FREE INDUCTION DECAY IN DIPOLAR SYSTEMS

E. Rémy Bacos

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ABSTRACT

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A method of approximation is used in the second derivative of the free induction decay function F(t), as applied to a crystal with magnetic dipole-dipole interactions, in the high-temperature limit. The approximation is used in lowest order of $\chi(t)^4$ and the results are compared with those of Lowe and Norberg, who used the same approximation to much higher order, but in the function F(t) itself. The second and fourth moments ~~are shown~~ to be exact in this approximation. Part of the theoretical expression for the fourth moment is shown to vanish identically, by using the symmetry properties of the traces concerned. This reduces the calculation time for the fourth moment by a factor of about two.

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PART B

PART A

1. INTRODUCTION

The free-induction decay (fid) of the transverse magnetization in a dipolar-coupled rigid lattice is an important problem in magnetic resonance; it is directly related, by a Fourier transformation, to the magnetic resonance line shape. The many-body character of the interaction Hamiltonian is such that the problem has not yet yielded to exact solution. For this reason, efforts have been concentrated on finding moments of the resonance line. The first successfull attempt at such calculation was performed by Van-Vleck[1] in 1948, who found expressions for the 2nd and 4th moments. Recently Jensen and Hansen[2] in 1973, using computer techniques, found expressions for the 6th and 8th moments.

Attempts to find analytic expressions for the fid range from the trial function approach of Abragam[3], who fits certain parameters to the first few moments, to the Lowe and Norberg[4] approach, where the starting point is the exact theoretical expression and certain approximations are introduced. Other names associated with this problem are: Evans and Powles[5], Betsuyaku[6], Kubo and Tomita[7], Goldburg and Lee[8], Gade and Lowe[9] and Clough and McDonald.[10] Our testing ground for the various expressions is the dipolar magnetic system CaF_2. The fluorine nuclei are magnetic, with $I=\frac{1}{2}$. The first 8 zeros of the fid shape are known experimentally to high accuracy.[11] Another test of the various theories involves computer simulation techniques.[2] The variables in these comparisons are the direction of the external magnetic field and the spin of the individual nuclei.

Although agreement between the various theories and the CaF_2 experiments has been good, yet the problem cannot be regarded as satisfactorily solved. Only the first few zeros of the fid of $F(t)$ can be fitted.

Our approach to the problem has been to examine the consequences of making Lowe-Norberg-type[4] approximations in the second derivative $F''(t)$ of the fid, rather than in $F(t)$ itself. In this scheme, as in that of Lowe and Norberg, it is possible to verify immedialtely whether the resulting moments are the exact ones; this follows from the relation between the moments and the coefficients of the powers of t^2 in the small-t expansion of $F(t)$. When the first two terms in our Lowe and Norberg-type approximation of $F''(t)$ are retained, it turns out that the second moment M_2 is exact, but the fourth moment M_4, does not correspond to the <u>exact</u> theoretical expression for M_4. It was clear that this development would not be an improvement on previous theories (at this stage) unless M_4 were reproduced exactly. Rather than continue immediately to a higher stage of approximation, it was decided to multiply our approximate $F''(t)$ by $\exp(-M_4'/2M_2)$ where M_4' is the missing part of the fourth moment. Then both M_2 and M_4 would be given correctly.

The direct evaluation of M_4' is very time-consuming, involving many commutators and traces. The end result of this work was: $M_4' = 0$. That is, our second stage approximation for $F''(t)$ did indeed give M_4 correctly. It remained then (i) to compute $F(t)$ by doing the double integration and (ii) to explore alternative methods of obtaining the result $M_4' = 0$. We evaluated $F(t)$ for the simple cubic lattice for the static magnetic field in the z-direction. Our results are in good agreement with those of Lowe and Norberg for $t < 25$ micro-sec. This indicates that further terms in the approximation must be considered. The problem of $M_4' = 0$ was solved using rotational symmetry to show that certain traces vanish identically.

In the following pages, Part A, describes the resonance phenomenon and the relation between susceptibility and absorption. The Method of Moments is discussed and applied to the transverse magnetization, the free induction decay, when dipole-dipole interactions are considered.

This is followed by a brief summary of some theories and their appropriate approximations. Part B shows the approximation introduced in F''(t) leading to M_4; symmetry considerations are also investigated. The integration is clearly shown leading to the function F(t), which, after some hand calculations, were fed into the computer. The shape of F(t) is shown and conclusions are drawn.

2. THEORY OF MAGNETIC RESONANCE

2.1 Non-interacting spins

A spin "I" will interact with a static magnetic field H_0 through its magnetic moment

$$\underset{\sim}{\mu} = \gamma \hbar \underset{\sim}{I} \tag{2.1}$$

where γ is the gyromagnetic ratio.

The Hamiltonian is simply

$$\mathcal{H} = - \underset{\sim}{\mu} \cdot \underset{\sim}{H_0} \tag{2.2a}$$

$$= - \gamma \hbar I . \underset{\sim}{H_0} \tag{2.2b}$$

If H_0 is in the z direction,

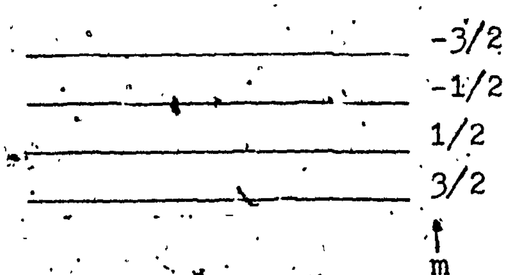
$$\mathcal{H} = - \gamma \hbar H_{0_z} I_z . \tag{2.3}$$

The eigenvalues E_m of this Hamiltonian are essentially proportional to the eigenvalues m of I_z, where $m = I, (I-1) \ldots . (-I)$.

i.e. $E_m = - \gamma \hbar H_{0_z} m$ (2.4)

For example, if $I = 3/2$, the system has eigenstates given by the following energy-level diagram (assuming $\gamma > 0$)

The levels are equidistant with spacing $\Delta E = \gamma \hbar H_{0_z}$



These levels can be detected by applying an oscillating magnetic field which will cause transitions. Energy is absorbed in the process. To satisfy conservation of energy this oscillating field must have an angular frequency ω such that the difference in energy between initial and final Zeeman states is given by $E_f - E_i = \hbar\omega$. The associated Hamiltonian $\mathcal{H}_{pert}$ must have non-vanishing matrix elements between these states if a transition is to occur. In our case

$$\mathcal{H}_{pert} = -\gamma\hbar H_x I_x \cos\omega t \tag{2.5}$$

The matrix element of the operator I_x between an initial state m and a final state m', $(m'|I_x|m)$, vanishes unless $m' = m \pm 1$; i.e., transitions occur only between adjacent levels. Thus, absorption will take place only for the frequency ω given by $\hbar\omega = \Delta E = \gamma\hbar H_0$

i.e., for $\omega = \gamma H_0$ (2.6)

From the foregoing we conclude that for this simple model we can compute the frequency needed to observe the resonance phenomenon if we know the value of the gyromagnetic ratio γ.

2.2 Macroscopic effect of an alternating field

If $\underset{\sim}{H}_1(t) = 2 H_1 \cos \omega t \, \underset{\sim}{i}$ is used, it could be analysed by breaking it into two rotating components, each of amplitude H_1, one rotating clockwise and the other counterclockwise. This situation would be described by

$$\underset{\sim}{H}_1(t) = H_1(\underset{\sim}{i} \cos\omega_z t + \underset{\sim}{j} \sin\omega_z t) + H_1(\underset{\sim}{i} \cos\omega_z t - \underset{\sim}{j} \sin\omega_z t) \quad (2.7)$$

where ω_z is positive. The second term can be neglected near resonance. The spin will interact with a combination of $H_1(t)$ and the static-field $\underset{\sim}{Ho} = \underset{\sim}{k} H_o$. We are interested in the equation of motion of the spin in the field $(\underset{\sim}{Ho} + \underset{\sim}{H}_1(t))$. Thus

$$\frac{d\underset{\sim}{\mu}}{dt} = \underset{\sim}{\mu} \times \gamma(\underset{\sim}{H}_o + \underset{\sim}{H}_1(t)) \quad (2.8)$$

One can eliminate the time dependence of $\underset{\sim}{H}_1(t)$ by using a coordinate system rotating at frequency ω_z. In such a coordinate system $\underset{\sim}{H}_1$ and $\underset{\sim}{H}_o$ will be static. The net result is a static field

$$\underset{\sim}{H}_{eff} = \underset{\sim}{k}(H_o - \frac{\omega}{\gamma}) + H_1 \underset{\sim}{i} \quad (2.9)$$

In the rotating frame, the moment acts as though it experienced the static magnetic field $\underset{\sim}{H}_{eff}$.

As a consequence, the moment precesses (in the rotating system) in a cone of fixed angle about the direction of $\underset{\sim}{H}_{eff}$ at the angular frequency γH_{eff}. At resonance $\omega = \gamma H_o$, i.e. $\underset{\sim}{H}_{eff} = H_1 \underset{\sim}{i}$, and μ will precess in the yz plane, remaining perpendicular to $\underset{\sim}{H}_1$. If $\underset{\sim}{H}_1$ is applied for a short time "t_w" the moment will precess through an angle $\theta = \gamma H_1 t_w$. If t_w is choosen such that $\theta = \pi$, the pulse would simply invert the moment (called 180 deg. pulse). But if $\theta = \pi/2$ the magnetic moment is turned from the z direction to the y direction. By turning off $\underset{\sim}{H}_1$, the moment will then remain at rest in the rotating frame and will precess in the laboratory in a plane normal to $\underset{\sim}{H}_o$ at the frequency γH_o. As a result the moment will produce a flux which will alternate as the spin precesses. The resultant induced e.m.f. can be observed. But the e.m.f. will not persist for very long, since the interaction of the spin with its surroundings cause a decay. The interaction of the precessing spin with other spins and the lattice carries away the energy absorbed from the alternating field.

2.3 Power absorbed from the oscillating magnetic field

A magnetic field oscillating in the x direction is applied to a sample. We may express the alternating field as

$$H_x = 2\, H_1 \cos \omega t \tag{2.10}$$

where we consider H_x as the real part of $2H_1 \exp i\omega t$. We introduce the complex susceptibility

$$\chi = \chi' - i\chi'' \tag{2.11}$$

where χ' and χ'' are real and $\chi = \chi(\omega)$

We define the complex magnetization as M_x^c.

From the definition of the magnetization we can then write:

$$M_x^c = \chi(2\, H_1 \exp i\omega t) \qquad (2,12)$$

The real part of the complex magnetization could then be written as:

$$M_x = \mathrm{Re}\, M_x^c$$

$$= \mathrm{Re}(\chi' - i\chi'')(2H_1 \cos \omega t + i2H_1 \sin \omega t) \tag{2.13}$$

$$M_x' = \chi' 2H_1 \cos \omega t + \chi'' 2H_1 \sin \omega t \tag{2.14}$$

The system will absorb energy from the oscillating field.

The rate at which energy is absorbed, $A(\omega)$, averaged over one cycle is:

$$A(\omega) = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} H\,\frac{dM}{dt}\,dt \tag{2.15}$$

$$= \frac{\omega}{2\pi}\int_0^{2\pi/\omega} (2H_1\cos\omega t)\,\frac{d}{dt}\,(\chi' 2H_1\cos\omega t + \chi'' 2H_1\sin\omega t)\,dt$$

i.e.

$$A(\omega) = 2\,H_1^{\,2}\,\omega\,\chi''(\omega) \tag{2.16}$$

For the non-interacting case considered on page 5, $A(\omega) = \text{const}\,\delta(\omega - \omega_0)$ where $\omega_0 = \gamma H_0$. When there are interactions between the nuclei, one expects $A(\omega)$ to be peaked near $\omega = \omega_0$ as in fig. 1, provided the interaction terms are small compared to the Zeeman terms.

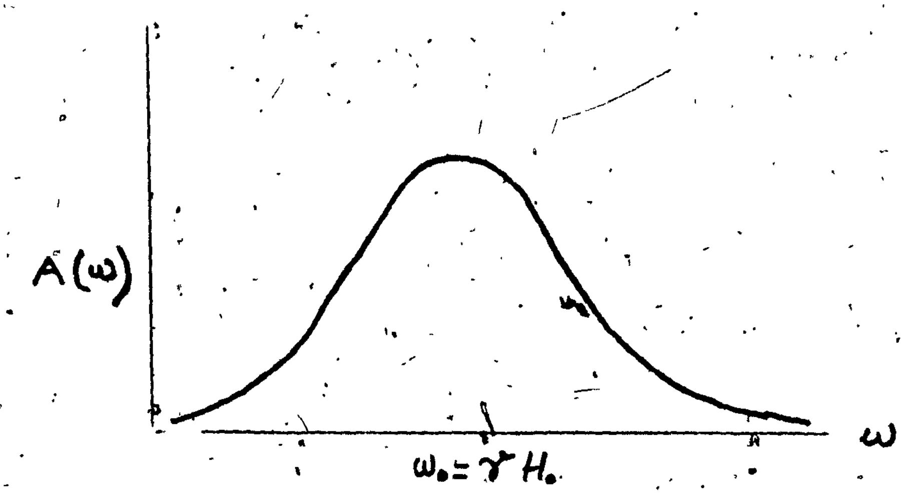


fig. 1

2.4 Microscopic treatment of the absorption.[12]

In this section we look for an expression for $A(\omega)$. Since the alternating magnetic field couples to the magnetic moment μ_{xk} of the kth spin, our perturbing Hamiltonian will be:

$$\mathcal{H}_{pert} = -\sum_k \mu_{xk} 2H_{1x} \cos\omega t \tag{2.17a}$$

$$= - M_x 2H_{1x} \cos \omega t \tag{2.17b}$$

where

$$M_x = \sum_k \mu_{xk}$$

In the absence of the perturbation, the Hamiltonian consists of the interactions of the spins with the external static field, and of the coupling between spins j and k. Thus

$$\mathcal{H} = -\sum_k \mu_{zk} H_1 + \sum_{jk} \mathcal{H}_{jk} \tag{2.18}$$

Denote the eigenvalues of energy of this many-spin Hamiltonian by E_a, E_b,...with corresponding many-spin wave functions $|a\rangle$, $|b\rangle$,... . Because of the large number of degrees of freedom, there will be a great number of energy levels. The most general wave function will be a linear combination of such eigenstates:

$$\Psi = \sum_a c_a |a\rangle e^{-iE_a t/\hbar} \tag{2.19}$$

where $|c_a|^2$ gives the probability of finding the system in the eigenstate a ;

i.e. $p(a) = |c_a|^2$ (2.20)

At thermal equilibrium all states will be occupied to some extent. The probability of occupation p(a) is given by the Boltzman factor

$$p(E_a) = \exp(-E_a/kT)/\sum_c \exp(-E_c/kT) \quad (2.21)$$

The denominator is the partition function denoted by "Z". The sum over E_c goes over the entire eigenvalue spectrum, and it is easily verified that

$$\sum_a p(E_a) = 1 \quad (2.22)$$

Let $\bar{P}_{ab}$ be the rate of energy absorption due to transition between states a and b of the entire system, then

$$\bar{P}_{ab} = \hbar\omega W_{ab} \left(p(E_b) - p(E_a) \right) \quad (2.23)$$

where W_{ab} is the probability per unit time that a transition is induced from a to b, if the system is entirely in state "a" initially; $\hbar\omega = E_b - E_a$ and $W_{ab} = W_{ba}^*$.

Under the perturbation $H_1(t)$, W_{ab} is given by Fermi's

* For the r.f. inducing transition probability

golden rule:

$$W_{ab} = \frac{2\pi}{\hbar} |\langle a|\mathcal{H}_1(t)| \rangle|^2 \delta(E_a - E_b - \hbar\omega) \qquad (2.24)$$

By substituting equation (2.24) into equation (2.23) and summing over all states with $E_a > E_b$ and equating to the energy absorbed $A(\omega)$ we get:

$$A(\omega) = \sum_{a,b(E_a>E_b)} P_{ab} = 2\pi\omega H_1{}^2 \sum_{E_a>E_b} (p(E_b)-p(E_a)) |\langle a| M_x| b\rangle|^2 \delta(E_a-E_b-\hbar\omega) \qquad (2.25)$$

or, using equation (2.16),

$$\chi''(\omega) = \pi \sum_{E_a>E_b} (p(E_b)-p(E_a)) |\langle a| M_x | b\rangle|^2 \delta(E_a-E_b-\hbar\omega) \qquad (2.26)$$

Substituting (2.21) into (2.26) and using the high temperature approximation, i.e. $E_a-E_b \ll kT$ we get for $\chi''(\omega)$ the expression

$$\chi''(\omega) = \frac{\pi\hbar\omega}{kTZ} \sum_{E_a>E_b} e^{-E_a/kT} |\langle a | M_x | b\rangle|^2 \delta(E_a - E_b - \hbar\omega) \qquad (2.27)$$

"$E_a > E_b$" means that as long as $E_a > E_b$ only positive ω will give absorption because of the délta function. Removal of this restriction ($E_a > E_b$) extends the meaning of $\chi''(\omega)$ to negative ω. Then defining the shape function $f(\omega)$ by

$$\chi'' = \omega f(\omega) \qquad (2.28)$$

we have:

$$f(\omega) = \sum_{a,b} e^{-E_a/kT} \left|\langle a| M_x | b\rangle\right|^2 \delta(E_a - E_b - \hbar\omega) \qquad (2.29)$$

$A(\omega)$ is obtained from (2.27),(2.28),(2.29) and(2.16) The shape function $f(\omega)$ describes the spread of the Larmor frequencies among the various spins. The time dependence of the amplitude of the precessing magnetization, obtained after a 90° pulse, is described by the inverse Fourier transform of the shape function $G(t)$, and may be measured experimentally.

2.5 Derivation of the Moments of the Shape Function

From equation (2.29) and using the integral representation of the delta function

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp\,(ixt)\, dt \qquad (2.30)$$

and by putting

$$M_x(t) = \exp(i\mathcal{H}t/\hbar)\, M_x\, \exp(-i\mathcal{H}t/\hbar) \qquad (2.31)$$

where $\mathcal{H}$ is the total Hamiltonian, we get:

$$f(\omega) = \frac{1}{2kTZ} \int_{-\infty}^{+\infty} \mathrm{Tr}\,(\,M_x(t)M_x)\; e^{-i\omega t}\, dt \qquad (2.32)$$

Equation (2.32) states that $f(\omega)$ is given by the Fourier transform of the correlation function

$$\mathrm{Tr}\,(\,M_x(t)M_x) \equiv G(t) \qquad (2.33)$$

We are interested in G(t) as well because it can be measured directly and thus has a physical interpretation (see Section 3.4, on fid). Taking the Fourier transform of equation (2.32),

$$(1/2kTZ)(G(t)) = (1/2\pi) \int_{-\infty}^{+\infty} f(\omega)\; e^{i\omega t}\, d\omega \qquad (2.34)$$

At t= 0, we get

$$(1/2kTZ)\ \mathrm{Tr}\ (M_x(0)M_x) = (1/2\pi)\int_{-\infty}^{+\infty} f(\omega)\ d\omega \qquad (2.35)$$

Now, taking the nth derivative of equation (2.34) and then putting t = 0, we get:

$$\frac{1}{2kTZ}\frac{d^n}{dt^n}\ \mathrm{Tr}(M_x(t)M_x)_{t=0} = \frac{i^n}{2\pi}\int_{-\infty}^{+\infty} \omega^n\ f(\omega)\ d\omega \qquad (2.36)$$

The nth moment of a shape function is defined by:

$$\langle\omega^n\rangle = \frac{\int_{-\infty}^{+\infty} \omega^n\ f(\omega)\ d\omega}{\int_{-\infty}^{+\infty} f(\omega)\ d\omega} \qquad (2.37)$$

Substituting equations (2.36) and (2.35) into equation (2.37), we get:

$$\langle\omega^n\rangle = \frac{i^{-n}\left[(d^n/dt^n)\ \mathrm{Tr}(M_x(t)M_x)\right]_{t=0}}{\mathrm{Tr}\ (M_x(0)M_x)} \qquad (2.38)$$

The second moment about $\omega = 0$ for a general Hamiltonian $\mathcal{H}$ is then

$$\langle\omega^2\rangle = -\frac{1}{\hbar^2}\frac{\mathrm{Tr}[\mathcal{H},M_x]}{\mathrm{Tr}\{M_x^2\}} \qquad (2.39)$$

This formalism provides a simple method for generating expressions for the higher moments. Note that the odd moments vanish.

3. INTERACTIONS BETWEEN NEIGHBORING PARAMAGNETIC IONS

3.1 Dipole-dipole Interaction.

With no interactions, $f(\omega) = C\,\delta(\omega - \omega_0)$, but magnetic dipole-dipole interactions between paramagnetic neighbors broaden the line. This broadening depends upon the spatial location of the neighbors, and on the relative orientations of their magnetic moments. The local field at a particular site due to the magnetic dipolar interactions will take on values from near zero to several times a typical measure of the nearest-neighbor dipole field, which is βr_o^{-3} where r_o is the nearest-neighbor distance and β is the Bohr magneton. The line shape, then, reflects the distribution of these dipolar fields, and will have a width comparable to, or greater than, βr_o^{-3}.

The classical interaction energy E between two magnetic moments $\underset{\sim}{\mu}_1$ and $\underset{\sim}{\mu}_2$ is

$$E = (\underset{\sim}{\mu}_1 \cdot \underset{\sim}{\mu}_2)/r^3 - 3(\underset{\sim}{\mu}_1 \cdot \underset{\sim}{r})(\underset{\sim}{\mu}_2 \cdot \underset{\sim}{r})/r^5 \tag{3.1}$$

where $\underset{\sim}{r}$ is the radius vector between $\underset{\sim}{\mu}_1$ and $\underset{\sim}{\mu}_2$, i.e. ($\underset{\sim}{r} = \underset{\sim}{r}_2 - \underset{\sim}{r}_1$). For the quantum mechanical Hamiltonian

μ_1 and μ_2 are to be treated as operators. We know that

$$\mu_1 = \gamma_1 \hbar I_1 \tag{3.2a}$$

and

$$\mu_2 = \gamma_2 \hbar I_2 \tag{3.2b}$$

For a sample with N spins the dipolar Hamiltonian becomes:

$$\mathcal{H}_d = \tfrac{1}{2}\sum_{j=1}^{N}\sum_{k=1}^{N}\{(\mu_j \mu_k / r_{jk}^3) - 3(\mu_j \cdot r_{jk})(\mu_k \cdot r_{jk})/r_{jk}^5\} \tag{3.3}$$

3.2 The truncated Hamiltonian

Writing the Hamiltonian in a form that is particularly convenient for computing matrix elements:

$$\mathcal{H}_d = \frac{\gamma_1 \gamma_2}{r^3}(A + B + C + D + E + F) \tag{3.4}$$

where

$A = I_{1z}I_{2z}(1 - 3\cos^2\theta)$

$B = -\tfrac{1}{4}(I_1^+ I_2^- + I_1^- I_2^+)(1 - 3\cos^2\theta)$

$C = -(3/2)(I_1^+ I_{2z} + I_{1z} I_2^+)\sin\theta\cos\theta\exp(-i\phi)$

$D = -(3/2)(I_1^- I_{2z} + I_{1z} I_2^-)\sin\theta\cos\theta\exp(i\phi)$

$E = (-3/4)\ I_1^+ I_2^+ \sin^2\theta\exp(-2i\phi)$

$F = -(3/4) I_1^- I_2^- \sin^2\theta\exp(2i\phi)$

Note: $\gamma_1\gamma_2\hbar^2/r^3$ corresponds to the interaction of a nuclear moment with a field of about 1 Gauss, whereas the Zeeman Hamiltonian

$$\mathcal{H}_z = -\gamma_1 \hbar H_o I_{1z} - \gamma_2 \hbar H_o I_{2z} \tag{3.6}$$

corresponds to an interaction with a field of 10^4 Gauss. It is well known[12] that the effect of the terms C,D,E, and F is to give absorption near " 0 " and " $2\omega_o$", where the peaks at zero and $2\omega_o$ are very small and may be disregarded for our purpose; we drop them from the Hamiltonian. Then

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_1 \tag{3.7}$$

where

$$\mathcal{H}_z = \sum_k \left(-\gamma \hbar H_o I_{zk} \right) \tag{3.8}$$

and

$$\mathcal{H}_1 = A + B$$

$$= \frac{1}{4} \gamma^2 \hbar^2 \sum_{jk} \left(\frac{1-3\cos^2\theta_{jk}}{r^3_{jk}} \right) \left(3I_{jz}I_{kz} - I_j \cdot I_k \right) \tag{3.9}$$

$\mathcal{H}_z$ and $\mathcal{H}_1$ commute. $\mathcal{H}_1$ is called the truncated Hamiltonian. θ_{jk} is the angle of r_{jk} with the z-axis.

3.3 Relation between correlation and reduced auto-correlation function.

Consider

$$M_x(t) = \exp(i\mathcal{H}t)\, M_x\, \exp(-i\mathcal{H}t)$$

where $\hbar = 1$

$$= \exp i(\mathcal{H}_z + \mathcal{H}_1)\, M_x\, \exp -i(\mathcal{H}_z + \mathcal{H}_1) \qquad (3.10)$$

from equation (3.7).

Since $\mathcal{H}_z$ and $\mathcal{H}_1$ commute, and

$$\mathcal{H}_z = -\gamma H_0 I_z$$
$$= -\omega_0 I_z,$$

then

$$M_x(t) = \exp(i\mathcal{H}_1 t)(M_x \cos\omega_0 t + M_y \sin\omega_0 t)\exp(-i\mathcal{H}_1 t) \qquad (3.11)$$

where we have used the identity[12]

$$\exp(-iI_z\phi)I_x\exp(iI_z\phi) = I_x\cos\phi + I_y\sin\phi \qquad (3.12)$$

Now

$$G(t) = \mathrm{Tr}(M_x(t)M_x)$$
$$= \cos\omega_0 t\, \mathrm{Tr}\{\exp(i\mathcal{H}_1 t)M_x\exp(-i\mathcal{H}_1 t)M_x\}$$
$$+ \sin\omega_0 t\, \mathrm{Tr}\{\exp(i\mathcal{H}_1 t)M_y\exp(-i\mathcal{H}_1 t)M_x\} \qquad (3.13)$$

The second trace on the right-hand side is zero, as can be seen as follows:

Perform a 180 degree rotation about the x axis. Then

$$M_x \to M_{x'} = M_x$$

$$M_y \to M_{y'} = -M_y$$

$$M_z \to M_{z'} = -M_z$$

$\mathcal{H}_1$ is invariant under this rotation, i.e. $\mathcal{H}_1' = \mathcal{H}_1$. This term is seen to equal its negative and so vanishes. Then

$$Tr(M_x(t)M_x) = \cos\omega_0 t \; Tr \exp(i\mathcal{H}_1 t) M_x \exp-(i\mathcal{H}_1 t) M_x \tag{3.14}$$

Since this is the Fourier transform of the shape function $f(\omega)$, we see that the correlation function $G(t)$ consists of a term, $\cos\omega_0 t$, multiplied by an envelope function. Defining $M_x^*(t) = \exp(i\mathcal{H}_1 t)\, M_x \exp-(i\mathcal{H}_1 t)$, we get the following expression:

$$G(t) = G_1(t)\cos\omega_0 t \tag{3.15}$$

where $G(t) = Tr(M_x'(t)M_x)$ and $G_1(t) = Tr(M_x^*(t)M_x)$.

$G(t)$ is called the correlation function or relaxation function, whereas $G_1(t)$ is called the reduced auto-correlation function of the magnetization. $G(t)$ tells us how

M_x at one time is correlated to its value at a later time. $G_1(t)$ is the function we measure experimentally. By writing $\cos\omega t = \frac{1}{2}(e^{i\omega t} + e^{-i\omega t})$, we can say that the two exponentials correspond to lines at positive and negative. We wish to discuss only the line at positive ω; we denote the corresponding function by $f_+(\omega)$: then

$$f_+(\omega) = (1/4kTZ)\int_{-\infty}^{+\infty} Tr(M^*_x(t)M_x)\exp(-i\omega t)\exp(+i\omega_0 t)\,dt \qquad (3.16)$$

and obtaining its transform

$$(1/4kTZ)\exp(i\omega_0 t)Tr(M^*_x(t)M_x) = (1/2\pi)\int_{-\infty}^{+\infty} f_+(\omega)\exp(i\omega t)\,d\omega \quad (3.17)$$

or

$$(1/4kTZ)Tr(M^*_x(t)M_x) = (1/2\pi)\int_{-\infty}^{+\infty} f_+(\omega)\exp(\omega - \omega_0)it\,d\omega \; (3.17)$$

and by taking derivative as before, we get:

$$(d^n/dt^n)\; Tr(M^*_x(t)M_x)/\,Tr(M^*_x(0)M_x) = \frac{i^n\int_{-\infty}^{+\infty}(\omega-\omega_0)^n f_+(\omega)\,d\omega}{\int_{-\infty}^{+\infty} f_+(\omega)\,d\omega} = i^n\langle(\omega-\omega_0)^n\rangle \qquad (3.18)$$

This gives the nth moment w.r.t. the frequency. By following steps as before we get:

$$\langle(\omega - \omega_0)^2\rangle = \frac{\mathrm{Tr}\left\{[\mathcal{H}_1', M_x]^2\right\}}{\mathrm{Tr}\left\{M_x^{\,2}\right\}} \tag{3.19}$$

where $\mathcal{H}_1'$ = A + B terms.

3.4 Experimental meaning of the reduced correlation function, $G_1(t)$.

To see that $G_1(t)$ is proportional to the amplitude of the free precession signal after a 90 degree r.f. pulse (which may be measured directly) let us assume the following:

Before the r.f. pulse, the spin system is in thermal equilibrium and described by a statistical operator

$$\rho_{eq} \propto \exp(-\mathcal{H}/kT) \doteqdot 1 - \mathcal{H}/kT$$
$$= 1 - (\omega_0/\gamma kT)\, M_z \tag{3.20}$$

Then at t = 0 a rotating field H_1 is applied along the oy axis of a frame rotating with an angular velocity $\omega = \omega_0$ for a duration t' such that $H_1 t' = \pi/2$. The net effect of the 90° r.f. pulse is to transform the operator $\mathcal{M}_z$ into $\mathcal{M}_x$ in the rotating frame, and into

$$e^{i\omega I_z t'}\mathcal{M}_x e^{-i\omega I_z t'} = \mathcal{M}_x \cos \omega t' - \mathcal{M}_y \sin \omega t' \qquad (3.21)$$

in the Laboratory frame. The statistical operator after the end the pulse, i.e: after t' sec., will be:

$$\rho(t') = 1 - \frac{\omega_0}{kT}(\mathcal{M}_x \cos \omega_0 t' - \mathcal{M}_y \sin \omega_0 t') \qquad (3.22)$$

since $\omega = \omega_0$. From now on $\rho(t')$ is governed by the total Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$, where $\mathcal{H}_1$ could be replaced by the secular parts $\mathcal{H}_1'$ i.e. (A + B) terms. Thus at time t, $\rho(t)$ will be:

$$\rho(t) = 1 - \frac{\omega_0}{\gamma kT} e^{i(\mathcal{H}_0 + \mathcal{H}_1')(t-t')}(\mathcal{M}_x \cos \omega_0 t' + \mathcal{M}_y \sin \omega t') \times e^{-i(\mathcal{H}_0 + \mathcal{H}_1')(t - t')} \qquad (3.23)$$

Since $\mathcal{H}_0$ and $\mathcal{H}_1'$ commute, then

$$\rho(t) = 1 - \frac{\omega_0}{kT} e^{i\mathcal{H}_1'(t-t')}\mathcal{M}_x e^{-i\mathcal{H}_1'(t-t')} \cos \omega_0 t - e^{i\mathcal{H}_1'(t-t')}\mathcal{M}_y e^{-i\mathcal{H}_1'(t-t')} \sin \omega_0 t \qquad (3.24)$$

and subsequently

$$M_x(t) = \langle \mathcal{M}_x(t) \rangle = \mathrm{Tr}\left\{ \rho(t)\mathcal{M}_x \right\} \qquad (3.25)$$

then

$$M_x(t) = -\frac{\omega_0}{\gamma kT} \cos \omega_1 t \; \mathrm{Tr}\left\{ e^{i\mathcal{H}_1' t} \mathcal{M}_x \, e^{-i\mathcal{H}_1' t} \mathcal{M}_x \right\} \qquad (3.26)$$

In writing (3.26) use has been made of the fact that

$$\mathrm{Tr}\left\{ e^{i\mathcal{H}_1' t} \mathcal{M}_x \, e^{-i\mathcal{H}_1' t} \mathcal{M}_y \right\} = 0 \qquad (3.27)$$

and of the assumption $\mathcal{H}_1' t \ll 1$.

Equation(3.26) means that $G_1'(t)$, the reduced auto-correlation function, is proportional to the time-dependent amplitude of the precessing magnetization of the sample.

4. RESUME OF SOME THEORIES

4.1 Work of Lowe and Norberg

The calculation of Lowe and Norberg (LN) is based upon the following remark:

$\mathcal{H}_1$ is a sum of 2 terms, α and β, where

$$\alpha = -\frac{\gamma^2\hbar}{3}\sum_{j<k} B_{jk}\, \underset{\sim}{I}_j\cdot\underset{\sim}{I}_k \qquad (4.1)$$

$$\beta = h\gamma^2\sum_{j<k} B_{jk}\, I_{jz}I_{kz} \qquad (4.2)$$

with

$$B_{jk} = \frac{3}{2}\left(1 - 3\cos^2\theta_{jk}\right)/r^3_{jk}$$

$$\underset{\sim}{r}_{jk} = \underset{\sim}{r}_k - \underset{\sim}{r}_j$$

θ_{jk} the angle of $\underset{\sim}{r}_{jk}$ with the z axis.

It is easy to show that: $[\alpha,\beta] \neq 0$, $[\beta, M_x] \neq 0$, but $[\alpha, M_x] = 0$

If α and β did commute, $G_1(t)$ could be evaluated in closed form, since α would disappear from the calculation, as follows:

$$G_1(t) = \mathrm{Tr}\left\{e^{i\mathcal{H}_1 t}\, M_x\, e^{-i\mathcal{H}_1 t}\, M_x\right\} \qquad (4.3)$$

$$= \mathrm{Tr}\left\{ e^{i(\alpha+\beta)t} \; M_x \; e^{-i(\alpha+\beta)t} \; M_x \right\}$$

$$= \mathrm{Tr}\left\{ e^{i\alpha t} e^{i\beta t} M_x e^{-i\alpha t} e^{-i\beta t} M_x \right\}$$

$$= \mathrm{Tr}\left\{ e^{i\beta t} \; M_x \; e^{-i\beta t} \; M_x \right\}$$

if $[\alpha, \beta] = 0$

The operator β is diagonal in the M_j representation. Then the trace is easily evaluated:

$$G_1(t) = \prod_k \cos\,(B_{jk}t/2\hbar) \qquad (4.4)$$

But since α and β do not commute, Lowe and Norberg write $\exp(i\,\mathcal{H}_1 t)$ in the form:

$$e^{i(\alpha+\beta)} = e^{+i\beta t}\;\chi(t)\;e^{i\alpha t} \qquad (4.5)$$

where

$$\chi(t) = \exp(i\alpha t)\exp\left[-it(\alpha+\beta)\right]\exp(i\beta t)$$

The deviation of $\chi(t)$ from unity is expected to have a small effect. Then

$$G_1(t) = \mathrm{Tr}\left\{ e^{i\beta t}\;\chi(t)\;M_x\;\chi^{\dagger}(t)\;e^{-i\beta t}\;M_x \right\} \qquad (4.6)$$

$\chi(t)$ is expanded as a power series in t:

$$\chi(t) = 1 + \sum_n \frac{C_n}{n!} t^n . \qquad (4.7)$$

where the C_n are operators.

This leads to the series expansion

$$F(t) = \frac{G_1(t)}{Tr(M_x^2)} = \sum_{n=0} F_n(t) \frac{t^n}{n!} \qquad (4.8)$$

where

$$F_n(t) = \sum_{\substack{p,q=0 \\ (p+q=n)}} \frac{n!}{p!q!} Tr \left\{ e^{i\beta t} C_p M_x C_q^+ e^{-i\beta t} M_x \;/ Tr(M_x^2) \right\} \qquad (4.9)$$

$G_1(t)$ is arbitrarily divided by $Tr(M_x^2)$ to give F(t), in order to have a function which is normalized to 1 at t = 0. In equation (4.9)[12] $C_0=1$, $C_1=0$, $C_2=[\alpha,\beta]=\lambda$; Only terms up to n = 4 in the expansion of $G_1(t)$ were considered. $F_2(t)$ and $F_4(t)$ were evaluated analytically and the result compared with experiment. Moderately good agreement was obtained for small t. For large t the approximation used is no longer valid and agreement with experiment breaks down. The convergence of this type of expansion is an open question. Its main justification is its a posteriori agreement with experiment.

4.2 The work of Gade and Lowe

The work of Gade and Lowe is a generalization of LN for any spin. They derived theoretical formula for fid of a system of identical particles of spin " I ". They showed that the fid is largely insensitive to the value of I.

4.3 The work of Clough and McDonald 1965.

Clough and McDonald tried a general method for the relaxation function $G_1(t)$. They introduced approximations depending upon the short- or long-term development of $G_1(t)$. By introducing another type of approximation they derived the equation of Lowe and Norberg. Their first approximation gives a curve that differs slightly from that of LN over the range of t for which LN is in good agreement with experiment. For larger t, the disagreement with expriment is less severe, though the characteristic oscillation of $G_1(t)$ is present with too large an amplitude. The second approximation gives a curve which, though overdamped, provides a better description of the approach of the spin system to equilibrium.

4.4 The work of Evans and Powles, (1966).

Evans and Powles (EP) used the expression for $F(t)$ in the related form

$$F(t) = 2^{1-N} \sum_{f,g} \mathrm{Tr}\, \exp(-i\mathcal{H}t)\, I_f^+ \exp(i\mathcal{H}t)\, I_g$$

$$= 2^{1-N} \sum_{f,g} \mathrm{Tr}\, I_f^+(-t) I_g \qquad (4.10)$$

Now α commutes with I_f^+ a[redacted]es not affect the time development of $I_f^+($[redacted]ctly, but only through the term β. They there[redacted]used a Dyson-type expansion in powers of α :

$$I_f^+(-t) = \exp(-i\beta t) I_f^+ \exp(i\beta t) + i\exp(-i\beta t) \int_0^t dt' \left[\alpha(t'), I_f^+\right] \exp(i\beta t) + \exp(-i\beta t)\left(\int_0^t dt' \int_0^{t'} dt'' \left[\alpha(t'), \left[\alpha(t''), I_f^+\right]\right]\right) \times \exp(i\beta t) + \ldots \qquad (4.11)$$

where $\alpha(t) = \exp(i\beta t)\,\alpha\, \exp(-i\beta t)$

This leads to a corresponding series for Bloch decay:

$$F(t) = B_0(t) + B_1(t) + B_2(t) + \ldots \qquad (4.12)$$

The result for $B_o(t)$ is given by:

$$B_o(t) = F_o(t) \tag{4.13}$$

where $F_o(t)$ is the LN lowest order approximation.

They evaluated $B_1(t)$:

$$B_1(t) = (1/3)\sum_{k\neq j} B_{kj}\sin(B_{kj}t)\left[t\prod_{g\neq j,k}\cos(B_{gj}t) - \int_0^t dt' \times \prod_{g\neq j,k}\cos\left\{B_{gj}(t-t') + B_{gk}t'\right\}\right] \tag{4.14}$$

They computed $B_o(t)$ and $B_1(t)$ and compared their sum with the experimental curve of Barnaal and Lowe.[16] They found that the earlier experimental results of LN fit their curve better than the later results of Barnaal and Lowe.[16] $B_2(t)$ was not calculated, as they felt that this would only become necessary when the experimental F(t) became known for larger values of t.

4.5 The work of Betsuyaku (1970).

Betsuyaku noted that the theory of EP, truncated at $G_1(t)$, does not give the correct 4th moment. He included higher order terms ignored in the EP theory and investigated the possible connections among the LN, CM, and EP theories. He calculated $G_2(t)$ which gives the correct 4th moment and plays an important role in determining the long-time behavior of the fid function.

He says that the LN and CM formulas are valid for short t, but his function G(t), which has been expanded in terms of α, has no restriction as to time, and is adequate to investigate long-time behavior.

Good agreement is found between theory and experiment for ^{19}F fid in a single crystal of CaF_2. However the calculated beat amplitude is about 25% larger than the experimental amplitude.

PART B

5. SECOND DERIVATIVE APPROXIMATION

5.1 Approximation method in the second derivative of F(t).

The expression for the free induction decay is given by;

$$F(t) = Tr(M_x(t)M_x)/Tr(M_x^2) \quad (5.1)$$

where $M_x(t) = \exp(i\mathcal{H}_1 t)\, M_x \exp(-i\mathcal{H}_1 t)$ and $\alpha + \beta = \mathcal{H}_1$, is our Hamiltonian for the dipole-dipole interaction.

As mentioned in the introduction, our tentative approximation is made on the second derivative

$$F''(t) = -\, Tr\left\{\left[\left[M_x, \mathcal{H}_1\right], \mathcal{H}_1\right] \exp(-i\mathcal{H}_1 t) M_x \exp(i\mathcal{H}_1 t)\right\} /Tr(M_x^2) \quad (5.2)$$

We write

$$\exp(-i\mathcal{H}_1 t)M_x\exp(i\mathcal{H}_1 t) = \exp-i(\alpha+\beta)t\; M_x\; \exp i\,(\alpha+\beta)t$$

$$\cong \exp(-i\beta t)\exp(-i\alpha t)M_x\exp(i\alpha t)\exp(i\beta t)$$

$$= \exp(-i\beta t)\; M_x\; \exp(i\beta t), \quad (5.3)$$

where the LN-type approximation

$$\exp i(\alpha+\beta)t \cong \exp(i\alpha t)\exp(i\beta t)$$

has been made. Then our approximate second derivative is given by:

$$F_a''(t) = -\mathrm{Tr}\left\{\left[\left[M_x,\mathcal{H}_1\right],\mathcal{H}_1\right]\exp(-i\beta t)M_x\exp(i\beta t)\right\}/\mathrm{Tr}(M_x^2) \qquad (5.4)$$

where the subscript "a" stands for "approximation".

We now investigate the second and fourth moments resulting from this approximation. The second moment M_2 of the fid is given by:

$$M_2 = -F''(t)_{t=0} \qquad (5.5)$$

So,

$$M_2^a = -\mathrm{Tr}\left\{\left[\left[M_x,\mathcal{H}_1\right],\mathcal{H}_1\right]M_x\right\} \qquad (5.6)$$

Equation (5.6) is the exact second moment.
Our fourth moment is:

$$M_4^a = F_a^{iv}(t)_{t=0} = \mathrm{Tr}\left\{\left[\left[M_x,\mathcal{H}_1\right],\mathcal{H}_1\right]\left[\left[M_x,\beta\right],\beta\right]\right\}/\mathrm{Tr}(M_x^2) \qquad (5.7)$$

It is seen that M_4^a does not have the same form as M_4, where

$$M_4 = F^{iv}(t)_{t=0} = \mathrm{Tr}\left\{\left[\left[M_x,\dot{\mathcal{H}}\right],\dot{\mathcal{H}}\right]\left[\left[M_x,\dot{\mathcal{H}}\right],\dot{\mathcal{H}}\right]\right\}/\mathrm{Tr}(M_x^{\;2}) \qquad (5.8)$$

As indicated in the introduction, sufficient motivation existed for a search for the difference $M_4' \equiv M_4 - M_4^a$. A short calculation yields:

$$M_4' = \mathrm{Tr}\left\{\left[\gamma,M_x\right]\left[\dot{\mathcal{H}},\left[\dot{\mathcal{H}},M_x\right]\right]\right\}/\mathrm{Tr}(M_x^{\;2}) \qquad (5.9)$$

where $\gamma = [\alpha,\beta]$.

M_4' will be evaluated in the next section.

5.2 Direct calculation of M_4'.

The method used for the calculation of M_4' is the direct evaluation of the commutators involved, and the taking of the traces. In the first part of this section we give an indication of the procedures followed for the evaluation of M_4'; in the second part we explain the method used to evaluate the traces. From equation (5.9), since ($M_x \propto I_x$) we get:

$$M_4' \mathrm{Tr}(I_x^2) = \mathrm{Tr}\left\{\left[\left[I_x, \beta\right], \alpha\right]^2\right\} + \mathrm{Tr}\left\{\left[\left[I_x, \beta\right], \alpha\right]\left[\left[I_x, \beta\right], \beta\right]\right\} \tag{5.10}$$

where α and β are given by equations (4.1) and (4.2). We adopt the convention that $B_{jk} \equiv 0$ if $j = k$; this allows us to remove the restriction in the summation of the following equations. Then taking commutators one obtains:

$$\frac{2}{(i)^2}\left[\left[I_x, \beta\right], \alpha\right] =$$

$$- (1/3) \sum_{jk\ell} \left\{ B_{jk} B_{\ell k} I_{jx} I_{\ell z} I_{kz} + B_{jk} B_{\ell j} I_{\ell z} I_{jz} I_{kz} \right.$$

$$\left. - B_{jk} B_{k\ell} I_{jx} I_{ky} I_{\ell y} - B_{jk} B_{j\ell} I_{jy} I_{\ell y} I_{kx} \right\}$$

$$+ B_{jk}B_{k\ell}I_{jy}I_{kx}I_{\ell y} + B_{jk}B_{j\ell}I_{jx}I_{\ell y}I_{ky}$$

$$- B_{jk}B_{k\ell}I_{jz}I_{\ell z}I_{kx} - B_{jk}B_{\ell j}I_{\ell z}I_{jx}I_{kz} \Big\} \qquad (5.11)$$

Noting that $I_{\ell z}$ and I_{jx} commute for $\ell \neq j$; our expression reduces to:

$$\Big[\big[I_x, \beta\big], \alpha\Big] = (1/6) \sum_{jk\ell} \Big\{ (B_{jk}B_{\ell k} - B_{jk}B_{\ell j}) I_{jx}I_{\ell z}I_{kz}$$

$$+ (B_{jk}B_{\ell j} - B_{jk}B_{k\ell}) I_{\ell z}I_{jz}I_{kx}$$

$$+ (B_{jk}B_{k\ell} - B_{jk}B_{j\ell}) I_{jy}I_{\ell y}I_{kx}$$

$$+ (B_{jk}B_{j\ell} - B_{jk}B_{k\ell}) I_{jx}I_{\ell y}I_{ky} \Big\} \qquad (5.12)$$

Now changing dummy indices and introducing the notation $I_{jx} \equiv j_x$, and defining $C_{jk\ell} = B_{\ell k} - B_{\ell j}$, our expression may be written:

$$\Big[\big[I_x, \beta\big], \alpha\Big] =$$

$$(1/6) \sum_{jk\ell} B_{jk}C_{jk} \, (j_x \ell_z k_z + j_y \ell_y k_x - \ell_z j_z k_x - j_x \ell_y k_y) \qquad (5.13)$$

One must now square and take the trace. After some simplification, thirteen separate terms result. A typical term is:

$$\sum_{jk\ell pqr} B_{jk}B_{pq}C_{jk\ell}C_{pqr}\,Tr(j_x \ell_z k_z p_x r_z q_z) \qquad (5.14)$$

This term was handled in the following way: one must have j = p, otherwise the trace would give zero; this is due to the invariance of the trace under rotations, in particular under a rotation about the z-axis of 180° Writing j = p, we get:

$$\sum_{jk\ell qr} B_{jk}B_{jq}C_{jk\ell}C_{jqr}\,Tr(j_x \ell_z k_z j_x r_z q_z) \qquad (5.15)$$

Now writing the mutually exclusive indices in a way suitable for summation of the traces; we get:

The first possibility is $\ell = r = k = q \neq j$
The second possibility is $j = \ell = r \neq k = q$
The third possibility is $j \neq \ell = r \neq k = q \neq j$
The fourth possibility is $j \neq \ell = k \neq r = q \neq j$
The fifth possibility is $j \neq \ell = q \neq r = k \neq j$

All other possibilities give zero automatically, due to the vanishing of the coefficients of the traces for these cases.

Introducing the five possibilities into equation (5.15) we get:

$$\sum_{jk}{}' B_{jk}^2 C_{jkk} \, Tr \, j_x^2 \, Tr \, k_z^4 + \sum_{jk}{}' B_{jk} C_{jkj}^2 \, Tr(j_x j_z)^2 Tr \, k_z^2$$

$$+ \sum_{jk\ell}{}' B_{jk}^2 C_{jk}^2 \, Tr \, j_x^2 \, Tr \, k_z^2 \, Tr \, \ell_z^2 \; +$$

$$\sum_{jkq}{}' B_{jk} B_{jq} C_{jkk} C_{jqq} \, Tr \, j_x^2 \, Tr \, k_z^2 \, Tr \, q_z^2 \; +$$

$$\sum_{jkq}{}' B_{jk} B_{jq} C_{jkq} C_{jqk} \, Tr \, j_x^2 \, Tr \, k_z^2 \, Tr \, q_z^2 \qquad (5.16)$$

where the prime means summation over unequal indices only. We proceeded in a similar way for the other twelve terms. The second trace in equation (5.2) was expanded using the same method.

(ii) Evaluation of the traces.

Certain traces are easy to evaluate directly. For example,

$$\mathrm{Tr}_j\, j_z = \sum_{m=-I}^{m=+I} m = 0 \qquad (5.17)$$

$$\mathrm{Tr}_j\, j_z^2 = \sum_{m=-I}^{I} m^2 = \frac{1}{3} I(I+1)(2I+1) \, . \qquad (5.18)$$

where the "j" in Tr_j means that the trace is performed over the subspace of spin j.

Again,

$$\mathrm{Tr}\, I_x^2 = \sum_{jk} \mathrm{Tr}\, j_x k_x$$

$$= \sum_j \mathrm{Tr}\, j_x^2 + \sum_{j\neq}\sum_k \mathrm{Tr}\, j_x k_x$$

$$= \sum_j (\mathrm{Tr}_j\, j_x^2)(2I+1)^{N-1} + \sum_{j\neq k}\sum \mathrm{Tr}_j\, j_x\, \mathrm{Tr}_k\, k_x\, (2I+1)^{N-2}$$

$$= N(2I+1)^{N-1} \cdot (1/3)\, I(I+1)(2I+1) \qquad (5.19)$$

where $\sum_{j\neq k} \mathrm{Tr}_j\, j_x\, \mathrm{Tr}_k\, k_x (2I+1)^{N-2} = 0$

The extra factors of (2I+1) arise from the traces of unity in the subspace of the spin indices not summed over. For more complicated terms use has been made of Ref. 13. After adding all terms, the answer was $M_4' = 0$; i.e. $M_4 = M_4'$. Our $F_a''(t)$ does in fact give M_4 correctly.

5.3 Symmetry considerations

The direct calculations of M_4' gave zero. This calculation, as indicated previously, was lengthy and time-consuming. In an effort to understand this result more deeply, we tried to take advantage of the symmetry properties of the traces involved in M_4'.

It is now convenient to define the following operators:

$$\beta_x = \sum_{j \neq k}^{N} B_{jk} I_{jx} I_{kx} \qquad (5.20\ a)$$

$$\beta_y = \sum_{j \neq k}^{N} B_{jk} I_{jy} I_{ky} \qquad (5.20\ b)$$

$$\beta_z = \sum_{j \neq k}^{N} B_{jk} I_{jz} I_{kz} \qquad (5.20\ c)$$

$$B_x = \mathrm{Tr}\left[\left[I_x, \beta_z\right], \alpha\right] \left[\left[I_x, \beta_z\right], \beta_x\right] / \mathrm{Tr}\ I_x^2 \qquad (5.21\ a)$$

$$B_y = \mathrm{Tr}\left[\left[I_x, \beta_z\right], \alpha\right] \left[\left[I_x, \beta_z\right], \beta_y\right] / \mathrm{Tr}\ I_x^2 \qquad (5.21\ b)$$

$$B_z = \mathrm{Tr}\left[\left[I_x, \beta_z\right], \alpha\right] \left[\left[I_x, \beta_z\right], \beta_z\right] / \mathrm{Tr}\ I_x^2 \qquad (5.21\ c)$$

That $M_4' = 0$, follows from

$$B_x = B_y = B_z$$

The proof that $B_y = B_z$ is accomplished by rotating the operators inside the trace for B_z by $\pm \pi/2$ about the x-axis. Since the trace is invariant under such an operation, then $\alpha \rightarrow \alpha$, $I_x \rightarrow I_x$, $\beta_z \rightarrow \beta_y$, and

$$B_z = Tr\left\{\left[\left[I_x, \beta_y\right], \alpha\right]\left[\left[I_x, \beta_y\right], \beta_y\right]\right\} / Tr(I_x^2) \qquad (5.22)$$

Now for the same reasons that $\left[I_x, \alpha\right] = 0$, (Section 4) one has

$$\left[I_x, \beta_x + \beta_y + \beta_z\right] = 0 \qquad (5.23)$$

But
$$\left[I_x, \beta_x\right] = 0 \qquad (5.24)$$

so that
$$\left[I_x, \beta_y\right] = -\left[I_x, \beta_z\right] \qquad (5.25).$$

Substituting equation (5.25) into (5.22) yields

$$B_y = B_z \qquad (5.26)$$

The proof that $B_x = B_y$ is not as straightforward. One considers the trace of the commutator of a judiciously selected operator " $\hat{O}$ ", with I_z:

$$Tr\left[\hat{O}, I_z\right] / Tr(I_x^2) = 0 \qquad (5.27)$$

(since Tr AB = Tr BA), where

$$\hat{O} = \left[\left[I_x, \beta_z\right], \alpha\right] \left[\left[I_y, \beta_z\right], \beta_x\right] \quad (5.28)$$

Three terms result, from the commutators of I_z with I_y, I_x and β_x. Equation (5.27) can then be written:

$$\gamma_1 + \gamma_2 + \gamma_3 = 0 \quad (5.29)$$

where

$$\gamma_1 = + i B_x \quad (5.30a)$$

$$\gamma_2 = -i \, \mathrm{Tr}\left\{\left[\left[I_y, \beta_z\right], \alpha\right] \left[\left[I_y, \beta_z\right], \beta_x\right]\right\} / \mathrm{Tr}(I_x^2) \quad (5.30b)$$

$$\gamma_3 = \mathrm{Tr}\left\{\left[\left[I_x, \beta_z\right], \alpha\right] \left[\left[I_y, \beta_z\right], \left[\beta_x, I_z\right]\right]\right\} / \mathrm{Tr}(I_x^2) \quad (5.30c)$$

A rotation of $\pm \pi/2$ about the x-axis ($I_x \rightarrow I_x$, $\alpha \rightarrow \alpha$, $\beta_z \rightarrow \beta_y$, $I_y \rightarrow \pm I_z$, $I_z \rightarrow \mp I_y$) gives:

$$\gamma_3 = - \mathrm{Tr}\left\{\left[\left[I_x, \beta_y\right], \alpha\right]\left[\left[I_z, \beta_y\right], \left[\beta_x, I_y\right]\right]\right\} / \mathrm{Tr}(I_x^2) \quad (5.31)$$

Using equation (5.25) and the similar equations

$$\left[I_y, \beta_x + \beta_z\right] = \left[I_z, \beta_x + \beta_y\right] = 0 \quad (5.32)$$

one obtains immediately

$$\gamma_3' = - \gamma_3 = \rho \tag{5.33}$$

A rotation of $\pm \pi/2$ about the z axis ($\beta_z \rightarrow \beta_y$, $\beta_x \rightarrow \beta_y'$; $I_y \rightarrow \pm I_x$) gives

$$\gamma_2' = - i\, B_y \tag{5.34}$$

From equations (5.29), (5.30a), (5.33), (5.34), one obtains

$$B_x = B_y \tag{5.35}$$

From (5.26) and (5.35) we get:

$$B_x = B_y = B_z \tag{5.36}$$

Now $\alpha = -(1/3)(\beta_x + \beta_y + \beta_z)$, so that with (5.36) and (5.1), we get:

$$M_4 = 0 \tag{5.37}$$

6.1 INTEGRATION OF THE FUNCTION F"(t) FOR CaF_2 (SPIN ½).

6.1a Explicit expression for F(t)

Rather than calculate out the traces in equation (5.4), it is noted that $F_a''(t)$ is the sum of two terms which appear in the theory of Lowe and Norberg, and which have been worked out by them:

$$F_a''(t) = F_o''(t)_{LN} + F_2(t)_{LN} \qquad (6.1)$$

(where the subscript LN refers to LN equations). Use has been made of the general expression for $F_n(t)$ given in ref. 9. Thus to get the fid we need to integrate equation (6.1):

$$F_a(t) = F_o(t) + \int_0^t\int_0^{t''} F_2(t')_{LN}\, dt'\, dt'' \qquad (6.2)$$

Before feeding this equation into the computer we first have to evaluate each term of the right-hand side in terms of the parameters involved and do some calculations by hand.

6.1b Computer calculations

For spin $\frac{1}{2}$, $F_o(t)$ is given by:[4]

$$F_o(t)_{LN} = \prod_{a'} \cos B_{aj} t/2\hbar \qquad (6.3)$$

$$\equiv Q(t) \text{ (independent of } j)$$

where a' means $a \neq j$; and $F_2(t')_{LN}$ is given by

$$F_2(t')_{LN} = \prod_{a'} \cos B_{aj} t'/2\hbar \left\{ \frac{1}{3}\frac{1}{N} \times \sum_{jk\ell} B_{jk}(B_{j\ell} - B_{k\ell}) \tan(B_{jk}t'/2\hbar)\tan(B_{j\ell}t'/2\hbar) \right\} \qquad (6.4)$$

Writing $F_a(t) = Q(t)U(t)$, we get for $U(t)$

$$U(t) = 1 - \frac{1}{3}\left\{ \sum_{k\neq\ell}\sum (B_{jk}/2\hbar)(B_{j\ell}/2\hbar)\tan(B_{jk}t/2\hbar)\tan(B_{j\ell}t/2\hbar) - \sum_{k\neq\ell}\sum (B_{jk}B_{k\ell}/4\hbar^2)\tan(B_{jk}t/2\hbar)\tan(B_{j\ell}t/2\hbar) \right\} \qquad (6.5)$$

The last summation is dropped since it contains odd functions of the B_{ij}; the lattice sums are negligible compared to the first summation.[4] Then $U(t) =$

$$1 - \frac{1}{3}\sum_{k\neq\ell}(B_{jk}/2\hbar)\tan(B_{jk}t/2\hbar)(B_{j\ell}/2\hbar)\tan(B_{j\ell}t/2\hbar) \qquad (6.5a)$$

$$= 1 - \frac{1}{3}\left[\left(\sum_{k}^{N} (B_{jk}/2h)\tan(B_{jk}t/2h)\right)^2 - \sum_{k}^{N}\left((B_{jk}/2h)\tan(B_{jk}t/2h)\right)^2\right] \quad (6.6)$$

where use has been made of

$$\sum_{\ell}\sum_{k\neq\ell} X_k X_\ell = \sum_k X_k \sum_\ell X_\ell - \sum_k {X_k}^2$$

The summation is handled in an approximate way. The near neighbors (of j) are treated exactly, while the far neighbors are treated as a continuum. Choosing the number of nearest neighbors to be treated exactly as 80, the summations in equation (6.6) are divided as follows:

$$\left(\sum_{k=1}^{80}(B_{jk}/2h)\tan B_{jk}t/2h + \sum_{81}^{N}(B_{jk}/2h)\tan B_{jk}t/2h\right)^2$$
$$- \sum_{k=1}^{80}\left((B_{jk}/2h)\tan B_{jk}t/2h\right)^2 - \sum_{81}^{N}\left((B_{jk}/2h)\tan B_{jk}t/2h\right)^2 \quad (6.6a)$$

The first summation is fed into the computer. The second summation is expanded to order t^2, the sums over the coefficients being approximated by integrals. For example,

$$\sum_{j=81}^{N} {B_{jk}}^2 = \int_0^{\pi}\int_0^{2\pi}\int_{\sqrt[3]{?}d}^{\infty} \frac{(1-3\cos^2\theta)^2}{r^6 d^3} \sin\theta \, d\theta \, d\phi \, r^2 dr, \quad (6.7)$$

$$= 0.14811/d^6$$

where d^{-3} is the number of spins/unit volume. The third and fourth summations are handled like the first and second, respectively. Then U(t) =

$$1 - \frac{1}{3}\left\{\left(\sum_{k=1}^{10}(B_{jk}/2\hbar)\tan B_{jk}t/2\hbar + 0.90625 \times 10^{-4}t\right)^2 - \sum_{k=1}^{80}(B_{jk}/2\hbar)\tan B_{jk}t/2\hbar)^2 - 0.006198 \times 10^{-8}t^2\right\} \qquad (6.8)$$

To compute Q(t), the product is again treated in terms of near and far neighbors, with expansion to order t^2 performed for the far-neighbors terms. The result is, for CaF_2,

$$Q(t) \cong \prod_{1}^{80}\cos\left\{(1/40.44)(1-3\cos^2\theta_{jk})/r_{jk}^3\right\} \left\{(1-0.45313 \times 10^{-4}t^2)\right\} \qquad (6.9)$$

where for CaF_2, $d/\gamma^2\hbar = 30.32\mu$sec., and d is the lattice constant. The direction of the static magnetic field H_0 is taken to be along one of the principal axes of a simple cubic crystal.

Finally the last equation will read:

$$\overset{\circ}{F}(t) = \prod_{jk}^{80} (\cos B_{jk}t/2\hbar)(1 - 0.45313 \times 10^{-4}\ t^3)$$

$$- (1/3)\int_0^t\int_0^{t''} Q(t')\left\{\left(\left(\sum_{k=1}^{80}(B_{jk}/2\hbar)\tan B_{jk}t'/2\hbar\right. + \right.\right.$$

$$\left.0.90625 \times 10^{-4}t' + 0.00089 \times 10^{-8}t'^3\right)^2$$

$$\left.- \sum_{k=1}^{80}\left((B_{jk}/2\hbar)\tan B_{jk}t'/2\hbar\right)^2\right\}dt'dt'' \qquad (6.10)$$

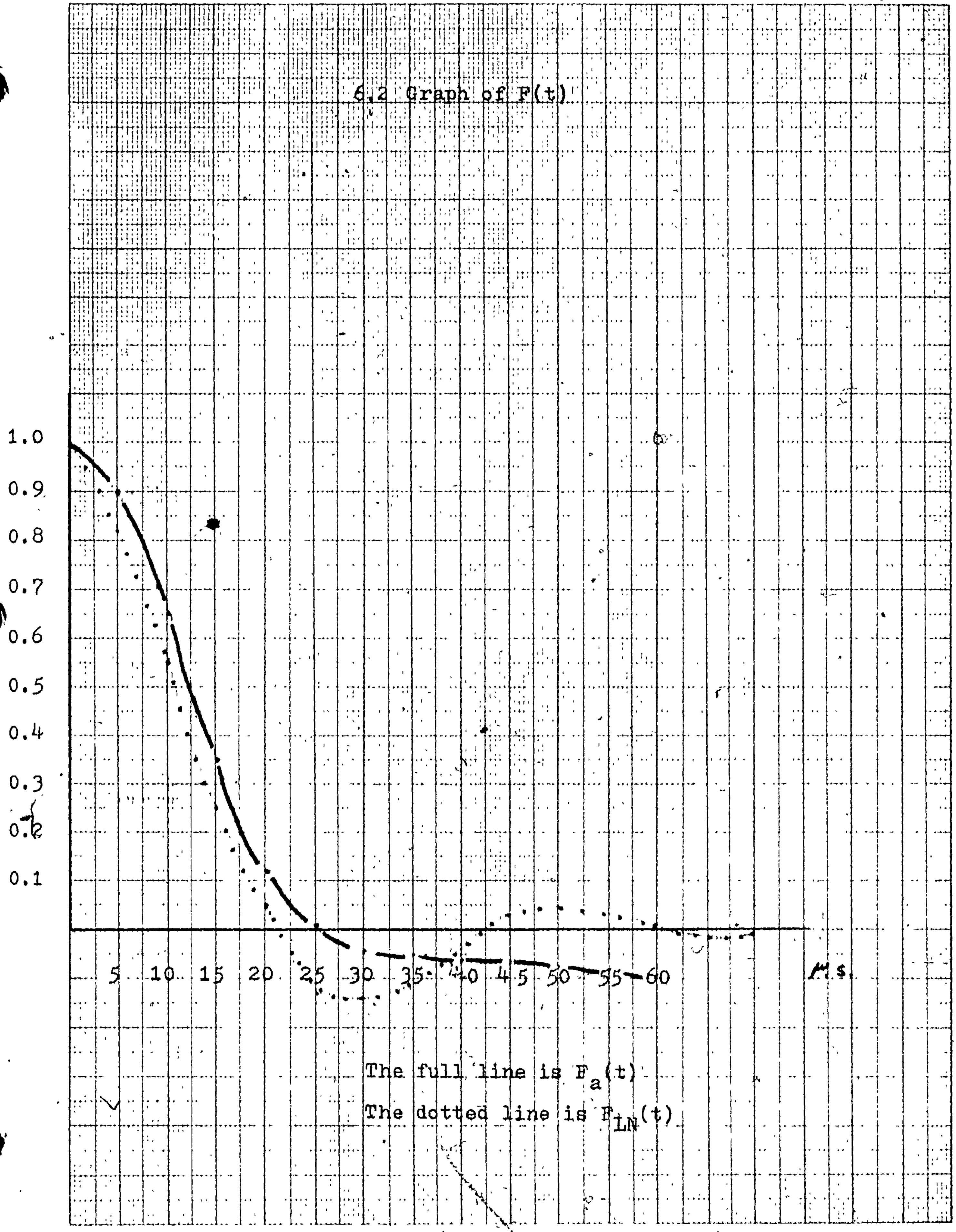
The double integral is reduced to single integrals by integrating by parts, i.e.

$$\int_0^t\int_0^{t''} f(t')dt'dt'' = t''\int_0^{t''} f(t')dt'\Big|_0^t - \int_0^t t''f(t'')dt'' \qquad (6.11)$$

$$= t\int_0^t f(t')dt' - \int_0^t t'f(t')dt'$$

A graph of the curves $F_a(t)$ obtained by us and $F_{LN}(t)$ obtained by Lowe and Norberg for CaF_2 is shown in the following page.

6.2 Graph of F(t)



DISCUSSION

The method of approximation for the fid line, used in this thesis, has been to assume the commutability of the α and β terms in the Hamiltonian which appears in the expression for the second derivative of F(t). This is equivalent to taking $\chi(t) = 1$. The method is similar to the one used by Lowe and Norberg, with two exceptions: 1) They made their approximation in the function F(t) itself, and 2) they expanded $\chi(t)$ to order t^4. Both methods yielded correct second and fourth moments. The LN method, however, gave much better agreement with experimental CaF_2 results, and up to higher values of t.

The main positive contribution of this thesis is a demonstration that certain terms in the theoretical expression for the fourth moment vanish identically. This was shown by symmetry. The result can also be generalized to higher moments.[15]

This work should be taken as the first stage in a more elaborate calculation of the fid, wherein further expansion of $\chi(t)$ in powers of t will be considered.

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