

# Pulsed Nuclear Magnetic Resonance

## 1 Purpose

To become familiar with NMR principles and techniques.

## 2 Introduction

Nuclear Magnetic Resonance is a quantum mechanical effect which has been well-studied in physics and has been put to extensive use in chemistry, and more recently in medicine as MRI (many people are scared of the word “nuclear”). Many nuclei, notably the proton, have spin angular momentum, and these magnetic moments will tend to align with an applied DC field. With a pulse of radio frequency (RF) magnetic field, the net magnetization can be rotated to an arbitrary angle, from where it will decay back to equilibrium. The timescales for growth toward equilibrium (parallel to the field) and decay of the transverse component of the magnetization are in general quite different, and can provide information about the nuclei’s environments.

Despite the fact that NMR is a quantum phenomenon, we recognize that most students in Physics 352 do not have the quantum background necessary to fully understand the derivation of NMR. A classical picture can be used to convince you of many of the effects you will observe, but keep in mind that they are the wrong way of looking at NMR. As long as you don’t think too hard about what’s going on or attempt to predict behaviour that isn’t mentioned, classical mechanics should be perfectly adequate. As an example of what can go wrong, the first sentence of the Theory section seems perfectly reasonable until you look up the radius of a proton or electron and compare the required speed with the speed of light. A short Appendix (section 11) is provided with a simplified quantum mechanical derivation of some of the main results.

### 3 Theory

Classically, nuclei with spin act like spinning charged spheres – you can convince yourself that these have both angular momentum and a magnetic moment. In this experiment, we will only concern ourselves with the hydrogen nucleus (a proton). The proton will have a magnetic moment  $\vec{\mu}$  and angular momentum  $\vec{J}$ , related by

$$\vec{\mu} = \gamma \vec{J} \quad (1)$$

where  $\gamma$  is called the gyromagnetic ratio (use caution when reading the references – the meaning of this term is highly source-dependent).  $\vec{J}$  is quantized in units of  $\hbar$ ,  $\vec{J} = \hbar \vec{I}$ , where  $\vec{I}$  is the nuclear spin.

The magnetic energy  $U$  of the nucleus in an applied  $\vec{B}$  field is

$$U = -\vec{\mu} \cdot \vec{B} \quad (2)$$

The direction of the applied field  $\vec{B}_o$  is taken to be the  $\hat{z}$  direction, so

$$U = -\mu_z B_o = -\gamma \hbar I_z B_o \quad (3)$$

The allowed values of  $I_z$ ,  $m_I$ , are quantized as  $m_I = I, I - 1, \dots, -I$ . Since the proton has spin one-half ( $I = \frac{1}{2}$ ), the allowed values of  $I_z$  are  $m_I = \pm \frac{1}{2}$ , so there are only two magnetic states. These are shown in figure 1. A key tenet of quantum mechanics is that energy and

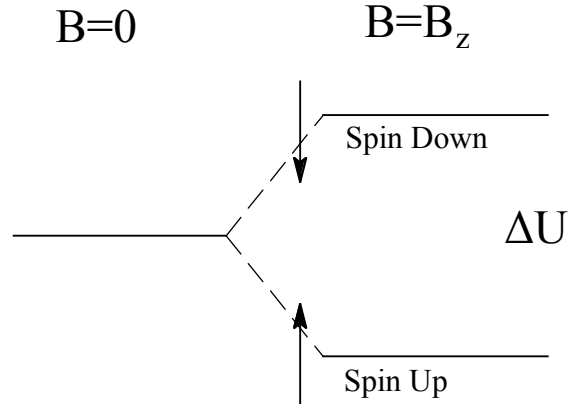


Figure 1: A proton's spin states.

frequency are proportional, with the constant of proportionality being Planck's constant, so the energy difference (splitting) between the two states may be written as an angular frequency:

$$\Delta U = 2 \left( \gamma \hbar \frac{1}{2} B_o \right) = \hbar \omega_o \quad (4)$$

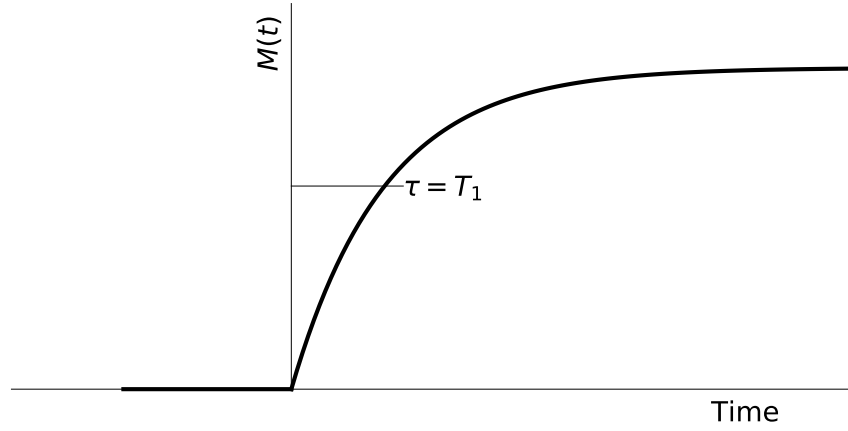


Figure 2: Exponential growth of the magnetization toward its equilibrium value.

So the resonant frequency  $\omega_o = \gamma B_o$ . For the proton,  $\gamma = 2.675 \times 10^8 \frac{\text{rad}}{\text{s} \cdot \text{T}}$ , or

$$f_o = 42.58 \frac{\text{MHz}}{\text{T}} B_o \quad (5)$$

Since we're working at non-zero temperature, the lower and higher energy states' populations ( $N_1$  and  $N_2$  respectively) will be governed by Boltzmann statistics:

$$\frac{N_2}{N_1} = e^{-\frac{\Delta U}{k_B T}} = e^{-\frac{\hbar \omega_o}{k_B T}} \quad (6)$$

giving the net magnetization

$$M_z = (N_1 - N_2) \mu_z = N \mu \tanh\left(\frac{\mu B}{k_B T}\right) \approx N \frac{\mu^2 B}{k_B T} \quad (7)$$

## 4 Spin-Lattice Relaxation Time

This equilibrium magnetization doesn't just appear;  $M_z$  grows exponentially toward equilibrium when placed in a magnetic field or displaced from equilibrium (see figure 2). The time constant governing this growth is called  $T_1$ , the spin-lattice relaxation time.

$$\frac{dM_z(t)}{dt} = \frac{M_o - M_z(t)}{T_1} \quad (8)$$

If an *unmagnetized* sample is placed in a magnetic field ( $M_z(0) = 0$ ), then direct integration of equation 8, with *these* initial conditions, gives

$$M_z(t) = M_o \left(1 - e^{-\frac{t}{T_1}}\right) \quad (9)$$

This is absolutely **NOT** what you will be dealing with in this experiment – you will have different initial conditions!

$T_1$  values can vary from microseconds to seconds for solid and liquid samples, and can be several weeks for some gas samples ( $^3\text{He}$  for example). If a particle finds itself in the higher-energy state when the field is turned on, it will be inclined to decay to the lower-energy state. In doing so, it must change not only its energy but also its angular momentum, and both the energy and angular momentum must be transferred out of the system, either through collisions or radiation. In order for it to decay in the first place, it requires an interaction of some sort (usually a collision), since the initial and final states are both eigenstates, and their orthogonality prohibits transitions under normal circumstances. The great variation in  $T_1$  is therefore due to the frequency and effectiveness of interactions between particles and their surroundings (the “lattice”, whether or not it actually is a lattice) at producing a transition and removing energy and angular momentum. The study of these processes is one of the major topics in NMR research.

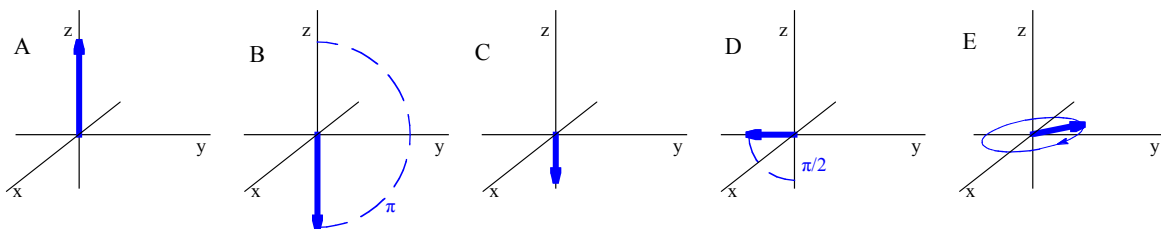


Figure 3: Measuring  $T_1$ : **a)** The initial magnetization is  $M_o\hat{z}$ . **b)** A  $\pi$  pulse is used to invert the magnetization to  $-M_o\hat{z}$ . **c)**  $M_z$  decays back toward equilibrium until  $t = \tau$ . . . **d)** when a  $\frac{\pi}{2}$  pulse is used to rotate the magnetization into the  $xy$  plane. . . **e)** where it precesses briefly, and can be measured, before it vanishes again. In these figures,  $\vec{B} = B_o\hat{z}$ .

In practice,  $T_1$  is measured using a sequence of two pulses of radio frequency radiation (RF). A  $\pi$  pulse is used to invert the magnetization, then after a delay of  $\tau$ , a  $\frac{\pi}{2}$  pulse rotates whatever magnetization there may be into the  $xy$  plane where it can be measured (see figure 3). How and why the magnetization can be rotated is described in section 6, and why it's measured in the  $xy$  plane is described in section 7.

## 5 Spin-Spin Relaxation Time

In thermal equilibrium, there is no magnetization in the  $xy$  plane, since angular momentum can only be known about one axis at a time. This can also be justified classically: The

torque  $\vec{\tau}$  on each is  $\vec{\mu} \times \vec{B}$ , but  $\vec{\tau} = \frac{d\vec{J}}{dt}$  and  $\vec{J} = \frac{\vec{\mu}}{\gamma}$  from equation 1, so

$$\vec{\mu} \times \vec{B} = \frac{1}{\gamma} \frac{d\vec{\mu}}{dt} \quad (10)$$

or, for the whole sample,

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B} \quad (11)$$

It can be shown from equation 11 that the magnetic moment will precess, with the precessional frequency  $\omega_o = \gamma B_o$  first seen in equation 4. Since the particles in the sample started out with random phases, they will continue summing to zero.

What would happen, though, if we started out with the magnetic moments rotating in phase in the  $xy$  plane? This situation is a combination of spin-up and spin-down states, and will decay exponentially with time constant  $T_2$ , the spin-spin relaxation time:

$$\frac{dM_{xy}}{dt} = -\frac{M_{xy}(t)}{T_2} \quad (12)$$

As the name suggests, this decay is due not only to the  $T_1$  processes, but also to the spins' magnetic moments interacting with each other. Each spin sees not only the large applied field  $\vec{B}_o$ , but the small fields from its neighbours. This means that different protons see different fields depending on their neighbours, and there is actually a range of precessional frequencies. Even if the spins started out in phase, they soon have random phases, and the rotating  $xy$  magnetization goes to zero.  $T_2$ , then, provides information on the distribution of local fields at the nuclear sites.

The sensible way to find  $T_2$  would seem to be flipping the equilibrium  $M_z$  into the  $xy$  plane and watching it decay. This is called the Free Induction Decay (FID). Unfortunately, the magnet in the lab has its own field inhomogeneities, such that the "sweet spot" in the middle allows a maximum 0.3ms decay time. If  $T_2 \lesssim 0.3\text{ms}$ , this isn't a problem, but most samples require an additional trick.

The spin-echo technique allows the measurement of any  $T_2$ , without the necessity of buying a better and more expensive magnet. If we first rotate the magnetization from  $\hat{z}$  into the  $xy$  plane, then rotate by a further  $\pi$  a time  $\tau$  later, the dephasing due to the magnet's inhomogeneity is reversed, and the spins rephase a further time  $\tau$  after that, for another FID. This works like the following egalitarian kindergarten footrace: Each kid runs in a straight line as fast as he or she can until the teacher blows a whistle, at which point the kids run back. The faster kids go farther, and must return a greater distance, so all return at the same time. The whistle in this case is the  $\pi$  rotation. The spins in larger fields precess faster by  $\Delta\theta(t)$  until  $t = \tau$ , at which point the magnetization is flipped  $\pi$ , and their headstart becomes an impediment. At  $t = 2\tau$ , the  $\Delta\theta$  from  $t = \tau$  to  $2\tau$  has completely cancelled the opposite  $\Delta\theta$  from  $t=0$  to  $\tau$ , and all spins are back in phase. The spin-spin interactions can't

be reversed in this manner, so the echo's height will be lower than the original FID, due to these  $T_2$  processes. A plot of echo height vs. delay time is a graph of the  $T_2$  decay with the magnet's inhomogeneity cancelled out.

## 6 Rotating $\vec{M}$ by $\pi$ or $\frac{\pi}{2}$

An RF magnetic field at  $\omega_o$  will rotate the magnetization, with the length of the pulse determining the angle. The quantum mechanical explanation is contained within the appendix (section 11). What follows is the classical explanation, using rotating co-ordinate frames.

If we add to our DC field a rotating (circularly polarized) field  $\vec{B}_1$ , our total field is

$$\vec{B}(t) = B_1 \cos \omega t \hat{x} + B_1 \sin \omega t \hat{y} + B_o \hat{z} \quad (13)$$

The convenient rotating co-ordinate frame for this problem has its axis along the static field and rotates at  $\omega$ . In this frame,  $B_o$  and  $B_1$  are joined by an effective field along the  $\hat{z}^*$  direction, of magnitude  $-\frac{\omega}{\gamma}$  (this keeps the magnetization stationary in our rotating frame, which is why we chose it). The effective field in the rotating co-ordinate frame is

$$\vec{B}_{eff}^* = B_1 \hat{x}^* + \left( B_o - \frac{\omega}{\gamma} \right) \hat{z}^* \quad (14)$$

The equation of motion from equation 11 is

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B}_{eff}^* \quad (15)$$

which shows that  $\vec{M}$  will precess about  $\vec{B}_{eff}^*$ .

If the rotating field is at  $\omega_o$ ,  $\frac{\omega}{\gamma} = \frac{\omega_o}{\gamma} = B_o$ , and  $\vec{B}_{eff}^* = B_1 \hat{x}^*$ . The magnetization precess about this effective field at a rate  $\omega_1 = \gamma B_1$ . If we turn off  $B_1$  at the instant that  $\vec{M}$  reaches the  $xy$  plane, we have created a coherent magnetization in the  $xy$  plane. This is a  $\frac{\pi}{2}$  pulse, rotating  $M_z$  into  $M_y$ . If we leave  $B_1$  on for twice as long, we have a  $\pi$  pulse, which inverts the original magnetization to  $-M_z$ . Keep in mind that the magnetizations thus created will decay back to equilibrium, and that any  $xy$  magnetization will rotate in the lab frame.

Now a graphical explanation of the spin echo is possible – see figure 4.

## 7 Apparatus

The glass sample vial is inside three mutually orthogonal coils (see figure 5). The large DC field required is provided by an 8.8kG (=0.88T, at 10A) water-cooled electromagnet. A

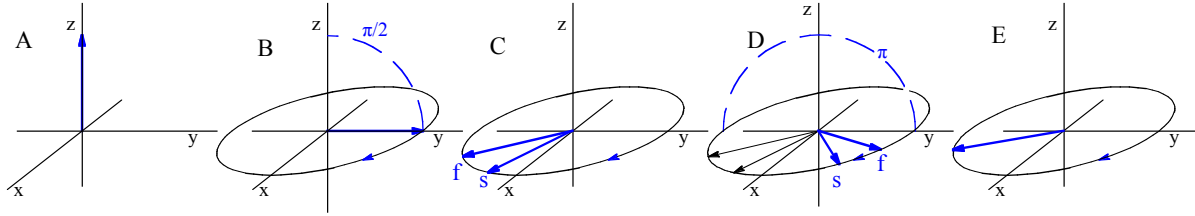


Figure 4: The spin echo: **a)** The initial magnetization is  $M_o\hat{z}$ . **b)** A  $\frac{\pi}{2}$  pulse is used to rotate the magnetization into the  $xy$  plane. **c)** The  $xy$  magnetization dephases (within the  $xy$  plane) due to inhomogeneous field distributions, with the extremes being  $\Delta M_{fast}$  (high field) and  $\Delta M_{slow}$  (low field), until  $t = \tau$ . **d)** when a  $\pi$  pulse is used to flip the magnetization (flip the  $xy$  plane like a pancake). The spins continue to precess as before, until... **e)**  $t = 2\tau$ , when they are again in phase, and an echo may be observed. After  $t = \tau$ , the spins again dephase, and the signal disappears. In these figures, the decay of the  $xy$  magnetization and the growth of  $M_z$  have been omitted for clarity.

smaller coil of similar shape (Helmholtz) is located toward and away from you as you look at the magnet, and a third, smaller, coil is wrapped around the space where you insert the sample vial. The innermost coil is the receiver, the other is the transmitter. Since you want the entire sample to be at the centre of all three coils, it's important that you only load  $\sim 4\text{-}5\text{mm}$  of sample into your vial.

As first mentioned in section 4, magnetization may only be measured in the  $xy$  plane. Left unmolested,  $M_z$  would grow to its equilibrium value and be completely boring, but any  $M_{xy}$  will precess with angular frequency  $\omega_o$  (see section 5). If you have rotating magnetization inside a coil, and the axis of rotation is not the coil's axis, an AC signal is induced in the coil – this is how AC wall power is generated, and it allows you to detect  $M_{xy}$ .

The NMR spectrometer unit consists of several parts (see figure 6): An RF source (the master oscillator), a pulse programmer to turn the RF on and off in short pulses, and the mixer. The mixer effectively multiplies the detector signal with the original RF, to generate an envelope waveform, which will have beats if the oscillator is not tuned to  $\omega_o$ . You have a dual-channel oscilloscope to let you view the detector and mixer signals simultaneously.

To allow the equilibrium magnetization  $\vec{M}_o$  to be established between repetitions of the experiment, one must wait at least  $3T_1$ , and preferably 6-10  $T_1$ 's, between pulse sequences. Water ( $T_1 \approx 3\text{s}$ ) would be annoying to work with, and you can imagine your frustration if you tried using  $^3\text{He}$  gas, with a  $T_1$  of about a week. Since several adjustments must be made before data can be taken, these samples would make for an infuriating experiment. Mineral oil has a  $T_1$  on the order of a few tens of milliseconds at  $25^\circ\text{C}$ , so a repetition time of 100-200 ms should be adequate.

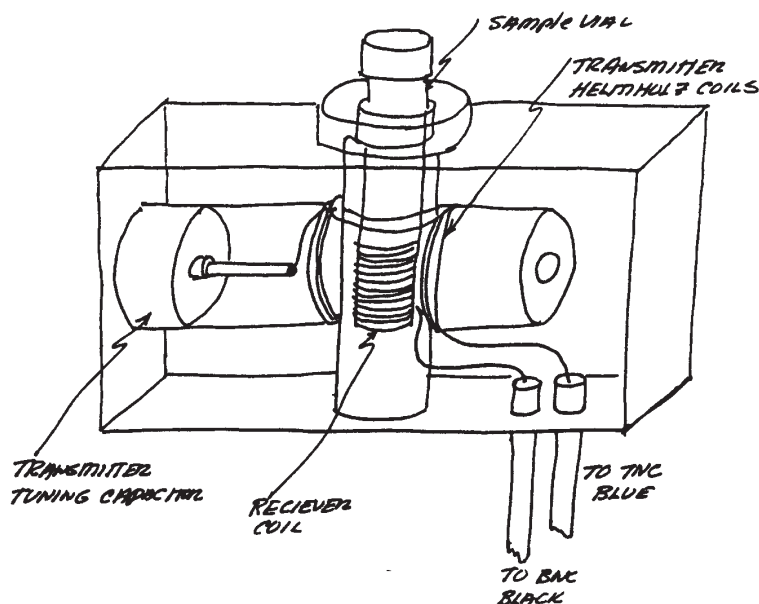


Figure 5: A sketch of the NMR probe.

## 8 Getting Started

At the beginning of the lab period, turn on the magnet and its water cooling. The magnet's field may never completely stabilize, but the greater its headstart, the easier your measurements will be.

Open LabView file "NMR"; this will set up the 'scope and allow you to save data.

### 8.1 Single Pulse

Typical NMR pulse widths range from 1-35  $\mu\text{s}$ . To start with, let's observe a single A pulse. The pulse programmer settings are:

A-width	halfway
Mode	Int
Repetition time	$\sim 500$ ms
Sync	A
A, B pulses	On, Off
Sync Out	To scope's external trigger input
A+B Out	To scope Channel 1

Set the oscilloscope to trigger on the rise of the sync pulse, use a sweep rate of 2-10  $\mu\text{s}/\text{cm}$ , and



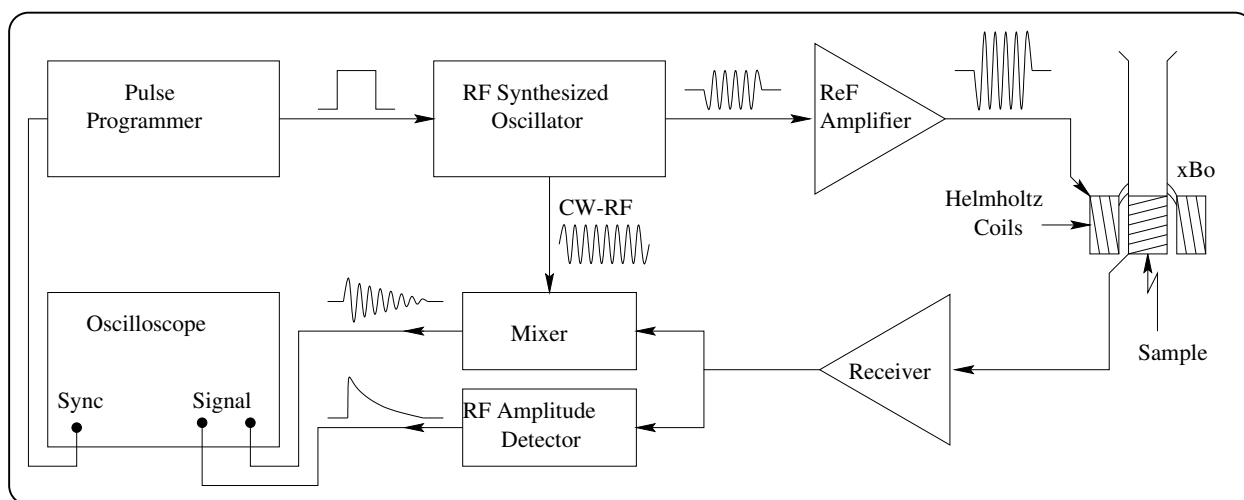


Figure 6: A block diagram of the NMR spectrometer.

1V/cm vertical scale. Change the A-width and observe the effect on the pulse. Switch the mode to Man, and observe the pulse when you press the “man” start button. Set the scope’s sweep rate to 1ms/cm and repetition time to 10ms, then change the variable repetition time from 10% to 100% – what do you observe?

## 8.2 The Pulse Sequence

To measure  $T_1$  or observe a spin echo, at least two pulses are required.

Delay Time	$0.10 \times 10^0$ (100 $\mu$ s)
Mode	Int
Repetition Time	$\sim 500$ ms
Sync	A
A, B pulses	On, On

The pulse train should now appear like figure 7. Change the A and B widths, change the delay time, change sync to B, turn off A, then B, change the number of repetitions, and observe what happens (i.e. fiddle with the equipment). Look at a two-pulse sequence with delay times from 1 to 100ms ( $1.00 \times 10^0$  to  $1.00 \times 10^2$ ). Be careful reading this number – note the decimal point.

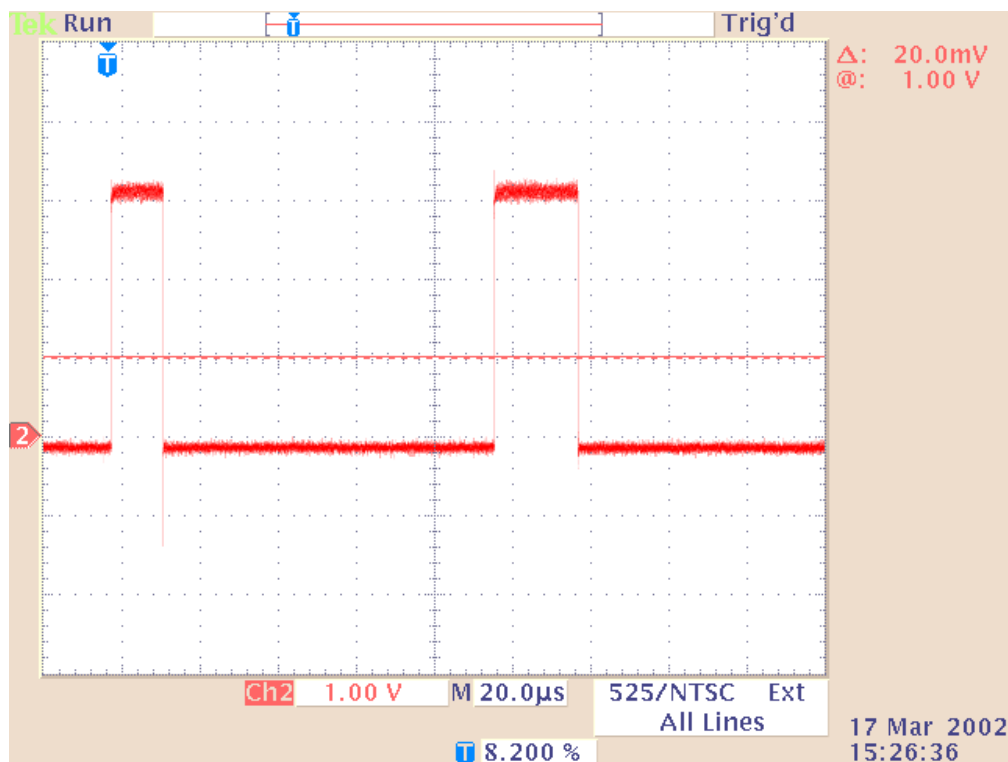


Figure 7: A two-pulse sequence

## 9 Procedure

Before you can do anything else, the spectrometer must be tuned to resonance, and this must be done for each measurement. When on resonance, the free induction signal will produce a zero-beat signal with the master oscillator as observed on the Mixer's output (see figure 8). Once the spectrometer is tuned to resonance, the shortest A pulse that produces a maximum FID amplitude is a  $\frac{\pi}{2}$  pulse. The setup is:

A-width	~20%
Mode	Int
Repetition Time	~ 500 ms
Sync	A
A, B pulses	On, Off
Time constant	0.01 ms
Gain	30%

Load a small sample of mineral oil (3-5 mm deep only) into one of the small sample vials, and adjust its height in the apparatus, using the rubber O-ring, to get a maximum signal. Tune the receiver input for maximum signal, then tune the frequency for a zero-beat signal. Find the pulse widths corresponding to  $\frac{\pi}{2}$  and  $\pi$  (a  $\pi$  pulse ideally leaves no magnetization

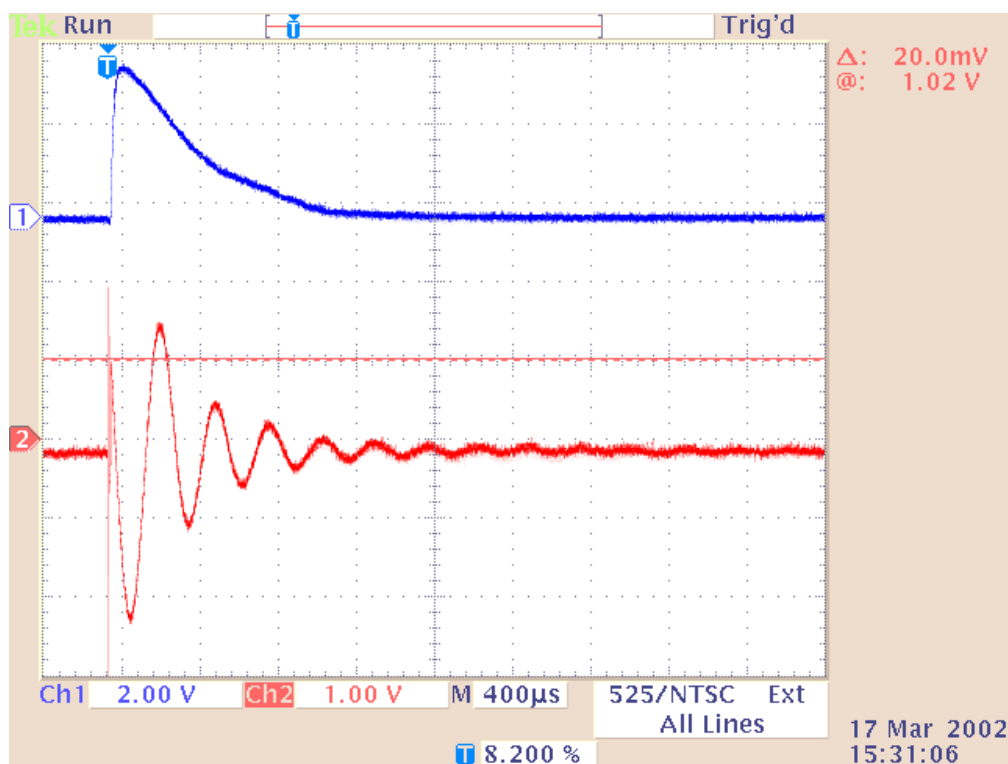


Figure 8: A free induction decay envelope and the detector signal mixed with the original RF, with the spectrometer not quite tuned to resonance. The beats are clearly visible.

in the  $xy$  plane, so it should have no signal following it). How are you going to do this?

## 9.1 Spin-Lattice Relaxation Time $T_1$

As the time constant for exchange of energy and angular momentum with the surroundings,  $T_1$  is one of the most important parameters to know and understand in NMR. Let's start with a quick, order-of-magnitude estimate:

1. Re-tune the spectrometer to resonance for a single pulse FID signal.
2. Change the repetition time, reducing the FID to roughly  $\frac{1}{2}$  of its largest value. This gives an idea of the order of magnitude of  $T_1$ .

At this repetition, the magnetization can't fully return to equilibrium, but does make it partway back. This measurement is useful as it gives you an idea of the time constant you want to measure, and helps you choose the delay settings.

The pulse sequence we'll use to find  $T_1$  is

$$\pi \xrightarrow{\tau} \frac{\pi}{2}, \text{ FID}$$

The  $\pi$  pulse inverts the magnetization ( $M_z \rightarrow -M_z$ ). A time  $\tau$  later, whatever magnetization exists gets rotated  $\frac{\pi}{2}$  into the  $xy$  plane for observation, where it decays in an FID. After the first pulse, the magnetization grows exponentially back from  $-M_z$  to  $M_z$  (it does **not** rotate!), but the spectrometer can only measure precessing  $xy$  magnetization, so the magnetization must be knocked over into the  $xy$  plane to be seen. The  $\frac{\pi}{2}$  pulse acts to sample  $M_z$  at the time selected.

You should be able to easily work out from equation 8 the equation governing the growth back to equilibrium. A two-digit value of  $T_1$  may be found by finding the zero-crossing point (which is not itself  $T_1$ ), but a better value is obtained by graphing the decay back to equilibrium and fitting to the correct function. Find  $T_1$  by both methods.

## 9.2 Spin-Spin Relaxation Time $T_2$

To find  $T_2$ , a simple  $\frac{\pi}{2}$  pulse will not suffice, due to inhomogeneities in the DC field. You'll need to use the spin-echo technique. The pulse sequence is

$$\frac{\pi}{2} \xrightarrow{\tau} \pi \xrightarrow{\tau} \text{echo}$$

The  $\frac{\pi}{2}$  pulse creates transverse ( $xy$  plane) magnetization, which dephases because of inhomogeneities in the applied field. The  $\pi$  pulse reverses these dephasing effects, and the magnetization eventually rephases, forming an echo signal. The reduction in height from the original FID to the echo is due to  $T_2$  processes, so plotting the echo height versus the total delay time ( $2\tau$ ) will give  $T_2$ .

Determine  $T_2$ .

## 10 References

1. The Basics of NMR, by Joseph P. Hornak: <http://www.cis.rit.edu/htbooks/nmr><http://www.cis.rit.edu/htbooks/nmr>

## 11 Appendix: Quantum Mechanics of NMR

In NMR, the large DC magnetic field  $\vec{B}_o = B_o \hat{z}$  defines the system's  $\hat{z}$ -direction. Any particles which have spin angular momentum (e.g. protons, neutrons, or electrons), and

aren't already paired in full orbitals/states, will align parallel or anti-parallel to the field, so as to reduce the system's energy. In proton NMR, we're interested, not surprisingly, in protons. These particles are spin  $\frac{1}{2}$ , meaning that their allowed spin states are  $m_I = \pm\frac{1}{2}$ .

The portion of the Hamiltonian due to the magnetic field is

$$H = \frac{e}{2m} g \vec{B}_o \cdot \vec{I} = \frac{eg}{2m} B_o \left( \pm \frac{1}{2} \hbar \right). \quad (16)$$

For free protons,  $g = 5.586$ , and is usually called the Landé g-factor.  $\vec{I}$  is the nuclear spin.

For anything interesting to happen, we must add a small, time-varying magnetic field  $\vec{B}_1 = B_1 \hat{x} \cos \omega t + B_1 \hat{y} \sin \omega t$ . In order to deal with this field in a comparatively straightforward manner, I must now introduce some notation:

I will be using spinors, because life becomes much simpler when the problem can be turned into  $2 \times 2$  matrices. The first time you see spinors, they usually look like a bizarre way to represent spin, but once you wrap your mind around them, they can be *extremely* handy. Spin up ( $\hat{z}$ -direction)  $\equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ , spin down  $\equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ . These are identical to the  $\uparrow$  and  $\downarrow$  you know and love from first year chem. All possible spin states can be constructed from these two spinors. For example, it can be shown that the state where spin is up in the  $\hat{x}$  direction corresponds to  $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} (\uparrow + \downarrow)$ . In quantum mechanics, you can know the angular momentum around only one axis at a time. If you know the spin about the  $x$ -axis, the particle is in some superposition of spin-up and spin-down states in the  $\hat{z}$  direction.

Using spinors, the Hamiltonian with both magnetic fields is

$$H = \frac{eg\hbar}{4m} \begin{pmatrix} B_o & B_1 e^{j\omega t} \\ B_1 e^{j\omega t} & -B_o \end{pmatrix} \quad (17)$$

The wavefunction  $\psi = \begin{pmatrix} a \\ b \end{pmatrix}$ , where  $a$  and  $b$  are time-varying and  $a^2 + b^2 = 1$ . When  $B_1$  is first turned on, it finds the spin in its equilibrium state  $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ , so  $a(0) = 1$  and  $b(0) = 0$ . In order to minimize mess, I must now introduce a couple more  $\omega$ 's. As above,  $\omega$  is the angular frequency of the applied field, but we now have  $\omega_o$ , the resonant (Larmor) frequency from field  $B_o$ , and  $\omega_1$ , which is the  $B_1$  equivalent. I.e.

$$\frac{\omega_o}{2} \equiv \frac{eg}{4m} B_o \quad \text{and} \quad \frac{\omega_1}{2} \equiv \frac{eg}{4m} B_1 \quad (18)$$

If we apply the Schrödinger equation ( $j\hbar\partial_t\psi = H\psi$ ) to  $\begin{pmatrix} a \\ b \end{pmatrix}$ , we get

$$j\hbar\partial_t \begin{pmatrix} a \\ b \end{pmatrix} = H \begin{pmatrix} a \\ b \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} \omega_o & \omega_1 e^{j\omega t} \\ \omega_1 e^{j\omega t} & -\omega_o \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} \quad (19)$$

This gives

$$j\partial_t a = \frac{\omega_o}{2} a + \frac{\omega_1}{2} b e^{j\omega t} \quad \text{and} \quad j\partial_t b = -\frac{\omega_o}{2} b + \frac{\omega_1}{2} a e^{j\omega t} \quad (20)$$

It is now convenient to define two new “constants”,  $A \equiv ae^{j\frac{\omega_o}{2}t}$  and  $B \equiv be^{-j\frac{\omega_o}{2}t}$ . Now,

$$j\partial_t A = \frac{\omega_1}{2} B e^{j(\omega_o - \omega)t} \quad \text{and} \quad j\partial_t B = \frac{\omega_1}{2} A e^{-j(\omega_o - \omega)t} \quad (21)$$

This can be solved by  $A = A(0)e^{j\lambda t}$  and  $B = B(0)e^{j\lambda t}e^{-j(\omega_o - \omega)t}$ , where the roots of  $\lambda$  are

$$\lambda_{\pm} = \frac{\omega_o - \omega \pm \sqrt{(\omega_o - \omega)^2 + \omega_1^2}}{2} \quad (22)$$

The general solution for  $A$  is then

$$A = A_+ e^{j\lambda_+ t} + A_- e^{j\lambda_- t} \quad (23)$$

Substituting this into the first part of equation 21 gives

$$B = -\frac{2}{\omega_1} e^{-j(\omega_o - \omega)t} [\lambda_+ A_+ e^{j\lambda_+ t} + \lambda_- A_- e^{j\lambda_- t}] \quad (24)$$

The initial conditions  $A(0) = a(0) = 1$  and  $B(0) = b(0) = 0$  imply that  $A_+ + A_- = 1$  and  $\lambda_+ A_+ + \lambda_- A_- = 0$ , or

$$A_+ = \frac{\lambda_-}{\lambda_- - \lambda_+} \quad \text{and} \quad A_- = -\frac{\lambda_+}{\lambda_- - \lambda_+} \quad (25)$$

We can now obtain a result for the probability that the spin has flipped to down (or how much “down” there is in the superposition of states):

$$\begin{aligned} P_{a \rightarrow b}(t) &= |b|^2 = |B|^2 = \frac{4}{\omega_1^2} \left| \frac{\lambda_+ \lambda_-}{\lambda_- - \lambda_+} e^{j\lambda_+ t} - \frac{\lambda_+ \lambda_-}{\lambda_- - \lambda_+} e^{j\lambda_- t} \right|^2 \\ &= \frac{\frac{4}{\omega_1^2} \left[ \frac{(\omega_o - \omega)^2}{4} - \frac{(\omega_o - \omega)^2 + \omega_1^2}{4} \right]^2}{\left[ -\sqrt{(\omega_o - \omega)^2 + \omega_1^2} \right]^2} \left| e^{j\frac{\omega_o - \omega}{2}t} \left( e^{j\frac{\sqrt{(\omega_o - \omega)^2 + \omega_1^2}}{2}t} - e^{-j\frac{\sqrt{(\omega_o - \omega)^2 + \omega_1^2}}{2}t} \right) \right|^2 \\ &= \frac{\frac{\omega_1^2}{4}}{(\omega_o - \omega)^2 + \omega_1^2} \left| e^{j\frac{\omega_o - \omega}{2}t} 2j \right|^2 \sin^2 \frac{\sqrt{(\omega_o - \omega)^2 + \omega_1^2}}{2} t \\ &= \frac{\omega_1^2}{(\omega_o - \omega)^2 + \omega_1^2} \sin^2 \frac{\sqrt{(\omega_o - \omega)^2 + \omega_1^2}}{2} t \end{aligned} \quad (26) \quad (27)$$

At this point, it should suddenly become clear why the spectrometer needs to be tuned to resonance ( $\omega = \omega_o$ ). The simplification is dramatic:

$$P_{a \rightarrow b}(t) = \sin^2 \frac{\omega_1}{2} t \quad (28)$$

It should also be clear now what  $\frac{\pi}{2}$  and  $\pi$  pulses correspond to. It should be noted that, while this was derived for a single particle, the same result works for the system as a whole, with the energies multiplied by  $(N_1 - N_2)$ , where  $N_1$  and  $N_2$  are the numbers of particles in the lower and upper energy states respectively.