Some notes on ^{3}He and Water NMR

Jaideep Singh
University of Virginia
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Abstract

I will derive the NMR-AFP lineshape, specify the parameters that define the signal size, set up the equations to calculate the flux, and derive the water signal lineshape.

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1 Quantum Mechanical Treatment of AFP-NMR

1.1 Notation & Conventions

All quantities will be denoted in SI. Angular momentum operators will be unitless:

$$\hat{\vec{J}}^2 |J, m_J\rangle = J(J+1) |J, m_J\rangle \tag{1}$$
$$\hat{J}_z |J, m_J\rangle = m_J |J, m_J\rangle, m_J = -J..J \tag{2}$$
$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y \tag{3}$$
$$\hat{J}_\pm |J, m_J\rangle = \sqrt{J(J+1) - m_J(m_J \pm 1)} |J, m_J \pm 1\rangle \tag{4}$$

The statistical weight is denoted by $[J]$ and is defined by $[J] = 2J + 1$. The magnetic moment arising from spin will be written:

$$\vec{\mu}_S = \frac{\mu_S}{S}\vec{S} \tag{5}$$
$$\frac{\mu_S}{S} = g_S \mu_x \tag{6}$$

g is the unitless Landé factor. Note that the sign of the magnetic moment is carried implicitly in g or alternatively μ_J. For example, $g \approx -2$ for the electron, $g \approx 2(2.79)$ for the proton, and $g \approx 2(-1.91)$ for the neutron. Operators and matrices will be denoted by hats $\hat{M}$. Hamiltonians will be $\mathcal{H}$, energies will be E, frequencies will be ν (with units of Hz), and angular frequencies ω (with units of rad·Hz).

1.2 A Spin in a DC field

The hamiltonian of a spin half particle in a large DC field B is:

$$\mathcal{H}_0 = -\vec{\mu} \cdot \vec{B} \tag{7}$$
$$\vec{\mu} = g\mu_N \vec{S} = g\mu_N \frac{\vec{\sigma}}{2} \tag{8}$$
$$\vec{B} = (B_0 + \Delta B)\,\hat{z} \tag{9}$$

where we explicitly stipulate (without loss of generality) that $B_0 > 0$ and as usual $\vec{\sigma}$ are the Pauli matrices:

$$\sigma_x = \begin{bmatrix} 0 & +1 \\ +1 & 0 \end{bmatrix} \qquad \sigma_y = \begin{bmatrix} 0 & -i \\ +i & 0 \end{bmatrix} \qquad \sigma_z = \begin{bmatrix} +1 & 0 \\ 0 & -1 \end{bmatrix} \tag{10}$$

The eigenstates of $\hat{S}_z$ are also the eigenstates of $\hat{H}_0$:

$$\hat{H}_0 |\pm\rangle = -g\mu_N B \left(\frac{\pm 1}{2}\right) |\pm\rangle = \frac{\mp s\hbar}{2} (\omega_0 + \Delta) |\pm\rangle \tag{11}$$
$$\omega_0 = \frac{|g|\mu_N B_0}{\hbar} \tag{12}$$
$$\Delta = \frac{|g|\mu_N \Delta B}{\hbar} \tag{13}$$
$$s = \frac{g}{|g|} \tag{14}$$

Plugging these eigenstates, $|\pm\rangle$, into Schrodinger's equation:

$$i\hbar \frac{\partial |\pm\rangle}{\partial t} = \hat{H}_0 |\pm\rangle \tag{15}$$
$$\frac{\partial |\pm\rangle}{\partial t} = \frac{\pm is}{2} (\omega_0 + \Delta) |\pm\rangle \tag{16}$$
$$|\pm\rangle = \exp\left[\frac{\pm is}{2} (\omega_0 + \Delta)\, t\right] |\pm\rangle_0 \tag{17}$$

1.3 A Spin in a DC and RF Field

The hamiltonian of spin half particle in a DC field B and an AC field B_1 is:

$$\begin{aligned} \mathcal{H} &= -\vec{\mu}\cdot\vec{B}_{\mathrm{tot}} && (18)\\ \vec{B}_{\mathrm{tot}} &= (B_0+\Delta B)\,\hat{z} + 2B_1\cos(\omega_0 t)\,\hat{y} && (19) \end{aligned}$$

It is convienient to work in the interaction picture:

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0 + \mathcal{W}(t) && (20)\\ \hat{H}_0\left|n\right\rangle &= E_n\left|n\right\rangle = \hbar\omega_n\left|n\right\rangle && (21)\\ \left|\Psi\right\rangle &= \sum_n c_n(t)\exp(-i\omega_n t)\left|n\right\rangle && (22) \end{aligned}$$

where the time dependence of c_n is determined by the form of $\mathcal{W}$ only. Plugging $\left|\Psi\right\rangle$ into Schrodinger's equation and projecting both side with $\left|k\right\rangle$:

$$\begin{aligned} i\hbar\frac{\partial\left\langle k \mid \Psi\right\rangle}{\partial t} &= \left\langle k\right|\hat{H}\left|\Psi\right\rangle && (23)\\ i\hbar\sum_n\frac{\partial c_n(t)\exp(-i\omega_n t)}{\partial t}\left\langle k \mid n\right\rangle &= \sum_n c_n(t)\exp(-i\omega_n t)\left\langle k\right|\hat{H}_0+\hat{W}\left|n\right\rangle && (24)\\ i\hbar\left[\dot{c}_k - i\omega_k c_k\right]\exp(-i\omega_k t) &= \hbar\omega_k c_k(t)\exp(-i\omega_k t) + \sum_n c_n(t)\exp(-i\omega_n t)\left\langle k\right|\hat{W}\left|n\right\rangle && (25)\\ i\hbar\dot{c}_k\exp(-i\omega_k t) &= \sum_n c_n(t)\exp(-i\omega_n t)\left\langle k\right|\hat{W}\left|n\right\rangle && (26)\\ i\hbar\dot{c}_k &= \sum_n c_n(t)\exp(i\omega_{kn} t)\left\langle k\right|\hat{W}\left|n\right\rangle && (27) \end{aligned}$$

This equation is exact and results in two coupled differential equations:

$$\begin{aligned} i\hbar\dot{a} &= a(t)\left\langle +\right|\hat{W}\left|+\right\rangle + b(t)\exp(i\omega_{ab}t)\left\langle +\right|\hat{W}\left|-\right\rangle && (28)\\ i\hbar\dot{b} &= b(t)\left\langle -\right|\hat{W}\left|-\right\rangle + a(t)\exp(i\omega_{ba}t)\left\langle -\right|\hat{W}\left|+\right\rangle && (29) \end{aligned}$$

where the coefficients for the $\left|\pm\right\rangle$ state is labeled by $a(b)$. We will now evaluate the matrix element of $\mathcal{W}$ by first noting:

$$\begin{aligned} \omega_1 &= \frac{|g|\mu_N B_1}{\hbar} && (30)\\ \hat{S}_y &= \frac{\hat{S}_+ - \hat{S}_-}{2i} && (31)\\ \hat{W} &= -g\mu_N\hat{S}_y 2B_1\cos(\omega_0 t) = -is\hbar\omega_1\cos(\omega_0 t)\left(\hat{S}_- - \hat{S}_+\right) && (32) \end{aligned}$$

which gives:

$$\begin{aligned} \left\langle \pm\right|\hat{W}\left|\pm\right\rangle &= 0 && (33)\\ \left\langle \pm\right|\hat{W}\left|\mp\right\rangle &= -is\hbar\omega_1\cos(\omega_0 t)\left\langle \pm\right|\hat{S}_- - \hat{S}_+\left|\mp\right\rangle && (34)\\ &= \pm is\hbar\omega_1\cos(\omega_0 t)\left\langle \pm\right|\hat{S}_\pm\left|\mp\right\rangle && (35)\\ &= \pm is\hbar\omega_1\cos(\omega_0 t)\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right) - \frac{\mp 1}{2}\frac{\pm 1}{2}} && (36)\\ &= \pm is\hbar\omega_1\cos(\omega_0 t) && (37) \end{aligned}$$

Rearranging the following:

$$\begin{aligned} \cos(\omega_0 t) &= \frac{\exp(+i\omega_0 t)+\exp(-i\omega_0 t)}{2} && (38)\\ \omega_{ab} = -\omega_{ba} = &= -s(\omega_0+\Delta) && (39) \end{aligned}$$

allows us to write the coupled differential equations as:

$$\dot{a} = +\frac{sb\omega_1}{2}\left(1+\exp\left[-si2\omega_0 t\right]\right)\exp\left[-is\Delta\right] \quad (40)$$

$$\dot{b} = -\frac{sa\omega_1}{2}\left(1+\exp\left[+si2\omega_0 t\right]\right)\exp\left[+is\Delta\right] \quad (41)$$

1.4 Rotating Wave Approximation

At this point, we'll make the time honored rotating wave approximation and simply drop the term occurring at a frequency $2\omega_0$:

$$\dot{a} = +\frac{sb\omega_1}{2}\exp\left[-is\Delta\right] \quad (42)$$

$$\dot{b} = -\frac{sa\omega_1}{2}\exp\left[+is\Delta\right] \quad (43)$$

Note that this term *does* have a small effect:

1. The main resonance of interest is shifted to $\omega_0\left(1+\frac{\omega_1^2}{4\omega_0^2}+\cdots\right)$ [F. Bloch and A. Siegert, *Physical Review,* **57**, 522 (1940)]
2. There are, in general, resonances at frequencies $\omega = \frac{\omega_0}{2n+1}$ where $n \geq 0$. However all resonances for $n \neq 0$ are very weak under our conditions. [Abragam, A., *Principles of Nuclear Magnetism*, Oxford: OUP, II.A p22, 1961.]

1.5 Rabi Frequency

Solving for b and then differentiating wrt t gives:

$$b = \frac{2\dot{a}}{s\omega_1}\exp\left[+is\Delta\right] \quad (44)$$

$$\dot{b} = \frac{2}{s\omega_1}\exp\left[+is\Delta\right]\left(\ddot{a}+is\Delta\dot{a}\right) \quad (45)$$

Equating the two forms of $\dot{b}$, dividing out the exponential term, and rearranging a few things results in:

$$\ddot{a}+is\Delta\dot{a}+\frac{\omega_1^2}{4}a = 0 \quad (46)$$

This is solved straightforwardly using the substitution $a = e^{i\lambda t}$:

$$\lambda^2+s\Delta\lambda-\frac{\omega_1^2}{4} = 0 \quad (47)$$

$$\lambda = \frac{-s\Delta \pm \sqrt{\Delta^2+\omega_1^2}}{2} = \frac{-s\Delta \pm \Omega}{2} \quad (48)$$

where $\Omega = \sqrt{\Delta^2+\omega_1^2}$ is the venerable Rabi frequency [Rabi, I.I. *Phys. Rev.* **51**, 652654 (1937)]. Note that the rotation wave approximation is valid only for $\Omega \ll 2\omega_0$.

1.6 General Solution

The general solutions are:

$$a(t) = \exp\left[-is\frac{\Delta}{2}t\right]\left(a_1\exp\left[+i\frac{\Omega}{2}t\right]+a_2\exp\left[-i\frac{\Omega}{2}t\right]\right) \quad (49)$$

$$b(t) = \exp\left[+is\frac{\Delta}{2}t\right]\left(b_1\exp\left[+i\frac{\Omega}{2}t\right]+b_2\exp\left[-i\frac{\Omega}{2}t\right]\right) \quad (50)$$

where the constants a_1, a_2, b_1, b_2 are determined by boundary conditions and are constrained by unit normalization:

$$\langle \Psi \mid \Psi \rangle = |a_1|^2 + |a_2|^2 + 2\Re\left\{a_1^* a_2 \exp\left[-i\Omega t\right]\right\} + |b_1|^2 + |b_2|^2 + 2\Re\left\{b_1^* b_2 \exp\left[-i\Omega t\right]\right\} = 1 \tag{51}$$

and by the differential equations (42) & (43):

$$b_1 = +\frac{ia_1}{s\omega_1}\left(\Omega - s\Delta\right) \quad \leftrightarrow \quad a_1 = -\frac{ib_1}{s\omega_1}\left(\Omega + s\Delta\right) \tag{52}$$

$$b_2 = -\frac{ia_2}{s\omega_1}\left(\Omega + s\Delta\right) \quad \leftrightarrow \quad a_2 = +\frac{ib_2}{s\omega_1}\left(\Omega - s\Delta\right) \tag{53}$$

By first noting that:

$$b_1^* b_2 = -a_1^* a_2 \frac{\Omega^2 - \Delta^2}{\omega_1^2} = -a_1^* a_2 \tag{54}$$

$$|b_1|^2 = \frac{|a_1|^2}{\omega_1^2}\left(\Omega - s\Delta\right)^2 = |a_1|^2 \frac{\left(\Omega - s\Delta\right)^2}{\Omega^2 - \Delta^2} = |a_1|^2 \frac{\left(\Omega - s\Delta\right)\left(\Omega - s\Delta\right)}{\left(\Omega - s\Delta\right)\left(\Omega + s\Delta\right)} = |a_1|^2 \frac{\left[1 - s\frac{\Delta}{\Omega}\right]}{\left[1 + s\frac{\Delta}{\Omega}\right]} \tag{55}$$

$$|b_2|^2 = \frac{|a_2|^2}{\omega_1^2}\left(\Omega + s\Delta\right)^2 = |a_2|^2 \frac{\left[1 + s\frac{\Delta}{\Omega}\right]}{\left[1 - s\frac{\Delta}{\Omega}\right]} \tag{56}$$

the two constraints can be combined to give:

$$\frac{2|a_1|^2}{1 + s\frac{\Delta}{\Omega}} + \frac{2|a_2|^2}{1 - s\frac{\Delta}{\Omega}} = 1 = \frac{2|b_1|^2}{1 - s\frac{\Delta}{\Omega}} + \frac{2|b_2|^2}{1 + s\frac{\Delta}{\Omega}} \tag{57}$$

$$|a_2|^2 = \left(1 - s\frac{\Delta}{\Omega}\right)\left(\frac{1}{2} - \frac{|a_1|^2}{1 + s\frac{\Delta}{\Omega}}\right) \quad \leftrightarrow \quad |b_2|^2 = \left(1 + s\frac{\Delta}{\Omega}\right)\left(\frac{1}{2} - \frac{|b_1|^2}{1 - s\frac{\Delta}{\Omega}}\right) \tag{58}$$

$$|a_1|^2 = \left(1 + s\frac{\Delta}{\Omega}\right)\left(\frac{1}{2} - \frac{|a_2|^2}{1 - s\frac{\Delta}{\Omega}}\right) \quad \leftrightarrow \quad |b_1|^2 = \left(1 - s\frac{\Delta}{\Omega}\right)\left(\frac{1}{2} - \frac{|b_1|^2}{1 + s\frac{\Delta}{\Omega}}\right) \tag{59}$$

The phases of a_1 and a_2, thus far unspecified, are labeled ϕ_1 and ϕ_2. Finally we can write the general solution as:

$$|\Psi\rangle = A(t)\exp\left[-is\frac{\omega_0}{2}t\right]|+\rangle + B(t)\exp\left[+is\frac{\omega_0}{2}t\right]|-\rangle \tag{60}$$

$$A(t) = |a_1|\exp\left[+i\frac{\Omega}{2}t + i\phi_1\right] + |a_2|\exp\left[-i\frac{\Omega}{2}t + i\phi_2\right] \tag{61}$$

$$= |b_1|\sqrt{\frac{1 + s\frac{\Delta}{\Omega}}{1 - s\frac{\Delta}{\Omega}}}\exp\left[+i\frac{\Omega}{2}t + i\phi_1\right] + |b_2|\sqrt{\frac{1 - s\frac{\Delta}{\Omega}}{1 + s\frac{\Delta}{\Omega}}}\exp\left[-i\frac{\Omega}{2}t + i\phi_2\right] \tag{62}$$

$$B(t) = i|a_1|\sqrt{\frac{1 - s\frac{\Delta}{\Omega}}{1 + s\frac{\Delta}{\Omega}}}\exp\left[+i\frac{\Omega}{2}t + i\phi_1\right] - i|a_2|\sqrt{\frac{1 + s\frac{\Delta}{\Omega}}{1 - s\frac{\Delta}{\Omega}}}\exp\left[-i\frac{\Omega}{2}t + i\phi_2\right] \tag{63}$$

$$= i|b_1|\exp\left[+i\frac{\Omega}{2}t + i\phi_1\right] - i|b_2|\exp\left[-i\frac{\Omega}{2}t + i\phi_2\right] \tag{64}$$

1.7 Expectation Value of the Spin Vector

Experimentally, we can measure the expectation value of the three components of $\vec{\mu}$:

$$\langle \vec{\mu} \rangle = \langle \Psi \mid \vec{\mu} \mid \Psi \rangle = \frac{g\mu_N}{\hbar}\left[\left\langle \hat{S}_x \right\rangle \hat{x} + \left\langle \hat{S}_y \right\rangle \hat{y} + \left\langle \hat{S}_z \right\rangle \hat{z}\right] \tag{65}$$

where we'll make frequent use of:

$$\hat{S}_x = \frac{\hat{S}_+ + \hat{S}_-}{2} \quad \& \quad \hat{S}_y = \frac{\hat{S}_+ - \hat{S}_-}{2i} \tag{66}$$

$$\left\langle \pm \mid \hat{S}_z \mid \pm \right\rangle = \pm\frac{1}{2} \quad \& \quad \left\langle \mp \mid \hat{S}_z \mid \pm \right\rangle = 0 \tag{67}$$

$$\left\langle \pm \mid \hat{S}_\pm \mid \pm \right\rangle = 0 \quad \& \quad \left\langle \pm \mid \hat{S}_\mp \mid \pm \right\rangle = 0 \tag{68}$$

$$\left\langle \mp \mid \hat{S}_\mp \mid \pm \right\rangle = +1 \quad \& \quad \left\langle \mp \mid \hat{S}_\pm \mid \pm \right\rangle = 0 \tag{69}$$

This gives for each component:

$$\left\langle \hat{S}_x \right\rangle = \Re\left\{A^* B \exp\left[+is\omega_0 t\right]\right\} \tag{70}$$

$$\left\langle \hat{S}_y \right\rangle = \Im\left\{A^* B \exp\left[+is\omega_0 t\right]\right\} \tag{71}$$

$$\left\langle \hat{S}_z \right\rangle = \frac{|A|^2 - |B|^2}{2} \tag{72}$$

where we calculate each part as:

$$|A|^2 = |a_1|^2 + |a_2|^2 + 2\Re\{a_1^* a_2\} = |a_1|^2 + |a_2|^2 + 2|a_1||a_2|\cos\left(\Omega t + \phi\right) \tag{73}$$

$$|B|^2 = |b_1|^2 + |b_2|^2 + 2\Re\{b_1^* b_2\} = |b_1|^2 + |b_2|^2 - 2|b_1||b_2|\cos\left(\Omega t + \phi\right) \tag{74}$$

$$\begin{aligned} A^* B &= \left(|a_1| \exp\left[-i\frac{\Omega}{2}t - i\phi_1\right] + |a_2| \exp\left[+i\frac{\Omega}{2}t - i\phi_2\right]\right) \\ &\quad \times i\left(|b_1| \exp\left[+i\frac{\Omega}{2}t + i\phi_1\right] - |b_2| \exp\left[-i\frac{\Omega}{2}t + i\phi_2\right]\right) \qquad (75) \\ &= \exp\left[+i\frac{\pi}{2}\right]\left(|a_1||b_1| - |a_2||b_2| - |a_1||b_2|\exp\left[-i\Omega t - i\phi\right] + |a_2||b_1|\exp\left[+i\Omega t + i\phi\right]\right) \qquad (76) \end{aligned}$$

where we have replaced ϕ_1 and ϕ_2 with their relative difference $\phi \equiv \phi_1 - \phi_2$. Putting this altogether gives for each component of the spin vector, in general:

$$\left\langle \hat{S}_x \right\rangle = -\left(|a_1||b_1| - |a_2||b_2|\right)\sin\left(s\omega_0 t\right) + |a_1||b_2|\sin\left(s\omega_0 t - \Omega t - \phi\right) - |a_2||b_1|\sin\left(s\omega_0 t + \Omega t + \phi\right) \tag{77}$$

$$\left\langle \hat{S}_y \right\rangle = +\left(|a_1||b_1| - |a_2||b_2|\right)\cos\left(s\omega_0 t\right) - |a_1||b_2|\cos\left(s\omega_0 t - \Omega t - \phi\right) + |a_2||b_1|\cos\left(s\omega_0 t + \Omega t + \phi\right) \tag{78}$$

$$\left\langle \hat{S}_z \right\rangle = \frac{|a_1|^2 + |a_2|^2 - |b_1|^2 - |b_2|^2}{2} + \left(|a_1||a_2| + |b_1||b_2|\right)\cos\left(\Omega t + \phi\right) \tag{79}$$

It is interesting to note that, in general, the system responds at four different frequencies: $\omega_0, \Omega, \omega_0 \pm \Omega$.

1.8 Specific Solution

Now we'll define our boundary conditions based on requirements that $|\Delta| \gg \omega_1$ and the system is approximately in one of two eigenstates: $|\Psi\rangle \approx |\pm\rangle$. The four separate initial conditions that are of interest to us are listed in table (1).

For the case $a_2 = b_2 = 0$:

$$\left\langle \hat{S}_x \right\rangle = -|a_1||b_1|\sin\left(s\omega_0 t\right) = -\frac{1}{2}\sqrt{1 - \frac{\Delta^2}{\Omega^2}}\sin\left(s\omega_0 t\right) = -\frac{s}{2}\frac{\omega_1}{\Omega}\sin\left(\omega_0 t\right) \tag{80}$$

$$\left\langle \hat{S}_y \right\rangle = +|a_1||b_1|\cos\left(s\omega_0 t\right) = +\frac{1}{2}\frac{\omega_1}{\Omega}\cos\left(\omega_0 t\right) \tag{81}$$

$$\left\langle \hat{S}_z \right\rangle = \frac{|a_1|^2 - |b_1|^2}{2} = +\frac{s}{2}\frac{\Delta}{\Omega} \tag{82}$$

$s\Delta$	$\|\Psi\rangle$	$\|a_1\|^2$	$\|a_2\|^2$	$\|b_1\|^2$	$\|b_2\|^2$
$+$	$\|+\rangle$	$\frac{1}{2}\left(1+s\frac{\Delta}{\Omega}\right)$	0	$\frac{1}{2}\left(1-s\frac{\Delta}{\Omega}\right)$	0
$+$	$\|-\rangle$	0	$\frac{1}{2}\left(1-s\frac{\Delta}{\Omega}\right)$	0	$\frac{1}{2}\left(1+s\frac{\Delta}{\Omega}\right)$
$-$	$\|+\rangle$	0	$\frac{1}{2}\left(1-s\frac{\Delta}{\Omega}\right)$	0	$\frac{1}{2}\left(1+s\frac{\Delta}{\Omega}\right)$
$-$	$\|-\rangle$	$\frac{1}{2}\left(1+s\frac{\Delta}{\Omega}\right)$	0	$\frac{1}{2}\left(1-s\frac{\Delta}{\Omega}\right)$	0

Table 1: Values for coefficients of a_1, a_2, b_1, b_2 depending on sign of $s\Delta$ and the approximate state of the system when $|\Delta| \gg \omega_1$

For the case $a_1 = b_1 = 0$:

$$\left\langle \hat{S}_x \right\rangle = +|a_2||b_2|\sin(s\omega_0 t) = +\frac{s}{2}\frac{\omega_1}{\Omega}\sin(\omega_0 t) \quad (83)$$

$$\left\langle \hat{S}_y \right\rangle = -|a_2||b_2|\cos(s\omega_0 t) = -\frac{1}{2}\frac{\omega_1}{\Omega}\cos(\omega_0 t) \quad (84)$$

$$\left\langle \hat{S}_z \right\rangle = \frac{|a_2|^2 - |b_2|^2}{2} = -\frac{s}{2}\frac{\Delta}{\Omega} \quad (85)$$

1.9 Adiabatic Sweep Through Resonance

Finally we'll allow ourselves the freedom to vary Δ linearly in time at a very "slow" rate $\dot{\omega}$. The rate of change is considered "slow" if the fractional change in Ω over one period of Ω is very small:

$$\delta \equiv (\text{fractional change in } \Omega) \times (\text{one period of } \Omega) = \left(\frac{1}{\Omega}\frac{\partial\Omega}{\partial t}\right)\left(\frac{2\pi}{\Omega}\right) \ll 1 \quad (86)$$

This condition is most severly tested for the maximum value of δ:

$$\frac{\partial\delta}{\partial t} = 0 \quad \rightarrow \quad t_{\max} = \frac{\omega_1}{\dot{\omega}\sqrt{2}} \quad (87)$$

$$\delta_{\max}(t_{\max}) = \frac{4\pi}{\sqrt{27}}\frac{\dot{\omega}}{\omega_1^2} \ll 1 \quad \rightarrow \quad \frac{\dot{H}}{H_1^2} \ll \frac{|g|\mu_N\sqrt{27}}{4\pi\hbar} \approx 2|g|\ \frac{\text{Hz}}{\text{milligauss}} \quad (88)$$

This is called the adiabatic condition and under our exprerimental conditions $\dot{H} \approx 1200\ \frac{\text{milligauss}}{\text{sec}}$ and $H_1 \approx 65$ milligauss for ^{3}He, it is well statisfied ($0.03 \ll 1.00$).

The case $s\Delta = 0$ corresponds to resonance.

The case $s\Delta > 0$ corresponds to:

1. $s > 0$, $\dot{\omega} > 0$, $t > 0$: positive magnetic moment, ramp up, receding from resonance
2. $s > 0$, $\dot{\omega} < 0$, $t < 0$: positive magnetic moment, ramp down, approaching resonance
3. $s < 0$, $\dot{\omega} < 0$, $t > 0$: negative magnetic moment, ramp down, receding from resonance
4. $s < 0$, $\dot{\omega} > 0$, $t < 0$: negative magnetic moment, ramp up, approaching resonance

The case $s\Delta < 0$ corresponds to:

1. $s > 0$, $\dot{\omega} < 0$, $t > 0$: positive magnetic moment, ramp down, receding from resonance
2. $s > 0$, $\dot{\omega} > 0$, $t < 0$: positive magnetic moment, ramp up, approaching resonance
3. $s < 0$, $\dot{\omega} > 0$, $t > 0$: negative magnetic moment, ramp up, receding from resonance
4. $s < 0$, $\dot{\omega} < 0$, $t < 0$: negative magnetic moment, ramp down, approaching resonance

1.10 Density Matrix Approach

It is often useful to use the density matrix to describe a large ensemble of systems. The density operator is given by a statistical mixture (labeled by α) of many different quantum states $|\Psi_\alpha\rangle$ in the $\{n\}$ basis:

$$\hat{\rho} = \sum_\alpha p_\alpha |\Psi_\alpha\rangle \langle\Psi_\alpha| = \sum_\alpha p_\alpha \sum_n c_n^\alpha |n\rangle \sum_m c_m^{\alpha\,*} \langle m| = \sum_{\alpha,n,m} p_\alpha c_n^\alpha c_m^{\alpha\,*} |n\rangle \langle m| = \sum_{n,m} \rho_{nm} |n\rangle \langle m| \tag{89}$$

The time evolution of the density operator is derived taking advantage of the Schrodinger Equation:

$$\begin{aligned}
\frac{d\hat{\rho}}{dt} &= \sum_\alpha p_\alpha \left(\frac{d|\Psi_\alpha\rangle}{dt}\right) \langle\Psi_\alpha| + \sum_\alpha p_\alpha |\Psi_\alpha\rangle \left(\frac{d\langle\Psi_\alpha|}{dt}\right) &(90)\\
&= \sum_\alpha p_\alpha \left(\frac{\hat{H}|\Psi_\alpha\rangle}{i\hbar}\right) \langle\Psi_\alpha| + \sum_\alpha p_\alpha |\Psi_\alpha\rangle \left(\frac{\langle\Psi_\alpha|\hat{H}}{-i\hbar}\right) &(91)\\
&= \frac{\hat{H}}{i\hbar}\left(\sum_\alpha p_\alpha |\Psi_\alpha\rangle\langle\Psi_\alpha|\right) - \left(\sum_\alpha p_\alpha |\Psi_\alpha\rangle\langle\Psi_\alpha|\right)\frac{\hat{H}}{i\hbar} &(92)\\
&= \frac{\hat{H}\hat{\rho} - \hat{\rho}\hat{H}}{i\hbar} = \frac{\left[\hat{H}, \rho\right]}{i\hbar} &(93)
\end{aligned}$$

and is called the Liouville Equation. It is convienient to work in the interaction picture:

$$\begin{aligned}
\mathcal{H} &= \mathcal{H}_0 + \mathcal{W}(t) &(94)\\
\hat{H}_0 |n\rangle &= E_n |n\rangle = \hbar\omega_n |n\rangle &(95)\\
|\Psi_\alpha\rangle &= \sum_n c_n^\alpha(t) \exp(-i\omega_n t) |n\rangle &(96)
\end{aligned}$$

where the time dependence of $c_n^\alpha(t)$ is determined by the form of $\mathcal{W}$ only. The density operator in this picture is:

$$\hat{\rho} = \sum_{\alpha,n,m} p_\alpha c_n(t) c_m^*(t) \exp(-i\omega_{nm} t) |n\rangle\langle m| = \sum_{n,m} \rho_{nm} \exp(-i\omega_{nm} t) |n\rangle\langle m| \tag{97}$$

Inserting this form of the density operator into the Liouville equation gives:

$$\begin{aligned}
i\hbar\frac{d\hat{\rho}}{dt} &= \sum_{nm} i\hbar\left(\dot{\rho}_{nm} - i\omega_{nm}\rho_{nm}\right)\exp(-i\omega_{nm}t)|n\rangle\langle m| &(98)\\
&= \left[\hat{H}, \hat{\rho}\right] = \left[\hat{H}_0, \hat{\rho}\right] + \left[\hat{W}, \hat{\rho}\right] &(99)\\
&= \sum_n H_{0n} |n\rangle\langle n| \sum_{j,m} \rho_{jm} \exp(-i\omega_{jm}t)|j\rangle\langle m| \\
&\quad - \sum_{n,k} \rho_{nk}\exp(-i\omega_{nk}t)|n\rangle\langle k| \sum_m H_{0m}|m\rangle\langle m| \\
&\quad + \sum_{n,k} W_{nk}|n\rangle\langle k| \sum_{j,m}\rho_{jm}\exp(-i\omega_{jm}t)|j\rangle\langle m| \\
&\quad - \sum_{n,k}\rho_{nk}\exp(-i\omega_{nk}t)|n\rangle\langle k| \sum_{j,m} W_{jm}|j\rangle\langle m| &(100)\\
&= \sum_{n,m}\hbar\omega_n\rho_{nm}\exp(-i\omega_{nm}t)|n\rangle\langle m| - \sum_{n,m}\hbar\omega_m\rho_{nm}\exp(-i\omega_{nm}t)|n\rangle\langle m| \\
&\quad + \sum_{n,j,m} W_{nj}\rho_{jm}\exp(-i\omega_{jm}t)|n\rangle\langle m| - \sum_{n,j,m}\rho_{nj}W_{jm}\exp(-i\omega_{nj}t)|n\rangle\langle m| &(101)\\
&= \sum_{n,m}\hbar\omega_{nm}\rho_{nm}\exp(-i\omega_{nm}t)|n\rangle\langle m|
\end{aligned}$$

$$+\sum_{n,j,m}\left[W_{nj}\rho_{jm}\exp\left(-i\omega_{jm}t\right)-\rho_{nj}W_{jm}\exp\left(-i\omega_{nj}t\right)\right]|n\rangle\langle m| \quad (102)$$

$$i\hbar\dot{\rho}_{nm} = \sum_{j}\left[W_{nj}\rho_{jm}\exp\left(+i\omega_{nj}t\right)-\rho_{nj}W_{jm}\exp\left(+i\omega_{jm}t\right)\right] \quad (103)$$

For a two level system labeled by a, b for which $W_{nn} = 0$:

$$i\hbar\dot{\rho}_{aa} = W_{ab}\rho_{ba}\exp\left(+i\omega_{ab}t\right)-\rho_{ab}W_{ba}\exp\left(+i\omega_{ba}t\right) = +2i\Im\left\{\rho_{ba}W_{ab}\exp\left(+i\omega_{ab}t\right)\right\} \quad (104)$$

$$i\hbar\dot{\rho}_{bb} = W_{ba}\rho_{ab}\exp\left(+i\omega_{ba}t\right)-\rho_{ba}W_{ab}\exp\left(+i\omega_{ab}t\right) = -2i\Im\left\{\rho_{ba}W_{ab}\exp\left(+i\omega_{ab}t\right)\right\} \quad (105)$$

$$i\hbar\dot{\rho}_{ab} = \left[\rho_{bb}-\rho_{aa}\right]W_{ab}\exp\left(+i\omega_{ab}t\right) \quad (106)$$

$$i\hbar\dot{\rho}_{ba} = \left[\rho_{aa}-\rho_{bb}\right]W_{ba}\exp\left(+i\omega_{ba}t\right) \quad (107)$$

Specializing to our case and making the rotating wave approximation:

$$W_{ab} = \langle +|\,\hat{W}\,|-\rangle = is\hbar\omega_1\cos\left(\omega_0 t\right) \quad (108)$$

$$\omega_{ab} = -s\left(\omega_0+\Delta\right) \quad (109)$$

$$W_{ab}\exp\left(+i\omega_{ab}t\right) = \frac{si\hbar\omega_1}{2}\left[1+\exp\left(-si2\omega_0 t\right)\right]\exp\left(-si\Delta t\right) \quad (110)$$

$$\approx \frac{si\hbar\omega_1}{2}\exp\left(-si\Delta t\right) \quad (111)$$

gives the following:

$$\dot{\rho}_{aa} = \rho_{ba}\frac{s\omega_1}{2}\exp\left(-si\Delta t\right)+\rho_{ab}\frac{s\omega_1}{2}\exp\left(+si\Delta t\right) \quad (112)$$

$$\dot{\rho}_{bb} = -\rho_{ba}\frac{s\omega_1}{2}\exp\left(-si\Delta t\right)-\rho_{ab}\frac{s\omega_1}{2}\exp\left(+si\Delta t\right) \quad (113)$$

$$\dot{\rho}_{ab} = \left[\rho_{bb}-\rho_{aa}\right]\frac{s\omega_1}{2}\exp\left(-si\Delta t\right) \quad (114)$$

$$\dot{\rho}_{ba} = \left[\rho_{bb}-\rho_{aa}\right]\frac{s\omega_1}{2}\exp\left(+si\Delta t\right) \quad (115)$$

Defining three new quantites:

$$\rho_{ab} = (u+iv)\exp\left(-si\Delta t\right) \qquad w = \rho_{aa}-\rho_{bb} \quad (116)$$

and rewriting the four coupled differential equations as:

$$\dot{\rho}_{aa}+\dot{\rho}_{bb} = 0 \quad \rightarrow \quad \rho_{aa}+\rho_{bb} = \text{constant} \quad (117)$$

$$\dot{w} = s2\omega_1 u \quad (118)$$

$$\dot{u}+i\dot{v}-si\Delta u+s\Delta v = -\frac{s\omega_1}{2}w \quad (119)$$

$$\dot{u}-i\dot{v}+si\Delta u+s\Delta v = -\frac{s\omega_1}{2}w \quad (120)$$

Addiing and subtracting the last two equations gives:

$$2\dot{u}+2s\Delta v = s\omega_1 w \quad (121)$$

$$\dot{v}-s\Delta u = 0 \quad (122)$$

Combining all these equations we get:

$$\frac{\dot{w}}{s2\omega_1} = u \quad (123)$$

$$\frac{d^3w}{dt^3}+\left(\Delta^2+\omega_1^2\right)\dot{w} = 0 \quad (124)$$

$$\dot{v} = s\Delta u \quad (125)$$

Noting that w, u, v must all be real and $\Omega^2 = \Delta^2 + \omega^2$ yields the following general solutions:

$$w = c_0 + c_1 \cos(\Omega t) + c_2 \sin(\Omega t) \quad (126)$$

$$u = \frac{\Omega}{s 2\omega_1} \left[-c_1 \sin(\Omega t) + c_2 \cos(\Omega t) \right] \quad (127)$$

$$v = \frac{\Delta}{2\omega_1} \left[+c_1 \cos(\Omega t) + c_2 \sin(\Omega t) \right] + c_3 \quad (128)$$

where $c_0,\ c_1,\ c_2,\ \&\ c_3$ are chosen to suit a specific scenario. Connecting these results with our general solution for a single spin, equations (60) to (64), and requiring unit normalization $\mathrm{Tr}\{\hat{\rho}\} = 1$:

$$\rho_{aa} = \frac{1+w}{2} = \sum_k p_k \left| A_k \right|^2 \quad (129)$$

$$\rho_{bb} = \frac{1-w}{2} = \sum_k p_k \left| B_k \right|^2 \quad (130)$$

$$\rho_{ab} = (u + iv) \exp\left(-si\Delta t\right) = \sum_k p_k A_k B_k^* \quad (131)$$

$$\rho_{ba} = (u - iv) \exp\left(+si\Delta t\right) = \sum_k p_k A_k^* B_k \quad (132)$$

2 The Signal

2.1 Faraday's Law of Induction

The signal induced in the pick up coils by the flipping spins is given by:

$$\mathcal{E} = -\frac{d\Phi}{dt} = -\frac{d}{dt} \int \vec{B}(\vec{r}, t) \cdot d\vec{a} \quad (133)$$

where $\vec{B}$ is the field produced by the collection of spins at an infinitesismal element of area $d\vec{a}$ on the surface of the pick-up coil. Representing the field produced by the spins as the vector potential $\vec{A}(\vec{r}, t)$ and applying Stoke's Theorem, the flux integral over the area of the coils can be reduced to an integral around the path of the coils:

$$\Phi(t) = \int \vec{B}(\vec{r}, t) \cdot d\vec{a} = \int \left(\nabla \times \vec{A}(\vec{r}, t) \right) \cdot d\vec{a} = \oint \vec{A}(\vec{r}, t) \cdot d\vec{l} \quad (134)$$

The magnetic vector potential is defined as a volume integral over a region of magnetization $\vec{M}(\vec{u}, t)$:

$$\vec{A}(\vec{r}, t) = \frac{\mu_0}{4\pi} \int \frac{\vec{M}(\vec{u}, t) \times (\vec{r} - \vec{u})}{\left| \vec{r} - \vec{u} \right|^3} d^3u \quad (135)$$

Combining all this gives:

$$\mathcal{E} = -\frac{\mu_0}{4\pi} \int \oint \frac{\frac{d\vec{M}(\vec{u},t)}{dt} \times (\vec{r} - \vec{u})}{\left| \vec{r} - \vec{u} \right|^3} \cdot d\vec{l}\, d^3u \quad (136)$$

where $\vec{u}$ is the vector from the origin to the infinitesimal volume element d^3u and $\vec{r}$ is the vector from the origin to the infinitesimal line element $d\vec{l}$.

2.2 Magnetization

The magnetization is defined as the magnetic dipole moment per unit volume:

$$\vec{M}(\vec{u}, t) = \vec{\mu}(\vec{u}, t) \rho(\vec{u}, t) \quad (137)$$

where $\vec{\mu}$ is the magnetic dipole moment of the particle and ρ is the number density. We'll replace the classical magnetic dipole moment with it's quantum mechanical expectation value:

$$\langle\vec{\mu}(\vec{u},t)\rangle = g\mu_N P(\vec{u},t)\left[-\frac{s}{2}\frac{\omega_1}{\Omega}\sin(\omega_0 t)\,\hat{x} + \frac{1}{2}\frac{\omega_1}{\Omega}\cos(\omega_0 t)\,\hat{y} + \frac{s}{2}\frac{\Delta}{\Omega}\hat{z}\right] \tag{138}$$

If the measurement occurs on a timescale much faster than the timescale on which the polarization and density evolve (or if the polarization and density are at equilibrium), then the time dependence of both can be dropped. A possible polarization and/or density gradient will be contained in $f(\vec{u})$:

$$P(\vec{u})\rho(\vec{u}) = \langle P\rho\rangle\, f(\vec{u}) \tag{139}$$

$$\int f(\vec{u})\,\frac{d^3u}{V} = 1 \tag{140}$$

where $\langle P\rho\rangle$ is the volume averaged polarization density product. The quantity of interest is the time derivative of the magnetization:

$$\frac{d\vec{M}}{dt} = \frac{g\mu_N\langle P\rho\rangle f(\vec{u})}{2}\frac{d}{dt}\left[-s\frac{\omega_1}{\Omega}\sin(\omega_0 t)\,\hat{x} + \frac{\omega_1}{\Omega}\cos(\omega_0 t)\,\hat{y} + s\frac{\Delta}{\Omega}\hat{z}\right] \tag{141}$$

$$\frac{d}{dt}\left[\frac{\omega_1}{\Omega}\sin(\omega_0 t)\right] = +\frac{\omega_1\omega_0}{\Omega}\cos(\omega_0 t) - \frac{\omega_1\dot{\Omega}}{\Omega^2}\sin(\omega_0 t) \tag{142}$$

$$\frac{d}{dt}\left[\frac{\omega_1}{\Omega}\cos(\omega_0 t)\right] = -\frac{\omega_1\omega_0}{\Omega}\sin(\omega_0 t) - \frac{\omega_1\dot{\Omega}}{\Omega^2}\cos(\omega_0 t) \tag{143}$$

$$\frac{d}{dt}\left[\frac{\Delta}{\Omega}\right] = \frac{\Omega\dot{\Delta} - \Delta\dot{\Omega}}{\Omega^2} \tag{144}$$

$$\frac{d\vec{M}}{dt} = \frac{g\mu_N\langle P\rho\rangle f(\vec{u})\omega_0}{2}\left(\frac{\omega_1}{\Omega}\right)\left[-s\cos(\omega_0 t)\,\hat{x} - \sin(\omega_0 t)\,\hat{y} + \frac{\dot{\Omega}}{\omega_0\Omega}\vec{m}\right] \tag{145}$$

where we've isolated the relatively small terms and hidden them in $\vec{m}$ by using $\dot{\Omega} = \Delta\dot{\Delta}/\Omega$:

$$\vec{m} = +s\sin(\omega_0 t)\,\hat{x} - \cos(\omega_0 t)\,\hat{y} + s\frac{\omega_1}{\Delta}\hat{z} \tag{146}$$

There are two important things to note here:

1. The $\hat{z}$ term in $\vec{m}$ does not blow up at resonance ($\Delta = 0$) because the Δ in the term in front of $\vec{m}$ cancels with the Δ in the denominator.

2. The term in front of $\vec{m}$ is extremely small if the both adiabatic condition is satified and the rotating wave approximation is valid:

$$\frac{\dot{\Omega}}{\Omega} \ll \frac{\Omega}{2\pi} \ll \frac{\omega_0}{\pi} < \omega_0 \tag{147}$$

   Under our exprerimental conditions $\dot{H} \approx 1200\ \frac{\text{milligauss}}{\text{sec}}$, $H_1 \approx 65$ milligauss, and $H_0 \approx 28$ gauss for ^{3}He, these terms are quite small $\left(3\times 10^{-5} \ll 1\right)$.

Dropping the aforementioned small terms, we can the write the EMF as:

$$\mathcal{E} = \frac{g\mu_N\mu_0\langle P\rho\rangle\,\omega_0}{8\pi}\left(\frac{\omega_1}{\Omega}\right)\left[s\Phi_x\cos(\omega_0 t) + \Phi_y\sin(\omega_0 t)\right] \tag{148}$$

where $\Phi_{x,y}$ is called the flux factor.

2.3 Pick-up Coil Detection Circuit

make diagram ###### The EMF induced in the pick up coils is then transmitted through a BNC terminated coaxial cable to a preamplifier. After filtering and amplification, the signal is transmitted through a BNC terminate coaxial cable to the lockin. Both the pick-up coil/BNC circuit and the BNC cable can be modeled as three circuit elements in parallel [Leo, W.R. **Techniques for Nuclear and Particle Physics Experiments.** Springer: Berlin, p266 (1994)]. The main circuit element is a voltage source ($V_{\rm in}$), a resistor (R_s), and an inductor (L) in a series configuration. In addition to this circuit element are a parallel capacitor (C)and a parallel resistor (R_p). The output voltage is measured across any one of these parallel circuit elements and using the complex representation in the frequency domain is [Purcell, E.M. **Electricity and Magnetism** McGraw-Hill: New York, p297-322 (1985)]:

$$V_{\rm out} = V_{\rm in} + (i\omega L + R_s)(I_1) = \left(-\frac{i}{\omega C}\right)(-I_2) = R_p(-I_3) \tag{149}$$

Applying Kirchhoff's junction rule, we find that $I_1 = I_2 + I_3$ and therefore:

$$\frac{V_{\rm in}}{V_{\rm out}} = 1 + \left[i\omega C + \frac{1}{R_p}\right][i\omega L + R_s] \tag{150}$$

Calculating the modulus of this ratio gives:

$$Q(\omega) = \left|\frac{V_{\rm out}}{V_{\rm in}}\right| = \left[\left(1 + \frac{Q_p}{Q_s} - \frac{\omega^2}{\omega_0^2}\right)^2 + \left(Q_p + \frac{1}{Q_s}\right)^2 \frac{\omega^2}{\omega_0^2}\right]^{-\frac{1}{2}} \tag{151}$$

$$\tag{152}$$

where:

$$\omega_0 = \frac{1}{\sqrt{LC}} \qquad Q_s = \frac{\omega_0 L}{R_s} \qquad Q_p = \frac{\omega_0 L}{R_p} \tag{153}$$

Putting all this together, the signal voltage transmitted into the lock-in is:

$$V = Q_{\rm C2P}(\omega)G_{\rm P}(\omega)Q_{\rm P2L}(\omega)\left[\frac{g\mu_N\mu_0\langle P\rho\rangle\omega_0}{8\pi}\right][s\Phi_x\cos(\omega_0 t) + \Phi_y\sin(\omega_0 t)]\left(\frac{\omega_1}{\Omega}\right) \tag{154}$$

where the preamp gain has a frequency dependance due to its frequency filtering.

3 The Flux Factor

3.1 Analytic Form

The flux factor contains all the geometrical information about the system: the region enclosing the spins and the relative orientation of the pick up coils wrt the spin vector:

$$\Phi_n = \int\oint \frac{f(\vec{u})\hat{n}\times(\vec{r}-\vec{u})}{|\vec{r}-\vec{u}|^3}\cdot d\vec{l}\, d^3u \tag{155}$$

where $f(\vec{u}) = P(\vec{u})\rho(\vec{u})/\langle P\rho\rangle$ is the normalized polarization density gradient factor, $\hat{n}$ is one of the components of the spin vector, $\vec{r}$ is the position vector of the unit coil line element $d\vec{l}$, and $\vec{u}$ is the position vector of the unit volume element of spins d^3u. The position vectors are measured from the origin of the reference coordinate system. The integral is evaluated counterclockwise over the path of the coil and over the volume of the spins. The resulting value has units of area. In practice, it is easier to the consider the EMF as the sum of the EMF procduced by the different parts of the cell, labeled by c. This is done by the following substitution:

$$\langle P\rho\rangle\Phi_n = \sum_c \langle P\rho\rangle_c \Phi_n^c = \langle P\rho\rangle_{\rm tc}\Phi_n^{\rm tc}G_\Phi^n \tag{156}$$

where we've introduced a new a new quantity called the "flux gain," because most of the flux comes from the target chamber:

$$G_{\Phi}^{n} = 1 + \frac{\langle P\rho\rangle_{\mathrm{tt}}\,\Phi_n^{\mathrm{tt}} + \langle P\rho\rangle_{\mathrm{pc}}\,\Phi_n^{\mathrm{pc}}}{\langle P\rho\rangle_{\mathrm{tc}}\,\Phi_n^{\mathrm{tc}}} \tag{157}$$

which gives for the signal voltage into the lockin:

$$V = Q_{\mathrm{C2P}}(\omega)G_{\mathrm{P}}(\omega)Q_{\mathrm{P2L}}(\omega)\left[\frac{g\mu_N\mu_0\,\langle P\rho\rangle_{\mathrm{tc}}\,\omega_0}{8\pi}\right]\left[s\Phi_x G_{\Phi}^{x}\cos(\omega_0 t) + \Phi_y G_{\Phi}^{y}\sin(\omega_0 t)\right]\left(\frac{\omega_1}{\Omega}\right) \tag{158}$$

Note that, in principle, the flux must be calculated in both the x and y directions. These directions are any two orthogonal vectors that define the plane perpendicular to the axis determined by the holding field. In practice, the RF coils and pickup coils are orientated in such a way to maximize the flux factor in one direction and minimize it in the other.

3.2 Cell-Coil Coordinate System and Geometry

3.3 Numerical Evaluation

make diagram of coils and cell and show equations###### The algorithm for the numerical evalulation of the integral is:

1. Divide the cell into its basic subunits
2. Divide each subunit into many small cubes or volume elements
3. Represent each turn of the coil as a separate loop
4. Divide each loop into its (usually four) sides
5. Divide each side into a small line element
6. Choose an origin
7. Find the center of each subunit wrt the origin
8. Find the location of each cube wrt the center of the subunit
9. Find the location of each coil wrt the origin
10. Find the location of each loop wrt the coil
11. Find the location of each line element wrt the loop
12. Calculate the integrand
13. Sum over all line elements per side
14. Sum over all sides
15. Sum over all loops
16. Sum over all coils
17. Sum over all cubes
18. Sum over all subunits

4 Signal Detection with a Lock-In Amplifier

4.1 Fourier Transform

A lock-in amplifier is used to detect the NMR signal. This device essentially performs fourier cosine and sine transforms of the input signal at some reference frequency and outputs the RMS amplitudes of the two components [Manual for Model SR830 DSP Lock-In Amplifier, Stanford Research Systems, Revision 2.2 (6/2005), pages 3-1 to 3-3]. The lock-in "performs" the fourier transform using a mixer followed by a low pass filter. A mixer takes two signals, the input signal V_{in} and an oscillatory reference signal V_{ref}, and outputs their "triganometric" sum and difference:

$$\begin{aligned} V_{\text{in}}(t) &= V_{\text{DC}} + V_C(t)\cos(\omega_0 t) + V_S(t)\sin(\omega_0 t) + V_{\text{noise}} && (159) \\ V_{\text{ref}} &= 2\cos(\omega t + \phi) && (160) \\ V_{\text{mixer}} &= 2\left(V_{\text{DC}} + V'_{\text{noise}}\right)\cos(\omega t + \phi) + \left[V_C(t) + \mathcal{F}_C\left(V_{\text{noise}}\right)\right]\left[\cos(\omega_0 t - \omega t - \phi) + \cos(\omega_0 t + \omega t + \phi)\right] \\ &\quad + \left[V_S(t) + \mathcal{F}_s\left(V_{\text{noise}}\right)\right]\left[\sin(\omega_0 t - \omega t - \phi) + \sin(\omega_0 t + \omega t + \phi)\right] && (161) \end{aligned}$$

where ϕ is the phase of the reference signal wrt the input signal and V'_{noise} are frequency components outside a certain band around the reference frequency. For a fourier cosine (sine) transform, $\phi = \phi_L$ ($\phi = \phi_L - \frac{\pi}{2}$). The reference signal for the lockin is chosen to be the same as the frequency of the signal of interest $\omega = \omega_0$. This allows us to decompose the mixer output in to a "DC" and an AC component:

$$\begin{aligned} V_{\text{mixer}-\text{DC}} &= \left[V_C(t) + \mathcal{F}_C\left(V_{\text{noise}}\right)\right]\cos(\phi) + \left[V_S(t) + \mathcal{F}_s\left(V_{\text{noise}}\right)\right]\sin(-\phi) && (162) \\ V_{\text{mixer}-\text{AC}} &= 2\left(V_{\text{DC}} + V'_{\text{noise}}\right)\cos(\omega_0 t + \phi) + \left[V_C(t) + \mathcal{F}_C\left(V_{\text{noise}}\right)\right]\cos(2\omega_0 t + \phi) \\ &\quad + \left[V_S(t) + \mathcal{F}_s\left(V_{\text{noise}}\right)\right]\sin(2\omega_0 t + \phi) && (163) \end{aligned}$$

The signal of interest is now essentially a "DC" signal. A low pass filter in the form of an RC circuit is used to remove of the high frequency components of the mixer output and isolate the "DC" signal:

$$\begin{aligned} V_{\text{in}}(t) - I(t)R - \frac{Q(t)}{C} &= 0 && (164) \\ V_{\text{out}}(t) &= \frac{Q(t)}{C} && (165) \end{aligned}$$

By noting that $I = dQ/dt$ and defining a time constant as $\tau = RC$, we can write a differential equation for the output signal:

$$\frac{dV_{\text{out}}}{dt} = \frac{V_{\text{in}}(t) - V_{\text{out}}(t)}{\tau} \qquad (166)$$

If $V_{\text{in}}(t) = 0$, then the solution would simply be $V_{\text{out}}(t) = V_{\text{out}}(0)\exp\left(-\frac{t}{\tau}\right)$. With this in mind, we'll use the ansatz that the output voltage can be written in the following form:

$$\begin{aligned} V_{\text{out}}(t) &= f(t)\exp\left(-\frac{t}{\tau}\right) && (167) \\ \dot{V}_{\text{out}} &= \left(-\frac{f(t)}{\tau} + \dot{f}\right)\exp\left(-\frac{t}{\tau}\right) && (168) \end{aligned}$$

Substituting this form of $V_{\text{out}}(t)$ into the differential equation gives:

$$\begin{aligned} \left(-\frac{f(t)}{\tau} + \dot{f}\right)\exp\left(-\frac{t}{\tau}\right) &= \frac{V_{\text{in}}(t) - f(t)\exp\left(-\frac{t}{\tau}\right)}{\tau} && (169) \\ \dot{f} &= \exp\left(+\frac{t}{\tau}\right)\frac{V_{\text{in}}(t)}{\tau} && (170) \end{aligned}$$

Using u as a dummy integration variable, this differential equation can be directly integrated to give:

$$f(t) = \frac{1}{\tau}\int_{-\infty}^{t} \exp\left(+\frac{u}{\tau}\right) V_{\text{in}}(u)\ du \qquad (171)$$

Therefore the output of an RC low pass filter with time constant $\tau = RC$ and input $V_{\text{in}}(t)$:

$$V_{\text{out}}(t) = \frac{1}{\tau}\int_{-\infty}^{t} \exp\left(\frac{u-t}{\tau}\right) V_{\text{in}}(u)\; du \tag{172}$$

Note that since $-\infty < u \leq t$, the quantity $u - t$ will always be less than or equal to zero. The output signal is a time averaging of the input signal with exponential weighting. The time scale of averaging is given by τ and the output signal at some time t is only sensistive to the time history of the input signal over a range from t to roughly $t - 5\tau$. After about five time constants, the exponential weighting drops to less than 0.7% relative. To study the effect of the averaging, we'll perform a taylor expansion of $V_{\text{in}}(u)$ about some time t_0:

$$\begin{aligned} V_{\text{in}}(u) &= \sum_{n=0}^{\infty} \frac{(u-t_0)^n}{n!} V_{\text{in}}^{(n)}(t_0) && (173)\\ V_{\text{in}}^{(n)} &\equiv \frac{d^n V_{\text{in}}}{du^n} && (174) \end{aligned}$$

Plugging this into the integral equation for $V_{\text{out}}(t)$:

$$\begin{aligned} V_{\text{out}}(t) &= \frac{1}{\tau}\int_{-\infty}^{t} \exp\left(\frac{u-t}{\tau}\right) \sum_{n=0}^{\infty} \frac{(u-t_0)^n}{n!} V_{\text{in}}^{(n)}(t_0)\; du && (175)\\ &= \frac{1}{\tau}\exp\left(\frac{-t}{\tau}\right) \sum_{n=0}^{\infty} \frac{V_{\text{in}}^{(n)}(t_0)}{n!} \int_{-\infty}^{t} \exp\left(\frac{u}{\tau}\right)(u-t_0)^n\;\; du && (176)\\ &= \frac{1}{\tau}\exp\left(\frac{t_0-t}{\tau}\right) \sum_{n=0}^{\infty} \frac{V_{\text{in}}^{(n)}(t_0)}{n!} \int_{-\infty}^{t-t_0} \exp\left(\frac{v}{\tau}\right) v^n\;\; dv && (177)\\ &= \frac{1}{\tau}\exp\left(\frac{t_0-t}{\tau}\right) \sum_{n=0}^{\infty} \frac{V_{\text{in}}^{(n)}(t_0)}{n!} \left[I_n\left(t-t_0\right) - \lim_{b\to-\infty} I_n\left(b\right)\right] && (178) \end{aligned}$$

It is tedious but straightforward to show that:

$$I_n = \int \exp\left(\frac{v}{\tau}\right) v^n\;\, dv = \exp\left(\frac{v}{\tau}\right)\sum_{k=0}^{n}(-1)^k \tau^{k+1} v^{n-k} \frac{n!}{(n-k)!} \tag{179}$$

Using this sum form of the integral gives:

$$\begin{aligned} V_{\text{out}}(t) &= \frac{1}{\tau}\exp\left(\frac{t_0-t}{\tau}\right) \sum_{n=0}^{\infty} \frac{V_{\text{in}}^{(n)}(t_0)}{n!} \exp\left(\frac{t-t_0}{\tau}\right) \sum_{k=0}^{n} (-1)^k \tau^{k+1} \left(t-t_0\right)^{n-k} \frac{n!}{(n-k)!} && (180)\\ &= \sum_{n=0}^{\infty}\sum_{k=0}^{n}(-1)^k \tau^k \left(t-t_0\right)^{n-k} \frac{V_{\text{in}}^{(n)}(t_0)}{(n-k)!} && (181) \end{aligned}$$

We can write this is an more illuminating form by splitting the sum over k:

$$\begin{aligned} V_{\text{out}}(t) &= \left[\sum_{n=0}^{\infty} \frac{(t-t_0)^n}{n!} V_{\text{in}}^{(n)}(t_0)\right] + \left[\sum_{n=1}^{\infty}\sum_{k=1}^{n}(-1)^k \tau^k \left(t-t_0\right)^{n-k} \frac{V_{\text{in}}^{(n)}(t_0)}{(n-k)!}\right] && (182)\\ &= V_{\text{in}}(t) + \underbrace{\left[\sum_{n=1}^{\infty}\sum_{k=1}^{n}(-1)^k \tau^k \left(t-t_0\right)^{n-k} \frac{V_{\text{in}}^{(n)}(t_0)}{(n-k)!}\right]}_{\text{effect of averaging}} && (183) \end{aligned}$$

The output signal is simply a sum of the input signal with some other function that is proportional to powers of τ and time derivatives of the input signal. This is a very satisfying form of the solution because when there is no averaging $\tau = 0$, we immediateley see that the output signal equals the input signal.

We can also get a qualitative "feel" for how the time averaging affects the output signal by considering the first derivative of the input signal. If the first derivative is positive (negative) or in another words the signal is growing (decreasing), then the output underestimates (overestimates) the input signal. This can be thought of as a "lag" effect. Since the effect of averaging in the output signal as measured at a certain time t is only dependant on the recent time history of the input signal, the appropriate range for t_0 would be $t - 5\tau \leq t_0 \leq t$. We'll illustrate two reasonable choices for t_0:

$$V_{\text{out}}(t) - V_{\text{in}}(t) = \left[\sum_{n=1}^{\infty} (-\tau)^n \, V_{\text{in}}^{(n)}(t)\right] \qquad \text{for } \mathrm{t_0 = t} \tag{184}$$

$$= \left[\sum_{n=1}^{\infty}\sum_{k=1}^{n} (-1)^k \tau^n \frac{V_{\text{in}}^{(n)}(t-\tau)}{(n-k)!}\right] \qquad \text{for } \mathrm{t_0 = t} - \tau \tag{185}$$

In some cases, the time derivative of the input signal takes on a simple form for $t_0 = 0$:

$$V_{\text{out}}(t) - V_{\text{in}}(t) = \left[\sum_{n=1}^{\infty}\sum_{k=1}^{n} (-1)^k \tau^k t^{n-k} \frac{V_{\text{in}}^{(n)}(0)}{(n-k)!}\right] \qquad \text{for } \mathrm{t_0} = 0 \tag{186}$$

The remarkable fact of the time averaging is that we can calculate its effect to arbitrary precision using the above sums (assuming the time derivatives of the input signal is known). An interesting side note and another remarkable fact is that the output of an input with a polynomial form is simply the time shifted polynomial:

$$V_{\text{in}} = \sum_n c_n t^n \to V_{\text{out}} = \sum_n c_n \left(t - \tau\right)^n \tag{187}$$

Returning to the problem at hand, the end result is that the AC part of the mixer output is filtered or intergrated "away." The "DC" or more approapriately slow varying part of the mixer output is only slightly distorted due to the time averaging. To recap, a signal input into a lockin of the following form:

$$V_{\text{in}}(t) = V_{\text{DC}} + V_C(t)\cos(\omega_0 t) + V_S(t)\sin(\omega_0 t) + V_{\text{noise}} \tag{188}$$

results in the following output with a lockin reference frequency of ω_0, time constant τ, gain G_L, and reference signal phase ϕ_L:

$$S_x(t) = \frac{G_L}{\sqrt{2}}\left\{\left(V_C(t) + \left[\sum_{n=1}^{\infty} (-\tau)^n \, V_C^{(n)}(t)\right]\right)\cos(\phi_L) - \left(V_S(t) + \left[\sum_{n=1}^{\infty} (-\tau)^n \, V_S^{(n)}(t)\right]\right)\sin(\phi_L)\right\} \tag{189}$$

$$S_y(t) = \frac{G_L}{\sqrt{2}}\left\{\left(V_C(t) + \left[\sum_{n=1}^{\infty} (-\tau)^n \, V_C^{(n)}(t)\right]\right)\sin(\phi_L) + \left(V_S(t) + \left[\sum_{n=1}^{\infty} (-\tau)^n \, V_S^{(n)}(t)\right]\right)\cos(\phi_L)\right\} \tag{190}$$

4.2 Lineshaping Effects due to Time Constant

5 Lineshaping Effects in Water AFP due to Thermal Relaxation

5.1 Introduction

Suppose that the magnetic field has been constant for a long time. We'll soon discuss exactly how long a "long time" actually is. The thermal polarization of water is proportional to the magnetic field. A more precise way to put it is that the *equilibrium* thermal polarization is proportional to magnetic field.

Suppose now that the field is instantaneously doubled. The polarization of the water does not also *instantaneously* double. In this scenario, it takes a finite amount of time for the thermal polarization of the water to double. More generally, if one were to plot the thermal polarization of water as a function of time after an instantaneous change in magnetic field, then one would see a ”capacitor charging up”-like curve:

$$P(t) = P_{\infty}^{\mathrm{f}} \left[1 - \exp\left(-\frac{t}{T_1} \right) \right] + P_{\infty}^{\mathrm{i}} \exp\left(-\frac{t}{T_1} \right) \tag{191}$$

where P_{∞}^{f} is the *equilibrium* thermal polarization at the final magnetic field, P_{∞}^{i} is the *equilibrium* thermal polarization at the initial magnetic field, and T_1 is the characteristic time constant. T_1 is usually referred to as the “longintudinal spin relaxation time” and for pure deoxygenated water is typically 3 sec. note that T_1 is quite sensitive to any chemical impurities in the water. Going back to the question of how long a “long time” is: we can now say that several time constants T_1 is a long time. after about 5*T_1 (or 15 seconds for pure water), the thermal polarization of water is around 99.3% of it’s final equilbrium value.

Now let’s consider what happens when you sweep the magnetic field. for all of the following scenarios we’ll assume that:

1. the sweep is slow enough to be adiabatic (in the quantum mechanical sense of the word)
2. the low field is 18 gauss
3. the high field is 25 gauss
4. the up sweep is low field to high field
5. the down sweep is high field to low field
6. the up sweep time is the same as the down sweep time
7. ”a long time” is longer than 5*T_1
8. the resonance field is 21.5 gauss
9. ”signal size” is defined by the absolute value of the voltage measured at the resonance minus the voltage measured far from resonance, in other words: |peak − baseline|.

(note one technical detail: the *sign* of the up and dn sweeps should be opposite. one is positive while the other is always negative. which one is which depends on the setting of the lockin phase and the sign of the magnetic moment of the nucleus in question.)

Scenario A sequence of events:

1. wait at low field for a long time
2. up sweep
3. wait at high field for a long time
4. dn sweep
5. duration of field sweep is much *shorter* than T_1

in this case, the field sweep is so fast that the thermal polarization changes *little* from it’s starting value. therefore, the thermal polarizations at resonance are essentially the polarizations at the start of the sweep. the ratio of the signal size for the up and dn sweeps would be:

(up sweep)/(down sweep) = 18/25 = 0.72

Scenario B:

1. wait at low field for a long time
2. up sweep
3. wait at high field for a long time

4. dn sweep

5. duration of field sweep is much *longer* than $5*T_1$

in this case, the field sweep is so slow that the thermal polarization tracks the field as it is swept. therefore, the thermal polarizations at resonance are essentially the equilibrium polarizations at the resonance field and therefore the up and dn signals have the same size:

$$(upsweep)/(downsweep) = 21.5/21.5 = 1.00 \tag{192}$$

Under real conditions, as Vince mentioned, the sweep time is on order of the relaxation time T_1. Specifically for JLAB, the sweep rate is about 1.2 Gauss per second which gives a sweep time of about 5.8 secs. this leads to our third scenario:

Scenario C:

1. wait at low field for a long time

2. up sweep

3. wait at high field for a long time

4. dn sweep

5. duration of field sweep is on order of T_1

obviously, in this case, the situation is more complicated. while the field is being swept, the thermal polarization does change from it's starting value, but, does not quite catch up with the field sweep until the sweep ends and the field has been constant for a long time. in other words there is a time lag in the thermal polarization with respect to the field at any given time during the sweep. consider an up sweep: at resonance, the thermal polarization is higher than it's starting value, *but* it has not caught up to the *equilibrium* thermal polarization one would expect for the resonance field. the up sweep signal size is therefore between the 18 gauss value and the 21.5 gauss value. by the same token, the down sweep signal size is between the 25 gauss value and the 21.5 gauss value. this yields the following for the ratio of the signal sizes:

$$(upsweep)/(downsweep) = (18 + dB_up)/(25 - dB_dn) \tag{193}$$

which means that:

$$0.72 <= (upsweep)/(dnsweep) <= 1.00 \tag{194}$$

Scenarios A and B are really then just special cases of Scenario C for "extreme" values for the field sweep rate.

now the question is: "What are the exact values of dB_up and dB_dn?" the answer depends intimately on:

1. the field sweep rate

2. the locationof the resonance field relative to the start and end fields, and

3. the T_1 for the water sample used.

one must numerically solve the full Bloch equations to obtain the exact values of dB_up and dB_dn given the specific experimental conditions. under JLAB conditions, we get:

$$dB_up = 0.8 gauss dB_dn = 1.7 gauss \tag{195}$$

which gives for the ratio:

$$(upsweep)/(dnsweep) = 18.8/23.3 = 0.81 \tag{196}$$

for each of the scenarios above, step was "wait at high field for a long time." we do not do this at JLAB. the water signals we get here in the Hall during the experiments are very noisy. therefore we have to take around 1000 sweeps and then average them. to do this in a reasonable amount of time ($\tilde{8}$ hrs), we can't wait at the high field for the water to come to thermal equilibrium. therefore we start the down sweep before the spins reach thermal equilibrium. when the software and NMR system was first designed 8 years ago, it was decided that we would wait at the high field value for the same amount of time that it takes to do one sweep, namely about 5.8 sec.

another subtle point is "how much time should we wait between sets of up and dn sweeps?" it turns out that at JLAB, it takes about 24 seconds to download the data for one up/dn sweep pair from the lockin. this is essentially "a long time" based on our above definition:

24 sec/(T_1 = 3 sec) = 8 time constants =¿ roughly 99.97% of the equilibirum value

putting this all together gives our final scenario:

Scenario D:

1. wait at low field long enough since last up/dn sweep cycle
2. up sweep
3. wait at high field for a time equal to the sweep time
4. dn sweep
5. duration of field sweep is on order of T_1

in this case, the up sweep starts at thermal equilibrium; therefore, it is treated the same way as the up sweep for scenario C. on the other hand, as we have argued above, the dn sweep starts *before* the spins reached thermal equilibrium at the high field value. therefore the dn sweep starts "smaller" than the high field *equilibrium* thermal polarization. this introduces a second factor which now gives for the signal size ratio:

$$(upsweep)/(downsweep) = (18 + dB_up)/(25 - dB_dn_2 - dB_dn) \tag{197}$$

where dB_up and dB_dn have the same defintions as they did in scenario C and dB_dn_2 is due to the fact that we start the down sweep *before* we were at thermal equilibrium. again dB_dn_2 depends initmately on the experimental conditions and must be found from a numerical solution to the full Bloch equations. under JLAB conditions, we get roughly:

$$dB_up = 0.8 gauss dB_dn_2 + dB_dn = 2.6 gauss \tag{198}$$

finally this gives us the ratio for the up and dn "signal sizes" under JLAB experimental condtions:

$$(upsweep)/(dnsweep) = 18.8/22.4 = 0.84 \tag{199}$$

again, to be explicit, the signal size is defined as the absolute value of the voltage measured at the resonance peak minus the voltage measured far words: |peak − baseline|.

The polarization of the protons in water is proportional to the field. Since we perform field sweep AFP, the thermal polarization tracks the change in the holding field during the sweep. Since the relaxation time is on order of the sweep time, one must account for the change in the lineshape due to the thermal relaxation during the sweep.

5.2 Modified Bloch Equations in low fields

The equations that govern the time evolution of the magnetization at thermal equilbrium are the phenomenological Bloch equations where $T_{1(2)}$ is the longitudinal (transverse) relaxation time. At resonance, in the rotating frame, the effective field is solely the RF field. Therefore one must apply the modified Bloch equations in the *rotating frame* [Abragam, A., *Principles of Nuclear Magnetism*, Oxford: OUP, III.C p54, 1961.]:

$$\frac{dM_x}{dt} = -\frac{(M_x - \chi_0 H_1)}{T_2} + \Delta\omega M_y \tag{200}$$

$$\frac{dM_y}{dt} = -\Delta\omega M_x - \frac{M_y}{T_2} - \omega_1 M_z \tag{201}$$

$$\frac{dM_y}{dt} = \omega_1 M_y - \frac{M_z - M_0}{T_1} \tag{202}$$

where for now we assume $T_1 \neq T_2$. In the notation of Abragram, the magnitude of the magnetic field in the lab frame is H_0, the magnitude of the RF field in the rotating frame is H_1, and the rotational frequency of the rotating frame relative to the lab frams is ω. The choice of ω is motivated by the frequency of the RF field in the lab frame ν_{RF}. Specifically, the sign and magnitude of ω are chosen such that the RF field is *static* in the rotating field:

$$\omega \equiv -s_{\mathrm{mm}} 2\pi\nu_{\mathrm{RF}} \tag{203}$$

where $s_{\mathrm{mm}}(= g/|g|)$ is the sign of particle's magnetic moment. Although this is an awkward notational choice, it insures that ν_{RF} is always a positive quantity.

The relationships between the magnetization $\vec{M}$ & magnetic susceptibility χ_0 to the polarization $\vec{P}$ & "reduced" magnetic susceptibility χ are:

$$\vec{M} = \frac{g\mu_N\rho}{2}\vec{P} = \frac{\chi_0}{\chi}\vec{P} \qquad \chi = \frac{g\mu_N}{2kT} \qquad \chi_0 = \left(\frac{g\mu_N\rho}{2}\right)\chi \qquad M_0 = \chi_0 H_0 \tag{204}$$

Using the above and make the following substitutions:

$$\Delta\omega = \omega - \omega_0 \qquad \omega_0 = -\gamma H_0 \qquad \omega_1 = -\gamma H_1 \qquad \gamma = \frac{g\mu_N}{\hbar} \tag{205}$$

gives:

$$\frac{dP_x}{dt} = -\frac{(P_x - \chi H_1)}{T_2} + (\gamma H_0 - s_{\mathrm{mm}} 2\pi\nu_{\mathrm{RF}})\, P_y \tag{206}$$

$$\frac{dP_y}{dt} = -(\gamma H_0 - s_{\mathrm{mm}} 2\pi\nu_{\mathrm{RF}})\, P_x - \frac{P_y}{T_2} + \gamma H_1 P_z \tag{207}$$

$$\frac{dP_z}{dt} = -\gamma H_1 P_y - \frac{(P_z - \chi H_0)}{T_1} \tag{208}$$

In general T_2 is different than T_1 and depends on the impurities present in the water and the magnitude of the RF field H_1. It is usefull to set the scale of the polarization to the value at resonance, $p_u = P_u/\chi H_{\mathrm{res}}$:

$$\frac{dp_x}{dt} = -\frac{\left(p_x - \frac{H_1}{H_{\mathrm{res}}}\right)}{T_2} + (\gamma H_0 - s_{\mathrm{mm}} 2\pi\nu_{\mathrm{RF}})\, p_y \tag{209}$$

$$\frac{dp_y}{dt} = -(\gamma H_0 - s_{\mathrm{mm}} 2\pi\nu_{\mathrm{RF}})\, p_x - \frac{p_y}{T_2} + \gamma H_1 p_z \tag{210}$$

$$\frac{dp_z}{dt} = -\gamma H_1 p_y - \frac{\left(p_z - \frac{H_0}{H_{\mathrm{res}}}\right)}{T_1} \tag{211}$$

where $H_{\mathrm{res}} = 2\pi\nu_{\mathrm{res}}/|\gamma|$ is the resonance field. For field sweep AFP, H_{res} is fixed by choosing the frequency of the RF field, $\nu_{\mathrm{RF}} = \nu_{\mathrm{res}}$. For frequency sweep AFP, H_{res} is fixed by choosing the size of the magnetic field in the lab frame, $H_0 = H_{\mathrm{res}}$. For a static holding field and a fixed frequency RF field, the equilibrium solutions are:

$$p_x^{\mathrm{eq}} = \frac{P_x^{\mathrm{eq}}}{\chi H_{\mathrm{res}}} = \frac{H_1}{H_{\mathrm{res}}}\left[1 + s_{\mathrm{mm}} 2\pi\nu_{\mathrm{RF}} (\gamma H_0 - s_{\mathrm{mm}} 2\pi\nu_{\mathrm{RF}})\, T_2^2 \eta\right] \tag{212}$$

$$p_y^{\mathrm{eq}} = \frac{P_y^{\mathrm{eq}}}{\chi H_{\mathrm{res}}} = s_{\mathrm{mm}} 2\pi\nu_{\mathrm{RF}} T_2 \left(\frac{H_1}{H_{\mathrm{res}}}\right)\eta \tag{213}$$

$$p_z^{\mathrm{eq}} = \frac{P_z^{\mathrm{eq}}}{\chi H_{\mathrm{res}}} = \frac{H_0}{H_{\mathrm{res}}} - 2\pi\nu_{\mathrm{RF}}|\gamma| T_1 T_2 \left(\frac{H_1^2}{H_{\mathrm{res}}}\right)\eta \tag{214}$$

$$\eta = \left[1 + \gamma^2 H_1^2 T_1 T_2 + \left(\gamma H_0 - s_{\mathrm{mm}} 2\pi\nu_{\mathrm{RF}}\right)^2 T_2^2\right]^{-1} \tag{215}$$

which are found by setting the derivatives equal to 0.

In the absence of an RF field, $H_1 = 0$, it no longer makes sense to talk about the frequency of the RF field ν_{RF}. Therefore, we'll revert back to $-s_{\mathrm{mm}} 2\pi\nu_{\mathrm{RF}} \to \omega$. Now the most natural choice for the rotational frequency of rotating frame relative to the lab is given be the Larmor frequency of the spins $\omega = -\gamma H_0$. Putting this altoghether gives the satisfying results:

$$\frac{dP_{x,y,z}}{dt} = \frac{P_{x,y,z}^{\mathrm{eq}} - P_{x,y,z}}{T_{2,2,1}} \tag{216}$$

$$P_x^{\mathrm{eq}} = P_y^{\mathrm{eq}} = 0 \quad \& \quad P_z^{\mathrm{eq}} = \chi H_0 \tag{217}$$

$$P_{x,y,z}(t) = P_{x,y,z}^{\mathrm{eq}} + \left[P_{x,y,z}^{\mathrm{initial}} - P_{x,y,z}^{\mathrm{eq}}\right] \exp\left(-\frac{t}{T_{2,2,1}}\right) \tag{218}$$

Any transverse polarization relaxes to 0 with time constant of T_2 and any longitudinal polarization relaxes to it equilibrium value χH_0 with a time constant T_1.

5.3 Time Evolution of the Magnitude of the Polarization Vector

The magnitude and sign of the polarization vector in the rotating frame are both given by one equation:

$$p = s\sqrt{p_x^2 + p_y^2 + p_z^2} \tag{219}$$

The first time derivative is:

$$\frac{dp}{dt} = \frac{p_x \frac{dp_x}{dt} + p_y \frac{dp_y}{dt} + p_z \frac{dp_z}{dt}}{p} \tag{220}$$

and plugging in the equations from the modified Bloch equations *in the rotating frame* give in Abragam's notation:

$$\frac{dp}{dt} = \left[\frac{H_1}{H_{\mathrm{res}} T_2}\left(\frac{p_x}{p}\right) + \frac{H_0}{H_{\mathrm{res}} T_1}\left(\frac{p_z}{p}\right)\right] - \frac{1}{T_1 p}\left[\frac{T_1}{T_2}\left(p_x^2 + p_y^2\right) + p_z^2\right] \tag{221}$$

If we make the approximation that $p_y = 0$, then the polarization vector is parallel to effective field in the rotating frame:

$$\vec{H}_{\mathrm{eff}} = \left(H_0 - \frac{2\pi\nu_{\mathrm{RF}}}{|\gamma|}\right)\hat{z} + H_1 \hat{x}_{\mathrm{rot}} \tag{222}$$

Since the field sweep is adiabatic by design, the polarization vector remains parallel to the effective field throughout the sweep:

$$\frac{p_x}{p} = \frac{H_1}{\sqrt{H_1^2 + \left(H_0 - \frac{2\pi\nu_{\mathrm{RF}}}{|\gamma|}\right)^2}} \qquad \frac{p_y}{p} = 0 \qquad \frac{p_z}{p} = \frac{H_0 - \frac{2\pi\nu_{\mathrm{RF}}}{|\gamma|}}{\sqrt{H_1^2 + \left(H_0 - \frac{2\pi\nu_{\mathrm{RF}}}{|\gamma|}\right)^2}} \tag{223}$$

Using the above relations and making the approximation $T_2 = T_1 = T$ simplifies things greatly:

$$\frac{dp}{dt} = \frac{p_{\mathrm{eq}}(t) - p}{T} \tag{224}$$

where we have defined the equilibrium polarization when $dp/dt = 0$:

$$p_{\mathrm{eq}}(t) \equiv \frac{\left[H_1^2 + H_0\left(H_0 - \frac{2\pi\nu_{\mathrm{RF}}}{|\gamma|}\right)\right]}{H_{\mathrm{res}}\sqrt{H_1^2 + \left(H_0 - \frac{2\pi\nu_{\mathrm{RF}}}{|\gamma|}\right)^2}} \tag{225}$$

In direct analogy to the lockin time constant equation (172), we can immediately write down the integral form of this equation:

$$p(t) = \frac{1}{T}\int_{-\infty}^{t} \exp\left(\frac{u-t}{T}\right) p_{\text{eq}}(u)\ du \tag{226}$$

5.4 Approximate Analytic Solution for Field Sweep AFP

We will now derive an approximate analytic solution for $p(t)$ when the field (as opposed to the frequency) is swept. Before doing so, we'll make the following notational changes:

1. The magnetic field in the lab frame: $H_0 \to H(t)$.
2. The resonance field, $H_{\text{res}} \to H_0$.
3. The frequency of the RF field: $\nu_{\text{RF}} \to \frac{|\gamma|}{2\pi} H_0$.

where the frequency of the RF field now determines the resonance field. In this new notation, the equilibrium polarization when $dp/dt = 0$:

$$p_{\text{eq}}(t) \equiv \frac{\left[H_1^2 + H(t)\left(H(t) - H_0\right)\right]}{H_0\sqrt{H_1^2 + \left(H(t) - H_0\right)^2}} \tag{227}$$

We can separate the field sweep into 5 distinct time domains and make the following approximations within each:

1. $-\infty < t \le -t_0$, We'll assume $|H(-t_0) - H_0| \gg H_1$ and $p_{\text{eq}} = p_{\text{eq}}(-t_0) = \text{constant}$.
2. $-t_0 \le t \le -t_a$, We'll choose $|H(-t_a) - H_0| \gg H_1$.
3. $-t_a < t < +t_b$, We'll choose $|t_a|, |t_b| < T$.
4. $+t_b \le t \le +t_0$, We'll choose $|H(+t_b) - H_0| \gg H_1$.
5. $+\infty > t \ge +t_0$, We'll assume $|H(+t_0) - H_0| \gg H_1$ and $p_{\text{eq}} = p_{\text{eq}}(+t_0) = \text{constant}$.

To potentially take advantage of symmetry later, we'll set $t_a = t_b$. We'll also specify a linear field sweep such that:

$$\begin{aligned}
H(t) &= H_{\text{start}} + \alpha(t + t_0) = H_0\left(h_m + at\right) && (228)\\
H_{\text{end}} &= H_{\text{start}} + 2\alpha t_0 && (229)\\
h_m &\equiv \frac{H_{\text{start}} + H_{\text{end}}}{2H_0} = \frac{H_{\text{start}} + \alpha t}{H_0} && (230)\\
s &\equiv \alpha/|\alpha| && (231)\\
a &\equiv \frac{\alpha}{H_0} && (232)\\
z(t) &\equiv \frac{H(t) - H_0}{H_1} = \frac{\alpha t + H_{\text{start}} + \alpha t_0 - H_0}{H_1} = \frac{H_0}{H_1}\left(at + h_m - 1\right) && (233)\\
\delta z &\equiv \left(h_m - 1\right)\frac{H_0}{H_1} && (234)\\
z_a &= \frac{\alpha t_a}{H_1} && (235)
\end{aligned}$$

We'll make special note regarding the sign convention of the following approxiamtion:

$$p_{\text{eq}} = \frac{H_1^2 + H(H - H_0)}{\sqrt{H_1^2 + (H - H_0)^2}} \approx H\frac{H - H_0}{\sqrt{(H - H_0)^2}} = H\frac{\alpha}{|\alpha|} = sH \tag{236}$$

Using the above approximations and definitions result in the following for the equilibrium polarization:

$$P_{\mathrm{eq}}(u) = \left\{ \begin{array}{cc} -s\left(h_m + au\right) & u \leq -t_a \\ \frac{H_1}{H_0}\left[1 + \frac{H_0}{H_1}z(u) + z(u)^2\right]\left[1 + z(u)^2\right]^{-\frac{1}{2}} & |u| < t_a \leftrightarrow |z(u) - \delta z| < z_a \\ +s\left(h_m + au\right) & u \geq +t_a \end{array} \right\} \tag{237}$$

and in the time period around resonance ($|u| < t_a$), we expand the exponential as:

$$u - t = \beta(z(u) - z(t)) \tag{238}$$

$$\beta \equiv \frac{H_1}{\alpha T} = \frac{H_1}{aH_0T} \tag{239}$$

$$\exp\left(\frac{u-t}{T}\right) = \exp\left(-\beta z(t)\right)\sum_{n=1}^{\infty}\frac{\left[\beta z(u)\right]^n}{n!} \tag{240}$$

This results in the following group of integrals:

$$p(t) = \frac{1}{T}\int_{-\infty}^{t}\exp\left(\frac{u-t}{T}\right)p_{\mathrm{eq}}(u)\ du \tag{241}$$

$$p_1(t) = -\frac{s}{T}\left[h_m - at_0\right]\exp\left(-\frac{t}{T}\right)\int_{-\infty}^{t}\exp\left(\frac{u}{T}\right)\ du \tag{242}$$

$$p_2(t) = -\frac{s}{T}\exp\left(-\frac{t}{T}\right)\left\{\left[h_m - at_0\right]\int_{-\infty}^{-t_0}\exp\left(\frac{u}{T}\right)\ du + \int_{-t_0}^{t}\exp\left(\frac{u}{T}\right)\left[h_m + au\right]\ du\right\} \tag{243}$$

$$\begin{aligned} p_3(t) = &-\frac{s}{T}\exp\left(-\frac{t}{T}\right)\left\{\left[h_m - at_0\right]\int_{-\infty}^{-t_0}\exp\left(\frac{u}{T}\right)\ du + \int_{-t_0}^{-t_a}\exp\left(\frac{u}{T}\right)\left[h_m + au\right]\ du\right\} \\ &+\frac{\beta H_1}{H_0}\exp\left(-\beta z\right)\int_{-z_a+\delta z}^{z}\left[\sum_{n=0}^{\infty}\frac{\left(\beta z'\right)^n}{n!}\right]\left[1 + \frac{H_0}{H_1}z' + z'^2\right]\left[1 + z'^2\right]^{-\frac{1}{2}}\ dz' \end{aligned} \tag{244}$$

$$\begin{aligned} p_4(t) = &-\frac{s}{T}\exp\left(-\frac{t}{T}\right)\left\{\left[h_m - at_0\right]\int_{-\infty}^{-t_0}\exp\left(\frac{u}{T}\right)\ du + \int_{-t_0}^{-t_a}\exp\left(\frac{u}{T}\right)\left[h_m + au\right]\ du\right\} \\ &+\frac{\beta H_1}{H_0}\exp\left(-\beta z\right)\int_{-z_a+\delta z}^{+z_a+\delta_z}\left[\sum_{n=0}^{\infty}\frac{\left(\beta z'\right)^n}{n!}\right]\left[1 + \frac{H_0}{H_1}z' + z'^2\right]\left[1 + z'^2\right]^{-\frac{1}{2}}\ dz' \\ &+\frac{s}{T}\exp\left(-\frac{t}{T}\right)\int_{+t_a}^{t}\exp\left(\frac{u}{T}\right)\left[h_m + au\right]\ du \end{aligned} \tag{245}$$

$$\begin{aligned} p_5(t) = &-\frac{s}{T}\exp\left(-\frac{t}{T}\right)\left\{\left[h_m - at_0\right]\int_{-\infty}^{-t_0}\exp\left(\frac{u}{T}\right)\ du + \int_{-t_0}^{-t_a}\exp\left(\frac{u}{T}\right)\left[h_m + au\right]\ du\right\} \\ &+\frac{\beta H_1}{H_0}\exp\left(-\beta z\right)\int_{-z_a+\delta z}^{+z_a+\delta z}\left[\sum_{n=0}^{\infty}\frac{\left(\beta z'\right)^n}{n!}\right]\left[1 + \frac{H_0}{H_1}z' + z'^2\right]\left[1 + z'^2\right]^{-\frac{1}{2}}\ dz' \\ &+\frac{s}{T}\exp\left(-\frac{t}{T}\right)\left\{\left[h_m - at_0\right]\int_{+t_0}^{t}\exp\left(\frac{u}{T}\right)\ du + \int_{+t_a}^{+t_0}\exp\left(\frac{u}{T}\right)\left[h_m + au\right]\ du\right\} \end{aligned} \tag{246}$$

These integrals are evaluated by using the following:

$$\int\exp\left(\frac{u}{T}\right)\left[h_m + au\right]\ du = T\exp\left(\frac{u}{T}\right)\left[h_m + a\left(u - T\right)\right] \tag{247}$$

$$\beta\sum_{n=0}^{\infty}c_nI_n = \frac{\beta H_1}{H_0}\int\left[\sum_{n=0}^{\infty}\frac{\left(\beta z\right)^n}{n!}\right]\left[1 + \frac{H_0}{H_1}z + z^2\right]\left[1 + z^2\right]^{-\frac{1}{2}}\ dz \tag{248}$$

$$c_n = \left\{ \begin{array}{cc} \frac{H_1}{H_0} & n = 0 \\ \frac{\beta^{n-1}}{(n-1)!}\left[1 + \frac{H_1}{H_0}\left(\frac{n-1}{\beta} + \frac{\beta}{n}\right)\right] & n \geq 1 \end{array} \right\} \tag{249}$$

$$I_n = \int \frac{z^n}{\sqrt{1+z^2}} dz \tag{250}$$

For our purposes, truncating the sum in the resonance region integral at sixth order gives us considerable flexibility in choosing t_a:

$$\int \frac{1}{\sqrt{1+z^2}}\, dz = \mathrm{asinh}(z) \tag{251}$$

$$\int \frac{z}{\sqrt{1+z^2}}\, dz = \sqrt{1+z^2} \tag{252}$$

$$\int \frac{z^2}{\sqrt{1+z^2}}\, dz = \frac{z}{2}\sqrt{1+z^2} - \frac{1}{2}\mathrm{asinh}(z) \tag{253}$$

$$\int \frac{z^3}{\sqrt{1+z^2}}\, dz = \left[\frac{z^2}{3} - \frac{2}{3}\right]\sqrt{1+z^2} \tag{254}$$

$$\int \frac{z^4}{\sqrt{1+z^2}}\, dz = \left[\frac{z^3}{4} - \frac{3z}{8}\right]\sqrt{1+z^2} + \frac{3}{8}\mathrm{asinh}(z) \tag{255}$$

$$\int \frac{z^5}{\sqrt{1+z^2}}\, dz = \left[\frac{z^4}{5} - \frac{4z^2}{15} + \frac{8}{15}\right]\sqrt{1+z^2} \tag{256}$$

$$\int \frac{z^6}{\sqrt{1+z^2}}\, dz = \left[\frac{z^5}{6} - \frac{5z^3}{24} + \frac{5z}{16}\right]\sqrt{1+z^2} - \frac{5}{16}\mathrm{asinh}(z) \tag{257}$$

Finally, this gives:

$$p_1(t \le -t_0) = -s\left[h_m - at_0\right] \tag{258}$$

$$p_2(-t_0 \le t \le -t_a) = -s\left[h_m + at\right] + saT\left[1 - \exp\left(\frac{-t_0 - t}{T}\right)\right] \tag{259}$$

$$\begin{aligned} p_3(-t_a \le t \le +t_a) = {} & +\beta \exp\left[-\beta z\right]\sum_n c_n\left[I_n(z) - I_n(-z_a + \delta z)\right] \\ & -s\exp\left[\frac{-t_a - t}{T}\right]\left\{h_m - at_a - aT\left(1 - \exp\left[\frac{t_a - t_0}{T}\right]\right)\right\} \end{aligned} \tag{260}$$

$$\begin{aligned} p_4(+t_a \le t \le +t_0) = {} & +s\left[h_m + a\left(t - T\right)\right] - s\left[h_m + a\left(t_a - T\right)\right]\exp\left[\frac{t_a - t}{T}\right] \\ & +\beta \exp\left[-\beta z\right]\sum_n c_n\left[I_n(+z_a + \delta z) - I_n(-z_a + \delta z)\right] \\ & -s\exp\left[\frac{-t_a - t}{T}\right]\left\{h_m - at_a - aT\left(1 - \exp\left[\frac{t_a - t_0}{T}\right]\right)\right\} \end{aligned} \tag{261}$$

$$\begin{aligned} p_5(+t_0 \le t) = {} & +s\left[h_m + at_0\right] - s\exp\left[\frac{t_0 - t}{T}\right]\left\{\left[h_m + a\left(t_a - T\right)\right]\exp\left[\frac{t_a - t_0}{T}\right] + aT\right\} \\ & +\beta \exp\left[-\beta z\right]\sum_n c_n\left[I_n(+z_a + \delta z) - I_n(-z_a + \delta z)\right] \\ & -s\exp\left[\frac{-t_a - t}{T}\right]\left\{h_m - at_a - aT\left(1 - \exp\left[\frac{t_a - t_0}{T}\right]\right)\right\} \end{aligned} \tag{262}$$

Some notes about this group of equations:

1. It assumes that $T_2 = T_1$ & takes as input $T = T_1$ and it assumes that $p_y = 0$. A full numerical solution shows that the up sweep is too large by about a percent, the down sweep is too small by about a percent, and at most (near resonance) p_y is only about a percent of p_x.

2. It does not take into account lineshaping due to the lockin time constant, which for $\tau = 30$ms reduces both up and down peaks by several percent.

3. One has to choose at what order to truncate the integral sum at the resonance region and the value of t_a based on the $T1$ and the sweep rate α.
4. $h_m H_0$ is the center of the sweep, whereas H_0 is the location of the resonance. This is included to account for any possible timing offset.
5. If the sweep starts at a field below resonance, then the proton spins are pointing antiparallel to the effective field in the corotating frame.
6. If the sweep starts at a field above resonance, then the proton spins are pointing parallel to the effective field in the corotating frame.
7. Using these equations to fit the water AFP lineshape takes into account the different heights of the up and down sweep due to relaxation.

If the resonance region integral sum is truncated at 6th order, then it is accurate to better than 0.1% over one T. Therefore a reasonable value for the transition time t_a between the two approximations is:

$$t_a = \left\{ \begin{array}{ll} t_1 & T > t_1 \\ T & T \leq t_1 \end{array} \right\} \qquad t_1 = \frac{10 H_1}{\alpha} \tag{263}$$

6 Lineshaping Effects due to Magnetic Field Gradients