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A stochastic relaxation model for interstitial diffusion

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Abstract. A stochastic jump model is applied to calculate the relaxation of oriented probes diffusing interstitially through a rigid lattice. The whole dynamical range from immobile to rapidly diffusing probes is covered. In contrast to what was done in earlier work, the dipole–dipole interaction between probe and host is taken into account quantitatively. For the static case and the limiting case of rapid diffusion, respectively, well known expressions both for static linewidth as well as for relaxation rates are rederived. The results are compared with the theory of Kubo and Tomita, where the local fields are treated only phenomenologically.

1. Introduction

Nuclear magnetic resonance (NMR) is the classical microscopic method to study diffusion (Abragam 1961). Related techniques using radioactive probes are β-NMR (Ackermann *et al* 1983) and muon spin rotation (μ-SR) (*Proc. 7th Yamada Conference on μ-SR* 1983). In all these experiments the spin orientation of the probes is monitored, either by magnetic induction as in conventional NMR, or by the anisotropy of the radioactive decay. Diffusion of the probes leads to a loss of the spin orientation caused by fluctuating dipole–dipole interactions between the spins of the probe and of the host nuclei. Fluctuating electric field gradients may equally well destroy the orientation by their interaction with the probe's quadrupole moment, if present.

Essentially two different approaches have been applied to calculate the influence of the diffusion process on probe orientation. In the classical papers of Wangsness and Bloch (1953) and Redfield (1957) the fluctuating interactions are treated in second-order perturbation theory. Applying several approximations discussed in textbooks on NMR (see, e.g., Abragam 1961), an exponential relaxation of the spin orientation is obtained. The relaxation rates are proportional to spectral density functions, being Fourier transforms of autocorrelation functions of the fluctuating fields. Spectral density functions for different detailed jump models have been calculated by Sholl (1981) (see also references in this paper) and co-workers in a number of papers.

The relaxation theories mentioned above work only in the so-called narrowing region, where many jumps are performed by the probe during one precession of the spin about the local fields. These theories are not applicable at low temperatures where the probes sit immobile in the lattice. If the whole dynamic range from immobile to rapidly diffusing probes is to be described, stochastic relaxation theories have to be applied. Anderson (1954) and Kubo and Tomita (1954) studied in two pioneering works the influence of local field fluctuations on NMR line shapes and on the transverse polarisation

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of the probe. Markovian Gaussian fluctuations were assumed, the dipole–dipole interaction between probe and host nuclei was approximated by a Gaussian distribution of local fields. In the limit of infinitely long correlation times of the fluctuations, a Gaussian decay of the transverse polarisation was obtained, and for short correlations times the polarisation decreased exponentially. In more recent papers the assumption of Markovian Gaussian jumps was abandoned. Czech and Kehr (1986) (see also references given in this paper) treated the case of field fluctuations produced by a random walk of the probe. Again, a Gaussian decay was obtained for very long correlation times corresponding to immobile probes, and again for short correlation times an exponential decay was observed. The decay constant for the latter case, however, differed from that obtained under the Gaussian Markovian assumption.

In all papers known to the author the dipole–dipole interaction was taken into account only qualitatively. It is the aim of this paper to show that a quantitative treatment of the dipole–dipole interaction within the frame of stochastic theories is possible and, in fact, often is indispensable for the quantitative interpretation of experimental relaxation data.

The paper is organised as follows. In § 2 the stochastic model is introduced. It is a generalisation of existing models where only local jumps are treated (Dattagupta 1987) to the case of interstitial diffusion where the whole interstitial lattice is accessible to the probe. As a consequence, a Liouville Master-equation system for the components of density matrix is obtained depending on about 10^{22} variables. A variant of the effective medium approximation (Kirkpatrick 1973, Summerfield 1981) is applied in § 3 to solve this equation system. In § 4 well known expressions for static linewidth as well as for relaxation rates and spectral density functions are rederived for the two limiting cases of immobile and rapidly diffusing probes, respectively. In § 5 it is shown that the Kubo–Tomita theory (1954) is valid only for small jump rates compared to the Larmor frequencies of probe and host because of the phenomenological treatment of the local fields (see also Hayano *et al* 1979, Seeger 1984). The results of this paper, on the other hand, are not limited in this respect, since the dipole–dipole interactions between probe and host nuclei are taken explicitly into account. Several derivatives of a more technical nature are presented in three appendices.

2. The stochastic model

The Hamiltonian $\mathcal{H}$ for the probe–host interaction of an impurity diffusing through a lattice can be decomposed into a static part $\mathcal{H}_0$ and a fluctuating part $\mathcal{H}_1(r(t))$, changing with every jump,

$$\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(r(t)). \tag{2.1}$$

In the following it is assumed that an *isolated* impurity is diffusing *interstitially* through a rigid lattice of host nuclei. It is further assumed that no static electric field gradients are present, and that the dipole–dipole interactions between the host nuclei can be neglected for present purposes. Then $\mathcal{H}_0$ contains only the Zeeman interaction with the external induction B,

$$\mathcal{H}_0 = -\hbar\left(\omega_I I_z + \omega_S \sum_i S_{iz}\right) \tag{2.2}$$

where $\omega_I = \gamma_I B$, $\omega_S = \gamma_S B$. I denotes the spin of the impurity, and S_i the spins of the host nuclei. $\mathcal{H}_1(r(t))$ is given by the dipole–dipole interaction between impurity and host

nuclei

$$\mathcal{H}_1(r(t)) = \sum_i \mathcal{H}_{DD}(I, S_i, r(t) - r_i) \tag{2.3}$$

where $r(t)$ denotes the site of the impurity and r_i the site of the host nucleus i. The explicit form for $\mathcal{H}_{DD}$ can be found in every textbook on NMR (e.g., Abragam 1961; see also Appendix 2).

For host spins $S_i > \frac{1}{2}$ additional fluctuating quadrupole interactions are produced by the charge of the impurity at neighbouring host nuclei. These interactions are not considered here. They are of importance, however, if cross relaxation processes between impurity and host nuclei are to be considered (see, e.g., Kreitzmann 1986, Jäger *et al* 1987).

The density matrix ρ describing the change in the orientation of the impurity with time is obtained as solution of the Liouville equation

$$\dot{\rho} = (\mathrm{i}/\hbar)[\rho, \mathcal{H}_0 + \mathcal{H}_1(r(t))] = -\mathrm{i}\{L_0 + L_1(r(t))\}\rho \tag{2.4}$$

where the Liouville operators L_0 and $L_1(r(t))$ are defined by

$$L_0\rho = (1/\hbar)[\mathcal{H}_0, \rho] \qquad L_1(r(t))\rho = (1/\hbar)[\mathcal{H}_1(r(t)), \rho].$$

In further calculations it is assumed that $r(t)$ is piecewise constant and changes discontinuously with every jump. The jumps shall be *Markovian*, i.e., the transition probability is independent of the history of preceding jumps. It is further assumed that the process is *stationary*, i.e., the transition probability depends only on the time difference between successive jumps.

Assuming stationary Markovian jumps the density matrix ρ can be decomposed as follows

$$\rho = \sum_{r_n} \rho(r_n) \tag{2.5}$$

where the sum is over all possible interstitial sites r_n. The $\rho(r_n)$ obey a Liouville Master-equation system,

$$\dot{\rho}(r_n) = -\mathrm{i}L_0\rho(r_n) - \mathrm{i}L_1(r_n)\rho(r_n) + \sum [w(r_m, r_n)\rho(r_m) - w(r_n, r_m)\rho(r_n)]. \tag{2.6}$$

The first two terms describe the reorientation of the impurity at site r_n under the influence of external and local fields respectively, the following terms describe the jumps of the impurity between different sites. $w(r_m, r_n)$ is the jump rate from site r_m to site r_n. Because of the translational symmetry of the lattice the jump rate depends only on the difference of the jump vectors,

$$w(r_n, r_m) = w(r_n - r_m). \tag{2.7}$$

The derivation of equation (2.6) can be found in Dattagupta (1987, ch. VIII).

In an abbreviated notation equation (2.6) can be written as follows

$$\dot{\boldsymbol{\rho}} = -(\mathrm{i}L_0\mathbf{I} + \mathrm{i}\mathbf{L}_1 + \mathbf{W})\boldsymbol{\rho} \tag{2.8}$$

where $\boldsymbol{\rho}$ now is a 'super' vector with elements $\rho(r_n)$ and $\mathbf{I}$, $\mathbf{L}_1$ and $\mathbf{W}$ are 'super' matrices with elements

$$\begin{aligned} \langle r_n|\mathbf{I}|r_m\rangle &= \delta(r_n - r_m) \\ \langle r_n|\mathbf{L}_1|r_m\rangle &= \delta(r_n - r_m)L_1(r_n) \\ \langle r_n|\mathbf{W}|r_m\rangle &= \delta(r_n - r_m)\sum_{r_k} w(r_n - r_k) - w(r_m - r_n) \end{aligned} \tag{2.9}$$

where

$$\delta(r_n - r_m) = \begin{cases} 1 & \text{if } r_n = r_m \\ 0 & \text{if } r_n \neq r_m. \end{cases}$$

In experiments using radioactive impurities often only the time average of $\rho(t)$ is measured,

$$\bar{\rho}(\lambda) = \lambda \int_0^\infty \exp(-\lambda t)\rho(t)\,\mathrm{d}t \tag{2.10}$$

where λ is the decay constant of the impurity. By means of standard Laplace transform techniques, one obtains from equations (2.8) and (2.5)

$$\bar{\rho}(\lambda) = (\lambda/N) \sum_{r_n, r_m} \langle r_n | [(\lambda + \mathrm{i}L_0)\mathbf{I} + \mathrm{i}\mathbf{L}_1 + \mathbf{W}]^{-1} | r_m \rangle \rho(0). \tag{2.11}$$

$\rho(0)$ is the density matrix at time $t = 0$. It was assumed that there are N possible interstitial sites, each of which is populated with equal probability.

In the system of basis vectors $|r_n\rangle$ $\mathbf{L}_1$ is diagonal, but $\mathbf{W}$ is not (see equation (2.9)). This basis system is appropriate for low jump rates. In the case of rapid diffusion, on the other hand, basis vectors in the reciprocal lattice are useful, which are defined as

$$\begin{aligned} |k_\alpha\rangle &= (1/\sqrt{N}) \sum_{r_n} \exp(\mathrm{i}k_\alpha r_n)|r_n\rangle \\ |r_n\rangle &= (1/\sqrt{N}) \sum_{k_\alpha} \exp(\mathrm{i}k_\alpha r_n)|k_\alpha\rangle. \end{aligned} \tag{2.12}$$

Periodic boundary conditions were assumed. In the new basis $\mathbf{L}_1$ is no longer diagonal, but $\mathbf{W}$ becomes diagonal because of the translational invariance of the lattice,

$$\langle k_\alpha | \mathbf{L}_1 | k_\beta \rangle = (1/N) \sum_{r_n} \exp[-\mathrm{i}(k_\alpha - k_\beta)r_n] L_1(r_n) \tag{2.13}$$

$$\langle k_\alpha | \mathbf{W} | k_\beta \rangle = \delta(k_\alpha - k_\beta) \sum_{r_n} [1 - \exp(-\mathrm{i}k_\alpha r_n)] w(r_n) = \delta(k_\alpha - k_\beta)\hat{w}(k_\alpha).$$

For later use we note that

$$\hat{w}(k_0) = 0 \tag{2.14}$$

where $k_0 = (0, 0, 0)$ is the null vector in the reciprocal lattice. In the $|k_\alpha\rangle$ basis equation (2.11) can alternatively be written as follows

$$\bar{\rho}(\lambda) = \lambda \langle k_0 | [(\lambda + \mathrm{i}L_0)\,\mathbf{I} + \mathrm{i}\,\mathbf{L}_1 + \mathbf{W}]^{-1} | k_0 \rangle \rho(0). \tag{2.15}$$

If only the orientation of the impurity is observed, equation (2.15) has to be averaged over the lattice spin variables,

$$\bar{\rho}(\lambda) = \lambda \langle k_0 | \bar{\mathbf{G}} | k_0 \rangle \rho(0) \tag{2.16}$$

where $\bar{\mathbf{G}}$ is given by

$$\bar{\mathbf{G}} = \mathrm{Tr}_S\{[(\lambda + \mathrm{i}L_0)\mathbf{I} + \mathbf{L}_1 + \mathbf{W}]^{-1} \rho_S(0)\}. \tag{2.17}$$

Whereas in equation (2.15) $\bar{\rho}(\lambda)$ and $\rho(0)$ denote the orientation of the coupled system of probe spin I and all host spins S_i, from now on the same symbols denote the orientation of the I spin alone. In the following, the Boltzmann orientation of the lattice spins is

assumed to be small compared with the orientation of the impurity (this situation is met, e.g., in experiments using muons or β-active nuclei). Then the S density matrix $\rho_S(0)$ reduces to the unity matrix (in equation (2.17), Tr denotes the *normalised* trace, i.e., $\mathrm{Tr}\,\mathbf{I} = 1$. This convention has been adopted to avoid normalisation prefactors).

Equation (2.17) can be transformed by use of the matrix identity

$$[(\lambda + \mathrm{i}L_0)\mathbf{I} + \mathrm{i}\mathbf{L}_1 + \mathbf{W}]^{-1} = (\mathbf{I} - \mathrm{i}\mathbf{G}_0\mathbf{L}_1)[(\lambda + \mathrm{i}L_0)\mathbf{I} + \mathbf{W} + \mathbf{L}_1\mathbf{G}_0\mathbf{L}_1]^{-1} \tag{2.18}$$

where

$$\mathbf{G}_0 = [(\lambda + \mathrm{i}L_0)\mathbf{I} + \mathbf{W}]^{-1}. \tag{2.19}$$

Because only even powers of $\mathbf{L}_1$ contribute to the trace over the S_i variables, one obtains from equations (2.17) and (2.18)

$$\bar{\mathbf{G}} = \mathrm{Tr}_S\{[(\lambda + \mathrm{i}L_0)\mathbf{I} + \mathbf{W} + \mathbf{L}_1\mathbf{G}_0\mathbf{L}_1]^{-1}\,\mathbf{I}_S\}. \tag{2.20}$$

This relation is still exact (within the limits of the stochastic model). From now on, however, the calculation is restricted to the case that the local fields are small compared with the external one. Then the term $(\lambda + \mathrm{i}L_0)\mathbf{I}$ is large compared to $\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1$, and all parts of $\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1$ not commuting with L_0 can be discarded. This corresponds to a neglection of terms of order $\mathbf{L}_1^3$, and all results derived below are correct only up to order $\mathbf{L}_1^2$. With this approximation one gets

$$\bar{\mathbf{G}} = \mathrm{Tr}_S\{[(\lambda + \mathrm{i}L_0)\mathbf{I} + \mathbf{W} + (\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1)_{\mathrm{trunc}}]^{-1}\,\mathbf{I}_S\}.$$

The operator L_0 can be written as a sum, $L_0 = L_{0I} + L_{0S}$, where L_{0I} acts only on the I spin variables, and L_{0S} only on the S_i spin variables. L_{0S} commutes with L_{0I}, $\mathbf{W}$ and $(\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1)_{\mathrm{trunc}}$. Furthermore, the action of L_{0S} on $\mathbf{I}_S$ gives zero. Therefore the above equation is equivalent to

$$\bar{\mathbf{G}} = \mathrm{Tr}_S\{[(\lambda + \mathrm{i}L_{0I})\mathbf{I} + \mathbf{W} + (\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1)_{\mathrm{trunc}}]^{-1}\,\mathbf{I}_S\}. \tag{2.21}$$

From equations (2.16) and (2.21) $\bar{\rho}(\lambda)$ can in principle be calculated. The number of possible interstitial sites, however, is of the order of the number of atoms in the probe. Thus the rank of the matrix to be inverted in equation (2.21) is of the order of 10^{22}, and further approximations are necessary.

3. The effective medium approximation

The trace over all S_i variables in equation (2.21) can be interpreted as an average over all possible spin configurations of the host lattice. This average can be simulated by replacing the operator $(\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1)_{\mathrm{trunc}}$ by an effective medium operator $\boldsymbol{\Omega}$ being independent of the S_i variables,

$$\bar{\mathbf{G}} = [(\lambda + \mathrm{i}L_{0I})\mathbf{I} + \mathbf{W} + \boldsymbol{\Omega}]^{-1}. \tag{3.1}$$

$\boldsymbol{\Omega}$ has to be determined such that equations (3.1) and (2.21) are consistent. To this end the following identity is used,

$$[(\lambda + \mathrm{i}L_{0I})\mathbf{I} + \mathbf{W} + (\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1)_{\mathrm{trunc}}]^{-1} = \bar{\mathbf{G}} - \bar{\mathbf{G}}\boldsymbol{\Delta}(1 + \bar{\mathbf{G}}\boldsymbol{\Delta})^{-1}\bar{\mathbf{G}} \tag{3.2}$$

where $\boldsymbol{\Delta}$ is defined by

$$\boldsymbol{\Delta} = (\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1)_{\mathrm{trunc}} - \boldsymbol{\Omega}. \tag{3.3}$$

Taking the trace over the S_i variables and using equation (2.21), we get

$$\mathrm{Tr}_S[\bar{\mathbf{G}}\boldsymbol{\Delta}(\mathbf{I} + \bar{\mathbf{G}}\boldsymbol{\Delta})^{-1}\bar{\mathbf{G}}] = 0$$

or, since $\bar{\mathbf{G}}$ is independent of the S_i variables

$$\mathrm{Tr}_S[\bar{\mathbf{G}}\boldsymbol{\Delta}(\mathbf{I} + \bar{\mathbf{G}}\boldsymbol{\Delta})^{-1}] = 0. \tag{3.4}$$

Equation (3.4) defines implicitly $\boldsymbol{\Delta}$ and thus $\boldsymbol{\Omega}$. Written in terms of matrix elements, (3.4) reads as follows

$$\sum_{r_k} \mathrm{Tr}_S[\langle r_n|\bar{\mathbf{G}}\boldsymbol{\Delta}|r_k\rangle\langle r_k|(\mathbf{I} + \bar{\mathbf{G}}\boldsymbol{\Delta})^{-1}|r_m\rangle] = 0. \tag{3.5}$$

Now, three approximations are applied:

(i) Since $\boldsymbol{\Delta}$ is the difference between the operator $(\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1)_{\mathrm{trunc}}$ (depending on actual local spin configurations) and the effective medium operator $\boldsymbol{\Omega}$, the operator $\bar{\mathbf{G}}\boldsymbol{\Delta}$ can be considered to be small compared with $\mathbf{I}$. Thus equation (3.5) can be replaced by

$$\mathrm{Tr}_S[\langle r_n|\bar{\mathbf{G}}\boldsymbol{\Delta}|r_m\rangle(\mathbf{I} + \langle r_m|\bar{\mathbf{G}}\boldsymbol{\Delta}|r_m\rangle)^{-1}] = 0. \tag{3.6}$$

(ii) The matrix elements $\langle r_n|\bar{\mathbf{G}}\boldsymbol{\Delta}|r_m\rangle$ and $\langle r_m|\bar{\mathbf{G}}\boldsymbol{\Delta}|r_m\rangle$ are assumed to be uncorrelated for $r_n \neq r_m$. Then the traces of $\langle r_n|\bar{\mathbf{G}}\boldsymbol{\Delta}|r_m\rangle$ and of $(1 + \langle r_m|\bar{\mathbf{G}}\boldsymbol{\Delta}|r_m\rangle)^{-1}$ can be performed separately. This leads to

$$\mathrm{Tr}_S\langle r_n|\bar{\mathbf{G}}\boldsymbol{\Delta}|r_m\rangle = 0 \qquad \text{if } r_n \neq r_m$$

or

$$\langle r_n|\bar{\mathbf{G}}\boldsymbol{\Omega}|r_m\rangle = \langle r_n|\bar{\mathbf{G}}\mathbf{R}|r_m\rangle \tag{3.7}$$

where

$$\mathbf{R} = \mathrm{Tr}_S(\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1)_{\mathrm{trunc}}.$$

It is easy to show that the parts of $\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1$ not commuting with L_0 do not contribute to the trace. Therefore we may write equivalently

$$\mathbf{R} = \mathrm{Tr}_S(\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1) \tag{3.8}$$

(iii) For $r_n = r_m$ one gets from equation (3.6)

$$\mathrm{Tr}_S[\langle r_n|\bar{\mathbf{G}}\boldsymbol{\Delta}|r_n\rangle/(\mathbf{I} + \langle r_n|\bar{\mathbf{G}}\boldsymbol{\Delta}|r_n\rangle)] = 0. \tag{3.9}$$

For the calculation of the trace we use the phenomenological *ansatz*

$$\mathrm{Tr}_S f[(\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1)_{\mathrm{trunc}}] = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \exp(-z^2/2) f[z^2\,\mathrm{Tr}_S(\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1)]\,\mathrm{d}z. \tag{3.10}$$

Equation (3.10) can be motivated as follows: $\mathbf{L}_1$ describes the dipole–dipole interaction between probe and all host nuclei. In the classical approximation this interaction can be replaced by the interaction of the probe with the local magnetic fields, and the trace over the S spins can be replaced by an average over the local fields. Assuming a Gaussian distribution of local fields one gets equation (3.10). For the special case $f(x) = x$ the equation gives an identity.

Applying equation (3.10) to (3.9) one gets, after some straightforward transformations,

$$\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \frac{\exp(-z^2/2)\,\mathrm{d}z}{1 - \langle r_n|\bar{\mathbf{G}}\boldsymbol{\Omega}|r_n\rangle + z^2\langle r_n|\bar{\mathbf{G}}\mathbf{R}|r_n\rangle} = 1. \tag{3.11}$$

Thus $\langle r_n|\bar{\mathbf{G}}\boldsymbol{\Omega}|r_n\rangle$ is a function of $\langle r_n|\bar{\mathbf{G}}\mathbf{R}|r_n\rangle$,

$$\langle r_n|\bar{\mathbf{G}}\boldsymbol{\Omega}|r_n\rangle = F(\langle r_n|\bar{\mathbf{G}}\mathbf{R}|r_n\rangle) \tag{3.12}$$

where $F(x)$ is implicitly defined by

$$\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\frac{\exp(-z^2/2)\,dz}{1-F(x)+xz^2}=1. \tag{3.13}$$

In Appendix 1 it is shown that $\bar{\mathbf{G}}$ can be determined without any further approximation using only equations (3.7) and (3.12). The result is

$$\bar{\mathbf{G}}=[(\lambda+iL_{0I})\mathbf{I}+\mathbf{W}+\mathbf{R}]^{-1}\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\frac{\exp(-z^2/2)\,dz}{1-A+Az^2} \tag{3.14}$$

where the operator A is given by

$$A=(1/N)\sum_{k_\alpha}\langle k_\alpha|[(\lambda+iL_{0I})\mathbf{I}+\mathbf{W}+\mathbf{R}]^{-1}\mathbf{R}|k_\alpha\rangle. \tag{3.15}$$

Since $\mathbf{R}=\mathrm{Tr}_S(\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1)$ is invariant against translations of the lattice, it is diagonal in the reciprocal-lattice basis,

$$\langle k_\alpha|\mathbf{R}|k_\beta\rangle=\delta(k_\alpha-k_\beta)R(k_\alpha). \tag{3.16}$$

$R(k_\alpha)$ is given by

$$R(k_\alpha)=\sum_{r_n r_m}\exp[-ik_\alpha(r_n-r_m)]\,\mathrm{Tr}_S[L_{DD}(I,S,r_n)\times P(\lambda+iL_0,r_n-r_m)L_{DD}(I,S,r_m)] \tag{3.17}$$

(see Appendix 2). $L_{DD}(I,S,r_n)$ is the Liouville operator for the dipole–dipole interaction between impurity spin I and host lattice spin S at distance r_n (see equation (2.3)), and

$$P(\lambda+iL_0,r_n)=(1/N)\sum_{k_\alpha}\frac{\exp(-ik_\alpha r_n)}{\lambda+iL_0+\hat{w}(k_\alpha)}. \tag{3.18}$$

Using equations (3.16) and (2.13), A can be written as

$$A=(1/N)\sum_{k_\alpha}[(\lambda+iL_{0I})+\hat{w}(k_\alpha)+R(k_\alpha)]^{-1}R(k_\alpha). \tag{3.19}$$

Substituting (3.14) into (2.16), one finally gets

$$\bar{\rho}(\lambda)=[\lambda+iL_{0I}+R(k_0)]^{-1}\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\frac{\exp(-z^2/2)\,dz}{1-A+Az^2}\lambda\rho(0) \tag{3.20}$$

where equation (2.14) was used. *Equation* (3.20) *is the main result of this paper.* A closed expression for $\bar{\rho}(\lambda)$ is obtained. The main computational effort lies in the calculation of $R(k_\alpha)$ by means of equation (3.17). This is a straightforward but rather tedious task. The expressions simplify considerably if $\hat{w}(k_\alpha)$ in equations (3.18) and (3.19) is approximated by an averaged jump rate $\bar{w}$ (it will be seen later that this approximation will lead to BPP-like spectral density functions (Bloembergen *et al* 1948). One obtains from (3.17)

$$R(k_\alpha)=\sum_{r_n}\mathrm{Tr}_S\{L_{DD}(I,S,r_n)(\lambda+iL_0+\bar{w})^{-1}L_{DD}(I,S,r_n)\} \tag{3.21}$$

where $R(k_\alpha)=R$ is now independent of k_α. Substituting this expression into equations (3.19) and (3.20), one gets

$$A=(\lambda+iL_{0I}+\bar{w}+R)^{-1}R \tag{3.22}$$

and

$$\bar{\rho}(\lambda) = \frac{\lambda + iL_{0I} + \bar{w} + R}{\lambda + iL_{0I} + R} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\exp(-z^2/2)\,dz}{\lambda + iL_{0I} + \bar{w} + Rz^2} \lambda\rho(0). \tag{3.23}$$

In order to calculate $\rho(t)$ from $\bar{\rho}(\lambda)$, an inverse Laplace transform has to be performed. This can be done only numerically for the exact expression (3.20). In the case of approximation (3.23) or in the limiting cases of slow and rapid diffusion, however, the inverse Laplace transform can be performed explicitly as will be shown in the next sections.

4. Limiting cases

4.1. Rapid diffusion

In the limit of large jump rates $P(\lambda + iL_0, r_n)$ and thus $R(k_\alpha)$ are proportional to w^{-1} (see equations (3.17) and (3.18)). As a consequence, $A \to 0$ for rapidly diffusing probes, as can be seen from equation (3.19). Then equation (3.20) can be replaced by

$$\bar{\rho}(\lambda) = [\lambda + iL_{0I} + R(k_0)]^{-1}\lambda\rho(0). \tag{4.1}$$

The density matrix can always be decomposed into its irreducible components ρ_{lm},

$$\rho = \sum_{lm} \rho_{lm} T_{lm}(I).$$

From the orthogonality of the irreducible tensor operator $T_{lm}(I)$ one gets

$$\rho_{lm} = \mathrm{Tr}_I\{T^+_{lm}(I)\rho\} \tag{4.2}$$

where it is assumed that the $T_{lm}(I)$ are normalised,

$$\mathrm{Tr}_I\{T^+_{l_1m_1}(I)\, T_{l_2m_2}(I)\} = \delta_{l_1l_2}\delta_{m_1m_2}.$$

Several slightly deviating definitions for the ρ_{lm} can be found in the literature. The $T_{lm}(I)$ are eigenoperators to L_0 (see equation (2.2)),

$$L_0 T_{lm}(I) = -m\omega_I T_{lm}(I). \tag{4.3}$$

The $T_{lm}(I)$ are eigenoperators to $R(k_0)$, too, since $R(k_0)$ commutes with L_0 (this is a consequence of the truncation procedure applied in equation (2.21)). Using equations (4.2) and (4.3), one obtains from (4.1)

$$\bar{\rho}_{lm}(\lambda) = (\bar{\lambda} + R_{lm})^{-1}\lambda\rho_{lm}(0). \tag{4.4}$$

We have introduced the new variable

$$\bar{\lambda} = \lambda - im\omega_I. \tag{4.5}$$

Substitution of λ by $\bar{\lambda}$ corresponds to a transition into a coordinate system rotating with angular frequency $m\omega_I$ about the axis of the external induction B. R_{lm} is given by

$$R_{lm} = \mathrm{Tr}_I\{T^+_{lm}(I)R(k_0)T_{lm}(I)\}. \tag{4.6}$$

Expressions for R_{lm} are given in Appendix 3.

The case of dipolar orientation, $l = 1$, is of special interest. Applying the formulae of Appendix 3, one gets for R_{lm}

$$R_{10} = \hbar^2\gamma_I^2\gamma_S^2 S(S+1)\{\tfrac{1}{24}J_0[\bar{\lambda} - \mathrm{i}(\omega_I - \omega_S)] + \tfrac{1}{24}J_0[\bar{\lambda} - \mathrm{i}(\omega_S - \omega_I)] + \tfrac{3}{4}J_1(\bar{\lambda} - \mathrm{i}\omega_I) + \tfrac{3}{4}J_{-1}(\bar{\lambda} + \mathrm{i}\omega_I) + \tfrac{3}{8}J_2[\bar{\lambda} - \mathrm{i}(\omega_I + \omega_S)] + \tfrac{3}{8}J_{-2}[\bar{\lambda} + \mathrm{i}(\omega_I + \omega_S)]\}$$

$$R_{11} = \hbar^2\gamma_I^2\gamma_S^2 S(S+1)\{\tfrac{1}{6}J_0(\bar{\lambda}) + \tfrac{1}{24}J_0[\bar{\lambda} + \mathrm{i}(\omega_S - \omega_I)] + \tfrac{3}{4}J_{-1}(\bar{\lambda} + \mathrm{i}\omega_I) + \tfrac{3}{4}J_1(\bar{\lambda} - \mathrm{i}\omega_S) + \tfrac{3}{4}J_{-1}(\bar{\lambda} + \mathrm{i}\omega_S) + \tfrac{3}{8}J_{-2}[\bar{\lambda} + \mathrm{i}(\omega_S + \omega_I)]\}$$

$$R_{1-1} = R_{11}^*. \tag{4.7}$$

The complex spectral density functions are defined by

$$J_m(\lambda - \mathrm{i}\omega) = 2\sum_{r_\alpha r_\beta} F_m(r_\alpha)F_m^*(r_\beta)P(\lambda - \mathrm{i}\omega, r_\alpha - r_\beta) \tag{4.8}$$

where

$$F_0(r) = \frac{1 - 3\cos^2\vartheta}{|r|^3}$$

$$F_{\pm1}(r) = \frac{\sin\vartheta\cos\vartheta\exp(\mp\mathrm{i}\varphi)}{|r|^3}$$

$$F_{\pm2}(r) = \frac{\sin^2\vartheta\exp(\mp2\mathrm{i}\varphi)}{|r|^3} \tag{4.9}$$

$|r|$, ϑ, φ are the polar coordinates of r, and $P(\lambda - \mathrm{i}\omega, r)$ is given by equation (3.18).

The decrease of the tensor orientation ρ_{lm} does not follow a simple exponential law since R_{lm} depends on $\bar{\lambda}$. From the formulae for the inverse Laplace transform, however, it can be seen that this dependence can be neglected if the relaxation rate R_{lm} is small compared to the jump rate w. In this case the inverse Laplace transform of $\bar{\rho}_{lm}(\lambda)$ (see equation (4.4)) can easily be performed with the result

$$\rho_{lm}(t) = \exp(-\mathrm{i}m\omega_I t - R_{lm}t)\rho_{lm}(0). \tag{4.10}$$

If R_{lm} is real, equation (4.10) describes a precession of the tensor component ρ_{lm} with angular frequency $-m\omega_I$ and an exponential damping of the amplitude with time constant R_{lm}. Equation (4.6), however, shows that R_{lm} is real only for $m = 0$. For $m \neq 0$ only the real part of R_{lm} has the meaning of a relaxation rate, whereas the imaginary part leads to a small shift of the precession frequency.

Exactly the same results are obtained by perturbation theory. In the limit $\bar{\lambda} \to 0$ equations (4.7) reduce to well known expressions for longitudinal and transverse relaxation rates for the case of dipolar coupling between unlike spins (see Abragam 1961, ch VIII E). Equation (4.8) for $J_m(\lambda - \mathrm{i}\omega)$ is equivalent to the expression used, e.g., by Sholl and co-workers (1981) to evaluate random walk spectral density functions for a number of different jump models (with the only difference that in the present work the argument of J_m is complex). It should be noted, however, that in the works of Sholl *et al* the spectral density functions were obtained from perturbation theory, and the narrowing condition was assumed to hold. In the present work the jump model was incorporated already from the very beginning (equation (2.6)) without any *a priori* assumption about the jump rate.

If approximation (3.21) for $R(k_0)$ is applied, one obtains for the real part of $J_m(\lambda - \mathrm{i}\omega)$

$$\mathrm{Re}\,J_m(\lambda - \mathrm{i}\omega) = \sum_{r_\alpha} |F_m(r_\alpha)|^2 \frac{2(\lambda + \bar{w})}{(\lambda + \bar{w})^2 + \omega^2}. \tag{4.11}$$

In the limit $\lambda \ll \bar{w}$ equation (4.11) leads exactly to the BPP approximation for the spectral density function, if $\bar{w}^{-1}$ is identified with the correlation time τ_c entering as a phenomenological parameter into the BPP model.

4.2. Static case

In the case of immobile probes, $w = 0$, equation (3.20) simplifies to

$$\bar{\rho}(\lambda) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\exp(-z^2/2)\,\mathrm{d}z}{\lambda + \mathrm{i}L_{0I} + Rz^2}\, \lambda\rho(0). \tag{4.12}$$

This result can be obtained directly from equation (3.23) by taking $\bar{w} = 0$ (the substitution of $w(k_0)$ by $\bar{w}$, applied in the derivation of (3.23), is trivially correct, if $w = 0$). For the tensor component $\bar{\rho}_{lm}$ one obtains in an analogous way as above

$$\bar{\rho}_{lm}(\lambda) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\exp(-z^2/2)\,\mathrm{d}z}{\lambda - \mathrm{i}m\omega_I + R_{lm}z^2}\, \lambda\rho_{lm}(0). \tag{4.13}$$

For further discussion we restrict ourselves to the case $l = m = 1$. Equation (4.7) shows that for $w = 0$ the term $\frac{1}{6}J_0(\bar{\lambda})$ is large compared to all other contributions, i.e., R_{11} can be approximated by

$$R_{11} = \hbar^2\gamma_I^2\gamma_S^2 S(S+1)\tfrac{1}{6}J_0(\bar{\lambda}). \tag{4.14}$$

Inserting expression (4.8) for $J_0(\bar{\lambda})$, one obtains for $w = 0$

$$R_{11} = \sigma^2/(\lambda - \mathrm{i}\omega_I) \tag{4.15}$$

where

$$\sigma^2 = \hbar^2\gamma_I^2\gamma_S^2 \frac{S(S+1)}{3} \sum_{r_n} \frac{(1 - 3\cos^2\Theta_n)^2}{|r_n|^6}. \tag{4.16}$$

This is exactly the van Vleck expression for the dipolar linewidth due to interactions between unlike spins (van Vleck 1948). Inserting equation (4.15) into (4.13), one gets

$$\bar{\rho}_{11}(\lambda) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\lambda - \mathrm{i}\omega_I}{(\lambda - \mathrm{i}\omega_I)^2 + \sigma^2 z^2} \exp(-z^2/2)\,\mathrm{d}z\, \lambda\rho_{11}(0). \tag{4.17}$$

The inverse Laplace transform of (4.17) and the following z-integration can easily be performed with the result

$$\rho_{11}(t) = \exp(-\mathrm{i}\omega_I t - \tfrac{1}{2}\sigma^2 t^2)\rho_{11}(0). \tag{4.18}$$

The tensor orientation $\rho_{11}(t)$ precesses with angular frequency $-\mathrm{i}\omega_I$ about the axis of the magnetic field, the damping of the amplitude is Gaussian due to reorientation of the probes in the inhomogeneous local fields.

5. Discussion

The influence of stochastic jumps on the polarisation of diffusing probes was studied in a classical paper by Kubo and Tomita (1954). They obtain for the time dependence of the transversal dipolar polarisation

$$\rho_{11}(t) = \exp[-\mathrm{i}\omega_I t - \sigma^2\tau_c^2(\mathrm{e}^{-t/\tau_c} - 1 + t/\tau_c)]\rho_{11}(0). \tag{5.1}$$

σ is the dipolar linewidth as given by eq. (4.16), τ_c is a phenomenological correlation time being of the order of the reciprocal jump rate. In the derivation of equation (5.1) a stationary Gaussian Markov process was assumed (see, e.g., Kubo (1969) for details). The local fields were introduced purely phenomenologically, the nuclear dipole–dipole interaction was not taken into account explicitly.

In the two limiting cases of immobile and rapidly diffusing probes, respectively, equation (5.1) reduces to

$$\rho_{11}(t) = \rho_{11}(0)\exp(-i\omega_I t)\begin{cases}\exp(-\frac{1}{2}\sigma^2 t^2) & \text{immobile probe}\\ \exp(-\sigma^2\tau_c t) & \text{rapidly diffusing probe.}\end{cases} \tag{5.2}$$

Equation (5.2) is to be compared with the results derived in § 4 for the two limiting cases (see equations (4.10) and (4.18), respectively),

$$\rho_{11}(t) = \rho_{11}(0)\exp(-i\omega_I t)\begin{cases}\exp(-\frac{1}{2}\sigma^2 t^2) & \text{immobile probe}\\ \exp(-R_{11}t) & \text{rapidly diffusing probe}\end{cases} \tag{5.3}$$

where R_{11} is given by equation (4.7) with $\bar{\lambda} = 0$. It is seen that for immobile probes expressions (5.2) and (5.3) are identical. For rapidly diffusing probes, however, (5.2) and (5.3) are only consistent, if

$$R_{11} = \sigma^2\tau_c = \hbar\gamma_I^2\gamma_S^2\frac{S(S+1)}{3}\tau_c\sum_{r_n}|F_0(r_n)|^2. \tag{5.4}$$

Only the secular part of the dipole–dipole interaction $\mathcal{H}_{DD}$ contributes to the static linewidth σ, whereas both secular and non-secular contributions enter into R_{11}. The secular part of $\mathcal{H}_{DD}$ gives rise to the first term $\frac{1}{6}J_0(0)$ on the right-hand side of equation (4.7) for R_{11}. The other five terms can be attributed to the non-secular parts. Equation (5.4) is therefore at most valid if the latter contributions are small compared to the first one. This leads to

$$|\omega_I|, |\omega_S|, |\omega_I \pm \omega_S| \gg \bar{w} \tag{5.5}$$

where $\bar{w}$ is a typical jump rate. It has already been pointed out by Hayano *et al* (1979) that these conditions are necessary for the Kubo–Tomita formula to hold (see also Seeger 1984, appendix). Using equations (4.8) and (3.18), the remaining part of R_{11} follows

$$R_{11} = \hbar\gamma_I^2\gamma_S^2\frac{S(S+1)}{3}\sum_{r_n r_m}F_0(r_n)F_0^*(r_m)\frac{1}{N}\sum_{k_\alpha}\frac{\exp[-ik_\alpha(r_n - r_m)]}{\hat{w}(k_\alpha)}. \tag{5.6}$$

Equations (5.4) and (5.6) become identical only if additionally the BPP approximation, $\hat{w}(k_\alpha) = \bar{w}$, is applied, and if $\bar{w}^{-1}$ is identified with τ_c.

This discussion has shown that the connection between static linewidth σ and relaxation rate R_{11} as is predicted by the Kubo–Tomita theory (equation (5.4)) is correct *quantitatively only if* (i) relations (5.5) hold, and (ii) the BPP approximation is applied.

All the difficulties with the Kubo–Tomita theory discussed above have their cause in the qualitative treatment of the dipole–dipole interaction. For a quantitative understanding of the relaxation of interstitially diffusing probes, the formulae derived in this paper should be used. Considerable computational effort, however, is necessary to evaluate expression (3.20). If the explicit time dependence of $\rho(t)$ is needed, an additional inverse Laplace transform has to be applied which can be performed analytically only in the two limiting cases.

Things simplify considerably if the BPP approximation is applied. The calculation of $\bar{\rho}(\lambda)$ by means of expression (3.23) is straightforward (the integral can be expressed in terms of the error function). Even the inverse Laplace transform can be performed analytically. The latter statement holds even if the explicit λ-dependence of R is taken into account.

Appendix 1. Proof of equation (3.14)

The operator $\bar{\mathbf{G}}\boldsymbol{\Omega}$–$\bar{\mathbf{G}}\mathbf{R}$ is diagonal in the $|r_n\rangle$ basis by virtue of equation (3.7). Furthermore, the matrix element $\langle r_n|\bar{\mathbf{G}}\boldsymbol{\Omega}$–$\bar{\mathbf{G}}\mathbf{R}|r_n\rangle$ is independent of r_n because of the translational invariance of the lattice. Therefore, $\bar{\mathbf{G}}\boldsymbol{\Omega}$–$\bar{\mathbf{G}}\mathbf{R}$ is a multiple of the unity operator,

$$\bar{\mathbf{G}}\boldsymbol{\Omega}\text{–}\bar{\mathbf{G}}\mathbf{R} = \langle r_n|\bar{\mathbf{G}}\boldsymbol{\Omega}\text{–}\bar{\mathbf{G}}\mathbf{R}|r_n\rangle\mathbf{I}. \tag{A1.1}$$

With the definition

$$\mathbf{G}_{0I} = [\lambda + \mathrm{i}L_{0I})\mathbf{I} + \mathbf{W}]^{-1} \tag{A1.2}$$

one can write

$$\boldsymbol{\Omega} = \bar{\mathbf{G}}^{-1} - \mathbf{G}_{0I}^{-1} \tag{A1.3}$$

where equation (3.1) was used. Inserting expression (A1.3) into (A1.1) one gets

$$\bar{\mathbf{G}}(\mathbf{G}_{0I}^{-1} + \mathbf{R}) = [1 + x - F(x)]\mathbf{I} \tag{A1.4}$$

where

$$x = \langle r_n|\bar{\mathbf{G}}\mathbf{R}|r_n\rangle \tag{A1.5}$$

and

$$F(x) = \langle r_n|\bar{\mathbf{G}}\boldsymbol{\Omega}|r_n\rangle, \tag{A1.6}$$

(see equation (3.12)). From (A1.4) it follows that

$$\bar{\mathbf{G}}\mathbf{R} = [1 + x - F(x)](\mathbf{G}_{0I}^{-1} + \mathbf{R})^{-1}\mathbf{R}$$

and, by taking the diagonal matrix element in the $|r_n\rangle$ basis,

$$x = [1 + x - F(x)]\,A \tag{A1.7}$$

where A is defined as

$$A = \langle r_n|(\mathbf{G}_{0I}^{-1} + \mathbf{R})^{-1}\mathbf{R}|r_n\rangle. \tag{A1.8}$$

In the $|k_\alpha\rangle$ basis, equation (A1.8) can be alternatively written as

$$A = (1/N)\sum_{k_\alpha}\langle k_\alpha|\mathbf{G}_{0I}^{-1} + \mathbf{R})^{-1}\mathbf{R}|k_\alpha\rangle. \tag{A1.9}$$

Both $\mathbf{G}_{0I}$ and $\mathbf{R}$ are diagonals in the $|k_\alpha\rangle$ basis. From (A1.7) it follows that

$$1 - F(x) = x(A^{-1} - 1). \tag{A1.10}$$

Inserting this expression into (3.13), we obtain

$$x = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\frac{\exp(-z^2/2)\,\mathrm{d}z}{A^{-1} - 1 + z^2}.$$

Using (A1.4) and (A1.7), one finally gets

$$\bar{\mathbf{G}} = (\mathbf{G}_{0I}^{-1} + \mathbf{R})^{-1}A^{-1}x = (\mathbf{G}_{0I}^{-1} + \mathbf{R})^{-1}\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\frac{\exp(-z^2/2)\,\mathrm{d}z}{1 - A + Az^2}. \tag{A1.11}$$

Equation (A1.11) is equivalent to equation (3.14).

Appendix 2. Proof of equation (3.17)

The calculation of $\langle k_\alpha|R|k_\beta\rangle = \langle k_\alpha|\mathrm{Tr}_S(\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1)|k_\beta\rangle$ is performed in three steps:

(i) $$\langle r_n|\mathbf{G}_0|r_m\rangle = (1/N)\sum_{k_\alpha}\exp[-\mathrm{i}k_\alpha(r_n-r_m)][\lambda+\mathrm{i}L_0+\hat{w}(k_\alpha)]^{-1}$$
$$= P(\lambda+\mathrm{i}L_0, r_n-r_m). \tag{A2.1}$$

The fact was used that $\mathbf{G}_0$ is diagonal in the reciprocal lattice basis (see equation (2.19)).

(ii) $$\langle r_n|\mathbf{L}_1\mathbf{G}_0\mathbf{L}_1|r_m\rangle = L_1(r_n)P(\lambda+\mathrm{i}L_0, r_n-r_m)L_1(r_m)$$
$$= \sum_{ij} L_{\mathrm{DD}}(I, S_i, r_n-r_i)P(\lambda+\mathrm{i}L_0, r_n-r_m)L_{\mathrm{DD}}(I, S_j, r_m-r_j) \tag{A2.2}$$

where equation (2.3) was used.

(iii) $$\langle k_\alpha|R|k_\beta\rangle = (1/N)\sum_{r_n r_m}\exp[\mathrm{i}(k_\beta r_m - k_\alpha r_n)]$$
$$\times\sum_{r_i}\mathrm{Tr}_S[L_{\mathrm{DD}}(I, S, r_n-r_i)P(\lambda+\mathrm{i}L_0, r_n-r_m)L_{\mathrm{DD}}(I, S, r_m-r_i)].$$

Shifting the summation variables r_n and r_m by r_i, one gets the final result

$$\langle k_\alpha|R|k_\beta\rangle = (1/N)\sum_{r_n r_m r_i}\exp[\mathrm{i}(k_\beta(r_m+r_i)-k_\alpha(r_n+r_i)]$$
$$\times\mathrm{Tr}_S[L_{\mathrm{DD}}(I, S, r_n)P(\lambda+\mathrm{i}L_0, r_n-r_m)L_{\mathrm{DD}}(I, S, r_m)]$$
$$= \delta(k_\alpha-k_\beta)\sum_{r_n r_m}\exp[-\mathrm{i}k_\alpha(r_n-r_m)]$$
$$\times\mathrm{Tr}_S[L_{\mathrm{DD}}(I, S, r_n)P(\lambda+\mathrm{i}L_0, r_n-r_m)L_{\mathrm{DD}}(I, S, r_m)]. \tag{A2.3}$$

Appendix 3. An expression for R_{lm} (equation (4.6))

With help of expression (A2.3) for $R(k_0)$, equation (4.6) can be written as

$$R_{lm} = \sum_{r_\alpha r_\beta}\mathrm{Tr}_{I,S}\{[L_{\mathrm{DD}}(I, S, r_\alpha)T_{lm}(I)]^+ P(\lambda+\mathrm{i}L_0, r_\alpha-r_\beta)$$
$$\times[L_{\mathrm{DD}}(I, S, r_\beta)T_{lm}(I)]\}. \tag{A3.1}$$

The Hamiltonian for the dipole–dipole interaction can be written in irreducible tensor notation as

$$\mathcal{H}_{\mathrm{DD}}(I, S, r) = \hbar\sum_{m_1 m_2} f^*_{m_1+m_2}(r)c(112, m_1 m_2)I_{m_1}S_{m_2} \tag{A3.2}$$

where

$$f_m(r) = \hbar\gamma_I\gamma_S\left(\frac{24\pi}{5}\right)^{1/2}\frac{Y_{2m}(\vartheta, \varphi)}{|r|^3} \tag{A3.3}$$

$c(112, m_1, m_2)$ is a Clebsch–Gordon coefficient, and I_m, S_m are the irreducible components of I, S. From (A3.2) it follows that

$$L_{\mathrm{DD}}(I, S, r)T_{lm}(I) = -\sum_{m_1 m_2} f^{*lm}_{m_1 m_2}(r)T_{lm+m_1}(I)S_{m_2} \tag{A3.4}$$

where

$$f^{lm}_{m_1m_2}(r) = [l(l+1)]^{1/2} c(112, m_1m_2)c(111, m_1m) f_{m_1+m_2}(r). \tag{A3.5}$$

Inserting expression (A3.4) into (A3.1) one gets

$$R_{lm} = \frac{S(S+1)}{3} \sum_{m_1m_2r_\alpha r_\beta} f^{lm}_{m_1m_2}(r_\alpha) f^{*lm}_{m_1m_2}(r_\beta)$$

$$P[\lambda - \mathrm{i}(m+m_1)\omega_I - \mathrm{i}m_2\omega_s, r_\alpha - r_\beta] \tag{A3.6}$$

where it has been assumed that $T_{lm+m_1}(I)S_{m_2}$ is an eigenoperator to L_0. For the special case $l = 1$, expressions (4.7) are obtained.

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References

Abragam A 1961 *The Principles of Nuclear Magnetism* (Oxford: Clarendon)
Ackermann H, Heitjans P and Stöckmann H-J 1983 *Springer Topics in Current Physics* vol 31, ed. J Christiansen (Berlin: Springer) p 291
Anderson P W 1954 *J. Phys. Soc. Japan* **9** 316
Bloembergen N, Purcell E M and Pound R V 1948 *Phys. Rev.* **73** 679
Czech R and Kehr K W 1986 *Phys. Rev.* B **34** 261
Dattagupta S 1987 *Relaxation Phenomena in Condensed Matter Physics* (London: Academic)
Hayano R S, Uemura Y J, Imazato J, Nishida N, Yamazaki T and Kubo R 1979 *Phys. Rev.* B **20** 850
Jäger E, Ittermann B, Stöckmann H-J, Bürkmann K, Fischer B, Frank H-P, Sulzer G, Ackermann H and Heitjans P 1987 *Phys. Lett.* **123A** 39
Kirkpatrick S 1973 *Rev. Mod. Phys.* **45** 574
Kreitzmann S R 1986 *Hyperfine Interact.* **31** 13
Kubo R 1969 *Stochastic Processes in Chemical Physics; Advances in Chemical Physics* vol 16, ed. K E Shuler (New York: Wiley) p 101
Kubo R and Tomita K 1954 *J. Phys. Soc. Japan* **9** 888
Proc. 7th Yamada Conf. Muon Spin Rotation and Associated Problems (Shimoda) 1983 1984 *Hyperfine Interact.* **17–19**
Redfield A G 1957 *IBM J. Res. Dev.* **1** 19
Seeger A 1984 *Hyperfine Interact.* **17–19** 75
Sholl C A 1981 *J. Phys. C: Solid State Phys.* **14** 1479
Summerfield S 1981 *Solid State Commun.* **39** 401
Van Vleck J H 1948 *Phys. Rev.* **74** 1168
Wangsness R K and Bloch F 1953 *Phys. Rev.* **89** 728