

NMR Procedure

A. Pulse Programmer

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 ms. Let's begin by observing a single A pulse like that shown in Figure 12. 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

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. Change the repetition time, notice the changes in the intensity of the scope signal on the analog scope. 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?

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 μ s)
 Mode: Int
 Repetition time: 100 ms variable 10%
 Number of B Pulses: 01
 Sync: A
 A: on B: on
 Sync Out: To ext. sync input on scope.
 A & B out: Verticle input on scope

The pulse train should appear like Figure 5.2, lower trace, if the time base on the oscilloscope is 20 μ s / 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)

3. Multiple Pulse Sequence

The Carr-Purcell or Meiboom-Gill pulse train 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%
 Number of B pulses: 02
 Sync A
 A: On B: On
 Oscilloscope Sweep 0.1 ms / cm
 A & B out : Verticle 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. Before you tune the receiver to a real magnetic resonance signal, you can tune it to the oscillator frequency (which should be set at the estimated resonance frequency) using a special "dummy signal" probe. This probe is connected to the cw rf oscillator. The loop end is placed inside the sample probe where it induces an *EMF* in the receiver coil like the precessing spins. The "dummy signal" is induced into the receiver with the A or B pulses turned **OFF**. This dummy signal allows you to tune the receiver and observe the rf and detected signals as a function of tuning and 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. 1.3. 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. Check them against the block diagram, Figure 1.2.

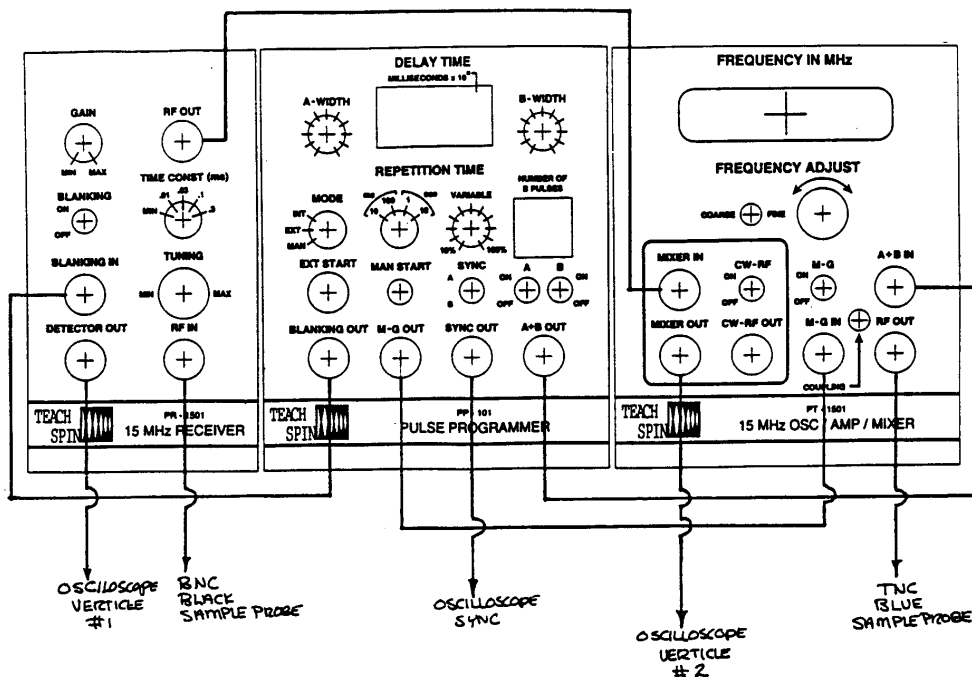


Fig. 1.3

D. Single Pulse NMR Experiment - Free Precession (Induction) Decay

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 the magnet or by the real spin-spin relaxation time T_2 , whichever is shorter. Fig. 9.2 shows the free precession decay of mineral oil, after the 90° pulse.

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 sample fills the receiver coil and the pulsed magnetic field is uniform over this volume. Larger samples will not experience uniform rf magnetic. In that case all the spins are not rotated the same amount during the pulse. Such sample can cause serious errors in the measurements of T_2 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 Fig. 2.3.

E. Magnetic field contours

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 mineral oil, the real T_2 is much longer than the free induction decay time.

F. Rotating Coordinate Systems (Optional Experiments)

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

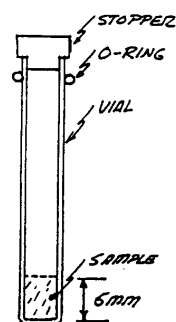


Fig. 2.3

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.

G. Spin Lattice Relaxation Time, 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. Let's start with an order of magnitude estimate of the time constant using the standard mineral oil 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.

1. 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:

$180^\circ - \tau$ (variable) -90° free induction decay

The first pulse (180°) inverts the thermal equilibrium magnetization, that is ; $M_z \rightarrow -M_z$. Then the spectrometer waits a time τ before a second pulse rotates the magnetization that exists at this later time by 90° . 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 $+M_z$. Fig. 3.3 shows a pictorial representation of the process. The magnetization grows exponentially towards its thermal equilibrium value.

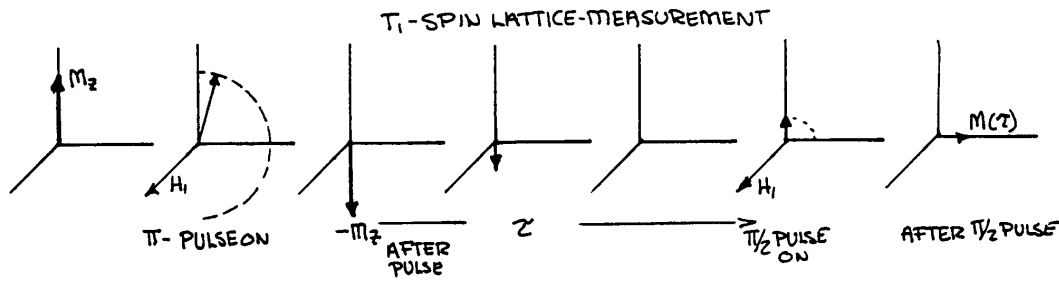


Fig. 3.3

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.

2. 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? The analysis of these experiments is left to the student.

Note: 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.

H. Spin-Spin Relaxation Time - T_2

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 .

1. Two Pulse-Spin Echo

We have already discussed the way a 180° pulse following a 90° pulse reverses the x-y magnetization and causes a rephasing of the spins at a later time. 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:

$$90^\circ \text{ -- } \tau \text{ -- } 180^\circ \text{ -- } \tau \text{ -- } \text{echo}(2\tau)$$

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

2. Multiple Pulse - Multiple Spin Echo Sequences.

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 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:

$$90^\circ - \tau / 2 - 180^\circ - \tau - 180^\circ - \tau - 180^\circ - \text{etc}$$

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

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 90° and the 180° 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 phase shift.

C. Self Diffusion

Carr and Purcell showed that self diffusion leads to the decay of the echo amplitude given by the expression

$$M(\tau) = M_0 e^{-\gamma^2 \left(\frac{\partial H}{\partial z} \right)^2 \frac{D\tau^3}{12}}$$

for the case where the field gradient $\frac{\partial H}{\partial z}$ is in the z-direction.

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