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Mixed magnetic and quadrupolar relaxation in the presence of a dominant static Zeeman Hamiltonian

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Abstract. We discuss the multi-exponential nuclear magnetization recovery which occurs in spin–lattice relaxation when NMR lines are split by quadrupole interaction. We treat the general situation in which both magnetic and quadrupolar fluctuations are present and consider three cases differing in their initial conditions: (1) a short radio-frequency pulse is applied selectively to one of the transitions; (2) all lines are saturated at once; (3) a selected line is saturated by continuous waves or by means of a long comb of pulses. Exact solutions are presented for spin $I = 1$ and $I = 3/2$, whereas for spin $I = 5/2$, exact solutions are given for special cases and approximate solutions for the general case. The spin $I = 7/2$ case is treated for magnetic fluctuations only. The detailed analysis reveals that the form of the recovery law is surprisingly insensitive to an additional relaxation channel, e.g. quadrupolar fluctuations in the presence of predominantly magnetic fluctuations or vice versa.

1. Introduction

The work presented in this paper has been motivated by the feature of condensed matter NMR experiments that quite often both magnetic and quadrupolar time-dependent interactions are present causing spin–lattice relaxation. The question arises of whether it is possible to deduce, directly from the experiment, the admixture of a weak contribution, for instance due to quadrupolar interaction, to the overall relaxation. In other words, how sensitive is the form of the magnetization recovery law to the two types of interaction?

If the nucleus under consideration has two magnetic isotopes as in the case of copper (^{63}Cu and ^{65}Cu), the admixture can be estimated from the ratio of the relaxation times, T_1. However, if the two contributions have about the same strength and the relaxation law is multi-exponential, one may question whether the ratio T_1 obtained is accurate. Furthermore, is the approximation using a *single* relaxation time meaningful or is it more appropriate to describe the system using *separate* probabilities for the transitions induced by magnetic and quadrupolar fluctuations?

The literature contains mainly calculations of multi-exponential magnetization recovery laws for the case of either *purely* magnetic or *purely* quadrupolar fluctuations, with Andrew and Tunstall [1] being the first to treat the case of a static quadrupolar perturbed Zeeman Hamiltonian (spin $I = 3/2, 5/2$). These calculations were extended to higher spins [2–4] and to the case of a static quadrupolar Hamiltonian [5–8]. MacLaughlin *et al* [9] treated the case of a static quadrupolar Hamiltonian ($\eta = 0$) with mixed fluctuations in a kind of perturbation expansion, whereas Rega [10] presented, for this case, an exact solution in the limit of time approaching zero.

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Since the emergence of high-temperature superconductors, extensive studies have been concerned with the copper relaxation which is dominated by magnetic interaction and in which, in some cases, the presence of a (small) quadrupolar contribution is suspected [11]. In particular, special consideration has been devoted to copper NMR in small external magnetic fields, for which the static Hamiltonian is the sum of a Zeeman term and a quadrupolar term which are of comparable magnitude. This case, in the limit of purely magnetic fluctuations, has been treated by Takigawa *et al* [12] and Horvatić [13].

In this publication we will present calculations for a static quadrupolar perturbed Zeeman Hamiltonian in the presence of mixed magnetic and quadrupolar fluctuations. These were carried out for three cases differing in their initial conditions and for spins $I = 1$, $I = 3/2$ and $I = 5/2$; spin $I = 7/2$ is treated for magnetic fluctuations only. Most of the results are exact; approximate solutions were found for the general case of $I = 5/2$. We analyse the whole parameter space constructed from the probabilities for transitions induced by magnetic and quadrupolar fluctuations. This is a necessity when dealing with single crystals or partially oriented powders, since in these cases the different contributions of the fluctuations depend on the angle that they form with the external magnetic field, $\boldsymbol{B}_0$; i.e. by changing the direction of $\boldsymbol{B}_0$, one samples another part of the parameter space. We also investigated how sensitive the form of the recovery law for the magnetization is to additional fluctuations (e.g. additional quadrupolar fluctuations in the presence of predominantly magnetic fluctuations), in order to determine whether it is possible to extract directly from the recovery law the magnetic and quadrupolar contributions.

2. Basic relations and the master equation

Our starting point is the following Hamiltonian:

$$\mathcal{H}_{\mathrm{tot}} = \mathcal{H}_0 + \mathcal{H}_1(t)$$

where $\mathcal{H}_0 = \mathcal{H}_{\mathrm{Z}} + \mathcal{H}_{\mathrm{Q}}$ describes the time-independent (or 'static') Hamiltonian which comprises the Zeeman interaction, $\mathcal{H}_{\mathrm{Z}}$, with the external magnetic field and the quadrupolar interaction, $\mathcal{H}_{\mathrm{Q}}$, with the electric field gradient (EFG) tensor. $\mathcal{H}_1(t)$ takes into account fluctuations; it is the sum of a magnetic and a quadrupolar contribution:

$$\mathcal{H}_1(t) = \mathcal{H}_{\mathrm{mag}}(t) + \mathcal{H}_{\mathrm{quad}}(t) \tag{1}$$

where

$$\mathcal{H}_{\mathrm{mag}}(t) = -\hbar\gamma_{\mathrm{n}}\boldsymbol{I}\cdot\boldsymbol{h}(t)$$

$$\mathcal{H}_{\mathrm{quad}}(t) = \frac{eQ}{4I(2I-1)}\sum_{k=-2}^{2} V_k(t)T_{2k}(\boldsymbol{I}).$$

Here, $\boldsymbol{I}$ is the nuclear spin operator, $\boldsymbol{h}(t)$ is a fluctuating magnetic field, $V_k(t)$ is a component of the fluctuating EFG and $T_{2k}(\boldsymbol{I})$ are spherical tensor operators [14, 15].

In equation (1), nuclear spin-exchange terms are omitted. If the quadrupolar splitting, due to $\mathcal{H}_{\mathrm{Q}}$, is large compared to the nuclear spin-exchange coupling, the time evolution of the spin–lattice relaxation proceeds by means of direct coupling to the lattice. Cases in which the nuclear spin-exchange terms are important are discussed in references [1, 16].

The relaxation of the spin system towards its thermodynamic equilibrium is described by the so-called master equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{P}(t) = \mathbf{W}\{\boldsymbol{P}(t) - \boldsymbol{P}(0)\}. \tag{2}$$

Here, $\boldsymbol{P}(t)$ is the population vector of the different energy levels with $\boldsymbol{P}(0)$ being the equilibrium value. The relaxation matrix, $\mathbf{W}$, is, in second-order perturbation theory, given by [14]

$$W_{\alpha\beta} \overset{\alpha\neq\beta}{=} \frac{1}{\hbar^2}\int_{-\infty}^{\infty} \mathrm{d}\tau\ \exp(\mathrm{i}\omega_{\alpha\beta}\tau)\overline{\langle\alpha|\mathcal{H}_1(\tau)|\beta\rangle\langle\beta|\mathcal{H}_1(0)|\alpha\rangle}$$

$$W_{\alpha\alpha} = -\sum_{\beta\neq\alpha} W_{\alpha\beta}$$

where $|\alpha\rangle$, $|\beta\rangle$ are eigenstates of $\mathcal{H}_0$ and $\omega_{\alpha\beta} = (\langle\alpha|\mathcal{H}_0|\alpha\rangle - \langle\beta|\mathcal{H}_0|\beta\rangle)/\hbar$ are transition frequencies. Ensemble averages are denoted by $\overline{\langle\cdots\rangle}$.

As long as the eigenfunctions of $\mathcal{H}_0$ can be approximated by the eigenfunctions of a Zeeman Hamiltonian, i.e. $\mathcal{H}_\mathrm{Z} \gg \mathcal{H}_\mathrm{Q}$, the relevant relaxation matrix terms for magnetic and quadrupolar relaxation are given as follows:

$$W_{\alpha\beta}^{\mathrm{mag}} = J(\omega_{\alpha\beta})\{|\langle\alpha|I^+|\beta\rangle|^2 + |\langle\alpha|I^-|\beta\rangle|^2\}$$

$$W_{\alpha\beta}^{\mathrm{quad},1} = J^{(1)}(\omega_{\alpha\beta})\{|\langle\alpha|I^+I_z + I_zI^+|\beta\rangle|^2 + |\langle\alpha|I^-I_z + I_zI^-|\beta\rangle|^2\}$$

$$W_{\alpha\beta}^{\mathrm{quad},2} = J^{(2)}(\omega_{\alpha\beta})\{|\langle\alpha|(I^+)^2|\beta\rangle|^2 + |\langle\alpha|(I^-)^2|\beta\rangle|^2\}.$$

The Js are the spectral densities of the fluctuating fields:

$$J(\omega) = \frac{\gamma_\mathrm{n}^2}{2}\int_{-\infty}^{\infty} \mathrm{d}\tau\ \exp(\mathrm{i}\omega\tau)[h_+, h_-]$$

$$J^{(1,2)}(\omega) = \left(\frac{eQ}{\hbar}\right)^2\int_{-\infty}^{\infty} \mathrm{d}\tau\ \exp(\mathrm{i}\omega\tau)[V_{+1,2}, V_{-1,2}]$$

with

$$[A, B] = (1/2)\overline{(A(\tau)B(0) + B(\tau)A(0))}$$

and $h_\pm = h_x \pm \mathrm{i}h_y$.

If $\mathcal{H}_\mathrm{Z}$ and $\mathcal{H}_\mathrm{Q}$ are of similar magnitude, the situation is more complicated. The case of *purely magnetic fluctuations*, for $\|\mathcal{H}_\mathrm{Z}\| \approx \|\mathcal{H}_\mathrm{Q}\|$, has been treated by various authors [12, 13].

In this paper we will deal with the case in which $\mathcal{H}_\mathrm{Z} \gg \mathcal{H}_\mathrm{Q}$ and make the additional assumption that the spectral densities can be approximated by a single value. This means that the inverse of the correlation time, τ_c^{-1}, of the fluctuating fields is large compared to $\omega_{\alpha\beta}$, that is $\omega_{\alpha\beta}\tau_c \ll 1$. One then obtains

$$J(\omega) \simeq J(0) =: W$$

$$J^{(1,2)}(\omega) \simeq J^{(1,2)}(0) =: W_{1,2}$$

and the resulting transition probabilities become

$$W_{m\to m-1}^{\mathrm{mag}} = W(I+m)(I-m+1) \tag{3}$$

$$W_{m\to m-1}^{\mathrm{quad},1} = W_1\frac{(2m-1)^2(I-m+1)(I+m)}{2I(2I-1)^2} \tag{4}$$

$$W_{m\to m-2}^{\mathrm{quad},2} = W_2\frac{(I+m)(I+m-1)(I-m+1)(I-m+2)}{2I(2I-1)^2}. \tag{5}$$

Our calculations were performed in the high-temperature limit, i.e. for $\hbar\omega_{\alpha\beta} \ll k_BT$, so there is a further simplification: $W_{\alpha\to\beta} \simeq W_{\beta\to\alpha}$. Figure 1 shows sketches of the various transition probabilities which are possible for a spin-5/2 system. We assume the spacings between the levels to be sufficiently unequal to suppress spin-exchange transitions.

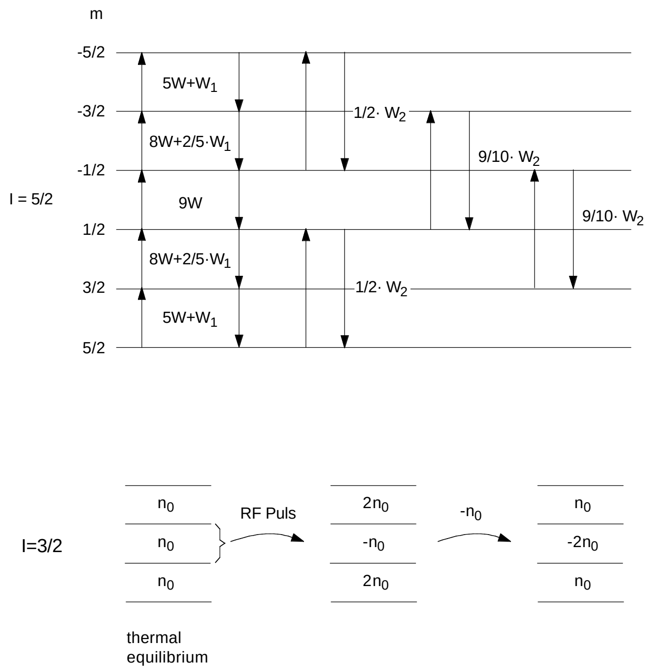

Figure 1. Top: transitions between the spin energy levels effected by magnetic and quadrupolar spin–lattice relaxation processes for $I = 5/2$. Bottom: population differences for the *case I* experiment; see the text.

To solve the master equation, equation (2), it is convenient to introduce some abbreviations. The population of level m is P_m and we define the difference in population between adjacent levels by $P_{m+1/2} = P_{m+1} - P_m$; the equilibrium value of this difference is $n_0 = P_{m+1}(0) - P_m(0)$. The deviation of the population difference from its equilibrium value is denoted by $N_{m+1/2} = P_{m+1/2} - n_0$; the values $N_{m+1/2}$ form the vector $\boldsymbol{N}$.

Given the transition probabilities shown in figure 1, we can write down, in compact form, the following 'reduced' master equation for $\boldsymbol{N}$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{N} = \mathbf{R}\boldsymbol{N} \tag{6}$$

where $\mathbf{R}$ is the reduced relaxation coefficient matrix. The solution of equation (6) is of the form

$$N_j(t) = \sum_i \left[(\mathbf{E}^{\mathrm{T}})^{-1}\boldsymbol{N}(0)\right]_i E_{ij} \exp(t\lambda_i) \tag{7}$$

where λ_i and $\mathbf{E}$ are the eigenvalues and the eigenvector matrix of $\mathbf{R}$, respectively. $\boldsymbol{N}(0)$ is the vector describing the initial condition of the spin system into which it has been brought during a certain preparation period.

Once the $N_j(t)$ are known, the time-dependent magnetization, $M(t)$, is obtained:

$$M(t) = M(\infty)\left[1 - \sum_i a_i \exp(t\lambda_i)\right] \tag{8}$$

and the a_i are given by

$$a_i = -\frac{1}{n_0}\left[(\mathbf{E}^{\mathrm{T}})^{-1}\boldsymbol{N}(0)\right]_j E_{ji} \tag{9}$$

where the index j refers to the corresponding line which will be observed, e.g. the central transition. Usually the irradiated line and the observed line are the same.

In the following sections we will consider three different cases of initial conditions.

Case I: with the system initially in equilibrium, a short radio-frequency (RF) pulse is applied selectively to one of the transitions (the central line or one satellite). This type of experiment is used in an inversion–recovery pulse sequence or for the selective saturation of a single line. Figure 1 illustrates the population difference before (on the left) and just after application (centre) of the $\theta = \pi$ pulse to the central line, where θ is the angle between $\boldsymbol{B}_0$ and $\langle \boldsymbol{M} \rangle$. On the right are shown the *deviations* of the population differences from their equilibrium values. Hence, the elements of the initial condition vector, $\boldsymbol{N}(0)$, are given as follows: $-2n_0$ for the inverted transition and n_0 for the others; e.g. for the inversion of the $I = 3/2$ central line we have $\boldsymbol{N}(0) = n_0[1, -2, 1]$. For this case $\sum_i a_i = 2$, whereas in the general case of a θ-pulse, $\sum_i a_i = 1 - \cos(\theta)$.

Case II: with the system initially in equilibrium, *all* of the lines are saturated at once. These conditions remain the same if one suddenly applies an external magnetic field to a system which has achieved thermal equilibrium in zero magnetic field. In both cases, the initial vector is simply $\boldsymbol{N}(0) = n_0[-1, \ldots, -1]$.

Case III: we assume that a selected line (q) is saturated, for instance by a long comb of pulses such that the comb length $\tau_{\mathrm{tot}} \gg 1/\min(W, W_1, W_2)$ and the pulse spacing τ within the comb satisfies the condition $5T_2 < \tau \ll 1/\max(W, W_1, W_2)$. In contrast to the previous cases, the initial condition is not obtained readily; instead it must be calculated, since the stimulating RF field causes transitions, with transition rate P_{rf}, between the levels $q + 1/2$ and $q - 1/2$. Thus, for calculating the initial condition vector, the rate equation (6) must be extended in the following way:

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{N} = (\mathbf{R} + \mathbf{S})\boldsymbol{N} + n_0\boldsymbol{P}.$$

$\mathbf{S}$ is a square matrix with all elements zero except $S_{q\pm1,q} = P_{\mathrm{rf}}$, $S_{q,q} = -2P_{\mathrm{rf}}$. $\boldsymbol{P}$ is a vector with all elements zero except $P_{q\pm1} = P_{\mathrm{rf}}$, $P_q = -2P_{\mathrm{rf}}$. For dynamic equilibrium, when $\mathrm{d}\boldsymbol{N}/\mathrm{d}t = 0$, we have

$$\boldsymbol{N}(\infty) = -n_0(\mathbf{R} + \mathbf{S})^{-1}\boldsymbol{P}.$$

$\boldsymbol{N}(\infty)$, which becomes the initial condition vector $\boldsymbol{N}(0)$ for solving equation (6), is calculated under the assumption that $P_{\mathrm{rf}} \gg \max(W, W_1, W_2)$.

We close this section by listing in table 1, to the best of our knowledge, all of the references to previous calculations of spin–lattice relaxation rates based on the above formalism. The references are summarized for given values of $\mathcal{H}_0$ and $\mathcal{H}_1$ and various spin values.

3. Exact solutions for $I = 1$

In this section we will present exact solutions of the reduced master equation (6) for the case in which the eigenfunctions of the Hamiltonian $\mathcal{H}_0$ can be approximated by the Zeeman eigenfunctions and $\mathcal{H}_1$ contains both magnetic and quadrupolar interactions.

The rate matrix $\mathbf{R}$ is obtained from equations (3)–(6):

$$\mathbf{R} = \mathbf{R}_{\mathrm{mag}} + \mathbf{R}_{\mathrm{quad}}$$
$$\mathbf{R}_{\mathrm{mag}} = W\begin{bmatrix} -4 & 2 \\ 2 & -4 \end{bmatrix} \qquad \mathbf{R}_{\mathrm{quad}} = \begin{bmatrix} -2(W_1 + W_2) & W_1 - 2W_2 \\ W_1 - 2W_2 & -2(W_1 + W_2) \end{bmatrix}.$$

Table 1. This table contains, as far as we are aware, all of the work on multi-exponential recovery laws due to spin–lattice relaxation carried out so far. The second column indicates whether the unperturbed Hamiltonian is a Zeeman Hamiltonian $\mathcal{H}_Z$ or a quadrupole Hamiltonian $\mathcal{H}_Q$ or the sum of these. The third column indicates the kind of fluctuation treated and the last column the spin for which the calculation was carried out.

Reference	$\mathcal{H}_0$	$\mathcal{H}_1$	I
[1]	$\mathcal{H}_Z$	$\mathcal{H}_{mag}/\mathcal{H}_{quad}$	$3/2, 5/2$
[2]	$\mathcal{H}_Z$	$\mathcal{H}_{quad}$	$7/2, 9/2$
[5]	$\mathcal{H}_Q$, $\eta = 0$	$\mathcal{H}_{quad}$	$5/2$
[3]	$\mathcal{H}_Z$	$\mathcal{H}_{mag}$	$5/2, 7/2$
[9]	$\mathcal{H}_Q$, $\eta = 0$	$\mathcal{H}_{mag} + \mathcal{H}_{quad}$	$3/2, 5/2$
[4]	$\mathcal{H}_Z$	$\mathcal{H}_{quad}$	$3/2$–$9/2$
[6]	$\mathcal{H}_Q$	$\mathcal{H}_{quad}$	$5/2$–$9/2$
[7]	$\mathcal{H}_Q$	$\mathcal{H}_{mag}$	$3/2, 5/2$
[10]	$\mathcal{H}_Q$	$\mathcal{H}_{mag} + \mathcal{H}_{quad}$, $M(t)\|_{t\to 0}$	$7/2$
[12]	$\mathcal{H}_Z + \mathcal{H}_Q$	$\mathcal{H}_{mag}$	$3/2$
[13]	$\mathcal{H}_Z + \mathcal{H}_Q$	$\mathcal{H}_{mag}$	$3/2$
[8]	$\mathcal{H}_Q$	$\mathcal{H}_{quad}$	$7/2$

Table 2. Coefficients a_i of the magnetization recovery law for spin $I = 1$, for different cases (see the text). For case III, $\alpha = W_2/(2W + W_1 + 2W_2)$.

	Case I	Case II	Case III
$\mathbf{N}(0)/n_0$	$[1, -2]$	$[-1, -1]$	$[2\alpha, -1]$
a_1	$3/2$	0	$1/2 + \alpha$
a_2	$1/2$	1	$1/2 - \alpha$

The eigenvalues $\boldsymbol{\lambda}$ and the eigenvector matrix $\mathbf{E}$ of $\mathbf{R}$ are, respectively,

$$\boldsymbol{\lambda} = \begin{bmatrix} -3(2W + W_1) \\ -(2W + W_1 + 4W_2) \end{bmatrix} \qquad \mathbf{E} = \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix}.$$

We now calculate the magnetization recovery laws for the three cases mentioned above. For spin $I = 1$, in contrast to the other cases, there is only one recovery law for a specified initial condition. The a_i-coefficients of equation (9) are given in table 2.

Figure 2 illustrates the results for two situations: (a) vanishing quadrupolar fluctuations, i.e. $W_1 = W_2 = 0$, and (b) strong quadrupolar fluctuations, namely $W_1 = W$, $W_2 = W/2$. We note that even a strong additional quadrupolar relaxation (situation (b)) does not change the form of the curve very much; that means that it is still possible to make all of the curves nearly coincide if a normalized abscissa is used. This is true over a surprisingly large proportion of the parameter space W, W_1, W_2. The reason for this behaviour is that the eigenvalues λ_i are only weak and linear functions of W, W_1, W_2. We will discuss this in section 7.

4. Exact solutions for $I = 3/2$

Like in the case for $I = 1$, we will present exact solutions of the reduced master equation and will consider again the three different cases discussed in the previous section.

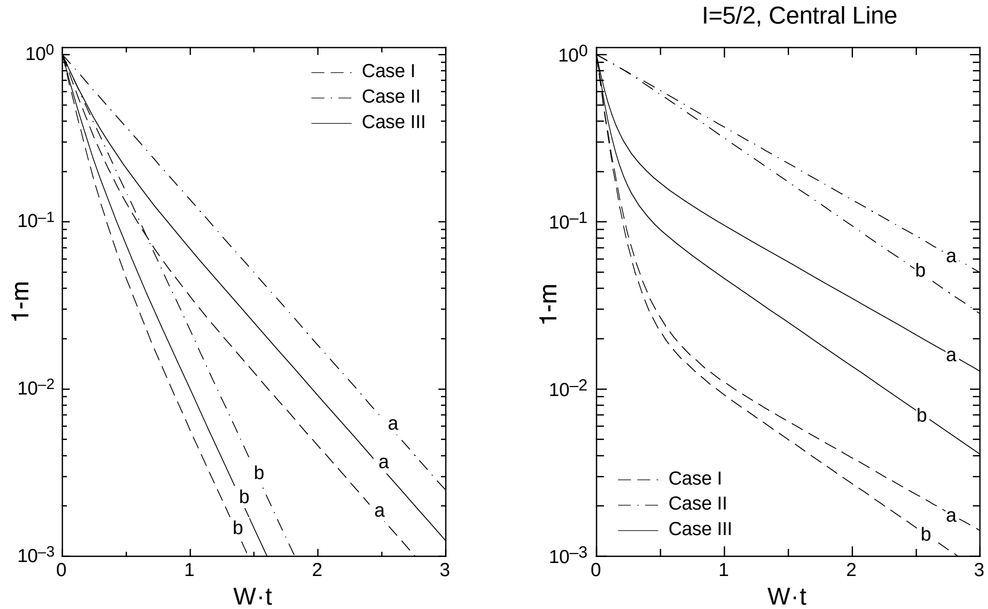

Figure 2. Recovery laws for the normalized magnetization, $m = M(t)/M(\infty)$, for an $I = 1$ (left-hand graph) and an $I = 5/2$ system [17]. The maximum of the function $1 - m$ is normalized to 1. Curves labelled 'a' refer to $W_1 = W_2 = 0$, while the 'b' curves refer to $W_1 = W,\ W_2 = W/2$.

The two terms of the reduced relaxation matrix, **R**, are

$$\mathbf{R}_{\text{mag}} = W \begin{bmatrix} -6 & 4 & 0 \\ 3 & -8 & 3 \\ 0 & 4 & -6 \end{bmatrix}$$

$$\mathbf{R}_{\text{quad}} = \begin{bmatrix} -(2W_1 + W_2) & 0 & W_2 \\ W_1 - W_2 & -2W_2 & W_1 - W_2 \\ W_2 & 0 & -(2W_1 + W_2) \end{bmatrix}.$$

The eigenvalues and the eigenvector matrix of **R** are, respectively

$$\boldsymbol{\lambda} = \begin{bmatrix} -(7W + W_1 + W_2) + \beta \\ -(6W + 2(W_1 + W_2)) \\ -(7W + W_1 + W_2) - \beta \end{bmatrix} \qquad \mathbf{E} = \begin{bmatrix} 1 & (\lambda_1 + 2W_1 + 6W)/(4W) & 1 \\ 1 & 0 & -1 \\ 1 & (\lambda_3 + 2W_1 + 6W)/(4W) & 1 \end{bmatrix}.$$

with

$$\beta = \sqrt{(W_1 - W_2)^2 + 6W(W_1 - W_2) + 25W^2}.$$

We now calculate the magnetization recovery laws for the three cases.

4.1. Case I

The initial condition vector for inversion of the central transition is $\boldsymbol{N}(0) = n_0[1, -2, 1]$. This yields the a_i-coefficients:

$$a_{1c} = \frac{-1}{8W\beta}(7W + (W_1 - W_2) - \beta)(W - (W_1 - W_2) - \beta)$$

$$a_{2c} = 0$$

$$a_{3c} = \frac{1}{8W\beta}(7W + (W_1 - W_2) + \beta)(W - (W_1 - W_2) + \beta).$$

The corresponding values for the satellites are

$$a_{1s} = \frac{-1}{2\beta}(3W + (W_1 - W_2) - \beta)$$
$$a_{2s} = 1$$
$$a_{3s} = \frac{1}{2\beta}(3W + (W_1 - W_2) + \beta).$$

The limiting values (e.g. for $W_{1,2} \to 0$) of the a_i agree with the literature values for all situations.

4.2. Case II

The initial vector is now $\boldsymbol{N}(0) = n_0[-1, -1, -1]$ and the a_i-coefficients become, for the central transition,

$$a_{1c} = \frac{-1}{8W\beta}(W - (W_1 - W_2) - \beta)(5W - (W_1 - W_2) + \beta)$$
$$a_{2c} = 0$$
$$a_{3c} = \frac{1}{8W\beta}(W - (W_1 - W_2) + \beta)(5W - (W_1 - W_2) - \beta)$$

and for the satellites

$$a_{1s} = \frac{1}{2\beta}(5W - (W_1 - W_2) + \beta)$$
$$a_{2s} = 0$$
$$a_{3s} = \frac{-1}{2\beta}(5W - (W_1 - W_2) - \beta).$$

The limiting values (e.g. for $W_{1,2} \to 0$) of the a_i agree with the literature values for all situations.

4.3. Case III

If the *central* line is irradiated, we have $\boldsymbol{N}(0) = n_0[\mu_1, -1, \mu_1]$, with $\mu_1 = W_2/(3W + W_2)$, and the coefficients a_i become

$$a_{1c} = \frac{-1}{8W\beta}((4 - \mu_1)W + \mu_1(W_1 - W_2) - \mu_1\beta)(W - W_1 + W_2 - \beta)$$
$$a_{2c} = 0$$
$$a_{3c} = \frac{1}{8W\beta}((4 - \mu_1)W + \mu_1(W_1 - W_2) + \mu_1\beta)(W - W_1 + W_2 + \beta).$$

For the satellites, the initial condition vector is $\boldsymbol{N}(0) = n_0[-1, \mu_2, \mu_3]$, where $\mu_2 = W_2(3W + 2W_2)/(12W^2 + 14WW_2 + 3W_2^2)$ and $\mu_3 = -W_2^2/(12W^2 + 14WW_2 + 3W_2^2)$, and the coefficients are

$$a_{1s} = \frac{1}{4\beta}((1 - 8\mu_2 - \mu_3)W - (1 - \mu_3)(W_1 - W_2) + (1 - \mu_3)\beta)$$
$$a_{2s} = \frac{1}{2}(1 + \mu_3)$$
$$a_{3s} = \frac{-1}{4\beta}((1 - 8\mu_2 - \mu_3)W - (1 - \mu_3)(W_1 - W_2) - (1 - \mu_3)\beta).$$

The remarks made concerning the case of $I = 1$ apply also to spin 3/2 and will be discussed in section 7.

5. Solutions for spin $I = 5/2$

The two terms of the reduced relaxation matrix, $\mathbf{R}$, are

$$\mathbf{R}_{\mathrm{mag}} = W \begin{bmatrix} -10 & 8 & 0 & 0 & 0 \\ 5 & -16 & 9 & 0 & 0 \\ 0 & 8 & -18 & 8 & 0 \\ 0 & 0 & 9 & -16 & 5 \\ 0 & 0 & 0 & 8 & -10 \end{bmatrix}$$

$$\mathbf{R}_{\mathrm{quad}} = \begin{bmatrix} -\frac{1}{2}(4W_1+W_2) & \frac{2}{5}(W_1+W_2) & \frac{9}{10}W_2 & 0 & 0 \\ \frac{1}{2}(2W_1-W_2) & -\frac{1}{5}(4W_1+7W_2) & 0 & \frac{9}{10}W_2 & 0 \\ \frac{1}{2}W_2 & \frac{2}{5}(W_1-W_2) & -\frac{9}{5}W_2 & \frac{2}{5}(W_1-W_2) & \frac{1}{2}W_2 \\ 0 & \frac{9}{10}W_2 & 0 & -\frac{1}{5}(4W_1+7W_2) & \frac{1}{2}(2W_1-W_2) \\ 0 & 0 & \frac{9}{10}W_2 & \frac{2}{5}(W_1+W_2) & -\frac{1}{2}(4W_1+W_2) \end{bmatrix}.$$

Since the exact solution of the reduced master equation, equation (6), is too complex to provide physical insight, we expanded the eigenvalues as well as the eigenvectors around $(W_1, W_2) = (0, 0)$ and used the exact form for λ_2, λ_4 only. All of the functions involved vary weakly in the subspace (W_1, W_2) around $(0, 0)$; hence the solution is accurate within a few per cent as long as $W_1, W_2 \leqslant 3W$. However, for the case in which $W_1 = W_2$, the eigenvalues and eigenvectors given below reduce to the exact solution.

Within this approximation, the eigenvalues are given by

$$\boldsymbol{\lambda} = \begin{bmatrix} -\left(2W + 0.031\,43W_1 + 0.768\,57W_2 + 0.003\,889\frac{(W_1^2+W_2^2)}{W} - 0.007\,778\frac{W_1W_2}{W}\right) \\ -(13W + (7/5)(W_1+W_2) - \gamma) \\ -\left(12W + 1.84W_1 + 1.46W_2 + 0.039\,14\frac{(W_1^2+W_2^2)}{W} - 0.078\,28\frac{W_1W_2}{W}\right) \\ -(13W + (7/5)(W_1+W_2) + \gamma) \\ -\left(30W + 0.928\,57W_1 + 0.571\,43W_2 + 0.035\,249\frac{(W_1^2+W_2^2)}{W} - 0.070\,498\frac{W_1W_2}{W}\right) \end{bmatrix}$$

with

$$\gamma = \{49W^2 + (19/25)W_1^2 + (61/100)W_2^2 - (22/25)W_1W_2 + (32/5)WW_1 + (17/5)WW_2\}^{1/2}.$$

The corresponding approximated eigenvector matrix is

$$\mathbf{E} = \begin{bmatrix} 1 & 1+\frac{10}{51}\Delta & 1+\frac{100}{358}\Delta & 1+\frac{10}{51}\Delta & 1 \\ -1+\frac{1}{8}\Delta & -\frac{1}{2}-\frac{5}{112}\Delta & -\frac{1}{160}(W_2/W)\Delta & \frac{1}{2}+\frac{3}{28}\Delta & 1 \\ 1 & -\frac{1}{4}+\frac{5}{154}\Delta & -\frac{2}{3}-\frac{4}{59}\Delta & -\frac{1}{4}+\frac{5}{154}\Delta & 1 \\ -1-\frac{1}{20}\Delta & \frac{5}{4}-\frac{1}{56}\Delta & -\frac{1}{160}(W_2/W)\Delta & -\frac{5}{4}+\frac{9}{112}\Delta & 1 \\ 1 & -\frac{5}{2}+\frac{500}{1931}\Delta & \frac{10}{3}-\frac{100}{209}\Delta & -\frac{5}{2}+\frac{500}{1931}\Delta & 1 \end{bmatrix}$$

with $\Delta = (W_1 - W_2)/W$. The coefficients a_i are summarized in table 3.

Table 3. Mixed relaxation for $I = 5/2$. The coefficients are valid in the region where $W_1, W_2 \leqslant 3W$. (We have used the notation $X = 1 + \mu_{12}/\zeta_3$ to help with the layout.)

	Case I		
	Central transition	First satellite	Second satellite
a_1	$2/35 + 0.007\,574\Delta$	$2/35 + 0.001\,58\Delta$	$2/35 + 0.011\,37\Delta$
a_2	0	$3/28 + 0.026\,102\Delta$	$3/7 - 0.079\,264\Delta$
a_3	$16/45 + 0.062\,1838\Delta$	$1/20 - 0.026\,934\Delta$	$4/5 - 0.022\,874\Delta$
a_4	0	$25/28 - 0.010\,478\Delta$	$4/7 + 0.066\,764\Delta$
a_5	$100/63 - 0.069\,7586\Delta$	$25/28 + 0.009\,728\Delta$	$1/7 + 0.024\,004\Delta$
	Case II		
	Central transition	First satellite	Second satellite
a_1	$1 + 0.1179\Delta$	$1 + 0.0346\Delta$	$1 - 0.1615\Delta$
a_2	0	0	0
a_3	-0.1093Δ	-0.0410Δ	0.1640Δ
a_4	0	0	0
a_5	-0.0085Δ	0.0064Δ	-0.0026Δ

We will list below the initial condition vectors, $\boldsymbol{N}(0)$, together with their components, for the cases in which the central line, the inner satellite and the outer satellite are saturated (case III).

(a) Central line

$$\boldsymbol{N}(0) = n_0\left[\frac{\mu_4}{\zeta_1}, \frac{\mu_5}{\zeta_1}, -1, \frac{\mu_5}{\zeta_1}, \frac{\mu_4}{\zeta_1}\right]$$
$$\mu_4 = -9W_2^2$$
$$\mu_5 = 45W_2(10W + 2W_1 + W_2)$$
$$\zeta_1 = 800W^2 + 200WW_1 + 8W_1^2 + 220WW_2 + 32W_1W_2 + 9W_2^2.$$

(b) Inner satellite

$$\boldsymbol{N}(0) = n_0\left[\frac{\mu_6}{\zeta_2}, -1, \frac{\mu_6}{\zeta_2}, \frac{\mu_7}{\zeta_2}, \frac{\mu_8}{\zeta_2}\right]$$
$$\mu_6 = W_2(8000W^3 + 2000W^2W_1 + 80WW_1^2 + 3800W^2W_2 + 720WW_1W_2 + 16W_1^2W_2 + 440WW_2^2 + 46W_1W_2^2 + 9W_2^3)$$
$$\mu_7 = -9W_2^2(10W + 2W_1 + W_2)^2$$
$$\mu_8 = 9W_2^3(10W + 2W_1 + W_2)$$
$$\zeta_2 = 80\,000W^4 + 36\,000W^3W_1 + 4800W^2W_1^2 + 160WW_1^3 + 8200W^2W_2^2 + 46\,000W^3W_2 + 16\,800W^2W_1W_2 + 1680WW_1^2W_2 + 32W_1^3W_2 + 2060WW_1W_2^2 + 108W_1^2W_2^2 + 530WW_2^3 + 64W_1W_2^3 + 9W_2^4.$$

(c) Outer satellite

$$\boldsymbol{N}(0) = n_0\left[-1, \frac{\mu_9}{\zeta_3}, \frac{\mu_{10}}{\zeta_3}, \frac{\mu_{11}}{\zeta_3}, \frac{\mu_{12}}{\zeta_3}\right]$$
$$\mu_9 = W_2(8000W^3 + 2000W^2W_1 + 80WW_1^2 + 3800W^2W_2 + 720WW_1W_2 + 16W_1^2W_2 + 440WW_2^2 + 46W_1W_2^2 + 9W_2^3)$$

Table 3. (Continued)

	Case III
	Central transition
a_1	$\frac{1}{35}\left(9-10\frac{\mu_4}{\zeta_1}-16\frac{\mu_5}{\zeta_1}\right)+\Delta\left(0.029\,94-0.035\,18\frac{\mu_4}{\zeta_1}-0.052\,30\frac{\mu_5}{\zeta_1}\right)$
a_2	0
a_3	$\frac{4}{45}\left(3+5\frac{\mu_4}{\zeta_1}-2\frac{\mu_5}{\zeta_1}\right)+\Delta\left(0.005\,73+0.064\,35\frac{\mu_4}{\zeta_1}+0.050\,72\frac{\mu_5}{\zeta_1}\right)$
a_4	0
a_5	$\frac{10}{63}\left(3-\frac{\mu_4}{\zeta_1}+4\frac{\mu_5}{\zeta_1}\right)-\Delta\left(0.035\,67+0.028\,73\frac{\mu_4}{\zeta_1}-0.001\,58\frac{\mu_5}{\zeta_1}\right)$
	First satellite
a_1	$\frac{1}{35}\left(8-14\frac{\mu_6}{\zeta_2}-8\frac{\mu_7}{\zeta_2}-5\frac{\mu_8}{\zeta_2}\right)+$ $\Delta\left(0.014\,27-0.026\,95\frac{\mu_6}{\zeta_2}+0.000\,02\frac{\mu_7}{\zeta_2}+0.006\,58\frac{\mu_8}{\zeta_2}+0.008\left(\frac{\mu_6}{\zeta_2}-\frac{\mu_8}{\zeta_2}\right)\frac{W_2}{W}\right)$
a_2	$\frac{1}{28}\left(4-5\frac{\mu_6}{\zeta_2}+4\frac{\mu_7}{\zeta_2}+5\frac{\mu_8}{\zeta_2}\right)+$ $\Delta\left(0.0195-0.012\,89\frac{\mu_6}{\zeta_2}+0.0195\frac{\mu_7}{\zeta_2}+0.012\,89\frac{\mu_8}{\zeta_2}\right)$
a_3	$\frac{1}{60}\left(2-\frac{\mu_6}{\zeta_2}-2\frac{\mu_7}{\zeta_2}+5\frac{\mu_8}{\zeta_2}\right)-$ $\Delta\left(0.021\,396-0.015\,86\frac{\mu_6}{\zeta_2}-0.013\,063\frac{\mu_7}{\zeta_2}+0.009\,3146\frac{\mu_8}{\zeta_2}-0.000\,31\left(\frac{\mu_6}{\zeta_2}-\frac{\mu_8}{\zeta_2}\right)\frac{W_2}{W}\right)$
a_4	$\frac{5}{28}\left(2+\frac{\mu_6}{\zeta_2}+2\frac{\mu_7}{\zeta_2}-\frac{\mu_8}{\zeta_2}\right)-$ $\Delta\left(0.019\,497-0.028\,52\frac{\mu_6}{\zeta_2}+0.019\,497\frac{\mu_7}{\zeta_2}+0.028\,517\frac{\mu_8}{\zeta_2}\right)$
a_5	$\frac{5}{84}\left(4+7\frac{\mu_6}{\zeta_2}-4\frac{\mu_7}{\zeta_2}+\frac{\mu_8}{\zeta_2}\right)+$ $\Delta\left(0.007\,13-0.004\,53\frac{\mu_6}{\zeta_2}-0.013\,08\frac{\mu_7}{\zeta_2}+0.018\,359\frac{\mu_8}{\zeta_2}-0.001\,116\left(\frac{\mu_6}{\zeta_2}-\frac{\mu_8}{\zeta_2}\right)\frac{W_2}{W}\right)$
	Second satellite
a_1	$\frac{1}{35}\left(5-8\frac{\mu_9}{\zeta_3}-9\frac{\mu_{10}}{\zeta_3}-8\frac{\mu_{11}}{\zeta_3}-\frac{\mu_{12}}{\zeta_3}\right)-$ $\Delta\left(0.009\,59-0.030\,55\frac{\mu_9}{\zeta_3}-0.041\,89\frac{\mu_{10}}{\zeta_3}-0.044\,839\frac{\mu_{11}}{\zeta_3}-0.034\,591\frac{\mu_{12}}{\zeta_3}+0.000\,804X\frac{W_2}{W}\right)$
a_2	$\frac{1}{14}\left(5-4\frac{\mu_9}{\zeta_3}+4\frac{\mu_{11}}{\zeta_3}+5\frac{\mu_{12}}{\zeta_3}\right)-$ $\Delta\left(0.050\,747-0.022\,23\left(\frac{\mu_9}{\zeta_3}-\frac{\mu_{11}}{\zeta_3}\right)+0.050\,747\frac{\mu_{12}}{\zeta_3}\right)$
a_3	$\frac{1}{15}\left(5+2\frac{\mu_9}{\zeta_3}+6\frac{\mu_{10}}{\zeta_3}+2\frac{\mu_{11}}{\zeta_3}-5\frac{\mu_{12}}{\zeta_3}\right)+$ $\Delta\left(0.022\,698-0.068\,27\frac{\mu_9}{\zeta_3}-0.032\,084\frac{\mu_{10}}{\zeta_3}-0.034\,936\frac{\mu_{11}}{\zeta_3}-0.006\,032\frac{\mu_{12}}{\zeta_3}+0.001\,25X\frac{W_2}{W}\right)$
a_4	$\frac{1}{7}\left(1+2\frac{\mu_9}{\zeta_3}-2\frac{\mu_{11}}{\zeta_3}+\frac{\mu_{12}}{\zeta_3}\right)+$ $\Delta\left(0.031\,997+0.002\,7697\left(\frac{\mu_9}{\zeta_3}-\frac{\mu_{12}}{\zeta_3}\right)+0.031\,997\frac{\mu_{12}}{\zeta_3}\right)$
a_5	$\frac{1}{42}\left(1+4\frac{\mu_9}{\zeta_3}+6\frac{\mu_{10}}{\zeta_3}+4\frac{\mu_{11}}{\zeta_3}-\frac{\mu_{12}}{\zeta_3}\right)+$ $\Delta\left(0.005\,6431+0.012\,717\frac{\mu_9}{\zeta_3}-0.009\,8054\frac{\mu_{10}}{\zeta_3}-0.015\,098\frac{\mu_{11}}{\zeta_3}-0.009\,8098\frac{\mu_{12}}{\zeta_3}-0.000\,446X\frac{W_2}{W}\right)$

$$\mu_{10} = -W_2^2(800W^2 + 200WW_1 + 8W_1^2 + 220WW_2 + 32W_1W_2 + 9W_2^2)$$
$$\mu_{11} = 9W_2^3(10W + 2W_1 + W_2)$$
$$\mu_{12} = -9W_2^4$$
$$\zeta_3 = 128\,000W^4 + 38\,400W^3W_1 + 2880W^2W_1^2 + 64WW_1^3 + 83\,200W^3W_2 + 20\,160W^2W_1W_2 + 1056WW_1^2W_2 + \frac{64}{5}W_1^3W_2 + 16\,240W^2W_2^2 + 2744WW_1W_2^2 + \frac{336}{5}W_1^2W_2^2 + 980WW_2^3 + \frac{392}{5}W_1W_2^3 + 9W_2^4.$$

Figure 2 presents the magnetization recovery curves for the central transition for the three cases I, II and III. Again, the remarks made concerning the case of $I = 1$ apply also to spin 5/2.

Table 4. Pure magnetic relaxation for $I = 7/2$.

	Case I			
	Central transition	First satellite	Second satellite	Third satellite
a_1	1/42	1/42	1/42	1/42
a_2	0	1/42	2/21	3/14
a_3	3/22	2/33	1/66	6/11
a_4	0	18/77	25/154	50/77
a_5	75/182	1/546	200/273	75/182
a_6	0	49/66	49/66	3/22
a_7	1225/858	392/429	98/429	8/429
	Case II			
	Central transition	First satellite	Second satellite	Third satellite
	$a_1 = 1$, others 0			
	Case III			
	Central transition	First satellite	Second satellite	Third satellite
a_1	4/21	5/28	1/7	1/12
a_2	0	5/84	4/21	1/4
a_3	2/11	5/66	1/66	7/22
a_4	0	27/154	15/154	5/22
a_5	20/91	1/1092	80/273	5/52
a_6	0	35/132	7/33	1/44
a_7	175/429	35/143	7/143	1/429

6. Spin $I = 7/2$

If only magnetic fluctuations are present, the reduced relaxation matrix is given by

$$\mathbf{R}_{\mathrm{mag}} = W\begin{bmatrix} -14 & 12 & 0 & 0 & 0 & 0 & 0 \\ 7 & -24 & 15 & 0 & 0 & 0 & 0 \\ 0 & 12 & -30 & 16 & 0 & 0 & 0 \\ 0 & 0 & 15 & -32 & 15 & 0 & 0 \\ 0 & 0 & 0 & 16 & -30 & 12 & 0 \\ 0 & 0 & 0 & 0 & 15 & -24 & 7 \\ 0 & 0 & 0 & 0 & 0 & 12 & -14 \end{bmatrix}.$$

The eigenvalues are

$$\boldsymbol{\lambda} = -W\,[\,2 \quad 6 \quad 12 \quad 20 \quad 30 \quad 42 \quad 56\,]$$

and the corresponding eigenvector matrix is

$$\mathbf{E} = \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ -3 & -2 & -1 & 0 & 1 & 2 & 3 \\ 6 & 1 & -2 & -3 & -2 & 1 & 6 \\ -10 & 5 & 6 & 0 & -6 & -5 & 10 \\ 15 & -20 & 1 & 15 & 1 & -20 & 15 \\ -3 & 7 & -7 & 0 & 7 & -7 & 3 \\ 4 & -14 & 28 & -35 & 28 & -14 & 4 \end{bmatrix}.$$

The coefficients a_i are given in table 4.

7. Discussion

The results of the previous sections have clearly shown that a separation of the total relaxation into its magnetic and quadrupolar contributions is not straightforward since the form of the relaxation law is very robust against additional contributions. We will discuss now the 'worst case', namely how large a certain contribution, either magnetic or quadrupolar, can be without being detected as a contribution to the total relaxation.

As an example, let us assume the following. (i) We 'believe' that a certain system relaxes by pure magnetic fluctuations with a rate $\widetilde{W}$; hence the relaxation time 'seems to be' $T_1 = (2\widetilde{W})^{-1}$. (ii) In reality, however, the system under consideration also has a quadrupolar relaxation channel and therefore the *real* magnetic relaxation, W, is different from $\widetilde{W}$. In other words, we are actually measuring the decay of a magnetization $M(W, W_1, W_2, t)$, which depends on W, W_1 and W_2, although we 'believe' that the magnetization is of the form $M(\widetilde{W}, 0, 0, t)$. We want to know how strong, compared to W, the quadrupolar relaxation rates, W_1, W_2, can be without being revealed experimentally and therefore not revealing that our assumption of 'pure magnetic fluctuations' is incorrect.

A measure of the deviation between the two magnetizations is provided by the following quantity:

$$\Gamma_{\mathrm{m}} = \int_0^{t_{\mathrm{co}}} \mathrm{d}t\ \{M(W, W_1, W_2, t) - M(\widetilde{W}, 0, 0, t)\}^2. \tag{10}$$

We introduced a cut-off time, t_{co}, in order to prevent an overestimation of the tail of the magnetization decay at very large times, because usually only the first three decades of this decay can be measured. We used a value $t_{\mathrm{co}} = 1/(3W)$ although the results are only marginally altered if one shifts t_{co} to even larger times.

The derivative $\partial\Gamma_{\mathrm{m}}/\partial\widetilde{W} = 0$ yields the 'optimal' value $\widetilde{W}_{\mathrm{opt}}$. In figure 3, we have plotted, for the central line for $I = 5/2$, contour lines of $\widetilde{W}_{\mathrm{opt}}/W$ (for the range from 1 to 1.3) in the (W_1, W_2) parameter space. Obviously, $\widetilde{W}_{\mathrm{opt}}$ is a slowly varying function of W_1, W_2. This is also true for the $I = 5/2$ satellites as well as for all $I = 1, 3/2$ lines.

Having obtained $\widetilde{W}_{\mathrm{opt}}$, we define an accuracy function:

$$\varepsilon_{\mathrm{m}} = \begin{cases} 1 & M(W, W_1, W_2, t) - \delta M < M(\widetilde{W}_{\mathrm{opt}}, 0, 0, t) < M(W, W_1, W_2, t) + \delta M \ \forall t \\ 0 & \text{otherwise.} \end{cases}$$

Here, $\delta M = nM(W, W_1, W_2, t = \infty)$ is the typical experimental uncertainty of the magnetization, where n is the relative error.

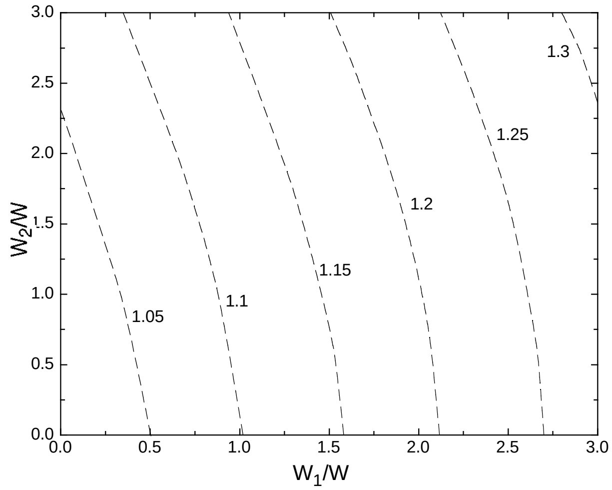

Figure 3. A contour plot of $\widetilde{W}_{\mathrm{opt}}/W$ (case I, for values between 1 and 1.3) in the parameter space (W_1, W_2) for the central line for $I = 5/2$.

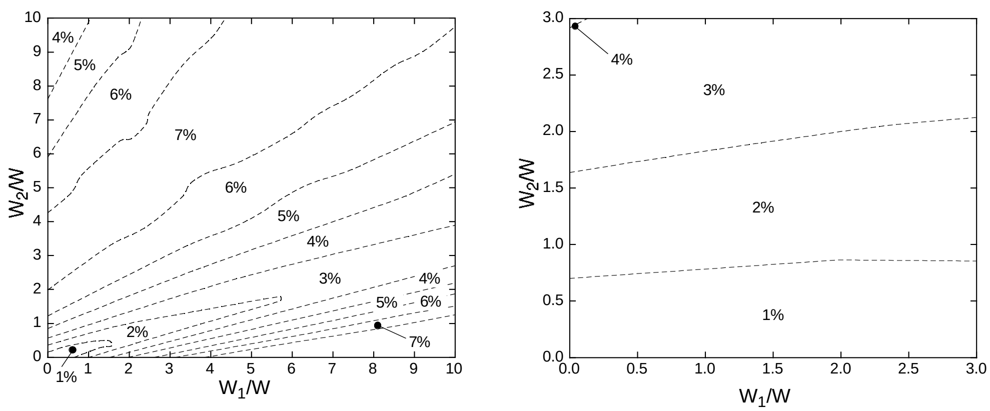

Figure 4. Regions in the (W_1, W_2) parameter space where the relative experimental uncertainty of the magnetization has a certain value, n, given in per cent. Left-hand graph: the central transition for $I = 3/2$; right-hand graph: the central transition for $I = 5/2$; both for case I.

In figure 4, we have drawn the regions in the (W_1, W_2) parameter space, separated by dashed lines, where n has a certain value. Since relative uncertainties of 7% and lower are very often below the usual experimental errors, the regions in figure 4 correspond to those experiments in which the case of mixed relaxation, that is $W_1, W_2 \neq 0$, *cannot* be distinguished from that of 'pure' magnetic relaxation with a relaxation rate $\widetilde{W}_{\mathrm{opt}}$. The results of figure 4 are for the central line for spin $I = 3/2$ (the left-hand part) and spin $I = 5/2$ (the right-hand part); similar plots (not shown here) apply for spin $I = 1$. In the case of spin $I = 5/2$, the situation is even worse, in the sense that the uncertainty region in the (W_1, W_2) parameter space is much larger.

In the most general case of mixed relaxation, the concept of a *single* typical timescale, T_1, breaks down and all of the transition probabilities W, W_1, W_2 must be considered according to equation (8). Since the above analysis revealed that the recovery law is rather insensitive to additional relaxation channels around $(W_1, W_2) = (0, 0)$, an approximation with a single $T_1 = 1/\widetilde{W}_{\mathrm{opt}}$ is still meaningful over an appreciable region of the parameter space (W_1, W_2). This is an acceptable situation if one can allow a relatively low precision and the neglect of details of the relaxation mechanism. The extracted ratio T_1 may yield significant information about the predominant relaxation channel, e.g. its temperature dependence.

The above treatment of a 'presumably' pure magnetic relaxation can be applied to the opposite case of a 'presumably' pure *quadrupolar* relaxation, i.e. we 'believe' that we measure a magnetization $M(0, \widetilde{W}_1, \widetilde{W}_2, t)$ with $\widetilde{W}_1, \widetilde{W}_2$ assumed to be pure quadrupolar relaxation rates, whereas the true magnetization is of the form $M(W, W_1, W_2, t)$. Again, in analogy to equation (10), we define a 'measure of deviation':

$$\Gamma_{\mathrm{q}} = \int_0^{t_{\mathrm{co}}} \mathrm{d}t \ \{M(W, W_1, W_2, t) - M(0, \widetilde{W}_1, \widetilde{W}_2, t)\}^2.$$

with t_{co} as defined before. Γ_{q} becomes minimal for $\widetilde{W}_{1,\mathrm{opt}}$ and $\widetilde{W}_{2,\mathrm{opt}}$.

As above, we define an accuracy function:

$$\varepsilon_{\mathrm{q}} = \begin{cases} 1 & M(W, W_1, W_2, t) - \delta M < M(0, \widetilde{W}_{1,\mathrm{opt}}, \widetilde{W}_{2,\mathrm{opt}}, t) < M(W, W_1, W_2, t) + \delta M \forall t \\ 0 & \text{otherwise.} \end{cases}$$

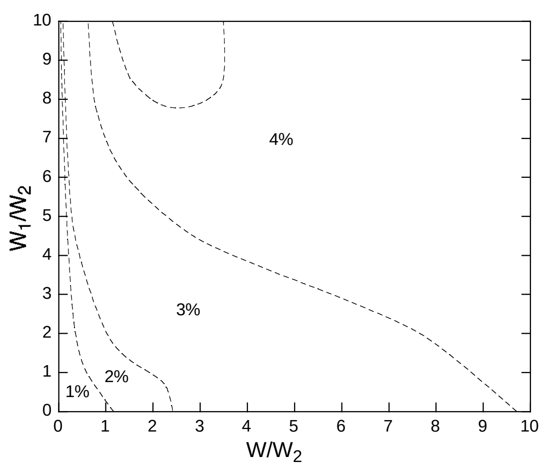

Figure 5. Regions in the (W, W_1) parameter space where the relative experimental uncertainty of the magnetization has a value n given in per cent. The data are for $I = 3/2$, the central line transition, case I.

Figure 5 shows regions in the parameter space (W, W_1), separated by dashed lines, where n has a certain value. The regions where the 'pure' quadrupolar relaxation cannot be distinguished from the situation with $W \neq 0$ are even more pronounced than in the case of almost 'pure' magnetic relaxation. The main reason for this is that there are two 'free' parameters $\widetilde{W}_1, \widetilde{W}_2$ to 'compensate' for the magnetic contribution.

So far, our discussion has shown that, in the presence of mixed relaxation, the two contributions cannot be separated if the experimental errors are in the range 10% or more. We thus conclude that additional information or a different procedure is needed to demonstrate *quantitatively* the existence or non-existence of the non-dominant relaxation. What possibilities do we have?

Since the above considerations refer to a *single* transition, one might suppose that a comparison of *several* transitions provides an alternative. However, we noticed that this procedure does not strongly affect the 'uncertainty' regions.

Another possibility is to use different initial conditions and to compare the respective results. This is what Rega [10] proposed for special cases, although he did not choose the correct initial conditions for case III. One determines the slope of the magnetization at time zero:

$$s_j(W, W_1, W_2) = \left(\frac{\mathrm{d}M}{\mathrm{d}t}\right)^j_{t\to 0} = \sum_i a_i \lambda_i \tag{11}$$

where j labels the chosen initial condition. One then takes the ratio of two such slopes, both expressed in a normalized form:

$$R_{ij} = \left(\frac{s_i(W, W_1, W_2)}{s_i(W, 0, 0)}\right) \Big/ \left(\frac{s_j(W, W_1, W_2)}{s_j(W, 0, 0)}\right). \tag{12}$$

Typical examples are shown in figure 6. For $R_{ij} = 1$, mixed relaxation is indistinguishable from pure magnetic relaxation. For an integer spin, $R_{ij} = 1$ is simply given by $W_2 = 0$ since the magnetic and the quadrupolar $\Delta m = 1$ relaxation channels connect the same energy levels (see equations (3)–(5)). On the other hand, the $(1/2, -1/2)$ transition for a half-integer spin is not allowed for the quadrupolar $\Delta m = 1$ relaxation channel and therefore a non-trivial result, $R_{ij} = 1$, follows.

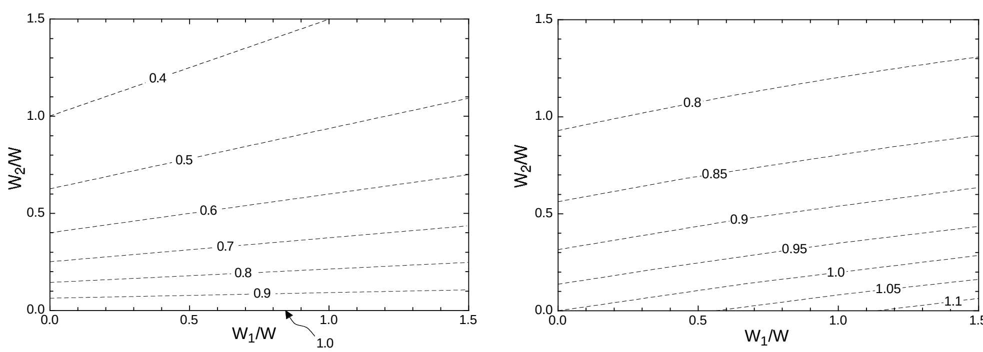

Figure 6. A contour plot of R_{ij} (see equation (12)). Left: $I = 1$ with i and j referring to cases I and II, respectively. Right: $I = 3/2$ and the central transition with i and j referring to cases I and III, respectively.

For spin $I = 1$, there is hope of separating quadrupolar from magnetic relaxation if W_2 is not too small. For half-integer spin, however, the indistinguishable regions for mixed relaxation in the (W_1, W_2) space are almost the same for the R_{ij}-approach as for the fitting of the whole time evolution of the magnetization; this can easily be seen from a comparison of figure 4 and figure 6. Therefore, here again, in general, additional information is needed to separate magnetic from quadrupolar contributions.

8. Summary and conclusions

We have discussed the multi-exponential nuclear magnetization recovery which occurs in spin–lattice relaxation when NMR lines are split by quadrupole interaction. We have treated the case of a static quadrupolar perturbed Zeeman Hamiltonian in the presence of both magnetic and quadrupolar fluctuations under the assumption that the spin-exchange coupling can be omitted and that the eigenfunctions of the static Hamiltonian can be approximated by Zeeman eigenfunctions.

The calculations were carried out for three cases differing in their initial conditions. *Case I:* with the system initially in equilibrium, a short radio-frequency (RF) pulse is applied selectively to one of the transitions (the central line or one satellite). *Case II:* with the system initially in equilibrium, *all* of the lines are saturated at once. *Case III:* a selected line (q) is saturated by continuous waves or by means of a long comb of pulses.

We have presented exact solutions for spin $I = 1$ and $I = 3/2$. For spin $I = 5/2$, we found an exact solution for the case in which the quadrupolar transition probabilities W_1 and W_2 are equal and an approximate solution for the general case of $W_1 \neq W_2$. Spin $I = 7/2$ is treated for magnetic fluctuations only.

We found that, over a surprisingly large region of the (W, W_1, W_2) parameter space, it is almost impossible, within experimental errors, to separate magnetic and quadrupolar contributions to the relaxation. Instead, the 'dominant' contribution determines the time evolution of the recovery law, i.e. the system can be approximately described using a single time constant, T_1^{eff}. In other words, even if the initial assumption of the experimentalist is wrong (let us say, the assumption of pure magnetic fluctuations is made), the extracted ratio T_1 is of the right order of magnitude.

Thus, to test any hypotheses about the origin of the spin–lattice relaxation in the system under consideration, additional information is necessary. This may be provided by the temperature dependence of the relaxation or by the different results obtained for different isotopes of the element considered. If single crystals are available, the relaxation's angular dependence yields valuable information. Because of the different transformation behaviour of the electric field gradient tensor, $V_{\alpha\beta}$, and the external magnetic field, a certain relaxation channel may vanish for a given orientation. For instance, for fluctuations along the principal axis of $V_{\alpha\beta}$, the quadrupolar W_1-channel is exactly zero.

Acknowledgment

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[17] Since we can only present some example graphs in this paper, we provide small programs for different packages (matlab, MapleV, Mathematica, proFit) on the Internet. The address is: http://www.physik.unizh.ch/∼asuter. These programs calculate for a given set (W, W_1, W_2) the corresponding eigenvalues $\boldsymbol{\lambda}$, as well as the coefficients a_i for the initial conditions discussed in this paper.