TOPICAL REVIEW

Spin dynamic simulations of solid effect DNP: the role of the relaxation superoperator

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Relaxation plays a crucial role in the spin dynamics of dynamic nuclear polarisation. We review here two different strategies that have recently been used to incorporate relaxation in models to predict the spin dynamics of solid effect dynamic nuclear polarisation. A detailed explanation is provided on how the Lindblad–Kossakowski form of the master equation can be used to describe relaxation in a spin system. Fluctuations of the spin interactions with the environment as a cause of relaxation are discussed and it is demonstrated how the relaxation superoperator acting in Liouville space on the density operator can be derived in the Lindblad–Kossakowski form by averaging out non-secular terms in an appropriate interaction frame. Furthermore we provide a formalism for the derivation of the relaxation superoperator starting with a choice of a basis set in Hilbert space. We show that the differences in the prediction of the nuclear polarisation dynamics that are found for certain parameter choices arise from the use of different interaction frames in the two different strategies. In addition, we provide a summary of different relaxation mechanisms that need to be considered to obtain more realistic spin dynamic simulations of solid effect dynamic nuclear polarisation.

Keywords: Lindblad–Kossakowski master equation; Liouville space; solid effect dynamic nuclear polarisation; relaxation superoperator; spin dynamics

1. Introduction

Dynamic nuclear polarisation (DNP) can be used to substantially enhance the nuclear spin polarisation. There is currently an increased interest in the use of DNP by the magnetic resonance community since with the availability of robust hardware this strategy may help to overcome the sensitivity limitations of a wide range of applications including magic angle spinning nuclear magnetic resonance (NMR) spectroscopy and magnetic resonance imaging [1–3]. Several DNP pathways in solid state have been described in the literature. Depending on the number of electrons that interact with the same nuclei and the linewidth of the electron resonance spectrum, solid effect DNP (SE DNP), cross effect DNP and DNP by thermal mixing have been distinguished [4,5]. SE DNP relies on (1) a spin system with negligible interactions between electrons, so it is sufficient to consider only one electron interacting with an ensemble of nuclear spins. Nuclear spins are coupled to the electron through the hyperfine interaction and form a coupled network through their dipolar interactions between each other. (2) The electron linewidth is smaller than the Zeeman splitting of the nuclear spins and hence spectral diffusion effects across the electron resonance line can be neglected. (3) The saturation of either the zero- or double-quantum transition frequency in the electron resonance spectrum. An important feature of DNP is relaxation processes that form the response of the spin system to the perturbation caused by the microwave (MW) irradiation. In combination, both the continuous irradiation and the relaxation processes lead to an establishment of a quasi equilibrium for the spin system in which the population differences for the NMR transitions are enhanced in comparison with the thermal equilibrium state.

The quantum mechanical description of the SE DNP process that leads to an increase of the nuclear spin polarisation in a sample can provide insight into the parameters that limit the achievable spin polarisation and control the time required to reach it. In particular, such models are useful to predict the performance of chemical compounds with unpaired electrons in DNP. A number of models have been proposed to simulate the spin dynamics of samples in the solid state either including sample rotation around the magic angle [6,7] or considering samples at rest [8–11]. We discuss in this contribution the challenges to incorporate relaxation in the quantum mechanical simulations and compare the different approaches that have been proposed in this respect.

2. The master equation

Our objective is to calculate the dynamics of a model spin system consisting of one electron spin $S$ coupled by hyperfine interactions to $n$ nuclear spins $I_k$ during the constant irradiation with a MW field. The general master
equation for the density operator $\sigma$, in the frame rotating with the MW irradiation frequency $\omega_0$, is the Liouville–von Neumann equation

$$\dot{\sigma} = -i [\mathcal{H}, \sigma] - \Gamma \sigma,$$

where $\mathcal{H} = [H, \cdot]$ is the Hamiltonian commutation superoperator and $\Gamma$ is the relaxation superoperator whose form we specify later. We assume that the relaxation superoperator has been appropriately thermalised in such a way that it ensures relaxation of the system back to the thermal equilibrium using the approach suggested by Levitt and di Bari [12]. The Hamiltonian $H$ of the spin system consists of the following terms:

$$H = H_Z + H_{IS} + H_d + H_{MW} = H_0 + H_{MW},$$

where the first term represents the Zeeman interaction of the electron and the nuclei with the external static magnetic field, the second term describes the hyperfine interaction between the electron and the nuclear spins and the third term represents the dipolar interaction between the nuclear spins. The fourth term represents the MW irradiation applied orthogonally to the direction of the static magnetic field. The stationary Hamiltonian $H_0$ consists of only the interaction terms without the term arising from the MW irradiation. The Zeeman interaction is defined by

$$H_Z = \omega_S S_z + \omega_I \sum_k I_{kz}.$$ 

The hyperfine interaction and the nuclear interaction can be written in terms of tensor products

$$H_{IS} = \sum_k I_k \cdot D_k \cdot S, \quad H_{II} = \sum_{k \neq j} I_k d_{kj} I_j.$$ 

After transferring the master equation into a frame rotating with the carrier frequency of the applied MW field $\omega_0$ we obtain

$$H'_Z = \Delta_S S_z + \omega_I \sum_k I_{kz},$$

where $\Delta_S = \omega_S - \omega_0 = \pm \omega_I$ since we can choose either to irradiate the zero- or the double-quantum transition of the electron–nuclear spin system. The hyperfine interaction term of the Hamiltonian simplifies using the high-field approximation

$$H'_{IS} = \sum_k A_{k0} S_z I_{kz} + \frac{1}{2} \sum_k A_{k+} S_z I_{k+} + \frac{1}{2} \sum_k A_{k-} S_z I_{k-},$$

and the dipolar interaction between nuclear spins can now be written in the truncated form

$$H'_d = \sum_{j<k} d_{jk} (3 I_{jz} I_{kz} - I_j \cdot I_k).$$

Note that $H'_0 = H'_Z + H'_{IS} + H'_{II}$ is the truncated stationary Hamiltonian.

The irradiation of the spin system at the MW frequency $\omega_0$ that is offset from the electron Larmor frequency by $\pm \omega_I$ is given by

$$H_{MW} = \frac{\omega_I}{2} (S_+ + S_-).$$

The appropriate Liouville space $\mathcal{L}$ for this quantum mechanical problem is spanned by the Zeeman basis using direct products of the single-spin unity operator, the Zeeman operators $I_{kz}, S_z$ and the raising and lowering operators $I_{k+}, S_\pm$.

The number of spins that can be included in a coupled network in a quantum mechanical simulation of the solid effect is limited due to the exponential scaling of the dimensions of the Liouville space with the size of the spin ensemble. A careful analysis of the participation of all states to the spin dynamics of the solid effect shows that mainly states belonging to the zero quantum coherence subspace contribute to it [13].

All other states are only weakly populated. We have recently proposed to calculate an effective Hamiltonian [13] based on an averaging procedure published by Krylov and Bogolyubov [14,15]. The averaging procedure confines the dynamics of SE DNP to the zero quantum coherence subspace. A prerequisite for this strategy is the use of the Zeeman basis for the calculations.

To maximise the number of spins in a model for SE DNP we want (1) to reduce the required state space as much as possible while still obtaining a close approximation of the spin dynamics and (2) avoid the use of any diagonalisation of operators since the required mathematical procedure imposes a limit to the quantum mechanical dimensions and thus the number of spins that can be included in the model.

In the following we describe our approach to include relaxation in a model for SE DNP, keeping the above restrictions in mind. We discuss how our strategy fits the general formalism for the description of dissipative quantum systems. Furthermore, we compare our approach to models proposed by other groups and discuss the differences in the model predictions that arise from the assumptions made in each of these models.

### 3. Fluctuations as the origin of relaxation

Relaxation in a spin system arises from the fluctuations of the interactions of the spins with their environment. We refer to the term ’environment’ to describe interactions with the lattice and other spins, which have an effect on the relaxation processes of the spin system under consideration. We can add to the stationary Hamiltonian $H_0$ of a quantum system a random time-dependent term $H_f(t)$ to account for the fluctuations,

$$H = H_0 + H_f(t).$$
The fluctuating part is represented by the Hermitian operator \( H_f(t) \) whose matrix elements describe random stationary processes with zero averages. The relaxation superoperator can be found in the following three steps [16].

First, we proceed to an appropriate spin interaction frame to take into account the periodic perturbation of the spin system due to the MW irradiation. We proceed to the frame to take into account the periodic perturbation of the Hamiltonian.

Furthermore, at the solid effect DNP resonance \( \omega_z \pm \omega_I \), the polarisation dynamics is effectively reduced to the subspace of operators commuting with the resonant part of the Zeeman interaction.

Thus, the dynamics is described in the spin interaction frame,

\[
\sigma = e^{-iH_Z t} \bar{\sigma} \equiv e^{-iH_Z t} \bar{\sigma} e^{iH_Z t},
\]

\[
H_Z \equiv [H_Z, \cdot], \quad H_Z = \omega_S S_z + \omega_I \sum I_z,
\]

(2)

where the higher order Krylov–Bogolyubov method should be used to accurately average out non-secular terms [13]. The effective relaxation superoperator in this case commutes with the commutation superoperator \( H_Z \).

We use the rule to transfer the time-dependent Hamiltonian into the interaction frame

\[
H_f(t) \rightarrow H'_f(t) = e^{iH_Z t} H_f(t) e^{-iH_Z t},
\]

(3)

where \( H_Z \) denotes the Zeeman part of the unperturbed Hamiltonian \( H_0 \).

Second, we calculate the second-order approximation leading to the following double-commutator superoperator:

\[
\hat{\Gamma}(t) = \frac{1}{2} \int_{-\infty}^{+\infty} [H'_f(t), [H'_f(t - \tau), \cdot]] d\tau,
\]

(4)

where the overline means the temporal ensemble average.

Third, non-secular terms in \( \hat{\Gamma}(t) \) should be neglected by taking the time average

\[
\hat{\Gamma}(t) \rightarrow \hat{\Gamma}_0 = \langle \hat{\Gamma}(t) \rangle \equiv \lim_{t \rightarrow +\infty} \frac{1}{t} \int_0^t \hat{\Gamma}(t) dt.
\]

(5)

It is important to note that when calculating the time average (5), it is assumed that the minimal difference between eigenvalues of \( H_Z \) is much larger than the maximal relaxation rate caused by the fluctuating part. This is usually the case at high magnetic field when working in the Zeeman basis. For example, in the SE DNP case the eigenvalues of \( H_Z \) are

\[
\Omega_{pq} = p \omega_I + q \omega_S, \quad |p| \leq n, \quad |q| \leq 1,
\]

(6)

where the integer sum \( p + q \) is equal to the coherence order of the corresponding eigenstates. The minimal difference between the eigenvalues (at least in the subspaces with less than 500 quantum coherences) is \( |\omega_I| \). At typical high field, this is much larger than any relaxation rate observed in experiments. In this respect, the Zeeman frame (3) is universal and provides the maximal elimination of non-secular terms.

It is instructive to analyse whether it is possible to use a different frame instead of the Zeeman frame to average out the non-secular terms in \( \hat{\Gamma}(t) \). In the frame corresponding to the rotation defined by an arbitrary Hermitian operator \( H_i \) we make the change

\[
\sigma \rightarrow \sigma' = e^{iH_i t} \sigma e^{-iH_i t}.
\]

(7)

Let \( \sigma_{kj}' \) be the matrix elements of \( \sigma' \) in the basis of eigenstates \( \lambda_k \) of \( H \),

\[
\sigma_{kj}' = (\lambda_k | \sigma' | \lambda_j).
\]

According to the fluctuations approach, under the action of the relaxation superoperator, the matrix element \( \sigma_{kj}' \) changes in time as [16]

\[
\frac{d}{dt} \sigma_{kj}' = \sum_{k',j'} \Omega_{kj,k'j'} R_{kj,k'j'} \sigma_{kj}' ,
\]

(8)

where \( R_{kj,k'j'} \) are some time-independent relaxation rates. The terms with

\[
\Omega_{kj,k'j'} \neq 0
\]

are called non-secular terms. For \( k, j, k', j' \) such that

\[
\left| \frac{R_{kj,k'j'}}{\Omega_{kj,k'j'}} \right| = \epsilon_{kj,k'j'} \ll 1,
\]

the time-dependence in Equation (6) is fast oscillating, and the corresponding non-secular terms in the sum can be neglected. Otherwise, terms with \( k, j, k', j' \) such that the rate \( R_{kj,k'j'} \) is of the same order of magnitude or larger than \( \Omega_{kj,k'j'} \) (i.e. \( \epsilon_{kj,k'j'} \approx 1 \) or larger) are not fast oscillating. Their effect on the spin dynamics of the spin system can be appreciable, so they cannot be neglected.

All non-secular terms can be removed in the case when

\[
\forall k, j, k', j' \quad \Omega_{kj,k'j'} = 0 \quad \text{or} \quad \left| \frac{R_{kj,k'j'}}{\Omega_{kj,k'j'}} \right| \ll 1.
\]

(9)

Condition (7) is violated if there exists at least a pair of eigenstates of \( H \) with differences between the eigenvalues much smaller than the corresponding relaxation rates. For
example, if

\[ 0 \neq |\lambda_k - \lambda_j| \ll |R_{kj,ik}| \]

then

\[ \Omega_{kj,ik} = 2(\lambda_k - \lambda_j) \neq 0, \quad \frac{|R_{kj,ik}|}{|\Omega_{kj,ik}|} \gg 1. \]

Thus, not any operator $H$ can be used in the removal of the non-secular terms and not any rates $R_{kj,ik}$ can be chosen except those for which condition (7) is satisfied. This condition is always satisfied if $H = H_Z$, because the smallest non-zero difference between the eigenvalues of $H_Z$ is $|\omega_l|$, which is always much bigger than any relaxation rates in the system.

4. **Lindblad–Kossakowski relaxation superoperator**

If we use a specific form of the relaxation superoperator $\hat{\Gamma}$, the LvN equation (1) can be written in the so-called Lindblad–Kossakowski form [17,18]. We retain the coherent part of the LvN equation (1) with the commutation superoperator $\hat{H}$ and write the superoperator $-\hat{\Gamma}$ that describes the relaxation or decoherent part of the LvN equation (1) with the commutation

\[ -\hat{\Gamma}\sigma = \sum_{k,j=1}^{N^2-1} C_{kj} \left[ M_k \sigma M_j^* - \frac{1}{2} \left( \sigma M_j^* M_k + M_j^* M_k \sigma \right) \right], \]

(8)

where $\{M_k\}_{k=1}^{N^2-1}$ is an orthonormal set of traceless operators in the $N$-dimensional Hilbert space and $C_{kj}$ is a positive matrix of relaxation rates. The operators $M_k$ stand for the coupling to the environment of the spin ensemble whose statistical properties are represented by the density operator $\sigma$. The Lindblad–Kossakowski form guarantees that the master equation preserves the trace and the positiveness of the density operator for any initial value.

Due to the positiveness of $C_{kj}$, there always exists a unitary transformation

\[ L_s = \sum_{k=1}^{N^2-1} u_{sk} M_k, \quad s \in 1, N^2 - 1 \]

that leads to the diagonal form of the relaxation superoperator $\hat{\Gamma}$, which in this form is frequently called the Lindbladian,

\[ -\hat{\Gamma}\sigma = \sum_{k=1}^{N^2-1} \gamma_k \left[ L_k \sigma L_k^* - \frac{1}{2} \left( \sigma L_k^* L_k + L_k^* L_k \sigma \right) \right]. \]

(9)

Here $\{L_k\}_{k=1}^{N^2-1}$ is again an orthonormal set of traceless operators and $\gamma_k$ are non-negative rates. The condition of normalisation for $L_k$ is actually not necessary, because any normalisation can be achieved by a suitable choice of the rates $\gamma_k \geq 0$.

The set $\{L_k\}$ and the rates $\gamma_k$ (or the set $\{M_k\}$ and the rates $C_{kj}$) can be specified if a choice is made in respect to the origin of the relaxation mechanisms that cause transitions between populations and the loss of coherences in the quantum system.

It is possible to show (see Appendix A.1) that the relaxation superoperator in the Lindblad–Kossakowski form is invariant to a transformation into the interaction frame if the set of Lindblad–Kossakowski operators $L_k$ are an orthogonal set of traceless eigenoperators of the Zeeman superoperator $\hat{H}_Z$.

We show also in Appendix A.2 that, based on the assumption that the time-dependent Hamiltonian $H_I$ is built of a full set $\{F_{pq,m}\}$ of orthonormal eigenvectors of $\hat{H}_Z$, it is always possible to derive the relaxation superoperator $\hat{\Gamma}$ in the Lindblad–Kossakowski form.

5. **Uncorrelated random field model**

As the simplest model for a relaxation mechanism we can consider isotropic uncorrelated fluctuations of the local magnetic field (along the three spatial directions with no specific preference) [21,22]. The assumption of this model determines the choice of the set $\{L_k\}$ of Lindblad–Kossakowski operators for which the set of single-spin-order operators written in terms of Zeeman components and lowering and raising operators can be used,

\[ \{L_k\} = \{S_z, S_\pm, I_{sz}, I_{sz}, s \in \{1, n\} \}. \]

Starting from this set of traceless operators the relaxation superoperator can be built (see Appendix A.3) and we get

\[ \hat{\Gamma}\sigma = R_3 \hat{\Sigma}_3^z \sigma + R_1^+ (\hat{\Sigma}_+ \hat{\Sigma}_- + \hat{\Sigma}_- \hat{\Sigma}_+) \sigma + R_3 (S_\pm \sigma S_- - S_- \sigma S_+ + \sigma S_+ S_- + S_- \sigma) + \sum_{k=1}^{n} \left[ R_{2k} \hat{I}_k^z \sigma + R_{1k} (\hat{I}_k^+ \hat{I}_k^\mp + \hat{I}_k^- \hat{I}_k^+) \sigma + R_{3k} (\hat{I}_k^+ \sigma \hat{I}_k^- - \hat{I}_k^- \sigma \hat{I}_k^+ + \sigma \hat{I}_k^+ \hat{I}_k^-) \sigma \right], \]

(10)

where $R_j$, $r_{kj}$ are some rates to be specified.

At cryogenic temperatures of about 1 K, typical for dissolution DNP experiments, and modest magnetic fields of 3.5 T, the thermal density operator is well approximated using only the Zeeman part of the stationary Hamiltonian,

\[ \sigma_{th} = \frac{e^{-\beta H_0}}{Tr e^{-\beta H_0}} \sim \sigma_{th} = \frac{e^{-\beta H_Z}}{Tr e^{-\beta H_Z}}, \quad \beta = \frac{\hbar}{k_B T}. \]
Furthermore, since $|\omega_0| \gg |\omega_f|$, the following approximation can be used:

$$\sigma_0' = \frac{1}{N} \left( 1 - 2 p_0 S_z \right), \quad p_0 = \tanh \frac{\beta \omega_0}{2}.$$ 

We can assume that

$$\hat{\Gamma} S_z = \frac{1}{T_{1e}} S_z, \quad \hat{\Gamma} S_h = \frac{1}{T_{2e}} S_h,$$

where $T_{1e}, T_{2e}$ are the longitudinal and transverse relaxation times of the electron, respectively, which can be experimentally obtained. Relaxation does not affect the thermal equilibrium, $\hat{\Gamma} \sigma_0' = 0$, hence we obtain

$$R_1 = \frac{1}{4T_{1e}}, \quad R_2 = \frac{1}{2T_{2e}}, \quad R_3 = \frac{p_0}{2T_{1e}}, \quad r_{3k} = 0.$$  

Note that the two terms in Equation (10) with the two factors $R_3$ or $r_{3k}$ ensure that the spin system relaxes back to the thermal state $\sigma_0$. Using the experimental nuclear longitudinal and transverse relaxation times $T_{1n,k}$ and $T_{2n,k}$, respectively, the remaining rates can be obtained as

$$r_{1k} = \frac{1}{4T_{1n,k}}, \quad r_{2k} = \frac{1}{2T_{2n,k}} - \frac{1}{2T_{1n,k}}.$$  

The relaxation superoperator (10) with the rates (11) and (12) corresponds to the uncorrelated random field relaxation model adapted to the thermal relaxation in the spin interaction frame.

It should be mentioned that the way in which we have introduced the nuclear longitudinal relaxation rate by assuming $\hat{\Gamma} I_z = (1/T_{1n}) I_z$ can create an inconsistency to the conventional relaxation model if the pseudosecular interaction strength (in frequency units) is comparable to the Zeeman frequency of the nuclear spins. This problem arises from the fact that with increasing strength of the pseudosecular part of the hyperfine interaction the quantisation axis of the nuclear spin is rotated away from the external magnetic field direction. The problem can be avoided as suggested by Vega et al. by diagonalisation of the stationary Hamiltonian $H_0$ and defining longitudinal relaxation as the process that changes populations of the eigenstates $[8,9,23]$. However, as we will discuss in Section 7, another issue that affects the spin dynamic calculation can arise from this approach.

At this point it is also important to note that we could have chosen a more complex relaxation model which includes fluctuations of the hyperfine interaction between electrons and nuclear spins. In such case we would have to include also second-order spin correlation operators to build the corresponding relaxation superoperator. We will discuss such more complex models in Section 8.

6. Constructing the relaxation superoperator starting from a basis set in Hilbert space

In the following section we discuss a different approach to derive the relaxation superoperator in the Lindblad–Kossakowski form. We select a set of basis vectors in Hilbert space, construct a set of elementary traceless operators and build the relaxation superoperator in the corresponding Liouville space. Furthermore, we introduce relaxation rates for both longitudinal relaxation and transverse relaxation without using any specific relaxation model. The motivation for this analysis is a recent string of publications by the Vega group using a related concept to include relaxation in DNP simulations $[8,9,23]$.

First, we choose an orthonormal basis $\{v_{i}\}_{i=1}^{N}$ of the Hilbert space. As a specific example this could be the eigenbasis of the stationary Hamiltonian $H_0$. Consider the set of operators in the Hilbert space

$$\{ O_{s'} = v_{i} v_{i}^{*} \}_{i,s=1}^{N}.$$ 

The $(ss')$-matrix element of the operator $O_{s'}$ in the basis $\{ v_{i} \}$ equals $1$ and all other elements are zero, so the set $\{ O_{s'} \}$ is orthogonal in the trace norm. The non-diagonal subset $\{ O_{s', s} \}$ is traceless and hence fulfills the condition for Lindblad operators. For the diagonal operators contained in the subset $\{ O_{s} \}$ the trace is always $1$. However, we can use this subset as an orthogonal basis to construct from linear combinations of the operators $O_{s}$ a new set of traceless operators

$$O_{q} = \sum_{s=1}^{N} c_{qs} O_{ss}, \quad q \in 1, N - 1,$$

where due to requirement of the tracelessness and orthogonality the coefficients $c_{qs}$ must satisfy the conditions

$$\forall q \sum_{s=1}^{N} c_{qs} = 0, \quad \forall q \neq q' \sum_{s=1}^{N} c_{qs} c_{qs}^{*} = 0.$$  

Following this strategy we can construct a complete orthogonal set of traceless operators

$$\{ L_{k} \} = \{ O_{ss} \}_{s \neq s'}^{N} + \{ O_{q} \}_{q=1}^{N-1}$$

that we can use to build the relaxation superoperator in the Lindblad–Kossakowski form $[1]$

$$-\hat{\Gamma}_{0} \sigma = \sum_{s \neq s'} \Gamma_{ss'} \left[ O_{ss} \sigma O_{s' s} - \frac{1}{2} \left( \sigma O_{s' s} + O_{s' s} \sigma \right) \right]$$

$$+ \sum_{q} \Gamma_{q} \left[ O_{q} \sigma O_{q}^{*} - \frac{1}{2} \left( \sigma O_{q}^{*} O_{q} + O_{q} O_{q} \sigma \right) \right].$$  

(14)
Note that this expression corresponds to the definition of the diagonal Lindbladian in Equation (9). We can conclude that in principle it is possible to derive the relaxation superoperator in the Lindblad form by choosing a basis set first without selecting a relaxation model as we did in Section 5. As a consequence, no formal time averaging of non-secular terms is required in the derivation of the time-independent Lindbladian (Equation (14)). However, as we will discuss in more details in the next section, an implicit assumption must be made in the derivation of the Lindbladian that the frame fixed by the choice of the basis enables the full removal of non-secular terms and condition (7) in Section 3 is fulfilled.

The full set of the elementary operators \( O_{ss'} \) generated by the basis \( \{ \nu_i \} \) can be used as an orthonormal basis in the Liouville operator space. It is then possible to introduce rates that describe the changes of the states represented by the Liouville operator space. It is then possible to introduce a rate \( R \) that corresponds to a change of populations in Hilbert space. Therefore we associate a rate \( R_1 \) for longitudinal relaxation with it. Correspondingly, the action of the relaxation superoperator on a state \( O_{ss'} \) corresponds to a change of populations in Hilbert space and therefore we associate a rate \( R_2 \) for transverse relaxation with this process. It follows from the form (14) that

\[
\hat{R}_0 O_{kk} = \sum_{s \neq k} R_{1,sk}(O_{kk} - O_{ss}), \quad \hat{R}_0 O_{kj} = R_{2,kj}O_{kj},
\]

\( k \neq j \),

\[
R_{1,sk} = \Gamma_{sk}, \quad R_{2,kj} = \frac{1}{2} \left[ \sum_{s \neq k} \Gamma_{sk} + \sum_{s \neq j} \Gamma_{sj} + \sum_q \Gamma_q \left( |c_{qj}|^2 + |c_{qk}|^2 - 2c_{qk}c_{qj}^* \right) \right].
\]

To ensure that the spin system relaxes back to the thermal state \( \sigma_{th} \), we have to weight the rates with the appropriate Boltzmann factors. The density operator at thermal equilibrium in the Boltzmann statistics is given by the formula

\[
\sigma_{th} = \frac{e^{-\beta H_0}}{Tr e^{-\beta H_0}}, \quad \beta = \frac{\hbar}{k_B T}.
\]

The relaxation superoperator acts trivially on \( \sigma_{th} \). Using the expansion

\[
\sigma_{th} = \sum_{k,j=1}^N p_{kj} O_{kj},
\]

we obtain then

\[
0 = \hat{R}_0 \sigma_{th} = \sum_{k \neq j} p_{kj} R_{2,kj} O_{kj} + \sum_k p_{kk} \sum_{s \neq k} R_{1,sk}(O_{kk} - O_{ss}).
\]

This gives

\[
\forall k \neq j \quad p_{kj} R_{2,kj} \equiv 0, \quad p_{kk} R_{1,sk} \equiv 0.
\]

As long as conditions (13) and (17) are satisfied and no additional conditions are imposed on the spin dynamics, the choice of the basis \( \{ \nu_i \} \) and the coefficients \( c_{qs} \), defining the set \( \{ L_k \} \) of Lindblad–Kossakowski operators, and the non-negative rates \( \Gamma_{ss'} \), \( \Gamma_q \) can be arbitrary. For example, it is feasible to use the eigenvectors of the time-independent Hamiltonian \( H_0 \) to construct the Lindblad–Kossakowski operators, build the relaxation superoperator and choose a set of rates. Formulas (15) in conjunction with the definitions of the rates taken from [8] can be used to reproduce the matrix representation of the relaxation superoperator as it is provided in [8].

It is noteworthy that this strategy only works for specific choices of the elementary operator set \( O_{ss'} \). For instance, it is not possible to define a basis \( \{ \nu_i \} \) in Hilbert space that can be used to construct the operators

\[
S_z, \quad I_{rz}, \quad I_{r\pm}, \quad s \in \Gamma, n,
\]

which we have used as a set of Lindblad–Kossakowski operators to derive the relaxation superoperator based on the uncorrelated random field model. This is due to the fact that the raising and lowering operators can only be defined as combinations of elementary operators \( O_{ss'} \) in the Zeeman basis.

7. Comparison between the different strategies

We compare now in more detail the two different strategies that we discussed in the previous sections for incorporating relaxation in a spin dynamics model for SE DNP. The motivation for this comparison arises from the different mathematical operations that these strategies require. The uncorrelated random field strategy relies on the choice of a relaxation model (such as uncorrelated random fluctuations) and the assumption that mixing of the states due to the pseudosecualar part of the hyperfine interaction is negligible for the derivation of the relaxation superoperator. If the pseudosecualar term of the hyperfine interaction is comparable to the Zeeman frequency of the nuclear spins, the rates for the longitudinal and transverse relaxation of the nuclear spins become mixed, and an inconsistency of the conventional relaxation model can occur. The positive feature is that the Zeeman basis can be used for the spin dynamics calculations and that a diagonalisation of the stationary Hamiltonian \( H_0 \) is not required. This provides a particular advantage when trying to simulate the dynamics of quantum systems containing many coupled spins since diagonalisation becomes impossible for the large matrices that appear in these simulations. On the other hand working in the eigenbasis of the stationary Hamiltonian has the
advantage that any mixing of states due to the non-secular part of the hyperfine interaction is accounted for and the diagonal density operator in Hilbert space provides directly the populations of the different energy levels.

In general, the uncorrelated random field model in the interaction frame (10) built of eigenoperators of the commutation superoperator \( \hat{H}_Z \) and the model-free strategy (14) based on eigenoperators of the commutation superoperator \( \hat{H}_0 \) is inconsistent, because both relaxation superoperators are diagonal in the form (9) but use different Lindblad–Kossakowski operator sets \( \{ L_k \} \). The former uses single-spin orders \( S_z, S_{\pm}, I_{z_k}, I_{k,\pm} \) according to the uncorrelated random field model, the latter uses the elementary operators \( O_{kj} \) in the basis of eigenstates of the stationary Hamiltonian \( H_0 \). Expectedly, the spin dynamics described by these two, in principle different models, can be different.

Apart from the choice of the bases, there is also a subtle but crucial difference in respect of the use of the interaction frame. If the eigenstates of the stationary Hamiltonian \( H_0 \) are used as a basis and no transformation of the Lindbladian into the interaction frame is carried out, an assumption is made that the relaxation processes during MW irradiation are equivalent to free relaxation of the spin system after it was perturbed by a driving field. Using a truncated Hamiltonian \( H_0' \) as it is done by Hovav et al. \cite{8} will eliminate this issue. A more important issue becomes evident when using the truncated stationary Hamiltonian \( H_0' \) instead of the Zeeman Hamiltonian \( H_Z \) as a reference frame to derive the relaxation superoperator using the random fluctuations model. For this reference frame it can be shown that for certain choices of parameters, which lead to strong mixing of the Zeeman states and if also high transverse relaxation rates are assumed, the condition (7) is not always fulfilled. This has the consequence that not all non-secular terms can be averaged out. This issue is not immediately apparent when following the strategy described in Section 6 since non-secular terms do not appear in the formalism. However, it makes this formalism inconsistent with a relaxation model based on fluctuating interactions between spins and their environment.

7.1. Numerical simulations

We present now a set of numerical simulations to illustrate our analysis. For the simplest two-spin system consisting of one electron and one nuclear spin (1e–1n), there is a good agreement between the model (14) when using the eigenbasis of the truncated Hamiltonian \( H_0' \) described in Section 6 and the model based on the uncorrelated field fluctuations (Equation (10)) provided that we assume isotropic random fluctuations along all three spatial directions (Figure 1 (A)).\cite{2} Comparing these simulations with the one obtained by using the model by Hovav et al. \cite{8} that is based on the assumption of fluctuations only along the \( x \)-direction to avoid the mixing of the longitudinal and transverse relaxation processes, it is clear that for relatively strong hyperfine interactions with pseudosecular strength of a few hundred kHz, a significant discrepancy occurs with the spin polarisation decreasing in dependence of the hyperfine pseudosecular interaction strength \( A_+ \) (Figures 1(B) and 1(D)). In this case the quantisation axis for the nuclear spins is rotated in respect to the static field direction and the assumptions made when defining the rates in the random fluctuation model cause a decrease of the nuclear spin polarisation due to the fact that fast transverse relaxation processes also affect the spin populations. If fluctuations along the \( z \)-axis are also included in the model by Hovav et al. \cite{8}, the same behaviour is reproduced (Figure 1(C)).

If the spin system consists of several nuclear spins and one electron spin, we demonstrate that there could be a substantial discrepancy in the spin dynamics predictions depending on the strength of the nuclear dipolar interaction in comparison with the difference of the strength of the secular term of the hyperfine interactions of the nuclei with the electron.

For the further analysis we use as an example a model spin system consisting of one electron and two nuclear spins. Suppose that, calculating the basis of eigenstates of \( H_0 \), we can neglect terms not commuting with \( H_Z \), i.e. we assume \(|A_k| \ll |\omega| \). This leads to the simplified truncated stationary Hamiltonian

\[
H'_0 = H_Z + \sum_{k<j} d_{kj} \left( 2I_kz I_jz - \frac{1}{2} I_kz I_jz - \frac{1}{2} I_kz I_jz \right) + \sum_k A_{k,0} I_kz S_z.
\] (18)

7.2. The case when the nuclear dipolar interaction is quenched by the hyperfine interaction – the core nuclei

First, we consider the case when the dipolar interaction between the nuclei is much smaller than the difference between the strength of the secular terms of the hyperfine interaction that describes their coupling to the electron spin. The nuclei are in this case close to the electron and the dipolar interaction between them is quenched by their coupling to the electron. In DNP models such nuclear spins belong to the core,

\[
\forall k \neq j \quad \frac{|d_{kj}|}{|A_{k,0} - A_{j,0}|} \ll 1.
\]

Under these conditions the nuclear interaction term is negligible and the basis of eigenstates of \( H'_0 \) is well approximated by the Zeeman basis \( \{ v \} \). We show in Appendix A.4 that in this case the two models can be modified in such a way that their predictions of the SE DNP spin dynamics are very close. Using the additional conditions that the transverse relaxation time constants are much shorter than the
Figure 1. Simulation of the nuclear steady state polarization for a system of one electron with one nuclear spin. The strength of the pseudosecular interaction $A_j$ is changed between 1 kHz and 10 MHz. (A) Comparison between uncorrelated random fluctuation model (10) (black) and the strategy (14) that involves the choice of the eigenbasis $H'_0$ (red). (B) Comparison between random fluctuation model (10) (black) and the model used by Hovav et al. [8], with fluctuations only assumed along $I_x$ (blue). (C) Comparison between random fluctuation model (10) (black) and the model used by Hovav et al., but this time with additional fluctuations assumed along $I_z$ (green). (D) Difference between the simulations. Red refers to (A), blue to (B) and green to (C). Note the logarithmic scale and the large discrepancy between simulations in (C) that disappears when fluctuations along $I_x$ and $I_z$ are assumed in the model by Hovav et al. [8]. The rugged appearance of the red line is due to numerical errors that become pronounced due to the low absolute error in the comparison. Model parameters: $\omega_I = 144$ MHz, $MW = 0.1$ MHz, $R_{1e} = 1$, $R_{2e} = 1E5$, $r_{1n} = 1E-2$, $r_{2n} = 1E4 s^{-1}$.

We show the good agreement for the two models (10) and (14) in Figures 2(A) and 2(C). Note that the absolute error between the two simulations is very small.

7.3. The case when the dipolar interaction is not quenched by the hyperfine interaction – the bulk nuclei

If the nuclei are relatively far away from the electron, the nuclear dipolar interaction can be larger than the difference between the strengths of the secular hyperfine interactions of the nuclei. Such conditions can be found for bulk nuclei. The first of conditions (19) is physically reasonable and normally satisfied. The second condition, however, can be violated. In this case, the two relaxation models predict different dynamics for the spin polarization (see Figures 2(B)}
Figure 2. Comparison between the two models (10) (red) and (14) (black). (A) Time course of the polarisation of the electron and two nuclear spins, \( \omega_I = 144 \text{ MHz}, MW = 0.1 \text{ MHz}, R_1 = 1, R_2 = 1E5, r_{1n} = 1E-2, r_{2n} = 1E4 \text{ s}^{-1}, A_0 = [0.155, -0.016] \times 1E6 \text{ Hz}, A_+ = [0.466, 0.015] \times 1E6 \text{ Hz}, d = 64.57 \text{ Hz}. \) (C) shows the difference between the two simulations in (A). (B) All parameters are the same apart from the interaction strengths \( A_0 = [-0.015, -0.015] \text{ MHz}, A_+ = [0.43, 0.015] \text{ MHz}, d = 15 \text{ Hz}. \) (D) shows the difference between the two simulations in (B). The maximal absolute error is more than 30% of the spin polarisation.

They are inconsistent whatever rates \( R_{1, ki}, R_{2, ki} \) we choose. To provide more insight we discuss in the following an instructive example.

Let us have two nuclei and assume as before that the ‘effective Hamiltonian’ commutes with \( H_Z \), i.e. has the form (18). Generally, there exists the unique basis in which both \( H'_0 \) and \( H_Z \) are diagonal. In terms of Zeeman states (with the first nucleus in the first position, the second nucleus in the second position and the electron separated with the comma), this basis is

\[
\begin{align*}
|\lambda_1\rangle &= |\alpha\alpha, \alpha\rangle, \\
|\lambda_2\rangle &= |\alpha\alpha, \beta\rangle, \\
|\lambda_3\rangle &= |\alpha\alpha, \beta\rangle, \\
|\lambda_4\rangle &= |\beta\beta, \beta\rangle, \\
|\lambda_5\rangle &= \cos \phi_+ |\alpha\beta, \alpha\rangle + \sin \phi_+ |\beta\alpha, \alpha\rangle, \\
|\lambda_6\rangle &= \cos \phi_+ |\beta\alpha, \beta\rangle - \sin \phi_+ |\alpha\beta, \beta\rangle, \\
|\lambda_7\rangle &= \cos \phi_- |\alpha\beta, \beta\rangle + \sin \phi_- |\beta\alpha, \beta\rangle, \\
|\lambda_8\rangle &= \cos \phi_- |\beta\alpha, \beta\rangle - \sin \phi_- |\alpha\beta, \beta\rangle,
\end{align*}
\]

\[
\tan \phi_\pm = \pm \frac{1}{d_{12}} \left( \Delta_A - \sqrt{\Delta_A^2 + d_{12}^2} \right), \quad \Delta_A = \frac{A_{10} - A_{20}}{2}.
\]

The second of conditions (19) is violated if \(|d_{12}| \gg |\Delta_A|\).

In this case, \( \tan \phi_\pm \sim \pm \text{sign} \ d_{12} \) and the following mixing of Zeeman states occurs (for \( d_{12} > 0 \)):

\[
\begin{align*}
|\lambda_5\rangle &= \frac{|\alpha\beta, \alpha\rangle - |\beta\alpha, \alpha\rangle}{\sqrt{2}}, \quad |\lambda_6\rangle = \frac{|\beta\alpha, \alpha\rangle + |\alpha\beta, \alpha\rangle}{\sqrt{2}}, \\
|\lambda_7\rangle &= \frac{|\alpha\beta, \beta\rangle + |\beta\alpha, \beta\rangle}{\sqrt{2}}, \quad |\lambda_8\rangle = \frac{|\beta\alpha, \beta\rangle - |\alpha\beta, \beta\rangle}{\sqrt{2}}.
\end{align*}
\]

We have, for example,

\[
\begin{align*}
O_{56} &= \frac{1}{2} \left( \frac{1}{2} + S_z \right) (I_{1+}I_{2-} - I_{1-}I_{2+} + I_{1z} - I_{2z}), \\
\Gamma O_{56} &= \frac{1}{2} \left[ (c_1 + c_2 S_z)(I_{1+}I_{2-} - I_{1-}I_{2+}) + (r_1 + d_1 S_z)I_{1z} - (r_2 + d_2 S_z)I_{2z} \right].
\end{align*}
\]
\[ c_1 = \frac{1}{2} \sum_{k=1}^{2} \frac{1}{T_{2n,k}} , \quad c_2 = \frac{1 + p_0}{T_{1e}} + 2c_1 , \quad r_k = \frac{1}{2T_{1n,k}} , \]

\[ d_k = \left( \frac{1 + p_0}{T_{1e}} + \frac{1}{T_{1n,k}} \right) . \]

Projecting onto \( O_{56} \) gives

\[ \hat{\Gamma} O_{56} = R O_{56} + P , \]

where

\[ R = T r \left( (\hat{\Gamma} O_{56}) O_{65} \right) \sim c_1 , \]

\[ O_{56} \perp P = \hat{\Gamma} O_{56} - R O_{56} \sim c_1 \left( \frac{1}{2} + S_c \right) \times \left( I_1 + I_2 - I_3 \right) = -c_1 O_{65} . \]

We see that the projection \( R O_{56} \) and the orthogonal component \( P \) are of the same order \( \sim c_1 \) which is the average between the transverse rates \( 1/T_{2n,1} \) and \( 1/T_{2n,2} \). This means that the action of the relaxation superoperator \( \hat{\Gamma} \) on the non-diagonal element \( O_{56} \) is strongly unproportional to \( O_{56} \). This will be the case for any non-diagonal elements \( O_{ij} \) composed of strongly mixed Zeeman states. On the other hand, using the model based on the choice of the eigenbasis of \( H'_0 \), we have always \( \hat{\Gamma}_0 O_{ij} = R_{2,kj} O_{kj} , k \neq j \).

Thus, the predictions of both models are inconsistent if the first of conditions (19) is satisfied while the second one is violated. The reason for this discrepancy is the use of the stationary Hamiltonian \( H'_0 \) as a reference frame for the relaxation model (14) that is based on the choice of the eigenbasis of \( H'_0 \) and that was described in Section 6. The choice of that reference frame leads the interaction parameters used in the simulation to a violation of condition (7). To demonstrate this, we provide a list of the values \( \epsilon_{kj,k'j'} = [\rho_{kj,k'j'}/\rho_{kj,k'j'}] \) calculated (see formula (6)) for the simulation shown in Figure 2 in Table 1. Condition (7) which requires \( \epsilon_{kj,k'j'} < 1 \) is not fulfilled for 3.6\% of the 1447 non-zero elements (4096 in total). Therefore, the intrinsic assumption made during the derivation of the superoperator in Section 7 that non-secular terms can always be neglected in this strategy is not valid and the predictions made by model (14) will deviate from the predictions arising from the random fluctuation model (10). For the core nuclei with much stronger hyperfine interactions, the values of \( \rho_{kj,k'j'} \) are always bigger then the relaxation rate \( R_{kj,k'j'} \) and hence there is a good agreement between the two models, if the non-secular hyperfine interaction is weak in comparison to the nuclear Zeeman frequency.

Figure 3 provides another example of the deviations between the two models. In this case we have assumed a spin chain of four nuclear spins and one electron with only the first nuclear spin coupled to the electron and all other nuclear spins interacting through dipolar interaction with each other (this is a similar configuration as described in [9]).

This further example demonstrates that the polarisation dynamics can substantially deviate between the uncorrelated fluctuation model (10) and the model that was built from the eigenbasis of the truncated stationary Hamiltonian \( H'_0 \). An analysis of the values for \( \epsilon_{kj,k'j'} \) again shows that condition (7) for the removal of the non-secular terms during averaging the time-dependent relaxation superoperator is severely violated. Again a substantial fraction of the \( \epsilon_{kj,k'j'} \) are in the order of \( 10^9 \), demonstrating that \( H'_0 \) cannot be used to fully remove the non-secular terms arising in a random field relaxation model. We can conclude that the use of the \( H'_0 \) frame can lead to spin dynamics predictions that cannot be explained by spin relaxation arising from a physically reasonable fluctuation model. The relaxation model summarised in Section 7 can only be used for spin systems for which condition (19) is satisfied.

| \( \epsilon_{kj,k'j'} \) | Bulk | Core |
|----------------|------|------|
| 1.96608E+9 | 2.12767E-5 |
| 1.96608E+9 | 2.12767E-5 |
| 1.96325E+9 | 2.12767E-5 |
| 1.96325E+9 | 2.12767E-5 |
| 1.80224E+9 | 2.12757E-5 |
| 1.80224E+9 | 2.12757E-5 |
| 1.80224E+9 | 2.12757E-5 |
| 1.80224E+9 | 2.12757E-5 |
| 1.80224E+9 | 2.12757E-5 |
| 1.80224E+9 | 2.12757E-5 |
| 1.80224E+9 | 2.12757E-5 |
| 1.80224E+9 | 2.12757E-5 |
| 1.64132E+9 | 2.12757E-5 |
| 1.64132E+9 | 2.12757E-5 |
| 1.63840E+9 | 2.12757E-5 |
| 1.63840E+9 | 2.12757E-5 |
| 8.21487E+2 | 2.12757E-5 |
| 8.21487E+2 | 2.12757E-5 |
| 8.21009E+2 | 2.12757E-5 |
| 8.21009E+2 | 2.12757E-5 |
| 9.08939E-1 | 2.12757E-5 |
8. Extension to more complex relaxation models

In this section we extend the discussion to more complex relaxation mechanisms. Three examples are given based on the fluctuations approach described in Section 5. The examples illustrate the typical mechanisms of relaxation in solids and are applicable to the electron–nuclear spin system in an SE DNP model: the electronic relaxation caused by the g-anisotropy, the nuclear relaxation caused by the electron as a paramagnetic centre and the electron–nuclear relaxation caused by vibrations of the crystalline lattice near the electronic spin.

8.1. Electron relaxation caused by g-anisotropy

The Zeeman interaction of the electronic spin $S$ with the static field $B_0$ is mediated by the $g$-tensor, $B_0 \cdot g \cdot S$. The tensor $g$ depends on the surroundings of the electron and is generally anisotropic, i.e. not represented by a simple scalar product between the vectors $B_0$ and $S$. In a sufficiently symmetric environment, the $g$-anisotropy is relatively small, but can be appreciable in non-symmetric cases.

Considering an ensemble of electronic spins ${\{S_k\}}$, we have to assume that each electron in the ensemble has its own $g$-tensor $g_k$, even when the anisotropic parts of them are small. In this case

$$g_k = g_0 \cdot 1 + g_{k,a}, \quad \|g_{k,a}\| \ll \|g_0\|.$$  

Statistically the electronic ensemble is well represented by a single electron $S$ in such a way that the Zeeman interaction becomes

$$H_Z = \omega_S S_z + B_0 \cdot g_a \cdot S, \quad \omega_S = g_0 |B_0|,$$

where $g_a$ is a random spatially distributed tensor. Using the ergodicity principle, we can assume that the tensor $g_a = g_a(t)$ is a random function of time, interpreting this as that anisotropies of different electron spins have different effective times, which are randomly distributed between them. An analogous assumption is made in liquid state NMR when we regard the spatially distributed ensemble molecular motion as a random temporal motion of a single molecule.

Thus, we can write

$$H_Z = \omega_S S_z + H_f(t),$$

$$H_f(t) = f_z(t) S_z + f_+(t) S_+ + f_-(t) S_-$$

with random scalar functions $f_\beta(t), \beta = z, \pm$. We can assume that $f_\beta(t)$ are random stationary processes with zero ensemble averages and some correlation functions

$$f_\beta(t) = 0, \quad g_{\alpha\beta}(\tau) = \frac{f_\alpha(t)f_\beta^*(t-\tau)}{|g_0|^2},$$

so we follow the fluctuations approach described in Section 5.

The operators $S_\beta, \beta = z, \pm$ are eigenvectors of the superoperator $\hat{H}_Z$ with the eigenvalues $0, \pm \omega_S$, respectively.
This leads to the formula
\[ \hat{\Gamma}_S = R_2 \hat{S}_z + R_1 (\hat{S}_+ \hat{S}_- + \hat{S}_- \hat{S}_+) \] (21)
with
\[ R_2 = \frac{1}{2} \int_{-\infty}^{+\infty} g_{zz}(\tau) \, d\tau, \quad R_1 = \frac{1}{2} \int_{-\infty}^{+\infty} g_{++}(\tau)e^{i\omega_\tau} \, d\tau \]
\[ d\tau = \frac{1}{2} \int_{-\infty}^{+\infty} g_{--}(\tau)e^{i\omega_\tau} \, d\tau. \]

8.2. Nuclear relaxation caused by electron as paramagnetic centre

To describe the electron–nuclear hyperfine interaction in a dielectric solid between a radical centre with a locally confined electron and the surrounding nuclei we can focus mainly on the dipolar interaction and ignore the Fermi contact interaction. Taking into account the huge electronic Larmor frequency \( \omega_e \) in the electron vicinity. The hyperfine interaction term can be written in the form of a random field seen by the nuclei via spontaneous fluctuations, which leads to the superoperator

\[ \hat{H}_{IS} = VS_z, \quad V = \sum_k (2A_{k0}I_{kz} + A_{k+}I_{k+} + A_{k-}I_{k-}). \]

The role of the electron as a paramagnetic centre (or impurity) can be described in the following way [24]. It is assumed that during the evolution a spontaneous exchange occurs between the subspaces of the ‘up’ and ‘down’ states of the electronic spin. Due to the presence of the terms with \( I_{k\pm}S_z \) in \( H_{IS} \), this random process affects the nuclear spins in the form of a random field seen by them via spontaneous changes of the sign of the coefficients \( A_{k\pm} \). These fluctuations are seen simultaneously by all nuclei grouped to the corresponding hyperfine interaction term. The typical correlation time is comparable with the electronic longitudinal time \( T_{1e} \), so can lead to processes with longer times than \( T_{1e} \). However, this can be appreciable and crucial for the nuclei in close electron vicinity.

In terms of fluctuations, this gives
\[ H_f(t) = f(t)V_+ + f^*(t)V_-, \quad V_\pm = \sum_k A_{k\pm}I_{k\pm}, \]
where \( f(t) \) is a random scalar function of time. We can assume that it describes a stationary process with zero average and some correlation function
\[ \langle f(t) \rangle = 0, \quad g(\tau) = \langle f(t)f(t-\tau) \rangle. \]

The operators \( V_\pm \) are eigenoperators of \( \hat{H}_z \) with the eigenvalues \( \pm \omega_f \). Using the fluctuations approach, this leads to the following superoperator:
\[ \hat{\Gamma}_I = \tau_0 (\hat{V}_+ \hat{V}_- + \hat{V}_- \hat{V}_+), \quad \tau_0 = \frac{1}{2} \int_{-\infty}^{+\infty} g(\tau)e^{i\omega_\tau} \, d\tau. \] (22)

The simplest realisation
\[ g(\tau) = g(-\tau) = \frac{1}{4} \exp \left( -\frac{\vert \tau \vert}{T_{1e}} \right) \]
leads to the formula
\[ \tau_0 = \frac{1}{4} \frac{T_{1e}}{1 + \omega_f^2 T_{1e}^2} \sim \frac{1}{4 \omega_f^2} \frac{1}{T_{1e}}. \]

It can be seen that the relaxation rates are \( \sim \epsilon_k/T_{1e} \) with \( \epsilon_k = |A_{k\pm}/\omega_f|^2 \), so they tend to be larger for nuclei closer to the electron and smaller for remote nuclei.

8.3. Electron–nuclear relaxation via vibrations of crystalline lattice near electron

The electron–nuclear interaction can lead to another mechanism connected with vibrations of the crystalline lattice in the electron vicinity.

Even at low temperatures, the position of the electronic spin (unlike the nuclear spins) is not fixed in space; it is found randomly in time in some volume near its average position. This is connected with vibrations of the crystalline lattice near the electron in the form of phonon lattice sound. This random noise affects the nuclear spins via fluctuations of the coefficients of the hyperfine interaction which depend on orientations of the electron–nuclear pairs and so depend on the random electron position. In the Zeeman frame with large Larmor frequencies \( \omega_f \), the dominating part of the electron–nuclear interaction is the purely Zeeman part
\[ H_{IS,Z} = 2 \sum_k A_{k0}I_{kz}S_z. \]

The fluctuations of the coefficients \( A_{k0} \) caused by the above vibrations can be written as
\[ H_f(t) = \sum_k f_k(t)V_k, \quad V_k = 2A_{k0}I_{kz}S_z, \]
where \( f_k(t) \) are real scalar functions of time describing random stationary processes with zero averages and some correlation functions
\[ \langle f_k(t) \rangle = 0, \quad g_{kj}(\tau) = \langle f_k(t)f_j(t-\tau) \rangle. \]

The operators \( V_k \) belong to the zero eigenspace of \( \hat{H}_Z \). This leads to the superoperator
\[ \hat{\Gamma}_{IS} = \sum_{k,j} \tau_{kj} \hat{V}_k \hat{V}_j, \quad \tau_{kj} = \frac{1}{4} \int_{-\infty}^{+\infty} g_{kj}(\tau) \, d\tau. \] (23)

It can be seen that \( \hat{\Gamma}_{IS} \) affects only non-Zeeman operators with rates proportional to \( A_{k0}A_{j0} \).
Combining the models (21)–(23) and applying the thermalisation, we obtain

$$\dot{\sigma} = -i \hat{H} \sigma - \hat{\Gamma} \sigma$$

with

$$\hat{\Gamma} \sigma = \hat{\Gamma}_s \sigma + \hat{\Gamma}_f \sigma + \hat{\Gamma}_t \sigma + \hat{\Gamma}_{ih},$$

$$\hat{\Gamma}_t \sigma = 2p_0R_1(S_+\sigma S_- - S_-\sigma S_+ + S_z\sigma + \sigma S_z).$$

(24)

To find connections between $R_{1,2}$, $\tau_0$, $\tau_{kj}$ and the effective transverse and longitudinal relaxation times, we can evaluate Equation (24),

$$\hat{\Gamma} S_z = 4R_1 S_z, \quad \hat{\Gamma} S_{\pm} = \left( R_2 + 2R_1 + \sum_k \tau_{kk}|A_{k0}|^2 + \sum_{k \neq j} \tau_{kj}|A_{k0}|^2 \right) S_{\pm},$$

$$\hat{\Gamma}_t I_z = 4\tau_0|A_{k\pm}|^2 I_z + 8p_0R_1 I_z S_z,$$

$$\hat{\Gamma}_t I_{\pm} = \left( 2\tau_0|A_{k\pm}|^2 + \tau_{kk}|A_{k0}|^2 \right) I_{\pm} + 8p_0R_1 I_{k\pm} S_z,$$

to obtain

$$\frac{1}{T_{1w,k}} = 4R_1, \quad \frac{1}{T_{2w,k}} = R_2 + 2R_1 + \sum_k \tau_{kk}|A_{k0}|^2.$$

In Figure 4 the polarisation dynamics is compared for a spin system consisting of four $^{13}$C nuclei calculated using the simple uncorrelated random fluctuation model (10) and a model taking all other mechanisms into account. Note as the main difference that in the case of the comprehensive model all nuclear spins reach eventually the same polarisation level.

9. Conclusions and outlook

The polarisation enhancement of the nuclear spin ensemble by solid effect DNP is the result of both the irradiation of either the double- or zero-quantum transition $(\omega_S \pm \omega_I)$, and the relaxation processes in response to this perturbation. Relaxation needs to be carefully incorporated into a quantum mechanical model for SE DNP to make it possible to calculate the spin dynamics that can be compared with experimental data. We reviewed and compared two strategies and pointed out under which conditions these strategies provide predictions in close agreement and discussed under which conditions they fail to agree. Working in the Zeeman interaction frame has the advantage that no diagonalisation of the Hamiltonian is required and hence it becomes easier to extend such a model to systems containing a large number of coupled spins using time averaging strategies such as the Krylov–Bogoliubov method that we proposed [13]. The choice of this interaction frame has also the advantage that in the derivation of a relaxation model that is based on random field fluctuations, all non-secular terms can be completely averaged out and a time-independent relaxation superoperator can be obtained. On the other hand, the use of the Zeeman interaction frame can lead to an inconsistency of the conventional relaxation model if the strength of the pseudosecular part of the hyperfine interaction is big in comparison with the nuclear Larmor frequency. In this case the nuclear longitudinal and transverse relaxation processes can become mixed with the consequence that the populations of the energy levels are also affected by transverse relaxation processes. However, this issue arises only if the distance between the electron and the nuclear spins is kept small in the model system. For instance, for the relaxation parameters used in Figure 1 this effect is negligible as along as the interspin distance between electron and nuclear $^1H$ nuclei is larger than 4.9 Å (for a nuclear transverse relaxation rate $r_{2n} = 1E4 s^{-1}$ or 3.3 Å for $r_{2n} = 1E3 s^{-1}$ or 3.1 Å for $^{13}C$ nuclei with $r_{2n} = 1E4 s^{-1}$).

The problem of the mixing of longitudinal and transverse relaxation processes can be avoided by defining the rates for these relaxation processes in the frame of the truncated stationary Hamiltonian $H'_0$ [8,9,23]. Processes that affect the populations in the eigenbasis of the stationary
Hamiltonians are classified as longitudinal relaxation processes while the processes that lead to a decay of coherences are identified as transverse relaxation processes. However, due to the small differences in the energy levels in this interaction frame for spin systems in which the hyperfine interaction is weak relative to the nuclear dipolar interaction, it can be shown that in the case of fast transverse relaxation rates the relaxation superoperator does not properly account for non-secular terms that arise from a fluctuation model. Significant deviations can in this case occur when comparing predictions based on this model to calculations of the spin dynamics obtained using the Zeeman interaction frame and a relaxation model based on uncorrelated magnetic field fluctuations.

It is worthwhile to emphasise that for many parameter choices both models provide predictions of the spin dynamics that differ by less than 5%. Since the use of the Zeeman interaction frame makes an extension of the spin dynamics obtained using the Zeeman interaction frame and a relaxation model based on uncorrelated magnetic field fluctuations.

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Notes
1. See Appendix A.5 for a detailed explanation on how to implement this formalism numerically.
2. Basically we have to calculate \( \frac{1}{\Gamma_{\text{rel}}^n} = \gamma_k^2 \left| \langle \lambda_k | S_i | \lambda_i \rangle \right|^2 + 4 \sum_{\ell=1}^n \frac{1}{\gamma_k^2} \left| \langle \lambda_k | I_i | \lambda_i \rangle \right|^2 \left| \langle \lambda_k | S_i | \lambda_i \rangle \right|^2 + 4 \sum_{\ell=1}^n \frac{1}{\gamma_k^2} \left| \langle \lambda_k | I_i | \lambda_i \rangle \right|^2 \).

3. We assume that the magnitudes \( \Omega_{in} \) are all well distinguished, which is true for protons at high field. This is true also for nuclei with smaller gyromagnetic ratios because in this case \( n < |\omega|/\omega_0|\).

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Appendix
A.1. Invariance of the relaxation superoperator in the Lindblad–Kossakowski form
After proceeding to the interaction frame by the rule (2), the relaxation superoperator (9) is transformed to

\[-\tilde{\Gamma}^n \tilde{\sigma} = \sum_{k=1}^{N^2-1} \gamma_k \left[ \tilde{L}_k \tilde{\sigma} - \frac{1}{2} (\tilde{\sigma} \tilde{L}_k \tilde{L}_k^* + \tilde{L}_k^* \tilde{L}_k \tilde{\sigma}) \right] \, ,

\[ \tilde{L}_k = e^{i H_k t} L_k \, . \]
It is possible to expand the Liouville space into eigenspaces $V_{pq}$ of the superoperator $\hat{H}_Z$ ($n$ is the number of nuclei)\footnote{Using the expansions $V_{pq}$ eigenspaces \{9\} in the interaction frame is such that the set $\{L_k\}$ of Lindblad–Kossakowski operators is an orthogonal set of traceless eigenoperators of the superoperator $\hat{H}_Z$.}. Taking Hermitian conjugate and permuting indices, we obtain

$\bar{L}_k \bar{\sigma} \bar{L}_k^\dagger = \frac{1}{2} \left( \bar{\sigma} \bar{L}_k \bar{L}_k^\dagger + \bar{L}_k^\dagger \bar{L}_k \bar{\sigma} \right) = \sum_{p,q,p',q'} \exp\left[ i(\Omega_{pq} - \Omega_{p'q'}) \alpha_{k,pq} \alpha_{k,p'q'}^* \right] \times \left[ \bar{l}_{k,pq} \bar{\sigma} \bar{l}_{k,p'q'}^* - \frac{1}{2} \left( \bar{\sigma} \bar{l}_{k,pq} \bar{l}_{k,p'q'}^* + \bar{l}_{k,pq}^* \bar{l}_{k,p'q'} \bar{\sigma} \right) \right].$ \hspace{1cm} (A2)

Effectively, the non-secular terms are averaged out, so $\hat{\Gamma}$ should be time-independent. This means

$\alpha_{k,pq} \alpha_{k,p'q'}^* = 0, \quad (pq) \neq (p'q'),$

so each $L_k$ belongs completely to one and only one of the eigenspaces $V_{pq}$, i.e. each $L_k$ is an eigenoperator of the Zeeman superoperator $\hat{H}_Z$.

Thus, we conclude that the effective relaxation superoperator (9) in the interaction frame is such that the set $\{L_k\}$ of Lindblad–Kossakowski operators is an orthogonal set of traceless eigenoperators of the superoperator $\hat{H}_Z$.

### A.2. Derivation of the relaxation superoperator in the Lindblad–Kossakowski form starting from a fluctuation model

We can assume that the fluctuation $H_f$ is built of a full set $\{F_{pq,m}\}$ of orthonormal eigenoperators of $\hat{H}_Z$. In the case that some eigenoperators are absent, we assign the zero value to the corresponding coefficient. Taking into account the multiplicities of eigenvalues, $p \in \{-n, n\}, q \in \{-1, 1\}, m \in \overline{1, \dim V_{pq}}$. We have

$\forall m \quad \hat{H}_Z F_{pq,m} = \Omega_{pq} F_{pq,m}, \quad \Omega_{pq} = p\omega_l + q\Omega_S,

F_{pq,m}' = \exp\left[ i\Omega_{pq}\tau \right] F_{pq,m}.$

Hence,

$\hat{H}_f(t) = \sum_{p,q} \sum_m f_{pq,m}(t) \exp\left[ i\Omega_{pq}\tau \right] F_{pq,m}$

and rewrite $\hat{\Gamma}$ as

$\hat{\Gamma}' = \sum_{p,q} \sum_{m,m'} C_{pq,mn'} (\hat{F}_{pq,m}^* \hat{F}_{pq,m'} + \hat{F}_{pq,m'}^* \hat{F}_{pq,m}).$

This gives

$\hat{\Gamma} = \frac{1}{2} \sum_{p,q} \sum_{m,m'} C_{pq,mn'} (\hat{F}_{pq,m}^* \hat{F}_{pq,m'} + \hat{F}_{pq,m'}^* \hat{F}_{pq,m}).$

Consider the two superoperators

$\hat{U}_{pq,mn}^+ = F_{pq,mn} F_{pq,mn}', -\frac{1}{2} \left( \sigma F_{pq,mn}^* F_{pq,mn} + F_{pq,mn}^* F_{pq,mn}' \right),$

$\hat{U}_{pq,mn}^- = F_{pq,mn}' F_{pq,mn} -\frac{1}{2} \left( \sigma F_{pq,mn}^* F_{pq,mn} + F_{pq,mn} F_{pq,mn}' \right)$

and rewrite $\hat{\Gamma}$ as

$\hat{\Gamma}' = \sum_{p,q} \sum_{m,m'} C_{pq,mn} (\hat{U}_{pq,mn}^+ + \hat{U}_{pq,mn}^-)$

In accordance with the formula

$\hat{F}_{pq,m}^* \hat{F}_{pq,m'} + \hat{F}_{pq,m'}^* \hat{F}_{pq,m} = -2(\hat{U}_{pq,mn}^+ + \hat{U}_{pq,mn}^-)$
the superoperator $\hat{\Gamma}'$ is in the Lindblad–Kossakowski form and coincides with $\hat{\Gamma}$ for $C^+_{pq,mn'} = 0$. We can choose $C^+_{pq,mn}$ in such way that

$$\hat{\Gamma}'\sigma_{th} = 0.$$ 

Then the master equation

$$\dot{\sigma} = -i \hat{H}_0\sigma - \hat{\Gamma}'\sigma$$

is the needed homogeneous Lindblad–Kossakowski form where the full density operator should be used. Here we can apply the approximation

$$\sigma_{th} = \frac{1}{N} (1 - 2p_0 S_z), \quad p_0 = \tanh \frac{\hbar \Omega_{S_z}}{2k_B T}.$$ 

**A.3. Derivation of the relaxation superoperator based on the uncorrelated random fluctuation model**

Let us introduce the superoperators

$$\hat{U}_z\sigma = S_z\sigma S_z - \frac{1}{2} (\sigma S_z S_z + S_z S_z \sigma),$$

$$\hat{U}_+\sigma = S_+ \sigma S_+ - \frac{1}{2} (\sigma S_+ S_+ + S_+ S_+ \sigma),$$

$$\hat{u}_{kz}\sigma = I_{kz} \sigma I_{kz} - \frac{1}{2} (\sigma I_{kz} I_{kz} + I_{kz} I_{kz} \sigma),$$

$$\hat{u}_{k\pm}\sigma = I_{k\pm} \sigma I_{k\pm} - \frac{1}{2} (\sigma I_{k\pm} I_{k\pm} + I_{k\pm} I_{k\pm} \sigma)$$

and the commutation superoperators

$$\hat{L} = [L, \cdot], \quad L = S_z, S_+, I_{kz}, I_{k\pm}.$$ 

Due to the relations valid for any spin 1/2

$$I_z^2 = \frac{1}{4}, \quad I_+ I_- = \frac{1}{2} \pm I_z,$$

we have

$$\hat{U}_z = -\frac{1}{2} \hat{S}_z^2, \quad \hat{u}_{kz} = -\frac{1}{2} \hat{I}_{kz}^2,$$

$$\hat{U}_+ + \hat{U}_- = -\frac{1}{2} (\hat{S}_+ \hat{S}_- + \hat{S}_- \hat{S}_+),$$

$$\hat{u}_{k+} + \hat{u}_{k-} = -\frac{1}{2} (\hat{I}_{k+} \hat{I}_{k-} - \hat{I}_{k-} \hat{I}_{k+}),$$

$$(\hat{U}_+ - \hat{U}_-)\sigma = S_+ \sigma S_- - S_- \sigma S_+ + \sigma S_z + S_z \sigma,$$

$$(\hat{u}_{k+} - \hat{u}_{k-})\sigma = I_{k+} \sigma I_{k-} - I_{k-} \sigma I_{k+} + \sigma I_{kz} + I_{kz} \sigma.$$ 

This gives

$$\hat{\Gamma}\sigma = R_z \hat{S}_z^2 \sigma + R_1 (\hat{S}_+ \hat{S}_- + \hat{S}_- \hat{S}_+) \sigma$$

$$+ R_3 (S_+ \sigma S_- - S_- \sigma S_+ + \sigma S_z + S_z \sigma)$$

$$+ \sum_{k=1}^n \left[ r_{2k} \hat{I}_{kz}^2 \sigma + r_{4k} (\hat{I}_{k+} \hat{I}_{k-} + \hat{I}_{k-} \hat{I}_{k+}) \sigma$$

$$+ r_{3k} (I_{k+} \sigma I_{k-} - I_{k-} \sigma I_{k+} + \sigma I_{kz} + I_{kz} \sigma) \right]. (A4)$$

where $R_j, r_{jk}$ are some rates to be specified.

**A.4. Comparison of the action of the two models $\Gamma_0$ and $\Gamma$ for core nuclei**

In this basis, each non-diagonal element $O_{kj} = \nu_k \nu_j^*$, $k \neq j$, is represented by one of the following forms:

$$O_{kj} = S_{\beta} O_z \prod_{i=1}^m I_{\beta_i}, \quad O_{kj} = \left( \frac{1}{2} \pm S_z \right) O_z \prod_{i=1}^m I_{\beta_i},$$

$$\beta, \beta_i = \pm, \quad m \geq 1,$$

where $O_z$ is a combination of Zeeman orders built of spins other than $S, I_z$. For example (the electronic state is separated with the comma),

$$|\alpha\beta, \alpha\beta, \beta\beta, \alpha\beta\rangle \langle \beta\beta, \beta\beta, \alpha\beta, \alpha\beta| = S_{\alpha} I_{\alpha} \left( \frac{1}{2} + S_{\beta} \right) I_{\beta} \left( \frac{1}{2} - I_{\beta} \right).$$

Since $T_{2\alpha}, T_{2\alpha,\beta} \ll T_{1\alpha}, T_{1\alpha,\beta}$, the action of our relaxation superoperator $\hat{\Gamma}$ on $O_{kj}$ in the first case is well approximated as

$$\hat{\Gamma} O_{kj} = R_{z,kj}^+ O_{kj}, \quad R_{z,kj}^+ = \frac{1}{T_{2\alpha}} + \sum_{i=1}^m \frac{1}{T_{2\alpha,\beta}}.$$ 

In the second case,

$$\hat{\Gamma} O_{kj} \sim \left( \frac{1}{2} \sum_{s=1}^m \frac{1}{T_{2\alpha,s}} \right) O_Z \prod_{i=1}^m I_{\beta_i},$$

$$+ \left( \frac{p_0 \pm 1}{k_B T} \sum_{s=1}^m \frac{1}{T_{2\alpha,s}} \right) O_Z S_z \prod_{i=1}^m I_{\beta_i},$$

which leads to the approximation

$$\hat{\Gamma} O_{kj} = R_{z,kj}^{\prime \prime} O_{kj}, \quad R_{z,kj}^{\prime \prime} = \sum_{i=1}^m \frac{1}{T_{2\alpha,s}}.$$ 

This means that the result of action of $\hat{\Gamma}$ on $O_{kj}$ is approximately proportional to $O_{kj}$. Hence, in the model $\hat{\Gamma}_0$, we should let

$$\hat{\Gamma}_0 O_{kj} = R_{z,kj} O_{kj}, \quad R_{z,kj} = Tr ((\hat{\Gamma}_0 O_{kj}) O_{kj}).$$

In this case, the ‘transverse parts’ of both relaxation superoperators will be close.
The action of the relaxation superoperator \( \hat{\Gamma} \) on \( O_{kk} \) gives a traceless combination of Zeeman orders. Any such combination is expanded into a combination of operators less combination of Zeeman orders. Any such combination is obtained from the eigenvectors of the stationary Hamiltonian in the Hilbert space. The requirement that the operators \( O_{kk} \) can be fulfilled by setting up a linear combination of the former:

\[
\hat{\Gamma}_0 O_{kk} = \sum_{s \neq k} R_{1,sk}(O_{sk} - O_{sj}), \quad R_{1,sk} = -Tr(\langle \hat{\Gamma}_o O_{sk} \rangle O_{jj})
\]

and the ‘longitudinal parts’ close to each other.

### A.5. Numerical implementation of the Lindblad–Kossakowski relaxation superoperator form

In this appendix we briefly recapitulate some of the information already presented in Sections 6 and 7 and explain how the Lindblad–Kossakowski form of the relaxation superoperator for the model-free approach (14) can be conveniently calculated. The Lindblad–Kossakowski form of the relaxation superoperator is given by (Equation (14))

\[
-\hat{\Gamma}_0 \sigma = \sum_{s \neq s'} \Gamma_{ss'} \left[ O_{ss'} \sigma O_{s's'} - \frac{1}{2} (\sigma O_{s's'} + O_{s's'} \sigma) \right] + \sum_q \Gamma_q \left[ O_q \sigma O_q - \frac{1}{2} (\sigma O_q O_q + O_q O_q \sigma) \right],
\]

where \( \hat{\Gamma}_0 \) is a matrix of the relaxation superoperator defined in Equation (15), \( O_{ss'} = v_s v_{s'}^\ast \) are the eigenoperators constructed from the eigenvectors of the stationary Hamiltonian in the Hilbert space. The requirement that the operators \( O_{kk} \) are traceless can be fulfilled by setting up a linear combination of the former:

\[
O_{kk} = \sum_{s=1}^N c_s O_{ss}.
\]

The coefficients \( c_s \) are found by solving a set of equations given in Equation (15). To avoid these cumbersome calculations we can further simplify Equation (14), the second term can be rewritten in the non-diagonal form

\[
\sum_q \Gamma_q \left[ O_q \sigma O_q - \frac{1}{2} (\sigma O_q O_q + O_q O_q \sigma) \right] = \sum_{s,s'} \hat{\Gamma}_{ss'} \left[ O_{ss'} \sigma O_{s's'} - \frac{1}{2} (\sigma O_{s's'} O_{s's'} + O_{s's'} O_{s's'} \sigma) \right]
\]

\[
= \sum_{s,s'} \hat{\Gamma}_{ss'} O_{ss'} \sigma O_{s's'}
\]

where the rates \( \hat{\Gamma}_{ss'} \) are expressed via \( \Gamma_q \) and \( c_q \). It follows from the form of Equation (14) that

\[
\hat{\Gamma}_0 O_{kk} = \sum_{s \neq k} R_{1,sk}(O_{sk} - O_{sj}), \quad \hat{\Gamma}_0 O_{kj} = R_{2,kj} O_{kj}, \quad k \neq j.
\]

which in terms of the rates \( \hat{\Gamma}_{ss'} \) gives

\[
R_{2,kj} = \frac{1}{2} \left( \Gamma_{kk} + \Gamma_{jj} - 2 \Gamma_{kj} + \sum_{s \neq k} \Gamma_{sk} + \sum_{s \neq j} \Gamma_{sj} \right),
\]

\[
R_{1,sk} = \Gamma_{sk}.
\]

If the rates \( R_{1,sk}, R_{2,kj} \) are known, it is possible to invert the relation in Equation (A6) to find \( \hat{\Gamma}_{ss'} \) and \( \Gamma_{ss'} \), letting further \( \hat{\Gamma}_{ss'} = 0 \) we obtain

\[
\Gamma_{sk} = R_{1,sk}, \quad \hat{\Gamma}_{kj} = \frac{1}{2} \left( \sum_{s \neq k} R_{1,sk} + \sum_{s \neq j} R_{1,sj} \right) - R_{2,kj}.
\]

The rates \( R_{1,sk}, R_{2,kj} \) can be found from the projection of the eigenoperators \( O_{kj} \)

\[
R_{2,kj} = Tr(\langle \hat{\Gamma} O_{kj} \rangle O_{kk}), \quad R_{1,sj} = -Tr(\langle \hat{\Gamma} O_{ks} \rangle O_{ss}).
\]

where \( \hat{\Gamma} \) is the relaxation superoperator for the uncorrelated random field model given by Equation (10). To calculate the projection, operators \( O_{kj} \) have to be represented column-wise as vectors. Either the trace is taken in the case that the product of \( \langle \hat{\Gamma} O_{kj} \rangle \) is transformed back into the operator representation, or the scalar product is calculated in the case that both \( \hat{\Gamma} O_{kj} \) and \( O_{kk} \) are in the vector form. Finally, the following expression for the relaxation superoperator matrix of the model-free approach is obtained:

\[
-\hat{\Gamma}_0 \sigma = \sum_{s \neq s'} \hat{\Gamma}_{ss'} \left[ O_{ss'} \sigma O_{s's'} - \frac{1}{2} (\sigma O_{s's'} + O_{s's'} \sigma) \right] + \sum_{s \neq s'} \hat{\Gamma}_{ss'} O_{ss'} \sigma O_{s's'}.
\]

The advantage of the form (A9) is that it contains only the operators \( O_{ss'} \) and rates \( \Gamma_{ss'} \). This form is especially convenient if operators \( O_{ss'} \) are expressed as the left/right superoperators (operators in Liouville space), i.e. \( \hat{O}_{ss'} = O_{ss'} \otimes 1, \hat{O}_{ss'}^\ast = 1 \otimes O_{ss'}^\ast \). It is worthwhile to note that Equation (A9) gives the thermalised form of the relaxation superoperator, thus the homogeneous form of the master equations is preserved and an exponential solution can be used. The above-mentioned treatment can be adopted in one of the available spin dynamics simulation software packages, e.g. Spinach [25].