Nuclear Magnetic Resonance

1 Introduction

Nuclear magnetic resonance is a phenomenon that in 1952 won Nobel prizes for its discoverers. It is widely used to investigate the properties of nuclei and their environments in various materials. It has found wide use in medicine to provide images of internal organs of the body. This is the field of *Magnetic Resonance Imaging*, or MRI for short. To allay public fears, the word "Nuclear" was dropped!

Recall that the proton is the nucleus of a hydrogen atom. It behaves like a tiny bar magnet that can either point along the direction of a steady external magnetic field, of strength B_0, or in the opposite direction. These two states have different energies $-\mu B_0$ and $+\mu B_0$, respectively, where μ is the magnetic moment of the proton expressed in Joules/Tesla, so their energy separation depends linearly on the strength of the magnetic field as well as the magnetic moment: $E = 2\mu B_0$. (Here the *magnetic moment of the proton*, μ, is defined to be the magnitude of the component of the proton's magnetic moment along the direction of the magnetic field, this being the experimentally measurable quantity.) If the protons are placed in an additional weak radio frequency magnetic field that oscillates at just the right frequency (f), a proton in the lower state can absorb energy from the oscillating field and flip its orientation so that it is in the upper state. A second process also occurs: a proton in the upper state can be stimulated by the external field to emit radiation and flip into the lower state. The probability of this *stimulated emission* for each proton in the upper state is equal to the probability of absorption for each proton in the lower state. In thermal equilibrium, there are slightly more protons in the lower state than in the upper (the relative numbers are determined by the so-called *Boltzmann factor*), so that the absorption process is the dominant one (although barely so). By varying the frequency of the weak oscillating magnetic field until absorption of energy is detected, we can then achieve the resonance condition with $h\,f = 2\mu\,B_0$.

Chemists commonly obtain NMR spectra for determining structural information of molecules since the resonance is highly sensitive to the effective local field or environment for the nuclei (typically hydrogen). In particular, different chemical bonds can lead to small (parts per million) shifts in the resonant frequency.

Further information can be obtained by examining the dynamical characteristics of the resonance, using a pulsed NMR in which a radio-frequency (RF) field is applied for only short periods of time. Two commonly measured time constants are known as T_1 and T_2. The time constant T_1 refers to the characteristic (longitudinal) decay time for a system of spins to align with the steady state field (by tradition in the z direction). In other words, if you prepare the nuclear magnetic moments

to point along the direction of the magnetic field, T_1 describes the time it takes for the magnetic moments of the nuclei to reorient and point in another direction. It's often called the spin-lattice relaxation time, since aligning spins necessarily means a change in energy which must be compensated somewhere, typically from the surroundings known as the lattice. The time constant T_2 refers to the characteristic decay time in the x-y or transverse direction (perpendicular to the steady state field). In this case the magnetic moments point perpendicular to the spin. This leads to precession of the magnetic moment around the external magnetic field. The *coherence time* of the precession (how long the magnetic moment precesses before reorienting) is described by T_2 . It's also called the spin-spin relaxation time, since no energy transfer is necessary. The observed relaxation times can provide insight into coupling and diffusion mechanisms in the material of interest. The times are used to give contrast in MRI applications.

2 Objectives

The main objective of this experiment is to learn the basic physics of nuclear magnetic resonance. You will be using a teaching NMR which performs all the major functions of a modern instrument. After tuning a simple spectrometer for optimal operation, you will be able to observe nuclear magnetic resonance in a sample of mineral oil or glycerin. In addition to extracting information about the applied steady state and oscillating magnetic fields, you will determine the two relaxation time constants T_1 and T_2.

3 Pre-lab Questions

1. In this lab, the sample is placed in a large dc magnetic field, B_0 and a pulsed oscillating field B_1 is applied. Assuming B_0 and B_1 cannot be changed, what parameter can you vary to make a $\frac{\pi}{2}$ pulse into a π pulse?

2. Briefly (2-3 sentences) describe, in your own words, how you will measure T_2^*. How many and what kind of pulses will you apply? What parameters will you vary?

3. Briefly (2-3 sentences) describe, in your own words, how you will measure T_1. How many and what kind of pulses will you apply? What parameters will you vary?

4 Preparation

- Read the following materials
  - The introduction to the TeachSpin manual.
  - The conceptual tour of TeachSpin's pulsed NMR.
  - George E. Pake, "Nuclear Magnetic Resonance in Bulk Matter," *Physics Today* Oct. 1993, page 46.

- Some other reference materials that you may find useful include
  - E.R. Andrew, *Nuclear Magnetic Resonance*, Cambridge University Press (1955).
  - H. Mark and T.N. Oison *Experiments in Modern Physics* Chapter 9, McGraw-Hill (1966).

5 Equipment List

- TeachSpin Pulsed NMR PS1-D, and mineral oil or glycerin sample.
- Tektronix 200 MHz digital storage oscilloscope and computer.
- Lakeshore 410 hand-held Gaussmeter probe.
- Rulers, vernier calipers as needed.
- BNC cables and 50 Ω terminator.

6 Procedure

CAUTIONARY NOTES

1. The magnet is very fragile, so take care when inserting samples. Keep the cover in place. DO NOT put any small magnetic objects (e.g. paper clips) or magnetically sensitive items (e.g. credit cards) near the magnet assembly.
2. Limit how much other electrical equipment is in the presence of the 15 MHz. The pickup coil can pick up other electrical signals too.

6.1 Identifying the Equipment

The first thing to do is to familiarize yourself with the apparatus.

1. Examine the TeachSpin magnet and coil assembly. A couple of sketches of the assembly are shown below. Make sure you understand everything in the sketches.
2. Look over the control electronics (an sketch of the front panel is shown in Fig. 2). There are three distinct modules. From left to right
   (i) The Receiver: Controls the signal received from the pickup coil surrounding the sample.
   (ii) The Pulse Programmer: Controls the sequence and timing of the pulse of rf field.
   (iii) The Oscillator/Amplifier/Mixer: Controls the frequency of the rf field and has an amplifier and mixer to check for resonance.

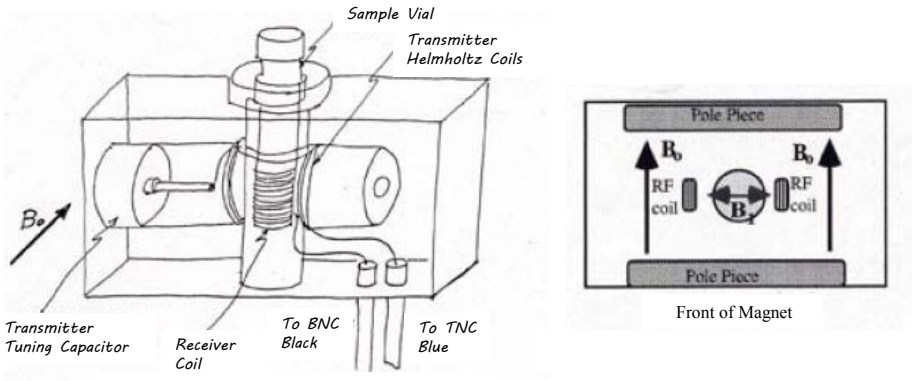

Figure 1: An "artist's" sketch of the magnet-coil assembly and a schematic picture of the magnet and coil assembly. Figures are taken from TeachSpin *Conceptual Tour of Pulsed NMR*.

3. You will use the Tektronix oscilloscope to look at and collect your data. The scope is connected to a computer through a GPIB cable. The LabView program "TDS2002 LocalSettings" program will allow you to collect the data from the oscilloscope. The program records the time and voltages in a txt file. Open the program (a shortcut is on the desktop) and play around with collecting data from the scope. Make a folder in the P314 folder to keep all of your data. The computer is not connected to the network or internet so you'll have to transfer the data with a flash drive. If you do not have one of your own see me and I'll lend you one.

6.2 Investigating the Pulse Programmer

The goal in this section is to familiarize you with the pulse programmer and figure out how to generate π and $\frac{\pi}{2}$ pulses.

1. Turn on the TeachSpin apparatus (the switch is on the back of the control electronics).

2. The pulse programmer can generate a single pulse (A) or two pulses (A and B). We'll start by just considering a single pulse at first. Set the programmer settings to

   A Width Turn knob halfway
   Mode INT
   Repetition Time 10 ms, variable knob set to 10%
   Sync A
   A On
   B Off
   Sync Out Connect to oscilloscope trigger
   A & B Out Connect to channel 1 of oscilloscope.

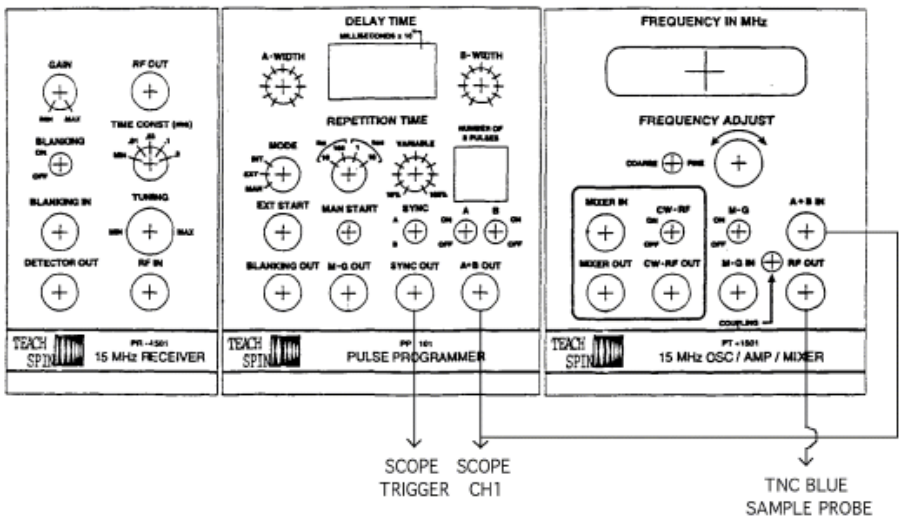

Figure 2: Front panel of control electronics. Figure are taken from TeachSpin manual.

3. Good settings to start out with on the oscilloscope are

   Trigger External
   CH1 1 V/div
   Sweep time $5 - 10\,\mu s$

4. Play around with the A-width control and the repetition time (adjust the scope setting as needed). Make sure you understand what you're looking at and what the controls are doing.

5. Now explore the two-pulse sequence by changing the following settings on the pulse programmer

   Delay Time 0.1×10^0 (100 μs)
   Number of B Pulses 1
   B On

6. Vary the B-width, delay time, and number of B pulses and see what happens. You should also try changing the SYNC to B instead of A. Make sure you understand all of the controls on the pulse programmer.

6.3 Measuring the Strength of the Magnetic Fields

1. Use the hand-held gaussmeter to measure the strength of the dc magnetic field (B_0). Pay attention to the orientation of the probe. It works on the Hall effect, which is direction dependent.

2. The oscillating rf magnetic field is generated by the Helmholtz coils and is too fast to measure with the gaussmeter. Instead, we can measure the strength of

the oscillating field by making use of Faraday's law. The TeachSpin instrument comes with two coils embedded in epoxy and attached to BNC cables. The coils are designed to slip into the sample housing. Figure out which coil you should use to measure the oscillating field (you may want to look back to Fig. 1).

3. Place the appropriate coil into the sample holder. Connect it to a tee and a 50 Ω impedance terminator and to one of the channels of the oscilloscope.

4. In order to see a signal you need to tell the pulse programmer to generate an rf pulse to send to the Helmholtz coils. Adjust the pulse programmer settings back to the settings you had when you were investigating the single pulse.

5. Use a tee to connect A&B OUT to the OSC/AMP MIXER module's A&B IN as well as to the oscilloscope.

6. Connect the blue TNC cable from the Helmholtz coils to the RF OUT connection on the OSC/AMP MIXER module. Adjust the frequency of the oscillator to 15.16 MHz, the nominal resonant frequency of the system. (You will see that this frequency is temperature dependent so you might have to adjust this more later.)

7. You should now see both the rf pulse and a signal from the coil. Align the coil for maximal signal; you might want to place an o-ring around it to control its adjustment in the vertical direction. Save a copy of your best measurement and use this (along with whatever other measurements you might need) to estimate the magnitude of the oscillating rf field, B_1. (You may need to review Faraday's law from Physics 111/311.)

8. This rf pulse is what you'll use to rotate the magnetic moments of your sample. Estimate the pulse time (A-width) necessary to rotate the magnetization by 90°. You may want to look through the introduction section of the TeachSpin manual.

6.4 Measuring the Free-Induction Decay

Now that you've figured out how the system works we're ready to start making some measurements. The first thing we'll look at is the free-induction decay. This will give us a value of T_2^*.

1. Remove the test coil and insert a sample of either mineral oil or glycerin.

2. Set the pulse-programmer to generate a single pulse with a width equal to the width you calculated above; that is, a single $\frac{\pi}{2}$ pulse. The repetition time should be set to 1 s with the variable knob turned to 20-30%. The number of B pulses should be zero.

3. The idea here is that initially the magnetic moments of the protons in our sample are pointing along the direction of B_0 (which is taken to be along the

z axis). The rf pulse will tip the magnetic moments into the x-y plane and the protons will begin precessing around the z axis. Since our pick up coil is sensitive to a changing magnetic field in the y direction (vertical with our set up) the pick up coil will detect the precession as a sinusoidal variation in the magnetic flux. The frequency of this precession is exactly equal to the resonant frequency of the protons. (Think about why this is true.) Let's take a look at that precession frequency. Connect the thin black coax cable that is coming from the pickup coils to the 15 MHz Receiver RF IN port. Hook up the RF OUT port on the receiver to the oscilloscope. You should see some significant signals. Take a minute and figure out what you're looking at.

4. Connect the BLANKING OUT (on the Pulse Programmer Module) to the BLANKING IN (on the Receiver Module). Leave the BLANKING OFF for now.

5. Much of the signal that you are seeing is due to the Helmholtz coils. Remove you sample and see how your signal changes. What portion of the signal was due to the atoms?

6. Turn the BLANKING ON. This tells the receiver to turn off when the rf pulse is being applied and gets rid of the signal from the Helmholtz coils.

7. Put your sample back in and look at the signal with the BLANKING OFF.

8. For measuring T_2^* we don't really care about the oscillations, but rather the envelope of the oscillations. The DETECTOR OUT port gives you the rectified envelope. Connect that to the scope instead of the RF OUT and record how it compares to the RF OUT.

9. A true $\frac{\pi}{2}$ pulse should lead to all of the magnetic moments being tipped into the x-y plane, which will result in a maximal signal in the pickup coil. Adjust the A pulse width in order to maximize the signal. Once you have the width optimized measure in on the scope and see well it agrees with your calculated value.

10. Adjust the time constant and observe the signal. In general, ≈ 0.01 ms should be sufficient for our studies.

11. With the pulse parameters set we now want to adjust the frequency of the rf field to hit the resonance of the atoms. We will do this by comparing the precession frequency to the rf frequency that we're applying and adjust the rf frequency we are applying until the two are equal. We can accomplish this by use of the MIXER unit on 15 MHz OSC/AMP/MIXER moudule. Attach the RF OUT to the MIXER IN. The mixer multiplies the RF OUT signal with the rf signal being generated by the 15 MHz oscillator. This multiplication results in a signal that has two characteristic frequencies, one at the sum of the two frequencies $(f_1 + f_2)$ and the other at the difference of the two frequencies $(f_1 - f_2)$ (the beat frequency). This difference frequency is sent to the MIXER OUT port. Hook up the MIXER OUT to the oscilloscope. You should see a

signal which is oscillating at the difference frequency of the applied rf field and the precession frequency. Make sure the CW-RF is ON; this switch controls whether or not the oscillator output is sent to the mixer or not. Adjust the frequency of the oscillator so that the beat frequency is zero.

12. **NOTE:** The dc magnetic field B_0 is temperature dependent so it may change over the course of the experiment. You may need to adjust the frequency of the oscillator and the pulse width throughout the experiment.

13. Once you've got a good looking signal save the DETECTOR OUT signal on the oscilloscope to the computer. Use this plot to extract T_2^*. This serves as a lower limit to T_2.

6.5 Measuring T_1

In this section our goal is to measure T_1. In thermal equilibrium the atoms will point along the direction of the magnetic field, B_0. If the magnetic moments in the sample are tipped by 180° so that they point in the opposite direction of B_0 they will eventually decay to the lower energy state where they again point along B_0. The time constant T_1 describes the decay time for this process. We'll try to measure T_1 in a couple of different ways and see how they compare.

1. It is possible to get a rough estimate of T_1 using a single pulse sequence similar to the one you used for measuring T_2^*. Using the same pulse width, decrease the repetition time until the maximum amplitude of the free-induction decay signal is reduce to about $\frac{1}{3}$ of its largest value. The repetition time for which this occurs is a rough estimate of T_1. Explain why this works.

2. For a more accurate measurement a two-pulse sequence is used. The key point here is that our pickup coil cannot directly measure the magnetization in the z direction, but only the changing magnetization in the y direction. We will use a two-pulse sequence to overcome this limitation and get an indirect measurement of the magnetization along the z axis. The first step is to rotate the spins by 180° by use of a π pulse. Some time later we will apply a second pulse to tip the spins 90° into the x-y plane with a $\frac{\pi}{2}$ pulse. The amplitude of the free-induction decay right after the second pulse is a measure of the magnitude of the magnetization along the z axis. By varying the time delay between the two pulses it is possible to map out the magnitude of the magnetization along the z axis. If the second pulse closely follows the first pulse the magnetic moments will not have a chance to decay and will still be pointing in the $-z$ direction. There will be a large peak amplitude in the pickup coil, followed by the free-induction decay. If the time delay between the two pulses is increased, there will be a smaller net magnetization along the $-z$ axis so the peak signal after the second pulse will be smaller. At some point during the decay there will be a net zero magnetization along the z axis so there will be no signal after the $\frac{\pi}{2}$ pulse. As the delay is further increase the signal after the $\frac{\pi}{2}$ pulse will return as there will be a net magnetization along the $+z$ axis.

Set up the pulse generator to produce the π pulse (with A) and the $\frac{\pi}{2}$ pulse (with B).

3. Using the scope cursors measure the initial amplitude of the free-induction decay relative to the zero level. Be sure to measure the zero-level amplitude at long time scales (when the atoms have returned to point along $+z$) very carefully.

4. Plot the magnetization as a function of the delay time and fit it to determine T_1.

6.6 Measuring T_2 via Spin Echo

If you reverse the order of the two pulses you used above, apply a $\frac{\pi}{2}$ pulse then a π pulse, you can make a measurement of T_2 via the spin echo technique. You should be quite familiar with the apparatus at this point so you are left to devise a measurement procedure of your own on this section. Look back over the reference material if you are stuck. You can also refer to page 33 of the TeachSpin NMR Manual if you need a bit of guidance. Be sure to explain your procedure.

6.7 More Complicated Pulse Sequences

If you have time you can investigate some more complicated pulse sequences as described in the TeachSpin NMR Manual.

7 Reporting Your Results

1. As mentioned in the introduction and in several of the references, the difference in the number of protons aligned either with or against the dc magnetic field B_0 is governed by a Boltzmann factor:

$$\frac{N_1}{N_2} = e^{-\frac{\Delta E}{k_B T}}, \tag{1}$$

where ΔE is the energy difference between the two states, k_B is Boltzmann's constant, and T is the temperature. For a bunch of independent protons in a material at room temperature and in a field B_0 with the strength you had in your experiments, determine the fraction of spins aligned with the field vs. against. What does this say about the portion of the spins that are sensitive to the pulsed NMR technique? Be quantitative!

2. From your measurement of the frequency of the resonant rf field and the literature value for the proton magnetic moment, determine the value of the dc field. Include your uncertainties. How does this value compare to what you measured with the Hall probe? Which one is more accurate? Explain any possible discrepancies.

3. Describe/derive a relationship for extracting a value for T_1 using the two-pulse-sequence method. What was your value for T_1 and how did it compare

to the quick estimate you made of T_1 by adjusting the repetition time of the single pulse?

4. Attach plots of the data you used to extract the values of T_2^*, T_2, and T_1. How do the values compare? Include an uncertainty budget for your measurements.

5. Explain why the two-pulse spin-echo technique allows for a more intrinsic value of T_2 in the presence of field inhomogeneities.