Nuclear spin relaxation due to motion on inequivalent sites

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Abstract.   It was shown by Jaroszkiewicz and Strange in 1985 that nuclear spin relaxation due to dipolar coupling between like spins diffusing on inequivalent sites involves magnetization recoveries which are linear combinations of exponentials. An alternative approach to obtaining the relevant rate equations is described, which starts from the well known expressions for dipolar relaxation of pairs of spins. The method can be extended easily to other inequivalent-site systems involving both like and unlike diffusing spins. The results for the multiexponential magnetization recoveries can be calculated by routine numerical methods.

1. Introduction

The basic theory of nuclear spin relaxation due to magnetic dipolar coupling between pairs of spins undergoing relative diffusion is well known (Abragam 1961). For like spins moving on equivalent crystal sites the resultant magnetization recovery is an exponential, while for unlike spins the magnetization recoveries of each spin species are, in general, sums of two exponentials. It has been shown by Jaroszkiewicz and Strange (1985) (to be referred to as JS) that the magnetization recoveries of like spins diffusing on inequivalent sites also involve a sum of exponentials. There are therefore several relaxation rates possible corresponding to the exponents of the various exponentials. A relaxation rate can also show more complicated behaviour as a function of temperature than is the case for diffusion on equivalent sites, with more than a single maximum possible. The theory was applied by JS to analyse relaxation data for the ionic conductor LaF_3 in which the mobile fluorine anions diffuse on several inequivalent sites. Another example of a single nuclear species diffusing on inequivalent sites is the diffusion of hydrogen in some complex metal–hydrogen systems (Barnes 1997). In such cases the diffusing spins may also have significant dipolar interaction with another species of fixed spins, such as F–La interactions in LaF_3 and H–metal nuclei interactions in metal–hydrogen systems. It is sometimes possible to measure the magnetization recoveries for both the diffusing and the fixed nuclear species separately.

In order to deduce information about the possible jump rates from the experimental data it is necessary to relate the magnetization recoveries to the spectral density functions of the fluctuations of the dipolar fields. The analysis used by JS was a first-principles development of these expressions using time-dependent perturbation theory. An aim of this paper is to show that such results can also be obtained more directly from the Abragam expressions for relaxation of a pair of interacting like or unlike spins. The magnetization components are sums of the contributions from expectation values of the corresponding spin components on each type of site. These expectation values are assumed to be simple superpositions of the relaxation due to all possible interactions with other spins and include jumps between

inequivalent sites which change the site type of the magnetization to which they contribute. Each contribution to the relaxation from spin pairs is obtained from the basic Abragam expressions. This approach gives a direct physical interpretation of the processes involved. It also provides a straightforward method of extending the theory to other situations.

2. Derivation of rate equations

The system to be considered is a set of mobile nuclear species I diffusing on a set of crystal sites which can be subdivided into subsets of inequivalent sites $\alpha = 1, 2, \ldots, n$. As shown by JS, the rate equations for the components of magnetization M^α of the I spins on the α-sublattice are of the form

$$\frac{\mathrm{d}M^\alpha}{\mathrm{d}t} = -\sum_{\beta=1}^{n} C_{\alpha\beta} M^\beta \qquad \alpha = 1, 2, \ldots, n \tag{1}$$

where the time-independent coefficients $C_{\alpha\beta}$ depend on the spectral density functions of the magnetic dipolar fluctuations and the rates of jumps between sublattices. The notation M here refers to the longitudinal component M_z, or transverse component M_x of the magnetization in the laboratory frame, or the component M_x in the rotating frame in a spin-locking field. For a single set of equivalent sites the coefficient C becomes the corresponding relaxation rate T_1^{-1}, T_2^{-1} or $T_{1\rho}^{-1}$, respectively, for each of these cases.

There are two contributions to changes in magnetization in (1): the physical jumping of spins between inequivalent sites, and the relaxation induced by the magnetic dipolar fluctuations between pairs of spins. The contributions to $C_{\alpha\beta}$ from the physical jumping are

$$C_{\alpha\beta} = \begin{cases} -\Gamma_{\beta\alpha} & \alpha \neq \beta \\ \sum_{\beta' \neq \alpha} \Gamma_{\alpha\beta'} & \alpha = \beta \end{cases} \tag{2}$$

where $\Gamma_{\alpha\beta}$ is the jump frequency for a spin from a particular site of type α to any site of type β.

The contributions to the coefficients $C_{\alpha\beta}$ from the dipolar fluctuations can be obtained from the well known expressions for relaxation of like- and unlike-spin pairs (Abragam 1961) provided the interaction of I spins on different sublattices are deduced from the expressions for unlike spins. The Abragam expressions provide differential equations for the expectation values of the components of the spin operators. These equations can be expressed in the form of (1) by summing over the appropriate sites and expressing the equations in terms of magnetization components. The interactions of spins on different sublattices need to be treated as unlike spins so that the magnetization on each sublattice can be calculated.

For longitudinal relaxation in the laboratory frame, with both spins on the same sublattice, equations (75) and (76) on p 291 of Abragam (1961) give

$$C_{\alpha\alpha} = K \left\{ \frac{3}{2} J_{\alpha\alpha}^{(1)}(\omega) + \frac{3}{2} J_{\alpha\alpha}^{(2)}(2\omega) \right\} \tag{3}$$

where $K = \gamma^4 \hbar^2 I(I+1)$, γ is the gyromagnetic ratio of an I spin and $\omega = \gamma B_0$ is the resonant frequency of an I spin in an applied field B_0. The functions $J_{\alpha\beta}^{(p)}(\omega)$ are spectral density functions which are the temporal Fourier transforms of the correlation functions of the magnetic dipolar fluctuations of a pair of spins on sublattices α and β at time t, averaged over the possible starting configurations of the spins at time zero, as described by JS.

For each of the pair of spins on different sublattices, equations (87) and (88) on p 295 of Abragam (1961) give

$$C_{\alpha\alpha} = K \sum_{\beta' \neq \alpha} \left\{ \frac{1}{12} J^{(0)}_{\alpha\beta'}(0) + \frac{3}{2} J^{(1)}_{\alpha\beta'}(\omega) + \frac{3}{4} J^{(2)}_{\alpha\beta'}(2\omega) \right\} \tag{4}$$

$$C_{\alpha\beta} = K \frac{N^\alpha}{N^\beta} \left\{ -\frac{1}{12} J^{(0)}_{\alpha\beta}(0) + \frac{3}{4} J^{(2)}_{\alpha\beta}(2\omega) \right\} \qquad \alpha \neq \beta \tag{5}$$

where N^α is the number of sublattice sites of type α. The term N^α/N^β arises from summing the expectation values of spin operators to form the corresponding magnetizations. The above expression has used $I = S$ in the Abragam equations.

For transverse relaxation in the laboratory frame, with both spins on the same lattice, equation (79) on p 292 of Abragam (1961) gives

$$C_{\alpha\alpha} = K \left\{ \frac{3}{8} J^{(2)}_{\alpha\alpha}(2\omega) + \frac{15}{4} J^{(1)}_{\alpha\alpha}(\omega) + \frac{3}{8} J^{(0)}_{\alpha\alpha}(0) \right\}. \tag{6}$$

If each of the spins are on different sublattices, equation (89) on p 296 gives, again taking $I = S$,

$$C_{\alpha\alpha} = K \sum_{\beta' \neq \alpha} \left\{ \frac{5}{24} J^{(0)}_{\alpha\beta'}(0) + \frac{9}{4} J^{(1)}_{\alpha\beta'}(\omega) + \frac{3}{8} J^{(2)}_{\alpha\beta'}(2\omega) \right\}. \tag{7}$$

In this case, however, there are additional secular terms to those considered by Abragam (1961) in equation (41) on p 279, which arise for like spins which are on inequivalent sites. Evaluating these terms gives

$$C_{\alpha\beta} = K \frac{N^\alpha}{N^\beta} \left\{ \frac{1}{6} J^{(0)}_{\alpha\beta}(0) + \frac{3}{2} J^{(1)}_{\alpha\beta}(\omega) \right\} \qquad \alpha \neq \beta. \tag{8}$$

It can be seen that the sum of (7) and (8) reduces to (6) when the sublattices are identical, as expected.

The expressions for $C_{\alpha\beta}$ in (1) can finally be obtained by adding the contributions above. The equations for longitudinal relaxation are obtained by adding (2)–(5) and the equations for transverse relaxation obtained by adding (2) and (6)–(8). The resulting equations for $I = \frac{1}{2}$ are identical to the corresponding terms in (2.30) and (2.31) of JS (except for a term M_x^β missing in the first term of the last line of (2.30) in JS).

JS also included in their relaxation theory the dipolar interaction between diffusing I spins and fixed S spins, where the S spins are on a separate set of sites. In general, the relaxation of the S magnetization then also needs to be included in (1) which increases the number of equations and dependent variables from n to $n+1$. The additional magnetization will be denoted M^s. This I–S interaction can also be incorporated in the above scheme by using the corresponding Abragam equations above for unlike spins I and S. For longitudinal magnetization, equation (88) on p 295 of Abragam (1961) gives

$$C_{\alpha\alpha} = K \frac{S(S+1)\gamma_S^2}{I(I+1)\gamma_I^2} \left\{ \frac{1}{12} J^{(0)}_{\alpha s}(\omega - \omega_s) + \frac{3}{2} J^{(1)}_{\alpha s}(\omega) + \frac{3}{4} J^{(2)}_{\alpha s}(\omega + \omega_s) \right\} \tag{9}$$

$$C_{\alpha s} = K \frac{S(S+1)\gamma_S^2}{I(I+1)\gamma_I^2} \frac{N^\alpha}{N^s} \left\{ -\frac{1}{12} J^{(0)}_{\alpha s}(\omega - \omega_s) + \frac{3}{4} J^{(2)}_{\alpha s}(\omega + \omega_s) \right\} \tag{10}$$

with similar results for $C_{s\alpha}$ by interchanging I and S, and where $\omega_s = \gamma_s B_0$ is the resonant frequency of the S spins. These terms can then be added to the previous contributions to form the coefficients in (1) for the $n + 1$ equations.

JS assumed that the S spins affect the I spins but remain unaffected by them. This is equivalent to omitting the terms (10) above and the number of equations in (1) is not increased. Adding in the remaining terms (9) gives agreement with the full JS equations for laboratory frame relaxation for $I = \frac{1}{2}$.

For transverse relaxation, equation (89) on p 296 of Abragam (1961) gives

$$C_{\alpha\alpha} = K \frac{S(S+1)\gamma_S^2}{I(I+1)\gamma_I^2} \left\{ \frac{1}{6} J_{\alpha s}^{(0)}(0) + \frac{1}{24} J_{\alpha s}^{(0)}(\omega - \omega_s) + \frac{3}{4} J_{\alpha s}^{(1)}(\omega) + \frac{3}{2} J_{\alpha s}^{(1)}(\omega_s) \right.$$
$$\left. + \frac{3}{8} J_{\alpha s}^{(2)}(\omega + \omega_s) \right\} \tag{11}$$

and $C_{\alpha s} = 0$. This again leads to agreement with the corresponding terms in (2.30) of JS.

It is possible to deduce the coefficients in (1) for relaxation in the rotating frame from the corresponding expressions in the laboratory frame using the method of Kelly and Sholl (1992) for interactions between like, but not necessarily equivalent, spins. In this method the rotating frame expressions are obtained by replacing $J^{(p)}(p\omega)$ in the laboratory frame expressions by $J_p(\omega_1, \omega)$, where $\omega_1 = \gamma B_1$ is the resonant frequency in the rotating field B_1, and where

$$J_0(\omega_1, \omega) = \frac{1}{4} J^{(0)}(0) + \frac{9}{8} J^{(2)}(2\omega) \tag{12}$$

$$J_1(\omega_1, \omega) = \frac{1}{2} J^{(1)}(\omega) + \frac{1}{8} J^{(2)}(2\omega) \tag{13}$$

$$J_2(\omega_1, \omega) = \frac{1}{4} J^{(0)}(2\omega_1) + 2 J^{(1)}(\omega) + \frac{1}{8} J^{(2)}(2\omega). \tag{14}$$

Following this procedure gives agreement with (2.45) of JS for all the terms arising from interactions between I spins. The terms arising from interactions between unlike spins cannot be deduced in this way since the Kelly and Sholl relations are only valid for like spins.

The above theory enables the coefficients $C_{\alpha\beta}$ in the rate equations to be written down from the basic Abragam relations for relaxation due to a pair of like or unlike spins undergoing relative diffusion. It is then necessary to obtain expressions for the spectral density functions. As discussed by JS the evaluation of these functions taking into account the details of the diffusion between the inequivalent sublattices is a formidable task. A simple model is to assume that the correlation between a pair of spins is destroyed completely as soon as either of the pair of spins has a jump. The probability that no jump has occurred in a time t is $\exp(-\tilde{\Gamma}t)$, where $\tilde{\Gamma}$ is the mean jump frequency for a jump of either spin. The corresponding density function for a polycrystalline sample is then (JS)

$$J_{\alpha\beta}^{(q)} = \frac{4C^q}{15} \frac{\tilde{\Gamma}}{\omega^2 + \tilde{\Gamma}^2} \sum_{i(\alpha\beta)} \frac{p(r_i)}{r_i^6} \tag{15}$$

where $C^0 = 6, C^1 = 1, C^2 = 4$, the summation is over all sites on sublattice β relative to a site on sublattice α and $p(r_i)$ is the probability of the site on the β-sublattice being occupied by a spin.

3. Solution of the rate equations

The rate equations (1) may be written in matrix form as

$$\frac{\mathrm{d}\mathcal{M}}{\mathrm{d}t} = -\mathbf{C}\mathcal{M} \tag{16}$$

where $\mathcal{M}$ is a column matrix of dimension n, each element of which is the appropriate component of the magnetization M^α of the I spins on the α-sublattice. The matrix $\mathbf{C}$ is square with elements $C_{\alpha\beta}$ which can be expressed in terms of appropriate spectral density functions. The solution of this equation can be written as

$$\mathcal{M}(t) = \mathbf{X}e^{-\mathbf{D}t}\mathbf{X}^{-1}\mathcal{M}(0) \tag{17}$$

where $\mathbf{D}$ is the diagonal matrix of eigenvalues of $\mathbf{C}$, $\mathbf{X}$ is the matrix of corresponding eigenvectors and $\mathcal{M}(0)$ is the initial magnetization on each sublattice. The ratios of the components of $\mathcal{M}(0)$ are determined by the relative occupation probabilities of the sublattices by the spins.

The observed magnetization is the sum of the contributions $M^\alpha(t)$ over the sublattices which can be occupied by spins of a particular type. For the examples in the previous section, where the S spins are unaffected by the I spins, the sum is over all sublattices. In these cases an explicit expression for the observed magnetization recovery to equilibrium $M(t)$ is

$$M(t) = \sum_{\alpha=1}^{n} M^\alpha(t) = \sum_{i=1}^{n} A_i e^{-\lambda_i t} \tag{18}$$

where λ_i are the eigenvalues of $\mathbf{C}$ and the coefficients A_i are given by

$$A_i = \sum_{j,k=1}^{n} X_{ji} X_{ik}^{-1} M^k(0). \tag{19}$$

Equations (5.2) and (5.3) of JS are the expressions (18) and (19) above evaluated explicitly for $n = 2$. While the algebraic complexity of explicit solutions increases rapidly for larger n, it is straightforward to evaluate λ_i and A_i in (16) using standard numerical matrix methods. If the relaxation of the fixed S spins was included in the above theory the magnetization recoveries $M^s(t)$ could also be evaluated in a similar manner.

4. Discussion

A model of spin occupancies on particular sublattices, and how the spins diffuse between them, enables the matrix $C_{\alpha\beta}$ in (1) to be constructed in terms of parameters describing the rates of jumps, $\Gamma_{\alpha\beta}$, of spins between sublattices. The form of the magnetization recoveries for longitudinal or transverse relaxation in the laboratory frame, or relaxation in the rotating frame, can then be calculated from equations (18) and (19). The magnetization recoveries will consist of n exponentials corresponding to the number of sublattices involved, but not all of these will necessarily be observable. This is because some of the eigenvalues λ_i may be very large, and hence the decay component is too rapid to be observed, or because their weightings A_i are too small to be significant. It could even be the case that only a single-exponential recovery is observed.

The aim in general is to obtain a fit to the observed relaxation data, typically measured as a function of temperature at possibly several different frequencies, by a suitable choice of parameters specifying the jump rates. The fitting can involve data for both the eigenvalues λ_i and the weighting A_i of each component in the magnetization as functions of temperature and frequency. For complex systems the number of parameters could make the analysis of the data quite difficult and some simplification of the model based on physical arguments would usually be necessary, as was the case for LaF$_3$ considered by JS. In cases where only a limited number of exponentials are observed in the magnetization recoveries it should be

possible to show from the above analysis that this is a result of the unobserved terms having either large eigenvalues or small weightings.

The general procedure outlined above for the analysis of nuclear spin relaxation in systems with inequivalent sites can be immediately generalized to other examples, such as the inclusion of quadrupolar relaxation, or the diffusion of mixed spin species on inequivalent sites, such as H and D in metal–hydrogen systems. There are additional complications for the case of quadrupolar nuclei with non-zero static quadrupole interactions which have been described by Schimmele *et al* (1987).

In all such cases, the coefficients of the relaxation matrix can be written down immediately for a particular model of the diffusion between sublattices. While the number of parameters involved can be a complicating factor, there are also more data for analysis than is the case for simple systems because of the multiexponential nature of the relaxation.

References

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