Spin 1/2 systems perturbed by fluctuating, arbitrary fields; relaxation and frequency shifts, a new approach to Redfield theory

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The usual approach to considerations of spin relaxation and frequency shifts due to fluctuating fields is through the density matrix [6]. Here we treat the problem of the influence of fluctuating fields on a spin 1/2 system based on direct solution of the Schrödinger equation in contrast to the usual treatment. Our results are seen to be in agreement with the known results in the literature (9, 6, 5, 8), as they must, but our derivation directly from the Schrödinger equation allows us to see the role of the necessary assumptions in a somewhat clearer way.

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I. INTRODUCTION

The behavior of a system of spins interacting with static and time varying magnetic fields is a very broad topic and has been the subject of intense study for decades. A very important application is to the study of spins interacting with the randomly fluctuating fields associated with a thermal reservoir. Bloembergen, Purcell and Pound, [1], have treated this problem using physical arguments based on Fermi’s golden rule and showed that the relaxation induced by the fields associated with a thermal reservoir is proportional to the power spectrum of the fluctuating fields evaluated at the Larmor frequency, which is given by the Fourier transform of the auto-correlation function of these fields. Wangsness and Bloch, [2], and then Bloch, [3], have approached the problem using second order perturbation theory applied to the equation of motion of the density matrix and Redfield, [4], [5] (see also [6]) has carried this calculation forward to show that the relaxation, indeed, depends on the spectrum of the auto-correlation of the fluctuating fields.

Another source of randomly fluctuating fields is the stochastic motion of spins (e.g. diffusion) through a region with an inhomogeneous magnetic field. To study this problem Torrey, [7] introduced a diffusion term into the Bloch equation applied to the bulk magnetization of a sample containing many spins (Torrey equation). Cates, Schaeffer and Hopper, [8] then rewrote the Torrey equation to apply to the density matrix and solved this equation to second order in the varying fields using an expansion in the eigenfunctions of the diffusion equation. McGregor, [9] applied the Redfield theory to this problem using diffusion theory to calculate the auto-correlation function of the fluctuating fields seen by spins diffusing through a (constant gradient) inhomogeneous field. Recently Golub et al, [10] have shown that these two approaches, [8], [9] are identical.

A useful review of the field is [11].
Another problem which can be treated by these methods is the case of a gas of spins contained in a vessel subject to inhomogeneous magnetic fields and a strong electric field as is the case in experiments to search for a non-zero electric dipole moment of neutral particles such as the neutron,\[12\] or various atoms or molecules,\[13\]. This was shown by Pendlebury et. al.,\[14\], using a second order perturbation approach to the classical Bloch equation, to lead to an unwanted, linear in electric field, frequency shift, (often called a 'geometric phase' effect) which can be the largest systematic error in such experiments.

Lamoreaux and Golub,\[15\] have shown, using a standard density matrix calculation (Redfield theory), that the 'geometric phase' frequency shift is given, to second order, by certain correlation functions of the fields seen by the moving particles.

Pignol and Roccia,\[16\] have given general results for this effect valid in the non-adiabatic limit.

Barabanov et al \[18\] have given analytic expressions for the relevant correlation functions for a gas of particles moving in a cylindrical vessel exposed to a magnetic field with a linear gradient along with an electric field. Petukhov, et al \[19\] and Clayton \[20\] have shown how to determine the correlation functions for arbitrary geometries and spatial field dependence for cases where the diffusion theory applies, while Swank et al,\[21\] have shown how to calculate the spectra of the relevant correlation functions for gases in rectangular vessels in magnetic fields of arbitrary position dependence even in those cases where the diffusion theory does not apply.

Recently Steyerl et al,\[22\] have approached the problem of a gas of spin 1/2 particles subject to time varying magnetic fields by directly solving the Schroedinger equation to second order. They showed that this approach leads to the same results as previous work \[14\], \[15\] for the 'geometric phase' effect in cylindrical vessels and applied the technique to several problems of interest such as the frequency shift produced by the field of a magnetic dipole in the vessel. They have also given solutions for a general linear gradient as has been discussed in \[16\], and higher order gradients as well.

In the present work we use the methods of \[22\] to obtain a general solution for spin 1/2 valid in all cases where second order perturbation theory can be applied, including coherent and stochastic fields and long and short times. In doing this we clarify the meaning of the assumptions necessary to obtain the Redfield theory.
II. SOLUTION OF THE SCHROEDINGER EQUATION FOR AN ARBITRARY PERTURBATION

We apply the method introduced by Steyerl et al. starting with the Hamiltonian

$$H = -\frac{1}{2} \begin{bmatrix} \omega'_o & \omega_x - i\omega_y \\ \omega_x + i\omega_y & -\omega'_o \end{bmatrix} = -\begin{bmatrix} \omega_o & \Omega^* \\ \Omega & -\omega_o \end{bmatrix}$$

where $\omega'_o = \gamma B_o$, $\gamma$ is the gyromagnetic ratio and $B_o$ represents the magnitude of the volume average field in the cell and the $z$ axis is its direction, $\omega_o = \omega'_o / 2$, $\Omega = (\omega_x + i\omega_y) / 2$.

The Schrödinger equation is then:

$$i\frac{\partial}{\partial t} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = H \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$  \hspace{1cm} (1)

Introducing the rotating frame

$$\alpha = \alpha_r e^{i\omega_o \tau}$$
$$\beta = \beta_r e^{-i\omega_o \tau}$$  \hspace{1cm} (2)

$$-i\dot{\alpha} = \omega_o \alpha + \Omega^* \beta$$  \hspace{1cm} (3)
$$i\dot{\alpha}_r = -\Omega^* \beta_r e^{-i2\omega_o \tau}$$  \hspace{1cm} (4)

$$i\dot{\beta} = -\Omega \alpha + \omega_o \beta$$  \hspace{1cm} (5)
$$i\dot{\beta}_r = -\Omega \alpha_r e^{i2\omega_o \tau}$$  \hspace{1cm} (6)

$$i\ddot{\alpha}_r = -\dot{\Omega}^* \beta_r e^{-i2\omega_o \tau} - \Omega^* \dot{\beta}_r e^{-i2\omega_o \tau} + i2\omega_o \Omega^* \beta_r e^{-i2\omega_o \tau}$$  \hspace{1cm} (7)
$$\ddot{\alpha}_r - \left( \frac{\dot{\Omega}^*}{\Omega^*} - i2\omega_o \right) \dot{\alpha}_r = -|\Omega|^2 \alpha_r$$  \hspace{1cm} (8)

A. Perturbation theory

We now treat the rhs of (8) as a perturbation and obtain the zero order solution by placing this equal to zero:

let

$$\dot{\alpha}_r^{(0)} = y_o$$  \hspace{1cm} (9)
\[ \dot{y} = \left( \frac{\dot{\Omega}^*}{\Omega^*} - i2\omega_o \right) = \frac{d}{dt} \ln y \]  
\[ \alpha_i^{(0)} = -C_2^{(0)} \int \Omega^* e^{-i2\omega_o t} dt + C_1^{(0)} \]

Now we substitute this into the rhs of (8) to get the next lowest order solution

\[ \dot{y}_1 - \left( \frac{\dot{\Omega}^*}{\Omega^*} - i2\omega_o \right) y_1 = -|\Omega|^2 \left( -C_2^{(0)} \int \Omega^* e^{-i2\omega_o t} dt + C_1^{(0)} \right) \]

this is of the form

\[ \dot{y}_1 - P(t) y = q(t) \]

with

\[ P(t) = \left( \frac{\dot{\Omega}^*}{\Omega^*} - i2\omega_o \right) \]
\[ q(t) = -|\Omega|^2 \left( -C_2^{(0)} \int \Omega^* e^{-i2\omega_o t} dt + C_1^{(0)} \right) \]

then by substituting

\[ y = e^{\int P dt} f \]

we find

\[ \dot{f} = e^{-\int P dt} q(t) \]
\[ y = e^{\int P dt} \int_t^t dt' e^{-\int P dt'} q(t') \]

Now, using (14)

\[ \int P dt = \int dt \left( \frac{\dot{\Omega}^*}{\Omega^*} - i2\omega_o \right) = \ln(-\Omega^*) - i2\omega_o t + K' \]
\[ e^{\int P dt'} = -K\Omega^* e^{-i2\omega_o t} \]

and then

\[ y_1 = -\Omega^* e^{-i2\omega_o t} \int_t^t dt' e^{i2\omega_o t'} \left[ \Omega \left( -C_2^{(0)} \int_t^{t'} \Omega^* e^{-i2\omega_o t''} dt'' + C_1^{(0)} \right) \right] \]
(note $K$ drops out). The $C_2(0)$ term is higher order in the perturbation so we only have to consider the $C_1$ term

$$y_1 = -C_1(0)^* e^{-i2\omega_o t} \int^t dt' e^{i2\omega_o t'} [\Omega]$$

$$\alpha_r^{(1)} = -C_1(0) \int^t dt' \Omega^* e^{-i2\omega_o t'} \int^t dt'' e^{i2\omega_o t''} [\Omega]$$

Combining the two terms for $\alpha_r$:

$$\alpha_r = -C_1(0) \int^t dt' \Omega^* \left\{ e^{-i2\omega_o t'} \int^t dt'' e^{i2\omega_o t''} [\Omega] \right\} - C_2 \int^t \Omega^* e^{-i2\omega_o t'} dt' + C_2(0)$$

and we calculate $\beta_r$ from (2):

$$\beta_r = -i\frac{\alpha_r}{\Omega^*} e^{i2\omega_o t}$$

$$= i \left( C_1(0) \Omega_i (t) + C_2 \right)$$

where

$$\Omega_i (t) = \int^t dt' e^{i2\omega_o t'} \Omega (t')$$

Applying the initial conditions, $\alpha_r (0) = 1$, $\beta_r (0) = 0$ we have

$$C_2 = -C_1(0) \Omega_i (t = 0)$$

$$1 - C_1(0) = C_1(0) \left[ |\Omega_i (t = 0)|^2 - F (0) \right]$$

with

$$F (t) = \int^t dt' \Omega^* (t') e^{-i2\omega_o t'} \Omega_i (t')$$

$$\langle F (t) - F (t_o) \rangle = \int^t dt' \int^t dt'' e^{-i2\omega_o (t' - t'')} \Omega^* (t') \Omega (t'')$$

Then (correct to second order)

$$C_1(0) = 1 - |\Omega_i (t = 0)|^2 + F (0)$$

$$C_2 = -\Omega_i (t = 0) \left( 1 - |\Omega_i (t = 0)|^2 + F (0) \right)$$

Putting it together

$$\alpha_r = 1 - (F (t) - F (0)) + \Omega_i (0) (\Omega^* (t) - \Omega^* (0))$$

$$\alpha_r = 1 - \left( \int_0^t dt' \int_0^{t'} dt'' e^{-i2\omega_o (t' - t'')} (\Omega^* (t') \Omega (t'')) \right)$$

$$\beta_r = i (\Omega_i (t) - \Omega_i (0)) = i \int_0^t dt' e^{i2\omega_o t'} \Omega (t')$$
putting $t_o = 0$.

The above solution is for a system that starts in the spin up state ($\alpha_r (0) = 1$). Combining with the solution where the system starts in the spin down state ($\beta_r (0) = 1$) we get the general solution in terms of a matrix

$$\psi_r (t) = \begin{bmatrix} a_r (t) \\ b_r (t) \end{bmatrix} = \begin{bmatrix} \alpha_r (t) & -\beta_r^* (t) \\ \beta_r (t) & \alpha_r^* (t) \end{bmatrix} \begin{bmatrix} a (0) \\ b (0) \end{bmatrix}$$ (36)

where the matrix is seen to be unitary if $\alpha_r, \beta_r$ are normalized.

Transforming back to the lab system:

$$\psi(t) = \begin{bmatrix} e^{i\omega_o \tau} a_r (t) \\ e^{-i\omega_o \tau} b_r (t) \end{bmatrix} = \begin{bmatrix} e^{i\omega_o \tau} & 0 \\ 0 & e^{-i\omega_o \tau} \end{bmatrix} \begin{bmatrix} \alpha_r (t) & -\beta_r^* (t) \\ \beta_r (t) & \alpha_r^* (t) \end{bmatrix} \begin{bmatrix} a (0) \\ b (0) \end{bmatrix}$$ (37)

Equation (36) or (37) together with (34) and (35) represent the complete general solution valid for coherent and incoherent fluctuating fields and all times, as long as the second order perturbation approximation is valid, i.e. those times for which the deviations from the initial values are small (however see below).

**B. Example, solution for a constant magnetic field gradient and constant Electric field (‘geometric phase’)**

This case is interesting because it results in a serious systematic error in searches for a particle electric dipole moment [14], [15], [16], [18]. In this case

$$\Omega = a + ibt$$ (38)

where $a = \gamma \left( \frac{\partial B_z}{\partial z} x + \frac{E}{c} v_y \right)$, $b = \gamma \frac{\partial B_z}{\partial z} y$, and the coordinate system is defined so that the particle is moving in the $y$ direction.

Substituting this into equations (34) and (35) we obtain the solutions

$$\alpha_r = 1 - z$$ (39)

$$z = \frac{1}{2\omega_o^2} b^2 t^2 + i \left( -\frac{1}{3\omega_o} b^2 t^3 + \frac{a}{\omega_o^2} (-\omega_o a + b) t \right) - \frac{1}{\omega_o^4} \left( e^{-i\omega_o t} (i (b - a\omega_o) b t\omega_o) \right)$$ (40)

$$\beta_r = \left( \frac{1}{\omega_o^2} e^{i\omega_o t} (-ibt\omega_o + (b - a\omega_o)) - \frac{1}{\omega_o^2} (b - a\omega_o) \right)$$ (41)
This solution is what was obtained in [22] by a similar method and was shown there to lead to the known result [14], [15] for the frequency shift. We see that our method (34), (35) applies to all times for which the perturbation theory holds, i.e. those times for which the deviations from the initial values are small.

III. PHASE SHIFTS, FREQUENCY SHIFTS AND RELAXATION

We now consider an ensemble of particles moving on a stochastic set of trajectories. Each trajectory will be characterized by a given \( \Omega(t) \) and we have to take an ensemble average of the frequency shifts and relaxation rates calculated for each trajectory.

We start by calculating \( \sigma_+ = (\sigma_x + i\sigma_y) \) and take the initial state to be \( \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \) corresponding to the experimentally common situation of a system immediately after being exposed to a \( \pi/2 \) pulse.

so that from (36)

\[
\psi(t) = \begin{bmatrix} a(t) \\ b(t) \end{bmatrix} = \begin{bmatrix} \alpha_r(t) & -\beta^*_r(t) \\ \beta_r(t) & \alpha^*_r(t) \end{bmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \frac{1}{\sqrt{2}} = \begin{bmatrix} \alpha_r - \beta^*_r \\ \beta_r + \alpha^*_r \end{bmatrix} \frac{1}{\sqrt{2}} \quad (42)
\]

Referring to the wave function (42) we evaluate \( \sigma_+ \) in the rotating frame.

\[
\langle \sigma_+ \rangle_r = 2a^*b = (\alpha^*_r - \beta_r)(\beta_r + \alpha^*_r) \quad (43)
\]

\[
= (\alpha^*_r - \beta_r^2) \quad (44)
\]

Using (34, 35)

\[
\langle \sigma_+ \rangle = 1 - 2 \left( \int_0^t dt' \int_0^{t'} dt'' e^{i2\omega_o(t' - t'')} \langle \Omega(t') \Omega^*(t'') \rangle \right)
\]

\[
+ \int_0^t dt' e^{i2\omega_o t'} \Omega(t') \int_0^{t'} dt'' e^{i2\omega_o t''} \Omega(t'') \quad (45)
\]

\[
= 1 - 2 \int_{t_0}^t dt' \int_0^{t'} d\tau e^{i2\omega_o \tau} \langle \Omega^*(t' - \tau) \Omega(t') \rangle
\]

\[
+ \int_0^t dt' e^{i2\omega_o (2t')} \int_0^{t'} d\tau e^{-i2\omega_o \tau} \Omega(t') \Omega(t' - \tau) \quad (46)
\]

\[
\langle \sigma_+ \rangle = 1 - 2 \int_{t_0}^t dt' \int_0^{t'} d\tau e^{i2\omega_o \tau} \langle \Omega^*(t' - \tau) \Omega(t') \rangle \quad (47)
\]
where the last term in (46) vanishes because the integrand is a rapidly varying function of $t'$. From the behavior of $\langle \sigma_+ \rangle$ we can obtain the frequency shift, $\delta \omega$, and the transverse relaxation rate, $1/T_2$.

A. Phase shifts and frequency shifts

Now $\langle \sigma_+ \rangle = 1 + z_2$ where $z_2 = z_2' + iz_2''$ is second order in the perturbation, so that (from (47))

$$\langle \delta \phi \rangle = \arg \langle \sigma_+ \rangle = \arg (1 + z_2) = \tan^{-1} \left( \frac{z_2''}{1 + z_2'} \right)$$

$$\simeq z_2'' = -2 \Im \int^t dt' \int^t_0 d\tau e^{i2\omega_0 \tau} \langle \Omega^* (t' - \tau) \Omega (t') \rangle$$

Then differentiating w.r.t. $t$ to get the frequency shift we have

$$\delta \omega = 2 \Im \left( \int^t_0 d\tau e^{-i2\omega_0 \tau} \langle \Omega^* (t) \Omega (t - \tau) \rangle \right)$$

$$\delta \omega = \frac{1}{2} \Im \left( \int^t_0 d\tau \begin{pmatrix} \cos \omega_o \tau & \sin \omega_o \tau \\ -i \sin \omega_o \tau & \cos \omega_o \tau \end{pmatrix} \langle (\omega_x (t) - i \omega_y (t)) (\omega_x (t - \tau) + i \omega_y (t - \tau)) \rangle \right)$$

$$= \frac{1}{2} \int^t_0 d\tau \begin{pmatrix} \cos \omega_o \tau & -i \sin \omega_o \tau \\ \sin \omega_o \tau & \cos \omega_o \tau \end{pmatrix} \langle (\omega_x (t) \omega_y (t) - \omega_y (t) \omega_x (t - \tau)) (\omega_x (t - \tau) + \omega_y (t - \tau)) \rangle$$

which is in agreement with previous results, [14], [15], [18], [16].

There has been some discussion in the literature, [16], concerning the correct signs in this expression. After discussions with the author, [17] and reworking of some previous calculations we have shown that all results agree with (51).

1. An assumption of Redfield theory

Redfield and other authors [4], [6] have taken $t$ large enough in (47) so that the correlation functions vanish at that time, i.e. $t > \tau_c$ where $\tau_c$ is the time it takes $\langle \Omega^* (t) \Omega (t - \tau) \rangle$ to go to zero and the upper limit of integration can then be taken to be infinite. This then results
in the integral giving the Fourier transform of the correlation function of the fluctuating field as introduced by Bloembergen, Pound and Purcell. However as is well known (see [6]) this step is not necessary, it is introduced only to allow writing the results in terms of the Fourier transform, the results (34 and 35) are valid for short times as well and also apply to the case of coherent fields as shown above.

\[ T_2 \text{ Relaxation} \]

With \( \langle \sigma_+ \rangle = 1 + z_2 \) we calculate

\[
|\langle \sigma_+ \rangle|^2 = 1 + 2 \Re z_2 = 1 + 2 \Re z_2 + z_2^2
\]

\[
|\langle \sigma_+ \rangle| = 1 + (z_2 + z_2^*)/2 = 1 - \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{i2\omega_0(t'-t'')} \langle \Omega^* (t'') \Omega (t') \rangle - \text{c.c.}
\]

using (47). c.c. is the complex conjugate of the second term.

We now specialize to the case of a stationary system where \( \langle \Omega^* (t') \Omega (t'') \rangle \) is a function of \( (t' - t'') \) only. Consider a square region of the \( t'', t' \) plane between \( (t_o, t_o), (t_o, t), (t, t_o) \) and \( (t, t) \). (See (23) for a discussion of this argument). Then the double integral over the top half \( (t' > t'') \) is seen to be the complex conjugate of the integral over the bottom half \( (t' < t'') \), so the last two terms are given by the integral over the entire square.

As a result of this we have (again putting \( t' - t'' = \tau \))

\[
|\sigma_+| = 1 - \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{-i2\omega_0(t'-t'')} \langle \Omega^* (t') \Omega (t'') \rangle
\]

\[
= 1 - \int_{-t}^{t} d\tau (t - |\tau|) e^{-i2\omega_0\tau} \langle \Omega^* (t') \Omega (t' - \tau) \rangle
\]

\[
= 1 - t \int_{-t}^{t} d\tau e^{-i2\omega_0\tau} \langle \Omega^* (t') \Omega (t' - \tau) \rangle
\]

\[
|\sigma_+| = 1 - \frac{t}{T_2}
\]

1. \textbf{Comparison to Redfield theory}

The step leading to (53) is based on taking \( t \gg \tau_c \) (following Redfield), where \( \tau_c \) is the correlation time or the time that it takes \( \langle \Omega^* (t') \Omega (t' - \tau) \rangle \) to go to zero. (See above). For
shorter times we would not have a linear but (for, say, the non-adiabatic limit, \( \omega_o \tau_c << 1 \)), a quadratic decay.

The result (54) obtained in second order perturbation theory is valid only as long as subsequent terms can be neglected. This requires that \( (t/T_2 << 1) \) or that the changes in the wave function remain small. In the Redfield treatment we assume that we are dealing with times short enough that we can replace \( \rho(0) \) by \( \rho(t) \) in the equation for \( \dot{\rho}(t) \) (\( \rho(t) \) is the spin density matrix) obtaining an equation

\[
\frac{\partial \rho}{\partial t} = \Gamma \cdot \rho(t) \tag{55}
\]

where \( \Gamma \) is the ‘relaxation matrix’. This equation is then valid for times so long that the changes in the system are significant as discussed by Slichter, p. 204 [6].

In our case we can formulate the argument in a slightly different way. Consider (54) after a time \( \delta t \),

\[
|\sigma_+| = 1 - \frac{\delta t}{T_2} \tag{56}
\]

as the initial condition for the interval \( t = \delta t \) to \( t = 2\delta t \) after which time we will have

\[
|\sigma_+| = \left(1 - \frac{\delta t}{T_2}\right)^2 \tag{57}
\]

Continuing the argument, after a time \( t \) we will have

\[
|\sigma_+| = \left(1 - \frac{\delta t}{T_2}\right)^{\frac{t}{\delta t}} = e^{-t/T_2} \tag{58}
\]

if we take the limit as \( \delta t \to 0 \).

C. \( T_2 \) Relaxation continued

Thus from (53) and (54)

\[
\frac{1}{T_2} = \int_{-\infty}^{\infty} d\tau e^{-i2\omega_o \tau} \langle \Omega^* (t') \Omega (t' - \tau) \rangle \tag{59}
\]

\[
= \frac{1}{4} \int_{-\infty}^{\infty} d\tau \left( \cos \omega_o \tau \langle \omega_x (t) \omega_x (t - \tau) + \omega_y (t) \omega_y (t - \tau) \rangle 
+ \sin \omega_o \tau \langle \omega_y (t) \omega_x (t - \tau) - \omega_x (t) \omega_y (t - \tau) \rangle \right) \tag{60}
\]

where the imaginary terms vanish as expected because their integrands are odd. We have replaced \( \omega_i \) by \(-\omega_i/2\) as discussed above. The second term is absent in the usual treatments as it is normally assumed that the cross correlation between the components of the fluctuating field vanishes.
1. Contribution of fluctuating $B_z$

For simplicity we consider the effects of a fluctuating $B_z$ independently of the other components and will add the results.

In that case the Hamiltonian is:

$$H = -\frac{1}{2} \begin{vmatrix} \omega'_o + \omega'_z & 0 \\ 0 & -(\omega'_o + \omega'_z) \end{vmatrix}$$

(61)

Here $\omega'_o$ represents the average value of $B_z$ while $\omega'_z$ corresponds to the fluctuations around this average. The Schroedinger equation is ($\omega_i = \omega'_i / 2$):

$$i \begin{bmatrix} \dot{\alpha} \\ \dot{\beta} \end{bmatrix} = - \begin{bmatrix} (\omega_o + \omega_z) \alpha \\ -(\omega_o + \omega_z) \beta \end{bmatrix}$$

(62)

$$i \dot{\alpha} = -(\omega_o + \omega_z) \alpha$$

(63)

$$i \dot{\alpha}_r = -\omega_z \alpha_r$$

(64)

using (2). Then

$$\ln (\alpha_r) = i \int_0^t \omega_z dt' + C$$

(65)

$$\alpha_r = e^{i \int_0^t \omega_z dt'}$$

(66)

$$\beta_r = 0$$

(67)

since we want a solution that is in the $\sigma_z = +1$ state at $t = 0$.

Combining with the solution for $\sigma_z = -1$ as the initial state we have, now taking a state with the spin along the $x$ axis as the initial state

$$\psi (t) = \begin{bmatrix} \alpha_r & 0 \\ 0 & \alpha^*_r \end{bmatrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} \alpha_r \\ \alpha^*_r \end{bmatrix}$$

so that

$$\langle \sigma_+ \rangle = (\alpha^*_r)^2 = \langle e^{-2i \int_0^t \omega_z dt'} \rangle$$

$$\approx 1 - 2i \left\langle \int_0^t \omega_z dt' \right\rangle - 2 \left\langle \left[ \int_0^t \omega_z dt' \right]^2 \right\rangle$$

(69)

$$\approx 1 - 2 \left\langle \int_0^t \omega_z dt' \int_0^t \omega_z dt'' \right\rangle$$

(70)
where we used the fact that the average of the fluctuating fields is zero by definition. Thus
\[ \langle \sigma_+ \rangle \approx 1 - 2 \int_0^t dt' \int_0^{t'} dt'' \langle \omega_z (t') \omega_z (t'') \rangle \]
\[ \approx 1 - 2 \int_{-t}^t d\tau (t - |\tau|) \langle \omega_z (t') \omega_z (t' - \tau) \rangle \]
\[ \approx 1 - 2t \int_{-\infty}^{\infty} d\tau \langle \omega_z (0) \omega_z (\tau) \rangle \]
where we have again taken \((t > \tau_c)\) in order to obtain the Fourier transform. We now have
\[ \frac{1}{T_2^{(z)}} = \frac{1}{2} \int_{-\infty}^{\infty} d\tau \langle \omega_z' (0) \omega_z' (\tau) \rangle \]
which is to be added to (60) to obtain the total transverse relaxation rate.

**IV. T\textsubscript{1} RELAXATION**

To calculate the \(T_1\) relaxation we start in the up state:
\[ \psi(t) = \begin{bmatrix} a(t) \\ b(t) \end{bmatrix} = \begin{bmatrix} \alpha_r (t) & -\beta_r^* (t) \\ \beta_r (t) & \alpha_r^* (t) \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} \alpha_r \\ \beta_r \end{bmatrix} \]
and calculate
\[ \langle \sigma_z \rangle = |a|^2 - |b|^2 = \alpha_r \alpha_r^* - \beta_r \beta_r^* \]
From (34)
\[ \alpha_r = 1 - \left( \int_0^t dt' \int_0^{t'} dt'' e^{-i2\omega_o (t' - t'')} \langle \Omega^* (t') \Omega (t'') \rangle \right) \]
\[ = 1 - \varepsilon_2 \]
\[ \alpha_r \alpha_r^* = 1 - (\varepsilon_2 + \varepsilon_2^*) = 1 - 2 \text{Re} \int_0^t dt' \int_0^{t'} dt'' e^{-i2\omega_o (t' - t'')} \langle \Omega^* (t') \Omega (t'') \rangle \]
\[ = 1 - 2 \text{Re} \left( \int_0^t dt' \int_0^{t'} dt'' e^{-i2\omega_o (t' - t'')} \langle \Omega^* (t') \Omega (t'') \rangle \right) \]
as shown above. From (35)
\[ \beta_r = i \int_0^t dt' e^{i2\omega o t'} \Omega (t') \]
\[ \beta_r \beta_r^* = \int_0^t dt' \int_0^{t'} dt'' \langle \Omega^* (t') \Omega (t'') \rangle e^{-i2\omega o (t' - t'')} \]

\[ \langle \sigma_z \rangle = \alpha_r \alpha_r^* - \beta_r \beta_r^* \]
\[ = 1 - 2 \int_0^t dt' \int_0^{t'} dt'' \langle \Omega^* (t') \Omega (t'') \rangle e^{i2\omega o (t' - t'')} \]
\[ = 1 - 2 \int_{-t}^t d\tau (t - |\tau|) e^{-i2\omega o \tau} \langle \Omega^* (t') \Omega (t' - \tau) \rangle \]
\[ = 1 - t2 \int_{-\infty}^{\infty} d\tau e^{-i2\omega o \tau} \langle \Omega^* (t') \Omega (t' - \tau) \rangle \]

again specializing to \((t >> \tau_c)\)

\[ \frac{1}{T_1} = 2 \int_{-\infty}^{\infty} d\tau e^{-i2\omega o \tau} \langle \Omega^* (t') \Omega (t' - \tau) \rangle \]
\[ = \frac{1}{2} \int_{-\infty}^{\infty} d\tau \left( \cos \omega_o \tau \langle (\omega_x (t') - i\omega_y (t')) (\omega_x (t' - \tau) + i\omega_y (t' - \tau)) \rangle \right) \]
\[ = \frac{1}{2} \int_{-\infty}^{\infty} d\tau \left( \cos \omega_o \tau \langle \omega_x (t) \omega_x (t - \tau) + \omega_y (t) \omega_y (t - \tau) \rangle \right) \]
\[ + \sin \omega_o \tau \langle \omega_y (t) \omega_x (t - \tau) - \omega_x (t) \omega_y (t - \tau) \rangle \]
\[ = \frac{2}{T_2} \]

1/T'_2 is the relaxation rate without the contribution of the fluctuations in B_z \([60]\).

V. CONCLUSION

We have treated the problem of the influence of fluctuating fields on a spin 1/2 system
based on direct solution of the Schroedinger equation in contrast to the usual treatment
based on the density matrix (Redfield theory).

Our results are seen to be in agreement with the known results in the literature ([9], [6],
[5], [8]), as they must, but our derivation directly from the Schroedinger equation allows us
to see the role of the necessary assumptions in a somewhat clearer way.
To get the Redfield results from the general solution it is necessary to assume the field fluctuations are stationary and to limit ourselves to times much longer than the correlation time. However this is only necessary to get the result in the satisfying form of a Fourier transform. The general solution will be valid for times shorter than the correlation time as well. The requirements of second order perturbation theory that the change in the wave function must remain small can be relaxed by treating changes over consecutive small time periods similar to what is done in the density matrix treatment, [6].

Our results (34) and (35) are very general and can be applied to coherent and stochastic fields also in the case of short times.

The density matrix was introduced to simplify the treatment of ’mixed’ states, states described by an ensemble of systems in ’pure’ quantum states, i.e. systems where some parameter, e.g. a phase, is a stochastic variable. However the same results can always be obtained by calculating the wave function as if for a pure state and then averaging the results for observables over the stochastic parameters. In general, the solution of the Schroedinger equation is easier than the solution of the equation for the density matrix, but the calculation of observables (expectation values) from the results is easier in the case of the density matrix. Since the most difficult step is usually solving the differential equations we would argue that the wave function approach presented here is more often advantageous.

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