I. INTRODUCTION

A. OVERVIEW OF THE INSTRUMENT

Congratulations, you have acquired for your students the most versatile, sensitive, rugged and reliable nuclear magnetic resonance spectrometer designed specifically for instruction. The specifications of this unit rival any research grade unit in this frequency range in terms of sensitivity, stability, capabilities and state- of-the-art electronics. And yet, the unit was designed from the outset for student instruction. By that we mean that students, and not a computer, set all of the experimental parameters. Students can make many mistakes including miswiring the spectrometer and incorrectly setting any and all of the parameters without damaging the unit. For the one case where incorrect wiring might do some damage, the unit has special connectors which make those connections impossible with the cables provided.

All of the data is presented in analog form for examination on a digital storage oscilloscope or a computer. Students (and faculty) can then choose how they wish to perform data reduction or analysis. No proprietary software programs are needed to operate the unit, so no software updates are needed. TeachSpin is convinced that the "volt" will never go out of style, and that the mode of data storage and analysis is a choice best left to the individual user. Although data storage and analysis hardware and software is changing so rapidly that what is "hot" today may be obsolete tomorrow, your TeachSpin spectrometer, with its analog output signals, will be capable of taking research grade data long into the future.

Our first NMR instrument PS1-A,B is no longer available because some of its essential electronics components are no longer being manufactured. (It continues, however, to teach students pulsed NMR spectroscopy of protons at more than 170 institutions all over the world.) PS2 is a completely redesigned spectrometer. The many differences and innovations are presented in the following list.

1. Students can study NMR signals from **two** types of nuclei, protons (hydrogen nuclei) and fluorine. Since the field of the permanent magnet is constant, this is accomplished by changing the spectrometer frequency.

2. PS2 is both a pulsed and a continuous wave (CW) spectrometer.

3. The unit has both amplitude (envelope) and phase sensitive detection built into its receiver.

4. The RF probe head has a single coil and a 50 Ω input impedance; a matched unit.

5. The field and frequency have increased to 21 MHz proton for resonance.

6. The magnetic field is stabilized to 1 part in 2×10^6 over a 20 minute interval.

7. Adjustable electric shim coils that can be used to increase the magnetic field homogeneity are part of the RF sample probe system. They can also be used to create known gradients for measuring diffusion as well as for one-dimensional imaging.

8. The homogeneous high magnetic field allows direct detection of inequivalent fluorine and protons nuclei (chemical shifts) in the free induction decay signal.

9. A Lock-In detection module can detect CW signals from solids with wide lines.

10. Both magnetic field and RF frequency sweeps are built in for studying CW resonance.

11. Digital clock stability in both the RF frequency and the pulse width synthesis are integral to the design.

12. The receiver recovery time (after pulse) has been improved by a factor of five to approximately 15 μs, making signals from "soft" solids available for study.

13. An elongated sample coil and layered sample kit, designed for PS2-C in 2013, allows students to perform one-dimensional imaging on samples of up to five layers. (A retrofit kit is available for both PS-A and PS1-B.)

The electronics system was designed by Dr. Norman Jarosik of the Princeton University Physics Department. Norman is a staff scientist in the "gravity Group" and the chief engineer of WMAP, the satellite that has been sensing and mapping the anisotropies in the microwave radiation left over from the Big Bang of the early universe. He also designed the PS-1 A and B whose well deserved reputation for reliability, as well as sensitivity, is known world-wide. Norman has been involved with TeachSpin from its 1992 inception.

Nuclear magnetic resonance is a large and mature field of physics. There certainly is a lot to learn and a real potential for a student to explore his or her own ideas in this area, perhaps even to find a real research project. We cannot think of a better instrument for students to pursue their own open-ended sets of experiments. But a new student should not be intimidated by the prospect of learning this vast subject. TeachSpin has outlined a manageable way to begin the study of NMR. Students can begin with straight-forward experiments that will develop their confidence and understanding and then branch out to more advanced measurements. This instrument is accessible, after all, it was designed from the moment of inception for the student. Enjoy!

B. OUTLINE OF THE PHYSICS

B.1 Brief History

In 1946, nuclear magnetic resonance (NMR) in condensed matter was discovered simultaneously by Edward Purcell at Harvard and Felix Bloch at Stanford using different instrumentation and techniques. Both groups, however, placed a sample containing magnetic nuclei in a uniform magnetic field and observed the response of those nuclei to a continuous (CW) radio frequency magnetic field as the field was tuned through resonance. This discovery opened up a new type of spectroscopy which has become one of the most important tools available to physicists, chemists, geologists, and biologists.

In 1950, Erwin Hahn, a postdoctoral fellow at the University of Illinois, again placing his sample of condensed matter in a uniform magnetic field, explored the response of the magnetic nuclei to pulse bursts of these same radio frequency (RF) magnetic fields. Hahn was interested in observing transient effects on the magnetic nuclei after the RF bursts. During these experiments, he observed a "spin echo" signal; that is, a signal from the magnetic nuclei that occurred after a two pulse sequence, at a time equal to the delay time between the two pulses. This discovery, and his brilliant analysis of the experiments, gave birth to a new technique for studying magnetic resonance. This pulse method originally had only a few practitioners, but now it is the method of choice for most laboratories. For the first twenty years after its discovery, continuous wave (CW) magnetic

resonance apparatus was used in almost every research chemistry laboratory, and no commercial pulsed NMR instruments were available. However, since 1966 when Ernst and Anderson showed that high resolution NMR spectroscopy can be achieved using Fourier transforms of the transient response, and cheap fast computers made this calculation practical, pulsed NMR has become the dominant commercial instrumentation for most research applications.

Widely used in physics and chemistry to characterize materials, NMR is a microscopic method in the sense that it probes the nuclei and their immediate surroundings. Within a certain solid, for instance, there may be a variety of local magnetic fields. A magnetic measurement by a magnetometer measures an average field. NMR, on the other hand, is capable of measuring the local field at atomic nuclei. Another example would be a molecule containing a several atoms of the same element, for instance carbon, in various different configurations. The NMR signal will be different for each one of these configurations. The microscopic nature of the NMR measurement makes it extremely useful, and often unique. Of course, in order to have a signal of detectable magnitude, we need many molecules of the same configuration to occur within the sample. The nuclei investigated in this set of experiments, hydrogen (proton) and fluorine, are very abundant and give particularly strong signals.

This technology has also found its way into medicine. MRI (magnetic resonance imaging; the word "nuclear" being removed to relieve the fears of the scientifically illiterate public) scans are revolutionizing radiology. This imaging technique seems to be completely noninvasive, produces remarkable three dimensional images, and has the potential to give physicians detailed information about the inner working of living systems. For example, preliminary work has already shown that blood flow patterns in both the brain and the heart can be studied without dangerous catheterization or the injection of radioactive isotopes. Someday, MRI scans may be able to pinpoint malignant tissue without biopsies. MRI is only in its adolescence, and we will see many more applications of this diagnostic tool in the coming years.

You have purchased a pulsed and CW NMR spectrometer designed specifically for teaching. The PS2 is a complete spectrometer, including the magnet, magnet temperature controller, pulse generator, oscillator, pulse amplifier, sensitive receiver, linear amplitude and phase-sensitive detector, sample probe, gradient coils with dedicated current regulated supply and a CW lock-in detector. You need only supply the oscilloscope and the substances you wish to study. Now you are ready to learn the fundamentals of both CW and pulsed nuclear magnetic resonance spectroscopy.

Nuclear magnetic resonance is a vast subject. Tens of thousands of research papers and hundreds of books have been published on NMR. We will not attempt to explain or even to summarize this literature. Some of you may wish to do only a few simple experiments with the apparatus and achieve a basic conceptual understanding, while others may aim to understand the details of the density matrix formulation of relaxation processes and do some original research. The likelihood is that the majority of students will work somewhere in between these two extremes. In this section we will provide a brief theoretical introduction to many important ideas of PNMR. This will help you get started and can be referred to later. These remarks will be brief, not completely worked out from first principles, and not intended as a substitute for a careful study of the literature and published texts. An extensive annotated bibliography of important papers and books on the subject is provided at the end of this section.

B.2 Theory

Magnetic resonance is observed in systems where the magnetic constituents have **both a magnetic moment** and **an angular momentum**. Many, but not all, of the stable nuclei of ordinary matter have this property. In "classical physics" terms, magnetic nuclei act like a small spinning bar magnet. For this instrument, we will be concerned with only two nuclei, the nucleus of hydrogen, which is a single proton, and the nucleus of fluorine which contains both protons and neutrons. Both nuclei can be thought of as small spinning bar magnets with a magnetic moment μ and an angular momentum J, which are related by the vector equation:

$$\boldsymbol{\mu} = \gamma \, \mathbf{J} \qquad\qquad (1.1)$$

The proportionality factor γ is called the "gyromagnetic ratio" and its values are unique to each kind of nucleus in the experiment.

The nuclear angular momentum is quantized in units of $\hbar$ as:

$$\mathbf{J} = \hbar \, \mathbf{I} \qquad\qquad (1.2)$$

where **I** is the "spin" of the nucleus.

The magnetic energy U of the nucleus in an external magnetic field is:

$$U = - \boldsymbol{\mu} \cdot \mathbf{B} \qquad\qquad (1.3)$$

If the magnetic field is in the z-direction, then the magnetic energy is:

$$U = - \mu_z B_o = - \gamma \hbar \, I_z B_o \qquad\qquad (1.4)$$

Quantum mechanics requires that the allowed values I_z , m_1, be quantized as

$$m_1 = I, \, I - 1, \; I - 2, \; I - 3 \ldots \; -I. \qquad\qquad (1.5)$$

Both of the nuclei we are investigating, the proton (hydrogen nucleus) and the fluorine nucleus have spin one half ($I = 1/2$). Therefore, the allowed values of I_z are simply

$$m_1 = \pm \, 1/2 \qquad\qquad (1.6)$$

This means that there are only two magnetic energy states for these nuclei when residing in a constant magnetic field B_0. These states are described in Figure 1.1.

The energy separation between the two states, ΔU, can be written in terms of an angular frequency or as

$$\Delta U = \hbar \, \omega_0 = \gamma \hbar \, B_0$$

or

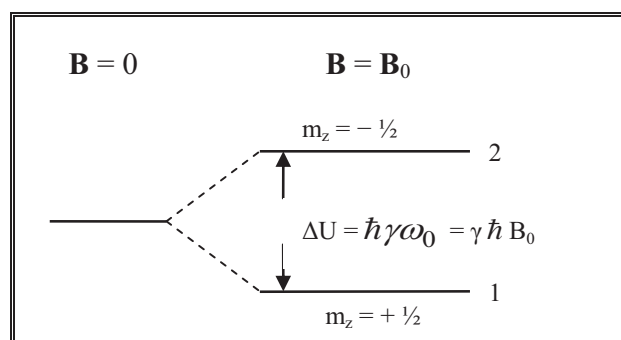$$\omega_0 = \gamma B_0 \qquad (1.7)$$

Figure 1.1 Energy State Separation in a Magnetic Field

Equation 1.7, $\omega_0 = \gamma B_0$ describes the fundamental resonance condition.

For the proton: γ_{proton} = 2.675 x 10^8 rad/sec-tesla

(1.8)

For Fluorine: $\gamma_{fluorine}$ = 2.517 x 10^8 rad/sec-tesla

For the proton, the numerical relationship between the resonant frequency and the constant magnetic field is worth remembering:

$$f_{proton} (MHz) = 42.58 \; B_0 \; tesla \qquad (1.9)$$

If a one milliliter (ml) sample of water (containing about 7×10^{19} protons) is placed in a magnetic field in the z-direction, a nuclear magnetization in the z-direction eventually becomes established. This nuclear magnetization occurs because of unequal population of the two possible quantum states. If N_1 and N_2 are the number of spins per unit volume in the respective states, then the population ratio (N_2 / N_1), in thermal equilibrium, is given by the Boltzmann factor as:

$$\frac{N_2}{N_1} = e^{\frac{\Delta U}{kT}} = e^{\frac{\hbar \omega_0}{kT}} \qquad (1.10)$$

and the magnetization is

$$M_Z = (N_1 - N_2) \, \mu \qquad (1.11)$$

The thermal equilibrium magnetization per unit volume for N magnetic moments is

$$M_0 = N\mu \tanh(\frac{\mu B}{kT}) \approx N \frac{\mu^2 B}{kT} \qquad (1.12)$$

$$where \; N = N_1 + N_2$$

This magnetization does **not** appear instantaneously when the sample is placed in the magnetic field. It takes a finite time for the magnetization to build up to its equilibrium value along the direction of the magnetic field (which we define as the z-axis). For most systems, the z-component of the magnetization is observed to grow exponentially as depicted in Figure 1.2. The differential equation that describes such a process assumes that the rate of approach to equilibrium is proportional to the difference between the equilibrium value M_0 and the instantaneous value $M_z(t)$:

$$\frac{dM_z(t)}{dt} = \frac{M_0 - M_z}{T_1} \qquad (1.13)$$

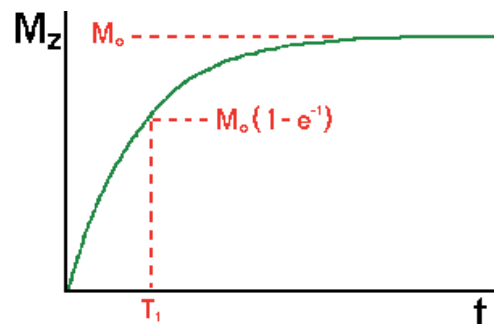where T_1 is called the spin-lattice relaxation time.

Figure 1.2 Magnetization vs. time for a sample placed in a magnetic field

If the unmagnetized sample is placed in a magnetic field, so that at t = 0, M_z = 0, then direct integration of equation 1.13, with these initial conditions, gives:

$$M_z(t) = M_0(1 - e^{-\frac{t}{T_1}})$$ (1.14)

The rate at which the magnetization approaches its thermal equilibrium value is characteristic of the particular sample. Typical values range from microseconds to seconds. What makes one material take 10 microseconds to reach equilibrium while another material (also with protons as the nuclear magnets) takes 3 seconds? Obviously, some processes in the material make the protons "relax" towards equilibrium at different rates. The study of these processes is one of the major topics in magnetic resonance.

Although we will not attempt to discuss these processes in detail, a few ideas are worth noting. In thermal equilibrium, more protons are in the lower energy state than the upper. When the unmagnetized sample was first put in the magnet, the protons occupied the two states equally that is ($N_1 = N_2$). During the magnetization process energy must flow *from* the nuclei *to* the surroundings, since the magnetic energy from the spins is reduced. The surroundings which absorb this energy are referred to as "the lattice", even for liquids or gases. Thus, the name "spin-lattice" relaxation time for the characteristic time of this energy flow.

However, there is more than energy flow that occurs in this process of magnetization. Each proton has angular momentum (as well as a magnetic moment) and the angular momentum must also be transferred from the spins to the surroundings during magnetization. In quantum mechanical terms, the "lattice" must have angular momentum states available when a spin goes from $m_1 = -1/2$ to $m_1 = +1/2$. In classical physics terms, the spins must experience a torque capable of changing their angular momentum. The existence of such states is usually the critical determining factor in explaining the enormous differences in T_1 for various materials. Pulsed NMR is ideally suited for making precise measurements of this important relaxation time. The pulse technique gives a direct and unambiguous measurement, where as CW spectrometers require a difficult, indirect, and imprecise technique to measure the same quantity.

What about magnetization in the x-y plane? In thermal equilibrium the only **net** magnetization of the sample is M_z, the magnetization along the external constant magnetic field. This can be understood from a simple classical model of the system. Think of placing a collection of tiny current loops in a magnetic field. The torque τ on the loop is μ x B and that torque causes the angular momentum of the loop to change, as given by:

$$\boldsymbol{\tau} = \frac{d\mathbf{J}}{dt} \quad \text{or} \quad \boldsymbol{\mu} \times \mathbf{B} = \frac{d\mathbf{J}}{dt}$$ (1.15)

For our nuclei, equation 1.15 becomes:

$$\boldsymbol{\mu} \times \mathbf{B} = \frac{1}{\gamma} \frac{d\boldsymbol{\mu}}{dt} \qquad (1.16)$$

Figure 1.3

Equation 1.16 is the classical equation describing the time variation of the magnetic moment of the proton in a magnetic field. It can be shown from equation 1.16 that the magnetic moment will execute precessional motion, depicted in 1.3. The precessional frequency $\omega_0 = \gamma B_0$, is just the resonant frequency in equation 1.7.

If we add up all the magnetization for the 10^{20} nuclei in our sample in thermal equilibrium, the μ_z components sum to M_z, but the x and y components of the individual magnetic moments add to zero.
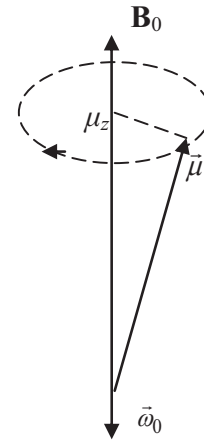
For the x-components of every nucleus to add up to some M_x, there must be a definite phase relationship among all the precessing spins.   For example, we might start the precessional motion with the x-component of the spins lined up along the x-axis. But that is not the case for a sample simply placed in a magnet. In thermal equilibrium, the spin components in the x-y plane are oriented randomly. Thus, in thermal equilibrium there is no transverse (x or y) component of the net magnetization of the sample. As we shall soon see, however, there is a way to *create* such a transverse magnetization using radio frequency pulsed magnetic fields. The idea is to quickly rotate the thermal equilibrium magnetization M_z into the x-y plane and thus create a temporary M_x and M_y. Let's see how this is done.

Equation 1.16 can be generalized to describe the classical motion of the net magnetization of the entire sample. It then becomes

$$\frac{d\mathbf{M}}{dt} = \gamma\, \mathbf{M} \times \mathbf{B} \qquad (1.17)$$

where **B** is any magnetic field, including time dependent rotating fields.

Suppose we apply not only a constant magnetic field $\mathbf{B}_0 \hat{k}$, but a rotating (circularly polarized) magnetic field of angular frequency ω the x-y plane so the **total** field is written as [†]

$$\mathbf{B(t)} = B_1 \cos\omega t\, \hat{i} + B_1 \sin\omega t\, \hat{j} + B_0 \hat{k} \qquad (1.18)$$

The analysis of the magnetization in this complicated time dependent magnetic field can best be carried out in a non-inertial rotating coordinate system. The coordinate system of choice is rotating at the same angular frequency as the rotating magnetic field with its axis in the direction of the static magnetic field. In this ***rotating coordinate system***, the rotating magnetic field appears to be stationary and aligned along the x* axis (Figure 1.4). However, from the point of view of the rotating coordinate system, B_0 and B_1 are not the only magnetic fields. An **effective field** along the z* direction, of $-\frac{\omega}{\gamma}\hat{k}*$ must also be included.

Let's justify this new effective magnetic field with the following physical argument.

Equations 1.16 and 1.17 predict the precessional motion of a magnetization in a constant magnetic field $B_o\hat{k}$. Suppose one observes this precessional motion from a rotating coordinate system which rotates **at the precessional frequency**. In this frame of reference the magnetization appears stationary, in some fixed position. The only way a magnetization can remain fixed in space is if there is no torque on it. If the magnetic field is zero in the reference frame, then the torque on **M** is always zero no matter what direction **M** is oriented. The magnetic field is zero (in the rotating frame) if we add the effective field $-\frac{\omega}{\gamma}\hat{k}*$ which is equal to $B_o\hat{k}*$
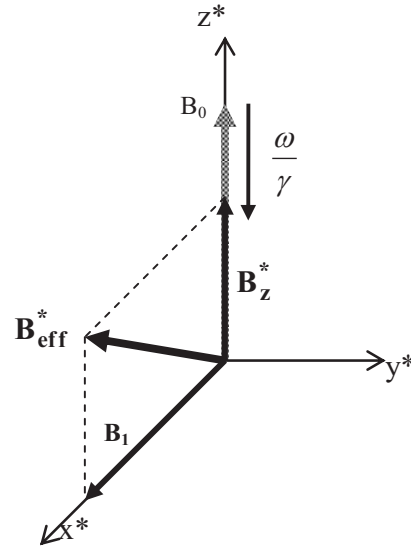
Figure 1.4

Transforming the magnetic field expression in equation (1.18) into such a rotating coordinate system, the total magnet field in the rotating frame B* is

$$\mathbf{B}*_{\text{eff}} = B_1\hat{i}* + (B_0 - \frac{\omega}{\gamma})\hat{k} \qquad (1.19)$$

Figure 1.4 is a representation of Equation 1.19. The classical equation of motion of the magnetization as observed in the rotating frame is then

$$\left.\frac{d\mathbf{M}}{dt}\right|_{rot} = \gamma\,\mathbf{M}\times\mathbf{B}*_{\text{eff}} \qquad (1.20)$$

which shows that **M** will precess about B*$_{\text{eff}}$ in the rotating frame.

[†]What is actually applied is an oscillating field $2B_1\cos\omega t\hat{i}$. But that can be decomposed into two counter rotating fields $B_1(\cos\omega t\hat{i} + \sin\omega t\hat{j}) + B_1(\cos\omega t\hat{i} - \sin\omega t\hat{j})$. One of the counter rotating fields can be shown to have no practical affects on the spin system and can be ignored in this analysis.

Suppose now, we create a rotating magnetic field at a frequency ω_0 as such that

$$\frac{\omega}{\gamma} = B_0 \qquad \text{or} \qquad \omega = \gamma B_0 = \omega_0 \tag{1.21}$$

In that case, $\mathbf{B}^*_{\text{eff}} = B_1 \hat{i}^*$, a constant magnetic field in the x* direction (Figure 1.5). Then, the magnetization M_z begins to precess about this magnetic field at a rate $\Omega = \gamma B_1$, (in the rotating frame). If we **turn off** the B_1 field at the instant the magnetization reaches the x-y plane, we will have created a transient (non-thermal equilibrium) situation where there **is** a net magnetization in the x-y plane. If this rotating field is applied for twice the time the transient magnetization will be - $\mathbf{M_z}$ and if it is left on four times as long the magnetization will be back where it started, with M_2 along the z* axis. These are called:

Figure 1.5

$$90° \text{ or } \pi/2 \text{ pulse} \rightarrow M_z \rightarrow M_y$$
$$180° \text{ or } \pi \text{ pulse} \rightarrow M_z \rightarrow -M_z$$
$$360° \text{ or } 2\pi \text{ pulse} \rightarrow M_z \rightarrow M_z$$
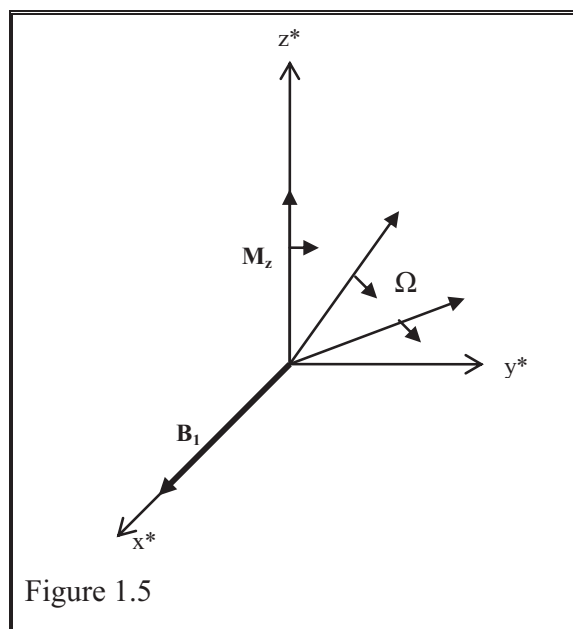
In the laboratory (or rest) frame, where the experiment is actually carried out, the magnetization not only precesses about B_1, but rotates about $\hat{k}$ during the pulse. **It is not possible, however, to observe the magnetization during the pulse**. Pulsed NMR signals are observed AFTER the transmitter pulse is over? But, what is there to observe AFTER the transmitter pulse is over? The spectrometer detects the **net magnetization precessing about the constant magnetic field** $B_0\hat{k}$ **in the x-y plane. Nothing Else!**

Suppose a 90° ($\pi/2$) pulse is imposed on a sample in **thermal equilibrium**. The net equilibrium magnetization will be rotated into the x-y plane where, after the pulse, it will precess about $B_0\hat{k}$. But the x-y magnetization will not last forever. For most systems, this magnetization decays exponentially as shown in Figure 1.6. The differential equations which describe the decay **in the rotating coordinate system are**:

$$\frac{dM_{x^*}}{dt} = -\frac{M_{x^*}}{T_2} \quad \text{and} \quad \frac{dM_{y^*}}{dt} = -\frac{M_{y^*}}{T_2} \tag{1.22}$$

whose solutions are

$$M_{x^*} = M_0 e^{-\frac{t}{T_2}} \quad \text{and} \quad M_{y^*} = M_0 e^{-\frac{t}{T_2}} \tag{1.23}$$

where the characteristic decay time T_2 is called the **Spin-Spin Relaxation Time**.

One simple way to understand this relaxation process, from the classical perspective, is to recall that each nucleus is itself a magnet and produces a magnetic field at its neighbors. Therefore, for a given distribution of nuclei, there must also be a distribution of *local* fields at the various nucleus sites. Thus, the nuclei precess about $B_0 \hat{k}$ with a distribution of frequencies, not a single frequency ω_0.
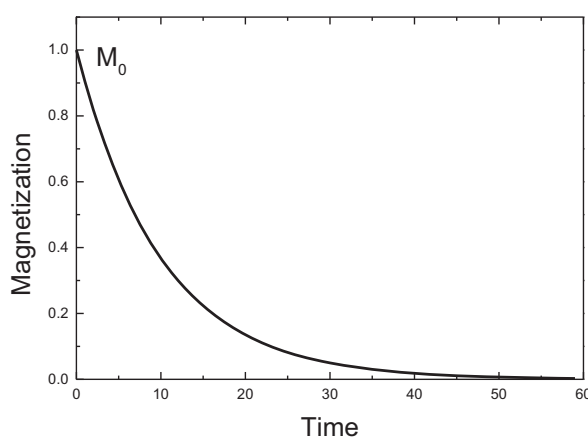

Figure 1.6

Even if all the nuclei begin in phase (after the 90° pulse), they will soon get out of phase and the net x-y magnetization will eventually go to zero. A measurement of T_2, the decay constant of the x-y magnetization, gives information about the distribution of local fields at the nuclear sites.

From this analysis, it would appear that the spin-spin relaxation time T_2 can be determined by simply plotting the decay of M_x(or M_y) after a 90° pulse. This signal is called the free *precession or free induction decay* (FID). If the field of the magnet were perfectly uniform over the entire sample volume, then the time constant associated with the free induction decay would, in fact, be T_2. But, in most cases, it is the nonuniformity of the magnet's field over the sample that is responsible for the observed decay constant of the FID. At its center, the PS2 magnet has sufficient uniformity to produce at least a .3 millisecond decay time. Using the electric shim coils (See Section II.F), students can improve the homogeneity so that decay time due to the magnet (called T_2^* in the jargon) is as long as 5 milliseconds, and, possibly, longer. Thus, for a sample whose $T_2 < 5$ ms, the free induction decay constant is also the T_2 of the sample. But what if T_2 is actually 5 msec or longer? The observed decay will still be about 5 ms. Here is where the genius of Erwin Hahn's discovery of the spin echo plays its crucial role.

Before the invention of pulsed NMR, the only ways to measure the real T_2 were to improve the magnet's homogeneity and to make the sample smaller. But, PNMR changed this.

Suppose we use a two pulse sequence, the first one 90° and the second one, turned on a time τ later, a 180° pulse. What happens? Figure 1.7 shows the pulse sequence and Figure 1.8 shows the progression of the magnetization in the rotating frame.
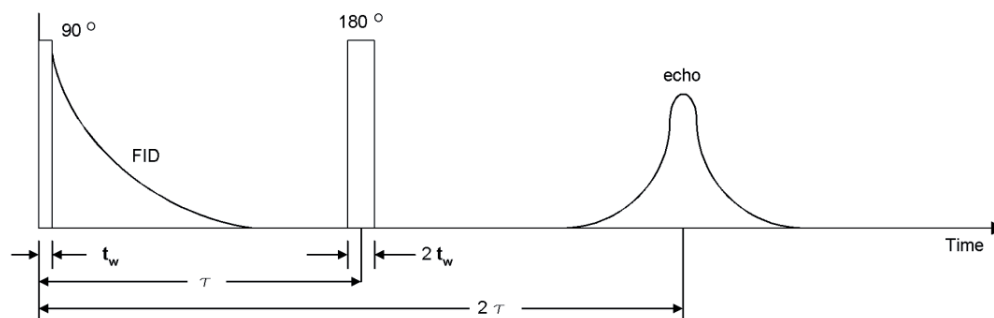

Figure 1.7: A 90° - 180° Pulse Sequence
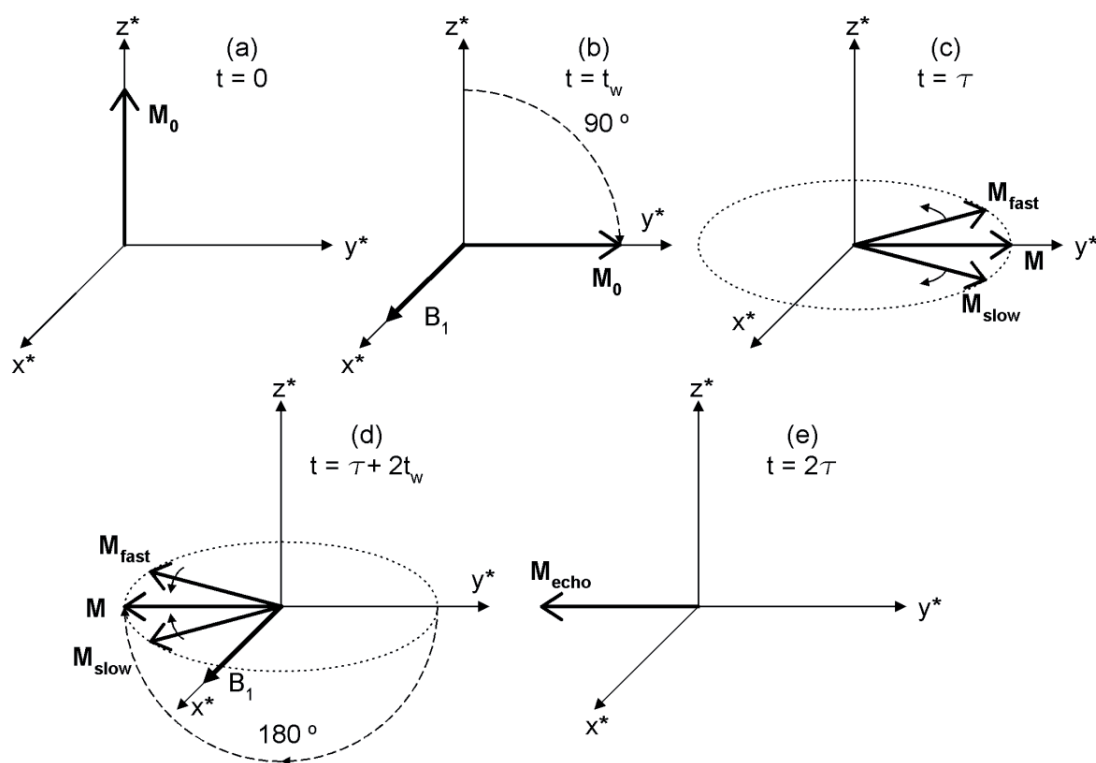
Figure 1.8: Progression of the Magnetization in the Rotating Frame
   a) Thermal equilibrium magnetization M_0 along the z axis before the rf pulse.
   b) M_0 rotated to the y-axis after the 90° pulse.
   c) The magnetization in the x-y plane is decreasing because some of the spins Δm_{fast} are in a higher field, and other spins Δm_{slow} are in a lower field static field.
   d) The spins are rotated 180° (visualize flipping the entire x-y plane like a pancake on the griddle) by the pulsed if magnetic field.
   e) The rephasing the three magnetization "bundles" to form an ***echo*** at t = 2t.

Study the diagrams in Figures 1.7 and 1.8 carefully. The 180° pulse allows the x-y magnetization to rephase to the value it would have had with a perfect magnet.

The echo process is analogous to an egalitarian and PC foot race for a kindergarten class, a race that makes all the children in the class winners, no matter how fast they can run. What if the race had the following rules? All the children are to line up at the starting line. At the first whistle, they are to run as fast as 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 pokes, who are now in the lead, the group comes together again "rephasing" as they pass the start line.

In Pulsed NMR, the 180° pulse is like that whistle. The spins in areas of larger field get out of phase by $+\Delta\theta$ in a time τ. After the 180° pulse, they continue to precess faster than M while the slower precessing spins do just the opposite. At 2τ all the spins return to the in-phase condition and then again dephase.

Yet some loss of $M_{x,y}$ magnetization has occurred and the maximum height of the echo is not the same as the maximum height of the FID. This loss of transverse magnetization occurs because of stochastic fluctuation in the local fields at the nuclear sites which is not rephasable by the 180° pulse. These are the real T_2 processes that we are interested in measuring. To find the "real" T_2, we use a series of $90° > \tau > 180°$ pulse experiments, varying τ, and then plotting the echo height as a function of time between the FID and the echo.

The transverse magnetization as measured by the maximum echo height is written as:

$$M_{xy}(2\tau) = M_0 e^{-\frac{2\tau}{T_2}}$$ (1.24)

That's enough theory for now. **Let's summarize**:

1. Magnetic resonance is observed in systems whose constituent particles have **both** a magnetic moment and angular momentum.

2. The resonant frequency of the system depends on the applied magnetic field in accordance with the relationship $\omega_0 = \gamma B_0$ where

$$\gamma_{proton} = 2.675 \times 10^8 \text{ radian/sec-tesla}$$

    or

$$f_{proton} = 42.58 \text{ MHz/tesla} \quad \text{(for protons)}$$

$$f_{fluorine} = 40.055 \text{ MHz/tesla} \quad \text{(for fluorine)}$$

3. The thermal equilibrium magnetization is parallel to the applied magnetic field, and approaches equilibrium following an exponential rise characterized by the constant T_1 the spin-lattice relaxation time.

4. Classically, the magnetization (which is the vector sum of the individual magnetic moments of the nuclei) obeys the differential equation

$$\frac{d\mathbf{M}}{dt} = \gamma(\mathbf{M} \times \mathbf{B})$$

where **B** may be a time dependent field.

5. Pulsed NMR employs a rotating radio frequency magnetic field described by

$$\mathbf{B}(t) = B_1 \cos\omega t \hat{i} + B_1 \sin\omega t \hat{j} + B_0 \hat{k}$$

6. The easiest way to analyze the motion of the magnetization during and after the rf pulsed magnetic field is to transform into a rotating coordinate system. If the system is rotating at an angular frequency ω along the direction of the magnetic field, a fictitious magnetic field must be added to the real fields such that the total effective magnetic field in the rotating frame is:

$$\mathbf{B}^*_{\mathbf{eff}} = B_1 \hat{i}* + (B_0 - \frac{\omega}{k})\hat{k}*$$

7. On resonance $\omega = \omega_0 = \gamma B_0$ and $\mathbf{B}^*_{\mathbf{eff}} = B_1 \hat{i}*$. In the rotating frame, during the pulse, the spins precess around $\mathbf{B}^*_{\mathbf{1}}$.

8. A 90° pulse is one where the pulse is left on just long enough (t_w) for the equilibrium magnetization M_0 to rotate to the x-y plane. That is;

$$\omega_1 t_w = \pi/2 \text{ radians or } t_w = \frac{\pi}{2\omega_1}$$

But

$$\omega_1 = \gamma B_1 \qquad \text{(since, on resonance, } B_1 \text{ is the only field in the rotating frame.)}$$

So,

$$t_w(90°) = \frac{\pi}{2\gamma B_1} \quad \text{duration of the 90° pulse} \quad (1.25)$$

9. T_2 - the spin-spin relaxation time - is the characteristic decay time for the nuclear magnetization in the x-y (or transverse) plane.

10. The spin-echo experiments allow the measurement of T_2 in the presence of a nonuniform static magnetic field. For those cases where the free induction decay time constant, (sometimes written T_2^*) is shorter than the real T_2, the decay of the echo envelope's maximum heights for various times τ, gives the real T_2.

C. REFERENCES

The following is a rather long list, and you certainly will not have the time all of them. In fact, you may only have time to read a rather small percentage of what is listed. But, you must take the time to read some of them so you have a basic understanding of magnetic resonance spectroscopy.

C.1 Books

C.P. Slichter: "Principles of Magnetic Resonance" Springer Series in Solid-State Sciences 1
                Third Edition (1990) Springer-Verlag
  A complete text with problems, clear explanations, appropriate for advanced undergraduate or graduate level students. **Any serious student of magnetic resonance should own it.** Everyone should read at least some of it. This reference contains a nearly complete bibliography of the important papers published in both NR and ESR spectroscopy. Consult this text for references to particular subjects.

T.C. Farrar, E.D. Becker: "Pulsed And Fourier Transform NMR", Academic Press 1971
  A good introduction, with simplified mathematics, to the subject. Gives students a physical feel for the basic ideas of PNMR.

G. E. Pake and T. L. Estle: "The Physical Principles of Electron Paramagnetic Resonance",
                Benjamin-Cummings, Menlo Park CA (1978)
  Don't let the title ESR scare you away from using this excellent text. It has clear discussions of important ideas of magnetic resonance, such as the rotating coordinate systems etc.

R. T. Schumacher: "Introduction to Magnetic Resonance", Benjamin-Cummings,
                Menlo Park CA 1970.

N. Bloembergen: "Nuclear. Magnetic Relaxation", W.A. Benjamin, New York 1961
  This is Bloembergen's Ph.D. thesis, reprinted, but it is like no other thesis you will ever read. Describes some of the classic ideas of magnetic resonance, still very worth reading, you will see why he is a Nobel Laureate.

A. Abragam: "Principles of Nuclear Magnetism", Clarendon, Oxford 1961
  This text is in a class by itself, but not easy for the beginner. Abragam has his own way of describing NMR. Important, but clearly for advanced students.

E. R. Andrew, "Nuclear Magnetic Resonance &' Cambridge University Press, New York, 1956
  A good general discussion of theory, experimental methods, and applications of NMR.

C. Kittel "Introduction to Solid State Physics" 5th edition, Wiley, New York 1976 in Chapter 16.
  A reasonable place to begin the subject of magnetic resonance, very brief, not fully worked out, but a good first overview;

D. M. S. Bagguley editor: "Pulsed Magnetic Resonance: NMR, ESR, and Optics, a Recognition of E.. L. Hahn, Clarendon Press, Oxford *1992*.
  A wonderful collection of historical reminisces and modem research applications of pulsed magnetic resonance. Useful for advanced students.

C.2 Papers

E. L. Hahn: "Spin echoes" Phys. Rev 80, 580-594 (1950)
  The first report oil PNMR and still a wonderful explanation, worth reading.

H. Y. Carr, E. M. Purcell: Effects of diffusion on free precession in nuclear magnetic resonance experiments. Phys Rev 94, 630-638 (1954)
  Anything Ed Purcell signs his name to is worth reading! This certainly is one such example. A must for PNMR.

N. Bloembergen, E. M. Purcell, and R. B. Pound: "Relaxation effects in Nuclear Magnetic Resonance absorption," Phys. Rev. 73, 679-712 (1948)
  A classic paper describing basic relaxation processes in NMR.

S. Meiboom, D. Gill: Rev of Sci Instruments 29, 6881 (1958)
  The description of the phase shift technique that opened up multiple pulse techniques to measuring very long T_2's in liquids.

K. Symon, "Mechanics" 3d ed. Addison-Wesley, Reading, MA (1971)
  A good place to learn about rotating coordinate systems, if you don't already understand them.

R. G. Beaver, E. L. Hahn, Scientific American 6, 251 (1984)
  A discussion of the echo phenomenon and mechanical memory.

III. GETTING STARTED

A. SPECTROMETER SET UP – PULSE MODE

There are three major parts to this spectrometer, the "MAGNET" (with RF Sample Probe mounted inside), the "MAINFRAME" (with the Receiver, Synthesizer, Pulse Programmer, Lock-In, and built-in DC Power supply) and the PS2 CONTROLLER (with Magnet Temperature and Field Gradient electronics). These three units are interconnected. All three are powered by a single regulated DC power supply (+ 5 V, ± 15 V) mounted inside the Mainframe case. You can see each of these components in Figure 3.1.
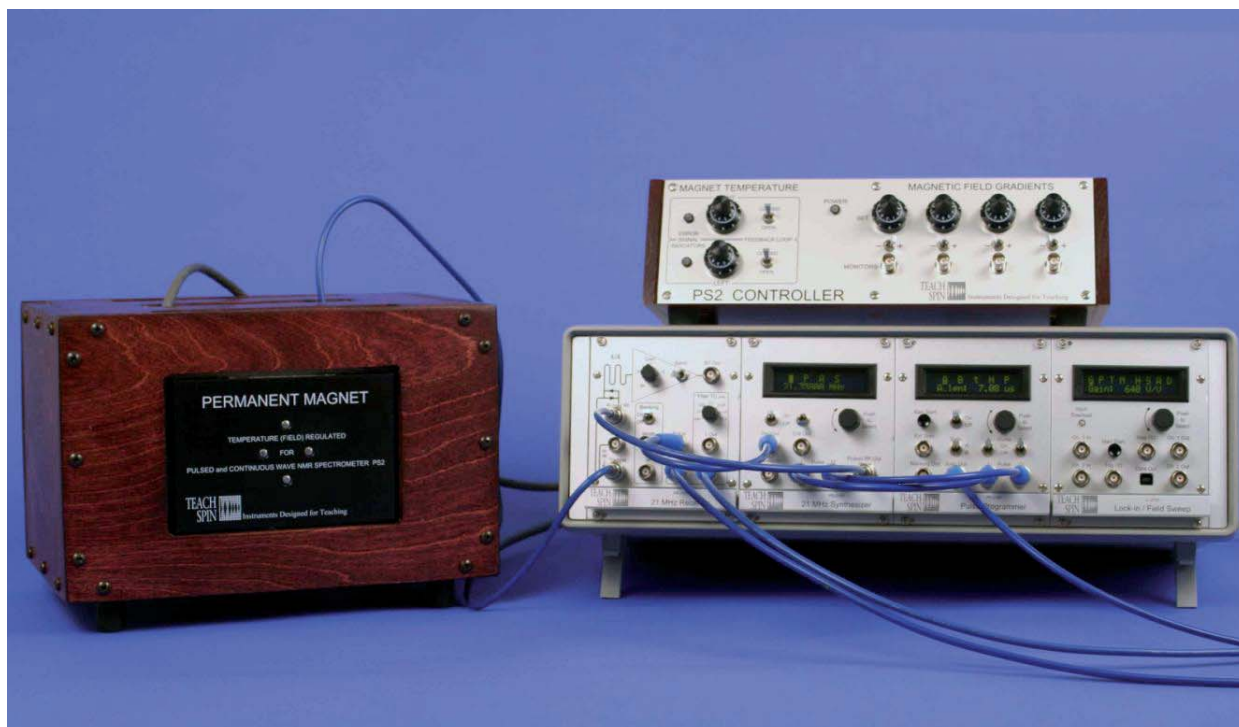

Figure 3.1 The PS2-A Spectrometer: Magnet, Mainframe and PS2 Controller

Begin by connecting up these three units. The gray cable from the PS2 Controller marked DC Input Power connects to the rear of the Mainframe. The blue coaxial cable, with the reverse gender BNC connector, attaches to the Receiver reverse gender panel connector marked "**Sample**". The gray cable from RF Sample Probe connects to the rear panel of the PS2 Controller marked "MAGNET GRADIENT/MODULATION". The gray cable from the lower part of the case of the magnet connects to the rear panel of the PS2 Controller marked "MAGNET TEMPERATURE". The AC power cable connects to the universal power entry plug on the rear of the Mainframe.

The rest of the connections are to be made with the blue BNC cables on the Mainframe and into your oscilloscope. TeachSpin recommends that students begin these experiments using a digital oscilloscope. A computer will also serve as a data storage device, but we believe it is more appropriate to use an oscilloscope first and then other options can be considered, after students have become thoroughly familiar with the spectrometer.

Connections and Basic Settings for Pulse Mode

1. Connect the blue 18 inch reverse gender cable from
    Pulsed RF Out (Synth) to Pulsed RF In (Rec)

2. The following are connections made with 12 inch blue BNC Cables:
    Q (PP) to Q (Synth)
    I (PP) to I (Synth)
    Blanking Out (PP) to Blanking in (Rec)
    Ref Out (Synth) to Ref In (Rec)

3. The following are connections made with 36 inch blue BNC cables to a two channel
    digital oscilloscope:
    Sync Out (PP) to Input Trigger
    Env. Out (Rec) to Channel 1
    Q Out or I Out (Rec) to Channel 2

4. Turn Off: CW Out (Synth), B Pulse (PP), MG (PP)
    Toggle Sync to A (PP)
    Toggle Pulse to A (PP)
    Ref Out (Synth) –Toggle Turn On
    Filter TC to .01 (Rec)
    Gain to 75% (Rec)
    Toggle Band to P (for proton) (Rec)
    Toggle Blanking (Rec) On, Width 75% (Rec)

    Do NOT connect to:
       Receiver – CW IN, RF Out
       Synthesizer – Sweep In, CW Out
       Pulse Programmer – Ext Start
       Lock-In – All Connectors.

If you have made all the connections specified, you have set up the spectrometer for your
first experiments. Turn it on with the power switch you will find on the rear panel of the
Mainframe, at the power entry plug. The only pilot lights that should go on are the one on
the PS2 Controller and the "error signal indicators". However, all three LCD displays should
light up and initially display "TeachSpin".

B. DIGITAL SETTING OF PARAMETERS

B.1 Overview

Before you attempt an experiment, you should get used to setting the parameters of the three
digital modules. Three of the modules on PS2-A's Mainframe, the Synthesizer, the Pulse
Programmer and the Lock-In/Field Sweep, are adjusted digitally with one knob in the upper right
hand corner. With this control the experimenter first selects the parameter and then changes its
value. The LCD screen at the top of the module displays both the name of the parameter and the
value selected.   It may take some practice to become proficient with this control, but in a short
time students will have the muscle memory needed to adjust these units seamlessly.

There is one disadvantage to this control system. The current value of only **one** parameter appears on the screen at any given time. The values of the other parameters can easily be obtained by scrolling through the menu. However, only one value at a time can be viewed or changed. Of course, students can always record the values they have chosen for each of the parameters. We trust that data books may still be in fashion. We encourage writing!

B.2 DEFAULT SETTINGS

The settings which have been preprogrammed into each unit of the PS2-A Mainframe electronics are listed below. You should check these to assure that the unit is operating correctly. In each module, the parameter we have shown as underlined appears on the screen as underlined and is flashing.

SYNTHESIZER	PULSE PROGRAMMER	LOCK-IN / FIELD SWEEP

<u>F</u> (flashing) –
   Frequency: 18.00000 mHz
P   Refer Phase: -180°
A   CW Pwr: - 10 dBm
S   Sweep: 0 kHz/V
	<u>A</u> (flashing)
	   A_len: 0.02 μs
	B B_len: 0. 02 μs
	τ tau: 0.0001 s
	N Num_B: 0
	P Period: 0.2 ms
		<u>G</u> (flashing) Gain: 80 V/V
		P Ref Phase: : -180°
		T Time Const: 0.5 s
		M Mod Amp: off
		H Fld off: 0.00 G
		S Swp Md: off
		A Swp Amp: 0.039 G
		D Swp Dur: 10 s

B.3 SETTING PARAMETERS

The push-to-select" knob is used in three stages.

1. Rotate the knob to display the desired parameter.
2. Push the knob into the panel and hold for a second or two until a beep indicates that the parameter has been selected.
3. Now you can change the value of the selected parameter by rotating the knob until your chosen value is displayed.

This process might best be explained by an example. Consider the synthesizer. If the Mainframe power has just been turned on, the capital letter F is both underlined and flashing and the number 18.00000 mHz appears on the screen. There are four functions that can be selected and varied by this control. They are:

F: the Frequency of the internal synthesizer

P: the relative Phase of the reference signal being routed to the receiver module

A: the Amplitude of the continuous wave (CW) rf output signal used when the spectrometer is configured for CW NMR detection.

S: the Sweep of the NMR rf frequency which is also used in CW NMR detection.

↑: the arrow is <u>not</u> a parameter. It is actually part of the menu and is used to return the control knob to the choices on the upper line of the menu.

Suppose you wish to set the synthesizer frequency to 21.350 mHz, the Larmor precession frequency for your particular unit, which was marked on the serial number label. How do you do this? Since the letter F is flashing, the default program has already selected Frequency for you. If you simply turn the knob, you will see the selected parameter change to P (phase), A (CW power), S (sweep).

To activate the parameter you wish to set, in this case frequency, start with the F flashing and then push the knob into the panel and hold it in until you hear the beep. The flashing will stop, but the F will still be underlined. Another underline will then appear at the 0.1 mHz decade on the display. Turning the knob will now change the frequency by 0.10 mHz per "click".

The coarse control of the frequency control has been activated and turning the knob can get us to 21.3 mHz, but that is not the value we want. Pushing in the knob and again waiting for the beep will move the underline to the .001 mHz position. Now, turning the knob will change the frequency in these smaller, 1 kHz steps. Another push and the underline will translate to .001 mHz or 10 Hz, the smallest frequency steps possible with the synthesizer.

By a combination of pushing and rotating, the entire menu of variables in each module can be accessed and the desired values assigned. Two things are important to remember. First, the chosen value of the parameter will only be set when the knob has been pushed in long enough for the "beep" to sound. This delay was installed to prevent accidental pushes, during rotations, from causing changes. Second, you must remember that the value of only ONE parameter at a time can be displayed. It might be wise to check all the parameters before beginning an experiment. Be sure to record these values!

An example: Perhaps you have "inherited" the spectrometer from your classmate who left the power on to the Mainframe. Supposing she was using it in the CW mode, with the frequency sweep option running. If you now attempt a pulsed experiment, without turning off the frequency sweep option, you will observe some bizarre signals. You might then incorrectly conclude that the spectrometer needs repair!

Even in a simple single 90° pulse experiment, where one is only observing the free precession decay (FID) of the proton spins, previously programmed parameters can cause serious problems. Suppose the period P (the time between repeated 90° pulses) is short compared to the spin-lattice relaxation time T_1. In such a case, the spins are not give sufficient time to return to thermal equilibrium magnetization before the 90° pulse of the RF occurs. Thus, the signal will be reduced in amplitude, possibly so much that it is not observable. There is nothing wrong with the spectrometer; it has just been set up incorrectly.

IT IS ESSENTIAL THAT ALL THE PARAMATERS HAVE BEEN INTERROGATED AND RECORDED BEFORE EMBARKING ON AN EXPERIMENT.

C. SINGLE PULSE EXPERIMENTS

C.1 Set Up

All of the experiments described in this section can be done with a single A pulse that is repeated with a period P. The first thing to do is to select a sample with a high density of protons. Mineral oil is a good choice. Two types are supplied with the unit. **It is essential that the correct volume of sample be used for all experiments**. Large errors are introduced into the measurements if too much sample is placed in the vials. The explanation for this systematic error is as follows:

The RF coil which surrounds the sample is a solenoid approximately 12 mm long.   The RF field from such a solenoid is only reasonable uniform over about half of its overall length. Therefore, if the sample only fills about 5 mm of the tube and is placed so that those 5 mm are in the center of the solenoid, all the spins in the sample will experience nearly the same magnitude of the RF magnetic field during the pulse burst. Thus, all of the spins will be "rotated" (tipped) the same amount. Figure 3.2 shows the correct volume and placement of a sample. Note that the O-Ring stop is located 39 mm from the center of the sample. This places the sample both at the center of the RF solenoid and at the center of the gradient and modulation coils.
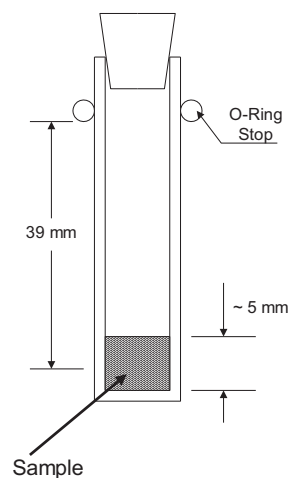
Figure 3.2 Schematic of Sample

Before you place the sample into the RF probe and search for your first NMR signal, you must tune the RF probe to the Larmor precession frequency of the proton in the ambient magnetic field. Since the spectrometer has no "pickoff points" in which you can examine the RF currents through the solenoid, TeachSpin has provided you with a "pickup probe" which can be inserted into the sample chamber to measure the RF fields DURING THE PULSE.

If the RF solenoid is tuned to resonance at the spectrometer's synthesized frequency (by the two tuning capacitors in the RF Sample Probe), then the RF magnetic field will also be at a maximum in the coil. The inserted pickup probe's voltage will also be a maximum when the sample solenoid is tuned to resonance.

Figure 3.3 Pickup Probe

Since the single solenoid coil in the RF Sample Probe serves as both a transmitter (to tip the spins) and a receiver (to produce an emf from the free precession of the magnetization), it is essential that it be tuned (or very nearly tuned) when searching for a signal. The unit is shipped from the factory tuned for a proton resonance. However, if this is your first attempt at PNMR with this unit, it is anybody's guess how the last user has left the tuning capacitors on the RF Sample Probe.

Place the coil end of RF pickup probe in the center of the sample solenoid. Secure it in place. Attach the BNC connector to Channel 1 of your oscilloscope. (The oscilloscope should have a bandwidth of at least 30 mHz.)

1. **Set the synthesizer frequency** to the frequency marked on the unit's labels. (Labels are on both the magnet and the Mainframe.)

2. **Set A_len** to 2.5 µ (or longer)
    Set P to 100 ms
    Leave all other settings as they have been set

3. **Set the parameters on the Oscilloscope**
    Trigger: Ext, Normal, Rising, > 0.1 Volt, positive slope
    Sweep: 2 µs/division
    Channel 1: 5 V/div, DC, Full bandwidth

With this time scale on your 'scope, you are observing the RF field inside the solenoid DURING THE PULSE. This is *not* a magnetic resonance signal. If the RF Sample Probe is properly tuned, you should observe an RF burst of about 40 volts peak-to-peak lasting about 3 µseconds. Try adjusting the two capacitors **on the tuning side**.

The tuning side is the side near the gray cable (the left side) coming out of the RF Sample Probe. The capacitor nearest the sample hole is a piston capacitor (1 – 30 pf fine tuning) and the one farthest from the hole is the compression capacitor (25 – 150 pf coarse tuning). Changing these capacitors should have a dramatic effect on the amplitude of the pickup signal.
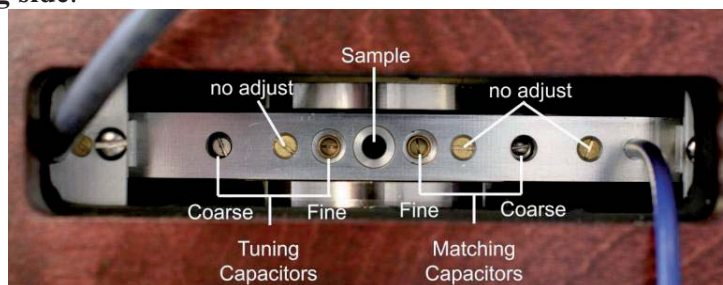

Figure 3.3b Tuning Capaciators Seen from Above

Adjust for maximum amplitude. If you cannot achieve about 40 V peak-to-peak voltage, something is wrong. Stop here and investigate the problem.

C.2 Free Induction Decays, FID (Free Precession); Protons

You are now ready to do your first magnetic resonance experiment with the PS2-A. Start with one of the mineral oil samples. Since you now wish to observe the precessing magnetization (collection of spins) AFTER THE RF PULSE HAS BEEN TURNED OFF, you need to change the time scale on the oscilloscope. The RF burst that tips the magnetization from its thermal equilibrium orientation along the z-axis (the direction of the DC magnetic field) to create some transient component along the x-y plane, does so on a time scale of microseconds (10^{-6} s). But this x-y magnetization precesses in the x-y plane for times of the order of milliseconds (10^{-3} s). Thus, the sweep times on the oscilloscope should be adjusted to 0.5 – 1.0 ms/div. Channel 1 of the 'scope should be connected Env Out from the receiver.

The second input on the oscilloscope should be connected to either the I or the Q output from the receiver. Remember (see Ch. 2, Sec. A.1) that the I and Q outputs are the *product* of the signal from the precessing *spins* multiplied by the *reference* signal from the oscillator. The equation is:

$$\sin(\omega_{ref}t) \cdot \sin(\omega_{spins}t) = \frac{1}{2}\cos(\omega_{ref} - \omega_{spins})t - \frac{1}{2}\cos(\omega_{ref} + \omega_{spins})t$$

Since the term $\omega_{ref} + \omega_{spins}$ is filtered out (it is approximately 40 MHz), it is the *difference signal* that is presented at the output. We call this the "beat" signal. It is essential that the beat frequency be at, or near, zero so that the oscillator has the same frequency as the precession frequency of the spins being examined.

Set all four potentiometers on the PS2 Controller – field gradients X, Y, Z, Z^2, to zero. Place your mineral oil sample in the RF Sample Probe and look for an FID signal. You should see one on the oscilloscope. Now there are many parameters to play with. Study their effects on the FID signal. You should do just that – play with them – vary them – record your results. You should try to explain everything you observe. If you cannot, talk with your instructor.

Some of the parameters to vary are listed below.

1. Gain	8. Phase
2. Filter TC	9. Magnetic Field Gradients
3. A_len (Pulse length)	10. Close the Temperature Control Loop
4. P period	11. Sample Placement in Solenoid
5. Tuning capacitors (RF Sample Probe)	12. Take the Fast Fourier Transform of the
6. Matching Capacitors	signal from either I or Q output from
7. Frequency	receiver – tune off resonance

The following is a list of things to do and questions you should be able to answer based on your experimentation with these single pulse measurements.

1. How do you know if you have a 90, 180, 270 or 360 degree "pulse"?
2. Calculate the approximate average B_1 field during the pulse.
3. Describe the differences in the signals from I, Q, Env Outputs.
4. How would you measure the field stability of the magnet?
5. Plot the magnetic field as a function of time after you close the temperature control loop.
6. What is the effect of the filter time constant on the signal?
7. Using a single 90 degree pulse, plot the maximum signal amplitude as a function of the period (repetition time). Explain your data.
8. How do you determine that the spectrometer is "on resonance" – namely that the free precession frequency is the same as that of the spectrometer's synthesizer?
9. Is there a signal when the spectrometer is off resonance? Explain. Suppose you tune it "way" off resonance? Is there a signal then? Keeping the A_len constant, tune the spectrometer's frequency away from resonance and explain what you observe. (Note: you should adjust the tuning capacitor in the RF Sample Probe for the maximum signal amplitude as you change the frequency.) A careful examination of effective fields in the rotating coordinate system will greatly help you understand your data.
10. Adjust the magnetic field gradient coils several times. Figure 3.4 shows our data from the Env. Output. Can you achieve this long – or maybe longer decay times?
11. Place some distilled water in a vial and repeat some of these measurements. What is the decay time? How does the signal depend on the period, on pulse length (A_len_, etc.? Explain what you observe. Which properties are the same and which are different between water and mineral oil?
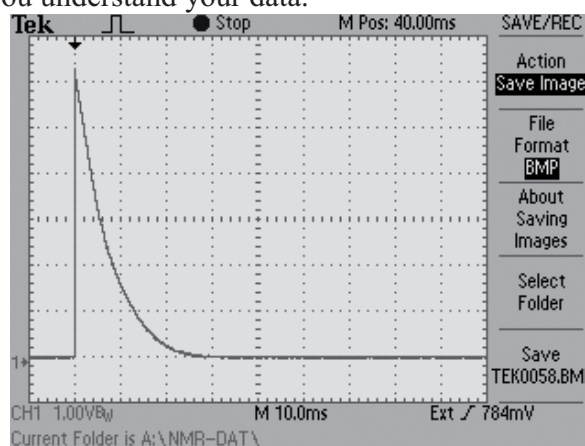

Figure 3.4 FID of Heavy Mineral Oil

C.3 The 180° Pulse

The experimental criterion for obtaining a 180° pulse, that is an RF burst that rotates the thermal equilibrium magnetization from the + z to – z axis, is a pulse approximately twice as long as a 90° pulse, yet one that leaves no FID signal after it. Why no signal? Well, if this pulse has rotated the magnetization exactly 180°, it has left no component of M_0 in the x-y plane. No x-y magnetization, no FID signal!

You may, however, have tried to obtain a 180° pulse and found a small signal after the pulse that you cannot eliminate by making the pulse time longer or shorter or even by changing the frequency. What is the problem?

To explain the effect, one must carefully examine what is happening during the RF pulse. When the signal for the pulse comes from the pulse programmer, the RF power is connected to the sample coil. An RF oscillating current rapidly builds up in the coil **at the synthesizer frequency**. It takes time, (~ 0.2 μs) to build up the current, since it is a tuned circuit. Then, the signal comes from the pulse programmer to turn off the current, to "open the switch" and end the pulse. The solenoid is disconnected from the synthesizer. But again, because the coil is part of a series resonant circuit, the current takes a finite time to die out. This is called **"ring-down"**.

Now, suppose that the resonant circuit of the sample coil was tuned to a frequency slightly different from the frequency of the synthesizer. When the coil is disconnected from the synthesizer, the RF oscillating current will decay to zero at this different frequency. Thus the spins have been subjected to **two different frequencies** during the entire burst of RF oscillating fields.

You should be able to show, with diagrams and by considering the effective field in the rotating frame, that one cannot obtain a true 180° pulse under this condition. One will always observe a FID signal after a pulse with two frequencies.

Luckily, you can easily eliminate the problem:

1. Tune the spectrometer to resonance and obtain the best 180° pulse possible by varying the pulse width.
2. Adjust the fine tuning capacitor in the RF Sample Probe a small amount. (Remember which way you changed it!)
3. Change the pulse width and see if the "tail" of the FID after the 180° pulse is smaller or larger. If it is smaller, continue to adjust the fine tuning the same direction. If larger, reverse your tuning direction.
4. Keep changing the pulse width and the tuning capacitor until you achieve a null after the 180° pulse.
5. Note, when you change the tuning capacitor, you are affecting **three** parameters of the spectrometer. They are:
   a) The amplitude of the RF magnetic field during the pulse.
   b) The "ring-down" frequency of the RF pulse.
   c) The amplitude of the FID signal (because the effective gain of the receiver changes).

6. How do you know if you have correctly tuned the RF Sample Probe? If it is correctly tuned for pulsed signals, the following criteria should be met:

    a) After a 180° pulse, there should be no (or very small) FID signal. You should achieve nearly perfect magnetization inversion.

    b) The 180° pulse width should be approximately twice as long as the 90° pulse, that is a 90° is 2.5 μs, a 180° is 5μs.

    c) The amplitude of the FID signal following a 90° pulse on a mineral oil sample should be comparable to the data taken at the factory and posted in this manual.

7. If the above criteria are not met, you may have tuned the system to some peculiar configuration that is incorrect. So start again.

    a) First: make sure your synthesizer frequency is actually at the Larmor procession frequency of the spins. As we pointed out before, this is done by creating a zero beat signal on either the Q or I phase detector. ***Look out for aliasing effects on your digital oscilloscope. They can badly mislead you.***

    b) Second: set the A pulse width (A_len) to 1μs, a pulse width that can, at best, produce about a 40° rotation of the magnetization. Set P to at least 0.3 seconds for a mineral oil sample. (For other samples, make sure P is at least three times the spin-lattice relaxation time.)

    c) Now adjust the tuning capacitor to maximize the signal. Note: If the signal increases, it may be due to all three effects listed in item 5 above. As long as you have correctly set the synthesizer frequency to the Larmor frequency of the spins, any increase in the FID signal amplitude will bring the probe closer to the correct setting.

    d) Change the pulse length to achieve a 180° pulse. Adjust the fine tuning capacitor to achieve a perfect 180° pulse as described in item 6 above.

What you are doing is simply tuning the series resonance circuit of the sample solenoid to the exact frequency of the synthesizer. When that has been accomplished, the spins only experience **one frequency** during the entire pulse burst. You should be able to achieve a near perfect result.

This is the best way to tune the spectrometer for all pulsed experiments. It assures that only one frequency is imposed on the spin system during the pulses. This "two frequency" effect cannot be observed from a 90° pulse, so it is best to tune the spectrometer with a 180° pulse before doing any experiments.

C.4 Free Precession; Fluorine

C.4.a Overview

The spectrometer comes with several fluorine liquids that should now be studied. In this spectrometer, the magnetic field is kept constant and it is the RF frequency that is changed to observe the fluorine NMR signals. It is necessary to retune the spectrometer to detect the fluorine free precession signals. But, before you do that, it important to adjust the magnetic field gradient coils so that the field at the sample has its maximum homogeneity. This can best be accomplished with the protons in the water sample.

The data shown in Figure 3.5 shows a decay time of about 25 ms due to the field inhomogeneities over the sample. (At this time, you will have to accept our word for that causality. You will soon see decay times that are due to the sample.) You should be able to adjust your spectrometer to have at least 5 ms decay times

The adjustment of the field gradients should be done **with the temperature control loop closed** and the magnetic field stabilized. This will prevent the field and the field gradients from drifting during the upcoming measurements of fluorine signals. A fluorine nucleus has a smaller magnetic moment than the proton so that, in the same magnetic field, the resonance frequency of the fluorine will be lower than that of the proton by about 6%.

Figure 3.5 FID of Water Sample

Important constants to note are:

Proton's NMR Frequency: 42.576 mHz/T

Fluorine's NMR Frequency: 40.044 mHz/T

$f_{fluorine}/f_{proton} = 0.9408$

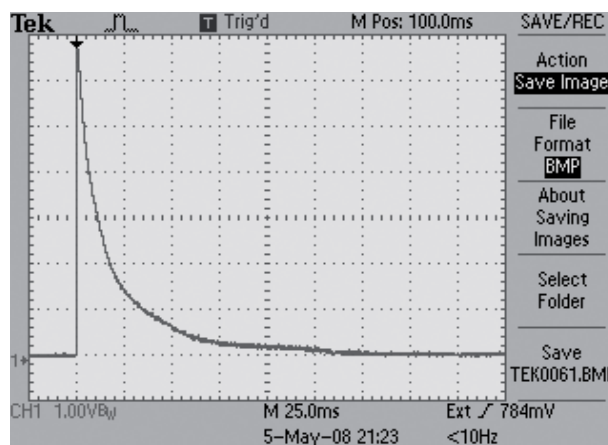C.4.b Fluorine Liquid FID

The following is a set of directions and questions to guide your exploration of the fluorine free induction decay signal.

1. Calculate the new resonant frequency for fluorine and set the frequency of the synthesizer to this new LOWER frequency.

2. Place the RF pickup probe in the sample chamber. Adjust the tuning capacitors in the RF Sample Probe for maximum signal. This should produce an approximately 40 volt peak-to-peak RF burst during the pulse.

3. Switch the BAND toggle on the receiver to f.

4. Start with the clear liquid sample labeled FC-770. Place a few drops in a sample vial. Place a black rubber stopper on it with an O-ring collar.

5. Adjust the A_len to produce a 180° pulse.

6. Tune the RF probe to achieve a near perfect 180° pulse (no "tail").

7. Adjust A_len to produce a 90° pulse.

8. Study the FID signal amplitude as a function of the period P. Vary P over a wide range and plot your data. Describe the ways this plot differs from what you found for the water and mineral oil samples.

C.5 Fast Fourier Transform

The FID signal from FC-770 looks very different from the mineral oil or water sample. The decay time is shorter and clearly not exponential. The explanation of this signal starts by considering the possibility that there is more than one "kind" of fluorine atoms in this liquid. By "kind," we do not mean different isotopes of fluorine. All of our nuclei are F^{19}. We mean that in this complex liquid, fluorine atoms may be located in different parts of the molecule with different local surroundings. These different local surroundings create different local magnetic fields. Since it is the total field at the nucleus that determines the nuclear precession frequency, different nuclear sites produce different precession frequencies. This very important property is essential for chemical and biological analysis of various samples. It has a name. It is call the **Chemical Shift.**

To analyze how many different fluorine sites there are in FC-770, we will look at the fast Fourier transform (FFT) of the FID signal from the phase sensitive detectors. To do this, it is essential that the spectrometer's frequency be **off** resonance so that the FID signal from Q looks like Figure 3.5. The FFT of this signal is shown in Figure 3.6.
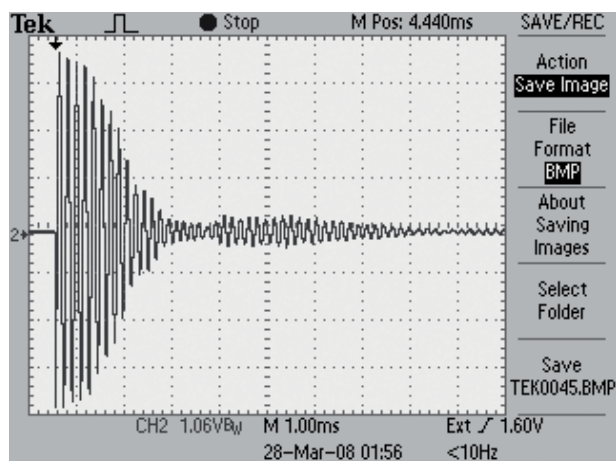
 Figure 3.5 FID of FC-770   Figure 3.6 FFT of FC-770
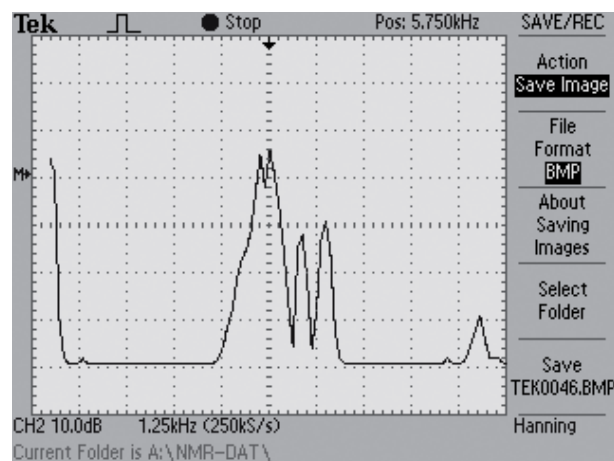
Clearly Figure 3.6 shows that there are three distinct peaks indicating at least 3 inequivalent fluorine sites. One peak, however, may actually be two peaks that are very close together. There may also be a fifth peak at a much smaller intensity. Chemists, especially organic chemists, use this technique to identify certain atomic clusters in molecules.

One can examine these spectra for different repetition periods P. What does this tell you?

Why didn't we see chemical shifts in mineral oil? It turns out that fluorine atoms typically have much larger chemical shifts than protons. Proton chemical shifts can be observed in some liquids by carefully adjusting the gradient coils for optimum field homogeneity and using a substance where these shifts are large. We have observed proton chemical shifts in ethyl alcohol and toluene, and many other substances can be used. But all of the principles of studying "chemical shifts" can be learned with your PS2-A using fluorine liquids. That's why we have provided you with several safe fluorine liquids to study.

C.6 Fluorine Solids FID

What differences can be observed between solids and liquids? Teflon is a common solid worth studying with these simple one pulse experiments. How does the Teflon compare with the fluorine liquids? You may not know that there are several kinds of Teflon – some made from recycled material and some "virgin". You might want to see if they exhibit any different NMR properties.

D. TWO PULSE EXPERIMENTS

Next we will consider experiments that have two pulses, A and B, which are separated in time. Here, a single pulse sequence consists of two bursts of RF magnetic field (whose length you can choose with A_len and B_len) separated by a variable time, τ. Thus, there are four parameters to program into the pulse programmer: A length, B length, τ (the time between A and B), and P, the repetition time of the entire A, B cycle.

D.1 Spin-Lattice Relaxation Time, T_1

D.1.a Overview

In the introduction section, we discussed the time it takes for the z-component of the magnetization to grow to its thermal equilibrium value. Equation 1.14 models the situation where the sample starts from zero magnetization $M_z(0) = 0$ and grows to $M(\infty) = M_0$, its thermal equilibrium magnetization value. T_1 is a very important physical parameter since it tells us about the mechanism of the spins interacting with their environment. There are materials that have T_1 values as short as microseconds and some that have T_1 values as long as several seconds. Let's examine some experimental ways of measuring it.

Actually, you have already made some crude estimates of T_1. You should have observed a decrease in the FID signal strength for decreasing repetition time P in the single pulse experiments. Sometimes, that decrease is not observed until P ~ 50 ms and for other samples, the decrease was noticeable for P ~ 1 second. The explanation for this, as you may have realized, is that too rapid a repetition time does not give sufficient time for the spins to return to their thermal equilibrium value before the 90° pulse. This condition is often referred to as **saturation**. By looking at these plots of signal vs. P, one can make a reasonable assessment as to the spin-lattice relaxation time.

D.1.b Measuring T_1

But let's do better than this estimate. A good sample to start with is mineral oil. The best place to begin is with the differential equation that governs the process of the spins returning to their thermal equilibrium value (1.13).

$$\frac{dM_z(t)}{dt} = \frac{M_0 - M_z(t)}{T_1} \qquad (1.13)$$

Now, however, we will consider a new set of **initial conditions**. The first pulse, A, will be a 180° pulse, which takes M_0, (in the + z direction) and rotates it 180° so that it is now in the – z direction. The magnetization will then return to M_0 in the +z direction with a time constant of T_1. From the differential equation we can see that the rate of return is **proportional to the difference** between the instantaneous value of $M_z(t)$ and the thermal equilibrium value M_0. Since the initial conditions are not the same as those described in Chapter 1, equation 1.14 will not be valid.   It is the job of the student to derive and plot the mathematical equation that describes the way the magnetization returns to equilibrium after an initial 180° pulse.

Once the equation has been determined, an interesting problem arises. How do you determine the instantaneous value of $M_z(t)$? Remember, the spectrometer never directly detects M_z. All of the spectrometer's NMR signals come from precessing magnetization **in the x-y plane.** This x-y precessing magnetization induces an emf in the sample coil. The "trick" is to follow the initial 180° pulse with **a 90° pulse to interrogate the z-magnetization.** This second pulse rotates the z-magnetization 90° into the x-y plane. The **initial amplitude** of the **FID** after the 90° pulse is proportional to the M_z magnetization **just before the pulse**. This two-pulse sequence in then repeated with different times, τ, between the A and B pulses. Note that for $\tau \gg T_1$, the initial amplitude of the FID should be proportional to M_0.

Using this two pulse sequence, measure the T_1 of your mineral oil sample. Do this in two ways.

1. There is a time, τ_0 such that the amplitude of the FID signal is zero. This *zero-crossing time* can be used to make a better estimate of T_1. Derive the expression for extracting T_1 from this time measurement.

2. Plot your data in any way you can support and extract T_1 from this plot. Estimate your systematic errors. Note: Having an accurate value of M_0 (or a signal proportional to M_0) is very important. Suppose, for example, that there is a 10% error in the measurement of M_0. How will that effect the measurement of T_1? Think of some clever ways to determine M_0 accurately.

Warning: All of the Bloch equations describing the spin systems start on the premise that the **spin system is in thermal equilibrium** before the first pulse is applied. Since these pulse sequences are applied every P seconds, it is essential that the spins be given adequate time after the last pulse in the sequence to recover to thermal equilibrium. How much time needed? At least 3 T_1, or better yet, 10 T_1 for accurate measurements. **It is crucial to make a good estimate of T_1 before you attempt an accurate experiment of any magnetic resonance parameter.**

D.2 Spin-Spin Relaxation Time, T_2

D.2.a Overview

The spin-spin relaxation time, T_2, is the time constant characteristic of the decay of the transverse magnetization of the system. Since the transverse magnetization does not exist in thermal equilibrium, a 90° pulse is needed to create it. The decay of the free induction signal following this pulse would give us T_2 if the sample was in a perfectly uniform magnetic field. As good as the PS2-A magnet is, it is not perfect. If the sample's T_2 is longer than a few milliseconds, a spin-echo experiment is needed to extract the real T_2. For $T_2 < 0.5$ ms, the free induction decay time constant is a good estimate of the real T_2 if the field gradients have been adjusted for maximum homogeneity over the sample.

D.2.b Two Pulse-Spin Echo

We have already discussed the way a 180° pulse following a 90° pulse reverses the x-y magnetization and causes a rephasing of the spins at a later time. (See Chapter I, Section B) This rephasing of the spins gives rise to a spin-echo signal that can be used to measure the "real" T_2. The pulse sequence is:

$$90° \text{ - - } \tau \text{ - - } 180° \text{ - - } \tau \text{- - echo maximum (total time, } 2\tau)$$

A plot of the echo amplitude as a function of the delay time 2τ will give the spin-spin relaxation time T_2. The echo amplitude decays because of stochastic processes among the spins, not because of inhomogeneity in the magnetic field. The decrease in the echo amplitude is our window into the "real" processes.

Figure 3.7

D.2.c Multiple Pulse – Multiple Spin Echo Sequences

D.2.c.1 Carr-Purcell

The two pulse system will give accurate results for liquids when the self diffusion times of the spin through the magnetic field gradients is slow compared to T_2. This is not often the case for common liquids in this magnet. Carr and Purcell devised a multiple pulse sequence which reduces the effect of diffusion on the measurement of T_2. In the multiple pulse sequence, a series of 180° pulses spaced a time τ apart is applied as:

$$90° \text{ - } \tau \text{ - } 180° \text{ - - } 2\tau \text{ - - } 180° \text{ - - } 2\tau \text{ - - } 180° \text{ - - } 2\tau \text{ - - } 180° \text{ - - etc.}$$

This creates a series of echoes equally spaced between the 180° pulses. The exponential decay of the maximum height of the echo envelope can be used to calculate the spin-spin

relaxation time. The time interval, 2τ, between the 180° pulses should be short compared to the time of self diffusion of the spins through the field gradients. If that is the case, this sequence significantly reduces the effects of diffusion on the measurement of T_2.

D.2.c.2 Meiboom-Gill

There is a serious practical problem with the Carr-Purcell pulse sequence. In any real experiment with real apparatus, it is not possible to adjust the pulse width and the frequency to produce an exact 180° pulse. If, for example, the spectrometer was producing 182° pulses, by the time the 20th pulse was turned on, the spectrometer would have accumulated a rotational error of 60°, a sizeable error. This error can be shown to affect the measurement of T_2. It gives values that are too small.

Meiboom and Gill devised a clever way to reduce this accumulated rotation error. Their pulse sequence provides a **phase shift** of 90° between the 90° and the 180° pulses which prevents the accumulated error to the first order. The M-G pulse train gives more accurate measurements of T_2. All of your final data on T_2 should be made with the Meiboom-Gill phase shift **on.** The only reason it is not permanently built into the instrument is to allow you to see the difference in the echo train with and without this phase shift.
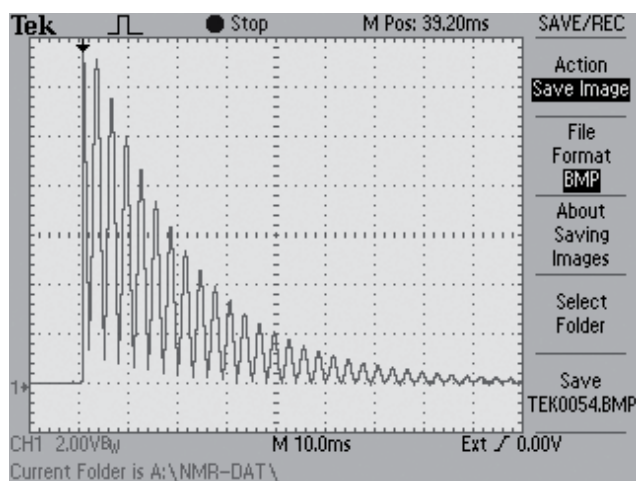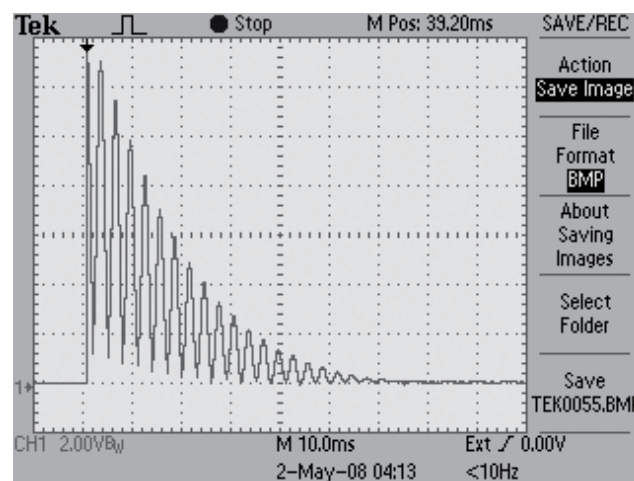

Figure 3.8 Meiboom-Gill Sequence   Figure 3.9 Carr-Purcell Sequence

D.2.c.3 Self Diffusion

Carr and Purcell showed that self diffusion leads to the decay of the echo amplitude. For the case where the field gradient, $\partial B/\partial z$, is in the z-direction, the magnitude of the echo gradient as a function of delay time τ is given by the expression:

$$M(\tau) = M_0 e^{-\gamma^2 (\frac{\partial B}{\partial z}) \frac{D\tau^3}{12}} \tag{3.1}$$

If the sample is placed in a known field gradient, it is possible to use this pulse sequence to measure D, the diffusion constant. This is an advanced experiment to be attempted only after mastering the basic measurements of T_1 and T_2.

A Conceptual Tour of Pulsed NMR*

Many nuclei, but not all, possess both a magnetic moment, μ, and an angular momentum, L. Such particles are said to have spin. When the angular momentum and magnetic moment are collinear, as they are in protons (hydrogen nuclei) and fluorine nuclei, both the particle and its surroundings can be investigated using various techniques of Nuclear Magnetic Resonance Spectroscopy. For these particles, the quantity μ/L, defined as the gyromagnetic ratio, is an important signature by which the particle can be identified and its behavior predicted or interpreted.

For our "tour" we will consider a specific collection of these magnetic nuclei, the protons in a liquid mineral oil sample. In the absence of a magnetic field, the spin axes of these particles are randomly oriented; there is no **net magnetization, M**, of the sample. We will begin our NMR experiment by placing our sample into a magnetic field, B_0. For PS2-A this is the field of our permanent magnet. There is *no instantaneous* net magnetization. In time, however, a net magnetization does develop which is collinear with the direction of our B_0 field. This is the **thermal-equilibrium condition**. The time constant for the build-up of this **net magnetization, M**, which is almost always exponential, is called the **spin-lattice relaxation time, T_1**. (For certain kinds of MRI, the "image" is nothing more than a grayscale map of the T_1 for the tissue.)

We'll begin our discussion of TeachSpin's Pulsed NMR with the probe head tuned to investigate protons and our proton containing mineral oil sample already located in the field of the magnet and the net magnetization of the spins already in the thermal equilibrium condition.

Figure 1 shows a side view sketch of the basic system. The sample sits in the **Sample coil**, a tightly wound solenoid which has its axis perpendicular to the constant magnetic field, B_0, of the permanent magnet. This coil serves **two** purposes. In the role of **transmitter coil,** it supplies an oscillating RF (radio frequency) field which can change the orientation of the net magnetization. In the vernacular, we say that the RF pulse "tips the spins" away from the B_0 direction. After such an RF pulse, the net magnetization vector will then freely precess around B_0. Once the spins have been tipped, the solenoid switches roles to become a **pickup coil** "sensing" the precession of any component of the magnetization which is in x-y plane. This three-dimensional process is easier to understand with some diagrams.

Figure 1 is a very simplified schematic. Figure 2, shows the relative directions of the magnetic fields we are discussing. The cylinder represents the solenoid/sample coil. The dark arrows represent the field, B_0, created by the permanent magnet. The thermal equilibrium magnetization of the protons is represented by the thinner arrow labeled M_0. The dashed double ended arrow, B_1, shows the direction of the oscillating RF field used to tip the spins
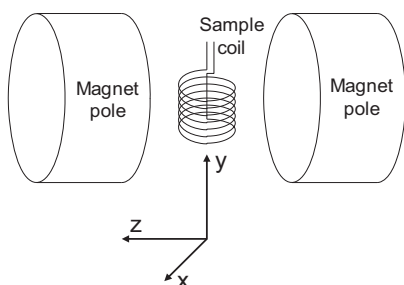
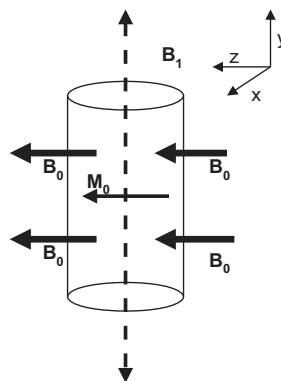

Figure 1 – Artist Sketch of Basic System

Figure 2 – Vector Fields

* This "tour" is a *conceptual* introduction to the basic ideas of NMR and the way they can be explored with the TeachSpin apparatus. For hands-on operation, the manual is the best guide.

The duration of a short burst of the RF field, (a pulse) can be adjusted to cause the magnetization **M** to rotate into the x-y plane. For the pulsed experiments we will be describing, it is important that the frequency of the oscillating RF matches the **Larmor frequency**, the frequency at which protons precess around **B₀**. In this "on resonance" condition, if a pulse lasting some time t tips the spins into the x-y plane, a pulse lasting twice as long, 2t, will tip the spins until the net magnetization is pointing in a direction, opposite to **B₀**. In NMR jargon, these are referred to as 90° and 180° pulses. (TeachSpin's Magnetic Torque apparatus provides a hands-on classical analog for this spin-flip mechanism.)

Figure 3a is a top view of the sample before and after a 90° pulse. In this view, the oscillating RF field **B₁** is directed perpendicular to the page. The gray line labeled **M₀** represents the initial thermal equilibrium magnetization of the spins parallel to **B₀**. The vector **M_T** represents the net magnetization of the sample the instant that the 90° RF pulse has ended. The net magnetization has been rotated into the x-y plane and will now precess, as shown in Figure 3b. This "free" precession creates an alternating emf in the solenoid surrounding the sample. This is clearly a non-equilibrium or transient condition. The rate at which the amplitude of the free precession signal diminishes, and the causes for that decrease, will be discussed later.
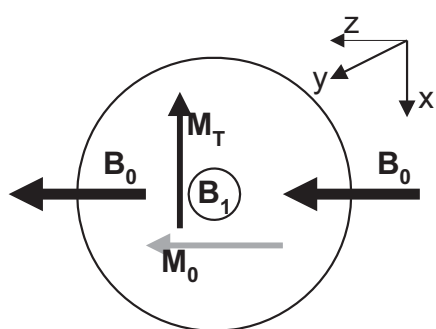

Fig. 3a Top view of the Sample showing the effect of a 90° pulse on the magneti-zation **M** of the sample. The thermal equilibrium magnetization **M₀** has been rotated to the transient **M_T**.
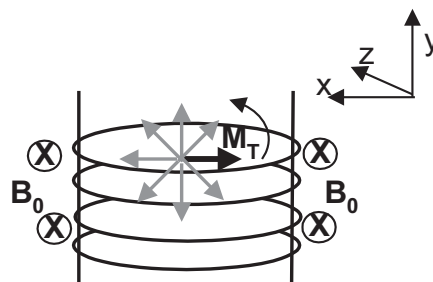
Fig. 3b Side view of the sample with, **B₀**, the field of the permanent magnet, directed into the page. Following a 90° pulse, the net magnetization, **M_T**, precesses around **B₀**.

The PS2-A electronics system is composed of four modules, only three of which are involved in Pulsed NMR. The black knobs on the **Synthesizer** and **Pulse Programmer** are used first to select the aspect of the signal to be changed, and then rotated to change magnitude. The RF signal used to "tip" the spins is created by the **Synthesizer**. The **Pulse Programmer** module is used to determine the duration and spacing of the RF signals produced by the Synthesizer. The **Receiver** plays several roles. The connection labeled **Sample** first transmits the RF pulse to the solenoid surrounding the sample to tip the spins and then receives the resulting signal coming from the free precessing spins.

Let's follow the progression of the signal. The module is in bold; the connector titles are shown in parenthesis. **Pulse Programmer** (*Pulse Out*) ▶ (*Pulse In*) **Synthesizer** (*Pulsed RF Out*) ▶ (*Pulsed RF*) **Receiver** (*Sample*) ▶ Solenoid acts as RF transmitter > Spins "tip" > Solenoid acts as Pickup Coil ▶ (*Sample*) **Receiver** (*Env. Out*) ▶ Oscilloscope, Channel 1

One role of the **Receiver** module is to amplify and "forward" the signal coming from the solenoid/pickup coil. As the spins precess inside the solenoid, they induce a voltage which rises and falls as a sine wave with each rotation. The sinusoidal signal can be observed at the *RF Out* connector. The signal usually associated with NMR, however, and shown in the lower trace of the oscilloscope capture in Figure 4, comes from the connector labeled *Env. Out* (envelope out). In this case, the signal is first "rectified" so that all values become positive and then only the maximum amplitudes for each cycle are selected. It is this rectified envelope which is referred to as the **free induction decay or FID**.

Set on *F*, the **Synthesizer** module displays the frequency in MHz of the RF (radio frequency) pulse being used to tip the spins, and change the direction of the net magnetization of the sample. As we have mentioned, for on resonance operation, this frequency must be adjusted to match, with high precision, the Larmor 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.)

The **Receiver** module also houses the electronics which are used monitor the relationship between the **Synthesizer** and Larmor frequencies. As already discussed, the portion of the **Synthesizer** signal coming from the connector labeled *Pulsed RF Out*, enters the **Receiver** via connection *Pulsed RF* and is then used to tip the spins of the sample.

Another portion of the synthesized signal becomes a reference signal that is used to monitor the Synthesizer/Free Precession frequency match. It goes from the **Synthesizer** connector *Ref Out* into the *Ref In* connector of the **Receiver**. An internal connection in the **Receiver** diverts part of the signal coming from the precessing protons to a phase detector system where it is "multiplied" with the reference signal coming from the **Synthesizer**. The output is monitored from either the *I Out* or *Q Out* connector on the **Receiver**. This is the signal shown as the upper trace of Figure 4.
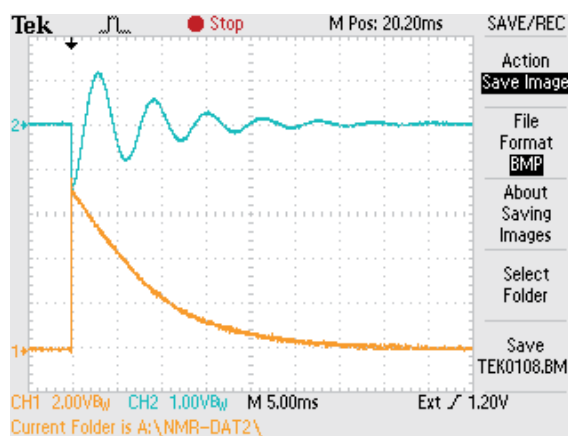

Figure 4 – Upper Trace: Mixer Signal
Lower Trace: FID Envelope

But how does this signal multiplication work; how does tell us if we are on resonance? We get an answer to this by looking at what happens when we "multiply" two sign wave expressions mathematically. If the synthesized frequency is ω_1 and the free precession frequency is ω_2, a bit of trigonometry gives $2 \sin\omega_1 \sin \omega_2 = \cos (\omega_1 - \omega_2) + \cos (\omega_1 + \omega_2)$. A low pass filter inside the **Receiver** allows only difference signals to reach the *I* and *Q* outputs. When the oscillator is properly tuned to the resonant frequency $\omega_1 = \omega_2$ and the signal from either of the phase detector outputs should show no "beats." The upper trace of Figure 4 indicates that when this measurement was made the system was not exactly "on resonance," but is very close and requires only a little tweaking. In many permanent magnet NMR systems, 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 B_0 and thus in the precession frequency. The PS2-A, however, has a temperature and thus field stability of one part per million over 25 minutes.

The **Pulse Programmer** determines the duration of individual RF pulses as well as the number of pulses in a series, the spacing between pulses, and how often an entire series is repeated. The PS2 pulse programmer provides two different pulses, A and B, both at the same frequency. Duration and number of pulses, however, are independent. The selected pulse pattern is sent from the *Pulse Out* connectors of the **Pulse Programmer** to the *Pulse In* connectors of the **Synthesizer**. For the experiments in this discussion, *Sync Out* connects to the oscilloscope. The *Sync* toggle switch can be set to either pulse. Now let's look at how each of the pulse parameters is controlled by the settings on the **Pulse Programmer**.

A_len and B_len control the length of time each of these RF pulses persists. (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.)

N indicates the number of pulses to be used. The PS2 provides only one A pulse, but there can be anywhere from 0 to 100 B pulses in a given series.

The τ setting indicates the delay time, 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. We will see why this matters later.

The *P*, or Period setting determines how often an entire pulse sequence is repeated. This is also called the repetition time.

The total time for the pulse series itself, is determined by the combination of *N* and τ. This must be less than the repetition time *P* so that the digital logic does not lock up. In addition, *P* must be long enough so that, after the pulse series had ended, the net magnetization has time to realign with the primary field. If *P* is too short, a pulse sequence will begin before the system has returned to thermal equilibrium and the FID will make little sense. **In fact the repetition time *P*, 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

As we have discussed, the Pulsed NMR experiments we are describing involve the sum of the magnetic moments of many protons, the net magnetization. (By contrast, Magnetic Torque works with the spin of only one "proton" which is represented by the ball.) When the sample is in thermal equilibrium, the net magnetization of the protons of the sample is aligned with the field of the permanent magnet, $\mathbf{B_0}$. Any change in the orientation of the spins decays back to an alignment with this "primary" field. The time constant of this usually exponential return to thermal equilibrium magnetization is the $\mathbf{T_1}$ relaxation time. But TeachSpin's PS2 can actually be used to measure two **different kinds of relaxation times**, referred to as T_1 and T_2. $\mathbf{T_1}$, the **spin-lattice** relaxation time already described, is the time characteristic of establishing thermal-equilibrium magnetization in the $\mathbf{B_0}$ direction. The **spin-spin** relaxation time, $\mathbf{T_2}$, is the time constant for the exponential loss of x-y magnetization due to dephasing of the spins. The variation in the "local" field surrounding individual protons, which is created by magnetic properties of nearby atoms, changes the local precession frequency. This dephasing is thus an indication of important qualities of the sample.

A First Exploration

Once the probe-head of the TeachSpin Pulsed NMR has been tuned to the proton frequency, we can investigate the PNMR signal following a single pulse. The duration of TeachSpin's A and B pulses are set independently. Start with both pulse widths set to 0, the repetition time, P, 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 length and examine the effect. (To be sure the RF pulse is in resonance, check the phase signal on the oscilloscope and tweak the **Synthesizer** frequency until there is a zero beat condition.) Pulse length determines the time allowed for the RF to tip the spins. The longer the RF is on, the farther the spins tip. As the time, A_len, increases, you will notice that the initial height of the FID (the signal on the oscilloscope) first rises to a maximum, indicating a 90° pulse, then decreases to close to 0 at about twice the 90° pulse time. This indicates a 180° rotation. After a 180° rotation there is no x-y magnetization and thus no signal. Continuing to increase the pulse time shows the signal increase to another maximum for a 270° rotation etc.

The repetition time can be used to estimate T_1, the time characteristic of re-establishing thermal equilibrium magnetization in the z-direction. Set the A pulse length for the first maximum. Decrease the repetition time, *P,* 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 90° pulse. We have found a rough measure of T_1. This effect becomes more dramatic as the repetition time decreases.

Measuring T_1, the spin-lattice relaxation time
(Time characteristic of establishing equilibrium magnetization in the z-direction)

A more precise measurement of T_1 requires a two pulse sequence. The net magnetization, M_o, is first tipped by 180° to $-M_o$ or the –z direction. The z-magnetization is then interrogated as it returns to its thermal equilibrium value, M_o. We have a problem however. Our spectrometer cannot directly detect M_z. Only precession in the x-y plane induces an emf in the sample coil. The "trick" we will use is to follow this initial 180° pulse with a 90° B pulse.

To tip the magnetization to - M_o, the length of the A pulse is increased until it has passed through the first maximum and returned 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 A pulse is then turned off and the width of the B pulse is adjusted to the first maximum signal, indicating a 90° 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. This second pulse rotates the z-magnetization into the x-y plane where it can be detected. 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 pickup 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 Q or I phase detector signal will show a 180° phase shift as the z-axis 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_0 - M, which changes exponentially. The equation is:

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

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.
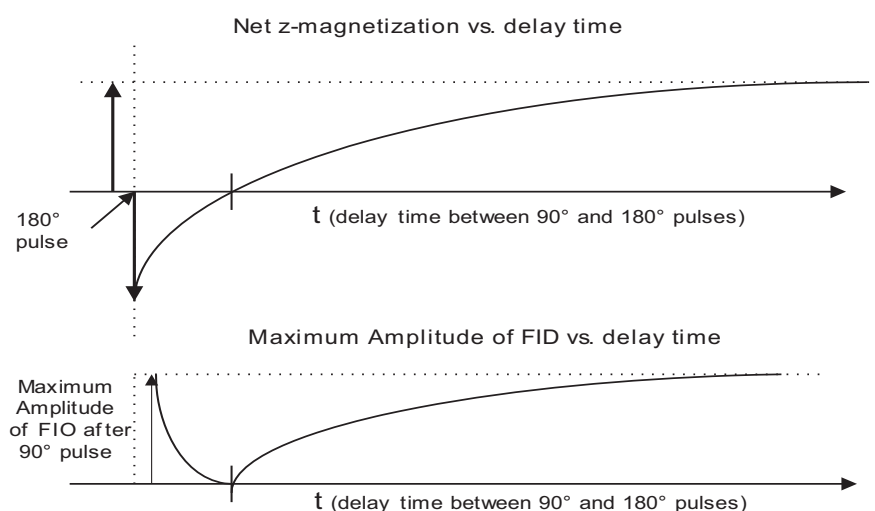

Figure 5 – Upper Diagram: Net z magnetization vs. delay time
Lower Diagram: Maximum Amplitude of FID vs. delay time

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. As good as the PS2 magnet is, it is not perfect. If the T_2 of the ample is less than 0.5 ms, the FID time constant can be used as a good measure of the real T_2. However, if the spin-spin relaxation time of the sample is longer than a few milliseconds we will need to use a spin echo experiment to measure it.

Spin Echo

In 1950, Irwin Hahn found a way to compensate for the apparent decay of the x-y magnetization due to inhomogeneity in 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 our initial 90° pulse, the spins in areas of stronger than average fields precess faster than average and those in weaker fields more slowly. The spins "dephase" and the induced emf fades. After the 180º flip, however, the 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 initial dephasing and then 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.
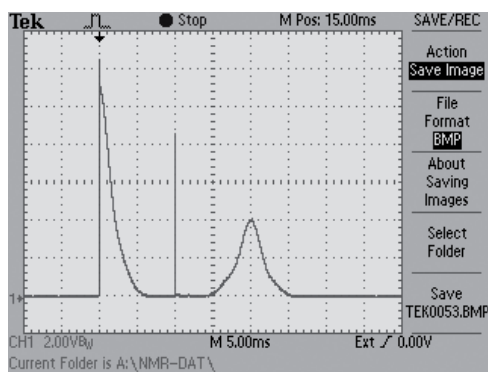

Figure 6a: Oscilloscope trace showing 180° pulse spike and spin echo.
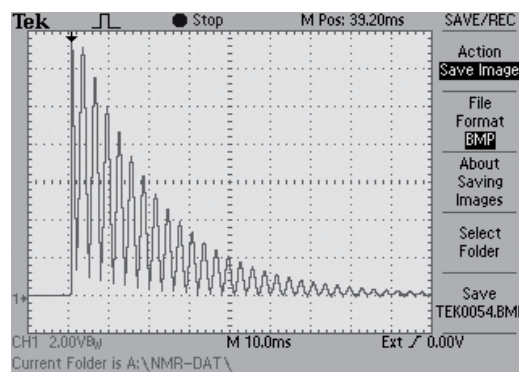

Figure 6 – Oscilloscope Trace of Multiple Echoes

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, change one of the gradient settings so that the magnetic field at the sample becomes less homogeneous. 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.