{int}, which strongly depends on both S and the field strength for arbitrary S. Hence, *an accurate description in terms of a Bloch equation holds even for the nonlinear response of a giant spin*.

Thus, we have explicitly demonstrated for noninteracting spins in an external magnetic field that the existing methods of solution of the classical Fokker–Planck equation (continued fractions, which can be evaluated by iterating a simple algorithm, integral representation of relaxation times, and so on.) seamlessly carry over to the quantum case. Again, the methods suggest new closed form quantum results via the corresponding classical ones. An example being the quantum integral relaxation time, Eq. (442). We have illustrated the phase space method via the rudimentary problem of the longitudinal relaxation of a spin in a uniform magnetic field of arbitrary strength directed along the Z-axis [the relaxation of the transverse components of the magnetization can be treated in a like manner using the master equation (405) and the associated quantum recurrence equation (418)]. This problem is the simplest example of the phase space method for spins and may be considered as the rotational analog of the Agarwal problem for the translational harmonic oscillator model [120] described by the master equation equation (168). Just as with translational oscillators, the phase space master equation (419) for spins has a Fokker–Planck equation form. This is not, however, true in general, for example, for nonaxially symmetric magnetocrystalline anisotropy and external field potentials, where the corresponding master equation may have

a very complicated form. Nevertheless, the simple noninteracting spins problem indicates how one may treat the influence of spin number S on the relaxation behavior using the phase space method. A factor that is both essential in the formation of magnetic clusters and for nanomagnets in the quest for macroscopic quantum tunneling.

C.   Longitudinal Relaxation of Uniaxial Nanomagnets

In contrast to the phase space approach used before, we shall now apply the density matrix method. We shall consider a uniaxial nanomagnet of arbitrary spin number S in an external *constant* magnetic field **H** applied along the Z-axis, that is, the axis of symmetry, with the Hamiltonian $\hat{H}_S$ defined by Eq. (370) with $\sigma \neq 0$ and $\xi \neq 0$. Furthermore, we shall use the method in the form based on the relation between the averages of polarization operators and the averages of spherical harmonics as described in Section III.A.2 (see also Section II.A.4). However, as mentioned earlier, Garanin and García-Palacios *et al.* [80–82] have also treated a uniaxial nanomagnet in a uniform longitudinal field via the quantum Hubbard operator representation of the evolution equation for the spin density matrix. Now in the axially symmetric Hamiltonian equation (370), the diagonal terms of the density matrix *decouple* from the non-diagonal ones. Hence, only the former contribute to the time evolution of the longitudinal component of the spin operator, so facilitating a treatment of the problem. Thus, in order to describe the longitudinal relaxation of a uniaxial nanomagnet, in which case only the *diagonal* terms of the density matrix are involved, the evolution equation (371) with the collision kernel given by Eq. (375) simplifies to

$$\frac{\partial \hat{\rho}_S}{\partial t} = -\frac{1}{\tau_N}\left\{ e^{-\frac{\sigma}{2S^2}-\frac{\xi}{2S}}\left[\hat{S}_{-1}e^{-\frac{\sigma}{S^2}\hat{S}_0}\hat{\rho}_S, \hat{S}_{+1}\right] + e^{\frac{\sigma}{2S^2}+\frac{\xi}{2S}}\left[\hat{S}_{+1}e^{\frac{\sigma}{S^2}\hat{S}_0}\hat{\rho}_S, \hat{S}_{-1}\right] \right\}.$$
(463)

This simplified method will be described in detail in Section III.C.2. Now, the associated evolution equation for the phase space distribution function $W_S(z = \cos\vartheta, t)$ corresponding to Eq. (371) is then given by Eq. (378), namely,

$$\frac{\partial W_S}{\partial t} = \frac{1}{2\tau_N}\frac{\partial}{\partial z}\left((1-z^2)\left[\frac{\partial}{\partial z}\left(R_+^{\prime(S)}W_S\right) + z\frac{\partial}{\partial z}\left(R_-^{\prime(S)}W_S\right) + 2SR_-^{\prime(S)}W_S\right]\right)$$
(464)

(because the azimuthal angle ϕ dependence of W_S may be ignored in longitudinal relaxation). In the classical limit, Eq. (464), further reduces to the Fokker–Planck equation for a classical uniaxial nanomagnet in a dc magnetic field, namely [5, 6, 23],

$$\frac{\partial W}{\partial t} = \frac{1}{2\tau_N}\frac{\partial}{\partial z}\left[(1-z^2)\left(\frac{\partial W}{\partial z} + W\frac{\partial V}{\partial z}\right)\right],$$
(465)

where $V(z) = -\sigma z^2 - \xi z$ is the normalized classical free energy.‘

1. Calculation of the Observables

As before, we suppose that the magnitude of an external uniform dc magnetic field is suddenly altered at time $t = 0$ from $\mathbf{H_I}$ to $\mathbf{H_{II}}$ (the magnetic fields $\mathbf{H_I}$ and $\mathbf{H_{II}}$ are applied parallel to the Z-axis of the laboratory coordinate system in order to preserve axial symmetry). Thus, we study as in the classical case [5], the nonlinear transient longitudinal relaxation of a system of spins starting from an equilibrium state I, say with density matrix $\hat{\rho}_{eq}^{I}$ ($t \leq 0$) to a new equilibrium state II, say with density matrix $\hat{\rho}_{eq}^{II}$ ($t \to \infty$), see Fig. 14. Simultaneously, the longitudinal component of the spin $\langle \hat{S}_Z \rangle (t)$ relaxes from the equilibrium value $\langle \hat{S}_Z \rangle_I$ to the new value $\langle \hat{S}_Z \rangle_{II}$, the ensuing transient response being described by the relaxation function $\langle \hat{S}_Z \rangle (t) - \langle \hat{S}_Z \rangle_{II}$. The transient response so formulated is again truly *nonlinear* because the *change* in amplitude $H_I - H_{II}$ of the external dc magnetic field is now *arbitrary* (the linear response is the particular case $\beta \mu_0 \mu |H_I - H_{II}| \to 0$). Now, the equilibrium phase space distributions W_{eq}^{I} and W_{eq}^{II} corresponding to the equilibrium spin density matrices $\hat{\rho}_{eq}^{I}$ and $\hat{\rho}_{eq}^{II}$ comprise the appropriate stationary (time-independent) solutions of Eq. (464). These equilibrium distributions have been extensively studied in Sec. II.D and are given by Eq. (299), namely,

$$(S + 1/2) W_{eq}^{i}(\vartheta) = \sum_{L=0}^{2S} (L + 1/2) \langle P_L \rangle_i P_L(\cos \vartheta), \qquad (466)$$

where $i = $ I, II and $\langle P_L \rangle_i$ are the equilibrium averages of the Legendre polynomials P_L defined by Eq. (300).

As far as the transient response is concerned, according to the multi-term differential recurrence relation (389) for the relaxation functions $c_L(t) = \langle \hat{T}_{L0}^{(S)} \rangle (t) - \langle \hat{T}_{L0}^{(S)} \rangle_{II}$ in terms of polarization operators, the behavior of any selected $c_L(t)$ is coupled to that of all the others so forming as usual a *finite* hierarchy of the averages of operators (because the index L ranges only between 0 and $2S$). The solution of such a multi-term recurrence relation may always be obtained (as we saw) by rewriting it as a first-order linear matrix differential equation with constant coefficients. Thus, we first construct the column vector $\mathbf{C}(t)$ such that

$$\mathbf{C}(t) = \begin{pmatrix} c_1(t) \\ c_2(t) \\ \vdots \\ c_{2S}(t) \end{pmatrix}. \qquad (467)$$

The column vector $\mathbf{C}(t)$ formed by Eq. (467) now contains just $2S$ rows (the index L ranges between 1 and $2S$) since the evolution equation for the function $c_0(t)$ is simply $\partial_t c_0(t) = 0$ with the trivial solution $c_0(t) = $ const. The initial conditions

for the relaxation functions $c_L(t)$ are

$$c_L(0) = \left\langle \hat{T}_{L0}^{(S)} \right\rangle_{\mathrm{I}} - \left\langle \hat{T}_{L0}^{(S)} \right\rangle_{\mathrm{II}}. \tag{468}$$

Hence, the matrix representation of the recurrence equations for the functions $c_L(t)$ becomes the linear matrix differential equation

$$\dot{\mathbf{C}}(t) + \mathbf{X}\mathbf{C}(t) = 0, \tag{469}$$

where $\mathbf{X}$ is the $2S \times 2S$ system matrix with matrix elements given by

$$(\mathbf{X})_{n,m} = -\tau_N^{-1} g_{n,m}^S \tag{470}$$

with $g_{n,m}^S$ given by Eq. (390). For example, for $S = 1$, the system matrix $\mathbf{X}$ takes the simple two-by-two form

$$\mathbf{X} = \frac{e^{-\sigma/2}}{\tau_N} \begin{pmatrix} \cosh\dfrac{\xi_{\mathrm{II}}}{2} & \dfrac{1}{\sqrt{3}}(2e^{\sigma} - 1)\sinh\dfrac{\xi_{\mathrm{II}}}{2} \\ -\sqrt{3}\sinh\dfrac{\xi_{\mathrm{II}}}{2} & (2e^{\sigma} + 1)\cosh\dfrac{\xi_{\mathrm{II}}}{2} \end{pmatrix}. \tag{471}$$

Now, in general, the solution of the homogeneous matrix equation (469) is [96]

$$\mathbf{C}(t) = e^{-\mathbf{X}t}\mathbf{C}(0), \tag{472}$$

which may be written in a more useful form as

$$\mathbf{C}(t) = \mathbf{U}e^{-\Lambda t}\mathbf{U}^{-1}\mathbf{C}(0), \tag{473}$$

where Λ is a diagonal matrix composed of the eigenvalues $\lambda_1, \lambda_2, \ldots \lambda_{2S}$ of the system matrix $\mathbf{X}$ and $\mathbf{U}$ is a right eigenvector matrix composed of all the eigenvectors of $\mathbf{X}$, namely,

$$\mathbf{U}^{-1}\mathbf{X}\mathbf{U} = \Lambda.$$

All the λ_k are real and positive. The one-sided Fourier transform of Eq. (472) also yields the spectrum $\tilde{\mathbf{C}}(\omega)$ of the column vector, namely,

$$\tilde{\mathbf{C}}(\omega) = \int_0^\infty \mathbf{C}(t)e^{-i\omega t}dt = (\mathbf{X} + i\omega\,\mathbf{I})^{-1}\,\mathbf{C}(0). \tag{474}$$

The function $\tilde{c}_1(0)$ is the first row of the column vector $\tilde{\mathbf{C}}(0)$ which itself in accordance with Eq. (474) is given by

$$\tilde{\mathbf{C}}(0) = (\mathbf{X})^{-1}\,\mathbf{C}(0). \tag{475}$$

The formal matrix solutions (472) and (474) will then yield the longitudinal relaxation function $\left\langle \hat{S}_Z \right\rangle (t) - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}}$ (cf. Eq. 86), namely,

$$\left\langle \hat{S}_Z \right\rangle (t) - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}} = \sqrt{\frac{S(S+1)(2S+1)}{3}} c_1(t), \tag{476}$$

and its spectrum as well as the effective and integral relaxation times from their definitions (see Appendix E and Ref. 5)

$$\tau_{ef} = -\frac{c_1(0)}{\dot{c}_1(0)}, \tag{477}$$

$$\tau_{int} = \frac{1}{\left\langle \hat{S}_Z \right\rangle_{\mathrm{I}} - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}}} \int_0^t \left[\left\langle \hat{S}_Z \right\rangle (t) - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}} \right] dt = \frac{\tilde{c}_1(0)}{c_1(0)}, \tag{478}$$

where

$$\tilde{c}_1(\omega) = \int_0^\infty c_1(t) e^{-i\omega t} dt.$$

In accordance with the matrix Eqs. (473) and (475), the relaxation function $c_1(t)$ and the effective integral relaxation times are given by [5]

$$c_1(t) = \sum_{k=1}^{2S} u_{1k} r_k e^{-\lambda_k t}, \tag{479}$$

$$\tau_{ef} = \frac{\sum_{k=1}^{2S} u_{1,k} r_k}{\sum_{k=1}^{2S} u_{1,k} r_k \lambda_k}, \tag{480}$$

$$\tau_{int} = \frac{\sum_{k=1}^{2S} u_{1k} r_k \lambda_k^{-1}}{\sum_{k=1}^{2S} u_{1k} r_k}, \tag{481}$$

where the u_{lk} are the matrix elements of the eigenvector matrix $\mathbf{U}$ defined before and r_k are those of the associated column vector $\mathbf{U}^{-1} \mathbf{C}(0)$. As usual, both the integral and effective relaxation times each contain contributions from *all* the eigenvalues λ_k, and so they characterize the overall relaxation behavior, while the inverse of the smallest nonvanishing eigenvalue λ_1 characterizes the spin reversal time. Furthermore, because the influence of the high-frequency relaxation modes on the low-frequency relaxation may often be ignored, λ_1 usually provides adequate information concerning the low-frequency dynamics of the system (see Section III.C.3).

Obviously, the matrix method also allows us to evaluate the *linear response* of a spin system due to infinitesimally small changes in the magnitude of the dc field, evaluated in Refs. [80–82] via the spin density matrix. Thus, we again suppose that the uniform dc field $\mathbf{H}_{II}$ is directed along the Z-axis of the laboratory coordinate system and that a small probing field $\mathbf{H}_1$ ($\mathbf{H}_1 \parallel \mathbf{H}_{II}$), having been applied to the assembly of spins in the distant past ($t = -\infty$) so that equilibrium conditions obtain at time $t = 0$, is switched off at $t = 0$. The only difference lies in the initial conditions. Instead of the *general* equation (468) pertaining to the transient response of *arbitrary strength*, in *linear response*, $\xi_I - \xi_{II} = \varepsilon << 1$, they become

$$
\begin{aligned}
c_L(0) &= \left\langle \hat{T}_{L0}^{(S)} \right\rangle(0) - \left\langle \hat{T}_{L0}^{(S)} \right\rangle_{II} \\
&\approx \frac{\varepsilon}{\beta} \mathrm{Tr} \left\{ \hat{\rho}_{eq}^{II} \int_0^\beta \hat{S}_0(-i\lambda\hbar) d\lambda \left(\hat{T}_{L0}^{(S)} - \left\langle \hat{T}_{L0}^{(S)} \right\rangle_{II} \hat{I}^{(S)} \right) \right\}.
\end{aligned}
\tag{482}
$$

Here, we have used the following identity concerning an exponential function of two operators [75]

$$
e^{\beta(\hat{a}+\hat{b})} = e^{\beta\hat{a}} \left(1 + \int_0^\beta e^{-\lambda\hat{a}} \hat{b} e^{\lambda(\hat{a}+\hat{b})} d\lambda \right).
\tag{483}
$$

Furthermore, $c_1(t)/c_1(0)$ reduces to the normalized equilibrium longitudinal correlation function $C(t)$ given by [33,75] [cf. Eq. (448)]

$$
\begin{aligned}
C(t) &= \lim_{\varepsilon \to 0} \frac{c_1(t)}{c_1(0)} \\
&= \frac{1}{\beta\chi} \left\langle \int_0^\beta \left[\hat{S}_Z(-i\lambda\hbar) - \left\langle \hat{S}_Z \right\rangle_{II} \right] \left[\hat{S}_Z(t) - \left\langle \hat{S}_Z \right\rangle_{II} \right] d\lambda \right\rangle_{II},
\end{aligned}
\tag{484}
$$

where

$$
\begin{aligned}
\chi &= \frac{1}{\beta} \left\langle \int_0^\beta \left[\hat{S}_Z(-i\lambda\hbar) - \left\langle \hat{S}_Z \right\rangle_{II} \right] \left[\hat{S}_Z(0) - \left\langle \hat{S}_Z \right\rangle_{II} \right] d\lambda \right\rangle_{II} \\
&\approx \left\langle \hat{S}_Z^2 \right\rangle_{II} - \left\langle \hat{S}_Z \right\rangle_{II}^2
\end{aligned}
\tag{485}
$$

is the normalized static susceptibility. Then, we have the dynamic susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ [75], namely,

$$
\frac{\chi(\omega)}{\chi} = 1 - i\omega\tilde{C}(\omega),
\tag{486}
$$

where the one-sided Fourier transform $\tilde{C}(\omega)$ is defined by Eq. (451). We have also as in the classical case [5] the integral and effective relaxation times,

$$\tau_{cor} = \tilde{C}(0), \tag{487}$$

$$\tau_{ef} = -\frac{1}{\dot{\tilde{C}}(0)}, \tag{488}$$

which now represent the characteristic times governing the behavior of the autocorrelation function $C(t)$.

According to the formal definitions embodied in Eqs. (479) and (486), the dynamic susceptibility is once more a finite sum of Lorentzians, namely,

$$\frac{\chi(\omega)}{\chi} = \sum_{p=1}^{2S} \frac{c_p}{1 + i\omega/\lambda_p}, \tag{489}$$

where

$$c_p = \frac{u_{1,p} r_p}{\sum\limits_{m=1}^{2S} u_{1,m} r_m}$$

and

$$\sum_{p=1}^{2S} c_p = 1.$$

Moreover, in the low- ($\omega \to 0$) and high- ($\omega \to \infty$) frequency limits, the behavior of the dynamic susceptibility can be easily evaluated as in the classical case [5]. For example by means of Eqs. (481) and (480), we have from the general equation (489) for the limits $\omega \to 0$ and for $\omega \to \infty$, respectively

$$\chi(\omega) \approx \chi \left(1 - i\omega\tau_{cor} + \ldots\right), \quad \omega \to 0, \tag{490}$$

$$\chi(\omega) \sim \chi \left(i\omega\tau_{ef}\right)^{-1} + \ldots, \quad \omega \to \infty. \tag{491}$$

Furthermore, the equilibrium averages $\langle \hat{S}_Z \rangle_{\mathrm{I}}$, $\langle \hat{S}_Z \rangle_{\mathrm{II}}$, and $\langle \hat{S}_Z^2 \rangle_{\mathrm{II}}$ can all be expressed in terms of either the density matrix or the phase space distribution as

$$\langle \hat{S}_Z \rangle_i = \sum_{m=-S}^{S} m \rho_m^i, \tag{492}$$

$$\langle \hat{S}_Z^2 \rangle_i = \sum_{m=-S}^{S} m^2 \rho_m^i, \tag{493}$$

$$\left\langle \hat{S}_Z \right\rangle_i = \left(S + \tfrac{1}{2}\right)(S+1)\int_{-1}^{1} z W_S^i(z)\,dz, \tag{494}$$

$$\left\langle \hat{S}_Z^2 \right\rangle_{\mathrm{II}} = \left(S + \tfrac{1}{2}\right)(S+1)\int_{-1}^{1} \left[(S + \tfrac{3}{2})z^2 - \tfrac{1}{2}\right] W_S^{\mathrm{II}}(z)\,dz, \tag{495}$$

because the Weyl symbols of the operators $\hat{S}_Z$ and $\hat{S}_Z^2$ are, respectively,

$$S_Z = (S+1)\cos\vartheta$$

and

$$S_Z^2 = (S+1)\left[(S + \tfrac{3}{2})\cos^2\vartheta - \tfrac{1}{2}\right].$$

Our method allows one to calculate numerically the integral (τ_{ef} and τ_{cor}), effective (τ_{ef}), and longest ($\tau = 1/\lambda_1$) relaxation times as well as the dynamic susceptibility $\chi(\omega)$ for a uniaxial nanomagnet. Moreover, all these observables can be calculated analytically.

2. Analytic Equations for the Characteristic Relaxation Times and Dynamic Susceptibility

Although, in general, the method of determining observables based on the correspondence between averages of polarization operators discussed in Sections II.A.4 and III.A.2 circumvent the phase space equation a much simpler method of treating axially symmetric problem exists. This is so because as already mentioned, for the axially symmetric Hamiltonian equation (370), the diagonal elements of the density matrix *decouple* from the non-diagonal ones. Hence, only the former contribute to the time evolution, so forming the basis of our simple treatment which we now explain. To appreciate this, we first transform the reduced density matrix evolution equation (463) into an evolution equation for its *individual* matrix elements. Thus, we have directly from Eq. (463) a three-term differential recurrence equation for the *diagonal* matrix elements $\rho_m = \rho_{mm}$ of the density matrix, namely,

$$\tau_N \frac{\partial \rho_m(t)}{\partial t} = q_m^- \rho_{m-1}(t) + q_m \rho_m(t) + q_m^+ \rho_{m+1}(t), \quad t > 0, \tag{496}$$

where $m = -S, -S+1, \ldots, S$,

$$q_m = -a_m^- e^{-(2m-1)\frac{\sigma}{2S^2} - \frac{\xi_{\mathrm{II}}}{2S}} - a_m^+ e^{(2m+1)\frac{\sigma}{2S^2} + \frac{\xi_{\mathrm{II}}}{2S}}, \tag{497}$$

$$q_m^\pm = a_m^\pm e^{\mp(2m\pm1)\frac{\sigma}{2S^2} \mp \frac{\xi_{\mathrm{II}}}{2S}}, \tag{498}$$

$$a_m^\pm = -S_{mm\pm1}^{\mp1} S_{m\pm1m}^{\pm1} = (S \mp m)(S \pm m + 1)/2. \tag{499}$$

Here

$$S^{\pm 1}_{m\pm 1 m} = \mp \sqrt{(S \mp m)(S \pm m + 1)/2}$$

(cf. Eq. A.7) are the matrix elements of the spherical spin operators $\hat{S}_{\pm 1}$. Equation (496) is accompanied by the initial condition $\rho_m(0) = \rho^{\mathrm{I}}_m$. Because of our usual *Ansatz* that the equilibrium spin density matrix $\hat{\rho}_{eq}$ must render the collision kernel zero, substitution of the final equilibrium matrix element $\rho^{\mathrm{II}}_m = e^{\sigma m^2/S^2 + \xi_{\mathrm{II}} m/S}/Z^{\mathrm{II}}_S$ with partition function $Z^{\mathrm{II}}_S = \sum_{m=-S}^{S} e^{\sigma m^2/S^2 + \xi_{\mathrm{II}} m/S}$ into the right-hand side of Eq. (496) requires

$$q^{-}_m \rho^{\mathrm{II}}_{m-1} + q_m \rho^{\mathrm{II}}_m + q^{+}_m \rho^{\mathrm{II}}_{m+1} = 0. \tag{500}$$

Consequently, ρ^{II}_m is by inspection the stationary solution of Eq. (496).

To determine the integral relaxation time as defined by Eq. (478), we introduce the set of relaxation functions $f_m(t)$ defined by

$$f_m(t) = \rho_m(t) - \rho^{\mathrm{II}}_m. \tag{501}$$

Then, the $f_m(t)$ also satisfy the recurrence equation (496) with the initial conditions

$$f_m(0) = \rho^{\mathrm{I}}_m - \rho^{\mathrm{II}}_m. \tag{502}$$

Because

$$\left\langle \hat{S}_Z \right\rangle (t) - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}} = \sum_{m=-S}^{S} m f_m(t)$$

and

$$\left\langle \hat{S}_Z \right\rangle (0) - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}} = \left\langle \hat{S}_Z \right\rangle_{\mathrm{I}} - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}},$$

the Fourier–Laplace transform $\tilde{c}_1(\omega)/c_1(0)$ of the normalized relaxation function $c_1(t)/c_1(0)$ is

$$\frac{\tilde{c}_1(\omega)}{c_1(0)} = \frac{1}{\left\langle \hat{S}_Z \right\rangle_{\mathrm{I}} - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}}} \sum_{m=-S}^{S} m \tilde{f}_m(\omega), \tag{503}$$

so that the integral relaxation time is as usual by definition (cf. Eq. 478)

$$\tau_{int} = \frac{1}{\left\langle \hat{S}_Z \right\rangle_{\mathrm{I}} - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}}} \sum_{m=-S}^{S} m \tilde{f}_m(0), \tag{504}$$

where

$$\left\langle \hat{S}_Z \right\rangle_i = \sum_{m=-S}^{S} m\rho_m^i. \tag{505}$$

The spectrum $\tilde{c}_1(\omega)/c_1(0)$ and the integral relaxation time τ_{int} can now be calculated analytically using continued fractions, which starting from Eq. (496) we describe as follows. For convenience, we first introduce a new index n defined as $n = m+S$. Thus, the differential recurrence equation (496) can then be rearranged as one for the relaxation functions $f_n(t)$ defined by Eq. (501), namely,

$$\tau_N \frac{\partial f_n}{\partial t} = p_n^- f_{n-1} + p_n f_n + p_n^+ f_{n+1}, \tag{506}$$

where the new coefficients $p_n^\pm$ and p_n are (cf. Eqs. 497–499)

$$p_n = -\frac{n(2S-n+1)}{2} e^{-(2n-2S+1)\frac{\sigma}{2S^2} - \frac{\xi_{\text{II}}}{2S}}$$
$$- \frac{(n+1)(2S-n)}{2} e^{(2n-2S+1)\frac{\sigma}{2S^2} + \frac{\xi_{\text{II}}}{2S}} \tag{507}$$

$$p_n^+ = \frac{1}{2}(2S-n)(n+1)e^{-(2n-2S-1)\frac{\sigma}{2S^2} - \frac{\xi_{\text{II}}}{2S}}, \tag{508}$$

$$p_n^- = \frac{n}{2}(2S-n+1)e^{(2n-2S-1)\frac{\sigma}{2S^2} + \frac{\xi_{\text{II}}}{2S}}. \tag{509}$$

Consequently, the new recurrence relation given Eq. (506) can be written in the *homogeneous* matrix form

$$\tau_N \dot{\mathbf{F}}(t) = \mathbf{\Pi} \cdot \mathbf{F}(t), \tag{510}$$

where the column vector $\mathbf{F}(t)$ and the tridiagonal system matrix $\mathbf{\Pi}$ are

$$\mathbf{F}(t) = \begin{pmatrix} f_0(t) \\ f_1(t) \\ \vdots \\ f_{2S}(t) \end{pmatrix}, \tag{511}$$

$$\mathbf{\Pi} = \begin{pmatrix} p_0 & p_0^+ & 0 & \cdots & & 0 \\ p_1^- & p_1 & p_1^+ & \cdots & & \vdots \\ \vdots & \vdots & \vdots & \ddots & & p_{2S-1}^+ \\ 0 & \cdots & 0 & & p_{2S}^- & p_{2S} \end{pmatrix}. \tag{512}$$

The tridiagonal system matrix $\mathbf{\Pi}$ has exactly the same eigenvalues as the actual system matrix $\mathbf{X}$ given by Eq. (470) except that it possesses an additional zero

eigenvalue $\lambda_0 = 0$ corresponding to the thermal equilibrium state. Clearly, the matrix recurrence given by equation (510) could again be solved numerically by the matrix methods described in Section II.A.4. Rather, we prefer to obtain the *exact analytic solution* in terms of continued fractions. Applying the general method of solution of inhomogeneous three-term recurrence relations to the Fourier–Laplace transform of the scalar equation (506) [5, section 2.7.3], we have the solution

$$\tilde{f}_n(\omega) = \Delta_n(\omega)p_n^-\tilde{f}_{n-1}(\omega) + \tau_N\left(p_{n-1}^+\right)^{-1}\sum_{l=n}^{2S}\prod_{k=n}^{l}\left(p_{k-1}^+\Delta_k(\omega)\right)f_l(0), \quad (513)$$

where $\Delta_n(\omega)$ are the continued fractions defined by the two-term recurrence equation

$$\Delta_n(\omega) = \frac{1}{i\omega\tau_N - p_n - p_n^+ p_{n+1}^- \Delta_{n+1}(\omega)}$$

with $0 \leq n \leq 2S$ and $\Delta_{2S+1}(\omega) = 0$. The spectrum $\tilde{c}_1(\omega)/c_1(0)$ from the definition Eq. (503) is then given by

$$\frac{\tilde{c}_1(\omega)}{c_1(0)} = \frac{1}{\left\langle\hat{S}_Z\right\rangle_{\mathrm{I}} - \left\langle\hat{S}_Z\right\rangle_{\mathrm{II}}}\sum_{n=1}^{2S}n\tilde{f}_n(\omega). \quad (514)$$

For $\omega = 0$, Eq. (513) simplifies yielding the two-term recurrence equation

$$\tilde{f}_n(0) = d_n\tilde{f}_{n-1}(0) + r_n, \quad (515)$$

where the coefficients are

$$d_n = e^{(2n-2S-1)\frac{\sigma}{S^2}+\frac{\xi_{\mathrm{II}}}{S}},$$

$$r_n = \frac{2\tau_N e^{(2n-2S-1)\frac{\sigma}{2S^2}+\frac{\xi_{\mathrm{II}}}{2S}}}{n(2S-n+1)}\sum_{l=n}^{2S}f_l(0)$$

because $\Delta_n(0) = \left(p_{n-1}^+\right)^{-1}$. However, the three-term recurrence equations for the relaxation functions defined by Eq. (506) are no longer *linearly independent*, because the determinant of the matrix $\mathbf{\Pi}$ generated from Eq. (506) is zero $(\det \mathbf{\Pi} = 0)$. Thus, all the subsequent $\tilde{f}_n(0)$ needed to calculate the integral relaxation time can be determined only in terms of $\tilde{f}_0(0)$. However, in order to calculate $\tilde{f}_0(0)$, we can now utilize the normalization properties of the density matrix, namely,

$$\sum_{m=-S}^{S}f_m(t) = \sum_{m=-S}^{S}\left(\rho_m(t) - \rho_m^{\mathrm{II}}\right) = 0,$$

so that

$$\sum_{m=-S}^{S} \tilde{f}_m(0) = 0. \tag{516}$$

Now because of Eqs. (515) and (516), we have the identity

$$\tilde{f}_0(0) + \sum_{n=1}^{2S} \left(d_n \tilde{f}_{n-1}(0) + r_n \right)$$

$$= \tilde{f}_0(0) + d_1 \tilde{f}_0(0) + r_1 + \sum_{n=2}^{2S} \left(d_n d_{n-1} \tilde{f}_{n-2}(0) + d_n r_{n-1} + r_n \right) \tag{517}$$

$$= \tilde{f}_0(0) + \tilde{f}_0(0) \sum_{n=1}^{2S} \prod_{l=1}^{n} d_l + \sum_{n=1}^{2S} \frac{r_n}{d_n} \sum_{k=n}^{2S} \prod_{l=n}^{k} d_l = 0,$$

where the products are given by

$$\frac{1}{d_n} \prod_{l=n}^{k} d_l = \frac{e^{(k-S)^2 \frac{\sigma}{S^2} + (k-S) \frac{\xi_{\mathrm{II}}}{S}}}{e^{(n-S)^2 \frac{\sigma}{S^2} + (n-S) \frac{\xi_{\mathrm{II}}}{S}}},$$

$$\prod_{l=1}^{n} d_l = e^{\xi_{\mathrm{II}} - \sigma} e^{(n-S)^2 \frac{\sigma}{S^2} + (n-S) \frac{\xi_{\mathrm{II}}}{S}}.$$

However,

$$e^{(2k-1) \frac{\sigma}{2S^2} + \frac{\xi_{\mathrm{II}}}{2S}} = \sqrt{\frac{\rho_k^{\mathrm{II}}}{\rho_{k-1}^{\mathrm{II}}}}, \tag{518}$$

so that Eq. (517) immediately yields a closed form expression for $\tilde{f}_0(0)$, namely,

$$\tilde{f}_0(0) = -\frac{2\tau_N e^{\sigma - \xi_{\mathrm{II}}}}{Z} \sum_{k=1-S}^{S} \frac{\sum_{m=k}^{S} \left(\rho_m^{\mathrm{I}} - \rho_m^{\mathrm{II}} \right) \sum_{j=k}^{S} \rho_j^{\mathrm{II}}}{[S(S+1) - k(k-1)] \sqrt{\rho_k^{\mathrm{II}} \rho_{k-1}^{\mathrm{II}}}}. \tag{519}$$

Thus, we have

$$\sum_{n=1}^{2S} n \tilde{f}_n(0) = \tilde{f}_0(0) e^{\xi_{\mathrm{II}} - \sigma} \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}}$$

$$+ \sum_{n=1}^{2S} r_n e^{-(n-S)^2 \frac{\sigma}{S^2} - (n-S) \frac{\xi_{\mathrm{II}}}{S}} \sum_{k=n}^{2S} k e^{(k-S)^2 \frac{\sigma}{S^2} + (k-S) \frac{\xi_{\mathrm{II}}}{S}}. \tag{520}$$

Hence, by substituting Eqs. (519) and (520) into the definition equation (504), we finally have the integral relaxation time rendered in explicit series form as follows:

$$
\tau_{int} = \frac{\sum\limits_{n=1}^{2S} n \tilde{f}_n(0)}{\left\langle \hat{S}_Z \right\rangle_{\mathrm{I}} - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}}}
$$

$$
= \frac{2\tau_N}{\left\langle \hat{S}_Z \right\rangle_{\mathrm{I}} - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}}} \sum_{k=1-S}^{S} \frac{\sum\limits_{m=k}^{S} \left(\rho_m^{\mathrm{I}} - \rho_m^{\mathrm{II}} \right) \sum\limits_{j=k}^{S} \left(j - \left\langle \hat{S}_Z \right\rangle_{\mathrm{II}} \right) \rho_j^{\mathrm{II}}}{[S(S+1) - k(k-1)] \sqrt{\rho_k^{\mathrm{II}} \rho_{k-1}^{\mathrm{II}}}}.
\tag{521}
$$

Both the eigensolution given by the formal equation (481) and the explicit equation (521) as determined from the definition of the integral relaxation time via the zero-frequency limit of the normalized relaxation function $\tilde{c}_1(\omega)/c_1(0)$ yield exactly the same numerical result. Thus, τ_{int} for various nonlinear transient responses (i.e., the rise, decay, and rapidly reversing field transients) may be easily evaluated from the explicit equation (521). Equation (521) is also valid for an *arbitrary* axially symmetric potential $\hat{H}_S(\hat{S}_Z)$, because the precise form of the potential is involved only in the *equilibrium* matrix elements of the density operator ρ_m^{II} and in the averages $\left\langle \hat{S}_Z \right\rangle_{\mathrm{I}}$ and $\left\langle \hat{S}_Z \right\rangle_{\mathrm{II}}$. Furthermore, it is useful to recall that in the classical limit $S \to \infty$, the nonlinear integral relaxation time τ_{int} of the longitudinal relaxation function $c_1(t) = \langle \cos \vartheta \rangle(t) - \langle \cos \vartheta \rangle_{\mathrm{II}}$ of a classical uniaxial nanomagnet with a free energy density

$$
\beta V(\vartheta) = -\sigma \cos^2 \vartheta - \xi_{\mathrm{II}} \cos \vartheta
\tag{522}
$$

is given by [5] (see Appendix D for details)

$$
\tau_{int} = \frac{2\tau_N}{\langle \cos \vartheta \rangle_{\mathrm{I}} - \langle \cos \vartheta \rangle_{\mathrm{II}}} \int_{-1}^{1} \frac{\Phi(z)\Psi(z)e^{-\sigma z^2 - \xi_{\mathrm{II}} z}}{1 - z^2} \, dz,
\tag{523}
$$

where

$$
\Phi(z) = \int_{-1}^{z} [W_{\mathrm{I}}(x) - W_{\mathrm{II}}(x)] \, dx
$$

$$
= \frac{\pi^{1/2} e^{-\sigma h_{\mathrm{II}}^2}}{2\sigma^{1/2} Z_{\mathrm{II}}} \left\{ \mathrm{erfi}[(z + h_{\mathrm{II}})\sqrt{\sigma}] + \mathrm{erfi}[(1 - h_{\mathrm{II}})\sqrt{\sigma}] \right\}
$$

$$
- \frac{\pi^{1/2} e^{-\sigma h_{\mathrm{I}}^2}}{2\sigma^{1/2} Z_{\mathrm{I}}} \left\{ \mathrm{erfi}[(z + h_{\mathrm{I}})\sqrt{\sigma}] + \mathrm{erfi}[(1 - h_{\mathrm{I}})\sqrt{\sigma}] \right\},
$$

$$\Psi(z) = \int_{-1}^{z} (x - \langle\cos\rangle_{II})e^{\sigma(x^2+2h_{II}x)}dx$$

$$= \frac{1}{2\sigma}\left[e^{\sigma(z^2+2h_{II}z)} - e^{\sigma(1-2h_{II})}\right] - e^{\sigma(1-h_{II}^2)}\frac{\sqrt{\pi}\sinh(2\sigma h_{II})}{2\sqrt{\sigma^3}Z_{II}}$$

$$\times\left\{\mathrm{erfi}[(z+h_{II})\sqrt{\sigma}] + \mathrm{erfi}[(1-h_{II})\sqrt{\sigma}]\right\},$$

$$\langle\cos\vartheta\rangle_i = \frac{e^{\sigma}\sinh(2\sigma h_i)}{\sigma Z_i} - h_i, \tag{524}$$

$$Z_i = \frac{e^{-\sigma h_i^2}}{2}\sqrt{\frac{\pi}{\sigma}}\left\{\mathrm{erfi}[(1+h_i)\sqrt{\sigma}] + \mathrm{erfi}[(1-h_i)\sqrt{\sigma}]\right\}, \tag{525}$$

where $h_i = \xi_i/(2\sigma)$ and the error function of imaginary argument $\mathrm{erfi}(x)$ is [105]

$$\mathrm{erfi}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{t^2}dt. \tag{526}$$

The nonlinear relaxation time τ_{int} for the rise transient response as a function of the anisotropy parameter σ and the spin number S is plotted in Fig. 18, indicating a pronounced dependence of this time on the field (ξ_{II}), anisotropy (σ), and spin (S) parameters; in particular that time decreases with increasing field strength ξ_{II} It is apparent from Fig. 18 that for large S, the quantum solutions reduce to the corresponding classical ones. Typical values of S for the quantum classical crossover are $\sim$20–40. *The smaller the anisotropy σ, the smaller the S value required for convergence of the quantum equations to the classical ones.*

In Fig. 19, we have plotted the real part of the normalized relaxation function spectrum $\tilde{c}_1(\omega)/c_1(0)$ versus the normalized frequency $\omega\tau_N$ for the rise transient response, $\xi_I = 0 \rightarrow \xi_{II} \neq 0$. Like the classical case [5], knowledge of λ_1 alone is enough to accurately predict the low-frequency part of $\tilde{c}_1(\omega)/c_1(0)$ as well as the long-time behavior of the relaxation function $c_1(t)/c_1(0)$. Here, the single-mode approximation

$$\frac{\tilde{c}_1(\omega)}{c_1(0)} \approx \frac{\tau_{int}}{1 + i\omega/\lambda_1}, \tag{527}$$

where τ_{int} is given by Eq. (521) and λ_1 is the smallest nonvanishing eigenvalue of the system matrix $\mathbf{X}$ defined by Eq. (470), is shown for comparison indicating that τ_{int} and λ_1 comprehensively describe the low-frequency behavior of the spectrum $\tilde{c}_1(\omega)/c_1(0)$ as in the classical case. In the time domain, the single-mode approximation equation (527) amounts to assuming that the relaxation function $c_1(t)$ as determined by Eq. (479) (comprising $2S$ exponentials) may be
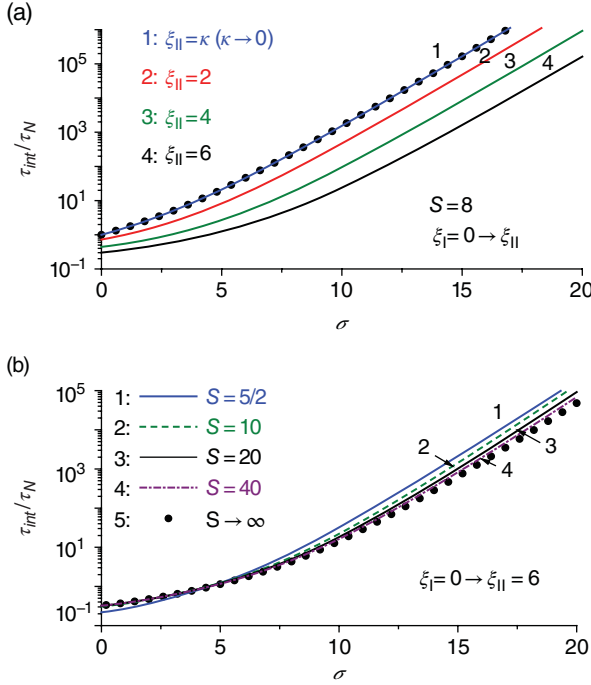
Figure 18. Nonlinear integral relaxation time τ_{int}/τ_N for the rise transient response as a function of the barrier parameter σ (a) for $S = 8$, $\xi_I = 0$, and various $\xi_{II} = \kappa \to 0, 2, 4, 6$; and (b) for $\xi_I = 0$ and $\xi_{II} = 6$; and various values of spin $S = 5/2, 10, 20, 40$, and $S \to \infty$. Solid lines: calculations from Eq. (521); circles: Eq. (531) (Color on line).

approximated for $t > 0$ by a *single* exponential. Consequently, the long-time relaxation behavior may once again be accurately approximated by a *single* exponential with relaxation time $T_1 = 1/\lambda_1$, and thus is again governed by the Bloch equation (462).

We may also evaluate the *linear response* of a uniaxial nanomagnet corresponding to infinitesimally small changes in the magnitude of the dc field, so that the integral relaxation time now becomes the correlation time. In linear response, that is, considering transient relaxation between the states I and II with respective Hamiltonians

$$\hat{H}_S^I = \frac{\sigma}{S^2}\hat{S}_Z^2 + \frac{\xi_{II} + \varepsilon}{S}\hat{S}_Z \quad \text{and} \quad \hat{H}_S^{II} = \frac{\sigma}{S^2}\hat{S}_Z^2 + \frac{\xi_{II}}{S}\hat{S}_Z,$$

where ε is a small external field parameter, the initial conditions $f_m(0)$ and $\left\langle \hat{S}_Z \right\rangle_I - \left\langle \hat{S}_Z \right\rangle_{II}$ reduce to
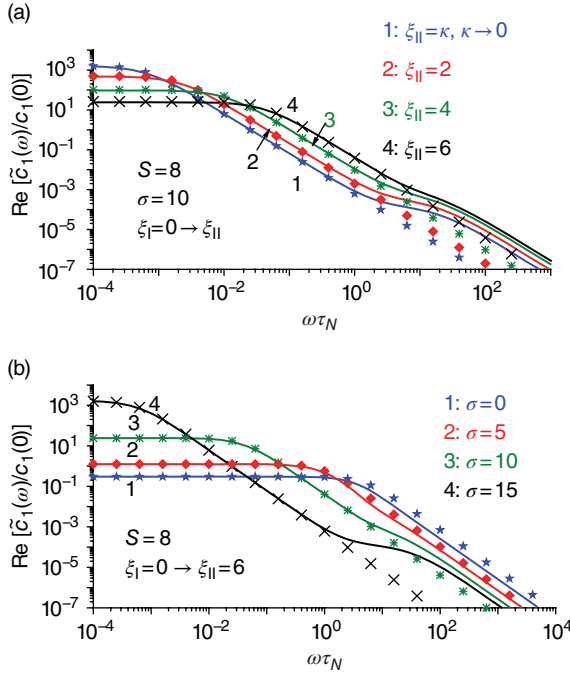
Figure 19. Real parts of the relaxation function spectrum $\tilde{c}_1(\omega)/c_1(0)$ versus the normalized frequency $\omega\tau_N$ for the rise transient response (a) for $S = 8$, $\sigma = 10$, $\xi_I = 0$ and various $\xi_{II} = \kappa \to 0, 2, 4, 6$; and (b) for $\xi_I = 0$, $\xi_{II} = 6$, $S = 8$, and various anisotropy parameters σ. Solid lines: calculations from Eq. (474); stars: Eq. (527) (Color on line).

$$f_m(0) = \frac{1}{Z_S} e^{\frac{\sigma}{S^2}m^2 + \frac{\xi_{II}+\varepsilon}{S}m} - \frac{1}{Z_S^{II}} e^{\frac{\sigma}{S^2}m^2 + \frac{\xi_{II}}{S}m} \approx \frac{\varepsilon}{S}\left(m - \left\langle\hat{S}_Z\right\rangle_{II}\right)\rho_m^{II}, \qquad (528)$$

$$\left\langle\hat{S}_Z\right\rangle_I - \left\langle\hat{S}_Z\right\rangle_{II} \approx \frac{\varepsilon}{S}\chi, \qquad (529)$$

where

$$\chi = \left\langle\hat{S}_Z^2\right\rangle_{II} - \left\langle\hat{S}_Z\right\rangle_{II}^2 = \sum_{m=-S}^{S} m^2\rho_m^{II} - \left(\sum_{m=-S}^{S} m\rho_m^{II}\right)^2. \qquad (530)$$

Thus, in the limit $\varepsilon \to 0$, Eq. (521) yields the correlation time τ_{cor} in the explicit series form

$$\tau_{cor} = \frac{2\tau_N}{\chi} \sum_{k=1-S}^{S} \frac{\left(\sum_{m=k}^{S}\left(m - \left\langle\hat{S}_Z\right\rangle_{II}\right)\rho_m^{II}\right)^2}{[S(S+1) - k(k-1)]\sqrt{\rho_k^{II}\rho_{k-1}^{II}}}. \qquad (531)$$

Equation (531) in the limit $S \to \infty$ yields numerical results concurring with the classical ones (cf. Eq. 552).

Furthermore, for the model embodied in Eq. (496), we can also calculate the effective relaxation time τ_{ef} given by Eq. (E.2). Thus, τ_{ef} yielding precise information on the initial decay of $c_1(t)$ in the time domain and defined as usual by [5]

$$\tau_{ef} = -\frac{c_1(0)}{\dot{c}_1(0)} = -\frac{S \, \partial_\varepsilon \left\langle \hat{S}_Z \right\rangle_{\text{I}} \big|_{\varepsilon=0}}{\sum\limits_{m=-S}^{S} m \dot{f}_m(0)} = -\frac{\chi}{\sum\limits_{m=-S}^{S} m \dot{f}_m(0)}, \tag{532}$$

is given by

$$\tau_{ef} = \frac{2\chi \tau_N}{\sum\limits_{k=1-S}^{S} [S(S+1) - k(k-1)] \sqrt{\rho_k^{\text{II}} \rho_{k-1}^{\text{II}}}}, \tag{533}$$

where noting Eqs. (508), (509), and (528) we have used and that

$$\sum_{m=-S}^{S} m \dot{f}_m(0) = \sum_{n=1}^{2S} n \left[p_n^- f_{n-1}(0) + p_n f_n(0) + p_n^+ f_{n+1}(0) \right]$$

$$= \sum_{n=1}^{2S} \left[(n-1) p_{n-1}^+ \rho_n^{\text{II}} - n p_n^- \rho_{n-1}^{\text{II}} \right]$$

$$= \frac{1}{2\tau_N} \sum_{k=1-S}^{S} [S(S+1) - k(k-1)] \sqrt{\rho_k^{\text{II}} \rho_{k-1}^{\text{II}}}.$$

Finally, the longest relaxation time τ, which is associated with the spin reversal time, can be calculated via the smallest *nonvanishing* eigenvalue λ_1 of the matrix $\tau_N^{-1} \boldsymbol{\Pi}$ given by Eq. (512) as $\tau = \lambda_1^{-1}$ from the deterministic equation

$$\det \left(\tau_N^{-1} \boldsymbol{\Pi} - \lambda \mathbf{I} \right) = 0. \tag{534}$$

The left-hand side of Eq. (534) represents the polynomial of the order $2S + 1$, namely,

$$\left(k_{2S+1} \lambda^{2S} + k_{2S} \lambda^{2S-1} + \cdots + k_2 \lambda + k_1 \right) \lambda = 0, \tag{535}$$

where

$$k_1 = -\sum_{i=0}^{2S} M_i^i, \tag{536}$$

$$k_2 = \sum_{i=0}^{2S-1} \sum_{j=i+1}^{2S} M_{ij}^{ij}, \tag{537}$$

and so on, and we have noted that $\det(\mathbf{\Pi}) = 0$. Here, the $M_i^{i'}$ are the first minors of the matrix $\mathbf{\Pi}$, which are in turn the determinants of square matrices as reduced from $\tau_N^{-1}\mathbf{\Pi}$ by removing the ith row and the i'th column of $\tau_N^{-1}\mathbf{\Pi}$ while the $M_{ij}^{i'j'}$ are the minors of the matrix $\tau_N^{-1}\mathbf{\Pi}$ which are the determinants of the square matrix reduced from $\tau_N^{-1}\mathbf{\Pi}$ by removing two (the ith and the jth) of its rows and two (the i'th and the j'th) columns. Now the smallest *nonvanishing* eigenvalue λ_1 can be readily evaluated numerically from Eq. (534), for example, using MATHEMATICA. However, in the high-barrier approximation when $\lambda_1 \ll 1$, it can be evaluated analytically by neglecting all higher-powers of λ^n with $n > 2$ in Eq. (535). Thus, we have

$$\lambda_1 \approx -\frac{k_1}{k_2}. \tag{538}$$

Equation (538) can be written equivalently in matrix form as

$$\lambda_1 \approx \frac{\mathrm{Tr}\left(\mathbf{M}^{(1)}\right)}{\mathrm{Tr}\left(\mathbf{M}^{(2)}\right)}, \tag{539}$$

where $\mathbf{M}^{(1)}$ is the matrix formed from the all first minors

$$\mathbf{M}^{(1)} = \begin{pmatrix} M_{2S}^{2S} & M_{2S}^{2S-1} & \cdots & M_{2S}^0 \\ M_{2S-1}^{2S} & M_{2S-1}^{2S-1} & \cdots & M_{2S-1}^0 \\ \vdots & \vdots & \ddots & \vdots \\ M_0^{2S} & M_0^{2S-1} & \cdots & M_0^0 \end{pmatrix}, \tag{540}$$

and the matrix $\mathbf{M}^{(2)}$ contains all the $M_{ij}^{i'j'}$ minors

$$\mathbf{M}^{(2)} = \begin{pmatrix} M_{2S,2S-1}^{2S,2S-1} & M_{2S,2S-1}^{2S,2S-2} & \cdots & M_{2S,2S-1}^{0,0} \\ M_{2S,2S-2}^{2S,2S-1} & M_{2S,2S-2}^{2S,2S-2} & \cdots & M_{2S,2S-2}^{0,0} \\ \vdots & \vdots & \ddots & \vdots \\ M_{0,0}^{2S,2S-1} & M_{0,0}^{2S,2S-2} & \cdots & M_{0,0}^{0,0} \end{pmatrix}. \tag{541}$$

The matrices $\mathbf{M}^{(1)}$ and $\mathbf{M}^{(2)}$ have, respectively, the dimensions $n \times n$ and $n(n-1)/2 \times n(n-1)/2$, where $n = 2S + 1$. Furthermore, the ordering of the elements in the matrix $\mathbf{M}^{(2)}$ is such that reading across or down the final matrix the successive lists of positions appear in lexicographic order. Now, $\mathrm{Tr}\left(\mathbf{M}^{(1)}\right)$ and $\mathrm{Tr}\left(\mathbf{M}^{(2)}\right)$ can be calculated analytically as

$$
\mathrm{Tr}\left(\mathbf{M}^{(1)}\right) = \frac{(-1)^{2S}}{\tau_N^{2S}} \sum_{i=0}^{2S} \prod_{s=1}^{i} p_s^- \prod_{r=i}^{2S-1} p_r^+ = \frac{(2S)!}{2^{2S}\tau_N^{2S}} \sum_{i=0}^{2S} e^{(i^2-2iS)\frac{\sigma}{S^2}+(i-S)\frac{\xi_{\mathrm{II}}}{S}}
$$

$$
= \frac{(2S)!}{2^{2S}\tau_N^{2S}} \sum_{k=-S}^{S} e^{(k^2-S^2)\frac{\sigma}{S^2}+k\frac{\xi_{\mathrm{II}}}{S}} = \frac{(2S)!e^{-\sigma}}{2^{2S}\tau_N^{2S}} Z_S \tag{542}
$$

and

$$
\mathrm{Tr}\left(\mathbf{M}^{(2)}\right) = \frac{(-1)^{2S+1}}{\tau_N^{2S-1}} \sum_{i=0}^{2S-1} \sum_{j=i+1}^{2S} \left(\prod_{s=1}^{i} p_s^- \prod_{r=j}^{2S-1} p_r^+ \sum_{m=1}^{j-i} \prod_{u=j+2-m}^{j} p_u^- \prod_{v=i}^{j-m-1} p_v^+ \right)
$$

$$
= \frac{(2S)!e^{-\sigma}}{2^{2S-1}\tau_N^{2S-1}} \sum_{k=-S}^{S-1} \sum_{n=k+1}^{S} \sum_{m=1}^{n-k}
$$

$$
\times \frac{e^{[2k^2-2n-1+2m(2n-m+1)]\frac{\sigma}{2S^2}+(2k+2m-1)\frac{\xi_{\mathrm{II}}}{2S}}}{(S+n-m+1)(S-n+m)}. \tag{543}
$$

Here, we have noted that $\prod\limits_{m=a}^{b} p_m^\pm = 1$ if $b < a$. Thus in the high-barrier approximation, the longest relaxation time $\tau \approx \lambda_1^{-1}$ is given by the following approximate equation:

$$
\tau \approx \frac{2\tau_N}{Z_S} \sum_{k=-S}^{S-1} \sum_{n=k+1}^{S} \sum_{m=1}^{n-k} \frac{e^{[2k^2-2n-1+2m(2n-m+1)]\frac{\sigma}{2S^2}+(2k+2m-1)\frac{\xi_{\mathrm{II}}}{2S}}}{(S+n-m+1)(S-n+m)}. \tag{544}
$$

We remarked before that the linear response has been previously studied by Garanin [80] and Garcia-Palacios and Zueco [81] using the spin density matrix whereby they also gave analytic expressions for τ_{cor}, τ_{ef}, and $\tau \approx \lambda_1^{-1}$ for more general models of linear and bilinear spin–bath interactions with superohmic damping. Using Garanin's method [80], the longest relaxation time τ can be found in a similar manner for the model embodied in Eq. (496) yielding

$$
\tau = \frac{2\tau_N}{\chi_\Delta} \sum_{k=1-S}^{S} \frac{\left(\sum\limits_{m=k}^{S} \left(m - \langle \hat{S}_Z \rangle_{\mathrm{II}}\right) \rho_m^{\mathrm{II}} \right) \left(\sum\limits_{m=-S}^{k-1} [\Delta - \mathrm{sgn}(m - m_b)] \rho_m^{\mathrm{II}} \right)}{[S(S+1) - k(k-1)]\sqrt{\rho_k^{\mathrm{II}} \rho_{k-1}^{\mathrm{II}}}}, \tag{545}
$$

where m_b is the quantum number corresponding to the top of the barrier, with

$$\Delta = \sum_{m=-S}^{S} \text{sgn}(m - m_b)\rho_m^{\text{II}}$$

and

$$\chi_\Delta = \sum_{m=-S}^{S} m \, \text{sgn}(m - m_b)\rho_m^{\text{II}} - \left(\sum_{m=-S}^{S} m\rho_m^{\text{II}}\right)\left(\sum_{m=-S}^{S} \text{sgn}(m - m_b)\rho_m^{\text{II}}\right).$$

Furthermore, via the replacement $k + 1 \to k$ and then via

$$\sum_{m=k}^{S} \left(m - \langle \hat{S}_Z \rangle_{\text{II}}\right)\rho_m^{\text{II}} = -\sum_{m=-S}^{k-1} \left(m - \langle \hat{S}_Z \rangle_{\text{II}}\right)\rho_m^{\text{II}},$$

one can rearrange Eq. (545) as follows:

$$\tau = \frac{2\tau_N}{\chi_\Delta}\sum_{k=-S}^{S-1} \frac{\left(\sum\limits_{m=-S}^{k} \left(m - \langle \hat{S}_Z \rangle_{\text{II}}\right)\rho_m^{\text{II}}\right)\left(\sum\limits_{m=-S}^{k} [\text{sgn}(m - m_b) - \Delta]\rho_m^{\text{II}}\right)}{[S(S+1) - k(k+1)]\sqrt{\rho_k^{\text{II}}\rho_{k+1}^{\text{II}}}}.$$

$$(546)$$

For $\xi_{\text{II}} < \sigma$, the relative deviation of τ given Eq. (546) from λ_1^{-1} calculated numerically does not exceed 1%.

All the foregoing expressions have been derived via the density matrix method. They can also be obtained using the phase space formalism, thereby exemplifying how they may reduce to the classical expressions. For example, τ_{ef} as rendered by Eq. (533) can be written as

$$\tau_{ef} = 2\tau_N e^{\xi/(2S)} \frac{\langle \hat{S}_Z^2 \rangle_{\text{II}} - \langle \hat{S}_Z \rangle_{\text{II}}^2}{\langle \hat{\mathbf{S}}^2 - \hat{S}_Z^2 + \hat{S}_Z \rangle_{\text{II}}}, \tag{547}$$

where $\langle \hat{S}_Z \rangle_{\text{II}}$ and $\langle \hat{S}_Z^2 \rangle_{\text{II}}$ can also be given via the phase space equations (494 – 495) and the denominator is given by the phase space average

$$\langle \hat{\mathbf{S}}^2 - \hat{S}_Z^2 + \hat{S}_Z \rangle_{\text{II}} = (S+1)\left(S+\tfrac{1}{2}\right)\int_{-1}^{1}\left[S\left(1 - z^2\right) + \tfrac{1}{2} + z - \tfrac{3}{2}z^2\right]W_S^{\text{II}}(z)dz,$$

$$(548)$$

on recalling that the Weyl symbol of the operator $\hat{\mathbf{S}}^2 - \hat{S}_Z^2 + \hat{S}_Z$ is

$$\hat{\mathbf{S}}^2 - \hat{S}_Z^2 + \hat{S}_Z \to (S+1)\left[S\left(1 - \cos^2\vartheta\right) + \cos\vartheta - \frac{3}{2}\cos^2\vartheta + \frac{1}{2}\right]. \tag{549}$$

Clearly, Eq. (547) is simply a quantum analog of the long-established equation for the longitudinal effective relaxation time τ_{ef} of classical macrospins, namely [5, 6],

$$\tau_{ef} = 2\tau_N \frac{\langle\cos^2\vartheta\rangle_{\mathrm{II}} - \langle\cos\vartheta\rangle_{\mathrm{II}}^2}{1 - \langle\cos^2\vartheta\rangle_{\mathrm{II}}}, \tag{550}$$

where

$$\langle\cos^2\vartheta\rangle_{\mathrm{II}} = \frac{1}{Z_{\mathrm{II}}} \int_{-1}^{1} x^2 e^{\sigma(x^2 + 2h_{\mathrm{II}}x)} dx$$

$$= \frac{e^{\sigma}[\cosh(2\sigma h_{\mathrm{II}}) - h\sinh(2\sigma h_{\mathrm{II}})]}{\sigma Z_{\mathrm{II}}} + h_{\mathrm{II}}^2 - \frac{1}{2\sigma} \tag{551}$$

and $\langle\cos\vartheta\rangle_{\mathrm{II}}$ and the partition function Z_{II} are defined by Eqs. (524) and (525), respectively. Furthermore, the corresponding integral (correlation) time τ_{cor} is given by [5, 6, 151, 153]

$$\tau_{cor} = \frac{2\tau_N}{Z_{\mathrm{II}}\left(\langle\cos^2\vartheta\rangle_{\mathrm{II}} - \langle\cos\vartheta\rangle_{\mathrm{II}}^2\right)}$$

$$\times \int_{-1}^{1} \left[\int_{-1}^{z} (x - \langle\cos\vartheta\rangle_{\mathrm{II}}) e^{\sigma(x^2 + 2h_{\mathrm{II}}x)} dx\right]^2 \frac{e^{\sigma(z^2 + 2h_{\mathrm{II}}z)}}{1 - z^2} dz. \tag{552}$$

For linear response, the correlation time τ_{cor} and overbarrier time λ_1^{-1} are plotted in Fig. 20 as a function of the field parameter $h = \xi_{\mathrm{II}}/(2\sigma)$ and the barrier height parameter σ for $S = 10$. Like the classical case, the behavior of τ_{cor} and λ_1^{-1} is similar only for *small* external fields. In a strong external field, $h \geq 0.2$, $1/\lambda_1$ can diverge exponentially from τ_{cor}. This divergence effect for a classical uniaxial nanomagnet was discovered numerically by Coffey *et al.* [152] and was later explained quantitatively by Garanin [153] (Ref. 5, ch. 1). He showed analytically that the contribution of relaxation modes other than the overbarrier one to either the integral relaxation time becomes significant for high external fields due to population depletion of the shallower of the two potential wells of a bistable potential under the action of an external applied field. The field is far less than that needed to destroy the bistable nature of the potential [5]. Furthermore, τ_{cor} and $1/\lambda_1$, are also plotted in Fig. 21 as a function of S for various values of ξ_{II} and σ. Clearly, even for relatively small $S \sim 20$, the quantum formulas are very close to the classical ones.

In Figs. 22 and 23, we show the real and imaginary parts of the dynamic susceptibility $\chi(\omega)/\chi$. Clearly, like the classical case, two bands appear in the spectrum of the imaginary part $-\mathrm{Im}\,[\chi(\omega)]$. The low-frequency band is due to the slowest "overbarrier" relaxation mode and can be described by a *single* Lorentzian. The characteristic frequency and the half-width of this band are determined by λ_1.
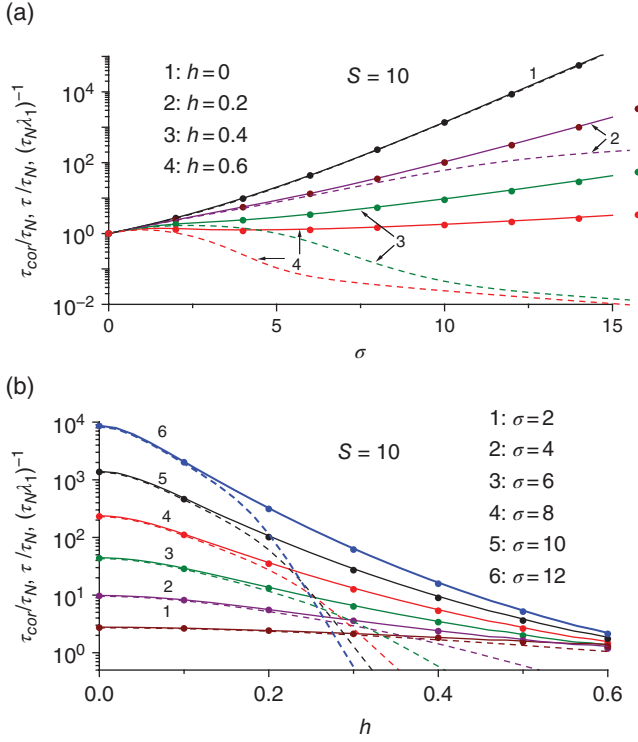
Figure 20. The correlation time τ_{cor} (Eq. (531); dashed lines), the inverse of the smallest eigenvalue λ_1 (filled circles) and its approximation τ (Eq. (545); solid line) (a) as a function of the barrier height parameter σ for various field parameters $h = \xi_{\text{II}}/(2\sigma)$ and (b) as a function of the field parameter h for various σ ($S = 10$) (Color on line).

The high-frequency band of $-\text{Im}\,[\chi(\omega)]$ is due to high-frequency well modes corresponding to the near-degenerate eigenvalues λ_k ($k \geq 2$). These individual "intrawell" modes are again indistinguishable in the spectrum of $-\text{Im}\,[\chi(\omega)]$ appearing merely as a single high-frequency Lorentzian band. Thus, like in the classical case [5], we may describe the behavior of $\chi(\omega)$ via the two-mode approximation [5], that is, by supposing that it is given as a sum of two Lorentzians, namely,

$$\frac{\chi(\omega)}{\chi} \approx \frac{1 - \delta}{1 + i\omega\tau} + \frac{\delta}{1 + i\omega\tau_W}, \tag{553}$$

where τ_W is a characteristic relaxation time of the near-degenerate high-frequency well modes and δ in the present context is a parameter characterizing
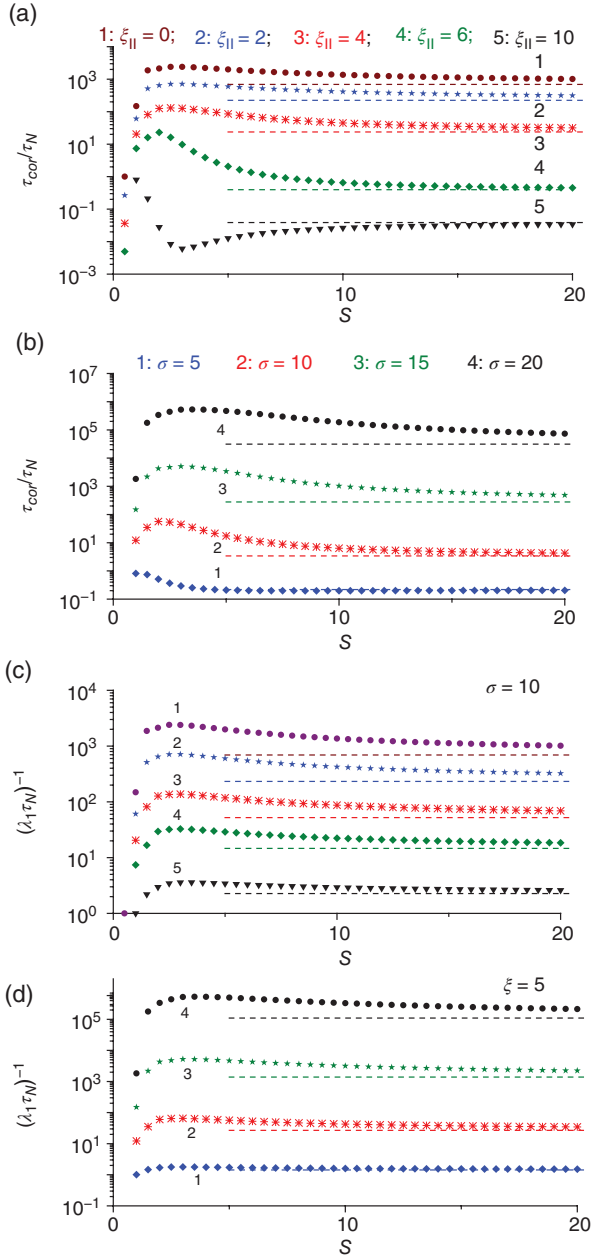
Figure 21. Correlation time τ_{cor}/τ_N (a), (b) and $(\lambda_1\tau_N)^{-1}$ (c), (d) versus the spin number S for various field parameters ξ_{II} for anisotropy barrier parameter σ =10 and for different σ and field parameters $\xi_{\mathrm{II}} = 5$. Dashed lines: classical limit (Color on line).
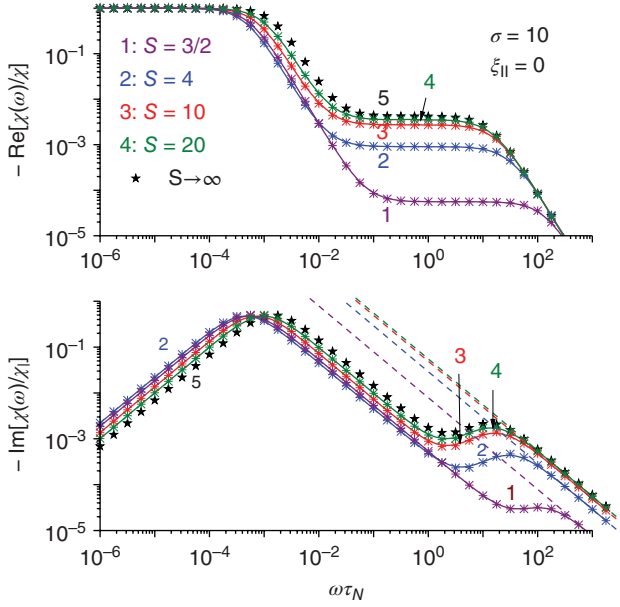
Figure 22. Normalized susceptibility $\chi(\omega)/\chi$, Eq. (489), versus $\omega\tau_N$ for barrier parameter $\sigma = 10$, the uniform field parameter $\xi_{\parallel} = 0$ (*symmetrical wells*), and various spin numbers S. Asterisks: the two-mode approximation, Eq. (553). Straight dashed lines: the high-frequency asymptote, Eqs. (491) and (533). Stars: the classical limit, Eqs. (491) and (550) (Color on line).

the contribution of these high-frequency modes to the susceptibility defined as [155]

$$\delta = \frac{\frac{\tau_{cor}}{\tau} + \frac{\tau}{\tau_{ef}} - \frac{\tau_{cor}}{\tau_{ef}} - 1}{\frac{\tau_{cor}}{\tau} + \frac{\tau}{\tau_{ef}} - 2}, \quad \tau_W = \frac{\tau_{cor} - \tau}{1 - \frac{\tau}{\tau_{ef}}} \tag{554}$$

and τ_{cor}, τ_{ef}, and $\tau \approx \lambda_1^{-1}$ are given by the quantum expressions of Eqs. (531), (533), and (546), respectively. The parameters δ and τ_W in Eqs. (553) and (554) have been determined by imposing the condition that the approximate two-mode equation (553) must obey the *exact* asymptotic equations (490 and 491). Now the longest relaxation time τ must be related to the frequency ω_{max} of the low-frequency peak in the magnetic loss spectrum $-\text{Im}[\chi(\omega)]$, where it attains a maximum, and/or the half-width $\Delta\omega$ of the spectrum of the real part of the susceptibility $\text{Re}[\chi(\omega)]$ via

$$\tau \approx \omega_{max}^{-1} \approx \Delta\omega^{-1}. \tag{555}$$

In the low-frequency region ($\omega\tau \leq 1$), where the effect of the high-frequency modes may be ignored, $\chi(\omega)$ may be approximated as follows:

$$\frac{\chi(\omega)}{\chi} \approx 1 - \frac{i\omega\tau_{int}}{1 + i\omega\tau}. \tag{556}$$
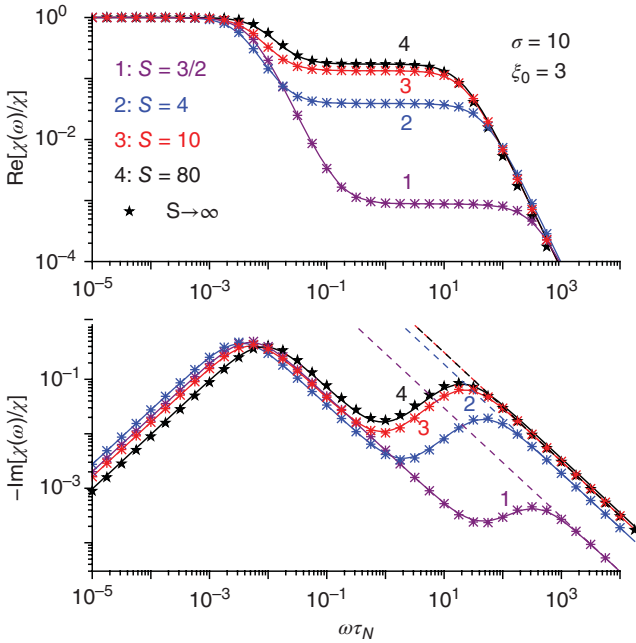
Figure 23. The normalized susceptibility $\chi(\omega)/\chi$, Eq. (489), versus normalized frequency $\omega\tau_N$ for barrier parameter $\sigma = 10$, the uniform field parameter $\xi_{\text{II}} = 3$ and various spin numbers S. Asterisks: the two-mode approximation, Eq. (553). Straight dashed lines: the high-frequency asymptote as rendered by Eq. (491) and the effective relaxation time by Eq. (533). Stars: the classical limit as rendered by Eq. (491) and the effective relaxation time Eq. (550).

We remark that Garcia-Palacios and Zueco [82] have shown that the two-mode approximation that was originally developed for classical systems [5, 155] accurately describes the linear response of quantum uniaxial nanomagnets at all frequencies of interest.

In order to illustrate the accuracy of the two-mode approximation for the quantum behavior, we plot in Figs. 22 and 23 the real and imaginary parts of $\chi(\omega)/\chi$ as calculated from the matrix solution, Eq. (489), representing a finite sum of Lorentzians and the approximate two-mode equation (553) for zero dc field, $\xi_{\text{II}} = 0$ (symmetrical wells) and for nonzero dc field, $\xi_{\text{II}} = 3$ (asymmetrical wells). It is apparent from Figs. 22 and 23 that at low frequencies, no *practical difference exists between the numerical solution and the two-mode approximation* (the maximum relative deviation between the corresponding curves does not exceed a few percent). In the classical limit, $S \rightarrow \infty$, the axially symmetric Hamiltonian equations (370 or 557) correspond to a free energy V given by Eq. (522). Here, both τ_{cor} and τ_{ef} can be expressed in closed form, namely Eqs. (552) and (550). The classical limit is also shown in Figs. 22 and 23 for comparison.

198 YURI P. KALMYKOV, WILLIAM T. COFFEY, AND SERGUEY V. TITOV

We have studied here the transient nonlinear longitudinal relaxation of a quantum uniaxial nanomagnet of arbitrary spin S in the high-temperature and weak spin–bath coupling limit. The principal result is that one may once again determine the transition from quantum elementary spin relaxation to the classical superparamagnetic relaxation pertaining to a giant classical spin as a function of the spin number S. Furthermore, one may accurately estimate the value of S (typically in the range 20–40) wherein the crossover to classical superparamagnetic behavior takes place. Thus, one may assign a range of validity as a function of the spin number S to the classical Néel–Brown treatment of magnetic nanoparticles with the simplest uniaxial magnetocrystalline anisotropy and Zeeman energy given earlier. The exact continued fraction solution based on the diagonal elements of the density matrix yields in closed form the dependence of the longitudinal spin relaxation function on the spin number S, which is dominated by a single exponential with time constant the longest relaxation time $1/\lambda_1$. Thus, *a simple description of the long-time behavior of the longitudinal relaxation function as a Bloch equation again holds for the nonlinear response of a quantum nanomagnet for arbitrary spin S*. In linear response, the approach so developed reproduces the results (with some modifications due to the symmetrized collision kernel used) previously obtained by Garanin [80] and Garcia-Palacios and Zueco [81, 82].

We have treated the longitudinal relaxation in two superficially distinct ways; the phase space formalism embodied in the Wigner–Stratonovich bijective mapping and the density matrix. *The high-temperature and weak spin-bath coupling limit-being understood in each case*. Thus, we have provided a vital check on the validity of both methods by explicitly demonstrating their equivalence. Again, we emphasize that a very useful feature of the phase space representation is that existing powerful computational techniques for the Fokker–Planck equation may be extended to the quantum domain, which also suggest new closed form quantum results via corresponding classical ones. For example, the integral and effective relaxation times, Eqs. (521) and (547), are clearly quantum analogs of the corresponding classical expressions given by Eqs. (523) and (550).

Next, we shall apply our methods to the nonlinear ac stationary responses of quantum nanomagnets by generalizing the known solutions for classical spins driven by a strong ac field to treat quantum effects in their ac nonlinear response [5, ch. 9]. The investigation is prompted by the fact that it has been shown experimentally (see e.g., Ref. 163) for the molecular magnet Mn_{12} with $S = 10$ that the nonlinear susceptibility of quantum nanomagnets differs from that of classical spins.

3. Nonlinear Longitudinal Relaxation in Superimposed ac and dc Magnetic Fields

Now the spin reversal process in quantum systems with finite spin number S has a strong field dependence causing nonlinear effects in the dynamic susceptibility

[68], stochastic resonance [69], and so on. In general, the nonlinear response to an external field poses an extremely difficult problem because the response now always depends on the precise nature of the stimulus [5]. Thus, no *unique* response function valid for all stimuli exists unlike in linear response. These difficulties are compounded in quantum systems so that the literature available on them is relatively sparse. The nonlinear longitudinal relaxation of a quantum nanomagnet arising from a sudden change in the magnitude of a strong external dc field was treated in Section III.C.2 using an evolution equation for the reduced density matrix. The solution of the evolution equation was then written as a finite series of the polarization operators, where the coefficients of the series (statistical averages of the polarization operators) were found from differential recurrence relations. Moreover, it was shown that the matrix solution simplifies for axially symmetric Hamiltonians Eq. (557) because the *diagonal terms of the density matrix decouple from the non-diagonal ones so that only the former partake in the time evolution*. We now show how this technique is also applied to the nonlinear dynamic magnetic susceptibility of a quantum nanomagnet with arbitrary S in superimposed ac and dc magnetic uniform fields amounting to the calculation of the nonlinear ac stationary response of the nanomagnet to an arbitrary ac field in the presence of the thermal agitation. Now calculations of the *nonlinear* ac response of quantum uniaxial nanomagnets have hitherto been made via perturbation theory (e.g., Ref. 163) by supposing that the potential energy of a spin in external magnetic fields is less than the thermal energy so that a small parameter exists. In the response to an ac field of *arbitrary strength*, however, such small parameters do not exist. The approach we shall use is, in some respects, analogous to that used in Ref. 164 for nonlinear dielectric relaxation behavior of polar molecules in a strong ac electric field and in Refs. 165 and 166 for the nonlinear magnetization relaxation of magnetic nanoparticles in superimposed ac and dc magnetic fields. The difference as usual is that for a finite spin number S the solution of the evolution equation is rendered as a finite sum of spherical harmonics in contrast to the classical case, where the solution of the evolution equation involves an infinite sum of them. We shall, in particular, demonstrate that our quantum results in the classical limit, $S \rightarrow \infty$, correspond to those of Ref. 165. Moreover, for small values of the ac applied fields (linear response), they agree with the results of Section III.C.2 calculated via the switch-off of a small longitudinal uniform field.

As an explicit example, we consider a uniaxial nanomagnet of arbitrary spin number S subjected to both a *uniform* external magnetic field $\mathbf{H}_0$ and to an ac external field $\mathbf{H}(t)$ applied along the Z-axis, that is, the axis of symmetry. The Hamiltonian $\hat{H}_S$ has the axially symmetric form (cf. Eq. 370)

$$\beta \hat{H}_S(t) = -\frac{\sigma}{S^2} \hat{S}_Z^2 - \frac{\xi_0 + \xi \cos \omega t}{S} \hat{S}_Z, \qquad (557)$$

where σ is again the dimensionless anisotropy parameter, and $\xi_0 = \beta S \hbar \gamma H_0$ and $\xi = \beta S \hbar \gamma H$ are the dc bias and ac field parameters, respectively. This Hamiltonian

as before comprises a uniaxial anisotropy term plus the Zeeman term, representing as usual a generic model for quantum spin relaxation phenomena in molecular magnets, nanoclusters, and so on.

The density matrix evolution equation describing the longitudinal relaxation of a uniaxial nanomagnet with the Hamiltonian defined by Eq. (557) is similar to Eq. (463) and is given by

$$\frac{\partial \hat{\rho}_S}{\partial t} = -\frac{1}{\tau_N} \left\{ e^{-\frac{\sigma}{2S^2} - \frac{\xi_0 + \xi \cos \omega t}{2S}} \left[\hat{S}_{-1} e^{-\frac{\sigma}{S^2} \hat{S}_0} \hat{\rho}_S, \hat{S}_{+1} \right] \right.$$
$$\left. + e^{\frac{\sigma}{2S^2} + \frac{\xi_0 + \xi \cos \omega t}{2S}} \left[\hat{S}_{+1} e^{\frac{\sigma}{S^2} \hat{S}_0} \hat{\rho}_S, \hat{S}_{-1} \right] \right\}. \tag{558}$$

For our purposes, the use of the symmetrized form of collision kernel equation (558) is very significant as it allows a correct description of the harmonics of spectral moments in the nonlinear response when an ac stimulus is imposed, namely the *absence* of the even harmonics for symmetric double-well potentials. Here, the magnitude of the ac field ξ is supposed to be so large that the energy of a spin is either comparable to or higher than the thermal energy kT, that is, $\xi \geq 1$, so that one always faces with an intrinsically nonlinear problem which is solved as follows.

We recall that for axially symmetric Hamiltonians such as that given by Eq. (557), the transformation of the evolution equation for the density matrix $\hat{\rho}_S$ into differential recurrence equations for its individual matrix elements can be radically simplified because the diagonal entries of $\hat{\rho}_S$ decouple from the non-diagonal ones. Hence, only the former contribute to the longitudinal spin relaxation. As before, we have from Eq. (558) the following three-term differential recurrence equation for the *diagonal* entries $\rho_m = \rho_{mm}$ (cf. Eqs. 496–498)

$$\tau_N \frac{d\rho_m(t)}{dt} = q_m^-(t)\rho_{m-1}(t) + q_m(t)\rho_m(t) + q_m^+(t)\rho_{m+1}(t), \tag{559}$$

where $m = -S, -S+1, \ldots, S$, $\tau_N = (2D_\perp)^{-1}$ is the characteristic (free diffusion) time, and now the time-dependent coefficients are as follows:

$$q_m(t) = -a_m^- e^{-(2m-1)\frac{\sigma}{2S^2} - \frac{\xi_0 + \xi \cos \omega t}{2S}} - a_m^+ e^{(2m+1)\frac{\sigma}{2S^2} + \frac{\xi_0 + \xi \cos \omega t}{2S}}, \tag{560}$$

$$q_m^\pm(t) = a_m^\pm e^{\mp(2m\pm1)\frac{\sigma}{2S^2} \mp \frac{\xi_0 + \xi \cos \omega t}{2S}}, \tag{561}$$

$$a_m^\pm = (S \mp m)(S \pm m + 1)/2. \tag{562}$$

Since we are solely concerned with the ac response corresponding to the stationary state, which is independent of the initial conditions, in calculating the longitudinal component of the magnetization defined as

$$\left\langle \hat{S}_Z \right\rangle (t) = \sum_{m=-S}^{S} m\rho_m(t), \tag{563}$$

we may seek the diagonal elements $\rho_m(t)$ as the Fourier series, namely,

$$\rho_m(t) = \sum_{k=-\infty}^{\infty} \rho_m^k(\omega)e^{ik\omega t}. \tag{564}$$

According to Eqs. (563) and (564), $\left\langle \hat{S}_Z \right\rangle (t)$ is then automatically rendered as a Fourier series, namely,

$$\left\langle \hat{S}_Z \right\rangle (t) = \sum_{k=-\infty}^{\infty} S_Z^k(\omega)e^{ik\omega t}, \tag{565}$$

where the amplitudes $S_Z^k(\omega)$ are themselves given by the finite series

$$S_Z^k(\omega) = \sum_{m=-S}^{S} m\rho_m^k(\omega). \tag{566}$$

Next, the time-dependent coefficients $q_m(t)$ and $q_m^{\pm}(t)$ in Eqs. (560) and (561) can also be expanded into the Fourier series using the known Fourier–Bessel expansion [105]

$$e^{\pm \frac{\xi}{2S} \cos \omega t} = \sum_{k=-\infty}^{\infty} I_k \left(\pm \frac{\xi}{2S} \right) e^{ik\omega t}, \tag{567}$$

where $I_k(z)$ are the modified Bessel functions of the first kind [105]. Thus, by direct substitution of Eq. (564) and the Fourier series for $q_m(t)$ and $q_m^{\pm}(t)$ into Eq. (559), we obtain a recurrence relation between the Fourier coefficients $\rho_m^k(\omega)$, namely,

$$
\begin{aligned}
ik\omega\tau_N \rho_m^k(\omega) = \sum_{k'=-\infty}^{\infty} & \left\{ a_m^- e^{\frac{\sigma(2m-1)}{2S^2} + \frac{\xi_0}{2S}} I_{k-k'} \left(\frac{\xi}{2S} \right) \rho_{m-1}^{k'}(\omega) \right. \\
& + a_m^+ e^{-\frac{\sigma(2m+1)}{2S^2} - \frac{\xi_0}{2S}} I_{k-k'} \left(-\frac{\xi}{2S} \right) \rho_{m+1}^{k'}(\omega) \\
& - \left[a_m^- e^{-\frac{\sigma(2m-1)}{2S^2} - \frac{\xi_0}{2S}} I_{k-k'} \left(-\frac{\xi}{2S} \right) \right. \\
& \left. \left. + a_m^+ e^{\frac{\sigma(2m+1)}{2S^2} + \frac{\xi_0}{2S}} I_{k-k'} \left(\frac{\xi}{2S} \right) \right] \rho_m^{k'}(\omega) \right\}. \tag{568}
\end{aligned}
$$

The recurrence relation given by Eq. (568) can be solved exactly for $\rho_m^k(\omega)$ via matrix continued fractions as follows. By introducing the column vector

$$\boldsymbol{\rho}_n = \begin{pmatrix} \vdots \\ \rho_n^{-1}(\omega) \\ \rho_n^0(\omega) \\ \rho_n^1(\omega) \\ \vdots \end{pmatrix}, \tag{569}$$

$(n = m + S)$, we have the following matrix recurrence equation between the $\boldsymbol{\rho}_n$, namely,

$$\mathbf{Q}_n^- \boldsymbol{\rho}_{n-1} + \mathbf{Q}_n \boldsymbol{\rho}_n + \mathbf{Q}_n^+ \boldsymbol{\rho}_{n+1} = \mathbf{0}, \tag{570}$$

where the matrix elements of the infinite matrices $\mathbf{Q}_n$ and $\mathbf{Q}_n^\pm$ are given by

$$[\mathbf{Q}_n]_{k,k'} = -i\omega\tau_N k\delta_{kk'} - a_n^+ e^{(2n-2S+1)\frac{\sigma}{S^2} + \frac{\xi_0}{S}} I_{k-k'}\left(\frac{\xi}{2S}\right)$$
$$- a_n^- e^{-(2n-2S-1)\frac{\sigma}{2S^2} - \frac{\xi_0}{2S}} I_{k-k'}\left(-\frac{\xi}{2S}\right),$$

$$[\mathbf{Q}_n^\pm]_{k,k'} = a_n^\pm e^{\mp(2n-2S\pm1)\frac{\sigma}{2S^2} \mp \frac{\xi_0}{2S}} I_{k-k'}\left(\mp\frac{\xi}{2S}\right).$$

Now according to the general method of solution of three-term recurrence relations [5, 71], all higher order column vectors $\boldsymbol{\rho}_n$ defined by Eq. (569) can be expressed in terms of the *lowest order* column vector $\boldsymbol{\rho}_0$ as

$$\boldsymbol{\rho}_n = \mathbf{S}_n \mathbf{S}_{n-1} \ldots \mathbf{S}_1 \boldsymbol{\rho}_0, \tag{571}$$

where the $\mathbf{S}_m$ are finite matrix continued fractions defined by the matrix recurrence relation

$$\mathbf{S}_m = \left[-\mathbf{Q}_m + \mathbf{Q}_m^+ \mathbf{S}_{m+1}\right]^{-1} \mathbf{Q}_m^-. \tag{572}$$

Now the zero-order column vector $\boldsymbol{\rho}_0$ itself can be found from the normalization condition for the density matrix elements, namely,

$$\sum_{n=0}^{2S} \rho_n(t) = \sum_{k=-\infty}^{\infty} \sum_{n=0}^{2S} \rho_n^k(\omega) e^{i\omega k t} = 1 \tag{573}$$

thereby immediately yielding the inhomogeneous equation for $\boldsymbol{\rho}_0$, namely,

$$\sum_{n=0}^{2S} \boldsymbol{\rho}_n = (\mathbf{I} + \mathbf{S}_1 + \mathbf{S}_2 \mathbf{S}_1 + \cdots + \mathbf{S}_{2S} \cdots \mathbf{S}_2 \mathbf{S}_1) \boldsymbol{\rho}_0 = \mathbf{v}, \tag{574}$$

where $\mathbf{I}$ is the unit matrix and the infinite column vector $\mathbf{v}$ has only the single nonvanishing element $v_k = \delta_{k0}$, $-\infty < k < \infty$. Consequently, we have

$$\boldsymbol{\rho}_0 = (\mathbf{I} + \mathbf{S}_1 + \mathbf{S}_2\mathbf{S}_1 + \ldots + \mathbf{S}_{2S}\ldots\mathbf{S}_2\mathbf{S}_1)^{-1}\,\mathbf{v}. \tag{575}$$

Having calculated the zero-order column vector $\boldsymbol{\rho}_0$, we can then determine via Eq. (571) all the other column vectors $\boldsymbol{\rho}_n$, and thus we can evaluate, all the $S_Z^k(\omega)$ from Eq. (566) yielding the nonlinear stationary ac response of a uniaxial nanomagnet.

Initially, we treat the *frequency-dependent* fundamental component of the magnetization $S_Z^1(\omega)$ in Eq. (565). For a weak ac field, $\xi \to 0$, the normalized fundamental component $S_Z^1(\omega)/S_Z^1(0)$ yields the normalized linear dynamic susceptibility, namely,

$$\frac{S_Z^1(\omega)}{S_Z^1(0)} \to \frac{\chi(\omega)}{\chi}, \tag{576}$$

concurring with the linear-response solution given in Section III.C.3. In strong ac fields, $\xi > 1$, like in linear response, two distinct absorption bands again appear in the spectrum of $-\mathrm{Im}[S_Z^1(\omega)/S_Z^1(0)]$ so that two accompanying dispersion regions occur in the spectrum of $\mathrm{Re}[S_Z^1(\omega)/S_Z^1(0)]$. However, due to the pronounced nonlinear effects, the low-frequency parts of $\mathrm{Re}[S_Z^1(\omega)/S_Z^1(0)]$ and $-\mathrm{Im}[S_Z^1(\omega)/S_Z^1(0)]$ may no longer be approximated by a *single* Lorentzian (see Fig. 24). Nevertheless, the frequency ω_{max} of the maximum loss and/or the half-width $\Delta\omega$ of the spectrum of $\mathrm{Re}[S_Z^1(\omega)/S_Z^1(0)]$ may still be used to estimate an effective reversal time τ as defined in Eq. (555). The behavior of the low-frequency peak of $-\mathrm{Im}[S_Z^1(\omega)/S_Z^1(0)]$ as *a function of the ac field amplitude* crucially depends on whether or not a dc field is applied. For strong dc bias, $\xi_0 > 1$ (see Fig. 24), the low-frequency peak shifts to lower frequencies reaching a maximum at $\xi \sim \xi_0$, thereafter shifting to higher frequencies with increasing ξ_0. In other words, as the dc field increases, the reversal time of the spin *initially increases* and having attained its maximum at some critical value $\xi \sim \xi_0$ thereafter decreases. For small dc bias, $\xi_0 < 0.5$, the low-frequency peak shifts monotonically to higher frequencies with increasing ξ. This behavior is very similar to that that observed in the classical case [165, 166].

Now a striking feature of the nonlinear response is that the effective reversal time may also be evaluated from either the spectrum of the (now) frequency-dependent dc component $S_Z^0(\omega)$ (only for nonzero dc bias, $\xi_0 \neq 0$) or those of the higher order harmonics $S_Z^k(\omega)$ with $k > 1$ because the low-frequency parts of these spectra are themselves, like the spectra of the fundamental, dominated by overbarrier relaxation processes. For illustration, the real and imaginary parts of the normalized second and third harmonic components $S_Z^2(\omega)/S_Z^2(0)$ and $S_Z^3(\omega)/S_Z^3(0)$ are shown in Fig. 25. Like the fundamental, the behavior of both
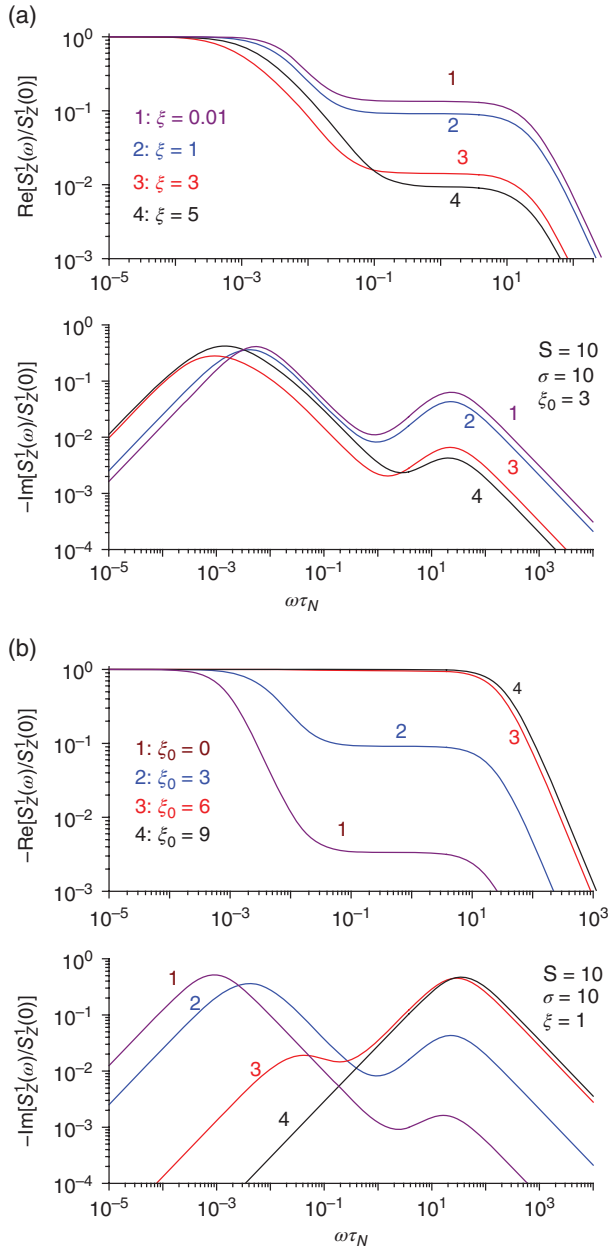
Figure 24. The real and imaginary parts of the normalized fundamental component $S_Z^1(\omega)/S_Z^1(0)$ versus normalized frequency $\omega\tau_N$ (a) for various applied ac fields ξ and the uniform field parameter $\xi_0 = 3$ and (b) for various dc field parameters ξ_0 and $\xi = 1$; the spin number $S = 10$ and anisotropy parameter $\sigma = 10$ (Color on line).
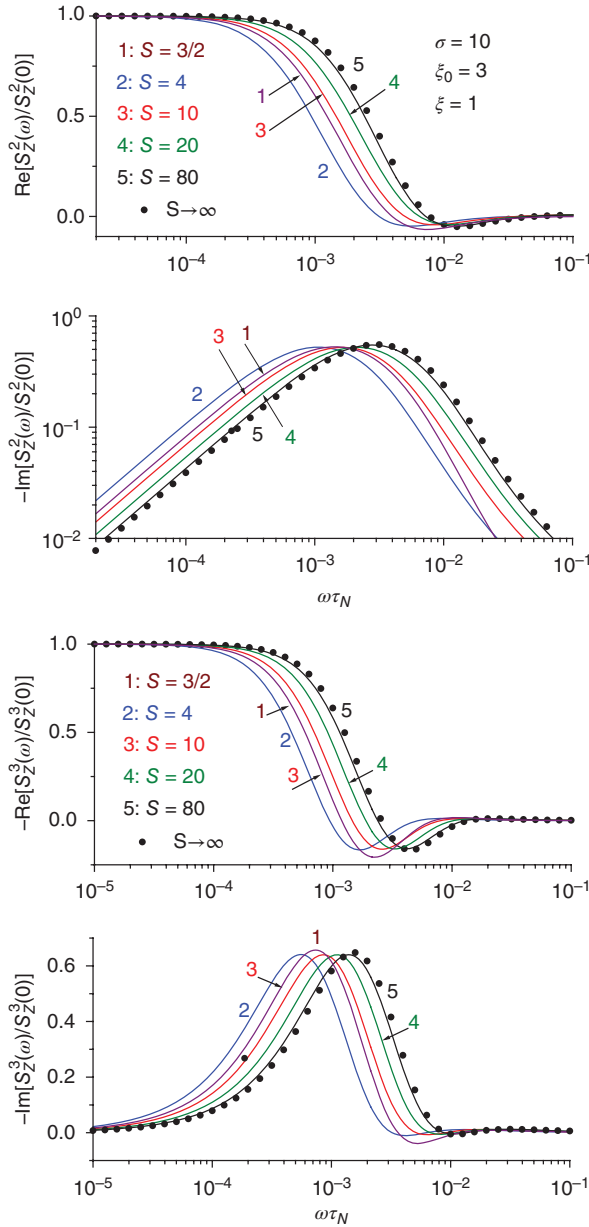
Figure 25. The real and imaginary parts of the normalized second and third harmonic components $S_Z^2(\omega)/S_Z^2(0)$ and $S_Z^3(\omega)/S_Z^3(0)$ of the nonlinear response vs. normalized frequency $\omega\tau_N$ for barrier parameter $\sigma = 10$, the uniform field parameter $\xi_0 = 3$ (*nonsymmetrical wells*), the ac field parameter $\xi = 1$, and various spin numbers S. Filled circles: the classical limit (*Color on line*).

$-\text{Im}\left[S_Z^2(\omega)/S_Z^2(0)\right]$ and $-\text{Im}\left[S_Z^3(\omega)/S_Z^3(0)\right]$ depends on whether or not a dc field is applied. For *weak* dc bias, $\xi_0 < 0.5$, on the one hand, the low-frequency peak shifts monotonically to higher frequencies. For *strong* dc bias, $\xi_0 > 1$, on the other hand, the low-frequency peak shifts to lower frequencies reaching a maximum at $\xi \sim \xi_0$, thereafter decreasing with increasing ξ.

Thus, in the nonlinear relaxation of a uniaxial quantum nanomagnet with arbitrary spin number S subjected to superimposed ac and dc magnetic fields in the high-temperature and weak spin–bath coupling limit, we may determine once again the transition from elementary spin relaxation to that pertaining to a giant spin as a function of the spin number S. Here, only uniaxial nanomagnets have been treated. Those with nonaxially symmetric anisotropies (cubic, biaxial, and so on.) can be considered in a like manner but with considerably more mathematical manipulation.

4. Dynamic Magnetic Hysteresis

We recall that nanoparticle magnetism has many novel applications, particularly in the (applied) area of information storage [167] and in medicine, for example, in hyperthermia occasioned by induction heating of nanoparticles [168, 169] with the dynamic magnetic hysteresis (DMH) induced in nanomagnets by an external ac field constituting a topic of special interest, which we now study in the quantum case. Here, the temperature directly influences the re-magnetization conditions, strongly affecting the effective rates, so altering the loop shape, coercive force, and specific power loss in nanomagnets. The theory of DMH in single-domain magnetically *isotropic* nanoparticles subjected to thermal fluctuations having been proposed by Ignachenko and Gekht, [170] was later extended to uniaxial superparamagnetic particles with moderate to high internal barriers [171–175]. Our approach as applied to quantum spins is analogous to that of Refs. [174] and [175] for DMH of single-domain ferromagnetic particles, where perturbation theory cannot be used. For purposes of exposition, we take a uniaxial nanomagnet of arbitrary spin number S subjected to uniform external magnetic field $\mathbf{H}_0$ and ac external field $\mathbf{H}(t)$ applied *along the Z-axis*, that is, the axis of symmetry, with the Hamiltonian $\hat{H}_S$ given by the axially symmetric equation (557). Again, our results will coincide with the classical ones in the limit $S \to \infty$.

The stationary ac response of the longitudinal component $\langle\hat{S}_Z\rangle(t)$ was treated in Section III.C.3 and is given by Eq. (565). Now, the DMH loop represents a parametric plot of the normalized magnetization as a function of the ac field, that is,

$$m(t) = \left\langle\hat{S}_Z\right\rangle(t)/S \text{ vs. } h(t) = H(t)/H = \cos\omega t.$$

Just as in the classical case [172–174], the normalized area of the DMH loop A_n (which is the energy loss per particle and per cycle of the AC field) is given by the exact equation

$$A_n = \frac{1}{4H} \oint m(t)dH(t) = -\frac{\pi}{2S} \text{Im} \left[S_Z^1(\omega) \right]. \tag{577}$$

In Figs. 26–32, we show the effects of ac and dc bias magnetic fields on the DMH loops in a uniaxial nanomagnet with arbitrary S. For a *weak* ac field, $\xi \to 0$,
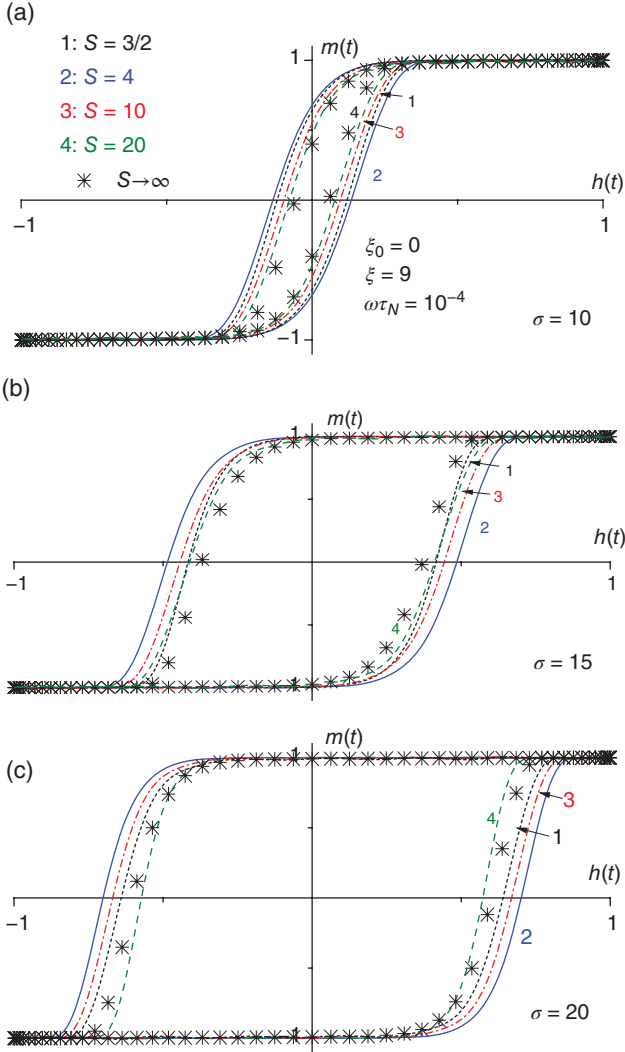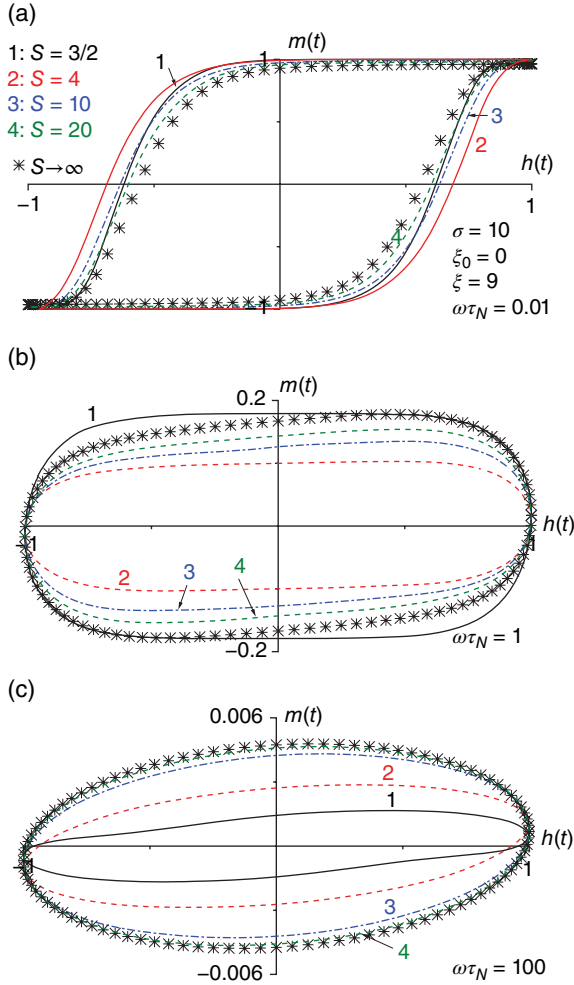

Figure 26. DMH loops for various anisotropy parameters $\sigma = 10$ (a), 15 (b), and 20 (c) and various spin numbers $S = 3/2$ (1: short-dashed lines), 4 (2: solid lines), 10 (3: dashed-dotted lines), 20 (4: dashed lines), and ∞ (asterisks) at $\omega\tau_N = 10^{-4}$, $\xi_0 = 0$, and $\xi = 9$ (Color on line).
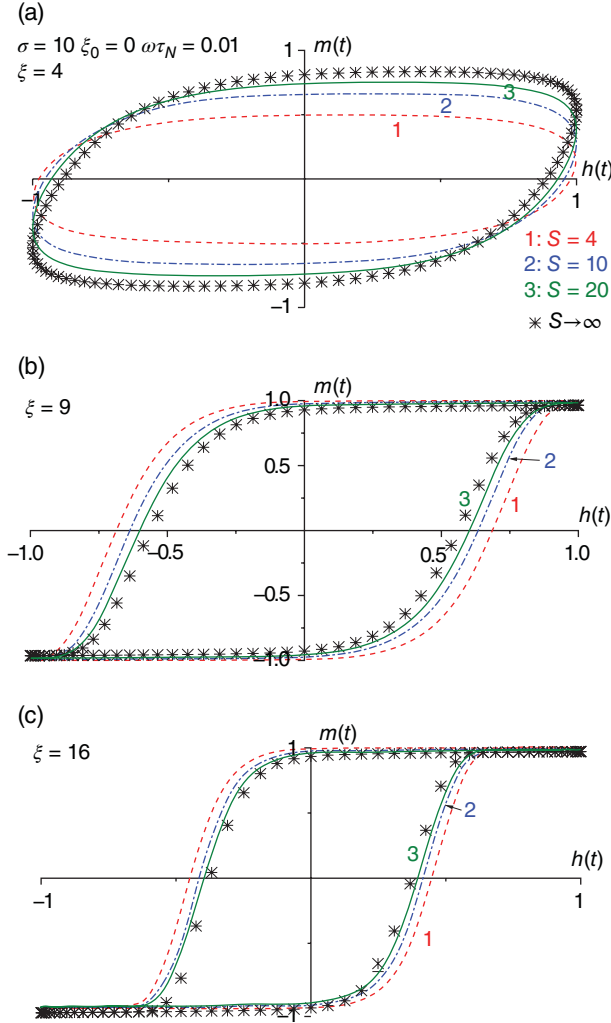
Figure 27. DMH loops for various ac external field parameters $\xi = 4$ (a), 9 (b), and 16 (c) and various spin numbers $S = 4$ (1: dashed lines), 10 (2: dashed-dotted lines), 20 (3: solid lines), and ∞ (asterisks) at $\sigma = 10$, $\xi_0 = 0$, and $\omega\tau_N = 10^{-2}$ (Color on line).

and low frequencies, $\omega\tau \leq 1$, the DMH loops are ellipses with normalized area A_n given by Eq. (577), with the behavior of $A_n \sim -\mathrm{Im}\left[S_Z^1(\omega)\right] \sim \chi''(\omega)$ being similar (cf. Eq. 577) to that of $\chi''(\omega)$ (see Figs. 22 and 23). Indeed, the two-mode approximation for the susceptibility given by Eq. (553) implies that the overall relaxation process consists of two distinct entities, namely, the slow thermally activated overbarrier (or interwell) process and the fast intrawell relaxation in the wells. Now, at low frequencies and for large barriers between the wells, only the

Figure 28. DMH loops for various frequencies $\omega\tau_N = 10^{-2}$ (a), 1 (b), and 10^2 (c) and various spin numbers $S = 3/2$ (1: solid lines), 4 (2: dashed lines), 10 (3: dashed-dotted lines), 20 (4: short-dashed lines), and ∞ (asterisks) at $\sigma = 10$, $\xi_0 = 0$, and $\xi = 9$ (Color on line).

first term on the right-hand side in Eq. (556) for $-\text{Im}\left[S_Z^1(\omega)\right]$ need be considered. Furthermore, for *weak dc bias fields*, $\xi_0/(2\sigma) << 1$, the approximation $\delta \approx 1$ may always be used in Eq. (553) so that the *normalized* magnetization $m(t) = \left\langle \hat{S}_Z \right\rangle(t)/S$ is given by the simple linear-response formula [174]

$$m(t) = \frac{1}{S}\left\langle \hat{S}_Z \right\rangle_0 + \frac{\chi\xi}{S}\frac{\cos\omega t + \omega\tau\sin\omega t}{1+\omega^2\tau^2}. \tag{578}$$
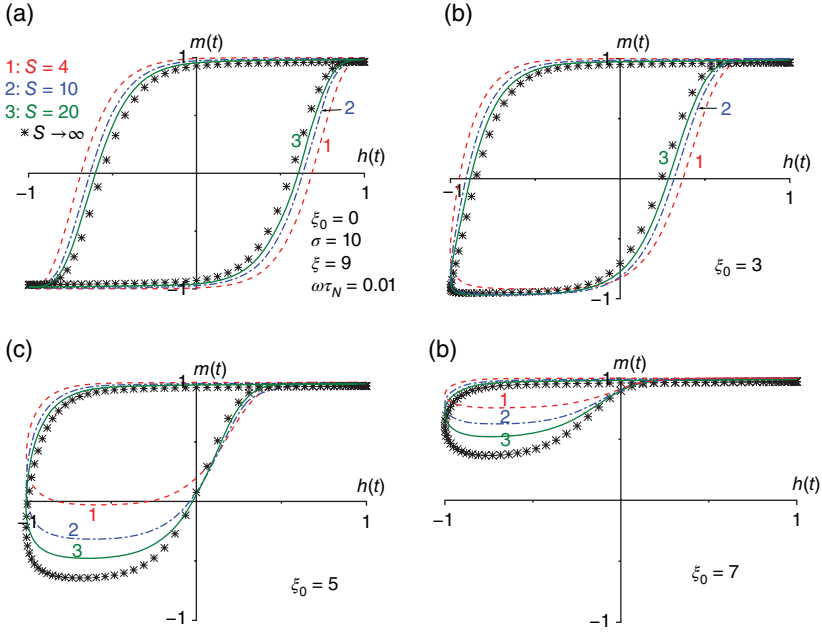
Figure 29.   DMH loops for various dc bias field parameters $\xi_0 = 0$ (a), 3 (b), 5 (c), and 7 (d) and various spin numbers $S = 4$ (1: dashed lines), 10 (2: dashed-dotted lines), 20 (3: solid lines), and ∞ (asterisks) at $\xi = 9$, $\sigma = 10$, and $\omega\tau_N = 10^{-2}$ (Color on line).

If we introduce the variables x and y defined as

$$x = h(t) = \cos\omega t \quad \text{and} \quad y = \frac{Sm(t) - \left\langle \hat{S}_Z \right\rangle_0}{\chi\xi},$$

we can then conclude from Eq. (578) that in the linear-response approximation, a low-frequency DMH loop in the (x, y) plane is an ellipse, namely, [174]

$$x^2 + \frac{1}{\omega^2\tau^2}\left[\left(1 + \omega^2\tau^2\right)y - x\right]^2 = 1. \tag{579}$$

This ellipse is centered at $(0, 0)$ and its major axis is inclined to the x-axis at an angle $\frac{1}{2}\arctan\left[2/(\omega\tau)^2\right]$.

For *moderate* ac fields, $0.5 < \xi \leq 1$, the DMH loops still have approximately an ellipsoidal shape implying that only a few harmonics actually contribute to the weakly nonlinear response. In contrast, in *strong* ac fields, $\xi > 1$, the shape alters substantially, and so the normalized area A_n now exhibits a pronounced dependence on the frequency ω and the ac and dc bias field amplitudes ξ and ξ_0
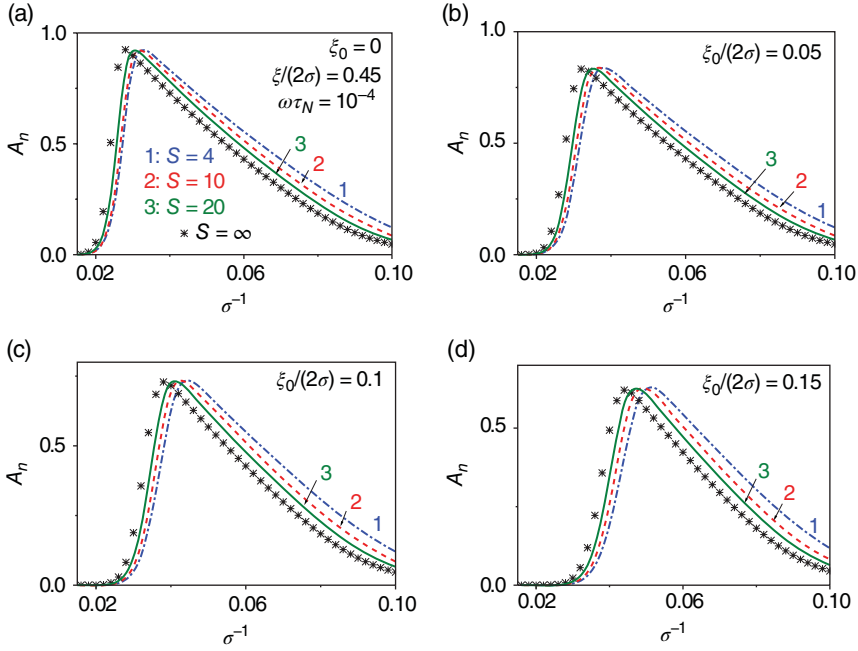
Figure 30. Normalized area of the DMH loop A_n versus the dimensionless temperature σ^{-1} under variation of the dc bias field parameter $h_0 = \xi_0/(2\sigma) = 0$ (a), 0.05 (b), 0.1 (c), and 0.15 (d) for various spin numbers $S = 4$ (dashed-dotted lines), 10 (dashed lines), 20 (solid lines), and ∞ (asterisks) at the frequency $\omega\tau_N = 10^{-4}$ and the ac field amplitude $\xi/(2\sigma) = 0.45$ (Color on line).

as well as on the anisotropy parameter σ and the spin number S (see Figs. 26–29). In this regime, the external ac field is able to saturate the paramagnet magnetic moment as well as induce its inversion (i.e., switching between the directions of the easy axis). In Figs. 25 and 26, we plot the loops for various S and anisotropy (σ) and ac field (ξ) parameters exemplifying how their shapes (and consequently their areas) alter as these parameters vary. Clearly, the re-magnetization time is highly sensitive to variations of these parameters. For example, with a strong ac driving field, the Arrhenius dependence of the reversal time on temperature $\log \tau \propto 1/T$, which accurately accounts for the linear-response regime, is modified because the strong ac field intervenes so drastically reducing the effective response time of the nanomagnet. Thus, the nonlinear behavior facilitates re-magnetization regimes, which are never attainable with weak ac fields, the reason being that the dc bias component under the appropriate conditions *efficiently tunes* this effect by either *enhancing* or *blocking* the action of the strong ac field. The *pronounced* frequency dependence of the loops is highlighted in Fig. 28 for various S. At low frequencies, the field changes are *quasiadiabatic*, so that the magnetization reverses due to the
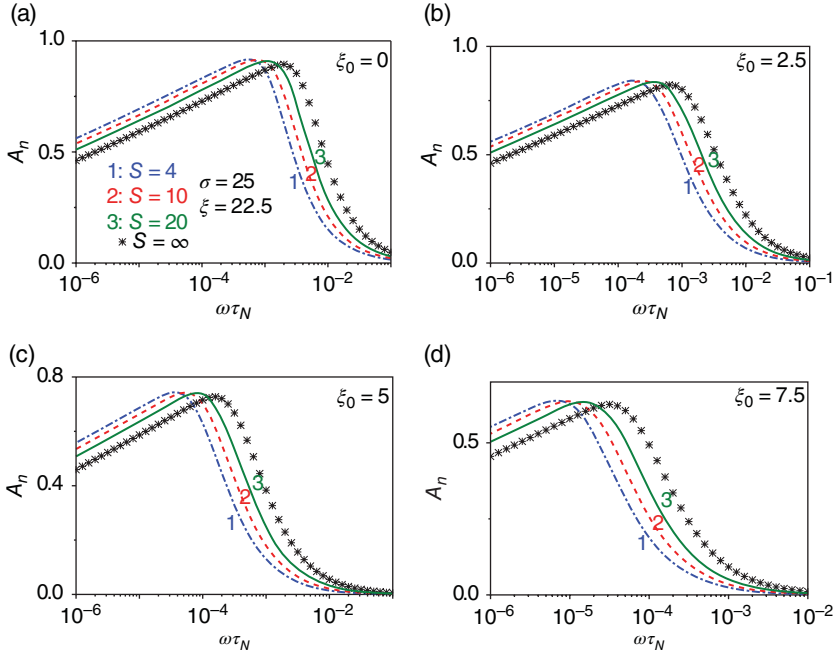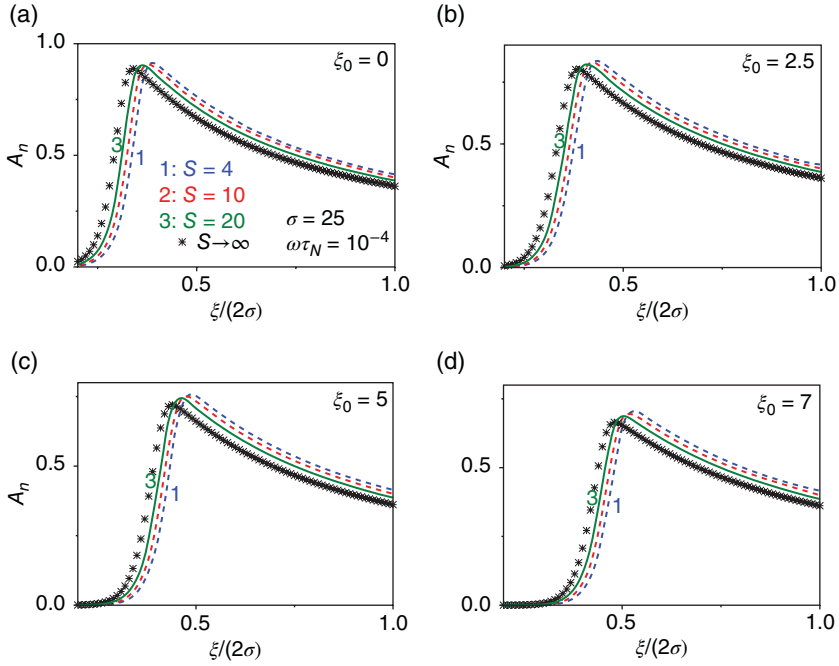
Figure 31. Normalized area of the DMH loop A_n versus the dimensionless frequency $\omega\tau_N$ under variation of the dc bias field $\xi_0 = 0$ (a), 2.5 (b), 5 (c), and 7.5 (d) for various spin numbers $S =4$ (dashed-dotted lines), 10 (dashed lines), 20 (solid lines), and ∞ (asterisks); the anisotropy parameter $\sigma = 25$ and the ac field parameter $h = 0.45$ (Color on line).

cooperative shuttling action of thermal agitation combined with the ac field. The dc bias field effects on the DMH are illustrated in Fig. 29 showing the changes in the DMH caused by varying ξ_0 for various spin numbers S. In order to understand the effect of the dc bias field on the loop area, one must first recall that the magnetic relaxation time depends on the actual value of the applied field. Under the conditions of Fig. 29, the *positive limiting* (saturation) value of $m(t) \rightarrow 1$ corresponds to a total field $H_0 + H$, thus *favoring* the magnetization relaxation to the positive saturation value $m(t) \rightarrow 1$. However, for *negative* $h(t)$, the total field $H_0 - H$ is much weaker, and so cannot induce relaxation to the negative saturation value $m(t) \rightarrow -1$. Therefore, the "center of area" of the loop moves upward. In the classical limit, $S \rightarrow \infty$, our results concur with those for classical uniaxial nanomagnets [175].

The temperature dependence of the DMH is governed by the dimensionless anisotropy (inverse temperature) parameter $\sigma \propto 1/T$. The normalized DMH area A_n as a function of σ^{-1} is shown in Fig. 30 for various S, showing that the tuning action of the dc bias field described before is effective over a certain temperature

Figure 32. Normalized area of the DMH loop A_n as a function of the ac field amplitude $h = \xi/(2\sigma)$ under variation of the dc bias field parameter $\xi_0 = 0$ (a), 2.5 (b), 5 (c), and 7 (d) for various spin numbers $S = 4$ (dashed-dotted lines), 10 (dashed lines), 20 (solid lines), and ∞ (asterisks); the anisotropy parameter $\sigma = 25$ and the frequency $\omega\tau_N = 10^{-4}$ (Color on line).

interval. This conclusion once again indicates that the relaxation of the magnetization is mostly caused by thermal fluctuations, implying that the magnetic response time still retains a corresponding strong temperature dependence. The normalized area as a function of the frequency ω and ac field parameter $\xi/(2\sigma)$ is shown in Figs. 31 and 32, respectively. Clearly, A_n can invariably be represented as a nonmonotonic curve with a maximum the position of which is determined by S as well as by the other model parameters. The peak in A_n (Fig. 31) is caused by the field-induced modifications of the reversal time as strongly tuned by the dc bias field. As in Fig. 31, variation of the dc field strength shifts the frequency, where the maximum is attained, by several orders of magnitude. The normalized loop area presented in Fig. 32 illustrates the dependence of A_n on the ac field amplitude, which is similar to that of classical nanomagnets.

The DMH in uniaxial nanomagnets has been treated already without any *a priori* assumptions regarding the potential barrier height, temperature, the magnetizing field strength, and/or spin number S. In general, it appears that given appropriate conditions, a small bias dc field (in comparison with the

internal anisotropy field) can profoundly affect the shape of the DMH loops in nanomagnets accompanied by a strong dependence on the spin number S.

5.   Quantum Effects in Stochastic Resonance

Yet another aspect of the Brownian motion of particles and spins in a potential is the *stochastic* resonance (SR) [175] whereby a weak periodic forcing *synchronized* with the thermally activated hopping of particles or spins between the wells greatly enhances the rate of switching between them. The archetypal theoretical model of SR [5, 176] is the motion of a heavily damped (so that inertial effects can be ignored) Brownian particle in a bistable potential $V(q)$ subjected to noise arising from a thermal bath (see Fig. 33). If we now apply a weak periodic forcing $f_0 \cos \Omega t$ of frequency Ω, the double-well potential will be tilted up and down, thereby periodically raising and lowering the potential barriers ΔV [176]. Consequently, if Ω is close to the rate of transitions (escape rates) between the wells despite the fact that the amplitude of the periodic forcing is insufficient to induce the transitions by *itself alone*, noise-induced hopping between potential wells may become *synchronized* with it so facilitating the transition. This statistical synchronization takes place when the average waiting (escape) time between two noise-induced transitions is comparable with half the period $\tau_\Omega = 2\pi/\Omega$ of the periodic forcing. Consequently, switching may occur only by the *combined* effect of the regular ac force and the noise. The spectral density $\Phi(\omega)$ of the motion at the forcing frequency $\omega = \Omega$ is then evaluated, and the resulting SNR (or the spectral power amplification coefficient) is analyzed as a function of the noise intensity D. Now, the curve of SNR versus D has a bell-like shape, that is, it passes through a maximum thus exhibiting *stochastic resonance.*
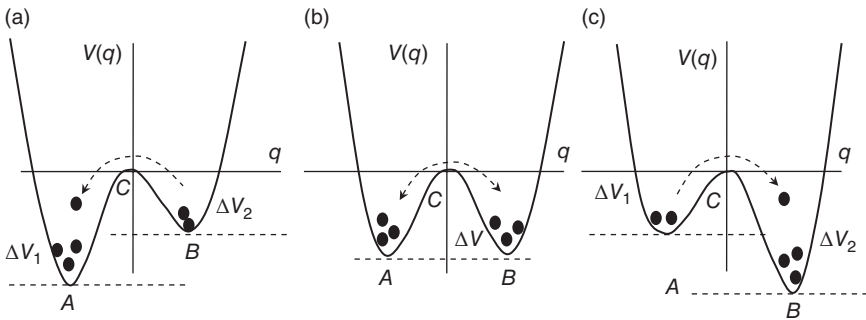
Figure 33.   Double-well potential as used in stochastic resonance [5]. The minima are located at A and B. In the absence of a periodic forcing function (b), the barrier heights ΔV_1 and ΔV_2 are equal to ΔV, so that the potential is symmetric. The periodic forcing function causes the double-well potential to tilt back and forth, thereby raising and lowering the potential barriers of the right and left wells, respectively, in an antisymmetric cyclic fashion: (a) and (c).

The maximum in the SNR is interpreted as being due to the remarkable ability of noise to *enhance* the intensity of the interwell hopping in the system. Stochastic resonance is, therefore, an important effect allowing one to control the behavior of periodic signals passing through noisy systems. As a manifestation of cross-coupling between stochastic and regular motions, the SR effect is universal in physics (e.g., optics, mechanics of solids, superconductivity, and surface science), communications engineering (optimal detection and tracing of signals) as well as in various branches of chemistry and biology. Comprehensive reviews of diverse aspects of SR are available in Refs. 176–178.

Now the behavior of magnetic nanosystems (i.e., magnetic nanoparticles, nanoclusters, and molecular magnets) forced by a weak ac magnetic field is yet another important manifestation of SR. Here, the magnetic anisotropy provides the multistable states for the magnetization $\mathbf{M}$, while the thermal fluctuations or random field due to the bath, which is in perpetual thermal equilibrium at temperature T, are the source of the noise. These conditions give rise to *magnetic stochastic resonance* which again may be defined as the enhancement of the SNR due to noise [179]. The magnetic SR was first predicted theoretically [180–182] and shortly afterward observed experimentally [183]. The SNR of the magnetic moment fluctuations is of some interest in information storage and in the crossover between classical and quantum behavior of the magnetization since we saw that single-domain particles exhibit essentially classical behavior, while smaller entities such as free nanoclusters made of many atoms, molecular clusters, and molecular magnets exhibit pronounced quantum behavior.

The main features of the magnetic SR in single-domain particles (classical spins) [184–188] may be completely understood in terms of the classical Brown (macrospin) model [23, 24]. Here, each particle behaves like a paramagnetic atom having a magnetic moment $\sim 10^4 - 10^5 \mu_B$, that is., $S \sim 10^4 - 10^5$. In the presence of a dc bias field $\mathbf{H}_0$, the normalized magnetic free energy density V of a *uniaxial* nanomagnet is given by the asymmetric bistable potential

$$\beta V(\vartheta) = -\sigma \left(\cos^2 \vartheta + 2h \cos \vartheta \right), \tag{580}$$

where $\sigma = vK/(kT)$ is the dimensionless barrier height parameter, v is the volume of the particle, K is the anisotropy constant, and $h = \mu_0 M_S H_0/(2K)$ is the bias field parameter (M_S is the saturation magnetization). Without the dc field, the magnetization of the uniaxial particle has two equivalent stable orientations at $\vartheta = 0$ and $\vartheta = \pi$, so that it is an ideal example of a bistable system subjected to noise. Here, the reversal of the classical spin is due to thermal activation and the rate of transitions between the potential wells is controlled by the anisotropy or inverse temperature parameter σ. Thus, one may regard $1/\sigma$ as the *dimensionless temperature*, that is, the *noise intensity*. A dc bias field $\mathbf{H}_0$ when applied to the particle parallel to its anisotropy axis breaks the bidirectional symmetry of

the potential. However, an asymmetric two-minima profile of the potential $V(\vartheta)$ survives as long as the bias field parameter $h \leq 1$. Now for $h = 0$, the basic concept of magnetic stochastic resonance has been well described by Raikher and Stepanov [184]. In the presence of noise, a weak alternating spatially uniform field of frequency Ω favoring the transitions between two equilibrium positions at $\vartheta = 0$, π is applied. Under these conditions, the SNR determined from the spectral density $\Phi_M(\omega)$ of the magnetic moment (i.e., the frequency response to the applied field), evaluated at the frequency Ω of the weak applied ac field, first *increases* with increasing noise strength kT, then on attaining a *pronounced maximum*, finally *decreases* again. This is the (magnetic) *stochastic resonance effect*, whereby the periodic response in both amplitude and phase may be manipulated by altering the noise strength.

In contrast to the classical case, in magnetic SR of nanomagnets with *smaller* spin numbers $S \sim 10$–100 both quantum effects and quantum-classical crossover appear. Here, the spin reversal is either due to thermal activation or tunneling or a combination of both. The quantum effects are not the same as those in the SR for translational Brownian motion (see, e.g., Refs. 189, 190 and references cited therein) because despite some analogies the quantum spin dynamics essentially differs from those of Brownian particles owing to the different symmetries of the rotational and translational groups. Here, we shall treat quantum effects in the SR for magnetic spin systems modeled by a uniaxial nanomagnet of arbitrary S in superimposed dc and ac external *uniform* magnetic fields $\mathbf{H}_0 + \mathbf{H} \cos \Omega t$ applied along the Z-axis, that is, the axis of symmetry, so that the time-dependent Hamiltonian $\hat{H}_S$ is (cf. Eq. 557)

$$\beta \hat{H}_S(t) = -\frac{\sigma}{S^2} \hat{S}_Z^2 - \frac{\xi_0 + \xi \cos \Omega t}{S} \hat{S}_Z, \tag{581}$$

where σ is the anisotropy constant, ξ_0 and ξ are the external dc and ac magnetic field parameters. The longitudinal relaxation of uniaxial nanomagnets interacting with a thermal bath has been treated in Section III.C via the respective evolution equations for the reduced density matrix and phase space distribution function using the methods already available for classical spins. In the large spin limit, we also saw in Section III.C that the quantum solutions reduce to those of the Fokker–Planck equation for a classical uniaxial nanomagnet, while for linear response and finite S, the results agree with those predicted by the solutions of Garanin [80] and García-Palacios and Zueco [81, 82]. Here, we apply these findings to the SNR for uniaxial quantum nanomagnets.

Now, we saw in Section III.C that the normalized longitudinal dynamic susceptibility of a quantum nanomagnet is defined in linear response as

$$\frac{\chi(\Omega)}{\chi} = 1 - i\Omega \int_0^\infty C(t)\, e^{-i\Omega t} dt, \tag{582}$$

where $C(t)$ is the normalized equilibrium correlation function defined by Eq. (484), $\chi = \beta\mu_0\mu^2 N\chi_0$ is the static susceptibility, N is the number of nanomagnets per unit volume,

$$\chi_0 = \frac{1}{S^2}\left[\left\langle\hat{S}_Z^2\right\rangle_0 - \left\langle\hat{S}_Z\right\rangle_0^2\right]$$

$$= \frac{1}{S^2}\left[\sum_{m=-S}^{S} m^2\rho_m - \left(\sum_{m=-S}^{S} m\rho_m\right)^2\right] \tag{583}$$

is the normalized static susceptibility,

$$\rho_m = \frac{e^{\sigma\left(m^2/S^2 + 2hm/S\right)}}{\sum_{m=-S}^{S} e^{\sigma\left(m^2/S^2 + 2hm/S\right)}} \tag{584}$$

and $h = \xi_0/(2\sigma)$. For a uniaxial nanomagnet, both $C(t)$ and $\chi(\Omega)$ have been calculated in Section III.C.3. In particular, we recall that $C(t)$ may formally be written as the finite discrete set of relaxation modes, namely, (cf. Eq. 456)

$$C(t) = \sum_{k=1}^{2S} c_k e^{-\lambda_k t}, \tag{585}$$

where λ_k are the eigenvalues of the system matrix $\mathbf{X}$, Eq. (470), with the replacement $\xi_{\mathrm{II}} \to \xi_0$. Consequently, Eqs. (582) and (585) allow us to *formally* write $\chi(\Omega)$ as the finite discrete set of Lorentzians (cf. Eq. 489)

$$\frac{\chi(\Omega)}{\chi} = \sum_{k=1}^{2S} \frac{c_k}{1 + i\Omega/\lambda_k}. \tag{586}$$

The asymptotic behavior of $\chi(\Omega)$ in the extreme cases of very low and very high frequencies is given as before by Eqs. (490) and (491), namely,

$$\frac{\chi(\Omega)}{\chi} \sim \begin{cases} 1 - i\Omega\tau_{cor} + \cdots, & \Omega \to 0 \\ -i\left(\Omega\tau_{ef}\right)^{-1} + \cdots, & \Omega \to \infty \end{cases}, \tag{587}$$

where τ_{cor} is the integral relaxation time and τ_{ef} is the effective relaxation time defined in terms of the eigenvalues λ_k as follows:

$$\tau_{cor} = \sum_{k=1}^{2S} c_k/\lambda_k \quad \text{and} \quad \tau_{ef} = \left(\sum_{k=1}^{2S} c_k\lambda_k\right)^{-1}. \tag{588}$$

Furthermore, the smallest nonvanishing eigenvalue λ_1 may as usual be associated with the long-time behavior of $C(t) \sim e^{t/\tau}$, $t >> \tau = 1/\lambda_1$, which is characterized by the longest relaxation (or the reversal) time τ. Now in Section III.C.3, it has

been shown that all these times are given by simple analytic formulas, Eqs. (531), (533), and (546), respectively.

Again (see Section III.C.3), two distinct bands appear in the spectrum of the imaginary part $\chi''(\Omega)$ of the susceptibility for a uniaxial quantum nanomagnet. As usual the low-frequency band is due to the slowest "interwell" relaxation mode. The characteristic frequency and the half-width of this band are determined by the smallest nonvanishing eigenvalue λ_1, and as usual the latter is associated with the long-time behavior of $C(t) \sim e^{-t/\tau}$, $t \gg \tau$, which is dominated by the longest relaxation (or the reversal) time τ. The high-frequency band in $\chi''(\Omega)$ is due to the individual near-degenerate high-frequency modes corresponding to the eigenvalues $\lambda_k \gg \lambda_1$ ($2S \geq k \geq 2$). Thus, if one is interested solely in the low-frequency region ($\Omega\tau \leq 1$), where their effect may be ignored, $\chi(\Omega)$ may be approximated as the single Lorentzian [69] (cf. Eq. 556)

$$\frac{\chi(\Omega)}{\chi} \approx 1 - \frac{i\Omega\tau_{cor}}{1 + i\Omega\tau},\tag{589}$$

where τ_{cor} and τ are defined by Eqs. (531) and (545), respectively.

Now, magnetic SR may be generally described using linear-response theory as follows [5]. The Fourier component M_ω of the longitudinal components of the magnetic moment is related to that of the applied ac field H_ω via the complex magnetic susceptibility $\chi(\omega)$ as follows:

$$M_\omega = \chi(\omega)H_\omega.\tag{590}$$

The spectral density $\Phi_M^{(s)}(\Omega)$ of the forced magnetic oscillations in the ac field $H(t) = H\cos\Omega t$ at the excitation frequency Ω is [175]:

$$\Phi_M^{(s)}(\Omega) = \frac{1}{2}\lim_{\Delta\Omega\to 0}\int_{\Omega-\Delta\Omega}^{\Omega+\Delta\Omega}(H\chi_0\,|\chi(\Omega)|)^2\,[\delta(\omega+\Omega)+\delta(\omega-\Omega)]\,d\omega,$$

where the parity condition $\chi^*(\omega) = \chi(-\omega)$ is used. The noise-induced part $\Phi_M^{(n)}(\Omega)$ is obtained using the fluctuation–dissipation theorem as follows [184]:

$$\Phi_M^{(n)}(\Omega) = \frac{\chi''(\Omega)}{\pi\beta\,\Omega}.$$

Thus on combining these equations, we have the SNR of the magnetic moment fluctuations, namely,

$$\text{SNR} = \frac{\Phi_M^{(s)}(\Omega)}{\Phi_M^{(n)}(\Omega)} = \frac{\beta\pi\,\Omega H^2\,|\chi(\Omega)|^2}{2\chi''(\Omega)}.\tag{591}$$

The linear-response theory result given by Eq. (591) is very useful on account of its generality because it automatically reduces the calculation of the SNR to that of the dynamic susceptibility, which is a fundamental dynamical characteristic of any relaxing system. By analogy with the SNR for a classical nanomagnet [5, 184], Eq. (591) can be written as

$$\text{SNR} = \frac{\pi \beta \chi_0 H^2}{2\tau_N \sigma} R_\Omega,$$ (592)

where the dimensionless SNR factor R_Ω is given by

$$R_\Omega = \frac{\sigma \tau_N \Omega \, |\chi(\Omega)|^2}{\chi''(\Omega)}.$$ (593)

Thus, the relevant quantity is R_Ω. In general, R_Ω, besides the obvious dependence on the noise intensity (temperature), the constant (bias) field strength parameter h, and the frequency of the exciting field Ω, depends on the spin number S. On the one hand, in the adiabatic limit, $\Omega \to 0$, with Eqs. (586), (588), and the correlation time equation (531), the SNR factor equation (593) simplifies yielding

$$R_0 = \frac{\tau_N \sigma \, \chi_0}{\tau_{cor}} = \frac{\dfrac{\sigma}{2S^2} \left[\displaystyle\sum_{m=-S}^{S} m^2 \rho_m - \left(\displaystyle\sum_{m=-S}^{S} m \rho_m \right)^2 \right]^2}{\displaystyle\sum_{k=1-S}^{S} \dfrac{\left(\displaystyle\sum_{m=k}^{S} \left(m - \displaystyle\sum_{n=-S}^{S} n \rho_n \right) \rho_m \right)^2}{[S(S+1)-k(k-1)] \sqrt{\rho_k \rho_{k-1}}}}.$$ (594)

On the other hand, in the opposite very high-frequency limit, $\Omega \to \infty$, Eq. (593) reduces to

$$R_{\Omega \to \infty} = \frac{\tau_N \sigma \, \chi_0}{\tau_{ef}} = \frac{\sigma}{2S^2} \sum_{m=1-S}^{S} [S(S+1) - m(m-1)] \sqrt{\rho_m \rho_{m-1}}$$ (595)

with Eqs. (550), (586), and (588). In the classical limit, $S \to \infty$, the normalized $\chi(\Omega)$ is also given by the linear-response equation (582), where $\chi_0 = \langle \cos^2 \vartheta \rangle_0 - \langle \cos \vartheta \rangle_0^2$ and the correlation function $C(t)$ becomes

$$C(t) = \frac{\langle \cos \vartheta(t) \cos \vartheta(0) \rangle_0 - \langle \cos \vartheta \rangle_0^2}{\langle \cos^2 \vartheta \rangle_0 - \langle \cos \vartheta \rangle_0^2}.$$ (596)

Here,

$$\langle \cos \vartheta \rangle_0 = \frac{1}{Z} \int_{-1}^{1} x e^{\sigma(x^2 + 2hx)} dx$$

and

$$\langle \cos^2 \vartheta \rangle_0 = \frac{1}{Z} \int_{-1}^{1} x^2 e^{\sigma(x^2 + 2hx)} dx$$

are given by the analytical equations (524 and 551), respectively. The classical analogs of the quantum equations (594 and 595) are simply

$$R_0 = \frac{\tau_N \sigma}{\tau_{cor}} \left(\langle \cos^2 \vartheta \rangle_0 - \langle \cos \vartheta \rangle_0^2 \right), \tag{597}$$

$$R_\infty = \frac{\tau_N \sigma}{\tau_{ef}} \left(\langle \cos^2 \vartheta \rangle_0 - \langle \cos \vartheta \rangle_0^2 \right). \tag{598}$$

Here, the classical relaxation times τ_{ef} and τ_{cor} are given by Eqs. (550) and (552).

The SNR factor R_0 in the adiabatic limit $\Omega = 0$ as a function of the dimensionless temperature parameter σ^{-1} is shown in Figs. 34 and 35 for various spin
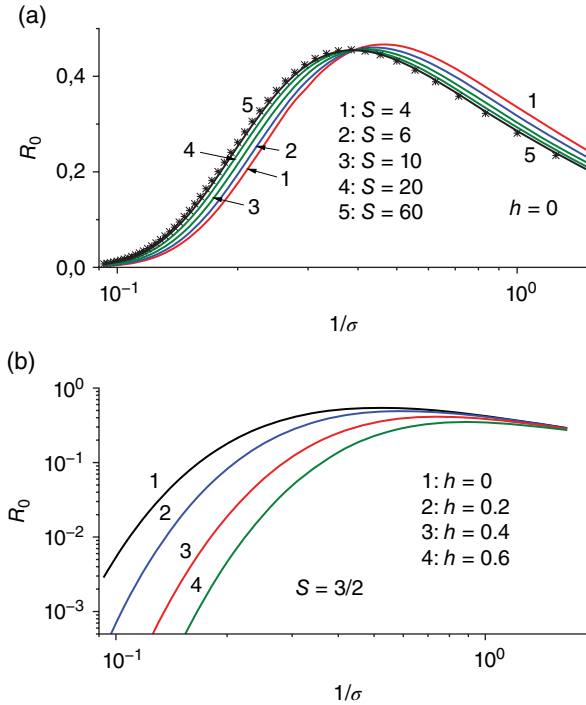
Figure 34. Signal-to-noise ratio R_0 versus the dimensionless temperature parameter σ^{-1} (a) for various spin numbers S in the absence of the dc bias field ($h = 0$) and (b) for various field parameters h and $S = 3/2$ in the adiabatic limit $\Omega = 0$. Asterisks: classical limit $S \to \infty$ (Color on line).
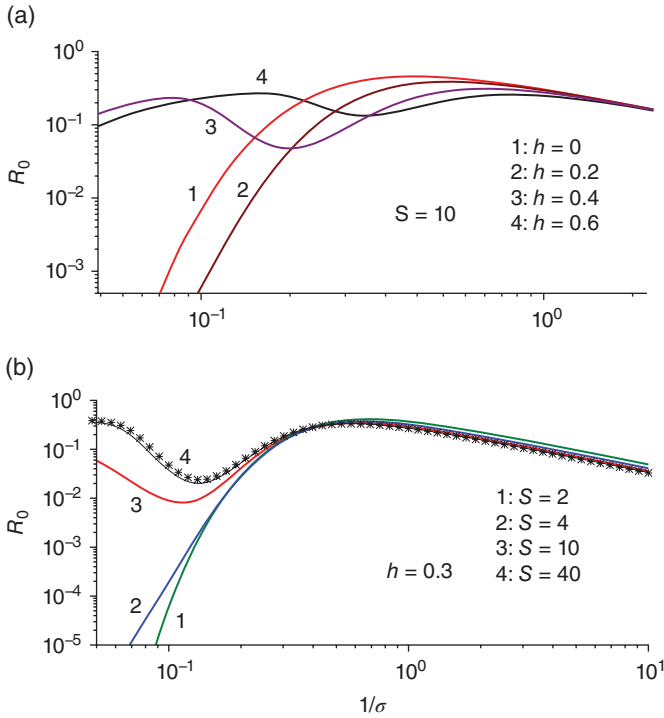
Figure 35. SNR R_0 as a function of dimensionless temperature σ^{-1} for nonzero values of the applied constant field (a) for various values of h and $S = 10$ and (b) for various values of S and $h = 0.3$ in the adiabatic limit $\Omega = 0$. Solid lines: exact solution. Asterisks: classical limit $S \to \infty$ (Color on line).

numbers S and field parameter h. Usually, the maximum of R_0 is attained in the range $\sigma^{-1} \sim 0.3-0.5$ (corresponding to $T \sim 30\,\mathrm{K}$ for the molecular magnet Mn$_{12}$ acetate with $S = 10$). Moreover, that maximum shifts to higher temperatures with increasing h because the bias field radically alters the temperature dependence of the static susceptibility. In a nonzero bias field, the effect of saturation of the magnetization is crucial causing R_0 to tend to zero at zero temperature. Although in the low-temperature limit, $\sigma^{-1} \to 0, R_0 \to 0$ for *both small S and h*; nevertheless, as long as S increases at *finite h* or as h increases at *finite S, $R_0 \to$* constant (see Fig. 35). This is due to the temperature dependence of τ_{cor}, which causes the latter to progressively lose its Arrhenius character with increasing h. In general, the quantum effects can lead to both amplification and attenuation of the SNR. The frequency-dependent SNR R_Ω versus the dimensionless temperature parameter σ^{-1} is shown in Figs. 36 for various spin numbers S and finite values of the forcing frequency Ω. Clearly, this figure exemplifies *the quantum effects via a pronounced*
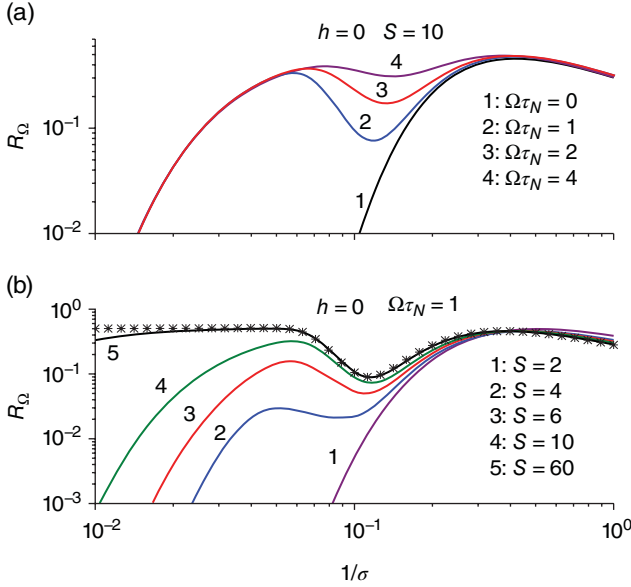
Figure 36. SNR R_{Ω} versus the dimensionless temperature σ^{-1} (a) for various normalized frequencies $\Omega\tau_N$ and $S = 10$ and (b) for various S and $\Omega\tau_N = 1$ in the absence of the dc bias field ($h = 0$). Solid lines: exact solution, Eqs. (582)–(588), and (593), Asterisks: classical limit, $S \to \infty$ (Color on line).

deviation of the quantum SNR curves from the corresponding classical ones (up to several orders of magnitude at low temperatures). Now, the SNR as a function of the dimensionless forcing frequency $\Omega\tau_N$ is also presented in Figs. 37. Here, the SNR monotonically increases from its low-frequency limit given by Eq. (594) to its plateau value given by Eq. (595).

We have studied the magnetic SR of a quantum uniaxial nanomagnet of arbitrary spin S in the high-temperature and weak spin–bath coupling limit. The principal result is that one may determine the transition from the SR corresponding to quantum elementary spin relaxation to that pertaining to a giant spin as a function of the spin size S. Hence, one may accurately estimate the value of S (typically in the range 20–40) at which the crossover from quantum to classical behavior takes place. Thus, one may assign a range of validity to the classical Néel–Brown treatment of a nanomagnet with the simplest uniaxial anisotropy and Zeeman energy. The relatively elementary calculation outlined before is also fundamental toward gaining an understanding of the SR of spin systems characterized by nonaxially symmetric Hamiltonians. The extension to particular nonaxially symmetric spin systems such as biaxial, cubic, etc., would also allow one to include spin number effects in important technological applications of magnetic relaxation such as the magnetization reversal time, the switching field and hysteresis curves, and so on.
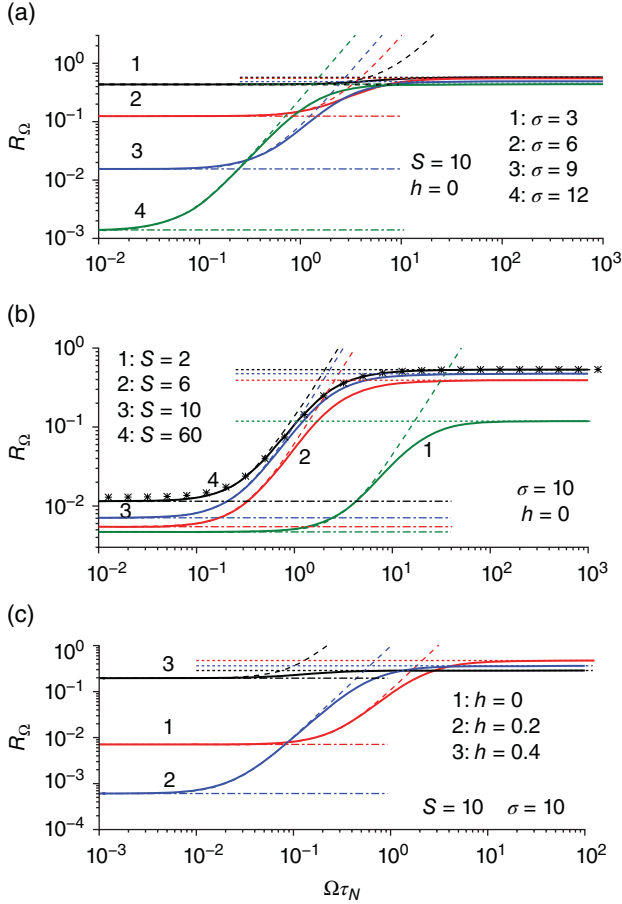
Figure 37.   SNR R_Ω versus the normalized frequency $\Omega\tau_N$ (a) for various σ, $S = 10$, and $h = 0$, (b) for various S, $\sigma = 10$, and $h = 0$, and (c) for various h, $S = 10$ and $\sigma = 10$. Solid lines: exact solution. Dashed lines: the low-frequency asymptote, Eqs. (593) and (589). Dashed-dotted lines: the adiabatic limit $\Omega = 0$, Eq. (594). Dotted lines: the high-frequency limit given by Eq. (595).

IV.   MASTER EQUATION IN PHASE SPACE FOR NONAXIALLY SYMMETRIC SYSTEMS

A.   Uniaxial Nanomagnet Subjected to a dc Bias Field of Arbitrary Orientation

Clearly, the analogy between the quantum and classical formulations provided by the phase space representation via the Wigner–Stratonovich map will also enable the powerful statistical moment method for classical Fokker–Planck equations

[5, 71] for an *arbitrary* Hamiltonian (which may be expanded in spherical harmonics) to be carried over into the quantum domain. Here, our objective is to illustrate this method for the formal phase space master equation (252) pertaining to a Hamiltonian $\hat{H}_S$ as accomplished for the Fokker–Planck equation for classical spins for arbitrary magnetocrystalline anisotropy–Zeeman energy potentials [5, 144]. We shall illustrate how the magnetization and its relaxation times may be evaluated in the *linear-response approximation* and how the solution of the corresponding classical problem [5, 6] carries over into the quantum domain. In view of the formal difficulties associated with both the derivation and the direct solution of phase space master equation, we will again proceed indirectly using the method of Section II.C. In this way, the *explicit* solution is written for an *arbitrary* spin Hamiltonian $\hat{H}_S$ as a *finite* series of spherical harmonics analogous to the (infinite) Fourier series representation of the classical case governed by the Fokker–Planck equation (3). Therefore, the expansion coefficients, that is, the statistical averages of the spherical harmonics, may be determined as before from a differential recurrence relation yielding the stochastic spin dynamics for arbitrary spin number S. For large S, the differential recurrence relations reduce to those generated by the Fokker–Planck equation. Thus, the spin dynamics may once again be treated in a manner transparently linking to the classical representations, thereby providing quantum corrections to classical averages.

1. Differential Recurrence Equations for Statistical Moments

In accordance with the Wigner–Stratonovich map, the formal solution of the phase space master equation (252) for arbitrary $\hat{H}_S$ may be written as a *finite* linear combination of the spherical harmonics $Y_{L,M}(\vartheta, \varphi)$ embodied in the phase space distribution Eq. (231). As shown in Section II.C.3, by substituting Eq. (231) into the master equation (252), we then formally have a *finite* set of differential recurrence relations for the statistical moments $\langle Y_{LM} \rangle (t)$ which becomes for $s = -1$ (i.e., for the Q-function) (cf. Eq. 256)

$$\frac{d}{dt} \langle Y_{LM} \rangle (t) = \sum_{L',M'} p'_{L'M';LM} \langle Y_{L'M'} \rangle (t), \tag{599}$$

where

$$p'_{L'M';LM} = (-1)^{M-M'} \sqrt{\frac{(2S - L')!(2S + L' + 1)!}{(2S - L)!(2S + L + 1)!}} g_{L'-M';L-M} \tag{600}$$

with the expansion coefficients $g_{L'M';LM}$ given by Eq. (76). In the classical limit, $S \to \infty$, Eq. (599) reduces to the classical hierarchy, that is, the recurrence relation given by Eq. (D.18) [5, 144]. Now the differential recurrence relations given by Eq. (599) can be solved by direct matrix diagonalization, involving the calculation of the eigenvalues and eigenvectors of the system matrix. Thus, it is evident that it is

relatively easy to generalize the phase space formalism to non-axially symmetric problems for an arbitrary spin Hamiltonian in a manner exactly analogous to that given for the classical Fokker–Planck equation (3) in Ref. 144.

Here, we shall take, as an illustrative example, a uniaxial nanomagnet of arbitrary S in an external dc magnetic field $\mathbf{H}_0$ at an *arbitrary angle* to the Z-axis (i.e., the easy axis), which is a quantum analog of the most basic nonaxially symmetric model in superparamagnetism. Thus, the Hamiltonian $\hat{H}_S$ has the nonaxially symmetric form

$$\hat{H}_S = -vK\hat{S}_Z^2 - \gamma\hbar\left(\mathbf{H}_0 \cdot \hat{\mathbf{S}}\right). \tag{601}$$

Without the loss of generality, we may suppose that $\mathbf{H}_0$ lies in the XZ plane of the laboratory coordinate system so that the spin Hamiltonian (601) becomes

$$\beta\hat{H}_S = -\frac{\sigma}{S^2}\hat{S}_Z^2 - \frac{\xi}{S}\left(\cos\psi\,\hat{S}_Z + \sin\psi\,\hat{S}_X\right), \tag{602}$$

where

$$\xi = \beta\mu_0\mu H_0 \quad\text{and}\quad \sigma = \beta vKS^2$$

are the dimensionless precession frequency and anisotropy constant, and ψ is the angle between the constant field $\mathbf{H}_0$ and the Z-axis taken as the easy axis of the nanomagnet. Using MATHEMATICA for the matrix algebra with the polarization and spin operators as defined in Appendix B, the expansion coefficients $p'_{L'M';LM}$ in Eq. (599) can then be evaluated from the symmetrized Hubbard form of the collision operator equation (76) and consequently Eq. (600) as specialized to Eq. (602).

The calculation of the observables proceeds by solving the corresponding hierarchy of moment equations, Eq. (599). That hierarchy can conveniently be rewritten for the relaxation functions $c_{L,M}(t) = \langle Y_{LM}\rangle(t) - \langle Y_{LM}\rangle_0$ as

$$\frac{d}{dt}c_{L,M}(t) = \sum_{L',M'} p'_{L'M';LM}c_{L',M'}(t) \tag{603}$$

because the equilibrium averages $\langle Y_{LM}\rangle_0$ themselves satisfy the homogeneous recurrence relation

$$\sum_{L',M'} p'_{L'M';LM}\langle Y_{LM}\rangle_0 = 0. \tag{604}$$

Here, the angular brackets $\langle\ \rangle_0$ designate the equilibrium average defined by

$$\langle Y_{LM}\rangle_0 = \frac{2S+1}{4\pi}\int_0^\pi\int_0^{2\pi} Y_{LM}(\vartheta,\varphi)W_S^{eq}(\vartheta,\varphi)\sin\vartheta\,d\vartheta\,d\varphi, \tag{605}$$

where $W_S^{eq}(\vartheta, \varphi)$ is the equilibrium quasiprobability distribution which can then be evaluated explicitly as described in Section II.D.2). Alternatively, $\langle Y_{LM} \rangle_0$ can be evaluated directly via the average polarization operators as

$$\langle Y_{LM} \rangle_0 = \sqrt{\frac{2S+1}{4\pi}} C_{SSL0}^{SS} \langle \hat{T}_{LM}^{(S)} \rangle_0 = \sqrt{\frac{2S+1}{4\pi}} C_{SSL0}^{SS} \mathrm{Tr}\left(\hat{\rho}_{eq} \hat{T}_{LM}^{(S)} \right), \qquad (606)$$

where the equilibrium density matrix $\hat{\rho}_{eq}$ is given by

$$\hat{\rho}_{eq} = \frac{e^{\frac{\sigma}{S^2} \hat{S}_Z^2 + \frac{\xi}{S}\left(\cos\psi \hat{S}_Z + \sin\psi \hat{S}_X \right)}}{\mathrm{Tr}\left\{ e^{\frac{\sigma}{S^2} \hat{S}_Z^2 + \frac{\xi}{S}\left(\cos\psi \hat{S}_Z + \sin\psi \hat{S}_X \right)} \right\}}. \qquad (607)$$

We note that for the axially symmetric case $\psi = 0$, the hierarchy defined by Eq. (603) reduces to the particular recurrence relation given by Eq. (391) already derived in Section III.A.2. For another particular case, namely, an individual spin in an external uniform magnetic field $\mathbf{H}_0$ directed along the Z-axis of the laboratory coordinate system, where $\beta \hat{H}_S = -\xi \hat{S}_Z / S$, Eq. (603) also yields the very simple *three-term* differential recurrence relation given by Eq. (418) for the relaxation functions $c_{L,M}(t)$, which *decouple* for different m and, as shown in Section III.B.3, can be solved *exactly* using continued fractions [62].

In the classical limit, $S \to \infty$ and $\hbar S \to$ constant, the hierarchy given by Eq. (603) associated with Eq. (602) reduces to the differential recurrence equations for a classical uniaxial nanomagnet subjected to a dc bias field of arbitrary orientation (see Refs. 166, 175, and 191–194 for details). Here, the number of recurring equations is *infinite* ($S \to \infty$) again constituting the principal difference between the hierarchies for classical and quantum spins; in the latter case, the number of equations is *finite*. Actually, in the classical limit, $S \to \infty$, the Hamiltonian (602) corresponds to a free energy V given by

$$\frac{V(\vartheta, \varphi)}{kT} = -\sigma \cos^2 \vartheta - \xi(\cos\vartheta \cos\psi + \sin\psi \sin\vartheta \cos\varphi). \qquad (608)$$

To describe the stochastic dynamics of a classical spin with magnetic moment $\boldsymbol{\mu}$, we may use Gilbert's equation [26] for the motion of the magnetic moment augmented by a random field, Eq. (2). In the weak coupling limit, $\alpha \ll 1$, the solution of the stochastic differential equation (2) with V defined by Eq. (608) reduces to the solution of the *infinite* hierarchy of moment equations for the relaxation functions $c_{l,m}(t) = \langle Y_{lm} \rangle(t) - \langle Y_{lm} \rangle_0$, namely, [5, 191, 192]

$$\tau_N \frac{d}{dt} c_{n,m}(t) + \left[\frac{n(n+1)}{2} + \frac{i\xi m}{2\alpha} \cos\psi - \sigma \frac{n(n+1) - 3m^2}{(2n-1)(2n+3)} \right] c_{n,m}(t)$$

$$= \left(\xi \frac{n+1}{2} \cos\psi - \frac{im\sigma}{\alpha} \right) \sqrt{\frac{n^2 - m^2}{4n^2 - 1}} c_{n-1,m}(t)$$

$$- \left(\xi \frac{n}{2} \cos\psi + \frac{im\sigma}{\alpha} \right) \sqrt{\frac{(n+1)^2 - m^2}{(2n+3)(2n+1)}} c_{n+1,m}(t)$$

$$- \frac{\xi \sin\psi}{4} \left[n \sqrt{\frac{(n-m+1)(n-m+2)}{(2n+3)(2n+1)}} c_{n+1,m-1}(t) \right.$$

$$+ i \frac{\sqrt{(n-m+1)(n+m)}}{\alpha} c_{n,m-1}(t)$$

$$\left. + (n+1) \sqrt{\frac{(n+m)(n+m-1)}{4n^2 - 1}} c_{n-1,m-1}(t) \right]$$

$$+ \frac{\xi \sin\psi}{4} \left[n \sqrt{\frac{(n+m+1)(n+m+2)}{(2n+3)(2n+1)}} c_{n+1,m+1}(t) \right.$$

$$- i \frac{\sqrt{(n+m+1)(n-m)}}{\alpha} c_{n,m+1}(t)$$

$$\left. + (n+1) \sqrt{\frac{(n-m)(n-m-1)}{4n^2 - 1}} c_{n-1,m+1}(t) \right]$$

$$+ \frac{\sigma(n+1)}{2n-1} \sqrt{\frac{(n^2 - m^2)[(n-1)^2 - m^2]}{(2n-3)(2n+1)}} c_{n-2,m}(t)$$

$$- \frac{n\sigma}{2n+3} \sqrt{\frac{[(n+2)^2 - m^2][(n+1)^2 - m^2]}{(2n+5)(2n+1)}} c_{n+2,m}(t). \tag{609}$$

For $S \to \infty$, the hierarchy of quantum relaxation equations (603) reduces to the classical equation (609) so that all the quantum results agree with the classical ones. By solving Eq. (609) for the one-sided Fourier transforms of $c_{1,0}(t)$ and $c_{1,\pm1}(t)$ as described in detail in Refs. 5 and 192, we can determine all relevant observables (see, e.g., Figs. 39–41). We shall compare later the predictions of the classical model with those of the quantum one with finite S.

2. *Characteristic Relaxation Times and Dynamic Susceptibility*

We now evaluate the *linear response* of the uniaxial nanomagnet with the Hamil-tonian equation (601) due to infinitesimally small changes in the magnitude of

the dc field. Thus, we suppose as usual that a small probing field $\mathbf{H}$ ($\mathbf{H} \parallel \mathbf{H}_0$), having been applied to the nonaxially symmetric system in the distant past ($t = -\infty$) so that equilibrium conditions obtain at time $t = 0$, is switched off at $t = 0$. By solving the hierarchy in (603) for $c_{1,0}(t)$ and $c_{1,\pm1}(t)$, we then have all relevant quantities, namely the integral, effective, and reversal times of the magnetization, the dynamic susceptibility, DMH loops, and so on. This conclusion again follows from linear response theory. Here, the decay of the magnetization $\langle M_H \rangle (t)$ defined as

$$\langle M_H \rangle (t) \sim \gamma\hbar \left\langle \left(\mathbf{H} \cdot \hat{\mathbf{S}} \right) \right\rangle (t)$$

when a small uniform external field $\mathbf{H}$ parallel to $\mathbf{H}_0$, $\beta\mu_0\mu H << 1$, has been switched off at time $t = 0$, is given by

$$\langle M_H \rangle (t) - \langle M_H \rangle_0 = \chi H C(t). \tag{610}$$

In Eq. (610), $C(t)$ is the normalized relaxation function defined in this particular instance as

$$C(t) = \frac{\sqrt{2}\cos\psi\, c_{1,0}(t) + \sin\psi [c_{1,-1}(t) - c_{1,1}(t)]}{\sqrt{2}\cos\psi\, c_{1,0}(0) + \sin\psi [c_{1,-1}(0) - c_{1,1}(0)]}, \tag{611}$$

and χ is the static magnetic susceptibility, given by

$$\chi = \sqrt{\frac{2\pi}{3}} \left\{ \sqrt{2}\cos\psi\, c_{1,0}(0) + \sin\psi [c_{1,-1}(0) - c_{1,1}(0)] \right\} \frac{\gamma\hbar(S+1)}{H}. \tag{612}$$

Furthermore, in writing Eqs. (610)–(612), we have again used the correspondence rules of spin operators and c-numbers (cf. the Weyl symbols given by Eqs. (239) and (241) for $s = 1$), namely,

$$\hat{S}_Z \to \sqrt{\frac{4\pi}{3}}(S+1)Y_{10}(\vartheta, \varphi)$$

and

$$\hat{S}_X \to \sqrt{\frac{2\pi}{3}}(S+1)\left(Y_{1-1}(\vartheta, \varphi) - Y_{11}(\vartheta, \varphi)\right).$$

The initial conditions $c_{L,M}(0)$ in Eqs. (611) and (612) are

$$c_{L,M}(0) = \lim_{\xi_1 \to 0} \xi_1^{-1} \left(\langle Y_{LM} \rangle_{\xi_1} - \langle Y_{LM} \rangle_0 \right)$$

$$= \sqrt{\frac{2S+1}{4\pi}} C_{SSL0}^{SS} \lim_{\xi_1 \to 0} \xi_1^{-1} \left(\left\langle \hat{T}_{LM}^{(S)} \right\rangle_{\xi_1} - \left\langle \hat{T}_{LM}^{(S)} \right\rangle_0 \right). \tag{613}$$

Moreover, in calculating the equilibrium averages $\left\langle \hat{T}_{L,M}^{(S)} \right\rangle_{\xi_1}$, we have also used the equilibrium Boltzmann distribution function ρ_{ξ_1} for the Hamiltonian equation (602), namely

$$\rho_{\xi_1} = \frac{e^{\frac{\sigma}{S^2}\hat{S}_Z^2 + \frac{\xi+\xi_1}{S}\left(\cos\psi\hat{S}_Z + \sin\psi\hat{S}_X\right)}}{\text{Tr}\left\{ e^{\frac{\sigma}{S^2}\hat{S}_Z^2 + \frac{\xi+\xi_1}{S}\left(\cos\psi\hat{S}_Z + \sin\psi\hat{S}_X\right)} \right\}}.$$

The corresponding dynamic susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ is as usual

$$\frac{\chi(\omega)}{\chi} = 1 - i\omega\,\tilde{C}(\omega), \tag{614}$$

where the spectrum

$$\tilde{C}(\omega) = \int_0^\infty C(t)\, e^{-i\omega t} dt. \tag{615}$$

We can also evaluate the integral relaxation time $\tau_{cor} = \tilde{C}(0)$ (in linear response the correlation time of $C(t)$) and the effective relaxation time $\tau_{ef} = -1/\dot{C}(0)$. In the frequency domain, these characteristic times as usual determine the low- and high-frequency behavior of the dynamic susceptibility $\chi(\omega)$ via Eqs. (490) and (491), namely,

$$\frac{\chi(\omega)}{\chi} \approx \begin{cases} 1 - i\omega\tau_{cor} + \cdots, & \omega \to 0 \\ (i\omega\tau_{ef})^{-1} + \cdots, & \omega \to \infty \end{cases}. \tag{616}$$

As before, yet another relevant quantity is the inverse of the smallest nonvanishing eigenvalue λ_1 of the transition matrix of the system (Eq. 618), which we recall is the time constant associated with the *long-time behavior* of the correlation function $C(t)$ comprising the slowest (lowest frequency) relaxation mode. Thus, λ_1^{-1} may again be associated with the spin reversal time. Furthermore, because the influence of the high-frequency relaxation modes on the low-frequency relaxation may often be ignored, λ_1 again provides more or less complete information concerning the low-frequency dynamics of the system and may be extracted from the eigenvalues of the transition matrix $\mathbf{X}$ given by Eq. (618). In the low-temperature limit and a weak external dc field, the relation between the time constants defined before is as follows:

$$\lambda_1^{-1} > \tau_{cor} \gg \tau_N \gg \tau_{ef}. \tag{617}$$

Thus, to determine the magnetization kinetics, we require (cf. the response function given by Eq. (611)) the one-sided Fourier transforms of $c_{1,0}(t)$ and

$c_{1,\pm 1}(t)$. According to the differential recurrence equation (603), these relaxation functions are as usual coupled to all the others, so forming (unlike the classical case) a *finite* hierarchy of averages as before (because the index L in Eq. (603) ranges only between 0 and $2S$). Once again, the solution of such a multi-term recurrence relation may always be obtained by rewriting it as a first-order linear matrix differential equation like Eq. (80) for a column vector $\mathbf{C}(t)$ given by Eq. (79) with a transition supermatrix $\mathbf{X}$ of dimension $4S(S+1) \times 4S(S+1)$ with matrix elements

$$(\mathbf{X})_{L,L'} = \mathbf{G}^{S}_{L,L'}, \quad \left[\mathbf{G}^{S}_{L,L'}\right]_{M,M'} = -p_{L'M';LM}. \tag{618}$$

Having solved the matrix equation (80) as described in detail in Section II.A.4, we have the relaxation functions $c_{1,0}(t)$ and $c_{1,\pm 1}(t)$, their spectra, and all desired observables such as characteristic times τ_{cor}, τ_{ef}, $\tau = 1/\lambda_1$, and the dynamic susceptibility $\chi(\omega)$. For simplicity, we shall suppose that the diffusion coefficients are given by $D_1 = D_{-1} = 2D_0 = 2D$ (i.e., isotropic diffusion). To compare with the semiclassical case, we simply write $\tau_N = 1/(2D)$ and $\alpha = \hbar S \beta D$.

The relaxation time τ_{cor} and inverse of the smallest nonvanishing eigenvalue $1/\lambda_1$ (the longest relaxation time) as a function of the oblique angle ψ, the anisotropy parameter σ, and the dimensionless damping α are plotted in Figs. 38–40, respectively, for various spin numbers S and of the field parameter $h = \xi/(2\sigma)$. The classical solutions [5, 192] corresponding to $S \to \infty$ are also shown for comparison. Both τ_{cor} and $\tau = 1/\lambda_1$ exhibit a pronounced dependence on the oblique angle ψ, the field h, anisotropy σ, damping α, and spin number S parameters. It is apparent from Figs. 38–40 that for large S, the quantum solutions reduce to the corresponding classical ones, while in contrast they differ markedly from each other for small S. Typical values of S for the quantum classical crossover are ~ 20–40. The smaller the anisotropy σ, the smaller the S value required for convergence of the quantum results to the classical ones. Now the *intrinsic* damping (α) dependence of these characteristic relaxation times for the oblique field configuration shown in Fig. 39 represents coupling between the longitudinal and precessional modes of the magnetization. Hence, it should be possible to determine α by fitting the theory to the experimental dependence of the reversal time on the angle ψ and dc bias field strength. Here, the sole fitting parameter is α, which can be determined at different temperatures T, exposing its temperature dependence. As before, the behavior of τ_{cor} and $\tau = 1/\lambda_1$ is similar only for small external fields, $h << 1$; in a strong external field, $h > 0.2$, τ can diverge exponentially from τ_{cor} as for classical spins (see Fig. 40). This effect as we have previously explained was discovered numerically for classical spins by Coffey *et al.* [152] and later interpreted quantitatively by Garanin [153] (see also Ref. 5, ch. 1 for details).

In Figs. 41–44, we have plotted the real and imaginary parts of $\chi(\omega)/\chi$ versus normalized frequency ω/D for various model parameter values. Clearly, three
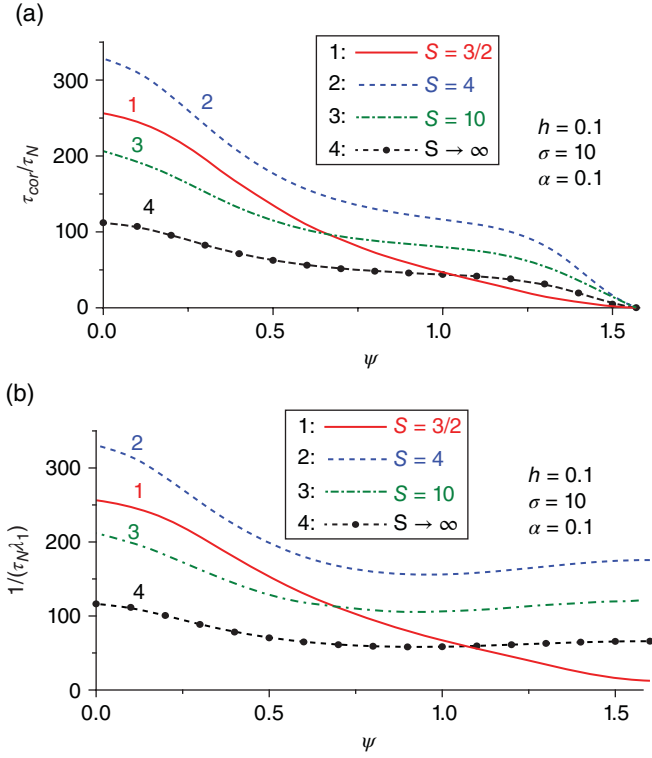
Figure 38. Correlation time τ_{cor} (a) and overbarrier time $1/\lambda_1$ (b) versus the oblique angle ψ for various spin numbers S and anisotropy parameter $\sigma = 10$, dimensionless damping $\alpha = 0.1$, and field parameter $h = 0.1$ (Color on line).

bands now appear in $\chi''(\omega)$ two of which are like those in axial symmetry, while a third resonance band appears due to high-frequency precession of the spin in the effective field. The low-frequency relaxation band is as usual due to the slowest relaxation mode where the characteristic frequency and bandwidth are determined by λ_1. Like the classical case, λ_1 is sufficient to accurately predict the behavior of the low-frequency part of $\chi(\omega)$ as well as the long-time behavior of $C(t)$. Thus, if one is interested solely in the low-frequency region ($\omega/\lambda_1 \leq 1$), where the effect of the high-frequency modes may be ignored, $\chi(\omega)$ may be again approximated by the single Lorentzian equation (556), which implies that $C(t)$ may be approximated for $t > 0$ by a *single* exponential with relaxation time $T_\parallel = 1/\lambda_1$. It is apparent from Figs. 41–44 since the influence of the high-frequency relaxation modes on the low-frequency relaxation may be ignored, that the simple Lorentzian formula given by Eq. (556) again accurately describes the entire low-frequency dynamics. The second far weaker high-frequency relaxation
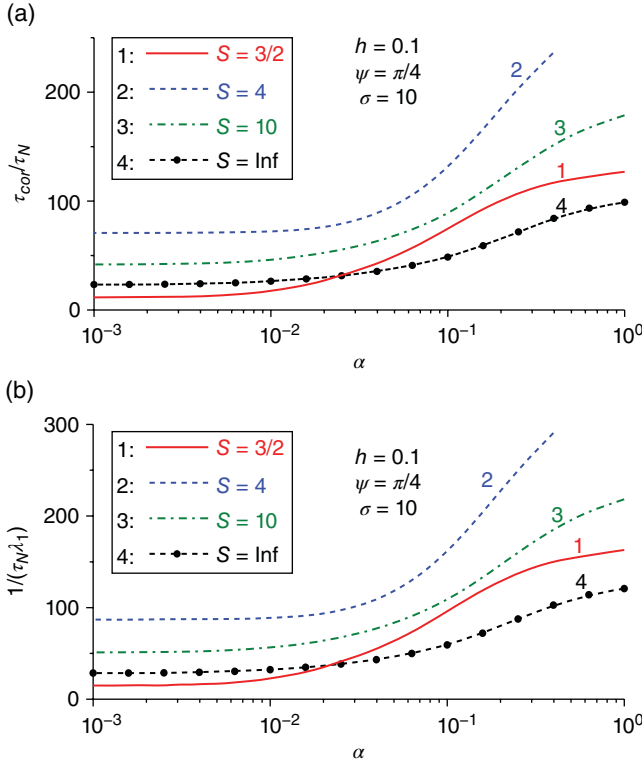
Figure 39. Correlation time τ_{cor} (a) and overbarrier time $1/\lambda_1$ (b) versus dimensionless damping α for various spin numbers S and oblique angle $\psi = \pi/4$, anisotropy parameter $\sigma = 10$, and field parameter $h = 0.1$ (Color on line).

band in $\chi''(\omega)$ is once more due to high-frequency longitudinal "intrawell" modes. The individual "intrawell" modes are indistinguishable in the spectrum of $\chi''(\omega)$ appearing merely as a single high-frequency Lorentzian band. This "intrawell" relaxation band is more pronounced when the external field coincides with the easy axis, that is, for $\psi = 0$. However, in general, it is masked by the third sharp resonance band due to excitation of transverse modes having frequencies close to the precession frequency of the spin which strongly manifests itself at high frequencies. For $\psi = 0$, the resonance peak disappears because the transverse modes are no longer excited. In contrast, it is most pronounced when $\psi = \pi/2$.

In this section, we have solved the differential recurrence equation (599) for the evolution of the statistical moments (average spherical harmonics) for a *nonaxially symmetric* spin Hamiltonian, namely, Eq. (602). For purposes of illustration, the analysis was carried out for a uniaxial nanomagnet subjected to a dc external field applied at an *arbitrary* angle to the easy axis. In particular, we have evaluated
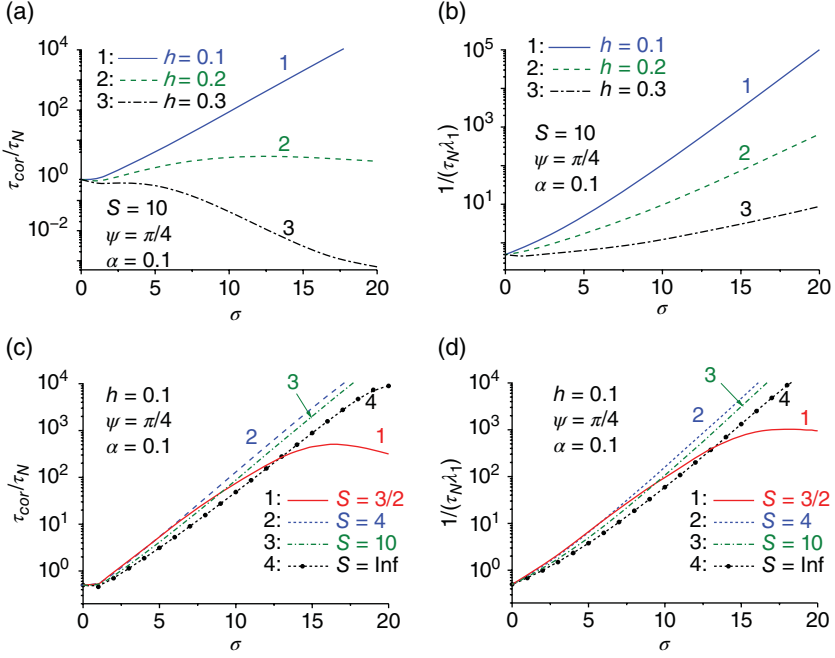
Figure 40. Correlation time τ_{cor} and overbarrier time $1/\lambda_1$ versus the anisotropy parameter σ for various field parameters h and spin number $S = 4$, (a) and (b), for various S with field parameter $h = 0.1$, (c) and (d); dimensionless damping $\alpha = 0.1$ and oblique angle $\psi = \pi/4$ (Color on line).

the characteristic relaxation times along with the linear dynamic susceptibility via obvious generalizations of the methods previously used for classical spins [5, 191, 192]. Thus, the phase space representation (because it is closely allied to the classical one) again transparently illustrates how quantum distributions reduce to the classical ones. When the direction of the external fields coincides with the easy axis, that is, for $\psi = 0$, our method reproduces the results for nanomagnets subjected to a longitudinal field previously obtained in Section III.C.2. The method may also be extended to other non-axially symmetric multi-well systems such as biaxial, cubic, mixed, and so on. Furthermore, the model can be generalized to time-dependent Hamiltonians as in Section III.C.3, so that we can also determine quantum effects in the nonlinear ac stationary response of quantum nanomagnets in the nonaxially symmetric problem we have just considered.

V. CONCLUSION

We have treated numerous illustrative examples of spin relaxation problems using Wigner's phase space formulation of quantum mechanics of particles and spins.
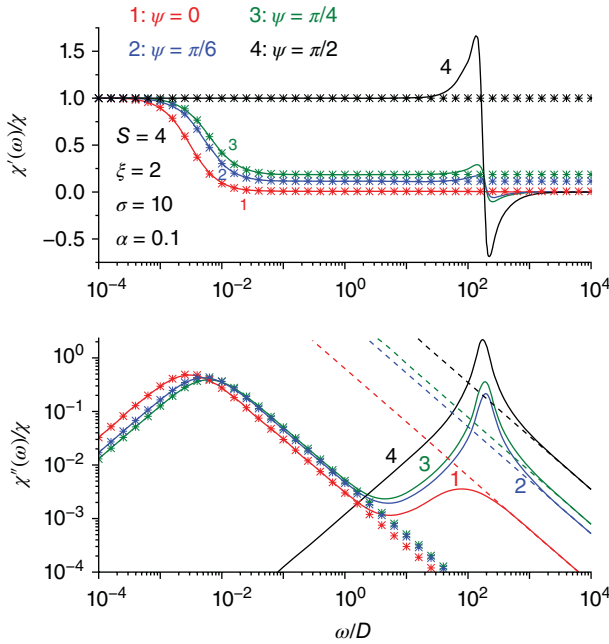
Figure 41. Real and imaginary parts of the dynamic susceptibility $\chi(\omega)$ versus the normalized frequency ω/D for various oblique angles ψ and field parameter $h = 0.1$, anisotropy parameter $\sigma = 10$, damping $\alpha = 0.1$, and spin $S = 4$. Asterisks: the single Lorentzian approximation, Eq. (556), while the straight dashed lines are the high-frequency asymptotes, Eq. (616) (Color on line).

This formulation, first envisaged for closed spin systems by Stratonovich [49] formally represents the quantum mechanics of spins as a statistical theory in the representation space of polar angles (ϑ, φ) which has a clear classical meaning. This procedure effectively generalizes the results of Wigner [41] who represented the quantum mechanics of a particle with Hamiltonian $\hat{H} = \hat{p}^2/2m + V(\hat{q})$ in Hilbert space as a statistical theory in a classically meaningful phase space with the canonical variables position and momentum (q, p). Stratonovich [49] proceeded by introducing a quasiprobability density (Wigner) function on the sphere, defined as the linear invertible bijective map onto the representation space comprising the trace of the product of the system density matrix and the irreducible tensor operators, the analysis being carried out via the finite series in spherical harmonics embodied in the bijective Wigner–Stratonovich map. Hence, the average value of a quantum spin operator may be calculated via its Weyl symbol just as the corresponding classical function in the representation space of polar angles (ϑ, φ). This may be accomplished essentially because the *polarization operators transform under rotation in the same way as the spherical harmonics*. Thus, the Stratonovich representation for spins [49] is well suited to the development of
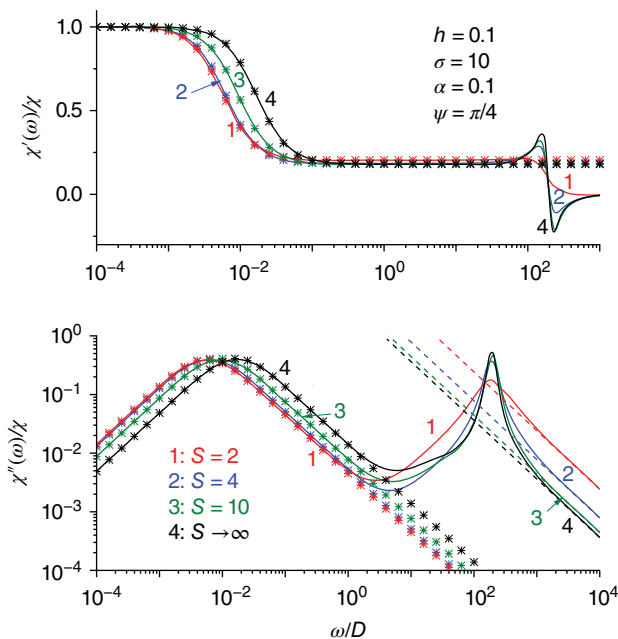
Figure 42. Real and imaginary parts of $\chi(\omega)$ versus the normalized frequency parameter ω/D for various spin numbers S and $h = 0.1$, $\sigma = 10$, $\alpha = 0.1$, and $\psi = \pi/4$. Asterisks are the single Lorentzian approximation, Eq. (556), while the straight dashed lines are the high frequency asymptotes, Eq. (616) (Color on line).

semiclassical methods of treatment of spin relaxation phenomena allowing one to obtain quantum corrections in a manner closely analogous to the classical case.

The merit of the phase space formalism as applied to spin relaxation problems is that only master equations for the phase space distributions akin to Fokker–Planck equations for the evolution of classical phase space distributions in configuration space are involved so that operators are unnecessary. The *explicit* solution of these equations can be expanded for an *arbitrary* spin Hamiltonian in a *finite* series of spherical harmonics equation (231) like in the classical case where an infinite number of spherical harmonics is involved. The expansion coefficients (statistical moments or averages of the spherical harmonics which are obviously by virtue of the Wigner–Stratonovich map the averages of the polarization operators) may be determined from a differential recurrence relation given by Eq. (253) in a manner similar to the classical case. Although the form of the phase space master equation is in general very complicated, we can circumvent the problem of determining differential recurrence relations by directly using the one-to-one correspondence between averages of polarization operators and those of spherical harmonics as outlined in Section II.C.3. Moreover, we have described this procedure via
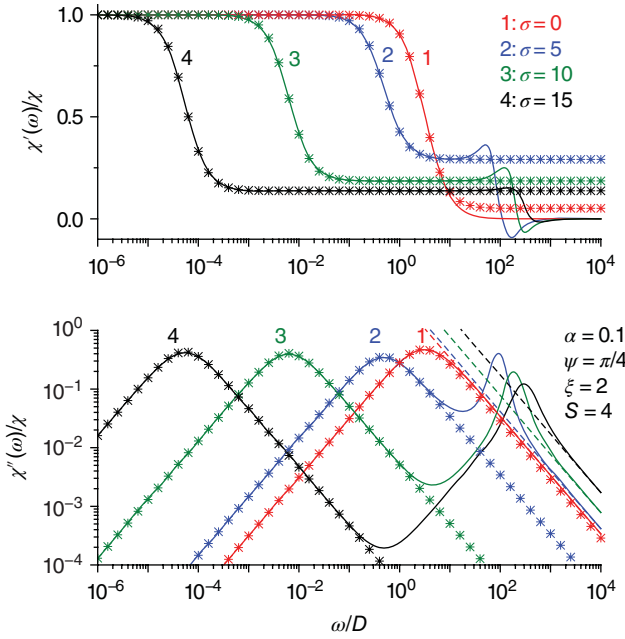
Figure 43.   Real and imaginary parts of $\chi(\omega)$ versus the normalized frequency ω/D for various anisotropy parameters σ and spin number $S = 4$, field parameter $\xi = 2$, dimensionless damping $\alpha = 0.1$, and oblique angle $\psi = \pi/4$. Asterisks are the single Lorentzian approximation, Eq. (556), while the straight dashed lines are the high-frequency asymptotes, Eq. (616) (Color on line).

several illustrative examples. Thus, we still have a method of treating the spin relaxation for *arbitrary* spin number S which is closely allied to the classical one even though a phase space master equation may not be explicitly involved. In the classical limit, the quantum differential recurrence relation reduces to that yielded by the classical Fokker–Planck equation for *arbitrary* magnetocrystalline–Zeeman energy potentials. Furthermore, the phase space representation via the Weyl symbol of the relevant spin operator suggests how powerful computation techniques developed for Fokker–Planck equations (matrix continued fractions, mean first passage time, integral representation of relaxation times, and so on [5, 71]) may be transparently extended to the quantum domain indeed suggesting new closed form quantum results via the corresponding classical ones. A specific example is the determination of the quantum integral relaxation time for a spin in a uniform magnetic field of arbitrary strength directed along the *Z*-axis, Eq. (442). Therefore, having solved the phase space master equation, one can then, in principle, evaluate via obvious generalizations of the methods previously used for classical spins [5, 6] all desired observables. These include the magnetization itself, the magnetization reversal time, the linear and nonlinear dynamic
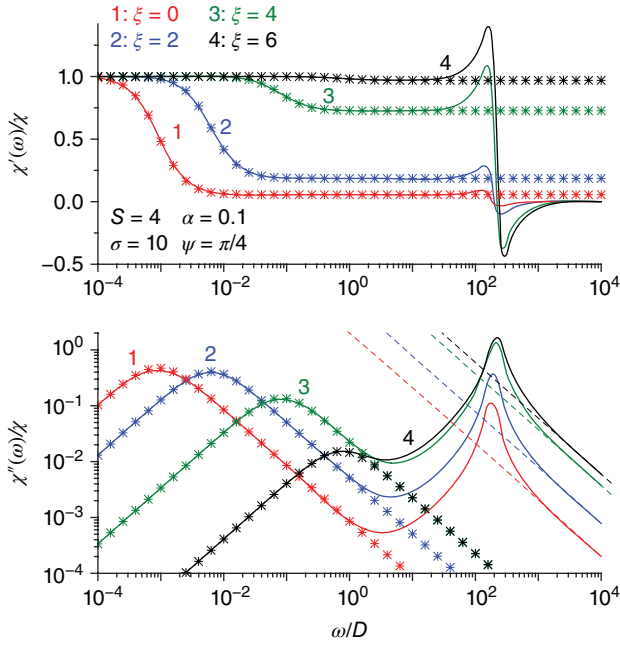
Figure 44. Real and imaginary parts of $\chi(\omega)$ versus the normalized frequency ω/D for various field parameters ξ and anisotropy parameter $\sigma = 10$, spin number $S = 4$, dimensionless damping $\alpha = 0.1$, and oblique angle $\psi = \pi/4$. Asterisks are the single Lorentzian approximation, Eq. (556), while the straight dashed lines are the high-frequency asymptotes, Eq. (616) (Color on line).

susceptibilities, the temperature dependence of the switching fields, the dynamic hysteresis loops, etc). In this way, one can study the transition of the relaxation behavior from that of an elementary spin to molecular magnets ($S \sim 10$), to nanoclusters ($S \sim 100$), and to classical superparamagnets ($S \geq 1000$). Thus, all *quantum effects in the spin relaxation phenomena can be treated in a manner linking directly to the classical representations*. Furthermore, by treating a variety of spin relaxation problems, we have also amply demonstrated that although the density matrix and phase space methods may yield results in *outwardly very different forms*, nevertheless, both approaches yield *identical* numerical values for the *same* physical quantities (i.e., relaxation times and susceptibility). Hence, we have established a vital corollary between the phase space and the density matrix methods, thereby demonstrating that they are essentially equivalent while simultaneously providing an important check on the validity of the phase space method. Thus, the phase space representation, because it is closely allied to the classical representation, besides being complementary to the operator one, transparently illustrates how quantum phase space distributions reduce to the classical ones in the limit $S \to \infty$.

APPENDIX A: SPIN AND POLARIZATION OPERATORS

The spin operator $\hat{\mathbf{S}}$ is Hermitian $\hat{\mathbf{S}}^\dagger = \hat{\mathbf{S}}$, and it is usually represented by a set of three (since the spin vector $\hat{\mathbf{S}}$ has three components) square $(2S+1) \times (2S+1)$ matrixes with S being the spin number [95]. For the Cartesian components of $\hat{\mathbf{S}}$, namely, for the operators $\hat{S}_X$, $\hat{S}_Y$, and $\hat{S}_Z$, the Hermitian property takes on the form $\hat{S}_i^\dagger = \hat{S}_i$, $(i = X, Y, Z)$, while for the spherical components $\hat{S}_{\pm 1}$ and $\hat{S}_0$ that property becomes $\hat{S}_\mu^\dagger = (-1)^\mu \hat{S}_\mu$. The relations between the Cartesian and spherical components of $\hat{\mathbf{S}}$ are given by [95]

$$
\begin{aligned}
\hat{S}_{+1} &= -\frac{1}{\sqrt{2}}\left(\hat{S}_X + i\hat{S}_Y\right), \quad \hat{S}_X = \frac{1}{\sqrt{2}}\left(\hat{S}_{-1} - \hat{S}_{+1}\right), \\
\hat{S}_{-1} &= \frac{1}{\sqrt{2}}\left(\hat{S}_X - i\hat{S}_Y\right), \quad \hat{S}_Y = \frac{i}{\sqrt{2}}\left(\hat{S}_{-1} + \hat{S}_{+1}\right), \\
\hat{S}_0 &= \hat{S}_Z, \quad \hat{S}_Z = \hat{S}_0.
\end{aligned}
\tag{A.1}
$$

Polarization states of particles are described by spin functions $\chi_{Sm} = |S, m\rangle$, which depend on the spin variable σ being the spin projection on the Z-axis. This variable takes $2S+1$ values, $\sigma = -S, -S+1, \ldots, S-1, S$. The dependence of the spin functions $\chi_{Sm}(\sigma)$ on the spin variable σ is given by $\chi_{Sm}(\sigma) = \delta_{m\sigma}$ [95]. The spin functions $\chi_{Sm} = |S, m\rangle$ are eigenfunctions of the spin operators $\hat{\mathbf{S}}^2$ and $\hat{S}_Z$, namely, [95]

$$
\hat{\mathbf{S}}^2 \chi_{Sm} = S(S+1)\chi_{Sm}, \tag{A.2}
$$

$$
\hat{S}_Z \chi_{Sm} = m\chi_{Sm} \tag{A.3}
$$

with $m = -S, -S+1, \ldots, S-1, S$. The spin functions each have $2S+1$ components and describe polarization states of a particle with definite spin S and spin projection m onto the Z-axis. They can be rewritten as column matrixes [95]

$$\chi_{SS} = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad \chi_{SS-1} = \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix}, \quad \dots, \quad \chi_{S-S} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 1 \end{pmatrix}. \tag{A.4}$$

Furthermore, the vector representation shows that the spin functions χ_{Sm} constitute a complete set of functions with the orthonormality and completeness conditions

$$\chi_{Sm'}^{\dagger} \chi_{Sm} = \delta_{mm'}, \tag{A.5}$$

$$\sum_{m=-S}^{S} \chi_{Sm} \chi_{Sm}^{\dagger} = \hat{I}, \tag{A.6}$$

where $\hat{I}$ is the unit $(2S+1) \times (2S+1)$ matrix.

Now, the spherical components of the spin operator $\hat{\mathbf{S}}$ may be expressed using the Clebsch–Gordan coefficients in terms of the spin functions as [95]

$$\hat{S}_{\mu} = \sqrt{S(S+1)} \sum_{m,m'} C_{Sm'1\mu}^{Sm} \chi_{Sm} \chi_{Sm'}^{\dagger}, \quad (\mu = 0, \pm 1). \tag{A.7}$$

The operators $\hat{S}_{\mu}$ satisfy the following commutation relation: [95]

$$\left[\hat{S}_{\mu}, \hat{S}_{v} \right] = -\sqrt{2} C_{1\mu 1v}^{1\lambda} \hat{S}_{\lambda}, \quad \left[\hat{\mathbf{S}}^2, \hat{S}_{\mu} \right] = 0 \quad (\mu, v, \lambda = 0, \pm 1). \tag{A.8}$$

The matrix elements of $\hat{S}_{\mu}$ are given by [95]

$$\left[\hat{S}_{\mu} \right]_{m'm} = \chi_{Sm'}^{\dagger} \hat{S}_{\mu} \chi_{Sm} = \sqrt{S(S+1)} C_{Sm1\mu}^{Sm'} \tag{A.9}$$

with the only nonvanishing elements being

$$\left[\hat{S}_0 \right]_{mm} = m, \tag{A.10}$$

$$\left[\hat{S}_{\pm 1} \right]_{m \pm 1m} = \mp \frac{1}{\sqrt{2}} \sqrt{(S \mp m)(S \pm m + 1)}. \tag{A.11}$$

The Cartesian and spherical components of $\hat{\mathbf{S}}$ are related by Eq. (A.1). For example, in the particular case $S = 1/2$, the operators $\hat{S}_i (i = X, Y, Z)$ and $\hat{S}_{\mu}$ ($\mu = 0, \pm 1$) are square 2×2 matrixes given by [95]

$$\hat{S}_X = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{S}_Y = \frac{i}{2} \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \quad \hat{S}_Z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{A.12}$$

$$\hat{S}_{+1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -1 \\ 0 & 0 \end{pmatrix}, \quad \hat{S}_0 = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \hat{S}_{-1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \tag{A.13}$$

while for $S = 1$, these operators are the square 3×3 matrixes given by [95]

$$
\hat{S}_X = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \hat{S}_Y = \frac{i}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix},
$$

$$
\hat{S}_Z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \tag{A.14}
$$

$$
\hat{S}_{+1} = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{S}_0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \hat{S}_{-1} = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}. \tag{A.15}
$$

Now, in order to describe a polarization (spin) state of a particle, the polarization operators are often used. These operators denoted by $\hat{T}_{LM}^{(S)}$, where $L = 0, 1, \dots, 2S$ and $M = -L, -L+1, \dots L$, are matrixes, which act on spin functions. However, the explicit form of $\hat{T}_{LM}^{(S)}$ depends on the representation chosen for the spin functions. In particular, the matrix elements $T_{m'm} = \left[\hat{T}_{LM}^{(S)} \right]_{m'm}$ of the polarization operator $\hat{T}_{LM}^{(S)}$ which has the explicit form

$$
\hat{T}_{LM}^{(S)} = \begin{pmatrix} T_{SS} & \cdots & T_{S-S} \\ \vdots & \ddots & \vdots \\ T_{-SS} & \cdots & T_{-S-S} \end{pmatrix} \tag{A.16}
$$

are related to those of the spin functions in the spherical basis representation via [95]

$$
T_{m'm} = \chi_{Sm'}^{\dagger} \hat{T}_{LM}^{(S)} \chi_{Sm} = \sqrt{\frac{2L+1}{2S+1}} C_{SmLM}^{Sm'}. \tag{A.17}
$$

For example, the operator $\hat{T}_{00}^{(S)}$ is proportional to the unit $(2S+1) \times (2S+1)$ matrix

$$
\hat{T}_{00}^{(S)} = \frac{1}{\sqrt{2S+1}} \hat{I}, \tag{A.18}
$$

while for $L = 1$, the operators $\hat{T}_{L\mu}^{(S)}$ are proportional to the spherical components of the spin operator

$$
\hat{T}_{1\mu}^{(S)} = \frac{1}{\sqrt{2a}} \hat{S}_\mu, \tag{A.19}
$$

where

$$a = \sqrt{\frac{S(S+1)(2S+1)}{6}}. \tag{A.20}$$

Likewise, the Cartesian components of $\hat{\mathbf{S}}$ given by Eq. (A.1) may also be expressed via the polarization operators $\hat{T}_{10}^{(S)}$ and $\hat{T}_{1\pm1}^{(S)}$ as follows:

$$\begin{aligned}
\hat{S}_X &= a\left(\hat{T}_{1-1}^{(S)} - \hat{T}_{11}^{(S)}\right), \\
\hat{S}_Y &= ia\left(\hat{T}_{1-1}^{(S)} + \hat{T}_{11}^{(S)}\right), \\
\hat{S}_Z &= \sqrt{2}a\hat{T}_{10}^{(S)}.
\end{aligned} \tag{A.21}$$

The polarization operators $\hat{T}_{LM}^{(S)}$ are normalized and satisfy the relations [95]

$$\hat{T}_{LM}^{\dagger(S)} = (-1)^M \hat{T}_{L-M}^{(S)} \tag{A.22}$$

and

$$\mathrm{Tr}\left(\hat{T}_{L,M}^{(S)}\right) = \sqrt{(2S+1)}\delta_{L0}\delta_{M0}, \tag{A.23}$$

that is, all $\hat{T}_{LM}^{(S)}$ have zero trace except of $\hat{T}_{00}^{(S)}$. Furthermore, the operators $\hat{T}_{LM}^{(S)}$ also constitute an orthonormal basis in the space of $(2S+1) \times (2S+1)$ matrixes with S integer or half-integer. Hence, it follows that an *arbitrary* square $(2S+1) \times (2S+1)$ matrix operator $\hat{A}$ may be expanded as a series of the polarization operators [95]

$$\hat{A} = \sum_{L=0}^{2S} \sum_{M=-L}^{L} A_{LM} \hat{T}_{LM}^{(S)}, \tag{A.24}$$

where the expansion coefficients A_{LM} are given by

$$A_{LM} = \mathrm{Tr}\left(\hat{T}_{LM}^{\dagger(S)}\hat{A}\right). \tag{A.25}$$

If the matrix $\hat{A}$ is Hermitian ($\hat{A}^\dagger = \hat{A}$), then

$$A_{LM}^* = (-1)^M A_{L-M}. \tag{A.26}$$

Moreover, the matrix products of the spin functions χ_{Sm} and $\chi_{Sm'}^{\dagger}$ (as arranged in the form of Eq. A.4) are themselves square $(2S + 1) \times (2S + 1)$ matrixes and, therefore, may also be expanded as a finite series of polarization operators, namely, [95]

$$\chi_{Sm}\chi_{Sm'}^{\dagger} = \sum_L \sqrt{\frac{2L+1}{2S+1}} C_{Sm'LM}^{Sm} \hat{T}_{LM}^{(S)}. \tag{A.27}$$

Furthermore, products of two polarization operators may be written in the form of the Clebsch–Gordan series [95]

$$\hat{T}_{L_1M_1}^{(S)} \hat{T}_{L_2M_2}^{(S)} = \sqrt{(2L_1+1)(2L_2+1)} \sum_L (-1)^{2S+L} \begin{Bmatrix} L_1 L_2 L \\ S S S \end{Bmatrix} C_{L_1M_1L_2M_2}^{LM} \hat{T}_{LM}^{(S)}, \tag{A.28}$$

where $\begin{Bmatrix} L_1 L_2 L \\ S S S \end{Bmatrix}$ is Wigner's 6j-symbol [95]. The polarization operators also satisfy the commutation relations [95]

$$\left[\hat{T}_{L_1M_1}^{(S)}, \hat{T}_{L_2M_2}^{(S)}\right] = \sqrt{(2L_1+1)(2L_2+1)} \sum_L (-1)^{2S+L}$$
$$\times \left[1 - (-1)^{L_1+L_2+L}\right] \begin{Bmatrix} L_1 L_2 L \\ S S S \end{Bmatrix} C_{L_1M_1L_2M_2}^{LM} \hat{T}_{LM}^{(S)}. \tag{A.29}$$

Equation (A.29) then automatically yields the commutation relation for the spherical components of the spin operator $\hat{S}_{\mu}$ and polarization operator $\hat{T}_{LM}^{(S)}$, namely [95],

$$[\hat{S}_{\mu}, \hat{T}_{LM}^{(S)}] = \sqrt{L(L+1)} C_{LM1\mu}^{LM+\mu} \hat{T}_{LM+\mu}^{(S)} \tag{A.30}$$

or

$$[\hat{S}_0, \hat{T}_{LM}^{(S)}] = \sqrt{L(L+1)} C_{LM10}^{LM} \hat{T}_{LM}^{(S)} = M\hat{T}_{LM}^{(S)}, \tag{A.31}$$
$$[\hat{S}_{\pm 1}, \hat{T}_{LM}^{(S)}] = \sqrt{L(L+1)} C_{LM1\pm1}^{LM\pm1} \hat{T}_{LM\pm1}^{(S)}$$
$$= \mp\sqrt{\frac{L(L+1) - M(M \pm 1)}{2}} \hat{T}_{LM\pm1}^{(S)}. \tag{A.32}$$

Finally, traces of products of the polarization operators are given by [95]

$$\mathrm{Tr}\left(\hat{T}_{L_1M_1}^{(S)} \hat{T}_{L_2M_2}^{(S)}\right) = (-1)^{M_1} \delta_{L_1L_2}\delta_{M_1-M_2}, \tag{A.33}$$
$$\mathrm{Tr}\left(\hat{T}_{LM}^{\dagger(S)} \hat{T}_{L'M'}^{(S)}\right) = \delta_{LL'}\delta_{MM'}, \tag{A.34}$$

$$\text{Tr}\left(\hat{T}^{(S)}_{L_1M_1}\hat{T}^{(S)}_{L_2M_2}\hat{T}^{(S)}_{L_3M_3}\right) = (-1)^{2S+L_3+M_3}\sqrt{(2L_1+1)(2L_2+1)}$$

$$\times C^{L_3-M_3}_{L_1M_1L_2M_2}\begin{Bmatrix}L_1L_2L_3\\SSS\end{Bmatrix}, \tag{A.35}$$

and so on.

Finally, under rotation of coordinate system defined by the Euler angles α, β, γ, the basis spin functions $\chi_{Sm'}$ are transformed by the rotation operator $\hat{D}^S(\alpha, \beta, \gamma)$ given by [95]

$$\hat{D}^S(\alpha, \beta, \gamma) = e^{-i\alpha\hat{S}_X}e^{-i\beta\hat{S}_Y}e^{-i\gamma\hat{S}_Z}$$

$$= \sum_{L,M,m,m'}\frac{2L+1}{2S+1}C^{Sm}_{Sm'LM}D^S_{mm'}(\alpha, \beta, \gamma)\hat{T}^{(S)}_{LM}, \tag{A.36}$$

yielding

$$\chi'_{Sm'} = \hat{D}^S(\alpha, \beta, \gamma)\chi_{Sm'} = \sum_m D^S_{mm'}(\alpha, \beta, \gamma)\chi_{Sm}, \tag{A.37}$$

where $\chi'_{Sm'}$ describe quantum states with definite spin S and spin projection m' on the new Z'-axis and $D^S_{mm'}(\alpha, \beta, \gamma)$ are the Wigner D functions. Similarly, the polarization operators $\hat{T}^{(S)}_{LM}$, which are irreducible tensors of rank L, are transformed by the operator $\hat{D}^L(\alpha, \beta, \gamma)$ given by Eq. (A.36) with $S = L$.

APPENDIX B: SPHERICAL HARMONICS

A spherical harmonic $Y_{lm}(\vartheta, \varphi)$ is a complex function of two arguments, namely, the colatitude $0 \le \vartheta \le \pi$ and the azimuth $0 \le \varphi \le 2\pi$ and may be defined as [95]

$$Y_{lm}(\vartheta, \varphi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}e^{im\varphi}P^m_l(\cos\vartheta), \tag{B.1}$$

$$Y_{l-m} = (-1)^m Y^*_{lm}, \tag{B.2}$$

where $P^m_l(x)$ are the associated Legendre functions defined as [95]

$$P^m_l(\cos\vartheta) = \frac{(-1)^m}{2^l l!}(\sin\vartheta)^m\frac{d^{l+m}}{(d\cos\vartheta)^{l+m}}\left(\cos^2\vartheta - 1\right)^l \tag{B.3}$$

with $m = l, l-1, \ldots l$, and the asterisk denotes the complex conjugate. For the particular case $m = 0$, $Y_{l0}(\vartheta, \varphi)$ is given by

$$Y_{l0}(\vartheta, \varphi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\vartheta), \tag{B.4}$$

where $P_l(\cos\vartheta)$ is the Legendre polynomial of order l [95,105]. In particular, Eq. (B.1) yields

$$Y_{10}(\vartheta, \varphi) = \sqrt{\frac{3}{4\pi}}\cos\vartheta, \quad Y_{1\pm1}(\vartheta, \varphi) = \mp\sqrt{\frac{3}{8\pi}}e^{\pm i\varphi}\sin\vartheta, \cdots \tag{B.5}$$

In quantum mechanics, the spherical harmonics $Y_{lm}(\vartheta, \varphi)$ play an important role describing the distribution of particles that move in spherically symmetric field with the orbital angular momentum l and projection on the quantization axis m [95]. The spherical harmonics $Y_{lm}(\vartheta, \varphi)$ are the eigenfunctions of the square of the angular momentum operator $\hat{\mathbf{L}}$ and its projection $\hat{L}_Z$ onto the Z-axis, namely,

$$\hat{\mathbf{L}}^2 Y_{lm}(\vartheta, \varphi) = l(l+1)Y_{lm}(\vartheta, \varphi), \tag{B.6}$$

$$\hat{L}_Z Y_{lm}(\vartheta, \varphi) = mY_{lm}(\vartheta, \varphi), \tag{B.7}$$

where

$$\hat{\mathbf{L}}^2 = -\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) - \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2} \tag{B.8}$$

and

$$\hat{L}_Z = -i\frac{\partial}{\partial\varphi}. \tag{B.9}$$

The completeness relation for the spherical harmonics is [95]

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l} Y_{lm}^*(\vartheta, \varphi)Y_{lm}(\vartheta', \varphi') = \delta(\varphi - \varphi')\delta(\cos\vartheta - \cos\vartheta'), \tag{B.10}$$

while the normalization and orthogonality relation of the spherical harmonics is given by [95]

$$\int_0^{2\pi}\int_0^{\pi} Y_{lm}(\vartheta, \varphi)Y_{l'm'}^*(\vartheta, \varphi)\sin\vartheta\, d\vartheta\, d\varphi = \delta_{ll'}\delta_{mm'}. \tag{B.11}$$

Thus, an arbitrary function $f(\vartheta, \varphi)$ defined on the interval $0 \le \vartheta \le \pi$ and $0 \le \varphi \le 2\pi$ (the unit sphere) which satisfies the square integrability condition

$$\int_0^{2\pi}\int_0^{\pi} |f(\vartheta, \varphi)|^2 \sin\vartheta\, d\vartheta\, d\varphi < \infty$$

can be expanded in a series of the spherical harmonics as [95]

$$f(\vartheta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} a_{lm} Y_{lm}(\vartheta, \varphi), \tag{B.12}$$

where the expansion coefficients a_{lm} are defined by

$$a_{lm} = \int_{0}^{2\pi} \int_{0}^{\pi} f(\vartheta, \varphi) Y_{lm}^{*}(\vartheta, \varphi) \sin \vartheta \, d\vartheta \, d\varphi. \tag{B.13}$$

Moreover, a product of two spherical harmonics may be expanded in the Clebsch–Gordan series as follows [95]:

$$Y_{l_1 m_1} Y_{l_2 m_2} = \sum_{L,M} \sqrt{\frac{(2l_1 + 1)(2l_2 + 1)}{4\pi (2L + 1)}} C_{l_1 0 l_2 0}^{L0} C_{l_1 m_1 l_2 m_2}^{LM} Y_{LM}. \tag{B.14}$$

Some useful recurrence relations for the spherical harmonics are [95]

$$\cos \vartheta \, Y_{lm} = \sqrt{\frac{(l+1)^2 - m^2}{(2l+3)(2l+1)}} Y_{l+1m} - \sqrt{\frac{l^2 - m^2}{(2l+1)(2l-1)}} Y_{l-1m}, \tag{B.15}$$

$$\sin \vartheta \, \frac{\partial Y_{lm}}{\partial \vartheta} = l \sqrt{\frac{(l+1)^2 - m^2}{(2l+3)(2l+1)}} Y_{l+1m} - (l+1) \sqrt{\frac{l^2 - m^2}{(2l+1)(2l-1)}} Y_{l-1m}. \tag{B.16}$$

The second derivative of $Y_{l,m}(\vartheta, \varphi)$ is given by [95]

$$\frac{\partial^2 Y_{lm}}{\partial \vartheta^2} = \left(\frac{m^2}{\sin^2 \vartheta} - l(l+1) \right) Y_{lm} - \cot \vartheta \, \frac{\partial Y_{lm}}{\partial \vartheta}. \tag{B.17}$$

One of the known trigonometric identities for the spherical harmonics, which has been used in the main text (cf. Eq. 211) is [95]

$$Y_{LM}^{*}(\vartheta, \varphi) = \frac{\cos^{4S}(\vartheta/2)}{C_{SSL0}^{SS}} \sqrt{\frac{2L+1}{4\pi}}$$
$$\times \sum_{m=-S}^{S} \frac{(2S)! C_{Sm-MLM}^{Sm} (\tan(\vartheta/2))^{2S-2m+M} e^{-iM\varphi}}{\sqrt{(S+m-M)!(S-m+M)!(S+m)!(S-m)!}}. \tag{B.18}$$

Because the spherical harmonics $Y_{lm}(\vartheta, \varphi)$ are components of some irreducible tensor of rank l, under arbitrary rotation of the coordinate system described by the Euler angles α, β, γ, the spherical harmonics $Y_{lm}(\vartheta, \varphi)$ are transformed according to the following rule [95] (cf. Eq. A.37):

$$Y_{lm'}(\vartheta', \varphi') = \sum_{m} Y_{lm}(\vartheta, \varphi) D_{mm'}^{l}(\alpha, \beta, \gamma). \tag{B.19}$$

Here ϑ, φ and ϑ', φ' are polar angles of the position vector in the original and final coordinate systems, and $D_{mm'}^{l}(\alpha, \beta, \gamma)$ are the Wigner D functions.

APPENDIX C: DERIVATION OF THE MASTER EQUATION FOR A UNIAXIAL PARAMAGNET SUBJECTED TO A DC MAGNETIC FIELD

In order to find the phase space representation of the density matrix evolution equation (371), we must transform the following integrands of Eq. (376) into the phase space representation, namely,

$$\frac{\sigma}{S^2}\left[\hat{S}_0^2, \hat{w}\right] + \frac{\xi}{S}\left[\hat{S}_0, \hat{w}\right], \tag{C.1}$$

$$\left[\hat{S}_0, \hat{w}\hat{S}_0\right] + \left[\hat{S}_0\hat{w}, \hat{S}_0\right], \tag{C.2}$$

$$\left[\hat{S}_1 e^{\frac{\sigma}{S^2}\hat{S}_0}\hat{w}, \hat{S}_{-1}\right] + \left[\hat{S}_1, \hat{w}e^{\frac{\sigma}{S^2}\hat{S}_0}\hat{S}_{-1}\right], \tag{C.3}$$

$$\left[\hat{S}_{-1}, \hat{w}e^{-\frac{\sigma}{S^2}\hat{S}_0}\hat{S}_1\right] + \left[\hat{S}_{-1}e^{-\frac{\sigma}{S^2}\hat{S}_0}\hat{w}, \hat{S}_1\right]. \tag{C.4}$$

We start with the commutation relation $\left[\hat{S}_0^2, \hat{w}\right]$ in Eq. (C.1) and its analogous differential operator in configuration space. In order to accomplish this, we observe that we have from the polarization operator expansion given by Eq. (230) of the Wigner–Stratonovich kernel $\hat{w}$, the following commutation relation indicated by the Liouville term of the integrand of Eq. (376), namely,

$$\left[\hat{S}_0^2, \hat{w}\right] = \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{SSL0}^{SS}\right)^{-1} Y_{LM}^{*} \left[\hat{S}_0^2, \hat{T}_{LM}^{(S)}\right]. \tag{C.5}$$

However, the spin operator $\hat{S}_0^2$ must first be written in terms of the polarization operators $\hat{T}_{LM}^{(S)}$ by using Eqs. (A.20) and (A.28), namely,

$$\hat{S}_0^2 = \frac{\sqrt{S(S+1)(2S+1)}}{3}\left(\frac{\sqrt{(2S-1)(2S+3)}}{\sqrt{5}} T_{20}^{(S)} + \sqrt{S(S+1)}T_{00}^{(S)}\right). \tag{C.6}$$

Now, the polarization operator $T_{0,0}^{(S)}$ is given by Eq. (A.18) and is proportional to the unit matrix. However, the commutator of any polarization operator with the unit matrix is zero. Thus, the last term in Eq. (C.6) can be discarded. Next, we can use Eq. (A.29) regarding commutators of polarization operators from Appendix A to get

$$\left[\hat{T}_{20}^{(S)}, \hat{T}_{LM}^{(S)}\right] = 2\sqrt{5(2L+1)}(-1)^{2S+L+1}$$

$$\times \left(\begin{Bmatrix} 2 & L & L+1 \\ S & S & S \end{Bmatrix} C_{2,0,L,M}^{L+1,M} \hat{T}_{L+1,M}^{(S)} + \begin{Bmatrix} 2 & L & L-1 \\ S & S & S \end{Bmatrix} C_{20LM}^{L-1M} \hat{T}_{L-1M}^{(S)}\right)$$

from which we conclude that

$$\left[\hat{S}_0^2, \hat{T}_{LM}^{(S)}\right] = M\sqrt{\frac{\left[(L+1)^2 - M^2\right]\left[(2S+1)^2 - (L+1)^2\right]}{(2L+3)(2L+1)}} \hat{T}_{L+1M}^{(S)}$$

$$+ M\sqrt{\frac{(L^2 - M^2)\left[(2S+1)^2 - L^2\right]}{(2L-1)(2L+1)}} \hat{T}_{L-1M}^{(S)}. \tag{C.7}$$

Therefore, we have from Eqs. (C.5)–(C.7)

$$\left[\hat{S}_0^2, \hat{w}\right] = \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{SSL0}^{SS}\right)^{-1} M Y_{LM}^*$$

$$\times \left\{\sqrt{\frac{\left[(L+1)^2 - M^2\right]\left[(2S+1)^2 - (L+1)^2\right]}{(2L+3)(2L+1)}} \hat{T}_{L+1M}^{(S)}\right.$$

$$\left. + \sqrt{\frac{(L^2 - M^2)\left[(2S+1)^2 - L^2\right]}{(2L-1)(2L+1)}} \hat{T}_{L-1M}^{(S)}\right\}. \tag{C.8}$$

Next, by means of the replacement $L \pm 1 \to L$ in Eq. (C.8) and subsequently using the explicit expression for the Clebsch–Gordan coefficients C_{SSL0}^{SS} from Eq. (212), we then have

$$\int W_S \left[\hat{S}_0^2, \hat{w}\right] d\Omega$$

$$= \sqrt{\frac{4\pi}{2S+1}} \int W_S \sum_{L=0}^{2S} \left(C_{SSL0}^{SS}\right)^{-1} \sum_{M=-L}^{L} \hat{T}_{LM}^{(S)} M$$

$$\times \left[L\sqrt{\frac{(L+1)^2 - M^2}{(2L+3)(2L+1)}} Y_{L+1M}^* - (L+1)\sqrt{\frac{L^2 - M^2}{4L^2 - 1}} Y_{L-1M}^* \right. \tag{C.9}$$

$$\left. + 2(S+1)\left(\sqrt{\frac{(L+1)^2 - M^2}{(2L+3)(2L+1)}} Y_{L+1M}^* + \sqrt{\frac{L^2 - M^2}{4L^2 - 1}} Y_{L-1M}^*\right)\right] d\Omega.$$

In Eq. (C.9), the terms containing the spherical harmonics $Y_{2S+1,M}$ are omitted because they vanish on averaging (due to the orthogonality relations and because

the quasi-distribution function W_S contains only the Y_{LM} up to order $L = 2S$). By using the recursion relations of the Y_{LM}, Eqs. (B.15) and (B.16), we then have the simplified expression

$$\int W_S \left[\hat{S}_0^2, \hat{w}\right] d\Omega = \sqrt{\frac{4\pi}{2S+1}} \int W_S \sum_{L=0}^{2S} \left(C_{SSL0}^{SS}\right)^{-1} \sum_{M=-L}^{L} \hat{T}_{LM}^{(S)} M$$
$$\times \left[\sin\vartheta \frac{\partial}{\partial\vartheta} Y_{LM}^* + 2(S+1)\cos\vartheta\, Y_{LM}^*\right] d\Omega. \quad (C.10)$$

Thus, via Eq. (187), we obtain by inspection the closed form

$$\int W_S \left[\hat{S}_0^2, \hat{w}\right] d\Omega = i \int W_S \left[\sin\vartheta \frac{\partial}{\partial\vartheta} + 2(S+1)\cos\vartheta\right] \frac{\partial}{\partial\varphi} \hat{w} d\Omega, \quad (C.11)$$

that is, we have found in the *configuration representation* that the analog of the commutator $\left[\hat{S}_0^2, \hat{w}\right]$ is the differential operator

$$i\left[\sin\vartheta\, \partial_\vartheta + 2(S+1)\cos\vartheta\right] \partial_\varphi \hat{w}.$$

Finally, using integration by parts in Eq. (C.11) in order to render it in the standard form of an inverse Wigner–Stratonovich transformation, Eq. (235), we have the desired transformation via the inverse map of a Weyl symbol

$$\int W_S \left[\hat{S}_0^2, \hat{w}\right] d\Omega = i \int \hat{w} \left[\frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta} \sin^2\vartheta - 2(S+1)\cos\vartheta\right] \frac{\partial}{\partial\varphi} W_S d\Omega. \quad (C.12)$$

This derivation has been given in detail merely as an illustration of how the inverse Wigner–Stratonovich map, Eq. (235), ultimately leads to the phase space representation of the density matrix evolution equation via the integrand of Eq. (C.12) and associated equations, which follow.

Next, we have the following commutation relation indicated by the second Liouville term $\left[\hat{S}_0, \hat{w}_S\right]$ in Eq. (C.1), namely,

$$\left[\hat{S}_0, \hat{w}\right] = \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{SSL0}^{SS}\right)^{-1} Y_{LM}^* \left[\hat{S}_0, \hat{T}_{LM}^{(S)}\right]$$
$$= \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} M \left(C_{SSL0}^{SS}\right)^{-1} Y_{LM}^* \hat{T}_{LM}^{(S)} \quad (C.13)$$
$$= i\sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{SSL0}^{SS}\right)^{-1} \frac{\partial Y_{LM}^*}{\partial\varphi} \hat{T}_{LM}^{(S)}.$$

Here, we used Eqs. (230), (A.1), (A.21), (A.29), (B.7), and (187). Thus, we have from Eq. (C.13)

$$\left[\hat{S}_0, \hat{w}\right] = i\frac{\partial \hat{w}}{\partial \varphi}. \tag{C.14}$$

Equations (C.13) and (C.14) (again via integration by parts) then yield the Liouville (deterministic) part of the master equation for W_S via the inverse map of a Weyl symbol

$$\int W_S \left\{ \frac{\sigma}{S^2}\left[\hat{S}_0^2, \hat{w}\right] + \frac{\xi}{S}\left[\hat{S}_0, \hat{w}\right] \right\} d\Omega$$
$$= i\frac{\sigma}{S^2}\int \hat{w}\left(2S\cos\vartheta - \sin\vartheta\frac{\partial}{\partial\vartheta} - \frac{S\xi}{\sigma}\right)\frac{\partial W_S}{\partial\varphi}d\Omega. \tag{C.15}$$

Next, we consider the commutator $\left[\hat{S}_0\hat{w}, \hat{S}_0\right] + \left[\hat{S}_0, \hat{w}\hat{S}_0\right]$ and determine its phase space representation. We have

$$\left[\hat{S}_0\hat{w}, \hat{S}_0\right] + \left[\hat{S}_0, \hat{w}\hat{S}_0\right]$$
$$= -\sqrt{\frac{4\pi}{2S+1}}\sum_{L=0}^{2S}\sum_{M=-L}^{L}M^2\left(C_{SSL0}^{SS}\right)^{-1}Y_{LM}^*\hat{T}_{LM}^{(S)} \tag{C.16}$$
$$= \sqrt{\frac{4\pi}{2S+1}}\sum_{L=0}^{2S}\sum_{M=-L}^{L}\left(C_{SSL0}^{SS}\right)^{-1}\frac{\partial^2 Y_{LM}^*}{\partial\varphi^2}\hat{T}_{LM}^{(S)} = \frac{\partial^2 \hat{w}}{\partial\varphi^2}$$

so that integrating by parts, we again obtain the standard inverse map of a Weyl symbol, namely,

$$\int W_S\left[\hat{S}_0\hat{w}, \hat{S}_0\right] + \left[\hat{S}_0, \hat{w}\hat{S}_0\right]d\Omega = \int \hat{w}\frac{\partial^2 W_S}{\partial\varphi^2}d\Omega. \tag{C.17}$$

Now, we consider the remaining commutators (which are more difficult to treat) in the collision operator $St(\hat{w})$, namely,

$$e^{\frac{\sigma}{2S^2}\pm\frac{\xi}{2S}}\left(\left[\hat{S}_{\pm1}e^{\pm\frac{\sigma}{S^2}\hat{S}_0}\hat{w}, \hat{S}_{\mp1}\right] + \left[\hat{S}_{\pm1}, \hat{w}e^{\pm\frac{\sigma}{S^2}\hat{S}_0}\hat{S}_{\mp1}\right]\right)$$
$$= \left[\hat{S}_{\pm1}\hat{P}_{\pm}^{(S)}\hat{w}, \hat{S}_{\mp1}\right] + \left[\hat{S}_{\pm1}, \hat{w}\hat{P}_{\pm}^{(S)}\hat{S}_{\mp1}\right], \tag{C.18}$$

where for convenience we have introduced the matrix exponential operators $\hat{P}_{\pm}^{(S)} = e^{\frac{\sigma}{2S^2}\pm\frac{\xi}{2S}}e^{\pm\frac{\sigma}{S^2}\hat{S}_0}$ in Eq. (C.18). However, they too can also be expanded as a series of the polarization operators (see Eq. (A.34) *et seq.*), namely,

$$\hat{P}_{\pm}^{(S)} = e^{\frac{\sigma}{2S^2}\pm\frac{\xi}{2S}}\sum_{l=0}^{2S}a_l^{\pm}\hat{T}_{l0}^{(S)}, \tag{C.19}$$

where the scalar expansion coefficients $a_l^{\pm}$ can be found using the orthogonality property, Eq. (A.34) of the polarization operators and the explicit form of their matrix elements in terms of the Clebsch–Gordan coefficients given by Eq. (A.17) (see Appendix A). The expansion coefficients are then as usual given by the trace

$$a_l^{\pm} = \mathrm{Tr}\left(e^{\pm\frac{\sigma}{S^2}\hat{S}_0}\hat{T}_{l0}^{(S)}\right) = \sqrt{\frac{2l+1}{2S+1}}\sum_{m=-S}^{S} C_{Sm\,l0}^{Sm}e^{\pm\frac{\sigma}{S^2}m}. \qquad (C.20)$$

However, Eq. (C.20) may be further simplified for $l=0$ using $C_{Sm\,00}^{Sm}=1$ to yield the closed form

$$a_0^{\pm} = \sqrt{\frac{2l+1}{2S+1}}\sum_{m=-S}^{S} e^{\pm\frac{\sigma}{S^2}m} = \frac{\sinh\frac{\sigma(S+1/2)}{S^2}}{\sqrt{2S+1}\sinh\frac{\sigma}{2S^2}}. \qquad (C.21)$$

The higher order expansion coefficients may now be found because differential recurrence relations, which allow one to determine $a_l^{\pm}$ may be derived as follows. We first use Eq. (A.28) concerning products of polarization operators to write

$$\hat{T}_{10}^{(S)}\hat{T}_{l-10}^{(S)} = \frac{l\sqrt{3(2S-l+1)(2S+l+1)}}{2\sqrt{(2l+1)(2l-1)S(S+1)(2S+1)}}\hat{T}_{l0}^{(S)}$$
$$+ \frac{(l-1)\sqrt{3(2S-l+2)(2S+l)}}{2\sqrt{(2l-3)(2l-1)S(S+1)(2S+1)}}\hat{T}_{l-20}^{(S)}. \qquad (C.22)$$

Next, by substituting $\hat{T}_{l0}^{(S)}$ as extracted from Eq. (C.22) into the left-hand side of Eq. (C.20), we have

$$a_l^{\pm} = \mathrm{Tr}\left(e^{\pm\frac{\sigma}{S^2}\hat{S}_0}\hat{T}_{l0}^{(S)}\right)$$
$$= \frac{2\sqrt{(2l+1)(2l-1)S(S+1)(2S+1)}}{l\sqrt{3(2S-l+1)(2S+l+1)}}\mathrm{Tr}\left(e^{\pm\frac{\sigma}{S^2}\hat{S}_0}\hat{T}_{10}^{(S)}\hat{T}_{l-10}^{(S)}\right) \qquad (C.23)$$
$$- \frac{(l-1)\sqrt{(2l+1)(2S-l+2)(2S+l)}}{l\sqrt{(2l-3)(2S-l+1)(2S+l+1)}}\mathrm{Tr}\left(e^{\pm\frac{\sigma}{S^2}\hat{S}_0}\hat{T}_{l-20}^{(S)}\right).$$

Now,

$$e^{\pm\frac{\sigma}{S^2}\hat{S}_0}\hat{T}_{10}^{(S)}\hat{T}_{l-10}^{(S)} = \pm S\sqrt{\frac{3S}{(S+1)(2S+1)}}\frac{\partial}{\partial\sigma}\left(e^{\pm\frac{\sigma}{S^2}\hat{S}_0}\hat{T}_{l-10}^{(S)}\right), \qquad (C.24)$$

therefore we have the desired differential recurrence relation for the expansion coefficients

$$a_l^{+} = \frac{2S^2}{l}\sqrt{\frac{4l^2-1}{(2S+1)^2-l^2}}\frac{\partial}{\partial\sigma}a_{l-1}^{+} + \frac{l-1}{l}\sqrt{\frac{(2l+1)[(2S+1)^2-(l-1)^2]}{(2l-3)[(2S+1)^2-l^2]}}a_{l-2}^{+}$$
$$\qquad (C.25)$$

with

$$a_l^+ = (-1)^l a_l^-. \tag{C.26}$$

Next, mindful of the matrix exponential operator $e^{\pm\frac{\sigma}{s^2}\hat{S}_0}$ embodied in Eq. (C.19) and prompted by that equation, we may regard the polarization operator $\hat{T}_{l0}^{(S)}$ as a (matrix) operator acting on the transformation kernel $\hat{w}$ and, consequently, may denote the corresponding differential operator by $P_l^{(S)}$ and its associated form $\bar{P}_l^{(S)}$. Both of these differential operators are defined in obvious fashion via

$$\int W_S \hat{T}_{l,0}^{(S)} \hat{w} d\Omega = \int W_S P_l^{(S)} \hat{w} d\Omega = \int \hat{w} \bar{P}_l^{(S)} W_S d\Omega. \tag{C.27}$$

The last term in Eq. (C.27), which serves to define the differential operator $\bar{P}_l^{(S)}$, has now the desired form, namely an inverse Wigner–Stratonovich map. In Eq. (C.27), the differential operator $\bar{P}_l^{(S)}$ is obtained from the differential operator $P_l^{(S)}$ using integration by parts in the middle term. The operator expansion defined by Eq. (C.19) involving $\hat{P}_{\pm}^{(S)}$ now allows one to express both of the phase space differential operators $P_{\pm}^{(S)}$ and $\bar{P}_{\pm}^{(S)}$ as suggested by that equation in terms of the phase space differential operators $P_l^{(S)}$ and $\bar{P}_l^{(S)}$ [as defined in Eq. (C.27)] corresponding to the polarization operators $\hat{T}_{l,0}^{(S)}$ as

$$\begin{pmatrix} P_{\pm}^{(S)} \\ \bar{P}_{\pm}^{(S)} \end{pmatrix} = e^{\frac{\sigma}{2S^2}\pm\frac{\xi}{2S}} \sum_{l=0}^{2S} a_l^{\pm} \begin{pmatrix} P_l^{(S)} \\ \bar{P}_l^{(S)} \end{pmatrix} \tag{C.28}$$

with $a_l^{\pm}$ defined by the recurrence relations: Eqs. (C.25) and (C.26). The differential operators $P_l^{(S)}$ and $\bar{P}_l^{(S)}$ on the right-hand side of Eq. (C.28) may now be determined by upward iteration. In order to find them explicitly, we first recall the expression for the product of the polarization operators embodied in Eq. (C.22), which may be rearranged as the upward operator recurrence equation

$$\hat{T}_{l0}^{(S)} = A_{l-1}\hat{T}_{10}^{(S)}\hat{T}_{l-10}^{(S)} - A_{l-2}\hat{T}_{l-20}^{(S)},$$

with coefficients A_{l-1} and A_{l-2} given by

$$A_{l-1} = \frac{2}{l}\sqrt{\frac{S(S+1)(2S+1)(4l^2-1)}{3[(2S+1)^2-l^2]}}, \tag{C.29}$$

$$A_{l-2} = \frac{l-1}{l}\sqrt{\frac{(2l+1)[(2S+1)^2-(l-1)^2]}{(2l-3)[(2S+1)^2-l^2]}}. \tag{C.30}$$

However, by virtue of the correspondence expressed in Eq. (C.27), the phase space differential operators $P_l^{(S)}$ and $\bar{P}_l^{(S)}$ must also satisfy a similar recurrence equation, namely,

$$\begin{pmatrix} P_l^{(S)} \\ \bar{P}_l^{(S)} \end{pmatrix} = A_{l-1} \begin{pmatrix} P_{l-1}^{(S)} P_1^{(S)} \\ \bar{P}_1^{(S)} \bar{P}_{l-1}^{(S)} \end{pmatrix} - A_{l-2} \begin{pmatrix} P_{l-2}^{(S)} \\ \bar{P}_{l-2}^{(S)} \end{pmatrix} \tag{C.31}$$

so that we have explicitly for the first two members of the hierarchy of operator recurrence relations

$$P_0^{(S)} = \bar{P}_0^{(S)}(2S+1)^{-1/2} \tag{C.32}$$

and

$$\begin{pmatrix} P_1^{(S)} \\ \bar{P}_1^{(S)} \end{pmatrix} = \frac{1}{2}\sqrt{\frac{3}{S(S+1)(2S+1)}} \left[(2S+1\pm 1)\cos\vartheta \pm \sin\vartheta \frac{\partial}{\partial\vartheta} \pm i\frac{\partial}{\partial\varphi} \right]. \tag{C.33}$$

Thus, it is now obvious that, in general, differential operators of arbitrary order will be involved. To establish the second member as in Eq. (C.33), we made the following steps:

$$\hat{T}_{10}^{(S)}\hat{w} = \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{SSL0}^{SS}\right)^{-1} Y_{LM}^* \frac{1}{2}\sqrt{\frac{3}{S(S+1)(2S+1)}} \left[M\hat{T}_{LM}^{(S)} \right.$$
$$+ \frac{\sqrt{(L-M+1)(L+M+1)(2S-L)(2S+L+2)}}{\sqrt{(2L+3)(2L+1)}} \hat{T}_{L+1M}^{(S)} \tag{C.34}$$
$$+ \left. \frac{\sqrt{(L-M)(L+M)(2S-L+1)(2S+L+1)}}{\sqrt{(2L-1)(2L+1)}} \hat{T}_{L-1M}^{(S)} \right].$$

Next, by the replacement $L \pm 1 \to L$ in Eq. (C.34), and then using the explicit expression for the Clebsch–Gordan coefficients C_{SSL0}^{SS} from Eq. (212), we have

$$\hat{T}_{10}^{(S)}\hat{w} = \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{SSL0}^{SS}\right)^{-1} \hat{T}_{LM}^{(S)} \sqrt{\frac{3}{S(S+1)(2S+1)}}$$
$$\times \left[\frac{M}{2} Y_{LM}^* + \frac{2S-L+1}{2}\sqrt{\frac{(L-M)(L+M)}{(2L+1)(2L-1)}} Y_{L-1M}^* \right.$$
$$+ \left. \frac{2S+L+2}{2}\sqrt{\frac{(L-M+1)(L+M+1)}{(2L+1)(2L+3)}} Y_{L+1M}^* \right] \tag{C.35}$$
$$= \sqrt{\frac{3}{S(S+1)(2S+1)}} \left[(S+1)\cos\vartheta + \frac{1}{2}\sin\vartheta\frac{\partial}{\partial\vartheta} + \frac{i}{2}\frac{\partial}{\partial\varphi} \right]\hat{w}$$
$$= P_1^{(S)}\hat{w}.$$

Consequently, by substituting Eq. (C.35) into the defining equation (C.27) and integrating by parts, we have Eq. (C.33).

Returning to the phase space representation of the commutators in Eq. (C.18), the matrix exponential operators $\hat{P}_{\pm}^{(S)}$, act on the *polarization operators* in the expansion of transformation kernel $\hat{w}$, while its phase space correspondents $P_{\pm}^{(S)}$ from Eq. (C.28), in contrast, represent sets of differential operators acting on the *spherical harmonics* in $\hat{w}$ leading in the end to the same result, namely,

$$\int W_S[\hat{S}_{\pm 1}\hat{P}_{\pm}^{(S)}\hat{w}, \hat{S}_{\mp 1}]d\Omega = \int \bar{P}_{\pm}^{(S)} W_S[\hat{S}_{\pm 1}\hat{w}, \hat{S}_{\mp 1}]d\Omega. \qquad (C.36)$$

Because the commutator $[\hat{S}_{\pm 1}\hat{P}_{\pm}^{(S)}\hat{w}, \hat{S}_{\mp 1}]$ gives the differential operator, which is complex conjugate to that corresponding to $[\hat{S}_{\pm 1}, \hat{P}_{\pm}^{(S)}\hat{w}\hat{S}_{\mp 1}]$ in the right-hand side of Eq. (C.18), we need to consider only the commutator $[\hat{S}_{\pm 1}\hat{P}_{\pm}^{(S)}\hat{w}, \hat{S}_{\mp 1}]$. We have

$$[\hat{S}_{\pm 1}\hat{w}, \hat{S}_{\mp 1}] = \frac{\sqrt{4\pi}}{\sqrt{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{SSL0}^{SS}\right)^{-1} Y_{LM}^*(\vartheta, \varphi) \left[\hat{S}_{\pm 1}\hat{T}_{LM}^{(S)}, \hat{S}_{\mp 1}\right],$$
$$(C.37)$$

where

$$\left[\hat{S}_{\pm 1}\hat{T}_{LM}^{(S)}, \hat{S}_{\mp 1}\right]$$
$$= -\frac{1}{4}\left[(L \mp M)(L \pm M + 1)\hat{T}_{LM}^{(S)}\right.$$
$$\mp \frac{(L \pm M + 2)\sqrt{(L+M+1)(L-M+1)(2S-L)(2S+L+2)}}{\sqrt{(2L+3)(2L+1)}}\hat{T}_{L+1M}^{(S)}$$
$$(C.38)$$
$$\left.\pm \frac{(L \mp M - 1)\sqrt{(L+M)(L-M)(2S-L+1)(2S+L+1)}}{\sqrt{(2L-1)(2L+1)}}\hat{T}_{L-1M}^{(S)}\right].$$

Next, via the replacement $L \pm 1 \rightarrow L$ in Eq. (C.8) and then using the explicit expression for the Clebsch–Gordan coefficients C_{SSL0}^{SS} from Eq. (212), we have

$$[\hat{S}_{\pm 1}\hat{w}, \hat{S}_{\mp 1}] = -\frac{1}{4}\frac{\sqrt{4\pi}}{\sqrt{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{SSL0}^{SS}\right)^{-1}\hat{T}_{LM}^{(S)}\left[(L \mp M)(L \pm M + 1)Y_{LM}^*\right.$$
$$\mp \frac{(2S+L+2)(L \pm M+1)\sqrt{(L+M+1)(L-M+1)}}{\sqrt{(2L-1)(2L+1)}}Y_{L-1M}^*$$
$$\left.\pm \frac{(2S-L+1)(L \mp M)\sqrt{(L+M)(L-M)}}{\sqrt{(2L+3)(2L+1)}}Y_{L+1M}^*\right]. \qquad (C.39)$$

Now, we can ultimately write Eq. (C.39) in differential form using properties of the angular momentum operators L_μ and $\hat{L}^2$ (see Appendix B), namely,

$$\hat{L}^2 Y^*_{LM} = -\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial^2\varphi}\right] Y^*_{LM} \qquad\text{(C.40)}$$
$$= L(L+1)Y^*_{LM},$$

$$\hat{L}_0 Y^*_{LM} = -i\frac{\partial}{\partial\varphi}Y^*_{LM} = -MY^*_{LM}, \qquad\text{(C.41)}$$

$$\hat{L}_{\pm 1} Y^*_{LM} = -\frac{1}{\sqrt{2}}e^{\pm i\varphi}\left(\frac{\partial}{\partial\vartheta} \pm i\cot\vartheta\frac{\partial}{\partial\varphi}\right) Y^*_{LM\mp 1}$$
$$= \pm\sqrt{\frac{L(L+1)-M(M\mp 1)}{2}}Y^*_{LM\mp 1}, \qquad\text{(C.42)}$$

and

$$\hat{L}_\pm\hat{L}_\mp Y^*_{LM} = \frac{1}{2}\left(\frac{\partial^2}{\partial\vartheta^2} + \cot\vartheta\frac{\partial}{\partial\vartheta} \pm i\frac{\partial}{\partial\varphi} + \cot^2\vartheta\frac{\partial^2}{\partial^2\varphi}\right) Y^*_{LM}$$
$$= -\frac{1}{2}(L\mp M)(L\pm M+1)Y^*_{LM}. \qquad\text{(C.43)}$$

Thus, we can rearrange the commutator given by Eq. (C.37) as the differential form

$$[\hat{S}_{\pm 1}\hat{w}, \hat{S}_{\mp 1}] = \sqrt{\frac{\pi}{2S+1}}\sum_{L=0}^{2S}\sum_{M=-L}^{L}\left(C^{SS}_{SSL0}\right)^{-1}\hat{T}^{(S)}_{LM}$$
$$\times\left[\frac{1}{2}\left(\frac{\partial^2}{\partial\vartheta^2} + \cot\vartheta\frac{\partial}{\partial\vartheta} \pm i\frac{\partial}{\partial\varphi} + \cot^2\vartheta\frac{\partial^2}{\partial^2\varphi}\right)\right.$$
$$+ i(S+1)\cos\vartheta\frac{\partial}{\partial\varphi} - \left(S+\frac{1}{2}\right)\sin\vartheta\frac{\partial}{\partial\vartheta} + \frac{i}{2}\sin\vartheta\frac{\partial}{\partial\vartheta}\frac{\partial}{\partial\varphi}$$
$$\qquad\text{(C.44)}$$
$$\left. -\frac{1}{2}\cos\vartheta\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial^2\varphi}\right]\right] Y^*_{LM}.$$

By substituting Eq. (C.44) into Eq. (C.36) and integrating the latter by parts, we then have that equation rendered as *the inverse map of a Weyl symbol*, namely,

$$\int W_S[\hat{S}_{\pm 1}\hat{P}^{(S)}_\pm\hat{w}, \hat{S}_{\mp 1}]d\Omega = -\frac{1}{4}\int\hat{w}\left\{i\left(\sin\vartheta\frac{\partial}{\partial\vartheta} - 2S\cos\vartheta\mp 1\right)\frac{\partial}{\partial\varphi}\right.$$
$$+ \frac{1}{\sin\vartheta}\left[\frac{\partial}{\partial\vartheta}\left(\sin\vartheta(1\pm\cos\vartheta)\frac{\partial}{\partial\vartheta} \pm 2S\sin^2\vartheta\right)\right.$$
$$\left.\left. + \cot\vartheta(\cos\vartheta\pm 1)\frac{\partial^2}{\partial\varphi^2}\right]\right\}\bar{P}^{(S)}_\pm W_S d\Omega. \qquad\text{(C.45)}$$

In the derivation of Eq. (C.45), the recurrence properties of the spherical harmonics given in Appendix B, namely, Eqs. (C.14)–C.17), have been used. Finally, because the commutator $[\hat{S}_{\pm 1}\hat{P}^{(S)}_{\pm}\hat{w}, \hat{S}_{\mp 1}]$ gives the differential operator which is complex conjugate to that corresponding to $[\hat{S}_{\pm 1}, \hat{P}^{(S)}_{\pm}\hat{w}\hat{S}_{\mp 1}]$, we have once again the standard inverse Wigner–Stratonovich map of a Weyl symbol via

$$\int W_S \left([\hat{S}_{\pm 1}\hat{P}^{(S)}_{\pm}\hat{w}, \hat{S}_{\mp 1}] + [\hat{S}_{\pm 1}, \hat{w}\hat{P}^{(S)}_{\pm}\hat{S}_{\mp 1}]\right) d\Omega$$

$$= e^{\frac{\sigma}{2S^2} \pm \frac{\xi}{2S}} \int W_S \left([\hat{S}_{\pm 1}e^{\pm\frac{\sigma}{S^2}\hat{S}_0}\hat{w}, \hat{S}_{\mp 1}] + [\hat{S}_{\pm 1}, \hat{w}e^{\pm\frac{\sigma}{S^2}\hat{S}_0}\hat{S}_{\mp 1}]\right) d\Omega$$

$$= -\frac{1}{2}\int \hat{w}\operatorname{Re}\left\{\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\,(1 \pm \cos\vartheta)\frac{\partial}{\partial\vartheta} \pm 2S\sin^2\vartheta\right)\right.\right. \quad (C.46)$$

$$+ \frac{1}{\sin\vartheta}\cot\vartheta\,(\cos\vartheta \pm 1)\frac{\partial^2}{\partial\varphi^2}$$

$$\left.\left. + i\left(\sin\vartheta\frac{\partial}{\partial\vartheta} - 2S\cos\vartheta \mp 1\right)\frac{\partial}{\partial\varphi}\right]\bar{P}^{(S)}_{\pm}\right\} W_S d\Omega.$$

Then due to Eq. (376), we have from the Weyl symbols of Eqs. (C.15), (C.17), and (C.46) the master equation for the phase space distribution $W_S(\vartheta, \varphi, t)$, namely,

$$\frac{\partial W_S}{\partial t} - \frac{\sigma}{\hbar\beta S^2}\left(2S\cos\vartheta - \sin\vartheta\frac{\partial}{\partial\vartheta} - \frac{S\xi}{\sigma}\right)\frac{\partial W_S}{\partial\varphi} = \operatorname{St}\{W_S\}, \quad (C.47)$$

where the collision kernel $\operatorname{St}\{W_S\}$ is

$$\operatorname{St}\{W_S\} = D_{\parallel}\frac{\partial^2}{\partial^2\varphi}W_S + D_{\perp}\frac{\cot\vartheta}{\sin\vartheta}\left(\cos\vartheta\frac{\partial^2}{\partial^2\varphi}R'^{(S)}_{+} + \frac{\partial^2}{\partial^2\varphi}R'^{(S)}_{-}\right)W_S$$

$$+ \frac{D_{\perp}}{\sin\vartheta}\left[\frac{\partial}{\partial\vartheta}\sin\vartheta\left(\frac{\partial}{\partial\vartheta}R'^{(S)}_{+} + \cos\vartheta\frac{\partial}{\partial\vartheta}R'^{(S)}_{-} + 2S\sin\vartheta R'^{(S)}_{-}\right)\right]W_S$$

$$\quad (C.48)$$

$$+ D_{\perp}\left[\left(\sin\vartheta\frac{\partial}{\partial\vartheta} - 2S\cos\vartheta\right)\frac{\partial}{\partial\varphi}R''^{(S)}_{+} - \frac{\partial}{\partial\varphi}R''^{(S)}_{-}\right]W_S$$

with the phase space differential operators $R^{(S)}_{\pm}$ generally involving differential operators of arbitrary order (cf. Eq. (C.28)) defined as follows:

$$R^{(S)}_{\pm} = R'^{(S)}_{\pm} + iR''^{(S)}_{\pm} = \bar{P}^{(S)}_{+} \pm \bar{P}^{(S)}_{-}. \quad (C.49)$$

In the classical limit, we see that since all the terms involving derivatives in the differential operator expansion (Eq. (C.28) *et seq.*) now vanish, the operator $\bar{P}^{(S)}_{l}$ simply reduces to the Legendre polynomial of order l

$$\bar{P}^{(S\gg 1)}_{l} \to Y_{l0}(\vartheta, \varphi)\sqrt{\frac{4\pi}{2S+1}}. \quad (C.50)$$

Thus, in this limit by substituting the Legendre polynomials into the operator series equation (C.28), we must then have

$$\bar{P}_{\pm}^{(S \to \infty)} = e^{\frac{\sigma}{2S^2} \pm \frac{\xi}{2S}} \sqrt{\frac{4\pi}{2S+1}} \sum_{l=0}^{2S} a_l^{\pm} Y_{l0}(\vartheta, \varphi) = e^{\frac{\sigma}{2S^2} \pm \frac{\xi}{2S}} F_{\pm}^{(0)}(\vartheta, \varphi),$$

in which the series

$$F_{\pm}^{(s)}(\vartheta, \varphi) = \sqrt{\frac{4\pi}{2S+1}} \sum_{l=0}^{2S} \left(C_{SSL0}^{SS} \right)^{-s} a_l^{\pm} Y_{l0}(\vartheta, \varphi)$$

represents the Weyl symbol of the Hilbert space operator $e^{\pm \sigma \hat{S}_0 / S^2}$. For large S,

$$F_{\pm}^{(s)}(\vartheta, \varphi) \to e^{\pm(\sigma/S) \cos \vartheta}$$

so that proceeding to the limit $S \to \infty$, we have

$$\lim_{S \to \infty} S \left(e^{[\sigma \cos \vartheta + (\sigma/S + \xi)/2]/S} - e^{[-\sigma \cos \vartheta + (\sigma/S - \xi)/2]/S} \right) = \xi + 2\sigma \cos \vartheta$$

and

$$\lim_{S \to \infty} e^{(\xi + \sigma/S + 2\sigma \cos \vartheta)/S} = 1.$$

Hence, it follows that in the classical limit, $S \to \infty$, Eq. (C.47), reduces to the corresponding classical Fokker–Planck equations for isotropic rotational diffusion of a magnetic dipole in the uniaxial potential [5] (if $D_{\perp} = D_{\parallel}$)

$$\frac{\partial W}{\partial t} = \frac{\gamma}{\mu \sin \vartheta} \frac{\partial V}{\partial \vartheta} \frac{\partial W}{\partial \varphi}$$
$$+ D_{\perp} \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial W}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 W}{\partial \varphi^2} + \frac{\beta}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \, W \frac{\partial V}{\partial \vartheta} \right) \right],$$
$$(C.51)$$

where $\mu = \gamma \hbar S / \mu_0$ is the magnetic dipole moment and

$$\beta V(\vartheta) = -\sigma \cos^2 \vartheta - \xi \cos \vartheta$$

is the normalized free energy density.

The master equation (C.47) for the evolution of the phase space quasiprobability distribution $W_S(\vartheta, \varphi, t)$ for a uniaxial spin system in contact with a heat bath at temperature T was derived in the weak coupling limit, that is, it was supposed that the correlation time characterizing the bath is so short that the stochastic process originating from it is Markovian so that one may assume frequency-independent damping. This has been accomplished by expressing the reduced density matrix master equation (371) in terms of the inverse Wigner–Stratonovich transformation. In order to achieve this objective, various commutators involving the spin operators occurring in the integrand of Eq. (376) have then been evaluated

by means of the orthogonality and recurrence properties of the polarization operators and the corresponding spherical harmonics to yield their analogs in phase space. Thus, we have expressed the master equation as a partial differential equation for the distribution function in the phase space of the polar angles. Despite the superficial resemblance of the quantum diffusion equation (C.47) to the corresponding classical Fokker–Planck equation for a classical spin in a uniaxial potential equation (C.51), it is in reality much more complicated. The complications arise because Eq. (C.47) involves the complicated differential operators $R_{\pm}^{(S)}$ only simplifying for large spin numbers ($S \to \infty$) when the higher order derivatives, as indicated by Eq. (C.49), occurring in the operators $R_{\pm}^{(S)}$ may be ignored. Consequently, it is often much easier to use the density matrix formulation where for axially symmetric problems only the diagonal terms partake in the time evolution.

APPENDIX D: BROWN'S THEORY OF THE BROWNIAN MOTION OF A CLASSICAL SPIN

The rigorous treatment of the magnetization dynamics of fine magnetic particles in the presence of thermal agitation was set in the context of the general theory of stochastic processes by W.F. Brown [23, 24] via the classical theory of the Brownian motion using by analogy ideas originating in the Debye theory of dielectric relaxation of polar dielectrics [7, 8]. The starting point of Brown's treatment [23, 24] of the dynamical behavior of the magnetization **M** for a single-domain particle was Gilbert's equation [26], namely, (cf. Eq. (2))

$$\dot{\mathbf{u}} = \gamma \left[\mathbf{u} \times \left(\mathbf{H}_{ef} - \alpha \dot{\mathbf{u}}/\gamma \right) \right] \tag{D.1}$$

(here $\mathbf{u} = M_S^{-1} \mathbf{M}$ is a unit vector in the direction of **M**). In general,

$$\mathbf{H}_{ef} = -\partial V/\partial \mathbf{M} \text{ and } -\alpha \dot{\mathbf{u}}/\gamma \tag{D.2}$$

represent the *conservative* and *dissipative* parts of an "effective field," respectively. Brown now supposes in order to treat thermal agitation that the dissipative "effective field" $-\alpha \dot{\mathbf{u}}/\gamma$ describes only the *statistical average* of the rapidly fluctuating random field due to thermal agitation, and that this term for an individual particle must become

$$-\alpha \dot{\mathbf{u}}/\gamma \to -\alpha \dot{\mathbf{u}}/\gamma + \mathbf{h}(t),$$

where the random field $\mathbf{h}(t)$ has the white noise properties

$$\overline{h_i(t)} = 0, \quad \overline{h_i(t_1) h_j(t_2)} = \frac{2kT\alpha}{v\gamma\mu_0 M_S} \delta_{ij} \delta\left(t_1 - t_2\right). \tag{D.3}$$

Here, the indices $i, j = 1, 2, 3$ in Kronecker's delta δ_{ij} and h_i correspond to the Cartesian axes X,Y,Z of the laboratory coordinate system $OXYZ$, $\delta(t)$ is the Dirac delta function, and the overbar means the statistical average over an ensemble of particles that all have at time t the *same* magnetization $\mathbf{M}$. The random field accounts for the thermal fluctuations of the magnetization of an individual particle without which the random orientational motion would not be sustained.

Brown was then able to derive, after a long and tedious calculation using the methods of Wang and Uhlenbeck [195], the Fokker–Planck equation (3) for the distribution function $W(\vartheta, \varphi, t)$ of the orientations of the magnetic moment vector $\mu = v\mathbf{M}$ (v is the volume of the particle) on the surface of the unit sphere. This lengthy procedure may be circumvented, however, by using an alternative approach also given by him [23], which appears to be based on an argument originally due to Einstein [196] in order to heuristically derive the Smoluchowski equation for point particles. Einstein accomplished this by adding a diffusion current representing the effect of the heat bath on the deterministic drift current due to an external force. In order to illustrate this method, we first write (cross-multiplying vectorially by $\mathbf{u}$ and using the triple vector product formula) Gilbert's equation in the absence of thermal agitation (noiseless equation) as an explicit equation for (D.1) $\dot{\mathbf{u}}$. Transposing the α term, we have

$$\dot{\mathbf{u}} + \alpha \left[\mathbf{u} \times \dot{\mathbf{u}}\right] = \gamma \left[\mathbf{u} \times \mathbf{H}_{ef}\right]. \tag{D.4}$$

Cross-multiplying vectorially by $\mathbf{u}$ in Eq. (D.4), using the triple vector product formula

$$\left[\left[\mathbf{u} \times \dot{\mathbf{u}}\right] \times \mathbf{u}\right] = \dot{\mathbf{u}} - \mathbf{u}(\mathbf{u} \cdot \dot{\mathbf{u}}), \tag{D.5}$$

we obtain

$$\left[\dot{\mathbf{u}} \times \mathbf{u}\right] = -\alpha\dot{\mathbf{u}} + \gamma \left[\left[\mathbf{u} \times \mathbf{H}_{ef}\right] \times \mathbf{u}\right] \tag{D.6}$$

because $(\mathbf{u} \cdot \dot{\mathbf{u}}) = 0$. Substituting Eq. (D.6) into Eq. (D.4) yields the explicit solution for $\dot{\mathbf{u}}$ in the Landau-Lifshitz form [25, 94]

$$\dot{\mathbf{u}} = \alpha^{-1} h' M_S \left[\mathbf{u} \times \mathbf{H}_{ef}\right] + h' M_S \left[\left[\mathbf{u} \times \mathbf{H}_{ef}\right] \times \mathbf{u}\right], \tag{D.7}$$

where h' is Brown's parameter defined as $h' = \gamma/[(\alpha + \alpha^{-1})M_S]$. With Eq. (D.2), Eq. (D.7) becomes

$$\dot{\mathbf{u}} = -\frac{h'}{\alpha} \left[\mathbf{u} \times \frac{\partial V}{\partial \mathbf{u}}\right] + h' \left[\mathbf{u} \times \left[\mathbf{u} \times \frac{\partial V}{\partial \mathbf{u}}\right]\right]. \tag{D.8}$$

Now the instantaneous orientation (ϑ, φ) of the magnetization $\mathbf{M}$ of a single-domain particle may be represented by a point on the unit sphere $(1, \vartheta, \varphi)$. As the magnetization changes its direction, the representative point moves over the
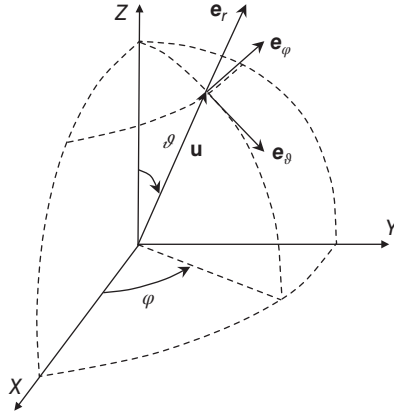
Figure D.1. Spherical polar coordinate system.

surface of the sphere. Following Refs. 5 and 23, consider now a statistical ensemble of identical particles and let $W(\vartheta, \varphi, t)d\Omega$ be the probability that **u** has orientation (ϑ, φ) within the solid angle $d\Omega = \sin\vartheta\,d\vartheta\,d\varphi$ (see Fig. D.1). The time derivative of $W(\vartheta, \varphi, t)$ is then related to the probability current **J** of such representative points swarming over the surface S of the sphere by the continuity equation

$$\dot{W} + \text{div}\mathbf{J} = 0. \tag{D.9}$$

Equation (D.9) states that the swarming representative points are neither created nor destroyed, merely moving to new positions on the surface of the sphere. Now, in the absence of thermal agitation, we have the deterministic drift current $\mathbf{J} = W\dot{\mathbf{u}}$, where $\dot{\mathbf{u}}$ is given by Eq. (D.8). Next, add to this deterministic **J** a diffusion term $-k'\partial_{\mathbf{u}}W$ (k' is a proportionality constant to be determined later), which represents the effect of thermal agitation; its tendency is to smooth out the distribution, that is, to make it more uniform. Recall the alternative and equivalent Langevin picture of a systematic retarding torque tending to slow down the spin superimposed on a rapidly fluctuating white noise random torque maintaining the rotational motion. This intuitive procedure essentially due to Einstein gives for the components of **J** (on evaluating $[\mathbf{u} \times \partial_{\mathbf{u}}V]$, etc, in spherical polar coordinates)

$$J_\vartheta = -h'\left[\left(\frac{\partial V}{\partial \vartheta} - \frac{1}{\alpha \sin\vartheta}\frac{\partial V}{\partial \varphi}\right)W + \frac{k'}{h'}\frac{\partial W}{\partial \vartheta}\right], \tag{D.10}$$

$$J_\varphi = -h'\left[\left(\frac{1}{\alpha}\frac{\partial V}{\partial \vartheta} + \frac{1}{\sin\vartheta}\frac{\partial V}{\partial \varphi}\right)W + \frac{k'}{h'\sin\vartheta}\frac{\partial W}{\partial \varphi}\right]. \tag{D.11}$$

Equations (D.10) and (D.11), when substituted into the continuity equation (D.9), now yield Brown's Fokker–Planck equation for the surface density of magnetic moment orientations on the unit sphere, which may be written as

$$
\frac{\partial W}{\partial t} = \frac{1}{2\tau_N \sin \vartheta} \left\{ \left[\frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} W \right) + \frac{1}{\sin \vartheta} \frac{\partial^2 W}{\partial \varphi^2} \right] \right.
$$
$$
\left. + \frac{v}{kT} \left[\frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial V}{\partial \vartheta} - \alpha^{-1} \frac{\partial V}{\partial \varphi} \right) W + \frac{\partial}{\partial \varphi} \left(\alpha^{-1} \frac{\partial V}{\partial \vartheta} + \frac{1}{\sin \vartheta} \frac{\partial V}{\partial \varphi} \right) W \right] \right\},
$$
(D.12)

or, equivalently, in the compact vector form of Eq. (3). Here,

$$
\tau_N = \frac{v \mu_0 M_S (\alpha + \alpha^{-1})}{2 \gamma kT}
$$

is the free diffusion time and the constant $k' = kTh'/v = (2\tau_N)^{-1}$ was evaluated by requiring that the Boltzmann distribution $W_{eq}(\vartheta, \varphi) = A e^{-vV(\vartheta,\varphi)/(kT)}$ of orientations (A is a normalizing constant) should be the stationary (equilibrium) solution of the Fokker–Planck equation (D.12). Here, we have given Brown's intuitive derivation of his magnetic Fokker–Planck equation (D.2), for the isotropic Brownian motion of the classical spin. A rigorous derivation of that equation from the Gilbert–Langevin equation is given elsewhere [5, 23, 193].

Now, Brown's Fokker–Planck equation for the probability density function $W(\vartheta, \varphi, t)$ of orientations of the unit vector **u** in configuration space (ϑ, φ) can be solved by separation of the variables. This gives rise to a Sturm–Liouville problem so that $W(\vartheta, \varphi, t)$ can be written as

$$
W(\vartheta, \varphi, t) = W_0(\vartheta, \varphi) + \sum_{k=1}^{\infty} \Phi_k(\vartheta, \varphi) e^{-\lambda_k t},
$$
(D.13)

where $\Phi_k(\vartheta, \varphi)$ and λ_k are the eigenfunctions and eigenvalues of the Fokker–Planck operator L_{FP} and $W_0(\vartheta, \varphi)$ is the stationary solution of that equation, that is, $L_{FP} W_0 = 0$, corresponding to the Boltzmann equilibrium. Then, the reversal time of the magnetization τ can be estimated [5, 6] via the inverse of the smallest nonvanishing eigenvalue λ_1 of the operator L_{FP} in Eq. (2), namely,

$$
\tau = \frac{1}{\lambda_1}.
$$
(D.14)

An alternative method involving the observables directly is to expand $W(\vartheta, \varphi, t)$ as a Fourier series of appropriate orthogonal functions forming an orthonormal basis related to them; here, these are the spherical harmonics $Y_{lm}(\vartheta, \varphi)$ (see Appendix B), namely,

$$
W(\vartheta, \varphi, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{lm}^*(\vartheta, \varphi) \langle Y_{lm} \rangle (t),
$$
(D.15)

where by orthogonality the expectation values of the spherical harmonics are given by

$$\langle Y_{lm} \rangle (t) = \int\limits_{0}^{2\pi} \int\limits_{0}^{\pi} W(\vartheta, \varphi, t) Y_{lm}(\vartheta, \varphi) \sin \vartheta \, d\vartheta \, d\varphi. \tag{D.16}$$

Moreover, for *arbitrary* magnetocrystalline anisotropy, which can be expressed in terms of spherical harmonics as

$$\frac{vV(\vartheta, \varphi)}{kT} = \sum_{R=1}^{\infty} \sum_{S=-R}^{R} A_{R,S} Y_{RS}(\vartheta, \varphi), \tag{D.17}$$

we have by assuming a solution in the form of the Fourier expansion equation (D.15) for the Fokker–Planck equation (2), an infinite hierarchy of differential recurrence equations for the statistical moments $\langle Y_{lm} \rangle (t)$, namely, (details are in Refs. 5 and 144)

$$\tau_N \frac{d}{dt} \langle Y_{lm} \rangle (t) = \sum_{s,r} e_{l,m,l+r,m+s} \langle Y_{l+r m+s} \rangle (t). \tag{D.18}$$

In Eq. (D.18), the $e_{l,m,l',m\pm s}$ are the matrix elements of the Fokker–Planck operator expressed as

$$
\begin{aligned}
e_{l,m,l',m\pm s} = &-\frac{l(l+1)}{2} \delta_{ll'} \delta_{s0} + (-1)^m \frac{1}{4} \sqrt{\frac{(2l+1)(2l'+1)}{\pi}} \\
&\times \sum_{r=s}^{\infty} A_{r,\pm s} \left\{ \frac{\left[l'(l'+1) - r(r+1) - l(l+1) \right]}{2\sqrt{2r+1}} C_{l0l'0}^{r0} C_{lml'-m\mp s}^{r\mp s} \right. \\
&+ \frac{i}{\alpha} \sqrt{\frac{(2r+1)(r-s)!}{(r+s)!}} \sum_{\substack{L=s-\varepsilon_{r,s}, \\ \Delta L = 2}}^{r-1} \sqrt{\frac{(L+s)!}{(L-s)!}} C_{l0l'0}^{L0} \\
&\times \left. \left[m C_{lml'-m\mp s}^{L\mp s} \pm s \sqrt{\frac{(l\mp m)(l\pm m+1)}{(L+s)(L-s+1)}} C_{lm\pm1 l'-m\mp s}^{L\mp s\pm1} \right] \right\}, \tag{D.19}
\end{aligned}
$$

where $s \geq 0$ and $C_{lml'm'}^{rs}$ are the Clebsch–Gordan coefficients. We remark that Eq. (D.19) determines the coefficients of the linear combination $e_{l,m,l',m'}$ for *arbitrary* magnetocrystalline anisotropy and Zeeman energy densities. The Gilbert–Langevin equation (2) can also be reduced to the moment system for $\langle Y_{lm} \rangle (t)$, Eq. (D.18), by an appropriate transformation of variables and by direct averaging (without recourse to the Fokker–Planck equation) of the stochastic equation thereby obtained [5,144]. Examples of explicit calculations of the $e_{l,m,l',m'}$ for particular magnetocrystalline anisotropies are available in Refs. 5 and 6 and further references therein.

The recurrence Eq. (D.18) may always be written in matrix form as

$$\dot{\mathbf{X}}(t) = \mathbf{A}\mathbf{X}(t), \tag{D.20}$$

where $\mathbf{A}$ is the system matrix and $\mathbf{X}(t)$ is an infinite column vector formed from $\langle Y_{lm} \rangle(t)$. The general solution of Eq. (E.7) is determined by successively increasing the size of $\mathbf{A}$ until convergence is attained. Alternatively, we can always transform the moment systems, Eq. (D.18) into the tri-diagonal vector differential recurrence equation

$$\tau_N \dot{\mathbf{C}}_n(t) = \mathbf{Q}_n^- \mathbf{C}_{n-1}(t) + \mathbf{Q}_n \mathbf{C}_n(t) + \mathbf{Q}_n^+ \mathbf{C}_{n+1}(t), \tag{D.21}$$

where $\mathbf{C}_n(t)$ are column vectors arranged in an appropriate way from $\langle Y_{lm} \rangle(t)$ and $\mathbf{Q}_n^\pm, \mathbf{Q}_n$ are matrixes with elements $e_{l',m',l,m}$. As shown in Ref. 197 (see also Ref. 5), the *exact matrix continued fraction solution* of Eq. (D.21) for the Laplace transform of $\mathbf{C}_1(t)$ is given by

$$\tilde{\mathbf{C}}_1(s) = \tau_N \Delta_1(s) \left\{ \mathbf{C}_1(0) + \sum_{n=2}^{\infty} \left[\prod_{k=2}^{n} \mathbf{Q}_{k-1}^+ \Delta_k(s) \right] \mathbf{C}_n(0) \right\}, \tag{D.22}$$

where

$$\tilde{\mathbf{C}}_1(s) = \int_0^{\infty} \mathbf{C}_1(t) e^{-st} dt,$$

$\Delta_n(s)$ is the matrix continued fraction defined by the recurrence equation

$$\Delta_n(s) = \left[\tau_N s \mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^+ \Delta_{n+1}(s) \mathbf{Q}_{n+1}^- \right]^{-1}, \tag{D.23}$$

and $\mathbf{I}$ is the unit matrix. Having determined $\tilde{\mathbf{C}}_1(s)$, one may evaluate all the relevant observables.

Hitherto, we have used Gilbert's form of the Langevin equation (2) and its accompanying Fokker–Planck equation (D.12). Equations (2) and (D.12) often occur in stochastic magnetization dynamics. Brown [23, 24] justified his use of the Gilbert equation because all the terms in it can be derived from a Lagrangian function and a Rayleigh dissipation function. Moreover, Gilbert's equation fits naturally into escape-rate theory in all damping ranges if the damping torque is regarded as the time average of a fluctuating torque, whose instantaneous value contains also a random term with statistical properties. However, in the literature, alternative forms of the Langevin equations governing the magnetization $\mathbf{M}(t)$ have also been proposed. Two other frequently used Langevin equations for stochastic spin dynamics are the Landau–Lifshitz (see e.g., Ref. 25) and Kubo [27, 90, 91] forms, respectively,

$$\dot{\mathbf{u}}(t) = \gamma \mathbf{u}(t) \times \left[\mathbf{H}_{ef}(t) + \mathbf{h}(t) \right] - \gamma \alpha \mathbf{u}(t) \times \left[\mathbf{u}(t) \times \left[\mathbf{H}_{ef}(t) + \mathbf{h}(t) \right] \right] \tag{D.24}$$

and

$$\dot{\mathbf{u}}(t) = \gamma \mathbf{u}(t) \times \left[\mathbf{H}_{ef}(t) + \mathbf{h}(t)\right] - \gamma \alpha \mathbf{u}(t) \times \left[\mathbf{u}(t) \times \mathbf{H}_{ef}(t)\right]. \qquad \text{(D.25)}$$

The difference between these two models is that in the Kubo equation (D.25), the random field $\mathbf{h}(t)$ appears only in the gyromagnetic term. In general, the explicit form of the infinite hierarchy of differential recurrence equations for the statistical moments depends on the Langevin equation. Furthermore, the corresponding Fokker–Planck equation is also determined by that equation. Nevertheless, all the Langevin equations (2, D.24, and D.25) yield very similar hierarchies and Fokker–Planck equations, the only difference being in the definition of the free diffusion time τ_N (see for details Ref. 5 and 6). Moreover, the Kubo and Landau–Lifshitz models, despite the different forms of the Langevin equations (D.24 and D.25), yield *identical* mathematical forms for the corresponding Fokker–Planck equations. Thus the Gilbert, Kubo, and Landau–Lifshitz models for Brownian motion of classical spins, irrespective of the Langevin equations, yield the *same* form of the corresponding Fokker–Planck equations, as well as the same infinite hierarchy of differential recurrence equations for the statistical moments, the only difference being in the free-diffusion time constant, a difference that is negligible at low damping [5, 6] (the most interesting damping range from an experimental point of view). However, only Gilbert's model where a damping term is introduced via the customary Lagrangian formulation of the classical equations of motion for the angular momentum, can be used in all damping ranges. In contrast, neither the Kubo nor the Landau–Lifshitz models can be used for high damping, because under this condition they may predict unphysical behavior of the observables (relaxation times, escape rates, and so on.).

Finally, we remark that in the more general treatment of the isotropic Brownian motion of the classical spin, the memoryless assumption, that is,

$$\phi\,(t_1 - t_2) = \alpha/(v\gamma\mu_0 M_S)\,\delta\,(t_1 - t_2)$$

is discarded. Thus, the random field $\mathbf{h}(t)$ has no longer white noise properties, namely,

$$\overline{h_i(t)} = 0, \overline{h_i(t_1)h_j(t_2)} = 2kT\delta_{ij}\phi\,(t_1 - t_2)\,, \qquad \text{(D.26)}$$

and the generalized stochastic magnetic Langevin equation becomes [198, 199]

$$\dot{\mathbf{u}}(t) = \gamma\left[\mathbf{u}(t) \times \left(\mathbf{H}_{ef}(t) + \mathbf{h}(t)\right)\right] - \left[\mathbf{u}(t) \times \int_0^t \phi(t - t')\dot{\mathbf{u}}(t')dt'\right]. \qquad \text{(D.27)}$$

Here, Eq. (D.27) takes into account memory effects and the random field correlation function $\phi\,(t - t')$ has the meaning of a memory function.

APPENDIX E: CHARACTERISTIC TIMES OF RELAXATION AND CORRELATION FUNCTIONS

We have seen by solving the differential recurrence equations for the statistical moments how we can evaluate the characteristic times of the relaxation and/or correlation functions $C_i(t)(i = X, Y, Z)$ of the longitudinal and transverse components of spin operators (or vectors in the classical case). Now, to characterize the overall time behavior of $C_i(t)$, we may formally introduce (see Ref. 5) the integral relaxation time τ_{int}^i, namely,

$$\tau_{int}^i = \frac{1}{C_i(0)} \int_0^\infty C_i(t)dt, \qquad (E.1)$$

which is the area under the decay curve of $C_i(t)$. Yet another time constant characterizing the time behavior of $C_i(t)$ is the effective relaxation time τ_{ef}^i defined by

$$\tau_{ef}^i = -\frac{C_i(0)}{\dot{C}_i(0)} \qquad (E.2)$$

(yielding precise information on the initial decay of $C_i(t)$ in the time domain). For spin systems with dynamics governed by Fokker–Planck equations, the times τ_{int}^i and τ_{ef}^i may equivalently be defined using the eigenvalues (λ_k^i) of the Fokker–Planck operator from the evolution equation (2) because (Ref. 5, ch. 2) the normalized relaxation function $C_i(t)/C_i(0)$ may formally be written as

$$\frac{C_i(t)}{C_i(0)} = \sum_k c_k^i e^{-\lambda_k^i t}, \qquad (E.3)$$

so that, from Eqs. (E.1), (E.2), and (E.3), we have

$$\tau_{int}^i = \sum_k c_k^i / \lambda_k^i \qquad (E.4)$$

and

$$\tau_{ef}^i = \sum_k \lambda_k c_k^i. \qquad (E.5)$$

Now, the relaxation times τ_{int}^i and τ_{ef}^i each contain contributions from *all* the eigenvalues λ_k^i. Therefore, in general, in order to evaluate both $C_i(t)$, τ_{int}^i, and τ_{ef}^i numerically, a knowledge of each individual λ_k and c_k^i is required. However, in the low-temperature (high-barrier) limit, for the *longitudinal* relaxation of the magnetization, $\lambda_1^Z << |\lambda_k^Z|$ and $c_1^Z \approx 1 >> c_k^Z$ $(k \neq 1)$ provided the wells of the potential remain equivalent or nearly equivalent, the approximation $\tau_{int}^Z \approx 1/\lambda_1^Z$

is valid. In other words, the inverse of the smallest nonvanishing eigenvalue λ_1^Z closely approximates the longitudinal relaxation time τ_{int}^Z in the low-temperature limit for zero or very weak external fields. Furthermore, in the *longitudinal* relaxation of the magnetization, the smallest nonvanishing eigenvalue(s) λ_1^Z of the Fokker–Planck operator characterizes the long-time behavior of

$$\left\langle \hat{S}_Z \right\rangle(t) - \left\langle \hat{S}_Z \right\rangle_{eq} \sim C_{\parallel}(t) \sim e^{-\lambda_1^Z t} = e^{-t/\tau}, t >> \tau. \tag{E.6}$$

Thus, it may be associated with the longest relaxation (reversal) time of the magnetization. In order to evaluate the reversal time τ numerically, we note that the recurrence equations for the statistical moments may always be written in matrix form as

$$\dot{\mathbf{X}}(t) = \mathbf{A}\mathbf{X}(t), \tag{E.7}$$

where $\mathbf{A}$ is the system matrix and $\mathbf{X}(t)$ is an infinite column vector formed from the statistical moments. The τ may then be determined from the smallest nonvanishing root of the characteristic equation

$$\det(\lambda \mathbf{I} - \mathbf{A}) = 0 \tag{E.8}$$

by selecting a sufficiently large number of equations. The general solution of Eq. (E.7) is determined by successively increasing the size of $\mathbf{A}$ until convergence is attained.

The integral relaxation times τ_{int}^i can also be calculated via the one-sided Fourier transform of the appropriate correlation function $\tilde{C}_i(-i\omega) = \int_0^\infty C_i(t)e^{i\omega t}dt$ as

$$\tau_{int}^i = \frac{\tilde{C}_i(0)}{C_i(0)}.$$

Here, we may evaluate the reversal time τ via the one-sided Fourier transform of the longitudinal correlation function $\tilde{C}_Z(-i\omega) = \int_0^\infty C_Z(t)e^{i\omega t}dt$ as follows. We consider the long-time behavior of $C_Z(t)$ which is dominated by an exponential, namely,

$$C_Z(t) \approx C_0 e^{-t/\tau}. \tag{E.9}$$

Then, the longest relaxation time τ can then be extracted from $\tilde{C}_Z(-i\omega)$ (by eliminating C_0) as follows [5]:

$$\tau = \lim_{\omega \to 0} \frac{C_Z(0) - \tilde{C}_Z(-i\omega)}{i\omega \tilde{C}_Z(-i\omega)}. \tag{E.10}$$

In practical applications, such as to magnetization reversal, matrix continued fractions due to their rapid convergence are much better suited to numerical calculations than standard direct matrix inversion based on the matrix representation,

Eq. (E.7), of the infinite system of linear differential recurrence relations for the averaged spherical harmonics.

In the general case, the integral relaxation time can only be evaluated numerically. However, for systems with dynamics governed by single-variable Fokker–Planck equation, it can be calculated analytically for both linear and nonlinear transient responses.

Here, we first derive following Ref. 5, an exact analytic equation for the *nonlinear transient response* relaxation time of a system governed by a one-dimensional Fokker–Planck equation for the probability distribution function $W(z, t)$ of a single variable z, namely,

$$\frac{\partial W}{\partial t} = \mathrm{L}_{FP}W, \tag{E.11}$$

where the Fokker–Planck operator L_{FP} may be represented as follows [71]:

$$\mathrm{L}_{FP}W = \frac{\partial}{\partial z}\left[D_2(z)\left(\frac{\partial W}{\partial z} + D_1(z)W\right)\right]. \tag{E.12}$$

Here, $D_1(z)$ and $D_2(z)$ are the coordinate-dependent coefficients and z is defined in the range t1 $\leq z \leq 1$). Moreover, we assume that the relaxation dynamics of spins obey the single-variable Fokker–Planck equation (E.11). Suppose that at time $t = 0$, the external field H is suddenly altered from H_{I} to H_{II} (see Fig. 14). We are interested in the relaxation of the system starting from an equilibrium (stationary) state I with the distribution function $W_{\mathrm{I}}(z)$, which evolves under the action of the stimulus of arbitrary strength to another equilibrium (stationary) state II with the distribution function $W_{\mathrm{II}}(z)$. This problem is intrinsically nonlinear, because *changes in the magnitude of the potential are arbitrary*. Thus, the concept of relaxation functions and relaxation times must now be used, rather than correlation functions and correlation times.

Following Ref. 200 we may define the relaxation function $f_A(t)$ of a dynamical variable A by

$$f_A(t) = \begin{cases} \langle A \rangle(t) - \langle A \rangle_{\mathrm{II}}, & (t > 0), \\ \langle A \rangle_{\mathrm{I}} - \langle A \rangle_{\mathrm{II}}, & (t \leq 0), \end{cases} \tag{E.13}$$

where $\langle A \rangle(t)$ is the time-dependent average and $\langle A \rangle_{\mathrm{I}}$ and $\langle A \rangle_{\mathrm{II}}$ are equilibrium (stationary) averages defined as follows:

$$\langle A \rangle(t) = \int_{-1}^{1} A(z)W(z, t)dz, \tag{E.14}$$

$$\langle A \rangle_i = \int_{-1}^{1} A(z)W_i(z)dz \quad (i = \mathrm{I}, \mathrm{II}). \tag{E.15}$$

Our goal is to evaluate the integral relaxation time τ_{int} of the relaxation function $f_A(t)$, which is defined as

$$\tau_{int} = \frac{1}{f_A(0)} \int_0^\infty f_A(t)dt$$

$$= \frac{1}{f_A(0)} \lim_{s \to 0} \int_0^\infty e^{-st} f_A(t)dt = \frac{\tilde{f}_A(0)}{f_A(0)}, \tag{E.16}$$

where $\tilde{f}_A(s)$ is the Laplace transform of $f_A(t)$. The relaxation time, Eq. (E.16), may be written as

$$\tau_{int} = \frac{1}{\langle A \rangle_{\mathrm{I}} - \langle A \rangle_{\mathrm{II}}} \int_{-1}^1 [A(z) - \langle A \rangle_{\mathrm{II}}] \tilde{W}(z, 0)dz, \tag{E.17}$$

where

$$\tilde{W}(z, 0) = \lim_{s \to 0} \tilde{W}(z, s)$$

and

$$\tilde{W}(z, s) = \int_0^\infty W(z, t) e^{-st} dt.$$

Now, $\tilde{W}(z, 0)$ in Eq. (E.11) can be calculated analytically via the final-value theorem of Laplace transformation [105], namely,

$$\lim_{s \to 0} s\tilde{W}(z, s) = \lim_{t \to \infty} W(z, t) = W_{\mathrm{II}}(z).$$

Thus, we obtain, from the Fokker–Planck equation (E.11), for $t > 0$, the ordinary differential equation

$$W_{\mathrm{II}}(z) - W_{\mathrm{I}}(z) = \frac{d}{dz} \left[D_2(z) \left(\frac{d}{dz} \tilde{W}(z, 0) + D_1(z) \tilde{W}(z, 0) \right) \right]. \tag{E.18}$$

The particular solution of Eq. (E.18) is

$$\tilde{W}(z, 0) = W_{\mathrm{II}}(z) \int_{-1}^1 \frac{\Phi(y)dy}{D_2(y) W_{\mathrm{II}}(y)}, \tag{E.19}$$

where

$$\Phi(y) = \int_{-1}^{y} [W_{II}(z) - W_{I}(z)]dz \qquad (E.20)$$

and $W_{II}(z)$ is the stationary solution of the equation

$$\frac{d}{dz}\left[D_2(z)\left(\frac{d}{dz}W_{II}(z) + D_1(z)W_{II}(z)\right)\right] = 0. \qquad (E.21)$$

Hence, using the definitions, Eq. (E.17) and Eq. (E.19), we have

$$\tau_{int} = \frac{1}{\langle A \rangle_I - \langle A \rangle_{II}} \int_{-1}^{1} [A(x) - \langle A \rangle_{II}] W_{II}(x) \int_{-1}^{x} \frac{\Phi(y)dy}{D_2(y)W_{II}(y)} dx$$

or, by integration by parts [200],

$$\tau_{int} = \frac{1}{\langle A \rangle_{II} - \langle A \rangle_I} \int_{-1}^{1} \frac{\Phi(x)\Psi(x)}{D_2(x)W_{II}(x)} dx, \qquad (E.22)$$

where for convenience we have written

$$\Psi(x) = \int_{x_1}^{x} [A(y) - \langle A \rangle_{II}] W_{II}(y)dy. \qquad (E.23)$$

Equation (E.22) is an *exact* equation for the *nonlinear transient-response relaxation time*. Examples of applications of Eq. (E.22) to nonlinear-response problems have been given in the present review and in Ref. 5.

If we now suppose that the change in the magnitude of the external field H from H_I to H_{II} is very small, that is, $|H_{II} - H_I| \to 0$, the problem becomes intrinsically linear, because *changes in the magnitude of the potential are insignificant*. Thus, linear-response theory and the concept of correlation functions and correlation times rather than relaxation functions and relaxation times can now be used. The *equilibrium* (stationary) correlation function $C_{AB}(t)$ is defined by

$$C_{AB}(t) = \langle A[z(0)] B[z(t)]\rangle_0 - \langle A \rangle_0 \langle B \rangle_0$$

$$= \int_{-1}^{1} [A(z) - \langle A \rangle_0]e^{L_{FP}t}[B(z) - \langle B \rangle_0]W_0(z)dz. \qquad (E.24)$$

Here, W_0 is the stationary (equilibrium) distribution function satisfying $L_{FP}W_0 = 0$; the symbols $\langle \rangle$ and $\langle \rangle_0$ designate the statistical averages over W and W_0, respectively. Now, the salient feature of one-dimensional systems is that an *exact integral formula* for the correlation time τ_{cor}

$$\tau_{cor} = \frac{1}{C_{AB}(0)} \int_0^\infty C_{AB}(t)dt \tag{E.25}$$

(defined as the area under the curve of the normalized correlation function $C_{AB}(t)$) exists because the relevant Fokker–Planck equation (E.11) may be integrated by quadratures as with the nonlinear responses [5, 71]. The details of the derivation are given in Refs. 5 and 71, so we merely quote the final analytic expression for τ_{cor}, namely,

$$\tau_{cor} = \frac{1}{C_{AB}(0)} \int_{-1}^1 \frac{\psi_A(x)\psi_B(x)dx}{D_2(x)W_0(x)}, \tag{E.26}$$

where

$$\psi_A(x) = \int_{-1}^x [A(y) - \langle A \rangle_0]W_0(y)dy, \tag{E.27}$$

$$\psi_B(x) = \int_{-1}^x [B(y) - \langle B \rangle_0]W_0(y)dy. \tag{E.28}$$

For $A = B$, Eq. (E.26) reduces to

$$\tau_{cor} = \frac{1}{\langle A^2 \rangle_0 - \langle A \rangle_0^2} \int_{-1}^1 \frac{\psi_A^2(x)dx}{D_2(x)W_0(x)}. \tag{E.29}$$

The relaxation time in integral form, Eq. (E.29), was first given by Szabo [201], and later reproduced by other authors under different guises [5, 151, 153, 200, 202, 203].

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