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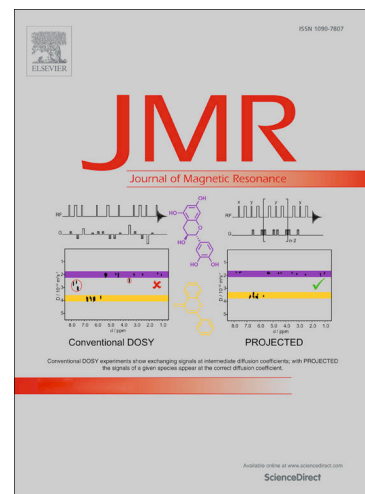
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A master equation for spin systems far from equilibrium

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ABSTRACT

The quantum dynamics of spin systems is often treated by a differential equation known as the master equation, which describes the trajectories of spin observables such as magnetization components, spin state populations, and coherences between spin states. The master equation describes how a perturbed spin system returns to a state of thermal equilibrium with a finite-temperature environment. The conventional master equation, which has the form of an inhomogeneous differential equation, applies to cases where the spin system remains close to thermal equilibrium, which is well satisfied for a wide variety of magnetic resonance experiments conducted on thermally polarized spin systems at ordinary temperatures. However, the conventional inhomogeneous master equation may fail in the case of hyperpolarized spin systems, when the spin state populations deviate strongly from thermal equilibrium, and in general where there is a high degree of nuclear spin order. We highlight a simple case in which the inhomogeneous master equation clearly fails, and propose an alternative master equation based on Lindblad superoperators which avoids most of the deficiencies of previous proposals. We discuss the strengths and limitations of the various formulations of the master equation, in the context of spin systems which are far from thermal equilibrium. The method is applied to several problems in nuclear magnetic resonance and to spin-isomer conversion.

1. Introduction

Nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) experiments are usually performed on samples which are allowed to reach thermal equilibrium in a large magnetic field, perturbed by radiofrequency (for NMR) or microwave (for EPR) pulses resonant with the Zeeman transitions in order to induce an observable electromagnetic response, and allowed to return to thermal equilibrium before the process is repeated. Under most circumstances, the behaviour of the spin system is described by a differential equation which is usually known as the *inhomogeneous master equation* (IME) and is given by [1–14]

$$\frac{d}{dt}\rho(t) = -i[H_{\text{coh}}(t), \rho(t)] + \hat{\Gamma}(\rho(t) - \rho_{\text{eq}}) \quad (1)$$

Here $\rho(t)$ is the spin density operator which describes the quantum state of the ensemble of spin systems, and is given by

$$\rho = \overline{|\psi\rangle\langle\psi|} \quad (2)$$

where $|\psi\rangle$ is the quantum state of an individual member of the spin ensemble, and the bar represents an average over all ensemble members. The term H_{coh} is the coherent part of the spin Hamiltonian, which is uniform for all spin ensemble members. The relaxation of the spin system is described by a relaxation superoperator, denoted $\hat{\Gamma}$, and which may be constructed from the fluctuating part of the spin Hamiltonian; some construction procedures are discussed later in this paper. The spin density operator at thermal equilibrium with the molecular environment is denoted ρ_{eq} . The last term in equation 1 depends on the deviation of the spin density operator from its thermal equilibrium value, and causes the density operator to reach thermal equilibrium when left unperturbed for a long time.

For example, consider an operator Q which commutes with the coherent Hamiltonian H_{coh} and which is also an eigensuperoperator of $\hat{\Gamma}$:

$$[Q, H_{\text{coh}}] = 0 \quad (3)$$

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$$\hat{\Gamma}Q = -T_Q^{-1}Q \quad (4)$$

where T_Q is the relaxation time constant of spin density components proportional to the operator Q . The expectation value of Q follows the trajectory

$$\langle Q \rangle(t) = \langle Q \rangle_{\text{eq}} + (\langle Q \rangle(0) - \langle Q \rangle_{\text{eq}}) \exp\{-t/T_Q\} \quad (5)$$

where

$$\langle Q \rangle(t) = \text{Tr}\{Q^\dagger \rho(t)\} \quad (6)$$

and

$$\langle Q \rangle_{\text{eq}} = \text{Tr}\{Q^\dagger \rho_{\text{eq}}\} \quad (7)$$

Equation 5 indicates that the deviation of the expectation value of Q from its thermal equilibrium value decays exponentially, so that $\langle Q \rangle(t)$ tends to $\langle Q \rangle_{\text{eq}}$ at long times t . Another corollary of Equation 5 is that the trajectory of the expectation value for the relaxation eigenoperator Q depends *only* on the initial value of the same expectation value and the time constant T_Q , and *not on any other expectation values*.

All of this seems unremarkable, and indeed, equation 1 has been a fixture in spin dynamical theory for a long time. This is despite the caveats used by the early developers of spin relaxation theory, including Bloch and Wangsness [1, 2], Redfield [3], Abragam [4], and Hubbard [5]. For example, in the derivation in his 1957 paper [3], Redfield used the following phrase at a key step: “unless the system is prepared in an unusual way”.

So what is “a system prepared in an unusual way”? The discussion in the Redfield paper makes it clear that the term implies a large deviation of the density operator from thermal equilibrium, such that the density operator ventures outside the *high-temperature* and *weak-order* approximation:

$$\|H_{\text{coh}}/k_B T\| \ll 1 \quad (8)$$

$$\|\rho - N^{-1} \mathbb{1}\| \ll 1 \quad (9)$$

where $\mathbb{1}$ is the unity operator, N is the dimension of Hilbert space and the Frobenius norm is defined

$$\|A\| = \sum_{r,s} |\langle r|A|s\rangle|^2 \quad (10)$$

In his classic textbook [4], Abragam makes the same approximations *en route* to the derivation of the IME (at the top of pages 287 and 288).

Hence, equation 1 only applies in the high-temperature limit for spin systems exhibiting a small degree of order, and this restriction was well-known at the time this equation was first developed.

There is great current interest in the preparation of nuclear spin systems “in an unusual way”, i.e. far from equilibrium, or with large amounts of spin order. Such preparations include hyperpolarized spin systems with a large level of Zeeman polarization, enhanced with respect to thermal equilibrium polarization by many orders of magnitude [15–28], as prepared by methods such as dynamic nuclear polarization (DNP) [15–18] and optical pumping [19–22]. In addition, nuclear spin systems may be prepared in states corresponding to non-equilibrium spin isomer distributions, such as hydrogen enriched in the *para* spin isomer [23–29] and rapidly rotating methyl groups prepared with non-equilibrium distributions of populations between the spin isomers of the three equivalent protons [30–36]. In some circumstances these different modes of non-equilibrium spin order interconvert, leading for example to the phenomena of parahydrogen-induced hyperpolarization (PHIP), in which the non-equilibrium singlet spin order of *para*-enriched hydrogen gives rise to large magnetization components after a chemical reaction [25–28], and quantum-rotor-induced polarization (QRIP) in which non-equilibrium methyl rotor order also gives rise to enhanced NMR signals [30–36]. In many cases, hyperpolarization leads to a situation in which the populations of long-lived states are strongly enhanced, or greatly depleted [34, 35, 37–45].

A “thought experiment” involving the preparation of a sample “in an unusual way” is shown in Figure 1(a). Consider an ensemble of nuclear spin-1/2 pairs. The magnetic environments of the two spins-1/2 are considered to be

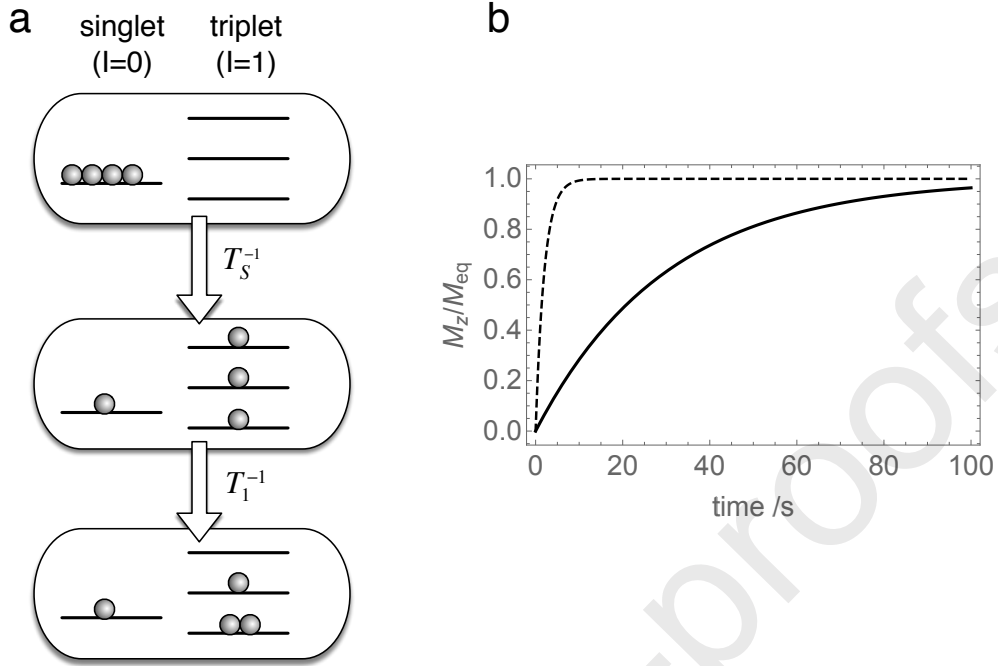


Figure 1: An experiment which illustrates the failure of the IME for spin systems far from equilibrium. The horizontal lines represent the Hamiltonian eigenvalues (energy levels) and the balls represent state populations. (a) An ensemble of spin-1/2 pairs is prepared so that only the non-magnetic ($I = 0$) singlet state is populated. Conversion from the singlet state to the magnetic triplet states ($I = 1$) occurs with a time constant T_S . The triplet manifold reaches thermal equilibrium in a magnetic field with time constant T_1 , such that $T_1 \ll T_S$. (b) Trajectories of the spin magnetization along the field M_z , normalized to the thermal equilibrium value. The IME predicts recovery of M_z with time constant T_1 (dashed line), which is physically unreasonable. The correct behaviour is that M_z recovers with the much longer time constant T_S (solid line). The simulations are for the case $T_1 = 2$ s and $T_S = 22.5$ s.

either identical (magnetic equivalence) or nearly identical (near-equivalence) [41], so that the Hamiltonian eigenstates are given, to a good approximation, by the singlet state and the three triplet states, defined as follows:

$$\begin{aligned}
 |S_0\rangle &= 2^{-1/2}(|\alpha\beta\rangle - |\beta\alpha\rangle) \\
 |T_{+1}\rangle &= |\alpha\alpha\rangle \\
 |T_0\rangle &= 2^{-1/2}(|\alpha\beta\rangle + |\beta\alpha\rangle) \\
 |T_{-1}\rangle &= |\beta\beta\rangle
 \end{aligned} \tag{11}$$

These states are eigenstates of total spin angular momentum with quantum number $I = 0$ for the singlet state and $I = 1$ for the triplet states. Hence, the singlet state is non-magnetic and all NMR observables are associated with the triplet states. In a magnetic field, the degeneracy of the triplet states is split by the nuclear Larmor frequency. Suppose that the sample is prepared “in an unusual way”, such that only the singlet state is populated, see Figure 1(a, top). Clearly, there can be no nuclear magnetization in this $I = 0$ state. Now suppose that relatively inefficient processes enable the slow conversion of the singlet state to the triplet states, and denote the corresponding time constant T_S . Assume also, for the sake of simplicity, that the transition probabilities are the same for all three triplet states. In this case, there is no magnetization associated with the triplet manifold when it is first populated by conversion from the singlet state, see Figure 1(a, middle). However, the triplet manifold rapidly magnetizes in the magnetic field due to spin-lattice relaxation, leading to the establishment of a Boltzmann distribution between its Zeeman-split energy levels, see Figure 1(a, bottom). Assume that the spin-lattice relaxation time constant T_1 is much smaller than the time constant T_S for singlet-to-triplet conversion. Now we ask: what is the time constant for the build-up of Zeeman magnetization along the field? The answer is obvious: since the singlet state has no nuclear spin, and no nuclear magnetization, the singlet population must convert to triplet populations before any magnetization can build up. Since the rate of singlet-

to-triplet conversion is much smaller than the rate of triplet relaxation, the rate of magnetization build-up is determined by the slowest process, which is the singlet-to-triplet conversion. Hence, the magnetization builds up along the field with a slow time constant of the order of T_S . This is illustrated by the solid line in Figure 1(b), which was simulated using the techniques described later in the paper.

This result is obvious, but it is *not* predicted by the standard master equation of equation 1! The IME predicts that the expectation value z -magnetization builds up with a time constant T_1 , irrespective of the initial distribution of singlet and triplet populations, and even in the case that the triplet states are totally unpopulated. The standard IME leads to the prediction given by the dashed line in Figure 1(b), with the magnetization building up with the fast time constant T_1 . The IME therefore predicts that a sample in which only the non-magnetic singlet state is populated somehow rapidly acquires a magnetization which is almost as large as a sample in full thermal equilibrium and with a triplet:singlet population ratio of 3:1. This makes no physical sense.

A real experiment of this form has been performed on a material containing freely rotating water molecules encapsulated in fullerene (C_{60}) cages [46]. This experiment utilizes the spin isomerism of freely rotating water molecules, in order to generate the required over-population of the non-magnetic singlet state. In freely rotating water molecules, the nuclear singlet state is associated with the *para* spin isomer of water, which has a significantly lower rotational energy than the triplet states, which belong to the *ortho* spin isomer. It is therefore possible to enrich the endofullerene sample in the *para* spin isomer of water by leaving it to equilibrate at low temperature, as verified by low-temperature NMR and electrical measurements [47, 48]. The *para*-enriched material is brought rapidly to room temperature using a fast dissolution apparatus, and the NMR signal observed in the presence of a large magnetic field. The NMR signal slowly increases in time since the *para*-water molecules, which are in a non-magnetic nuclear singlet state providing no NMR signal, convert into *ortho*-water molecules, which have nuclear spin-1, and rapidly polarize along the field, providing an NMR signal upon radiofrequency excitation. The slow increase in the NMR signal with time therefore allows determination of the *para*-to-*ortho* spin-isomer conversion kinetics. The time constant for this signal build-up was found to be about 30 seconds, while the measured value of T_1 is only 0.75 s. [46]. This is in clear contradiction with the prediction of the IME.

Although this experimental example exploits spin isomerism in order to prepare the required initial state, the phenomenon of spin isomerism is by no means essential for highlighting the problematic features of the IME. Identical behaviour would be observed for molecules lacking spin isomers, but which still exhibit slow conversion between singlet and triplet states. Such examples are widespread [34, 35, 37–45]. In one case, the singlet-triplet conversion time constant exceeds 1 hour [43]. If a system of this kind were prepared in a pure singlet state through hyperpolarization techniques, the recovery of the longitudinal magnetization in a strong magnetic field would also be on a timescale far longer than T_1 , in contradiction to the predictions of the inhomogeneous master equation.

The early pioneers of NMR relaxation theory [1–5, 49] did not address the problem of nuclear spin relaxation far from equilibrium. For a long time there was no need, since the vast majority of NMR experiments are performed on spin systems which are very close to equilibrium. The inhomogeneous master equation (equation 1) rapidly became established as a fixture in the field and plays a central role in standard textbooks [6].

A series of alternative master equations were proposed in the 1980's and 1990's [50–53]. However, the primary motivation was *not* to address the relaxation dynamics of far-from-equilibrium spin systems, but to circumvent the mathematical inconvenience of the IME, which has the form of an inhomogeneous differential equation. The alternative master equations have the form of a *homogeneous* differential equation, of the type

$$\frac{d}{dt}\rho(t) = -i[H_{\text{coh}}(t), \rho(t)] + \hat{\Gamma}^\theta \rho(t) \quad (12)$$

where $\hat{\Gamma}^\theta$ is a “thermalized” variant of the relaxation superoperator $\hat{\Gamma}$, adjusted in such a way that the spin density operator ρ tends to the correct thermal equilibrium value ρ_{eq} in thermal equilibrium with the environment [50–57]. A spin dynamical equation of the form in equation 12 is referred to here as a *homogeneous master equation* (HME).

Some proposed forms for $\hat{\Gamma}^\theta$ are examined below. Although this was not their primary intention, some of the HME formulations do provide a partial treatment of far-from-equilibrium spin systems, as well as being mathematically more convenient than the IME. However none of the proposed solutions treat the behaviour of coherences correctly far from equilibrium. The rest of this paper discusses the construction of an alternative HME which does not suffer from these restrictions and which retains validity for spin systems far from equilibrium.

This class of problem is, of course, not unique to nuclear magnetic resonance. Other forms of coherent spectroscopy, such as electron paramagnetic resonance (EPR) and coherent optical spectroscopies, also encounter quantum

systems which are strongly ordered or in transient states which are far from equilibrium. The large field of research into *open quantum systems* addresses the problems of quantum dynamics of systems which exchange energy with a thermal reservoir [58–63]. Some of the techniques presented in the current paper will be familiar to open quantum theorists, so we do not claim great originality. Nevertheless, techniques such as Lindbladian superoperators, which are widely used in open quantum theory, are seldom encountered in magnetic resonance, with notable exceptions [64, 65].

Our aim in this paper is to make an explicit connection between magnetic resonance theory on the one hand, and open quantum theory on the other, in order to address the pressing issue of how to treat the behaviour of nuclear spin systems far from equilibrium.

2. Theoretical Background

The theoretical background of NMR relaxation theory is reviewed briefly in order to establish the notation and to resolve ambiguities in some of the key terms.

2.1. Hilbert space

The sample is considered to consist of a large number of duplicates of identical spin systems, each consisting of N coupled spins with spin quantum numbers $\{I_1, I_2 \dots I_N\}$. The quantum state of each system may be described by a state vector $|\psi\rangle$ which is an element of a Hilbert space \mathcal{H} . The dimension of Hilbert space is equal to the number of independent spin states, and is given by

$$N_{\mathcal{H}} = \prod_{i=1}^N (2I_i + 1) \quad (13)$$

Spin operators may be represented by $N_{\mathcal{H}} \times N_{\mathcal{H}}$ -dimensional matrices in Hilbert space.

2.2. Liouville space and Superoperators

2.2.1. Liouville space

A complete set of linear operators forms a linear vector space called Liouville space, with dimension $N_{\mathcal{L}} = N_{\mathcal{H}}^2$. An operator O may be regarded as a vector of length $N_{\mathcal{L}}$ in this space and denoted $|O\rangle$. The inner product between any two operators (called the *Liouville bracket*) is defined as follows:

$$(M|N) = \text{Tr}\{M^\dagger N\} \quad (14)$$

A set of $N_{\mathcal{L}}$ basis operators $\{|O_p\rangle\}$ with $p \in \{1, 2 \dots N_{\mathcal{L}}\}$ is said to be orthonormal if it satisfies the condition

$$(O_p|O_q) = \delta_{pq} \quad (15)$$

Such a set of operators forms a suitable basis for Liouville space.

2.2.2. Superoperators

Superoperators transform operators into other operators [50, 66]. The following superoperators are used in the current article:

1. The *left-multiplication superoperator* is denoted here by $M\bullet$, where the bullet symbol \bullet is a placeholder for an operator argument. The superoperator $M\bullet$ multiplies its operand by an operator from the left, as follows:

$$(M\bullet)|O\rangle = |MO\rangle \quad (16)$$

2. The *right-multiplication superoperator* is denoted here by $\bullet M$, and multiplies its operand by an operator from the right, as follows:

$$(\bullet M)|O\rangle = |OM\rangle \quad (17)$$

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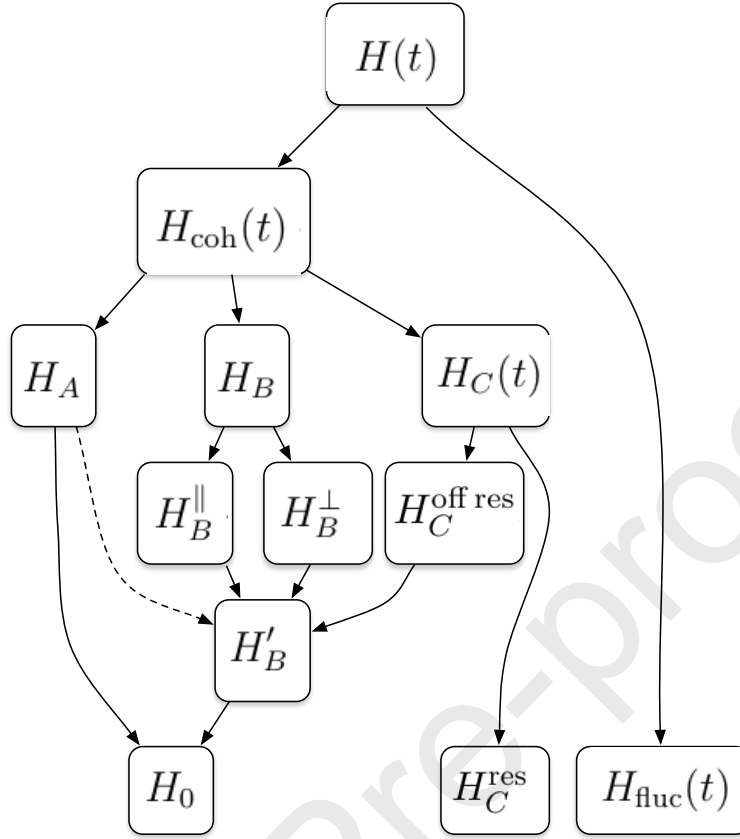


Figure 2: The organization of spin Hamiltonian terms used in this article. The Hamiltonian $H(t)$ consists of a coherent term $H_{\text{coh}}(t)$ and a fluctuating term $H_{\text{fluc}}(t)$. The coherent term contains a dominant part H_A , a static (or quasi-static) perturbation H_B , and a time-dependent perturbation $H_C(t)$. The static perturbation may be decomposed into a secular part H_B^{\parallel} which commutes with H_A , and a non-secular part H_B^{\perp} , which does not. The time-dependent perturbation H_C may be divided into a resonant part H_C^{res} and an off-resonant part $H_C^{\text{off res}}$. Standard approximations lead to a corrected perturbation H'_B which commutes with H_A . The main coherent Hamiltonian H_0 is constructed by adding H_A and H'_B .

3. The *commutation superoperator* is defined as follows:

$$\widehat{M} = (M \bullet) - (\bullet M) \quad (18)$$

such that

$$\widehat{M} |N\rangle = |[M, N]\rangle = |MN - NM\rangle \quad (19)$$

In the current article, a symbol of the form \widehat{M} implies a general superoperator of unspecified type, unless M is already defined as the symbol for an operator, in which case \widehat{M} implies the commutation superoperator of the operator M .

The matrix representation of a superoperator in a particular operator basis has matrix elements defined as follows:

$$[\widehat{M}]_{rs} = (O_r | \widehat{M} | O_s) = \text{Tr}[O_r^\dagger \widehat{M} O_s] \quad (20)$$

2.3. Spin Hamiltonian

The organization of the spin Hamiltonian terms for the individual ensemble members is shown in figure 2. The spin Hamiltonian is expressed as a sum of coherent and fluctuating contributions:

$$H(t) = H_{\text{coh}}(t) + H_{\text{fluc}}(t) \quad (21)$$

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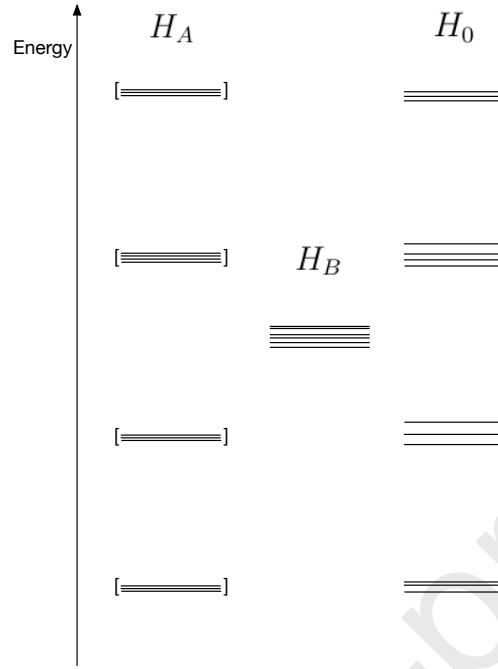


Figure 3: Schematic eigenvalue spectra of the coherent Hamiltonian terms H_A and H_B . Degenerate eigenvalues are indicated by square brackets. The eigenvalue spectrum of H_A consists of degenerate or widely-spaced eigenvalues, such that the eigenvalue spacing is large compared to $\|H_B\|$, and also $\|H_C\|$ and $\|H_{\text{fluc}}\|$ (not shown). Degeneracy is broken when H_0 is constructed by combining H_A and H_B , after correction for non-secular and off-resonant contributions (equation 32).

The coherent part is assumed to be the same for each member of the ensemble, whereas the fluctuating part may differ for ensemble members at a given point in time, and is responsible for the relaxation of the system. For typical solution-state NMR experiments the coherent part consists of Zeeman, chemical shift and scalar coupling interactions [4, 6, 12]. Other interactions are readily accommodated, such as residual dipole-dipole couplings and quadrupolar interactions in anisotropic phases.

2.3.1. Coherent Hamiltonian

The discussion below makes extensive use of a division of the coherent Hamiltonian into three parts, called H_A , H_B and H_C , as follows:

$$H_{\text{coh}}(t) = H_A + H_B + H_C(t) \quad (22)$$

The properties of these three terms is as follows:

- *The dominant Hamiltonian H_A .* The term H_A is much larger than the H_B , H_C and H_{fluc} terms:

$$\|H_A\| \gg \|H_B\|, \|H_C\|, \|H_{\text{fluc}}\| \quad (23)$$

The operators H_B and H_C may therefore be regarded as perturbations to the dominant Hamiltonian H_A . In this article we also demand that all eigenvalues of H_A are either degenerate or widely spaced compared to the corresponding matrix elements of the perturbations H_B and H_C in the eigenbasis of H_A (see figure 3). This strong constraint on the eigenvalue spectrum of H_A is very important and underpins much of the theory described below.

Denote the eigenvalues and eigenstates of the dominant term H_A by ω_r^A and $|r\rangle^A$ respectively:

$$H_A |r\rangle^A = \omega_r^A |r\rangle^A \quad (24)$$

where $r \in \{1, 2 \dots N_H\}$, and the eigenstates are orthogonal:

$$\langle r|^A |s\rangle^A = \delta_{rs} \quad (25)$$

The perturbations H_B and H_C are both assumed to fulfil the following condition:

$$\langle r|^A H_B |s\rangle^A, \langle r|^A H_C(t) |s\rangle^A \ll |\omega_r^A - \omega_s^A| \quad \forall \omega_r^A \neq \omega_s^A \quad (26)$$

Equation 26 implies that the matrix representations of H_B and H_C , expressed in the eigenbasis of H_A , has off-diagonal terms which are either between degenerate states of H_A , or which are always small in magnitude compared to the corresponding separation of non-degenerate H_A eigenvalues.

In typical high-field NMR experiments, H_A represents the dominant Zeeman interaction with a strong external magnetic field. However in some cases, a different Hamiltonian, such as an exchange interaction, is included in the H_A term (see section 6.4).

- *The (quasi)static perturbation term H_B .* The term H_B is assumed to be small in magnitude with respect to H_A (equation 23) and either time-independent or with a slow time-dependence. The latter condition may be written as follows:

$$\left| \frac{d}{dt} \langle r|^A H_B |s\rangle^A \right| \ll |\omega_r^A - \omega_s^A| \quad \forall \omega_r^A \neq \omega_s^A \quad (27)$$

In typical high-field NMR applications, the term H_B contains spin-spin couplings, chemical shift terms, and interactions with slowly varying fields such as magnetic field gradient pulses. In solid-state NMR, anisotropic spin interactions such as chemical shift anisotropies, quadrupolar interactions, and dipole-dipole couplings are also included. These terms may acquire a slow time-dependence satisfying equation 27 through sample rotation. Since the eigenvalues of H_A are combinations of the Larmor frequencies for the nuclides in the spin system, equation 26 implies the validity of a high-field approximation for the nuclear spin Hamiltonian.

The H_B term may be further subdivided into a “secular” term H_B^{\parallel} and a “non-secular” term H_B^{\perp} :

$$H_B = H_B^{\parallel} + H_B^{\perp} \quad (28)$$

where H_B^{\parallel} commutes with H_A , while H_B^{\perp} does not:

$$\begin{aligned} [H_A, H_B^{\parallel}] &= 0 \\ [H_A, H_B^{\perp}] &\neq 0 \end{aligned} \quad (29)$$

- *The time-dependent perturbation term $H_C(t)$.*

The term H_C is also small in magnitude with respect to H_A (equation 23) but has a rapid time-dependence such that the following condition is satisfied:

$$\left| \frac{d}{dt} \langle r|^A H_C(t) |s\rangle^A \right| \not\ll |\omega_r^A - \omega_s^A| \quad \forall \omega_r^A \neq \omega_s^A \quad (30)$$

In typical NMR experiments, $H_C(t)$ includes the interaction of the spin system with a resonant radiofrequency field. The $H_C(t)$ term may be further divided into a term $H_C^{\text{res}}(t)$ with frequency components close to resonance and an off-resonance term $H_C^{\text{off res}}(t)$ with frequency components far from resonance. For example, in the case of an amplitude-modulated radiofrequency field, the near-resonant term which rotates in the same sense as the Larmor frequency is included in H_C^{res} , while the counter-rotating term is included in $H_C^{\text{off res}}$.

Since equation 26 is assumed to be satisfied, the “non-secular” term H_B^{\perp} may either be ignored, or treated approximately by a small correction to the eigenvalues of H_B^{\parallel} (second-order quadrupolar shifts are a typical example [67]).

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The off-resonant term $H_C^{\text{off res}}(t)$ also gives rise to small shifts which may be taken into account through a small correction to H_B . For simplicity, we now assume that any non-secular corrections induced by H_B^\perp , and any off-resonance shifts induced by $H_C^{\text{off res}}$ (for example, Bloch-Siegert shifts [68]), are incorporated into a corrected version of H_B , denoted H'_B , which commutes with H_A :

$$[H_A, H'_B] = 0 \quad (31)$$

The main part of the coherent Hamiltonian, denoted here H_0 , is now constructed by combining the H_A and H'_B terms:

$$H_0 = H_A + H'_B \quad (32)$$

The operators H_A and H_0 commute:

$$[H_A, H_0] = 0 \quad (33)$$

Hence it is possible to define a set of states that form a simultaneous eigenbasis of both operators. The states which form this simultaneous eigenbasis are denoted $\{|1\rangle \dots |N_{\mathcal{H}}\rangle\}$, where $N_{\mathcal{H}}$ is the dimension of Hilbert space. The corresponding eigenequations are as follows:

$$\begin{aligned} H_0 |r\rangle &= \omega_r |r\rangle \\ H_A |r\rangle &= \omega_r^A |r\rangle \end{aligned} \quad (34)$$

where $\langle r|s\rangle = \delta_{rs}$.

Note that although the eigenvalues ω_r^A of H_A are the same as in equation 24, the set of eigenstates $|r\rangle$ may not be identical to the set of eigenstates $|r\rangle^A$, since eigenstates belonging to degenerate subspaces of H_A may be mixed by the H_B term.

The term H_0 determines the coherent dynamics of the spin system. In typical NMR experiments in high field, H_0 contains the Zeeman interaction of the nuclei with the static magnetic field, as well as the secular parts of the chemical shift and spin-spin coupling terms.

The H_0 eigenstates may be used to define a set of transition operators (or shift operators) X_{rs} , as follows:

$$X_{rs} = |r\rangle\langle s| \quad (35)$$

where the states $|r\rangle$ satisfy equation 34. The operator X_{rs} converts the state $|s\rangle$ into the state $|r\rangle$. There are $N_{\mathcal{L}} = N_{\mathcal{H}}^2$ transition operators since the indices r and s both run from 1 to $N_{\mathcal{H}}$.

The set of all eigenstate transition operators $\{X_{rs}\}$ forms an orthonormal operator basis of Liouville space, being orthonormal in both indices:

$$(X_{rs} | X_{kl}) = \delta_{rk} \delta_{sl} \quad (36)$$

The eigenstate transition operators X_{rs} are eigenoperators of the commutation superoperator of H_0 :

$$\hat{H}_0 | X_{rs} \rangle = \omega_{rs} | X_{rs} \rangle \quad (37)$$

where the transition frequencies are given by

$$\omega_{rs} = \omega_r - \omega_s \quad (38)$$

The eigenstate transition operators X_{rs} are also eigenoperators of the commutation superoperator of H_A , but with different eigenvalues:

$$\hat{H}_A | X_{rs} \rangle = \omega_{rs}^A | X_{rs} \rangle \quad (39)$$

where

$$\omega_{rs}^A = \omega_r^A - \omega_s^A \quad (40)$$

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In the case that H_A is chosen to be the Zeeman Hamiltonian for the spin system, the eigenvalues ω_{rs}^A are given by linear combinations of the nuclear Larmor frequencies of the relevant nuclides.

The transition operators X_{rs} have inconvenient rotational properties which derive from the complexity and low rotational symmetry of the operator H_B . It proves convenient to define a new eigenoperator basis for \hat{H}_A , with operators $|A_\alpha\rangle$ satisfying the eigenequation:

$$\hat{H}_A |A_\alpha\rangle = \omega_\alpha^A |A_\alpha\rangle \quad (41)$$

where the set of eigenoperators $\{|A_1\rangle \dots\}$ is orthonormal:

$$(A_\alpha | A_{\alpha'}) = \delta_{\alpha\alpha'} \quad (42)$$

The eigenvalues are denoted ω_α^A with $\alpha \in \{0, 1 \dots N_L\}$. Each eigenvalue ω_α^A corresponds to one of the frequencies ω_{rs}^A in equation 40, and each eigenoperator may be expressed as a linear superposition of transition operators with the same eigenvalue of \hat{H}_A :

$$|A_\alpha\rangle = \sum_{r=1}^{N_H} \sum_{s=1}^{N_H} |X_{rs}\rangle (X_{rs} | A_\alpha) \times \delta(\omega_{rs}^A - \omega_\alpha^A) \quad (43)$$

where $\delta(x) = 1$ for $x = 0$ and 0 otherwise.

It is desirable to choose eigenoperators $\{|A_1\rangle \dots\}$ which have convenient properties under three-dimensional rotations of the nuclear spin angular momenta. Whether this is possible depends on the commutation properties of the dominant Hamiltonian H_A .

In high-field NMR, the dominant Hamiltonian H_A is usually identified with the Zeeman Hamiltonian, ignoring any chemical shifts or other perturbations:

$$\text{high-field NMR:} \quad H_A = H_Z \quad (44)$$

$$H_Z = \sum_{i=1}^N \omega_i^0 I_{iz} \quad (45)$$

In cases involving spin isomerism, the nuclear exchange interaction may also be included in H_A (see section 6.4).

The commutation properties of the Zeeman Hamiltonian are different for homonuclear and heteronuclear systems:

- In *homonuclear* systems (all nuclides of the same type), all Larmor frequency terms ω_i^0 are identical, and hence H_A is proportional to the total angular momentum operator along the z-axis, $I_z = \sum_{i=1}^N I_{iz}$. In this case H_A commutes with the total spin angular momentum along the field, and also the total square angular momentum of all nuclei:

$$[H_A, I_z] = [H_A, I^2] = 0 \quad (46)$$

where $I^2 = I_x^2 + I_y^2 + I_z^2$ and $I_\nu = \sum_{i=1}^N I_{i\nu}$; $\nu \in \{x, y, z\}$. Hence, each eigenoperator $|A_\alpha\rangle$ may be identified with an irreducible spherical tensor operator (ISTO) $|T_{\lambda\mu}^\alpha\rangle$:

$$|A_\alpha\rangle = c_\alpha |T_{\lambda\mu}^\alpha\rangle \quad (47)$$

obeying the following standard eigenequations:

$$\begin{aligned} \hat{I}^2 |T_{\lambda\mu}^\alpha\rangle &= \lambda_\alpha(\lambda_\alpha + 1) |T_{\lambda\mu}^\alpha\rangle \\ \hat{I}_z |T_{\lambda\mu}^\alpha\rangle &= \mu_\alpha |T_{\lambda\mu}^\alpha\rangle \\ \hat{I}^2 &= (\hat{I}_x)^2 + (\hat{I}_y)^2 + (\hat{I}_z)^2 \end{aligned} \quad (48)$$

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Here \hat{I}_x is the commutation superoperator of the total angular momentum along the x-axis, $I_x = \sum_{i=1}^N I_{ix}$, and similarly for the x and y-operators [69]. Note that $(\hat{I}_x)^2$ is *not* the same superoperator as $\sum_{i=1}^N \hat{I}_{ix}^2$. The rotational rank and azimuthal quantum number of the eigenoperator $|A_\alpha\rangle$ are denoted λ_α and μ_α respectively. The normalization factor c_α in equation 47 ensures that $(A_\alpha|A_\alpha) = 1$.

- In *heteronuclear* systems, the Zeeman Hamiltonian does not commute with the total square angular momentum operator of all spins but with the total square angular momentum operators of individual groups of spins, organized by their isotopic types $\{I, S, \dots\}$. If the numbers of spins of the different isotopic types are denoted $\{N_I, N_S, \dots\}$, the relevant z- angular momentum operators are denoted $I_z = \sum_{i=1}^{N_I} I_{iz}$, $S_z = \sum_{s=1}^{N_S} S_{sz}$, etc. and the total-square angular momentum operators by

$$\begin{aligned} I^2 &= \sum_{i=1}^{N_I} (I_{ix}^2 + I_{iy}^2 + I_{iz}^2) \\ S^2 &= \sum_{s=1}^{N_S} (S_{sx}^2 + S_{sy}^2 + S_{sz}^2) \end{aligned} \quad (49)$$

The following commutation relationships apply:

$$\begin{aligned} [H_A, I_z] &= [H_A, I^2] = [H_A, S_z] = [H_A, S^2] = 0 \quad \dots \\ [I_z, S_z] &= [I^2, S^2] = 0 \quad \dots \end{aligned} \quad (50)$$

An appropriate set of \hat{H}_A eigenoperators is given by the tensor product of the individual spherical tensor operator sets:

$$\{A_\alpha\} = \{T_{\lambda,\mu}^I\} \otimes \{T_{\lambda,\mu}^S\} \otimes \dots \quad (51)$$

Each eigenoperator has the form

$$|A_\alpha\rangle = c_\alpha \left| T_{\lambda,\mu}^{I,\alpha} T_{\lambda,\mu}^{S,\alpha} \right\rangle \quad (52)$$

with a set of rotational ranks $\{\lambda_\alpha^I, \lambda_\alpha^S, \dots\}$ and azimuthal quantum numbers $\{\mu_\alpha^I, \mu_\alpha^S, \dots\}$ for the spin species $\{I, S, \dots\}$.

2.3.2. Fluctuating Hamiltonian

The fluctuating Hamiltonian H_{fluc} , which is responsible for spin relaxation, typically contains contributions from several different nuclear spin interactions:

$$H_{\text{fluc}}(t) = H_{\text{fluc}}^{\Lambda_1}(t) + H_{\text{fluc}}^{\Lambda_2}(t) + \dots \quad (53)$$

The interactions $\{\Lambda_1, \Lambda_2, \dots\}$ typically include nuclear dipole-dipole interactions, chemical shift anisotropies, etc. The random fluctuations of these interactions, due to molecular motion, are responsible for nuclear spin relaxation. In general, the fluctuations of different interactions are correlated with each other.

Each fluctuating Hamiltonian term may be expressed as a superposition of \hat{H}_A eigenoperators, as follows:

$$|H_{\text{fluc}}^\Lambda(t)\rangle = \sum_\alpha F_\alpha^\Lambda(t) |A_\alpha\rangle \quad (54)$$

where the coefficients are defined as follows:

$$F_\alpha^\Lambda(t) = (A_\alpha | H_{\text{fluc}}^\Lambda(t)) \quad (55)$$

and have the following correlation functions:

$$G_{\alpha\alpha'}^{\Lambda\Lambda'}(\tau) = \overline{F_\alpha^{\Lambda*}(t + \tau) F_{\alpha'}^{\Lambda'}(t)} \quad (56)$$

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where the overbar indicates an ensemble average. The correlation functions $G_{\alpha\alpha'}^{\Lambda\Lambda'}(\tau)$ are assumed to be independent of t (stationary assumption), and have the form

$$G_{\alpha\alpha'}^{\Lambda\Lambda'}(\tau) = G_{\alpha\alpha'}^{\Lambda\Lambda'}(0)g_{\alpha\alpha'}^{\Lambda\Lambda'}(\tau) \quad (57)$$

where $g_{\alpha\alpha'}^{\Lambda\Lambda'}(0) = 1$. The correlation functions are assumed to decay monotonically with increasing τ and become vanishingly small for τ larger than an interval called the correlation time denoted τ_c . In general the correlation time may be different for different mechanisms, but we will overlook this complication here, for the sake of simplicity.

In the case of rotational diffusion, the correlation functions may be shown to decay approximately exponentially [70], with the following form

$$g_{\alpha\alpha'}^{\Lambda\Lambda'}(\tau) \simeq \exp\{-|\tau/\tau_c|\} \quad (58)$$

For simplicity we assume that the correlation time is independent of the interaction and eigenoperator indices.

The spectral density functions are defined as the Fourier transform of the correlation functions:

$$\begin{aligned} J_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega) &= \int_{-\infty}^{\infty} G_{\alpha\alpha'}^{\Lambda\Lambda'}(\tau) \exp\{i\omega\tau\} d\tau \\ j_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega) &= \int_{-\infty}^{\infty} g_{\alpha\alpha'}^{\Lambda\Lambda'}(\tau) \exp\{i\omega\tau\} d\tau \end{aligned} \quad (59)$$

such that

$$J_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega) = j_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega)G_{\alpha\alpha'}^{\Lambda\Lambda'}(0) \quad (60)$$

For an exponential correlation function (equation 58), the real part of the spectral density has the simple form of an absorption-mode Lorentzian:

$$\text{Re}\{j_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega)\} = \frac{2\tau_c}{1 + \omega^2\tau_c^2} \quad (61)$$

An alternative approach is to expand the fluctuating Hamiltonian in transition operators as follows:

$$|H_{\text{fluc}}^{\Lambda}(t)\rangle = \sum_{r,s} \langle r| H_{\text{fluc}}^{\Lambda}(t)|s\rangle |X_{rs}\rangle \quad (62)$$

The correlation functions of the fluctuating matrix elements are defined as follows:

$$G_{ijkl}^{\Lambda\Lambda'}(\tau) = \overline{\langle i| H_{\text{fluc}}^{\Lambda}(t+\tau)|j\rangle \langle k| H_{\text{fluc}}^{\Lambda'}(t)|l\rangle} \quad (63)$$

which are again assumed to be independent of t through the assumption of stationary random processes. The spectral density functions of the transition matrix elements are defined as follows:

$$J_{ijkl}^{\Lambda\Lambda'}(\omega) = \sum_{\Lambda,\Lambda'} J_{ijkl}^{\Lambda\Lambda'}(\omega) \quad (64)$$

from which the contributions of the individual correlation functions are given by:

$$J_{ijkl}^{\Lambda\Lambda'}(\omega) = \int_{-\infty}^{\infty} G_{ijkl}^{\Lambda\Lambda'}(\tau) \exp\{i\omega\tau\} d\tau \quad (65)$$

Their real parts are again proportional to absorption-mode Lorentzians, as in equation 61.

2.4. Equation of Motion

2.4.1. Liouville-von Neumann equation

The density operator of a single ensemble member is defined as follows:

$$|\sigma\rangle = |\psi\rangle\langle\psi| \quad (66)$$

The time evolution of the density operator in Liouville space is governed by the Liouville-von-Neumann (LvN) equation, and takes the form:

$$\begin{aligned} \frac{d}{dt} |\sigma(t)\rangle &= -i\hat{H}(t) |\sigma(t)\rangle \\ \hat{H}(t) &= \hat{H}_0 + \hat{H}_C^{\text{res}} + \hat{H}_{\text{fluc}}(t) \end{aligned} \quad (67)$$

The solution to the LvN may be written as

$$|\sigma(t)\rangle = \hat{U}(t, t_a) |\sigma(t_a)\rangle \quad (68)$$

where $t \geq t_a$ and the propagation superoperator is given by a time-ordered product of exponential superoperators:

$$\hat{U}(t, t_a) = \hat{T} \exp \left\{ -i \int_{t_a}^t \hat{H}(t') dt' \right\} \quad (69)$$

2.4.2. Ensemble density operator

The ensemble-averaged density operator is defined

$$|\rho\rangle = \overline{|\sigma\rangle} = \overline{|\psi\rangle\langle\psi|} \quad (70)$$

where the overbar denotes an average over ensemble members.

It is assumed that the evolution of the system may be approximated by an equation of the type:

$$|\rho(t)\rangle = \hat{V}(t, t_a) |\rho(t_a)\rangle \quad (71)$$

where the propagation superoperator \hat{V} is in general not unitary. The primary aim of relaxation theory is the systematic construction of \hat{V} valid within appropriate limits. Methods which have been used include semi-classical (SC) relaxation theory [1, 3, 4], the generalized cumulant expansion method [71–73] or the Fokker-Plank formalism frequently encountered in EPR. [74, 75] A conceptually different approach is the Quantum Monte Carlo approach, which is widely used in the field of quantum optics. [76–78]

3. Semi-classical relaxation theory

The semi-classical relaxation theory of nuclear spin systems is widely covered in the standard literature [1, 2, 4, 6–11]. To underpin the later discussion we give a concise overview of the basic concepts and key approximations. We also include a brief discussion of the handling of the relaxation superoperator in the interaction frame, which is the source of occasional confusion.

3.1. Semi-classical relaxation superoperator

In order to prepare for the application of second-order perturbation theory, the spin Hamiltonian is expressed in the interaction frame of the dominant part of the coherent Hamiltonian H_A :

$$\tilde{H}(t) = \exp \left\{ +i\hat{H}_A t \right\} H(t) \quad (72)$$

In the case that H_A is identified with the Zeeman Hamiltonian, as is common in high-field NMR, the interaction frame is also known as the “rotating frame”.

The LvN equation, in the interaction frame, is given by

$$\begin{aligned} \frac{d}{dt} |\tilde{\sigma}(t)\rangle &= -i\tilde{H}(t) |\tilde{\sigma}(t)\rangle \\ \tilde{H}(t) &= \tilde{H}_{\text{coh}} + \tilde{H}_{\text{fluc}}(t) \end{aligned} \quad (73)$$

with the interaction-frame fluctuating Hamiltonian:

$$\tilde{H}_{\text{fluc}}(t) = \exp\left\{+i\hat{H}_A t\right\} H_{\text{fluc}}(t) \quad (74)$$

and the interaction-frame coherent Hamiltonian:

$$\tilde{H}_{\text{coh}}(t) = H_0 - H_A + \tilde{H}_C^{\text{res}}(t) \quad (75)$$

In the case of single-frequency near-resonant irradiation, H_A may be chosen so that \tilde{H}_C^{res} is piecewise time-independent, the time-independent “pieces” corresponding to the elements of the applied pulse sequence.

The solution to the LvN equation for the time evolution of individual ensemble members may be approximated by time-dependent perturbation theory [4, 6–11, 62, 63]. The following standard approximations and assumptions are made:

- The density operator and the fluctuating contributions are uncorrelated.
- The ensemble average of the fluctuating contributions vanishes.
- The fluctuating contributions represent a weakly stationary process, so that two-time correlations only depend on their time difference $t' - t = \tau$.
- There exists a correlation time τ_C such that the ensemble average becomes negligible for time differences $\tau \gg \tau_C$.
- The terms H_B , H_C and H_{fluc} are all sufficiently small that $\|H_B \tau_C\| \ll 1$, $\|H_C \tau_C\| \ll 1$ and $\|H_{\text{fluc}} \tau_C\| \ll 1$, so that the interaction frame density operator does not change significantly over the timescale of τ_C .

Note that there is *no* assumption at this stage, of the spin system being close to equilibrium.

These assumptions lead to the following equation of motion for the ensemble-average density operator in the interaction frame:

$$\frac{d}{dt} |\tilde{\rho}(t)\rangle = \hat{\tilde{\mathcal{L}}}_{SC}(t) |\tilde{\rho}(t)\rangle \quad (76)$$

where the semi-classical Liouvillian superoperator, in the interaction frame, is given by

$$\hat{\tilde{\mathcal{L}}}_{SC} = -i\hat{\tilde{H}}_{\text{coh}} + \hat{U}_A^\dagger(t) \hat{\Gamma}_{SC}^{\text{lab}} \hat{U}_A(t) \quad (77)$$

and the relaxation superoperator in the laboratory frame is as follows [1, 3]:

$$\hat{\Gamma}_{SC}^{\text{lab}} = - \int_{-\infty}^0 \overline{\hat{H}_{\text{fluc}}(0) \hat{H}_{\text{fluc}}(\tau)} d\tau \quad (78)$$

If small dynamic frequency shifts are neglected [1, 3, 4, 62, 63], this may be written as follows:

$$\hat{\Gamma}_{SC}^{\text{lab}} = -\frac{1}{2} \sum_{\Lambda, \Lambda'} \sum_{\alpha, \alpha'} J_{\alpha\alpha'}^{\Lambda\Lambda'} (\omega_{\alpha'}^A) \hat{A}_\alpha \hat{A}_{\alpha'}^\dagger \quad (79)$$

Equation 79 is a convenient expression for the semi-classical relaxation superoperator. This form is basis-independent and gives no special status to the eigenstates of the coherent Hamiltonian. It has been used for many purposes in solution NMR, and proves particularly useful for the analysis of long-lived states [34, 35, 37–45, 79–84].

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An alternative expression, making use of the transition operators between the eigenstates of the Hamiltonian H_0 , is as follows:

$$\hat{\Gamma}_{SC}^{\text{lab}} = -\frac{1}{2} \sum_{i,j,k,l} J_{ijkl}(\omega_{kl}) \hat{X}_{ij} \hat{X}_{kl}^{\dagger} \quad (80)$$

where the spectral densities are given in equation 64, and the differences ω_{kl}^A between eigenvalues of the dominant Hamiltonian H_A are defined in equation 40.

Most spin dynamical calculations are performed in the interaction frame of the dominant Hamiltonian H_A , since this greatly simplifies the treatment of resonant radiofrequency fields. However, the interaction-frame Liouvillian given in equation 77 is difficult to use, because of the time-dependent terms $\hat{U}_A(t)$. This problem is avoided by making another approximation. The laboratory frame relaxation superoperator is expanded in eigenoperators of \hat{H}_A :

$$\hat{\Gamma}_{SC}^{\text{lab}} = \sum_{\alpha,\alpha'} |A_{\alpha}\rangle \langle A_{\alpha'}| \times (A_{\alpha} | \hat{\Gamma}_{SC}^{\text{lab}} | A_{\alpha'}) \quad (81)$$

This allows the second term in equation 77 to be written as follows:

$$\hat{U}_A^{\dagger}(t) \hat{\Gamma}_{SC}^{\text{lab}} \hat{U}_A(t) = \sum_{\alpha,\alpha'} |A_{\alpha}\rangle \langle A_{\alpha'}| \times (A_{\alpha} | \hat{\Gamma}_{SC}^{\text{lab}} | A_{\alpha'}) \exp\{i(a_{\alpha} - a_{\alpha'})t\} \quad (82)$$

The rapidly oscillating terms in this equation may be ignored under the assumption that the relaxation rate constants are small compared to the eigenvalue separation of the dominant Hamiltonian H_A . Note that this approximation is readily defensible for the eigenvalues of H_A , since these are defined to be either degenerate or widely spaced, but would not be fully justifiable if the Hamiltonian H_0 had been used to construct the interaction frame, since H_0 may have near-degenerate eigenvalues. The omission of rapidly oscillating components in equation 82 allows use of the following *secularized relaxation superoperator* in the interaction frame:

$$\hat{\Gamma}_{SC}^{\text{sec}} \simeq \sum_{\alpha,\alpha'} |A_{\alpha}\rangle \langle A_{\alpha'}| \times (A_{\alpha} | \hat{\Gamma}_{SC}^{\text{lab}} | A_{\alpha'}) \delta(a_{\alpha} - a_{\alpha'}) \quad (83)$$

where $\delta(x) = 1$ if $x = 0$ and $\delta(x) = 0$ otherwise. The Liouvillian superoperator in the interaction frame of H_A is therefore given, to a very good approximation, by

$$\hat{\mathcal{L}}_{SC} \simeq -i\hat{H}_{\text{coh}} + \hat{\Gamma}_{SC}^{\text{sec}} \quad (84)$$

where $\hat{\Gamma}_{SC}^{\text{sec}}$ is time-independent. Spin dynamical calculations may therefore be conducted in the interaction frame of the dominant Hamiltonian H_A , using the interaction-frame coherent Hamiltonian \tilde{H}_{coh} and the secularized semi-classical relaxation superoperator $\hat{\Gamma}_{SC}^{\text{sec}}$ of equation 83.

In the solution NMR of homonuclear spin systems in high magnetic field, H_A may be chosen to equal the dominant Zeeman interaction. In this case, selection rules on the rotational correlation functions [85] render the secularization procedure in equation 83 unnecessary, since the matrix elements $(A_{\alpha} | \hat{\Gamma}_{SC}^{\text{lab}} | A_{\alpha'})$ vanish in any case for $a_{\alpha} \neq a_{\alpha'}$. However, this is not always true for heteronuclear spin systems. An example of relaxation superoperator secularization in heteronuclear systems may be found in reference 35.

For simplicity, the secularized relaxation superoperator in the interaction frame is now simply denoted as $\hat{\Gamma}$:

$$\hat{\Gamma} = \hat{\Gamma}_{SC}^{\text{sec}} \quad (85)$$

From the definition of $\hat{\Gamma}_{SC}^{\text{sec}}$, this superoperator is identical when expressed in the laboratory frame:

$$\hat{\Gamma}^{\text{lab}} = \hat{U}_A \hat{\Gamma} \hat{U}_A^{\dagger} = \hat{\Gamma} \quad (86)$$

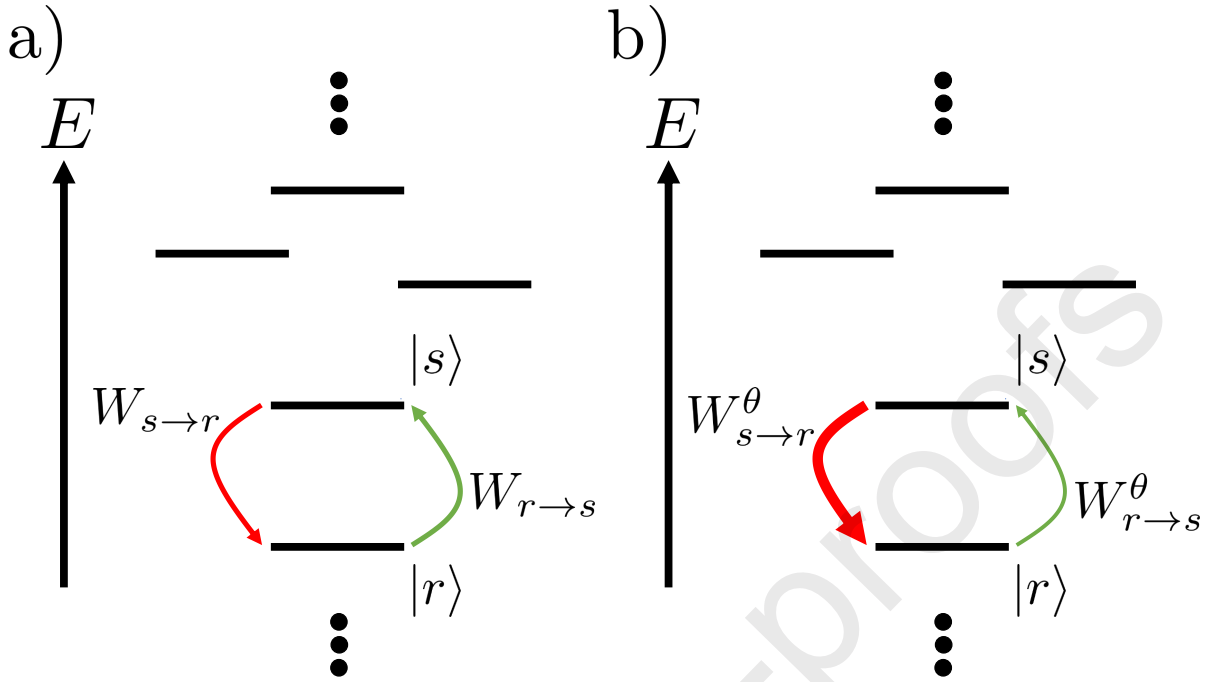


Figure 4: A section of the energy level structure of an arbitrary quantum system. Relaxation phenomena induce transitions between the states $|r\rangle$ and $|s\rangle$. Transitions that cause the system to gain energy are indicated in green, transitions that cause the system to lose energy are indicated in red. **(a)** Semi-classical transition probabilities. The “upwards” and “downwards” transition probabilities $W_{r \rightarrow s}$ and $W_{s \rightarrow r}$ are equal. **(b)** After thermalization, the “downwards” transition probability $W_{s \rightarrow r}^\theta$ (thick arrow) is larger than the “upwards” transition probability $W_{r \rightarrow s}^\theta$ (thin arrow).

3.2. Transition probabilities

The transition probability per unit time from an eigenstate $|r\rangle$ of H_0 to a different eigenstate $|s\rangle$ may be derived from the secularized relaxation superoperator as follows [6]:

$$W_{r \rightarrow s} = -(X_{ss} | \hat{\Gamma} | X_{rr}) = J_{sr sr}(\omega_{sr}) \quad (87)$$

The semi-classical approach leads to identical rate coefficients for forward and backward transitions, as sketched in figure 4(a):

$$W_{r \rightarrow s} = W_{s \rightarrow r} \quad (88)$$

As is well-known, symmetrical transition probabilities are incompatible with the establishment of thermal equilibrium at a finite temperature [1–14].

3.2.1. Coherence decay rate constants

The decay rate constant for a coherence between the eigenstates $|r\rangle$ and $|s\rangle$ of the coherent Hamiltonian H_0 may be expressed as:

$$\lambda_{rs} = -(X_{rs} | \hat{\Gamma} | X_{rs}) \quad (89)$$

which may be written as the sum of an “adiabatic” and “non-adiabatic” contributions [4, 6–10]:

$$\lambda_{rs} = \lambda_{rs}^{\text{ad}} + \lambda_{rs}^{\text{na}} \quad (90)$$

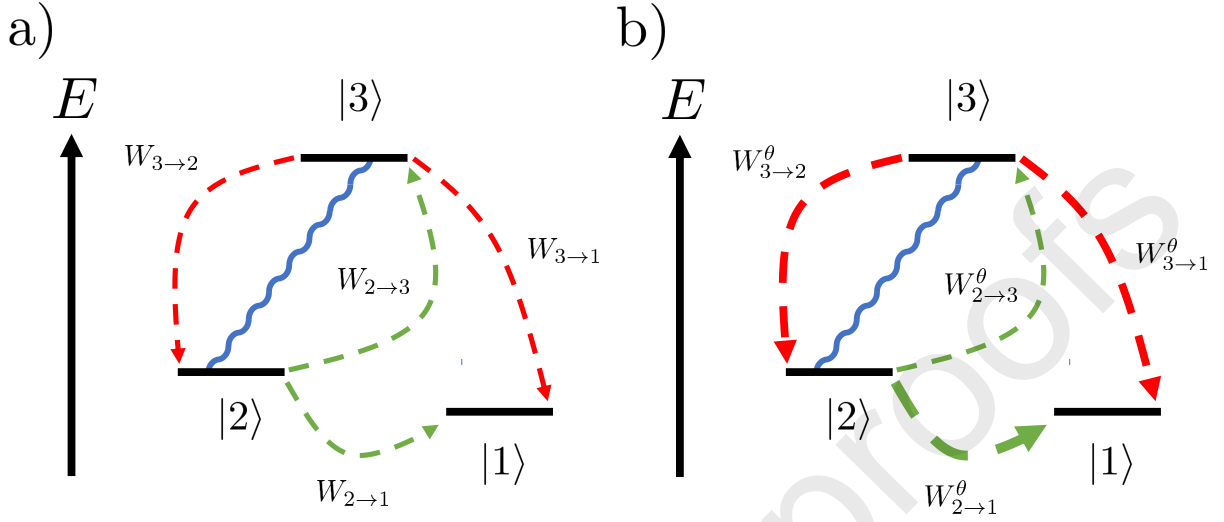


Figure 5: Energy levels of a three-level quantum system. A coherence between the states $|2\rangle$ and $|3\rangle$ is indicated by a blue wavy line. The non-adiabatic contribution to the coherence decay process is given by the summed transition probability for all transitions out of the states $|2\rangle$ and $|3\rangle$ as indicated by the arrows. **(a)** In the semi-classical treatment, “upwards” and “downwards” transition probabilities are equal. **(b)** At finite temperature the non-adiabatic contributions to the coherence decay rate must be adjusted to reflect the different transition probabilities in the two directions.

with

$$\lambda_{rs}^{\text{ad}} = \int_{-\infty}^0 \frac{(\langle r | \tilde{H}_{\text{fluc}}(0) | r \rangle - \langle s | \tilde{H}_{\text{fluc}}(0) | s \rangle)(\langle r | \tilde{H}_{\text{fluc}}(\tau) | r \rangle - \langle s | \tilde{H}_{\text{fluc}}(\tau) | s \rangle) d\tau}{2} = \frac{1}{2} \sum_{\Lambda, \Lambda'} \left(J_{rrrr}^{\Lambda\Lambda'}(0) - J_{rrss}^{\Lambda\Lambda'}(0) - J_{ssrr}^{\Lambda\Lambda'}(0) + J_{ssss}^{\Lambda\Lambda'}(0) \right) \quad (91)$$

and

$$\lambda_{rs}^{\text{na}} = \frac{1}{2} \left(\sum_{k \neq r} W_{r \rightarrow k} + \sum_{k \neq s} W_{s \rightarrow k} \right) \quad (92)$$

The adiabatic contributions are due to random fluctuations of the energy levels. The non-adiabatic contributions arise from the finite lifetimes of the spin states, due to transitions to other states. As an illustrative example, the non-adiabatic contribution for an arbitrary three-level system is illustrated in figure 5(a). The coherence between states $|2\rangle$ and $|3\rangle$ is indicated by a wavy line. The non-adiabatic contribution to the decay of this coherence is due to all transitions out of the states $|2\rangle$ and $|3\rangle$.

3.3. Semi-classical equation of motion

The master equation for the dynamics of the spin density operator, under semiclassical relaxation theory, is therefore given by

$$\frac{d}{dt} |\rho\rangle = \hat{\mathcal{L}}_{\text{SC}} |\rho\rangle \quad (93)$$

where the Liouvillian is

$$\hat{\mathcal{L}}_{\text{SC}} \simeq -i\{\hat{H}_0 + \hat{H}_C^{\text{res}}(t)\} + \hat{\Gamma}_{\text{SC}} \quad (94)$$

and the secularized semi-classical relaxation superoperator is given by equation 83.

Since the semi-classical relaxation superoperator predicts equal probabilities for transitions gaining and losing energy (equation 88), the true thermal equilibrium state of the spin density operator is not correctly predicted by equations 93 and 94. This problem is often addressed by arbitrarily introducing a thermal equilibrium term in the relaxation part, leading to the widely used inhomogeneous master equation (IME) of the form [1–14]:

$$\frac{d}{dt} |\rho\rangle = -i(\hat{H}_0 + \hat{H}_C^{\text{res}}(t)) |\rho\rangle + \hat{\Gamma}_{\text{SC}} (|\rho\rangle - |\rho_{\text{eq}}\rangle) \quad (95)$$

However, as described in the introduction, equation 95 gives incorrect results in general for spin systems which are far from equilibrium. In this article we present a deeper solution.

4. Thermalization

4.1. Thermal Equilibrium

At thermal equilibrium the spin-state populations adopt the Boltzmann distribution, leading to the following expression for the thermal equilibrium density operator:

$$|\rho_{\text{eq}}\rangle = \frac{|\exp\{-\beta_\theta H_0\}\rangle}{\text{Tr}[\exp\{-\beta_\theta H_0\}]} \quad (96)$$

where the temperature parameter is defined as follows:

$$\beta_\theta = \frac{\hbar}{k_B T} \quad (97)$$

An initially perturbed system eventually returns to thermal equilibrium for sufficiently long times in the absence of time-dependent perturbations.

The semi-classical relaxation superoperator of equation 79 fails to predict the correct thermal equilibrium state, since the transition probabilities are symmetric, as in eq. 88. Instead the state of complete disorder represents the stationary distribution of $\hat{\Gamma}_{\text{SC}}$ and lies in its null-space:

$$\hat{\Gamma}_{\text{SC}} |\mathbb{1}\rangle = |0\rangle \quad (98)$$

The semi-classical relaxation superoperator $\hat{\Gamma}_{\text{SC}}$ therefore drives the system to the unphysical state of infinite temperature.

4.2. Thermal Corrections

The correct thermal equilibrium state may be forced by adjusting the semi-classical relaxation superoperator using a procedure known as “thermalization”. Most techniques [50–54] achieve this by multiplying the SC-relaxation superoperator by a thermal correction superoperator $\hat{\Theta}$:

$$\hat{\Gamma}^\theta = \hat{\Gamma}_{\text{SC}} \hat{\Theta} \quad (99)$$

where $\hat{\Theta}$ forces $|\rho_{\text{eq}}\rangle$ into the null-space of $\hat{\Gamma}^\theta$:

$$\hat{\Gamma}^\theta |\rho_{\text{eq}}\rangle = |0\rangle \quad (100)$$

The thermalized equation of motion for the density operator is given by

$$\frac{d}{dt} |\rho\rangle = (-i\hat{H}_{\text{coh}} + \hat{\Gamma}^\theta) |\rho\rangle \quad (101)$$

where \hat{H}_{coh} is the commutation superoperator of the coherent Hamiltonian H_{coh} .

The thermalized relaxation superoperator should have the following properties:

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- **preserves the trace:** This condition captures the fact that the sum of all populations should be a constant of motion. Populations are free to be redistributed among each other, but there is no "loss" of populations.

$$\frac{d}{dt}(\mathbb{1}|\rho(t)) = (\mathbb{1}|\frac{d}{dt}\rho(t)) = (\mathbb{1}|\hat{\Gamma}^\theta|\rho(t)) = 0 \quad (102)$$

- **preserves hermiticity:** The density matrix must remain hermitian at all points in time to be in agreement with the statistical interpretation of quantum mechanics.

$$\frac{d}{dt}\rho_{rs}(t) = \frac{d}{dt}\rho_{sr}^*(t) \quad (103)$$

- **obeys detailed balance:** At thermal equilibrium the detailed balance condition applies [63]. The transition probabilities of $\hat{\Gamma}^\theta$ should therefore fulfill the following condition:

$$\frac{\rho_{eq}^{ss}}{\rho_{eq}^{rr}} = \frac{\hat{\Gamma}_{ssrr}^\theta}{\hat{\Gamma}_{rrss}^\theta} = \frac{W_{r \rightarrow s}^\theta}{W_{s \rightarrow r}^\theta} = \exp\{\beta_\theta \omega_{rs}\} \quad (104)$$

The detailed balance condition indicates that transitions from higher energy states to lower energy states are slightly more likely than vice versa. It follows that $|\rho_{eq}\rangle$ is a stationary distribution and lies in the null-space of $\hat{\Gamma}^\theta$ [86].

- **predict consistent coherence decay rates:** The thermalized coherence decay rate constants are composed of adiabatic and non-adiabatic contributions:

$$\lambda_{rs}^\theta = \lambda_{rs}^{\theta,ad} + \lambda_{rs}^{\theta,na} \quad (105)$$

The adiabatic contributions to the coherence decay rate constants should be independent of the thermal correction:

$$\lambda_{rs}^{\theta,ad} = \lambda_{rs}^{ad} \quad (106)$$

The non-adiabatic contributions, on the other hand, depend on the transition probabilities and should be adjusted according to the detailed balance condition, as follows:

$$\lambda_{rs}^{\theta,na} = \frac{1}{2} \left(\sum_{k \neq r} W_{r \rightarrow k}^\theta + \sum_{k \neq s} W_{s \rightarrow k}^\theta \right) \quad (107)$$

A variety of methods have been proposed for the thermalization of the relaxation superoperator. Their properties and limitations are summarized in table 1.

4.2.1. Jeener's Method

Jeener's seminal article on superoperators in magnetic resonance [50] contains a proposed thermalization method for relaxation superoperators. This is based on the *energy superoperator* $\hat{\mathcal{E}}$ defined as follows:

$$\begin{aligned} \hat{\Theta}_J &= \exp\{\beta_\theta \hat{\mathcal{E}}\} \\ \hat{\mathcal{E}} &= \frac{1}{2}(\hat{H}_0 \bullet + \bullet \hat{H}_0) \end{aligned} \quad (108)$$

The thermally corrected relaxation superoperator is given by:

$$\hat{\Gamma}_J^\theta = \hat{\Gamma}_{sc} \hat{\Theta}_J = \hat{\Gamma}_{sc} \exp\{\beta_\theta \hat{\mathcal{E}}\} \quad (109)$$

The method works by transforming the thermal equilibrium density operator $|\rho_{eq}\rangle$ into $|\mathbb{1}\rangle$. This may be seen as follows: The action of the energy superoperator on a population operator of the coherent Hamiltonian is given by:

$$\hat{\mathcal{E}}|X_{kk}\rangle = \omega_k |X_{kk}\rangle \quad (110)$$

Table 1

The methods for treating nuclear spin relaxation discussed in this paper, and their properties in the context of a finite-temperature molecular environment. The following abbreviations are used: SC = semi-classical relaxation theory; IME = inhomogeneous Master equation; Jeener = Jeener's thermalized relaxation superoperator [50]; LdB = Levitt-di Bari method for thermalizing the relaxation superoperator [51–53]; sLdB = simplified Levitt-di Bari method as implemented in *SpinDynamica* 3.2 software[87]; LB = Lindblad method.

	SC	IME	Jeener	LdB	sLdB	LB
correct thermal equilibrium	×	✓	✓	✓	✓	✓
valid outside high-temperature regime	×	×	✓	✓	×	✓
valid outside weak-order regime	×	×	✓	✓	×	✓
transition probabilities fulfil detailed balance	×	×	✓	✓	×	✓
coherence decay rates: correct adiabatic contributions	✓	✓	×	✓	✓	✓
coherence decay rates: correct non-adiabatic contributions	×	×	×	×	×	✓
equation number	83	1,95	108,109	118,119	125	140
references	1, 3	1, 3, 4	50	51, 52	51–53	this article

The thermal equilibrium density operator may be expressed in terms of the population operators:

$$\begin{aligned} |\rho_{\text{eq}}\rangle &= Z^{-1} \sum_k \exp\{-\beta_\theta \omega_k\} |X_{kk}\rangle \\ Z &= \sum_k \exp\{-\beta_\theta \omega_k\} \end{aligned} \quad (111)$$

According to equations 110 and 111, the result of applying the total energy superoperator to the thermal equilibrium density operator is given by:

$$\begin{aligned} \hat{\mathcal{E}}|\rho_{\text{eq}}\rangle &= Z^{-1} \sum_k \omega_k \exp\{-\beta_\theta \omega_k\} |X_{kk}\rangle \\ \hat{\Theta}_J|\rho_{\text{eq}}\rangle &= Z^{-1} \sum_k \exp\{-\beta_\theta \omega_k\} \sum_n \frac{(\beta_\theta \omega_k)^n}{n!} |X_{kk}\rangle = Z^{-1} |\mathbb{1}\rangle \end{aligned} \quad (112)$$

Since the state of total disorder lies within the null-space of the SC-relaxation superoperator, ρ_{eq} lies in the null-space of $\hat{\Gamma}_J^\theta$:

$$\hat{\Gamma}_J^\theta |\rho_{\text{eq}}\rangle = Z^{-1} \hat{\Gamma}_J |\mathbb{1}\rangle = |0\rangle \quad (113)$$

The transition probabilities per unit time are modified in the following way:

$$W_{r \rightarrow s}^{\theta, J} = (X_{ss} | \hat{\Gamma}_J^\theta | X_{rr}) = (X_{ss} | \hat{\Gamma} \exp\{\beta_\theta \hat{\mathcal{E}}\} | X_{rr}) = \exp\{\beta_\theta \omega_r\} W_{r \rightarrow s} \quad (114)$$

and the ratio between forward and backwards transition probabilities is given by:

$$\frac{W_{r \rightarrow s}^{\theta, J}}{W_{s \rightarrow r}^{\theta, J}} = \exp\{\beta_\theta \omega_{rs}\} \quad (115)$$

showing that the thermalized transition probabilities obey the detailed balance condition (equation 104).

However, Jeener's method does not handle the coherence decay rate constants correctly. The thermalized decay rate constants of a particular coherence are given by:

$$\begin{aligned} \lambda_{rs}^{\theta, J} &= (X_{rs} | \hat{\Gamma}_J^\theta | X_{rs}) = \exp\{\beta_\theta (\omega_r + \omega_s)\} \lambda_{rs} \\ \lambda_{sr}^{\theta, J} &= (X_{sr} | \hat{\Gamma}_J^\theta | X_{sr}) = \exp\{\beta_\theta (\omega_r + \omega_s)\} \lambda_{sr} \end{aligned} \quad (116)$$

The equality $\lambda_{rs}^{\theta, J} = \lambda_{sr}^{\theta, J}$ follows from $\lambda_{rs} = \lambda_{sr}$ and maintains the hermiticity of the density operator. However, there is still a problem. The adiabatic and non-adiabatic contributions to the coherence decay rate constants are given in

Jeener's method by:

$$\begin{aligned}\lambda_{rs}^{\theta, \text{ad}, J} &= \exp\left\{\frac{1}{2}\beta_\theta(\omega_r + \omega_s)\right\} \lambda_{rs}^{\text{ad}} \\ \lambda_{rs}^{\theta, \text{na}, J} &= \exp\left\{\frac{1}{2}\beta_\theta(\omega_r + \omega_s)\right\} \lambda_{rs}^{\text{na}}\end{aligned}\quad (117)$$

where the adiabatic and non-adiabatic rate constants are given by equations 91 and 92 respectively. The terms $\lambda_{rs}^{\theta, \text{ad}, J}$ and $\lambda_{rs}^{\theta, \text{na}, J}$ are both in conflict with the requirements of equations 106 and 107. In particular, Jeener's method adjusts the adiabatic contributions to the coherence decay rates, which does not make physical sense, since the adiabatic contributions are not related to state transitions and are energy-preserving.

The properties of the Jeener method are summarized in table 1. The Jeener method fulfils most of the required conditions of a thermalization method, but does not treat the coherence decay rate constants correctly. To the best of our knowledge, no application of the Jeener thermalization method has been reported in the literature.

4.2.2. Levitt-di Bari and Levante-Ernst method

An alternative thermalization technique was proposed by Levitt and di Bari [51, 52] and further developed by Levante and Ernst [53]. This method is termed here the LdB method and uses projection superoperators onto the population operators of the coherent Hamiltonian, weighted by the eigenvalue of the associated eigenstate:

$$\hat{\omega} = \sum_k \omega_k |X_{kk}\rangle \langle X_{kk}| \quad (118)$$

The thermal correction superoperator is given by:

$$\hat{\Theta}_{\text{LdB}} = \exp\{-\beta_\theta \hat{\omega}\} \quad (119)$$

The action of $\hat{\omega}$ onto the thermal equilibrium density operator is identical to the action of $\hat{\mathcal{E}}$ (compare with equation 112).

$$\hat{\omega}|\rho_{\text{eq}}\rangle = Z^{-1} \sum_k \omega_k \exp\{-\beta_\theta \omega_k\} |X_{kk}\rangle \quad (120)$$

As a result $\hat{\Theta}_{\text{LdB}}$ transforms the thermal equilibrium density operator into the state of total disorder:

$$\hat{\Theta}_{\text{LdB}}|\rho_{\text{eq}}\rangle = Z^{-1} |\mathbb{1}\rangle \quad (121)$$

and ρ_{eq} lies in the null-space of $\hat{\Gamma}_{\text{LdB}}^\theta$.

$$\hat{\Gamma}_{\text{LdB}}^\theta |\rho_{\text{eq}}\rangle = |0\rangle \quad (122)$$

The modification of the transition probabilities is identical to Jeener's method:

$$W_{r \rightarrow s}^{\theta, \text{LdB}} = (X_{ss} | \hat{\Gamma}_{\text{LdB}}^\theta | X_{rr}) = (X_{ss} | \hat{\Gamma}_{SC} \exp\{\beta_\theta \hat{\omega}\} | X_{rr}) = \exp\{\beta_\theta \omega_r\} W_{r \rightarrow s} \quad (123)$$

Hence the transition probabilities of $\hat{\Gamma}_{\text{LdB}}^\theta$ obey the detailed balance condition.

A defect of the LdB method is that the coherence decay rates are not adjusted at all, since the coherence operators lie in the null-space of $\hat{\omega}$.

$$\begin{aligned}\hat{\omega}|X_{rs}\rangle &= |0\rangle \implies \exp\{\beta_\theta \hat{\omega}\} |X_{rs}\rangle = |X_{rs}\rangle \\ \lambda_{rs}^{\theta, \text{LdB}} &= (X_{rs} | \hat{\Gamma}_{SC} \exp\{\beta_\theta \hat{\omega}\} | X_{rs}) = (X_{rs} | \hat{\Gamma}_{SC} | X_{rs}) = \lambda_{rs}\end{aligned}\quad (124)$$

Hence the Levitt-di Bari method obeys the condition of equation 106 for the adiabatic decay rate contribution, but not that of 107 for the non-adiabatic contribution.

A master equation for spin systems far from equilibrium

A simplified version of the LdB method (sLdB), which employs the high-temperature and weak-order approximations, is currently implemented in version 3.3.2 of the *SpinDynamica* software package [87]. This method uses the following thermalization correction:

$$\hat{\Theta}_{\text{sLdB}} = \hat{\mathbb{I}} - |\rho_{\text{eq}}\rangle\langle\mathbb{I}| \quad (125)$$

The thermally adjusted transition probabilities are given by:

$$W_{r \rightarrow s}^{\theta, \text{sLdB}} = W_{r \rightarrow s} - \sum_j W_{j \rightarrow s} \langle j | \rho_{\text{eq}} | j \rangle \quad (126)$$

whereas the coherence decay rates remain unchanged:

$$\lambda_{rs}^{\theta, \text{sLdB}} = \lambda_{rs} \quad (127)$$

The sLdB method generates the correct thermal equilibrium density operator in the high-temperature approximation but does not obey detailed balance in general, and fails to handle coherence decay rate constants correctly.

5. Lindblad Thermalization

In this article we propose a different thermalization method, called the Lindblad (LB) method, based on a quantum-mechanical treatment of the molecular environments and incorporating thermal corrections to the spectral densities to account for the finite sample temperature [1, 2, 58–60]. Unlike the Jeener, LdB and sLdB methods, the LB method does not lead to a relaxation superoperator which may be expressed as the product of the semi-classical relaxation superoperator and a thermal correction superoperator, as in equation 99. Instead one performs thermal corrections to the individual components of the relaxation superoperator.

A Lindbladian formulation of relaxation processes has been extensively used in quantum optics, quantum computing, quantum information theory and laser physics [76, 78]. Lindbladian description of relaxation of nuclear spin relaxation is used rarely [64, 65], presumably because the inhomogeneous master equation is sufficient in most cases.

5.1. Quantum-Mechanical Spectral Densities

The starting point of the Lindblad method is to treat both the environment and the spin system quantum mechanically [1, 2, 5, 60–63]. The fluctuating contributions are replaced by a Hamiltonian of the following type:

$$H_{\text{fluc}}^{\Lambda} = \sum_{\alpha} A_{\alpha} \otimes B_{\alpha}^{\Lambda} \quad (128)$$

where B_{α}^{Λ} is an environmental (“bath”) operator.

The environment represents a thermal reservoir with sufficient heat capacity to always remain close to thermal equilibrium due to its size and complexity, and is described by a density operator $\rho_{\text{eq}}^{\text{bath}}$. It is not necessary to assume that the *spin system* remains close to equilibrium. The combined density operator of the spin system and the environment is assumed to be of the form:

$$\rho_{\text{tot}}(t) = \rho(t) \otimes \rho_{\text{eq}}^{\text{bath}} \quad (129)$$

The relaxation superoperator may be derived by substituting the expression for $H_{\text{fluc}}^{\Lambda}$ from equation 128 into equation 78, and taking the trace over the environmental degrees of freedom [4, 5, 62, 63].

$$\begin{aligned} \hat{\Gamma}_{\text{QM}}^{\text{lab}} = & - \sum_{\Lambda, \Lambda'} \sum_{\alpha, \alpha'} \int_{-\infty}^0 (A_{\alpha} \cdot A_{\alpha'}^{\dagger} - A_{\alpha'}^{\dagger} \cdot A_{\alpha}) \langle B_{\alpha'}^{\Lambda'}(\tau) B_{\alpha}^{\Lambda}(0) \rangle \exp\{i\omega_{\alpha'}^{\Lambda} \tau\} \\ & - \sum_{\Lambda, \Lambda'} \sum_{\alpha, \alpha'} \int_{-\infty}^0 (A_{\alpha'}^{\dagger} \cdot A_{\alpha} - A_{\alpha} A_{\alpha'}^{\dagger}) \langle B_{\alpha}^{\Lambda}(0) B_{\alpha'}^{\Lambda'}(\tau) \rangle \exp\{i\omega_{\alpha'}^{\Lambda} \tau\} \end{aligned} \quad (130)$$

Here $\langle B_{\alpha'}^{\Lambda'}(\tau) B_{\alpha}^{\Lambda}(0) \rangle$ are quantum-mechanical correlation functions, defined as follows:

$$\langle B_{\alpha'}^{\Lambda'}(\tau) B_{\alpha}^{\Lambda}(0) \rangle = \text{Tr}_{\text{bath}} \left\{ U_{\text{bath}}(\tau) B_{\alpha'}^{\Lambda'} U_{\text{bath}}^{\dagger}(\tau) B_{\alpha}^{\Lambda} \rho_{\text{eq}}^{\text{bath}} \right\} = \langle B_{\alpha'}^{\Lambda'}(0) B_{\alpha}^{\Lambda}(-\tau) \rangle \quad (131)$$

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Since the system-bath interaction is hermitian it is permissible to replace the second part of equation 130 by its hermitian conjugate:

$$\begin{aligned}\hat{\Gamma}_{\text{QM}}^{\text{lab}} = & - \sum_{\Lambda, \Lambda'} \sum_{\alpha, \alpha'} \int_{-\infty}^0 (A_{\alpha} \cdot A_{\alpha'}^{\dagger} - \bullet A_{\alpha'}^{\dagger} A_{\alpha}) \langle B_{\alpha'}^{\Lambda'}(\tau) B_{\alpha}^{\Lambda}(0) \rangle \exp\{i\omega_{\alpha'}^A \tau\} \\ & - \sum_{\Lambda, \Lambda'} \sum_{\alpha, \alpha'} \int_{-\infty}^0 (A_{\alpha'} \cdot A_{\alpha}^{\dagger} - A_{\alpha}^{\dagger} A_{\alpha'} \bullet) \langle B_{\alpha}^{\Lambda}(0) B_{\alpha'}^{\Lambda'}(\tau) \rangle \exp\{-i\omega_{\alpha'}^A \tau\}\end{aligned}\quad (132)$$

The sum is invariant under the exchange of the labels ($\alpha \leftrightarrow \alpha'$) and ($\Lambda \leftrightarrow \Lambda'$) which we perform on the second part.

$$\begin{aligned}\hat{\Gamma}_{\text{QM}}^{\text{lab}} = & - \sum_{\Lambda, \Lambda'} \sum_{\alpha, \alpha'} \int_{-\infty}^0 (A_{\alpha} \cdot A_{\alpha'}^{\dagger} - \bullet A_{\alpha'}^{\dagger} A_{\alpha}) \langle B_{\alpha'}^{\Lambda'}(\tau) B_{\alpha}^{\Lambda}(0) \rangle \exp\{i\omega_{\alpha'}^A \tau\} \\ & - \sum_{\Lambda, \Lambda'} \sum_{\alpha, \alpha'} \int_{-\infty}^0 (A_{\alpha} \cdot A_{\alpha'}^{\dagger} - A_{\alpha'}^{\dagger} A_{\alpha} \bullet) \langle B_{\alpha'}^{\Lambda'}(-\tau) B_{\alpha}^{\Lambda}(0) \rangle \exp\{-i\omega_{\alpha'}^A \tau\}\end{aligned}\quad (133)$$

A simple transformation of variables ($\tau \mapsto -\tau$) in the second sum leads to the following expression:

$$\begin{aligned}\hat{\Gamma}_{\text{QM}}^{\text{lab}} = & - \sum_{\Lambda, \Lambda'} \sum_{\alpha, \alpha'} \int_{-\infty}^0 (A_{\alpha} \cdot A_{\alpha'}^{\dagger} - \bullet A_{\alpha'}^{\dagger} A_{\alpha}) \langle B_{\alpha'}^{\Lambda'}(\tau) B_{\alpha}^{\Lambda}(0) \rangle \exp\{i\omega_{\alpha'}^A \tau\} \\ & - \sum_{\Lambda, \Lambda'} \sum_{\alpha, \alpha'} \int_0^{\infty} (A_{\alpha} \cdot A_{\alpha'}^{\dagger} - A_{\alpha'}^{\dagger} A_{\alpha} \bullet) \langle B_{\alpha'}^{\Lambda'}(\tau) B_{\alpha}^{\Lambda}(0) \rangle \exp\{i\omega_{\alpha'}^A \tau\}\end{aligned}\quad (134)$$

By considering only the secular contributions $\omega_{\alpha} = \omega_{\alpha'}$ and neglecting dynamical frequency shifts, the two sums may be combined to form a complete Fourier transform (see Appendix A.1):

$$\hat{\Gamma}_{\text{QM}}^{\text{sec}} = \sum_{\Lambda, \Lambda'} \sum_{\alpha, \alpha'} \hat{D}[A_{\alpha}, A_{\alpha'}^{\dagger}] K_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega_{\alpha'}^A) \delta(\omega_{\alpha}^A - \omega_{\alpha'}^A) \quad (135)$$

where the quantum-mechanical spectral densities are given by

$$K_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega) = \int_{-\infty}^{\infty} \langle B_{\alpha'}^{\Lambda'}(\tau) B_{\alpha}^{\Lambda}(0) \rangle \exp\{i\omega\tau\} d\tau \quad (136)$$

and \hat{D} defines the so-called Lindbladian dissipator [62, 63]:

$$\hat{D}[A, B] = A \bullet B - \frac{1}{2} (BA \bullet + \bullet BA) \quad (137)$$

In contrast to the classical correlation functions, the quantum mechanical correlation functions are not symmetric with respect to frequency, i.e. $K(\omega) \neq K(-\omega)$. In thermal equilibrium they obey the Kubo-Martin-Schwinger(KMS)-condition [4, 5, 62, 63].

$$K_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega) = K_{\alpha'\alpha}^{\Lambda\Lambda'}(-\omega) \exp\{\beta_{\theta}\omega\} \quad (138)$$

Detailed knowledge of the quantum mechanical spectral densities is rarely available. Nevertheless they may be approximated by classical spectral densities by an invoking an appropriate quantum mechanical correction [88]. One possibility is given by the Schofield method [89]:

$$K_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega) \mapsto J_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega) \exp\left\{-\frac{1}{2}\beta_{\theta}\omega\right\} \quad (139)$$

Corrections of this form have been previously used in the description of vibrational relaxation effects [90].

This leads to the following expression for the secularized relaxation superoperator:

$$\hat{\Gamma}_{\text{LB}}^{\theta} = \sum_{\Lambda, \Lambda'} \sum_{\alpha, \alpha'} \hat{D}[A_{\alpha}, A_{\alpha'}^{\dagger}] J_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega_{\alpha}^A) \exp\left\{-\frac{1}{2}\beta_{\theta}\omega_{\alpha}^A\right\} \delta(\omega_{\alpha} - \omega_{\alpha'}) \quad (140)$$

where $J_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega)$ are the classical spectral densities defined in equation 64.

Equation 140 is the central result of this paper. It has a clear relationship with the semiclassical form of equation 79. The double commutation superoperator is replaced by a Lindbladian dissipator (multiplied by -1/2), and thermal correction factors $\exp\left\{\frac{1}{2}\beta_\theta\omega_\alpha^A\right\}$ are introduced.

It might appear that a similar result would be obtained by simply introducing the thermal factors $\exp\left\{-\frac{1}{2}\beta_\theta\omega_\alpha^A\right\}$ into the semi-classical relaxation superoperator of equation 79. Indeed, this construction was proposed by Abragam (see page 288) as part of the quantum-mechanical treatment of relaxation [4]. However, that version of the quantum-mechanical procedure fails for spin systems exhibiting a large degree of spin order, as is clear from the context of Abragam's expressions (see top of page 288). The double-commutator form does *not* provide a clear separation of the forward and backwards transition probabilities and is therefore incompatible with detailed balance at finite temperature, even after the inclusion of thermal corrections. It is only at infinite temperature that the Lindblad formalism and double commutator formalism coincide. These issues are discussed in more detail in Appendices A.2 and A.3.

The Lindblad dissipators have a clear relationship with the physical picture of figure 4. They may be understood as inducing forward and backward transition processes as illustrated below:

$$\begin{aligned}(X_{ss}|\hat{\mathcal{D}}[X_{ij}, X_{ij}^\dagger]|X_{rr}) &= \delta_{is}\delta_{jr} \\ (X_{ss}|\hat{\mathcal{D}}[X_{ij}^\dagger, X_{ij}]|X_{rr}) &= \delta_{js}\delta_{ir}\end{aligned}\quad (141)$$

Terms $\hat{\mathcal{D}}[X_{ij}, X_{ij}^\dagger]$ and $\hat{\mathcal{D}}[X_{ij}^\dagger, X_{ij}]$ are associated with relaxation processes across the same pair of H_0 eigenstates but in opposite directions. The transition probabilities per unit time are given by

$$W_{r\rightarrow s}^{\theta, \text{LB}} = (X_{ss}|\hat{\Gamma}_{\text{LB}}^\theta|X_{rr}) = \exp\left\{-\frac{1}{2}\beta_\theta\omega_{sr}\right\} W_{r\rightarrow s} \quad (142)$$

Hence the transition probabilities for the forward and backwards processes are related as follows:

$$W_{r\rightarrow s}^{\theta, \text{LB}} = W_{s\rightarrow r}^{\theta, \text{LB}} \exp\{-\beta_\theta\omega_{sr}\} \quad (143)$$

in agreement with the detailed balance condition and the physical picture in figure 4.

The Lindbladian formalism also handles the coherence decay rate constants correctly. The adiabatic contributions to the coherence decay rates are unaffected by thermalization, as should be the case:

$$\lambda_{rs}^{\theta, \text{ad}} = \lambda_{rs}^{\text{ad}} \quad (144)$$

The non-adiabatic contributions to the coherence decay rate constants are sums of thermalized transition probabilities. This is also physically reasonable (see figure 5).

$$\begin{aligned}\lambda_{rs}^{\theta, \text{na}} &= \frac{1}{2} \left(\sum_{k \neq r} \exp\left\{-\frac{1}{2}\beta_\theta\omega_{kr}\right\} W_{r\rightarrow k} + \sum_{k \neq s} \exp\left\{-\frac{1}{2}\beta_\theta\omega_{ks}\right\} W_{s\rightarrow k} \right) \\ &= \frac{1}{2} \left(\sum_{k \neq r} W_{r\rightarrow k}^{\theta, \text{LB}} + \sum_{k \neq s} W_{s\rightarrow k}^{\theta, \text{LB}} \right)\end{aligned}\quad (145)$$

It follows that the thermalized Lindblad representation of equation 140 preserves the trace and hermiticity of the density operator, obeys the detailed balance condition, and handles coherence decay processes correctly.

6. Case Studies

In this section the Lindblad approach is applied to some simple cases. The first two cases concern "ordinary" high-field NMR in the high-temperature and weak-order approximation, where the LB formulation reproduces well-known results which may also be derived using the inhomogeneous master equation. In the last two examples we consider a spin system far from equilibrium, where the conventional IME equation breaks down.

6.1. Homonuclear spin-1/2 pairs

Consider an ensemble of rigid molecules undergoing rotational diffusion, with each molecule containing a homonuclear spin-1/2 pair. The electronic environments of the two spins are distinct (chemical inequivalence). The nuclear spin relaxation is assumed to be dominated by dipole-dipole relaxation. The dipole-dipole coupling constant is given by $b_{12} = -(\mu_0/4\pi)\gamma_I^2\hbar r_{12}^{-3}$ where γ_I is the magnetogyric ratio and r_{12} is the internuclear distance. The rotational correlation time is denoted τ_C .

In the presence of resonant radiofrequency irradiation, the coherent Hamiltonian is given in the laboratory frame, by

$$H_{\text{coh}} = H_A + H_B + H_C \quad (146)$$

The dominant part of the Hamiltonian (see section 2.3.1) is given in the laboratory frame by

$$H_A = \omega^0(1 + \delta_{\text{ref}})(I_{1z} + I_{2z}) \quad (147)$$

while the terms H_B and H_C are given in the interaction frame of H_A (rotating frame) by:

$$\begin{aligned} H_B &= \Omega_1 I_{1z} + \Omega_2 I_{2z} + 2\pi J_{12} \mathbf{I}_1 \cdot \mathbf{I}_2 \\ H_C &= \omega_{\text{nut}}(I_x \cos \phi + I_y \sin \phi) \end{aligned} \quad (148)$$

The Larmor frequency is $\omega^0 = -\gamma B^0$ and the chemical shift offsets are given by $\Omega_i = \omega^0(\delta_i - \delta_{\text{ref}})$, where $\{\delta_1, \delta_2\}$ are the chemical shifts of the two sites and δ_{ref} is the chemical shift position of the carrier frequency of the radiofrequency irradiation. The amplitude of the resonant field is specified in terms of the nutation frequency ω_{nut} and its phase is denoted ϕ . These choices of H_A , H_B and H_C fulfil the constraints in section 2.3.1: The eigenvalues of H_A are either degenerate or spaced by multiples of the spectrometer reference frequency $|\omega^0(1 + \delta_{\text{ref}})|$, which is much larger than the matrix elements of H_B and H_C .

Following equation 47, the eigenoperators of the commutation superoperator \hat{H}_A are proportional to the irreducible spherical tensor operators, as in equation 48. The corresponding eigenvalues of \hat{H}_A are given by:

$$\omega_\alpha^A = \mu_\alpha \omega^0 \quad (149)$$

The fluctuating part of the spin Hamiltonian, which is responsible for the dipole-dipole relaxation, takes the form [6]:

$$H_{\text{fluc}}(t) = \sum_{\mu=-2}^{+2} F_{2\mu}(\Omega_{\text{PL}}^{(12)}(t))^* T_{2\mu}^{(12)} \quad (150)$$

where both $F_{2\mu}$ and $T_{2\mu}^{(12)}$ transform as second-rank irreducible spherical tensors under rotations. The operator $T_{2\mu}^{(12)}$ indicates coupling of spins I_1 and I_2 as defined in Appendix 2.

The spatial components $F_{2\mu}$ depend on the Euler angles $\Omega_{\text{PL}}^{(12)}(t)$ that relate the principal axis system of the dipole-dipole coupling to the laboratory frame. This transformation is time-dependent due to rotational diffusion of the molecule. We assume a single exponential decay for the corresponding correlation functions as indicated by equation 58, leading to Lorentzian spectral densities.

Following the recipe of equation 140, and assuming isotropic rotational diffusion, the secular and thermalized relaxation superoperator may be expressed as follows:

$$\hat{\Gamma}_{\text{LB}}^\theta = \frac{6}{5} b_{12}^2 \sum_{\mu=-2}^{+2} \hat{D}[T_{2\mu}^{(12)}, T_{2\mu}^{(12)\dagger}] J^\theta(\mu\omega^0) \quad (151)$$

where the thermally corrected spectral density functions are given by

$$J^\theta(\omega) = \exp\left\{-\frac{1}{2}\beta_\theta\omega\right\} J(\omega) \quad (152)$$

and

$$J(\omega) = \frac{2\tau_C}{1 + \omega^2\tau_C^2} \quad (153)$$

The Lindbladian \hat{D} is defined in equation 137.

The thermalized relaxation superoperator may be represented as a 16×16 matrix in a basis of orthogonal operators. One possible basis involves all ket-bra products for the singlet and triplet states of the 2-spin-1/2 system, defined in equation 11. The 4×4 block involving the population operators for these states is as follows:

$$\left[\hat{\Gamma}_{LB}^\theta \right]_{4 \times 4} = \frac{6}{5} b_{12}^2 \times$$

$ S_0\rangle\langle S_0 $	$ T_{+1}\rangle\langle T_{+1} $	$ T_0\rangle\langle T_0 $	$ T_{-1}\rangle\langle T_{-1} $
0	0	0	0
0	$-\frac{1}{8}J^\theta(-\omega^0) - \frac{1}{4}J^\theta(-2\omega^0)$	$\frac{1}{8}J^\theta(\omega^0)$	$\frac{1}{4}J^\theta(2\omega^0)$
0	$\frac{1}{8}J^\theta(-\omega^0)$	$-\frac{1}{8}(J^\theta(-\omega^0) + J^\theta(\omega^0))$	$\frac{1}{8}J^\theta(\omega^0)$
0	$\frac{1}{4}J^\theta(-2\omega^0)$	$\frac{1}{8}J^\theta(-\omega^0)$	$-\frac{1}{8}J^\theta(\omega^0) - \frac{1}{4}J^\theta(2\omega^0)$

(154)

The row and column of zeros indicate that the singlet population is disconnected from the triplet populations under dipole-dipole relaxation processes. The population of the singlet state is therefore a long-lived state [79–84], in the case that coherent Hamiltonian terms mixing the singlet and triplet states are suppressed. In the current example, the relevant singlet-triplet mixing term is proportional to the chemical shift frequency difference $|\Omega_1 - \Omega_2|$. The long-lived nature of the singlet population is revealed by suppressing this mixing term, either by transporting the sample to a region of low magnetic field [91], or by applying a resonant radiofrequency field [83].

The thermalized relaxation superoperator $\hat{\Gamma}_{LB}^\theta$ may also be used to treat well-known relaxation phenomena such as the transient and steady-state nuclear Overhauser (NOE) effects [11, 12]. The simulations shown in Figure 6 were performed by integrating the homogeneous equation of motion in the interaction frame (equation 101) using *SpinDynamica* software [87].

Figure 6(a) shows a transient NOE effect in which inversion of the magnetization of one set of spins induces a transient increase in the magnetization of the second set of spins through dipole-dipole cross-relaxation. Figure 6(b) shows a steady-state NOE effect. Saturation of the longitudinal magnetization of one set of spins by a continuous resonant rf field establishes a steady state in which the magnetization of the second set of spins is enhanced with respect to thermal equilibrium.

These phenomena are well understood and the simulated trajectories using the Lindblad method agree with the literature [51, 52]. For the steady-state NOE it is straightforward to show that within the fast motion limit ($\omega^0\tau_C \ll 1$) and high-temperature approximation the maximal achievable polarisation enhancement on the passive spin is given by $\epsilon_{NOE}^{SS} = \frac{3}{2}$ which is in agreement with figure 6(b) [11, 12].

6.2. Heteronuclear spin-1/2 pairs

In the case of heteronuclear spin pairs (one I -spin coupled to one S -spin, with magnetogyric ratios γ_I and γ_S), the dominant part of the coherent Hamiltonian, in the laboratory frame, is given by

$$H_A = \omega_I^0(1 + \delta_{ref}^I)I_z + \omega_S^0(1 + \delta_{ref}^S)S_z \quad (155)$$

where $\omega_I^0 = -\gamma_I B^0$ and $\omega_S^0 = -\gamma_S B^0$ are the Larmor frequencies of the two species, and $\{\delta_{ref}^I, \delta_{ref}^S\}$ are the chemical shifts of the two spectrometer reference frequencies.

The H_B and H_C components of the coherent spin Hamiltonian have the following form in the interaction frame of H_A :

$$\begin{aligned} H_B &= \Omega_I I_z + \Omega_S S_z + 2\pi J_{IS} I_z S_z \\ H_C &= \omega_{nut}^I (I_x \cos \phi_I + I_y \sin \phi_I) + \omega_{nut}^S (S_x \cos \phi_S + S_y \sin \phi_S) \end{aligned} \quad (156)$$

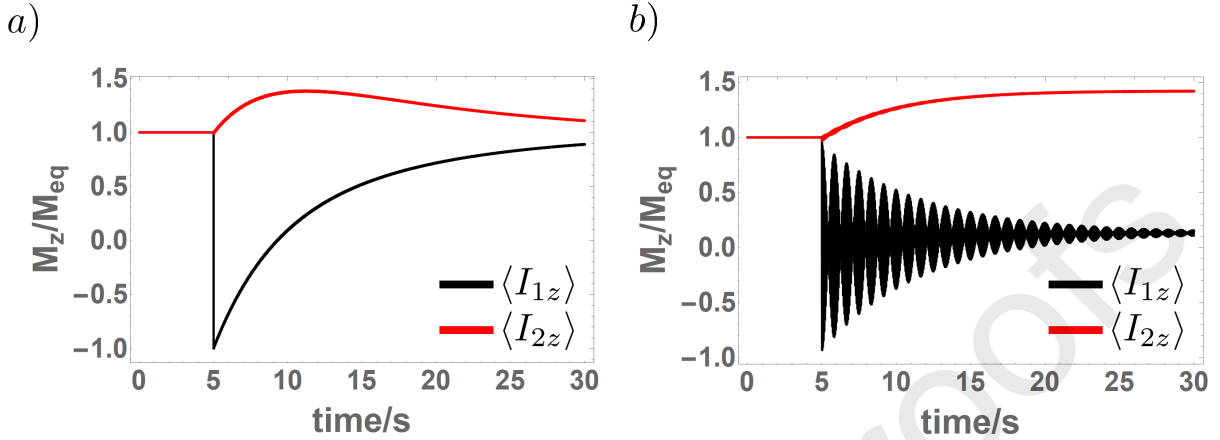


Figure 6: Simulations of nuclear Overhauser effects (NOE) in a system of homonuclear proton pairs at a temperature of 300 K and a magnetic field of 11.4 T using the Lindbladian form of the relaxation superoperator (equation 151). The vertical scales correspond to the ratio of the longitudinal spin magnetization M_z to its thermal equilibrium value M_{eq} . (a) Simulation of the transient NOE. Starting from thermal equilibrium, a selective π -rotation is applied to one set of spins at time point $t = 5$ s, and the expectation values of the z-magnetization components tracked in the subsequent interval. No resonant rf field is applied ($\omega_{nut} = 0$). (b) Simulation of the steady-state NOE. Starting at $t = 5$ s, a continuous rf irradiation with nutation frequency $\omega_{nut} = 2\pi \times 2.5$ Hz is applied to a thermal equilibrium state. The simulation parameters are as follows: $\Omega_1 = 0$, $\Omega_2 = 2\pi \times 200$ Hz, $J_{12} = 15$ Hz, $b_{12} = -2\pi \times 30$ kHz, and $\tau_C = 10$ ps. The resulting T_1 time constant is 5.64 s.

The chemical shift offset frequencies for the two isotopes are given by $\Omega_I = \omega_I^0(\delta_I - \delta_{ref}^I)$ and $\Omega_S = \omega_S^0(\delta_S - \delta_{ref}^S)$, where δ_I and δ_S are the chemical shifts of the two spin species. Resonant radiofrequency fields applied to the two spin species have amplitudes corresponding to the nutation frequencies $\{\omega_{nut}^I, \omega_{nut}^S\}$, and phases $\{\phi_I, \phi_S\}$.

According to Equation 51, the eigenoperators of H_A are given in the heteronuclear case by products of spherical tensor operators. These may be labelled by their individual total and z-angular momentum ($T_{\lambda_1 \lambda_2 \mu_1 \mu_2}^{(ij)}$). The relevant eigenoperators for heteronuclear dipolar relaxation are given by column $(\lambda_1, \lambda_2) = (1, 1)$ of table 3. The thermalized relaxation superoperator for the heteronuclear case may be expressed as follows:

$$\hat{\Gamma}_{LB}^\theta = \frac{6}{5} b_{12}^2 \sum_{\mu'_1, \mu'_2 = -2}^{+2} \sum_{\mu_1, \mu_2 = -2}^{+2} \hat{D}[T_{11\mu_1\mu_2}^{(12)}, T_{11\mu'_1\mu'_2}^{(12)\dagger}] J^\theta(\omega_{\mu_1\mu_2}^A) \delta(\omega_{\mu_1\mu_2}^A - \omega_{\mu'_1\mu'_2}^A) \quad (157)$$

The relaxation dynamics of the Zeeman spin state populations are governed by the following matrix:

$$\left[\hat{\Gamma}_{\text{LB}}^{\theta} \right]_{4 \times 4} = \frac{6}{5} b_{12}^2 \times$$

$ \alpha\alpha\rangle\langle\alpha\alpha $	$ \beta\alpha\rangle\langle\beta\alpha $	$ \alpha\beta\rangle\langle\alpha\beta $	$ \beta\beta\rangle\langle\beta\beta $
$-\frac{1}{16}J^{\theta}(-\omega_I^0)$ $-\frac{1}{16}J^{\theta}(-\omega_S^0)$ $-\frac{1}{4}J^{\theta}(-(\omega_I^0 + \omega_S^0))$	$\frac{1}{16}J^{\theta}(\omega_I^0)$	$\frac{1}{16}J^{\theta}(\omega_S^0)$	$\frac{1}{4}J^{\theta}(\omega_I^0 + \omega_S^0)$
$\frac{1}{16}J^{\theta}(-\omega_I^0)$	$-\frac{1}{16}J^{\theta}(\omega_I^0)$ $-\frac{1}{16}J^{\theta}(-\omega_S^0)$ $-\frac{1}{24}J^{\theta}(\omega_I^0 - \omega_S^0)$	$\frac{1}{24}J^{\theta}(-\omega_I^0 + \omega_S^0)$	$\frac{1}{16}J^{\theta}(\omega_S^0)$
$\frac{1}{16}J^{\theta}(-\omega_S^0)$	$\frac{1}{24}J^{\theta}(\omega_I^0 - \omega_S^0)$	$-\frac{1}{16}J^{\theta}(-\omega_I^0)$ $-\frac{1}{16}J^{\theta}(\omega_S^0)$ $-\frac{1}{24}J^{\theta}(-\omega_I^0 + \omega_S^0)$	$\frac{1}{16}J^{\theta}(\omega_I^0)$
$\frac{1}{4}J^{\theta}(-(\omega_I^0 + \omega_S^0))$	$\frac{1}{16}J^{\theta}(-\omega_S^0)$	$\frac{1}{16}J^{\theta}(-\omega_I^0)$	$-\frac{1}{16}J^{\theta}(\omega_I^0)$ $-\frac{1}{16}J^{\theta}(\omega_S^0)$ $-\frac{1}{4}J^{\theta}(\omega_I^0 + \omega_S^0)$

(158)

Simulations of the z-magnetisation dynamics during heteronuclear transient-NOE and steady-state-NOE experiments [11, 12] involving pairs of ^{13}C and ^1H spins are shown in figure 7. The trajectories were generated by *Spin-Dynamica* software [87] using equation 157. The maximum achievable enhancement of the ^{13}C magnetization for a coupled ^{13}C - ^1H pair in the steady-state NOE experiment is given by $\epsilon \simeq 3$. The numerical simulations of figure 7(b) confirm that this well-known result [11, 12] may be reproduced by using the Lindbladian relaxation superoperator.

6.3. Singlet-Triplet conversion

We now return to the problem given in the introduction: namely, the build-up of longitudinal magnetization in a system of magnetically equivalent (or near-equivalent) spin-1/2 pairs, prepared “in an unusual way” such that only the singlet state is populated. In this section, we consider an ensemble of “conventional” two-spin-1/2 systems which do not exhibit spin isomerism. The problem of spin-isomer conversion is examined in the next section.

As explained in the introduction, the inhomogeneous master equation (equation 1) incorrectly predicts a build-up of longitudinal magnetization with the ordinary rate constant T_1^{-1} , starting from a pure singlet population. In reality, longitudinal magnetization builds up with the much slower rate constant T_S^{-1} for the singlet-triplet conversion (see figure 1). We now examine how this problem may be addressed by using the Lindbladian form of the relaxation superoperator.

The dominant and perturbative parts of the coherent Hamiltonian in the absence of resonance rf fields are given by:

$$\begin{aligned} H_A &= \omega^0(I_{1z} + I_{2z}) \\ H_B &= 2\pi J_{12}\mathbf{I}_1 \cdot \mathbf{I}_2 \end{aligned} \quad (159)$$

This assignment of H_A and H_B assumes that the scalar coupling interaction is much smaller than the Zeeman interaction. This condition is easily met for NMR under ordinary conditions.

The relaxation of the system may be modelled as a superposition of the dipole-dipole (DD) and fluctuating random field mechanisms. The fluctuating random field mechanism may include spin-rotation interactions as well as external random fields deriving from, for example, paramagnetic species in solution. The DD mechanism does not induce spin-isomer conversion, which is entirely driven by uncorrelated random fields. Using spherical tensor operators as the eigenoperators of \hat{H}_A , the relaxation superoperator in the Lindblad formalism is given by:

$$\hat{\Gamma}_{\text{LB}}^{\theta} = \hat{\Gamma}_{\text{LB}}^{\theta, \text{DD}} + \hat{\Gamma}_{\text{LB}}^{\theta, \text{ran}} \quad (160)$$

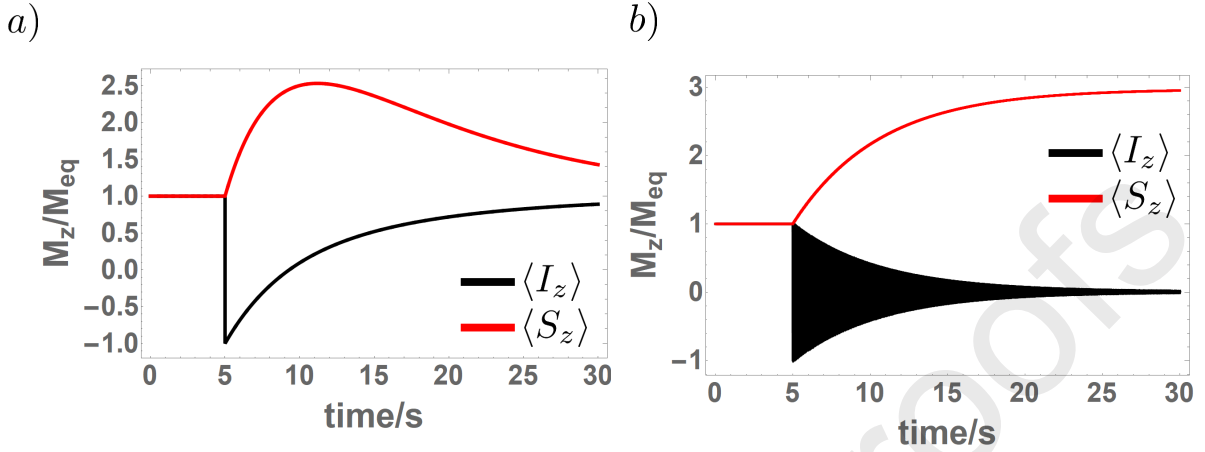


Figure 7: Simulations of heteronuclear Overhauser effects (NOE) in a system of ^1H - ^{13}C pairs at a temperature of 300 K and a magnetic field of 11.4 T using the Lindbladian form of the relaxation superoperator (equation 151). The black curves show the ratio of the ^1H (I -spin) magnetization M_z^I to its thermal equilibrium value M_{eq}^I . The red curves show the ratio of the ^{13}C (S -spin) magnetization M_z^S to its thermal equilibrium value M_{eq}^S . (a) Simulation of the transient NOE. Starting from thermal equilibrium, a selective π -rotation is applied to the ^1H spins at time point $t = 5$ s and the expectation values of the z -angular momentum components of both spin species tracked in the subsequent interval. No resonant rf field is applied ($\omega_{nut}^I = \omega_{nut}^S = 0$). (b) Simulation of the steady-state NOE. Starting from a thermal equilibrium state, continuous rf irradiation with nutation frequency $\omega_{nut}^I = 2\pi \times 100$ Hz is applied to the ^1H spins, starting at time point $t = 5$ s. No rf field is applied to the ^{13}C spins ($\omega_{nut}^S = 0$). The dipolar relaxation was treated using equation 157. The simulation parameters are as follows: $\Omega_I = \Omega_S = 0$, $\tau_C = 10$ ps, $b_{12} = -2\pi \times 30$ kHz. For this choice of parameters the ^1H and ^{13}C T_1 time constants are $T_1^I = T_1^S = 5.62$ s.

where the dipole-dipole term is given by equation 151. A suitable relaxation superoperator for the fluctuating random fields is given by the following expression:

$$\hat{\Gamma}_{LB}^{\theta, \text{ran}} = \sum_{i,j=1}^2 \kappa_{ij} \omega_{\text{rms}}^{(i)} \omega_{\text{rms}}^{(j)} \sum_{\mu=-1}^{+1} \hat{\mathcal{D}}[T_{1\mu}^{(i)}, T_{1\mu}^{(j)*}] J_{\text{ran}}^{\theta}(m\omega^0) \quad (161)$$

where

$$J_{\text{ran}}^{\theta}(\omega) = J_{\text{ran}}(\omega) \exp\left\{-\frac{1}{2} \beta_{\theta} \omega\right\} \quad (162)$$

and the spectral density function for random-field fluctuations is given by

$$J_{\text{ran}}(\omega) = \frac{2\tau_{\text{ran}}}{1 + \omega^2 \tau_{\text{ran}}^2} \quad (163)$$

The term $\omega_{\text{rms}}^{(j)}$ is the root-mean-square amplitudes of the local field fluctuations at the location of spin I_j . The random fields are assumed to be isotropic and with the same rms value for the two sites ($\omega_{\text{rms}} = \omega_{\text{rms}}^{(1)} = \omega_{\text{rms}}^{(2)}$). The coefficient $-1 \leq \kappa_{12} \leq 1$ describes the correlation between random field fluctuations at spin sites I_1 and I_2 . By definition, $\kappa_{11} = \kappa_{22} = 1$. Perfectly correlated random fields are described by $\kappa_{12} = 1$ while uncorrelated random fields have $\kappa_{12} = 0$.

In the extreme narrowing limit, the spectral density functions are frequency-independent ($J(\omega) \simeq 2\tau_C$). The relaxation rate constant R_1 is given by

$$R_1 = R_1^{\text{DD}} + R_1^{\text{ran}} \quad (164)$$

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where the individual contributions to R_1 are given by the following matrix elements:

$$R_1^{\text{DD}} = -\frac{(I_z | \hat{\Gamma}_{\text{LB}}^{\theta, \text{DD}} | I_z)}{(I_z | I_z)} = \frac{3}{10} b_{12}^2 \tau_C \left(\cosh(\frac{1}{2} \beta_\theta \omega^0) + 4 \cosh(\beta_\theta \omega^0) \right) \quad (165)$$

$$R_1^{\text{ran}} = -\frac{(I_z | \hat{\Gamma}_{\text{LB}}^{\theta, \text{ran}} | I_z)}{(I_z | I_z)} = 2 \omega_{\text{rms}}^2 \tau_{\text{ran}} \cosh(\frac{1}{2} \beta_\theta \omega^0)$$

The relaxation rate constant for singlet order (the mean population difference between the singlet and triplet states) is given by the following matrix element:

$$R_S = R_S^{\text{ran}} = -\frac{(\mathbf{I}_1 \cdot \mathbf{I}_2 | \hat{\Gamma}_{\text{LB}}^{\theta, \text{ran}} | \mathbf{I}_1 \cdot \mathbf{I}_2)}{(\mathbf{I}_1 \cdot \mathbf{I}_2 | \mathbf{I}_1 \cdot \mathbf{I}_2)} = \frac{4}{3} \omega_{\text{rms}}^2 \tau_{\text{ran}} (1 - \kappa_{12}) \left(1 + 2 \cosh(\frac{1}{2} \beta_\theta \omega^0) \right) \quad (166)$$

There is no dipole-dipole contribution to R_S .

In the Lindblad formalism, the temperature-dependence of the relaxation rate constants derives not only from the temperature-dependence of the correlation time τ_C , but also from the explicit temperature dependence of the hyperbolic functions in equations 165 and 166.

In the high-temperature limit, which is applicable to NMR at ordinary temperatures, the rate constants are given by

$$R_1 \simeq \frac{3}{2} b_{12}^2 \tau_C + 2 \omega_{\text{rms}}^2 \tau_{\text{ran}} \quad (167)$$

$$R_S \simeq 4 \omega_{\text{rms}}^2 \tau_{\text{ran}} (1 - \kappa_{12})$$

The relaxation rate constant for singlet order R_S vanishes for perfectly correlated random fields ($\kappa_{12} = 1$).

As shown in Appendix A.5, the trajectory of the z-magnetisation is well approximated within the fast-motion and high-temperature limit by the following expression:

$$\langle I_z(t) \rangle / \langle I_z \rangle_{\text{eq}} \simeq 1 + A_1 \exp\{-R_1 t\} + A_S \exp\{-R_S t\} \quad (168)$$

where the coefficients are

$$A_1 = \frac{R_S}{2(R_1 - R_S)} \quad (169)$$

$$A_S = \frac{-2R_1 + R_S}{2(R_1 - R_S)}$$

The first exponential in equation 168 represents the fast equilibration of the outer triplet states due to T_1 processes. The second exponential represents the singlet-triplet conversion process. The coefficients approach $A_1 \rightarrow 0$ and $A_S \rightarrow -1$ in the limit $R_1 \gg R_S$, in which case the recovery of z-magnetization is dominated by the small rate constant R_S for the singlet-triplet conversion.

The solid line in figure 1b shows the solution to equation 168 with the following parameters: $\omega_{\text{rms}} = 2\pi \times 10$ kHz, $\tau_{\text{ran}} = 60.31$ ps, $\kappa_{12} = 0.955$, $\tau_C = 107$ fs and $b_{12} = -2\pi \times 34.88$ kHz. The resulting relaxation time constants are given by: $T_1 = 2$ s and $T_S = 22.5$ s. In contrast to the IME, the Lindblad method correctly describes the recovery of the longitudinal magnetization starting from a pure singlet population, with the long time constant $T_S \gg T_1$.

6.4. Ortho-para conversion

In the example above, it was assumed that the scalar coupling term $\mathbf{I}_1 \cdot \mathbf{I}_2$ is much smaller than the Zeeman term, allowing the Zeeman Hamiltonian to be assigned to the dominant term H_A , while the scalar coupling is assigned to the perturbation H_B (see equation 159). This assumption is well-satisfied for the vast majority of physical systems, but breaks down at low temperatures for systems exhibiting spin isomerism. In such cases the scalar coupling term acquires a large contribution from the nuclear exchange interaction, which derives from the Pauli-principle restrictions

on the spatial quantum states accessible to nuclear spin states of a given symmetry. In some cases, nuclear exchange interactions exceed the nuclear Zeeman interactions by several orders of magnitude [92]. This can be the case, for example, for dihydrogen (H_2), and for freely-rotating water molecules (H_2O) encapsulated in symmetrical cavities, such as fullerenes [46–48].

In spin-1/2 pair systems with a large nuclear exchange interaction, the spin Hamiltonian terms may be assigned as follows:

$$\begin{aligned} H_A &= \omega^0(I_{1z} + I_{2z}) + \zeta(T)\mathbf{I}_1 \cdot \mathbf{I}_2 \\ H_B &= 2\pi J_{12}\mathbf{I}_1 \cdot \mathbf{I}_2 \end{aligned} \quad (170)$$

In general, the temperature-dependent exchange splitting $\zeta(T)$ is given by the thermally-averaged energy difference between the spatial quantum states accessible to the different nuclear spin isomers. For example, in the case of freely-rotating diatomic molecules such as H_2 in the gas phase, this exchange splitting is given by

$$\hbar\zeta(T) = \overline{E_{\text{ortho}}(T)} - \overline{E_{\text{para}}(T)} \quad (171)$$

where

$$\begin{aligned} \overline{E_{\text{ortho}}(T)} &= \sum_{J=1,3,\dots} g_J E_J \exp\{-E_J/k_B T\} / \sum_{J=1,3,\dots} g_J \exp\{-E_J/k_B T\} \\ \overline{E_{\text{para}}(T)} &= \sum_{J=0,2,\dots} g_J E_J \exp\{-E_J/k_B T\} / \sum_{J=0,2,\dots} g_J \exp\{-E_J/k_B T\} \end{aligned} \quad (172)$$

Here E_J is the rotational energy of the spatial quantum state with rotational quantum number J , and the degeneracies of the rotational levels are $g_J = 2J + 1$. The use of equation 172 for the average exchange splitting assumes that the transitions between rotational states (caused by collisions, in the case of a liquid) are much faster than all terms in the spin Hamiltonian. The exchange splitting (*ortho-para* splitting) becomes very small at temperatures large compared to the rotational level splittings, but may exceed hundreds of GHz at low temperature. In such cases, the exchange splitting $\zeta(T)$ may be larger than the thermal energy $k_B T$.

In triatomic molecules displaying spin isomerism, such as H_2O , equation 172 should be modified to reflect the more complex relationship between the rotational quantum numbers and the nuclear spin states [93]. However, the principle is the same and the form of the exchange Hamiltonian is identical. Similar phenomena are observed for tunneling methyl groups [30–35].

The theory above requires identification of the eigenoperators $|A_\alpha\rangle$ of the commutation superoperator \hat{H}_A (equation 41). Although, the zero- and second-rank spherical tensor operators $|T_{00}^\Lambda\rangle$ and $|T_{2\mu}^\Lambda\rangle$, defined in equation 47, are already eigenoperators of \hat{H}_A as defined in equation 170, this is not the case for the first-rank spherical tensor operators $|T_{1\mu}^\alpha\rangle$. Nine first-rank eigenoperators are constructed from symmetrical combinations of the single-spin and spin-pair spherical tensor operators of rank 1. The 16 \hat{H}_A eigenoperators $\{|A_\alpha\rangle\}$, with $\alpha \in \{1 \dots 16\}$, are given by:

$$\begin{aligned} \{|A_\alpha\rangle\} = & \left\{ |T_{2-2}^{12}\rangle, |T_{1-1}^g\rangle, |T_{1-1}^{u+}\rangle, |T_{1-1}^{u-}\rangle, |T_{2-1}^{12}\rangle, |T_{00}^0\rangle, |T_{00}^{12}\rangle, |T_{10}^g\rangle, \right. \\ & \left. |T_{10}^{u+}\rangle, |T_{10}^{u-}\rangle, |T_{20}^{12}\rangle, |T_{11}^g\rangle, |T_{11}^{u+}\rangle, |T_{11}^{u-}\rangle, |T_{21}^{12}\rangle, |T_{22}^{12}\rangle \right\} \end{aligned} \quad (173)$$

where the symmetrical combinations are:

$$\begin{aligned} |T_{1\mu}^{(u+)}\rangle &= \left| \sqrt{2}T_{1\mu}^{(12)} + \frac{1}{2}T_{1\mu}^{(1)} - \frac{1}{2}T_{1\mu}^{(2)} \right\rangle \\ |T_{1\mu}^{(u-)}\rangle &= \left| \sqrt{2}T_{1\mu}^{(12)} - \frac{1}{2}T_{1\mu}^{(1)} + \frac{1}{2}T_{1\mu}^{(2)} \right\rangle \\ |T_{1\mu}^g\rangle &= \left| \frac{1}{\sqrt{2}}(T_{1\mu}^{(1)} + T_{1\mu}^{(2)}) \right\rangle \end{aligned} \quad (174)$$

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with $\mu \in \{-1, 0, +1\}$. The subscripts u and g refer to operators that are antisymmetric and symmetric with respect to particle exchange, respectively. The corresponding eigenvalues of \hat{H}_A are given by:

$$\{\omega_\alpha^A\} = \left\{ -2\omega^0, -\omega^0, -\zeta - \omega^0, \zeta - \omega^0, -\omega^0, 0, 0, 0, -\zeta, \zeta, 0, \omega^0, -\zeta + \omega^0, \zeta + \omega^0, \omega^0, 2\omega^0 \right\} \quad (175)$$

These eigenoperators and eigenvalues may be used to construct the Lindbladian form of the relaxation superoperator for the fluctuating random field mechanism:

$$\hat{\Gamma}_{\text{LB}}^{\theta, \text{ran}} = \sum_{i,j=1}^2 \kappa_{ij} \omega_{\text{rms}}^{(i)} \omega_{\text{rms}}^{(j)} \sum_{\alpha, \alpha'=1}^{16} \hat{D}[A_\alpha^A, A_{\alpha'}^{A\dagger}] J_{\text{ran}}^\theta(\omega_\alpha^A) \delta(\omega_\alpha^A - \omega_{\alpha'}^A) \quad (176)$$

The thermal equilibrium density operator may be derived from the null-space of this superoperator, i.e. by solving the equation

$$\hat{\Gamma}_{\text{LB}}^{\theta, \text{ran}} \left| \rho_{\text{eq}} \right\rangle = 0 \quad (177)$$

with the constraint $\text{Tr}\{\rho_{\text{eq}}\} = 1$. The solution is as follows:

$$\begin{aligned} \rho_{\text{eq}}(T) = & Z^{-1} \left\{ |S_0\rangle \langle S_0| + \exp\{-\beta_\theta(\zeta(T) + \omega^0)\} |T_{+1}\rangle \langle T_{+1}| \right. \\ & \left. + \exp\{-\beta_\theta\zeta(T)\} |T_0\rangle \langle T_0| + \exp\{-\beta_\theta(\zeta(T) - \omega^0)\} |T_{-1}\rangle \langle T_{-1}| \right\} \end{aligned} \quad (178)$$

where the partition function is:

$$Z = 1 + \exp\{-\beta_\theta(\zeta(T) + \omega^0)\} + \exp\{-\beta_\theta\zeta(T)\} + \exp\{-\beta_\theta(\zeta(T) - \omega^0)\} \quad (179)$$

Note that ρ_{eq} depends on temperature through the exchange splitting $\zeta(T)$.

The singlet state $|S_0\rangle$ may be identified with the *para* spin isomer, while the triplet states $|T_M\rangle$, $M \in \{-1, 0, +1\}$, belong to the *ortho* spin isomer. The equilibrium *para* and *ortho* populations are given by:

$$\begin{aligned} p_{\text{para}}^{\text{eq}}(T) &= \left(|S_0\rangle \langle S_0| \left| \rho_{\text{eq}} \right\rangle \right) = Z^{-1} \\ p_{\text{ortho}}^{\text{eq}}(T) &= 1 - p_{\text{para}}^{\text{eq}}(T) \end{aligned} \quad (180)$$

This displays the well-known temperature dependence of *ortho-para* equilibrium. In equilibrium at high temperature $\beta_\theta \rightarrow 0$, the partition function tends to $Z \rightarrow 4$, all four states are approximately equally populated, and the *ortho* and *para* populations tend to $p_{\text{ortho}}^{\text{eq}} \rightarrow 3/4$ and $p_{\text{ortho}}^{\text{eq}} \rightarrow 1/4$. At very low temperature, on the other hand ($\beta_\theta \rightarrow \infty$), the partition function tends to $Z \rightarrow 1$, and only the *para* state $|S_0\rangle$ is populated at thermal equilibrium.

The Lindbladian superoperator in equation 176 also allows analysis of the dynamics of spin-isomer conversion, under the fluctuating random field model. Since singlet order corresponds to the difference between the population of the singlet state and the mean population of the triplet states, the rate constant for spin-isomer conversion is equal to the decay rate constant R_S for singlet order. This is given by the following matrix element:

$$\begin{aligned} R_S = & - \frac{(\mathbf{I}_1 \cdot \mathbf{I}_2 | \hat{\Gamma}_{\text{LB}}^{\theta, \text{ran}} | \mathbf{I}_1 \cdot \mathbf{I}_2)}{(\mathbf{I}_1 \cdot \mathbf{I}_2 | \mathbf{I}_1 \cdot \mathbf{I}_2)} = \frac{1}{6} (1 - \kappa) \omega_{\text{rms}}^2 \left(J_{\text{ran}}^\theta(-\zeta) + J_{\text{ran}}^\theta(-\zeta + \omega^0) + J_{\text{ran}}^\theta(-\zeta - \omega^0) \right) \\ & + \frac{1}{2} (1 - \kappa) \omega_{\text{rms}}^2 \left(J_{\text{ran}}^\theta(+\zeta) + J_{\text{ran}}^\theta(+\zeta + \omega^0) + J_{\text{ran}}^\theta(+\zeta - \omega^0) \right) \end{aligned} \quad (181)$$

where the explicit temperature dependence of the *ortho-para* splitting has been suppressed for simplicity. Note that the spin-isomer conversion requires spectral density of the random fields at combinations of the exchange splitting frequency ζ and the Larmor frequency ω^0 , and that the conversion process is suppressed for correlated random fields ($\kappa \rightarrow 1$).

These results are unsurprising. Nevertheless, it should be emphasized that the semi-classical relaxation method, and the inhomogeneous master equation, are incapable of generating them.

This formalism may readily be extended to include additional nuclei and mechanisms in the relaxation processes. Such techniques were used to analyze quantum-rotor-induced polarization effects in fullerene-encapsulated ^{17}O -labelled water, in which the quadrupolar ^{17}O nucleus catalyzes the generation of antiphase magnetization during the spin-isomer conversion of *para*-water to *ortho*-water, at the same time as undergoing rapid quadrupolar relaxation [46, 94].

7. Conclusions

The correct treatment of spin systems in contact with a thermal reservoir is one of the oldest problems in magnetic resonance theory. The early founders of semiclassical relaxation theory were fully aware that semiclassical relaxation theory fails to describe thermal equilibration correctly and that the most readily available “fix” (the inhomogeneous master equation, IME) is of limited validity. Nevertheless, this venerable equation has served the nuclear magnetic resonance community well for more than 60 years, presumably because the underpinning assumptions (weakly ordered and near-equilibrium spin systems) were well-satisfied for the vast majority of systems under study.

In the period 1980–2000, there was interest in formulating homogeneous master equations as alternatives to the IME [50–54]. The main motivating factor for these developments was the mathematical inconvenience of the IME. Much insight into spin dynamical problems such as steady-state NMR properties could be gained by expressing the nuclear spin dynamics, including thermally induced relaxation, as solutions to a homogeneous differential equation. This formulation allowed the development and application of attractive theoretical approaches such as the average Liouvillian theory [52, 55]. This provided an intuitive tool for understanding how certain relaxation processes may effectively be turned on and off by applying resonant radiofrequency fields, allowing unusual insights into phenomena such as the steady-state nuclear Overhauser effect [11, 12]. Insights of this kind played a role in the development of techniques exploiting long-lived spin states [34, 35, 37–45]. However, although the mathematical awkwardness of the IME was widely recognized, its validity was not generally called into question at this time. Its restriction to near-equilibrium and weakly-ordered spin systems was largely overlooked or forgotten. [50–57]

More recently, technological developments have made spin systems which are prepared “in an unusual way”, to use the phrase of Redfield [3], increasingly accessible to the magnetic resonance community. Hyperpolarization techniques such as dynamic nuclear polarization [15–18], optical pumping [19–22], quantum-rotor-induced polarization [30–36], parahydrogen-induced polarization [23–29], and chemically-induced dynamic nuclear polarisation [95–97] all involve spin systems which are far from equilibrium. As discussed in the current article, the relaxation behaviour of these systems is not always consistent with the IME, and in some cases, very substantial deviations from the IME are observed, as illustrated in figure 1.

Some variants of the homogeneous master equation do succeed in describing certain features of non-equilibrium nuclear spin dynamics correctly. Nevertheless the Lindbladian formalism, as described in the current article, seems to be the only one which passes all tests (subject to its own restrictions and approximations, of course, as indicated above). This will not come as a great surprise to researchers in many other spectroscopies, where the approximations underpinning the IME were never valid in the first place, and where Lindbladian techniques have been current for a long time.

We hope that the current work will help bring the magnetic resonance community into mutual contact with other research areas facing similar problems, including the vigorous theoretical field of open quantum systems [62, 63, 76–78].

8. Acknowledgements

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A. Appendix

A.1. Lindblad form

First consider the Fourier transformation of the unit-step function.

$$\int_{-\infty}^{\infty} h(t) \exp\{i\omega t\} dt = \int_0^{\infty} \exp\{i\omega t\} dt = \pi \delta(\omega) - i \text{PV} \left(\frac{1}{\omega} \right) \quad (182)$$

where $h(t)$ denotes the unit-step function and PV the Cauchy principal value.

The bath correlation functions are related to the spectral densities as follows:

$$\langle B_{\alpha'}^{\Lambda' \dagger}(\tau) B_{\alpha}^{\Lambda}(0) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} K_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega) \exp\{-i\omega\tau\} d\omega \quad (183)$$

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The one-sided Fourier transformation of the bath correlation functions in equation 134 may then be expressed as shown below:

$$\begin{aligned}
 \int_0^\infty \langle B_{\alpha'}^{\Lambda'\dagger}(\tau) B_\alpha^\Lambda(0) \rangle \exp\{i\omega\tau\} d\tau &= \frac{1}{2\pi} \int_0^\infty \int_{-\infty}^\infty K_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega') \exp\{i(\omega - \omega')\tau\} d\omega' d\tau \\
 &= \frac{1}{2\pi} \int_{-\infty}^\infty K_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega') \int_0^\infty \exp\{i(\omega - \omega')\tau\} d\tau d\omega' \\
 &= \frac{1}{2\pi} \int_{-\infty}^\infty K_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega') \left\{ \pi \delta(\omega - \omega') - i \text{PV} \left(\frac{1}{\omega - \omega'} \right) \right\} d\omega' \\
 &\quad \frac{1}{2} K_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega) - \frac{i}{2\pi} \int_{-\infty}^\infty K_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega') \text{PV} \left(\frac{1}{\omega - \omega'} \right) d\omega'
 \end{aligned} \tag{184}$$

in a similar manner one can show the following:

$$\int_{-\infty}^0 \langle B_{\alpha'}^{\Lambda'\dagger}(\tau) B_\alpha^\Lambda(0) \rangle \exp\{i\omega\tau\} d\tau = \frac{1}{2} K_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega) + \frac{i}{2\pi} \int_{-\infty}^\infty K_{\alpha\alpha'}^{\Lambda\Lambda'}(\omega') \text{PV} \left(\frac{1}{\omega - \omega'} \right) d\omega' \tag{185}$$

The above representations of the one-sided Fourier transformation may then be substituted into equation 134.

The combination of the principal value leads to a commutator that is known as dynamic frequency shift.

The decaying part is proportional to the spectral density $K_{\alpha\alpha'}(\omega)$. The minus sign preceding the sum of equation 134 and the factor of 1/2 are usually absorbed into the definition of the Lindbladian resulting in the presented Lindblad equation.

A.2. Double commutator thermalization

In this section we show that thermal adjustment of the correlation functions within the double commutator formalism does not lead to a correct thermalization of the relaxation superoperator.

This may be demonstrated by making use of the eigenoperator formulation of the relaxation superoperator as presented in equation 80. A thermally adjusted and secularized double-commutation form of the relaxation superoperator is as follows:

$$\hat{\Gamma}^\theta = -\frac{1}{2} \sum_{ij} \exp\left\{-\frac{1}{2}\beta_\theta \omega_{ij}\right\} J_{ijij}(\omega_{ij}) \hat{X}_{ij} \hat{X}_{ij}^\dagger \tag{186}$$

The transition probability per unit time $W_{k \rightarrow l}$ from the eigenstate $|k\rangle$ to the eigenstate $|l\rangle$ of the Hamiltonian H_A may be identified with the following matrix element:

$$W_{k \rightarrow l} = (X_{ll} | \hat{\Gamma}^\theta | X_{kk}) = -\frac{1}{2} \sum_{ij} \exp\left\{-\frac{1}{2}\beta_\theta \omega_{ij}\right\} J_{ijij}(\omega_{ij}) (\delta_{li} \delta_{kj} - \delta_{li} \delta_{kj} - \delta_{lj} \delta_{ki} + \delta_{lj} \delta_{kj}) \tag{187}$$

Similarly, the transition probability for the reverse process is given by

$$W_{l \rightarrow k} = (X_{kk} | \hat{\Gamma}^\theta | X_{ll}) = -\frac{1}{2} \sum_{ij} \exp\left\{-\frac{1}{2}\beta_\theta \omega_{ij}\right\} J_{ijij}(\omega_{ij}) (\delta_{ki} \delta_{li} - \delta_{ki} \delta_{li} - \delta_{kj} \delta_{li} + \delta_{kj} \delta_{li}) \tag{188}$$

Clearly these two transition probabilities are equal:

$$W_{k \rightarrow l} = W_{l \rightarrow k} \tag{189}$$

This indicates that forward and backward transitions are equally likely, violating detailed balance, except at infinite temperature. It follows that thermal correction of the spectral density functions within the double commutator formalism cannot lead to a valid thermalized relaxation superoperator, at finite temperature.

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$\mu \backslash \lambda$	2	1
± 2	$\frac{1}{2} I_1^\pm I_2^\pm$	-
± 1	$\mp \frac{1}{2} (I_1^\pm I_{2z} + I_{1z} I_2^\pm)$	$\mp \frac{1}{\sqrt{2}} I_j^\pm$
0	$-\frac{1}{2\sqrt{6}} (I_1^+ I_2^- + I_1^- I_2^+ - 4 I_{1z} I_{2z})$	I_{jz}

Table 2

Eigenoperators of \hat{H}_A for a homonuclear coupled spin-1/2 pair.

A.3. Equivalence of double commutator and Lindbladian at infinite temperature

The Lindblad formalism and the double commutator formalism only coincide at infinite temperature, because the spectral densities become temperature-independent. To see this the relaxation superoperator in the double-commutator formalism at infinite temperature may be written as shown below:

$$\hat{\Gamma}^\theta = -\frac{1}{2} \sum_{ij} J_{ijij}(\omega_{ij}) \{ \frac{1}{2} (\hat{X}_{ij} \hat{X}_{ij}^\dagger + \hat{X}_{ji} \hat{X}_{ji}^\dagger) \} \quad (190)$$

since $\exp\left\{-\frac{1}{2}\beta_\theta \omega_{ij}\right\} = 1$ for $T \rightarrow \infty$. To proceed the following identity is employed:

$$\frac{1}{2} (\hat{X}_{ij} \hat{X}_{ij}^\dagger + \hat{X}_{ji} \hat{X}_{ji}^\dagger) = -(\hat{\mathcal{D}}[X_{ij}, X_{ij}^\dagger] + \hat{\mathcal{D}}[X_{ji}, X_{ji}^\dagger]) \quad (191)$$

The relaxation superoperator in the double-commutator formalism is then readily expressed in Lindblad form:

$$\begin{aligned} \hat{\Gamma}^\theta &= \frac{1}{2} \sum_{ij} J_{ijij}(\omega_{ij}) (\hat{\mathcal{D}}[X_{ij}, X_{ij}^\dagger] + \hat{\mathcal{D}}[X_{ji}, X_{ji}^\dagger]) \\ \hat{\Gamma}^\theta &= \frac{1}{2} \sum_{ij} J_{ijij}(\omega_{ij}) \hat{\mathcal{D}}[X_{ij}, X_{ij}^\dagger] + J_{ijij}(\omega_{ij}) \hat{\mathcal{D}}[X_{ji}, X_{ji}^\dagger] \\ \hat{\Gamma}^\theta &= \frac{1}{2} \sum_{ij} J_{ijij}(\omega_{ij}) \hat{\mathcal{D}}[X_{ij}, X_{ij}^\dagger] + J_{jiji}(\omega_{ji}) \hat{\mathcal{D}}[X_{ji}, X_{ji}^\dagger] \\ \hat{\Gamma}^\theta &= \sum_{ij} J_{ijij}(\omega_{ij}) \hat{\mathcal{D}}[X_{ij}, X_{ij}^\dagger] \end{aligned} \quad (192)$$

by noticing that $J_{ijij}(\omega_{ij}) = J_{jiji}(\omega_{ji})$ at infinite temperature.

A.4. Eigenoperators

The relevant eigenoperators of \hat{H}_A for the homonuclear case are summarised in Table 2. The eigenoperators are denoted by $T_{\lambda\mu}^{(ij)}$. The superscript (ij) indicates angular momentum coupling of spins I_i and I_j resulting in a spherical tensor operator of total angular momentum λ and z-angular momentum μ .

The relevant eigenoperators of \hat{H}_A for the heteronuclear case are summarised in Table 3. The eigenoperators are denoted by $T_{\lambda_1\lambda_2\mu_1\mu_2}^{(ij)}$. For the heteronuclear case the superscript (ij) indicates the direct product of spherical tensor operators of spins I_i and I_j with total angular momentum λ_1 and λ_2 and z-angular momentum μ_1 and μ_2 , respectively.

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$(\mu_1, \mu_2) \backslash (\lambda_1, \lambda_2)$	(1,1)	(1,0)	(0,1)	(0,0)
$(\pm 1, \pm 1)$	$\frac{1}{2} I_1^\pm I_2^\pm$	-	-	
$(\mp 1, \pm 1)$	$-\frac{1}{2\sqrt{6}} I_1^\mp I_2^\pm$	-	-	
$(\pm 1, 0)$	$\mp \frac{1}{2} I_1^\pm I_{2z}$	$\mp \frac{1}{\sqrt{2}} I_1^\pm$	-	-
$(0, \pm 1)$	$\mp \frac{1}{2} I_{1z} I_2^\pm$	-	$\mp \frac{1}{\sqrt{2}} I_2^\pm$	-
$(0, 0)$	$\sqrt{\frac{2}{3}} I_{1z} I_{2z}$	I_{1z}	I_{2z}	-

Table 3

Eigenoperators of \hat{H}_A for a heteronuclear coupled spin-1/2 pair.

A.5. Longitudinal recovery for spin-isomer-conversion

We briefly outline the derivation of equation 168. First we project out the population block of the relaxation superoperator.

$$\left[\hat{\Gamma}_{\text{LB}}^\theta \right]_{4 \times 4} = \begin{bmatrix} |S_0\rangle\langle S_0| & |T_{+1}\rangle\langle T_{+1}| & |T_0\rangle\langle T_0| & |T_{-1}\rangle\langle T_{-1}| \\ -\Sigma_1 & \frac{1}{2}(1-\kappa)R_1^{\text{ran}}\theta(-\omega^0) & \frac{1}{2}(1-\kappa)R_1^{\text{ran}} & \frac{1}{2}(1-\kappa)R_1^{\text{ran}}\theta(\omega^0) \\ \frac{1}{2}(1-\kappa)R_1^{\text{ran}}\theta(\omega^0) & -\Sigma_2 & \frac{1}{10}\theta(\omega^0)(2R_1^{\text{DD}} + 5(1+\kappa)R_1^{\text{ran}}) & \frac{2}{5}R_1^{\text{DD}}\theta(2\omega^0) \\ \frac{1}{2}(1-\kappa)R_1^{\text{ran}} & \frac{1}{10}\theta(-\omega^0)(2R_1^{\text{DD}} + 5(1+\kappa)R_1^{\text{ran}}) & -\Sigma_3 & \frac{1}{10}\theta(\omega^0)(2R_1^{\text{DD}} + 5(1+\kappa)R_1^{\text{ran}}) \\ \frac{1}{2}(1-\kappa)R_1^{\text{ran}}\theta(-\omega^0) & \frac{2}{5}R_1^{\text{DD}}\theta(-2\omega^0) & \frac{1}{10}\theta(-\omega^0)(2R_1^{\text{DD}} + 5(1+\kappa)R_1^{\text{ran}}) & -\Sigma_4 \end{bmatrix} \quad (193)$$

$$\theta(\omega) = \exp\left\{(-\frac{1}{2}\omega^0\beta_\theta)\right\}$$

where Σ_j indicates the sum over all the other elements in one column.

To proceed it is advantageous to perform a change of basis. The transformation matrix is given by the expression below:

$$X = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{1}{2} & -\frac{1}{2\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{2} & -\frac{1}{2\sqrt{3}} & \sqrt{\frac{2}{3}} & 0 \\ \frac{1}{2} & -\frac{1}{2\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \end{bmatrix} \quad (194)$$

To simplify notation we denote the transformed population block as follows:

$$X^{-1} \left\{ \left[\hat{\Gamma}_{\text{LB}}^\theta \right]_{4 \times 4} \right\} X = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & \sigma_{22} & 0 & \sigma_{24} \\ 0 & 0 & \sigma_{33} & \sigma_{34} \\ \sigma_{41} & \sigma_{42} & \sigma_{43} & \sigma_{44} \end{bmatrix} \quad (195)$$

and enumerate the transformed populations:

$$\begin{bmatrix} P_1 \\ P_2 \\ P_3 \\ P_4 \end{bmatrix} = X^{-1} \begin{bmatrix} |S_0\rangle\langle S_0| \\ |T_{+1}\rangle\langle T_{+1}| \\ |T_0\rangle\langle T_0| \\ |T_{-1}\rangle\langle T_{-1}| \end{bmatrix} \quad (196)$$

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To a good approximation the dynamics of P_2 are decoupled from the dynamics of P_4 .

$$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & \sigma_{22} & 0 & \sigma_{24} \\ 0 & 0 & \sigma_{33} & \sigma_{34} \\ \sigma_{41} & \sigma_{42} & \sigma_{43} & \sigma_{44} \end{bmatrix} \approx \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & \sigma_{22} & 0 & 0 \\ 0 & 0 & \sigma_{33} & \sigma_{34} \\ \sigma_{41} & \sigma_{42} & \sigma_{43} & \sigma_{44} \end{bmatrix} \quad (197)$$

leading to the following set of equations:

$$\frac{d}{dt} \begin{bmatrix} P_1(t) \\ P_2(t) \\ P_3(t) \\ P_4(t) \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & \sigma_{22} & 0 & 0 \\ 0 & 0 & \sigma_{33} & \sigma_{34} \\ \sigma_{41} & \sigma_{42} & \sigma_{43} & \sigma_{44} \end{bmatrix} \begin{bmatrix} P_1(t) \\ P_2(t) \\ P_3(t) \\ P_4(t) \end{bmatrix} \quad (198)$$

The solution for $P_1(t)$ and $P_2(t)$ are easily found:

$$P_1(t) = P_1(0) \quad P_2(t) = \exp\{(\sigma_{22}t)\} P_2(0) \quad (199)$$

The solution for $P_3(t)$ is formally given by:

$$P_3(t) = \exp\{(\sigma_{33}t)\} P_3(0) + \sigma_{34} \int_0^t \exp\{(\sigma_{33}(t-s))\} P_4(s) ds \quad (200)$$

We interpret the variable $(t-s)$ as a "memory time" and perform a 0-th order Markov approximation [98].

$$P_3(t) \approx \exp\{(\sigma_{33}t)\} P_3(0) + \frac{\sigma_{34}}{\sigma_{33}} P_4(t) \quad (201)$$

The dynamics for $P_4(t)$ then reduce to the following:

$$\frac{d}{dt} P_4(t) = \sigma_{41} P_1(0) + \sigma_{42} \exp\{(\sigma_{22}t)\} P_2(0) + \sigma_{43} \left\{ \exp\{(\sigma_{33}t)\} P_3(0) + \frac{\sigma_{34}}{\sigma_{33}} P_4(t) \right\} + \sigma_{44} P_4(t) \quad (202)$$

which is easily solved.

The solution may then be transformed back into the original representation. Using the appropriate initial conditions: $P_1(0) = \frac{1}{2}$, $P_2(0) = \frac{\sqrt{3}}{2}$, $P_3(0) = 0$ and $P_4(0) = 0$ in combination with the high-temperature and fast-motion approximation results in equation 168.

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- * The inhomogeneous master equation fails in general far from equilibrium.
- * A simple thought-experiment illustrates the failure of the standard equation.
- * A Lindbladian approach is described which retains validity far from equilibrium.
- * Case studies are provided illustrating the new master equation.

