

Nuclear Magnetic Resonance (NMR)

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1 Theory

Read Section 14.4 of Shankar, Spin Dynamics, including the optional digression on negative absolute temperature.

2 Prelab

1. Do exercise 14.4.1 in Shankar. *Hint:* Use the Ehrenfest Theorem to evaluate the time derivative,

$$\frac{d}{dt} \langle \vec{L} \rangle = \frac{-i}{\hbar} \langle [\vec{L}, H] \rangle.$$

2. Do exercise 14.4.4 in Shankar, with the following modifications. Consider a proton, not an electron, and use a field strength of 10 Gauss instead of 100 Gauss. (Careful! He uses cgs units.)
3. Consider a collection of independent protons at room temperature in a magnetic field of 4kG. Approximately what fraction of these protons will be aligned parallel with the magnetic field, as opposed to antiparallel?
4. If we disturb this distribution, say with a 180° pulse, we may expect the system to decay back to thermal equilibrium with some characteristic time T_1 . Phenomenologically, we can modify the precession equation

for the net magnetization \vec{M} to include this decay term.

$$\begin{aligned}\dot{M}_x &= \gamma (\vec{M} \times \vec{B})_x \\ \dot{M}_y &= \gamma (\vec{M} \times \vec{B})_y \\ \dot{M}_z &= \gamma (\vec{M} \times \vec{B})_z + (M_0 - M_z) / T_1\end{aligned}$$

where M_0 is the equilibrium magnetization along $\vec{B} = B_0 \hat{\mathbf{k}}$.

Consider a system in thermal equilibrium for time $t < 0$. Let a 180° pulse be applied just before $t = 0$ so that, at $t = 0$, $\vec{M} = -M_0 \hat{\mathbf{k}}$. Solve for $\vec{M}(t)$ for time $t \geq 0$, and plot $M_z(t)$ from $t = 0$ to $t = 3T_1$. For what value of t is the net magnetization zero?

5. For this exercise and the next one, consider the case of a non-uniform magnetic field. Here, each spin feels a slightly different value of B_0 and thus precesses at a slightly different frequency. In this case, it will be useful for us to consider the net magnetization as the sum of the individual magnetic moments of each proton.

$$\vec{M} = \sum_{i=1}^N \vec{\mu}_i,$$

where each magnetic moment $\vec{\mu}_i$ is a classical vector of constant magnitude $e\hbar/2Mc$, obeying the precession equation

$$\dot{\vec{\mu}}_i = \gamma \vec{\mu}_i \times \vec{B}_i.$$

(Recall that we can do this because of the result of Shankar's Exercise 14.4.1.) Now model the magnetic field at each proton as

$$\vec{B}_i = (B_0 + b_i) \hat{\mathbf{k}},$$

where B_0 is the average field value, and the individual variations b_i have a mean of zero. In the rotating reference frame, the precession equations then become

$$\dot{\vec{\mu}}_i = \gamma \vec{\mu}_i \times (b_i \hat{\mathbf{k}}_r).$$

Let us consider, as in the last exercise, a system in thermal equilibrium for times $t < 0$, with $\vec{M} = M_0 \hat{\mathbf{k}}$. This time, however, let's apply a 90°

pulse at $t = 0$, instead of a 180° pulse, with rotation being about \hat{i}_r in the rotating reference frame. At $t = 0$, then, the magnetic moment of each proton becomes, in this rotating frame,

$$\vec{\mu}_i(0) = \frac{e\hbar}{2Mc} \hat{i}_r,$$

and hence the magnetization is $\vec{M}(0) = M_0 \hat{i}_r$.

Solve the precession equations for the individual moments $\vec{\mu}_i$ in the rotating frame for times $t \ll T_1$, then evaluate the sum to get the net magnetization $\vec{M}(t)$. Show that this net magnetization decays due to dephasing with a characteristic timescale

$$\frac{1}{T_2} = \gamma \sqrt{\langle b_i^2 \rangle}.$$

Hint: What you will get here is a sum of phases, of the form

$$\sum_{n=1}^N e^{i\phi_n}$$

To evaluate this sum, expand each phase as a series, then sum each order in ϕ separately.

$$\begin{aligned} \sum_{n=1}^N e^{i\phi_n} &= \sum_{n=1}^N \left\{ 1 + i\phi_n + \frac{1}{2}(i\phi_n)^2 + \dots \right\} \\ &= N + \sum_{n=1}^N i\phi_n + \frac{1}{2} \sum_{n=1}^N (i\phi_n)^2 + \dots \end{aligned}$$

The series you wind up with will have an (approximate) exponential representation, with a characteristic decay time equal to T_2 .

6. Now apply a 180° pulse at a much later time $t = \tau$ when the initial free-induction-decay signal has long since died away, *i.e.* $\tau > T_2$. Show that the magnetization will return to its full initial value at time $t = 2\tau$, then decay again with the same time constant T_2 . This phenomenon is known as *spin echo*.

Hint: Replace the x-y plane in the rotating frame with the real and imaginary axes of the complex plane, write the vector $\vec{\mu}_i$ as a complex

number, and express the precession equation in this complex notation. Remember that the 180° pulse essentially rotates all of the spins around the x-axis, in the rotating reference frame, and this will be particularly easy to represent if the complex plane is used to represent the x-y plane. This is the starting point for a lot of NMR dephasing analysis and is widely used in the NMR literature.

We can describe both dephasing and thermal relaxation with the following phenomenological modifications to the precession equations.

$$\begin{aligned}\dot{M}_x &= \gamma (\vec{M} \times \vec{B})_x - M_x/T_2 \\ \dot{M}_y &= \gamma (\vec{M} \times \vec{B})_y - M_y/T_2 \\ \dot{M}_z &= \gamma (\vec{M} \times \vec{B})_z + (M_0 - M_z)/T_1\end{aligned}$$

These are known as the *Bloch Equations*, after Felix Bloch. If there are several, uncorrelated mechanisms that cause the variation in \vec{B}_i , then the dephasing rates for each just add to give a total dephasing rate T_2^* .

$$\frac{1}{T_2^*} = \frac{1}{T_2^A} + \frac{1}{T_2^B} + \dots$$

Two examples of sources of nonuniformity are

1. Inhomogeneities in the field of the permanent magnet used to supply the field \vec{B} , and
2. Interactions between individual spins.

If you were doing research, you would probably want to look at the interactions between the spins and be uninterested in the inhomogeneities of the magnet. Because the inhomogeneities in the magnet do not change with time, any dephasing they cause can be recovered using this spin-echo technique. The spin-spin interactions, however, change over time, and the dephasing they cause cannot be recovered by spin-echo.

We may expect the net magnetization, then, to decay immediately following the initial 90° pulse as

$$M(t) \sim M(0)e^{-t/T_2^*}.$$

This initial decay is known as the *free-induction decay*, or FID. Spin-spin interactions should keep the spin echo signal from returning to its full initial height $M(0)$, and the height of the spin echo should decay as

$$M(2\tau) = M(0)e^{-2\tau/T_2}.$$

This provides us with a way of separating the irreversible dephasing time T_2 from the total dephasing time T_2^* . Because T_2 is intrinsic to the sample and T_2^* depends on your apparatus, it is usually T_2 that you are interested in.

3 NMR Techniques: First lab session

In a well-funded research lab, you would probably not build your own NMR apparatus. Instead, you would buy a research-grade instrument, just as you would buy a cryostat or oscilloscope. Research-grade NMR spectrometers usually include strong, superconducting magnets, computer control, digital signal processing, and sometimes cryogenic sample spaces for studying NMR at low temperatures.

The instrument you will use in this lab is a TeachSpin PS1-A, a pulsed NMR apparatus designed for teaching the physics behind NMR measurements. It focuses on the use of 90° and 180° pulses for measuring T_1 , T_2 , and T_2^* . The pulse and measurement process is made transparent by making all of the signal paths accessible from the front panel.

The samples you will use, at least for the first half of this lab, are pretty simple. Remember, however, that the purpose of this lab is not to study the physics of relaxation mechanisms, but to learn how the measurements are made. The zero-crossing and spin-echo techniques you learn here are exactly the same ones you would use to measure T_1 and T_2 in a research environment. Even MRI, Magnetic Resonance Imaging, used for generating beautiful maps of the interiors of living things, is just a repeated application of these measurement techniques. Spatial information in these images comes from a strong magnetic field gradient, which allows us to correlate the positions of spins by their precession frequency, or the strength of the field felt.

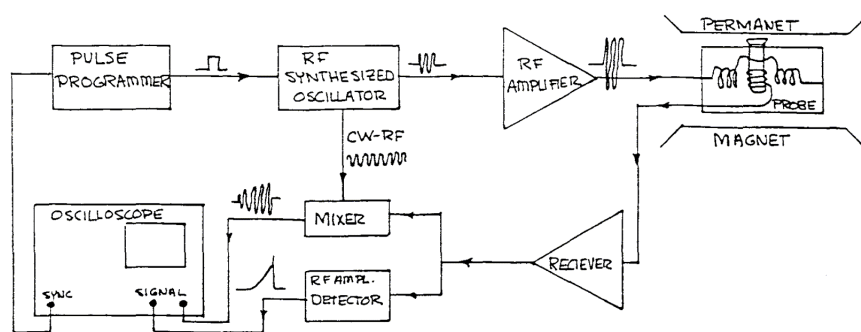


Figure 1: A block diagram of the pulsed-NMR apparatus used in this lab. In this setup, an RF synthesized oscillator is gated by a pulse programmer to produce, through an RF amplifier, an oscillating magnetic field B in the sample. Note carefully the orientation of the coils around the sample! As shown in this figure, the permanent magnetic field is applied perpendicular to the page; the applied magnetic field B is orthogonal to the axis of the sample tube; and the axis of the receiver coil is parallel to the test tube's axis. The output of the receiver goes both to a mixer (analog multiplier) and to an RF amplitude detector (rectifier), and the outputs of these are displayed on an oscilloscope.

3.1 Apparatus

A block diagram of the TeachSpin apparatus is shown in Figure 1. A permanent magnet supplies the field B_0 along the z-axis (which in this instrument is not vertical but parallel to the table). The rotating magnetic field B is supplied by a Helmholtz coil with its axis perpendicular to the axis of the sample test tube. The field this coil supplies, of course, is actually linear, not rotating, but any linearly polarized field can be thought of as the sum of two counter-rotating fields. In our case only the component that matters is the one rotating along with the precessing spins. The other one can be neglected. The magnetization produced by the sample does rotate, and because of this the receiver coil, labeled "probe" in Figure 1, can be oriented perpendicular to the Helmholtz coil.

3.2 Applied RF field and 90° pulses

The first thing we are going to do is look at the applied magnetic field B . Supplied with the instrument are two vials with small loops of wire embedded in epoxy and coaxial cables connected to these loops. We will observe B and measure its amplitude by placing one of these coils in the sample space and looking at the voltage induced by the oscillating B field.

Notice that the two coils have different orientations. One is designed for measuring B , and the other, which we will not use in this lab, is designed for generating a false signal in the pickup coil. For the orientation of coils shown in Figure 1, which coil should you use to measure B ? What is the relationship between the voltage generated across the coil and B ? What property of the coil do you need to measure to convert between this voltage and B ? (This will just be a rough estimate, so don't spend too much time on precision here. 20% or so will be fine.) Clearly describe your procedure for measuring B in your lab book, along with the formula you use for converting your observed voltage to B and how you arrived at it.

Note: When you attach the cable connected to your measurement coil to your oscilloscope, set the input impedance of that channel to be 50 Ω .

If there are any cables connected to the front panel of the TeachSpin electronics bin, disconnect them and turn the instrument on. (The switch is in the back.) Locate the A+B OUT port, in the PULSE PROGRAMMER module. Using a tee, connect this to the A+B IN port on the 15 MHz OSC/AMP/MIXER module and then to the other channel of your oscillo-

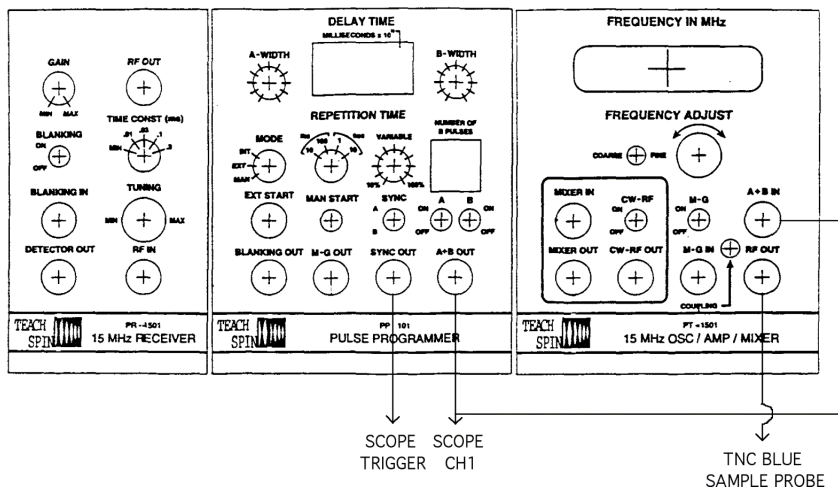


Figure 2: Wiring diagram for observing pulse gating signal and measuring B .

scope. Trigger the scope off of the SYNC OUT signal, provided by the pulse programmer module. The blue cable attached to the sample holder with the TNC connector on the end of it supplies current to the Helmholtz coil. Plug this into the RF OUT port on the 15 MHz OSC/AMP/MIXER module.

Because this instrument is only designed for pulsed NMR, it does not supply a continuous RF signal to the Helmholtz coils. Instead, the RF oscillator is gated by the pulse programmer. When the voltage going into the A+B IN port is high, a signal is applied to the coils. When it is low (zero), no current flows through the coils, and no magnetic field is applied. The length of time over which the field is applied is set by the A-WIDTH knob on the pulse programmer module. On the pulse programmer module, make sure that MODE is set to INT, the SYNC switch is set to A, the A switch is ON, and the B switch is OFF.

You should now see both the gating signal and an RF signal, as detected by the coil you placed in the sample space, on your oscilloscope screen. Make sure your coil is optimally aligned, measure the amplitude of the RF signal you observe, and use this to estimate the magnitude of B . Estimate how long this signal should be applied to produce a 90° pulse, and set the A-WIDTH

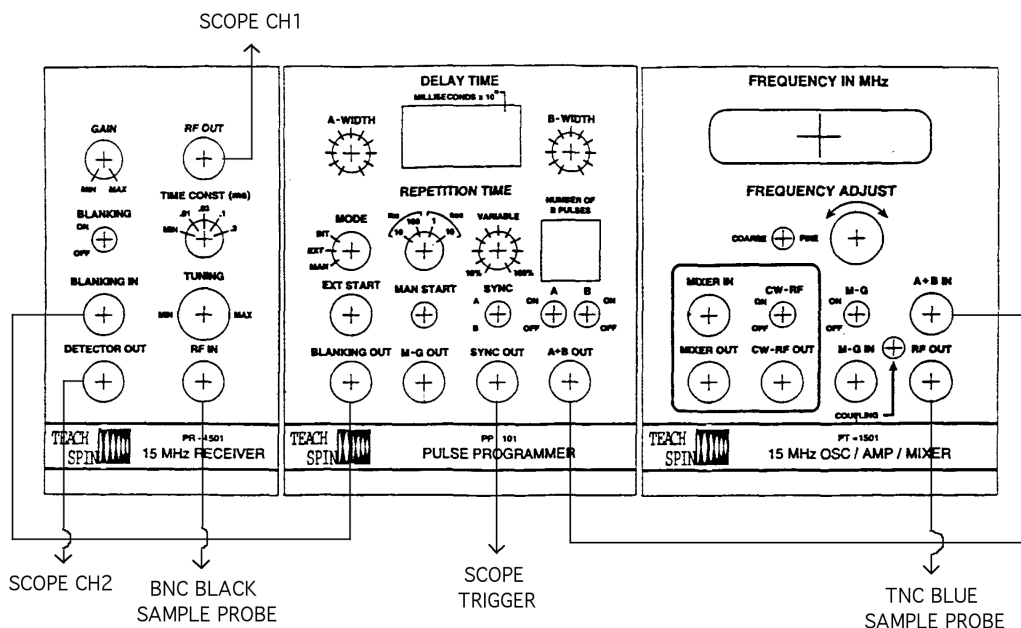


Figure 3: Wiring diagram for observing free-induction decay (FID).

to this value. Take a screenshot, print it out, and include it in your lab book.

3.3 Single-pulse free-induction decay

Now remove the test coil from the sample space and disconnect it from your oscilloscope. The RF pickup coil, wrapped around the sample space inside the sample holder assembly, is connected to a thin, black coaxial cable with an ordinary BNC connector at the other end. Connect this cable to the RF IN port in the 15 MHz RECEIVER module. Send the RF OUT signal to your scope, and send the BLANKING OUT signal to the BLANKING IN port. Start with the BLANKING switch OFF.

There is, as you should observe, considerable crosstalk between the Helmholtz coils and the receiver coil! The blanking signal here is essentially the opposite of the A+B gating signal you looked at in the last section. With blanking

on, whenever an RF signal is applied to the Helmholtz coils, the RF receiver is turned off. Look at the RF OUT and A+B OUT signals on your scope with blanking on and off. Take screenshots of both cases, and include them in your lab book. Now switch blanking on and leave it there.

Pick out a sample, either mineral oil or glycerin, and insert it into the sample space. Adjust the scale on your scope until you can see the free induction decay signal as it appears after the A pulse ends. Play with the GAIN and TUNING knobs to get a good signal, then take screenshots with the sample in and out to demonstrate that the signal you see really does come from the sample. (Adjust the tuning to maximize your signal and the gain to keep it from saturating.)

Now we are at a point where we no longer need to look at the gating signal. Disconnect the A+B signal from your scope, and replace it with the DETECTOR OUT signal. (This is just a rectified version of the RF OUT signal.) In the last section, you set the A-WIDTH to approximate a 90° pulse. Now you should fine-tune the A-WIDTH to a more precise 90° pulse by maximizing your observed free-induction decay. Measure T_2^* , and record your result in your lab book.

Play around with the TIME CONSTANT knob to see what that does. Record your observations. (*Hint:* If you are at all familiar with passive filters, it does exactly what you'd expect.)

3.4 Mixer

We have adjusted the receiver circuit to optimize our signal, but we have not yet paid any attention to our oscillator. For resonance to occur, recall that the applied RF magnetic field must be at the same frequency as the natural proton precession frequency in the constant magnetic field B_0 . If we are close, we will still be able to stimulate some precession, but for accurate measurements of T_1 and T_2 we will need to meet the resonance condition with a fair degree of precision.

We can compare our oscillator's frequency with the protons' precession frequency by using a *mixer*, contained in the 15 MHz OSC/AMP/MIXER module. A mixer is a nonlinear, passive electronic device that essentially multiplies two signals. Recall that the product of two sine waves at different frequencies has the form

$$\sin(\omega_1 t) \sin(\omega_2 t) = \frac{1}{2} \{ \cos[(\omega_1 - \omega_2)t] - \cos[(\omega_1 + \omega_2)t] \}.$$

If the two inputs of a mixer contain signals at different frequencies, the output contains signals at both the sum ($\omega_1 + \omega_2$) and difference ($\omega_1 - \omega_2$) frequencies.

In the TeachSpin apparatus, one of the mixer's inputs is internal and not accessible from the front panel. If the CW-RF switch is ON, this internal input receives a signal from the 15 MHz oscillator, which also appears on the CW-RF OUT port. The other input is accessible from the front panel and is labeled MIXER IN. Connect the RF OUT port (on the receiver module) to the MIXER IN port, and send the MIXER OUT signal to your oscilloscope. Note that you will only see the difference-frequency signal, as the sum-frequency signal, at ~ 30 MHz, is filtered out inside the module. During a free-induction decay, you should see a beat signal, on the output of the mixer, between the oscillator and the FID signal, which oscillates at the precession frequency. Tune the oscillator frequency to get it as close as you can to the natural precession frequency. Record the precession frequency, and use it to calculate the value of B_0 . Record a screenshot of the optimized mixer-out signal in your lab book.

(This tuning procedure will be familiar to anyone who plays a stringed musical instrument. When tuning a guitar, for example, you compare some reference tone to that produced by a string, adjusting the tension on that string to eliminate audible beats between the two tones.)

Once you have tuned the oscillator frequency, verify that your A-WIDTH, TUNING, and GAIN settings are still optimized. Correct them if they are not. From now on, you should monitor the MIXER OUT signal any time you are performing a measurement, to make sure your oscillator is still tuned to resonance. The permanent magnet is very sensitive to temperature drifts, and the precession frequency is likely to drift over time.

4 Multiple pulse sequences

Now that you have learned how to tune the system to produce clean 90° pulses and observed a single-pulse free-induction decay, we are ready to start investigating properties of the sample. In particular, we will explore techniques for measuring T_1 and T_2 . For this you will need to apply sequences of pulses, and the PS1-A has the capability to do that.

Look at the A+B OUT signal on your scope again, only this time switch B to ON. Start with the following settings:

DELAY TIME	1.00×10^1 ms
MODE	INT
REPETITION TIME	1 s
NUMBER OF B PULSES	02
SYNC	A
A: ON	B: ON

You should see three pulses on your scope screen. Play around with the settings to get a feel for what they do. Change the A and B widths. (Don't forget to record the A width first so that you can go back to a good 90° pulse later.) Change the delay time, sync source, A and B switches on and off, and the repetition time.

4.1 Zero-crossing measurement of T_1

In your prelab exercises (# 4) you saw how the magnetization would decay back to equilibrium after a 180° pulse, and how the zero-crossing point of this decay provides a measure of T_1 . Set your system up to produce only two pulses, one A pulse and one B pulse. Set the A-width to produce a 180° pulse and the B-width to produce a 90° pulse. The first, 180° pulse inverts the sign of the magnetization along the z-axis, and the second pulse is used to measure the net magnetization. Do this for several values of the DELAY TIME, the time between the A and B pulses, and plot the net magnetization versus the time after a 180° pulse. Fit your theory from prelab Exercise 4 to your data, and use this to measure T_1 .

Notes:

- Tune the A and B pulses separately to make sure they are good 180° and 90° pulses, respectively. We saw earlier how to tune the pulse width to produce a good 90° pulse by maximizing the free-induction decay. What should the free-induction decay be like for a perfect 180° pulse? Why?
- Note that we do not need to convert the amplitude of the initial FID following the B pulse to an actual magnetization. As you saw in the prelab exercises, the zero-crossing technique gives T_1 without requiring us to know the actual value of $M(t)$, only its shape.
- The magnetization decay curve you observe has one distinct difference from the one you predicted in the prelabs. Why is what you observe

different from what you predicted?

4.2 Spin-echo and T_2

Now reverse the order of the pulses. Set the A pulse to be a 90° pulse and the B width for a 180° pulse. Again, tune each separately, using the A and B switches to isolate each one. See if you can observe a single spin echo. (It may be useful to plot, on your scope, A+B OUT and DETECTOR OUT simultaneously. A good delay time to start with here is $100\mu s$.) Take a screenshot of your spin-echo signal, and record it in your lab book.

We could now just vary the delay time and plot the height of the spin echo to get T_2 , but there is a less tedious and more accurate way to do this measurement. Increase the number of B pulses from one to twenty or more, and make sure the M-G switch is set to OFF. Observe all of the subsequent spin-echo pulses, and from this infer an initial estimate of T_2 .

One thing to be careful about here is that, if the B-widths are not perfect, the B-pulses will not produce exactly 180° of rotation. If the B-pulses produce, say, only 175° of rotation, then after ten pulses an error of 50° has built up. This will substantially attenuate the spin echo and contaminate your measurement of T_2 ! To see how sensitive the spin echo is to the B width, slightly adjust the B width to try and maximize the amplitude of the spin-echo train. As you can see, your measurement of T_2 by this method is not very reliable. Take a screenshot of your optimized spin-echo train, and record it in your lab book.

One way around this dilemma is to alternate the sign of the 180° pulses for every other B pulse. Now, if one B pulse only produces 175° of rotation, the next pulse will rotate the system by -175° , for a net accumulated error of zero. This alternating-sign technique is named after its inventors, Meiboom and Gill, and it is applied in the PS1-A by connecting the M-G OUT port on the pulse programmer to the M-G IN port on the oscillator module, and switching M-G to ON. Do this, and use the Meiboom-Gill technique to get a refined measurement of T_2 .

(The first method, that of applying a train of what-you-hope-are- 180° pulses, is known as the Carr-Purcell method, after the first discoverers of NMR.)

5 Experiments: Second lab session

The study of relaxation mechanisms in condensed matter is an area of active research, and there are a large number of experiments we could now do with the PS1-A. For this part of the lab, choose a material that contains hydrogen (protons), and study its relaxation times T_1 and T_2 as you vary some property of the material. Here are some examples of appropriate projects.

Paramagnetic doping: In pure water, the coupling between the protons' spins and the rest of the water is weak. For very pure, deionized water, relaxation times on the order of $T_1 > 1\text{sec}$ are not unheard of. Paramagnetic ions dissolved in the water strongly affect the coupling between the protons and the bath and can dramatically reduce T_1 . For this project, obtain some distilled or deionized water and some water-soluble paramagnetic ions. (CuSO_4 and $\text{Fe}(\text{NO}_3)_3$ will work and may even be available in the lab.) Study T_1 and T_2 as a function of the concentration of the ions.

Self diffusion and viscosity: One way to produce irreversible dephasing is by diffusion. If a proton has diffused significantly between an initial 90° pulse and a subsequent 180° pulse, designed to produce a spin echo, then the magnetic field it feels will be different enough to lead to irreversible dephasing. The dephasing time constant for this mechanism was shown by Carr and Purcell to be

$$\frac{1}{T_2^D} = -\gamma^2 \frac{\partial H}{\partial x} \frac{D}{12},$$

for the case where the field gradient $\partial H/\partial x$ is in the x-direction. (Here D is the diffusion constant.) The PS1-A's sample holder can be moved along both the x- and y-axes, using the knobs on the front of the magnet assembly, and you can use this degree of freedom to measure the field gradient. (Remember, the value of the field is got from the precession frequency.) For this project, get some glycerin and distilled water and mix them in various ratios. The viscosity, and hence the diffusion constant, should depend on this mixing ratio. Measure the field contours in both the x- and y-axes, then study the effects of the mixing ratio on D .

5-minute epoxy and diffusion: Epoxy is a hydrocarbon and therefore contains lots of protons. It also, after mixing, makes a transition from liquid to solid over the course of its curing time. We might expect the relaxation time(s) to increase as the epoxy cures. For this project, you could obtain some 5-minute epoxy and measure its relaxation times as a function of time while it cures.

You can also come up with your own projects.

References

1. Ramamurti Shankar, *Principles of Quantum Mechanics*, Plenum Press, New York (1980).
2. Brian Cowan, *Nuclear Magnetic Resonance and Relaxation*, Cambridge University Press, Cambridge UK (1997).