Steady State in Magnetic Resonance Pulse Experiments

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Relaxation during multiple-pulse magnetic resonance experiments is treated by an average Liouvillian technique. The finite lattice temperature is taken into account by means of phenomenological correction terms. Both the transient and long-term response of the spin system are readily treated. We predict and verify a novel steady state of correlated spin polarizations in a spin-pair system under a periodic sequence of strong π pulses.

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We report a new formulation of average Liouvillian theory for treating the behavior of a nuclear spin system during multiple-pulse irradiation. In contrast with previous approaches [1,2], spin-lattice relaxation is included, within the limitations of a high-temperature assumption for the spin system. The method is applicable to any nuclear spin system weakly coupled to a thermal reservoir. We illustrate the theory by predicting an unusual steady state of correlated spin polarizations for coupled nuclear spin pairs exposed to a sequence of strong radio-frequency π pulses.

It has long been recognized that spin-lattice relaxation is awkward to treat theoretically. Semiclassical relaxation theories [3] provide a treatment of the relaxation *rates* but predict a false *equilibrium position* involving the destruction of spin order rather than a Boltzmann population distribution. A phenomenological term σ^{eq} is usually added to the evolution equation of the spin density operator σ so as to impose the correct thermal equilibrium state: Under well-known approximations, this "master equation" is [3–5]

$$(d/dt)\sigma = -i\hat{\mathcal{H}}\sigma + \hat{\Gamma}(\sigma - \sigma^{eq}), \tag{1}$$

where $\hat{\mathcal{H}}$ is the commutation superoperator for the coherent spin-spin and spin-field interactions, and $\hat{\Gamma}$ is the relaxation superoperator (a single caret indicates a superoperator).

Equation (1) is awkward to use since it is homogeneous in neither σ nor $\sigma - \sigma^{eq}$. The spin evolution cannot be represented as a linear transformation in Liouville space. This greatly complicates the task of formulating the interplay of relaxation and external irradiation. It has not been possible to formulate an "average relaxation superoperator" analogous to the "average Hamiltonian" used for the coherent evolution [1]. A general theory of the steady-state under multiple-pulse irradiation does not exist.

In the following treatment we use the following notation: A spin system has n eigenstates $|r\rangle$ defined by $\mathcal{H}^{lab}|r\rangle = \omega_r|r\rangle$ where ω_r are the state energies (angular frequency units). A superspace of n^2 orthonormal spin operators $\{\cdots|Q_j\rangle\cdots\}$, denoted by bold kets, is constructed [5]: The superspace metric is $\langle Q_j|Q_k\rangle = \mathrm{Tr}\{Q_j^\dagger Q_k\} = \delta_{jk}$; the matrix elements of a superoperator $\hat{S}$ are given by $S_{jk} = \langle Q_j|\hat{S}|Q_k\rangle$. The density operator is represented by a superket $|\sigma\rangle$ and the unit operator by $|\mathbb{1}\rangle$ with $\langle\mathbb{1}|\mathbb{1}\rangle = n$. The population operator (projector) $|r\rangle\langle r|$ of the spin state $|r\rangle$ is denoted by $|P_r\rangle$. The symbol $\hat{P}_r$ denotes a *superprojector* onto the ket $|P_r\rangle$, i.e., $\hat{P}_r = |P_r\rangle\langle P_r|$. The superprojector onto the unity operator is defined $\hat{P}_{\mathbb{1}} = n^{-1}|\mathbb{1}\rangle\langle\mathbb{1}|$.

Jeener [5] showed that Eq. (1) may be rendered homogeneous by "improving" $\hat{\Gamma}$ rather than adding a σ^{eq} term. In Liouville space the new master equation has the form

$$(d/dt)|\sigma\rangle = (-i\hat{\mathcal{H}} + \hat{\Upsilon})|\sigma\rangle \tag{2}$$

with the adjusted relaxation superoperator

$$\hat{\Upsilon} = \hat{\Gamma} + \hat{\Theta}.$$

$\hat{\Theta}$ may be derived as follows: The matrix elements $\langle P_r|\hat{\Gamma}|P_s\rangle$ of the relaxation superoperator are the state transition probabilities W_{rs}: For a lattice of temperature T, the probability W_{sr} for a transition $|r\rangle \rightarrow |s\rangle$ differs from that for the transition $|s\rangle \rightarrow |r\rangle$ by the small factor $\exp\{(\omega_r - \omega_s)\tau_\theta\}$, where $\tau_\theta = \hbar/kT$ (dimensions of time). This suggests the following form for the adjusted relaxation superoperator:

$$\hat{\Upsilon} = \hat{\Gamma}\exp\{\hat{\omega}\tau_\theta\}, \tag{3}$$

where

$$\hat{\omega} = \sum_r \omega_r \hat{P}_r, \tag{4}$$

and the mean energy is assumed to be zero ($\langle\mathbb{1}|\hat{\omega}|\mathbb{1}\rangle = 0$). The thermal correction is therefore $\hat{\Theta} \simeq \hat{\Gamma}\hat{\omega}\tau_\theta$ correct to first order in τ_θ. In practice it is convenient to insert an additional projector and write

$$\hat{\Theta} \simeq \hat{\Gamma}\hat{\omega}\hat{P}_{\mathbb{1}}\tau_\theta. \tag{5}$$

This is possible since those density operator components which are perpendicular to the unity operator have small magnitudes $\simeq ||\hat{\omega}\tau_\theta||$.

We now consider a specific Liouville basis such that the first ket is given by the normalized unity operator $|Q_1\rangle = n^{-1/2}|\mathbb{1}\rangle$, and all the other kets are operators with zero trace. The matrix elements of $\hat{\Theta}$ are given in terms of the Redfield matrix elements Γ_{jl} by

$$\Theta_{jk} = n^{-1}\mathrm{Tr}\{Q_k\}\sum_r \langle Q_j|\hat{\Gamma}|P_r\rangle\omega_r\tau_\theta$$
$$\simeq n^{-1/2}\delta_{k1}\sum_{l,\mu}\Gamma_{jl}\langle Q_l|I_{\mu z}\rangle\omega_\mu^0\tau_\theta, \quad (6)$$

where each spin I_μ has a longitudinal angular momentum operator $|I_{\mu z}\rangle$ and a Larmor frequency ω_μ^0. The last expression is valid in the high-field limit (Larmor frequency much larger than all other interactions).

Unlike $\hat{\Gamma}$, the corrected relaxation matrix $\hat{\Upsilon}$ is *asymmetric*. It represents a unidirectional flow from $|Q_1\rangle$ into the other spin operators, where the order is redistributed and dissipated. Since $\langle\mathbb{1}|\hat{\Gamma}=0$, the first row of $\hat{\Upsilon}$ contains only zeros, and the eigenvalues of $\hat{\Upsilon}$ are the same as those of $\hat{\Gamma}$: The finite lattice temperature affects the position but not the rates of thermal equilibration (in the high-temperature approximation). The steady-state density operator for time-independent $\hat{\mathcal{H}}$ and $\hat{\Gamma}$ may be calculated from the null space of $-i\hat{\mathcal{H}}+\hat{\Upsilon}$. For $\hat{\mathcal{H}}=0$, the correct thermal equilibrium density operator

$$|\sigma^{eq}\rangle = n^{-1}(\hat{1}-\hat{\omega}\tau_\theta)|\mathbb{1}\rangle$$

is predicted.

For time-dependent $\hat{\mathcal{H}}$ an interaction frame and/or Magnus expansion technique may be used [1]. An interaction frame density operator $|\tilde{\sigma}(t)\rangle = \hat{V}(t)^\dagger|\sigma\rangle$ is defined where $\hat{V}$ satisfies

$$(d/dt)\hat{V}(t) = -i\hat{\mathcal{H}}(t)\hat{V}(t).$$

The equation of motion is

$$(d/dt)|\tilde{\sigma}(t)\rangle = \hat{\tilde{\Upsilon}}(t)|\tilde{\sigma}(t)\rangle$$

where

$$\hat{\tilde{\Upsilon}}(t) = \hat{V}(t)^\dagger\hat{\Upsilon}\hat{V}(t).$$

The Magnus expansion is used to estimate an average relaxation superoperator over a time τ, under the usual convergence conditions (1):

$$|\tilde{\sigma}(\tau)\rangle = \exp\{\hat{\bar{\Upsilon}}(\tau)\}|\tilde{\sigma}(0)\rangle,$$
$$\hat{\bar{\Upsilon}}(\tau) = \hat{\bar{\Upsilon}}^{(0)}(\tau)+\hat{\bar{\Upsilon}}^{(1)}(\tau)+\cdots,$$

where

$$\hat{\bar{\Upsilon}}^{(0)}(\tau) = \tau^{-1}\int_0^\tau dt_1\hat{\tilde{\Upsilon}}(t_1),$$
$$\hat{\bar{\Upsilon}}^{(1)}(\tau) = (2\tau)^{-1}\int_0^\tau dt_2\int_0^{t_2}dt_1[\hat{\tilde{\Upsilon}}(t_2),\hat{\tilde{\Upsilon}}(t_1)],$$

and so on. Irradiation schemes may be designed such that $\hat{\bar{\Upsilon}}^{(0)}$ has desirable properties (such as the suppression of undesirable relaxation pathways), while the correction terms $\hat{\bar{\Upsilon}}^{(1)}+\cdots$ are kept as small as possible. This average Liouvillian method improves on average Hamiltonian theory by making it possible to treat the long-term as well as the short-term spin response.

As an example consider a system of two unlike spins $-1/2$ I and S in a liquid ($n=4$), in the presence of a variety of relaxation mechanisms including motional modulational of the chemical shift anisotropy (CSA) and the dipole-dipole coupling between the spins (DD), not excluding cross correlation between these two mechanisms [6]. Under the secular approximation [3], the matrix elements of $\hat{\Upsilon}$ are written in the base of the four normalized Cartesian product operators [4] $\{|\frac{1}{2}\mathbb{1}\rangle, |I_z\rangle, |S_z\rangle, 2I_zS_z\rangle\}$ as follows:

$$\hat{\Upsilon} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ \theta_I & -\rho_I & -\sigma_{IS} & -\delta_{I.IS} \\ \theta_S & -\sigma_{IS} & -\rho_S & -\delta_{S.IS} \\ \theta_{IS} & -\delta_{I.IS} & -\delta_{S.IS} & -\rho_{IS} \end{pmatrix}. \quad (7)$$

Here ρ_I, ρ_S, and ρ_{IS} are decay rates for longitudinal spin order, σ_{IS} is the cross-relaxation rate constant, and $\delta_{I.IS}$, $\delta_{S.IS}$ are rate constants for the transfer of one-spin order to two-spin order driven by CSA and DD cross correlation [6,7].

From Eq. (6), the thermal correction terms are

$$\theta_I = -\tfrac{1}{2}(\rho_I\omega_I^0+\sigma_{IS}\omega_S^0)\tau_\theta,$$
$$\theta_S = -\tfrac{1}{2}(\sigma_{IS}\omega_I^0+\rho_S\omega_S^0)\tau_\theta, \quad (8)$$
$$\theta_{IS} = -\tfrac{1}{2}(\delta_{I.IS}\omega_I^0+\delta_{S.IS}\omega_S^0)\tau_\theta,$$

where ω_I^0,ω_S^0 are the Larmor frequencies of the I and S spins.

Now consider two simple experiments involving periodic π pulse sequences. In Experiment A, the π pulses are applied to the I spins alone. In Experiment B, the π pulses are applied simultaneously to both spin species. In both cases, the π pulses are repeated at intervals of $\tau/2$. We consider the properties of the effective Liouvillian over the element $[\tau/4-\pi-\tau/2-\pi-\tau/4]$, which is cyclic in the sense that $\hat{V}(\tau)=\hat{1}$. Since the interaction frame is symmetric $[\hat{V}(\tau-t)=\hat{V}(t)]$, $\hat{\bar{\Upsilon}}^{(1)}$ and all odd Magnus powers vanish [1]. We assume that the pulsing rate τ^{-1} is much faster than the relaxation and consider only the zeroth-order Magnus term $\hat{\bar{\Upsilon}}^{(0)}$ (the average Liouvillian over the cycle).

For infinitely short π pulses the interaction frame superoperator toggles between two values, $\hat{\Upsilon}$ and $\hat{\Pi}^\dagger\hat{\Upsilon}\hat{\Pi}$, where $\hat{\Pi}$ is the superoperator for the π pulse. Ideal π pulses transform the four basis operators according to

$$\hat{\Pi}|Q_j\rangle = \pi_j|Q_j\rangle, \quad (9)$$

where $\pi_j=\pm1$ is the *parity* of $|Q_j\rangle$. The average Liouvillian is the sum of a *gerade* component $\bar{\Upsilon}_g$, and an *ungerade* component $\bar{\Upsilon}_u$, where $\bar{\Upsilon}_g$ has matrix elements only between operators with even parity (including $|\frac{1}{2}\mathbb{1}\rangle$), and $\bar{\Upsilon}_u$ has matrix elements only between operators with odd parity.

Experiment A: π pulses applied to I spins. The *gerade* subspace is spanned by the operators $\{|\frac{1}{2}\mathbb{1}\rangle,|S_z\rangle\}$, and the *ungerade* space by the operators $\{|I_z\rangle,|2I_zS_z\rangle\}$. The two components of the average Liouvillian are given

by

$$\hat{\Upsilon}_g = \begin{array}{c} \begin{matrix} |\tfrac{1}{2}\mathbb{1}\rangle & |S_z\rangle \end{matrix} \\ \begin{pmatrix} 0 & 0 \\ \theta_S & -\rho_S \end{pmatrix} \end{array},$$

$$\hat{\Upsilon}_u = \begin{array}{c} \begin{matrix} |I_z\rangle & |2I_zS_z\rangle \end{matrix} \\ \begin{pmatrix} -\rho_I & -\delta_{I,IS} \\ -\delta_{I,IS} & -\rho_{IS} \end{pmatrix} \end{array}. \tag{10}$$

The *gerade* superoperator is asymmetric and represents a flow of order in which the S spins acquire a Zeeman polarization $\langle S_z\rangle = \langle S_z|\sigma\rangle$ at a rate $\theta_S\langle\frac{1}{2}\mathbb{1}\rangle$, and lose it at a rate $\rho_S\langle S_z\rangle$. At long times, a steady-state S spin polarization is attained, for which these two rates become equal: This is readily evaluated in terms of the thermal equilibrium S-spin polarization $\langle S_z\rangle^{eq} = \langle S_z|\sigma^{eq}\rangle$ as

$$\frac{\langle S_z\rangle^{ss}}{\langle S_z\rangle^{eq}} = 1 + \frac{\sigma_{IS}\omega_I^0}{\rho_S\omega_S^0} \tag{11}$$

which is just the ordinary steady-state nuclear Overhauser effect [8], here arising naturally from an average Liouvillian description.

The *ungerade* superoperator represents a redistribution and dissipation of order in the subspace $\{|I_z\rangle, |2I_zS_z\rangle\}$. The transfer rates are affected only by the CSA and DD cross correlation, offering a means for isolating and measuring these weak processes, in similar fashion to Burghardt, Konrat, and Bodenhausen [9], as will be described in detail elsewhere. Since $\hat{\Upsilon}_u$ has only negative eigenvalues, no order remains in the *ungerade* subspace at long times.

Experiment B: π pulses applied simultaneously to I and S spins. This time the *gerade* subspace is spanned by the operators $\{|\frac{1}{2}\mathbb{1}\rangle, |2I_zS_z\rangle\}$, and the *ungerade space by the operators* $\{|I_z\rangle, |S_z\rangle\}$. The components of the average Liouvillian are

$$\hat{\Upsilon}_g = \begin{array}{c} \begin{matrix} |\tfrac{1}{2}\mathbb{1}\rangle & |2I_zS_z\rangle \end{matrix} \\ \begin{pmatrix} 0 & 0 \\ \theta_{IS} & -\rho_{IS} \end{pmatrix} \end{array},$$

$$\hat{\Upsilon}_u = \begin{array}{c} \begin{matrix} |I_z\rangle & |S_z\rangle \end{matrix} \\ \begin{pmatrix} -\rho_I & -\sigma_{IS} \\ -\sigma_{IS} & -\rho_S \end{pmatrix} \end{array}. \tag{12}$$

The dynamics in the *ungerade* subspace represent a redistribution of Zeeman order between the I spins and S spins under the influence of the cross-relaxation rate σ_{IS}, free from perturbation by cross correlation. As before, all order dies out in the ungerade subspace at long times.

The behavior of the *gerade* subspace is particularly interesting. By analogy with experiment A, a *steady-state of two-spin order* is predicted at long times, given in terms of the thermal equilibrium S-spin Zeeman polarization by

$$\frac{\langle 2I_zS_z\rangle^{ss}}{\langle S_z\rangle^{eq}} = \frac{\delta_{I,IS}\omega_I^0 + \delta_{S,IS}\omega_S^0}{\rho_{IS}\omega_S^0}. \tag{13}$$

According to its sign, the steady-state value of $\langle 2I_zS_z\rangle$ indicates a persistent (anti)correlation of the spin polarizations along the field. It arises when the driving fields and the microscopic interactions causing relaxation are both correlated. The effect can be quite considerable and offers a sensitive measurement of cross correlation. The value of $\langle 2I_zS_z\rangle$ is easily estimated from the asymmetry of the J-coupled doublet after Fourier transformation of the signal induced by a $\pi/2$ pulse applied to one of the spin species.

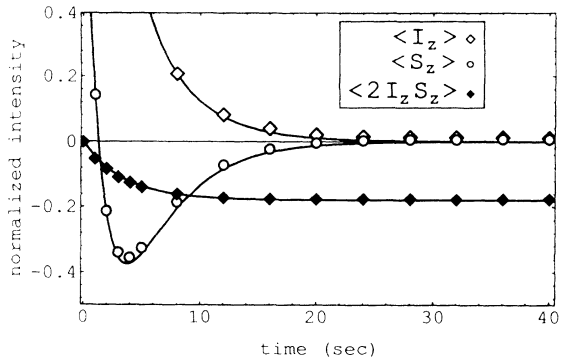

FIG. 1. Trajectories of $\langle I_z\rangle$, $\langle S_z\rangle$, and $\langle 2I_zS_z\rangle$ as a function of time during a periodic sequence of composite π pulses applied to both spin species (normalized with respect to $\langle S_z\rangle^{eq}$). Solid curves are simulations (see text).

Figure 1 shows some experimental results for ^{13}C-labeled chloroform in ethylene glycol solution ($I = {}^1H$, $S = {}^{13}C$) in a field of 4.7 T at 300 K. The values of $\langle I_z\rangle$, $\langle S_z\rangle$, and $\langle 2I_zS_z\rangle$ are shown after an increasing number of cycles $[-\tau/4-\pi-\tau/2-\pi-\tau/4]$ applied to a thermal equilibrium density operator. The cycle period was $\tau = 200$ ms: Composite π pulses with flip angles $\{\pi/2, 2\pi, \pi/2\}$ and phases $\{0, 2\pi/3, 0\}$ were used throughout to compensate radio-frequency field inhomogeneity [10]. The Zeeman magnetizations $\langle I_z\rangle$ and $\langle S_z\rangle$ decay to zero while $\langle 2I_zS_z\rangle$ gradually builds up to a steady state of -18% of $\langle S_z\rangle^{eq}$. The simulated curves are based on Eq. (12), with parameters as in Ref. [7], except for $\delta_{S,IS} = 13.7\times10^{-3}\,s^{-1}$.

In summary, we have demonstrated an average Liouvillian approach which resolves long-standing problems concerning the proper treatment of spin-lattice relaxation in multiple-pulse sequences. The theory is capable of generating existing results such as the steady-state nuclear Overhauser effect in a simple and intuitive way, as well as predicting new and surprising results such as the establishment of steady-state two-spin order in the

presence of a long π pulse train. This appears to open up an entirely new approach to magnetic resonance pulse sequence design based on manipulating the steady-state behavior of pulse sequences rather than exploiting their short-term transient performance. When relaxation is fast this may be particularly advantageous. Although immediate applications are likely in nuclear magnetic resonance, a similar approach may be expected to be useful in microwave and optical spectroscopy as well (bearing in mind the limitations of the high-temperature approximation). Indeed spin-lattice relaxation (or spontaneous decay) is of even more significance in those cases.

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