# Nuclear Spin Dynamics ($I = 1/2$) under the Influence of Random Perturbation Fields in the "Strong Collision" Approximation

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We investigate the relaxation of a spin 1/2 system by random perturbation fields in the strong collision approximation. In contrast to prior studies no assumptions are made about the fluctuation frequency or about the magnitude of the perturbation fields. A general result for the Laplace transform of the spin lattice and phase relaxation is derived. We discuss the result for phase relaxation induced by a perturbation field with only two opposite modes along the $x$, $y$ and $z$ axis. Using the method of the general moment approximation we demonstrate how the spin lattice relaxation can be approximated by a sum of exponentials, and we discuss approximations by a single exponential and a bi-exponential function.

## 1. Introduction

In the presence of an external static magnetic field nuclear spins are aligned along its axis leading to a total nuclear magnetization vector which is parallel to this field vector. After perturbing such a system of nuclear spins, it will relaxate towards its equilibrium state. The relaxation of the magnetization component parallel to the external field is denoted as spin lattice relaxation, the relaxation of the perpendicular component is called phase relaxation [1]. Spin relaxation is induced by perturbation fields [1] due to the environment of a nuclear spin. If one considers for instance biological tissues, which become a heterogeneous magnetic environment in the presence of an external magnetic field [2], the perturbation fields may be due to susceptibility differences of adjacent compartments, or to fields induced by magnetic compounds as ferritin [3, 4].

Nuclear spin relaxation is determined by the magnitude of the perturbation fields and the dynamics of the perturbation field modulation [1, 5]. In general, this dynamics is given by a superposition of a deterministic and stochastic component of the perturbation field modulation [5]. For instance, in the case of nuclear spin relaxation via magnetic dipol-dipol interactions between a nuclear spin and another spin (electron or nuclear spin) the deterministic component is given by the precession of the second spin in the external magnetic field, the stochastic one is due to the rotational and translational diffusion motion of both spins [5, 6].

In general, the dynamics of interactions inducing spin relaxation are very complex. Therefore analytical approaches for the calculation of spin relaxation are only feasible in special cases where certain assumptions of perturbation field dynamics are employed. If this dynamics is a stationary process, it can be characterized by the temporal autocorrelation function $K(\Delta t)$ of the stochastic interaction part $V(t)$ of the Hamiltonian [5] $K(\Delta t) = \langle V(t_0 + \Delta t) V(t_0) \rangle$ where the brackets $\langle X \rangle$ denote the average value of an observable $X$ of the spin system. The temporal autocorrelation function reveals information about how long on average the dynamics of a nuclear spin is affected by the particular perturbation $V(t_0)$. A simple and well known approach is the assumption of a single exponential decay for $K(\Delta t)$ [1, 5, 7], i.e. $K(\Delta t) = \langle V(t_0)^2 \rangle \cdot \exp(-\Delta t/\tau)$, with the

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correlation time $\tau$. This correlation time is the average duration of the influence of a perturbation field form $V(t_0)$ on the dynamics of a nuclear spin [1]. The assumption of a single exponential decay was successful for the description of spin relaxation by translational diffusion motion in aqueous solutions of paramagnetic ions [5, 7, 8], by rotational diffusion motion in the presence of intramolecular spin-spin interactions [6] and by local fluctuating magnetic fields [1]. In these applications the fluctuation rate $\tau^{-1}$ of the perturbation fields is much greater than their precession frequency (*motional narrowing limit*). This condition allows the description of nuclear spin relaxation by means of the quantum mechanical perturbation theory. Taking into account the assumption of the mono exponential decay of $K(\Delta t)$ this approach yields an analytical solution of the spin lattice and phase relaxation time.

Only in the motional narrowing limit the single exponential autocorrelation function $K(\Delta t)$ provides enough information for the determination of spin lattice relaxation [5]. In general one has to consider also autocorrelation functions of higher order.

$$K_n = \langle V(t_0)\, V(t_0 + \Delta t_1) \ldots V(t_0 + \sum_{j=1}^{n} \Delta t_j) \rangle ,$$

for the evaluation of the perturbation field dynamics and its influence on spin relaxation [9]. An important group of stochastic field fluctuations are those in which the stochastic modulation is governed by a stationary Markov process [10–12]. Such a process implies that the probability for a nuclear spin to jump from the influence of one perturbation field form $V(t)$ to the influence of another $V(t + \mathrm{d}t)$ is independent from perturbation field forms in the past $V(t - \mathrm{d}t)$, $V(t - 2\mathrm{d}t)$, .... A special case is the *Random phase approximation* (RPA) or *strong collision* model which makes the additional assumption that the transition probability of two perturbation field forms $V(t)$ and $V(t + \mathrm{d}t)$ is independent of $V(t)$ [10]. This independence implies that two successive perturbation field forms are uncorrelated, i.e. it is not possible to determine the perturbation field forms having influenced a nuclear spin in the past. The RPA model was applied to the description of spin relaxation by fluctuating magnetic fields [10, 13]. This model however was mainly developed to reveal fundamental relationships between perturbation field dynamics and spin relaxation [10], and not to apply to special physical situations.

Though the RPA model appears to be rather simple, analytical approaches for the quantum mechanical description of spin relaxation were only made in the case of very long or very short correlation times [10]. In this paper we will present an analytical approach for the calculation of the frequency spectrum of phase and spin lattice relaxation of a spin system ($I = 1/2$) within the RPA model. We will assume that the distribution function of the perturbation field components is symmetrical in each of the three coordinate axis. Additionally the $x$ and $y$ components are assumed to be identically distributed, i.e. this includes the cylindric and isotropic distribution as special cases. No assumptions are made about the magnitude of the correlation time and about perturbation fields or the relationship of both.

In the following we will consider the relaxation of a nuclear spin system in an external magnetic field where relaxation is induced by uncorrelated fluctuating perturbation fields (RPA model). The time evolution of this system will be determined by the stochastic Liouville equation [10, 12]. From this equation we will derive the Laplace transform $\hat{\varrho}(s)$ of the spin density operator $\varrho(t)$. We will reveal simple expressions for the Laplace transform of spin lattice and phase relaxation which easily lead to the determination of the frequency spectra of the corresponding relaxation process. As an example we will consider a fluctuating perturbation field with only two opposite field forms in each space axis. The frequency spectrum of phase relaxation will be discussed for various correlation times. In the last chapter we will demonstrate by means of the Laplace transform, how the algorithm of the *generalized moment approximation* (GMA) provides an appropriate approximation of the spin lattice relaxation by a sum of exponentials. Especially the approximation by a single exponential function will be discussed, and we will show that in the *motional narrowing limit* the relaxation time derived from the GMA algorithm is equivalent to the well known result obtained from perturbation theory. Furthermore we will use the GMA to approximate spin lattice relaxation by a bi-exponential function.

## 2. Mathematical Analysis of Spin Relaxation in the RPA Model

In the presence of an external magnetic field $\boldsymbol{B} = \omega_L/\gamma \cdot \boldsymbol{e}_z$ and additional stochastically fluctuating perturbation fields $\boldsymbol{b}(t) = \boldsymbol{\Omega}(t)/\gamma$ the time evolution of the spin density operator $\varrho(t)$ is determined by the Liouville equation

$$\partial_t \varrho = -\mathrm{i} \cdot (-\omega_L \cdot \boldsymbol{I}_z^{\mathrm{l}} - \boldsymbol{\Omega}(t) \cdot \boldsymbol{I}^{\mathrm{l}})\varrho , \tag{2.1}$$

where $\gamma$ denotes the gyromagnetic ratio, $\boldsymbol{e}_z$ the unit vector in $z$ direction, $\omega_L$ and $\Omega$ the precession frequency of the external field and the perturbation field, respectively; $\boldsymbol{I}$ is the spin operator. The superscript $^{\mathrm{l}}$ defines a Liouville operator, i.e. $\boldsymbol{I}^{\mathrm{l}}\varrho = [\boldsymbol{I}, \varrho]$ [14]. Liouville operators are superoperators which means that they are operators which themselves act on operators, in this case spin density operators [14].

When the dynamics of perturbation field fluctuations is determined by a Markov process, the transition rate $r_{i,j}$ between two perturbation field forms $\boldsymbol{\Omega}_j$, $\boldsymbol{\Omega}_i$ is independent from interactions in the past. The time evolution of the density operator $\varrho_i(t)$, which describes the behavior of nuclear spins under the influence of the perturbation field $\boldsymbol{\Omega}_i$ at the time $t$, is determined by the stochastic Liouville equation [12],

$$\partial_t \varrho_i = -\mathrm{i}(H_0^{\mathrm{l}} + V_i^{\mathrm{l}})\varrho_i + \sum_j r_{i,j}\varrho_j , \tag{2.2}$$

with

$$H_0^{\mathrm{l}} = -\omega_L \cdot \boldsymbol{I}_z^{\mathrm{l}} , \tag{2.3}$$

$$V_i^{\mathrm{l}} = -\boldsymbol{\Omega}_i \cdot \boldsymbol{I}^{\mathrm{l}} . \tag{2.4}$$

he formal solution of Eq. (2) is given by the expression

$$(t) = \exp\left(-it \cdot \sum_i (H_0^i + V_i^i)\mathbf{F}_i + t \cdot \mathbf{R}\right)\underline{\varrho}(t=0), \qquad (2.5)$$

here the transition rates $r_{i,j}$ are comprised in the rate matrix $\mathbf{R}$, and the spin density operators $\varrho_i$ in the vector $\underline{\varrho}$. The matrix $\mathbf{F}_i = (F_{n,m})_i$ has the components $F_{n,m} = 1$ for $n = m = i$, and $F_{n,m} = 0$ else.

Under thermal equilibrium conditions the probability distribution of the perturbation field forms is determined by the stationary solution $\mathbf{P}_0 = (p_{0,i})$ of the rate matrix $\mathbf{R}$. If the initial ($t = 0$) state of a spin system is given by the spin density operator $\varrho_0$, the vector $\underline{\varrho}(t=0)$ has the form $\underline{\varrho}(t=0) = (p_{01} \cdot \varrho_0, p_{02} \cdot \varrho_0, \ldots)^+$. According to Eq. (5) the time development of the spin density operator $\varrho(t)$ is given by

$$t) = \mathbf{1}^+ \exp\left(-it \cdot \sum_i (H_0^i + V_i^i)\mathbf{F}_i + t \cdot \mathbf{R}\right)\mathbf{P}_0 \cdot \varrho_0, \qquad (2.6)$$

ith the vector $\mathbf{1}^+ = (1, 1, \ldots)$ and with the relation $\varrho(t) = \varrho_i$ *). Thus, the Laplace transform $\hat{\varrho}(s)$ of the spin density operator $\varrho(t)$ has the form

$$s) = \int_0^\infty dt e^{-s \cdot t} \cdot \varrho(t), \qquad (2.7)$$

$$= \mathbf{1}^+ \frac{1}{s + i\sum_i (H_0^i + V_i^i)\mathbf{F}_i - \mathbf{R}} \mathbf{P}_0 \cdot \varrho_0 . \qquad (2.8)$$

the case of the RPA model the transition rates $r_{i,j}$ in q. (2) take the values [10]

$$= \begin{cases} \frac{1}{\tau} \cdot p_{0i}, & i \neq j, \\ \frac{1}{\tau} \cdot (p_{0i} - 1), & i = j, \end{cases} \qquad (2.9)$$

ere $\tau$ denotes the correlation time, i.e. the mean time a clear spin experiences the influence of a perturbation field rm. The quantity $\lambda = \tau^{-1}$ is the fluctuation frequency [5]. q. (9) reveals that the transition rates from an initial state o a state $i$ do not depend on the initial state, i.e. both ates are uncorrelated. If the transition rates have the form Eq. (9), the Laplace transform of Eq. (8) can be considbly simplified [10],

$$) = \frac{\sum_i (s + \lambda + iH_0^i + iV_i^i)^{-1} \cdot p_{0i}}{1 - \lambda \cdot \sum_i (s + \lambda + iH_0^i + iV_i^i)^{-1} \cdot p_{0i}} \cdot \varrho_0 . \qquad (2.10)$$

*) More precisely, one should replace the spin density operators $\varrho(t)$ and $\varrho_0$ by the operators $\varrho(t) - \varrho_{eq}$ and $\varrho_0 - \varrho_{eq}$, respectively, where $\varrho_{eq}$ denotes the density operator in the equilibrium state of the spin system [1]. However, in the remaining part of this paper the above notation will be used.

To solve this Laplace transform, the super operator

$$u(s) = \sum_i (s + \lambda + iH_0^i + iV_i^i)^{-1} \cdot p_{0i} \qquad (2.11)$$

$$= \left\langle \frac{1}{\tilde{s} + iH_i^i} \right\rangle$$

with $\tilde{s} = s + \lambda$, $H_i^i = H_0^i + V_i^i$ has to be determined first. The brackets $\langle\ \rangle$ denote the average for all perturbation field forms.

In the following, we will solve Eq. (11) for a spin system $I = 1/2$. Since every spin density operator of such a spin system can be written as a linear superposition of the Pauli spin matrices $\sigma_i$ together with the $2 \times 2$ unity matrix $e = (\delta_{i,j})$ [15], the superoperator in Eq. (11) can be written as a matrix within this base of the matrices. As the Liouville operators $H_0^i$ and $V_i^i$ satisfy the relations $H_0^i e = 0$ and $V_i^i e = 0$, one obtains for the operator $u(s)$ in Eq. (11)

$$u(s)e = (s + \lambda)^{-1} e . \qquad (2.12)$$

The fact that the Lioville operators $H_0^i$ and $V_i^i$ project Pauli matrices into the vector space given by these Pauli matrices, $[\sigma_1, \sigma_2, \sigma_3]$, can be expressed by the relation

$$H_0^i \sigma_j, V_i^i \sigma_j \in [\sigma_1, \sigma_2, \sigma_3] . \qquad (2.13)$$

From the relations (12), (13) one can derive

$$u(s)([\sigma_1, \sigma_2, \sigma_3]) \subseteq [\sigma_1, \sigma_2, \sigma_3] . \qquad (2.14)$$

The Eq. (12) and the relation (14) show that the superoperator $u(s)$ has only to be considered in the vector space of the Pauli matrices.

Employing the algebra of Pauli matrices [15], one can write the superoperator $\tilde{s} + iH_i^i$ within this matrix base in the form

$$\tilde{s} + iH_i^i = \begin{pmatrix} \tilde{s} & -(\omega_L + \Omega_{i,z}) & \Omega_{i,y} \\ \omega_L + \Omega_{i,z} & \tilde{s} & -\Omega_{i,x} \\ -\Omega_{i,y} & \Omega_{i,x} & \tilde{s} \end{pmatrix}, \qquad (2.15)$$

with

$$d_i = \tilde{s} \cdot (\tilde{s}^2 + \omega_L^2 + \Omega_i^2 + 2\omega_L \Omega_{i,z}) \qquad (2.16)$$

being the determinant of the matrix $\tilde{s} + iH_i^i$. Inversion of this matrix reveals the components $\langle(\tilde{s} + iH_i^i)^{-1}\rangle = (c_{\nu,\mu})$

$$c_{1,1} = \langle d_i^{-1} \cdot (\tilde{s}^2 + \Omega_{i,x}^2)\rangle ,$$

$$c_{1,2} = \langle d_i^{-1} \cdot \tilde{s} \cdot (\omega_L + \Omega_{i,z})\rangle ,$$

$$c_{1,3} = 0 ,$$

$$c_{2,1} = \langle d_i^{-1} \cdot \tilde{s} \cdot (-\omega_L - \Omega_{i,z})\rangle ,$$

$$c_{2,2} = \langle d_i^{-1} \cdot (\tilde{s}^2 + \Omega_{i,y}^2)\rangle ,$$

$$c_{2,3} = 0 ,$$

$$c_{3,1} = 0 ,$$

$$c_{3,2} = 0 ,$$

$$c_{3,3} = \langle d_i^{-1} \cdot (\tilde{s}^2 + (\omega_L + \Omega_{i,z})^2)\rangle ,$$

where we made use of the symmetry of the distribution function of the perturbation fields. Transformating from the base of the Pauli matrices $\sigma_i$ to the base of polar spin matrices

$$(\sigma_1, \sigma_2, \sigma_3) \rightarrow (\sigma_+, \sigma_-, \sigma_3),$$

with $\sigma_\pm = \sigma_1 \pm i \cdot \sigma_2$, one observes that the operator $\langle(\tilde{s} + iH_i^!)^{-1}\rangle$ is a diagonal matrix within this new base with the diagonal elements being

$$\langle(\tilde{s}+iH_i^!)^{-1}\rangle_{\pm,\pm} = \langle d_i^{-1}(\tilde{s}^2 + \Omega_{i,x}^2)\rangle \pm i \cdot \langle d_i^{-1}\tilde{s}\cdot(\omega_L + \Omega_{i,z})\rangle, \tag{2.17}$$

$$\langle(\tilde{s} + iH_i^!)^{-1}\rangle_{3,3} = \langle d_i^{-1}(\tilde{s}^2 + (\omega_L + \Omega_{i,z})^2)\rangle . \tag{2.18}$$

Since the operator $\langle(\tilde{s} + iH_i^!)^{-1}\rangle$ is a diagonal matrix within the base of the polar spin matrices, the superoperator in Eq. (10) must be a diagonal matrix within this base, too. Due to this fact it is possible to determine the Laplace transform of the spin lattice and phase relaxation. If one considers for instance a spin system which is initially polarized in $z$ direction, i.e. the initial spin density operator has the form $\varrho_0 = b \cdot \sigma_3 + 1/2 \cdot e$ [15]*), the Laplace transform $\hat{M}(s)$ of the normalized nuclear magnetization

$$M(t) = \frac{m_z(t) - m_{z,eq}}{m_{z,0} - m_{z,eq}}, \tag{2.19}$$

is given by

$$\hat{M}(s) = \frac{\langle(\tilde{s} + iH_i^!)^{-1}\rangle_{3,3}}{1 - \lambda\langle(\tilde{s} + iH_i^!)^{-1}\rangle_{3,3}}, \tag{2.20}$$

where we made use of Eqs. (10) and (18). A similar expression can be derived for the phase relaxation where the subscript (3,3) in Eq. (20) has to be replaced by $(+,+)$ or $(-,-)$.

### 3. Magnetic Field Fluctuating in Six Space Directions

In this chapter we will present an application of the result given by Eq. (2.17). The frequency spectrum of phase relaxation will be determined for various correlation times in the case when relaxation is induced by a stochastically fluctuating perturbation field with only two opposite field forms in each cartesian space axis. There are six perturbation field forms $\boldsymbol{b}_j = \boldsymbol{n}(j) \cdot \Omega/\gamma$, $j = 1, 2, \ldots 6$, where the vectors $\boldsymbol{n}(j)$ are positive or negative unit vectors along the $x$, $y$ nd $z$ axis. The probability that a nuclear spin is affected by the perturbation field $\boldsymbol{b}_j$ is assumed to be $\frac{1}{6}$, i.e. all perturbation field forms $\boldsymbol{b}_1, \boldsymbol{b}_2, \ldots \boldsymbol{b}_6$ have the same probability. We will consider a system of nuclear spins precessing in the $x-y$ plane, i.e. the initial spin density operator is given by $\varrho_0 = b_+ \cdot \sigma_+$ (polar presentation) [15], where $b_+$ denotes the initial magnitude of the nuclear spin magnetization.

*) The number $b$ is determined from $b = (m_{z,0} - m_{z,eq})/N\gamma\hbar$ [1], where $m_{z,0}$, $m_{z,eq}$ is the nuclear magnetization in $z$ direction at $t = 0$ and in the equilibrium state respectively. $N$ denotes the nuclear spin density.

The frequency spectrum $I(\omega)$ of the relaxation process from the transverse nuclear magnetization*) is given by

$$I(\omega) = \frac{1}{\pi} \cdot \mathrm{Re}(\hat{M}_+(i\omega)), \tag{3.1}$$

where $\mathrm{Re}(z)$ denotes the real part of $z$. The evaluation of $\hat{M}_+(s)$ requires the determination of $\langle(\tilde{s} + iH_i^!)^{-1}\rangle$ in Eq. (2.17). For the perturbation field described above one obtains

$$\begin{aligned}\langle(\tilde{s}+i\cdot H_i^!)^{-1}\rangle_{+,+} = {} & \frac{1}{6}\left(\frac{1}{\tilde{s}-i(\omega_L+\Omega)} + \frac{1}{\tilde{s}-i(\omega_L-\Omega)}\right) \\ & + \frac{1}{3}\left(\frac{\tilde{s}+i\omega_L}{\tilde{s}^2+\omega_L^2+\Omega^2}\right) \\ & + \frac{1}{3}\left(\frac{\tilde{s}^2+\Omega^2+\tilde{s}\cdot\omega_L}{\tilde{s}\cdot(\tilde{s}^2+\omega_L^2+\Omega^2)}\right).\end{aligned} \tag{3.2}$$

In our example we will assume the Larmor frequency $\omega_L$ to be that of a proton spin in a magnetic field of 1 Tesla i.e. $\omega_L = 2.67 \cdot 10^8\ s^{-1}$. The magnitude of the perturbation field is 1 Gauß, i.e. $\Omega = 2.67 \cdot 10^4\ s^{-1}$ which implies that the relation $\Omega/\omega_L \ll 1$ is valid. Figs. 1a and 1b show the frequency distribution of the transverse magnetization decay given by Eq. (1) for four different correlation times $\tau$. The fields fluctuating in $z$ direction induce the secular, the fields fluctuating in the $x-y$, plane the nonsecular part of the transverse relaxation [1]. For $\tau \gg \Omega^{-1}$, three maxima can be seen in the frequency spectrum (Fig. 1a). For an explaination one has to consider the influence of the fluctuating field in $z$ direction seperately from that of the fields in the $x-y$ plane. Due to the relation $\tau \gg \Omega^{-1}$ a nuclear spin which is under the influence of a perturbation field in $z$ direction precesses a long time either with the precession frequency $\omega_L + \Omega$ or with $\omega_L - \Omega$. The nuclear spins precessing with those frequencies are responsible for the side maxima in Fig. 1a. The $x$, $y$ fields have much less influence on the precession frequency as the following consideration will show. A nuclear spin which is under the influence of a $x-y$ perturbation field sees a total magnetic field of the magnitude

$$\begin{aligned}B_{ges} &= \sqrt{((\omega_L/\gamma)^2 + (\Omega/\gamma)^2)}, \\ &\approx \omega_L/\gamma \cdot (1 + 1/2 \cdot (\Omega/\omega_L)^2),\end{aligned}$$

Thus, the precession frequency becomes $\omega_L + 1/2 \cdot \Omega^2/\omega_L$, and the difference from $\omega_L$ is $\Omega/\omega_L$ times smaller than the one induced by the perturbation fields in $z$ direction. If, as it is the case in our example, the perturbation fields are much smaller than the external field, the nuclear spins have a precession frequency which is nearly identical with the one of the external field. Hence, the central maximum is induced by spin relaxation due to the $x$, $y$ perturbation fields.

*) We consider the normalized transverse magnetization, i.e. $M_+(t = 0) = 1$.

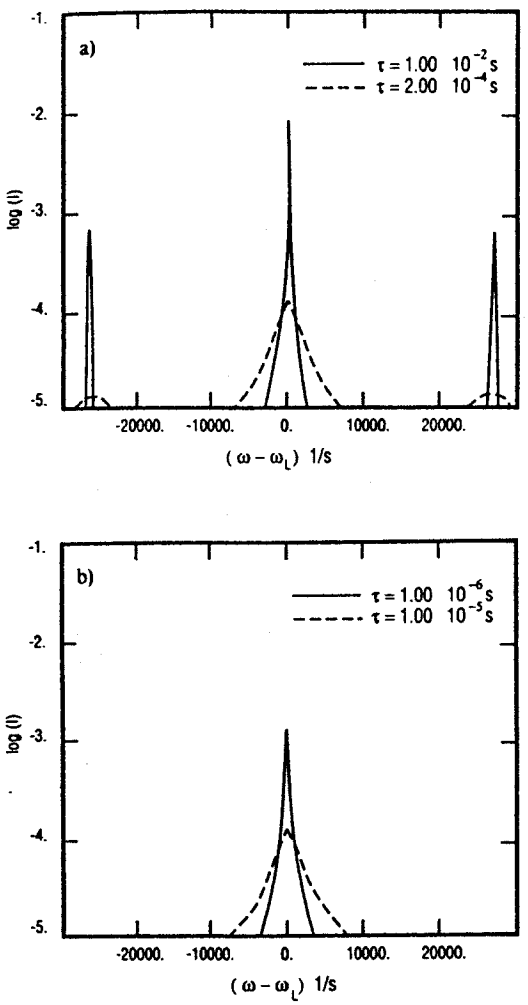


Fig. 1a, b
Frequency spectrum $I$ of phase relaxation for four different correlation times $\tau$ of the fluctuating perturbation fields. The magnitude of the external field is 1 Tesla, that of the perturbation field is 1 Gauß

For correlation times decreasing down to $\tau \approx \Omega^{-1}$ the spectra beneath the maxima spread and their height decreases until the side maxima vanish (Figs. 1a, 1b). For correlation times in the range of $\Omega^{-1}$ ($\tau = 2.0 \cdot 10^{-4}$s to $1 \cdot 10^{-5}$s), the influence of a perturbation field is too short for a nuclear spin to precess with either of the frequencies $\approx \omega_L$ ($x-y$ perturbation fields) or $\omega_L \pm \Omega$ ($z$ perturbation fields). Thus, the frequency spectrum is widely spread around the maxima. Since the phase coherence of the nuclear spins dissipates very fast due to this widely spread frequency spectrum, the phase relaxation is markedly enhanced.

For fluctuation frequencies $\lambda = \tau^{-1}$ greater than the precession frequency of the perturbation field $\Omega$, only a central maximum of the frequency spectrum is present (Fig. 1b). Due to the fast field fluctuations a nuclear spin does not precess with any of the perturbation field frequencies. Instead, the spin precesses with the Larmor frequency of the external field, $\omega_L$, and the perturbation fields only cause stochastic modulations of the precession frequency around $\omega_L$. The higher the fluctuation frequency the smaller becomes the variance around $\omega_L$ (*motional narrowing* effect) (Fig. 1b) meaning that the relaxation speed decreases.

## 4. Approximation of Spin Lattice Relaxation by Generalized Moment Approximation

In principle every observable $M(t)$ can be reconstructed from its Laplace transform $\hat{M}(s)$ by backward transformation [16]. However, for complex expressions as in Eq. (2.20) enormous difficulties are encountered so that backward transformation fails in gaining an analytical result for the observable.

In this chapter we will demonstrate that by means of the generalized moment approximation (GMA) [17] the spin lattice relaxation can be approximated by a sum of single exponentials. Particularly the approximation by a single exponential function will be discussed, which is denoted as the *mean relaxation time approximation* (MRT approximation) [17]. We will show that in the *motional narrowing* limit (short correlation time and small perturbation field) the spin lattice relaxation time derived from the MRT approximation is identical with the well known result [1] from perturbation theory.

Once the Laplace transform of an observable, for instance the spin lattice relaxation (s. Eq. (2.19)), is known, the low-frequency moments of $(n+1)$-th order are given by [17]

$$\mu_{-n-1} = \frac{(-1)^n}{n!} \cdot \frac{d^n \hat{M}(s)}{ds^n}_{s \to 0} \tag{4.1}$$

$$= \frac{1}{n!} \cdot \int_0^\infty \mathrm{d}t\, t^n \cdot M(t), \tag{4.2}$$

and the high-frequency moments of $n$-th order are

$$\mu_n = \frac{(-1)^n}{n!} \cdot \frac{d^n(s \cdot \hat{M}(s))}{d(1/s)^n}_{s \to \infty} \tag{4.3}$$

$$= \frac{d^n}{dt^n} M(t)_{t \to 0}. \tag{4.4}$$

The low-frequency moments characterize the long time behavior, while the high-frequency moments determine the short temporal behavior of an observable. It has been shown that the Laplace transform of a relaxation function, e.g. $\hat{M}(s)$, can be approximated by a series of Lorentzians [18]

$$\hat{M}(s) \approx \hat{m}(s),$$

$$\hat{m}(s) = \sum_{n=0}^{N-1} f_n \cdot \frac{1}{s + \Gamma_n}, \tag{4.5}$$

representing an $[N-1, N]$ Padé approximant where $\hat{m}(s)$ correctly describes the $N_k$ high- and $N_l$ low-frequency moments of the Laplace transform $\hat{M}(s)$ ($N_k + N_l = 2N$) [18]. With this requirement Eq. (5) represents a two sided Padé approximation around $s = 0$ and $s = \infty$ [19], which we will call $(N_k, N_l)$ generalized moment approximation (GMA)

[17]. The parameters $f_n$ and $\Gamma_n$ of Eq.(5) are determined from the generalized moments $\mu_m$, $m = -N_l, -N_l+1, \ldots 1, \ldots N_k-1$ through the relations [18]

$$\sum_{n=0}^{N-1} f_n \cdot \Gamma_n^m = \mu_m \,. \tag{4.6}$$

Eq.(5) means that with the GMA the relaxation function $M(t)$ can be approximated by a sum of single exponentials

$$M(t) \approx \sum_{n=0}^{N-1} f_n \cdot \exp(-\Gamma_n t) \,. \tag{4.7}$$

### 4.1. Mean Relaxation Time Approximation

Knowing the moments $\mu_n$, the solution of Eq.(6) provides an approximation of the relaxation function by a sum of exponentials that can be tailored to an arbitrary exactness. Generally, the coefficients $f_n$ and the rate constants $\Gamma_n$ in the exponent can only be determined numerically. An exception is the (1,1) or *mean relaxation time approximation* [17]. In this special case the relaxation function $M(t)$ is approximated by a single exponential function.

$$M(t) \approx \mu_0 \cdot \exp(-t/\theta), \tag{4.8}$$

with the relaxation time [17]

$$\theta = \mu_{-1}/\mu_0 \tag{4.9}$$

Since we consider the normalized magnetization $M(t)$, we have $\mu_0 = 1$ and therefore $\theta = \mu_{-1}$. In the RPA model the first low-frequency moment has the form (s. Eqs. (2.18) and (2.20))

$$\mu_{-1} = \hat{M}(s=0) \,,$$

$$= \frac{\left\langle \dfrac{\lambda^2 + (\omega_L + \Omega_z)^2}{\lambda(\lambda^2 + \Omega_x^2 + \Omega_y^2 + (\omega_L + \Omega_z)^2)} \right\rangle}{1 - \lambda \cdot \left\langle \dfrac{\lambda^2 + (\omega_L + \Omega_z)^2}{\lambda(\lambda^2 + \Omega_x^2 + \Omega_y^2 + (\omega_L + \Omega_z)^2)} \right\rangle} \,. \tag{4.10}$$

Under the condition of short correlation times and small perturbation fields (*motional narrowing*), i.e.

$$\lambda \gg |\boldsymbol{\Omega}| \tag{4.11}$$

and

$$|\boldsymbol{\Omega}| \ll \omega_L \,, \tag{4.12}$$

the approximations $\omega_L + \Omega_z \approx \omega_L$ and, therefore

$$\left\langle \frac{\lambda^2 + (\omega_L + \Omega_z)^2}{\lambda^2 + \Omega_x^2 + \Omega_y^2 + (\omega_L + \Omega_z)^2} \right\rangle \approx \left(1 + \frac{\langle \Omega_x^2 + \Omega_y^2 \rangle}{\lambda^2 + \omega_L^2}\right)^{-1}$$

can be made. The relaxation rate $1/\theta = 1/\mu_{-1}$ is then given by

$$\frac{1}{\theta} = \frac{\lambda}{\lambda^2 + \omega_L^2} \cdot \langle \Omega_x^2 + \Omega_y^2 \rangle \,. \tag{4.13}$$

The spin lattice relaxation rate derived by GMA in Eq.(13) is equivalent to the result obtained from perturbation theory [1]. In contrast to the latter approach, however, Eq.(10) provides the relaxation rate even without the restriction (11).

### 4.2. Approximation by a Bi-Exponential Function

As a further application of the GMA we will study the approximation of spin lattice relaxation by a bi-exponential function. We will try to find the best approximation to long time behavior, i.e. we choose a (1,3) approximation. All perturbation field forms are assumed to have the same magnitude $\Omega$ and to be cylindric symmetrically distributed in the $x-y$ plane. The Laplace transform is then given by (Eq.(2.20))

$$\hat{M}(s) = \frac{\tilde{s}^2 + \omega_L^2}{\lambda\Omega^2 + s(\tilde{s}^2 + \omega_L^2 + \Omega^2)} \,. \tag{4.14}$$

According to Eq.(6) the parameters $f_i$ and $\Gamma_i$ are determined from the relation

$$f_1 \cdot \Gamma_1^m + f_2 \cdot \Gamma_2^m = \mu_m \,, \tag{4.15}$$

with $m = 0, -1, -2-, -3$. The moments $\mu_n$ are

$$\mu_0 = 1 \,, \tag{4.16}$$

$$\mu_{-1} = \frac{\lambda^2 + \omega_L^2}{\lambda\Omega^2} \,, \tag{4.17}$$

$$\mu_{-2} = \mu_{-1}^2 \cdot \left(1 + \Omega^2 \cdot \frac{\omega_L^2 - \lambda^2}{(\omega_L^2 + \lambda^2)^2}\right), \tag{4.18}$$

$$\mu_{-3} = \mu_{-1}^3 \cdot \left(1 + 2\Omega^2 \cdot \frac{\omega_L^2 - \lambda^2}{(\omega_L^2 + \lambda^2)^2} + \Omega^2 \cdot \frac{\omega_L^2 \Omega^2}{(\lambda^2 + \omega_L^2)^3}\right). \tag{4.19}$$

The rates $\Gamma_{1,2}$ are then calculated to

$$\Gamma_{1,2}^{-1} = \frac{A \pm \sqrt{A^2 - 4BC}}{2B} \,, \tag{4.20}$$

with $A = \mu_0\mu_{-3} - \mu_{-1}\mu_{-2}$, $B = \mu_0\mu_{-2} - \mu_{-1}^2$ and $C = \mu_{-1}\mu_{-3} - \mu_{-2}^2$. The coefficients are

$$f_{1,2} = \pm \frac{\mu_{-1} - \Gamma_{2,1}^{-1}}{\Gamma_1^{-1} - \Gamma_2^{-1}} \,. \tag{4.21}$$

Eqs. (18) and (19) demonstrate that the terms depending on the magnitude of perturbation field are of the order of $\Omega^2/\lambda^2$ and $\Omega^4/\lambda^4$. In the *motional narrowing* limit ($\lambda \gg \Omega$) this results in $\mu_{-2} \to \mu_{-1}^2$ and $\mu_{-3} \to \mu_{-1}^3$. Thus, one obtains $f_1 = f_2 = 1/2$ and $\Gamma_1 = \Gamma_2 = \mu_{-1}^{-1}$, which means that in the *motional narrowing* limit the bi-exponential function con-

verges to a single-exponential function, with the relaxation rate given by the rate of the MRT approximation (s. Eq. (9)).

As an application of the approximation of spin lattice relaxation by a bi-exponential function we dicuss the extreme case of a very slowly fluctuating perturbation field, i.e. we consider a situation opposite to the motional narrowing limit. The fluctuation frequency $\lambda$ is assumed to be smaller than the perturbation frequency $\Omega$, $\lambda = 0.1 \cdot \Omega$. Furthermore we assume that the magnitude of the perturbation field is in the range of the external field $\omega_L$, i.e. $\Omega = \omega_L$. Obviously, this example cannot be treated by a perturbation approach. Spin lattice relaxation is characterized by its frequency spectrum $I(\omega)$, which is determined by $I(\omega) = 1/\pi \cdot \mathrm{Re}(\tilde{M}(i\omega))$.

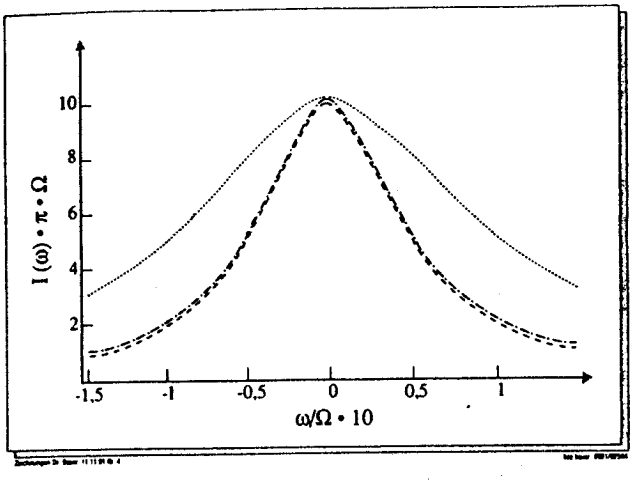


Fig. 2
Frequency spectrum $I(\omega)$ of the spin lattice relaxation for a very slowly flucutating perturbation field $\Omega$. The fluctuation frequency $\lambda$ was assumed to be $\lambda = 0.1 \cdot \Omega$, the magnitude of the perturbation field is equivalent to the one of the external field i.e. $\Omega = \omega_L$. The spectrum of the exact relaxation decay (dashed line) according to Eq. (14), the single exponential approximation (dotted) and the bi-exponential approximation (dashed-dotted)

Fig. 2 shows the frequency spectrum of the exact relaxation process (dashed line) according to Eq. (14) as well as the approximation by a single exponential (MRT) (dotted line) and a bi-exponential function (dashed-dotted line). The frequency spectra were obtained from the Laplace transforms which were derived according to Eq. (5). Obviously the single exponential approach is a very bad approximation in the low frequency range, i.e. the frequencies which are relevant for the long time behavior. In contrast the bi-exponential is an excellent approximation of the exact frequency spectrum in the low frequency range.

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