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Phase-space formulation of the nonlinear longitudinal relaxation of the magnetization in quantum spin systems

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Nonlinear longitudinal relaxation of a spin in a uniform external dc magnetic field is treated using a master equation for the quasiprobability distribution function of spin orientations in the configuration space of polar and azimuthal angles (analogous to the Wigner phase space distribution for translational motion). The solution of the corresponding classical problem of the rotational Brownian motion of a magnetic moment in an external magnetic field essentially carries over to the quantum regime yielding in closed form the dependence of the longitudinal spin relaxation on the spin size S as well as an expression for the integral relaxation time, which in linear response reduces to that previously given by D. A. Garanin [Phys. Rev. E **55**, 2569 (1997)] using the density matrix approach. The nonlinear relaxation is dominated by a single exponential having as time constant the integral relaxation time. Thus a simple description in terms of a Bloch equation holds even for the nonlinear response of a giant spin.

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I. INTRODUCTION

Spin relaxation is fundamental in the physics and chemistry of condensed phases, e.g., on an *atomic* level, nuclear magnetic and related spin resonance experiments probe the time evolution of the elementary spins of nuclei, electrons, muons, etc. [1,2]. On a larger scale the time evolution of magnetic *molecular clusters* exhibiting relatively large quantum effects [3] with spins of order $15-25\mu_B$ is currently of interest in the context of molecular magnets. Finally, on a *nanoscale* level, we have magnetic fluids composed of single domain ferromagnetic particles (constituting a single giant spin of magnitude $10^4-10^5\mu_B$) 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 overcome via thermal agitation anisotropy, potential barriers inside the particle and the Debye (or Brownian) relaxation [7] due to physical rotation of the suspended particles in the presence of an applied field and the heat bath. Here quantum effects are expected to be much smaller.

Spin relaxation experiments in nuclear magnetic or electron spin resonance are usually interpreted via the phenomenological Bloch [8] equations and their later modifications [1,2]. They describe relaxation of an assembly of elementary spins in a sample subjected to an external magnetic field and coupled to a heat bath. 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 by two time constants, the so-called relaxation times. They provide a substantially correct [1] quantitative description for liquid samples. Microscopic theories of the relaxation in quantum spin systems have been developed by Bloembergen, Purcell, and Pound [9], and other authors (see, e.g., [10–12]).

Proceeding to larger scales, in magnetic molecular clusters comprising a few spins the relaxation behavior as a function of spin is of paramount importance as strong quantum effects are expected to manifest themselves as the spin decreases, while in single domain (giant spin) nanoparticles suspended in a fluid carrier the relaxation is usually assumed to be classical. Thus the Néel mechanism of the magnetization reversal [6] occurring inside the ferromagnetic particles is described by a classical Langevin equation for the time evolution of the magnetization as adapted to magnetic moments by Brown [13,14] while the Debye theory [7] of dielectric relaxation of polar molecules is used to describe the relaxation by physical rotation of the suspended particles [4,15]. In the description of the Néel mechanism [13,14], the Langevin equation is the phenomenological Landau-Lifshitz [16] or Gilbert equation [17] for the magnetization $\mathbf{M}(t)$ (used originally to study the motion of a domain wall) augmented by random magnetic fields due to the heat bath [18]. This equation leads [4,13,14] to the Fokker-Planck equation in the space of polar angles for the surface distribution of the magnetic moment orientations. For simplicity it is commonly assumed that the solid state and Brownian relaxation mechanisms may be treated independently. A discussion of the limitations of that assumption has been given in Refs. [4,15]. Moreover, memory effects are ignored, however, they may also be included as in [19–21]. It is immediately apparent that treating magnetization relaxation via the Landau-Lifshitz equation augmented by stochastic terms is essentially just another problem concerning the rotational Brownian motion under the combined effect of an external field and the internal magnetocrystalline anisotropy. Many particular cases have been treated [5,13,14] by using the Kramers escape rate [22] as adapted to magnetic relaxation [14,23,24] in order to calculate the reversal time of the magnetization over the internal potential barrier. Moreover, the results have been exhaustively compared [5] with exact solutions yielded by the Fokker-Planck equation. Now it has been suggested by Bean and Livingston [25] that in addition to the overbarrier relaxation mechanism mentioned above the magnetization may also reverse by quantum tunneling through the barrier. This relaxation mechanism represents *macroscopic quantum tunneling* since a giant spin is always involved [26].

These considerations merit a systematic way of introducing quantum effects into the spin dynamics simultaneously linking to the classical representation and allowing one to study quantum effects. The method proposed here utilizes the coherent state representation of the density matrix introduced by Glauber and Sudarshan commonly used in quantum optics (see, e.g., [27,28]). This method when applied to spin systems [29,30] allows one to analyze quantum spin relaxation using a master equation for a *quasiprobability distribution function* $W^{\sigma}(\vartheta,\varphi,t)$ of spin orientations in a phase (here configuration) space (ϑ,φ); ϑ and φ are the polar and azimuthal angles, constituting the canonical variables. Here σ parametrizes quasiprobability functions of spins belonging to the SU(2) rotation group, and $\sigma=0$ and $\sigma=\pm 1$ correspond to the Stratonovich [31] and Berezin [32] contravariant and covariant functions, respectively (the latter are directly related to the P and Q symbols, which appear naturally in the coherent state representation; see Refs. [33,34] for a review and Appendix A for details. We consider $W^{-1}(\vartheta,\varphi,t)$ only and drop the superscript. Such a mapping of the quantum spin dynamics onto c-number quasiprobability density evolution equations clearly shows how these reduce to the Fokker-Planck equation in the classical limit [29,30]. The function $W(\vartheta,\varphi,t)$ was originally introduced by Stratonovich [31] for zero dissipation, i.e., for closed systems, and further developed both for closed and open spin systems (e.g., [29,30,32–42] and is entirely analogous to the translational Wigner distribution $W(x,p,t)$ in phase space (x,p) [43], which is the quasiprobability representation of the density operator except that certain differences arise [29] because of the angular momentum commutation relations. The Wigner function $W(\vartheta,\varphi,t)$ of spin orientations in a configuration space, just as the Wigner function $W(x,p,t)$ for the translational motion of a particle in phase space, enables the expected value $\langle\hat{A}\rangle(t)$ of a quantum spin operator $\hat{A}$ to be calculated via the corresponding (c number) function $A(\vartheta,\varphi)$. For example, for the spin operator $\hat{S}_Z$, the correspondence rules of operators and c numbers yield $\hat{S}_Z\rightarrow(S+1)\cos\vartheta$, while the expected value $\langle\hat{S}_Z\rangle(t)$ is

$$\langle\hat{S}_Z\rangle(t)=\frac{2S+1}{4\pi}\int_0^{\pi}\int_0^{2\pi}(S+1)\cos\vartheta W(\vartheta,\varphi,t)\sin\vartheta d\vartheta d\varphi$$

(see Appendix A for details). The phase-space formalism allows quantum mechanical averages involving the density matrix to be calculated just as classical ones and so is eminently suited to the calculation of quantum corrections because it formally represents quantum mechanics as a statistical theory on classical phase space [44]. Indeed $W(x,p,t)$ has been recently used [45–48] for quantum corrections to the classical theory of the translational Brownian motion via perturbation theory in $\hbar^2$ ($\hbar$ is Planck's constant). The formalism is easy to implement because semiclassical master equations in phase space enable techniques (e.g., continued fractions [49]) originally developed for the solution of the Fokker-Planck equation to be seamlessly carried over into the quantum domain [45,47]. In particular (which is relevant in the present context), we note the semiclassical quantum master equation in phase space for the translational harmonic quantum oscillator in the weak coupling limit (originally studied by Agarwal [50])

$$\frac{\partial W}{\partial t}+\frac{p}{m}\frac{\partial W}{\partial x}-m\omega_0^2 x\frac{\partial W}{\partial p}=\frac{\varsigma}{m}\frac{\partial}{\partial p}\left[pW+\langle p^2\rangle_{\mathrm{eq}}\frac{\partial W}{\partial p}\right], \qquad (1)$$

where ς, m, and ω_0 are the "friction" coefficient, mass, and oscillator frequency, respectively, $\langle p^2\rangle_{\mathrm{eq}}=(m\hbar\omega_0/2)\coth(\beta\hbar\omega_0/2)$, $\beta=1/(kT)$, and kT is the thermal energy. Equation (1) is the same as the Fokker-Planck equation (here the Klein-Kramers equation) for a classical Brownian oscillator [5] except the diffusion coefficient $D_{pp}=\varsigma\langle p^2\rangle_{\mathrm{eq}}/m$ is altered to include the quantum effects. Thus it is unnecessary to resort to perturbation theory because the dynamical equation for the Wigner function for a quadratic Hamiltonian $\hat{H}=\hat{p}^2/2m+m\omega_0^2\hat{x}^2/2$ in the absence of dissipation ($\varsigma=0$) coincides with the corresponding classical Liouville equation.

Now for a spin in an external uniform field if the coherent state representation is transferred to the conventional polar and azimuthal angle representation (ϑ,φ), the master equation describing the time evolution of $W(\vartheta,\varphi,t)$ again has essentially the same form as the corresponding classical Fokker-Planck equation [30]. Hence the problem is analogous to the Agarwal harmonic oscillator model [50] thus serving as the most simple example of the application of the phase-space method to open spin systems [29,30,41,42] as we demonstrate here. We remark that the master equation has been solved by continued fractions in Ref. [41] for the longitudinal relaxation for *particular* small values of the spin $S=1/2$, 1, and 3/2. Here we shall present both the *exact* and an approximate general solution for the linear and *nonlinear* relaxation of the averaged longitudinal component of the spin $\langle\hat{S}_Z\rangle(t)$ as a function of all spin values S in a uniform magnetic field of *arbitrary* strength. We shall show how the solution of the corresponding classical problem [5,51–54] carries over into the quantum domain and how the exact solution for the integral relaxation time for an *arbitrarily strong* change in the uniform field may be obtained. In the *linear response approximation* the exact solution reduces to that previously given by Garanin [55] using the spin density matrix in the second order of perturbation theory in the spin bath coupling and later rederived by García-Palacios and Zueco [56] who (again using the density matrix) considered the linear longitudinal relaxation for arbitrary S. Furthermore, we shall demonstrate that the relaxation of the spin $\langle\hat{S}_Z\rangle(t)$, comprising $2S$ exponentials, may be accurately approximated by a *single* exponential with a definite relaxation time T_1, which strongly depends on S and the field strength for arbitrary S. In other words, even for a giant spin ($S \gg 1$), $\langle \hat{S}_Z \rangle(t)$ still obeys the Bloch equation

$$\frac{d}{dt}\langle \hat{S}_Z \rangle(t) + (\langle \hat{S}_Z \rangle(t) - \langle \hat{S}_Z \rangle_{\text{eq}}) \big/ T_1 = 0, \tag{2}$$

where $\langle \hat{S}_Z \rangle_{\text{eq}}$ is the equilibrium average of the operator $\hat{S}_Z$. We remark in passing that Garanin and García-Palacios *et al.* [55–57] evaluated the response for a more general spin system (a uniaxial paramagnet in a uniform field). They have given a quantum treatment of the spin dynamics by proceeding from the quantum Hubbard operator representation of the evolution equation for the spin density matrix. However, they considered a *small* longitudinal ac field superimposed on a longitudinal dc field so that by linear response theory their solution is strictly limited to the response consequent on a small perturbation in the dc field unlike ours, which is valid for arbitrary changes in the dc field, thus no longer necessarily bearing any relation to the ac response.

II. BASIC EQUATIONS FOR THE LONGITUDINAL RELAXATION

Following [30,41,42] we consider the dynamics of a spin $\hat{\mathbf{S}}$ in an external dc magnetic field $\mathbf{H}_0$ 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 so that the Hamiltonian $\hat{H}$ is

$$\hat{H} = \hat{H}_S + \hat{H}_{SB} + \hat{H}_B,$$

where $\hat{H}_S = -\hbar\omega_0 \hat{S}_Z$, $\omega_0 = \gamma H_0$ is the precession (Larmor) frequency, γ is the gyromagnetic ratio, the term $\hat{H}_{SB} = -\hbar\gamma \mathbf{h}\cdot\hat{\mathbf{S}}$ describes interaction of the spin with the thermostat, and $\hat{H}_B$ characterizes the thermostat. The equation of motion for the density matrix $\hat{\rho}$ is then

$$\frac{\partial \hat{\rho}}{\partial t} + \frac{i}{\hbar}[\hat{H}_S, \hat{\rho}] = \hat{Q}(\hat{\rho}), \tag{3}$$

where $\hat{Q}(\hat{\rho}) = -(i/\hbar)[\hat{H}_{SB} + \hat{H}_B, \hat{\rho}]$ is the collision kernel operator. The reduced density matrix $\hat{\sigma} = \text{Tr}_B\, \hat{\rho}$ (i.e., that averaged over the density matrix of the bath) obeys the following equation [30]:

$$\frac{\partial \hat{\sigma}}{\partial t} = i\omega_0[\hat{S}_0, \hat{\sigma}] + B^* e^{\beta\hbar\omega_0}[\hat{S}_+\hat{\sigma}, \hat{S}_-] + B e^{\beta\hbar\omega_0}[\hat{S}_+, \hat{\sigma}\hat{S}_-] + B[\hat{S}_-\hat{\sigma}, \hat{S}_+] + B^*[\hat{S}_-, \hat{\sigma}\hat{S}_+] + C[\hat{S}_0\hat{\sigma}, \hat{S}_0] + C^*[\hat{S}_0, \hat{\sigma}\hat{S}_0],$$

where $\hat{S}_+$, $\hat{S}_-$, and $\hat{S}_0 = \hat{S}_Z$ are the spin operators in spin coherent state representation (defined in Ref. [30]) and

$$B = (\gamma/2)^2 \int_0^\infty \langle h^-(t) h^+(0) \rangle_B e^{-i\omega_0 t} dt,$$

$$C = \gamma^2 \int_0^\infty \langle h^0(t) h^0(0) \rangle_B dt.$$

Here the averages are over the equilibrium bath density matrix (assuming axial symmetry about the Z axis and that the averaged field components $\langle h^{\pm}(t) \rangle_B = 0$ and $\langle h^0(t) \rangle_B = 0$). In the longitudinal relaxation, the azimuthal dependence of W may be ignored so that the corresponding evolution equation for $W(\vartheta, t)$ is [30]

$$\frac{\partial W}{\partial t} = \frac{b(e^{\beta\hbar\omega_0} - 1)}{\sin\vartheta} \frac{\partial}{\partial\vartheta} \left\{ (\sin\vartheta[\coth(\beta\hbar\omega_0/2) + \cos\vartheta]) \frac{\partial W}{\partial\vartheta} + 2S \sin^2\vartheta W \right\}, \tag{4}$$

where $b = \text{Re}(B)$ is the effective "diffusion" coefficient related to the random magnetic field imposed by the reservoir on the spin. Equation (4) applies in the narrowing limit case when the correlation time τ_c of the random field $\mathbf{h}(t)$ acting on the spin satisfies the condition $\gamma H \tau_c \ll 1$, where H is the averaged amplitude of the random magnetic field. The left hand side of Eq. (4) is the quantum analog of the Liouville equation for a spin, which in this instance is the same as the classical case just as the corresponding result 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. Conditions for the validity of Eq. (4) are discussed in detail elsewhere (see, e.g., [30]). Essentially, Eq. (4) follows from the equation of motion of the reduced density matrix where the interactions between the spin and the heat bath are small enough to allow one to use the weak coupling limit and the correlation time characterizing the bath is so short that we can regard the stochastic process originating in the bath as Markovian [30]. Thus one may assume frequency independent damping. This approximation may be used in the high temperature limit. In the parameter range, where such an approximation is invalid (e.g., throughout the very low temperature region), a more general form of the master equation with time dependent diffusion coefficients [41,42] should be used. We have chosen Eq. (4) in the approximation of frequency independent damping because our objective is merely to understand in semiclassical fashion how quantum effects alter the rotational Brownian motion and nonlinear longitudinal relaxation of a classical spin. We also remark that in the case of longitudinal relaxation, Eq. (4) may be plausibly derived (see Appendix B) by postulating (just as in the phase space treatment of the quantum translational Brownian motion [46,48]) a master equation for the Wigner function W 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 $\hat{\rho}_{\text{eq}} = e^{-\beta\hat{H}_S}/\text{Tr}\{e^{-\beta\hat{H}_S}\}$, renders the collision kernel equal to zero.

Now the Wigner function $W_{\text{eq}}(\vartheta)$, which is the stationary solution of Eq. (4), is [30]

$$W_{\mathrm{eq}}(\vartheta)=Z_S^{-1}\left[\cosh\left(\frac{1}{2}\beta\hbar\omega_0\right)+\sinh\left(\frac{1}{2}\beta\hbar\omega_0\right)\cos\vartheta\right]^{2S}, \tag{5}$$

where

$$\begin{aligned}Z_S&=\left(S+\frac{1}{2}\right)\int_{-1}^{1}\left[\cosh\left(\frac{1}{2}\beta\hbar\omega_0\right)+\sinh\left(\frac{1}{2}\beta\hbar\omega_0\right)z\right]^{2S}dz\\&=\sinh\left[\left(S+\frac{1}{2}\right)\beta\hbar\omega_0\right]\Big/\sinh\left(\frac{1}{2}\beta\hbar\omega_0\right)\end{aligned}$$

is the partition function. The average longitudinal component of the spin at equilibrium is

$$\begin{aligned}\langle\hat{S}_Z\rangle_{\mathrm{eq}}&=\left(S+\frac{1}{2}\right)\int_0^{\pi}(S+1)\cos\vartheta W_{\mathrm{eq}}(\vartheta)\sin\vartheta d\vartheta\\&=SB_S(\beta\hbar\omega_0 S),\end{aligned} \tag{6}$$

where $B_S(x)$ is the Brillouin function defined as [49]

$$B_S(x)=\frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}x\right)-\frac{1}{2S}\coth\left(\frac{x}{2S}\right). \tag{7}$$

Equation (6) is in complete agreement with the well-known result for the equilibrium magnetization of a spin in a uniform magnetic field [58]. In the classical limit, $\beta\to 0$, $S\to\infty$, and βS=const, the equilibrium distribution $W_{\mathrm{eq}}(\vartheta)$ and the Brillouin function $B_S(x)$ tend, respectively, to the Boltzmann distribution, i.e., $(S+\frac{1}{2})W_{\mathrm{eq}}(\vartheta)\to Z_{\mathrm{cl}}^{-1}e^{S\beta\hbar\omega_0\cos\vartheta}$, and the Langevin function, i.e., $B_S(x)\to L(x)=\coth(x)-1/x$, where Z_{cl} is the classical partition function. Quantum effects become important when $\hbar\gamma H_0/(kTS)\geqslant 1$, i.e., either at small S or at very low temperatures T or for an intense field H_0.

III. EXACT SOLUTION OF THE MASTER EQUATION (4)

We suppose that the magnitude of an externally uniform dc magnetic field is suddenly altered at time $t=0$ from $\mathbf{H}_{\mathrm{I}}$ to $\mathbf{H}_{\mathrm{II}}$ (the magnetic fields $\mathbf{H}_{\mathrm{I}}$ and $\mathbf{H}_{\mathrm{II}}$ are assumed to be applied parallel to the Z axis of the laboratory coordinate system). Thus we study as in the classical case [5,59] the transient longitudinal relaxation of a system of spins starting from an equilibrium state I with the distribution function $W_{\mathrm{eq}}^{H_{\mathrm{I}}}$ $(t\leqslant 0)$ to a new equilibrium state II with the distribution function $W_{\mathrm{eq}}^{H_{\mathrm{II}}}$ $(t\to\infty)$. Here the longitudinal component of the spin $\langle\hat{S}_Z\rangle(t)$ relaxes from the equilibrium value $\langle\hat{S}_Z\rangle_{\mathrm{eq}}^{\mathrm{I}}$ to the value $\langle\hat{S}_Z\rangle_{\mathrm{eq}}^{\mathrm{II}}$, the transient being described by an appropriate relaxation function (see Fig. 1). The transient response so formulated is truly nonlinear because the change in amplitude $H_{\mathrm{I}}-H_{\mathrm{II}}$ of the external dc magnetic field is *arbitrary* (the linear response can be treated as the particular case $|H_{\mathrm{I}}-H_{\mathrm{II}}|\to 0$).

The master equation (4) for the evolution of $W(z,t)$ (with $z=\cos\vartheta$) can be given in the form of a single variable Fokker-Planck equation for $t>0$ [30],

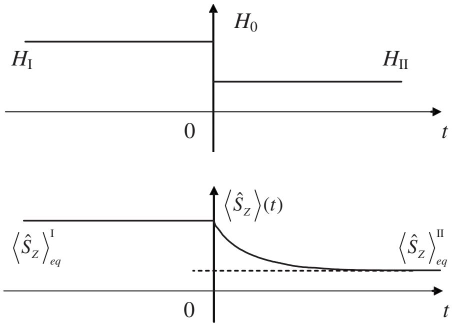

FIG. 1. Schematic representation of the longitudinal nonlinear transient response.

$$\frac{\partial W}{\partial t}=\frac{\partial}{\partial z}\left(D^{(2)}(z)\frac{\partial}{\partial z}W-D^{(1)}(z)W\right), \tag{8}$$

where $D^{(1)}(z)$ and $D^{(2)}(z)$ are, respectively, the drift and diffusion coefficients given by

$$D^{(1)}(z)=S(e^{\xi/S}-1)(1-z^2)/(2\tau_N), \tag{9}$$

$$D^{(2)}(z)=(e^{\xi/S}+1)[1+z\tanh(\xi/2S)](1-z^2)/(4\tau_N), \tag{10}$$

$\tau_N=1/(4b)$ is the characteristic time of the free rotational "diffusion" of the spin, and the dimensionless field parameter ξ is defined as

$$\xi=\beta\hbar\gamma H_{\mathrm{II}}S. \tag{11}$$

We remark that the explicit form of $D^{(1)}(z)$ and $D^{(2)}(z)$ can be obtained from the Fokker-Planck equation (8) using the equilibrium distribution Eq. (5) alone exactly as in the translational Brownian motion [48] (see Appendix B).

The solution of Eq. (8) is obtained by expanding the distribution function $W(z,t)$ in a series of Legendre polynomials $P_n(z)$

$$W(z,t)=W_{\mathrm{eq}}^{\xi}(z)+\sum_{n=0}^{2S}\frac{2n+1}{2S+1}P_n(z)f_n(t), \tag{12}$$

where the equilibrium distribution $W_{\mathrm{eq}}^{\xi}(z)$ is defined as [c.f., Eq. (5)]

$$\begin{aligned}W_{\mathrm{eq}}^{\xi}(z)&=Z_S^{-1}[\cosh(\xi/2S)+\sinh(\xi/2S)z]^{2S}\\&=\sum_{n=0}^{2S}\frac{2n+1}{2S+1}P_n(z)\langle P_n\rangle_{\mathrm{eq}}^{\xi},\end{aligned} \tag{13}$$

and

$$\langle P_n\rangle_{\mathrm{eq}}^{\xi}=\left(S+\frac{1}{2}\right)\int_{-1}^{1}P_n(z)W_{\mathrm{eq}}^{\xi}(z)dz \tag{14}$$

is the equilibrium average of $P_n(z)$. In particular, we have $\langle P_1\rangle_{\mathrm{eq}}^{\xi}=[S/(S+1)]B_S(\xi/S)$. Substituting Eq. (12) into Eq. (8) and noting the orthogonality and recurrence properties of the Legendre polynomials [60] as in the classical case [5] we have a differential-recurrence relation for the relaxation functions $f_n(t)=\langle P_n\rangle(t)-\langle P_n\rangle_{\rm eq}^{\xi}$, viz.,

$$\tau_n \dot{f}_n(t) = q_n^- f_{n-1}(t) + q_n f_n(t) + q_n^+ f_{n+1}(t), \tag{15}$$

where $1\leqslant n\leqslant 2S$, $f_0(t)=f_{2S+1}(t)=0$,

$$\tau_n = 2\tau_N/[n(n+1)], \quad q_n = -(1+e^{\xi/S})/2,$$

$$q_n^{\pm} = \mp \frac{2S\pm n+(3\pm 1)/2}{2(2n+1)}(e^{\xi/S}-1),$$

and the brackets $\langle\ \rangle(t)$ designate statistical averaging defined as $\langle\odot\rangle(t)=\left(S+\frac{1}{2}\right)\int_{-1}^{1}\odot W(z,t)dz$.

Using the properties of the one-sided Fourier transform, we have from Eq. (15)

$$(i\omega\tau_n - q_n)\tilde{f}_n(\omega) - q_n^-\tilde{f}_{n-1}(\omega) - q_n^+\tilde{f}_{n+1}(\omega) = \tau_n f_n(0), \tag{16}$$

where $\tilde{f}_n(\omega)=\int_0^\infty e^{-i\omega t}f_n(t)dt$. The inhomogeneous three-term recurrence Eq. (16) can be solved exactly for $\tilde{f}_1(\omega)$ using continued fractions just as the corresponding classical problem (see for details Ref. [5], Chap. 2) yielding

$$\tilde{f}_1(\omega) = \frac{2\tau_N}{(e^{\xi/S}-1)}\sum_{n=1}^{2S} a_n \prod_{k=1}^{n}\Delta_k^{\parallel}(\omega,\xi). \tag{17}$$

Here the finite continued fraction $\Delta_n^{\parallel}(\omega,\xi)$ is defined by the recurrence relation

$$\Delta_n^{\parallel}(\omega,\xi) = q_n^-[i\omega\tau_n - q_n - q_n^+\Delta_{n+1}^{\parallel}(\omega,\xi)]^{-1},$$

with $\Delta_{2S+1}^{\parallel}(\omega,\xi)=0$ and

$$a_n = \frac{f_n(0)}{n(n+1)(S+1)}\prod_{k=1}^{n}\frac{q_{k-1}^+}{q_k^-}$$

$$= (-1)^{n+1}f_n(0)\frac{(2n+1)(2S+n+1)!(2S-n)!}{n(n+1)(S+1)(2S+1)!(2S)!}.$$

Noting that the initial value for the distribution function is $W(z,0)=W_{\rm eq}^{\xi+\delta}(z)$, where $\delta=\beta\hbar\gamma S(H_{\rm II}-H_{\rm I})$ (that is, the perturbation strength), the initial values for the $f_n(t)$ are

$$f_n(0) = \langle P_n\rangle_{\rm eq}^{\xi+\delta} - \langle P_n\rangle_{\rm eq}^{\xi}. \tag{18}$$

The equilibrium averages $\langle P_n\rangle_{\rm eq}^{\xi}$ given by Eq. (14) can also be evaluated in terms of $\Delta_n^{\parallel}(0,\xi)$ since $\langle P_n\rangle_{\rm eq}^{\xi}$ satisfies the three-term recurrence relation

$$q_n^-\langle P_{n-1}\rangle_{\rm eq}^{\xi} + q_n\langle P_n\rangle_{\rm eq}^{\xi} + q_n^+\langle P_{n+1}\rangle_{\rm eq}^{\xi} = 0, \tag{19}$$

so that $\Delta_n^{\parallel}(0,\xi)=\langle P_n\rangle_{\rm eq}^{\xi}/\langle P_{n-1}\rangle_{\rm eq}^{\xi}$ and

$$\langle P_n\rangle_{\rm eq}^{\xi} = \prod_{k=1}^{n}\Delta_k^{\parallel}(0,\xi). \tag{20}$$

Equation (17) is the exact solution for the one-sided Fourier transform of the nonlinear 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 normalized magnetization $\langle\hat{M}_Z\rangle(t)=\langle\hat{S}_Z\rangle(t)-\langle\hat{S}_Z\rangle_{\rm eq}^{\xi}$ may be evaluated because

$$\langle\hat{M}_Z\rangle(t) = (S+1)f_1(t), \tag{21}$$

where $\langle\hat{S}_Z\rangle_{\rm eq}^{\xi}=SB_S(\xi/S)$. In particular, we mention the rise, decay, and rapidly reversing field transient responses. In some cases, the general equation (17) can be considerably simplified. For example, let us now suppose that a strong constant field $\mathbf{H}_{\rm II}$ is suddenly switched on at time $t=0$ (so that $\mathbf{H}_{\rm I}=\mathbf{0}$ or $\delta=-\xi$). Thus we are interested in the nonlinear relaxation of a system of spins starting from an equilibrium state I with the isotropic distribution function $W_{\rm eq}^{0}=(2S+1)^{-1}$ $(t\leqslant 0)$ to another equilibrium state II with the distribution function $W_{\rm eq}^{\xi}$ $(t\to\infty)$. Noting Eq. (20), Eq. (17) becomes

$$\tilde{f}_1(\omega) = i[\Delta_1^{\parallel}(0,\xi) - \Delta_1^{\parallel}(\omega,\xi)]/\omega. \tag{22}$$

Equation (22) allows one to easily calculate $\tilde{f}_1(\omega)$ for the rise transient.

IV. NONLINEAR LONGITUDINAL RELAXATION TIME

The overall transient behavior of the relaxation function $f_1(t)$ [hence the magnetization $\langle\hat{M}_Z\rangle(t)$] is characterized by the integral relaxation time [the area under the normalized relaxation function $f_1(t)/f_1(0)$] [5]

$$\tau_{\rm int} = \frac{1}{f_1(0)}\int_0^\infty f_1(t)dt = \frac{\tilde{f}_1(0)}{f_1(0)}, \tag{23}$$

where $f_1(0)=[B_S(\xi+\delta)-B_S(\xi)]S/(S+1)$. This time can be evaluated from Eqs. (17) and (20) and is given by

$$\tau_{\rm int} = \frac{2\tau_N}{(e^{\xi/S}-1)f_1(0)}\sum_{n=1}^{2S} a_n\langle P_n\rangle_{\rm eq}^{\xi}. \tag{24}$$

This expression can also be presented in an equivalent integral form by noting that the master equation (8) has the form of a single variable Fokker-Planck equation. As shown in Refs. [5,59], for any system, with dynamics governed by a single variable Fokker-Planck equation, e.g., Eq. (8), the integral relaxation time $\tau_{\rm int}$ characterizing the nonlinear relaxation behavior of $f_1(t)=\langle P_1\rangle(t)-\langle P_1\rangle_{\rm eq}^{\xi}$ can be obtained in closed integral form (just as for linear response) in terms of the equilibrium distribution and the diffusion coefficient $D^{(2)}(z)$ only. Hence on applying these results to Eq. (8), we obtain just as in the classical case [5,59] the exact equation for $\tau_{\rm int}$, viz.,

$$\tau_{\rm int} = \frac{(S+1/2)}{f_1(0)}\int_{-1}^{1}\frac{\Phi(z)\Psi(z)}{D^{(2)}(z)W_{\rm eq}^{\xi}(z)}dz, \tag{25}$$

where $\Psi(z)=\int_{-1}^{z}(x-\langle P_1\rangle_{\rm eq}^{\xi})W_{\rm eq}^{\xi}(x)dx$ and $\Phi(z)=\int_{-1}^{z}[W_{\rm eq}^{\xi+\delta}(x)-W_{\rm eq}^{\xi}(x)]dx$. For the limiting case $S=1/2$, $\tau_{\rm int}$ is independent of the perturbation strength δ and is given by

$$\tau_{\rm int} = 2\tau_N/(e^{2\xi}+1), \tag{26}$$

while in the classical limit $(S\to\infty)$

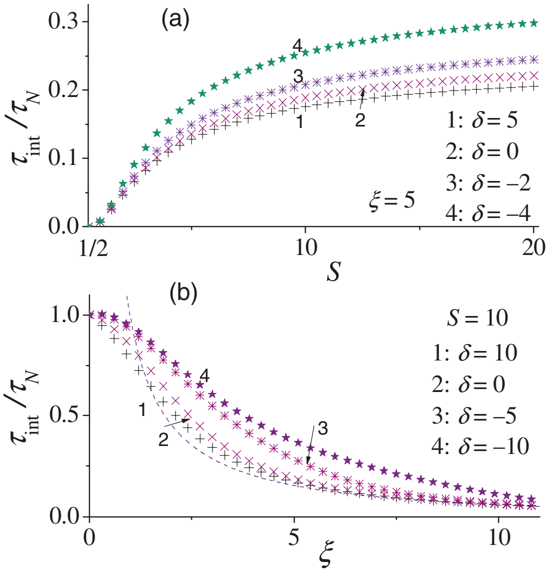

FIG. 2. (Color online) Normalized integral relaxation time $\tau_{\mathrm{int}}/\tau_N$ from Eq. (25) as a function of S (a) and ξ (b) for various values of δ (symbols). Dashed line: Eq. (28).

$$\tau_{\mathrm{int}} = \frac{2\tau_N}{f_1(0)}\int_{-1}^{1}\frac{\phi(z)\psi(z)e^{-\xi z}}{1-z^2}dz, \tag{27}$$

where $\phi(z)=\int_{-1}^{z}[W_{\mathrm{cl}}^{\xi+\delta}(x)-W_{\mathrm{cl}}^{\xi}(x)]dx$, $\psi(z)=\int_{-1}^{z}(\cos z' - \langle P_1\rangle^{\xi})e^{\xi z'}dz'$, $f_1(0)=\langle P_1\rangle^{\xi}-\langle P_1\rangle^{\xi+\delta}$, $\langle P_1\rangle^{\xi}=\coth\xi-1/\xi$, and $W_{\mathrm{cl}}^{\xi}(z)=\xi e^{\xi z}/(2\sinh\xi)$, agreeing entirely with the classical result [59].

Numerical calculations show that both Eqs. (24) and (25) yield exactly the same result. Thus τ_{int} for various nonlinear transient responses (such as the rise, decay, and rapidly reversing field transients) may be easily evaluated from Eq. (25). The normalized relaxation time $\tau_{\mathrm{int}}/\tau_N$ from Eq. (25) is shown in Fig. 2 as a function of S and ξ for various values of δ. The figure indicates that the relaxation time decreases with increasing field strength ξ and, moreover, strongly depends on *both* S and δ. The nonlinear effect comprising accelerated relaxation in the external field also exists for classical dipoles [5,59]. An explanation may be given as follows. In the absence of the field $\mathbf{H}_{\mathrm{II}}$ ($\xi=0$), the relaxation time of the spin is the free diffusion relaxation time τ_N, viz., $\tau_{\mathrm{int}}=\tau_N$. In a strong field ($\xi \gg 1$) and $S \gg 1$, the relaxation time is determined by the damped diffusion of the spin in the field $\mathbf{H}_{\mathrm{II}}$ and the characteristic frequency is now the frequency of the spin oscillation about $\mathbf{H}_{\mathrm{II}}$ (in the vicinity of $z=0$), which is determined by the inverse of the field induced probability current $\sim 2D_1(0)=\xi/\tau_N$ so that $\tau_{\mathrm{int}}\sim\tau_N/\xi$. This asymptotic formula may be used to estimate τ_{int} for $\xi\gg 1$ and $\delta>0$ and $|\delta|\ll\xi$. The influence of the parameter δ, which enters into the integral relaxation time due to the initial distribution function $W_{\mathrm{eq}}^{\xi+\delta}$, is more pronounced for negative values of δ and field strengths $\xi\sim 2-7$ (see Fig. 2). For $\delta\sim-\xi$, a more accurate formula is given by $\tau_{\mathrm{int}}\sim\tau_N/[\xi-1-\xi(\xi+\delta)]$. The enhanced dependence of τ_{int} on δ for negative values of δ can be understood because these cases correspond to rise and rapidly reversing transients, where the initial and final distributions differ considerably. As far as the *spin dependence* of τ_{int} is concerned, τ_{int} substantially depends on S (due to the strong spin dependence of the field induced probability current) and is given for $\xi\gg 1$ and $\delta>0$ and $|\delta|\ll\xi$ (where the δ dependence of the relaxation time may be ignored in the first approximation) by,

$$\tau_{\mathrm{int}} \sim [2D_1(0)]^{-1} = (\tau_N/S)(e^{\xi/S}-1)^{-1}. \tag{28}$$

This asymptote is also shown in Fig. 2 (see also Fig. 3).

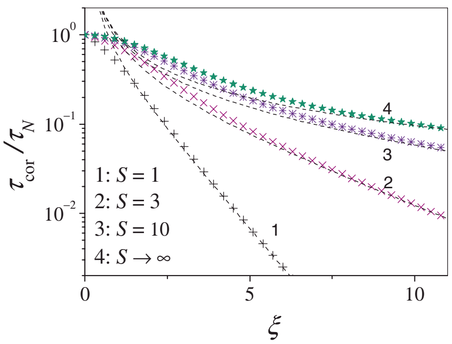

FIG. 3. (Color online) Normalized correlation time $\tau_{\mathrm{cor}}/\tau_N$ from Eq. (32) as a function of ξ for various values of S (symbols). Dashed lines: Eq. (28).

V. LINEAR RESPONSE

We may also evaluate the *linear response* of a spin system to infinitesimally small changes in the magnitude of the dc field, which is of particular interest as the corresponding integral relaxation time becomes the correlation time, which we stress has already been evaluated [55–57] using the spin density matrix. Thus we again suppose that the uniform dc field $\mathbf{H}_{\mathrm{II}}$ is directed along the Z axis of the laboratory coordinate system and that a small probing field $\mathbf{H}_1(\mathbf{H}_1\|\mathbf{H}_{\mathrm{II}})$ having been applied to the assembly of spins in the distant past ($t=-\infty$) so that equilibrium conditions are fulfilled at time $t=0$, is switched off at $t=0$. Here $\delta\to 0$ and $f_1(t)/f_1(0)$ reduces to the normalized longitudinal dipole equilibrium correlation function $C_{\|}(t)$ [61], that is,

$$\lim_{\delta\to 0}\frac{f_1(t)}{f_1(0)} = C_{\|}(t) = \frac{\beta^{-1}}{\chi_{\|}}\int_0^{\beta}\langle\hat{M}_Z(-i\lambda\hbar)\hat{M}_Z(t)\rangle_{\mathrm{eq}}^{\xi}d\lambda, \tag{29}$$

where $\chi_{\|}$ is the static susceptibility defined as

$$\chi_{\|} = \beta^{-1}\int_0^{\beta}\langle\hat{M}_Z(-i\lambda\hbar)\hat{M}_Z(0)\rangle_{\mathrm{eq}}^{\xi}d\lambda = S^2\frac{\partial}{\partial\xi}B_S(\xi) \tag{30}$$

and

$$S^2\frac{\partial}{\partial\xi}B_S(\xi) = \frac{1}{4}\left[\operatorname{csch}^2\left(\frac{\xi}{2S}\right) - (2S+1)^2\operatorname{csch}^2\left(\frac{2S+1}{2S}\xi\right)\right].$$

According to linear response theory (see, e.g., [61]), having determined the one-sided Fourier transform $\tilde{C}_{\|}(\omega)$

$=\int_0^\infty C_\parallel(t)e^{-i\omega t}dt$ [the spectrum of the equilibrium correlation function $C_\parallel(t)$], one may evaluate the dynamic susceptibility $\chi_\parallel(\omega)=\chi'_\parallel(\omega)-i\chi''_\parallel(\omega)$ [61] via

$$\chi_\parallel(\omega)/\chi_\parallel = 1 - i\omega\tilde{C}_\parallel(\omega). \tag{31}$$

In the linear response approximation, the integral relaxation time, that is, the correlation time $\tau_{\mathrm{int}}|_{\delta\to 0}=\tau_{\mathrm{cor}}=\tilde{C}_\parallel(0)$ of $C_\parallel(t)$, follows from Eq. (25) in the limit $\delta\to 0$ and is given by

$$\tau_{\mathrm{cor}} = \frac{(S+1)(S+1/2)}{S\partial B_S(\xi)/\partial\xi}\int_{-1}^{1}\frac{1}{D_2(z)W_{\mathrm{eq}}^{\xi}(z)}\int_{-1}^{z}\frac{\partial}{\partial\xi}W_{\mathrm{eq}}^{\xi}(x)dx \times\int_{-1}^{z}\left(y-\frac{SB_S(\xi)}{S+1}\right)W_{\mathrm{eq}}^{\xi}(y)dydz, \tag{32}$$

where

$$\frac{\partial}{\partial\xi}W_{\mathrm{eq}}^{\xi}(z) = \frac{\mathrm{csch}(\xi/2S) - (2S+1)\mathrm{csch}(\xi+\xi/2S)(\cosh\xi - z\sinh\xi)}{2S[\cosh(\xi/2S)+z\sinh(\xi/2S)]}W_{\mathrm{eq}}^{\xi}(z).$$

For the limiting case $S=1/2$, τ_{cor} is equal to τ_{int} from Eq. (26), while in the limit $S\to\infty$,

$$\tau_{\mathrm{cor}} = \frac{\tau_N\xi\,\mathrm{csch}\,\xi}{1+\xi^{-2}-\coth^2\xi}\int_{-1}^{1}[z-\coth\xi+e^{-\xi(1+z)}(1+\coth\xi)]^2\frac{e^{\xi z}dz}{1-z^2}, \tag{33}$$

agreeing entirely with the classical result ([5], Chap. 7). In the low field limit ($\xi\ll 1$), the correlation time may be approximated as $\tau_{\mathrm{cor}}/\tau_N=1-\xi/(2S)+O(\xi^2)$; in the classical limit $S\to\infty$, one has [5] $\tau_{\mathrm{cor}}/\tau_N=1-\xi^2/9+O(\xi^4)$. As far as the spin and field dependence of τ_{cor} for $\xi\gg 1$ is concerned, a simple asymptotic formula for $\tau_{\mathrm{cor}}=\tau_{\mathrm{int}}|_{\delta\to 0}$ is given by Eq. (28). It varies smoothly from the power law ($\tau_{\mathrm{cor}}\sim\tau_N/\xi$) at $S\to\infty$ to exponential decrease ($\tau_{\mathrm{cor}}\sim 2\tau_N e^{-2\xi}$) at $S=1/2$. The qualitative behavior of $\tau_{\mathrm{cor}}=\tau_{\mathrm{int}}|_{\delta\to 0}$ has been discussed in Sec. IV. The normalized correlation time $\tau_{\mathrm{cor}}/\tau_N$ from Eq. (32) is plotted in Fig. 3 as a function of ξ for various values of S; the asymptotes from Eq. (28) are also shown here for comparison.

We remarked above that the linear response had been studied previously by Garcia-Palacios and Zueco [56] using the spin density matrix approach. They also gave an explicit expression for the linear response integral relaxation time first derived by Garanin [55]. Garanin derived his formula for a more general Hamiltonian than that treated in the present paper, namely, that corresponding to a uniaxial paramagnet in a uniform field $\hat{H}_S=-\hbar\omega_0\hat{S}_Z-D\hat{S}_Z^2$, which is also valid in the limit $D\to 0$, corresponding to the present case and which reads as follows (in our notation):

$$\tau_{\mathrm{cor}} = \frac{2\tau_N}{e^{\xi/S}\chi_\parallel}\sum_{m=-S}^{S-1}\frac{1}{\rho_m l_m^2}\left[\sum_{k=-S}^{m}(M-k)\rho_k\right]^2, \tag{34}$$

where $\rho_n=e^{\xi n/S}/Z_S$, $Z_S=\sum_{m=-S}^{S}e^{\xi m/S}$, $M=\sum_{m=-S}^{S}m\rho_m$, $\chi_\parallel=\sum_{m=-S}^{S}m^2\rho_m-M^2$, $l_m^2=S(S+1)-m(m+1)$, and we have taken a normalizing factor $\sim\tau_N$. Equations (32) and (34) have outwardly different forms; however, calculation shows that both equations yield exactly the same result establishing an essential corollary between the phase-space formulation considered here and the spin density matrix method in the second order of perturbation theory in the spin-bath coupling.

VI. SINGLE-MODE APPROXIMATION

Although the continued fraction solution given above 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 show how the single-mode approximation previously suggested by us to describe the relaxation of a classical spin ([5], Chap. 7), can be generalized to quantum systems. We first recall that the spectrum $\tilde{f}_1(\omega)$ from Eq. (17) on Fourier inversion indicates that the time behavior $f_1(t)$ comprises $2S$ exponentials

$$f_1(t) = f_1(0)\sum_{k=1}^{2S}c_k e^{-\lambda_k t}, \tag{35}$$

where the λ_k are the eigenvalues of the tridiagonal (transition) matrix $\mathbf{A}$ characterizing the dynamics of the system. The matrix elements $A_{q,p}$ of $\mathbf{A}$ are defined as

$$A_{q,p} = \delta_{p,q+1}q_p^- + \delta_{p,q}q_p + \delta_{p,q-1}q_p^+.$$

In the frequency domain, the spectrum $\tilde{f}_1(\omega)$ is thus the series of $2S$ Lorentzians

$$\frac{\tilde{f}_1(\omega)}{f_1(0)} = \sum_{k=1}^{2S}\frac{c_k}{\lambda_k+i\omega}. \tag{36}$$

According to Eq. (36), the finite number of relaxation modes (corresponding to the discrete eigenvalues λ_k) each contribute to the spectrum $\tilde{f}_1(\omega)$. However, as we shall see below, these near-degenerate individual modes are indistinguishable in the spectrum $\tilde{f}_1(\omega)$ appearing merely as a single band. Hence $\tilde{f}_1(\omega)$ may be approximated by the single Lorentzian

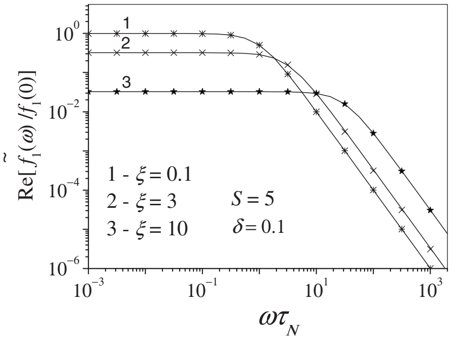

FIG. 4. The real parts of the normalized spectra $\tilde{f}_1(\omega)/f_1(0)$ vs the normalized frequency $\omega\tau_N$ evaluated from the exact continued fraction solution [Eq. (17): solid lines] for $S=5$, $\delta=0.1$, and various values of ξ compared with those calculated from the single Lorentzian approximation Eq. (37) (symbols).

$$\frac{\tilde{f}_1(\omega)}{f_1(0)} \approx \frac{\tau_{\mathrm{int}}}{1 + i\omega\tau_{\mathrm{int}}}, \tag{37}$$

where τ_{int} is given by Eq. (25). In the time domain, the single-mode approximation Eq. (37) amounts to assuming that the relaxation function $f_1(t)$ as determined by Eq. (35) (comprising $2S$ exponentials) may be approximated by a *single* exponential, viz.,

$$f_1(t) = f_1(0)e^{-t/\tau_{\mathrm{int}}}. \tag{38}$$

In order to verify the single-mode approximation we plot in Figs. 4 and 5 the real parts of the normalized spectra $\tilde{f}_1(\omega)/f_1(0)$ calculated from the exact continued fraction solution [Eq. (17)] and the approximate Eq. (37). Thus it is apparent from Figs. 4 and 5 that no practical difference exists between the exact solution and the single-mode approximation [the maximum relative deviation between the corresponding curves does not exceed a few percent]. Similar (or even better) agreement exists for *all* values of S, ξ, and δ. Just as in the classical case ([5], Chap. 7), the single-mode approximation is very accurate because the finite number ($2S$) of relaxation modes are *near degenerate* manifesting themselves merely as a single high-frequency band in the spectrum. Thus they may be effectively approximated by a single mode, i.e., both the linear and nonlinear longitudinal relaxation of the magnetization for all S is accurately described by the Bloch equation (2). We remark that García-Palacios and Zueco [56] have also used the single-mode approximation in the evaluation of the *linear* response of an isotropic spin system. In linear response, Eqs. (37) and (38) can be reformulated for the susceptibility $\chi_\parallel(\omega)$ and correlation function $C_\parallel(t)$ as

$$C_\parallel(t) = e^{-t/\tau_{\mathrm{cor}}} \quad \text{and} \quad \chi_\parallel(\omega) \approx \chi_\parallel/(1 + i\omega\tau_{\mathrm{cor}}).$$

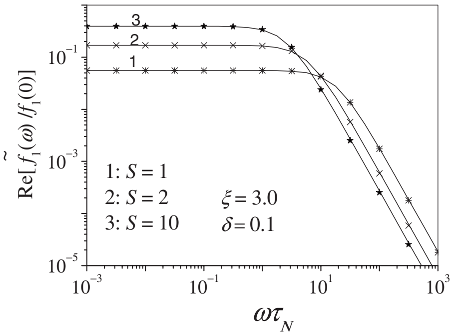

FIG. 5. The real parts of the normalized spectra $\tilde{f}_1(\omega)/f_1(0)$ vs $\omega\tau_N$ evaluated from the exact continued fraction solution [Eq. (17): solid lines] for $\xi=3$, $\delta=0.1$, and various values of S compared with those calculated from the single Lorentzian approximation Eq. (37) (symbols).

VII. CONCLUSIONS

We have treated nonlinear spin relaxation 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 which, in particular limiting cases, e.g., the correlation time Eq. (32), reduces to previously known results obtained using the equation of motion of the density matrix in the second order of perturbation theory in the spin-bath coupling so providing 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 in closed form the dependence of the longitudinal spin relaxation on the spin size S, which is dominated by a single exponential having as time constant the integral relaxation time. Thus a simple description in terms of a Bloch equation holds even for the nonlinear response of a giant spin.

We reiterate that 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 [31], formally represents the quantum mechanics of spins as a statistical theory in the representation space of polar angles (ϑ, φ) (which are now the canonical variables) just as accomplished by Wigner [43] who represented the quantum mechanics of a particle with Hamiltonian $\hat{H}=\hat{p}^2/2m+V(\hat{x})$ as a statistical theory in phase space with the canonical variables (x,p). Stratonovich [31] proceeded by introducing a quasiprobability density (Wigner) function on the sphere, defined as the linear invertible bijective map onto the representation space comprised of the trace of the product of the system density matrix and the irreducible tensor operators having matrix elements in the spherical basis representation given by the Clebsch-Gordan coefficients (see Appendix A). Hence the average value of a quantum spin operator may be calculated just as the corresponding classical function. Moreover, for a general (nonaxially symmetric) Hamiltonian the evolution equation for the quasiprobability density function of the closed system proposed by Stratonovich may be expanded for large spins $S \gg 1$ [39] in powers of the small parameter $\varepsilon \sim S^{-1}$ with the term linear in ε being the same as the classical Liouville equation (analogous to the result for particles), the next term being $O(\varepsilon^2)$ and so on. Thus the Stratonovich representation for spins [31], just as the well-known Wigner representation for particles [43], is well suited to the development of semiclassical methods of solution allowing one to obtain quantum corrections in a manner closely analogous to the classical case (see, e.g., [5], Chap. 7).

Thus one may conclude for spins (just as for particles) that the existing solution methods (matrix continued fractions which can be evaluated by iterating a simple algorithm, integral representation of relaxation times, etc.) seamlessly carry over to the quantum case indeed suggesting new closed form quantum results via the corresponding classical ones; for example, the quantum integral relaxation time, Eq. (25) above. We have illustrated the phase-space method by considering the simplest possible problem, namely, the longitudinal relaxation of an arbitrary 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 like manner using Eq. (4) just as in the classical case [5]). We remark that longitudinal relaxation in a uniform field is the simplest example of the phase method for spins as it is the rotational analog of the translational harmonic oscillator in the weak coupling limit considered by Agarwal [50] so that the quasiprobability density diffusion equation has the Fokker-Planck form for all S, hence perturbation theory is not required. This would not be true in general, e.g., for relaxation in nonaxially symmetric magnetocrystalline anisotropy and external field potentials, which invariably comprise two or more potential wells. Here perturbation theory in the small parameter $\varepsilon \sim S^{-1}$ is required in the evolution equation for the Wigner function (which unlike axially symmetric problems involves the conservative or Liouville term) just as perturbation theory in $\hbar^2$ is required in the corresponding quantum translational Brownian motion in an arbitrary potential $V(\hat{x})$. Nevertheless our simple isotropic spin problem demonstrates clearly how one may calculate, using the phase-space method, the influence of spin size (in the weak bath spin coupling limit) on the relaxation behavior.

ACKNOWLEDGMENT

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APPENDIX A: PHASE-SPACE DESCRIPTION OF SPIN SYSTEMS

To provide a phase-space description of spin systems, Stratonovich in 1956 [31] introduced the quasiprobability (Wigner) distribution function on the sphere. Alternative quasiprobability distribution functions for spins have also been proposed and discussed, e.g., in Refs. [32–40] using the spin coherent-state representation. Moreover, Várilly and Gracia-Bondía [33] have shown that the spin coherent-state approach is equivalent to the Stratonovich formalism (see also [39,40]). The Wigner quasiprobability distribution function on the surface of the unit sphere for a spin system given by Stratonovich [31] is defined by the invertible map [39]

$$W_\sigma(\vartheta,\varphi,t)=\mathrm{Tr}\{\hat{\rho}\hat{w}_\sigma(\vartheta,\varphi)\}, \tag{A1}$$

where σ parametrizes quasiprobability functions of spins belonging to the SU(2) dynamical symmetry group, $\hat{\rho}$ is the system density matrix, and $\hat{w}_\sigma(\vartheta,\varphi)$ is the Wigner-Stratonovich operator or kernel of the bijective transformation given by Eq. (A1) defined as

$$\hat{w}_\sigma(\vartheta,\varphi)=\sqrt{\frac{4\pi}{2S+1}}\sum_{L=0}^{2S}\sum_{M=-L}^{L}(C^{S,S}_{S,S,L,0})^{-\sigma}Y^{*}_{L,M}(\vartheta,\varphi)\hat{T}^{(S)}_{L,M}, \tag{A2}$$

such that $\mathrm{Tr}\{\hat{w}_\sigma(\vartheta,\varphi)\}=1$ and $\frac{2S+1}{4\pi}\int_{\theta,\varphi}\hat{w}_\sigma(\vartheta,\varphi)\sin\vartheta\, d\vartheta\, d\varphi=\hat{I}$. Here $\hat{I}$ is the identity matrix, $Y_{L,M}(\vartheta,\varphi)$ are the spherical harmonics [62], and the $\hat{T}^{(S)}_{L,M}$ are the irreducible tensor (polarization) operators with matrix elements given by [62]

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

$-S\leqslant m,m'\leqslant S-L<M<L$, $0\leqslant L\leqslant 2S$, and $C^{S,S}_{S,S,L,0}$ and $C^{S,m'}_{S,m,L,M}$ are the Clebsch-Gordan coefficients [62]. The density matrix $\hat{\rho}$ may then be expressed using the kernel Eq. (A2) as [39]

$$\hat{\rho}=\frac{2S+1}{4\pi}\int_{\theta,\varphi}\hat{w}_\sigma(\vartheta,\varphi)W^{-\sigma}(\vartheta,\varphi,t)\sin\vartheta\, d\vartheta\, d\varphi. \tag{A3}$$

Knowledge of the function $W^{-\sigma}(\vartheta,\varphi,t)$ now allows one to calculate the average value of an arbitrary spin operator $\hat{A}$ in the same way as the corresponding function for translational motion [39] because the $W^{-\sigma}(\vartheta,\varphi,t)$ provide the overlap relation

$$\langle\hat{A}\rangle=\mathrm{Tr}\{\hat{\rho}\hat{A}\}=\frac{2S+1}{4\pi}\int_{\theta,\varphi}A^{\sigma}(\vartheta,\varphi)W^{-\sigma}(\vartheta,\varphi,t)\sin\vartheta\, d\vartheta\, d\varphi, \tag{A4}$$

where $A^{\sigma}(\vartheta,\varphi)$ is the Weyl symbol of the operator $\hat{A}$ (see, e.g., [44]) defined as

$$A^{\sigma}(\vartheta,\varphi)=\mathrm{Tr}\{\hat{A}\hat{w}_\sigma(\vartheta,\varphi)\}. \tag{A5}$$

As an example, we evaluate $A^{\sigma}(\vartheta,\varphi)$ for the operator $\hat{S}_Z$. Noting Eqs. (A2) and (A5) and known relations $\hat{S}_Z=\sqrt{S(S+1)(2S+1)/3}\hat{T}^{(S)}_{1,0}$ and $\mathrm{Tr}\{\hat{T}^{(S)}_{L_1,M_1}\hat{T}^{(S)}_{L_2,M_2}\}=(-1)^{M_1}\delta_{L_1,L_2}\delta_{M_1,-M_2}$ [62], we obtain

$$\begin{aligned}S^{\sigma}_{Z}(\vartheta,\varphi)&=\mathrm{Tr}\{\hat{S}_Z\hat{w}_\sigma(\vartheta,\varphi)\}\\&=(C^{S,S}_{S,S,1,0})^{-\sigma}\sqrt{4\pi S(S+1)/3}Y^{*}_{1,0}(\vartheta,\varphi)\\&=S^{(1-\sigma)/2}(S+1)^{(1+\sigma)/2}\cos\vartheta.\end{aligned}$$

In particular, for $\sigma=1$ we have $S^{1}_{Z}(\vartheta,\varphi)=(S+1)\cos\vartheta$. Furthermore, at equilibrium, the phase-space distribution $W_{\mathrm{eq}}(\vartheta)=W^{-1}_{\mathrm{eq}}(\vartheta)$ from Eq. (5) corresponds to the equilibrium density matrix

$$\hat{\rho}_{\mathrm{eq}} = e^{\beta\hbar\omega_0 \hat{S}_Z}/Z_S, \tag{A6}$$

and vice versa. For $S=1/2$, this can readily be demonstrated by analytically substituting into Eqs. (A1)–(A3) and (A6) the known representation of the matrix exponential $e^{\alpha\hat{S}_Z}$ in terms of the irreducible tensor operators $\hat{T}^{(S)}_{L,M}$ ([62], Secs. 2.5 and 2.6), viz.,

$$e^{\alpha\hat{S}_Z} = \sqrt{2}[\hat{T}^{(1/2)}_{0,0}\cosh(\alpha/2) + \hat{T}^{(1/2)}_{1,0}\sinh(\alpha/2)].$$

Thus one obtains after some algebra [cf. Eq. (5)]

$$W^{-1}_{\mathrm{eq}}(\vartheta) = \left[\cosh\left(\frac{1}{2}\beta\hbar\omega_0\right) + \sinh\left(\frac{1}{2}\beta\hbar\omega_0\right)\cos\vartheta\right] \Big/ Z_{1/2}.$$

In the present paper, we consider $W^{-1}(\vartheta,t)$ only [corresponding to Eq. (4)]; thus we omit in all equations the superscript -1 in $W^{-1}(\vartheta,t)$ and $W^{-1}_{\mathrm{eq}}(\vartheta)$.

APPENDIX B: DERIVATION OF $D^{(1)}(z)$ AND $D^{(2)}(z)$

Knowing the functional form of the master equation (8) for the spin, the next crucial step is to determine the drift and diffusion coefficients $D^{(1)}(z)$ and $D^{(2)}(z)$. Hitherto calculations of $D^{(1)}(z)$ and $D^{(2)}(z)$ for a quantum spin subjected to a dc magnetic field $\mathbf{H}_0$ have been undertaken in Refs. [30,42] by starting from the master equation for the density matrix $\hat{\rho}$. Undoubtedly, many methods of determining these coefficients exist. Among a wide variety of options for determining $D^{(1)}(z)$ and $D^{(2)}(z)$, we shall select here the extension to the semiclassical case of a simple heuristic idea originally used by Einstein, Smoluchowski, Langevin, and Kramers in order to calculate drift and diffusion coefficients in the classical theory of the Brownian motion. Recently, we have applied this approach for the quantum translational Brownian motion [46,48].

In order to determine the explicit form of $D^{(1)}(z)$ and $D^{(2)}(z)$ in Eq. (8), we first recall that the equilibrium distribution $W_{\mathrm{eq}}(z)$ from Eq. (13) must be the equilibrium solution of the generic master equation (8), i.e., it must satisfy

$$\frac{\partial}{\partial z}\left(D^{(2)}(z)\frac{\partial}{\partial z}W_{\mathrm{eq}}(z) - D^{(1)}(z)W_{\mathrm{eq}}(z)\right) = 0. \tag{B1}$$

One may seek a solution for $D^{(1)}(z)$ and $D^{(2)}(z)$ in the form

$$D^{(1)}(z) = (1-z^2)[a_0^S + a_1^S z + a_2^S z^2 + \cdots], \tag{B2}$$

$$D^{(2)}(z) = (1-z^2)[b_0^S + b_1^S z + b_2^S z^2 + \cdots]. \tag{B3}$$

By substituting Eqs. (B2) and (B3) into Eq. (B1), one then finds if $W_{\mathrm{eq}}(z)$ from Eq. (13) is a solution of Eq. (B1), that only the coefficients a_0^S, b_0^S, and b_1^S are nonzero and $D^{(1)}(z)$ and $D^{(2)}(z)$ are given by

$$D^{(1)}(z) = 2Sb_0^S(1-z^2)\tanh\frac{\xi}{2S}$$

and

$$D^{(2)}(z) = b_0^S(1-z^2)\left[1 + z\tanh\frac{\xi}{2S}\right].$$

In order to define the normalizing coefficient b_0^S one can use the fluctuation-dissipation theorem [30] and the additional condition that in the classical limit ($\beta\to 0$, $S\to\infty$, and $\beta S\to$const), the drift and diffusion coefficients $D^{(1)}(z)$ and $D^{(2)}(z)$ must reduce to their classical counterparts for the rotational Brownian motion of a classical spin [5,18,19,30]

$$D^{(1)}(z) \to \xi(1-z^2)/2\tau_N \quad \text{and } D^{(2)}(z) \to (1-z^2)/2\tau_N,$$

so that $b_0^S=(e^{\xi/S}+1)/(4\tau_N)$ and $D^{(1)}(z)$ and $D^{(2)}(z)$ are given by Eqs. (9) and (10). In the derivation of $D^{(1)}(z)$ and $D^{(2)}(z)$ we have imposed the stationary solution of the master equation as the distribution $W_{\mathrm{eq}}(z)$, Eq. (5), corresponding to the equilibrium density matrix $\hat{\rho}_{\mathrm{eq}}$ given by Eq. (A6), which describes the system in thermal equilibrium without coupling to the thermal bath. It is known from the theory of quantum open systems [63], that the equilibrium state, in general, may deviate from the canonical distribution $\hat{\rho}_{\mathrm{eq}}$; the latter describes the thermal equilibrium of the system in the weak coupling and high temperature limits only. A detailed discussion of this problem is given, e.g., by Geva *et al.* [64]. The imposition of the phase-space distribution $W_{\mathrm{eq}}(z)$ as the equilibrium solution of Eq. (B1) so yielding $D^{(1)}(z)$ and $D^{(2)}(z)$, appears to be the exact analog of the *ansatz* used by Gross and Lebowitz [65] in their formulation of quantum kinetic models of impulsive collisions. According to [65], for a system with a time dependent Hamiltonian $\hat{H}$, the equation governing the time behavior of the density matrix $\hat{\rho}$ is Eq. (3), where the collision kernel operator $\hat{Q}$ satisfies the condition $\hat{Q}(\hat{\rho}_{\mathrm{eq}})=0$. Equation (B1) is entirely analogous to this condition. The condition $\hat{Q}(\hat{\rho}_{\mathrm{eq}})=0$ has also been used by Redfield [11] in the calculation of the matrix elements of the relaxation operator $\hat{Q}$ in the context of his theory of relaxation processes.

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