Pulsed Nuclear Magnetic Resonance (Pulsed NMR)

This manual is an abbreviated synopsis of the TeachSpin manual in the red binder. Please refer to the TeachSpin manual for additional information.

Reading

Please read the conceptual introduction to the instrument and Section I.B (Outline of the Physics) from the manual.

Power Switch

Turn on the power on the back left of the main unit.

Temperature Control

We want the temperature of the magnet to be as steady as possible.

- Adjust the two knobs on the left of the PS2 Controller until the LEDs go off.
- Flip the switches up to the CLOSED position.
- The switches should be left in the OPEN position when not in use.

Default Settings

- In the Receiver section of the main unit:
  - Gain: 75%
  - Band: p
  - Toggle Blanking: On
  - Filter TC: 0.01
- In the Synthesizer section:
  - Ref Out: On
  - CW Out: Off
- In the Pulse Programmer section:
  - Toggle B Pulse and MG: Off
  - Toggle Sync and Toggle Pulse: A

Adjust the Resonant Frequency of the Circuit

The instrument is designed to operate near one of two frequencies: the precession frequency of protons (hydrogen nuclei) in the magnetic field, and the precession frequency of fluorine nuclei in the magnetic field. Whenever we switch between protons and fluorine, we need to manually adjust the resonant frequency of the circuit that detects the rotating magnetic field in the sample.

- Set the frequency of the synthesizer to the resonant frequency of protons in our magnetic field. This frequency is written on the back of the instrument: 21.04 MHz.
  - When the cursor is over F in the Synthesizer unit, press the knob.
  - Turn the knob to select the digit you want to adjust, then press the knob.
  - Turn the knob to adjust the value.

    - Press the knob to restore the flashing cursor, then turn the knob to select the upward arrow.
    - Press the knob to return to the main menu.
- In the Pulse Programmer unit, set A_len to at least 2.5 μs, and set P to 100 ms.
- Disconnect the cable from Channel 1 of the oscilloscope. Connect the "pickup probe" to Channel 1. Place the probe in the holder in the magnetic field.
- Set the Channel 1 scale to 5 V. Set the horizontal scale to 2.5 μs. Press "Set to Zero" in the Horizontal section of the oscilloscope.
- We want to adjust the signal to the maximum. There are two screws you can adjust (to change the capacitances of tuning capacitors). Looking down, the leftmost screw is coarse adjust, and the third (NOT the second) screw is fine adjust. **Do not touch any screws except the first and third screws!**
- Once you've maximized the signal (it should exceed 30 V peak to peak), remove the pickup probe and reconnect the blue cable to Channel 1.

Samples

The samples in the black box are as follows (if nobody mixed them up):

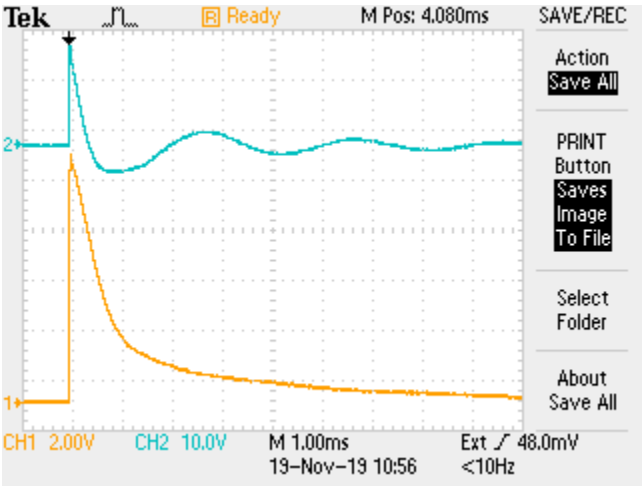
- 1A: light mineral oil
- 1B: heavy mineral oil
- 1C: FC-70 (a compound containing fluorine)
- 1D: two discs of "ultra strong" silicone
- 1E: three discs of "ultra strong" silicone
- 2A: one disc of FDA silicone
- 2B: two discs of FDA silicone
- 2C: three disc of FDA silicone

You're free, of course, to prepare additional samples. In any case, the rubber O-Ring on the vial should be **39 mm above** the center of the fluid. (This will place the fluid in the center of the magnetic field.)

Adjust Synthesizer Frequency

The resonant frequency will be slightly different from what's shown on the label.

- Place a sample of mineral oil in the sample holder.
- Set the period to 1 s. Adjust the horizontal scale on the oscilloscope.
- Adjust the Synthesizer frequency to minimize the oscillations in Channel 2. Make Channel 2 look as much like Channel 1 as possible. (Channel 1 is the "envelope" obtained by drawing a smooth line through the maxima of Channel 2.)



Saving Data

Save the images and data that you want on the flash drive.

Optimize Magnetic Field Uniformity

We want the magnetic field to be as uniform as possible. As the uniformity increases, the signal on Channel 1 lasts longer; the decay time increases. Adjust X, Y, Z, and Z^2 coils to maximize the decay time.

The 90° Pulse

The voltages we're plotting are proportional to magnetization in the x-y plane. Since equilibrium magnetization is in the z direction (parallel with the magnetic field), the spins need to be rotated 90° from equilibrium to maximize magnetization in the x-y plane. Increase A_len from 0 to maximize the signal, which shows "free induction decay."

Three Reasons the Amplitude Decays after a 90° Pulse

- The lowest energy state is equilibrium, in which the spins are aligned with the magnetic field. The hydrogen nuclei (protons) gradually release energy to neighboring atoms ("the lattice") to return to equilibrium. This process is called spin-lattice relaxation, and the time constant is called T_1.
- The magnetization in the x-y plane is significant only when all the spins are pointing in the same direction as they precess around the magnetic field. (This means all the spins are in phase.) The spins gradually "dephase" because the precession frequency is not the same for all hydrogen nuclei: the precession frequency depends on the neighboring atoms because these atoms affect the local magnetic field. This dephasing process is called spin-spin relaxation, and the time constant is T_2.
- The external magnetic field is nonuniform, causing the spins to dephase over time. The time constant of this process is called T_2*.
- So we need to come up with measurements that isolate the effects of T_1 and T_2 so that we can characterize our sample.

The 180° Pulse

The 180° pulse should be approximately double the 90° pulse. It should flip the spins 180° from equilibrium, so there should be no magnetization in the x-y plane. Since x-y magnetization is what's shown on Channel 1, we want to minimize the signal after 180° pulse.

- Adjust A_len to minimize the signal.
- Adjust the tuning capacitor to further minimize the signal.
- Iterate.

Measuring T_1

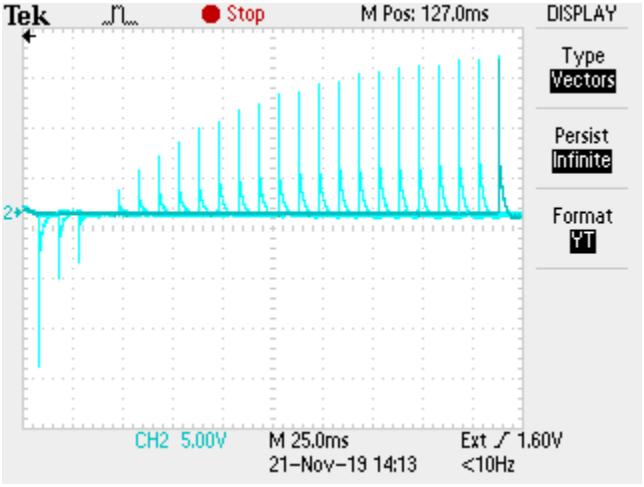
To determine T_1, we first use a 180° pulse to flip the magnetization from the +z direction to the –z direction. Then we want to see how M_z, the magnetization in the z direction, depends on time. M_z returns to equilibrium according to

$$\frac{dM_z(t)}{dt} = \frac{M_0 - M_z(t)}{T_1}, \quad (1)$$

where M_0 is the equilibrium magnetization.

We want to determine $M_z(t)$, but our system can measure magnetization only in the x-y plane. So, to determine M_z at a time t after the 180° pulse, we apply a 90° pulse at time t to rotate M_z into the x-y plane. The initial amplitude of the signal is $M_z(0)$.

- Make a crude estimate of T_1 by applying a 90° pulse with decreasing repetition time P until the signal begins to decrease (because the spins don't have time to return to equilibrium before the next pulse).
- Set A_len for a 180° pulse and B_len for a 90° pulse. Flip up the B Pulse toggle, and increase the number N of B pulses to 1.
- Adjust the period P to be much larger than your estimate of T_1 (to ensure that the system returns to equilibrium before the next pair of pulses).
- Adjust the time τ between pulses until the signal shrinks to 0. Determine T_1 by solving Eq. (1). (What is the initial condition, $M_z(0)$?)
- For a more accurate determination of T_1, measure $M_z(t=\tau)$ for a variety of τ and fit the data with the solution to Eq. (1). The figure below shows the Channel 2 signals (since Channel 1 is always positive) for a variety of τ. The "envelope" of these signals is the solution to Eq. (1).

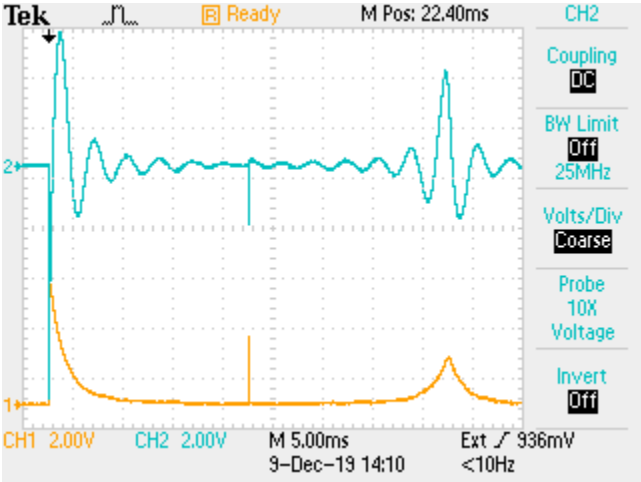


Spin Echo

A 90° pulse tips the spins into the x-y plane. These spins initially point all in the same direction, but they precess around the z axis (the magnetic field direction) at different speeds due to inhomogeneity in the magnetic field caused by neighboring atoms. Faster spins precess ahead of the slower spins until some have the opposite direction as others, and the total magnetization decays to 0.

Next, use a 180° pulse to reverse all the spins. Now the slower spins are ahead of the faster spins, so the precession causes the faster spins to catch up to the slower spins, producing a "spin echo." The spin echo is weaker than the original amplitude (after the 90° pulse) due to interactions between the spins. The decay of the echo amplitude allows us to determine T_2.

Apply a 90° pulse followed by a 180° pulse after some time τ. You should see the echo at 2τ. (Time τ coincides with the spike halfway between the original signal and the echo.)



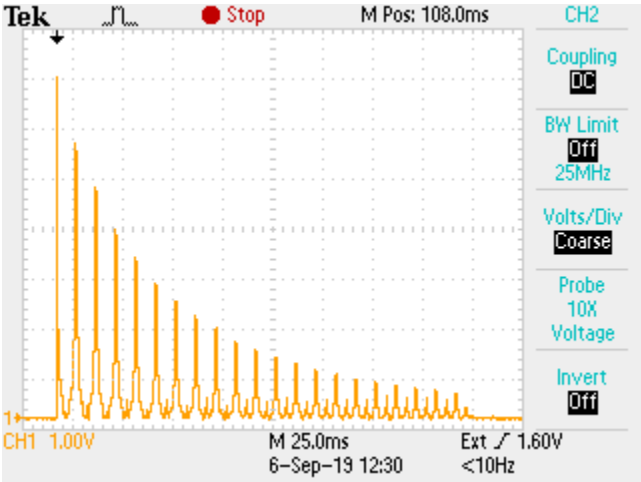
Measuring T_2

We can see how the echo amplitude decays over time by applying the following sequence of pulses:

90° pulse, delay of τ, 180° pulse, delay of 2τ, 180° pulse, delay of 2τ, 180° pulse, delay of 2τ, …

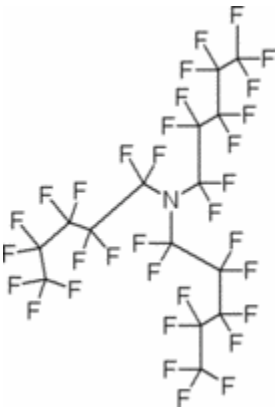
To reduce the accumulated error in repeated 180° pulses (that are really 180°±some error), we can use the Meiboom-Gill (MG) phase shift of 90° between the 90° pulse and the 180° pulses. This means (in a rotating reference frame) that the 90° pulse rotates the spins around the y axis, but the 180° pulses rotate the spins around the x axis. Why does this reduce accumulated error? A detailed and lucid explanation is in the original paper by Meiboom and Gill.

Increase Num_B and determine T_2 as the exponential decay constant of the echo amplitudes. Make sure the period is large enough.



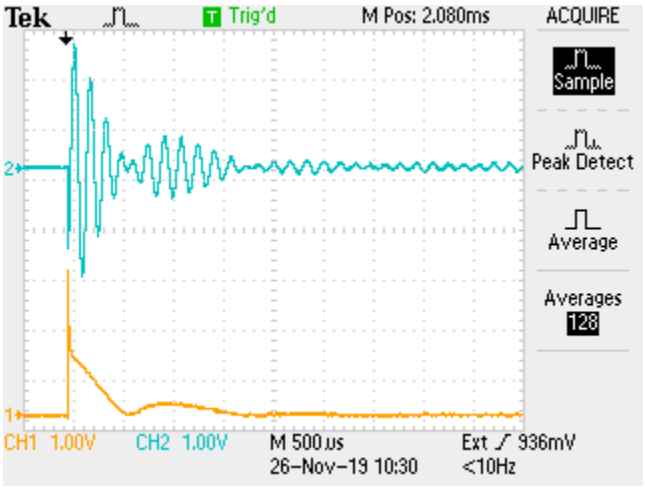
Probing Molecular Structure

The Larmor frequency of nuclei depends on neighboring atoms. Consider a molecule of FC-70 (figure from https://www.sigmaaldrich.com/catalog/product/sigma/f9880?lang=en&region=US):



Different fluorine atoms in this molecule may have different Larmor frequencies depending on where they are in the molecule. Chemists use the spectra of detected frequencies to identify the chemical composition of samples. How can we detect multiple frequencies?

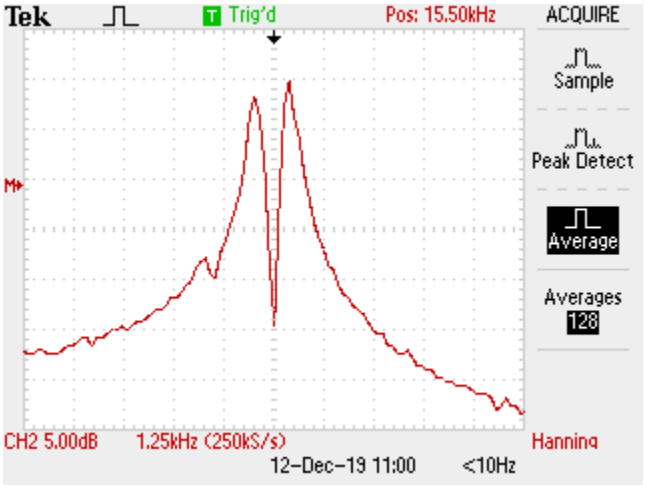
We need to recognize that the oscillations on Channel 2 (within the exponential envelope) are given by $\cos[(\omega_{ref} - \omega_{spins})t]$, where ω_{ref} is the synthesizer frequency (which we've been setting close to ω_{spins} by minimizing the oscillations in Channel 2). If we do a Fourier transform of Channel 2, we get a peak at $(\omega_{ref} - \omega_{spins})$. If there are multiple frequencies $\omega_{spins,1}$, $\omega_{spins,2}$, etc., then the Fourier transform shows multiple peaks at $(\omega_{ref} - \omega_{spins,1})$, $(\omega_{ref} - \omega_{spins,2})$, etc. To see these peaks in a Fourier transform, they can't be too close to 0, so the synthesizer frequency must be slightly off resonance (there should be some wiggles in Channel 2).



To measure fluorine spins, we need to change synthesizer frequency and the resonant frequency of the circuit.

- Flip the switch from p to F on the Receiver unit.
- Estimate the resonant frequency of F using $\omega_{fluorine}/\omega_{hydrogen} = 0.9408$.

- Set the synthesizer to this frequency.
- Place the pickup probe in the sample holder and adjust the tuning capacitors to maximize the signal during the pulse.
- Place a sample of FC-70 (from 3A in the box) in the sample holder.
- Apply a 90° pulse and observe free induction decay.
- Generate a fast Fourier transform (FFT) of the signal by pressing the MATH button on the oscilloscope.



Other Experiments

As time allows, perform other experiments described in the manual or based on your own creativity and imagination. The pulsed NMR spectrometer is a very versatile instrument.

A Math Problem To Include in Your Lab Report

Solve Eq. (1.16) in the printed TeachSpin manual (it's 17.1 in the old version found online) to prove that the magnetic moment precesses.