Introduction to the Yale NMR experiment

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This document is designed to provide a thorough introduction to the pulsed NMR experiment for the advanced laboratory at Yale University. The basic theory behind NMR, the two level quantum system, is described in detail and its connections to other systems are also discussed. Relaxation, an important mechanism in NMR experiments, is described along with spin echos, the main method to overcome some relaxation and, in fact, measure the relaxation. Finally, several possible investigations are suggestion in the last section for the student to choose to study.

I. INTRODUCTION TO NMR

Nuclear magnetic resonance (NMR), discovered in 1946 by Purcell and Bloch, is a widely used technique for experimental studies. In essence, NMR allows the experimenter to access information about the spin degree of freedom of the nucleus. Many nuclei have a spin, and therefore a magnetic moment, and can therefore be probed with NMR. Despite the fact that most of the periodic table is accessible by NMR, most experiments only work with hydrogen, since it has the largest magnetic dipole moment. Nonetheless, NMR finds many uses. For example, chemists use NMR extensively for compound determination. Medical doctors use NMR as an imaging technique commonly called MRI, magnetic resonance imaging. All these applications hinge on the basic nuclear magnetic resonance.

Physicists use NMR for a wide variety of experiments. Because a spin 1/2 nucleus in a mangetic field represents the ideal, two-level quantum system, it draws much attention in fields like quantum computing. Outside of nuclei themselves, the methods of NMR are used in almost any field where there is an ideal, two level system. For example, in experiments that use a superconducting device as an ideal two level system for quantum computing, they still refer to the Bloch sphere, π pulses, and T_1 relaxation times, all concepts originally developed for use in NMR. Understanding how population transfer works in the two level system can gain insight into a host of other probelms, for example, the two level neutrino mixing problem obeys the same physics!

In this introduction, we'll go over the quantum, two state system in the context of NMR.

A. Larmor Precession

In NMR, we place spins inside a static magnetic field, typically generated by an electromagnet, superconducting magnet, or a permanent magnet with typical strengths of 0.1 T to 10 T. The Hamiltonian in this system is given by

$$H = -\mu \cdot \mathbf{H} = -\gamma \mathbf{H} \cdot \mathbf{S} \,, \tag{1}$$

where $\mu = \gamma \mathbf{S}$ is the magnetic moment of the nucleus, γ is the so called gyromagnetic ratio, and $\mathbf{H}$ is the applied magnetic field. Since $\mathbf{S}$ has units of angular momentum, or $\hbar$, we know that the gyromagnetic ratio must have units of radians/(s·T). Let us now take this static field to be along z, $\mathbf{H} = H_0 \hat{z}$, making our Hamiltonian

$$H = -\gamma H_0 S_z \,.$$

Ehrenfest's theorem states that

$$\frac{d\langle O\rangle}{dt} = \frac{1}{i\hbar}\langle [O,H]\rangle + \left\langle \frac{\partial O}{\partial t}\right\rangle \,, \tag{2}$$

where O is any operator, $\langle O\rangle$ is the expectation value for that operator, and H is the Hamiltonian. Using this theorem, show that

$$\frac{d\langle S_x\rangle}{dt} = \gamma H_0 \langle S_y\rangle$$
$$\frac{d\langle S_y\rangle}{dt} = -\gamma H_0 \langle S_x\rangle$$
$$\frac{d\langle S_z\rangle}{dt} = 0 \,,$$

which, in concise form is

$$\frac{d\langle \mathbf{S}\rangle}{dt} = \gamma \langle \mathbf{S} \times \mathbf{H}\rangle \,. \tag{3}$$

Hint: use the fact that

$$[S_x, S_y] = i\hbar S_z \quad [S_z, S_x] = i\hbar S_y \quad [S_y, S_z] = i\hbar S_x \,.$$

Show that the expectation value of this spin wil precess about the magnetic field at a frequency given by $\omega = \gamma H_0$ (the Larmor precession frequency). This is most easily accomplished by taking the derivative of the equation for $\dot{S}_x$ and inserting the equation for $\dot{S}_y$. This yields

$$\frac{d^2 \langle S_x \rangle}{dt^2} + (\gamma H_0)^2 \langle S_x \rangle = 0 \ .$$

This is the equation for the harmonic oscillator, and its frequency is as advertised. Note that S_z is a constant, so if the spin starts off with some angle to the magnetic field, that angle will remain fixed.

Using the NIST website, look up gyromagnetic ratio for the proton (the gyromagnetic ratio is this factor of γ). Be careful with units - generally constants that are in units of 1/(s·T) imply radians/(s·T)! What is the magnetic field that corresponds to a Larmor frequency of 6.4 MHz? What is the Larmor frequency for a magnetic field of 0.4 T?

B. The rotating frame

In NMR, we apply pulses of oscillating magnetic field to the spins in order to tip them. We will now work out these dynamics. We direct the oscillationg magnetic field in a direction perpendicular to $\hat{z}$, the direction of the static magnetic field. Call this direction $\hat{x}$. Assuming this magnetic field is of the form $H_{RF}(t) = H_1 \cos(\omega t)$, write down the full Hamiltonian. Write down the time-dependent Schrödinger equation for this system. Use

$$\psi = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

as your ψ, and write down the two coupled differential equations which goven the motion of the spin up part and the spin down part.

Let us now make a transformation that will make this equation easier to solve - the transformation into the rotating frame. The transformation is as follows:

$$\begin{aligned} c_1^r &= c_1 e^{-i\omega t/2} \\ c_2^r &= c_2 e^{i\omega t/2} \end{aligned}$$

Let us show that this transformation does in fact rotate at the same frequency as the oscillating field. Let's start out with the state

$$|\psi\rangle_R = \frac{1}{\sqrt{2}} \left(|\uparrow\rangle + |\downarrow\rangle \right) \ ,$$

where $c_1^r = c_2^r = 1/\sqrt{2}$. This state is constantly pointing along the $\hat{x}$-axis in the rotating frame. In the lab frame this state is

$$|\psi\rangle_L = \frac{1}{\sqrt{2}} \left(e^{-i\omega t/2} |\uparrow\rangle + e^{i\omega t/2} |\downarrow\rangle \right)$$

Show that the expectation values in the lab frame are given by $\langle S_x \rangle = \cos(\omega t)$ and $\langle S_y \rangle = \sin(\omega t)$. This state clearly rotates with a frequency ω, the frequency of the oscillating field.

Now, apply this transformation to our Schrödinger equation. Note that you should get terms that look like

$$\cos(\omega t) e^{-i\omega t/2} \ .$$

Note that the term above is equal to

$$\frac{1}{2} \left(e^{i\omega t} + e^{-i\omega t}) e^{-i\omega t/2} \right) = \frac{1}{2} \left(e^{i\omega t/2} + e^{-3i\omega t/2} \right) \ .$$

The $e^{i\omega t/2}$ should divide out of the equation. We will neglect the second term, since near resonance ($\omega = \omega_0$), this term oscillates very fast and effectively averages to zero. The result is a small shift in the resonant frequency which we will ignore (see Ramsey, *Molecular Beams*, pg. 122, for more information). Our two equations should now read

$$\begin{aligned} i\dot{c}_1^r(t) &= \frac{1}{2} \left[-(\gamma H_0 - \omega) c_1^r(t) - \gamma H_1 c_2^r(t) \right] \qquad (4) \\ i\dot{c}_2^r(t) &= \frac{1}{2} \left[-\gamma H_1 c_1^r(t) + (\gamma B_0 - \omega) c_2^r(t) \right] \ . \end{aligned}$$

These two equations can be rewritten as

$$i\hbar |\psi\rangle = \frac{\hbar}{2} \left[-(\gamma H_0 - \omega) \sigma_z - \gamma H_1 \sigma_x \right] |\psi\rangle \ ,$$

which, itself can be written as

$$H = -\gamma \mathbf{S} \cdot \left[\left(H_0 - \frac{\omega}{\gamma} \right) \hat{z} + H_1 \hat{x} \right] \ , \qquad (5)$$

which states that my static magnetic field along $\hat{z}$ is reduced by ω/γ. When on resonance ($\omega = \gamma H_0$) the field along $\hat{z}$ dissappears, and now all I have to do is which clearly states that the direction of the perturbation is along $\hat{x}$. Assume that we are on resonance. In the rotating frame, the spin will now precess only about the $\hat{x}$-axis. In our expierment, we pulse (turn on) H_{RF} to rotate the spins around $\hat{x}$. How long should my pulse be in order to rotate the spin 90°? 180°? If I start with my spin aligned along z in the rotating frame and apply H_{RF} to rotate the spin 90°, what axis in the rotating frame do I end up along? This can be shown rigorously and the full quantum states can be computed rather easily - we will do this in the next subsection.

In the experiment, we of course work with a multitude of proton spins, not just one. These proton spin vectors add to create a net magnetization in the sample which is the source of our signal. This net magnetization is stationary in the rotating frame when we are on resonance, but what does it look like in the lab frame? This magnetization is contained within our NMR coil - what does it do to our NMR coil (what does it induce in the coil)? What does the signal look like? Now, imagine that instead of having my spins along $\hat{y}$ in the rotating frame I have my spins along $\hat{x}$ in the rotating frame. What does this signal look like with respect to $\hat{y}$ (rotating frame) signal?

Along the same lines, what can I do to $H_{RF}(t)$ to make it appear along $\hat{y}$ in the rotating frame? Show that this is the case by changing $H_{RF}(t)$ appropriately and rederiving the effective Hamiltonian in the rotating frame. We also apply these pulses. The axis of rotation for any given pulse is usually denoted by a subscript, for example 90°_y rotates a spin 90° about the $\hat{y}$-axis.

C. The Rabi Formula

Although we now have a basic quantitative description of NMR, we will now return to the two level system and derive the Rabi Formula - the formula that describes this rotation about the $\hat{x}$ axis in the most general case. As mentioned before, this is the fundamental equation for all two level problems - from superconducting quantum computing bits (qubits) to neturino mixing.

Return to Eq. 4. Take the derivative of the first equation and insert the second equation into the result. The result should decouple the equations and should leave you with the oscillator equation

$$\ddot{c}_1^r(t) + \left(\frac{\Omega_R}{2}\right)^2 c_1^r(t) = 0 \ ,$$

where

$$\Omega_R = \sqrt{(\gamma B_0 - \omega)^2 + (\gamma B_{RF})^2} \ .$$

The equation for $c_2^r(t)$ is identical.

Clearly the solution to the system is sines and cosines, e.g.

$$\begin{aligned} c_1^r(t) &= \alpha_1 \sin\left(\frac{1}{2}\Omega_R t\right) + \beta_1 \cos\left(\frac{1}{2}\Omega_R t\right) \\ c_2^r(t) &= \alpha_2 \sin\left(\frac{1}{2}\Omega_R t\right) + \beta_2 \cos\left(\frac{1}{2}\Omega_R t\right) \ , \end{aligned}$$

where $\alpha_{1,2}$ and $\beta_{1,2}$ are constants to be determined from the initial conditions. Apply the following initial conditions, $c_1^r(t=0) = 1$ and $c_2^r(t=0) = 0$. Show that the solution in this case is

$$\begin{aligned} c_2^r &= -i\frac{\gamma B_{RF}}{\Omega_R} \sin\left(\frac{1}{2}\Omega_R t\right) \\ c_1^r &= \cos\left(\frac{1}{2}\Omega_R t\right) + i\frac{\gamma B_0 - \omega}{\Omega_R} \sin\left(\frac{1}{2}\Omega_R t\right) \ . \end{aligned}$$

I now start off with my spin up, and apply a pulse that is timed such that

$$\Omega_R t = \frac{\pi}{2} \ .$$

What state do I end up in? What are the expectation values of x and y for this state? Along what axis am I pointed? About which axis did I rotate? This pulse is called a $(\pi/2)_x$ pulse - exactly the pulse that rotates us 90° that we found in the last section. Note that you can derive this transition probability for the general state by taking $c_1(t=0) = c_1^0$ and $c_2(t=0) = c_2^0$.

II. THE EXPERIMENTAL APPARATUS

This experiment uses either an electromagnet which can have its magnetic field tuned or a permanent magnet whose field is $B_0 \approx 0.4$ T $= 4$ kG to generate the static magnetic field. Try not to bring anything large and magnetizable near either of the magnets, as they could fall in. Also, be careful not to bring the hall probe nulling shield **anywhere near the magnet**. Magnetic shields are made of soft magnetic materials that can be easily magnetized. If you magnetize it; you'll have to degauss it.

The basic experimental setup is shown in Fig. 1. A function generator creates the frequency output that will be used both as a reference signal and as the signal that will be shaped into the pulses, amplified and delivered to the probe. The output of the function generator immediately goes into the "phase shifter" which splits the signal into two components, one which is in phase with the original signal and one which is 90° out of phase. This box must be tuned when the frequency is changed (see below for instructions).

Two of the outputs, one in phase and the other 90° shifted, are directed to RF switches which form the pulses. These RF switches are Minicircuits ( ). To open, control input 1 requires -8 V and control input 2 requires 0 V. The are controlled using the computer, which uses the analog outputs to time when the switches are open (pulse on) and when the switches are closed (pulse off). The timing accuracy of the analog outputs, also known as a digital-to-analog converter (DAC), is set by its sampling frequency. The greater the sampling frequency, the

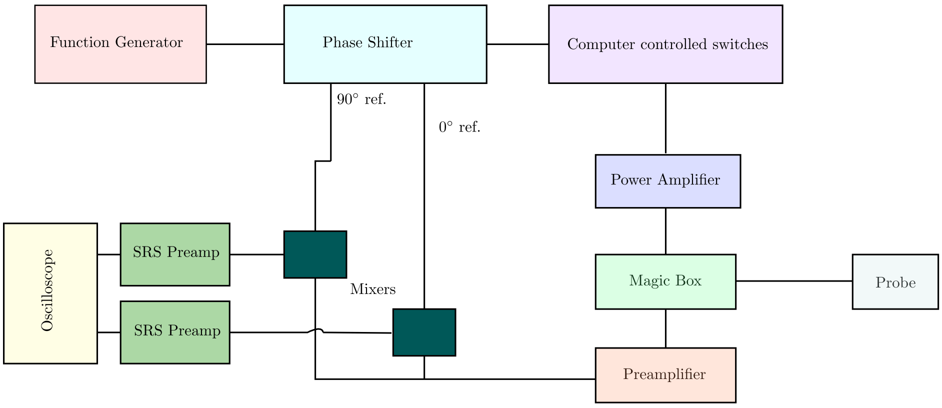

FIG. 1: A simplified schematic of the pNMR experiment at Yale.

greater the timing accuracy.

After the pulses are shaped by the switches, they proceed to an RF amplifier which amplifies the pulses and delivers them to the sample probe. The input of the RF amplifier should be 575 $\mathrm{mV_{RMS}}$ before the attenuator! The pulse proceeds through the so called "magic box" which forces a majority of the pulse energy in the probe. After the pulse has been delivered to the sample, the signal then proceeds out through the "magic box" to the preamplifier and detection circuitry.

The "magic box" works by using some slightly counter-intuitive RF principles. In RF circuits, the approximation that all parts of the circuit connected by a conductor are at the same voltage breaks down. Voltage changes, like any other information, can only travel at the speed of light. The speed at which voltage changes propograte down a coaxial cable is approximately $0.6c$ to $0.7c$, where c is the speed of light in a vacuum. Therefore, with RF circuits, you must consider wave type effects if the length of your circuit is on the order of the wavelength of your signal. The wavelength for a 10 MHz signal is around 20 m (just use $v = \lambda f$.

The predominant wave effect to consider is reflections. Consider a wave which is traveling down a string. If the string is tied to a rope that can hold a cruise ship at dock, the heavier rope will barely move, and most of the wave incident on the interface will be reflected. The best transmission occurs when the mass per unit length of the two ropes is identical. The same goes for RF lines. If the the radio frequency voltage traveling down a line encounters an impedance that does not equal the line, some, and in some cases almost all, of the power will be reflected. The typical impedance of most RF lines if 50 Ω.

One interesting case to consider is when you have a RF line that is equal to $\lambda/4$. In this case, a reflected wave can in general, intefere with the incident wave to create a standing wave on the line. If you solve the equations involved, you find that a $\lambda/4$ line is an "impedance transformer", the input impedance of the line is related to the output impedance by

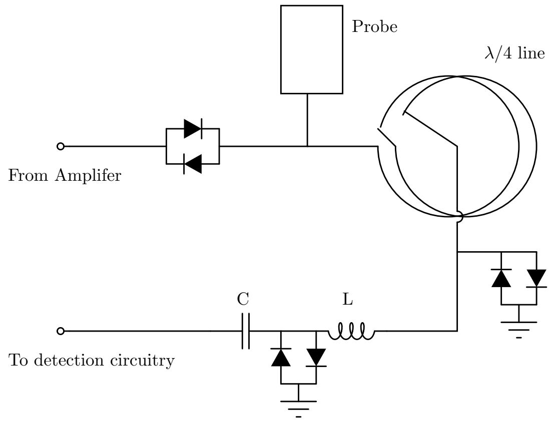

FIG. 2: The circuit diagram for the "magic box".

$$Z_{in} = \frac{Z_0^2}{Z_{out}} \ ,$$

where Z_{out} is the impedance on the far end of the line, Z_{in} is the impedance on the input of the line, and Z_0 is the characteristic impedance of the line, usually 50 Ω. Note that if $Z_{out} = 0$, e.g. the line is shorted at the far end, on the input side it looks like a break!

This is the principle upon which the "magic box" works. The circuit for the box is shown in Fig 2. The large RF signal enters the box and passes easily through the crossed diodes at its input (as these look like they are not even there for large signals). At the far end of the $\lambda/4$ line, there is another pair of crossed diodes. These diodes again look like a short for large signals, but this makes the input of the $\lambda/4$ line look like an open. Therefore, most of the power is directed to the probe. After the pulse, the probe begins to emit a signal, which is very small voltage. The diodes at the pulse input prevent any of these small signals from leaking towards the amplifier and any small noise from the amplifier to leak into the detection circuitry. Since small signals see crossed diodes as an infinite impedance, the small signals travel down the $\lambda/4$ line into a secondary filter.

The secondary filter works to filter out whatever part the pulse leaked through the $\lambda/4$ line. Consider how it works with no diodes present. The inductor and capacitor are tuned such that they are in resonance at the frequency of the pulse and signal. When in resonance, the impedance of the inductor exactly cancels the impedance of the capacitor and the signal passes through unimpeded. However, a large voltage builds up between the inductor and capacitor in this circuit. When the pulse comes, this voltage can be very large, and so the diodes short that voltage to ground, which helps to filter out more of the leaked pulse.

The small signal from the probe travels onward to a preamplifier (minicircuits model) which amplifies the signal and then it is split and fed into mixers where it is mixed with the 0° and 90° reference signals from the phase shifter. A mixer is a simple device which effectively multiplies two signals together. For example, if the reference signal goes as $\cos(\omega t)$ and the signal from the probe goes as $\cos(\omega_0 t)$, then the output signal is

$$\sim \cos(\omega t)\cos(\omega_0 t) = \frac{1}{2}\left[\cos((\omega-\omega_0)t)+\cos((\omega+\omega_0)t)\right] \ .$$

This output is then passed into SRS SR560 preamplifier/filter units which amplify the signal more and filter out the very fast $\omega+\omega_0$ signal (which typically oscillates at frequencies greater than 10 MHz, depending on the magnet which you are using).

Note that these mixers place us **in the rotating frame**. If we are detuned, we will see the spins moving in the rotating frame, rotating at a frequency given by $\omega-\omega_0$. Note also that because we have both 0° and 90° reference signals, we can detect along **two, orthogonal axes** in the rotating frame. This gives us not just information about the magnitude of the magnetization, but also its direction in the $\hat{x}-\hat{y}$ plane in the rotating frame.

The signals are read out on a Tektronics TDS3016B oscilliscope, which can transfer data to the computer using an antiquated communication protocol called GPIB. You can use either MATLAB or OpenChoice Desktop to download the data from the oscilliscope, although MATLAB is recommended.

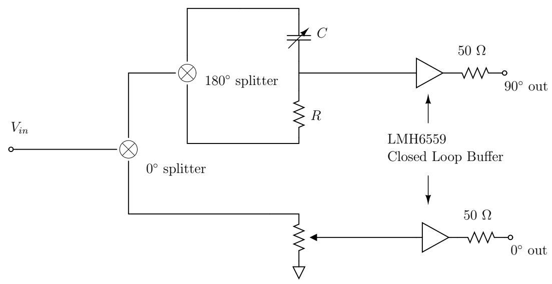

FIG. 3: The circuit diagram of the phase shifter.

A. Things that require optimization

Many of the circuits in this experiment require that they be tuned to 50 Ω, or in the parlence of the RF engineers, the circuits must be **impedance matched**. In RF electronics, tuning something to be 50 Ω is rather straightforward. If the impedance of any particular circuit is not 50 Ω, waves will be reflected from its input. Using a device called a directional coupler, you can view only the reflected waves. A directional coupler takes waves traveling from the "in" port to the "out" port and couples a certain fraction of these waves' power to the "coupled" port. You can place this device at the input of any circuit or component, drive a voltage into that circuit and use the coupler to see if there are any reflected waves. By driving these reflected waves to zero, you can ensure that any circuit or component has a 50 Ω impedance.

There are several things which the student can tune and, in some cases, must tune for proper operation of the experiment. This list appears in no particular order.

1. The phase shifter must be tuned to operate at the particular frequency at which the experiment is being run. The circuit that does the phase shifting is shown in Fig 3. Upon entering the circuit, the signal is split into two components. The first component is split again by a 180° splitter, e.g. the 2 outputs of that splitter are 180° out of phase. These two, inverted components then travel through a resistor and a capacitor, respectively. If the impedance of the capacitor ($1/j\omega C$) is equal to that of the resistor R, the output is 90° phase shifted. The other output of the first power splitter goes to a potenitometer, which allows you to tune the voltage output. The potenitometer and the 90° phase shifted wave are then fed into closed

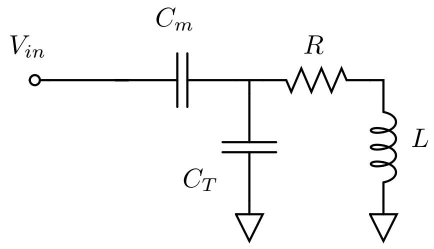

FIG. 4: The probe circuit. C_T and C_m are tunable capacitors.

loop buffer which drive the outputs of the box. Two outputs are used for reference signals, two outputs are used to deliver the pulses.

To tune the circuit, hook up the reference outputs to the oscilliscope and first tune the capacitor to make the two outputs 90° out of phase. **Make sure the input impedance of the oscilloscope is set to** 50 Ω. The oscilloscope can automatically measure the phase for you. After the phase is tuned, tune the potentiometer to bring the two signals to the same amplitude. Once this is complete, tune the function generator's output amplitude such that the RMS output voltage of **both** channels reads 575 mV. Much higher than this and the power amplifier that amplifies the pulses will saturate. Too much less, and you won't deliver as much power to the sample during the pulse.

2. The magic box must also be tuned. The primary thing to ensure is that for the frequency you are operating, the $\lambda/4$ wire is the correctly connected. There are 3 $\lambda/4$ cables in the lab, 6.4 MHz, 17 MHz (the delay box), and 10.7 MHz (generally unused). You can also tune the filter in the box be disconnecting all the diodes from ground, capping the output of the filter with a 50 Ω impedance and tune the capacitor until you see no reflections (e.g. the impedance appears to be 50 Ω at the source).

3. The probe must also be tuned such that it resonates at the desired frequency and has the standard characteristic impedance of 50 Ω. The circuit diagram for the probe is shown if Fig. 4. The details of the circuit derivation for this can be found in the MIT NMR document, Appendix A. The key here is that C_T (which is generally much larger than C_m) is used to get the circuit to resonate at the desired frequency,

$$\omega = \frac{1}{\sqrt{LC_T}}$$

where L is the known inductance of the NMR coil. R is some parasitic resistance that will accompany any probe. C_m is then used to transform the full impedance to 50 Ω.

To tune, one first should calculate the value of C_T and C_m that are requires to make the circuit work. Again, see the MIT NMR document for the details and equations. After the capacitors are chosen properly, one tunes the C_T capacitor until it resonates with the NMR probe. This will cause a huge drop in the reflected wave at the input of the probe. Then, changing C_m slightly, you can then retune C_T to once again find where the reflected wave is minimized.

A word of caution - the probes generally have very high Q's or "quality factors". What this means is they resonante very well at one frequency, say 6.4 MHz. With a Q of 200, if you move the frequency to 6.4 MHz + $\frac{1}{2}$6.4 MHz/200 = 6.416 MHz, the reflected wave from the probe will go from zero (perfectly tuned) to half of the total input power. Tuning the probe a mere 0.016 MHz will cause you to loose half the power you are applying to the sample! Because the time that you have to apply a pulse depends on the strength of that pulse, weakening the pulse in this way will require you to apply the pulse for a greater amount of time. We'll discuss more about the practical limits on how long you can make a pulse in the next section.

III. RELAXATION, DECAY, AND LINEWIDTH

Once the experiment is tuned and ready, you should be able to apply pulses to your sample and see signal from the protons. However, once you tip the spins such that they have some projection in the $\hat{x} - \hat{y}$ plane, the net magnetization (the vector some of all the proton's magnetic moments) of the sample does not just stick around forever. In fact, it tends to decay to zero through several mechanisms:

1. The field of the magnet is not perfectly uniform so that the protons in different parts of the sample precess at slightly different frequencies and get out of phase with one another, thereby gradually decreasing the net magnetization of the sample. This effect, although physically the least interesting, is always the dominant effect. The characteristic time of this decay is called T_2^*.

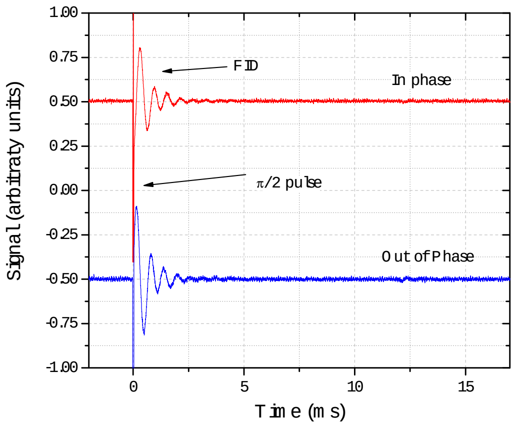

FIG. 5: An example of an free induction decay. The rotating frame is slightly detuned from resonance, e.g. $\omega \neq \omega_0$. The frequency of the beating in the decay is the difference frequency between the frequency of the rotating frame and the Larmor precession frequency. The exponential envolope is the result of the static field gradients, and is characterized by T_2^*.

2. Since each of the spins is in a slightly different environment, each spin is subjected to slightly different magnetic forces primarily through dipole-dipole interactions. These small perturbations work to dephase the sample on a time scale that is generally called T_2.

3. Gradually, through collisions and electromagnetic interactions, the energy imparted to the sample is lost to the environment, which returns the state to thermal equilibrium. The characteristic time for this to occur is called T_1, and can vary greatly from sample to sample.

Because of the relaxation mechanisms, what you actually see after a $\pi/2$ pulse may look like Fig. 5. This decay immediately after a $\pi/2$ pulse is called the free induction decay (FID). What you should notice is the magnetization of the sample is now in the $\hat{x}$-$\hat{y}$ plane where it can be detected. If you tune the frequency of the rotating frame (ω) such that it is different from the Larmor precession frequency (ω_0), you should be able to see this decay oscillate at the difference frequency ($|\omega - \omega_0|$, as seen if Fig. 5). The exponential envolope is characterized by a relaxation time T_2^*. When you are on resonance, you should be able to see only this exponential decay. Again, the decay here is caused by the dephasing of the spins due to inhomogeneity of the static magnetic field.

The Fourier transform of the FID is typically a Lorentzian (as the Fourier transform of any exponential decay is a Lorentzian). In frequency space, the full-width, half-max of this Lorentzian is the so called "linewidth". It is a measure of how wide the frequency spectrum of the protons are. In other words, the line shape tells you what the distribution of precesion frequencies of the protons are in the sample. Therefore, by doing pulses and acquiring just the time-dependent data are able to get the frequency spectrum of our sample as well.

Using the FID, one should be able to tune the optimal pulse times for the experiment. Before applying multiple pulses, one should figure out what is the optimal time for a $\pi/2$ pulse and a π pulse. The size of the FID should reach a maximum at a $\pi/2$ pulse, as the spins have now been tipped into the $\hat{x} - \hat{y}$ plane where they can be most efficiently detected. The FID should go to zero after a π pulse and back to a the maximum magnitude, but opposite sign at a $3\pi/2$ pulse. Mapping out how the FID changes with respect to pulse time is called a nutation curve. Finding the nutation curve and optimizing your pulse to be a $\pi/2$ or a π pulse is good practice before beginning any more complicated experiments.

The time for a 360° pulse (T_{360}) and the linewidth (or T_2^*) are important numbers to compare. If the case of $T_{360} \ll T_2^*$, the pulse takes so long to tip the spins that the phase coherence is lost long before the spin arrive in the $\hat{x} - \hat{y}$ plane. In addition, since the linewidth is wide compared to the pulse strength, some of the spins are on resonance with the pulse, but most are not in this limit. Likewise, in the limit of $T_{360} \gg T_2^*$, the pulse is nearly instantaneous compared to the time that it takes for the spins to decohere. This limit is called the "strong pulse" limit; the opposite pulse limit is called (not surprisingly) the "weak pulse" limit. So the practical upper limit on T_{360} for pulsed NMR experiments is T_2^*, ensuring that you maintain coherence throughout the multiple pulse experiment.

IV. SPIN ECHOS

One can counteract the effect of the dephasing due to the field by creating a spin echo, a schematic diagram of which is shown in Fig. 6. To see how one forms this, consider what happens in the resonant ($\omega = \omega_0$) case in the $\hat{x}$-$\hat{y}$ rotating frame. Although we are on resonance, some of the spins have a precssion frequency less than that of the ensemble average (colored blue in Fig 6) and some a have a precession frequency greater than that of the ensemble average (colored red in Fig. 6). After a $(\pi/2)_x$ pulse, all the spins end up along $\hat{y}$ (frame (a) in Fig. 6). As time elapses, the spins begin to dephase as the

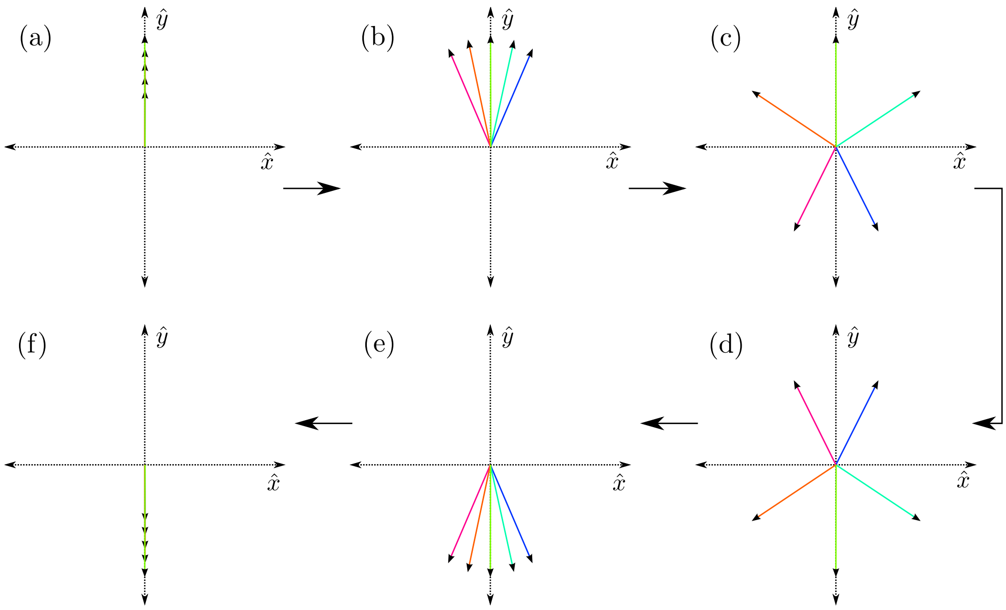

FIG. 6: Example of how a spin echo forms. Spins that are colored blue have a Larmor precession frequency that is smaller than the ensemble average Larmor precession frequency (ω_0). They move clockwise in this example. Spins that have a faster precession frequency (colored red) move counterclockwise in this example. Time flows in the direction of the arrows. A π pulse is delivered to bring the spins from (c) to (d). See the text for further information.

spins that move faster move clockwise away from $\hat{y}$ and the spins that move slower move counter . The spins with precession frequency greater than the average resonant frequency begin to fall move in front of the $\hat{y}$ axis (frame (b)). As this happens the net magnetization along $\hat{y}$ decreases - this is the FID. After enough time has elapsed, the spins find themselves distributed throughout the $\hat{x}$-$\hat{y}$ plane (frame (c)). If I then apply a $(\pi)_x$ pulse, the spins each rotate around the $\hat{x}$ axis by 180° ending up in the state shown in frame (d). Note that both the faster and slower spins will now move toward the $-\hat{y}$ axis as shown in frame (e). The time between the $(\pi/2)_x$ pulse and the $(\pi)_x$ pulse later they would rephase along $-\hat{y}$ frame (f). At this point, there is a large net magnetization in the $-\hat{y}$ direction and the echo is formed.

Another type of echo which is hard to depict is the $(\pi/2)_x - \tau - (\pi/2)_y$ echo. In this echo sequence, the distribution of the spins in the $\hat{x}$-$\hat{y}$ are kicked up out the plane. They recohere along $+\hat{y}$ in a pattern that resembles a figure 8. The expected echo height is 1/2 that of the original FID if T_2 and T_1 effects are neglected.

An example of such an echo is shown in Fig. 7. Although the scan was taken slightly off resonance, you can clearly see the effect of the spins recohering at 10 ms. This spin echo is a powerful tool, because it now lets us examine more about the spins themselves, disentangling the effects of the field from

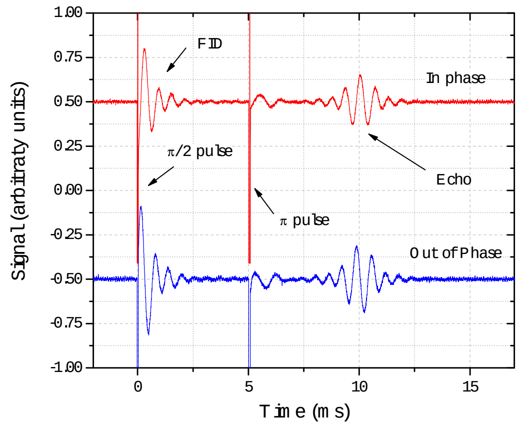

FIG. 7: An example of an spin echo. The rotating frame is slightly detuned from resonance, e.g. $\omega \neq \omega_0$. The frequency of the beating in the decay is the difference frequency between the frequency of the rotating frame and the Larmor precession frequency. Note that echo appears at exactly the same time after the π pulse as the π pulse is seperated from the $\pi/2$ pulse.

the T_2 and T_1 from the effects of the inhomogenous static magnetic field. In fact, to measure T_1 and T_2 one must use spin echos.

A. Measurement of T_2

One can use this simple $\pi/2 - \tau - \pi$ pulse sequence to measure T_2. In principle is the wait time between the two pulses is zero, then the combined pulses should be a $3\pi/2$ pulse, which should create as a strong of an FID as a $\pi/2$ pulse, excpeted pointed in the opposite direction in the $\hat{x}$-$\hat{y}$ plane. As you increase τ, the wait time between the two pulses, you give the spins more time to dechoere due to spin-spin interactions. The result is that the echo beccomes smaller and smaller as τ is increased. Since spin-spin interactions are the primary cause of this decoherence, measuring the pulse height as a function of τ will show an exponential decay like $e^{-\tau/T_2}$.

One can improve this mesaurement by repeating the π pulse multiple times. By doing $\pi/2$ - τ - π - 2τ - π - 2τ ...., you can make the spins recohere multiple times along the $-\hat{y}$ and $\hat{y}$ axis respectively. The subsequent echos in the series will grow smaller and smaller due to this spin-spin decoherence, and the height of each echo will follow an exponential decay as before. Because with each π pulse one rotates around the $\hat{x}$ axis, the pulses switch between negative and positive after every pulse. This method is called the Carl-Purcell (CP) method.

The CP method can be improved by applying not $(\pi)_x$ pulses as we have been but $(\pi)_y$ pulses instead. Using $(\pi)_y$ pulses, the magnetization will always recohere along $+\hat{y}$. Thus, all the echos will be along the same direction, making analysis significantly easier. This modified method is called CPMG.

B. Measurement of T_1

One can also use spin echos to measure T_1. One method is to apply a π pulse initially, which tips most of the spins to tip from $+\hat{z}$ to $-\hat{z}$. If at the end of the π pulse you were then to immediately apply a $\pi/2$ pulse, you have a a $3\pi/2$ pulse with its large FID again in the opposite direction of the FID of a $\pi/2$ pulse. However, if you were to wait a time τ between the π pulse and the $\pi/2$ pulse, some of the spins would fall back to $+\hat{z}$ direction as the exchange energy with the environment and fall back into thermal equilibrium. As this happens the size of the FID decreases, eventually goes to zero (when exactly half the spins have fallen back to $+\hat{z}$) and then switches sign and grows to a regular $\pi/2$ pulse FID as $\tau \to \infty$ and all the spins fall back into thermal equilibrium. Therefore, measuring the height of the FID as a function of the wait time between the two pulses should show an exponential dependence that looks something like $(2e^{-\tau/T_1} - 1)$.

Of course, seperating the ring-down of the pulse from the FID can, in principle, be very difficult. So this method can be improved by simply adding a π pulse that occurs a fixed time after the $\pi/2$ pulse. By measuring the echo, you can generally get a cleaner measurement, and by keeping the time between the last $\pi/2$ pulse and π pulse fixed, you can eliminate T_2 effects.

Another interesting way to measure T_1 is to blast the spins with a series of pulses that effectively randomize the distribution of the spins around the Bloch sphere. After delivering this series of random pulses, you then wait some time τ for the spins to come back to thermal equilibrium, e.g. to point along the $+\hat{z}$ axis again. After τ you can then apply a $\pi/2$ and π pulse to try to measure an echo. If none of the spins have yet to return to the $+\hat{z}$ axis, there will be no echo; if they have all returned, the echo will be the strongest available. By varying τ, the time between the randomizing pulses and the $\pi/2-\pi$ echo sequence and recording the echo height, you can measure T_1.

V. SUMMARY OF RELAXATION - TIMESCALES

These relaxation methods set the appropriate time scales in the system, which are shown schematically in Fig. 8. T_2^* sets the timescale for which the signal disappears after a $\pi/2$ pulse. As we saw in Section III, T_2^* also sets a practical upper limit on the duration of our pulses. Pulses that are on the order of T_2^* or longer will have significant dephasing during the pulse, leaving our final state not at all pure. T_2 sets the scale for how long we can recohere the signal using echos. This basically sets the scale for how long an experiment can last, an experiment being defined as a sequence of pulses. Once your experiment is concluded, you **must still wait** a few T_1's before applying another sequence of pulses to ensure that you begin each pulse sequence in the same state, namely the spins aligned with the $\hat{z}$ axis.

In liquid NMR, $T_2 \sim T_1$, so once your signal disappears you can generally assume that the sample has reobtained thermal equilibrium. However, *this is definitely not always the case.* For example, in solids, T_2 and T_1 can differ by several orders of magnitude. You may no longer see echos with a CPMG pulse sequence after only 1 ms (T_2), but you may still have to wait 10 s (T_1) before you apply another CPMG sequence. If you increase the viscocity of your liquid, you should expect the ratio T_2/T_1 to move from being approximately one to much much less than one.

I cannot overemphasize this - you must wait several T_1 before repeating the experiment! In this

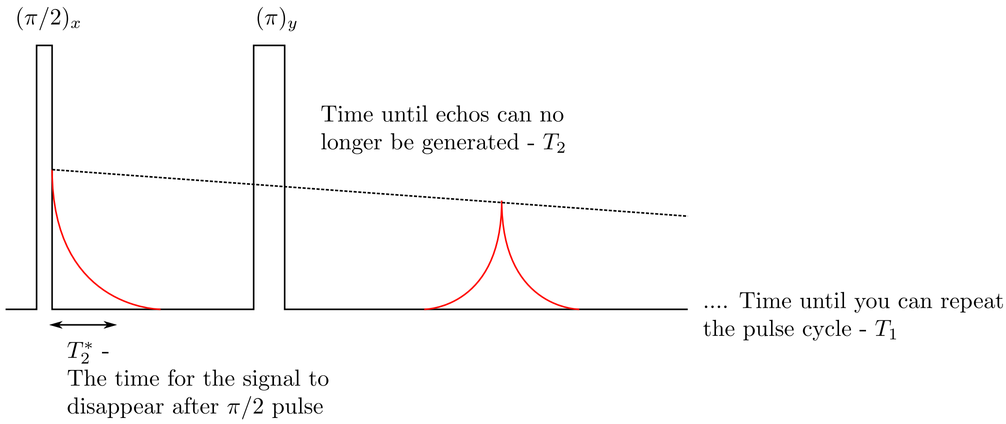

FIG. 8: The relative timescales in the system (see text for further explanation)

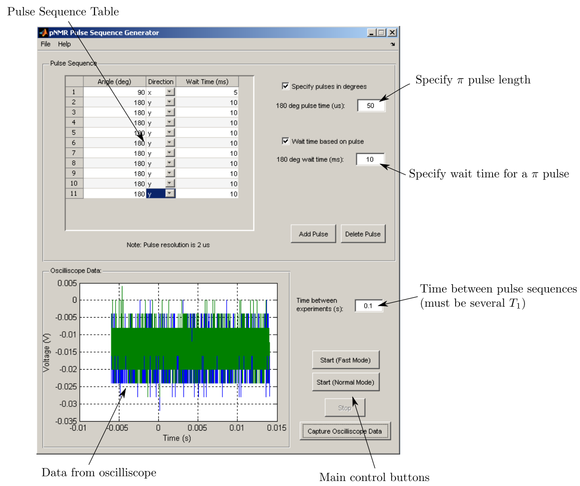

FIG. 9: `pNMRcontrol` software used in the pNMR lab.

lab, you will envariably average the results of several pulse sequences together to get your final data. If you do not wait several T_1 between pulse sequences, the second time you apply your pulse sequence you will be starting off in a state which is not the same as the first pulse sequence - and hence the results will be different and cannot be averaged!

VI. OPERATING THE SOFTWARE

MATLAB software was created to generate the pulse sequences. After opening MATLAB, run **pNMRcontrol** (You must first log into the computer, the password is **ErnestJoyce**). This will bring up the program shown in Fig. 9. On the top panel, you can edit the pulse sequence. The bottom panel shows any data that may have been captured from the oscilliscope. Lastly, the primary control buttons allow you to output and stop the pulses along with capturing data from the oscilliscope.

To generate a pulse sequence, you first must specify what individual pulses make up your pulse sequence. Using the "add" and "delete" buttons, you can change the number of pulses in your pulse sequence. For any particular pulse, you can specify the direction and length of the pulse. If you know how long a pulse must be applied in order to tip the spin 180°, you can check the box labeled "Specify pulses in degrees" and enter how long (in mircoseconds) a pulse needs to be applied to get a 180° rotation. Otherwise, you can specify the pulse length in microseconds. Be aware, however, that the resolution of the pulses is only 2 microseconds.

You must also specify the time to wait after that pulse before applying the next pulse. This is the pulse wait time, specified in milliseconds. You can specify each pulse's wait time individually using the third column in the table or you can have the program automatically determine this time based on the type of pulse. To do this, simply check the "Wait time based on pulse" box and specify the time to wait after a 180° pulse. If the pulse is 90°, the program will automatically wait half that time. If the pulse is 360°, the program will wait twice this specified time.

You must also specify how long the program will wait before applying the given pulse sequence. This is specified in the box "Time between experiments (s)". The units of this is seconds.

After creating a pulse sequence, you can start applying it to the sample by pressing one of the start buttons. Starting the program in normal mode will allow you to edit the pulse sequence while the program is running. However, the program will take at least 0.5 s before repeating the pulse sequence. If, on the other hand, you want the experiment to be repeated faster, you can start the program in "Fast

Mode". In this mode, you cannot edit the pulse sequence, but the amount of time that you specify between pulse sequneces in the "Time between experiments" box will be rigorously obeyed - if you want only 100 ms between pulse sequences, there will be only 100 ms between pulse sequences. Press "Stop" at any point to stop the pulse sequence from being applied.

You can save the data and pulse sequences at any time using the File menu of the program. Loading a saved pulse sequence can also be accessed using the "File" menu.

VII. QUESTIONS TO INVESTIGATE

Once you understand the fundamentals, there are many experiments to work on with this setup. You can choose one or more from this list to investigate:

1. T_2 is strongly dependent on the magnetic environment that each of the spins is in. One could look at what happens as you change that environment. For example, doping small amounts of glycerin in with water can increase the viscosity of the sample. How does greter viscosity effect T_2?

2. T_1 is dependent on what dissipative mechanisms exist for the nuclei to loose the energy imparted to them and return to thermal equilibrium. A standard way to decrease T_1 in water is to dope in $CuSO_4$, copper sulfate. The sulfate doesn't really matter, it just makes the compound soluble. What is special about Cu? Try measuring T_1 as a function of $CuSO_4$ doping. How much copper do you need to add to really have an effect on T_1? *Warning* - the T_1 of distilled water can be as high as 10 s!

3. How do T_2 and T_1 depend on the strength of the static magnetic field?

4. How does sample size effect T_2^* and why?

5. Is the model of field gradients an accurate one for T_2^*? Devise a way to measure the gradients and compare that to the predicted value of the gradients for T_2^*.

6. The static magnetic field is not the only field which gradient has an effect. H_1, the applied RF field has a gradient as well. By reducing the size of the sample relative to the NMR coil, you can minimize the effect of this gradient. What does this do to the nutation curve? What does this do for the quality of multiple pulse sequences like CP and CPMG.
7. The strong pulse limit, $\gamma H_1 \gg 1/T_2^*$ is a good limit to be in for multiple pulse sequences like CP or CPMG. What happens to the quality of the echos in this pulse sequence when you approach the limit where $\gamma H_1 \approx 1/T_2^*$? What happens in the limit $\gamma H_1 \ll 1/T_2^*$?

8. Do all three T_2 meamsurements - simple Hann echo, CP, CPMG - yield the same result for T_2? Why or why not?

Appendix A: Extra probe impedances at relavent frequencies

Table I contains information regarding the impedances of the coils that have been made for the NMR experiment. Some of these coils are no longer in use, some are made for larger samples, some just have significant differences. If switching our a probe, please consult this table before tuning.

Probe	17 MHz	6.4 MHz
#1	$L_s = 586$ nH, $R_s = 0.09\ \Omega$	$L_s = 562$ nH, $R_s = 0.05\ \Omega$
#2	$L_s = 907$ nH, $R_s = 0.25\ \Omega$	$L_s = 837$ nH, $R_s = 0.003\ \Omega$
#3 (curr perm)	$L_s = 384$ nH, $R_s = 0.034\ \Omega$	$L_s = 375$ nH, $R_s = 0.042\ \Omega$
#4 (curr EM)	no measurement	$L_s = 582$ nH, $R_s = 0.044\ \Omega$

TABLE I: Impedances of extra NMR coils in case they are to be used.