

## A Novel Relaxation Equation of Motion

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We present a novel form of the equation of motion from Bloch–Wangness–Redfield theory (BWRT) that is in a representation-independent operator form. The equation has no time restrictions on it and incorporates Boltzmann equilibrium. We show that this new form gives results consistent with traditional BWRT and limits to BWRT when the additional restrictions and approximations of BWRT are applied to the new equation of motion. The new form shows how the usual equations for relaxation may be easily modified to include detailed balance and to avoid the long-standing problem that certain relaxation rates incorrectly become large when the lattice fluctuation rates become small; that is, the relaxation rates determined from this new approach avoid the BWRT “catastrophe”. The new formulation leads to a more complete description of both longitudinal and transverse relaxation in magnetic resonance and takes into account the oscillatory nature of the relaxation of both transverse and longitudinal components in all motional regimes including the slow motion regime. The approach is of direct benefit to spectroscopists because it is described in terms of relaxation rates of observables.

### I. Introduction

Density matrix theory has been used in magnetic resonance (MR) in the form of Bloch–Wangness–Redfield theory (BWRT).<sup>1–3</sup> This theory has had enormous success and has been of practical utility to spectroscopists. However, there are two well-recognized flaws with BWRT.<sup>4</sup> The first is that it has been very difficult to reconcile approach of the system to thermal equilibrium with the original form of the equation of motion. In the original semiclassical form of BWRT, the system relaxes to zero not to a Boltzmann type equilibrium. This is equivalent to saying that detailed balance is not obeyed at finite temperature. A partial solution to this problem suggests that one replace the density matrix in the relaxation part of the BWRT equation of motion with the difference between the density matrix and its value at equilibrium.<sup>4</sup> However, this has the problem of still not fully satisfying detailed balance. Redfield addressed this issue in his original review article,<sup>3</sup> in which he noted the need for equilibrium terms and suggested where such terms needed to be placed in the relaxation expressions based primarily on the original treatment of Bloch.<sup>1</sup> The second problem with BWRT is that the predictions for the transverse relaxation rates go to infinity when the rates that describe lattice fluctuations approach zero. We find that both of these problems with BWRT may be overcome with minimal modifications to the existing theory. We develop the equations of motion of observables as well as the equation of motion of the density matrix; all expressions are kept in operator form and a basis set is never used to expand operators. We will show that this alternative formulation allows one to obtain insight over the traditional approach. This alternative form avoids approximations that are necessary when working directly with density matrix equations. We feel that casting the equations of motion in terms of observables is a more natural way for spectroscopists to think of relaxation. For the sake of clarity for a more general readership we do not use the super-operator formalism, which is the formalism of choice among many of the theoreticians in this field.<sup>5</sup> In the application section we show that the spin–

lattice and spin–spin relaxation rates, traditionally used in magnetic resonance, can be slightly modified to have more robust behavior.

Alternative methods have been developed to circumvent the drawbacks of traditional BWRT. The stochastic Liouville equation (SLE) approach has been widely used to simulate spectra where BWRT fails;<sup>6–8</sup> by which, variables driven by random processes are added to the total Hamiltonian representing bath or lattice coordinates. A SLE equation of motion for average density matrix components is inferred from a diffusion equation that governs the distribution of random variables representing the bath. The incorporation of the diffusion term for the random variables into the density matrix equation of motion parallels the derivation of the classical Langevin equation from Newton’s equation using randomly fluctuating forces. Defining quantum random bath variables is sufficiently complicated that a semiclassical treatment is typically sought. The cost of the semiclassical approach is that the equilibrium state remains undefined. However, unlike traditional BWRT the SLE does predict evolution of the density matrix even as the rate of bath fluctuations becomes arbitrarily slow. We compare the predictions of our reformulation of BWRT for spin–spin relaxation with the results of the SLE for the simple case of a two-site exchange process below and find exact correspondence of the two methods.<sup>7,8</sup>

The outline of the paper is as follows: In this section we introduce the basic equations of motion. In section II we develop the equation of motion for observables and the density matrix that we will use throughout. In section III we compare our results to the more traditional development of BWRT. (A more extensive treatment is found in Appendix C, Supporting Information.) In section IV we develop a specific form for the equilibrium quantum correlation functions (QCFs) for the lattice, following the work of Mazur and co-workers.<sup>9</sup> In section V we use the lattice correlation functions of section IV to obtain expressions for spin–lattice and spin–spin relaxation rates and

compare the new results with those of BWRT using a specific model for the QCF.

The fundamental equation of motion, of the combined system and lattice is

$$\frac{\partial \rho}{\partial t} = -i[H, \rho] \quad (1)$$

Here the complete Hamiltonian is the sum of the system (or spin),  $H_s$ , the lattice (or bath),  $H_l$ , and the coupling,  $H'$ , Hamiltonians:

$$H = H_o + H'$$

where  $H_o = H_s + H_l$ . The system and lattice Hamiltonians commute, and neither commutes with the coupling Hamiltonian. All Hamiltonians are in frequency units. We restrict our attention to coupling Hamiltonians that are bilinear,

$$H' = SF$$

Here  $S$  is a spin-system, Hermitian operator, and  $F$  is a bath-lattice, or handle, Hermitian operator. The development can be generalized to include coupling Hamiltonians that are sums of bilinear terms in a straightforward way. We consider only time independent Hamiltonians. The extension to time dependent Hamiltonians is possible, following what is done in other derivations.<sup>10</sup> Our restrictions here are made merely for the purposes of providing a simplified notation and a clear presentation of the equations of motion.

Corresponding to every observable of the system is a Hermitian operator,  $O_s$ . Any observable can be computed from the density matrix and the operator:  $\langle O_s \rangle = \text{tr}\{O_s \rho\}$ . The observables of the system can be written in terms of the expectation value of appropriate Hermitian operators. The complete set of all Hermitian operators,  $\{O_s\}$ , constitutes an operator basis set.<sup>11</sup> The density matrix equation of motion (1) can be rewritten into a *completely* equivalent equation in terms of the evolution of system observables, which is

$$\frac{d\langle O_s \rangle}{dt} = -i\langle [O_s, H_s] \rangle - \int_{\tau=0}^t \text{tr}\{([\tilde{O}_s(\tau), \tilde{S}(\tau)]S[\tilde{F}(\tau)F] - (F\tilde{F}(\tau)S[\tilde{O}_s(\tau), \tilde{S}(\tau)])\rho(t-\tau))\} d\tau \quad (2)$$

Here the system variables evolve only under the system Hamiltonian:

$$\tilde{S}(\tau) = U_s^\dagger(\tau) S U_s(\tau) \quad \text{where} \quad U_s(\tau) = e^{-i\tau H_s}$$

And the lattice variables evolve only under the lattice Hamiltonian:

$$\tilde{F}(\tau) = U_l^\dagger(\tau) F U_l(\tau) \quad \text{where} \quad U_l(\tau) = e^{-i\tau H_l}$$

Equation 2 is not a perturbation expansion. It is a reformulation of (1) as an integro-differential equation. Those unfamiliar with this equivalent form are encouraged to read Appendix A, Supporting Information. The development thus far parallels the approach of Zwanzig<sup>12</sup> in two respects: The relaxation term is in the form of a convolution integral over previous history; and the use of spin-system observables is similar to Zwanzig's use of projection operators. In the absence of any lattice coupling, system observables,  $\langle O_s \rangle$ , will evolve independently of the lattice and the first two terms of (2) constitute a proper, completely coherent equation for evolution of such observables. The

integrand on the rhs of eq 2, containing system–lattice coupling, leads to relaxation. The process by which (2) was obtained can be completely reversed to reconstruct eq 1. (See Appendix A.) We assumed in the development of (2), for simplicity and with no loss of generality, that the initial condition on the density matrix is such that the handle operator,  $F$ , is mean zero, i.e.,  $\text{tr}_l(\tilde{F}(t)\rho(0)) = 0$ , where the trace is taken over the lattice variables.

There are three general properties of eq 2 we wish to emphasize: The integrand inside the time integral of (2) is a pure real function of time, as may be seen by complex conjugation and permutation of operators under the trace. This guarantees that the values of the integral are always pure real. Second, the diagonal elements of the density matrix must remain nonnegative no matter what state  $\rho$  evolves into (positivity of the density matrix).<sup>11</sup> Positivity of the density matrix is ensured for eq 2 because of the exact equivalence of (2) with the original unitary equation of motion (1). Third, because eq 2 is just a reformulation of eq 1, the right-hand side (rhs) of (2) rigorously goes to zero when the density matrix is the Boltzmann equilibrium density matrix for the full Hamiltonian  $H = H_o + H'$ . It is our intention that the approximate equations that we develop in section II will retain these three features, which are characteristics of the exact formulation (2). However, we will use a density matrix that describes the evolution of the spin system alone. This is achieved by coupling the spin system to a lattice that is always at equilibrium. The idea of making the spin–lattice communication one way is common to most formulations that give an irreversible equation of motion. We differ, here, by how this assumption is implemented. We believe that the assumption of a dynamically independent lattice need not restrict the treatment of the spin system as severely as the assumptions of BWRT would indicate.

We make two standard approximations whose assumptions are coupled.<sup>4,10</sup> The first is that the density matrix can be written as the product of two density matrices: a lattice density matrix, which is always at equilibrium with its own Hamiltonian, ( $H_l$ ), oblivious to the system, and a spin-system density matrix that is otherwise arbitrary. The second approximation is that equilibrium for of the spin system is described by a Boltzmann density matrix with respect to its own Hamiltonian ( $H_s$ ) and at the same temperature as the lattice. The separation assumption is

$$\rho(t) = \rho_s(t) \cdot \rho_l^o = \rho_s(t) \cdot \frac{e^{-\hbar\beta \cdot H_l}}{\text{tr}\{e^{-\hbar\beta \cdot H_l}\}} \quad (3)$$

This assumption or ansatz is used in both magnetic resonance and the optical literature.<sup>5,13</sup> The question then is: Is there an equation of motion that can sustain both of these requirements but needs no modification of the convolution form or the memory form of the relaxation term found in eq 2? Goldman, in a recent review of BWRT, argues that it not possible and that one cannot know what happens to the spin density matrix at early times.<sup>10</sup> Our answer is yes, and we set about to find one such equation. The details are worked out in section II below. The final equation of motion for any spin-system observable, developed in section II, is

$$\frac{d\langle O_s \rangle}{dt} = -i\langle [O_s, H_s] \rangle - \Gamma[\rho_s, t] \quad (4)$$

where

$$\Gamma[\rho_s, t] = \text{tr}_s \left\{ O_s \int_{\tau=0}^t G(\tau, \beta) [S, U_s(\tau)] e^{-(\hbar\beta/2)H_s} \text{Se}^{(\hbar\beta/2)H_s} \rho_s(t-\tau) - \rho_s(t-\tau) e^{(\hbar\beta/2)H_s} \text{Se}^{-(\hbar\beta/2)H_s} U_s^\dagger(\tau) \right\} d\tau \quad (5)$$

Equation 5 is the central equation of this paper.  $\Gamma[\rho_s, t]$  is the relaxation contribution for the spin-system observable of interest and is a functional of the spin-system density matrix,  $\rho_s$ . The form of the terms in the integrand guarantees that  $\Gamma[\rho_s, t]$  is always pure real.  $G(\tau, \beta)$  is a generalized, real-valued, lattice correlation function that depends on both time,  $\tau$ , and reciprocal temperature,  $\beta = 1/k_B T$ , where  $k_B$  is Boltzmann's constant and  $T$  is the absolute temperature.  $G(\tau, \beta)$  will be given a precise definition in section II in terms of a quantum correlation function (QCF) that will be further elaborated upon in section IV. Boltzmann equilibrium and detailed balance enter into the equation of motion through the terms in the exponential operators containing  $\beta$ . These terms guarantee that when the system density matrix is at Boltzmann equilibrium the system is stationary; the integrand vanishes and  $\Gamma[\rho_s, t]$  does not change as a function of time. Thus, if the initial state is "close" to equilibrium then the system will relax to the equilibrium state defined by the Boltzmann density matrix for the spin system.

There is an associated equation of motion for the spin-system density matrix as well, which is easily obtained from (4) by projection of the observables. It is

$$\frac{d\rho_s(t)}{dt} = -i[H_s, \rho_s(t)] - \int_{\tau=0}^t G(\tau, \beta) ([S, U_s(\tau)] e^{-(\beta/2)\hbar H_s} \text{Se}^{+(\beta/2)\hbar H_s} \rho_s(t-\tau) - \rho_s(t-\tau) e^{+(\beta/2)\hbar H_s} \text{Se}^{-(\beta/2)\hbar H_s} U_s^\dagger(\tau)) d\tau \quad (6)$$

As noted, the assumption or ansatz of (3) is common to our approach and BWRT.<sup>3-5,14</sup> However, there is a distinction to be made in how this assumption was applied to arrive at eq 5. In BWRT, as will be discussed in section III and Appendix C, a time scale argument is concomitantly invoked. In BWRT the equations of motion are not to be interpreted on the time scale of lattice fluctuations, and the assumption of a lattice at constant and separate equilibrium is used to ascertain the solution to the equations of motion in an asymptotic sense. Goldman, in his extensive discussion of BWRT, emphasizes this point.<sup>10</sup>  $\rho_0 = \rho_s^0 \rho_l^0$  appears as a stationary solution to BWRT for all times; however, this is deceptive because the equation of motion is justified by the time scale argument. Thus, what constitutes an early time solution to the equation of motion is not well-defined elsewhere.<sup>10</sup> We develop an equation of motion that describes the evolution of the spin system from time zero. We imagine that the system and lattice are in contact and at equilibrium, in prehistory, where time is less than zero. Then at time zero, a pulse of energy is put selectively into the (spin) system such that the lattice is transparent to the pulse. The lattice density matrix will be sufficiently close to  $\rho_l^0$  because it is composed of many degrees of freedom. We view the pulse as effectively severing the spin-lattice communication, and ordering the spin density matrix arbitrarily. The pulse is turned off, and the system then evolves under the full Hamiltonian, where the density matrix is  $\rho(0) = \rho_s(0)\rho_l^0$  at time zero and  $\rho_s(0)$  is no longer the system equilibrium density matrix.

## II. Derivation of Eqs 4 and 5

The expression we seek is found by treating the effect of the lattice on the (spin) system in terms of quantum correlation functions (QCFs) defined under lattice equilibrium. To connect with correlation functions for the lattice, we invoke the assumption already introduced above (3):  $\rho(t) = \rho_s(t)\rho_l^0$ . This allows us to write the trace over the lattice in (2) in terms of correlation functions for of lattice variables alone at equilibrium. We define the quantum mechanical correlation function, QCF,  $C(\tau)$  for the lattice variable by the following relation:  $C(\tau) = \text{tr}_{\text{latt}}\{\tilde{F}(\tau)F\rho_l^0\} = \langle \tilde{F}(\tau)F \rangle_{\text{eq}}$ .

It follows from this definition and the product form of the density matrixes that  $\text{tr}_{\text{latt}}\{\tilde{F}(\tau)F\rho(t-\tau)\} = C(\tau)\rho_s(t-\tau)$ . From this definition of the correlation function we notice that the conjugate is  $C^*(\tau) = \text{tr}_{\text{latt}}\{F\tilde{F}(\tau)\rho_l^0\}$ . By assuming that the lattice is always at equilibrium, the quantum correlation functions represent stationary processes, i.e.,  $\langle \tilde{F}(t_1)F(t_2) \rangle_{\text{eq}} = \langle \tilde{F}(t_1-t_2)F \rangle_{\text{eq}}$ , and have special properties, which directly follow from the above definitions. The ones we will use are the following:<sup>5,13,14</sup>

$$\begin{aligned} C^*(\tau) &= C(\tau - i\hbar\beta) \\ C^*(\tau) &= C(-\tau) \quad \text{when } \tau \text{ is pure real} \\ C^*(iy) &= C(iy), \quad \text{or} \quad C(iy) \quad \text{is real for } y \text{ real} \\ C^*\left(t - i\frac{\hbar\beta}{2}\right) &= C\left(t - i\frac{\hbar\beta}{2}\right), \quad \text{or} \quad C\left(t - i\frac{\hbar\beta}{2}\right) \quad \text{is real and is an even function of } t \end{aligned}$$

It may seem a bit odd that the time argument can be complex and that we have  $\beta$  in the time argument. The evolution operator,  $U_1$ , and the equilibrium lattice density matrix,  $\rho_l^0$ , both depend on  $H_1$  as an argument in an exponential. The equilibrium lattice density matrix can be written in terms of the evolution operator with an imaginary argument. It is this correspondence that allows us to use imaginary time arguments in the correlation function with units of  $i\hbar\beta$ . We have included Appendix B (Supporting Information) for those unfamiliar with these relations.

When the separation ansatz is applied to the relaxation term in (2) it becomes

$$\frac{d\langle O_s \rangle}{dt} = -i\langle [O_s, H_s] \rangle - \Gamma[\rho_s, t] \quad (7)$$

$$\Gamma[\rho_s, t] = \int_{\tau=0}^t \text{tr}_s \{ [\tilde{O}_s(\tau), \tilde{S}(\tau)] S C(\tau) \rho_s(t-\tau) \} d\tau + \int_{\tau=0}^t \text{tr}_s \{ \rho_s(t-\tau) (C^*(\tau) S [\tilde{S}(\tau), \tilde{O}_s(\tau)]) \} d\tau$$

The function  $\Gamma[\rho_s, t]$  represents the relaxation contribution to any spin-system observable from the QCF of the lattice. There is an equivalent equation then for the spin-system density matrix:

$$\frac{d\rho_s(t)}{dt} = -i[H_s, \rho_s(t)] - \int_{\tau=0}^t (C(\tau)[S, U_s(\tau)S\rho_s(t-\tau)U_s^\dagger(\tau)] - C^*(\tau)[S, U_s(\tau)\rho_s(t-\tau)SU_s^\dagger(\tau)]) d\tau \quad (8)$$

The exact form in eq 2 has important features that must also be reflected in the new form of the equation of motion (7). The first feature is that the two parts of the integrand in (2) and of  $\Gamma[\rho, t]$  in (7) are Hermitian conjugates of one another. This implies that  $\Gamma[\rho, t]$  is pure real at all times when  $O_s$  is a Hermitian operator. The second feature is that the rhs of eq 2 vanishes when the entire system is at Boltzmann equilibrium. It is desirable that the integrand in (7) should vanish when the spin system is at Boltzmann equilibrium, because the first term vanishes at equilibrium.

To find a form of the equation of motion (7) that preserves the conjugation symmetry between the two distinct terms and allows the QCF to be factored, we perform the following change of variables on the two integrals of (7):

In the first integral, we do a change of variables to let  $z = \tau + i\hbar\beta/2$  and in the second integral we apply the correlation function identity  $C^*(\tau) = C(\tau - i\hbar\beta)$  and then do a change of variables to let  $z = \tau - i\hbar\beta/2$ . With these changes of integration variables on each of the two parts of the integral we have

$$\Gamma[\rho_s, t] = \text{tr}_s \left\{ O_s \left[ \int_{z=0+i(\hbar\beta/2)}^{t+i(\hbar\beta/2)} C\left(z - i\frac{\hbar\beta}{2}\right) \left[ S, U_s\left(z - i\frac{\hbar\beta}{2}\right) S\rho_s\left(t - z + i\frac{\hbar\beta}{2}\right) U_s^{-1}\left(z - i\frac{\hbar\beta}{2}\right) \right] dz - \int_{z=0-i(\hbar\beta/2)}^{t-i(\hbar\beta/2)} C\left(z - i\frac{\hbar\beta}{2}\right) \left[ S, U_s\left(z + i\frac{\hbar\beta}{2}\right) \rho_s\left(t - z - i\frac{\hbar\beta}{2}\right) SU_s^{-1}\left(z + i\frac{\hbar\beta}{2}\right) \right] dz \right] \right\}$$

The integration of these functions in the complex plane is well behaved, because both the time dependence due to the rotating frame acting on the spin operators and the lattice correlation functions are entire functions when extended to the complex plane. It seems reasonable then that the density matrix can be extended as an analytic function into the complex plane.

Cauchy's integral theorem, which states that the closed-contour integral must be the sum of the residues inside (which is zero in this case), may be used to rewrite this expression. Cauchy's integral theorem is applied to these two integrals separately: each integral is written in terms of the integrals over the real axis and the two integrals going on the imaginary axis from 0 to  $\pm i\hbar\beta/2$  at time 0 and time  $t$ . Therefore

$$\Gamma[\rho_s, t] = \text{tr}_s \left\{ O_s \left[ \int_{z=0}^t C\left(z - i\frac{\hbar\beta}{2}\right) \left[ S, U_s\left(z - i\frac{\hbar\beta}{2}\right) S\rho_s\left(t - z + i\frac{\hbar\beta}{2}\right) U_s^{-1}\left(z - i\frac{\hbar\beta}{2}\right) \right] dz - \int_{z=0}^t C\left(z - i\frac{\hbar\beta}{2}\right) \left[ S, U_s\left(z + i\frac{\hbar\beta}{2}\right) \rho_s\left(t - z - i\frac{\hbar\beta}{2}\right) SU_s^{-1}\left(z + i\frac{\hbar\beta}{2}\right) \right] dz \right] \right\} + \text{EI} \quad (9)$$

The extra integrals, or end-cap integrals, EI, are the integrals along the imaginary time (i.e., temperature) axis. And they may be written as

$$\text{EI} = \text{tr}_s \left\{ O_s \left[ \int_{z=0+i(\hbar\beta/2)}^0 C\left(z - i\frac{\hbar\beta}{2}\right) \left[ S, U_s\left(z - i\frac{\hbar\beta}{2}\right) S\rho_s\left(t - z + i\frac{\hbar\beta}{2}\right) U_s^{-1}\left(z - i\frac{\hbar\beta}{2}\right) \right] dz - \int_{z=0-i(\hbar\beta/2)}^0 C\left(z - i\frac{\hbar\beta}{2}\right) \left[ S, U_s\left(z + i\frac{\hbar\beta}{2}\right) \rho_s\left(t - z - i\frac{\hbar\beta}{2}\right) SU_s^{-1}\left(z + i\frac{\hbar\beta}{2}\right) \right] dz \right] \right\} + \text{tr}_s \left\{ O_s \left[ \int_{z=t+i0}^{t+i(\hbar\beta/2)} C\left(z - i\frac{\hbar\beta}{2}\right) \left[ S, U_s\left(z - i\frac{\hbar\beta}{2}\right) S\rho_s\left(t - z + i\frac{\hbar\beta}{2}\right) U_s^{-1}\left(z - i\frac{\hbar\beta}{2}\right) \right] dz - \int_{z=t+i0}^{t-i(\hbar\beta/2)} C\left(z - i\frac{\hbar\beta}{2}\right) \left[ S, U_s\left(z + i\frac{\hbar\beta}{2}\right) \rho_s\left(t - z - i\frac{\hbar\beta}{2}\right) SU_s^{-1}\left(z + i\frac{\hbar\beta}{2}\right) \right] dz \right] \right\}$$

Equation 9 may be written as (carrying along the EI terms)

$$\Gamma[\rho_s, t] = \text{tr}_s \left\{ O_s \left[ \int_{z=0}^t C\left(z - i\frac{\hbar\beta}{2}\right) \left[ S, U_s(\tau) e^{-(\beta/2)\hbar H_s} S\rho_s\left(t - \tau + i\frac{\hbar\beta}{2}\right) e^{+(\beta/2)\hbar H_s} U_s^\dagger(\tau) \right] d\tau - \int_{z=0}^t C\left(z - i\frac{\hbar\beta}{2}\right) \left[ S, U_s(\tau) e^{+(\beta/2)\hbar H_s} \rho_s\left(t - \tau - i\frac{\hbar\beta}{2}\right) S e^{-(\beta/2)\hbar H_s} U_s^\dagger(\tau) \right] d\tau \right] \right\} + \text{EI} \quad (10)$$

On the basis of our desire to have a form for  $\Gamma[\rho_s, t]$  that vanishes when  $\rho_s = e^{-\beta\hbar H_s/z_s}$ , we choose to neglect the extra integral, EI, terms. Direct inspection of the two remaining integrals in (10) shows that the integrands sum to zero when the spin density matrix is replaced by the Boltzmann equilibrium.

We need to relate the spin density matrix in the complex plane to that on the real axis. There is no exact method for extending the system density matrix off the real axis. Therefore, we suggest the simple prescription that

$$e^{-(\beta/2)\hbar H_s} \rho_s\left(t - \tau + i\frac{\hbar\beta}{2}\right) e^{+(\beta/2)\hbar H_s} \rightarrow \rho_s(t - \tau) \quad (11)$$

This is similar to the principle governing evolution by unitary operators. As an example: when the spin density matrix evolves under the spin Hamiltonian as  $\dot{\rho}_s = -i[H_s, \rho_s]$ , then it follows that  $\rho_s(t) = U_s(\tau) \rho_s(t-\tau) U_s^\dagger(\tau)$ . The approximation in (11) is analogous to the "slow moving" approximation for real values of the argument of the density matrix, which is based upon the idea that the density matrix evolution is dominated by the rotating frame motion generated by  $U_s(t)$ . We do not wish to invoke the "slow moving" approximation for the time arguments (real valued arguments), which is one of the time scale assumptions of BWRT.<sup>10</sup> The criterion for "slow evolution" of the density matrix under complex arguments need not in principle be governed by the same magnitude restriction as the real arguments. If, however, it is assumed that the same restriction applied to both real and complex numbers, the "time scale" of  $\hbar\beta$  is only competitive with frequencies on the order of  $10^{11}$  to  $10^{13}$  Hz over temperatures from 1 to



400 K, respectively. This means that the “slow moving” approximation would apply for most MR applications (frequencies below 100 GHz) over a wide temperature range.

Therefore, we substitute (11) into (10) and drop the EI terms to obtain

$$\Gamma[\rho_s, t] = \text{tr}_s \left\{ O_s \int_{\tau=0}^t C \left( \tau - i \frac{\hbar\beta}{2} \right) \left[ [S, U_s(\tau) e^{-(\beta/2)\hbar H_s} S e^{+(\beta/2)\hbar H_s} \rho_s(t-\tau) U_s^\dagger(\tau)] - [S, U_s(\tau) \rho_s(t-\tau) e^{+(\beta/2)\hbar H_s} S e^{-(\beta/2)\hbar H_s} U_s^\dagger(\tau)] \right] d\tau \right\} \quad (12)$$

This expression for  $\Gamma[\rho_s, t]$  is the relaxation part of a practical equation of motion that incorporates the Boltzmann equilibrium in an operator form and guarantees that the integrand to  $\Gamma[\rho_s, t]$  vanishes when the (spin) system density matrix is at its own Boltzmann equilibrium. The Cauchy integral theorem enabled us to transfer the equilibrium property of the lattice to that of the system. Inspection of the use of the QCF in the derivation of eq 12 illustrates that the complex nature of the QCF was necessary to establish detailed balance. For example, if the QCF is assumed to be real from the outset, then eq 8 assumes precisely the same form as eq 12, but with  $\beta$  set equal to zero. The complex valued nature of the QCF arises from the noncommutivity of the lattice operators referring to different times. Two commonly known formulations of relaxation theory demonstrate this. When transition rates among the diagonal elements of the density matrix are calculated with Fermi’s Golden rule, the noncommutivity of the lattice operators establishes the main difference between forward and backward rate processes,<sup>15</sup> as shown in Appendix D (Supporting Information). Also, it has been recognized historically that the quantum nature of the lattice variables are essential for inclusion of equilibrium itself, as illustrated in the semiclassical formulations of relaxation theory, which lack any sense of equilibrium.<sup>3</sup>

The form of the QCF of (12) contains a complex argument but is itself always a real valued function. This form of  $\Gamma[\rho_s, t]$  guarantees that the relaxation term is pure real for all time when the spin observable is Hermitian. We note that the original separation of the density matrix into a product of spin and lattice parts was made to have QCFs defined in terms of the lattice equilibrium alone. The additional approximations that we have made have been done to restore properties to the relaxation term  $\Gamma[\rho, t]$  that existed in the original form and were destroyed by the approximation associated with using equilibrium QCFs of the lattice. The two additional approximations we made were (1) neglecting the end-cap integrals and (2) rotation of the system density matrix back to the real axis. The derivation of (5) is complete when we identify the real correlation function,  $G(\tau, \beta)$ , as

$$G(\tau, \beta) = C \left( \tau - i \frac{\hbar\beta}{2} \right) \quad (13)$$

This gives a precise definition of a generalized real correlation function used in (5) in terms of a QCF. The use of the correlation function (13) in a practical equation of motion is novel to this paper.

Inserting  $O_s = 1$  in eq 12 shows that the trace of the spin-system density matrix is conserved. Whether the convolution eq 12 preserves positivity of the spin-system density matrix remains to be shown. It is well-known that the traditional BWRT equation of motion need not preserve positivity.<sup>13</sup> Necessary and sufficient criteria have been developed that ensure positivity under the assumption of a Markov master equation (equations of motion containing no memory effects).<sup>16</sup> The equation of motion from BWRT is an example of a master equation that is Markovian, but which does not satisfy the criteria necessary for positivity. The lack of positivity in the BWRT master equation has been ascribed to the standard approximations that remove memory effects of the type that we have retained in the convolution equation (12).<sup>17</sup> Sufficient conditions for positivity of a class of non-Markovian (convolution) equations have been developed by extension of the criteria for Markovian master equations, but eq 12 does not fit within this class.<sup>18</sup> The necessary conditions that restrict the form of the integrand of a convolution master equation have not been developed to our knowledge. We leave the question of whether the particular convolution form (12) guarantees positivity as an open question; given that there are no relevant general proofs or constructs guaranteed to give both the necessary and sufficient conditions for positivity within a memory form of the equation of motion. However, as a first step toward showing positivity, the temperature operators (such as  $e^{-(\beta/2)\hbar H_s}$ ) can be partitioned equally over all operators in eq 12. Then, for example, the equation of motion governs  $e^{+(\beta/4)\hbar H_s} \rho_s(t) e^{-(\beta/4)\hbar H_s}$  and its Hermitian conjugate. The observables  $O_s$  then also similarly transform. Positivity, if provable for  $e^{+(\beta/4)\hbar H_s} \rho_s(t) e^{-(\beta/4)\hbar H_s}$ , then gives positivity of the density matrix because the temperature transformations are positive definite operators. Therefore, the presence of the temperature-dependent operators would appear to add no more difficulty to the issues of whether the density matrix will preserve positivity.

### III. Relation of Eq 12 to Previous Treatments

We now compare the equation of motion (5) to the well-known form of BWRT developed by Abragam<sup>4</sup> and amplified by Goldman.<sup>10</sup> Two additional approximations, extensively discussed in Goldman’s paper,<sup>10</sup> are needed to derive the BWRT equation of motion from (5) and (12). First, the time dependence of the density matrix on the integration variable is removed by the approximate transformation:  $U_s(\tau) \rho_s(t-\tau) U_s^\dagger(\tau) \rightarrow \rho_s(t)$ . Second, the limit of time integration is taken to infinity:  $\int_0^t \rightarrow \int_0^\infty$ . These two approximations are generally taken concomitantly because their validity depends on the fast decay of the lattice correlation function, relative to the spin density matrix. These are similar to the approximations inherent in transition rate theory (Appendix D). With these approximations eq 5 becomes

$$\frac{d\langle O_s \rangle}{dt} = -i\langle [O_s, H_s] \rangle - \text{tr}_s \left\{ O_s \int_{\tau=0}^\infty G(\tau, \beta) [S, e^{-(\hbar\beta/2)H_s} \tilde{S}(-\tau) e^{(\hbar\beta/2)H_s} \rho_s(t) - \rho_s(t) e^{(\hbar\beta/2)H_s} \tilde{S}(-\tau) e^{-(\hbar\beta/2)H_s}] d\tau \right\} \quad (14)$$

The infinite temperature limit gives the conventional “double commutator” form of the master equation that is found when the lattice is treated semiclassically within the BWRT framework.<sup>3</sup> Equation 14 is related to Goldman’s finite temperature master equation<sup>10</sup> in Appendix C.

The temperature operators,  $e^{\pm(\hbar\beta/2)H_s}$ , in (14) enforce detailed balance at finite temperature. Each of the three terms on both sides of (14) vanishes individually when the spin density matrix assumes its equilibrium value,  $\rho_s(t) \rightarrow \rho_o = e^{-\beta\hbar H_s/z_s}$ . Consequently, the substitution  $\rho \rightarrow \rho - \rho_o$  can be made in the integrand on the rhs of eq 14, to give the equivalent form

$$\frac{d\langle O_s \rangle}{dt} = -i\langle [O_s, H_s] \rangle - \text{tr}_s \left\{ O_s \int_{\tau=0}^{\infty} G(\tau, \beta) [S, e^{-(\hbar\beta/2)H_s} \times \tilde{S}(-\tau) e^{(\hbar\beta/2)H_s} (\rho_s(t) - \rho_o) - (\rho_s(t) - \rho_o) e^{(\hbar\beta/2)H_s} \times \tilde{S}(-\tau) e^{-(\hbar\beta/2)H_s}] d\tau \right\} \quad (15)$$

The linear  $\beta$  temperature limit of (15) is now considered. The correlation function (13) is simply  $\text{Re}(C(\tau))$  in the linear  $\beta$  limit (see Appendix B). The temperature operators in the integrand of (15) are expanded in powers of  $\beta$  using the Baker–Campbell–Hausdorff series.

$$e^{-(\hbar\beta/2)H_s} \tilde{S}(-\tau) e^{(\hbar\beta/2)H_s} = \tilde{S}(-\tau) + \frac{\hbar\beta}{2} [\tilde{S}(-\tau), H_s] + O(\geq (\hbar\beta)^2)$$

To achieve simplification of (15), it must be assumed, in addition, that the density matrix is always sufficiently near equilibrium that  $\rho_s(t) - \rho_o = O(\geq \hbar\beta)$ . The latter assumption is the same as the standard assumption  $\rho(t)\rho_o^{-1} = 1 + O(\geq \hbar\beta) = \rho_o^{-1}\rho(t)$  used in the traditional derivation of the high-temperature equation of motion of BWRT.<sup>4,10</sup>

Equation 15, with the assumption that the density matrix is near equilibrium, and keeping terms only to linear order in  $\beta$ , becomes

$$\frac{d\langle O_s \rangle}{dt} = -i\langle [O_s, H_s] \rangle - \text{tr}_s \left\{ O_s \int_{\tau=0}^{\infty} \text{Re}(C(\tau)) [S, [\tilde{S}(-\tau), \rho_s(t) - \rho_o]] d\tau \right\} \quad (16)$$

The derivation of eq 16 shows that the effect of the temperature operators in (14) is the same as simply inserting the difference density matrix into the semiclassical double commutator form of the relaxation term from BWRT. It was demonstrated that this is only possible, however, by assuming a restricted density matrix that is near equilibrium, in the high-temperature limit. In conclusion, eq 12 may be cast in a form identical to BWRT by applying the same approximations that are used within BWRT.

#### IV. Development of the Correlation and Spectral Density Functions

The previous section developed the master equation under the approximation that the limit of the time integration could go to infinity (and the density matrix could be written in terms of time, independently of the variable of integration). We now remove those restrictions and go back to the fundamental form of the equation of motion (eq 5) to develop the lattice correlation functions that will be used in this master equation. With the lattice correlation functions we can concretely demonstrate how (spin) system observables are relaxed by the lattice toward equilibrium as a function of time. Here we begin with (5) or (12), which can be written equivalently as

$$\Gamma[\rho_s, t] = \int_{\tau=0}^t C\left(\tau - \frac{\hbar\beta}{2}\right) \text{tr}_s \left\{ [\tilde{O}_s(\tau), \tilde{S}(\tau)] e^{-(\hbar\beta/2)H_s} S e^{(\hbar\beta/2)H_s} \times \rho_s(t-\tau) + \text{H.C.} \right\} d\tau \quad (17)$$

H.C. stands for the Hermitian conjugate of the previous term. We have already shown that the use of Cauchy's integral theorem allowed for the transfer of Boltzmann equilibrium from the lattice to the (spin) system. The QCF,  $C(t - i\hbar\beta/2)$ , is a correlation function of the lattice. This correlation function evolves with frequencies associated with the lattice, not the system. We now explore how the correlation function transfers motion from the lattice to the (spin) system. The transfer of motion is solved in the Abragam–Goldman approach, in which the time integral is extended to infinity, by the Dirac  $\delta$  function that arises from a Fourier transform of a complex exponential at the difference of the (spin) system and lattice frequencies. The use of the  $\delta$  function in the context of the Abragam–Goldman approach is in keeping with the asymptotic solution found in that work. Physically, however, multiple frequency modes of the lattice contribute to spin relaxation at early times and are only limited as time goes to infinity, in keeping with the Fourier time/frequency relation. Therefore, we explore the consequences of considering the equations of motion at all times.

To proceed further, we need a model of the QCF,  $C(t - i\hbar\beta/2)$ , and for this we rely heavily on the work of Mazur.<sup>9</sup> The correlation functions that are used in practical formulations of magnetic resonance represent Gaussian Markov random processes. Mazur and co-workers have discussed how a mechanical model of the lattice (consisting of coupled harmonic oscillators) can produce the relations among correlation functions necessary for a Gaussian Markov process. Namely, exponentially decaying correlation functions are obtained in the limit of an infinite number of bath oscillators for an appropriate choice of coupling constants among the harmonic oscillators. Their analysis was carried out for both a classical system, and a quantum system. To make the connection to a Gaussian Markov process, in the quantum case, a canonical operator order of the quantum correlation functions was imposed, with the result that the ordered correlation functions were real.

Our system is like one oscillator connected to, or part of, a bath of similar oscillators. We want to know how that one oscillator evolves. In particular, we seek Markovian behavior, i.e., a characteristic exponential decay of the oscillator auto-correlation function as a result of being coupled to all the other oscillators. This implies a choice of coupling constants among the oscillators of the system. An alternative, equally valid, view is from the perspective normal modes, which oscillate with pure trigonometric correlation functions. Mazur showed that the choice of classical oscillator coupling constants needed to reproduce exponential decay of the classical auto correlation function of any particular oscillator chosen out of the assembly implies that the normal modes of the lattice have a Lorentzian power spectrum. The choice of coupling constants of the oscillators is equivalent to a choice of eigenfrequencies for the normal modes. The correlation functions are simply a weighted arithmetic average of the trigonometric mode functions over the spread of eigenfrequencies.

In the quantum case, with the canonical ordering in force, the correlation functions are the same simple trigonometric forms as in the classical case, but now include temperature-dependent amplitudes. Removing all temperature dependence from the power spectrum, in the quantum case, necessitates that the coupling constants would be temperature dependent. To avoid this problematic state of affairs, Mazur proposed using the classical spectrum of the eigenfrequencies without modification.<sup>9</sup> This implies that the *power spectrum* of the quantum correlation functions is Lorentzian with a temperature-dependent prefactor. The result of this is a quantum correlation function

that has both temperature and a correlation time as adjustable parameters. A correlation time is by definition given by the coupling constants of the lattice necessary to produce exponential decay at high temperature.

We follow Mazur's procedure and construct an assembly of noninteracting two-level systems having level separations (frequencies) distributed in analogy to the frequencies of the normal modes in his model. The dynamics of the two-level assembly in the high-temperature limit are formally equivalent to the lattice of normal mode eigenfunctions, running at frequency  $\omega_l$ . The QCF for a two-level system with the particular operator order indicated is

$$C_{\omega_l}(t) = \langle \tilde{F}(t)F \rangle_{\omega_l} = f_L^2 \left\{ \cos(\omega_l \cdot t) - i \tanh\left(\frac{\hbar\omega_l}{2}\right) \sin(\omega_l \cdot t) \right\}$$

See Appendix B. Just as Mazur et al. imposed a canonical ordering to ensure that their correlation functions were real, we obtain a real form for the expressions used in the relaxation master equations:

$$C_{\omega_l}\left(\tau - i\frac{\hbar\beta}{2}\right) = f_L^2 \frac{\cos(\omega_l \cdot \tau)}{\cosh(\hbar\omega_l \cdot \beta/2)}$$

The total correlation function for the assembly is the Lorentzian weighted average of oscillators over the frequencies  $\omega_l$ . The power spectrum representation of the lattice correlation function for the assembly of two-level systems is, in analogy to Mazur's development:

$$\begin{aligned} G(\tau, \beta) &= C_{\text{total}}\left(\tau - i\frac{\hbar\beta}{2}\right) \\ &= \frac{2}{\pi} \int_0^\infty \frac{1/\tau_c}{\omega_l^2 + (1/\tau_c)^2} C_{\omega_l}\left(\tau - i\frac{\hbar\beta}{2}\right) d\omega_l \\ &= \frac{2}{\pi} \int_0^\infty \frac{1}{\cosh(\hbar\omega \cdot \beta/2)} \frac{f_L^2/\tau_c}{\omega^2 + (1/\tau_c)^2} \cos(\omega \cdot \tau) d\omega \quad (18) \end{aligned}$$

It should be noted that the integration limits defining the total correlation function can be symmetrized due to the frequency symmetry of the two-level correlation function. This form of the correlation function vanishes in the zero-temperature limit, as can be shown using Cauchy's residue theorem by using the poles of the Lorentzian part of the integral. The vanishing of the correlation function is due to the vanishing of the amplitude of the lattice fluctuation. This is an advantage over alternative formulations that exhibit residual zero-point energy effects in the zero-temperature limit, as emphasized by Mazur.<sup>9</sup> For low temperature applications, however, zero-point fluctuations can be restored in the QCF though a procedure outlined by Mazur. The difficulty presented by zero-point energy is that the limit of an infinite lattice is ill-defined because an infinite quantity of zero-point energies are summed. Intuitively, if the lattice is limited to a large, but finite, number of oscillators, the truncation of the lattice size will result in an upper limit to the normal-mode eigenfrequencies of lattice fluctuations, and therefore, the integral in (18) must contain a cutoff. To include zero-point energy, the spectral density in (18) is simultaneously modified by the addition of Lorentzian-weighted zero-point energy. This new term would diverge if it were not for the simultaneous cutoff on the frequency integral. The applications presented

below do not focus on the zero-temperature limit, so the simpler form of the QCF (18) is used.

In the high-temperature, linear  $\beta$ , limit (18) becomes a single-exponential decaying with characteristic time,  $\tau_c$ , because  $\cosh(\hbar\omega \cdot \beta/2) \rightarrow 1$  and the correlation function then becomes the Fourier transform of a Lorentzian distribution.

Inserting the model correlation function (18) into (17), and interchanging the order of integration, gives

$$\Gamma[\rho_s, t] = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{J(\omega)}{\cosh(\hbar\omega \cdot \beta/2)} \left( \int_0^t \cos(\omega \cdot \tau) \text{tr}_s \{ [\tilde{O}_s(\tau), \tilde{S}(\tau)] \times e^{-(\hbar\beta/2)H_s} S e^{(\hbar\beta/2)H_s} \rho_s(t-\tau) + \text{H.C.} \} d\tau \right) d\omega$$

where the Lorentzian distribution is recognized as the conventional spectral density,  $J(\omega) = f_o^2 \tau_c / [1 + (\omega \tau_c)^2]$  with  $f_o^2 = f_{\text{SL}}^2 f_L^2$ ; that is we include both the amplitude of the true lattice-only fluctuations,  $f_L$ , with the spin-lattice coupling amplitude,  $f_{\text{SL}}$ , inherent from the definition of  $H' = SF$ . The finite time integral now connects the lattice frequencies,  $\omega$  or  $\omega_l$ , to the spin-system frequencies,  $\omega_s$ , that are present in the spin operator,  $\tilde{S}(\tau)$ . As will be demonstrated below, as time increases, the finite time integral selects only those lattice frequencies that match the spin-system frequencies and reflects the well-known Fourier time/frequency uncertainty relation that must be present in any theory that claims to evolve literally from time zero. At early times all lattice frequencies initially contribute to the total relaxation through the integral over the spectral density. As time increases, those frequencies are windowed down to frequencies near the spin-system frequencies. As time goes to infinity the windowing becomes a Dirac  $\delta$  and the lattice frequencies that contribute to relaxation must exactly match the spin-system frequencies.

The full equation of motion is now

$$\begin{aligned} \frac{d\langle O_s \rangle}{dt} &= -i \langle [O_s, H_s] \rangle - \\ &\int_0^t G(\tau, \beta) \text{tr}_s \{ [\tilde{O}_s(\tau), \tilde{S}(\tau)] (e^{-(\hbar\beta/2)H_s} S e^{(\hbar\beta/2)H_s} \rho_s(t-\tau) - \rho_s(t-\tau) e^{(\hbar\beta/2)H_s} S e^{-(\hbar\beta/2)H_s}) \} d\tau \quad (19) \end{aligned}$$

where

$$G(\tau, \beta) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{J(\omega)}{\cosh(\hbar\omega \cdot \beta/2)} \cos(\omega \tau) d\omega \quad (20)$$

This expression is the most profound one of this paper and is readily adaptable to practical application and usable for a wide range of problems. The choice of a Lorentzian form for  $J(\omega)$  was for convenience for motivating the result. The form of the spectral density function,  $J(\omega)$ , is arbitrary (as long as it is real) and may be chosen as appropriate for the problem of interest. Moreover,  $J(\omega)$  may be obtained from the correlation function in the classical limit.

Three points can be emphasized:

(1) Permuting the spin operators puts the rotating frame back on the density matrix. The usual time scale assumptions may be applied to the density matrix and integrand to get back to the BWRT form discussed above eq 14. The only step that has been taken is to use a specific form of the lattice correlation function.

(2) Because the integrand of the relaxation term vanishes when the Boltzmann spin density matrix is substituted for  $\rho_s(t-\tau)$ ,  $\rho_s(t-\tau)$  may be replaced by  $\rho_s(t-\tau) - \rho_s^o$  without affecting the term. This is the operator analogy to the situation



encountered in simple relaxation theory (see Appendix C). Namely, when rate elements satisfy detailed balance there is no difference in the governing rate laws if the equilibrium solution is removed from each element of the relaxation populations. It is important to realize that this follows from the fact that detailed balance is included in (19). The converse—if the form of the relaxation equation contains  $\rho_s(t-\tau) - \rho_s^0$ , then detailed balance holds—is *not* necessarily true; see Appendices C and D.

(3) The symmetry of the relaxation term under conjugation is still preserved. Therefore,  $\Gamma[\rho_s, t]$  remains pure real in (19). The construction of the correlation function requires that it remain pure real regardless of the particular model. This was required for the QCF,  $G(t, \beta)$ , and thus symmetry of the integrand of the relaxation term,  $\Gamma[\rho_s, t]$ , is preserved and remains pure real, as was implied in eq 5.

### V. Three Examples and Applications to MR

Equation 5 or 19 is unique in that the time is explicitly retained in the integral and the integrand is a convolution with the density matrix over all previous times. There has never been a worked example of relaxation, through equilibrium correlation functions in the MR literature, which explicitly involves time. Therefore, it is important to develop simple examples of this new form of relaxation and compare with previous results obtained using the more conventional forms. We now consider the spin–spin relaxation rate,  $R_2 = 1/T_2$ , and spin–lattice relaxation rate,  $R_1 = 1/T_1$ . In all of our examples the spin-system Hamiltonian will be  $H_s = \omega_s S_z$ , and the model for the lattice (developed in section IV) will be that of an ensemble of two-state systems, which is coupled to the spin system.

#### Example 1: Spin–Lattice Relaxation for a Spin $j$ System.

The system observable associated with spin–lattice relaxation is  $O_s = S_z$ . For simplicity we consider the spin–lattice coupling to be of the form  $H' = F \cdot S_x$ . The integrand of the relaxation term in (12) is

$$\text{tr}_s \{ [\tilde{O}_s(\tau), \tilde{S}(\tau)] (e^{-(\hbar\beta/2)H_s} \rho_s(t-\tau) - \rho_s(t-\tau) e^{(\hbar\beta/2)H_s} S_e^{-(\hbar\beta/2)H_s}) \} \quad (21)$$

The effect of finite temperature on  $S_x$  is

$$e^{-(\hbar\beta/2)H_s} S_e^{(\hbar\beta/2)H_s} = e^{-(\hbar\beta/2)\omega_s S_z} S_x e^{(\hbar\beta/2)\omega_s S_z} = S_x \cosh\left(\frac{\hbar\beta}{2}\omega_s\right) - i S_y \sinh\left(\frac{\hbar\beta}{2}\omega_s\right) \quad (22)$$

Using the permutation under the trace yields

$$\frac{d\langle O_s \rangle}{dt} = -i\omega_s \langle [O_s, S_z] \rangle - \cosh\left(\frac{\hbar\beta}{2}\omega_s\right) \int_{\tau=0}^t G(\tau, \beta) \langle [ [\tilde{O}_s(\tau), \tilde{S}_x(\tau)], S_x ]_{(t-\tau)} - i [ [\tilde{O}_s(\tau), \tilde{S}_x(\tau)], S_y ]_{(t-\tau)} \tanh\left(\frac{\hbar\beta}{2}\omega_s\right) \rangle d\tau$$

For the case where the observable  $O_s = S_z$ :

$$[\tilde{O}_s(\tau), \tilde{S}(\tau)] = U^{-1}(\tau) [S_z, S_x] U(\tau) = i\tilde{S}_y(\tau) = i(S_y \cos(\omega_s \tau) + S_x \sin(\omega_s \tau))$$

The rotated operators then are substituted into the equation of motion:

$$\frac{d\langle S_z \rangle}{dt} = -\cosh\left(\frac{\hbar\beta}{2}\omega_s\right) \int_{\tau=0}^t G(\tau, \beta) \langle \langle S_z \rangle_{(t-\tau)} \cos(\omega_s \tau) \rangle d\tau - \cosh\left(\frac{\hbar\beta}{2}\omega_s\right) \int_{\tau=0}^t G(\tau, \beta) \langle [S_y, S_y \cos(\omega_s \tau) + S_x \sin(\omega_s \tau)]_{(t-\tau)} \tanh\left(\frac{\hbar\beta}{2}\omega_s\right) \rangle d\tau \quad (23)$$

As a set of equations for observables, it is difficult to see how these equations maintain detailed balance. On closer inspection, however, the form is that which is anticipated by simple rate theory of diagonal matrix elements (see Appendix C eq C.11 and Appendix D). The set of equations in terms of observables maintain detailed balance by coupling to other, higher ordered observables through the temperature dependence in the  $\tanh[(\hbar\beta/2)\omega_s]$  term. Notice that there will be an observable in the integrand of the form  $\langle S_y^2 \rangle_{(t-\tau)}$  for example. To have full detailed balance then, one would have to generate the equation of motion for this observable as well, until the complete set of coupled observables was developed. The anti-commutator in (23) arises from the conjugation symmetry of the temperature terms. If the spin–lattice coupling Hamiltonian contained  $S_y$  instead of  $S_x$ , then the  $\sin(\omega_s \tau)$  term in the anti-commutator would appear with a negative sign, whereas the spin operator in the  $\cos(\omega_s \tau)$  term would involve  $S_x$ . Thus, if noncorrelated fluctuating fields about  $X$  and  $Y$  of equal amplitude are considered simultaneously, only a  $\cos(\omega_s \tau)$  term is present in the anti-commutator. In the spin  $1/2$  case discussed below the anti-commutator containing the  $\sin(\omega_s \tau)$  term vanishes identically, so that assuming fluctuation about  $X$  alone gives the same results as if we had included both  $X$  and  $Y$  fluctuations for that particular case. The  $\cos(\omega_s \tau)$  term of the anti-commutator also simplifies in the spin  $1/2$  case, but in general this term will couple  $\langle S_z \rangle$  to the expectation values of other, higher order, spin variables.

Boltzmann equilibrium is still enforced as the stationary solution. Inserting the equilibrium expectation values of the spin operators in the integrand shows that the integrand vanishes. From the operator form, of (19), it is clear that the integrand must vanish. To emphasize this, we will re-prove the stationary condition for any spin  $j$  in (23). The  $\tanh[(\hbar\beta/2)\omega_s]$  term arises naturally for all values of the spin,  $j$ .

Equilibrium is when  $\rho_0 = e^{-\hbar\beta\omega_s S_z} / \text{tr} \{ e^{-\hbar\beta\omega_s S_z} \}$ .  $\langle [S_x, S_y]_{+} \rangle_{\text{eq}} = 0$  because a  $\pi/2$  frame rotation generated about  $S_z$  may be inserted in the trace on one of the terms of the anti-commutator, and does not affect  $\rho_0$ ; however,  $S_x \rightarrow S_y$ ,  $S_y \rightarrow -S_x$ . This rotation also shows that  $\langle S_x^2 \rangle_{\text{eq}} = \langle S_y^2 \rangle_{\text{eq}}$ , and therefore,  $\langle [S_y, S_y]_{+} \rangle_{\text{eq}} = j(j+1) - \langle S_z^2 \rangle_{\text{eq}}$ . Substitution of these results into (23) yields the expression for the relaxation at equilibrium:

$$\Gamma[\rho_0, t] = \cosh\left(\frac{\hbar\beta}{2}\omega_s\right) \int_{\tau=0}^t G(\tau, \beta) \cos(\omega_s \tau) \langle \langle S_z \rangle_{\text{eq}} + \tanh\left(\frac{\hbar\beta}{2}\omega_s\right) (j(j+1) - \langle S_z^2 \rangle_{\text{eq}}) \rangle d\tau \quad (24)$$

which must be zero. We now show that the integrand of (24) is indeed zero.

The function  $Z(u) = \sum_{m=-j}^j e^{-m \cdot u} = \sinh((j+1/2)u) / \sinh(1/2u)$  is the generator of the equilibrium averages, i.e.,  $\langle S_z \rangle_{\text{eq}} = -(dZ(u)/du)/(Z)|_{u=\hbar\beta\omega_s}$ ,  $\langle S_z^2 \rangle_{\text{eq}} = (d^2Z(u)/du^2)/(Z)|_{u=\hbar\beta\omega_s}$ , etc.

The trigonometric expression for  $Z(u)$  follows from the summation of a geometric series. The vanishing of the integrand in (24) implies that  $Z(u)$  must also satisfy the differential equation:

$$-Z' + \tanh(u/2)(j(j+1)Z - Z'') = 0$$



Direct substitution of the definition of  $Z(u)$  in terms of the sinh functions into the differential equation shows that it is indeed a solution. A simpler method is to transform to  $\ln(Z(u)) = \ln(W(u)) - \int_{1/2}^u 1/\tanh(u/2) du = \ln(W(u)) - \ln(\sinh(u/2))$ , which gives the simpler differential equation  $W'' - (j + 1/2)^2 W = 0$ .

This differential equation in  $W$  is satisfied by  $W(u) = \sinh((j + 1/2)u)$ . Therefore, the expression for  $Z(u)$  given by summation of the geometric series is indeed a solution to the differential equation, and Boltzmann equilibrium, as defined by the spin Hamiltonian, is a stationary state for any value of  $j$ .

**Example 2: Spin–Lattice Relaxation for Spin  $1/2$ .** The case of  $j = 1/2$  is useful as a simple case to show how the finite time integral links spin-system and lattice frequencies. The operators may be evaluated for the spin  $1/2$  case, from (23) giving

$$\frac{d\langle S_z \rangle}{dt} = -\cosh\left(\frac{\hbar\beta}{2}\omega_s\right) \int_{\tau=0}^t G(\tau, \beta) \cos(\omega_s \tau) (\langle S_z \rangle_{(t-\tau)} - \langle S_z \rangle_{\text{eq}}) d\tau \quad (25)$$

where

$$\langle S_z \rangle_{\text{eq}} = -(1/2) \tanh\left(\frac{\hbar\beta}{2}\omega_s\right)$$

It is interesting to view this equation of motion in terms of the conventional time scale arguments on the density matrix and integration limits. If

$$\begin{aligned} \langle S_z \rangle_{(t-\tau)} &= \text{tr}\{S_z \rho(t-\tau)\} = \text{tr}\{\tilde{S}_z(-\tau) U(\tau) \rho(t-\tau) U^{-1}(\tau)\} \\ &= \text{tr}\{S_z U(\tau) \rho(t-\tau) U^{-1}(\tau)\} \approx \text{tr}\{S_z \rho(t)\} = \langle S_z \rangle_{(t)} \end{aligned}$$

i.e., the density matrix, when viewed in the rotating frame, is only slowly evolving compared to the time decay of  $G(\tau, \beta)$ .

Then from eq 23

$$\frac{d\langle S_z \rangle}{dt} \approx -\cosh\left(\frac{\hbar\beta}{2}\omega_s\right) \left( \int_{\tau=0}^t G(\tau, \beta) \cos(\omega_s \tau) d\tau (\langle S_z \rangle - \langle S_z \rangle_{\text{eq}}) \right) \quad (26)$$

The time integral in (26) is now isolated, and in the limit of infinite time, the integral becomes the inverse Fourier transform of  $G(\tau, \beta)$  at the spin frequency  $\omega_s$ . Thus, as time progresses the integral selects  $J(\omega)/\cosh(\hbar\beta\omega/2)$ , the spectral density and its temperature-dependent pre-factor, at the frequency  $\omega_s$ . The lattice prefactor cancels the factor in front of the integral, leaving the Lorentzian  $J(\omega)$  for the relaxation rate.

In finite time the integral in (26) can be stated in a convenient form and gives a criterion for how fast the infinite time Fourier transform limit is approached. Using (20) for  $G(\tau, \beta)$ , the integral component of (26) becomes

$$\int_{\tau=0}^t G(\tau, \beta) \cos(\omega_s \tau) d\tau = \int_{-\infty}^{\infty} \frac{J(\omega)}{\cosh(\hbar\beta\omega/2)} \left( \frac{\sin((\omega_s - \omega)t)}{\pi(\omega_s - \omega)} \right) d\omega$$

The symmetry of the frequency integration limits was used to complete the necessary cosine addition formula before performing the  $\tau$  integration.

The distribution (or window function),  $\sin((\omega_s - \omega)t)/[\pi(\omega_s - \omega)]$ , approaches a Dirac  $\delta$  function as time goes to infinity, selecting out the lattice spectral density function at the spin-

system frequency  $\omega_s$ . Furthermore, the  $\cosh(\hbar\beta\omega/2)$  temperature weighting in the denominator is selected at the spin-system frequency and cancels the similar term that arose purely from the action of spin-system operators on  $S$  in the numerator of the relaxation expressions (see (12) and (22)). The distribution function becomes a good approximation to the  $\delta$  function when its width becomes, as a function of time, much less than the width of  $J(\omega)/\cosh(\hbar\beta\omega/2)$ . The time must, at the very least, exceed the correlation time of the lattice process,  $\tau > \tau_c$ , as represented by the lattice spectral density width. Once the time has exceeded several correlation times the integral converges to the Fourier transform limit. This is a concrete demonstration of the well-used approximation in BWRT, namely that the time in the finite integral may be passed to infinity while the time derivative on the left-hand side of the equation of motion (26) is retained at finite time. Goldman emphasizes that this places a restriction on the interpretation of the equation of motion such that its solutions must necessarily correspond to the system response after several lattice time constants<sup>10</sup> (p 167b). The process described by our formulation is intuitive and valid at all times: Initially, all the lattice modes represented by the spectral density function must contribute to the spin-system evolution. The spin system samples the frequency of the lattice, in effect. The frequency spread presented by the lattice is resolved into a single component only after a sufficient interaction time with the spin system.

The extension of time in the integrand of the relaxation expression to infinity is one of the principal time scale arguments in the derivation of BWRT, and its basis has been concretely demonstrated here. The other time scale argument invoked is the slow evolution of the spin density matrix (as viewed in the rotation frame) over several correlation times of the lattice. The lattice must have a weak coupling to the spin system at the frequency of the rotating frame if the spin density matrix is expected to be nearly stationary for initial times within several lattice correlation time constants. The solution in Appendix E (Supporting Information) to (25) (the complete convolution equation) reveals that the weak coupling required in BWRT means that the lattice coupling, considered a coherent field in the rotating frame, must not cause significant spin precession over the correlation time or  $1 \gg f_0 \tau_c$ . Neither such restriction is present in our general formulation. A similar picture arises in the solution of relaxation of transverse components, discussed in the next example.

The solution of the convolution form of relaxation, (25), for the longitudinal magnetization is given in Appendix E, in the high-temperature limit. The general solution contains three exponentials and contains, in general, oscillatory components as well as exponential decay. The method of solution is similar to that used for the relaxation of the transverse magnetization discussed in the next example below. The principal regime of interest is when the spin–lattice coupling energy is a perturbation of the basic Zeeman spin Hamiltonian, that is,  $\omega_s > f_0$ . With this restriction, the short correlation time ( $1 \gg \tau_c f_0$ ) and the long correlation ( $\tau_c f_0 \gg 1$ ) limits are each dominated by a single rate:

$$R_1 = \frac{f_0^2/\tau_c}{\omega_s^2 + (1/\tau_c)^2} \Big|_{1 \gg \tau_c f_0} \quad \text{or} \quad \frac{f_0^2/\tau_c}{\omega_s^2 + f_0^2} \Big|_{\tau_c f_0 \gg 1}$$

It is tempting to combine both limits into one expression:

$$R_1 \approx \frac{f_0^2/\tau_c}{\omega_s^2 + (1/\tau_c)^2 + f_0^2} = \frac{\tau_c f_0^2}{1 + (\tau_c \omega_s)^2 + (\tau_c f_0)^2} \quad (27)$$

One motivation for this form is that it represents the solution for the rates to the linearized cubic equation given in Appendix E. This expression also applies in the intermediate regime, where  $\tau_c f_0 \approx 1$  as long as  $\omega_s > f_0$ . When  $\omega_s$ ,  $f_0$ , and  $1/\tau_c$  are nearly equal, a single spectral density is not appropriate, due to the presence of two other competitive rate components. These extra rates are due to coherent precession, which results from the contribution of the fluctuating field in the rotating frame, and are characterized as damped oscillation (see the general solution in Appendix E). The relative amplitudes of the pure decay and the oscillatory components are governed by a complicated competition of  $\omega_s$  with  $f_0$  and  $\tau_c$ . When  $f_0 \gg \omega_s$ , the rates are similar to the transverse (spin–spin) mechanism. In this regime, the “fast motion” case ( $1 \gg \tau_c f_0$ ) is dominated by the rate  $\tau_c f_0^2$ , alone. In the slow motion limit ( $\tau_c f_0 \gg 1$ ) relaxation is a mixture of pure decay and oscillatory components and does not have a single spectral density. In the no motion limit, the “perturbation” is coherently coupled to the evolution of the observable. The result obtained by the complete solution, Appendix E, is identical to that obtained from first principles (eq 1) in this limit. Therefore, the general solution limits to the exact, oscillatory answer as the correlation time goes to infinity, where there is no damped relaxation, or  $\text{Re}\{R_1\} = 0$ .

**Example 3: Spin–Spin Relaxation for Spin  $1/2$ .** Relaxation of the X component of the spin system is given as a result of the field fluctuations along Z. The coupling Hamiltonian is of the form  $H' = FS_z$ . The Zeeman magnetic field is still oriented along Z. The equation of motion for the X and Y components, which follow from (21) and (12), are

$$\frac{d\langle S_x \rangle}{dt} = -i\omega_s \langle -iS_y \rangle - \int_{\tau=0}^t G(\tau, \beta) \text{tr}\{[S_x, S_z] S_z U_s(\tau) \rho(t-\tau) U_s^{-1}(\tau) + \text{H.C.}\} d\tau$$

$$\frac{d\langle S_y \rangle}{dt} = -i\omega_s \langle iS_x \rangle - \int_{\tau=0}^t G(\tau, \beta) \text{tr}\{[S_y, S_z] S_z U_s(\tau) \rho(t-\tau) U_s^{-1}(\tau) + \text{H.C.}\} d\tau$$

or

$$\frac{d\langle S_x \rangle}{dt} = -\omega_s \langle S_y \rangle - \int_{\tau=0}^t G(\tau, \beta) \text{tr}\{S_x U_s(\tau) \rho(t-\tau) U_s^{-1}(\tau)\} d\tau$$

$$\frac{d\langle S_y \rangle}{dt} = \omega_s \langle S_x \rangle - \int_{\tau=0}^t G(\tau, \beta) \text{tr}\{S_y U_s(\tau) \rho(t-\tau) U_s^{-1}(\tau)\} d\tau \quad (28)$$

The connection with the conventional BWRT result is obtained by again applying the time scale assumption that  $U_s(\tau) \rho(t-\tau) U_s^{-1}(\tau) \rightarrow \rho(t)$ . So that

$$\begin{aligned} \frac{d\langle S_x \rangle}{dt} &= -\omega_s \langle S_y \rangle - \left( \int_{\tau=0}^t G(\tau, \beta) d\tau \right) \langle S_x \rangle \\ \frac{d\langle S_y \rangle}{dt} &= \omega_s \langle S_x \rangle - \left( \int_{\tau=0}^t G(\tau, \beta) d\tau \right) \langle S_y \rangle \end{aligned}$$

As time goes to infinity the integral becomes the inverse Fourier transform, and the zero-frequency term of the spectral density function is selected.

$$\lim_{t \rightarrow \infty} \int_{\tau=0}^t G(\tau, \beta) d\tau = \frac{J(0)}{\cosh\left(\frac{\hbar\beta}{2}\right)} = f_0^2 \tau_c$$

This is the famous result for the relaxation rate of the transverse components from BWRT. We note that the result has the problem that the relaxation rate diverges as the correlation time becomes large; this is the “BWRT Catastrophe”.

We now revisit (28) without invoking the traditional BWRT approximations. In so doing it is convenient to go into a rotating frame. The equation of motion is a convolution of the density matrix. The rotating frame is determined by the properties of the observables, not the density matrix. Here  $S_x$  and  $S_y$  are known to transform simply under a rotation generated about Z because of their commutation properties with the generator of the rotation,  $S_z$ . In general, a set of spin observables is constructed from the spherical tensor operators. Spherical tensor operators transform under rotation such that a frame change is possible in general.<sup>19</sup> Therefore, this problem is illustrative of a much larger class of problems that are of practical use. The expectation of  $S_x$  in the rotating frame is

$$\begin{aligned} \text{tr}\{S_x \tilde{\rho}(t)\} &= \text{tr}\{S_x U_s^{-1}(t) \rho(t) U_s(t)\} = \\ &= \text{tr}\{U_s(t) S_x U_s^{-1}(t) \rho(t)\} = \langle \tilde{S}_x(-t) \rangle \end{aligned}$$

The spin operators transform such that

$$\begin{pmatrix} \langle \tilde{S}_x(t) \rangle \\ \langle \tilde{S}_y(t) \rangle \end{pmatrix} = \begin{pmatrix} \cos(\omega_s t) & -\sin(\omega_s t) \\ \sin(\omega_s t) & \cos(\omega_s t) \end{pmatrix} \begin{pmatrix} \langle S_x \rangle \\ \langle S_y \rangle \end{pmatrix} \equiv R(t) \langle \vec{S} \rangle$$

The vector notation simplifies the algebra that follows. If  $R(-t)$  is applied to both sides of the equation of motion written in vector form:

$$R(-t) \frac{d\langle \vec{S} \rangle}{dt} = R(-t) \begin{pmatrix} 0 & -\omega_s \\ \omega_s & 0 \end{pmatrix} \langle \vec{S} \rangle - \int_{\tau=0}^t G(\tau, \beta) R(-t) \langle \vec{S}(\tau) \rangle_{(t-\tau)} d\tau$$

Then it follows that

$$\frac{d(\text{tr}\{\vec{S} \tilde{\rho}(t)\})}{dt} = - \int_{\tau=0}^t G(\tau, \beta) \text{tr}\{\vec{S} \tilde{\rho}(t-\tau)\} d\tau$$

because

$$\frac{dR(-t)}{dt} = \omega_s \begin{pmatrix} -\sin(\omega_s t) & \cos(\omega_s t) \\ -\cos(\omega_s t) & -\sin(\omega_s t) \end{pmatrix} = -R(-t) \begin{pmatrix} 0 & -\omega_s \\ \omega_s & 0 \end{pmatrix}$$

Denoting the expectation values in the rotating frame by  $\langle S_{\tilde{x}} \rangle_{(t)} \equiv \text{tr}\{S_x \tilde{\rho}(t)\}$ , the equation of motion for  $\langle S_{\tilde{x}} \rangle$  becomes, for example

$$\begin{aligned} \frac{d\langle S_{\tilde{x}} \rangle}{dt} &= - \int_{\tau=0}^t G(\tau, \beta) \langle S_{\tilde{x}} \rangle_{(t-\tau)} d\tau = \\ &= - \int_{\tau=0}^t G(t-\tau, \beta) \langle S_{\tilde{x}} \rangle_{(\tau)} d\tau \quad (29) \end{aligned}$$

When this equation of motion is compared to the analogue for  $\langle S_z \rangle$  given above, in (25), two differences become evident. First, the equilibrium state for  $\langle S_{\tilde{x}} \rangle$  is zero. Second, there is no spin-system frequency present (because the density matrix has been transformed into the rotating frame). Both of these differences are also characteristic of conventional BWRT and are well-known properties of the transverse magnetization. However, the

relaxation term has the form of a convolution. As will be shown, the convolution form of the relaxation term, unique to our formulation, prevents the “BWRT Catastrophe” and provides the fully coherent, correct form of the solution in the long correlation time limit.

The integral form of the equation of motion can be converted to a differential equation, as illustrated in Appendix E, by direct differentiation of both sides if the time derivative of  $G(t, \beta)$  is known. We use the high-temperature limit of (18). The factor  $1/\cosh(\hbar\omega\beta/2)$  has a spectral width on the order of  $1/\hbar\beta$  so that if  $1 \gg \hbar\beta/\tau_c$  then  $G(t, \beta \rightarrow 0) = f_o^2 e^{-t/\tau_c}$ . This criterion means that correlation times must be larger than  $10^{-14}$  s at room temperature, a criterion easily met, for example, by a rotational correlation function of a small molecule in water (considered as representative of the time scale of motion).

Upon differentiation the equation of motion (29) becomes

$$\frac{d^2 \langle S_{\bar{x}} \rangle}{dt^2} + \frac{1}{\tau_c} \frac{d \langle S_{\bar{x}} \rangle}{dt} + f_o^2 \langle S_{\bar{x}} \rangle = 0 \quad \text{with} \quad \left. \frac{d \langle S_{\bar{x}} \rangle}{dt} \right|_{t=0} = 0 \quad (30)$$

where the boundary condition is inherited from the original equation of motion.

The general solution contains exponentials with “rates”

$$R_2^\pm = \frac{1}{2\tau_c} \pm \sqrt{\left(\frac{1}{2\tau_c}\right)^2 - f_o^2}$$

This is a complete description of the relaxation of the transverse component of the (spin) system that covers the full range of possible correlation times. The rates may become imaginary when the correlation time is long, and this leads to damped oscillation. These rates are identical to the rates from the stochastic Liouville equation (SLE) of Kubo for a stochastically modulated two-state oscillator.<sup>7</sup> For this case the SLE has the form

$$\dot{X}(t) = \left[ i \begin{pmatrix} \omega_1 & 0 \\ 0 & -\omega_1 \end{pmatrix} + \frac{\gamma}{2} \begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \right] X(t) \quad (31)$$

where  $X(t)$  is the average value of the oscillator coordinate for each state as a function of time. To make the comparison with the spin relaxation problem treated here, the exchange rate,  $\gamma$ , is identified with the reciprocal of the correlation time and Kubo's  $\omega_1 = f_o$ . The eigenvalues of the matrix on the rhs of the SLE give the relaxation rates and are found to be identical to the rates obtained from our convolution equation. This correspondence is expected, given that our lattice is composed of two-state systems as well. The two states of  $X$  in eq 31 correspond to the two possible states of traverse spin precession (as seen in the rotating frame) that result from the two possible lattice states.

We now consider the individual cases of eq 30. There are three specific solutions of (30) depending on the relative magnitudes of  $\tau_c$  and  $f_o$ .

**Case 1:**  $1 > 2\tau_c f_o$

$$\langle S_{\bar{x}} \rangle = \langle S_{\bar{x}} \rangle_{t=0} e^{-t/2\tau_c} \left( \cosh\left(\frac{t}{2\tau_c} \sqrt{1 - (2\tau_c f_o)^2}\right) + \frac{1}{\sqrt{1 - (2\tau_c f_o)^2}} \sinh\left(\frac{t}{2\tau_c} \sqrt{1 - (2\tau_c f_o)^2}\right) \right)$$

In this case both relaxation rates are pure real. In the limiting

case  $1/2 \gg \tau_c f_o$  the radical may be expanded to second order in this product with the result

$$\langle S_{\bar{x}} \rangle = \langle S_{\bar{x}} \rangle_{t=0} \left( (1 + (\tau_c f_o)^2) e^{-\tau_c f_o^2 t} - (\tau_c f_o)^2 e^{-(1/\tau_c - \tau_c f_o^2) t} \right)$$

The first term is recognized as the rate from the conventional form of BWRT due to the zero-frequency component of the spectral density function. The second rate is larger than the first (faster decay) and is minor because its amplitude is weighted by  $(\tau_c f_o)^2$ .

**Case 2:**  $2\tau_c f_o = 1$

This limit, easily found from case 1, is

$$\langle S_{\bar{x}} \rangle = \langle S_{\bar{x}} \rangle_{t=0} e^{-t/2\tau_c} (1 + t/2\tau_c)$$

**Case 3:**  $2\tau_c f_o > 1$

$$\langle S_{\bar{x}} \rangle = \langle S_{\bar{x}} \rangle_{t=0} e^{-t/2\tau_c} \left( \cos\left(\frac{t}{2\tau_c} \sqrt{(2\tau_c f_o)^2 - 1}\right) + \frac{1}{\sqrt{(2\tau_c f_o)^2 - 1}} \sin\left(\frac{t}{2\tau_c} \sqrt{(2\tau_c f_o)^2 - 1}\right) \right)$$

In the limiting case  $2\tau_c f_o \gg 1$

$$\langle S_{\bar{x}} \rangle = \langle S_{\bar{x}} \rangle_{t=0} e^{-t/2\tau_c} \left( \cos(f_o t) + \frac{1}{2\tau_c f_o} \sin(f_o t) \right)$$

Here the terms oscillate, and the real part of the relaxation rate, the damping term, depends inversely on the correlation time, as opposed to case 1 where the relaxation rate was proportional to the correlation time. The physical interpretation of this answer is that the correlation time is so long or the amplitude of fluctuation is so strong that the fluctuating field causes appreciable coherent precession over a time period up to the lattice correlation time. Exactly the same answer is obtained for the  $Y$  component  $\langle S_{\bar{y}} \rangle$ . Both directions of induced precession are statistically present with equal probability because the fluctuations of  $f_o$  have zero mean. As a result, the induced average oscillation of  $\langle S_{\bar{x}} \rangle$  is linearly polarized, as viewed in the rotating frame. This coherence has an analogue in Kubo's solution for the motion of a stochastically modulated oscillator. In the regime where  $t \ll \tau_c$  it is found that “dynamical coherence is dominant for the short time approximation.”<sup>20</sup> The lattice amplitudes are assumed to be Gaussian distributed in the typical applications of Kubo, in contrast to the simple two-state distribution of our lattice. Our results exhibit the same persistence of coherence in the large correlation time limit that is found with the more complex models of the lattice considered by Kubo.

This example illustrates:

(1) Passage to the rotating frame is possible because an external rotation of the spin observables is generated by a transformation that acts on the spin operators, not the density matrix. This is particular to the physical properties of spherical tensor operators and their linear combinations.<sup>21</sup> If the fundamental equation of motion (5) were rewritten as a density matrix equation of motion (6), the ability to transform to a rotating frame would be lost. The convolution nature of these equations makes it impossible to perform a simple frame rotation directly on the density matrix. The ability to perform a frame change in the observables formalism underscores the importance of the observable formalism used in this paper.

(2) The conventional result of BWRT for spin–spin relaxation is obtained in the fast motion limit, i.e., when  $1 \gg \tau_c f_0$  and the effective  $R_2$  relaxation rate is  $\tau_c f_0^2$ .

(3) The effective  $R_2$  rate in the slow motion limit  $2\tau_c f_0 \gg 1$  does not diverge but is given by  $1/(2\tau_c)$ . This relaxation rate is also accompanied by amplitude modulation with frequency  $f_0$ . The same result was found for the spin–lattice relaxation in the limit of vanishing Larmor frequency (Appendix E).

The pure decay component of  $R_2$  may be summarized by the expression

$$R_2 \approx f_0^2 \frac{\tau_c}{1 + 2(\tau_c f_0)^2} \quad (32)$$

although the oscillatory behavior when  $\tau_c f_0 \gg 1$  must be emphasized. The form of the relaxation rate constant suggested by (32) conveys the character of the change in the rate constant from the fast to the slow motion region but does not take into account the abrupt change in the real part of the relaxation rates when  $1 \cong 2\tau_c f_0$ . In the no motion case, we recover the exact answer, which would be obtained by making the lattice fully coherent and solving for the evolution of the transverse components directly from (1). This solution, in the no motion limit, is a coherent free induction decay, or FID, with no damping, oscillating at frequency  $f_0$ . This result is in marked contrast to the predictions of BWRT in which the relaxation rate constant becomes infinite without oscillation.

## VI. Conclusions

We have developed a novel equation for relaxation of a system in the presence of a lattice. The issue of how to choose a QCF, and what form to put into the master equation, has always been a difficult one. We have given a precise definition of the form of the QCF needed in relaxation theory: One that guarantees the QCF will always be pure real, as seen in (18) and that guarantees that relaxation rates will be pure real as well for real observables of Hermitian operators. The form we have developed in eq 5 guarantees detailed balance. In terms of the operator formalism, when the (spin) system is at its own Boltzmann equilibrium at the temperature of the lattice, then relaxation no longer contributes to the evolution of system observables. A consequence of finite temperature in the equation of motion is the presence of cross relaxation terms that couple the expectation value of the spin operators to higher-order moments of the spin operators, as can be seen in eq 23. This work provides a practical, usable formulation of the effects of temperature on relaxation. The additional difficulty of working with the equations as a convolution, integro-differential equation, can be surmounted. The results are important to practicing spectroscopists because they make clear that relaxation rates can be well defined in nearly any dynamics limit. This theory does contain approximations. However, it is not a perturbation theory valid only in the high temperature, short correlation time limit like BWRT. This theory is valid at finite temperature and limits to the proper equation of motion when the correlation

time of the lattice fluctuations becomes infinitely long. The only approximation made was to admit a theory that used equilibrium lattice QCFs. The approximations made subsequently (mainly to neglect the EI terms and return the density matrix to the real axis) *restored* properties to the equation of motion lost due to the initial approximation. Although we chose a particularly simple form for the QCF, (18) (one in which the QCF vanishes at low temperature), any number of forms could be chosen. This work provides a well-defined way to include the QCF into the relaxation part of the equation of motion. One of the practical consequences of this work may be simply stated that the amplitude of the fluctuation,  $f_0$ , may be considered to be equivalent to a frequency that can be included in the denominator of any existing spectral density function as done in (27) and (32). The presence of this term guarantees that the spectral density functions are valid in all motional regimes and prevents the catastrophe of BWRT.

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**Supporting Information Available:** Text giving the equivalence of eqs 1 and 2 in the main text, properties of the quantum correlation functions, derivations of BWRT, transition state theory and density matrix formulation, and relaxation of longitudinal magnetization for spin  $1/2$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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