Dynamical theory of spin relaxation

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The dynamics of a spin system is usually calculated using the density matrix. However, the usual formulation in terms of the density matrix predicts that the signal will decay to zero, and does not address the issue of individual spin dynamics. Using stochastic calculus, we develop a dynamical theory of spin relaxation, the origins of which lie in the component spin fluctuations. This entails consideration of random pure states for individual protons, and how these pure states are correctly combined when the density matrix is formulated. Both the lattice and the spins are treated quantum mechanically. Such treatment incorporates both the processes of spin-spin and (finite temperature) spin-lattice relaxation. Our results reveal the intimate connections between spin noise and conventional spin relaxation.

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I. INTRODUCTION

The dynamics of a spin system is usually calculated using the density matrix, following Abragam [1], for instance. However, the usual formulation in terms of the density matrix predicts that the signal will decay exponentially to zero, and does not address the issue of spin dynamics from the point of view of an individual proton in the spin population. In this article, we draw on related mathematical ideas in the theory of electromagnetic scattering from random media [2] and apply the modern methods of stochastic calculus in combination with a detailed quantum mechanical description to develop a dynamical theory of spin relaxation, the origins of which lie in the fluctuations and dynamics of individual spins.

Our approach entails consideration of random pure states for individual protons, and how these pure states are correctly combined when the density matrix is formulated. Both the lattice and the spins are treated quantum mechanically. Such treatment incorporates both the processes of spin-spin and (finite temperature) spin-lattice relaxation. In our conceptual framework, the stochastic dynamics of a single spin, existing in a random pure state, is the primary object of consideration. The dynamics of each individual spin can be considered as a stochastic trajectory on the Bloch sphere. There is no violation of quantum mechanical unitarity in this picture, in which individual pure states evolve into random pure states. This dynamics is a spin noise process, from which an asymptotic probability distribution for an individual spin can be constructed. The existence of this asymptotic distribution rests alongside individual (proton) spin fluctuations that persist for all time. When referred to an ensemble, such distribution represents the spin population density in a steady state. In this framework, it is the autocorrelation properties of the dynamics of a single spin that are the origin of the standard spin relaxation parameters which pertain to an ensemble. Thus, the spin noise process is intimately related to the dephasing and other phenomena associated with conventional spin relaxation. Accordingly, we retain the raw, as opposed to ensemble averaged, density matrix which is constructed in terms of the probability-weighted sum of projection operators corresponding to the constituent pure states of the system.

A semiclassical treatment entails that the magnetic field fluctuations be treated classically and there be no interactions with the lattice; in effect, the lattice is absent (or equivalently considered to be at infinite temperature). Our analysis entails that the lattice also be treated quantum mechanically. Indeed, as Abragam [1] points out, a semiclassical description (where the coupling with the lattice is represented by classical random magnetic field fluctuations) leads to a steady state for the spin system described by an infinite temperature, i.e., one for which there is no Boltzmann fraction. Such a quantum mechanical treatment incorporates both the processes of spin-spin and (finite temperature) spin-lattice relaxation. A quantum mechanical treatment of the lattice modifies the equation of motion for the density matrix via an offset by the statistical equilibrium value. The (stochastic differential) equation of motion for the ensemble density matrix is accordingly modified. The effect of the lattice, in the presence of isotropic fluctuations, is to induce a polar drift which yields the desired Boltzmann fraction, and the process of $T1$ relaxation.

The paper is organized as follows. Section II introduces the quantum mechanical density matrix in geometric terms and the related notion of a (random) pure state. The significance of these quantities is explained in the context of NMR for an ensemble of spins with various examples. In Sec. III, we apply spinor geometry to develop the (stochastic) spin dynamics for an ensemble immersed in a random magnetic field environment such as encountered in NMR. A detailed account is provided of both the cases of axial and isotropic fluctuations and the resulting dynamics of a certain modified spin density, that scales with the square root of the spin population, is calculated explicitly. When coupled to thermal degrees of freedom (the "lattice"), the stochastic dynamics is also derived. The central result of the paper is a stochastic differential equation for the combined processes of spin-spin

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and spin-lattice relaxation in terms of the modified spin density. It is shown that, when an ensemble average is effected, the ordinary (deterministic) equations of spin-spin and spin-lattice relaxation are recovered and have the desired properties familiar from standard theory of NMR. With regard to quantum mechanical unitarity, we demonstrate that random pure states evolve into themselves under stochastic evolution, and explain the role of the lattice in this respect. The paper concludes in Sec. IV with a discussion of related issues in quantum foundations and experimental implications in NMR.

II. GEOMETRY OF THE NMR DENSITY MATRIX

Our analysis of spin dynamics will be expressed in relation to the concept of the quantum mechanical density matrix, which is the basic tool for describing dynamics of NMR. To set our results in the appropriate geometric context, we review here the essential features of the density matrix and extend these in geometrical terms (cf. [2]). Recall the following general expression for the quantum mechanical density matrix:

$$\hat{\sigma} = \sum_i p_i |\alpha_i\rangle\langle\alpha_i|, \tag{1}$$

where we assume $|\alpha_i\rangle$ are normalized, $\langle\alpha_i|\alpha_i\rangle = 1$. Thus, the density matrix arises as the probability-weighted sum of projection operators $\hat{\Pi}_i = |\alpha_i\rangle\langle\alpha_i|$ onto the state vectors $|\alpha_i\rangle$. On grounds of probability, we impose the unit trace condition $\mathrm{tr}[\hat{\sigma}] = 1$, which is equivalent to $\sum_i p_i \equiv 1$. In terms of the quantum statistical ensemble, we can interpret the density matrix as representing a system consisting of a large ensemble of states $|\alpha_i\rangle$ constituted in respective proportion p_i. Thus, p_i is equal to the classical probability that a state, drawn from the ensemble at random, is equal to $|\alpha_i\rangle$. Each component basis vector $|\alpha_i\rangle$ represents a "pure" quantum state and we shall consider a single proton as existing in such a (possibly unknown and random) state, obtained, e.g., by making a spin measurement and then allowing the state to undergo unitary evolution with a known Hamiltonian. Thus, pure states correspond to projection operators in the density matrix formalism. It is essential to appreciate in the present context of spin populations that the above resolution applies even if $\{|\alpha_i\rangle\}$ constitute a nonorthogonal (and possibly over-complete) basis set, i.e., $\langle\alpha_i|\alpha_j\rangle \neq 0$ for $i \neq j$. In the case of a spin-$\frac{1}{2}$ system with a two-dimensional basis $\{|\alpha\rangle,|\beta\rangle\}$, we can express the density matrix as

$$\hat{\sigma} = p_\alpha|\alpha\rangle\langle\alpha| + p_\beta|\beta\rangle\langle\beta|, \tag{2}$$

in which $p_\alpha + p_\beta = 1$.

Suppose a spin measurement is made in the z direction, e.g., by placing the system in a magnetic field aligned with the z axis. The eigenstates of the Hamiltonian are then the orthogonal states spin "up" and "down" ($|\uparrow\rangle$ and $|\downarrow\rangle$), respectively. According to classical probability laws applied to the ensemble $\mathbf{P}[A] \equiv \mathbf{P}[A|B]\mathbf{P}[B] + \mathbf{P}[A|\bar{B}]\mathbf{P}[\bar{B}]$ and quantum probability rules applied to the transition between a pair of pure states $\mathbf{P}[A|B] = |\langle\psi_A|\psi_B\rangle|^2$ (which is symmetric under $A \leftrightarrow B$), the probability of the outcome spin $\uparrow$ is given by

$$\mathbf{P}[\uparrow] = |\langle\uparrow|\alpha\rangle|^2 p_\alpha + |\langle\uparrow|\beta\rangle|^2 p_\beta. \tag{3}$$

In the quantum mechanical formalism, this can be conveniently expressed as

$$\mathbf{P}[\uparrow] = \langle\uparrow|\hat{\sigma}|\uparrow\rangle = \mathrm{tr}[\hat{\sigma}\,\hat{\Pi}_\uparrow]. \tag{4}$$

Corresponding expressions hold in the higher dimensional case for arbitrary states. Indeed, through the same type of reasoning, the expectation of any observable $\hat{O}$ is given by

$$\langle\hat{O}\rangle = \sum_\alpha \langle\alpha_i|\hat{O}|\alpha_i\rangle p_\alpha = \mathrm{tr}[\hat{\sigma}\,\hat{O}], \tag{5}$$

where, as before, the basis $\{|\alpha_i\rangle\}$ need not be orthogonal. The relation between classical (ensemble) and quantum probabilities can be illustrated further, in the context of the density matrix. Suppose $|\alpha\rangle,|\beta\rangle$ are equal to $|\uparrow\rangle,|\downarrow\rangle$, respectively, then $\mathbf{P}[\uparrow] = p_\alpha$ and $\mathbf{P}[\downarrow] = p_\beta$. It is important to appreciate that there is not such an immediate translation from the classical to quantum probabilities, in general. For example, if $|\alpha\rangle = |\uparrow\rangle$ and $|\beta\rangle \neq |\downarrow\rangle$, then

$$\mathbf{P}[\uparrow] = p_\alpha + |\langle\uparrow|\beta\rangle|^2 p_\beta \tag{6}$$

so $\mathbf{P}[\uparrow] \neq p_\alpha$ (unless $p_\beta = 0$, in which case $p_\alpha = 1$, a system of identically prepared spins in the positive z direction). Indeed, the formalism illustrates that some considerable care is needed in the passage between quantum and classical probabilities. For example, if a quantum ensemble is prepared as a classical mixture of (only) pure states $|\alpha\rangle,|\beta\rangle$ (i.e., a randomized collection of particles in either of these pure states mixed in the proportion $p_\alpha : p_\beta$) then we find, according to (4),

$$\mathbf{P}[\alpha] + \mathbf{P}[\beta] = 1 + |\langle\alpha|\beta\rangle|^2, \tag{7}$$

which exceeds unity for any pair of nonorthogonal states. The resolution of this apparent inconsistency is that quantum observables yield only orthogonal eigenbases as measurement outcomes.

A natural and pertinent question to consider at this stage is how many ways there are of representing a given density matrix in terms of pure states, according to (1). We confine our attention here to the case of spin-$\frac{1}{2}$ since we are concerned with protons in NMR, and in this case the geometry is particularly simple and illuminating. It is sufficient to consider a two-dimensional basis $\{|\alpha\rangle,|\beta\rangle\}$, as introduced above. We can choose to represent a given density matrix by a point P in the interior of the Bloch sphere S (see Fig. 1). Its resolution among Π_α is determined by passing a line L through P and finding its intersection with S, say at points A and B corresponding to the basis elements $|\alpha\rangle$ and $|\beta\rangle$. Thus, points on the surface of the sphere S represent pure states. The ensemble probabilities are then determined by the ratio of the distances d_{PA} and d_{PB} from P to A and P to B, respectively, according to

$$p_\alpha : p_\beta = d_{PB} : d_{PA}. \tag{8}$$

Therefore, as P approaches A, the density matrix approaches Π_α, which renders the system an ensemble of identical pure states $|\alpha\rangle$. Now, for points P that do not lie on S, this resolution is nonunique. Indeed, there exist infinitely many bases $\{|\alpha\rangle,|\beta\rangle\}$ that resolve a given density matrix, realized in the geometry by rotating the line L about the point P. Uniqueness is only obtained if we confine ourselves to an orthogonal basis by constructing L as the line joining P to the

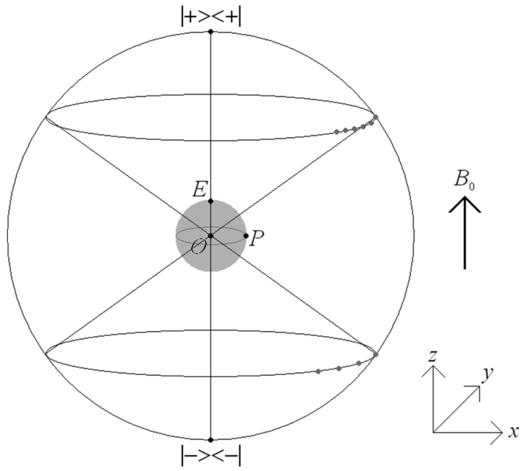

FIG. 1. Bloch sphere depicting the "NMR ball" of radius $\varepsilon = |2p - 1|$ where ε, p are given by Eqs. (10) and (85), respectively, and typically $\varepsilon \ll 1$, $p \approx \frac{1}{2}$.

center O of the interior of S (provided that $P \neq O$). Then, the points A and B are antipodal and $\langle \alpha \mid \beta \rangle = 0$. In the case that $P = O$, there exist infinitely many resolutions, all of which are orthogonal; the ensemble average then contains no "quantum information." It is a straightforward exercise to show that this metric geometry is statistically consistent under changes of basis. In other words, if we represent a given ensemble by P and determine the coefficients of a change of basis according to the metrical relation (8), then the quantum probabilities obtained via (4) are identical in the two bases. This geometry provides an illustrative tool for our discussion of NMR spin noise, which enables its key features to be readily interpreted. In the context of the density matrix geometry, NMR phenomena can be viewed as taking place within a small solid ball B_ε of radius ε (shaded in Fig. 1) centered at the origin of the interior of the sphere S. The size of the radius $\varepsilon \ll 1$ results from the value of the "Boltzmann fraction" which, according to statistical mechanics, is given by

$$N_{\text{upper}}/N_{\text{lower}} = \exp(-\Delta E/kT) > 1, \tag{9}$$

where k is Boltzmann's constant, T is the temperature, and N_{upper} / N_{lower} are the number of spins in the upper and lower half cones, respectively. This ratio exceeds, but is approximately equal to, unity in typical experimental situations. Thus, according to (8) we have

$$0 < \varepsilon = \frac{\exp(-\Delta E/kT) - 1}{\exp(-\Delta E/kT) + 1} \ll 1 \tag{10}$$

(see, e.g., [1]). The distance ε scales proportionately with the radius of the sphere, which here we have set equal to unity. The figure illustrates the semiclassical geometry of the density matrix for a spin-$\frac{1}{2}$ system in NMR. In this picture, the pure (proton) states are distributed over the intersections of the double cone with the sphere of pure states S. The angle θ of the double cone is determined by the spin quantum number j according to $\cos^2\theta = j^2/j(j+1)$ and so in the case of protons, for which $j = \frac{1}{2}$, we have $\cos\theta = 1/\sqrt{3}$ and so $\theta \approx 54.7^\circ$. As the spin quantum number tends to infinity, the angle of this cone tends to zero, which can be considered as the "classical limit" of this quantum geometry. In a fully quantum mechanical framework, as we shall develop in the sections that follow, the pure states are situated over the *entire* surface S with a certain distribution that conforms to the Boltzmann fraction mentioned above. We emphasize that the density matrix description is valid for quantum statistical ensembles of pure states that are nonorthogonal. Although this feature is understood within the foundations of quantum mechanics, it is not generally appreciated in the context of NMR. Our discussion of spin noise in NMR requires that we consider such ensembles, which arise asymptotically through the acquisition of a uniform phase distribution in the transverse magnetization, for a large number of pure states (proton spins). As an illustration, we recall the situation familiar in a pulsed NMR experiment. Let us assume that a rf pulse is applied at a pulse flip angle of 90° to the longitudinal B_0 direction. As a result, rf energy ΔE is absorbed, and the net local magnetization is rotated into the transverse plane. Each component spin vector then rotates about the longitudinal axis at (approximately) the Larmor precession frequency ω_0 governed by the relations $\Delta E = \hbar\omega_0 = h\gamma B_0/2\pi$, where γ is the gyromagnetic ratio (which varies throughout space depending on the details of the molecular environment). The resulting motion of the net local magnetization vector E_t can be understood by analogy with the Eulerian top in classical mechanics. As time progresses following the pulse, energy is transferred from the proton spins to the surroundings during the process of "spin-lattice" relaxation, and the longitudinal component of the net magnetization is gradually restored to the equilibrium value prior to the pulse being applied. Likewise, random exchange of energy between neighboring spins and small inhomogeneities in the total magnetic field cause perturbations in the phases of the transverse spin components and dephasing occurs, so that the net transverse component of magnetization decays to zero. Now, the situation of this experiment can be readily interpreted in the context of the geometry of the density matrix. At equilibrium, the density matrix can be conveniently represented in the $\{|\uparrow\rangle,|\downarrow\rangle\}$ basis according to (2) with $p_{\uparrow,\downarrow}$ determined by the Boltzmann fraction. However, following the 90° pulse, such a resolution among the projection operators for these orthogonal basis elements is no longer possible, as the geometry illustrates. In the $\{|\uparrow\rangle,|\downarrow\rangle\}$ basis, the density matrix now has nonzero components proportional to $|\uparrow\rangle\langle\downarrow|$ and $|\downarrow\rangle\langle\uparrow|$. Thus, the nonequilibrium character of NMR experiments involving radiation is represented in terms of off-diagonal elements in the density matrix or, alternatively, in terms of a resolution amongst projection operators in a basis that is not aligned to the background magnetic field; the coefficients of such are supplied by the metrical geometry. (It is a matter of convenience in terms of the calculations involved as to which basis is chosen.) At equilibrium (before a pulse is applied), the density matrix lies at the point E, which can be considered as arising from a uniform distribution of spins represented as points on the intersections of the upper and lower half cones with S. As indicated in the figure, the distribution is more concentrated on the upper cone which has lower energy, and thus the average of these pure spin states results in the point E situated above the origin O. After a 90° pulse is applied, the density matrix rotates to the transverse plane; correspondingly, the entire double cone rotates through the same angle about the positive y axis. The result is that the original density matrix is rotated to the point P shown. As explained above, the pure states are those situated on the Bloch sphere (i.e., the two-dimensional surface of the sphere); the spherical geometry results from the fact that we are concerned with a collection of protons, which have spin-$\frac{1}{2}$. The density matrix description is thus a convenient way of representing statistical ensembles of large numbers of quantum states and their average properties. Physically, the nonuniqueness described above suggests that the density matrix description is an incomplete one, at least on a microscopic scale. Our analysis that follows will demonstrate this incompleteness, and remedy the situation by providing a detailed description in terms of the dynamical properties of the constituent underlying pure states of the system. The process of ensemble averaging will necessarily recover the ordinary density matrix description, and we shall see how this arises explicitly.

III. SPIN DYNAMICS

A. Spinor geometry

We begin with an exposition of the spinor geometry of a spin-$\frac{1}{2}$ system. In homogeneous coordinates (ξ,η), we write a spin state vector as

$$|\psi\rangle = \xi|\uparrow\rangle + \eta|\downarrow\rangle, \tag{11}$$

which maps to the normalized state vector

$$|\psi\rangle = (\zeta|\uparrow\rangle + |\downarrow\rangle)/\sqrt{1+|\zeta|^2}, \quad \langle\psi|\psi\rangle = 1 \tag{12}$$

in which $\zeta = \xi/\eta$ is the familiar (inhomogeneous) stereographic coordinate for the Bloch sphere, and satisfies

$$\zeta_t = e^{i\phi_t}\cot\tfrac{1}{2}\theta_t \tag{13}$$

in polar coordinates (θ,ϕ). The projection operator onto this pure state vector is thus

$$\begin{aligned}|\psi\rangle\langle\psi| = \frac{1}{1+|\zeta|^2}[\zeta\zeta|\uparrow\rangle\langle\uparrow| + \zeta|\uparrow\rangle\langle\downarrow| \\ + \zeta^*|\downarrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|],\end{aligned} \tag{14}$$

which in density matrix form is

$$\sigma = \frac{1}{1+|\zeta|^2}\begin{pmatrix}\zeta\zeta^* & \zeta \\ \zeta^* & 1\end{pmatrix} \tag{15}$$

and in polar form

$$\sigma = \frac{1}{2}\begin{pmatrix}1+\cos\theta & e^{i\phi}\sin\theta \\ e^{-i\phi}\sin\theta & 1-\cos\theta\end{pmatrix}. \tag{16}$$

For an ensemble, we introduce the modified spin density

$$\Sigma = \frac{1}{N^{1/2}}\sum_{j=1}^{N}\sigma^{(j)}, \tag{17}$$

which differs from the standard density matrix in respect of the reciprocal scaling by the *square root* of the spin population, as opposed to the population itself [cf. (1)]. For single pure states and ensembles, respectively, in relation to (17), we shall write

$$\sigma_t = \begin{pmatrix}\sigma_t^{\uparrow\uparrow} & \sigma_t^{\uparrow\downarrow} \\ \sigma_t^{\downarrow\uparrow} & \sigma_t^{\downarrow\downarrow}\end{pmatrix}, \quad \Sigma_t = \begin{pmatrix}\Sigma_t^{\uparrow\uparrow} & \Sigma_t^{\uparrow\downarrow} \\ \Sigma_t^{\downarrow\uparrow} & \Sigma_t^{\downarrow\downarrow}\end{pmatrix}. \tag{18}$$

B. Random Hamiltonian

The unperturbed Hamiltonian is given by $H_0 = -\mu\cdot\mathbf{B}_0$ (taking due note of the minus sign) where the magnetic moment is $\mu = \gamma\mathbf{s}$ (γ is the gyromagnetic ratio) for spin $\mathbf{s} = \frac{1}{2}\hbar\sigma$ in which $(\sigma_x,\sigma_y,\sigma_z)$ are the Pauli matrices. In matrix notation, then we have

$$H_0 = \begin{pmatrix}E & 0 \\ 0 & -E\end{pmatrix}. \tag{19}$$

This implies a negative energy eigenvalue $E<0$ for $\mathbf{B}_0$ in the positive z direction and thus the spins tend to align *parallel* to the magnetic field [cf. (83) and the discussion of Sec. III E]. In what follows, we shall consider a time-dependent random perturbed Hamiltonian

$$H(t) = H_0 + H_1(t) = -\gamma\mathbf{s}\cdot\mathbf{B}(t) \tag{20}$$

in which $\mathbf{B}(t)$ is the effective random magnetic field environment experienced by an individual (proton) spin. This consists of the main field $\mathbf{B}_0$ plus a (rapidly) fluctuating field $\mathbf{B}_1(t)$ corresponding to the rapid (rotational) motion of the spin (nucleus) in its magnetic environment. We shall not be concerned with the specific interaction, e.g., dipole-dipole, chemical shielding, quadrupolar, that gives rise to the effective field fluctuations, and concentrate on the cases of axial and isotropic fluctuations in the "extreme narrowing" approximation where the autocorrelation time for $\mathbf{B}_1(t)$ is extremely small.

C. Axial fluctuations

Consider a transverse magnetization subject to magnetic field fluctuations in the axial z direction. According to the spinor geometry introduced above, the normalized transverse state vector, at an azimuth angle ϕ, can be expressed in terms of the spin $\uparrow$, $\downarrow$ state vectors by

$$|\rightarrow^{(\phi)}\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle + e^{i\phi}|\downarrow\rangle). \tag{21}$$

The projection operator for a transverse pure state is therefore

$$\begin{aligned}\hat{P}^{(\phi)} &= |\rightarrow^{(\phi)}\rangle\langle\rightarrow^{(\phi)}| \\ &= \tfrac{1}{2}(|\uparrow\rangle\langle\uparrow| + e^{i\phi}|\downarrow\rangle\langle\uparrow| + e^{-i\phi}|\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\downarrow|).\end{aligned} \tag{22}$$

In matrix form, we identify

$$\begin{aligned}|\uparrow\rangle\langle\uparrow| = \begin{pmatrix}1 & 0 \\ 0 & 0\end{pmatrix}, \quad |\downarrow\rangle\langle\uparrow| = \begin{pmatrix}0 & 0 \\ 1 & 0\end{pmatrix}, \\ |\uparrow\rangle\langle\downarrow| = \begin{pmatrix}0 & 1 \\ 0 & 0\end{pmatrix}, \quad |\downarrow\rangle\langle\downarrow| = \begin{pmatrix}0 & 0 \\ 0 & 1\end{pmatrix}\end{aligned} \tag{23}$$

and thus we find the "transverse" density matrix

$$\hat{P}_{\rightarrow}^{(\phi)} = \frac{1}{2}\begin{pmatrix}1 & e^{-i\phi} \\ e^{i\phi} & 1\end{pmatrix}. \tag{24}$$

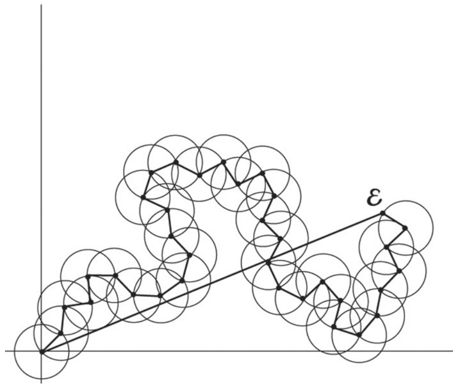

FIG. 2. Geometry of transverse magnetization for a spin ensemble.

Thus, for a spin ensemble, the transverse magnetization can be represented as

$$\mathcal{E}_t^{(N)} = \sum_{j=1}^{N} \overbrace{a_j \exp\left[i\varphi_t^{(j)}\right]}^{s^{(j)}} \tag{25}$$

in which the "form factors" a_j can be taken to have the uniform (over j) value $1/\sqrt{N}$ according to (17), so that all spins in the population carry equal weight. This has the mathematical structure of a random walk as applied in the theory of scattering from random media [3], and its geometry is depicted in Fig. 2.

1. Abragam's analysis

It is appropriate at this point to recount Abragam's treatment of the master equation for the density matrix (p. 276 in [1]). Abragam begins with the equation of motion for the density matrix in the presence of a perturbed Hamiltonian

$$\frac{1}{i}\frac{d\sigma}{dt} = -[H_0 + H_1(t),\sigma] \tag{26}$$

in which the perturbation $H_1(t)$ is a stationary operator-valued random process. Then, in the interaction representation with

$$\sigma^* = e^{iH_0t}\sigma e^{-iH_0t}, \quad H_1{}^*(t) = e^{iH_0t}H_1(t)e^{-iH_0t}, \tag{27}$$

Abragam [1] obtains

$$\frac{1}{i}\frac{d\sigma^*}{dt} = -[H_1{}^*(t),\sigma^*]. \tag{28}$$

[For a general operator A, the (Heisenberg) transformed operator is defined as $A \mapsto A^* \doteq e^{iH_0t}Ae^{-iH_0t}$. In the present context, applied to the density matrix σ and Hamiltonian H, this amounts to an overall rigid rotation of the Bloch sphere about the $\mathbf{B}_0$ axis at the Larmor frequency. In our calculations, we operate in a corotating frame, in NMR language "on resonance," and so the asterisk superscript can be dropped.] This equation is then integrated by successive approximations up to second order, which gives

$$\sigma^*(t) = \sigma^*(0) - i\int_0^t [H_1{}^*(t'),\sigma^*(0)]dt' - \int_0^t dt'\int_0^{t'} dt''[H_1{}^*(t'),[H_1{}^*(t''),\sigma^*(0)]]. \tag{29}$$

The time derivative of this equation, via a change of variable $\tau = t - t'$, yields

$$\frac{d\sigma^*}{dt} = -i[H_1{}^*(t),\sigma^*(0)] - \int_0^t d\tau[H_1{}^*(t),[H_1{}^*(t-\tau),\sigma^*(0)]]. \tag{30}$$

Abragam [Eq. (33), Ch. VIII in [1]] then concludes with an equation for the evolution of the *average* density matrix:

$$\frac{d\overline{\sigma^*}}{dt} = -\int_0^\infty d\tau\overline{[H_1{}^*(t),[H_1{}^*(t-\tau),\sigma^*(t)]]} \tag{31}$$

in which the overbar denotes an ensemble average. (The reader should consult p. 276 in [1] for details of certain technical assumptions involved in reaching this conclusion, which are not so immediately relevant for the present discussion.) It is precisely this average that removes the underlying spin noise process from Abragam's analysis. Thus, the status of Abragam's analysis and standard NMR description, in relation to the results we present here, can be summarized by the following:

Standard theory provides an exact quantum mechanical description of the ensemble average density matrix, in terms of which one can deduce the standard spin relaxation parameters (such as free induction exponential decay with a characteristic time scale of $T2$), which are deterministic ensemble properties. The underlying spin population, on the other hand, requires the analysis in terms of the raw, i.e., nonaveraged, density matrix. The results herein determine the component spin dynamics of the raw density matrix, thus accounting for real-time measurements of the NMR signal (such as observed spin noise), which is random. This reveals the origins of spin relaxation in terms of the fluctuations in individual spins which exist in random pure states.

It suffices to examine the above dynamics for a transverse component $|\rightarrow^{(\phi)}\rangle\langle\rightarrow^{(\phi)}|$ of the density matrix, and then extend via linearity of (30) in σ. Consider a perturbed Hamiltonian given by $H(t) = H_0 + H_1(t)$ in which the magnetic field perturbation is purely axial so that

$$H_1(t) = \frac{1}{2}\sigma\cdot(0,0,k^{1/2}\Gamma_t) = \frac{1}{2}k^{1/2}\Gamma_t\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}. \tag{32}$$

In this expression, Γ_t is a white noise process with the Dirac delta function autocorrelation property $\langle\Gamma_t\Gamma_{t'}\rangle = \delta(t-t')$. The description we provide here therefore aligns with the extreme narrowing approximation for which the spectral density of the perturbing Hamiltonian is independent of frequency and the (reciprocals of the) spin-spin and spin-lattice relaxation times $T1$ and $T2$ are equal. (We refer to Sec. III E for an explicit derivation of the latter property within our current framework.) The first commutator term in (30) can be computed explicitly as

$$\frac{1}{4}k^{1/2}\Gamma_t\left[\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix},\begin{pmatrix}1 & e^{-i\phi}\\ e^{i\phi} & 1\end{pmatrix}\right] = \frac{1}{2}k^{1/2}\Gamma_t\begin{pmatrix}0 & e^{-i\phi}\\ -e^{i\phi} & 0\end{pmatrix}. \tag{33}$$

Likewise, for the second commutator term, we have

$$\frac{1}{4}k\Gamma_t\Gamma_{t-\tau}\left[\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix},\left[\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix},\frac{1}{2}\begin{pmatrix}1 & e^{-i\phi}\\ e^{i\phi} & 1\end{pmatrix}\right]\right]$$
$$=\frac{1}{4}k\Gamma_t\Gamma_{t-\tau}\left[\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix},\begin{pmatrix}0 & e^{-i\phi}\\ -e^{i\phi} & 0\end{pmatrix}\right]$$
$$=\frac{1}{2}k\Gamma_t\Gamma_{t-\tau}\begin{pmatrix}0 & e^{-i\phi}\\ e^{i\phi} & 0\end{pmatrix}. \tag{34}$$

Thus, (30) yields the transverse density matrix stochastic dynamics:

$$\frac{d\hat{P}^{(\phi)}_{\rightarrow}}{dt}=-\frac{1}{2}ik^{1/2}\Gamma_t\begin{pmatrix}0 & e^{-i\phi}\\ -e^{i\phi} & 0\end{pmatrix}-\frac{1}{2}k\int_0^t d\tau\,\Gamma_t\Gamma_{t-\tau}\begin{pmatrix}0 & e^{-i\phi}\\ e^{i\phi} & 0\end{pmatrix}. \tag{35}$$

The corresponding differential projection operator is therefore

$$d\hat{P}^{(\phi)}_{\rightarrow}=-\frac{1}{2}ik^{1/2}\begin{pmatrix}0 & e^{-i\phi}\\ -e^{i\phi} & 0\end{pmatrix}dW_t^{(\phi)}-\frac{1}{2}k\begin{pmatrix}0 & e^{-i\phi}\\ e^{i\phi} & 0\end{pmatrix}\int_{\tau=0}^t(-dW_{t-\tau}^{(\phi)})\circ dW_t^{(\phi)}. \tag{36}$$

2. Stratanovich calculus

In the above, we use the relationship between stochastic differential equations (SDE) and Langevin representations, thus, $\Gamma_t = dW_t/dt$ for a Wiener process W_t, to be understood in this specific instance in the sense of Stratonovich since the original dynamics is presented in the form of an ordinary differential equation (ODE). In the above expression, the integral part is equal to $W_t \circ dW_t$ in which the symbol "$\circ$" indicates the Stratonovich interpretation. In other words, we can consider an approximate solution to an SDE

$$dX_t = b_t dt + \sigma_t dW_t \tag{37}$$

with drift b_t and volatility σ_t, generated by a sequence $x_t^{(n)}$ of solutions to the ODE $dx^{(n)}/dt = b + \sigma\Gamma^{(n)}$ in which $\Gamma_t^{(n)}$ is a sequence of processes whose integral $W_t^{(n)} = \int_0^t \Gamma_s^{(n)} ds$ converges to the Wiener process as $n \to \infty$. Then, the solution $x^{(n)}$ converges to the Stratonovich (as opposed to Ito) solution of the SDE (37). (Cf. [4] for a complete discussion concerning the relationship between ordinary and stochastic differential equations of relevance here.)

So, the resulting equation (36) should be understood in the sense of Stratonovich, which is the most natural from the point of view of an underlying ODE, as in (26). However, in order to make direct contact with more recent work in the theory of electromagnetic scattering from random media and the modern methods of stochastic calculus, we translate to the Ito interpretation via the identity

$$W_t dW_t \equiv W_t \circ dW_t - \tfrac{1}{2}dt \tag{38}$$

in which the left-hand side is an *Ito* differential. (It should be emphasized that such translation does not alter the stochastic process involved, rather, it is to be viewed as a different mathematical representation.) Accordingly, the expected value of the left-hand side above is zero. (See Appendix B in [3] for an exposition of the interrelationship between the Ito and Stratonovich interpretations of SDEs.) Observe that, in terms of the expression $\int_0^t \Gamma_t\Gamma_{t-\tau}d\tau$ arising above, the factor of $\frac{1}{2}$ can be considered to enter through the expectation of the same, $\langle\ldots\rangle = \int_0^t \delta(\tau)d\tau = \frac{1}{2}$, in which careful attention should be paid to the asymmetry in the interval of integration with respect to the peak in the delta distribution function. Thus, considering the perturbation expansion infinitesimally, i.e., as $t \to 0$, and using (38) we find that (36) becomes

$$d\hat{P}^{(\phi)}_{\rightarrow}=-\frac{1}{2}ik^{1/2}\begin{pmatrix}0 & e^{-i\phi_t}\\ -e^{i\phi_t} & 0\end{pmatrix}dW_t^{(\phi)}-\frac{1}{4}k\begin{pmatrix}0 & e^{-i\phi_t}\\ e^{i\phi_t} & 0\end{pmatrix}dt. \tag{39}$$

Since the Ito differential of a component spin random phasor is $d(e^{-i\phi_t}) = -ie^{-i\phi_t}d\phi_t - \frac{1}{2}e^{-i\phi_t}d\phi_t{}^2$, comparing with the components of $\hat{P}^{(\phi)}_{\rightarrow}$ in (24), we identify the phase dynamics

$$\phi_t = k^{1/2}W_t^{(\phi)}. \tag{40}$$

Hence, the azimuthal angle is a scaled Wiener process, in which the physical origin of the constant k is through the magnitude of the perturbing Hamiltonian $H_1(t)$, according to (32) above.

It is important to appreciate the *truncation* of the perturbation expansion (30) at second order in the case of the extreme narrowing approximation where the perturbing Hamiltonian $H_1(t)$ is modeled via a (differential of a) Wiener process. This feature can be understood to arise since the Wiener process satisfies the *exact* relations $dW_t^\alpha = 0$ for $\alpha > 2$, which express the fact that higher than second order moments of its increments (per unit of time) vanish. Consequently, the associated Kramers-Moyal expansion is second order, and in this case reduces to the heat equation. The vanishing higher moment property of the Wiener process implies that higher order (in H_1) terms of (30) are zero.

Observe that there is no violation of quantum mechanical unitarity in this picture, in which individual pure states evolve into random pure states.

D. Isotropic fluctuations

We have seen in the case of axial fluctuations that the state vector evolves as a Wiener process on the equatorial circle on the Bloch sphere. In the more general case, we shall consider a perturbation involving fluctuations in all directions:

$$H_1(t)=\frac{1}{2}k^{1/2}\sigma\left(\Gamma_t^{(x)},\Gamma_t^{(y)},\Gamma_t^{(z)}\right)=\frac{1}{2}k^{1/2}\begin{pmatrix}\Gamma_t^{(z)} & \Gamma_t^{(x)}-i\Gamma_t^{(y)}\\ \Gamma_t^{(x)}+i\Gamma_t^{(y)} & -\Gamma_t^{(z)}\end{pmatrix}. \tag{41}$$

Applying the same arguments to the case of isotropic fluctuations, via (41), we deduce that (26)–(30) lead to isotropic rotational diffusion, for which we develop the dynamics explicitly below.

1. Rotational diffusion

We construct an isotropic stationary diffusion process on the unit (Bloch) sphere. In spherical polar coordinates, the position vector of a point on the unit sphere (in ambient Euclidean coordinates) is $\mathbf{r}_t = (\sin\theta_t\cos\phi_t, \sin\theta_t\sin\phi_t, \cos\theta_t)$, and in terms of these coordinates the spherical Laplacian on the unit sphere is given by

$$\nabla^2 f = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2}. \tag{42}$$

The heat equation on the sphere can then be written as

$$\frac{\partial f}{\partial t} = \frac{1}{2}k\nabla^2 f \tag{43}$$

and expressed in these coordinates. The probabilistic interpretation of the function f in this equation is that, for an element of probability $\delta\mathbf{P}$, we have $\delta\mathbf{P} = f\delta^2 A$ where $\delta^2 A = \sin\theta\delta\theta\delta\phi$ is the area element on the unit sphere. [To see how this arises from an ambient diffusion in three-dimensional Euclidean space explicitly, consider the full 3-Laplacian in spherical polar coordinates $\nabla^2 = \frac{1}{r^2}\{\partial_r(r^2\partial_r) + \frac{1}{\sin^2\theta}\partial_\phi^2 + \frac{1}{\sin\theta}\partial_\theta(\sin\theta\partial_\theta)\}$ acting on $f^{(3)} = \rho^{(3)}/r^2\sin\theta$ so that $\delta\mathbf{P} = f^{(3)}\delta^3\mathbf{r}$. The resulting (Fokker-Planck) equation for $\partial\rho/\partial t$ contains ∂_r terms of the form $\partial_r(r^2\partial_r)(\frac{\rho}{r^2}) = \partial_r^2\rho - \partial_r(\frac{2\rho}{r})$. Removal of such ∂_r terms and setting $r = 1$ maps to zero the radial component of the generator of the diffusion (cf. Chap. 3 in [3]) and restricts the process to the unit sphere; locally the sphere process is two-dimensional Brownian motion in the tangent space at each point P. For the probability density in spherical coordinates $\rho(\theta,\phi)$, we make the identification $\rho \leftrightarrow f\sin\theta$. It follows that

$$\frac{\partial\rho}{\partial t} = \frac{1}{2}k\left[-\frac{\partial}{\partial\theta}(\rho\cot\theta) + \frac{\partial^2\rho}{\partial\theta^2} + \frac{1}{\sin^2\theta}\frac{\partial^2\rho}{\partial\phi^2}\right], \tag{44}$$

which is the *Fokker-Planck* equation. From this we can read off (see, e.g., [3]) a pair of coupled SDEs for the (θ_t,ϕ_t) process

$$d\theta_t = k^{1/2}dW_t^{(\theta)} + \tfrac{1}{2}k\cot\theta_t dt, \quad d\phi_t = \tfrac{k^{1/2}}{\sin\theta_t}dW_t^{(\phi)} \tag{45}$$

in which the Wiener processes $W_t^{(\theta)}$, $W_t^{(\phi)}$ are independent so that the product of their Ito differentials vanishes, $dW_t^{(\theta)}dW_t^{(\phi)} = 0$, and are normalized in the sense that $dW_t^{(\theta)2} = dt$, $dW_t^{(\phi)2} = dt$. Observe that, consistent with the requirement of isotropy, Eq. (45) implies (by applying Ito's formula to $\mathbf{r}_t$) that $d\mathbf{r}_t|_\theta^2 = d\mathbf{r}_t|_\phi^2$, i.e., the squared fluctuations due to the θ, ϕ motions separately are equal in magnitude (in other words, the diffusion tensor for the two-sphere process with respect to the ambient Euclidean metric is isotropic). Since the probability distribution for this process is uniform on the Bloch sphere (with area measure induced from the volume form in the ambient Euclidean 3-space), an element of probability satisfies $\frac{1}{4\pi}\sin\theta\, d\theta\, d\phi = \delta\mathbf{P} = p_{\theta\phi}d\theta\, d\phi$ for joint probability density function $p_{\theta\phi}$. Thus, we have the joint and marginal probabilities

$$p_{\theta\phi} = \frac{1}{4\pi}\sin\theta, \quad p_\theta = \frac{1}{2}\sin\theta, \quad p_\phi = \frac{1}{2\pi} \tag{46}$$

and, hence, θ, ϕ are statistically independent.

In this geometric context, for mathematical completeness, it is informative to consider the distribution of the stereographic coordinate ζ. Writing an element of probability as $p_{|\zeta|}d|\zeta| = p_\theta d\theta$ and using $|\zeta| = \cot\frac{1}{2}\theta$ and (46) for p_θ yields $p_{|\zeta|} = \frac{2|\zeta|}{(1+|\zeta|^2)^2}$. This distribution is heavy tailed: the first moment $\mathbf{E}[|\zeta|]$ exists, but all integer moments of higher order are infinite (thus, $|\zeta|$ has infinite variance). For the expected value we have $\mathbf{E}[\zeta] = 0$ since θ, ϕ are independent and $e^{i\phi}$ has zero mean (this is in spite of the corresponding state P being uniformly distributed on the Bloch sphere). It is important to appreciate here that, while the (polar and stereographic) *coordinates* depict a certain orientation, the situation as regards dynamics and distribution on the Bloch sphere is totally symmetric.

Observe for these dynamics that the probability that the two-sphere process hits a pole is zero, the event of which is analogous to a Wiener process in two dimensions hitting the origin (or any given point). This situation should be contrasted with the circle diffusion case where the probability of hitting an antipodal point is one. In this respect, it should be appreciated that the circle of azimuth is compactified to a single point at the poles. With regard to the behavior of the drift at the poles, locally we have diffusion on the Euclidean tangent plane. The polar angle measures the absolute distance from the origin (pole), which can be recognized as the *Bessel process*. Consistently, the polar drift, which is proportional to the cotangent of the polar angle, coincides with the Bessel drift for small angles (equal to the reciprocal angle). The (mathematical) reader should compare, e.g., Chap. 4 in [3] for a detailed account of the Bessel process in any number of dimensions. The process for the spin vector is described in terms of intrinsic polar coordinates so that it is constrained to lie on the Bloch sphere without imposing boundary conditions. In this way, the isotropic spin diffusion process, the origins via (41) of which lie in isotropic magnetic field fluctuations in the ambient 3-space, is described in terms of nonisotropic (polar) coordinates. Thus, the singularities that appear in (45) are "apparent," i.e., coordinate, ones.

2. Stereography

The differential of the stereographic coordinate can be calculated from the Ito product formula $d(A_tB_t) = A_t dB_t + B_t dA_t + dA_t dB_t$ where attention should be paid, in general, to the additional second order term. In our specific case

$$d\zeta_t = e^{i\phi_t}d\left(\cot\tfrac{1}{2}\theta_t\right) + (de^{i\phi_t})\cot\tfrac{1}{2}\theta_t, \tag{47}$$

and the second order term vanishes due to the independence between the polar and azimuthal fluctuations (the diffusion is isotropic). According to Ito's formula and (45),

$$\begin{aligned} d(e^{i\phi_t}) &= ie^{i\phi_t}d\phi_t - \frac{1}{2}e^{i\phi_t}d\phi_t^2 \\ &= ie^{i\phi_t}\left(\frac{k^{1/2}}{\sin\theta_t}dW_t^{(\phi)}\right) - \frac{1}{2}e^{i\phi_t}\left(\frac{k}{\sin^2\theta_t}\right)dt. \end{aligned} \tag{48}$$

Again, via Ito's formula, we have $d(\cot\frac{1}{2}\theta_t) = -\frac{1}{2}\csc^2\frac{1}{2}\theta_t d\theta_t + \frac{1}{4}\cot\frac{1}{2}\theta_t\csc^2\frac{1}{2}\theta_t d\theta_t^2$ and hence

$$\begin{aligned} d\zeta_t = e^{i\phi_t}\big(& -\tfrac{1}{2}\csc^2\tfrac{1}{2}\theta_t\big[k^{1/2}dW_t^{(\theta)} + \tfrac{1}{2}k\cot\theta_t dt\big] \\ & + \tfrac{1}{4}k\cot\tfrac{1}{2}\theta_t\csc^2\tfrac{1}{2}\theta_t dt \\ & + \big[ik^{1/2}\csc\theta_t dW_t^{(\phi)} - \tfrac{1}{2}k\csc^2\theta_t dt\big]\cot\tfrac{1}{2}\theta_t\big). \end{aligned} \tag{49}$$

Close inspection of the combined drift terms above (via the trigonometric t formulas for sine and cosine in terms of tangent of half the angle, for instance) reveals an overall *zero* drift. Thus, the stereographic coordinate for the spin relaxation process is a *martingale*. There remain two fluctuating terms in $dW_t^{(\phi)}$, $dW_t^{(\theta)}$ with volatilities expressed in angular form as read off from (49). Using the expressions $|\zeta| = \cot\frac{1}{2}\theta$, $\zeta/|\zeta| = e^{i\phi}$, the residual fluctuating terms can be more compactly expressed in terms of the stereographic coordinate alone, and thus

$$d\zeta_t = \frac{1}{2}k^{1/2}\zeta_t\left(\frac{1}{|\zeta_t|} + |\zeta_t|\right)\left(-dW_t^{(\theta)} + i\,dW_t^{(\phi)}\right). \tag{50}$$

The diffusion tensor for this process is therefore isotropic, $d\zeta_t^2 = 0$, and the magnitude of the diffusion or squared volatility depends (only) on $|\zeta|$ (the polar angle) according to

$$|d\zeta_t|^2 = \frac{1}{2}k|\zeta_t|^2\left(\frac{1}{|\zeta_t|^2} + 2 + |\zeta_t|^2\right)dt \tag{51}$$

in which the squared volatility coefficient can be recognized trigonometrically as $\frac{1}{2}k\csc^4\frac{1}{2}\theta_t$. In the limits $|\zeta| \to \infty$ and $|\zeta| \to 0$, corresponding to approach of the north (spin-↑) and south (spin-↓) poles of the Bloch sphere, this coefficient tends to infinity and $\frac{1}{2}k$, respectively, as we anticipate from the locally constant diffusion on the Bloch sphere and the nature of the stereographic mapping which sends the north pole to infinity in the complex ζ plane.

Remark. The results above should be compared and contrasted with the polar representation of two-dimensional Brownian motion $B_t = R_t e^{i\alpha_t} = X_t + iY_t$, where X, Y are (scaled) independent Brownian motions

$$dX_t = \kappa^{1/2}dW_t^{(x)}, \quad dY_t = \kappa^{1/2}dW_t^{(y)}. \tag{52}$$

The differentials of the modulus and phase components can then be computed, using the property $dB_t^2 = 0$, as

$$\begin{aligned} dR_t &= \frac{1}{2R_t}(B_t dB_t^* + B_t^* dB_t) + \frac{1}{4R_t}dB_t dB_t^* \\ &= \frac{1}{R_t}(X_t dX_t + Y_t dY_t) + \frac{1}{4R_t}\left(dX_t^2 + dY_t^2\right) \\ &= \kappa^{1/2}dW_t^{(R)} + \frac{\kappa}{2R_t}dt \end{aligned} \tag{53}$$

and

$$\begin{aligned} d\alpha_t &= \frac{1}{2i}\left(\frac{dB_t}{B_t} - \frac{dB_t^*}{B_t^*}\right) \\ &= \frac{1}{R_t^2}(-Y_t dX_t + X_t dY_t) = \frac{\kappa^{1/2}}{R_t}dW_t^{(\alpha)} \end{aligned} \tag{54}$$

in which we identify radial and angular Wiener processes from their Cartesian counterparts

$$\begin{aligned} dW_t^{(R)} &= \frac{1}{R_t}\left(X_t dW_t^{(x)} + Y_t dW_t^{(y)}\right), \\ dW_t^{(\alpha)} &= \frac{1}{R_t}\left(-Y_t dW_t^{(x)} + X_t dW_t^{(y)}\right). \end{aligned} \tag{55}$$

The above expression demonstrates explicitly the orthogonality property $dR_t d\alpha_t = 0$. Then, from the Ito product formula, we deduce

$$dB_t = \kappa^{1/2}e^{i\alpha_t}\left(i\,dW_t^{(\alpha)} + dW_t^{(R)}\right) \tag{56}$$

in which computation the drift terms that arise cancel. Thus, both the stereographic spin noise and two-dimensional Brownian motion processes are martingales, but the former has a distinct and intricate (stochastic) volatility structure encapsulated by (50).

3. Diagonal

We now proceed to calculate the dynamics of the density matrix for pure states and an ensemble. Via Ito's formula, we have $d\cos\theta_t = -\sin\theta_t d\theta_t - \frac{1}{2}\cos\theta_t d\theta_t^2$, and so from (45) and (16) the differential of the spin ↑↑ component of the density matrix is given by

$$d\sigma_t^{\uparrow\uparrow} = -k\left(\sigma_t^{\uparrow\uparrow} - \tfrac{1}{2}\right)dt - \tfrac{1}{2}k^{1/2}\sin\theta_t dW_t^{(\theta)}. \tag{57}$$

The differential of the spin ↓↓ component is then the negative of this:

$$d\sigma_t^{\downarrow\downarrow} = -d\sigma_t^{\uparrow\uparrow}, \tag{58}$$

which follows from the unit trace condition $\sigma^{\uparrow\uparrow} + \sigma^{\downarrow\downarrow} \equiv 1$ [as evident from (16)]. With regard to the fluctuating term in (57), define the following (real) processes pertaining to constituent pure states and the ensemble:

$$d\breve{\chi}_t^{(j)} \doteq \sin\theta_t^{(j)}dW_t^{(\theta)(j)}, \quad d\breve{\chi}_t \doteq \frac{1}{N^{1/2}}\sum_{j=1}^{N} d\breve{\chi}_t^{(j)}. \tag{59}$$

Taking the square of the second relation as pertains to the ensemble, we find

$$\lim_{N\to\infty} d\breve{\chi}_t^2 = \mathrm{E}[\sin^2\theta]dt = \tfrac{2}{3}dt \tag{60}$$

in which we have used (46) to calculate **E**. It follows that

$$d\breve{\chi}_t \doteq \sqrt{\frac{2}{3}}dW_t. \tag{61}$$

The fact that the sum in (59) yields a scaled Wiener process follows from the stability property of the Gaussian distribution (see, e.g., Appendix A in [3]). Now, for an ensemble, define

$$\Sigma^{\uparrow\uparrow} \doteq \frac{1}{N^{1/2}}\sum_{j=1}^{N}\sigma^{\uparrow\uparrow(j)}. \tag{62}$$

The dynamics for the spin ↑↑ component of the ensemble is thus determined by the following SDE:

$$d\Sigma_t^{\uparrow\uparrow} = -k\left(\Sigma_t^{\uparrow\uparrow} - \frac{1}{2}N^{1/2}\right)dt - \sqrt{\frac{k}{6}}dW_t. \tag{63}$$

4. Off diagonal

For mathematical convenience and a natural geometric interpretation, let us first introduce a new complex "transverse" coordinate adapted from the stereographic coordinate introduced earlier (and which differs from the off-diagonal component of the pure state density matrix by a factor of 2):

$$\tilde{\zeta} \doteq \frac{2\zeta}{1+|\zeta|^2}. \tag{64}$$

In polar form $\tilde{\zeta} = e^{i\phi}\sin\theta$ which, in the geometry of Fig. 1, is the projection along the z axis of a point on the Bloch sphere to the transverse plane. Thus, $0 \leqslant |\tilde{\zeta}| \leqslant 1$ and $\tilde{\zeta}_t$ is a process on the unit disk. According to this geometry, a given value of $\tilde{\zeta}$ has two associated values of ζ, and thus a given point in the transverse plane maps to a pair of equal longitude, opposite latitude points on the Bloch sphere with stereographic coordinates

$$|\zeta_\pm| = \frac{1}{|\tilde{\zeta}|}[1 \pm \sqrt{1-|\tilde{\zeta}|^2}], \tag{65}$$

for which $|\zeta_+||\zeta_-| \equiv 1$, and thus ζ_+, ζ_- represent inverse points. Observe that the $\uparrow\downarrow$ component of (15) does *not* determine the density matrix. Physically, this corresponds to the fact that a given pure state transverse magnetization has two equal and opposite possible z magnetizations. The differential of this new coordinate can be computed explicitly as

$$d\tilde{\zeta}_t = e^{i\phi_t}d(\sin\theta_t) + d(e^{i\phi_t})\sin\theta_t + d(e^{i\phi_t})d(\sin\theta_t) \tag{66}$$

in which the last quadratic differential term is zero in this case due to the independence of the θ and ϕ fluctuations. From Ito's formula, we have $d\sin\theta_t = \cos\theta_t d\theta_t - \frac{1}{2}\sin\theta_t d\theta_t^2$ and so combining with (45) we deduce

$$d\sin\theta_t = k^{1/2}\cos\theta_t dW_t^{(\theta)} + \tfrac{1}{2}k(\cos\theta_t\cot\theta_t - \sin\theta_t)dt. \tag{67}$$

It follows from (48) and (67) that

$$d\tilde{\zeta}_t = -k\tilde{\zeta}_t dt + k^{1/2}e^{i\phi_t}\left(\cos\theta_t dW_t^{(\theta)} + i\,dW_t^{(\phi)}\right). \tag{68}$$

Observe the complex valued nature of the fluctuating term in the above SDE, for which the polar fluctuations contribute in the instantaneous direction defined by $\tilde{\zeta}$ (weighted by a cosine stochastic volatility), while the azimuthal fluctuations contribute in the direction perpendicular to this (through multiplication by $\sqrt{-1}$). Note that, for a single spin, the magnitude of the radial fluctuations in the transverse plane is *less* than that of the angular fluctuations (unless the underlying state lies at either pole of the Bloch sphere); however, as we shall see in what follows, when an ensemble of spins is considered, the resulting fluctuating term has a circular symmetry (its diffusion tensor is isotropic). With regard to the linear drift term above, this has the effect of a mean reversion to zero. An ensemble average of (68) removes the fluctuating term on the right-hand side, while the residual drift term (which it should be appreciated contains second order derivative terms from Ito's formula) yields the familiar free induction decay (FID) which is *exponential on a time scale* k^{-1}.

Now, we map this single spin dynamics onto the behavior for an ensemble of spins. [It is worthwhile to remark that, owing to the stochastic volatility present in (68), the dynamics for a single spin is distinct from that we shall derive for an ensemble, the latter yielding a constant amplitude fluctuating term, as we shall derive.] As for the diagonal case, throughout our analysis each spin is assumed independent from every other spin. For the jth such spin, set $\tilde{\zeta} \mapsto \tilde{\zeta}^{(j)}$, and likewise for θ, ϕ, etc. With regard to the fluctuating terms in (68), define another family of processes pertaining to individual spins and the ensemble:

$$\begin{aligned} d\hat{\chi}_t^{(j)} &\doteq e^{i\phi_t^{(j)}}\left(\cos\theta_t^{(j)} dW_t^{(\theta)(j)} + i\,dW_t^{(\phi)(j)}\right), \\ d\hat{\chi}_t &\doteq \frac{1}{N^{1/2}}\sum_{j=1}^{N} d\hat{\chi}_t^{(j)}. \end{aligned} \tag{69}$$

Hence, taking the square of the component spin process above

$$d\hat{\chi}_t^{(j)2} = e^{2i\phi_t^{(j)}}\left(\cos^2\theta_t^{(j)} - 1\right)dt \tag{70}$$

and accordingly the resultant amplitude fluctuations have square

$$d\hat{\chi}_t^2 = \frac{1}{N}\sum_{j=1}^{N} d\hat{\chi}_t^{(j)2} = \frac{1}{N}\sum_{j=1}^{N} e^{2i\phi_t^{(j)}}\left(\cos^2\theta_t^{(j)} - 1\right)dt. \tag{71}$$

For the ensemble, in the limit of a large number of spins, via the law of large numbers, we have

$$\lim_{N\to\infty}\left[d\hat{\chi}_t^2\right] = \mathbf{E}[e^{2i\phi}(\cos^2\theta - 1)]dt = 0, \tag{72}$$

where the vanishing follows from the expectation values

$$\mathbf{E}[e^{2i\phi}] = 0, \quad \mathbf{E}[\cos^2\theta] = \tfrac{1}{3}, \tag{73}$$

which are a consequence of (46). In a similar way, using $d\hat{\chi}_t^{(j)} d\hat{\chi}_t^{(j)*} = (\cos^2\theta_t^{(j)} + 1)dt$, we find

$$d\hat{\chi}_t d\hat{\chi}_t^* = \frac{1}{N}\sum_{j=1}^{N} d\hat{\chi}_t^{(j)} d\hat{\chi}_t^{(j)*} = \frac{1}{N}\sum_{j=1}^{N}\left(\cos^2\theta_t^{(j)} + 1\right)dt, \tag{74}$$

which, for the spin ensemble, tends to

$$\lim_{N\to\infty}[d\hat{\chi}_t d\hat{\chi}_t^*] = \mathbf{E}[\cos^2\theta + 1]dt = \tfrac{4}{3}dt. \tag{75}$$

We deduce that the resultant fluctuation $\hat{\chi}_t$ is a scaled *complex* Wiener process with differential

$$d\hat{\chi}_t \equiv \frac{2}{\sqrt{3}}d\xi_t \tag{76}$$

in which $d\xi_t^2 = 0$ and $d\xi_t d\xi_t^* = dt$. The squared property $d\hat{\chi}_t^2 = 0$ implies that $\hat{\chi}_t$, when regarded as a process in the real plane $\mathbf{R}^2$, has an *isotropic diffusion tensor*; this fact follows from writing $d\hat{\chi}_t = e^{i\delta_t}(dx_t + i\,dy_t)$ for real δ, x, y with orthogonality $dx_t dy_t = 0$ (so that $e^{i\delta_t}$ represents an instantaneous principal axis of the diffusion tensor) and taking the square. Now, if we define

$$\tilde{\zeta}_t \doteq \sum_{j=1}^{N} \frac{1}{N^{1/2}} \tilde{\zeta}_t^{(j)}, \tag{77}$$

the resulting dynamics is

$$d\tilde{\zeta}_t = -k\tilde{\zeta}_t dt + \sqrt{\frac{4k}{3}} d\xi_t. \tag{78}$$

Correspondingly, if we introduce the spin $\uparrow\downarrow$ component of the ensemble modified spin density matrix

$$\Sigma_t^{\uparrow\downarrow} \doteq \sum_{j=1}^{N} \frac{1}{N^{1/2}} \sigma_t^{\uparrow\downarrow(j)}, \tag{79}$$

then this satisfies

$$d\Sigma_t^{\uparrow\downarrow} = -k\Sigma_t^{\uparrow\downarrow} dt + \sqrt{\frac{k}{3}} d\xi_t, \tag{80}$$

which is the dynamical equation for a *complex Ornstein-Uhlenbeck* process.

5. Statistics of fluctuating terms

To complete our analysis of the fluctuating terms pertaining to the spin $\uparrow\uparrow$ (longitudinal) versus $\uparrow\downarrow$ (transverse) components of the density matrix, we examine their statistical relationship. It follows from (59) and (69), together with the orthogonality of the polar and azimuthal fluctuations, that

$$d\widehat{\chi}_t d\breve{\chi}_t = \frac{1}{N} \sum_{j=1}^{N} e^{i\phi_t^{(j)}} \sin\theta_t^{(j)} \cos\theta_t^{(j)} dt, \tag{81}$$

and so for a large ensemble of spins we have

$$\begin{aligned} \lim_{N\to\infty} [d\widehat{\chi}_t d\breve{\chi}_t] &= \mathbf{E}[e^{i\phi} \sin\theta\cos\theta] dt \\ &= \mathbf{E}[e^{i\phi}]\mathbf{E}[\sin\theta\cos\theta] dt = 0 \end{aligned} \tag{82}$$

in which the last two equalities follow from (46). Thus, W_t and ξ_t are uncorrelated and, since they are Gaussian, statistically independent.

6. Scaling

If we define the quantity pertaining to an ensemble $Q \doteq \frac{1}{N^s} \sum_{j=1}^{N} q_t^{(j)}$ where the individual component differentials $dq_t^{(j)}$ have drifts $a - q_t^{(j)}$ for constant a, then the ensemble Q drift is $N^{1-s}a - Q_t$. In the present context, we are concerned with the case $s = \frac{1}{2}$ since the r.m.s. for spin noise is $N^{1/2}$; this yields a drift of the form $N^{1/2}a - Q_t$, as we shall see explicit instances of in what follows.

E. Effect of the lattice

According to a quantum statistical mechanical treatment of the lattice [1], there exists an equilibrium value for the density matrix

$$\sigma_0 = \exp[-\hbar H_0/kT]/\mathrm{tr}\{\exp[-\hbar H_0/kT]\}, \tag{83}$$

which can be written in the simple compact form

$$\begin{pmatrix} p & 0 \\ 0 & 1-p \end{pmatrix}, \tag{84}$$

where p is the longitudinal polarization (Boltzmann) fraction

$$p = \frac{1}{1 + \exp(2\hbar E/kT)}. \tag{85}$$

In the high field $E \to \pm\infty$ or equivalently low temperature $T \to 0$ limits, for antiparallel and parallel fields, we have $p \to 0, 1$, respectively. As we shall see explicitly, a contribution of spin noise is energy and temperature independent and thus persists in these limits. Mathematically, the coordinate ζ drifts toward zero (infinity) [as E is negative (positive)] and $\tilde{\zeta}$ drifts toward zero, while (spin noise) fluctuations persist (in a pulsed experiment the latter to be regarded as an asymptotic residual noise). On the Bloch sphere, this corresponds to a drift toward the south (north) poles as $\mathbf{B}_0$ is antiparallel (parallel) to the z axis.

1. Modified dynamics

According to Abragam [1], the effect of the lattice is to modify the equation for the density matrix via the transformation $\sigma^* \mapsto \sigma^* - \sigma_0$. Dynamically, this yields an extra contribution to the double commutator term in (30) equal to

$$\int_0^t d\tau [H_1(t),[H_1(t-\tau),\sigma_0]]. \tag{86}$$

As we shall see in our following analysis, this term amounts to a *drift* oriented to a pole of the Bloch sphere (the polarity depending on the sign of E). We evaluate the single commutator in (86) as

$$[H_1(t-\tau),\sigma_0] = \frac{1}{2} k^{1/2}(1-2p) \begin{pmatrix} 0 & \Gamma_{t-\tau}^{(w)*} \\ -\Gamma_{t-\tau}^{(w)} & 0 \end{pmatrix} \tag{87}$$

in which the quantity $\Gamma_t^{(w)} \doteq \Gamma_t^{(x)} + i\Gamma_t^{(y)}$ has been introduced for notational compactness. Hence, the contribution to the double commutator from the lattice via the additional equilibrium density matrix term is

$$\begin{aligned} &[H_1(t),[H_1(t-\tau),\sigma_0]] \\ &= \frac{1}{4} k(1-2p) \left[\begin{pmatrix} \Gamma_t^{(z)} & \Gamma_t^{(w)*} \\ \Gamma_t^{(w)} & -\Gamma_t^{(z)} \end{pmatrix}, \begin{pmatrix} 0 & \Gamma_{t-\tau}^{(w)*} \\ -\Gamma_{t-\tau}^{(w)} & 0 \end{pmatrix} \right] \\ &= \frac{1}{2} k(1-2p) \begin{pmatrix} -\Gamma_t^{(x)}\Gamma_{t-\tau}^{(x)} - \Gamma_t^{(y)}\Gamma_{t-\tau}^{(y)} & * \\ \Gamma_t^{(z)}\Gamma_{t-\tau}^{(w)} & - \end{pmatrix}, \end{aligned} \tag{88}$$

where the symbols "$*$" and "$-$" in the matrix of the last line indicate elements equal to the complex conjugate and negative of those diagonally opposite, respectively. Observe that, under certain circumstances, this lattice contribution vanishes. First, if the transverse fluctuations are zero ($\Gamma^{(x)} = \Gamma^{(y)} = 0$), then the lattice contribution vanishes, as expected since it is only transverse magnetic fields that can effect longitudinal relaxation. Second, in the infinite temperature and zero field limits, for which $p = \frac{1}{2}$, the equilibrium density matrix is proportional to the identity (situated at the center of the Bloch ball in Fig. 1). It therefore commutes with all operators and consistently the contribution (86) vanishes, as evident from (88).

Let us consider the off-diagonal and diagonal contributions to the differential $d\sigma$ separately. Following similar steps to the case of axial fluctuations considered in Sec. III C, a typical off-diagonal term in (88) yields a contribution to (86) of

$$\int_0^t d\tau\, \Gamma_t^{(z)}\Gamma_{t-\tau}^{(x)}dt = dW_t^{(z)} \circ \underbrace{\int_0^t -dW_{t-\tau}^{(x)}}_{W_t^{(x)}}$$
$$= W_t^{(x)} \circ dW_t^{(z)} \to 0, \tag{89}$$

where the limit is $t \to 0$; similarly, all such off-diagonal terms yield zero contribution. For the diagonal terms, however, a nonzero contribution arises. For a typical term, we find

$$\int_0^t d\tau\, \Gamma_t^{(x)}\Gamma_{t-\tau}^{(x)}dt = dW_t^{(x)} \circ \underbrace{\int_0^t -dW_{t-\tau}^{(x)}}_{W_t^{(x)}}$$
$$= W_t^{(x)} \circ dW_t^{(x)} \to \frac{1}{2}dt \tag{90}$$

and similarly for terms involving $\Gamma^{(y)}$. Hence, the additional contribution to relaxation due to the lattice is

$$d\sigma|_{\sigma_0} = \frac{1}{2}k(1-2p)\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} dt \tag{91}$$

and so the lattice contributes only to *longitudinal* relaxation. Grouping the terms in the way they arise in the above derivation (so that the drift induced by the finite temperature lattice appears separately as the final term) leads to the central result of the paper.

The combined processes of spin-spin and spin-lattice relaxation are determined by the following set of stochastic differential equations for the modified spin density:

$$d\Sigma_t = \begin{pmatrix} -k(\Sigma_t^{\uparrow\uparrow} - \frac{1}{2}N^{1/2}) & -k\Sigma_t^{\uparrow\downarrow} \\ * & - \end{pmatrix} dt$$
$$+ \begin{pmatrix} -\sqrt{k/6}\,dW_t & \sqrt{k/3}\,d\xi_t \\ * & - \end{pmatrix}$$
$$+ \frac{1}{2}k(1-2p)N^{1/2}\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} dt. \tag{92}$$

Once again, the symbols "$*$" and "$-$" in the bottom rows of the first two matrices appearing on the right-hand side of the above equation denote the complex conjugate and negative of the elements diagonally opposite, respectively. As derived previously in Sec. III D5, the fluctuating terms dW_t and $d\xi_t$ arising in (92) are statistically independent.

2. *Ensemble properties*

We examine closely the implications of the dynamics embodied by (92) for the spin ensemble. First, observe the cancellation of the N-dependent longitudinal relaxation drift term extant in the absence of the lattice [top line right-hand side of (92)] with a corresponding term that arises from the finite temperature lattice; this leaves a residual lattice drift term that scales as $N^{1/2}$. It follows from the general solution of the Ornstein-Uhlenbeck equation (see, e.g., Chap. 8 in [3]) that "spin noise" [the off-diagonal component of (92)] has asymptotic variance $\mathbf{E}[|\Sigma^{\uparrow\downarrow}|^2] = \frac{1}{3}$ which is *independent* of the strength of the magnetic field fluctuations prescribed by k; the constant k amounts to a time change in the stochastic differential equation for $\Sigma^{\uparrow\downarrow}$ and so does not affect the asymptotic stationary probability distribution. Thus, k determines (only) the $T2$ time scale of spin noise fluctuations, their magnitude scaling with the square-root of the spin population size $N^{1/2}$. Spin noise is manifestly *temperature independent* or, in other words, independent of the Boltzmann fraction since p features only in the diagonal component of (92). It is evident from (92) that the spin-spin and spin-lattice relaxation times are equal, $T1 = T2$, since the coefficients of $\Sigma^{\uparrow\uparrow}$ and $\Sigma^{\uparrow\downarrow}$ in the drift term are matching values $-k$. This is a familiar feature of extreme narrowing such as we consider here, where the autocorrelation times of the noise processes Γ in Eqs. (32) and (41) are zero. By solving the ensemble averaged equations for the density matrix (92), we can obtain the appropriate scaling with the spin population N, for both spin-spin and spin-lattice relaxation, and also the equilibrium Boltzmann value for $T1$ relaxation. Explicitly, the expected value $\mathbf{E}$ of (92) yields, for the $\uparrow\uparrow$ component,

$$\frac{d\Sigma^{\uparrow\uparrow}}{\Sigma^{\uparrow\uparrow} - N^{1/2}p} = -k\,dt, \tag{93}$$

which integrates to

$$\Sigma_t^{\uparrow\uparrow} = N^{1/2}p + (\Sigma_0^{\uparrow\uparrow} - N^{1/2}p)e^{-kt}. \tag{94}$$

This is the equation for *longitudinal relaxation*. Similarly, for the $\uparrow\downarrow$ component

$$\frac{d\Sigma_t^{\uparrow\downarrow}}{\Sigma_t^{\uparrow\downarrow}} = -k\,dt, \tag{95}$$

$$\Sigma_t^{\uparrow\downarrow} = \Sigma_0^{\uparrow\downarrow}e^{-kt}, \tag{96}$$

which is the equation for *transverse relaxation*.

In comparison to the square root N scaling of (17) if we define $\hat{\Sigma} \doteq \frac{1}{N}\sum_{j=1}^N \sigma^{(j)}$ (so that $\hat{\Sigma} = \Sigma/N^{1/2}$), then in the limit $N \to \infty$, via the law of large numbers, this tends to the expected value

$$\hat{\Sigma} \to \mathbf{E}[\sigma^{(j)}] = \mathbf{E}[\hat{\Sigma}]. \tag{97}$$

Thus, for an asymptotically large collection of spins, we can write

$$\hat{\Sigma} \equiv \mathbf{E}[\hat{\Sigma}] \tag{98}$$

and $\hat{\Sigma}$ becomes *nonrandom*. This property of $\hat{\Sigma}$, which is the object of consideration in conventional NMR, can be understood from the fact that it is an *ensemble average* quantity. Consistently, by scaling (92) [or the components of its ensemble average (93) and (95)] by $1/N^{1/2}$ in this limit, we obtain the system of deterministic differential equations:

$$d\hat{\Sigma} = -k\begin{pmatrix} \hat{\Sigma}^{\uparrow\uparrow} - p & \hat{\Sigma}^{\uparrow\downarrow} \\ * & - \end{pmatrix} dt. \tag{99}$$

Observe how the $1/N^{1/2}$ scaling removes the fluctuating terms in (92). The solution of this system is

$$\hat{\Sigma}_t^{\uparrow\uparrow} = p + (\hat{\Sigma}_0^{\uparrow\uparrow} - p)e^{-kt}, \quad \hat{\Sigma}_t^{\uparrow\downarrow} = \hat{\Sigma}_0^{\uparrow\downarrow}e^{-kt}. \tag{100}$$

Thus, for example, if $p = \frac{1}{2}$ (the case of zero field or infinite temperature), the asymptotic solution for $\hat{\Sigma}$ is proportional to the identity operator and the corresponding point in Fig. 1 is situated at the center of the Bloch ball. In this way, the deterministic results of conventional NMR are recovered, and moreover it is clear how they arise from the random fluctuations in the individual spins.

F. Unitarity and mixing

We examine how an initially pure state configuration evolves, with regard to unitarity and mixing and the effect of coupling with the lattice. For a system containing more than a single spin $N > 1$, in the absence of the lattice, it is immediate from the geometry we have described in Sec. II that an initial pure preparation (an ensemble with all component spins prepared in an identical pure state) evolves into a mixed state, via the following argument. For an ensemble, an initial pure state will evolve via stochastic evolution into an ensemble of distinct pure states, with probability one. Consider, then, the case of two spin states starting at the same point on the Bloch sphere which, at a later time, are situated at a pair of distinct points; the resulting ensemble is described by a mixed state whose density matrix is represented by the midpoint of the chord joining the two component pure states, in the solid *interior* of the Bloch sphere. Thus, it remains to study the case of a single spin $N = 1$. In the absence of the lattice, it is clear from the parametrization (16) that a pure state remains pure under stochastic evolution, which is rotational diffusion confined to the Bloch sphere according to (45). The situation in this respect when the effect of the lattice is included becomes more involved, however. We shall see that a state that is initially pure for the spin system evolves into a mixed state for the spin component $\mathcal{S}$ of the combined system $\mathcal{S} \otimes \mathcal{L}$, through its coupling with the lattice $\mathcal{L}$. Unitarity for the tensor product Hilbert space $\mathcal{H} = \mathcal{S} \otimes \mathcal{L}$ on which the full Hamiltonian acts requires that the combined state remain pure, although evolving into a random pure state in $\mathcal{S} \otimes \mathcal{L}$. To see how this arises explicitly, first we introduce Euclidean coordinates in the spinor representation

$$\sigma = \frac{1}{2}\begin{pmatrix} 1+z & x+iy \\ x-iy & 1-z \end{pmatrix}. \tag{101}$$

For a(n) (initial) pure state

$$x + iy = e^{i\phi}\sin\theta, \quad z = \cos\theta \tag{102}$$

so that (x,y,z) is a point on the (unit) Bloch sphere $x^2 + y^2 + z^2 = 1$. Now, a convenient measure of purity for a spin state is the determinant

$$D \doteq \sigma^{\uparrow\uparrow}\sigma^{\downarrow\downarrow} - \sigma^{\uparrow\downarrow}\sigma^{\uparrow\downarrow *}, \tag{103}$$

which we require to be constant for a pure state to remain pure under (stochastic) evolution. (The situation can be compared with two-component spinor geometry where the vanishing determinant corresponds to a null vector in Lorentzian space-time.) Dropping the process suffix t temporarily for notational simplicity, we obtain the (stochastic) differential

$$\begin{aligned} dD = {} & \sigma^{\uparrow\uparrow}d\sigma^{\downarrow\downarrow} + \sigma^{\downarrow\downarrow}d\sigma^{\uparrow\uparrow} + d\sigma^{\uparrow\uparrow}d\sigma^{\downarrow\downarrow} \\ & - \sigma^{\uparrow\downarrow}d\sigma^{\uparrow\downarrow *} - \sigma^{\uparrow\downarrow *}d\sigma^{\uparrow\downarrow} - d\sigma^{\uparrow\downarrow}d\sigma^{\uparrow\downarrow *}. \end{aligned} \tag{104}$$

This can be computed explicitly for a single spin using (92) and setting $N = 1$. Using the trace condition $\sigma^{\uparrow\uparrow} + \sigma^{\downarrow\downarrow} \equiv 1$, and its differential $d\sigma^{\uparrow\uparrow} = -d\sigma^{\downarrow\downarrow}$, we find

$$\begin{aligned} dD_t = {} & (1 - 2\sigma_t^{\uparrow\uparrow})\left[k(-\sigma_t^{\uparrow\uparrow} + p)dt - \sqrt{\frac{k}{6}}dW_t\right] - \frac{k}{6}dt \\ & - \left[\sigma_t^{\uparrow\downarrow}\left(-k\sigma_t^{\uparrow\downarrow *}dt + \sqrt{\frac{k}{3}}d\xi_t^*\right)\right. \\ & \left. + \sigma_t^{\uparrow\downarrow *}\left(-k\sigma_t^{\uparrow\downarrow}dt + \sqrt{\frac{k}{3}}d\xi_t\right) + \frac{k}{3}dt\right]. \end{aligned} \tag{105}$$

Observe that in the absence of fluctuations $k = 0$, there are no dynamics and this differential vanishes. The extra contribution to the differential of the determinant, due to the lattice, is evidently

$$dD_{\text{lattice}} = \tfrac{1}{2}k(1 - 2p)(\sigma^{\uparrow} - \sigma^{\downarrow}) \neq 0, \tag{106}$$

which is nonvanishing for $p \neq \frac{1}{2}$ unless the state is situated instantaneously on the equatorial plane, which occurs with probability measure zero. Thus, an effect of the lattice is that pure spin states evolve into mixed spin states, geometrically situated in the interior of the Bloch sphere in Fig. 1.

Removing the coupling with the lattice is mathematically equivalent to setting $p = \frac{1}{2}$, as evident from (92), for example. If we calculate dD_t explicitly in this case, we obtain a vanishing drift and a collection of fluctuating terms involving W_t, ξ_t which, on inspection using the results of Sec. III D, are seen also to vanish. This verifies what must be the case from the parametrization, namely, that in the absence of the lattice, a pure spin state remains pure under stochastic evolution. A corollary of this, via the spinor geometry of (101) and (103), is that a mixed spin state situated at a given radius in the Bloch ball remains on the concentric sphere of that radius under stochastic evolution.

IV. DISCUSSION

It is worthwhile to pinpoint the three separate time scales that arise in spin noise and relaxation, in an experimental context. The perturbation to the Hamiltonian has very rapid fluctuations on a time scale τ_c, corresponding to the rapid (rotational) motion of the nucleus in its magnetic environment and the precise nature of the interaction, e.g., dipole-dipole, chemical shielding, quadrupolar. This interaction is very weak so that, in mathematical terms, $k \ll 1$ in (41). The aforementioned weakness means that the motion of the density matrix, according to (30), is relatively *slow*, on a time scale τ_σ (even in the extreme narrowing approximation $\tau_c \approx 0$). These two time scales are inherent to the physical system under observation. A third time scale is the experimentally determined sample interval τ_s which, for observations of spin noise, should be chosen much less than the spin noise correlation time τ_σ (cf. [5]). Thus, a typical observation entails the following sequence of inequalities of three (independent) time scales:

$$\tau_c \ll \tau_s \ll \tau_\sigma. \tag{107}$$

The work is closely aligned to some issues in quantum foundations through the role of a random pure state, an essential ingredient in the derivation of the existence of spin noise (and therefore relaxation). In this paper, we have developed the idea that *a random pure state is both theoretically and experimentally distinct from a corresponding mixed state constructed from the asymptotic distribution pertaining to the former; moreover, spin noise is (an example of) experimental evidence of this distinction [5]*.

In relation to conventional NMR, our approach has shown how the approximations that Abragam [1] uses are justified within their domain of applicability, and we have demonstrated how the standard density matrix fits within our more general formulation. Our results reveal the intimate connections between spin noise and conventional spin relaxation. The advantage of this approach is both conceptual and experimental.

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