Experiment 5

Pulsed Nuclear Magnetic Resonance

5.1 Introduction: The Two Level System

Nuclear Magnetic Resonance (NMR) is the archetypal example of a very important concept in condensed matter physics referred to as the 2-level system. The dynamics of such a system are governed by 2 well defined energy levels, provided they are well separated from other energy levels.

Figure 5.1: A 2-level system well isolated from other energy levels.

However, such a system would be static if there were no interactions between the system and its environs - a means by which energy can be gained (excitation) or released (decay). Such interactions give rise to the concept of relaxation times for an excited state. This experiment will introduce the student to a phenomenological picture of NMR in which two distinct types of interactions, spin lattice and spin-spin, provide two distinct types of relaxation mechanisms.

5.2 A Phenomenological Picture of NMR

5.2.1 A Sample in a Static Field $\vec{B} = B_0\hat{z}$

Magnetic resonance is observed in systems where the magnetic constituents have 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 spinning magnetic dipoles. For this instrument, one need only be concerned with the nucleus of hydrogen, which is a single proton. The proton has a magnetic moment μ and an angular momentum $\vec{J}$ which are related by the vector equation

$$\vec{\mu} = \gamma \vec{J} \tag{5.1}$$

where γ is called the *gyromagnetic ratio.* For the case of a hydrogen nucleus, there shall be no *orbital* angular momentum, $\vec{L} = 0$. The nuclear angular momentum is quantized as $\vec{J} = \hbar m_I \hat{I}$ where $m_I = -I, -I+1, ..., I-1, I+1$ are the allowed spin projections and I is the spin of the nucleus.

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

$$U = -\vec{\mu} \cdot \vec{B} \tag{5.2}$$

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

$$U = -\mu_z B_0 = -\gamma\hbar m_I B_0 \tag{5.3}$$

For the proton, with spin one half ($I = 1/2$), the allowed values of m_I are simply $\pm 1/2$ which means there are only two magnetic energy states (a 2 level system) for a proton residing in a constant magnetic field B_0. These are shown in Fig. 5.1. The energy separation between the 2 states Δ can be written as

$$\Delta U = \hbar\omega_0 = \gamma\hbar B_0 \tag{5.4}$$

This is the fundamental resonance condition. For the proton, $\gamma_{proton} = 2.675 \times 10^8$ rad/sec T, so that the resonant frequency is related to the constant magnetic field for the proton by $f_0(MHz) = 42.58 B_0(\mathrm{T})$.

If a small sample containing a thermodynamically large ($\sim 10^{20}$) number of protons is placed in an external magnetic field $B_0\hat{z}$, then the population of spins will eventually establish a macroscopic magnetization, $\vec{M} = M_0\hat{z}$, due to the vector summation of the individual nuclear magnetic moments. The magnitude of M_0 will depend upon the equilibrium distributions of spins; let N_- represent the number of spins in the excited state ($m_I = -1/2$) and N_+ the number of spins in the ground state ($m_I = +1/2$). Using Boltzmann statistics, it can be shown that

$$\frac{N_-}{N_+} = e^{-\Delta\mu/k_BT} = e^{-\hbar\omega_o/k_BT} \tag{5.5}$$

and the net magnetization shall be

$$M_0 = \mu(N_+ - N_-) = \mu N \tanh\Big(\frac{\mu B}{k_BT}\Big) \tag{5.6}$$

where $N = N_- + N_+$.

Thus far, all mention of the magnetization in the xy plane has been avoided. In thermal equilibrium the only *net* magnetization is in the direction of the external field, $\vec{M} = M_0\hat{z}$. However, quantum mechanics dictates that individual nuclei will have spin in the xy plane, but they precess about the direction of the external field at the Larmor frequency, $\omega_o = \gamma B_0$. The key element here is coherence; the $\sim 10^{20}$ H nuclei in a typical NMR sample have definite spin in the $\hat{z}$ direction due to the external field, but they will be precessing in the xy plane with a random distribution of phases, hence they will not coherently add in the xy plane. Therefore $< M_x >=< M_y >= 0$.

From a semi-classical standpoint, one can understand the behavior of individual spins by recalling that a magnetic dipole $\vec{\mu}$ will experience a torque when subjected to an external field $\vec{B}$. The torque is equivalent to the rate of change of angular momentum.

$$\tau = \frac{\partial \vec{J}}{\partial t} = \vec{\mu} \times \vec{B} \tag{5.7}$$

By Eqn. 5.1

$$\frac{\partial \vec{\mu}}{\partial t} = \gamma\vec{\mu} \times \vec{B} \tag{5.8}$$

One can now perform a vector summation over all $\sim 10^{20}$ spins in the system to obtain the following key result;

$$\frac{\partial \vec{M}}{\partial t} = \gamma\vec{M} \times \vec{B} \tag{5.9}$$

Eqn. 5.9 is valid even if $\vec{B}$ contains time or spatial dependence.

5.2.2 A Sample in a Time Varying Field $\vec{B} = B_0\hat{z} + 2B_1\cos(\omega t)\hat{x}$

Consider a sample subjected to an external field $\vec{B} = B_0\hat{z}$ at $t = -\infty$ and then an additional time varying field $\vec{B} = B_0\hat{z} + 2B_1\cos(\omega t)\hat{x}$ at $t = 0$. For $t < 0$, the spins will be precessing about $\hat{z}$ direction at an angular frequency ω_o and produce a net magnetization $\vec{M} = M_0\hat{z}$. For $t > 0$, the spins will precess about the new field $\vec{B}$, and $\vec{M}$ will move away from the $\hat{z}$ orientation. The motion will be quite complicated in the xyz

laboratory frame of reference, and so it will be prudent to adopt a noninertial coordinate system $x^*y^*z^*$ that rotates about $\hat{z}$ at a frequency ω.

The change of coordinate systems requires a transformation of the external field. To begin, decompose the time varying field into a pair of *cw* and *ccw* circularly polarized fields:

$$\begin{aligned}\vec{B} &= B_0\hat{z} + 2B_1\cos(\omega t)\hat{x} \\ &= B_0\hat{z} + B_1(\cos(\omega t)\hat{x} + \sin(\omega t)\hat{y}) + B_1(\cos(\omega t)\hat{x} - \sin(\omega t)\hat{y})\end{aligned} \tag{5.10}$$

For convenience, choose the $x^*y^*z^*$ coordinate system to be rotating in the *cw* direction. The stationary field must be modified by a effective field - $\frac{\omega}{\gamma}\hat{z}$ (Why? Think about the motion of individual spins for $t < 0$: at what frequency do they precess in the $x^*y^*z^*$ rotating coordinate system?), the *ccw* field will be rotating at a frequency 2ω, and the *cw* field will become stationary (for convenience, assume it is oriented in the $\hat{x}^*$ direction). Thus the field will become

$$\vec{B}^*_{eff} = (B_0 - \frac{\omega}{\gamma})\hat{z}^* + B_1(\cos(2\omega t)\hat{x}^* + \sin(2\omega t)\hat{y}^*) + B_1\hat{x}^* \tag{5.11}$$

The field rotating at 2ω can be neglected for $\omega \approx \omega_0$. The reason for this is that radiation of energy $2\hbar\omega \gg \hbar\omega_0$, so it should not excite any spins in the 2-level system. Therefore, the effective field in the rotating coordinate system is

$$\vec{B}^*_{eff} = (B_0 - \frac{\omega}{\gamma})\hat{z}^* + B_1\hat{x}^* \tag{5.12}$$

Now return to the original problem. The net magnetization, initially at rest in the $\hat{z}^*$ direction, will now begin to precess about the field $\vec{B}^*_{eff}$, thus tilting the axis of precession. For the particular case $\omega = \omega_0$, $\vec{M}$ will precess about the $\hat{x}^*$ direction, as shown in Fig. 5.2. This is an astounding result, for it suggests that one can alter the orientation of a *coherent* population of spins by applying the rf field for a finite period of time.

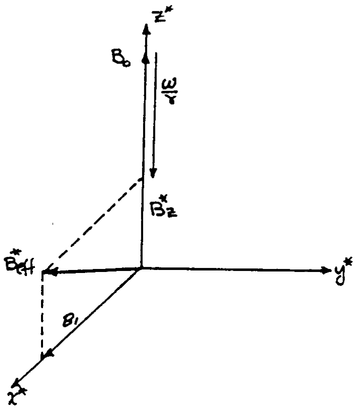

Figure 5.2: The effective magnetic field $\vec{B}^*_{eff}$ in the rotating frame of reference.

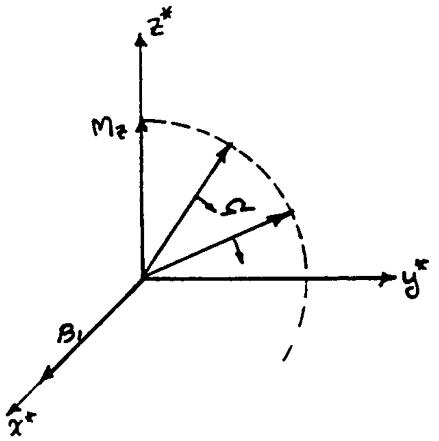

Figure 5.3: Rotation of the net magnetization about $\vec{B}^*_{eff}$for the case $\omega = \omega_o$.

$\pi/2$ Pulse

If the time varying field is turned off at a later time $\tau = (1/4)(2\pi)/\omega_o$, the net magnetization $\vec{M}$ will complete 1/4 of a rotation in the y^*z^* plane (see Fig. 5.3), thus stopping in the $\hat{y}^*$ direction. Therefore, it is possible to produce coherence in the laboratory xy plane by rotating the net magnetization vector away from its ground state. The student is encouraged to think about the quantum mechanical nature of this state at $t > \tau$. Recall that there are only two well defined states in this system, and they are in reference to the $\hat{z}^*$ direction.

π Pulse

If the time varying field is turned off at a later time $\tau = (1/2)(2\pi)/\omega_o$, then the net magnetization will complete 1/2 of a rotation in the y^*z^* plane (see Fig. 5.3), thus stopping in the $-\hat{z}^*$ direction. This corresponds to inverting the equilibrium distribution of spins, but the coherence remains in the z^* orientation.

5.2.3 Relaxation Dynamics

The model described thus far will not provide very interesting behavior *after* either a $\pi/2$ or π pulse, since by eq. 5.9 $\vec{M}$ will be stationary in the $x^*y^*z^*$ coordinate system.

$$\frac{\partial M_{x^*}}{\partial t} = \frac{\partial M_{y^*}}{\partial t} = \frac{\partial M_{z^*}}{\partial t} = 0$$

However, the inclusion of interactions will alter this simple picture considerably.

T_1 Spin-Lattice Relaxation Processes

Recall that a π pulse effectively moves all of the nuclei from the groundstate ($m_I = +1/2$) to the excited state ($m_I = -1/2$). This process involves changing two factors: energy and spin. Therefore, if a nucleus is to relax back into the groundstate, it must deposit both energy and spin into the surroundings (hereafter referred to as the lattice). Rather than delve into immense detail about spin-lattice relaxation mechanisms, assume that one can use a phenomenological relaxation time T_1 in the equation of motion for M_{z^*}.

$$\frac{\partial M_{z^*}}{\partial t} = -\frac{M_{z^*}}{T_1} \tag{5.13}$$

After a single π pulse, then M_{z^*} will evolve in the following manner;

$$M_{z^*}(t) = M_0(1 - 2e^{-t/T_1}) \tag{5.14}$$

Thus, T_1 is a measure of the interactions between a spin system and the lattice in which it resides.

T_2 Spin-Spin Relaxation Processes

A $\pi/2$ pulse moves the net magnetization to the $\hat{y}^*$ orientation in the rotating coordinate system. This corresponds to 1/2 of the spin population occupying the excited state, but there is now coherence in the xy plane. If there were only spin-lattice interactions, then this magnetization $M_0\hat{y}^*$ would decay with a characteristic time T_1. However, each magnetic dipole creates a field that will interact with those of neighbouring dipoles. Therefore, there will be local fluctuations in $\vec{B}$ inside of the sample. If $|\vec{B}| > B_0$ at some point in the sample, then spins in that region will precess at a frequency $\omega' > \omega_0$, and the converse is true if $|\vec{B}| < B_0$ at another point in the sample. With time, these fluctuations will become increasingly more random, thus dephasing the spins and destroying coherence in the xy plane.

In the rotating coordinate system, this corresponds to the macroscopic magnetization breaking into *cw* ($\omega' > \omega_0$) and *ccw* ($\omega' < \omega_0$) components.

As for spin-lattice relaxation, assume that the net effect of spin-spin interactions is to produce a characteristic relaxation timescale T_2.

$$\frac{\partial M_{y^*}}{\partial t} = -\frac{\partial M_{y^*}}{T_2} \tag{5.15}$$

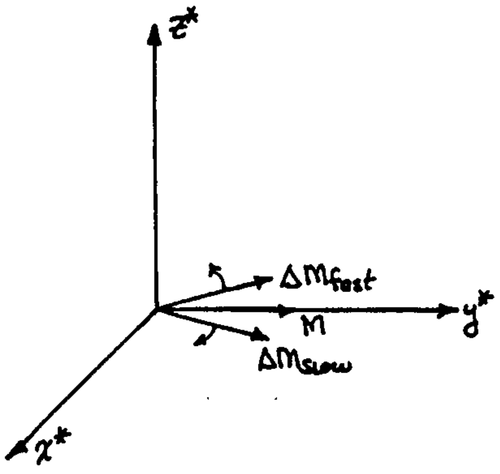

Figure 5.4: The loss of coherence in the xy plane due to spin-spin interactions, as pictured in the rotating frame of reference.

After a $\pi/2$ pulse, the magnetization in the xy plane will decay and follows:

$$M_{y^*}(t) = M_0 e^{-t/T_2} \tag{5.16}$$

Thus, T_2 is a measure of the interactions between spins within a spin system. This is very different from T_1, for spin-spin interactions do not transfer energy out of the spin system, rather they induce a loss of coherence. The decay after a $\pi/2$ pulse will hereafter be referred to as a *free induction decay* (FID).

5.3 Experiment

5.3.1 Apparatus and Samples

A sketch of the PNMR probe is shown in Fig. 5.5, along with the laboratory xyz coordinate system. Note that $\vec{B} = B_0\hat{z}$ and that the time varying field $\vec{B}_{rf} = 2B_1\cos(\omega_o t)\hat{x}$. The pickup coil is oriented in the $\hat{y}$ direction, and measures the magnitude of the precessing $\vec{M}$ in the xy plane via Lenz's law. The student is encouraged to consider the practical implications which led to this design.

For the experiment 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. Remember, all PNMR experiments begin by assuming a thermal equilibrium magnetization along the $\hat{z}$ direction. But this magnetization builds exponentially with a time constant, T_1. Each experiment, that is, each pulse sequence, must wait at least $3T_1$, (preferably 6-10 T_1's) before repeating the pulse train. For a single pulse experiment that means a repetition time of $6 - 10T_1$. If you choose pure water, with $T_1 = 3s$, you will have to wait a half a minute between each pulse. Since several adjustments are required to tune this spectrometer, pure water samples can be very time consuming and difficult to work with.

Glycerin has a T_1 of about $20ms$ at room temperature. That means that the repetition time can be set to $100ms$ and the magnetization will effectively attain thermal equilibrium at the start of each pulse sequence.

IMPORTANT NOTE: Do not fill vial with sample material. The standard samples which are approximately cubical (about 5 mm in height) are the appropriate size. This size of sample fills the receiver coil and the pulsed magnetic field is uniform over this volume. Larger samples will not experience uniform rf magnetic field. In that case all the spins are not rotated the same amount by a pulse. Such a sample 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.

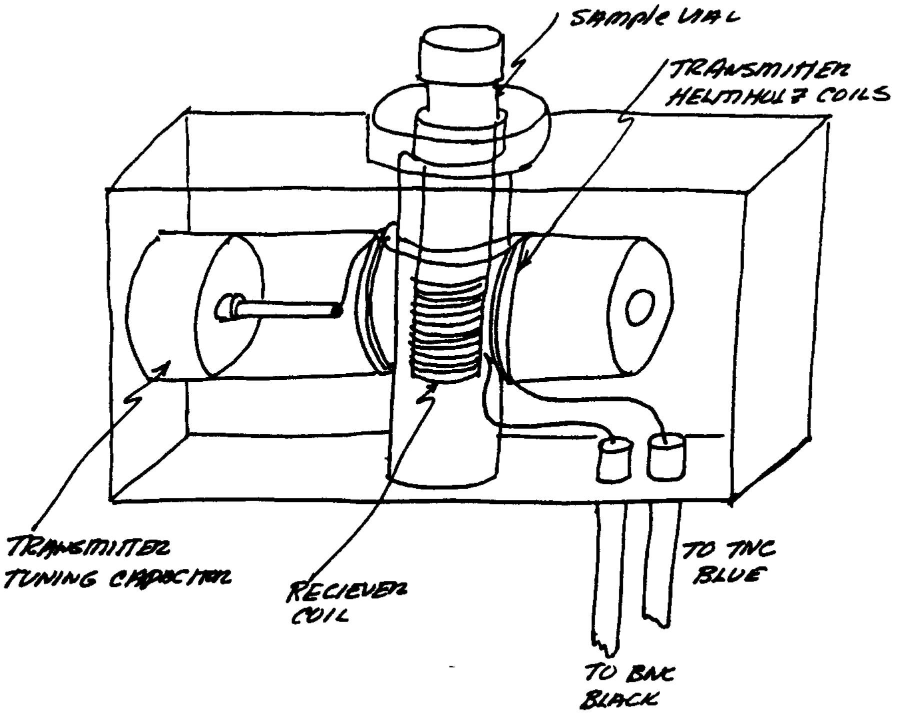

Figure 5.5: A sketch of the NMR probe.

Figure 5.6 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.

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 pulses are amplified and sent to the transmitter coils in the sample probe. The rf current bursts in these coils produce a homogenous 12 *Gauss* rotating magnetic field at the sample. The transmitter coils are wound in a Helmholtz configuration to optimize rf magnetic field homogeneity.

Nuclear magnetization precessing in the direction transverse to the applied constant magnetic field (the so called xy plane) induces an EMF in the receiver coil, which is then amplified by the receiver circuitry. This amplified radio frequency ($\sim$ 15 MHz) signal can be detected (demodulated) by two separate and different detectors. The rf **amplitude** detector rectifies the signal and has an output proportional 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 other 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 precessional frequency when a zero-beat output signal from the mixer is obtained. A dual channel scope allows simultaneous observations of the signals from both detectors. The field of the permanent magnet is temperature dependent so periodic adjustments in the frequency are necessary to keep the spectrometer on resonance.

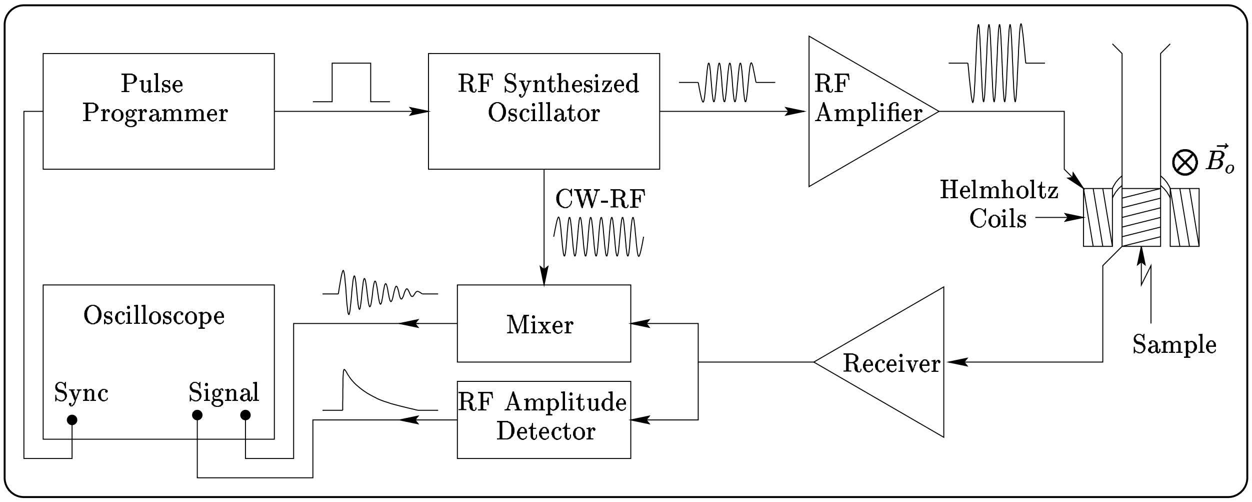

Figure 5.6: A block diagram of the NMR apparatus.

5.3.2 Preliminaries

Begin this experiment by turning on the cooling water and the magnet power supply 20 minutes prior to taking any measurements. This is necessary in order to stabilize the temperature of the magnet, thus ensuring a constant field strength.

After a sufficient wait, one can then proceed to tune the spectrometer. This can be accomplished by using a single A pulse arbitrarily set to $\sim$ 20% and a pulse repetition time $\sim 50ms$. Watch the output of the mixer carefully, adjust the frequency of the rf pulses until the beating is minimized. Next, adjust the A pulse width to maximize the height of the FID, and then tune again. A satisfying signal should be obtained within a few iterations of this procedure. By this means, you will simultaneously tune the apparatus and determine the 90^o pulse width.

5.3.3 Measuring T_1

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. Start with an order of magnitude estimate of the time constant using the standard glycerine sample.

1. Adjust the spectrometer to resonance for a single pulse free induction decay signal.
2. Lower the repetition time, 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^o 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.

Two Pulse-Zero Crossing

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

$$\pi \xrightarrow{\tau(\text{variable})} \frac{\pi}{2}(\text{free induction decay})$$

The first pulse (180^o) inverts the thermal equilibrium magnetization, $M_z \rightarrow -M_z$. Then the spectrometer waits a time τ before a second pulse rotates the magnetization that exists at this later time by 90^o.

After the first pulse inverts the thermal equilibrium magnetization, the net magnetization is **not** a thermal equilibrium situation. In time the magnetization will return to $+M_z$. Figure 5.7 shows a pictorial representation of the process. The magnetization grows exponentially towards its thermal equilibrium value.

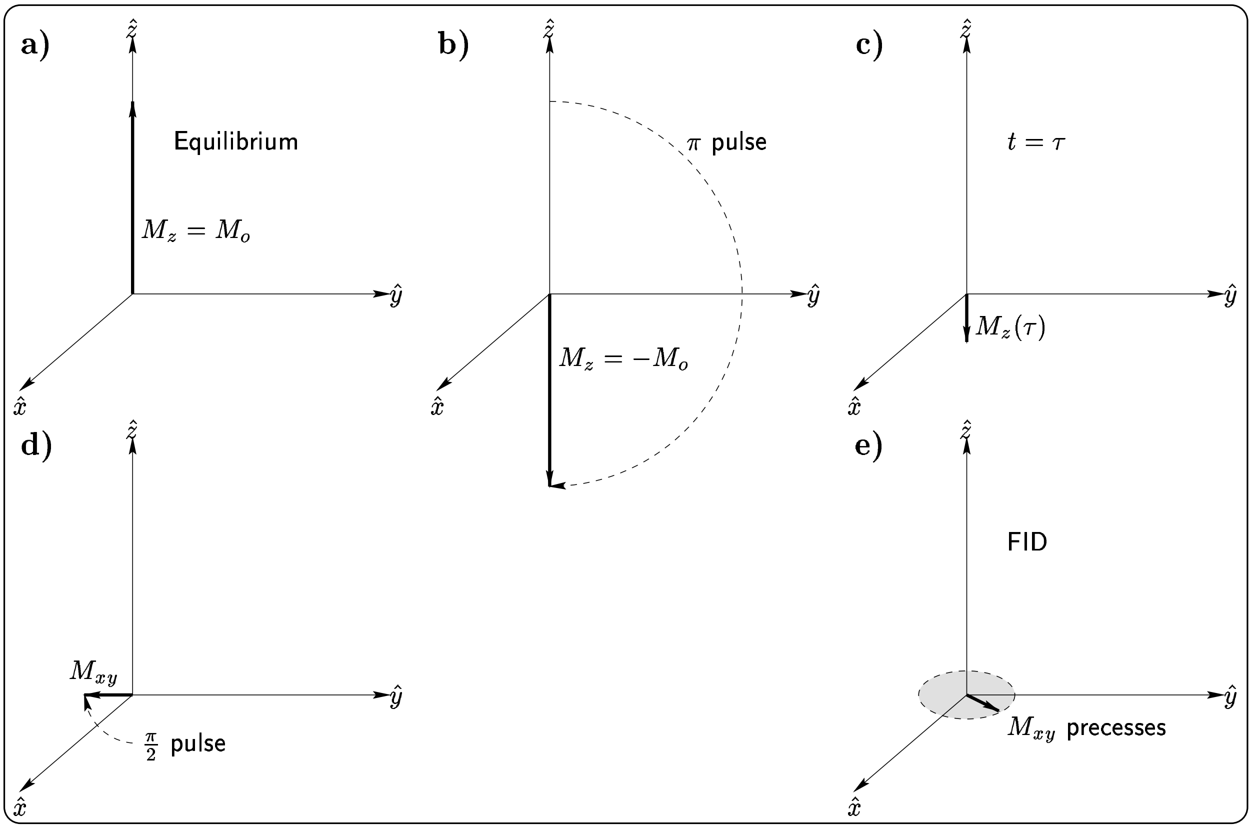

Figure 5.7: Measuring T_1: **a)** The initial magnetization is $M_o\hat{z}$. **b)** A π pulse is used to invert the magnetization to $-M_o\hat{z}$. **c)** M_z decays back toward equilibrium until $t = \tau\ldots$ **d)** when a $\frac{\pi}{2}$ pulse is used to rotate the magnetization into the xy plane... **e)** where it precesses briefly, and can be measured, before it vanishes again. In these figures, $\vec{B} = B_o\hat{z}$.

However, the spectrometer **cannot detect** magnetization along the z-axis; it only measures precessing **net** magnetization in the xy plane. That's where the second pulse plays its part. This pulse rotates **any net** magnetization in the z-direction into the xy plane where the magnetization can produce a measurable signal. In fact, the initial amplitude of the free induction decay following the 90^o pulse is proportional to the net magnetization along the z-axis ($M_z(\tau)$), **just before the pulse**. You should be able the 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. A more accurate method to determine T_1 uses the same pulse sequence just described, but plots $M(\tau)$ as a function of τ.

Note: A 180^o pulse is characterized by a pulse approximately twice the length of the 90^o pulse, which has no signal (free induction decay) following it. A true 180^o pulse should leave no magnetization in the xy plane after the pulse.

5.3.4 Measuring T_2

From previous discussion 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^o pulse. 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 magnet used in the experiment has sufficient uniformity to produce at least a 0.3 millisecond decay time.

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, PMNR changed this. Suppose a two pulse sequence is used: the first one 90^o, and the second one, turned on a time τ later, a 180^o pulse.

$$\frac{\pi}{2} \xrightarrow{\tau} \pi$$

What happens? Figure 5.8 shows pulse sequence and Fig. 5.9 shows the progression of the magnetization in the rotating frame. Study these diagrams carefully. The 180^o pulse allows the x^*y^* magnetization to rephase to the value it would have had with a perfect magnet. The spins in the larger field get out of phase by $\Delta\theta$ in a time τ. After the 180^o pulse, they continue to precess faster than $\vec{M}$, but at 2τ they return to the in-phase condition. The slower precessing spins do just the opposite, but again rephase at a time 2τ. The rephasing at 2τ is referred to as a spin echo. 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.

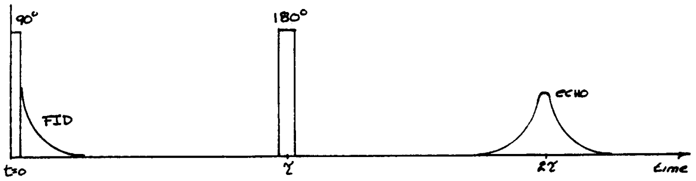

Figure 5.8: The pulse sequence used to elicit a spin echo.

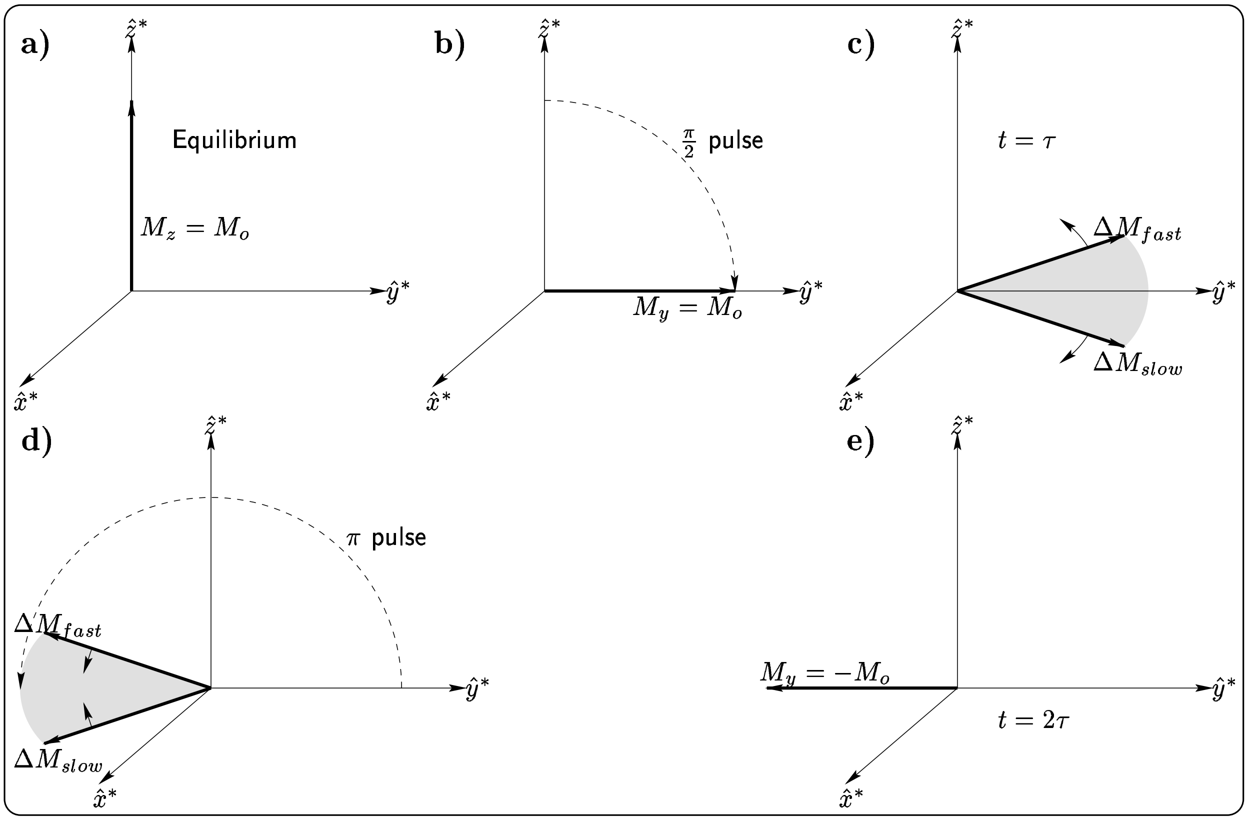

Figure 5.9: The spin echo: **a)** The initial magnetization is $M_o\hat{z}$. **b)** A $\frac{\pi}{2}$ pulse is used to rotate the magnetization into the xy plane. **c)** The xy magnetization dephases due to inhomogeneous field distributions, with the extremes being ΔM_{fast} (high field) and ΔM_{slow} (low field), until $t = \tau\ldots$ **d)** when a π pulse is used to flip the magnetization. The spins continue to precess as before, until… **e)** $t = 2\tau$, when they are again in phase, and an echo may be observed. After $t = \tau$, the spins again dephase, and the signal disappears again. In these figures, the decay of the xy magnetization and the growth of M_z have been omitted for clarity.

Carr-Purcell Pulse Sequence

The two pulse system will give accurate results for liquids when the self diffusion times of the spins through the magnetic field gradients are slow compared to T_2. This is not often the case for common liquids in the 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^o pulses spaced a time τ apart are applied

$$\frac{\pi}{2} \xrightarrow{\frac{\tau}{2}} \pi \xrightarrow{\tau} \pi \xrightarrow{\tau} \pi \rightarrow \text{ etc. } \ldots$$

thus creating a series of echoes equally spaced between the 180^o pulses. 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^o pulses τ should be short compared to the time of self diffusion of the spins through the field gradients. If that is the case, the Carr-Purcell sequence significantly reduces the effects of diffusion on the measurement of T_2.

Meiboom-Gill Pulse Sequence

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^o pulse. If, for example, the spectrometer was producing 183^o pulses, by the time the 20th pulse was turned on, the spectrometer would have accumulated a rotational error of 60^o, a sizable error. This error can be shown to erroneously reduce the measurement of T_2. Meiboom and Gill devised a clever way to reduce this accumulated rotation error. Their pulse sequence provides a **phase shift** of 90^o between the 180^o pulses, which cancels the error to the first order. The M-G pulse train gives more accurate measurements of T_2.

5.4 Selected References

C.P. Slichter, Principles of Magnetic Resonance. Springer-Verlag, New York U.S.A., 1978.

This text should be considered essential reading for those who wish to truly understand NMR. If a copy cannot be found in the library, then contact the teaching assistant.

D.J. Griffiths, Introduction to Quantum Mechanics. Prentice-Hall, Englewood Cliffs, U.S.A., 1994

I think this is the QM textbook used in your 4th year class. However, every elementary QM textbook should cover Larmor precession of an electron in a magnetic field.

TeachSpin PS1-A Manual. TeachSpin, Inc. Buffalo, U.S.A., 1997.

Inadequate theoretical description and slightly disorganized, but the primary technical reference for this experiment. Ask for the manual if you have questions concerning the equipment or desire suggestions for further experiments.