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## A relationship between nuclear spin relaxation in the laboratory and rotating frames for dipolar and quadrupolar relaxation

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**Abstract.** Density operator theory of nuclear spin relaxation due to fluctuating magnetic dipole or electric quadrupole interactions is based on a differential equation for the density operator which, in the weak collision limit, depends on the spectral density functions of the dipolar or quadrupolar fluctuations. It is shown that the differential equation for relaxation in the rotating frame may be expressed in a similar form to that for relaxation in the laboratory frame. Expressions for magnetization recoveries in the rotating frame can then be simply deduced from the laboratory frame expressions by replacing the spectral density functions in the laboratory frame results by linear combinations of spectral density functions. The method is applied to single-exponential relaxation for the dipolar mechanism and to single- and multiple-exponential relaxation for the quadrupole mechanism for both longitudinal and transverse magnetization recoveries.

### 1. Introduction

The measurement of nuclear spin relaxation caused by fluctuating magnetic fields or electric field gradients at nuclear sites due to diffusional motion has become a common technique for studying diffusion on an atomic scale. The basic theory of the relaxation, which gives the forms of the magnetization recoveries in terms of spectral density functions of the fluctuating fields, has been studied extensively in the weak collision limit for relaxation in the laboratory frame. The weak collision limit corresponds to the situation where many field fluctuations are required to produce significant relaxation and ensures that perturbation theory may be used in the analysis. Relaxation in the laboratory frame conventionally means relaxation of a non-equilibrium magnetization in the presence of a static magnetic field  $B_0$ .

An alternative technique, conventionally called relaxation in the rotating frame, corresponds to relaxation of a non-equilibrium magnetization in the presence of the static magnetic field  $B_0$  together with a transverse magnetic field  $B_1$  rotating at the nuclear Larmor frequency. This paper is concerned with deriving a relationship between the theories of relaxation in the laboratory and rotating frames. It is shown that, under quite general circumstances, expressions for rotating frame relaxation can be obtained from those for laboratory frame relaxation simply by replacing spectral density functions in the laboratory frame expressions by new linear combinations of spectral density functions.

The theory is based on the use of the density operator which provides a general approach to the theory of nuclear spin relaxation. The derivation of the equation

of motion of the density operator in the weak collision limit for laboratory frame relaxation is well described by Abragam (1961). Abragam shows that, for dipolar interactions between like spins, both longitudinal and transverse magnetization recoveries are described by single exponentials and derives expressions for the relaxation rates in terms of the spectral density functions. The situation is more complex for quadrupolar relaxation. The laboratory frame magnetization recoveries are then only describable by single exponentials if the nuclear spin  $I = 1$ , or in the extreme narrowing limit corresponding to very rapid diffusion (Abragam 1961), or if the secular part of the dipolar interaction can maintain a spin temperature (Wolf 1979). Otherwise the magnetization recoveries are linear combinations of exponentials (see, for example, Andrew and Tunstall 1961, Hubbard 1970, Gordon and Hoch 1978, Kelly 1991). Considerable effort has been devoted to understanding the many complications that can then occur and more information can be deduced about the diffusional processes when multiple-exponential behaviour can be observed than is the case for single-exponential recoveries.

The theory of relaxation in the rotating frame has been much less extensively studied. Expressions have been derived for longitudinal magnetization recoveries for like-spin dipolar interactions (Look and Lowe 1966) and for quadrupolar relaxation when a spin temperature exists in the rotating frame (Wolf 1979) but little progress seems to have been made concerning quadrupolar relaxation in the absence of a spin temperature or the theory of transverse magnetization recoveries in the rotating frame. The relationship between relaxation in the laboratory and rotating frames derived in this paper enables the details known from laboratory frame relaxation to be immediately extended to relaxation in the rotating frame for cases such as these.

In section 2, the equation of motion of the density operator in the laboratory frame is described and it is shown that, by applying appropriate transformations, the equation of motion of the density operator in the rotating frame can be expressed in a similar form. Some implications of this result for dipolar and quadrupolar relaxation are discussed in section 3.

## 2. Density operator theory

The equation of motion for the density operator  $\sigma$  of a system of nuclear spins, with Hamiltonian  $\mathcal{H}$ , in a static magnetic field  $B_0$  is

$$\frac{d\sigma}{dt} = \frac{i}{\hbar} [\sigma, \mathcal{H}] \quad (1)$$

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_1(t) \quad (2)$$

where  $\mathcal{H}_z$  is the Zeeman interaction of the spins with the field  $B_0$  and  $\mathcal{H}_1(t)$  is a time-dependent Hamiltonian which causes the relaxation. For electric quadrupolar relaxation the density operator may be taken as the operator for a single spin, if all the spins are identical and relax independently. For magnetic dipolar relaxation the density operator is the operator for a pair of spins with dipolar interaction, if each pair of spins relaxes independently. For both dipolar and quadrupolar relaxation  $\mathcal{H}_1(t)$  may be written in the form (Wolf 1979)

$$\mathcal{H}_1(t) = \sum_q A^{(q)} F^{(q)}(t) \quad (3)$$

where  $A^{(q)}$  are spin operators and  $F^{(q)}(t)$  are lattice variables with a stochastic time dependence. The detailed forms of the Hamiltonians are given in the appendix.

Equation (1) can be transformed to the frame of reference rotating about  $B_0$  with frequency  $\omega_0 = -\gamma B_0$ , where  $\gamma$  is the nuclear gyromagnetic ratio, by applying the operator transformation

$$U' = \exp(i\mathcal{H}_Z t/\hbar)U \exp(-i\mathcal{H}_Z t/\hbar) \quad (4)$$

to each of the operators. The equation of motion then becomes

$$\frac{d\sigma'}{dt} = \frac{i}{\hbar}[\sigma', \mathcal{H}'_1]. \quad (5)$$

A perturbative solution (weak collision limit) of this equation then leads to (Abragam 1961, p 279)

$$\frac{d\sigma'}{dt} = -\frac{1}{2\hbar^2} \sum_{qq', pp'} e^{i(\omega_p^{(q)} + \omega_{p'}^{(q')})t} [A_p^{(q')}, [A_p^{(q)}, \sigma']] J^{(q, q')}(\omega_p^{(q)}) \quad (6)$$

where the spectral density functions  $J^{(q, q')}(\omega)$  are

$$J^{(q, q')}(\omega) = \int_{-\infty}^{\infty} \overline{F^{(q)}(0)F^{(q')}(t)} \cos \omega t dt \quad (7)$$

and the bar denotes an ensemble average. For a Hamiltonian of the form of equation (3),  $\mathcal{H}'_1(t)$  is

$$\mathcal{H}'_1(t) = \sum_q A^{(q)'} F^{(q)}(t) \quad (8)$$

and the  $A_p^{(q)}$  and  $\omega_p^{(q)}$  in equation (6) are defined by

$$A^{(q)'} = \sum_p A_p^{(q)} \exp(i\omega_p^{(q)}t). \quad (9)$$

As discussed by Abragam (pp 286–9), the perturbative solution (6) is only valid for an infinite temperature but can also be applied in the weak-collision and high-temperature limits if  $\sigma'$  is interpreted as the difference between  $\sigma'$  and the equilibrium density operator.

Writing equation (6) in a Zeeman representation gives a set of coupled differential equations for the density matrix elements  $\sigma'_{\alpha, \beta}$  which are the Redfield equations (Redfield 1957). If the terms corresponding to  $\omega_p^{(q)} + \omega_{p'}^{(q')} \neq 0$  are omitted from the Redfield equations the solutions are a linear combination of exponentials with time constants  $T_i$ . It is therefore valid to omit such terms if  $(\omega_p^{(q)} + \omega_{p'}^{(q')})T_i \gg 1$  for all  $i, p, p', q, q'$  since they are then rapidly oscillating terms, which average to zero on a timescale of the smallest  $T_i$ , and will not contribute to relaxation.

For both dipolar and quadrupolar relaxation (see the appendix)

$$A^{(q)'} = A^{(q)} \exp(iq\omega_0 t) \quad (10)$$

so only a single value of  $p$  occurs in equation (9). Equation (6) then becomes, after omitting the oscillating terms,

$$\frac{d\sigma'}{dt} = -\frac{1}{2\hbar^2} \sum_q [A^{(q)}, [A^{(-q)}, \sigma']] J^{(q)}(q\omega_0) \quad (11)$$

where  $J^{(q)}(\omega) = J^{(q,-q)}(\omega)$ . The conditions for the validity of this equation are that  $(q - q')\omega_0 \gg T_i$  for  $q \neq q'$  and also that  $T_i \gg \tau$ , where  $\tau$  is the mean time between fluctuations of  $F^{(q)}(t)$ , which corresponds to the weak collision limit. Equation (11) describes the evolution of the density operator in a frame of reference rotating about  $B_0$  at the resonant frequency  $\omega_0$  and is the basis of evaluating the magnetization recoveries, both longitudinal and transverse, in the laboratory frame for any non-equilibrium magnetization as discussed in the following section.

For relaxation in the presence of the static field  $B_0$ , together with a magnetic field of magnitude  $B_1$  rotating at the resonant frequency  $\omega_0$  transverse to the static field  $B_0$ , the Hamiltonian (2) is replaced by

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_r(t) + \mathcal{H}_1(t) \quad (12)$$

where  $\mathcal{H}_r(t)$  is the Hamiltonian for the interaction of the spins with the rotating field (see the appendix). The density operator in the presence of  $\mathcal{H}_r(t)$  will be denoted by  $\rho$  and the equation of motion of  $\rho$  in the rotating frame of reference is then

$$\frac{d\rho'}{dt} = \frac{i}{\hbar} [\rho', \mathcal{H}'_r + \mathcal{H}'_1] \quad (13)$$

where  $\mathcal{H}'_r$  is independent of  $t$ . Applying the transformation

$$U'' = \exp(i\mathcal{H}'_r t/\hbar) U' \exp(-i\mathcal{H}'_r t/\hbar) \quad (14)$$

to equation (13) gives

$$\frac{d\rho''}{dt} = \frac{i}{\hbar} [\rho'', \mathcal{H}''_1]. \quad (15)$$

This interaction representation describes motion in the doubly rotating frame of a frame rotating about  $B_1$  which is rotating about  $B_0$ . Equation (15) therefore describes relaxation in the rotating frame analogously to equation (5) describing relaxation in the laboratory frame.

The form of  $\mathcal{H}''_1$  may be written as

$$\mathcal{H}''_1 = \sum_q A^{(q)\mu} F^{(q)}(t) \quad (16)$$

$$A^{(q)\mu} = \sum_p B_p^{(q)} \exp(i\Omega_p^{(q)} t) \quad (17)$$

similarly to equations (8) and (9). It is shown in the appendix that the  $B_p^{(q)}$  may be written as linear combinations of  $A^{(q)}$  and that  $\Omega_p^{(q)} = q\omega_0 + p\omega_1$ . The solution of equation (15) may be written down immediately by analogy with equation (6) and is

$$\frac{d\rho''}{dt} = -\frac{1}{2\hbar^2} \sum_{qq', pp'} e^{i(\omega_0(q+q')+\omega_1(p+p'))t} [B_{p'}^{(q')}, [B_p^{(q)}, \rho'']] J^{(q,q')}(q\omega_0 + p\omega_1). \quad (18)$$

In the absence of the oscillating terms corresponding to  $q + q' \neq 0$  and  $p + p' \neq 0$  the solution of equation (18) is again a linear combination of exponentials, with time constants  $T_{i\rho}$ . It is therefore valid to omit the oscillating terms if both  $(q + q')\omega_0 \gg T_{i\rho}$  and  $(p + p')\omega_1 \gg T_{i\rho}$  for all  $q, q', p, p'$  and  $i$ . The second inequality is the most stringent if, as is usually the case,  $\omega_1 \ll \omega_0$ . The validity of equation (18) also requires that  $T_{i\rho} \gg \tau$  corresponding to the weak collision limit. Equation (18) in the absence of the oscillating terms is

$$\frac{d\rho''}{dt} = -\frac{1}{2\hbar^2} \sum_{pq} [B_p^{(q)}, [B_{-p}^{(-q)}, \rho'']] J^{(q)}(q\omega_0 + p\omega_1) \quad (19)$$

similarly to equation (11).

It is helpful to make a further transformation to this equation given by

$$\hat{U} = \exp(i\pi I_y/2) U \exp(-i\pi I_y/2) \quad (20)$$

which corresponds to a rotation of  $\pi/2$  about the  $y$  axis. The reason for this transformation is that it can be shown that (see the appendix) the transformed operators  $\hat{B}_p^{(q)}$  are of the form

$$\hat{B}_p^{(q)} = c_p^{(q)} A^{(p)} \quad (21)$$

where  $c_p^{(q)} = c_{-p}^{(-q)}$  are constants and  $A^{(p)}$  are the operators in equation (3). Applying the transformation (20) to equation (19) and using equation (21) gives

$$\frac{d\rho''}{dt} = -\frac{1}{2\hbar^2} \sum_p [A^{(p)}, [A^{(-p)}, \rho'']] J_p(\omega_1, \omega_0) \quad (22)$$

$$J_p(\omega_1, \omega_0) = \sum_q (c_p^{(q)})^2 J^{(q)}(p\omega_1 + q\omega_0). \quad (23)$$

If  $\omega_1 \ll \omega_0$  the relation (23) reduces to

$$J_0(\omega_1, \omega_0) = \frac{1}{4} J^{(0)}(0) + \frac{9}{8} J^{(2)}(2\omega_0) \quad (24)$$

$$J_1(\omega_1, \omega_0) = \frac{1}{2} J^{(1)}(\omega_0) + \frac{1}{8} J^{(2)}(2\omega_0) \quad (25)$$

$$J_2(\omega_1, \omega_0) = \frac{1}{4} J^{(0)}(2\omega_1) + 2J^{(1)}(\omega_0) + \frac{1}{8} J^{(2)}(2\omega_0). \quad (26)$$

Equation (22) is now identical in form to equation (11) if  $J^{(q)}(q\omega_0)$  is replaced by  $J_q(\omega_1, \omega_0)$ . This is an extremely useful general result. It means that the solution of equation (22) for  $\rho''$ , the density operator in the doubly rotating frame for relaxation in the presence of  $\mathcal{H}_r(t)$ , can be simply deduced from the solution of equation (11) for  $\sigma'$ , the density operator in the singly rotating frame for relaxation in the absence of  $\mathcal{H}_r(t)$ .

The theory of relaxation in the absence of  $\mathcal{H}_r(t)$  has been studied extensively and the general result above means that corresponding results for relaxation in the rotating frame can be deduced from the theory of relaxation in the laboratory frame simply by replacing  $J^{(q)}(q\omega_0)$  in the appropriate expressions by  $J_q(\omega_1, \omega_0)$ . Examples are discussed in the following section in the limit  $\omega_1 \ll \omega_0$  for simplicity. The more general case can be similarly analysed using equation (23).

### 3. Relaxation

In the absence of a rotating field, a spin system which has been disturbed from equilibrium will relax according to

$$\langle I \rangle = \text{Tr}\{\sigma I\} \quad (27)$$

where  $\sigma$  is the laboratory frame density operator. The component of this equation along the direction of the magnetic field  $B_0$ , corresponding to longitudinal relaxation, is

$$\langle I_z \rangle = \text{Tr}\{\sigma I_z\} = \text{Tr}\{\sigma' I_z\} = \sum_{\alpha} \alpha \sigma'_{\alpha, \alpha} \quad (28)$$

where  $\sigma'_{\alpha, \alpha}$  is the Zeeman representation solution of equation (11) for the density operator in this rotating frame of reference. A non-equilibrium magnetization will precess about  $B_0$  at the Larmor frequency and the transverse component will relax, in the rotating frame, according to

$$\langle I_x \rangle' = \text{Tr}\{\sigma' I_x\} = \frac{1}{2} \sum_{\alpha} (Z_{\alpha}^{+} \sigma'_{\alpha+1, \alpha} + Z_{\alpha}^{-} \sigma'_{\alpha-1, \alpha}) \quad (29)$$

where  $Z_{\alpha}^{\pm} = [I(I+1) - \alpha(\alpha \pm 1)]^{1/2}$ .

In the presence of a field  $B_1$  rotating at the resonant frequency, the relaxation of a non-equilibrium spin system, in the frame rotating with  $B_1$ , is

$$\langle I \rangle' = \text{Tr}\{\rho' I\} \quad (30)$$

where  $\rho$  is the rotating frame density operator. The component of this equation along the field  $B_1$ , corresponding to longitudinal relaxation in the rotating frame, is

$$\langle I_x \rangle' = \text{Tr}\{\rho' I_x\} = \text{Tr}\{\rho'' I_x\} = \text{Tr}\{\hat{\rho}'' I_z\} = \sum_{\alpha} \alpha \hat{\rho}''_{\alpha, \alpha} \quad (31)$$

where the primes correspond to the transformations described in section 2. A non-equilibrium magnetization will precess about  $B_1$  at a frequency  $\omega_1 = -\gamma B_1$  and the component transverse to  $B_1$  will relax, in this doubly rotating frame, according to

$$\langle I_z \rangle'' = \text{Tr}\{\rho'' I_z\} = -\text{Tr}\{\hat{\rho}'' I_x\} = -\frac{1}{2} \sum_{\alpha} (Z_{\alpha}^{+} \hat{\rho}''_{\alpha+1, \alpha} + Z_{\alpha}^{-} \hat{\rho}''_{\alpha-1, \alpha}) \quad (32)$$

As shown in section 2, the solution of the equation for  $\hat{\rho}''$  can be obtained simply from that for  $\sigma'$  by appropriate substitutions for the spectral density functions. It therefore follows that, since the pairs of equations (28) and (31), and (29) and (32) are of similar forms, the relaxation expressions in the presence of a rotating field  $B_1$  can be deduced immediately from those in the absence of  $B_1$  provided the initial conditions are also the same. Some examples are given below.

### 3.1. Spin-temperature longitudinal relaxation

If the secular part of the magnetic dipolar interaction between nuclei is sufficiently effective, the spin system can exist in quasi-equilibrium, corresponding to a spin temperature  $T_s$ , as the longitudinal relaxation occurs. The density matrix is then of the form

$$\sigma = \exp(-\mathcal{H}_Z/kT_s) / \text{Tr}\{\exp(-\mathcal{H}_Z/kT_s)\} \quad (33)$$

for a strong Zeeman field (Wolf 1979). The longitudinal relaxation in the absence of a rotating field  $B_1$  is then described by a time-dependent  $T_s$ , with relaxation being caused by the non-secular dipolar interaction or quadrupolar relaxation. Using the result that  $\sigma' = \sigma$  and substituting the high-temperature approximation for the expression (33) into equation (11) yields a first-order differential equation for  $T_s^{-1}(t)$ . Since the longitudinal magnetization is proportional to  $T_s^{-1}$  this analysis shows that the longitudinal magnetization approaches equilibrium according to a single exponential with time constant  $T_1$ , the spin-lattice relaxation time, given by the Habel-Slichter equation (see, for example, Wolf 1979). Evaluating this equation for dipolar relaxation gives

$$\frac{1}{T_1(D)} = \frac{3}{2} \gamma^4 \hbar^2 I(I+1) [J_D^{(1)}(\omega_0) + J_D^{(2)}(2\omega_0)] \quad (34)$$

and for quadrupole relaxation gives

$$\frac{1}{T_1(Q)} = \frac{9}{160} \left( \frac{eQ}{\hbar I} \right)^2 \frac{(2I+3)}{(2I-1)} [J_Q^{(1)}(\omega_0) + J_Q^{(2)}(2\omega_0)] \quad (35)$$

where  $J_D^{(q)}(\omega)$  and  $J_Q^{(q)}(\omega)$  are the dipolar and quadrupolar spectral density functions respectively.

The corresponding expressions for the spin-lattice relaxation time  $T_{1\rho}$  in the rotating frame can be written down immediately, using the substitutions (24) to (26), for the case where a spin temperature exists in the rotating frame. The results are

$$\frac{1}{T_{1\rho}(D)} = \frac{3}{8} \gamma^4 \hbar^2 I(I+1) [J_D^{(0)}(2\omega_1) + 10J_D^{(1)}(\omega_0) + J_D^{(2)}(2\omega_0)] \quad (36)$$

$$\frac{1}{T_{1\rho}(Q)} = \frac{9}{640} \left( \frac{eQ}{\hbar I} \right)^2 \frac{(2I+3)}{(2I-1)} [J_Q^{(0)}(2\omega_1) + 10J_Q^{(1)}(\omega_0) + J_Q^{(2)}(2\omega_0)]. \quad (37)$$

The dipolar expression (36) agrees with the result obtained by Look and Lowe (1966).

### 3.2. Dipolar relaxation

An alternative analysis of relaxation which does not require the assumption of a spin temperature is due to Abragam (1961). This approach uses the equation of motion for the density operator to develop a differential equation for an observable and can be applied to both longitudinal and transverse dipolar relaxation. The longitudinal relaxation result is identical to the spin-temperature theory. The transverse relaxation,



in the absence of a rotating field, is also described by a single-exponential recovery for like spins, with time constant  $T_2$ , the transverse relaxation time, given by

$$\frac{1}{T_2(D)} = \frac{3}{8} \gamma^4 \hbar^2 I(I+1) [J_D^{(0)}(0) + 10J_D^{(1)}(\omega_0) + J_D^{(2)}(2\omega_0)]. \quad (38)$$

As expected physically, this is identical to the expression for  $T_{1\rho}^{-1}(D)$  when  $\omega_1 = 0$ .

Longitudinal relaxation in the rotating frame is achieved experimentally by applying a  $\pi/2$  pulse which rotates the equilibrium magnetization through  $\pi/2$  from the direction of  $B_0$  and then phase-shifting the  $B_1$  field to achieve spin locking. The magnetization in the rotating frame then relaxes along the direction of  $B_1$ . If the phase-shift of the  $B_1$  field is not  $\pi/2$ , the magnetization in the rotating frame will precess about  $B_1$  and relaxation of magnetization component transverse to  $B_1$  will occur. The time constant for this single-exponential relaxation is  $T_{2\rho}(D)$ , the transverse relaxation time in the rotating frame. The expression for it follows from equation (38) by making the substitutions given by equations (24) to (26). The result is

$$\frac{1}{T_{2\rho}(D)} = \frac{3}{32} \gamma^4 \hbar^2 I(I+1) [J_D^{(0)}(0) + J_D^{(0)}(2\omega_1) + 28J_D^{(1)}(\omega_0) + 10J_D^{(2)}(2\omega_0)]. \quad (39)$$

### 3.3. Quadrupolar relaxation

It is well known that, in the absence of a spin temperature, the magnetization recovers in a static magnetic field  $B_0$  may be a linear combination of exponentials for quadrupolar relaxation. The Redfield equations obtained by writing equation (11) in a Zeeman representation, give a set of  $(2I+1)^2$  coupled linear differential equations for the density matrix elements  $\sigma'_{\alpha,\beta}$ . The solution of these equations is a linear combination of exponentials with coefficients determined by initial conditions corresponding to the manner in which the spin system is disturbed from equilibrium. The magnetization recoveries may then be obtained from equations (28) and (29).

In the absence of a static quadrupole interaction the Zeeman energy levels are equally spaced and the entire magnetization may be disturbed from equilibrium and its recovery observed. There are then only  $I + \frac{1}{2}$  contributing exponentials for half-integral  $I$  and  $I$  exponentials for integral  $I$  (Hubbard 1970).

For  $I = 1$  the result for longitudinal relaxation is the same as the spin-temperature result and the spin-lattice relaxation times in the laboratory and rotating frames are given by equations (35) and (37) respectively. The transverse relaxation in the laboratory frame has a relaxation time given by (Hubbard 1970)

$$\frac{1}{T_2(Q)} = \frac{9}{128} \left( \frac{eQ}{\hbar} \right)^2 [J_Q^{(0)}(0) + 10J_Q^{(1)}(\omega_0) + J_Q^{(2)}(2\omega_0)]. \quad (40)$$

Making the substitutions given by equations (24) to (26) then gives the transverse relaxation time in the rotating frame as

$$\frac{1}{T_{2\rho}(Q)} = \frac{9}{512} \left( \frac{eQ}{\hbar} \right)^2 [J_Q^{(0)}(0) + J_Q^{(0)}(2\omega_1) + 28J_Q^{(1)}(\omega_0) + 10J_Q^{(2)}(2\omega_0)] \quad (41)$$

For  $I = \frac{3}{2}$  the laboratory frame longitudinal and transverse magnetizations approach equilibrium according to (Hubbard 1970)

$$\langle I_z \rangle = 0.8e^{-a_1 t} + 0.2e^{-a_2 t} \quad (42)$$

$$\langle I_x \rangle' = 0.6e^{-b_1 t} + 0.4e^{-b_2 t} \quad (43)$$

respectively when the entire magnetization is disturbed from equilibrium and its recovery observed. The parameters  $a_i$  and  $b_i$  are

$$a_1 = \frac{3}{32} \left( \frac{eQ}{\hbar} \right)^2 J_Q^{(2)}(2\omega_0) \quad (44)$$

$$a_2 = \frac{3}{8} \left( \frac{eQ}{\hbar} \right)^2 J_Q^{(1)}(\omega_0) \quad (45)$$

$$b_1 = \frac{1}{32} \left( \frac{eQ}{\hbar} \right)^2 [J_Q^{(0)}(0) + 6J_Q^{(1)}(\omega_0)] \quad (46)$$

$$b_2 = \frac{3}{64} \left( \frac{eQ}{\hbar} \right)^2 [4J_Q^{(1)}(\omega_0) + J_Q^{(2)}(2\omega_0)]. \quad (47)$$

The corresponding magnetization expressions in the rotating frame have the same coefficients but the  $a_i$  and  $b_i$  become

$$a_{1\rho} = \frac{3}{256} \left( \frac{eQ}{\hbar} \right)^2 [2J_Q^{(0)}(2\omega_1) + 16J_Q^{(1)}(\omega_0) + J_Q^{(2)}(2\omega_0)] \quad (48)$$

$$a_{2\rho} = \frac{3}{64} \left( \frac{eQ}{\hbar} \right)^2 [4J_Q^{(1)}(\omega_0) + J_Q^{(2)}(2\omega_0)] \quad (49)$$

$$b_{1\rho} = \frac{1}{256} \left( \frac{eQ}{\hbar} \right)^2 [2J_Q^{(0)}(0) + 24J_Q^{(1)}(\omega_0) + 15J_Q^{(2)}(2\omega_0)] \quad (50)$$

$$b_{2\rho} = \frac{3}{512} \left( \frac{eQ}{\hbar} \right)^2 [2J_Q^{(0)}(2\omega_1) + 32J_Q^{(1)}(\omega_0) + 5J_Q^{(2)}(2\omega_0)]. \quad (51)$$

In the extreme narrowing limit  $\omega_0 \rightarrow 0$  and  $\omega_1 \rightarrow 0$  all of the  $a_i, b_i, a_{i\rho}, b_{i\rho}$  become identical for a polycrystal for which the spectral density functions  $J^{(0)}, J^{(1)}, J^{(2)}$  are in the ratio 6:1:4.

For  $I > \frac{3}{2}$  the coefficients of the exponentials, as well as their exponents, are dependent on the spectral density functions. An analytic solution for relaxation in the laboratory frame is possible for  $I = 2$  (Körblein *et al* 1985) but for  $I > 2$  the analysis must be accomplished numerically. Detailed results for the laboratory frame have been obtained by Gordon and Hoch (1978) and Kelly (1991). All of these results can be extended to the corresponding relaxation in the rotating frame by employing the spectral density substitutions given by equations (24) to (26).

If the quadrupolar nuclei are in non-cubic environments, so that there is a static quadrupole interaction in the spin Hamiltonian, the situation is much more complex. The general analysis of the laboratory frame relaxation for this case has not

been achieved because of the difficulties associated with manipulating exponentials of the sum of non-commuting operators, but a general feature of the results is that there are additional exponentials which contribute to the magnetization recoveries. The presence of the static quadrupole interaction destroys the equal spacing of the Zeeman energy levels which has two important consequences. Firstly, it inhibits the secular dipolar interaction from maintaining a spin temperature, and so the multiple-exponential recoveries are more likely. Secondly, it allows selective excitation and observation of particular pairs of energy levels (Andrew and Tunstall 1961, Gordon and Hoch 1978, Kelly *et al* 1989, 1991, Kelly 1991). A common approximation in the analysis in this case is to take account of the static quadrupole effects in determining the initial conditions and which levels are observed in magnetization recoveries, but to neglect the effect of the static quadrupole interaction on the relaxation and to neglect the additional exponentials. This has the effect of giving the same exponentials as in the absence of a static quadrupole interaction, but with different coefficients. Such cases which are relevant in the rotating frame could also easily be deduced from the laboratory frame results by using the spectral density substitution relations derived in section 2.

#### 4. Discussion

In the weak collision limit the recoveries of the longitudinal and transverse magnetizations are all either single exponentials or a linear combination of exponentials, with time constants  $T_i$ , for relaxation in both the laboratory and rotating frames. The reciprocal time constants  $T_i^{-1}$  are linear combinations of spectral density functions  $J^{(q)}(\omega)$ . For a polycrystal the spectral density functions for  $q = 0, 1, 2$  are in the ratios 6:1:4 but this is not the case for single crystals and they then also depend on the direction of the static field  $B_0$  (Sholl 1986). It should also be noted that the dipolar and quadrupolar spectral density functions are different for the same diffusion mechanism. This is because the dipolar functions describe the relative motion of a pair of interacting spins and are therefore two-particle functions, whereas the quadrupolar functions describe the correlation between the total electric field gradient at a nuclear site at different times and the product of the sums of field gradient components results in two- and three-particle functions (Sholl 1967).

The usual procedure in analysing nuclear spin relaxation data is to use a spectral density function obtained either numerically or analytically (see for example, Sholl 1988) for some diffusion model and to deduce the parameters in the diffusion model from the data. It would be useful though to be able to deduce the spectral density functions directly from the spin relaxation data and attempts at doing this have been made by Halstead *et al* (1982). The observation of single-exponential magnetization recoveries in the rotating frame and multiple-exponential recoveries in both the laboratory and rotating frames are especially valuable because they can allow particular spectral density functions to be obtained directly. The connection between the laboratory and rotating frame relaxation expressions derived here provides the theoretical basis for analysing the rotating frame results. The analysis is particularly simple for  $I = \frac{3}{2}$ .

The observation of multiple-exponential recoveries requires the absence of a spin temperature. This will be the case if the energy conserving flip-flop dipolar interaction between pairs of spins is weak compared with the quadrupolar interactions causing

the relaxation. An example is if the dipolar interaction is between unlike spins since the flip-flop process does not then conserve energy. An extreme case of this is  $\beta$ -NMR (Ackermann *et al* 1983) in which relaxation of a transmuted nucleus is studied.

### Appendix. Hamiltonians

For electric quadrupolar relaxation the one-particle Zeeman Hamiltonian of a spin  $I$  in a magnetic field  $B_0$  is

$$\mathcal{H}_Z = \hbar\omega_0 I_z \quad (52)$$

where  $\omega_0 = -\gamma B_0$  and  $\gamma$  is the nuclear gyromagnetic ratio. The relaxation Hamiltonian  $\mathcal{H}_1(t)$  is

$$\mathcal{H}_1(t) = \sum_{q=-2}^2 A^{(q)}(I) F^{(q)}(t). \quad (53)$$

The spin operators  $A^{(q)}(I)$  are

$$A^{(0)} = -\frac{\delta_Q}{2}(3I_z^2 - I^2) \quad (54)$$

$$A^{(\pm 1)} = \frac{3}{2}\delta_Q(I_z I_{\pm} + I_{\pm} I_z) \quad (55)$$

$$A^{(\pm 2)} = \frac{3}{4}\delta_Q I_{\pm}^2 \quad (56)$$

where  $\delta_Q = -eQ/4I(2I-1)$  and  $Q$  is the nuclear electric quadrupole moment. The lattice functions  $F^{(q)}(t)$  are

$$F^{(0)} = -2(V_{zz} - \frac{1}{3}\nabla^2 V) \quad (57)$$

$$F^{(\pm 1)} = \frac{2}{3}(V_{zx} \mp iV_{zy}) \quad (58)$$

$$F^{(\pm 2)} = \frac{4}{3}[\frac{1}{2}(V_{xx} - V_{yy}) \mp iV_{xy}] \quad (59)$$

where  $V_{ij}$  are the electric field gradient components at a nuclear site relative to an orthogonal set of axes  $x, y, z$  with the  $z$  axis along the direction of the magnetic field  $B_0$ .

For magnetic dipolar relaxation the two-particle Zeeman Hamiltonian for a pair of identical spins  $I$  and  $S$  is

$$\mathcal{H}_Z = \hbar\omega_0(I_z + S_z). \quad (60)$$

The relaxation Hamiltonian  $\mathcal{H}_1(t)$  is

$$\mathcal{H}_1(t) = \sum_{q=-2}^2 A^{(q)}(I, S) F^{(q)}(t). \quad (61)$$

The spin operators  $A^{(q)}(I, S)$  are

$$A^{(0)} = -\frac{\delta_D}{2}(3I_x S_x - I \cdot S) \quad (62)$$

$$A^{(\pm 1)} = \frac{3\delta_D}{2}(I_x S_{\pm} + I_{\pm} S_x) \quad (63)$$

$$A^{(\pm 2)} = \frac{3}{4}\delta_D I_{\pm} S_{\pm} \quad (64)$$

where  $\delta_D = -\gamma^2 \hbar^2$ . The lattice functions  $F^{(q)}(t)$  are

$$F^{(0)} = r^{-3}(1 - 3 \cos^2 \theta) \quad (65)$$

$$F^{(\pm 1)} = r^{-3} \sin \theta \cos \theta \exp(\pm i\phi) \quad (66)$$

$$F^{(\pm 2)} = r^{-3} \sin^2 \theta \exp(\pm 2i\phi) \quad (67)$$

where  $\mathbf{r} = (r, \theta, \phi)$  is the internuclear vector relative to the direction of the magnetic field  $B_0$ . The above forms of the Hamiltonians are chosen, following Wolf (1979), to express the dipolar and quadrupolar  $\mathcal{H}_1(t)$  in similar forms. If the electric field gradient in equations (57) to (59) was due to a point charge the expressions (57) to (59) become proportional to the expressions (65) to (67).

The transformation of  $\mathcal{H}_1(t)$  to the rotating frame leads to the result

$$A^{(q)'} = A^{(q)} \exp(iq\omega_0 t) \quad (68)$$

for both the one-spin quadrupolar operators and two-spin dipolar operators (Abragam 1961, Wolf 1979).

The one-particle Hamiltonian  $\mathcal{H}_r(t)$  for a single nucleus interacting with a rotating magnetic field of magnitude  $B_1$  transverse to the static field is

$$\mathcal{H}_r(t) = \hbar\omega_1(I_x \cos \omega_0 t + I_y \sin \omega_0 t) = \hbar\omega_1 \exp(-i\omega_0 t I_z) I_x \exp(i\omega_0 t I_z) \quad (69)$$

where  $\omega_1 = -\gamma B_1$  and  $\omega_0$  is the resonant frequency. In the rotating frame of reference  $\mathcal{H}_r(t)$  therefore becomes  $\mathcal{H}_r'(t) = \hbar\omega_1 I_x$ . These results are also valid for the two-particle form of  $\mathcal{H}_r(t)$  if each operator  $I_i$  is replaced by  $I_i + S_i$ .

The transformation of  $A^{(q)}$  to the doubly rotating frame for the one-particle Hamiltonian is

$$A^{(q)''} = \exp(i\mathcal{H}_r' t / \hbar) A^{(q)'} \exp(-i\mathcal{H}_r' t / \hbar) = \exp(i\omega_1 t I_x) A^{(q)} \times \exp(-i\omega_1 t I_x) \exp(iq\omega_0 t). \quad (70)$$

Evaluating this expression gives

$$A^{(q)''} = \sum_{p=-2}^2 B_p^{(q)} \exp(i\Omega_p^{(q)} t) \quad (71)$$

where  $\Omega_p^{(q)} = q\omega_0 + p\omega_1$  and  $B_p^{(q)} = (-1)^{p-q} B_p^{(-q)}$ . The  $B_p^{(q)}$  can be expressed as linear combinations of  $A^{(q)}$  and are

$$B_0^{(0)} = \frac{2}{3} B_0^{(2)} = \frac{1}{4} (A^{(0)} + A^{(2)} + A^{(-2)}) \quad (72)$$

$$\pm B_{\pm 1}^{(1)} = -2B_{\pm 1}^{(2)} = \pm \frac{1}{4} (A^{(1)} + A^{(-1)}) - \frac{1}{2} (A^{(2)} - A^{(-2)}) \quad (73)$$

$$B_{\pm 2}^{(0)} = \pm \frac{1}{2} B_{\pm 2}^{(1)} = -2B_{\pm 2}^{(2)} = \frac{3}{8} A^{(0)} \pm \frac{1}{8} (A^{(1)} - A^{(-1)}) - \frac{1}{8} (A^{(2)} + A^{(-2)}) \quad (74)$$

$$B_{\pm 1}^{(0)} = B_0^{(1)} = 0. \quad (75)$$

A similar evaluation for the two-particle Hamiltonian for dipolar interactions gives the same result.

The transformation of  $B_p^{(q)}$  by a rotation of  $\pi/2$  about the  $y$  axis is

$$\hat{B}_p^{(q)} = \exp(i\pi I_y/2) B_p^{(q)} \exp(-i\pi I_y/2) \quad (76)$$

Evaluating this transformation for each of the terms in the equations (72) to (75) gives the simple result

$$\hat{B}_p^{(q)} = c_p^{(q)} A^{(p)} \quad (77)$$

where  $c_p^{(q)}$  are constants given by  $c_p^{(q)} = c_{-p}^{(-q)}$  and the matrix

$p \backslash q$	-2	-1	0	1	2
0	-3/4	0	-1/2	0	-3/4
1	-1/4	-1/2	0	-1/2	1/4
2	1/4	1	-1/2	1	1/4.

An explicit expression for  $c_p^{(q)}$  is

$$c_p^{(q)} = \text{Tr}\{\hat{A}^{(q)} A^{(-p)}\} / \text{Tr}\{A^{(p)} A^{(-p)}\} \quad (78)$$

which is obtained by using equation (71) at  $t = 0$ , the transformation (76), equation (77) and the result that  $\text{Tr}\{A^{(p)} A^{(p')}\}$  is zero for  $p \neq p'$ .

The above results are valid for both dipolar and quadrupolar interactions and equation (78) is valid more generally for any Hamiltonian of the form of equation (53) and for which  $\text{Tr}\{A^{(p)} A^{(p')}\}$  is zero for  $p \neq p'$ .

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