

Continuous Wave

Nuclear Magnetic Resonance

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Spontaneous Transitions

The term "spontaneous transitions" in NMR refers to those transitions which occur, not because of B_1 , but because of magnetic coupling between the nucleus of an atom (containing protons) and the surrounding atoms. (The coupling can be greatly increased by adding a small amount of paramagnetic ions to the sample.) The nucleon can make a spontaneous transition by emission or absorption of a phonon between itself and the surrounding atoms. This is equivalent to a transfer of thermal energy. A spontaneous transition from the higher energy state to the lower energy state ($|-\rangle \Rightarrow |+\rangle$) is called spin-lattice relaxation.

The rate of spontaneous transitions is independent of the rate of induced transitions. So, in order to describe spontaneous transitions when B_1 is on, we can look at the situation when B_1 is off. This is the equilibrium situation - the situation in which the sample of spin 1/2 particles is at thermal equilibrium and is not being subjected to a B_1 field. At equilibrium then, we can treat the NMR sample as a Boltzmann gas, and so the following relations are valid

$$N_+ = C e^{-\frac{E_+}{kT}}$$

$$N_- = C e^{-\frac{E_-}{kT}}$$

$$N = N_+ + N_-$$

N_+ = number density of particles in $|+\rangle$

N_- = number density of particles in $|-\rangle$

N = number density of particles

$n = N_+ - N_- \rightarrow$ population difference

$M_{z0} = M_z$ occurring when B_1 is off

Note that there are just slightly more protons in $|+\rangle$ than in $|-\rangle$.

($n/N \Rightarrow 1.6E-6$, for $B_0 \Rightarrow 5E3$ [gauss], $T \Rightarrow 300$ [K])

So,

$$\frac{N_+}{N_-} \rightarrow e^{\frac{E_- - E_+}{kT}} \rightarrow e^{\frac{\Delta E}{kT}} \rightarrow e^{\frac{\alpha \hbar B_0}{kT}}$$

In terms of the magnetization vector,

$$M_z \rightarrow \frac{\sum_{\Delta V} \mu_z}{\Delta V} \rightarrow N_+ \left(\frac{1}{2} \alpha \hbar \right) + N_- \left(-\frac{1}{2} \alpha \hbar \right) \rightarrow \frac{1}{2} \alpha \hbar N \left(\frac{e^{\frac{\alpha \hbar B_0}{kT}} - 1}{e^{\frac{\alpha \hbar B_0}{kT}} + 1} \right) \rightarrow \frac{1}{2} \alpha \hbar N \left(\frac{\frac{\alpha \hbar B_0}{kT}}{2} \right) \rightarrow \frac{N (\alpha \hbar)^2 B_0}{4 kT}$$

So, the rate of spontaneous transitions should agree with the above results

$\frac{dN_-}{dt} = N_+ S_- - N_- S_+$ $\frac{dN_+}{dt} = N_- S_+ - N_+ S_-$ $\frac{dn}{dt} = \frac{dN_+}{dt} - \frac{dN_-}{dt}$ $\left(\frac{dn}{dt} \right)_{\text{spontaneous}} = 2 (N_- S_+ - N_+ S_-)$ $\left(\frac{dn}{dt} \right)_{\text{spontaneous}} = -\frac{n - n_0}{T_1}$	$N_- [t] \rightarrow N \frac{S_-}{S_+ + S_-} + C e^{-(S_+ + S_-) t}$ $N_+ [t] \rightarrow N \frac{S_+}{S_+ + S_-} + C e^{-(S_+ + S_-) t}$	<p>$S_{+-} = S_- =$ rate of spontaneous transition from $+\rangle \rightarrow -\rangle$ $S_{-+} = S_+ =$ rate of spontaneous transition from $-\rangle \rightarrow +\rangle$</p> <p>Note that as $t \Rightarrow \infty$</p> $N_- \rightarrow N \frac{S_-}{S_+ + S_-}$ $N_+ \rightarrow N \frac{S_+}{S_+ + S_-}$ $\frac{N_+}{N_-} = \frac{S_+}{S_-}$ <p>(from above) $e^{\frac{\alpha \hbar B_0}{kT}} = \left(\frac{S_+}{S_-} \right)$</p>
<p>where</p> $n_0 = n[t \rightarrow \infty] \rightarrow N \frac{S_+ - S_-}{S_+ + S_-}$ $T_1 = \frac{1}{S_+ + S_-}$		

or, since $M_z = \frac{1}{2} \alpha \hbar n$

$$\dot{M}_z = -\frac{M_z - M_{z0}}{T_1} \quad (3)$$

So, if the populations are perturbed from their equilibrium values, n will return to its equilibrium value, n_0 , with decay time constant T_1 .

We can better understand the T_2 processes by understanding the T_1 processes. The T_1 processes occur due to the spontaneous transitions of particles. In other words, the particles have a finite lifetime in each spin state. So, the uncertainty in the energy of a state can be approximated using the uncertainty principle.

It is this variation in energy which causes particles to have slightly different Larmor frequencies, and hence to dephase - the T_2 processes.

For a quantum mechanical explanation of lifetimes, and the Lorentz curve see Gasiorowicz, *Quantum Physics*, "Special Topic 4 - Lifetimes, Linewidths, and Resonances"

$$\begin{cases} \Delta E \Delta t \geq \hbar \\ \Delta E T_1 \geq \hbar \\ \Delta E \geq \frac{\hbar}{T_1} \end{cases}$$

Induced Transitions

From quantum mechanics it can be shown that the probability of inducing a transition via a γ at ω_L is the same for both transitions. That is, $R_{+ \rightarrow -} = R_{- \rightarrow +} = R$

The rate of transition is proportional to the density of electromagnetic field quanta, or B_1^2 , and is approximately given by a univariate distribution in the frequency domain, ω , where ω is the (angular) frequency of B_1 .

$f[\omega]$ is a normalized function which peaks at $\omega = \omega_L$. More will be said about this function later.

$$R = \frac{\alpha^2 B_1^2}{4} f[\omega]$$

So,

$$\left(\frac{dn}{dt} \right)_{\text{induced}} \rightarrow \frac{dN_+}{dt} - \frac{dN_-}{dt} \rightarrow (N_- R_{+ \rightarrow -} - N_+ R_{- \rightarrow +}) - (N_+ R_{- \rightarrow +} - N_- R_{+ \rightarrow -}) \rightarrow -2 R n$$

Note that induced transitions tend to equalize the populations in the sample, that is, as $t \Rightarrow \infty$, $n \Rightarrow 0$. When B_1 is large, n is close to 0, and the sample is said to be saturated.

Power Absorption

Power absorption from the B_1 field by the sample is how the resonance condition is detected. Therefore, we would like to determine the magnitude of this power.

By combining both types of transitions we can determine the steady-state "RF" power absorption of the sample.

$$\begin{aligned} \frac{dn}{dt} &\rightarrow \left(\frac{dn}{dt} \right)_{\text{spontaneous}} + \left(\frac{dn}{dt} \right)_{\text{induced}} \rightarrow -2 R n - \frac{n - n_0}{T_1} \\ n[t = \infty] &\rightarrow \frac{n_0}{1 + 2 R T_1} \end{aligned}$$

The power absorption density of the sample is only due to the RF induced transitions, and therefore is given by

$$P \rightarrow N_+ R_- (\hbar \omega_L) + N_- R_+ (-\hbar \omega_L) \rightarrow \hbar \alpha B_0 R n \rightarrow \hbar \alpha B_0 \frac{R}{1 + 2 R T_1}$$

Bloch's Equations

By reviewing the discussion so far, we see that we have gathered 3 relations which completely describe the magnetization vector \mathbf{M} , which are valid for the situation when $B_1 \Rightarrow$ off. These are called Bloch's equations.

$$\begin{aligned} \dot{M}_x &= \omega_L M_y - \frac{M_x}{T_2} & \dot{M}_x &= \omega_L M_y - \frac{M_x}{T_2} \\ \dot{M}_y &= -\omega_L M_x - \frac{M_y}{T_2} & \dot{M}_y &= -\omega_L M_x - \frac{M_y}{T_2} \\ \dot{M}_z &= -\frac{M_z - M_{z0}}{T_1} & \dot{M}_z &= -\frac{M_z - M_{z0}}{T_1} \end{aligned} \quad \text{OR}$$

Returning to the vector model, we can modify these equations so that they are valid for $B_1 \Rightarrow$ on. Firstly, the vector situation with $B_1 \Rightarrow$ off must reproduce Bloch's equations above.

$$\dot{\vec{r}} = \dot{\vec{M}} \times \hat{B}_0$$

$$\dot{\vec{L}} = \dot{\vec{M}} \times \hat{B}_0$$

$$\dot{\vec{M}} = \alpha \dot{\vec{M}} \times \hat{B}_0$$

$$\dot{\vec{M}} \times \hat{B}_0 \rightarrow \frac{1}{\alpha} \left(\left(\omega_L M_y - \frac{M_x}{T_2} \right) \hat{x} + \left(-\omega_L M_x - \frac{M_y}{T_2} \right) \hat{y} + \left(-\frac{M_z - M_{z_0}}{T_1} \right) \hat{z} \right)$$

substituting the value for $\dot{\vec{M}}$ from Bloch's equations.

Now with B_1 on,

$$\dot{\vec{M}} = \alpha \dot{\vec{M}} \times \hat{B}$$

$$\hat{B} \rightarrow \hat{B}_0 + \hat{B}_1$$

$$\hat{B}_0 \rightarrow B_0 \hat{z}$$

$$\dot{\vec{M}} = \alpha (\dot{\vec{M}} \times \hat{B}_0 + \dot{\vec{M}} \times \hat{B}_1)$$

$$\hat{B}_1 \rightarrow B_1 (\cos[\omega t] \hat{x} + \sin[\omega t] \hat{y})$$

Substituting $\dot{\vec{M}} \times \hat{B}_0$ from above, expanding $\dot{\vec{M}} \times \hat{B}_1$, and making a change of basis vectors to the frame rotating at ω_L in the x-y plane such that

we find that
$$\dot{M}_{x'} = (\omega_L - \omega) M_{y'} - \frac{M_{x'}}{T_2}$$

$$\hat{x}' = \cos[\omega t] \hat{x} + \sin[\omega t] \hat{y}$$

$$\hat{y}' = -\sin[\omega t] \hat{x} + \cos[\omega t] \hat{y}$$

$$\hat{z}' = \hat{z}$$

\hat{B}_1 is chosen to be directed along \hat{x}'

$$\dot{M}_{y'} = -(\omega_L - \omega) M_{x'} + \alpha B_1 M_z - \frac{M_{y'}}{T_2}$$

$$\dot{M}_z = -\alpha B_1 M_{y'} - \frac{M_z - M_{z_0}}{T_1}$$

The steady-state solutions of these Bloch's equations (which are now valid for $B_1 \Rightarrow$ on) are

$$M_{x'} = M_{z_0} \frac{\alpha B_1 T_2^2 (\omega_L - \omega)}{1 + T_2^2 (\omega_L - \omega)^2 + \alpha^2 B_1^2 T_1 T_2}$$

$$M_{y'} = M_{z_0} \frac{\alpha B_1 T_2}{1 + T_2^2 (\omega_L - \omega)^2 + \alpha^2 B_1^2 T_1 T_2}$$

$$M_z = M_{z_0} \frac{1 + T_2^2 (\omega_L - \omega)^2}{1 + T_2^2 (\omega_L - \omega)^2 + \alpha^2 B_1^2 T_1 T_2}$$

The power absorption density of the sample can be determined as follows

$$P \rightarrow \hat{\omega} \cdot \dot{\vec{r}} \rightarrow \frac{B_1^2 \alpha^3 N \hbar B_0}{4 k T} \frac{\omega T_2}{1 + T_2^2 (\omega_L - \omega)^2 + \alpha^2 B_1^2 T_1 T_2}$$

So, the power absorption density (as a function of ω) has the form of a Lorentz curve. This is also the form of the normalized distribution $f[\omega]$ mentioned previously.

QUANTUM PHYSICAL, PRE-QUANTIZED EM FIELD, NMR THEORY

In this treatment, we examine 1, uncoupled, stationary in space, spin 1/2 particle. So, we take the possible states of the system to be $|+\rangle$ and $|-\rangle$, where, as usual, the notation refers to a state with the spin component in the

z direction being either $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$. We examine how the amplitudes to be in these states vary as a function of 1: time, and 2: the frequency of B_1 , when the particle is subjected to the previously discussed magnetic field.

The Shrodinger equation is

$$\hat{H} |\psi\rangle = i \hbar \frac{\partial}{\partial t} |\psi\rangle$$

$$i \frac{\alpha}{2} \begin{pmatrix} B_0 & B_1 e^{i\omega t} \\ B_1 e^{-i\omega t} & -B_0 \end{pmatrix} \begin{pmatrix} a_+[t] \\ a_-[t] \end{pmatrix} = \begin{pmatrix} \dot{a}_+[t] \\ \dot{a}_-[t] \end{pmatrix}$$

The 2 coupled differential equations we end up with are

$$-i \frac{2}{\alpha} \dot{a}_+[t] = B_0 a_+[t] + B_1 e^{i\omega t} a_-[t]$$

$$-i \frac{2}{\alpha} \dot{a}_-[t] = B_1 e^{-i\omega t} a_+[t] - B_0 a_-[t]$$

To solve these, we make the Ansatz

$$a_+[t] \rightarrow C_+ e^{i\Omega_+ t}$$

$$a_-[t] \rightarrow C_- e^{i\Omega_- t}$$

Substituting this we have

$$\frac{2}{\alpha} C_+ \Omega_+ = C_+ B_0 + C_- B_1 e^{i(\omega - \Omega_+ + \Omega_-) t}$$

$$\frac{2}{\alpha} C_- \Omega_- = C_+ B_1 e^{-i(\omega - \Omega_+ + \Omega_-) t} - C_- B_0$$

In order to eliminate the time dependence, we must have

$$\Omega_+ \rightarrow \Omega_- + \omega$$

We now have a set of algebraic equations which are, in matrix form,

$$\begin{pmatrix} \frac{2}{\alpha} \Omega_+ - B_0 & -B_1 \\ -B_1 & \frac{2}{\alpha} \Omega_- + B_0 \end{pmatrix} \begin{pmatrix} C_+ \\ C_- \end{pmatrix} = 0$$

In order for there to be a nonzero solution, the determinant of the above matrix must be zero. This yields that

$$\Omega_{\pm} \rightarrow \frac{\omega}{2} \pm \Delta\omega \quad \text{where } \Delta\omega \equiv \frac{1}{2} \sqrt{(\omega - \alpha B_0)^2 + (\alpha B_1)^2}$$

$$\Omega_- \rightarrow -\frac{\omega}{2} \pm \Delta\omega$$

where the Hamiltonian is

$$\hat{H} \rightarrow -\hat{\mu} \cdot \vec{B} \rightarrow -\alpha \frac{\hbar}{2} \begin{pmatrix} B_0 & B_1 e^{i\omega t} \\ B_1 e^{-i\omega t} & -B_0 \end{pmatrix}$$

and where

$$\hat{\mu} \rightarrow \alpha \hat{S} \rightarrow \alpha \frac{\hbar}{2} \hat{\sigma}$$

$$\hat{\sigma} \rightarrow \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right)$$

$$\vec{B} \rightarrow \vec{B}_0 + \vec{B}_1$$

$$\vec{B}_0 \rightarrow (0, 0, B_0)$$

$$\vec{B}_1 \rightarrow (B_1 \cos[\omega t], B_1 \sin[\omega t], 0)$$

$|\psi\rangle$ will be represented in column vector form for this treatment

$$|\psi\rangle \rightarrow \begin{pmatrix} a_+[t] \\ a_-[t] \end{pmatrix} \quad \text{where } \begin{matrix} a_+[t] \rightarrow \langle + | \psi \rangle \\ a_-[t] \rightarrow \langle - | \psi \rangle \end{matrix}$$

The most general solution is a linear combination of the possible individual solutions. So,

$$a_+[t] \rightarrow C_1 e^{i\frac{\omega}{2}t} e^{i\Delta\omega t} + C_2 e^{i\frac{\omega}{2}t} e^{-i\Delta\omega t}$$

$$a_-[t] \rightarrow C_3 e^{-i\frac{\omega}{2}t} e^{i\Delta\omega t} + C_4 e^{-i\frac{\omega}{2}t} e^{-i\Delta\omega t}$$

Imposing the initial condition that the particle is in the spin up state at $t=0$, using some of the previous relations to eliminate some of the "C" constants, and then normalizing, we have

$$a_+[t] \rightarrow \left(\cos[\Delta\omega t] - \frac{i \sin[\Delta\omega t] (\omega - \alpha B_0)}{2 \Delta\omega} \right) e^{i\frac{\omega}{2}t}$$

$$a_-[t] \rightarrow \frac{i \alpha B_1}{2 \Delta\omega} \sin[\Delta\omega t] e^{-i\frac{\omega}{2}t}$$

The associated probabilities are then

$$P_+[t] \rightarrow \cos^2[\Delta\omega t] + \frac{(\omega - \alpha B_0)^2}{(\omega - \alpha B_0)^2 + \alpha^2 B_1^2} \sin^2[\Delta\omega t]$$

$$P_-[t] \rightarrow \frac{\alpha^2 B_1^2}{(\omega - \alpha B_0)^2 + \alpha^2 B_1^2} \sin^2[\Delta\omega t]$$

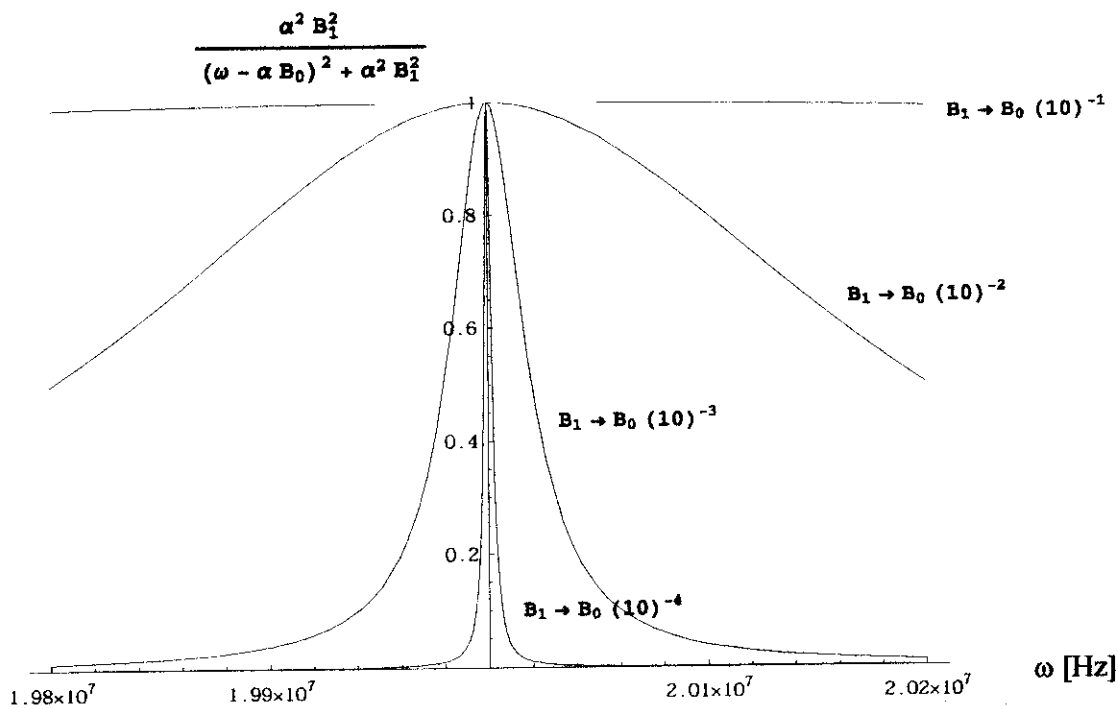
Comments

Looking at the result for $P[t]$ (the probability that the spin "flips" as a function of time) we see that it oscillates sinusoidally at a frequency $\Delta\omega$, and ranges between 0 and a maximum value of

$$\frac{\alpha^2 B_1^2}{(\omega - \alpha B_0)^2 + \alpha^2 B_1^2}$$

This value will be 1 when $\omega \Rightarrow \alpha B_0$, or ω_L , which is the Larmor frequency. Notice that this term exhibits the Lorentz line shape.

Usually, one wants to measure αB_0 very precisely. To do this, one needs to achieve a sharp curve. To achieve a sharp curve, or, in other words, to achieve a very narrow region in ω space in which the "spins flip" and hence the particles absorb power through spin relaxation (which is what one actually usually detects), the αB_1 term in the denominator (and hence B_1) needs to be small.



Example graph of Lorentz factor, using $\omega_L \Rightarrow 20$ [MHz].

EXPERIMENT

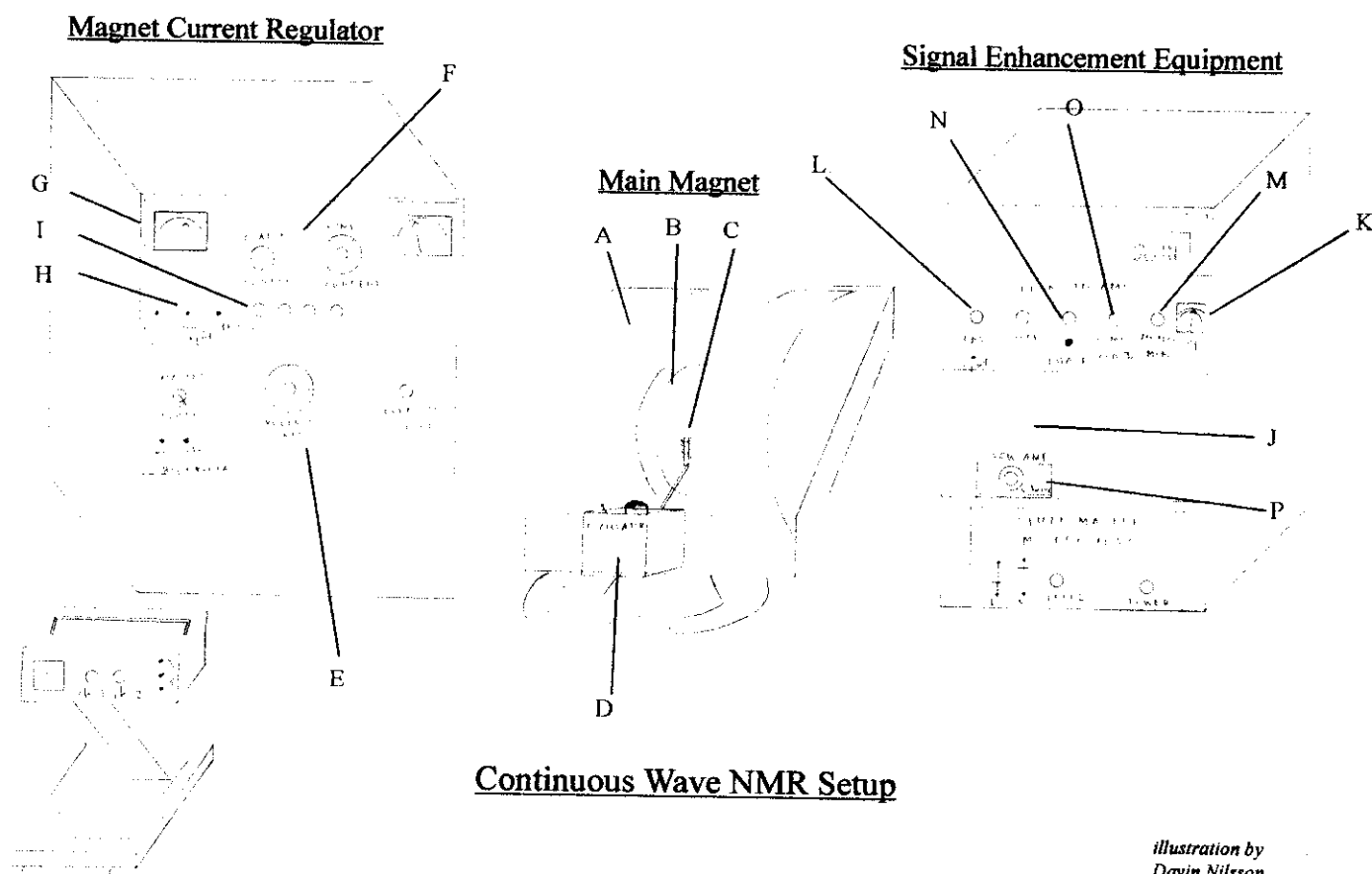


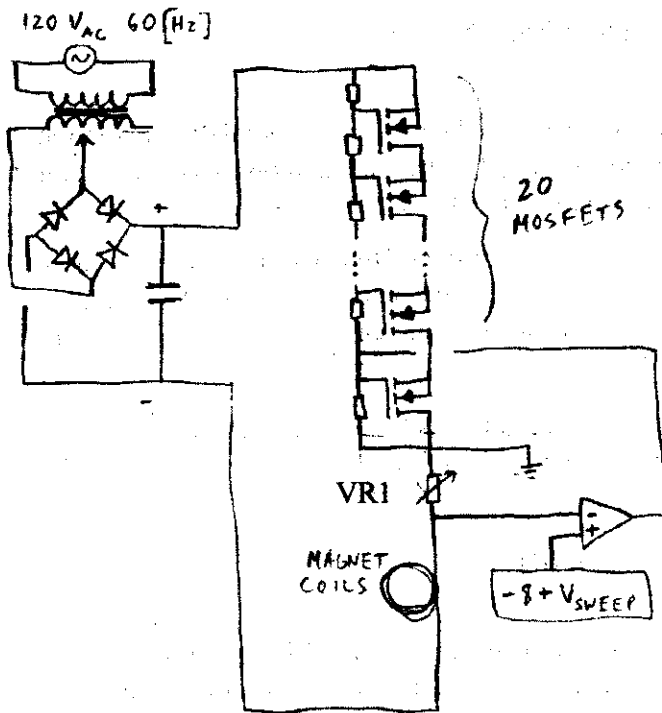
illustration by
Davin Nilsson

Main Magnet

- A Main Magnet. (.2 - .7 [Tesla]) This is the electromagnet that produces B_0 .
- B Modulating coils. These 2 coils have a smaller inductance than the main magnet. They are used to modulate the main magnetic field (usually at 25[Hz])
- C Sample apparatus. The sample is in a small cylindrical vial which is inside of an inductor. This inductor produces B_1 . The inductor has a fixed inductance. The inductor is connected to the oscillator (D) via a coax cable. Outside of the inductor are 2 more coils which are oriented in the same direction as (A) & (B). These coils have a lower inductance than (A) & (B), and are used to modulate the main magnetic field at a lower amplitude and higher frequency (60 [Hz]) than (B).
- D Marginal Oscillator. This device controls B_1 and detects the power absorption. A variable capacitor controls the frequency of B_1 (13 - 40 [MHz]). The amplitude is also adjustable. The power absorption is measured by the following. The marginal oscillator maintains a constant current amplitude through the LC circuit. The Q value of the inductor changes depending on the magnitude of power absorption by the sample. The Q value changes the effective L. Besides slightly changing the LC resonant frequency, this changes the voltage amplitude across the LC circuit. The output of the marginal oscillator is proportional to the amplitude of this voltage.

For more information on this and other NMR experiments see Melissinos, *Experiments in Modern Physics*, "Chapter 8 - Magnetic Resonance Experiments"

Magnet Current Regulator



- E Variac Voltage Control. This controls the voltage output that will be present across the “MOSFET stack” and the magnet coils. It effectively limits the maximum current possible through the magnet. Set this as low as possible for efficient current regulation.
- F Current Controls. These control the current through the main magnet. There is a coarse and fine control. On the schematic, these controls would be the variable resistor VR1. Rather than adjusting the oscillator frequency (D), the fine control is usually used to achieve the resonant situation.
- G Stack Voltage Meter. This meter shows the voltage across the MOSFET stack. The voltage across the stack should be high enough so as to enable current regulation, but not so high as to destroy the MOSFETs.

Schematic of the magnet current regulator

- H Sweep Input. The voltage at this input is attenuated by (I) and then summed to the reference voltage of the feedback op-amp. So, the sweep input voltage can be used to vary the magnet current regulator’s output current. The sweep input is used to slowly sweep the main magnetic field (usually ramp waveform input). The sweep is usually used with the lock-in amplifier. The sweep waveform can be generated by the LabView hardware and software, and output to the sweep input.
- I Sweep Attenuator. This control attenuates the sweep input. The attenuation is $n/10$, where n is the number on the dial.

Signal Enhancement Equipment

- J 60[Hz] Modulator. This device outputs current at 60[Hz]. The amplitude is adjustable. The output current usually goes to the coils described in (C). It is used to modulate the main magnetic field. If the “DC” magnitude of the main magnetic field is near the resonant value, then a small 60[Hz] variation in the magnetic field will cause the magnitude of the magnetic field to pass through the resonant value 120 times/sec. If the output of the marginal oscillator (D) is then shown on an oscilloscope which is triggered to 60[Hz] (AC line triggering), the signal will be stable on the screen. This method is usually used at first to obtain resonance.

Lock-In Amplifier *

- K Output Meter. This meter shows the voltage output of the RC stage of the lock-in. This voltage is the output of the lock-in. The output voltage can be input to the LabView hardware.

* For an explanation of lock-in amplification, see the section in this manual Lock-In Amplification p.10-12.

- L Sensitivity. This control adjusts the gain of the lock-in's input amplifier.
- M Output Gain. This control adjusts the gain of the output voltage (K).
- N Phase Control. This control adjusts the phase difference between the lock-in's internal 25[Hz] reference signal and its 25[Hz] current output which goes to the coils in (B). There are 2 knobs. One which adjusts the phase through 90° increments and one that varies continuously from -45° to 45°.
- O RC Time Constant Control. This control adjusts the RC Time Constant. Higher values will filter more narrowly about 25[Hz] but it takes longer for the RC filter to reach the actual value. So, if sweeping through a rapidly changing value, reducing the RC time constant (or increasing the sweep time) will allow more accurate reconstruction of the original NMR signal.
- P Lock-In Modulation Amplifier. The 25[Hz] modulation output of the lock-in is fed to this amplifier before it goes to the coils (B). There is a control to adjust the modulation amplitude.

SAMPLE PROCEDURE

This procedure is intended to familiarize you with the NMR equipment and the LabView program. In this experiment the sample will be distilled deionized water with a small amount of paramagnetic ions added to enhance the signal. The particle involved in the resonance will be the proton.

- 1 Place the water sample in the sample apparatus (C).
- 2 Turn on the cooler. This cools the magnet coils which usually dissipate 1.5[kW].
- 3 Set the current regulator's voltage control (E) to 0.
- 4 Turn on the Master Power switch.
- 5 Press the red High Voltage button.
- 6 Adjust the voltage control to .35 (black line).
- 7 Set the coarse current (G) to 7 (black line).

The ammeter should be in the range 80 \Leftrightarrow 100.

- 8 Turn on the marginal oscillator (D) by turning on the battery switch and the oscillator switch.
- 9 Set the oscillator frequency to ~ 18[MHz], and amplitude to the 10 position. (You can measure the frequency by connecting a frequency counter to the frequency output connector on the chassis)
- 10 The output of the oscillator should be connected to an oscilloscope which is in "line" triggering mode, 5[ms/div], 2[mV/div].
- 11 Turn on the 60[Hz] modulator (J) and set to medium amplitude.
- 12 Because the gyromagnetic ratio of the proton $\Rightarrow 5.585$, the magnitude of B_0 for which $\omega_L \Rightarrow 2 \pi 18$ [MHz], is 0.4225[Tesla] or 4225[gauss]. So, by adjusting the main magnetic field (using the fine current control for precision) the resonance signal should appear on the oscilloscope. The value of .4225[Tesla] usually corresponds to an ammeter reading of 0.9[A].

If the resonant signal is present, we will now switch to the lock-in amplifier.

- 13 Turn off the 60[Hz] modulator.
- 14 Disconnect the oscillator output from the oscilloscope and connect it to the input of the lock-in.
- 15 Turn on the lock-in amplifier.

- 16 Turn on the lock-in 25[Hz] modulation amplifier (P). Set the amplitude to a medium setting.
- 17 Set the sensitivity (L) to 5[mV]. Set the gain (M) to 10X. Set the RC time constant (O) to .3[s].
- 18 Adjust the magnet current regulator's fine current control to achieve the maximum value on the lock-in output meter.
- 19 Adjust the phase controls (N) so that the lock-in output meter deviates from 0 as little as possible as you manually sweep B_0 through resonance (using the fine current control). For maximum amplification, adjust the phase 90° from this phase. For positive polarity the 90° change should be such that the end phase is closer to 320° than 140° .

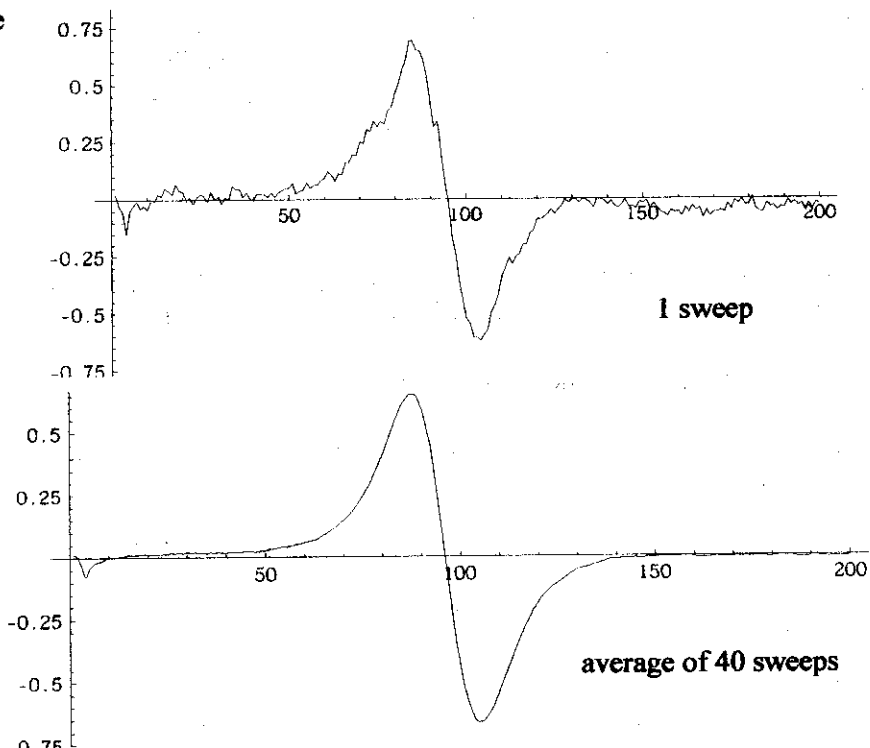
LabView Hardware & Software

- 20 The lock-in signal output should be going to the LabView input. The LabView output should be going to the sweep input (H).
- 21 Adjust the sweep attenuator (I) to 2.
- 22 Open the LabView NMR program.
 Use the following settings: number of sweeps \Rightarrow 2, sweep time \Rightarrow 20 [s], sweep voltage \Rightarrow 5[V]
 Run the program.

The NMR program will start at -5[V] and ramp to 5[V] then immediately start over at 5[V]. It will take 20[s] per sweep and do 2 sweeps. The top graph shows the output of the lock-in amplifier for each sweep. The bottom graph is an average of all of the iterations. The bottom graph's leftmost x-axis value corresponds to -5[V] and the rightmost to 5[V]. So, as the program does more sweeps, the bottom graph should look "cleaner" - less noisy. You can save this averaged data.

You should see something which resembles the derivative of a Lorentz curve. This curve is proportional to the derivative of the power absorption with respect to B_0 .

Here is an example of what you might see



Lock-In Amplification

This is an original analysis of Lock-In Amplification by Christian Malone

The lock-in amplifier is a device used to increase the signal-to-noise ratio by reducing the "1/f" noise factor. It is actually the combination of 2 devices. Device #1 inputs a sinusoidal signal into the experiment. Device #2 filters the output signal of the experiment at the same frequency. The experiment's output signal in the absence of the Lock-In Amplifier is then more accurately determined by reconstructing this signal from the output of Device #2.

Device #1 outputs a sinusoidal voltage (V_{STIM}) at frequency ω_{STIM} , which is used to cause small amplitude variations in a parameter of the experiment about the value of interest. The output signal of the experiment (V_{EXP}) will now contain a small varying signal near frequency ω_{STIM} . So, what was before a 0[Hz] "DC" output signal, now is the same "DC" signal but with a small amplitude variation near frequency ω_{STIM} . From this small varying signal, the original "DC" signal can be reconstructed - as will be shown. This method reduces the signal-to-noise ratio because the frequency domain of the experiment is shifted by ω_{STIM} , so that now the sinusoidal component of interest occurs at ω_{STIM} , rather than at 0. It is this shifting of the frequency of V_{EXP} 's sinusoidal component of interest to a *higher* value which improves the signal-to-noise ratio.

V_{EXP} 's ω_{STIM} component can now be filtered by Device #2 which is shown in Fig 5.

Let's examine the specific case in which

$$V_{EXP} \Rightarrow V_0 \cos[\Omega t + \theta]$$

so that the frequencies of V_{EXP} and V_{REF} (the square wave switching signal), are the same, where θ is the phase difference between the signals. So,

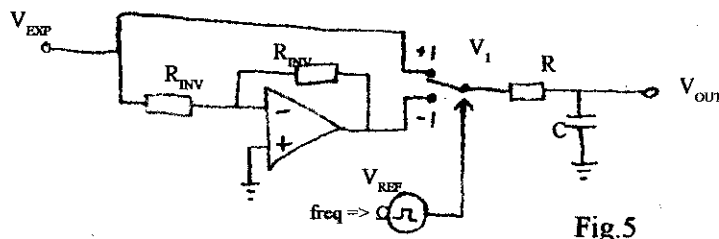


Fig.5

$$v_1[t] \rightarrow \begin{cases} \frac{2n}{\Omega} < t < \frac{(2n+1)\pi}{\Omega} & V_0 \cos[\Omega t + \theta] \\ \frac{(2n+1)\pi}{\Omega} < t < \frac{(2n+2)\pi}{\Omega} & -V_0 \cos[\Omega t + \theta] \end{cases}$$

After sampling and averaging many values of V_{OUT} , the value obtained is the average value of V_1 .

$$V_{1AVG} \rightarrow \frac{1}{\frac{2\pi}{\Omega}} \left(\int_0^{\frac{\pi}{\Omega}} V_0 \cos[\Omega t + \theta] dt + \int_{\frac{\pi}{\Omega}}^{\frac{2\pi}{\Omega}} -V_0 \cos[\Omega t + \theta] dt \right) \rightarrow -\frac{2V_0}{\pi} \sin[\theta]$$

For V_{EXP} frequencies other than Ω , such as $\Omega + \Delta\Omega$, the average values of V_1 during different $\frac{2\pi}{\Omega}$ intervals of time will be different. These average values will vary sinusoidally at frequency $\Delta\Omega$ and so will be attenuated by the low-pass RC filter stage. Sinusoidal components whose $\Delta\Omega \gg 1/RC$ will be heavily attenuated. Even without considering the attenuation, components other than those very near Ω ($\Delta\Omega \ll 1/RC$), will cause an oscillating V_{OUT} , and after sampling and averaging many values of V_{OUT} , the effects of these components will cancel out.

So, we see that $V_{OUTAVG} \rightarrow -\frac{2V_0}{\pi} \sin[\theta]$ where V_0 and θ refer to the sinusoidal component of V_{EXP} at frequency Ω .

Hence, this device effectively filters out the Ω -component of the input signal. Since we want the ω_{STIM} component, Ω and ω_{STIM} should be the same value (which will from now on be referred to as Ω) - in other words Ω should be set to ω_{STIM} .

There are some practical considerations for determining the value of Ω . The higher Ω , the better the signal-to-noise ratio. However, we don't want a Ω (or amplitude V_{STIM0}) so high that the amplitude of $\frac{\partial \text{PARAM}}{\partial t}$ is so high that transient effects occur in the experiment (thereby affecting V_{EXP}) which would otherwise, in the "DC" case, not occur. For this NMR experiment specifically, $\Omega \Rightarrow 25[\text{Hz}]$.

Signal Reconstruction

To represent the output value of an experiment as a function of its parameters we will use $f[C_1, C_2, \dots]$, where f represents the output value for a given combination of parameters $\{C_i\}$. Keep in mind that it is this f that we want to solve for, and we will want to solve for it in terms of the information output from the Lock-In, which is V_{OUTAVG} . If Ω and V_{STIM0} are small enough so that no transient effects occur, and if we call the stimulated parameter "B", then the output value of the experiment, which will vary over time, will be $f[C_1, C_2, \dots, B_0 + \beta \cos[\Omega t + \phi], C_n, \dots]$ where B_0 is the "DC" magnitude of parameter B, β is the modulation amplitude of B (which is related to V_{STIM0}), and ϕ is the phase of B relative to V_{REF} - which is not necessarily the same as the phase of f 's (V_{EXP} 's) Ω -component. For example, in the case of this experiment,

consider applying V_{STIM} across a resistor and inductor in series in order to vary the magnetic field, B , of the inductor. The phase of V_{STIM} , and the phase of the varied parameter, B , will be different.

We will abbreviate the notation of f and its dependence to $f[B_0 + \beta \cos[\Omega t + \phi]]$. Note that $f[B_0 + \beta \cos[\Omega t + \phi]]$ is called V_{EXP} in Fig.5. V_{OUTAVG} depends on the magnitude, V_0 , and phase, θ , of the Ω -component of $f[B_0 + \beta \cos[\Omega t + \phi]]$. So, as will be shown, $f[B_0]$ can be related to V_{OUTAVG} .

$$\text{Expanding } f \text{ in a trigonometric Fourier series, } f[B_0 + \beta \cos[\Omega t + \phi]] = \lim_{T \rightarrow \infty} \sum_{n=0}^{\infty} a_n \cos\left[\frac{n\pi}{T} t\right] + b_n \sin\left[\frac{n\pi}{T} t\right] \quad (1)$$

Because Device #2 filters through a voltage which is related only to the sinusoidal component of f at frequency Ω , we need to obtain this component, that is, we need to obtain the a_n & b_n corresponding to the frequency Ω . These values are termed $a_{n\Omega}$ & $b_{n\Omega}$, and occur at $n_{\Omega} \rightarrow \text{Round}\left[\frac{T\Omega}{\pi}\right]$

This sinusoidal component, $\lim_{T \rightarrow \infty} \left(a_{n\Omega} \cos\left[\frac{n_{\Omega}\pi}{T} t\right] + b_{n\Omega} \sin\left[\frac{n_{\Omega}\pi}{T} t\right] \right)$, can then be equated to $v_0 \cos[\Omega t + \theta]$ and the values V_0 & θ can be identified to $a_{n\Omega}$ & $b_{n\Omega}$.

$$V_0 \rightarrow \sqrt{a_{n\Omega}^2 + b_{n\Omega}^2}$$

$$\theta \rightarrow -\text{Atan}\left[\frac{b_{n\Omega}}{a_{n\Omega}}\right]$$

So that now, $V_{OUTAVG} \rightarrow -\frac{2}{\pi} V_0 \sin[\theta] \rightarrow \frac{2}{\pi} b_{n\Omega} \quad (2)$

$b_{n\Omega}$ can be solved for by,

$$\lim_{T \rightarrow \infty} \int_{-T}^T \sin\left[\frac{m\pi}{T} t\right] dt \left(f[B_0 + \beta \cos[\Omega t + \phi]] = \lim_{T \rightarrow \infty} \sum_{n=0}^{\infty} a_n \cos\left[\frac{n\pi}{T} t\right] + b_n \sin\left[\frac{n\pi}{T} t\right] \right)$$

$$b_n \rightarrow \begin{cases} n=0 & 0 \\ n>0 & \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T}^T f[B_0 + \beta \cos[\frac{n_{\Omega}\pi}{T} t + \phi]] \sin\left[\frac{n\pi}{T} t\right] dt \end{cases} \quad (\text{relabelling } m \text{ to } n)$$

In order to simplify the above expression for b_n , we expand $f[B_0 + \beta \cos[\frac{n_{\Omega}\pi}{T} t + \phi]]$ in a polynomial series about B_0 . After substituting $b_{n\Omega}$ into (2), we have,

Note that since (2) is valid for all B_0 , the B_0 dependence of V_{OUTAVG} can be included as in expression (3).

$$V_{OUTAVG}[B_0] = \lim_{T \rightarrow \infty} \frac{2}{\pi} \frac{1}{T} \int_{-T}^T \left(\sum_{j=0}^{\infty} \frac{1}{j!} f^{(j)}[B_0] (\beta \cos[\frac{n_{\Omega}\pi}{T} t + \phi])^j \right) \sin\left[\frac{n_{\Omega}\pi}{T} t\right] dt \quad (3)$$

$$V_{OUTAVG}[B_0] = \alpha \sum_{j=0}^{\infty} \left(\frac{1}{j!} \lim_{T \rightarrow \infty} \int_{-T}^T \cos\left[\frac{n_{\Omega}\pi}{T} t + \phi\right]^j \sin\left[\frac{n_{\Omega}\pi}{T} t\right] dt \right) \beta^j f^{(j)}[B_0] \quad (4)$$

From (3) to (4), the proportionality constant $\lim_{T \rightarrow \infty} \frac{2}{\pi} \frac{1}{T}$

$$V_{OUTAVG}[B_0] = \alpha \sum_{j=0}^{\infty} C_j \beta^j f^{(j)}[B_0] \quad (5)$$

$$\text{has been combined into } \alpha. \text{ Note that } V_{OUTAVG}[B_0] = -\alpha \sin[\phi] \sum_{j=0}^{\infty} C_j \beta^{2j+1} f^{(2j+1)}[B_0] \quad (6)$$

in spite of the limit, $\alpha \neq 0$. This is so, because it is not just 1 sinusoidal component at frequency Ω , infinitesimal in magnitude, which contributes to V_{OUTAVG} , but also (an infinite amount of) components near Ω , whose net effect is to cause a finite proportionality constant α . The a_n 's & b_n 's of these nearby components are almost the same, which is the reason that the finite constant α can be pulled outside the expression.

where,

$$C_j = \frac{1}{j!} \lim_{T \rightarrow \infty} \int_{-T}^T \cos\left[\frac{n_{\Omega}\pi}{T} t + \phi\right]^j \sin\left[\frac{n_{\Omega}\pi}{T} t\right] dt$$

$$C_j = -\frac{1}{\sin[\phi]} C_{2j+1}$$

some values of C_j and c_j are,

j	C_j	c_j
0	0	1
1	$-\sin[\phi]$	$\frac{1}{2^3}$
2	0	$\frac{1}{2^4 3}$
3	$-\frac{1}{8} \sin[\phi]$	$\frac{1}{2^{10} 3^2}$
4	0	$\frac{1}{2^{14} 3^2 5}$
5	$-\frac{1}{192} \sin[\phi]$	$\frac{1}{2^{17} 3^3 5^2}$
6	0	$\frac{1}{2^{20} 3^4 5^2 7}$
7	$-\frac{1}{9216} \sin[\phi]$	$\frac{1}{2^{25} 3^4 5^2 7^2}$

Since (6) is valid for all B_0 , it can be integrated and differentiated with respect to B_0 to yield useful relations. This is done, because we are solving for $f^{(0)}[B_0]$, which does not appear in (6), but appears in $\int (6) dB_0$. However this relation also involves $f^{(n)}[B_0]$ for $n > 0$, and so we need other relations involving the "variables" $f^{(n)}[B_0]$ ($n > 0$) in order to eliminate them. These relations are produced by differentiating (6). So, we have the following:

$$\begin{aligned}
 -\frac{1}{\alpha \sin[\phi]} v^{(-1)}[B_0] &= c_0 \beta f^{(0)}[B_0] + c_1 \beta^3 f^{(2)}[B_0] + c_2 \beta^5 f^{(4)}[B_0] + \dots & \text{where,} \\
 -\frac{1}{\alpha \sin[\phi]} v^{(0)}[B_0] &= c_0 \beta f^{(1)}[B_0] + c_1 \beta^3 f^{(3)}[B_0] + c_2 \beta^5 f^{(5)}[B_0] + \dots & v^{(-1)}[B_0] = \int_{-\infty}^{B_0} v[B_0'] dB_0' \\
 -\frac{1}{\alpha \sin[\phi]} v^{(1)}[B_0] &= c_0 \beta f^{(2)}[B_0] + c_1 \beta^3 f^{(4)}[B_0] + c_2 \beta^5 f^{(6)}[B_0] + \dots & (V_{\text{OUTAVG}} \text{ is abbreviated to } V) \\
 -\frac{1}{\alpha \sin[\phi]} v^{(2)}[B_0] &= c_0 \beta f^{(3)}[B_0] + c_1 \beta^3 f^{(5)}[B_0] + c_2 \beta^5 f^{(7)}[B_0] + \dots
 \end{aligned}$$

This can be written in matrix form as

$$\frac{1}{\alpha \sin[\phi]} \begin{pmatrix} v^{(-1)} \\ v^{(0)} \\ v^{(1)} \\ v^{(2)} \\ v^{(3)} \\ v^{(4)} \\ \vdots \end{pmatrix} = \begin{pmatrix} c_0 \beta & 0 & c_1 \beta^3 & 0 & c_2 \beta^5 & 0 & \dots \\ 0 & c_0 \beta & 0 & c_1 \beta^3 & 0 & c_2 \beta^5 & \dots \\ 0 & 0 & c_0 \beta & 0 & c_1 \beta^3 & 0 & \dots \\ 0 & 0 & 0 & c_0 \beta & 0 & c_1 \beta^3 & \dots \\ 0 & 0 & 0 & 0 & c_0 \beta & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & c_0 \beta & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} f^{(0)} \\ f^{(1)} \\ f^{(2)} \\ f^{(3)} \\ f^{(4)} \\ f^{(5)} \\ \vdots \end{pmatrix}$$

(the $[B_0]$ notation is dropped for convenience and to emphasize that for a fixed B_0 , the $f^{(n)}$ & $V^{(n)}$ can be thought of as variables and constants respectively)

This matrix relation can be solved for $f^{(0)}$.

$$f[B_0] \rightarrow -\frac{1}{\alpha \sin[\phi]} \sum_{n=0}^{\infty} d_n \beta^{2n-1} v^{(2n-1)}[B_0]$$

where the d_n can be given by the following recursion relation

$$\begin{aligned}
 d_0 &\rightarrow 1 \\
 d_n &\rightarrow -\sum_{i=1}^n c_i d_{n-i}
 \end{aligned}$$

$f[B_0]$ can also be written as

$$f[B_0] \rightarrow -\frac{1}{\alpha \sin[\phi]} \sum_{n=0}^{\infty} (-1)^n k_n c_n \beta^{2n-1} v^{(2n-1)}[B_0]$$

some values of d_n & k_n are

n	d_n	k_n
0	c_0	1
1	$-c_1$	1
2	c_2	1
3	$-7 c_3$	7
4	$13 c_4$	13
5	$-107 c_5$	107
6	$409 c_6$	409
7	$-56197 c_7$	56197

$f[B_0]$ can be approximated by

$$f[B_0] \rightarrow -\frac{1}{\alpha \sin[\phi]} \left(\frac{1}{\beta} \int_{-\infty}^{B_0} v[B_0'] dB_0' + \sum_{n=1}^{\infty} d_n \beta^{2n-1} v^{(2n-1)}[B_0] \right) \approx -\frac{1}{\alpha \beta \sin[\phi]} \int_{-\infty}^{B_0} v[B_0'] dB_0'$$

This approximation is valid when

$$\beta \ll \sqrt{\frac{1}{d_1} \frac{v^{(0)}[B_0]}{v^{(2)}[B_0]}}$$

PRACTICALITY CONSIDERATIONS

Since θ , and hence ϕ , is variable, one can maximize the signal strength of V_{OUTAVG} by doing the following. Vary θ until $V_{\text{OUTAVG}} \Rightarrow 0$. Here, you know that $\sin[\phi] \Rightarrow 0$, and hence $\phi \Rightarrow 0$. You should record this constant phase difference. Now for the max value of $\sin[\phi]$ (which is 1), increase θ , by 90° .

The above expressions for $f[B_0]$ involve an unknown scaling constant α . This constant not only lumps together the effect of nearby frequency components, but also the numerous electronic/mathematical amplification devices/processes that the signal goes through before its final destination (such as the graph in LabView). If it becomes necessary to know this constant, it will have to be calibrated for.