

Theory of nuclear magnetic relaxation

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A theory of nuclear magnetic relaxation centred around the rotation operator is proposed. The theory is applicable in principle to molecules of arbitrary shape, and account is taken of the effects of their inertia. Calculation of relaxation times associated with anisotropic chemical shift and spin-rotational interactions provides illustrations of how the theory may be employed.

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1 INTRODUCTION

The theory of nuclear magnetic relaxation associated with random thermal motion has been presented by Abragam¹ and Hubbard². In the present investigation a theory is proposed in which the rotation operator plays a central and explicit part. This is facilitated by employing results for the rotational Brownian motion of a rigid body of arbitrary shape, that were derived by calculations in which the effects of the inertia of the body are included³.

In the next section the stochastic rotation operator will be defined, and an outline will be given of the way in which the operator and its ensemble average are calculated. In section 3 it will be shown how relaxation times can be deduced from spectral densities associated with the rotation operator. This will be illustrated in section 4 by applications to relaxation by anisotropic chemical shift and by spin-rotational interactions.

2 THE STOCHASTIC ROTATION OPERATOR

The concept of rotation operator may be introduced by taking a set of rectangular coordinate axes Ox, Oy, Oz and a function $f(x, y, z)$ of the coordinates (x, y, z) of a fixed point P . Let us now rotate the coordinate axes about the origin to Ox', Oy', Oz' and consider the same function f of the new coordinates (x', y', z') of P . We write

$$f(x', y', z') = Rf(x, y, z) \quad (1)$$

and we say that R is the rotation operator associated with the rotation of axes and with the function f . When f has more than one component, equation (1) is to be interpreted as

$$f_i(x', y', z') = \sum_k R_{ik} f_k(x, y, z) \quad (2)$$

It is helpful to introduce infinitesimal generators of rotation J_x, J_y, J_z by

$$J_x = -i \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \quad J_y = -i \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \\ J_z = -i \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

If we rotate Ox, Oy, Oz through an angle χ about an axis specified by the unit vector \mathbf{e} , it is easily proved⁴ that

$$R = \exp[-i\chi(\mathbf{J} \cdot \mathbf{e})] \quad (3)$$

If a rigid body is rotating with angular velocity $\omega(t)$ about \mathbf{e} , it follows from equation (3) that

$$\frac{dR(t)}{dt} = -i(\mathbf{J} \cdot \omega(t))R(t) \quad (4)$$

The rotation of the coordinate axes may be achieved by rotating about the z -axis through an angle γ' , then about the y -axis through an angle β' and lastly about the z -axis through an angle α' ⁵. We see from equation (3) that R is now given by

$$R = e^{-i\alpha'J_z} e^{-i\beta'J_y} e^{-i\gamma'J_z} \quad (5)$$

If for this rotation we apply equation (2) to the set of spherical harmonics $Y_{jm}(\theta, \phi)$, where

$$x = r \sin\theta \cos\phi, \quad y = r \sin\theta \sin\phi, \quad z = r \cos\theta$$

then it is usual to write equation (2) as

$$Y_{jm}(\theta', \phi') = \sum_{m'=-j}^j D_{m'm}^j(\alpha', \beta', \gamma') Y_{jm}(\theta, \phi) \quad (6)$$

where $D_{m'm}^j$ are Wigner functions. Equation (6) shows that $D_{m'm}^j$ is the $m'm$ -element of the matrix representative of R in the representation with basis elements $Y_{j,-j}, Y_{j,-j+1}, \dots, Y_{jj}$; that is to say,

$$D_{m'm}^j(\alpha', \beta', \gamma') = R_{m'm}^j \quad (7)$$

We apply these ideas to a molecule that is undergoing steady state Brownian motion. Then the angular velocity $\omega(t)$ in equation (4) is a random variable, and so also is the solution of this equation. We refer to $R(t)$ as the stochastic rotation operator. To obtain information about ω we take axes fixed in the molecule with origin at the centre of mass and in the directions of the principal axes of inertia. We assume that the components of ω referred to the molecular coordinate system obey the Euler-Langevin

equations⁶

$$I_1 \frac{d\omega_1}{dt} - (I_2 - I_3)\omega_2\omega_3 = -I_1 B_1 \omega_1(t) + I_1 A_1(t), \text{ etc. (8)}$$

where I_1, I_2, I_3 are the principal moments of inertia, $\omega_1, \omega_2, \omega_3$ are the components of angular velocity, $I_1 A_1, I_2 A_2, I_3 A_3$ the components of the driving couple and $I_1 B_1 \omega_1, I_2 B_2 \omega_2, I_3 B_3 \omega_3$ the components of the frictional couple resisting the motion. From equation (8) we may deduce the value of the time-correlation function of two components of angular velocity, which will be useful for subsequent calculations.

In order to solve equation (4) we employ a method of solution of nonlinear differential equations that goes back to Krylov and Bogoliubov⁷. It is assumed that the solution $R(t)$ consists of a slowly varying ensemble average $\langle R(t) \rangle$, about which there are random fluctuations, and the solution is expressed as

$$R(t) = (I + \varepsilon F^{(1)}(t) + \varepsilon^2 F^{(2)}(t) + \dots) \langle R(t) \rangle \quad (9)$$

where I is the identity operator and ε is a small dimensionless parameter. $R(t)$ describes the rotation of the molecule from its orientation at time zero. The ensemble average $\langle R(t) \rangle$ is nonstochastic and it is supposed to satisfy some equation

$$\frac{d\langle R(t) \rangle}{dt} = (\varepsilon \Omega^{(1)}(t) + \varepsilon^2 \Omega^{(2)}(t) + \varepsilon^3 \Omega^{(3)}(t) + \dots) \langle R(t) \rangle \quad (10)$$

By using the knowledge that we have obtained from equation (8) we can often deduce from equations (4), (9) and (10) the values of $\varepsilon F^{(1)}(t), \varepsilon^2 F^{(2)}(t), \varepsilon \Omega^{(1)}(t), \varepsilon^2 \Omega^{(2)}(t), \dots$ for substitution into equations (9) and (10). We may then be able to solve equation (10) for $\langle R(t) \rangle$. Analytical solutions have in fact been found for a molecule that is spherical or linear or a symmetric top or even an asymmetric top³. For most n.m.r. problems the value of $\langle R(t) \rangle$ is all that we need. If we do need the value of $R(t)$, we can obtain it from equation (9).

BASIC THEORY OF NUCLEAR MAGNETIC RELAXATION

To study nuclear magnetic relaxation we take a set of cartesian axes fixed with respect to the laboratory. A constant strong magnetic field H_0 acts in the z -direction. If H_0 interacts with a nucleus spin I and gyromagnetic ratio γ , the field produces a Hamiltonian $-\gamma \hbar H_0 I_z$, denoted also by $\hbar \mathcal{H}_0$, with non-degenerate energy levels. We now use the normalized eigenfunctions of $\hbar \mathcal{H}_0$ as a basis to express matrix elements of operators. A relatively small perturbing Hamiltonian $\hbar G(t)$ like that arising from dipole-dipole, quadrupole, chemical shift or spin-rotational interactions causes a relaxation process, and the results are usually expressed in terms of longitudinal and transverse relaxation times T_1 and T_2 , T_1 referring to the z -direction. For any particular interaction one has two problems:

- (a) to express T_1 and T_2 in terms of spectral densities
- (b) to calculate the spectral densities.

The most direct way of handling problem (a) is to

employ a general method due to Redfield⁸. If M_r , with $r = x, y, z$ is a component of magnetic moment per unit volume due to the interaction and $\rho_{\beta\beta'}$ denotes an element of the density matrix, then

$$\frac{d\langle M_r \rangle}{dt} = \sum_{\alpha\alpha'\beta\beta'} R_{\alpha\alpha'\beta\beta'} \rho_{\beta\beta'} (M_r)_{\alpha\alpha'} \quad (11)$$

where

$$R_{\alpha\alpha'\beta\beta'} = J_{\alpha\beta\alpha'\beta'}(\omega_\alpha - \omega_\beta) + J_{\alpha\beta\alpha'\beta'}(\omega_\alpha - \omega_\beta) - \delta_{\alpha\beta} \sum_{\sigma} J_{\sigma\beta\sigma\alpha}(\omega_\sigma - \omega_\beta) - \delta_{\alpha\beta'} \sum_{\sigma} J_{\sigma\alpha\sigma\beta'}(\omega_\sigma - \omega_\beta) \quad (12)$$

$$J_{\alpha\alpha'\beta\beta'}(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} \langle G_{\alpha\alpha'}(0) G_{\beta\beta'}^*(t) \rangle e^{-i\omega t} dt \quad (13)$$

The $J_{\alpha\alpha'\beta\beta'}(\omega)$ is a spectral density referred to in (a) and (b), $G_{\alpha\alpha'}(t)$ is an abbreviation of $\langle \alpha | G(t) | \alpha' \rangle$, where $|\alpha\rangle, |\alpha'\rangle$ are eigenfunctions of $\hbar \mathcal{H}_0$. The energy of the state $|\alpha\rangle$ is $\hbar \omega_\alpha$. On substituting equations (12) and (13) into equation (11) we may obtain an equation

$$\frac{d\langle M_r \rangle}{dt} = -\lambda_r \langle M_r \rangle \quad (14)$$

From this would follow

$$\frac{1}{T_1} = \lambda_z \quad \frac{1}{T_2} = \lambda_x \quad (15)$$

To see how the spectral densities are to be calculated we shall first of all take a special form of $G(t)$, namely,

$$G(t) = \sum_{q=-2}^2 (-)^q F_{-q}(t) A_q \quad (16)$$

where $F_{-2}(t), F_{-1}(t), F_0(t), F_1(t), F_2(t)$ transform under rotations like the spherical harmonics

$$Y_{2,-2}(\theta(t), \phi(t)), Y_{2,-1}(\theta(t), \phi(t)), Y_{20}(\theta(t), \phi(t)), Y_{21}(\theta(t), \phi(t)), Y_{22}(\theta(t), \phi(t))$$

This will permit the application of equations (6) and (7) to $F_p(t)$. We have from equation (16)

$$G_{\alpha\alpha'}(t) = \sum_{q=-2}^2 (-)^q F_{-q}(t) \langle \alpha | A_q | \alpha' \rangle$$

$$G_{\beta\beta'}^*(t) = \sum_{q=-2}^2 (-)^q F_{-q}^*(t) \langle \beta | A_q | \beta' \rangle^*$$

$$= \sum_{q=-2}^2 (-)^q F_{-q}^*(t) \langle \beta' | A_q^+ | \beta \rangle$$

where A_q^+ is the adjoint of the operator A_q . We deduce that

$$\langle G_{\alpha\alpha'}(0) G_{\beta\beta'}(t) \rangle = \sum_{q,q'=-2}^2 (-)^{q+q'} \langle F_{-q}(0) F_{-q'}^*(t) \rangle \langle \alpha | A_q | \alpha' \rangle \times \langle \beta' | A_{q'}^+ | \beta \rangle \quad (17)$$

The angular brackets denote here an average over the random variables, that is to say, the angular velocity components, together with an average over the initial orientations of the molecule. A study of the transformation properties of spherical harmonics shows that⁹

$$\langle F_{-q}(0)F_{-q}^*(t) \rangle = \frac{1}{5}\delta_{qq'} \sum_{n,n'=-2}^2 \langle R(t) \rangle_{n'n} F_n^* F_{n'}$$

where $F_p = F_p(0)$, a constant, and $\langle R(t) \rangle$ is the ensemble average of the rotation operator for the molecule in question. We see that we may write

$$\int_{-\infty}^{\infty} \langle F_{-q}(0)F_{-q}^*(t) \rangle e^{-i\omega t} dt = J(\omega)$$

independent of q , and, from equations (13) and (17), that

$$J_{\alpha\alpha'\beta\beta'}(\omega) = \frac{1}{2}J(\omega) \sum_{q=-2}^2 (\alpha|A_q|\alpha')(\beta'|A_q^+|\beta) \quad (18)$$

where

$$J(\omega) = \frac{1}{5} \sum_{n,n'=-2}^2 F_n^* F_{n'} \int_{-\infty}^{\infty} \langle R(t) \rangle_{n'n} e^{-i\omega t} dt \quad (19)$$

We know F_q from the nature of the perturbing Hamiltonian that gives rise to the interaction and we know $\langle R(t) \rangle$ from the investigation of the rotational Brownian motion of the molecule. Hence we can in principle calculate $J(\omega)$ from equation (19) and consequently the relaxation times from equations (11), (12), (13), (15) and (18). Moreover, since the integral in equation (19) is independent of the interaction Hamiltonian $\hbar G(t)$, results for relaxation times can easily be taken over from one interaction satisfying equation (16) to another by replacing the values of F_q in equation (19).

4 CALCULATION OF RELAXATION TIMES

As applications of the Redfield theory we shall investigate two types of interaction that cause nuclear magnetic relaxation. The first is anisotropic chemical shift, which is an example of an interaction satisfying equation (16). The other is spin-rotational interaction, which does not obey equation (16).

For anisotropic chemical shift it may be shown that^{10,11}

$$\begin{aligned} A_0 &= 2H_0 I_z & A_1 &= -\frac{\sqrt{6}}{2}H_0 I_+ & A_{-1} &= \frac{\sqrt{6}}{2}H_0 I_- \\ & & A_2 &= A_{-2} = 0 \end{aligned} \quad (20)$$

where

$$I_{\pm} = I_x \pm iI_y$$

and that

$$F'_0 = \frac{1}{2}\gamma\delta_z \quad F'_{\pm 1} = 0 \quad F'_{\pm 2} = \frac{\zeta}{2\sqrt{6}}\gamma\delta_z \quad (21)$$

where the non-vanishing elements of the diagonalized anisotropic chemical shift tensor are

$$-\frac{1}{2}(1-\zeta)\delta_z, \quad -\frac{1}{2}(1+\zeta)\delta_z, \quad \delta_z$$

Hence, from equation (18),

$$J_{\alpha\beta\alpha'\beta'}(\omega_{\alpha'} - \omega_{\beta'}) = \frac{1}{2}J_{cs}(\omega_{\alpha'} - \omega_{\beta'}) \sum_{q=-1}^1 (\alpha|A_q|\beta)(\beta'|A_q^+|\alpha')$$

and $J_{cs}(\omega)$ is given by equation (19) with the values of F_q taken from equation (21). Since

$$\langle M_r \rangle = \gamma\hbar N \langle I_r \rangle$$

where N is the number per unit volume of nuclei taking part in the relaxation process, we may obtain the relaxation times by applying equations (11), (14) and (15) to I_r . Employing equation (20) we find after an elementary calculation that¹⁰

$$\frac{1}{T_1^{cs}} = 3H_0^2 J_{cs}(\omega_0) \quad (22)$$

$$\frac{1}{T_2^{cs}} = \frac{1}{2}H_0^2 [4J_{cs}(0) + 3J_{cs}(\omega_0)]$$

To complete the calculations we must obtain an expression for $J_{cs}(\omega)$ from equations (19) and (21). What was equivalently the same thing was done by Abragam but only for a spherical molecule and with inertial effects neglected¹². The explicit use of the rotation operator has allowed us to include the inertial effects and to extend the discussion to a linear molecule and to a symmetric top molecule¹⁰. We shall put down the result only for the latter case taking the nucleus to be at the centre and the axis of symmetry as the third coordinate axis in equation (8), so that $I_2 = I_1$, $B_2 = B_1$:

$$\begin{aligned} J_{cs}(\omega) &= \frac{1}{5}\gamma^2\delta_z^2 \left\{ \frac{3D_1 \left(1 + \frac{6D_1}{B_1}\right)}{36D_1^2 + \omega^2} \right. \\ &\quad \left. + \frac{1}{3}\zeta^2 \frac{(D_1 + 2D_3) \left(1 + \frac{2D_1}{B_1} + \frac{4D_3}{B_3}\right)}{(2D_1 + 4D_3)^2 + \omega^2} + \dots \right\}, \end{aligned}$$

where

$$D_1 = \frac{kT}{I_1 B_1} \quad D_3 = \frac{kT}{I_3 B_3} \quad (23)$$

The relaxation times follow from equation (22).

We can see from equations (16), (18) and (19) that, when the interacting Hamiltonian can be expanded as a linear combination of elements of a five-dimensional spherical tensor, we require only $\langle R(t) \rangle$ for the molecule in order to calculate the spectral density $J(\omega)$ and consequently the relaxation times. This procedure fails in the study of nuclear magnetic relaxation by spin-rotational interactions. Then

$$\hbar G = \hbar(\mathbf{I} \cdot \mathbf{C} \cdot \mathbf{J}) \quad (24)$$

where \mathbf{I} is the spin operator of the nucleus that interests us,

\mathbf{C} is the three-dimensional spin-rotational tensor and $\hbar\mathbf{J}$ is the angular momentum operator of the molecule that contains the nucleus. Since the number of independent elements of \mathbf{C} is not five, the G of equation (24) cannot be expanded as in equation (16).

A general theory of nuclear magnetic relaxation by spin-rotational interactions has been based on the stochastic rotation operator¹³. The angular momentum $\hbar\mathbf{J}$ is replaced by its classical value ($I_1\omega_1, I_2\omega_2, I_3\omega_3$). We have found that the Redfield method yields relaxation times T_1^{sr}, T_2^{sr} given by

$$\frac{1}{T_1^{sr}} = 2J_{sr}(\omega_0) \quad \frac{1}{T_2^{sr}} = J_{sr}(0) + J_{sr}(\omega_0) \quad (25)$$

where

$$J_{sr}(\omega) = \frac{1}{2}\{c(i\omega) + c(-i\omega)\} \quad (26)$$

$$c(s) = \frac{1}{3\hbar^2} \sum_{\mu,\nu=1}^3 \sum_{m,n=1}^1 (-)^m b_{n\mu} b_{m\nu} I_\mu I_\nu \times \left(\int_0^\infty e^{-st} \langle R(t) \omega_\mu(t) \omega_\nu(0) \rangle dt \right)_{n,-m} \quad (27)$$

$$b_{0\nu} = C_{3\nu} \quad b_{\pm 1,\nu} = \mp \frac{C_{1\nu} \mp iC_{2\nu}}{\sqrt{2}}$$

and $n, -m$ denotes matrix representation with respect to the basis $Y_{1,-1}, Y_{10}, Y_{11}$.

We can see from equations (25), (26) and (27) that a knowledge of $\langle R(t) \rangle$ is no longer adequate for the calculation of spectral densities and relaxation times. We must now use our knowledge of the values of $e^{F^{(1)}(t)}, e^{F^{(2)}(t)}, \dots$ and of $\langle R(t) \rangle$ to calculate $R(t)$ from equation (9). Then we must obtain $\langle R(t) \omega_\mu(t) \omega_\nu(0) \rangle$, calculate its Laplace transform and the matrix elements of this, evaluate $c(s)$ from equation (27) and employ equations (25) and (26) to deduce the relaxation times. This has been done in principle for an asymmetric molecule and with the inclusion of inertial effects. Explicit results can be given for molecules that are linear, axially symmetric or spherical.

For simplicity we shall report these results only in the extreme narrowing approximation of $\omega_0 \ll kT/(IB)$, where I and B stand generically for the moments of inertia and the friction constants in equation (8). Then T_1^{sr} and T_2^{sr} are equal, and we shall denote their common value by T_{sr} . In the case of a spherical molecule¹³

$$\frac{1}{T_{sr}} = \frac{2IkT}{3\hbar^2 B} \{ (C_{\parallel}^2 + 2C_{\perp}^2) - \kappa(C_{\perp} - C_{\parallel})^2 + \frac{1}{6}\kappa^2(C_{\perp} - C_{\parallel})^2 + \dots \} \quad (28)$$

where $\kappa = kT/(IB^2)$, the spin-rotational tensor component C_{\parallel} refers to the direction of the radius through the nucleus and C_{\perp} refers to a perpendicular direction. In the case of a molecule which has a principal axis of inertia through the centre of mass that passes through the nucleus and which is such that this principal axis is an axis of symmetry C_n for the molecule with $n \geq 3$ ¹⁴

$$\frac{1}{T_{sr}} = \frac{2kT}{3\hbar^2} \left\{ \frac{2I_1 C_{\perp}^2}{B_1 + D_1 + D_3} + \frac{I_3 C_{\parallel}^2}{B_3 + 2D_1} + kT \left[\left(\frac{2}{B_1^3} + \frac{2I_1}{I_3 B_1^2 B_3} - \frac{2I_3}{I_1 B_1^2 (B_1 + B_3)} \right) C_{\perp}^2 + \frac{2I_3 (C_{\parallel}^2 + 2C_{\perp} C_{\parallel})}{I_1 B_1 B_3 (B_1 + B_3)} \right] \right\} \quad (29)$$

In this equation C_{\parallel}, I_3, B_3 refer to the axis of symmetry, C_{\perp}, I_1, B_1 refer to a perpendicular axis and D_1, D_3 are defined in equations (23). In the case of a linear molecule¹⁵

$$\frac{1}{T_{sr}} = \frac{4kTIC_{\perp}^2}{3\hbar^2 B} \quad (30)$$

Calculations have been performed for the above molecular models, when inertial effects are ignored¹⁶. It has been found that equation (28) is altered to

$$\frac{1}{T_{sr}} = \frac{2IkT(C_{\parallel}^2 + 2C_{\perp}^2)}{3\hbar^2 B}$$

that equation (29) is altered to

$$\frac{1}{T_{sr}} = \frac{2kT}{3\hbar^2} \left\{ \frac{2I_1 C_{\perp}^2}{B_1} + \frac{I_3 C_{\parallel}^2}{B_3} \right\}$$

and that equation (30) is unaltered. The inclusion of inertial effects produces for the sphere and for the symmetric rotator corrections of order κ , which is at most a few per cent. There is zero correction for the linear molecule, even though the calculations have been performed to an accuracy of κ^2 .

5 CONCLUSION

An analytical theory of nuclear magnetic relaxation has been based on the stochastic rotation operator and on the Redfield method of establishing a differential equation for the ensemble average of the magnetic moment produced by a specified interaction mechanism. The theory has been applied to examples of two different classes of interaction, namely, anisotropic chemical shift and spin-rotational. The present theory is confined to the study of the behaviour of a single molecule.

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