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Nuclear Magnetic Relaxation by Quadrupole Interactions in Non-Spherical Molecules

James McConnell

**Dublin Institute for Advanced Studies,
Dublin 4, Ireland**

Abstract The nuclear magnetic relaxation times associated with quadrupole interactions are investigated by an analytical method for molecules that may be linear or symmetric rotators, or may be totally asymmetric. The molecules are subject to random thermal couples, and it is supposed that the consequent rotational motion is Brownian. The results are in agreement with those obtained otherwise by Hubbard for the special case of spherical molecules.

1. Introduction

The general theory of nuclear magnetic interaction by quadrupole interactions has been expounded by Abragam[1] and by Hubbard[2]. Employing a semi-classical theory and a Fokker-Planck equation Hubbard derived analytical expressions for relaxation times when the molecule under consideration is spherical and is undergoing steady-state rotational Brownian motion, inertial effects being included in the calculations. The purpose of the present paper is to make use of results deduced from Euler-Langevin equations in order to embrace the cases of molecules that are linear or symmetric rotators, or are asymmetric rotators. As in recent studies of dielectric[3] and of nuclear magnetic[4] relaxation the stochastic rotation operator R(t) will appear prominently in the calculation of Brownian motion effects. In the next section earlier results required for our calculations will be recalled and expressed in a form convenient for future use. In section 3 the linear rotator model will be considered. In section 4 the asymmetric model will be investigated, and results for a symmetric rotator molecule will be deduced as a special case in section 5.

2. Basic equations for quadrupole interactions

We recall some results derived by Abragam and by Hubbard, which will serve as a basis for our calculations. Selecting a molecule we fix our attention on one of its nuclei having spin angular momentum $\hbar \underset{\sim}{I}$, quadrupole moment Q and given gyromagnetic ratio, which is influenced by a constant magnetic field in a fixed direction taken to be the z-direction of the laboratory coordinate system S. We consider the interaction between the quadrupole moment and the electric field produced at the nucleus by all the other charges in the molecule. The interaction Hamiltonian $\hbar H_1$ is given by[5]

$$\hbar H_1 = \sum_{q=-2}^{2} (-)^q F_{-q} Q_q , \tag{1}$$

where

$$F_0 = \tfrac{1}{2} V_{zz} , \quad F_{\pm 1} = \mp \frac{1}{\sqrt{6}} \left(V_{zx} \pm i V_{zy} \right) \tag{2}$$
$$F_{\pm 2} = \frac{1}{2\sqrt{6}} \left(V_{xx} - V_{yy} \pm 2i V_{xy} \right),$$

$$Q_0 = \frac{eQ}{2I(2I-1)} \left[3I_z^2 - I(I+1) \right] \tag{3}$$
$$Q_{\pm 1} = \mp \frac{\sqrt{6}}{2} \frac{eQ}{2I(2I-1)} \left[I_z I_\pm + I_\pm I_z \right]$$
$$Q_{\pm 2} = \frac{\sqrt{6}}{2} \frac{eQ}{2I(2I-1)} I_\pm^2 , \quad I_\pm = I_x \pm i I_y .$$

The quantities on the right hand sides of (2) refer to the body in its position at time t. V is the electric potential at the nucleus of the other charges in the molecule and these charges are regarded as fixed with respect to the molecule. The subscripts to V denote partial derivatives. All the quantities in (1) refer to the frame S. If the quantities on the right hand sides of (2) were referred to a coordinate system S' fixed in the molecule, they would all be constants.

The set $F_0, F_{\pm 1}, F_{\pm 2}$ transforms under spatial rotations as the spherical harmonies $Y_{20}, Y_{2,\pm 1}, Y_{2,\pm 2}$ and so constitutes a spherical tensor of rank 2. For any spherical tensors $T_{km}, V_{k'm'}$, of ranks k, k', respectively, whose components are functions of time, the correlation function

$$\langle T^*_{km}(t)\, V_{k'm'}(0)\rangle = \frac{\delta_{kk'}\,\delta_{mm'}}{2k+1} \sum_{n,n'=-k}^{k} w^k_{nn'}(t)\, T'^*_{kn}\, V'_{kn'}, \tag{4}$$

where

$$w^k_{nn'}(t) = (2k+1)\left\langle D^k_{0n}(\alpha(t),\beta(t),\gamma(t))\, D^{k*}_{0n'}(\alpha(0),\beta(0),\gamma(0))\right\rangle.^{6)} \tag{5}$$

In (4) T,V indicate components in the frame S and T',V' components in S'. In (5) the $\alpha(t)$, $\beta(t)$, $\gamma(t)$ are Euler angles defining the orientation of S' at time t with respect to S, and we shall denote by R(t) the rotation operator which brings S' at time zero to its orientation at time t. Using well-known properties of Wigner functions[7] we deduce from (5) that

$$\begin{aligned} w^k_{nn'}(t) &= (2k+1)\left\langle D^k_{n'0}(-\gamma(0),-\beta(0),-\alpha(0))\, D^{k*}_{n0}(-\gamma(t),-\beta(t),-\alpha(t))\right\rangle \\ &= 4\pi\left\langle Y^*_{kn'}(-\beta(0),-\alpha(0))\, Y_{kn}(-\beta(t),-\alpha(t))\right\rangle. \end{aligned} \tag{6}$$

Employing the result

$$4\pi\left\langle Y^*_{kn'}(\beta(0),\alpha(0))\, Y_{kn}(\beta(t),\alpha(t))\right\rangle = \langle R^\dagger(t)\rangle^k_{n'n}$$

and the unitary property of R(t) we see from (6) that

$$w^k_{nn'}(t) = \langle R(t)\rangle^{k}_{n'n},$$

the n'n-element of the representative of $\langle R(t)\rangle$ with reference to the basis $Y_{k,-k}, Y_{k,-k+1}, \ldots Y_{kk}$. We may therefore express (4) as

$$\langle T^*_{km}(t)\, V_{k'm'}(0)\rangle = \frac{\delta_{kk'}\,\delta_{mm'}}{2k+1} \sum_{n,n'=-k}^{k} \langle R(t)\rangle^k_{n'n}\, T'^*_{kn}\, V'_{kn'}. \tag{7}$$

In future we shall work in the five-dimensional space of spherical tensors of rank 2. Applying (7) to F_q we obtain

$$\langle F^*_q(t)\, F_{q'}(0)\rangle = \frac{1}{5}\,\delta_{qq'} \sum_{n,n'=-2}^{2} \langle R(t)\rangle_{n'n}\, F'^*_n\, F'_{n'}, \tag{8}$$

the values of F_n',$F_{n'}'$, being constant as we saw above. We note that $\langle F^*_q(t) F_{q'}(0)\rangle$ vanishes for q'≠q, and that

$$\langle F^*_q(t)\, F_q(0)\rangle = \frac{1}{5} \sum_{n,n'=-2}^{2} \langle R(t)\rangle_{n'n}\, F'^*_n\, F'_{n'}, \tag{9}$$

which is independent of q. Since, from (2), $F^*_q = (-)^q F_{-q}$,

$$\begin{aligned} \langle F^*_q(t)\, F_q(0)\rangle^* &= \langle F_q(t)\, F^*_q(0)\rangle = \langle F^*_{-q}(t)\, F_{-q}(0)\rangle \\ &= \langle F^*_q(t)\, F_q(0)\rangle, \end{aligned} \tag{10}$$

so that $\langle F^*_q(t) F_q(0)\rangle$ is real. Moreover, since we are concerned only with steady state motion,

$$\begin{aligned} \langle F^*_q(-t)\, F_q(0)\rangle &= \langle F^*_q(0)\, F_q(t)\rangle = \langle F^*_q(t)\, F_q(0)\rangle^* \\ &= \langle F^*_q(t)\, F_q(0)\rangle, \end{aligned} \tag{11}$$

by (10), and so $\langle F^*_q(t) F_q(0)\rangle$ is also an even function of t. Then defining the Fourier transform $J(\omega)$ of $\langle F^*_q(t) F_q(0)\rangle$ by

$$J(\omega) = \int_{-\infty}^{\infty} \langle F^*_q(t)\, F_q(0)\rangle\, e^{-i\omega t}\, dt \tag{12}$$

we see from (11) that

$$J(\omega) = 2\int_0^{\infty} \langle F^*_q(t) F_q(0)\rangle \cos\omega t\, dt, \tag{13}$$

which shows that $J(\omega)$ is an even function of ω. We also see that

$$J(\omega) = \tau(\omega) + \tau(\omega)^*, \tag{14}$$

where

$$\tau(\omega) = \int_0^\infty \langle F_{q'}^*(t) F_q(0)\rangle e^{-i\omega t} dt. \tag{15}$$

Having established these preliminaries we are justified in accepting the results of calculations of Abragam which are required for the introduction of quadrupole interaction relaxation times[8]. If there exists an equation of the type

$$\frac{d\langle I_3\rangle}{dt} = -\frac{\langle I_3\rangle - \langle I_3\rangle_0}{T_1}, \tag{16}$$

where $\langle I_3\rangle_0$ is the ensemble average of I_3 for the equilibrium state, we call T_1 the longitudinal relaxation time. Similarly if there exists an equation

$$\frac{d\langle I_x\rangle}{dt} = -\frac{\langle I_x\rangle}{T_2}, \tag{17}$$

we say that T_2 is the transverse relaxation time. Equations (16) and (17) will exist when the molecule has spin one, and then in our notation

$$\frac{1}{T_1} = \frac{3}{4}\left(\frac{eQ}{\hbar}\right)^2 \left(J(\omega_0) + 4J(2\omega_0)\right) \tag{18}$$

$$\frac{1}{T_2} = \frac{1}{8}\left(\frac{eQ}{\hbar}\right)^2 \left(9J(0) + 15J(\omega_0) + 6J(2\omega_0)\right), \tag{19}$$

where ω_0 is the Larmor angular frequency. Equations (16) and (17) will also exist for an arbitrary spin I of the molecule in the extreme narrowing case where it is allowable to approximate ω_0 by zero in the arguments of the J-functions, and then

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3(2I+3)}{4I^2(2I-1)}\left(\frac{eQ}{\hbar}\right)^2 J(0). \tag{20}$$

Equations (18)-(20) are seen to agree with (2.44)-(2.46) of ref. 2 when it is noticed that, since F_0 is real,

$$J_Q(\omega) = J_{00}(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} \langle F_0(t)F_0(0)\rangle e^{i\omega t} dt = \frac{1}{2}\int_{-\infty}^{\infty} \langle F_0^*(t)F_0(0)\rangle e^{i\omega t} dt$$
$$= \frac{1}{2}\int_{-\infty}^{\infty} \langle F_0^*(t)F_0(0)\rangle e^{-i\omega t} dt = \frac{1}{2}J(\omega),$$

where we have employed (11).

It appears from the above that the shape of the molecule and its random motion enter into the calculation of the relaxation times only through $J(\omega)$. By (9) and (12)

$$J(\omega) = \frac{1}{5}\sum_{n,n'=-2}^{2} \int_{-\infty}^{\infty} \langle R(t)\rangle_{n'n} e^{-i\omega t} dt\, F_n'^* F_{n'}', \tag{21}$$

where $F_n', F_{n'}'$ given by (2) in the molecular frame are time independent. We may also express (21) by (14), where

$$\tau(\omega) = \frac{1}{5}\sum_{n,n'=-2}^{2} \int_0^{\infty} \langle R(t)\rangle_{n'n} e^{-i\omega t} F_n'^* F_{n'}', \tag{22}$$

by (9) and (15).

3. Relaxation in linear molecules

The value of $\langle R(t)\rangle$ when the molecule is linear has been expressed in a form convenient for our calculations by the equation[9]

$$\begin{aligned}\langle R(t)\rangle = \{ &\underset{\sim}{E} + \gamma(J^2-J_3^2)(1-e^{-B_1 t}) + \gamma^2[(2J^2-5J_3^2)(\tfrac{5}{4}-e^{-B_1 t}-B_1 t e^{-B_1 t}-\tfrac{1}{4}e^{-2B_1 t})\\ &+(J^2-J_3^2)^2(\tfrac{1}{2}-e^{-B_1 t}+\tfrac{1}{2}e^{-2B_1 t})] + \cdots\}\\ \times \exp\Big[&-\gamma B_1\{(J^2-J_3^2)+\gamma(J^2-\tfrac{5}{2}J_3^2)\\ &+\gamma^2(\tfrac{8}{3}J^2-\tfrac{29}{3}J_3^2+4[J^2-J_3^2]J_3^2)+\cdots\}t\Big].\end{aligned} \tag{23}$$

To derive this equation the motion was referred to the body frame coordinate system with origin at the centre and third axis along the line of the molecule. The moment of inertia about the first or second axis was denoted by I_1. The frictional couple about either axis is I_1B_1 times the corresponding component of angular velocity of the molecule and

$$\gamma = \frac{kT}{I_1 B_1^2}, \tag{24}$$

a small dimensionless constant. The identity operator is denoted in (23) by $\underset{\sim}{E}$. J^2 and J_3^2 are the usual rotation operators, the subscript 3 referring to the rotating axes as do the n,n' in (21) and (22). In the five-dimensional representation with basis $Y_{2,-2}, Y_{2,-1}, Y_{20}, Y_{21}, Y_{22}$

$$J^2 = \begin{bmatrix} 6 & 0 & 0 & 0 & 0 \\ 0 & 6 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & 6 & 0 \\ 0 & 0 & 0 & 0 & 6 \end{bmatrix}, \quad J_3^2 = \begin{bmatrix} 4 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 4 \end{bmatrix}, \tag{25}$$

the rows and columns being numbered in the order -2,-1,0,1,2. Since all the matrices in (23) are diagonal and the elements of each matrix are equal for n=±1 and for n=±2, we may simplify (21) in the present molecular model to

$$J(\omega) = \frac{1}{5}\int_{-\infty}^{\infty}\left\{\langle R(t)\rangle_{00}|F_0'|^2 + 2\langle R(t)\rangle_{11}|F_1'|^2 + 2\langle R(t)\rangle_{22}|F_2'|^2\right\}e^{-i\omega t}dt. \tag{26}$$

It is convenient to write the exponential in (23) as exp (-B₁Gt) with

$$G = \gamma\left\{(J^2 - J_3^2) + \gamma(J^2 - \tfrac{5}{2}J_3^2) + \gamma^2\left(\tfrac{8}{3}J^2 - \tfrac{29}{3}J_3^2 + 4[J^2 - J_3^2]J_3^2\right) + \cdots\right\}. \tag{27}$$

For convenience we write

$$G_{00} = G_0, \quad G_{11} = G_{-1,-1} = G_1, \quad G_{22} = G_{-2,-2} = G_2.$$

Then from (23), (25), (27)

$$\langle R(t)\rangle_{00} = \left\{1 + 6\gamma(1 - e^{-B_1 t}) + \gamma^2(33 - 48e^{-B_1 t} - 12B_1 t e^{-B_1 t} + 15e^{-2B_1 t}) + \cdots\right\}e^{-B_1 G_0 t} \tag{28}$$

$$G_0 = 6\gamma(1 + \gamma + \tfrac{8}{3}\gamma^2 + \cdots) \tag{29}$$

$$\langle R(t)\rangle_{11} = \left\{1 + 5\gamma(1 - e^{-B_1 t}) + \gamma^2(\tfrac{85}{4} - 32e^{-B_1 t} - 7B_1 t e^{-B_1 t} + \tfrac{43}{4}e^{-2B_1 t}) + \cdots\right\}e^{-B_1 G_1 t} \tag{30}$$

$$G_1 = 5\gamma(1 + \tfrac{7}{10}\gamma + \tfrac{79}{15}\gamma^2 + \cdots) \tag{31}$$

$$\langle R(t)\rangle_{22} = \left\{1 + 2\gamma(1 - e^{-B_1 t}) + \gamma^2(-8 + 4e^{-B_1 t} + 8B_1 t e^{-B_1 t} + 4e^{-2B_1 t}) + \cdots\right\}e^{-B_1 G_2 t} \tag{32}$$

$$G_2 = 2\gamma\,(1 - 2\gamma + \tfrac{14}{3}\gamma^2 + \cdots). \tag{33}$$

To perform the integrations in (26) we employ Laplace transforms. Let us put

$$\int_0^\infty \langle R(t)\rangle_{00}e^{-i\omega t}dt = \tau_{20}(\omega), \quad \int_0^\infty \langle R(t)\rangle_{11}e^{-i\omega t}dt = \tau_{21}(\omega)$$
$$\int_0^\infty \langle R(t)\rangle_{22}e^{-i\omega t}dt = \tau_{22}(\omega), \qquad \text{(}$$

so that, from (22) and (25),

$$\tau(\omega) = \frac{1}{5}\left\{\tau_{20}(\omega)|F_0'|^2 + 2\tau_{21}(\omega)|F_1'|^2 + 2\tau_{22}(\omega)|F_2'|^2\right\}. \qquad \text{(}$$

On writing $\omega/B_1 = \omega'$ we deduce from (28)-(34)

$$\tau_{20}(\omega) = \frac{1 + 6\gamma + 33\gamma^2 + \cdots}{B_1(G_0 + i\omega')} - \frac{6\gamma + 48\gamma^2 + \cdots}{B_1(1 + G_0 + i\omega')} - \frac{12\gamma^2 + \cdots}{B_1(1 + G_0 + i\omega')^2} + \frac{15\gamma^2 + \cdots}{B_1(2 + G_0 + i\omega')} + \cdots \qquad \text{(}$$

and in particular

$$\tau_{20}(0) = \frac{1 + 5\gamma - \frac{32}{3}\gamma^2 + \cdots}{6\gamma B_1}. \qquad \text{(:}$$

Similarly we find that

$$\tau_{21}(\omega) = \frac{1 + 5\gamma + \frac{85}{4}\gamma^2 + \cdots}{B_1(G_1 + i\omega')} - \frac{5\gamma + 32\gamma^2 + \cdots}{B_1(1 + G_1 + i\omega')} - \frac{7\gamma^2 + \cdots}{B_1(1 + G_1 + i\omega')^2} + \frac{\frac{43}{4}\gamma^2 + \cdots}{B_1(2 + G_1 + i\omega')} + \cdots \qquad \text{(3}$$

$$\tau_{21}(0) = \frac{1 + \frac{43}{16}\gamma - \frac{902}{75}\gamma^2 + \cdots}{5\gamma B_1} \qquad \text{(3}$$

$$\tau_{22}(\omega) = \frac{1 + 2\gamma - 8\gamma^2 + \cdots}{B_1(G_2 + i\omega')} + \frac{-2\gamma + 4\gamma^2 + \cdots}{B_1(1 + G_2 + i\omega')} + \frac{8\gamma^2 + \cdots}{B_1(1 + G_2 + i\omega')^2} + \frac{4\gamma^2 + \cdots}{B_1(2 + G_2 + i\omega')} + \cdots \qquad \text{(4}$$

$$\tau_{22}(0) = \frac{1 + 4\gamma - \frac{26}{3}\gamma^2 + \cdots}{2\gamma B_1}. \qquad \text{(4}$$

We may note in passing that the spectral density for the spherical harmonies $Y_{2,\pm m}$ is $(1/2\pi)\,\mathrm{Re}\,(\tau_{2m}(\omega))$ and that the correlation time is the real quantity $\tau_{2m}(0)$.

From (14), (35), (36), (38), (40) and (2)

$$J(\omega) = \frac{1}{5B_1}\Bigg[\Bigg\{\frac{2(1+6\gamma+33\gamma^2+\dots)G_0}{G_0^2+\omega'^2} - \frac{2(6\gamma+48\gamma^2+\dots)(1+G_0)}{(1+G_0)^2+\omega'^2}$$
$$- \frac{24\gamma^2[(1+G_0)^2+\omega'^2]}{[(1+G_0)^2+\omega'^2]^2} + \frac{30\gamma^2(2+G_0)}{(2+G_0)^2+\omega'^2}+\dots\Bigg\}\frac{1}{4}V_{zz}^2$$
$$+\Bigg\{\frac{4(1+5\gamma+\frac{85}{4}\gamma^2+\dots)G_1}{G_1^2+\omega'^2} - \frac{4(5\gamma+32\gamma^2+\dots)(1+G_1)}{(1+G_1)^2+\omega'^2} \tag{42}$$
$$- \frac{28\gamma^2[(1+G_1)^2+\omega'^2]}{[(1+G_1)^2+\omega'^2]^2} + \frac{43\gamma^2(2+G_1)}{(2+G_1)^2+\omega'^2}+\dots\Bigg\}\frac{1}{6}(V_{zx}^2+V_{zy}^2)$$
$$+\Bigg\{\frac{4(1+2\gamma-8\gamma^2+\dots)G_2}{G_2^2+\omega'^2} + \frac{4(-2\gamma+4\gamma^2+\dots)(1+G_2)}{(1+G_2)^2+\omega'^2}$$
$$+ \frac{32\gamma^2[(1+G_2)^2+\omega'^2]}{[(1+G_2)^2+\omega'^2]^2} + \frac{16\gamma^2(2+G_2)}{(2+G_2)^2+\omega'^2}+\dots\Bigg\}\frac{1}{24}\left[(V_{xx}-V_{yy})^2+4V_{xy}^2\right]\Bigg]$$

On substituting from (42) into (18) and (19) we may obtain the values of the longitudinal and transverse relaxation times for a molecule of spin one.

In the extreme narrowing case we have from (14) and (35)

$$J(0) = 2\tau(0) = \frac{2}{5}\left\{\tau_{20}(0)|F_0'|^2 + 2\tau_{21}(0)|F_1'|^2 + 2\tau_{22}(0)|F_2'|^2\right\},$$

and from (37), (39), (41)

$$J(0) = \frac{2}{5\gamma B_1}\Big(\frac{1}{6}[1+5\gamma-\frac{32}{3}\gamma^2+\dots]|F_0'|^2 + \frac{2}{5}[1+\frac{43}{10}\gamma-\frac{902}{75}\gamma^2+\dots]|F_1'|^2$$
$$+ [1+4\gamma-\frac{26}{3}\gamma^2+\dots]|F_2'|^2\Big).$$

Then from (2) and (24)

$$J(0) = \frac{2}{5}\frac{I_1B_1}{kT}\Big\{\frac{1}{24}(1+5\gamma-\frac{32}{3}\gamma^2+\dots)V_{zz}^2 + \frac{1}{15}(1+\frac{43}{10}\gamma-\frac{902}{75}\gamma^2+\dots)(V_{zx}^2+V_{zy}^2)$$
$$+ \frac{1}{24}(1+4\gamma-\frac{26}{3}\gamma^2+\dots)\left[(V_{xx}-V_{yy})^2+4V_{xy}^2\right]\Big\}.$$

It follows from (20) for a molecule of spin I that

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{1}{80}\,\frac{2I+3}{I^2(2I-1)}\left(\frac{eQ}{\hbar}\right)^2\frac{I_1B_1}{kT}$$
$$\times\Big\{(1+5\gamma-\frac{32}{3}\gamma^2+\dots)V_{zz}^2 + \frac{8}{5}(1+\frac{43}{10}\gamma-\frac{902}{75}\gamma^2+\dots)(V_{zx}^2+V_{zy}^2) \tag{43}$$
$$+(1+4\gamma-\frac{26}{3}\gamma^2+\dots)\left[(V_{xx}-V_{yy})^2+4V_{xy}^2\right].\Big\}$$

4 Relaxation in asymmetric molecules

To investigate the rotational Brownian motion of an asymmetric molecule one takes a body frame S' with origin at the centre of mass and coordinate axes coinciding with the principal axes of inertia, the relevant moments of inertia being I_1, I_2, I_3 and the frictional constants B_1, B_2, B_3. Ford, Lewis and McConnell[10)] derived an expression for $\langle R(t)\rangle$ and deduced from it the value of the operator $\sigma(\omega)$ defined by

$$\sigma(\omega) = \int_0^\infty \langle R(t)\rangle e^{-i\omega t}\,dt. \tag{44}$$

In our five-dimensional representation with basis $Y_{2,-2}, Y_{2,-1}, \dots Y_{22}$ the matrix representation of $\sigma(\omega)$ is given by[11)]

$$\sigma(\omega)_{nn'} = \begin{bmatrix} A & 0 & D & 0 & F \\ 0 & B & 0 & E & 0 \\ D & 0 & C & 0 & D \\ 0 & E & 0 & B & 0 \\ F & 0 & D & 0 & A \end{bmatrix} = \sigma(\omega)_{n'n}, \tag{45}$$

where

$$A = \frac{(ac-d^2)(1+\tilde{a})-ad\tilde{d}}{a(ac-2d^2)}, \quad B = \frac{b+b\tilde{b}-e\tilde{e}}{b^2-e^2}$$
$$C = \frac{a+a\tilde{c}-2d\tilde{d}}{ac-2d^2}, \quad D = \frac{-2d+(a+c)\tilde{d}-d(\tilde{a}+\tilde{c})}{2(ac-2d^2)} \tag{46}$$
$$E = \frac{-e+b\tilde{e}-e\tilde{b}}{b^2-e^2}, \quad F = \frac{d^2+d(d\tilde{a}-a\tilde{d})}{a(ac-2d^2)}.$$

In these relations

$$a = D_1+D_2+4D_3+i\omega, \quad b = \frac{5}{2}(D_1+D_2)+D_3+i\omega$$
$$c = 3(D_1+D_2)+i\omega, \quad d = \left(\frac{2}{3}\right)^{1/2}e = \left(\frac{3}{2}\right)^{1/2}(D_1-D_2)$$
$$\tilde{a} = \frac{D_1}{B_1}+\frac{D_2}{B_2}+\frac{4D_3}{B_3}, \quad \tilde{b} = \frac{5}{2}\left(\frac{D_1}{B_1}+\frac{D_2}{B_2}\right)+\frac{D_3}{B_3} \tag{47}$$
$$\tilde{c} = 3\left(\frac{D_1}{B_1}+\frac{D_2}{B_2}\right), \quad \tilde{d} = \left(\frac{2}{3}\right)^{1/2}\tilde{e} = \left(\frac{3}{2}\right)^{1/2}\left(\frac{D_1}{B_1}-\frac{D_2}{B_2}\right)$$

and

$$D_i = \frac{kT}{I_iB_i} + D_i^{(1)}, \tag{48}$$

where $D_i^{(2)}$ is a small correction given by eq. (4.8) of ref. 10.

In order to calculate $J(\omega)$ for the asymmetric molecule we note that for steady motion[12])

$$\langle R(-t)\rangle^{j}_{nn'} = \langle R(t)\rangle^{j\,*}_{n'n}. \qquad (49)$$

If then we define the operator $\rho(\omega)$ by

$$\rho(\omega) = \int_{-\infty}^{\infty} \langle R(t)\rangle\, e^{-i\omega t}\, dt, \qquad (50)$$

we deduce from (49) the general result

$$\rho(\omega)^{j}_{n'n} = \sigma(\omega)^{j}_{n'n} + \left(\sigma(\omega)^{j}_{nn'}\right)^{*}. \qquad (51)$$

Working in the five-dimensional representation and using (50) we express (21) as

$$J(\omega) = \frac{1}{5}\sum_{n,n'=-2}^{2} \rho(\omega)_{n'n}\, F'^{*}_{n} F'_{n'}. \qquad (52)$$

On substituting from (2), (45) and (51), eq. (52) yields

$$\begin{aligned} J(\omega) = \frac{1}{20}\Big\{ &(C+C^{*})V_{zz}^{2} + \frac{4}{\sqrt{6}}(D+D^{*})V_{zz}(V_{xx}-V_{yy}) \\ &+\frac{4}{3}(B+B^{*}-E-E^{*})V_{zx}^{2} + \frac{4}{3}(B+B^{*}+E+E^{*})V_{zy}^{2} \\ &+\frac{1}{3}(A+A^{*}+F+F^{*})(V_{xx}-V_{yy})^{2} \\ &+\frac{4}{3}(A+A^{*}-F-F^{*})V_{xy}^{2}\Big\}. \end{aligned} \qquad (53)$$

Equations (18) and (19) combined with (46)-(48), (53) provide the relaxation times T_1 and T_2 for a molecule with spin one.

In the extreme narrowing case $\sigma(\omega)_{nn'}$ is a real matrix and (53) reduces to

$$\begin{aligned} J(0) = \frac{1}{10}\Big\{ &C V_{zz}^{2} + \frac{4}{\sqrt{6}} D V_{zz}(V_{xx}-V_{yy}) + \frac{4}{3}(B-E)V_{zx}^{2} \\ &+\frac{4}{3}(B+E)V_{zy}^{2} + \frac{1}{3}(A+F)(V_{xx}-V_{yy})^{2} + \frac{4}{3}(A-F)V_{xy}^{2}\Big\} \end{aligned} \qquad (54)$$

with ω put equal to zero in (47). After some elementary calculation it is found from (20) and (54) that

$$\begin{aligned} \frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{40}\left(\frac{eQ}{\hbar}\right)^{2}\frac{2I+3}{I^{2}(2I-1)}\Bigg\{ &\frac{D_1+D_2+4D_3+6D_1D_2\left(\frac{1}{B_1}+\frac{1}{B_2}\right)+12D_3\left(\frac{D_1}{B_1}+\frac{D_2}{B_2}\right)}{12(D_2D_3+D_3D_1+D_1D_2)}V_{zz}^{2} \\ &+\frac{D_1+D_2+2D_1D_2\left(\frac{1}{B_1}+\frac{1}{B_2}\right)+\frac{4(D_1+D_2)D_3}{B_3}}{12(D_2D_3+D_3D_1+D_1D_2)}(V_{xx}-V_{yy})^{2} \\ &+\frac{4\left(1+\frac{4D_1}{B_1}+\frac{D_2}{B_2}+\frac{D_3}{B_3}\right)}{3(4D_1+D_2+D_3)}V_{yz}^{2}+\frac{4\left(1+\frac{D_1}{B_1}+\frac{4D_2}{B_2}+\frac{D_3}{B_3}\right)}{3(D_1+4D_2+D_3)}V_{zx}^{2}+\frac{4\left(1+\frac{D_1}{B_1}+\frac{D_2}{B_2}+\frac{4D_3}{B_3}\right)}{3(D_1+D_2+4D_3)}V_{xy}^{2} \\ &+\frac{-D_1+D_2+4D_1D_2\left(\frac{1}{B_1}-\frac{1}{B_2}\right)+2D_3D_1\left(\frac{1}{B_1}-\frac{1}{B_3}\right)+2D_2D_3\left(\frac{1}{B_3}-\frac{1}{B_2}\right)}{6(D_2D_3+D_3D_1+D_1D_2)}V_{zz}(V_{xx}-V_{yy}). \end{aligned} \qquad (55)$$

5 Relaxation in symmetric molecules

We consider what the results of the previous section yield when the third axis of the molecule is an axis of symmetry. Then $B_2=B_1$, $D_2=D_1$ and it follows from (46) and (47) that

$$d = e = \tilde{d} = \tilde{e} = 0\,, \quad D = E = F = 0$$

$$a = 2D_1+4D_3+i\omega\,, \quad b = 5D_1+D_3+i\omega\,, \quad c = 6D_1+i\omega$$

$$\tilde{a} = \frac{2D_1}{B_1}+\frac{4D_3}{B_3}\,, \quad \tilde{b} = \frac{5D_1}{B_1}+\frac{D_3}{B_3}\,, \quad \tilde{c} = \frac{6D_1}{B_1}$$

$$A = \frac{1+\frac{2D_1}{B_1}+\frac{4D_3}{B_3}}{2D_1+4D_3+i\omega}\,, \quad B = \frac{1+\frac{5D_1}{B_1}+\frac{D_3}{B_3}}{5D_1+D_3+i\omega}\,, \quad C = \frac{1+\frac{6D_1}{B_1}}{6D_1+i\omega}.$$

When these values of A,B,C are substituted into (53) we obtain

$$\begin{aligned} J(\omega) = \frac{1}{20}\Bigg\{ &\frac{12D_1\left(1+\frac{6D_1}{B_1}\right)}{36D_1^{2}+\omega^{2}}V_{zz}^{2} + \frac{\frac{8}{3}(5D_1+D_3)\left(1+\frac{5D_1}{B_1}+\frac{D_3}{B_3}\right)}{(5D_1+D_3)^{2}+\omega^{2}}\left(V_{zx}^{2}+V_{zy}^{2}\right) \\ &+\frac{\frac{4}{3}(D_1+2D_3)\left(1+\frac{2D_1}{B_1}+\frac{4D_3}{B_3}\right)}{4(D_1+2D_3)^{2}+\omega^{2}}\left[(V_{xx}-V_{yy})^{2}+4V_{xy}^{2}\right]\Bigg\}. \end{aligned} \qquad (56)$$

This will provide the relaxation times for symmetric molecules with spin one.

For the extreme narrowing case we put $\omega = 0$ in (56), so that

$$\begin{aligned} J(0) = \frac{1}{20}\Bigg\{ &\frac{1+\frac{6D_1}{B_1}}{3D_1}V_{zz}^{2} + \frac{8\left(1+\frac{5D_1}{B_1}+\frac{D_3}{B_3}\right)}{3(5D_1+D_3)}\left(V_{zx}^{2}+V_{zy}^{2}\right) \\ &+\frac{1+\frac{2D_1}{B_1}+\frac{4D_3}{B_3}}{3(D_1+2D_3)}\left[(V_{xx}-V_{yy})^{2}+4V_{xy}^{2}\right]\Bigg\}. \end{aligned}$$

Thus, from (20),

$$\frac{1}{T_1}=\frac{1}{T_2}=\frac{1}{80}\left(\frac{eQ}{\hbar}\right)^2\frac{2I+3}{I^2(2I-1)}\left\{\frac{1+\frac{6D_1}{B_1}}{D_1}V_{zz}^2+\frac{8\left(1+\frac{5D_1}{B_1}+\frac{D_3}{B_3}\right)}{5D_1+D_3}\left(V_{zx}^2+V_{zy}^2\right)\right.$$
$$\left.+\frac{1+\frac{2D_1}{B_1}+\frac{4D_3}{B_3}}{D_1+2D_3}\left[(V_{xx}-V_{yy})^2+4V_{xy}^2\right]\right\}. \tag{57}$$

Let us apply these results to a spherical molecule. Then $B_3=B_1$, $D_3=D_1$ and to a first approximation in γ as defined in (24) we have[13)]

$$D_1=\left(1+\tfrac{1}{2}\gamma\right)\frac{kT}{I_1B_1}.$$

Hence, from (56), in the same approximation

$$J(\omega)=\frac{1}{20}\left\{\frac{12\left(1+\frac{13}{2}\gamma\right)\frac{kT}{I_1B_1}}{36(1+\gamma)\left(\frac{kT}{I_1B_1}\right)^2+\omega^2}\left[V_{zz}^2+\frac{4}{3}\left(V_{zx}^2+V_{zy}^2\right)+\frac{1}{3}\left\{(V_{xx}-V_{yy})^2+4V_{xy}^2\right\}\right]\right\}. \tag{58}$$

In the extreme narrowing case we deduce from (57) that

$$\frac{1}{T_1}=\frac{1}{T_2}=\frac{1}{80}\left(\frac{eQ}{\hbar}\right)^2\frac{2I+3}{I^2(2I-1)}\frac{I_1B_1}{kT}\left(1+\frac{11}{2}\gamma\right)\left[V_{zz}^2+\frac{4}{3}\left(V_{zx}^2+V_{zy}^2\right)+\frac{1}{3}\left\{(V_{xx}-V_{yy})^2+4V_{xy}^2\right\}\right]. \tag{59}$$

For the sphere the axes of the molecular frame S' may be taken in any convenient direction. If we take them in the directions of the principal axes of the tensor with components $V_{xx}, V_{xy}, \cdots V_{yz}, V_{zz}$, then in terms of the new coordinates X,Y,Z the quantities V_{YZ}, V_{ZX}, V_{XY} vanish. We choose the labelling X,Y,Z such that $|V_{ZZ}|\geqslant|V_{XX}|\geqslant|V_{YY}|$ and put

$$\frac{V_{XX}-V_{YY}}{V_{ZZ}}=\eta.$$

Equations (58) and (59) are now expressible as

$$J(\omega)=\frac{1}{20}\,\frac{12\left(1+\frac{13}{12}\gamma\right)\left(1+\frac{1}{3}\eta^2\right)}{36(1+\gamma)+\left(\frac{I_1B_1\omega}{kT}\right)^2}\,\frac{I_1B_1}{kT}\,V_{ZZ}^2$$
$$\frac{1}{T_1}=\frac{1}{T_2}=\frac{1}{80}\,\frac{2I+3}{I^2(2I-1)}\,\frac{I_1B_1}{kT}\left(1+\frac{11}{2}\gamma\right)\left(1+\frac{1}{3}\eta^2\right)\left(\frac{eQ}{\hbar}V_{ZZ}\right)^2. \tag{60}$$

The investigation of the spherical molecule may be carried out directly and to two higher orders of approximation in γ by the method which we employed for the linear molecule. The results of many of the preliminary calculations are already available[14)]. To illustrate how they may be applied we consider only the extreme narrowing case.

Since for the sphere the matrix $\langle R(t)\rangle_{nn'}$ is real and a multiple of the unit matrix, we have from (9) and (13) that

$$J(0)=2\int_0^\infty\langle F_q^*(t)\,F(0)\rangle dt$$
$$=\frac{2}{5}\sum_{n,n'=-2}^{2}\int_0^\infty\langle R(t)\rangle_{n'n}\,F_n'^{*}F_{n'}'$$
$$=\frac{2}{5}\int_0^\infty\langle R(t)\rangle_{00}dt\sum_{n=-2}^{2}|F_n'|^2=\frac{2}{5}\tau_2\sum_{n=-2}^{2}|F_n'|^2,$$

where[15)]

$$\tau_2=\frac{I_1B_1}{6kT}\left(1+\frac{11}{2}\gamma-\frac{83}{6}\gamma^2+56\frac{49}{72}\gamma^3+\cdots\right) \tag{61}$$

Then from (2) and (20)

$$\frac{1}{T_1}=\frac{1}{T_2}=\frac{3}{40}\left(\frac{eQ}{\hbar}\right)^2\frac{2I+3}{I^2(2I-1)}\tau_2\left[V_{zz}^2+\frac{4}{3}\left(V_{zx}^2+V_{zy}^2\right)+\frac{1}{3}\left\{(V_{xx}-V_{yy})^2+4V_{xy}^2\right\}\right] \tag{62}$$

This comprises the result of Hubbard[16)] and of (59) and (60) above.

If τ_2 is calculated according to the Debye theory, (61) is replaced by[17)]

$$\tau_2=\frac{I_1B_1}{6kT}.$$

Thus the inclusion of inertial effects just gives a small correction of order γ to the common value of T_1 and T_2 in (62). This contrasts markedly with what occurs for dielectric absorption in the submillimetre region[18)].

6. Conclusion

The mathematical methods developed for the application of the theory of rotational Brownian motion to the study of dielectric relaxation problems have been found very useful for deriving analytical expressions for longitudinal and transverse relaxation times associated with nuclear magnetic relaxation arising from quadrupole interactions. When the molecule under consideration is linear, eq. (43) gives the relaxation times in the extreme narrowing case and (42) combined with (18) and (19) gives the times for spin one molecules when non-vanishing values of the Larmor frequency are used. Similar results are provided for asymmetric molecules by (53) and (55), and for symmetric molecules by (56) and (57). The relation of these with earlier results for spherical molecules is briefly discussed.

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18) ref. 3, section 14.2.