Pulsed NMR

1 Objective

This experiment is an introduction to pulsed nuclear magnetic resonance. [1] The goal is to become familiar with the basic physics of magnetic resonance and to carry out measurements of characteristic relaxation times: the spin-lattice (T_1) and spin-spin (T_2) relaxation times.

2 Guidelines for the experiment

Before making any measurements in this lab, you will need to read the introductory material in the apparatus manual and work out some of the details that describe the physics of NMR. This handout is only meant as a supplementary guide to the procedures. You will need to refer to this *and* to the manual as you become familiar with the apparatus. You will need to use a significant part of the three weeks allocated for the lab to understand the system and learn how to make the basic measurements. Once that's under control you can make some measurements on samples.

Work out the pre-measurement exercises in your lab notebook. then become familiar with the apparatus. This includes observing the signals produced from the NMR system, especially the generation of various pulse sequences to be used in the measurements, and making preliminary measurements. The remaining lab time will be used for completing measurements on the assigned sample.

3 Pre-measurement exercises

These exercises should be completed after you have read through at least pages 1-12 of the manual once or maybe twice. The exercises are intended to re-inforce the ideas by allowing you to fill in details of some of the arguments presented. You can discuss your solutions with the instructor before beginning measurements.

(1) Write out the three equations of eq. 17.1 on page 6 of the TeachSpin manual in component form, i.e. complete:

$$\frac{dM_x}{dt} = \ldots,$$

[1]Parts of this experiment are adapted from a similar experiment at Caltech.

$$\frac{dM_y}{dt} = \ldots,$$
$$\frac{dM_z}{dt} = \ldots.$$

In the following the time derivative is more compactly denoted by a dot, e.g. $\frac{dM_x}{dt} = \dot{M}_x$.

(2) Lab frame calculations [*This exercise is intended to lead you through the details of precession of classical spins in a magnetic field.*] Consider a special case of the equations in exercise (1) describing the magnetization in the lab frame in a static magnetic field.
(a) For the particular case of $\vec{B} = (0, 0, B_o)$, what are the three preceding equations?
(b) Differentiate the first equation ($\dot{M}_x = \ldots$) with respect to time and use the second equation ($\dot{M}_y$) to obtain a simple differential equation for M_x that does not include M_y or M_z.
(c) Assume that $M_x(t) = M_{ox}\cos(\omega t)$. What is ω (in terms of B_o and γ) in order for this to be a solution of the differential equation obtained in (b)?
(d) Find $M_y(t)$.
(e) Let the component of $\vec{M}$ in the xy plane be denoted as $\vec{M}_\perp(t)$ $(= M_x(t)\hat{\imath} + M_y(t)\hat{\jmath})$. From your solutions in (c) and (d) for $M_x(t)$ and $M_y(t)$, does $\vec{M}_\perp$ precess clockwise or counterclockwise around the z-axis when $B_o > 0$? (Assume you are looking down from the $+z$-axis.)

(3) Rotating frame calculations [*Effect of a pulsed magnetic field.*] Assume that $\vec{B} = (B_1, 0, 0)$ in the *rotating* reference frame during an RF burst to the Helmholtz coils, as will be seen by precessing protons. You can also assume the magnetization at the start of the pulse is given by the initial condition $\vec{M} = (0, 0, M_o)$ at $t = 0$.
(a) What is the $\dot{M}_y$ (or, in the notation of the TeachSpin manual, $\dot{M}_{y^*}$) equation in the rotating frame? (And not just at $t = 0$! Find the equations that apply throughout the B_1 pulse. Refer back to exercise 1.)
(b) What is the $\dot{M}_{x^*}$ equation in the rotating frame? What can you then say about M_{x^*} under these conditions at all times $t \geq 0$?
(c) Assume in the rotating frame only the direction of $\vec{M}$ changes during the pulse, while its magnitude remains at M_o. (M_o doesn't decay significantly during the pulse since it is short.) Use the consequences of part (b), which then imply that

$$M_{z^*} = \sqrt{M_o^2 - M_{y^*}^2} = M_o\sqrt{1 - \frac{M_{y^*}^2}{M_o^2}},$$

to help you integrate (a) to find $M_{y^*}(t)$. (Hint: it may help to make a change of variables to $u \equiv M_{y^*}/M_o$.)
(d) In terms of γ and B_1, how long does it take to rotate $\vec{M}$ from its initial alignment along the along z^* axis to along the y^*-axis in the rotating frame? That is, how long is a $\frac{\pi}{2}$ pulse?

(4) A single turn of wire 6 mm in diameter is placed in a uniform magnetic field oscillating sinusoidally at 15. MHz. The loop is connected to an oscilloscope and a peak-to-peak voltage of 1.0 V is observed when the plane of the coil is perpendicular to the field. Use Faraday's law to figure the amplitude of the oscillating magnetic field.

4 Experimental Procedure

Before beginning these measurements be certain you have completed and understood the exercises above.

You will want to capture and save data from the oscilloscope at various points to record your work in your notebook and for your report. Create a utility VI in LabVIEW to retrieve and save to a file data from the oscilloscope. Many instrument drivers already exist and are available from National Instruments that can do much of this for you. Mostly it will be a matter of understanding how to get the data you want out of the VI and save it for later use.

4.1 Preliminary measurements

Pulse Programmer: Verify that the pulse programmer module is operating properly by working through the procedures in part A of the 'Getting Started' section of the TeachSpin manual, beginning on p. 26. Be sure you understand what each of the controls does.

Using the oscilloscope, take screenshots of the output of the pulse programmer from both A+B OUT and M-G OUT.

Receiver: Insert the dummy signal coil (see sketches on p. 25a in the manual) into the sample space in the magnet housing. Connect the CW-RF OUT to the dummy signal coil with a BNC 'tee' and 50 Ω terminator. Connect the thin black receiver cable from the magnet housing to the RF input of the receiver module. Set the oscillator frequency to the nominal frequency marked on the magnet housing. Connect the RF OUT of the receiver and the DETECTOR OUT to the oscilloscope. Tune the receiver to maximize the amplitude of RF OUT or equivalently the DC level at the DETECTOR OUT, which is just a rectified and filtered version of RF OUT. Once this is done, the receiver is set-up to detect signals near this frequency as described in 'Getting Started' section B of the manual. You may need to reduce the receiver gain to prevent the amplifier from saturating as you tune the receiver. When finished, disconnect the CW-RF OUT and remove the dummy probe.

Pulsed field calibration: Wire up the system as described in section C of 'Getting Started.' Then figure the pulsed field strength as described in item 1 on p. 30 of section D in 'Getting Started.' Put the pick-up loop probe in the magnet sample space. Connect the pick-up probe to the oscilloscope. Observe and measure the voltage induced in the pick-up probe by the RF magnetic field from the Helmholtz coils during an A pulse. Be sure to orient the pick-up loop to maximize the observed signal. From the induced voltage, use Faraday's law to find the strength of the rotating field B_1 produced by the A pulse. In fact, this is a measurement of B_x; see the footnote on p. 6 of the instrument manual to avoid a factor of 2 error in determining the value of B_1 that is needed. From this rough value of B_1, estimate how long a pulse must be to make it a $\pi/2$ or 90° pulse.

Free induction decay: (See item 2 on p. 30 of 'Getting Started' section D.) Put the mineral oil or other sample assigned for you in the sample space in the magnet. Set the pulse programmer to generate only A pulses, and set the A pulse-width to the value calculated above. (You can temporarily disconnect the A+B OUT connection from the pulse programmer to the Osc/Amp/Mixer module, and look at the A+B OUT with the oscilloscope directly to set the A pulse-width. Once you've set it, reconnect the A+B OUT to A+B IN.) Find the free-induction decay (FID) signal from your sample by observing the Detector Out. Adjust the width of the A pulses to maximize the FID signal. You may find it helpful to increase the repetition time to 1 sec. Also adjust the vertical position of the sample to maximize your signal, thereby centering the sample in the detector coil. An O-ring around the vial will keep it in the optimal position.

Next adjust the oscillator frequency to maximize the amplitude of the rectified Detector Out signal. Tune the oscillator until the output of the mixer no longer shows any beat signal (oscillations). Beware: for the mixer output to be meaningful, the CW-RF switch must be on, even though nothing is connected to the CW-RF OUT BNC. If you observe too much noise, use the averaging feature of the oscilloscope in the normal triggering mode. (As room temperature drifts, so does the strength of the magnet and the resonant frequency. You are likely to observe that beats gradually re-appear at the mixer output; simply fine-tune the oscillator back onto resonance as needed.) You may want to re-check the tuning of the receiver after making these adjustments.

Now fine-tune the width of the A-pulses to maximize the amplitude of the Detector Out signal. Record both Detector Out and Mixer Out. Measure the width of the optimized $\pi/2$ pulse. (Look at it directly again with the oscilloscope.) From this $\pi/2$ pulse-width determine B_1 and compare to your earlier rough estimate from the pick-up probe measurements.

Record the precession frequency of the free-induction signal based on the final tuned oscillator frequency. Assuming that this signal is due to protons with the proton gyromagnetic ratio given in the manual, calculate the magnetic field B_0 of the instrument.

Spin echo: Adjust the pulse programmer to produce one B pulse $\tau = 5$ ms after the A pulse. Set the B pulse width to that required for a π pulse. Observe the spin echo after the FID at the Detector output. Verify that the echo appears 2τ after the A pulse. Fine tune the width of the B pulse to maximize the amplitude of the spin echo. Save the data from the oscilloscope of your spin echo.

Before proceeding further make sure you understand the physical processes you are observing during the FID and the spin echo. Omit procedures described in sections E and F of 'Getting Started.'

4.2 T_1 and T_2 measurements

$\mathbf{T_1}$ Follow the procedures outlined in section G of 'Getting Started' to measure the spin-lattice relaxation time T_1. Carry out only the first method: 'Two-pulse zero crossing.' Note that immediately after a π pulse, the z-magnetization starts at $-M_0$ and relaxes back to $+M_0$ exponentially:

$$M_z(t) = M_0 \left(1 - 2\, e^{-\frac{t}{T_1}}\right).$$

Solve this equation to find the time (denoted as τ_0 in the manual) after the initial spin-inverting pulse when M_z should equal zero. Your answer will be in terms of T_1. Applying a

$\pi/2$ pulse at this time should result in no FID since there is no M_z magnetization to tip into the x-y plane at that instant. Vary the delay time between the A (π) and B ($\pi/2$) pulses and find the delay that produces the smallest FID at the $\pi/2$ pulse. Figure out T_1 from that.

$\mathbf{T_2}$ Measure the spin-spin relaxation time T_2 and observe spin echoes ('Getting Started' section H). Begin by restoring the A pulse to a $\pi/2$ pulse and optimize the FID decay by re-tuning the oscillator and pulse width as needed. (You may want to re-examine the mixer output ot be sure you are still on resonance. Small temperature drifts change the magnetic field B_0 and consequently the resonant frequency.)

Set the instrument to produce only a single B pulse and set the width to that of a π-pulse. Observe a spin echo in your sample on the Detector Out after the free induction decay. Fine-tune the width of the B-pulse to maximize the spin-echo amplitude. Save your data from the scope.

Measure the spin-spin relaxation time T_2 of your sample material using the single spin-echo protocol: with a pulse sequence of A= $\pi/2$ followed by a single B= π pulse, measure the amplitude of the spin echo for a series of increasing A-B delay times, τ. From a graph of the decay of the amplitude as a function of delay time, determine T_2. (Refer to eq. 24.1 on p. 10 for ideas on how you might analyze such data to extract T_2. Describe in your report how you decided to analyze the data to find T_2.

Use the multiple B pulse – multiple echo protocol to measure T_2. Set the pulse programmer to generate 20 or more π B-pulses using the Meiboom-Gill pulse sequence (MG connected and on). Decide what makes for a good delay time. Make sure that your repetition rate is low enough to accommodate all your B-pulses. (Don't send another A pulse before all the B pulses have been sent!) Take a screenshot of the oscilloscope showing the sequence of echoes. You can also save the data itself for analysis. Extract a value for T_2 from this data. Explain how you get your value for T_2.

Further explorations: Determine T_1 and T_2 for a series of samples, starting with distilled or de-ionized water and progressing through some dilute but increasing concentrations of solutions containing some well-define and possibly paramagnetic ions that will alter the magnetic environment of the proton spins. Copper or iron sulfates might be interesting choices for solutions.