A Conceptual Tour of TeachSpin's Pulsed NMR

Pulsed nuclear magnetic resonance begins with the net magnetization of the protons of a sample in thermal-equilibrium in a strong magnetic field which is designated B_o. There is a net alignment of the spins with this field which is considered to be directed along the +z axis. In the TeachSpin PNMR, this is the field of the **permanent magnet**. The direction of the net magnetization is altered by one or more 90° or 180º rf pulses. The spins, tipped into the x-y plane, then precess around B_o creating a time varying voltage in a pick-up coil. The **pickup coil** monitors only magnetization in the x-y plane.

Figure 1shows an artist sketch of the sample probe. The transmitter coil is wound in a Helmholtz configuration with its axis perpendicular to the constant magnetic field, B_o, of the permanent magnet. The transmitter applies the oscillator's rf pulse to the sample "tipping" the spins. The receiver pickup coil is tightly wound in a solenoid configuration around the thin walled tube which holds the sample vial. The pickup coil's axis is perpendicular to both the axis of the transmitter coil and the magnetic field of the permanent magnet. The pickup coil "senses" the precession of the magnetization in the field of the permanent magnet.

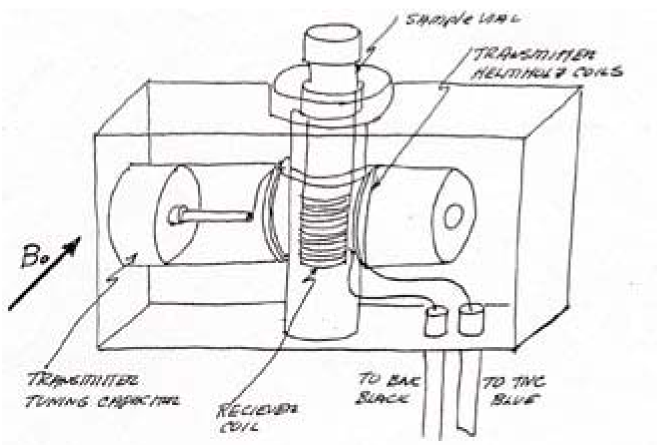

Figure 1 – Artist Sketch of Sample Probe

The precessing magnetization induces an emf in the pickup coil which is subsequently amplified by the circuitry in the receiver. The coaxial cables for both the transmitter and receiver coils are permanently mounted in the sample probe.

Figure 2 is a schematic showing a view of the system looking down into the magnet. In this view, the central circle represents the sample. The B_o arrows represent the magnetic field of the permanent magnet. The double ended arrow B_1, represents the rf field used to tip the spins.

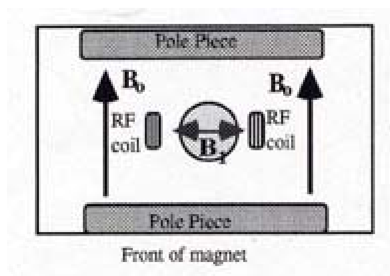

Figure 2 – Top View of Magnet

Initially, the net magnetization of the sample is aligned along B_o, the field of the permanent magnet. The rf coils produce a field, B_1, which can be visualized as the sum of two counter rotating fields. If the rf pulse is at the Larmor frequency, the spins will precess around the direction of the B_1 field. The duration of the pulse is adjusted to give a 90° spin flip orienting the net magnetization of the sample perpendicular to the page. After the B_1 pulse, the spins will precess around the B_o field.

Figure 3 is a front view of the sample after a 90° rotation. The net magnetization, shown as the arrow labeled μ, will precess around the Bo field, now shown as into the page. The coil, wrapped around the sample, is the pickup coil. The trace observed on the oscilloscope will indicate the positive detected amplitude of the 15 MHz precession of the magnetization.

The trace will diminish relatively quickly due to the inhomogeneity of the magnet which dephases the spins.

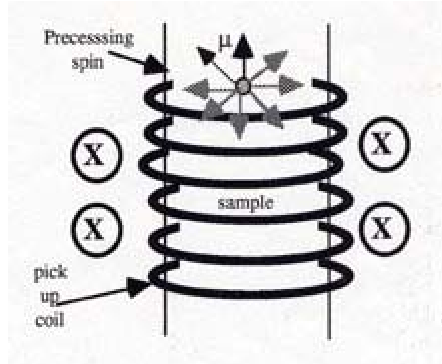

Figure 3 – Front View of Sample after a 90° rotation.

The **RECEIVER** amplifies the signal coming from the pickup coil. As the spins precess inside the pickup coil, they induce a voltage which rises and falls as a sine wave with each rotation. Due to interactions between the atoms, the magnitude of the signal decreases with time. This, however, is not the signal that the **DETECTOR** sends to the oscilloscope. The detector transmits only the maximum strength of the signal for each rotation. The signal is "rectified" so that only a positive magnitude is shown each time. It is this "rectified" envelope, shown in the first section of the lower trace of Figure 4, which represents the **free induction decay or FID**. (If you wish to observe the sinusoidal output of the pick-up coil, it is available at the **RF OUT** of the receiver.)

The **FREQUENCY IN MHz** read-out on the right side of the PNMR gives the radio frequency (rf) pulse being used to "tip the spins" and change the direction of the net magnetization of the sample. For proper on-resonance operation, this frequency must be the same as the precession frequency of the protons in the field of the permanent magnet. (In TeachSpin's Magnetic Torque simulation, this is equivalent to the frequency at which the small rotating field accessory is turned by hand. When doing this by hand, on the Magnetic Torque apparatus, the person turns the small magnet assembly so that it keeps up with the precession the ball has in the field generated by the coils.)

The actual proton precession frequency sensed by the pick up coil comes from the **RF OUT** on the receiver and is connected to **MIXER IN** on the mixer itself. An internal connection feeds the rf frequency of the rotating magnetic field into the mixer. The **MIXER** multiplies the rf signal from the transmitter coil with the actual precession frequency of the protons as sensed by the pick up coil. This allows the experimenter to see if they are the same. When the oscillator is properly tuned to the resonant frequency, the signal output of the mixer should show no "beats." **MIXER OUT** sends the signal to the oscilloscope. The mixer signal, shown in the upper trace of Figure 4, indicates that the system is not exactly "on resonance," but it is close.

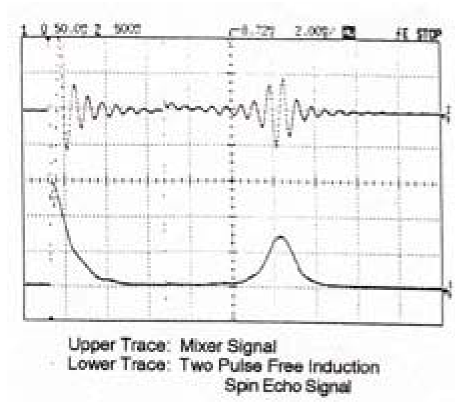

Figure 4 – Upper Trace: Mixer Signal
Lower Trace: Two Pulse Free Induction
Spin Echo Signal

The **FREQUENCY ADJUST** tuning can then be used to match the frequency of the rf pulse to the proton precession frequency. The precession frequency drifts because the temperature of the permanent magnet is not absolutely constant. Any change in magnet temperature causes a change in the magnetic field $\mathbf{B_0}$ and thus in the precession frequency.

There are **two different GAIN mechanisms**.

1. The **Gain** on the PNMR receiver module amplifies the signal coming from the pick up coil. The ability of the PNMR to magnify in this way does have limits. The oscilloscope will show a flat top on the signal if you have reached the maximum output signal.
2. The gain on the oscilloscope is basically an enlarger which just makes the "picture" of the signal on the scope larger. It also amplifies the noise.

Pulse width is a time measure. When starting from equilibrium, a 90º pulse tips the spins until they are perpendicular to the strong, constant, magnetic field of the permanent magnet, B_o. For a 90º pulse, the pulse width is the time it takes the rf magnetic field to tip the spin 90°. (In the Magnetic Torque apparatus, this "pulse" time is equivalent to how long you must rotate the horizontal field to get the ball's handle, and thus its magnetic moment, horizontal.)

A single isolated proton (or a Magnetic Torque snooker ball with **no** frictional effects) would maintain its tipped magnetization indefinitely. In reality, the spins do realign to the primary field and a characteristic of the time this takes is known as the **spin-lattice relaxation time, T_1**.

REPETITION TIME tells how often the entire pulse sequence is repeated. This time must be long enough for the net magnetization to realign with the primary field after the pulses are over. If it is too short, a pulse sequence will begin when the system is not in thermal equilibrium.

DELAY TIME, τ, is the time between the first and second pulses of a series. When more than two pulses are used, the system adjusts subsequent delay times between the second and third, third and fourth etc. to 2τ. The total time for an entire pulse series must be less than the repetition time so that the digital logic does not lock up. **Repetition time should be such that the time *after* the last echo or FID is long compared to T_1. To be safe it should be close to $10T_1$.**

Describing Relaxation Time

The PNMR responds to the sum of the magnetic moments of many protons, the net magnetization. (This is different from the Magnetic Torque Apparatus. Magnetic Torque works with the spin of only one "proton" which is represented by the ball.) The net magnetization of the protons of the sample becomes aligned with the field of the permanent magnet, B_o. Any change in the orientation of the spins decays back to an alignment with the "primary" field. The time characteristic of this return to thermal equilibrium magnetization is called a relaxation time. The TeachSpin PNMR can be used to measure two different quantities referred to as T_1 and T_2. T_1, the spin-lattice relaxation time is the time characteristic of establishing thermal-equilibrium magnetization in the z direction. T_2, spin-spin relaxation time, is the time characteristic of the loss of x-y magnetization. In PNMR, the x-y magnetization is created by tipping the spins 90º from their thermal equilibrium condition.

Getting Started – An Exploratory Experiment

Begin by investigating the PNMR signal following a single pulse. Start with all pulse width dials in the counter clockwise position, the repetition time set to about 0.10 seconds, the A pulse on, the B pulse off and the oscilloscope triggering on A.

Slowly increase the A pulse width and examine the effect. (To be sure the rf pulse is in resonance, check the mixer signal on the oscilloscope and tune it until there is zero beat condition.) Pulse width determines the time allowed for the rf to tip the spins. The longer the rf is on, the farther the spins tip. You will notice that the initial height of the FID (the signal on the oscilloscope), first reaches a maximum, indicating a 90° pulse, then decreases to close to 0 at about twice the 90º pulse width, indicating a 180º rotation. After a 180° rotation there is no x-y magnetization. Continuing to increase the pulse width shows the signal increase to another maximum for a 270º rotation etc.

The repetition time can be used to get a rough estimate of T_1, the time to re-establish the thermal equilibrium. Set the A pulse width at the first maximum. Decrease the repetition time until the signal maximum begins to shrink. This decrease in the initial height of the FID occurs because the z-magnetization has not returned to its thermal equilibrium value before the next 90º pulse. This effect becomes more dramatic as the repetition time decreases. To make sure the PNMR is giving accurate information, the repetition time for any pulse sequence should be set so that the time between the last pulse in the sequence and the beginning of the next sequence is at least 10 T_1.

Determining T_1, the spin-lattice relaxation time

(The time characteristic of establishing thermal equilibrium magnetization in the z direction)

To measure T_1, the net magnetization, M_o, is first tipped by 180º to $-M_o$. The z-magnetization is then interrogated as it returns to its thermal equilibrium value, M_o. Because the pickup coil only indicates precession in the x-y plane, this magnetization along the z-axis cannot be monitored directly. Therefore, the B pulse is adjusted to create a 90º pulse and the oscilloscope is trigged on the B pulse.

To tip the magnetization to $-M_o$, the width of the A pulse is increased until it has passed through the first maximum and returns to a 0 signal on the oscilloscope. This indicates a 180° pulse after which there is no net magnetization in the x-y plane. The width of the B pulse is adjusted to the first maximum signal, indicating a 90º pulse.

The key to this experiment is the fact that the B pulse, which tips *any* spin by 90°, is being used to interrogate what has happened to the magnetization along the z axis. The maximum amplitude of the Fee Induction decay (FID) signal which follows the B pulse is directly proportional to the magnitude of M_z at the time the B pulse occurs. For example, if the delay time for B, following A, were to be 0, the signal would be at a maximum because the spins would be tipped from -z to the x-y plane.

By changing the delay time between the A and B pulses, the rate at which the net magnetization returns to alignment with the “primary” magnetic field can be investigated. When the delay time results in a 0 signal in the pick up coil, it means that the net magnetization along the z-axis is zero. When the signal again reaches a maximum, the spins have “relaxed” back to alignment along the z-axis. Careful observation of the mixer signal will show a phase shift as the magnetization passes through 0.

If the maximum amplitude, M, of the FID following the 90° pulse is plotted against the delay time, the relaxation of the spins from -z to +z can be observed. To extract T_1 correctly, however, the difference between the FID maximum for long delay times, which is a measure of the thermal equilibrium magnetization, and the FID maxima at time t is plotted against delay time.   It is this difference, M_o - M, which changes exponentially. The equation is:

$$\frac{dM_z}{dt} = \frac{M(t) - M_o}{T_1}$$

An arbitrary scale can be used to plot the magnitude of the initial FID signal after the B pulse as a function of delay time. From the shape of this curve, T_1 can be calculated.

Figure 5 shows diagrams of both the actual net magnetization M and the maximum amplitude of the FID just after the 90° pulse as a function of time.

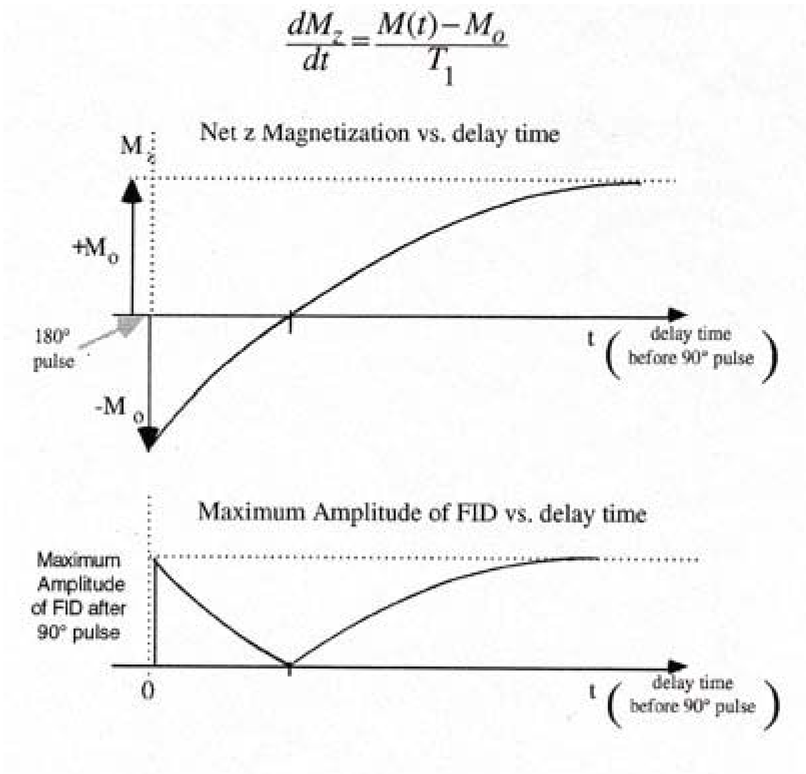

Figure 5 – Upper Diagram: Net z magnetization vs. delay time
Lower Diagram: Maximum Amplitude of FID vs. delay time

Measuring T_2, the spin-spin relaxation time

(The time characteristic of the loss of x-y magnetization)

The characteristic time for the spins to lose a non-thermal equilibrium x-y magnetization, which has been established by a 90º rf pulse, is called T_2. To measure this relaxation time, the width of the A pulse is adjusted to the first maximum signal, indicating a 90° pulse. The oscilloscope must trigger on A.

In the pick-up coil, the precessing spins induce a sinusoidally varying voltage which decays over time. As discussed at the beginning, the detector transmits only the absolute value of the maximum voltages during each precession. The rectified envelope represents the free induction decay or FID

Spin-spin relaxation occurs by two mechanisms:

1. The spins re-orient along the + z axis of the main magnetic field, B_o due to stochastic, T_1, processes.

2 The interaction of the spins themselves creates a variation in the local magnetic field of individual atoms. Because their precession frequency is proportional to the magnitude of the local magnetic field, the precessing spins dephase.

Understanding T2*

If the external magnetic field across the sample is not perfectly homogenous, spins in different physical locations will precess at different rates. This means that the precession of the individual spins is no longer in phase. Over time, the phase difference between the precessions of the individual protons increases and the net voltage induced in the pick-up coil decreases. The time for this loss of signal, which is not due to relaxation processes, is called T_2*. The free induction decay observed after a single 90º pulse is often due primarily to this effect. If, however, the external magnetic field is very homogeneous and T_2* is long compared to T_2, the free induction will represent a true measure of T_2.

Spin Echo

In 1950, Irwin Hahn found a way to compensate for the apparent decay in the x-y magnetization due to inhomogeneity of an external magnetic field. The external inhomogeneity creates a variation in the proton precession times around an average. The introduction of a 180° pulse, or spin flip, allows the spins to regroup before again dephasing. This creates a *spin echo* which allows us to measure the true T_2.

After the 180º flip, spins that were "ahead" because they are in a stronger field are now "behind." Because their protons are precessing faster, however, they will now "catch up" to the "average." In the same way, after the 180° pulse, "slow" spins are now "ahead" and the "average" will overtake them. The spins rephase momentarily and dephase again. This is why the oscilloscope trace after the first 180º pulse shows a rise to a maximum and then a decay. The rephasing and dephasing wings of the echo can be seen in the diagram below. The difference between the height of the initial signal and the echo maximum is due to the actual stochastic processes of T_2.

The magnitude T_2 can be investigated two ways. The time between the A and B pulses can be varied and T_2 determined by plotting the resulting echo maximum as a function of time. Another option is to introduce a series of 180° B pulses and look at the decrease of the maxima.

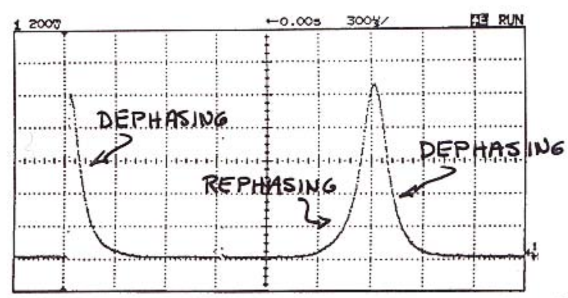

Figure 6 – Oscilloscope Trace Showing Spin Echoes

Understanding the effect of the 180º Spin Flip - a Jonathan Reichert analogy

Consider the plight of a kindergarten teacher who must devise a foot race which keeps all children happy, no matter how fast they run. What if the race has the following rules? All children are to line up at the starting line. At the first whistle they are to run as fast at they can down the field. At the second whistle they are to turn around and run back toward the starting line. First person back wins!! Of course, it is a tie, except for the ones who "interfere" with one another or fall down. As the children run away the field spreads out with the fastest ones getting farther and farther ahead. At some point there is no semblance of order. On the trip back, as the faster ones overtake the slow guys now in the lead, the group comes together again "rephasing" as they pass the start line.

This is a good analogy for the effect of the 180° spin flip which creates a spin echo. The effect of the 180º pulse is analogous to that of the kindergarten whistle. After the 180° pulse, the signal increases as the spins rephase, hitting a maximum somewhat lower than the initial height of the FID and decreasing as the spins again dephase. The decay of the maxima shows how the protons are losing the x-y magnetization. In our kindergarten analogy, this tells us the rate at which the children are actually interacting with each other.

The Output of the Mixer as a Phase Indicator

During a T_1 measurement the output of the mixer can be used to determine when the direction of the magnetization changes from the minus to the plus z direction. This cannot be inferred from detector output because it always gives a positive signal on the oscilloscope. By watching the mixer as delay time is changed you can see when the magnetization passes through the x-y plane. The initial signal of the mixer can have its maximum either above or below the time axis on the oscilloscope when the net magnetization of the sample has been driven to $-M_o$ by the A pulse. As the direction of the net magnetization changes from below (-z) to above (+z) the x-y plane, the mixer signal will reverse its orientation around the time axis of the oscilloscope. If you have truly caught the moment when the net magnetization is in the x-y plane, both the pick up signal and the mixer signal will be 0. The way this time can be used to give a very good estimate of T_1 is discussed in the PNMR manual.

An Interesting Activity

With the pulse series for determining T_2 on the oscilloscope screen (a MG pulse sequence), move the sample to a less homogeneous region of the magnet. Notice that although the widths of the individual echo traces narrow, the maximum heights of the peaks do not change. This shows that although the time for the spins to dephase due to inhomogeneity does decrease, the true time for the spins to return to their thermal equilibrium value, as indicated by the decay of the peaks, does not.