

The behaviour of an electron in a strong randomly rotating magnetic field

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1978 J. Phys. A: Math. Gen. 11 537

(<http://iopscience.iop.org/0305-4470/11/3/013>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 30/05/2010 at 18:47

Please note that [terms and conditions apply](#).

The behaviour of an electron in a strong randomly rotating magnetic field

A J O'Connor

School of Science, Griffith University, Nathan, Queensland 4111, Australia

Received 17 August 1977

Abstract. We study the behaviour of an electron sitting in a strong, randomly rotating magnetic field. The strength of the field is constant and its rotational movement is taken to be rotational Brownian motion. The decay time for the electron spin moment is found to be a simple fraction of the correlation time for the Brownian motion when the field is strong. It does not depend significantly on the field strength.

1. Introduction

In this paper we study the behaviour of a spin- $\frac{1}{2}$ particle sitting in a strong, randomly rotating magnetic field. We assume that the random angular motion of the field is rotational Brownian motion on the unit sphere. We have been motivated to study this problem by recent work of Pegg and Doddrell (1976a) and Pegg *et al* (1976). They use a different method and were lead to this problem of NMR experiments on solutions of paramagnetic transition-metal complexes.

In each of these molecules there are unpaired electrons which, in the molecular frame, experience strong static magnetic fields which are typically about 30 kG. The molecule rotates randomly in the solution and so as seen from an inertial laboratory frame each electron appears to be acted on by a randomly rotating field of constant strength H . We calculate the ensemble average of the expectation value of $S_z(t)$ (S_z is the electron spin) and find that $\langle S_z(t) \rangle$ decays to zero with a decay time which does not significantly depend on H when H is large. More precisely, if all electron spins point upwards at $t=0$ and initially the orientations of the molecules are uniformly distributed relative to the laboratory frame when we find that

$$\langle S_z(t) \rangle = \frac{1}{3} \cos \omega t e^{-\sigma t} + \frac{1}{6} e^{-2\sigma t}$$

(equation (19)). Here $\hbar\omega = gH$ and σ^{-1} is the correlation time for the rotational motion; usually ω will be so large that the oscillatory term will not be detectable hence $\langle S_z(t) \rangle$ has a decay time of one half the correlation time of the random field. This confirms the general conclusion in Pegg and Doddrell (1976a) and Pegg *et al* (1976) that the decay time is a simple fraction of the correlation time. Since the relaxation of the nuclear spin is determined by the relaxation of these electrons it is possible to verify this result (Pegg and Doddrell 1976a, b, Pegg *et al* 1976). We have not been able to include the effect of a static magnetic field but we present arguments in the final section which suggest that a static field would not greatly alter these results.

A more detailed explanation of the magnetic resonance phenomena can be found in Pegg and Doddrell (1976a) and Pegg *et al* (1976). Briefly however, if τ is the correlation time for the Brownian motion and τ_e the time constant for the electron spin relaxation we are here considering the case when $\tau_e < \tau$. The usual Redfield theory applies only when $\tau_e \gg \tau$. For many interesting complexes (especially those with sharp NMR lines) τ_e is less than τ . This may occur in complexes which have very anisotropic g tensors or large zero field splitting constants D . If D has a typical value of 30 cm^{-1} then the static field in the molecular reference frame is about 21 kG. This compares with a static field strength of about 30 kG in a typical spectrometer.

In § 2 we formulate the problem and solve it using a Fokker-Planck approach. In § 3 we present an alternative approach which confirms the results of § 2.

2. Formulation of the problem

In the inertial laboratory frame the magnetic field acting on the electron is $H\mathbf{n}(t)$ where $\mathbf{n}(t)$ is a randomly rotating unit vector. If ψ is the electron wavefunction then

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{1}{2} g H \mathbf{n}(t) \cdot \boldsymbol{\sigma} \psi, \quad (1)$$

$\mathbf{n}(t)$ can be written as

$$\mathbf{n}(t) = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta).$$

We can also parametrise ψ by three angles α , β and δ :

$$\psi = (e^{i(\delta-\beta)/2} \cos \frac{1}{2} \alpha, e^{i(\delta+\beta)/2} \sin \frac{1}{2} \alpha). \quad (2)$$

From (1) we have

$$\begin{aligned} \dot{\alpha} &= \omega \sin \theta \sin(\phi - \beta) \\ \dot{\beta} &= \omega (\cos \theta - \sin \theta \cos(\phi - \beta) \cos \alpha) \end{aligned} \quad (3)$$

where $\hbar\omega = gH$. We will measure time in units of ω^{-1} .

These equations can be written in a more classical form. If $\mathbf{a}(t)$ is the unit vector $(\sin \alpha \cos \beta, \sin \alpha \sin \beta, \cos \alpha)$ then (3) becomes

$$\frac{d\mathbf{a}}{dt} = \mathbf{n}(t) \times \mathbf{a}(t). \quad (4)$$

This represents the motion of a vector $\mathbf{a}(t)$ which is fixed on a sphere which rotates with angular velocity $\mathbf{n}(t)$. This problem arises in the dielectric relaxation of polar liquids. One recent study in which $\mathbf{n}(t)$ is a rotational Ornstein-Uhlenbeck process can be found in Lewis *et al* (1976).

Since $\theta(t)$ and $\phi(t)$ are Brownian random variables, $\alpha(t)$ and $\beta(t)$ are also random variables. The joint distribution of these quantities at time t is written as $p(\alpha, \beta, \theta, \phi; t)$; this is normalised by

$$\int p \, d\Omega = \left(\frac{1}{4\pi}\right)^2 \int \sin \alpha \, d\alpha \, d\beta \int \sin \theta \, d\theta \, d\phi p(\alpha, \beta, \theta, \phi; t) = 1. \quad (5)$$

Following Feller (1966) we can obtain the Fokker-Planck equation obeyed by p (details are given in the appendix):

$$\frac{\partial p}{\partial t} + i(\cos \theta L_z + \frac{1}{2} \sin \theta e^{-i\phi} L_+ + \frac{1}{2} \sin \theta e^{i\phi} L_-)p = \frac{1}{2} \sigma_* \Delta p. \quad (6)$$

Here L_x etc are the angular momentum operators in the variables α and β (e.g. $iL_z = \partial/\partial\beta$) and Δ is the spherical Laplacian in the θ, ϕ variables. Also $\sigma = \omega\sigma_*$ and $\sigma\tau = 1$, τ being the correlation time for the rotational Brownian motion.

At $t = 0$ we assume that all electrons have spin $+\frac{1}{2}$ in the laboratory frame and that the molecular magnetic field initially makes an angle θ_0 with the laboratory z axis (the value of ϕ_0 is unimportant and for convenience is taken as 0). To find the expected value of S_z when initially the orientations of the molecules are uniformly distributed we will only have to average over θ_0 .

So we take

$$p(\alpha, \beta, \theta, \phi; 0) = \delta(\alpha) \delta(\beta) \delta(\theta - \theta_0) \delta(\phi). \quad (7)$$

At a later time the ensemble average of S_z is

$$2\langle S_z(t) \rangle = \int p(\alpha, \beta, \theta, \phi; t) \cos \alpha \, d\Omega = \langle |\psi_+(t)|^2 - |\psi_-(t)|^2 \rangle. \quad (8)$$

To solve (6) we expand p in terms of the spherical harmonics $Y_{l,m}(\alpha, \beta)$.

$$p(\alpha, \beta, \theta, \phi; t) = \sum_{l,m} p_{l,m}(\theta, \phi, t) Y_{l,m}(\alpha, \beta). \quad (9)$$

One finds that $p_{1,0}$, $p_{1,-1}$ and $p_{1,1}$ are only related to one another. Writing p_0 for $p_{1,0}$ etc we get

$$\frac{\partial}{\partial t} \mathbf{p} + i\mathbf{M}(\theta, \phi)\mathbf{p} = \frac{1}{2} \sigma_* \Delta \mathbf{p} \quad (10)$$

where \mathbf{p} is the column vector with components p_{+1} , p_0 and p_{-1} and

$$\mathbf{M}(\theta, \phi) = \begin{bmatrix} \cos \theta & \frac{1}{\sqrt{2}} \sin \theta e^{-i\phi} & 0 \\ \frac{1}{\sqrt{2}} \sin \theta e^{i\phi} & 0 & \frac{1}{\sqrt{2}} \sin \theta e^{-i\phi} \\ 0 & \frac{1}{\sqrt{2}} \sin \theta e^{i\phi} & -\cos \theta \end{bmatrix}. \quad (11)$$

When H is large, σ_* is small and the method of multiple time scales (Nayfeh 1973, Muus and Atkins 1972) is well suited to this problem. Intuitively, over a time interval which is much shorter than σ_*^{-1} , θ and ϕ will hardly change while the angles α and β will precess rapidly about the axis defined by θ and ϕ . So there is a fast time scale (of order much less than σ_*^{-1}) and a slow time scale (of order σ_*). Our claim is that the decay of $\langle S_z(t) \rangle$ is only noticeable on the slow time scale.

We assume that for times much shorter than σ_*^{-2} , \mathbf{p} can be written as

$$\mathbf{p}(\theta, \phi, t) = \mathbf{p}_0(\theta, \phi; t, \sigma_* t) + \sigma_* \mathbf{p}_1(\theta, \phi; t, \sigma_* t) + \text{terms of order } \sigma_*^2. \quad (12)$$

We use the notation $t_0 = t$ and $t_1 = \sigma_* t$ and so

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial t_0} + \sigma_* \frac{\partial}{\partial t_1}.$$

Finally, notice that M is Hermitian and has eigenvalues 1, 0 and -1 whose eigenvectors are

$$\begin{aligned} e_1 &= \begin{bmatrix} \frac{1}{2}(1 + \cos \theta) e^{-i\phi} \\ \frac{1}{\sqrt{2}} \sin \theta \\ \frac{1}{2}(1 - \cos \theta) e^{i\phi} \end{bmatrix} & e_0 &= \begin{bmatrix} \frac{-1}{\sqrt{2}} \sin \theta e^{i\phi} \\ \cos \theta \\ \frac{1}{\sqrt{2}} \sin \theta e^{i\phi} \end{bmatrix} \\ e_{-1} &= \begin{bmatrix} \frac{1}{2}(1 + \cos \theta) e^{-i\phi} \\ \frac{-1}{\sqrt{2}} \sin \theta \\ \frac{1}{2}(1 + \cos \theta) e^{i\phi} \end{bmatrix} \end{aligned} \tag{13}$$

Writing $p_0 = f_+ e_1 + f_0 e_0 + f_- e_{-1}$ then from (10), (12) and (13) we get on equating powers of σ_*

$$\frac{\partial f_+}{\partial t_0} + i f_+ = 0, \quad \frac{\partial f_0}{\partial t_0} = 0, \quad \frac{\partial f_-}{\partial t_0} - i f_- = 0 \tag{14}$$

$$\frac{\partial p_1}{\partial t_0} + M p_1 = \frac{1}{2} \Delta p_0 - \frac{\partial p_1}{\partial t_1}. \tag{15}$$

(14) gives

$$\begin{aligned} f_{\pm}(\theta, \phi; t_0, t_1) &= f_{\pm}(\theta, \phi, t_1) e^{\pm i t_0} \\ f_0(\theta, \phi, t_0, t_1) &= f_0(\theta, \phi, t_1). \end{aligned} \tag{16}$$

The exact form of f_{\pm} can be found by remembering that p_1 has to remain bounded for all t . If p_1 is expanded in terms of e_1 etc, say, $p_1 = k e_1 + \dots$, then one has

$$\frac{\partial k}{\partial t_0} + i k = g.$$

Here g is the component of $\frac{1}{2} \Delta p_0 - (\partial p_0 / \partial t_1)$ parallel to e_1 . Clearly if g contains a term proportional to $e^{-i t_0}$ then k will grow linearly with t_0 . Hence g cannot contain terms involving $e^{-i t_0}$ and so we have an equation for f_+ . (More detailed explanations of this approach, which is standard in the method of multiple time scales can be found in Nayfeh (1973).)

Thus

$$\begin{aligned} 2 \frac{\partial f_+}{\partial t_1} &= \Delta f_+ - \frac{1}{\sin^2 \theta} f_+ - 2i \frac{\cos \theta}{\sin^2 \theta} \frac{\partial f_+}{\partial \phi} \\ 2 \frac{\partial f_+}{\partial t_1} &= \Delta f_0 - 2 f_0 \\ 2 \frac{\partial f_-}{\partial t_1} &= \Delta f_- - \frac{1}{\sin^2 \theta} f_- + 2i \frac{\cos \theta}{\sin^2 \theta} \frac{\partial f_-}{\partial \phi}. \end{aligned} \tag{17}$$

So calculating $2\langle S_z(t) \rangle = \langle \cos \alpha \rangle$ we get to first order

$$\langle \cos \alpha \rangle = \langle Y_{1,0}(\alpha, \beta), p_0 \rangle = \langle 1, p_{1,0} \rangle = \frac{1}{\sqrt{2}} (e^{-i\tau_0} \langle \sin \theta, f_+ \rangle - e^{i\tau_0} \langle \sin \theta, f_- \rangle) + \langle \cos \theta, f_0 \rangle$$

where the last averages are only over θ and ϕ .

The solutions of (17) which do not depend on ϕ are $P_l^1(\cos \theta) e^{-l(l+1)\tau_1/2}$ for f_+ and f_- and $P_l(\cos \theta) e^{-[1+l(l+1)/2]\tau_1}$ for f_0 . So

$$\begin{aligned} \langle \sin \theta, f_+ \rangle &= e^{-\tau_1} \langle \sin \theta, f_+(\theta, \phi, 0) \rangle \\ \langle \cos \theta, f_0 \rangle &= e^{-\tau_1} \langle \cos \theta, f_0(\theta, \phi, 0) \rangle \end{aligned}$$

and using (7) we get

$$\begin{aligned} \langle \cos \alpha(t) \rangle &= \cos t_0 e^{-\tau_1} \sin^2 \theta_0 + e^{-2\tau_1} \cos^2 \theta_0 \\ &= \cos \omega t e^{-\sigma t} \sin^2 \theta_0 + e^{-2\sigma t} \cos^2 \theta_0 \end{aligned} \tag{18}$$

in terms of the original variables.

Averaging over θ_0 gives

$$2\langle S_z(t) \rangle = \langle \cos \alpha(t) \rangle = \frac{2}{3} \cos \omega t e^{-\sigma t} + \frac{1}{3} e^{-2\sigma t}. \tag{19}$$

In real situations ω is too rapid to be detected and the nucleus sees (on average) an electron whose spin decays with a correlation time $\frac{1}{2}\tau$. If $H = 30$ kG then $\omega = 5 \times 10^{11}$ rad s⁻¹ and if τ for the rotational motion is about 5×10^{-11} s then $\omega\tau$ is about 25 and so σ_* is 0.04 which is reasonably small.

If a static field of 21 kG were also present the field of 30 kG seen by the electron in the molecular frame would now be replaced by a field which could vary from 9 to 51 kG. These are still strong fields and the intuitive picture of rapid precession about a relatively slowly moving axis still suggests that the decay time should depend primarily on τ and not on H . However it is not simple to incorporate this in calculations and we have not been able to do so. The method of Pegg and Doddrell (1976a) included the effect of a static field and our calculation confirms their results in the absence of a static field.

3. An exact approach

The decay properties of $\langle S_z(t) \rangle$ can be confirmed exactly. To do this we expand p_{+1} , p_{-1} and p_0 in terms of spherical harmonics:

$$\begin{aligned} p_0 &= \sum_{l=0}^{\infty} a_l P_l(\cos \theta) + \text{other terms} \\ p_1 &= \sum_{l=1}^{\infty} b_l P_l^1(\cos \theta) e^{-i\phi} + \text{other terms} \\ p_{-1} &= \sum_{l=1}^{\infty} c_l P_l^1(\cos \theta) e^{i\phi} + \text{other terms.} \end{aligned} \tag{20}$$

a_l etc depend only on t . Looking for a solution which decays as $e^{\lambda t}$ we obtain the equations

$$\begin{aligned}
 g(l)a_l + \frac{i}{\sqrt{2}} \frac{(l+1)(l+2)}{2l+3} b_{l+1}^+ - \frac{i}{\sqrt{2}} \frac{l(l-1)}{2l-1} b_{l-1}^+ &= 0 \\
 g(l)b_l + i \left(\frac{l+2}{2l+3} b_{l+1}^- + \frac{l-1}{2l-1} b_{l-1}^- \right) + i\sqrt{2} \left(\frac{a_{l-1}}{2l-1} - \frac{a_{l+1}}{2l+3} \right) &= 0 \\
 g(l)b_l^- + i \left(\frac{l+2}{2l+3} b_{l+1}^+ + \frac{l-1}{2l-1} b_{l-1}^+ \right) &= 0
 \end{aligned}
 \tag{21}$$

where $b_l^\pm = b_l \pm c_l$ and $g(l) = \lambda + \frac{1}{2} \sigma_* l(l+1)$.

It is a surprising and remarkable fact that one can obtain from these equations a very simple equation for b_l^\pm :

$$\begin{aligned}
 f(l)b_l^\pm &= 0 \\
 f(l) &= g(l)g(l-1)g(l+1) + \frac{1}{2l-1}g(l-1) + \frac{l+1}{2l+1}g(l+1).
 \end{aligned}
 \tag{22}$$

So only for special values of λ can b_l^\pm be non-zero. We want $a_0 \neq 0$ which requires that b_1^+ and b_2^- should be non-zero. So when $l = 1$ we have

$$\lambda(\lambda + \sigma_*)(\lambda + 3\sigma_*) + (\lambda + 2\sigma_*) = 0.
 \tag{23}$$

When σ_* is small the roots of this are nearly $\pm i - \sigma_*$ and $-2\sigma_*$. This confirms the results of the previous section and is more generally valid for all values of σ and H . However other correlations such as $\langle \sin \alpha e^{i\beta} \rangle$ cannot be calculated by this method whereas the method of multiple time scale always works.

Acknowledgments

It is a pleasure to acknowledge very helpful conversations with D M Doddrell and D T Pegg.

Appendix. Derivation of the Fokker-Planck equation for p

Recall that $\alpha(t)$ and $\beta(t)$ evolve according to the differential equations (12), so in an interval from t to $t + \Delta t$, β increases by $\dot{\beta} \Delta t + O(\Delta t)^2$ and α by $\dot{\alpha} \Delta t + O(\Delta t)^2$. θ and ϕ have stochastic increments $\Delta\theta$ and $\Delta\phi$. Debye (1929) has shown that

$$\begin{aligned}
 E(\Delta\theta) &= O(\Delta t)^2, & E(\Delta\theta) &= \frac{1}{2} \sigma \cot \theta \Delta t \\
 E(\Delta\phi)^2 &= \sigma \operatorname{cosec}^2 \theta \Delta t & E(\Delta\theta)^2 &= \sigma \Delta t \\
 E(\Delta\theta \Delta\phi) &= O(\Delta t)^2.
 \end{aligned}
 \tag{A.1}$$

Here we use E for the expected value of a quantity. From $\alpha(t)$, $\beta(t)$, $\theta(t)$ and $\phi(t)$ we can form any function of these random variables and find its ensemble average.

As t grows to $t + \Delta t$ we obtain

$$\begin{aligned}
 & Ef[\alpha(t + \Delta t), \beta(t + \Delta t), \theta(t + \Delta t), \phi(t + \Delta t)] \\
 &= E\left(f + \dot{\alpha} \frac{\partial f}{\partial \alpha} \Delta t + \dot{\beta} \frac{\partial f}{\partial \beta} \Delta t + \Delta \theta \frac{\partial f}{\partial \theta} + \Delta \phi \frac{\partial f}{\partial \phi} + \frac{1}{2} (\Delta \theta)^2 \frac{\partial^2 f}{\partial \theta^2} \right. \\
 &\quad \left. + \Delta \theta \Delta \phi \frac{\partial^2 f}{\partial \theta \partial \phi} + \frac{1}{2} (\Delta \phi)^2 \frac{\partial^2 f}{\partial \phi^2} + \dots \right). \tag{A.2}
 \end{aligned}$$

Hence we have

$$\frac{\partial}{\partial t} Ef = E\left(\dot{\alpha} \frac{\partial f}{\partial \alpha} + \dot{\beta} \frac{\partial f}{\partial \beta} + \frac{1}{2} \sigma \Delta f\right). \tag{A.3}$$

Since $Ef(\alpha(t), \beta(t), \theta(t), \phi(t)) = \int d\Omega p(\alpha, \beta, \theta, \phi; t) f(\alpha, \beta, \theta, \phi)$ one may integrate (A.3) by parts to obtain equation (6).

References

- Carrington A and McLachan A E 1967 *Introduction to Magnetic Resonance* (New York: Harper and Row)
 Debye P 1929 *Polar Molecules* (New York: Dover)
 Feller W 1966 *An Introduction to Probability Theory and its Applications* vol. 2 (New York: Wiley) p 313
 Lewis J T, McConnell J and Scaife B K P 1976 *Proc. R. Irish Acad. A* **79** 44
 Muus L T and Atkins P W (eds) 1972 *Electron Spin Relaxation in Liquids* (New York: Plenum)
 Nayfeh A H 1973 *Perturbation Methods* (New York: Wiley)
 Pegg D T and Doddrell D M 1976a *Chem. Phys. Lett.* **42** 607
 — 1976b *Aust. J. Chem.* **29** 1869
 Pegg D T, Doddrell D M, Bendall M R and Grigson A K 1976 *Aust. J. Chem.* **29** 1885