

NUCLEAR MAGNETIC RESONANCE¹

v2.2

Last Revision: R. A. Schumacher, February 2009

I. INTRODUCTION

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, observed the response of magnetic nuclei, placed in a uniform magnetic field, to a continuous (cw) radio frequency magnetic field as the field was tuned through resonance. This discovery opened up a new form of spectroscopy which has become one of the most important tools for physicists, chemists, geologists, biologists, and physicians.

In 1950 Erwin Hahn, a young postdoctoral fellow at the University of Illinois, explored the response of magnetic nuclei in condensed matter 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.

In medicine, MRI (magnetic resonance imaging; the word "nuclear" being removed to relieve the fears of the scientifically illiterate public) scans have revolutionized radiology. This imaging technique seems to be completely noninvasive, produces remarkable three dimensional images, and gives 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. MRI scans are able to pinpoint malignant tissue without biopsies, and we will see many more applications of this diagnostic tool in the coming years. The scans rely on measuring the “ T_1 ” and “ T_2 ” values in various body tissues: in this experiment you will learn what these are and how to measure them for a small sample.

You will be using the first pulsed NMR spectrometer designed specifically for teaching. The PS1-A is a complete spectrometer, including the magnet, the pulse generator, the oscillator, pulse amplifier, sensitive receiver, linear detector, and sample holder. Many substances can be studied.

Now you are ready to learn the fundamentals of pulsed nuclear magnetic resonance spectroscopy. We recommend that for this laboratory experiment you proceed as follows:

- 1) Read about nuclear spin and spin precession (start with Section III, below) so you grasp the basic ideas.
- 2) Try out the "TeachSpin" mechanical model and the induction coil until you understand the precession concepts, the notion of the rotating reference frame, and magnetic induction. Also try the VPython computer simulation of NMR that is available on the MPL web site (NucMagRes5.py). Your instructor can walk you through these visualizations to help you get started.
- 3) Read the discussion in Section IV to become familiar with the equipment.
- 4) Start a series of measurements as outlined in Section V. Go as far as you can in the time available. Quality of results is more important than quantity.

II. BACKGROUND READING

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. An extensive annotated bibliography of important papers and books on the subject is provided at the end of this section. The following references may provide additional useful background for the experiment and should be perused:

| <u>Reference</u> | <u>Sections</u> | <u>Pages</u> | <u>Topics</u> |
|------------------------------|------------------------------|--------------------|--|
| Melissinos ² | 8.1 - 8.4.1 8.4.2 - 8.4.4 | 340-359 361-374 | Magnetic Resonance basics Detection (but not the MPL way) |
| Cohen-Tannoudji ³ | F(IV) | 443-451 | Quantum vs classical descriptions |

III. THEORY OVERVIEW

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 only be concerned with one nucleus, the nucleus of hydrogen, which is a single proton. The proton can be thought of as a small spinning bar magnet with a magnetic moment μ and an angular momentum J , which are related by the vector equation:

$$\vec{\mu} = \gamma \vec{J} \quad (\text{III.1})$$

where γ is called the "gyromagnetic ratio." The nuclear angular momentum is quantized in units of \hbar as:

$$\vec{J} = \hbar \vec{j} \quad (\text{III.2})$$

where j is the unit-less "spin" of the nucleus. The magnetic energy U of the nucleus in an external magnetic field is

$$U = -\vec{\mu} \cdot \vec{B} \quad (\text{III.3})$$

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

$$U = -\mu_z B_0 = \gamma \hbar m_z B_0 \quad (\text{III.4})$$

Quantum mechanics requires that the allowed values of m_z be quantized as

$$m_z = j, j-1, j-2, \dots, -j \quad (\text{III.5})$$

For the proton, with spin one half ($j = 1/2$), the allowed values of m_z are simply

$$m_z = \pm 1/2 \quad (\text{III.6})$$

which means there are only two magnetic energy states for a proton residing in a constant magnetic field B_0 . These are shown in Figure III.1.

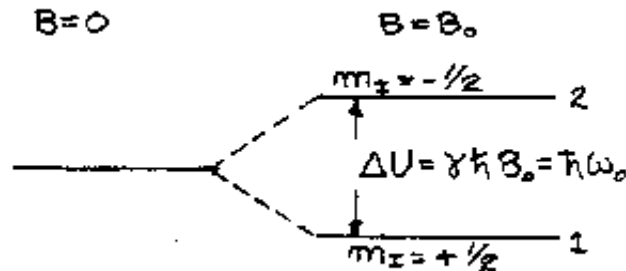


Figure III.1

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

$$\Delta U = \hbar \omega_o = \gamma \hbar B_o \quad \text{or} \quad \boxed{\omega_o = \gamma B_o} \quad (\text{III.7})$$

This is the fundamental resonance condition. For the simplest nucleus, a proton,

$$\gamma_{\text{proton}} = 2.675 \times 10^4 \text{ rad/sec/Gauss}^1 \quad (\text{III.8})$$

so that the resonant frequency is related to the constant magnetic field for the proton by

$$\boxed{f_o \text{ (MHz)} = 4.258 B_o \text{ (kG)}} \quad (\text{III.9})$$

a number worth remembering.

The connection between a spinning classical bar magnet and a 2-level quantum spin system is not trivial to learn, but it is not difficult if you have learned enough quantum mechanics. It can be shown, for example in Ref [3], that the algebra for quantum spins mimics that of classical angular momentum. It follows that we can successfully understand NMR almost entirely in terms of a classical vector model.

"Relaxation" along the external field:

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 factor³ as

$$\frac{N_2}{N_1} = e^{\frac{-\Delta U}{kT}} = e^{\frac{-\hbar \omega_o}{kT}} \quad (\text{III.10})$$

and the magnetization is

$$M_z = (N_1 - N_2)\mu \quad (\text{III.11})$$

The thermal equilibrium magnetization per unit volume for $N = N_1 + N_2$ magnetic moments is then

$$M_o = N\mu \tanh\left(\frac{\mu B}{kT}\right) = N \frac{\mu^2 B}{kT} \quad (\text{III.12})$$

Exercise 1: Derive Eq. III.12 from the preceding two equations.

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

¹ Gauss has been the traditional unit to measure magnetic fields in NMR but the Tesla is the proper SI unit, where 1 Tesla = 10^4 Gauss.

systems, the z-component of the magnetization is observed to grow exponentially as depicted in Figure III.2. The differential equation that describes such a process assumes the rate of approach to equilibrium is proportional to the separation from equilibrium:

$$\frac{dM_z}{dt} = \frac{M_o - M_z}{T_1} \quad (\text{III.13})$$

where T_1 is called the spin-lattice relaxation time. If the unmagnetized sample is placed in a magnetic field, so that at $t = 0$, $M_z = 0$, then direct integration of Equation III.13, with these initial conditions, gives

$$M_z(t) = M_o (1 - e^{-t/T_1}) \quad (\text{III.14})$$

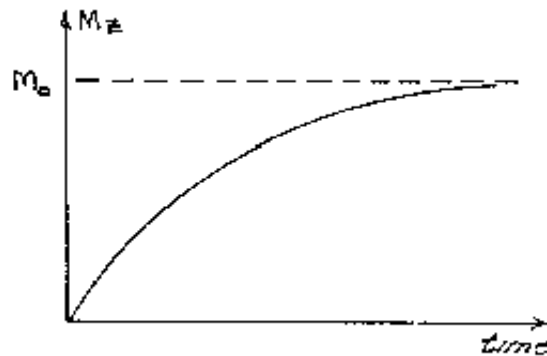


Figure III.2

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 $10 \mu\text{s}$ 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 is referred to as "the lattice", even for liquids or gases. Thus, the name "spin-lattice" relaxation time for the characteristic time, T_1 , 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 lattice during magnetization. In

quantum mechanical terms, the lattice must have angular momentum states available when a spin goes from $m_z = -\frac{1}{2}$ to $m_z = +\frac{1}{2}$. 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 unambiguous measurement, whereas cw spectrometers use a difficult, indirect, and imprecise technique to measure the same quantity.

Phase decoherence of the spins with respect to each other:

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 $\vec{\mu} \times \vec{B}$ and that torque causes the angular momentum of the loop to change, as given by:

$$\vec{\tau} = \frac{d\vec{J}}{dt} \quad \text{or} \quad \vec{\mu} \times \vec{B} = \frac{d\vec{J}}{dt} \quad (\text{III.15})$$

which for the protons becomes

$$\vec{\mu} \times \vec{B} = \frac{1}{\gamma} \frac{d\vec{\mu}}{dt} \quad (\text{III.16})$$

This is the classical equation describing the time variation of the magnetic moment of the proton in a magnetic field. It can be shown that the magnetic moment will execute precessional motion, depicted in Figure III.3.

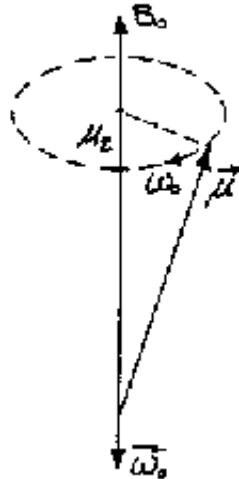


Figure III.3

Exercise 2: Show that the precessional frequency, ω_0 , is just the resonant frequency in Equation III.7.

If we add up all the magnetization for the 10^{20} protons 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 average to zero. For the x-components of every proton to add up to some finite 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 randomly positioned. Thus, in thermal equilibrium there is no transverse (x and y) component of the net magnetization of the sample. However, as we shall soon see, there is a way to *create* such a transverse magnetization using radio frequency pulsed magnetic fields. The idea is to 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 III.16 can be generalized to describe the classical motion of the net magnetization of the entire sample. It is

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B} \quad (\text{III.17})$$

where \vec{B} is any magnetic field, including time dependent rotating fields. Suppose we apply not only a constant magnetic field $B_0 \hat{z}$, but also a rotating (circularly polarized) magnetic field of frequency ω in the x-y plane, so the total field is written as

$$\vec{B}(t) = B_1 \cos \omega t \hat{x} + B_1 \sin \omega t \hat{y} + B_0 \hat{z} \quad (\text{III.18})$$

The analysis of the magnetization in this complicated time dependent magnetic field can best be carried out in a *rotating coordinate system*, 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 (Fig. III.4). However, from the point of view of the rotating coordinate system, B_0 and B_1 are not the only magnetic field components. An *effective field* along the z^* direction, of magnitude $-\omega/\gamma$ must also be included. The justification for this new effective magnetic field can be argued as follows.

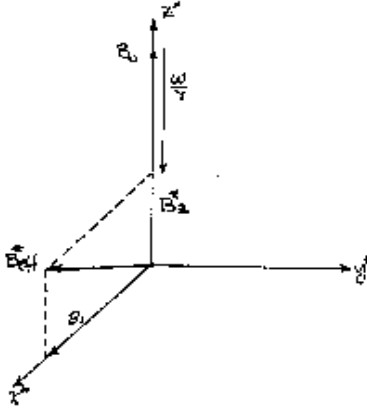


Figure III.4

Equations III.16 and III.17 predict the precessional motion of a magnetization in a constant magnetic field $B_0 \hat{z}$. 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. If it remains fixed in space 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 $-(\omega/\gamma) \hat{z}^*$ which is equal to $B_0 \hat{z}^*$.

Transforming the magnetic field expression in Equation (III.18) into such a rotating coordinate system, the total magnet field in the rotating frame is

$$\vec{B}_{eff}(t) = B_1 \hat{x}^* + \left(B_0 - \frac{\omega}{\gamma} \right) \hat{z}^* \quad (\text{III.19})$$

shown in Figure III.4. The classical equation of motion of the magnetization as observed in the rotating frame is then

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B}_{eff}^* \quad (\text{III.20})$$

which shows that M will precess about the effective field in the rotating frame.

How does one create a "rotating magnetic field"? What is actually applied is a field oscillating only along \hat{x} , of the form $2B_1 \cos \omega t \hat{x}$, but this can be decomposed into two counter-rotating fields $B_1 (\cos \omega t \hat{x} + \sin \omega t \hat{y}) + B_1 (\cos \omega t \hat{x} - \sin \omega t \hat{y})$. The second term can be shown to have no practical effects on the spin system and can be ignored in this analysis.

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

$$\frac{\omega}{\gamma} = B_o \quad \text{or} \quad \omega = \gamma B_o = \omega_o \quad (\text{III.21})$$

In that case $\vec{B}_{eff}(t) = B_1 \hat{x}^*$, a constant magnetic field in the \hat{x}^* direction. The \hat{z}^* component of the field is gone! Then the magnetization M_z begins to precess about this magnetic field at a rate $\Omega = \gamma B_1$ (in the rotating frame). This is illustrated in Figure III.5.

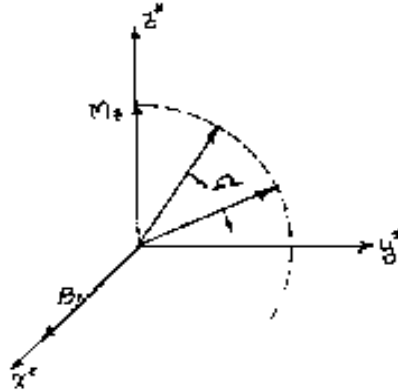


Figure III.5

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 $-M_z$ and if it is left on four times as long the magnetization will be back where it started, with M_z along the z axis. These are called:

| | |
|------------------------------|----------------------|
| 90° or $\pi/2$ pulse: | M_z goes to M_y |
| 180° or π pulse: | M_z goes to $-M_z$ |
| 360° or 2π pulse: | M_z goes to M_z |

In the laboratory (or rest) frame where the experiment is carried out, the magnetization not only precesses about B_1 but rotates about the x axis 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_z 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 it will precess about $B_0 \hat{z}^*$. But the x - y magnetization will not last forever. For most systems, this magnetization decays exponentially as shown in Figure III.6.

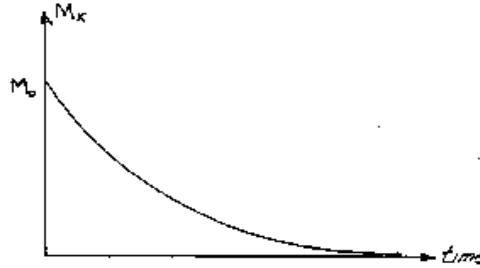


Figure III.6

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:

$$\Omega t_w = \frac{\pi}{2} \text{ radians, or } t_w = \frac{\pi}{2\Omega}$$

But, $\Omega = \gamma B_1$, since B_1 is the only field in the rotating frame on resonance, so the duration of the 90° pulse is

$$t_w = \frac{\pi}{2\gamma B_1} \quad (\text{III.22})$$

The differential equations which describe the decay in the rotating coordinate system are:

$$\frac{dM_{x^*}}{dt} = -\frac{M_{x^*}}{T_2} \quad \text{and} \quad \frac{dM_{y^*}}{dt} = -\frac{M_{y^*}}{T_2} \quad (\text{III.23})$$

whose solutions are of the form

$$M_{(x,y)^*} = -M_0 e^{-t/T_2} \quad (\text{III.24})$$

There is a new timescale here, called T_2 , or the "Spin-Spin Relaxation Time". A simple way to understand this relaxation process from the classical perspective, is to recall that each proton is itself a magnet and produces a magnetic field at its neighbors. Therefore, for a given distribution of these protons there must also be a distribution of local fields at the various proton sites. Thus, the protons precess about $B_0 \hat{z}^*$ with a narrow *distribution* of frequencies, not a single frequency ω_0 . Even if all the protons 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.

Remember that T_1 was the characteristic time it takes the spins to align to the constant external field, while T_2 is the characteristic time over which the spins lose phase coherence with respect to each other. They are not the same times, though at a fundamental level they are related.

The need for pulse sequences:

From this analysis it would appear that the spin-spin relaxation time T_2 can simply be determined by 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 magnet's field were perfectly uniform over the entire sample volume, then the time constant associated with the free induction decay would be T_2 . But in most cases it is the magnet's nonuniformity that is responsible for the observed decay constant of the FID. The PSI-A's magnet, at its "sweet spot," has sufficient uniformity to produce at least a 0.3 millisecond delay time. Thus, for a sample whose $T_2 < 0.3\text{ms}$ the free induction decay constant is also the T_2 of the sample. But what if T_2 is actually 0.4msec or longer? The observed decay will still be about 0.3 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 way to measure the real T_2 was to improve the magnets homogeneity and 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 t later, a 180° pulse. What happens? Figure III.7 shows pulse sequence and the progression of the magnetization in the *rotating* frame.

Study these diagrams carefully. The 180° pulse allows the x - y magnetization to rephase to the value it would have had with a perfect magnet. This is analogous to an egalitarian foot race for the kindergarten class; the race that makes everyone in the class a winner. Suppose you made the following rules. Each kid would run in a straight line as fast as he or she could and when the teacher blows the whistle, every child would turn around and run back to the finish line, again as fast as he or she can run. The faster runners go farther, but must return a greater distance and the slower ones go less distance, but all reach the finish line at the same time. The 180° pulse is like that whistle. The spins in the larger field get out of phase by $+\Delta\theta$ in a time τ . After the 180° pulse, they continue to precess faster than M but at 2τ they return to the in-phase condition. The slower precessing spins do just the opposite, but again rephase after a time 2τ .

Yet some loss of M_{xy} 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. A series of 90° - τ - 180° pulse experiments, varying τ , and plotting the echo height as a function of time between the FID and the echo, will give us the "real" T_2 . The transverse magnetization as measured by the maximum echo height is written as:

$$M_{(x,y)*}(t = 2\tau) = -M_o e^{-\frac{2\tau}{T_2}} \quad (\text{III.25})$$

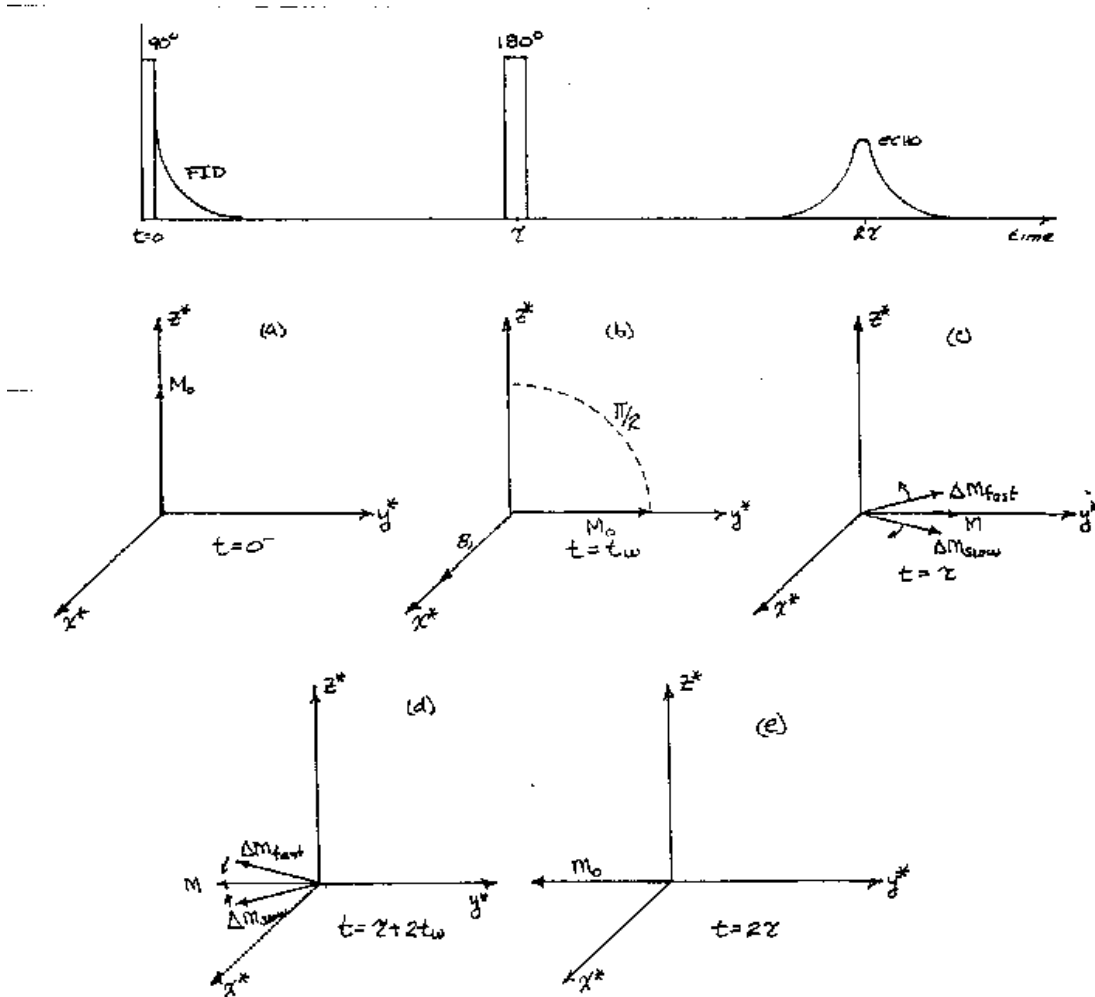


Figure III.7

Figure III.7: Top panel: Representation of rf pulses and the spin echo after time 2τ
 a) Thermal equilibrium magnetization 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 of the *rotating* frame is decreasing because some spins ΔM_{fast} are in a higher field, and some ΔM_{slow} in a lower field static field. d) spins are rotated 180° (flip the entire x - y plane like a pancake on the griddle) by the pulsed rf magnetic field. e) The rephasing the three magnetization "bundles" to form an echo at $t = 2\tau$.

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

$$\omega_o = \gamma B_o \quad \text{where} \quad \gamma_{\text{proton}} = 2.675 \times 10^4 \text{ rad/sec/Gauss}$$

or

$$f_o \text{ (MHz)} = 4.258 B_o \text{ (kG)}.$$

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 obeys the differential equation

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B} \quad \text{(III.17)}$$

where B may be a time dependent field.

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

$$\vec{B}(t) = B_1 \cos \omega t \hat{x} + B_1 \sin \omega t \hat{y} + B_o \hat{z} \quad \text{(III.18)}$$

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:

$$\vec{B}_{\text{eff}}(t) = B_1 \hat{x}^* + \left(B_o - \frac{\omega}{\gamma} \right) \hat{z}^* \quad \text{(III.19)}$$

7. On resonance $\omega = \gamma B_o = \omega_o$ and $\vec{B}_{\text{eff}}(t) = B_1 \hat{x}^*$ In this rotating frame, during the pulse, the spins precess around the x axis.

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

9. 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 .

IV. EXPERIMENTAL EQUIPMENT

This section of the write-up for this experiment gives the essential features of the equipment. More detailed information can be found in Appendix A.

Figure IV.1 shows a sketch of the sample probe. The transmitter coil is wound in a Helmholtz coil configuration so that the axis is perpendicular to the constant magnetic field. The receiver pickup coil is wound in a solenoid configuration tightly around the sample vial. The coil's axis is also perpendicular to the magnetic field. The precessing magnetization induces an EMF in this coil which is subsequently amplified by the circuitry in the receiver. Both coaxial cables for the transmitter and receiver coils are permanently mounted in the sample probe and should not be removed. Caution should be exercised if the sample probe is opened since the wires inside are delicate and easily damaged. Care should be exercised that no foreign objects, especially magnetic objects are dropped inside the sample probe. They can seriously degrade or damage the performance of the spectrometer.

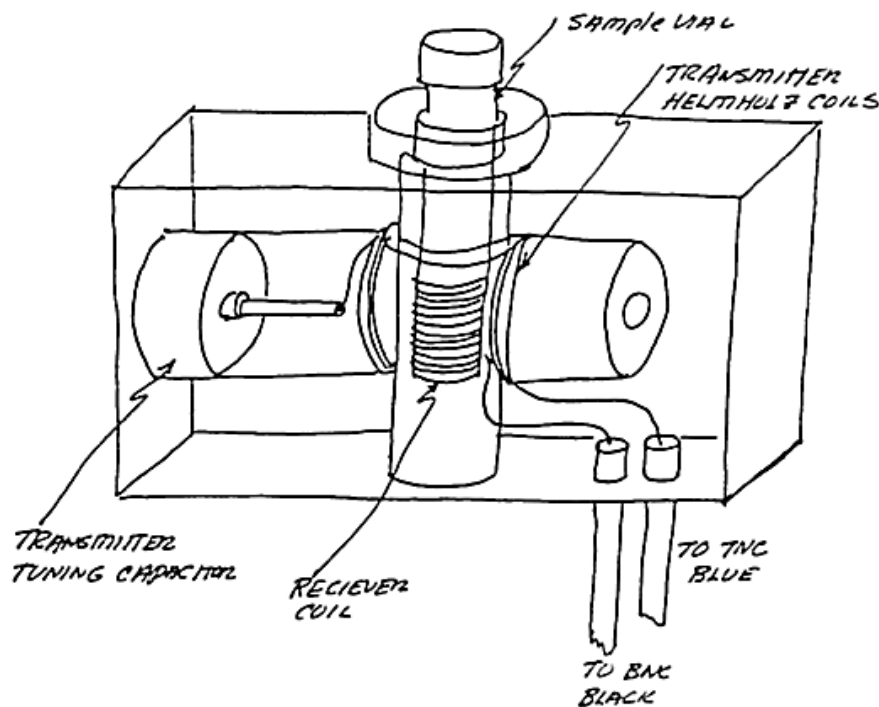


Figure IV.1

To remind yourself how induction of a precessing magnetic dipole can produce a signal in the pick-up coil, play with the separate demonstration setup that should be in the room with you.

The magnetic field strength has been measured at the factory. The value of the field at the center of the gap is recorded on the serial tag located on the back side of the yoke. Each magnet comes equipped with a carriage mechanism for manipulating the sample probe in the transverse (x - y) plane. The location of the probe in the horizontal direction is indicated on the scale located on the front of the yoke and the vertical position is determined by the dial indicator on the carriage. The vertical motion mechanism is designed so that one

rotation of the dial moves the probe 0.2 centimeters. The probe is at the geometric center of the field when the dial indicator reads 10.0.

Vertical Position 0.2 centimeters / turn
Field Center - Dial at 10.0 Turns

Do not move the carriage initially. Chances are it is already set at its "sweet spot" where the magnetic field is most uniform. (Presently: 8.5mm horizontal, 14.15 mm vertical.) It is important not to force the sample probe past its limits of travel. This can damage the carriage mechanism. The carriage should work smoothly, do not force it.

The clear plastic cover should be kept closed except when changing samples. Small magnetic parts, like paper clips, pins, small screws or other hardware, keys, etc. will degrade the field homogeneity of the magnet should they get inside. It is also possible that the impact of such foreign object could damage the magnet. Do not drop the magnet. The permanent magnets are brittle and can easily be permanently damaged. Do not hold magnetic materials near the gap. They will experience large forces that could draw your hand into the gap and cause you injury. Do not bring computer disks near the magnet. The fringe magnetic field is likely to destroy their usefulness.

All permanent magnets are temperature dependent. These magnets are no exceptions. The approximate temperature coefficient for these magnets is:

| |
|---|
| $\Delta B = 4 \text{ Gauss} / ^\circ\text{C} \quad \text{or} \quad 17 \text{ kHz} / ^\circ\text{C} \text{ for protons}$ |
|---|

It is therefore important that the magnets be kept at a constant temperature. It is usually sufficient to place them on a laboratory bench away from drafts, and away from strong incandescent lights. Although the magnetic field will drift slowly during a series of experiments, it is easy to tune the spectrometer to the resonant frequency and acquire excellent data before this magnetic field drift disturbs the measurement. It is helpful to pick a good location for the magnet in the laboratory where the temperature is reasonable constant.

Figure IV.2 is a simplified block diagram of the apparatus. The diagram does not show all the functions of each module, but it does represent the most important functions of each modular component of the spectrometer.

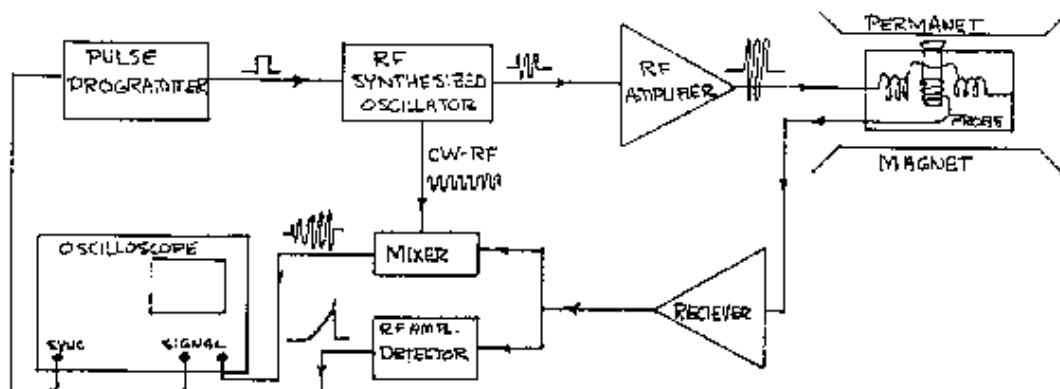


Figure IV.2

The Pulse Programmer creates the pulse stream that gates the synthesized oscillator into radio frequency pulse bursts, as well as triggering the oscilloscope on the appropriate pulse. The rf pulse bursts are amplified and sent to the transmitter coils in the sample probe. The rf current bursts in these coil produce a homogeneous 12 Gauss rotating magnetic field at the sample. These are the time dependent B_1 fields that produce the precession of the magnetization, referred to as the 90° or 180° pulses. The transmitter coils are wound in a Helmholtz configuration to optimize rf magnetic field homogeneity.

Nuclear magnetization precession in the direction transverse to the applied constant magnetic field (the so called x - y plane) induces an EMF in the receiver coil, which is then amplified by the receiver circuitry. This amplified radio frequency (15 MHz) signal can be detected (demodulated) by two separate and different detectors. The rf Amplitude Detector rectified the signal and has an output proportioned to the peak amplitude of the rf precessional signal. *This is the detector that you will use to record both the free induction decays and the spin echoes signals.*

The second detector is a Mixer, which effectively multiplies the precession signal from the sample magnetization with the master oscillator. Its output frequency is proportional to the difference between the two frequencies. This Mixer is essential for determining the proper frequency of the oscillator. The magnet and the nuclear magnetic moment of the protons uniquely determine the precessional frequency of the nuclear magnetization. The oscillator is tuned to this precession frequency when a zero-beat output signal of the mixers obtained. A dual channel scope allows simultaneous observations of the signals from both detectors. As stated above, the field of the permanent magnet is temperature dependent so periodic adjustments in the frequency are necessary to keep the spectrometer on resonance.

You have a modern digital (sampling) oscilloscope for your measurements. A digital oscilloscope can fool you because it samples its input signals at a fixed high frequency, which, if the signal you are measuring has similar frequency components, can lead to

spurious displays. Fortunately, with the modern scopes we have on hand this is seldom a problem. Trigger the digital scope using its external (EXT) input from the synchronization (SYCH) output of the controller. For most of the data taking, put the mixer output (beat signal) into channel 2 of the scope. Put the rectified detector output into channel 1.

V. EXPERIMENTAL PROCEDURE

V.1 Learning to use the equipment:

You might be tempted now to put a sample in the probe and try to find a free induction decay or even a spin echo signal right away. Some of you will probably do this, but we recommend a more systematic study of the instrument. In this way you will quickly acquire a clear understanding of the function of each part and develop the facility to manipulate the instrument efficiently to carry out experiments you want to perform. Consult Appendix A, as needed for details about the knobs and switches of the electronics.

A. Pulse Programmer

A.1. Single Pulse

Begin with the pulse programmer and the oscilloscope. The A and B pulses that are used in a typical pulsed experiment have pulse widths ranging from 1 to 35 μ s. Begin by observing a single A pulse like that shown in Figure V.1. The pulse programmer settings are:

A-width: half way
 Mode: Int
 Repetition time: 10 ms 10%
 Sync: A
 A: On
 B: Off
 Sync Out: Connected to ext. sync input to oscilloscope
 A & B Out: Connected to channel 1 vertical input of oscilloscope

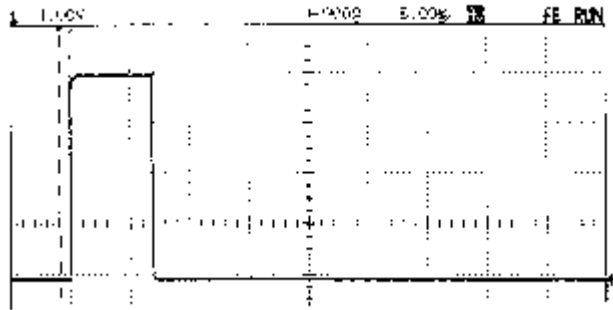


Figure V.1

Your oscilloscope should be set up for external sync pulse trigger on a positive slope; sweep time of 2, 5, or 10 $\mu\text{s}/\text{cm}$, and an input vertical gain of 1 V/cm. Turn the A-width and observe the change in the pulse width. Switch the mode to Man, and observe the pulse when you press the main start button. Set the oscilloscope time to 1.0 ms/cm and the repetition time to 10 ms and change the variable repetition time from 10% to 100%. What do you observe?

A.2. The Pulse Sequence

At least a two pulse sequence is needed to observe either a spin echo or to measure the spin lattice relaxation time T_1 . So let's look at a two pulse sequence on the oscilloscope.

Settings:

A, B Width: Arbitrary
 Delay Time: 0.10×10^0 (100 μs)
 Mode: Int
 Repetition time: 100 ms variable 10%
 B Pulses: 01
 Sync: A
 A, B: On
 Sync Out: To ext. sync input on scope
 A & B out: Vertical input on scope

The pulse train should appear like Figure V.2, lower trace, if the time base on the oscilloscope is 20 $\mu\text{s}/\text{cm}$ and the vertical gain is 1 V / cm. Now you should play. Change the A and B width, change delay time, change sync to B (you will now see only the B pulse since the sync pulse is coincident with B), turn A off, B off, change repetition time, and observe what happens. Look at a two pulse train with delay times from 1 to 100 ms (1.00×10^0 to 1.00×10^2).

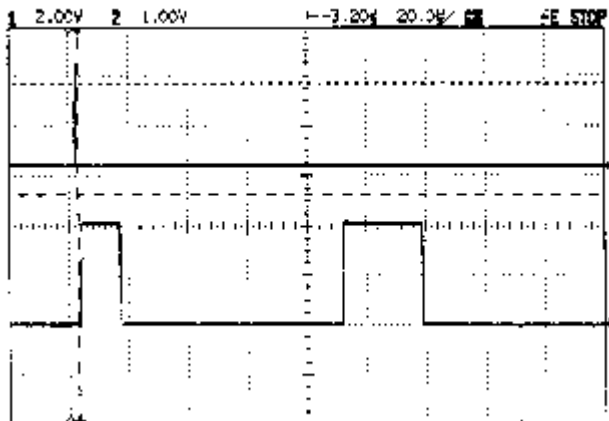


Figure V.2

A.3. Multiple Pulse Sequence

(You can postpone doing this section until later, if you wish.)

The Carr-Purcell and Meiboom-Gill pulse trains require multiple B pulses. In some cases you may use 20 or more B pulses. To see the pattern of this pulse sequence, we will start with a 3 pulse sequence.

A-width: 20%
B-width: 40%
Delay time: 0.10×10^0 (100 μ s)
Mode: Int
Repetition Time: 100 ms variable 10%
B pulses: 02
Sync A
A, B: On
Oscilloscope Sweep 0.1 ms / cm
A & B out: Vertical input on scope

Change the number of B pulses from 3 - 10. Note the width of B and the spacing between pulses. Change the mode switch to man and press the manual start button. Change the delay time to 2.00×10^0 ms and the oscilloscope to 2 ms / cm horizontal sweep. Notice that on this time scale the pulses appear as spikes, and it is difficult to observe any change in the pulse width when the B width is changed over its entire range.

B. Receiver

The receiver is designed to amplify the tiny voltages induced in the receiver coil by the magnetization precessing in the transverse (x - y) plane. The receiver coil is part of a parallel tuned resonant circuit with the tuning capacitor mounted inside the receiver module. It is important to tune this coil to the resonant frequency (the precession frequency) of the spin system in order to achieve optimum signal to noise and maximum gain. In preparation for a magnetic resonance experiment, the receiver should be tuned to the proton's resonance frequency in your magnet. Note: The strength of the magnetic field is registered on the blue serial label on the back side of the magnet yoke.

C. Spectrometer

Connect the spectrometer modules together using the BNC cables as shown in Fig. V.3. Please note the special TNC connector (rf out) which connects the power amplifier to the transmitter coils inside the sample probe. Connecting the blanking pulse is optional. There may be experiments that you attempt later where the sample has a very short T_2 and the blanking pulse will be helpful. It is not necessary to use it now. You cannot damage the electronics by making the wrong connections but you can certainly cause yourself grief. Most likely you will not see the signal. Check your connections carefully. Also check them against the block diagram, Figure IV.2.

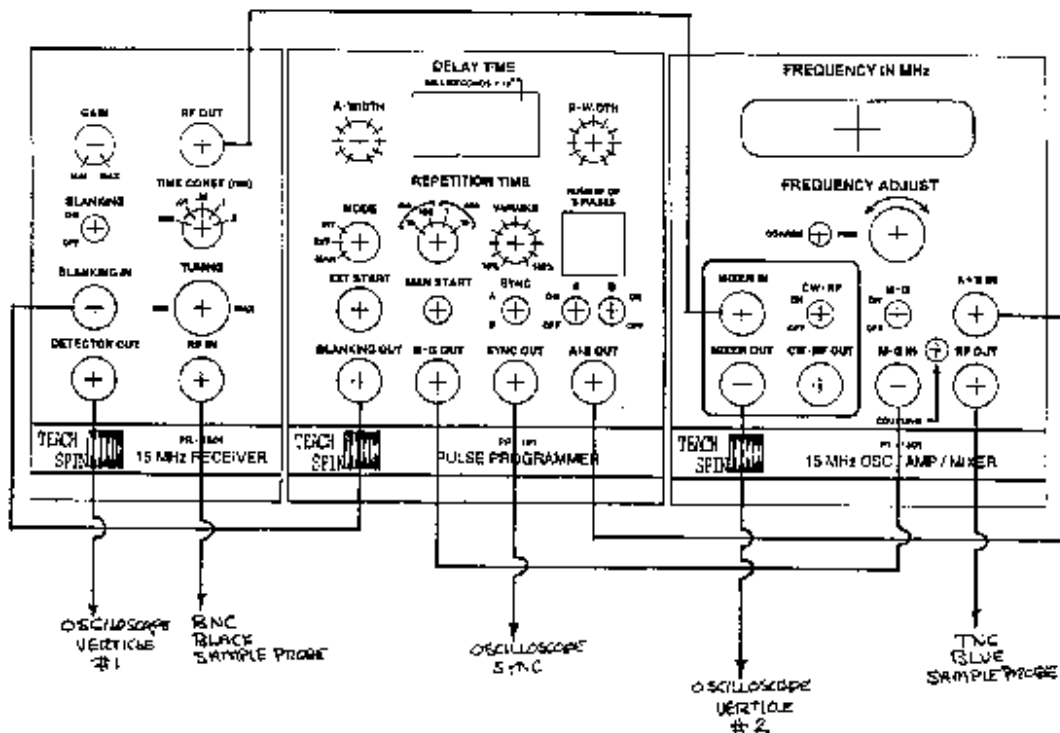


Figure V.3

D. The Sample Holder

Do not overfill the vial with sample material. The standard samples which are approximately cubical (about 5 mm in height) are the appropriate size. This size sample fills the receiver coil and the pulsed magnetic field is uniform over this volume. Larger samples will not experience uniform rf magnetic fields. In that case all the spins are not rotated the same amount during the pulse. Overfilled samples can cause serious errors in the measurements of T_1 and T_2 . It is important to adjust the sample to the proper depth inside the probe. A rubber o-ring, placed on the sample vial, acts as an adjustable stop and allows the experimenter to place the sample in the center of the rf field and receiver coil, see Figure V.4. A standard, pre-made sample should be available. The o-ring should be 38 mm from the bottom of the sample tube. The first sample to use with the spectrometer is glycerin. Note that glycerin is hygroscopic, and the presence of water in the glycerin will have drastic effects on the values obtained. Glycerin has a spin-lattice relaxation time (T_1) of 20 msec or less, and a roughly equal spin-spin (T_2) relaxation time. If you have difficulty getting good results, one issue may be that the same is contaminated with too much water.

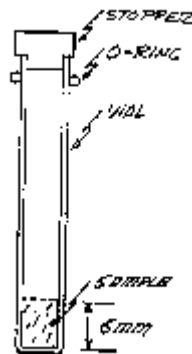


Figure V.4

V.2 Getting a FID signal and tuning the receiver circuitry

A "90° pulse", as it is called, produces the maximum amplitude of the free induction decay, since it rotates all of M_z into the x - y plane. But this is only true if the spectrometer is on resonance, so that the effective field in the rotating frame is B_1 along the (rotating) x axis. To assure yourself you are tuned to resonance, the free induction signal must produce a zero beat with the master oscillator as observed on the output of the mixer. If the zero beat condition is obtained, then the shortest A-width pulse that produces the maximum amplitude of the free induction decay is a 90° pulse. The setup is:

Sample: Glycerin
 A-width: ~20%
 Mode: Int
 Repetition time: 100 ms, 100%
 Number of B Pulses: 0
 Sync A
 A: on
 B: off
 Tune frequency adjust for zero-beat mixer output
 Tune receiver input for maximum signal
 Time constant: .01
 Gain: 30%

The apparatus will turn on with the oscillator frequency at 15.2 MHz. Depending on temperature (since the magnetic field of the permanent magnet is slightly temperature dependent), the proton resonance will occur at about 15.3 MHz. Use only the A pulse (B pulse switch "off" in Pulse Programmer unit), and adjust the A-width at or near minimum (ccw rotation). Adjust gain knob to 10 o'clock and assume for the time being that the tuning knob is correctly adjusted. Turn off the M-G control on the transmitter unit. The scope should be set for a sensitivity of 1.0 volts/division, and the sweep rate at 1 ms/division. It should be triggered by the sync pulse, and the pulse repetition frequency should be about 10/second. The y1-input of the scope should be connected to the Mixer Out BNC connector of the OSC/AMP/Mixer unit. You should see on the scope a signal that in fact is at about 100 kHz, with an envelope that decays in about 2 ms or less, depending on the field gradient at position of the sample in the magnet. The envelope of the signal is a proton free induction decay (FID) that is quite far off resonance. The mixer

signal shows the beat frequency formed when signal created by the precession of the protons in the permanent magnet's field is multiplied by the signal from the continuous wave (cw) oscillator from which the pulses are derived. Adjust the frequency of the transmitter (using the "coarse" position of the switch on the osc/amp/mixer unit) upward towards 15.3 MHz until the beat frequency goes to zero. Use the "fine" switch for final adjustments of the rf frequency. Change the gain of the receiver at this point until the peak value of the FID is about 3 or 4 volts.

You should examine also the FID from the detector signal in the receiver unit, and note that it is a little larger, always positive, and that it is relatively unaltered by slight mis-tunings of the oscillator frequency. It should not ever be larger than about 9 volts. Adjust the width of the A pulse to maximize the signal from the detector. Now tune the narrow bandpass filter on the receiver: Change the frequency of the bandpass using the tuning knob on the receiver unit. Turn it to maximize the detector signal. Then, looking at the mixer output and changing the frequency control on the transmitter, again minimize the beat frequency. (Concentrate on removing all wiggles on the trace for times beyond the FID.) Go back to the step where you maximized the detector signal by varying the A width and repeat the process. When all this is done, on resonance as determined by the zero beat condition of the FID as seen with the mixer output, then you have achieved a 90° or $\pi/2$ pulse.

Note that if the rf pulse repetition rate is too high the spins will not have all 'relaxed' back to their initial state precessing around the z axis. This results in your signal size "saturating" or being reduced. Test for this by watching the amplitude of response while varying the rep rate.

V.3 Measuring T_2^ for glycerin*

The first pulsed magnetic resonance experiment to attempt requires only a single rf pulse. The signal you are looking for is called by two different but equivalent names, the free precession or free induction decay (FID). The later name is more commonly used. The signal is due to a net magnetization precessing about the applied constant magnetic field B_0 in the transverse plane (x - y) Remember, in thermal equilibrium there is no transverse magnetization, since all the nuclear spins are precessing out of phase with each other. The transverse magnetization is clearly not in thermal equilibrium. So we have to create it. We begin by waiting long enough for the thermal equilibrium magnetization to become established in the z -direction. Now we apply a high power rf pulsed magnetic field B_1 to the sample for a time $t_w(90^\circ)$ sufficient to cause a precession of this magnetization 90° in the rotating frame. After the transmitter pulse has been turned off, the thermal equilibrium magnetization is left in the x - y plane where it precesses about the static magnetic field B_0 . The precession signal then decays to zero in a time determined either by imperfections in the magnet (called T_2^*) or by the real spin-spin relaxation time T_2 , whichever is shorter. Fig. A.3 (in Appendix A) shows the free precession decay of mineral oil after the 90° pulse.

For the first measurement of T_2 you want to choose a sample that not only has a large concentration of protons, but also a reasonably short spin-lattice relaxation time, T_1 . All PNMR experiments begin by assuming a thermal equilibrium magnetization along the z -

direction. But this magnetization builds exponentially with a time constant, T_1 . Each Measurement, that is, each pulse sequence, must wait at least $3 T_1$ (preferably $6-10 T_1$'s) before repeating the pulse train. For a single pulse experiment that means a repetition time of $6-10 T_1$. If you chose pure water as a sample, with $T_1 \approx 3$ sec, you would have to wait a half a minute between each pulse. Since several adjustments are required to tune this spectrometer, pure water samples would be very time consuming and difficult to work with. The effect of not fully recovering the z magnetization between pulse trains is called *saturation*.

Glycerin has a T_1 of roughly 20 ms at room temperature. That means the repetition time can be set 100 ms and the magnetization will be in thermal equilibrium at the start of each pulse sequence (or single pulse in this first experiment).

The actual shape of the T_2^* signal is neither exponential nor hyperbolic, but a “sinc” function. Later, you may be interested to consult a separate handout to learn about this shape. For now we will simply characterize the shape by its width:

Estimate T_2^* for glycerin by finding and recording the full-width at half maximum (FWHM) of the FID signal.

V.4 Quick First Estimate of the Spin-Lattice Relaxation Time, T_1 , for glycerin.

The time constant that characterizes the exponential growth of the magnetization towards thermal equilibrium in a static magnetic field, T_1 , is one of the most important parameters to measure and understand in magnetic resonance. With the PS1-A, this constant can be measured directly and very accurately. It also can be quickly estimated. Let's start with an order of magnitude estimate of the time constant using the standard glycerin sample.

1. Adjust the spectrometer to resonance for a single pulse free induction decay signal.
2. Change the Repetition Time, reducing the FID until the maximum amplitude of the FID is reduced to about $1/3$ of its largest value.

The order of magnitude of T_1 , is the repetition time that was established in step 2. Setting the repetition time equal to the spin lattice relaxation time does not allow the magnetization to return to its thermal equilibrium value before the next 90° pulse. Thus, the maximum amplitude of the free induction decay signal is reduced to about $1/e$ of its largest value. Such a quick measurement is useful, since it gives you a good idea of the time constant you are trying to measure and allow you to set up the experiment correctly the first time.

V.5 Two-Pulse Zero-Crossing Method for T_1

A two pulse sequence can be used to obtain a two significant figure determination of T_1 . The pulse sequence is:

180° pulse -- τ (variable) -- 90° pulse -- free induction decay

The first pulse (180°) inverts the thermal equilibrium magnetization, that is; M_z goes to $-M_z$. Then the spectrometer waits a time τ before a second pulse rotates the magnetization that exists at this later instant by 90°. τ is the delay time set on the Pulse Programmer. How can this pulse sequence be used to measure T_1 ?

After the first pulse inverts the thermal equilibrium magnetization, the net magnetization is $-M_z$. This is not a thermal equilibrium situation. In time the magnetization will return to $+M_z$. Figure V.5 shows a pictorial representation of the process. The magnetization grows exponentially towards its thermal equilibrium value.

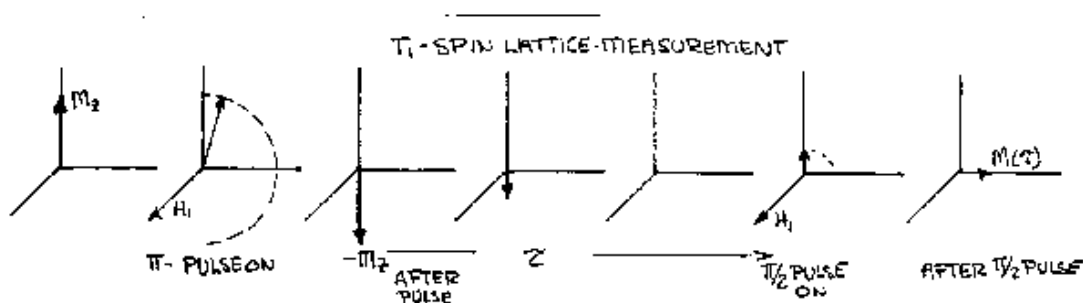


Figure V.5

But the spectrometer *cannot detect* magnetization along the z-axis. It only measures precessing net magnetization in the x-y plane. That's where the second pulse plays its part. This pulse rotates any net magnetization in the z-direction into the x-y plane where the magnetization can produce a measurable signal. In fact, the initial amplitude of the free induction decay following the 90° pulse is proportional to the net magnetization along the z-axis ($M_z(\tau)$), *just before the pulse*. You should be able to work out the algebraic expression for T_1 , in terms of the particular time τ_0 , where the magnetization $M_z(\tau_0) = 0$, the so-called zero crossing point. They are related by a simple constant.

V.6 A Better Two-Pulse Method for T_1

A more accurate method to determine T_1 , uses the same pulse sequence as we just described, but plots $M(\tau)$ as a function of τ . Since it is an exponential process, the plot is logarithmic. But be careful! There are some subtleties to watch out for. Hint: It is essential to measure $M_z(\infty)$, that is the thermal equilibrium magnetization along the z-direction, very accurately. Why? You may use the MPL fitting software (mpl_DATAFIT) on the local computers to fit your data.

A 180° pulse is characterized by a pulse approximately twice the length of the 90° pulse, which has no signal (free induction decay) following it. A true 180° pulse should leave no magnetization in the x-y plane after the pulse. Use this fact to carefully adjust the B width for the $\pi - \pi/2$ sequence. Also note: If $M_z(t)$ does not change with τ , you are not on resonance.

V.7 Spin-Spin Relaxation Time - T_2 for glycerin

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 PS1-A's 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 $T_2 < 0.3$ ms, the free induction decay time constant is a good estimate of the real T_2 .

V.8. Two-Pulse Spin Echo Method

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. 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° pulse -- τ (variable) -- 180° pulse -- τ --echo at 2τ

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.

Make sure that the M-G switch is off. Reset the A pulse width so that the FID is a maximum. Now set up the pulse sequencer unit for a single B pulse, and the B pulse delay to 5 ms. Set the length of the B-pulse to minimum by turning the knob all the way counter-clockwise, the scope sweep rate to 2 ms/division. Turn on the B-pulse switch, and slowly turn up the length of the B pulse until, simultaneously, the echo at 10 ms is maximized and the FID following the B pulse goes to zero. Understand why the echo is now a positive signal when viewed at the mixer output. Note all signals are always positive at the rectifier detector output. The latter just rectifies and filters the rf signal from the receiver coil. By contrast, the phase sensitive detector mixes that rf signal in a nonlinear device (the "mixer") with a rf signal at the oscillator frequency (which is the same as the signal frequency if one is on resonance), and then rectifies the low frequency component of the mixer output, keeping the component near dc. Iterate back and forth between the A width and B width until the echo amplitude is a maximum. You now have a pulse sequence as specified above.

The transverse magnetization following a $\pi/2$ pulse decays exponentially with the transverse, or spin-spin relaxation time T_2 . The echo following the pulse sequence is expected to decay according to the law

$$V(t = 2\tau) = V_0 e^{-\frac{t}{T_2}} \quad (\text{V.1})$$

where τ is the time between the $\pi/2$ and the π pulse, as set on the Pulse Programmer. A simple way to measure T_2 is to take data at a variety of times τ and plot $\ln(V(t))$ vs t , where $t=2\tau$, so the slope of the resulting straight line will be $(-1/T_2)$. Alternatively, fit the

exponential curve directly with a non-linear least-squares fitting algorithm. Make a good T_2 measurement for glycerin using the two-pulse echo method. Measure the height of the spin echo for enough values of τ using the two-pulse echo method and extract a value (using a fit) for T_2 .

There are several issues, some inherent in the apparatus, some inherent in the physics, that can result in the data not lying on a straight line. These can be classified as:

1. 'Nonlinearities' in the detector response.
2. Errors caused by improper use of the digital scope.
3. The actual decay may not be exponential under the conditions of the two pulse experiment, for some samples.

They are discussed here:

1. The echo amplitude is to be measured by using the output of the rectifying detector, not the phase sensitive detector, because the latter can be subject to small but easily observed fluctuations and the relative phase of the reference and the signal are not under experimental control. However, the signal detection rectifier response is nonlinear at low signal levels due to 'noise'. This can be easily seen by examining an echo amplitude that decays exponentially with τ at high signal levels, but non-exponentially at low signal levels. One can go from one regime to the other just by changing the gain of the receiver amplifier. For our purposes, *no signal less than about 0.4 volts should be used for amplitude measurements* unless you include corrections for the detector nonlinearity. How to identify and compensate for this effect is an exercise left to the student. Discuss it with the instructor.

2. In earlier times, the limited sampling rate of digital oscilloscopes could cause a particular illusion in what is seen called "aliasing". Beats in the FID signal at the scope sampling frequency will show up on the digital scope as a "flat" trace. If the spin echoes are too narrow, *i.e.*, too brief in time, then display of a chain of them on the digital scope will result in large fluctuations in the apparent amplitude of each of them. That is because each screen of the scope samples the input waveform only finite number of times. If the echo is too sharp for the sampling rate used it has information in a frequency range exceeding half the sampling rate. Fortunately, with present-day scopes this problem rarely shows up.

3. Physical diffusion of the spins in the sample: real physics. A spin randomly diffuses from one region to another in the sample. Since those regions have different static magnetic fields because of field inhomogeneity, the random movement will cause loss of phase memory of the spins. That phase memory loss occurs at a more rapid rate than simple exponential decay:

$$V(t = 2\tau) = V_0 e^{-\alpha t^3} e^{-\frac{t}{T_2}} \quad (\text{V.2})$$

where

$$\alpha = V_0 D\gamma (dB/dz)^2 / 12 \quad (\text{V.3})$$

In this equation, D is a diffusion constant for the material, and dB/dz is the local gradient of the external field. Because of the t^3 factor, this diffusion multiplicative factor is negligible for sufficiently short times and for very small diffusion constants D or small field gradients. When α is not negligible, the decay of the echo amplitude can begin exponentially, and then die away faster than exponentially as time between FID and echo gets longer. As you can see, the possibility of confusion with detector 'nonlinearity' exists in identifying the existence of diffusion. However, detector effects are sample independent and can be compensated for separately with samples for which T_2 is sufficiently short so that diffusion does not have time to occur. After correcting for any detector effects, do you see any evidence of diffusion in the T_2 measurement of glycerin?

V.9 Multiple Pulse Spin Echo Sequences for T_2 .

A. 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 (C-P) 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° pulse -- τ -- 180° pulse -- 2τ -- 180° pulse -- 2τ -- 180° pulse -- etc.

creating a series of echoes equally spaced between the 180° pulses. τ is the delay time set on the Pulse Programmer. The exponential decay of the maximum height of the echo envelope can be used to calculate the spin-spin relaxation time. The spacing between the 180° pulses τ 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 .

When the echo forms, the remaining magnetization (attenuated by $e^{-2\tau/T_2}$) is, except for a 180° phase shift in the rotating frame, in the same condition as after the $\pi/2$ pulse. Consequently one would expect another π pulse at τ after the first echo to form an echo at a time τ later, or 2τ after the first echo. The process can be repeated until no magnetization is left to recollect, resulting in a string of echoes 2τ apart, decaying exponentially with time. This observation was made by C-P in the early 1950's, after the effects of diffusion were identified by Torrey. The power of their observation is that diffusion occurs *independently* between each pair of echoes in the C-P technique, so that the exponent of Equation V.2 contains, instead of t^3 , the quantity $(2\tau)^3$, so the signal is

$$V(t = n(2\tau)) = V_0 e^{-\alpha(2\tau)^3} e^{-\frac{t}{T_2}} \quad (\text{V.4})$$

where t is the time of the n^{th} echo since the $\pi/2$ pulse. To appreciate the power of the C-P pulse sequence in overcoming the loss of phase memory from diffusion, compare the size of the signal $V(t=T_2)$ for a 2 pulse sequence using Equation V.2 and the signal when

there are 10 echoes in time T_2 , using the C-P technique. (The factor should be about 10^{-3} in the exponent.) You could now try to improve your value for T_2 using the C-P pulse sequence, but read on...

B. 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 183° pulses, by the time the 20th pulse was turned on, the spectrometer would have accumulated a rotational error of 60° , a sizable error. This error can be shown to effect 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 $\pi/2$ and the π pulses, which cancels the error to first order. The M-G pulse train gives more accurate measurements of T_2 . All your final data on T_2 should be made with the Meiboom-Gill pulse on. The only reason it is not permanently built into the instrument is to show you the difference in the echo train with and without this special phase shift.

The operation of the M-G pulse sequence is quite complex. If the student wishes, read the next paragraph and an extra handout available. At this point, you may choose to skip the explanation.

One obvious way to defeat the accumulated error is to reverse its sign at every pulse by applying the π pulses along the +x and -x axes in the rotating frame alternately. The M-G solution is more elegant. They introduced a 90° phase shift between the $\pi/2$ pulse and the chain of π pulses. Thus if the original rf field for the $\pi/2$ pulse were along the y-axis in the rotating frame, the subsequent π pulses would be along the x-axis. In the Teach-Spin apparatus the signal from the phase sensitive detector shows the difference readily because the phase of the reference rf is not altered; only the phase of the A pulse is altered relative to the B pulse. To see the result, examine a single echo output from the phase sensitive detector with the M-G switch on, and the apparatus tuned exactly to resonance. Then flip the M-G switch to off, and note that the echo, instead of being roughly bell shaped, is essentially flat, or, if not, looks more like the derivative of the M-G echo, with the magnitude being zero exactly where the M-G echo was maximum. Then turn on a second B pulse, and note that the shape of the second C-P echo is the same as the first, showing that the phase of the second B pulse was the same as the first. The shape of the echoes is a consequence of the reference rf being in quadrature with the signal rf. For more discussion of the M-G pulse sequence ask the instructor for the handout on the topic.

One of the difficulties of the M-G technique is adjusting the B pulse to exactly π . However, one trick can be used that is a considerable help. Since the error in the height of the C-P echoes increases as both as the number of pulses and as the length of the B pulse, switch to the C-P sequence and adjust the length of the B pulse to maximize the height of the echoes at the end of the sequence. Then keep that pulse length for the M-G sequence measurements.

Now measure T_2 for glycerin using M-G pulse sequence. Compare this result with your previous result using the two-pulse method. Try to separate the effect of diffusion from the value of T_2 .

V.10 Better Estimate of Diffusion Effects

We can use the various pulse sequences to separate the spin-spin relaxation and diffusion effects on the echo. If the time between the $\pi/2$ and the π pulse in the M-G sequence is τ , the echoes occur at $t_n = n(2\tau)$. From Equation V.2, using the fact that the echoes are equally spaced and the difference between any two is equal to $t_1 = 2\tau$:

$$V(t_n) = V(t_{n-1}) e^{-\alpha t_1^3} e^{-\frac{t_1}{T_2}} \quad (\text{V.5})$$

Recursive application of this relation gives

$$V(t_n = 2n\tau) = V(0) e^{-\alpha n t_1^3} e^{-\frac{n t_1}{T_2}} \quad (\text{V.6})$$

If one uses a *single* pulse to create an echo at a time t_n , then the required delay is $n\tau$, and the echo height after that time is

$$V_S(t_n) = V(0) e^{-\alpha (n t_1)^3} e^{-\frac{n t_1}{T_2}} \quad (\text{V.7})$$

The ratio, R , of Equation (6) to Equation (7) is

$$R(t_n = 2n\tau) = e^{-\alpha (n^3 - n) t_1^3} \quad (\text{V.8})$$

Thus, a plot of $\ln(R)$ vs. $(n^3 - n)$ would have a slope of αt_1^3 . Notice that T_2 has canceled out. You now have a method to measure the effects of diffusion through the field gradient of the magnet, $\alpha = D(\gamma dB/dz)^2/12$. Another test of the B pulse length being incorrect is that the points in the plot of $\ln(R)$ vs. $(n^3 - n)$ will alternate around the best fit line drawn through them, a clear indication that the M-G sequence does indeed correct the error from one pulse on the next pulse. Correct adjustment of the length of the B pulse will minimize that alternation.

Use the two-pulse and the M-G measurements together to determine $D(\gamma dB/dz)^2$ for glycerin at the position in the magnetic field where your sample sits. If you would like, ask for an extra handout which will give you a method to separately estimate dB/dz .

V.11 Examining water

Try this part of the lab only if you have successfully completed the previous parts.

Use the simple method described in Section V.4.2 to get an estimate of T_1 for distilled water. The full measurement would be tough. We can shorten the relaxation times by adding paramagnetic Cu^{++} ions to the water. Why? A CuSO_4 (cupric sulfate) solution has been prepared. For this solution, measure T_1 and then T_2 using the two-pulse and M-G

methods. Get $D(\gamma dB/dz)^2$ for the solution. From this result and the analogous result for glycerin, determine the ratio of the diffusion constants of glycerin and water.

Make T_1 and T_2 measurements for a series of different CuSO_4 solutions at different concentrations. As the ion concentration approaches zero, you are getting closer to pure water. The relaxation rate ($1/T_1$) should be proportional to the ion concentration. Is this true? Can you extrapolate to get T_1 of pure water - a measurement which was too hard for the straightforward approach?

V.12 Other Interesting Behavior

Try this part of the lab only if you have successfully completed the previous parts.

The magnet is not oriented on the table in an arbitrary way. To demonstrate that, set up a single echo and observe it on the scope with the PSD signal. Then reorient the magnet. Two things happen. One is the oscillator frequency necessary for resonance changes. Adjust the oscillator frequency so you are exactly on resonance again. Note the change in frequency - it can be translated into the difference in component of the static field in the laboratory parallel to the magnet field of the permanent magnet at the sample between the two orientations. Calculate the size of that field. [The resonance frequency of protons is 4.259 kHz/Gauss]. Secondly, careful observation will show that the echo is not stationary - it oscillates with time. If it does not do so obviously, adjust the pulse repetition frequency until the echo shape fluctuates slowly. That phenomenon shows there is a periodic component of the laboratory field as well (probably at 60 or 120 Hz). The original orientation of the magnet was chosen so that the oscillating component of the laboratory field is in the plane perpendicular to B_0 . Estimate the size of the oscillating field by seeing what frequency change of the oscillator produces the same shape change that you observe.

V.13 Magnetic Field Contours

Try this part of the lab only if you have successfully completed the previous parts.

After you have found a free induction decay signal and set up the spectrometer for a 90° pulse, it is time to examine the field contour of the magnet and find the place in the gap where the magnetic field has the best uniformity; the "sweet spot". The two controls on the sample carriage allow you to move the sample in the x - y plane. The magnetic field at the sample uniquely determines the frequency of the free-induction decay signal. This frequency can be measured directly by beating it against the master oscillator's frequency using the mixer. Plot the magnetic field as a function of position in the x - y plane.

Caution: The magnetic field in the gap changes with temperature. To create an accurate field plot, it is essential to make these measurements quickly in a well regulated temperature environment.

The field gradients over the sample can be estimated from the decay of the free induction signal. For glycerin, the real T_2 is much longer than the free induction decay time.

V.14 Rotating Coordinate Systems

This part is easy and may help you grasp the way the spin vectors respond to the static and the rotating fields.

What happens to our spin systems when the spectrometer is not tuned to resonance? Can a signal be observed? What is a 90° , a 180° pulse? These questions and more can be answered by a series of easy experiments that give somewhat puzzling results. These experiments can help you understand rotating coordinate systems and PNMR off resonance. They are all single pulse experiments that use mineral oil or some other equivalent sample with $T_1 < 50$ ms.

Tune the spectrometer to resonance using a single 90° pulse and observe the zero beat of the free induction decay. Put both detected signals on the oscilloscope display using both input channels. Now change the frequency of the oscillator, first going to higher frequency (about .7 MHz upfield) and later to lower frequencies. Note the free induction decay signals. Change the frequency until no signal appears (but make sure no signal reappears when the frequency is further changed). It may be necessary to slightly tune the receiver to see the signal. Adjust the pulse width at several frequencies off resonance. What do you observe? Is it possible to create a 360° pulse off resonance? How do you know it is 360° ?

Explain what you observed. Draw diagrams of the effective fields in the rotating frame off resonance. These will help you understand your observations. Although your explanations should be mostly qualitative, it helps to record some numerical data, such as signal amplitude and frequency.

APPENDIX A: ADDITIONAL DETAILS ABOUT THE EQUIPMENT

Pulse Programmer PP-101

The pulse programmer is a complete, self contained, pulse generator which creates the pulse sequences used in all the experiments. The pulses can be varied in width (pulse duration), spacing, number, and repetition time. Pulses are about 4 volt positive pulses with a rise time of about 15 ns. The controls and connectors are described below and pictured in Fig A.1

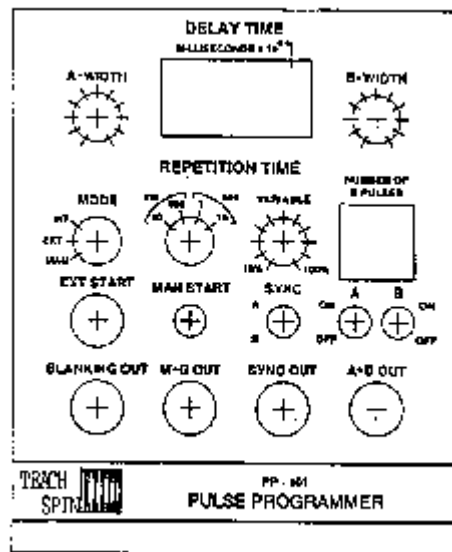


Figure A.1 The Pulse Programmer

A-width: width of A pulse 1-30 μ s continuously variable

B-width: width of B pulse 1-30 μ s continuously variable

Delay time:

1) with number of B pulses set at 1, this is the time delay between the A and B pulses.

2) with number of B pulses set at 2 or greater, this is the time between A and the first B pulse and one half of the time between the first B pulse and the second B pulse.

3) delay range can be varied from: 10 μ s (which appears as 0.01×10^0 ms) to 9.99 s (which appears as 9.99×10^3 ms)

Accuracy: 1 pt in 10^6 on all delay times.

Mode: This switch selects the signal that starts the pulse sequence.

There are three options:

Int (Internal): The pulse stream is repeated with a repetition time selected by the two controls at the right of the mode switch.

Ext (External): The pulse stream is repeated at the rising edge of a TTL pulse.

Man (Manual): The pulse stream is repeated every time the manual start button is pushed. This allows the experimenter to choose arbitrarily long repetition times for the experiment.

Repetition Time: four position 10ms, 100 ms, 1 s, 10 s, variable 10-100% on any of the four position. Thus for 100 ms and 50%, the repetition time is 50 ms. The range of repetition times is 10 ms 10% or 1 ms to 10 s, 100% or 10 s.

Number of B Pulses: This sets the number of B pulses from 0 to 99

Ext-Start: Rising edge of a TTL pulses will start a single pulse stream.

Man-Start: Manual start button which starts pulse stream on manual mode.

Sync Switch: This switch allows the experimenter to choose which pulse, A or B, will be in time coincides with the output sync pulse. In Fig. 5.2, the upper trace shows the sync pulse occurring at the beginning of the A pulse.

A-switch: turns on or off the A pulse output

B-switch: turns on or off the B pulse output

Blanking out: A blanking pulse used to block the receiver during the rf pulse and thus to improve the receiver recovery time. *Leave in during MPL experiments.*

M-G out: Meiboom-Gill phase shift pulse, connected to the oscillator, to provide a 90° phase shift after the A pulse.

Sync out: A fast rising positive 4 volt pulse of 200 ns duration used to trigger an oscilloscope or other data recording instrument. Fig. A.2, top trace shows the sync pulse coincident with the beginning of the B pulse (lower trace).

A & B OUT: 4 volt positive A & B pulses, shown in Fig. V.2.

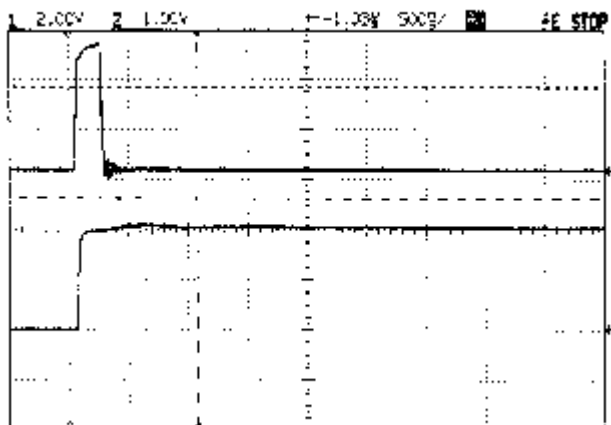


Figure A.2: Sync pulse coincident with B pulse.

15 MHz OSCILLATOR/AMPLIFIER/MIXER:

There are three separate functioning units inside this module. A tunable 15 MHz oscillator, an rf power amplifier, and a mixer. The oscillator is digitally synthesized and locked to a crystal oscillator so that its stability is better. Frequency in MHz is displayed on a seven digit LED readout at the top center of the instrument (See Fig. A.3). This radio frequency signal can be extracted as a continuous signal (CW-RF out, switch on) or as rf pulse burst in to the transmitter coil inside the sample probe.

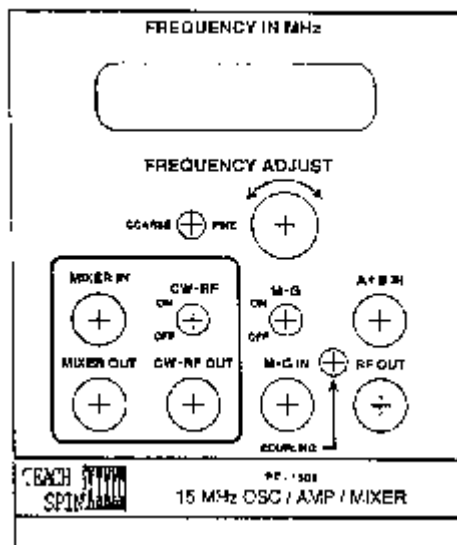


Figure A.3: Oscillator/Amplifier/Mixer

The second unit is the Power Amplifier. It amplifies the pulse bursts to produce 12 Gauss rotating radio frequency magnetic fields incident on the sample. It has a peak power output of about 150 watts.

The third unit is the Mixer. It is a nonlinear device that effectively multiplies the CW rf signal from the oscillator with the rf signals from the precessing nuclear magnetization. The frequency output of the mixer is proportional to the difference frequencies between the two rf signals. If the oscillator is properly tuned to the resonance, the signal output of the mixer should show no "beats", but if the two rf signals have different frequencies a beat structure will be super-imposed on the signal. The beat structure is clearly evident on the upper trace of the signals from a two-pulse free induction spin echo signal, shown in Fig. A.4. The mixer output and the detector output from the receiver module may have identical shape. It is essential, however, to tune the oscillator so as to make these two signals as close as possible and obtain a zero-beat condition. That is the only way you can be sure that the spectrometer is tuned to resonance for the magnetic field imposed.

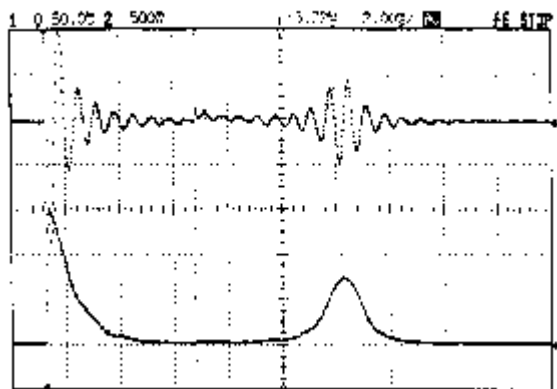


Figure A.4: Mixer output signal off resonance (top).

IMPORTANT: DO NOT OPERATE THE POWER AMPLIFIER WITHOUT ATTACHING TNC CABLE FROM SAMPLE PROBE. DO NOT OPERATE THIS UNIT WITH PULSE DUTY CYCLES LARGER THAN 1%. DUTY CYCLES OVER 1% WILL CAUSE OVERHEATING OF THE OUTPUT POWER TRANSISTORS. SUCH OVERHEATING WILL AUTOMATICALLY SHUT DOWN THE AMPLIFIER AND SET OFF A BUZZER ALARM. IT IS NECESSARY TO TURN OFF THE ENTIRE UNIT TO RESET THE INSTRUMENT. POWER WILL AUTOMATICALLY BE SHUT OFF TO THE AMPLIFIER IN CASE OF OVERHEATING AND RESET ONLY AFTER THE INSTRUMENT HAS BEEN COMPLETELY SHUT OFF AT THE AC POWER ENTRY.

Frequency in MHz: The LED displays the synthesized oscillator frequency in megahertz (10^6 cycles/second).

Frequency Adjust: this knob changes the frequency of the oscillator. When the switch (at its left) is on course control, each "click" changes the frequency by 1,000 Hz, when it is switched to fine, each click changes the frequency 10 Hz. The smallest change in this digitally synthesized frequency is 10 Hz.

The Mixer (inside black outline)

Mixer In - rf input signal from receiver, 50 mV rms (max.)

Mixer Out - detected output, proportional to the difference between cw-rf and rf from precessing magnetization. Level, 2 V rms (max.) bandwidth 500 kHz.

CW-RF switch: on-off switch for cw-rf output.

CW RF OUT: continuous rf output from oscillator - 13dbm into 50 Ω load.

M-G Switch: turns on phase shift of 90° between A and B pulse for multipulsed Meiboom-Gill pulse sequence.

A & B in: input for A & B pulses from pulsed programmer.

RF out: TNC connector output of amplifier to the transmitter coil inside sample probe. Radio frequency power bursts that rotate magnetization of the sample.

Coupling: This adjustment should only be made by the instructor using a small screwdriver. Adjusting the screw inside the module optimizes the power transfer to the transmitter coils in the sample probe. This adjustment has been made of the factory and should not need adjusting under ordinary operating conditions.

15 MHz Receiver

This is a low noise, high gain, 15 MHz receiver designed to recover rapidly from an overload and to amplify the radio frequency induced EMF from the precessing magnetization. The input of the receiver is connected directly to a high Q coil wrapped around the sample vials inside the sample probe. The tiny induced voltage from the precessing spins is amplified and detected inside this module. The module provides both the amplified rf signal as well as detected signal. The rf signal can be examined directly on the oscilloscope. For example, Fig. A.5 shows a free induction decay signal from precessing nuclear magnetization in mineral oil. This data was obtained on the HP 54600A digital oscilloscope. On this instrument, it is not possible to see the individual 15 MHz cycles, but with an analog scope, these cycles can be directly observed. Please note, these are *not* the beat cycles seen in the output of the mixer, but decaying 15 MHz oscillations of the free induction decay.

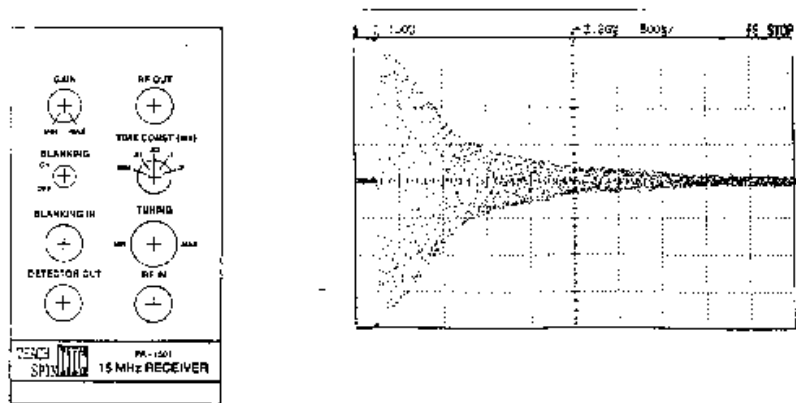


Figure A.5

Gain: continuously variable, range 60 dB (typical).

RF out: amplified radio frequency signal from the precessing nuclear magnetization.

Blanking: turns blanking pulse on or off.

Blanking In: input from blanking pulse, to reduce overload to the receiver during the power rf pulses.

Time Constant: selection switch for RC time constant on the output of the amplitude detector. The longer the time constant, the less noise that appears with the signal. However, the time constant limits the response time of the detector and may distort the signal. The longest time constant should be compatible with the fastest part of the changing signal.

Tuning: rotates a variable air capacitor which tunes the first stage of the amplifier. It should be adjusted for maximum signal amplitude of the precessing magnetization.

Detector Out: the output of the amplitude detector to be connected to the vertical scope input.

RF In: To be connected to the receiver coil inside the sample probe. This directs the small signals to the first stage of the amplifier.

Fig. A.6 shows a two pulse (90° - 180°) free induction decay - spin echo signal as observed from the rf output port (upper trace) and detector output port (lower trace) of the receiver. Again, it is not possible to observe the individual oscillation of the 15 MHz on this trace (with this time scale and the digital scope) but it is clear that the detector output rectifies the signal ("cuts" it in half) and passes only the envelope of the rf signal. It is also important to remember that the precession signal from spin system cannot be observed during the rf pulse from the oscillator/amplifier since these transmitter pulses induce voltages in the receiver coil on the order of 10 volts and the nuclear magnetization creates induced EMFs of about $10\mu\text{V}$; a factor of 10^6 smaller!

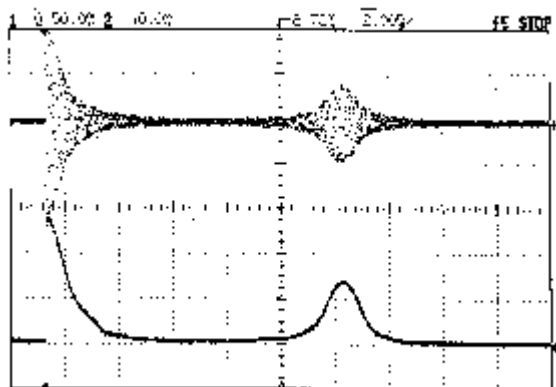


Figure A.6

Auxiliary Components (not used in present MPL setup)

1. PICKUP PROBE

A single loop of # 32 wire with a diameter of 6mm is used to measure the B_z of the rotating rf field. This loop is encapsulated with epoxy inside a sample vial and attached to a short coaxial cable. The coaxial cable has a female BNC connector at the other end. To effectively eliminate the effects of the coaxial cable on the pickup signal from the transmitter pulse, a 50 ohm termination is attached at the pickup loop end as shown in the diagram. Since the single loop has a very low impedance, the signal at the oscilloscope is essentially the same as the signal into an open circuit. Note: the orientation of the pickup loop inside the sample holder is important, since the plane of the loop must be perpendicular to the rf field. (Faraday's Law!)

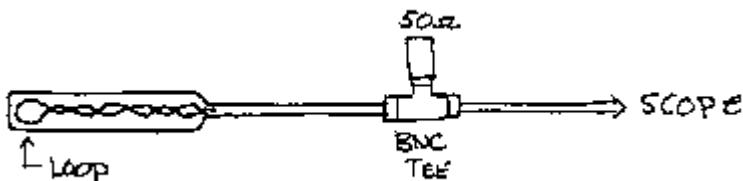


Figure A.7

2. DUMMY SIGNAL COIL

A second single loop of # 32 wire in series with a 22k resistor is used to create a "dummy signal". The probe is also placed in the sample holder at the proper depth to produce the maximum signal. The loop is also connected to the terminating resistor to eliminate cable effects. This probe is attached to the cw output of the oscillator to create a signal which can be used to tune and calibrate the spectrometer. The connections are shown in the diagram.

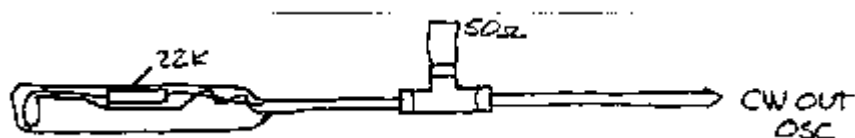


Figure A.8

References

- 1) This write-up is a combination of the "Teach-Spin" documentation sold with the apparatus (apparently uncopyrighted), with an older write-up by Robert Schumacher and Steve Garoff, and parts of even older write-ups by various other instructors. The present organization of the document, and some of the writing, is due to Reinhard Schumacher.
- 2) A. C. Melissinos, *Experiments in Modern Physics*, Academic Press, New York, 1966.
- 3) See, for example, R. Eisberg and R. Resnick, *Quantum Physics*, 2nd Ed. page 391.
- 4) C. Cohen-Tannoudji, B. Diu, F. Laloe, *Quantum Mechanics*, Hermann, Paris, 1977.
- 5) P. R. Bevington and D. K. Robinson *Data Reduction and Error Analysis for the Physical Sciences*, McGraw Hill Book Company, New York, 1992.

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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.

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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.

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