

# Pulsed Nuclear Magnetic Resonance

## 1 Background

What we call “nuclear magnetic resonance” (NMR) was developed simultaneously but independently by Edward Purcell and Felix Bloch in 1946. The experimental method and theoretical interpretation they developed is now called “continuous-wave NMR” (CWNMR). A different experimental technique, called “pulsed NMR” (PNMR), was introduced in 1950 by Erwin Hahn. Pulsed NMR is used in magnetic resonance imaging (MRI). Purcell and Bloch won the Nobel Prize in Physics in 1952 for NMR; more recently NMR was the subject of Nobel Prizes in Chemistry in 1991 and 2002. We have both NMR setups in the advanced labs: one is a variation of the CWNMR method, and the other is a pulsed NMR system.

The physics underlying NMR is the same for both the continuous and pulsed methods, but the information obtained may be different. Certainly, the words used to describe what is being done in the experiments are different. In *continuous-wave* NMR one tunes a *weak* radio-frequency oscillator to match the natural frequency of nuclear magnetic moments precessing in a static magnetic field. When the frequencies match, the moments “resonate” and energy transfer between the RF field and the sample is optimized; this resonance creates an electrical signal in a pickup coil. By sweeping the magnetic field, one can leave the RF frequency fixed but tune the resonance itself to excite the sample and then see how quickly the magnetization dies away by watching a “beat pattern.” In *pulsed* NMR, one applies a sequence of *strong* RF bursts or “pulses” to the sample that are very short in duration. The resulting signal, called the “free induction” is then optimized to tune the RF oscillator. The pulses are strong enough and short enough to reorient all of the spins in a coherent way. One can flip the magnetization upside down with a “ $\pi$ -pulse” (180 degrees) or sideways with a “ $\pi/2$ -pulse” (90 degrees). With the a sequence of *pi*-pulses, one can create the fascinating phenomenon of “spin echoes.” More on the two methods is given later in this introduction.

Below, we give a very simplified introduction based on classical ideas to the physics of NMR. More thorough discussions, focusing on the CWNMR technique, may be found in in the books by Preston and Dietz [1] and Melissinos [2] (see references). In particular, the chapter in Preston and Dietz gives a nice description of the connection between quantum-mechanical and semiclassical approaches to NMR physics. For a comprehensive treatment of NMR, see the book by Slichter [3].

### 1.1 Semiclassical ideas

To observe NMR, one needs nuclei with a non-zero angular momentum  $\vec{I}$  and magnetic moment  $\vec{\mu}$ . The relationship between these two quantities is

$$\vec{\mu} = \gamma \vec{I}, \tag{1}$$

where  $\gamma$  is called the *gyromagnetic ratio* (a scalar that may be positive or negative).

A simple classical calculation would give  $\gamma = q/2M$ , where  $q$  is the charge of the nucleus and  $M$  is its mass. But quantum mechanics requires this dimensionally correct result to be modified. In practice, we specify  $\gamma$  in units of the nuclear magneton  $\mu_n \equiv e\hbar/2m_p$  times a dimensionless

factor  $g$  called the “spectroscopic splitting factor” (often just “ $g$  factor”):

$$\gamma = \frac{g\mu_n}{\hbar} = \frac{ge}{2m_p}, \quad (2)$$

where  $e$  is the elementary charge and  $m_p$  is the mass of one proton. The  $g$  factor is on the order of unity. It is positive for some nuclei, and negative for others. For the proton,  $g = +5.586$ ; a table of various  $g$  factors may be found in Preston and Dietz.

When a nucleus of moment  $\vec{\mu}$  is placed in a magnetic field  $\vec{B}_0$  it will experience a torque causing a change in the angular momentum following Newton’s second law:

$$\vec{\tau} = \vec{\mu} \times \vec{B}_0 = \frac{d\vec{I}}{dt} = \frac{1}{\gamma} \frac{d\vec{\mu}}{dt}. \quad (3)$$

Figure 1 shows some of the vectors defined with  $\vec{B}_0$  lying along the  $z$  axis (which is horizontal in most lab setups, including ours). The rate of change of  $\vec{\mu}$  is, by Eq. (3), both perpendicular

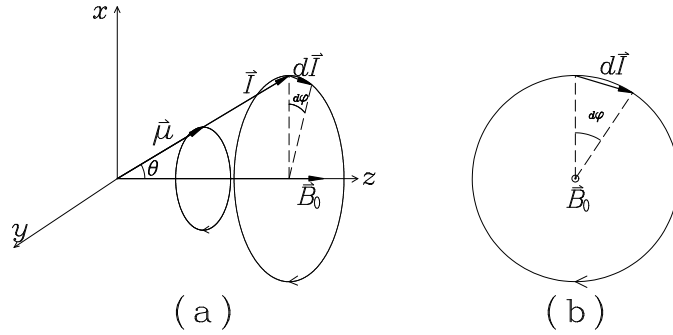


Figure 1: (a) Vectors defined in semiclassical picture of NMR. (b) Tip of angular momentum vector  $\vec{I}$ , viewed opposite to  $\vec{B}_0$ .

to  $\vec{B}_0$  and  $\vec{\mu}$  itself; hence  $\vec{\mu}$  precesses about the direction of  $\vec{B}_0$ . From Fig. 1 it is easy to derive from geometry that the vector magnitudes obey

$$\mu B_0 \sin \theta = \frac{\mu}{\gamma} \sin \theta \left( \frac{d\phi}{dt} \right); \quad (4)$$

thus

$$\omega_0 \equiv \frac{d\phi}{dt} = \gamma B_0, \quad (5)$$

which is the Larmor angular frequency.

When we deal with nuclei of spin  $I = 1/2$  (e.g., protons), quantum mechanics tells us that in a magnetic field  $\vec{B}_0$  the ground state splits into two sublevels, as shown in Fig. 2. The energies  $U$  of the two sublevels are given by

$$U = -\vec{\mu} \cdot \vec{B}_0 = -\mu_z B_0 = -\gamma \hbar m_I B_0, \quad (6)$$

where  $m_I$  is the angular momentum projection of  $I$  along the  $z$  direction defined by  $\vec{B}_0$ ,  $m_I = \pm 1/2$ . The difference in energy between the two sublevels is thus

$$\Delta U = U_- - U_+ = \gamma \hbar B_0, \quad (7)$$

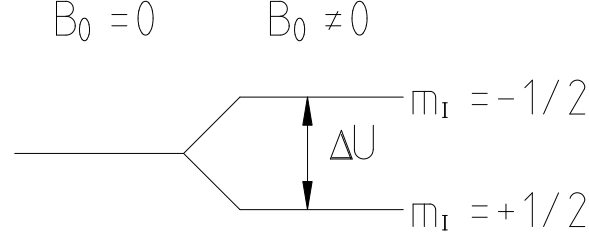


Figure 2: Splitting of nuclear energy levels due to applied magnetic field.

where  $U_{+/-}$  is the energy of the state corresponding to  $m_I = \pm 1/2$ . Transitions between the two energy sublevels may be induced by photons carrying one unit of angular momentum ( $\hbar$ ) and energy  $\hbar\omega_0$  such that

$$\hbar\omega_0 = \gamma\hbar B_0, \quad (8)$$

or  $\omega_0 = \gamma B_0$ , which is the same as the Larmor frequency, Eq. (5).

For free protons, the gyromagnetic ratio is (according to NIST, <https://physics.nist.gov/cuu>)

$$\gamma = 2.6752 \times 10^8 \text{ radians/seconds-Tesla},$$

so for fields in the 0.1–1 T range the frequencies will be in the megahertz range. These are radio frequencies (RF), and both of our setups—pulsed and continuous—work in this MHz range. (Historical note: There was an advantage to having NMR work in the RF range, as existing radio equipment and techniques were used for detection and modulation of NMR signals.) Given that magnetic fields in these experiments are frequently measured in kilogauss, a useful relationship to remember for protons is,

$$f_0 \text{ (MHz)} = 4.2577 \times B_0 \text{ (kilogauss)}, \quad (9)$$

where  $f_0 = \omega_0/2\pi$ .

In order to excite the magnetic resonance, the applied RF must be circularly polarized, optimally with the rotation axis along the  $z$  axis. This is shown in Fig. 3, where an applied field  $\vec{B}_1(t)$  lies in the  $x$ - $y$  plane and rotates about the  $z$  axis at the Larmor frequency and in the same direction as the Larmor precession. Now imagine observing the field from the reference frame that rotates

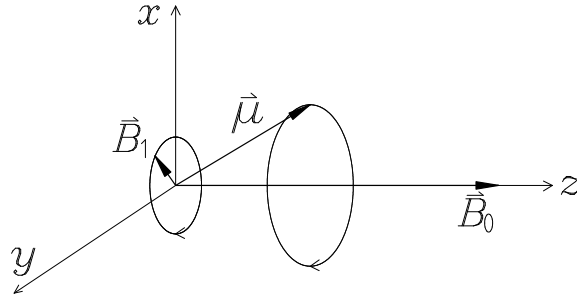


Figure 3: The RF  $\vec{B}_1$  field rotates with the precessing  $\vec{\mu}$  in the semiclassical picture.

along with the Larmor precession; the field  $\vec{B}_1$  would be seen as a *steady* field relative to the moment  $\vec{\mu}$ , and also perpendicular to  $\vec{B}_0$ . The effect of  $\vec{B}_1(t)$  would be to exert a torque in that rotating frame. However, if the RF were applied at a frequency different than the Larmor

frequency, the torque on  $\vec{\mu}$  in the rotating frame would vary in direction and strength over time, so the net work done by the field would be less, tending to zero as the RF angular frequency moves away from  $\omega_0$ . A little mathematics shows that this situation follows the standard picture of resonance phenomena—a resonance which involves the interaction between a *nucleus* with a *magnetic* field, hence the name *nuclear magnetic resonance*.

In the quantum-mechanical picture for a single nucleus we can say that the probability of a “spin-flip” between the  $m_I = +1/2$  and  $m_I = -1/2$  state is maximized when the RF photon has energy equal to  $\hbar\omega_0$ . One may well wonder whether a complete quantum mechanical approach would give different answers than the classical picture we have presented. It is somewhat surprising to discover that Bloch showed that the classical equations governing NMR can be derived from quantum mechanics. See the text by Slichter for a readable and thorough presentation of this result [3].

## 1.2 Net magnetization and relaxation

Clearly, any physical sample will consist of many atoms and the NMR signal measured by an experiment will be due to the combined effect of the magnetic field on them all. As an example, consider an assembly of  $N$  protons, say, in water, glycerin, mineral oil, or animal tissue. The net magnetization  $\vec{M}$  of the sample is the vector sum of all of the individual moments  $\vec{\mu}$ . For the example of spin- $\frac{1}{2}$  protons, the net magnetization along the  $z$ -axis,  $M_z$  would be given by

$$M_z = \sum_i \gamma \hbar m_{Ii} = \frac{1}{2} \gamma \hbar (N_+ - N_-) , \quad (10)$$

where  $m_{Ii}$  denotes the state of the  $i$ th proton, and  $N_+$ ,  $N_-$  are the numbers of protons in the  $+\frac{1}{2}$  and  $-\frac{1}{2}$  state, respectively. When an RF field  $\vec{B}_1(t)$  is applied, some protons have their spin flip to align *against*  $\vec{B}_0$ ; these absorb energy from the RF field. Other protons experience a spin-flip to align *with*  $\vec{B}_0$ ; these give energy back to the RF field. Thus, if the populations of the two sublevels were equal,  $M_z = 0$  and *no net energy would be absorbed from or given up to the field*.

At room temperature with no RF field but with the steady  $\vec{B}_0$  field there will be a small difference between the number of protons with spins aligned in the direction of  $\vec{B}_0$  and the number aligned opposite to it; the magnetic sublevel with  $m_I = +\frac{1}{2}$  will have a slightly larger population  $N_+$  than the population  $N_-$  in sublevel  $m_I = -\frac{1}{2}$ . The ratio of the populations is proportional to the ratio of the associated Boltzmann factors, according to the principles of statistical mechanics:

$$\frac{N_+}{N_-} = \frac{\exp(-U_+/kT)}{\exp(-U_-/kT)} = \frac{\exp(+\frac{1}{2}\gamma\hbar B_0/kT)}{\exp(-\frac{1}{2}\gamma\hbar B_0/kT)} = e^{\gamma\hbar B_0/kT} . \quad (11)$$

If one applies the RF  $\vec{B}_1(t)$  to this equilibrium population, energy goes into the system, since there is an imbalance in the number of up ( $+\frac{1}{2}$ ) spins versus down ( $-\frac{1}{2}$ ) spins. In a fairly short time, however, this imbalance will vanish, because the torque experienced by each moment will cause the populations  $N_+$  and  $N_-$  to become equal. At this point, the net energy transferred between the sample and the field drops to zero as  $M_z = 0$ , and the sample is said to be *saturated*.

There is still a tendency for the system to recover its equilibrium configuration, even while it is subject to the oscillating field. The collection of protons could continue to absorb energy

from an oscillating magnetic field  $\vec{B}_1(t)$  if the rate of equilibrium population recovery is greater than the rate of energy transfer from the field. The rate of  $M_z$  recovering its equilibrium (nonzero) value is due to energy exchanges between the proton magnetic moments and their local environments. The rate of energy transfer from the RF field depends on the amplitude of the RF field and how close its frequency matches the resonance frequency.

Let us consider the magnetization a bit more generally. The net magnetization  $\vec{M}$  is a vector, and thus can be broken into components. The component along the direction of the static field  $M_z$  is called the longitudinal magnetization, and the components along two orthogonal directions perpendicular to  $\vec{B}_0$  are called the transverse magnetizations  $M_x$  and  $M_y$ . Clearly, each of these components is the sum of the individual component moments  $\mu_z$ ,  $\mu_x$  and  $\mu_y$ , respectively, e.g.,  $M_x = \sum_i \mu_{xi}$ . Now look again at Fig. 3 which depicts a single moment precessing about  $\vec{B}_0$ . It should be obvious that for a collection of  $\vec{\mu}$ s at a particular time, each precessing independently about  $\vec{B}_0$ , one could have a nonzero  $M_z$  but a (possibly) zero  $M_x$  or  $M_y$ .

The equilibrium nonzero  $M_z$  exists because the moments aligned parallel to  $\vec{B}_0$  are at a lower energy than those aligned antiparallel. In order to return to equilibrium following absorption from the  $\vec{B}_1(t)$  field, the moments would need to give energy to their surroundings, conventionally called the “lattice” (even if we are dealing with liquid or gaseous materials). The relaxation of  $M_z$  to its equilibrium value is called the “longitudinal” or “spin-lattice” relaxation, and is associated with a characteristic time called  $T_1$ . In liquids,  $T_1$  is typically short: a few milliseconds to as long as a second or two in water or water-based ionic solutions. But in solids,  $T_1$  may be very long, e.g.,  $T_1 \approx 10,000$  s in ice. This is one reason why we use liquid samples in the continuous NMR setup, as the short  $T_1$  allows for a continuous input of energy from the oscillator coil.

A nonzero  $M_x$  or  $M_y$  is harder to obtain, as it requires a majority of the moments to be precessing in lock-step with each other. Even so,  $M_x$  and  $M_y$  cannot be constant in time, but at best oscillate between positive and negative values at the Larmor frequency. If one can contrive to force the moments to have a net projection onto, say, the  $x$ -axis (and indeed one can—we’ll see how), then the resulting oscillating  $M_x$  would decay because variation in the local magnetic field, some of which is due to the field of neighboring moments, would cause different moments to precess at different rates. This is called “spin-spin dephasing”, and the characteristic time for this process is called  $T_2$ , the “spin-spin” or “transverse” relaxation time. In most cases,  $T_2$  is shorter than  $T_1$ ; in solids it is much shorter, but in low viscosity liquids (like water or light oils)  $T_2$  approaches  $T_1$ .

With these two relaxation processes in mind, consider how one would detect the signal of these precessing and relaxing moments. Since they are magnetic, an obvious choice would be to use a pickup coil. The coil also needs to be oriented *transverse* to the static field in order to sense the precession, since in an orientation parallel to  $\vec{B}_0$ , the coil would only be sensitive to a slight change in flux from a non-oscillatory  $M_z$ ; whereas the transverse component  $M_x$  or  $M_y$  will oscillate between positive and negative values at the Larmor frequency  $\omega_0$ .

This arrangement is depicted schematically in Fig. 4, which is taken from the article by Hahn [4]. The top of the figure shows that at  $t = 0$ , all of the moments are aligned along the  $+z$  direction and the pickup coil has its axis along the  $y$ -axis. The static field  $\vec{B}_0$  points out of the page toward the viewer, thus the moments will precess in the clockwise direction (following the sense of  $\vec{M} \times \vec{B}_0$ ). The right side of the figure depicts the voltage measured across the pickup coil. Faraday’s law requires that this voltage be proportional to the *rate of change* of the flux

through the coil, and it is a simple matter to prove that the maximum signal from the coil will occur at  $t = 0$  in this setup. (Try it: let the field in the coil be  $\mu_0 \vec{M}$  which is rotating about the  $z$ -axis at  $\omega_0$ , and calculate the rate of change of the flux,  $d\Phi/dt$  from this.)

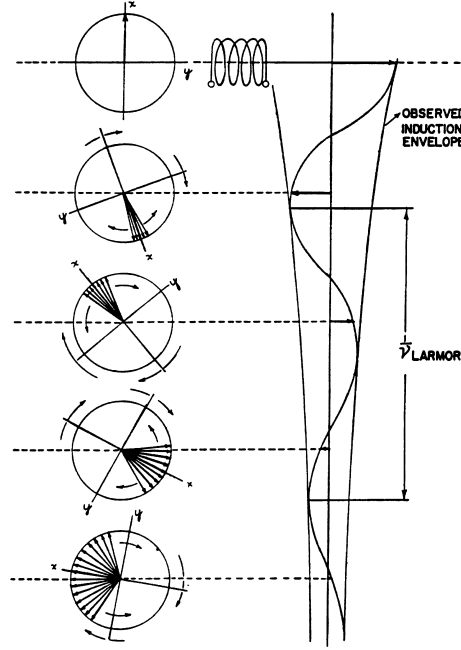


Figure 4: Induction signal measured by a pickup coil in the transverse plane following orientation of moments along the  $x$ -axis. Taken from the article by Hahn [4].

As the moments precess, the induced voltage oscillates at the Larmor frequency ( $\nu_{\text{LARMOR}}$  in the figure), and also decays. The decay is due to the spin-spin dephasing, shown as a spreading of the moments away from the principal rotating  $x$ -axis—the  $T_2$  process.

While the overall decay of the signal from the pickup coil comes from spin-spin relaxation, experimentally a third effect is often more predominate: spin-spin dephasing due to inhomogeneities in the external field  $\vec{B}_0$  over the volume of the sample. Taken together, the effects lead to a combined relaxation time  $T_2^*$  defined as

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma \Delta B_0, \quad (12)$$

where  $\Delta B_0$  is the variation in  $B_0$ . In effect,  $\gamma \Delta B_0$  is equal to a spread in Larmor frequencies  $\Delta \omega_0$  which, all else being equal, would cause spin-spin dephasing in a characteristic time of  $1/\Delta \omega_0$ . Similarly, one can assign an effective resonance width  $\Delta \omega_{\text{eff}} \sim 1/T_2^*$ .

In summary, two processes are involved in the relaxation of the net magnetization: 1) spin-lattice relaxation, which involves energy exchange with the environment, and is characterized by the time constant  $T_1$ ; 2) spin-spin relaxation, characterized by a time constant  $T_2$ , which is caused by loss of the phase relationships among the various moments and is due to the fact that each spin experiences a slightly different local magnetic field. In a practical setup, the measured signal comes from the oscillating transverse magnetization, characterized by a time constant  $T_2^*$  that is related to  $T_2$ , but is typically dominated by inhomogeneities in the static

field  $\vec{B}_0$ . It is important to note that the recovery to equilibrium following saturation follows  $T_1$ , but the decay of the detected *signal* follows  $T_2^*$ .

The two relaxation times  $T_1$  and  $T_2$  are related to each other. For non-viscous liquids, in which the molecules undergo very rapid motion on a small scale, theory predicts that  $T_1 \approx T_2$ . When the material becomes more viscous (like heavy oil or grease), there is a divergence between  $T_1$  and  $T_2$ , with  $T_2$  becoming shorter than  $T_1$  [3, pp. 210-214]. As required by Eq. (12),  $T_2^* < T_2$ , and in practice  $T_2^* \ll T_1$ .

### 1.3 The two experimental methods

In the continuous NMR method, the RF excitation producing the rotating  $\vec{B}_1$  field is applied all of the time. The resonance is created by having the  $\vec{B}_0$  field swept slowly through the value which satisfies Eq. (5). A pickup coil surrounding the sample detects the resonance, and this signal is mixed with the fixed RF signal to create “beats” (the term for the modulation of two signals which have nearly the same frequency). The effect of the beats can be seen on an oscilloscope. Once the resonant signal is found, the relationship between the magnetic field and the resonant frequency is fixed, and depending on the givens, the information can be used to extract  $B_0$  itself,  $\gamma$ , or related quantities. One can also crudely measure  $T_2^*$  by looking at the decay of the beat signal.

In the pulsed NMR method, the RF excitation is applied to the sample in a series of short bursts, or pulses. The application of the RF field for a short time (the “pulse width”) allows the applied torque to rotate the net magnetization  $\vec{M}$  by a specific amount. For example, one can apply a pulse of RF field to rotate all moments by  $90^\circ$ . If this pulse is applied to a sample initially at equilibrium with a net magnetization  $\vec{M} = M_z \hat{\mathbf{k}}$ , then  $\vec{M}$  will become  $M_z \hat{\mathbf{i}}$  (i.e., the same magnitude of magnetization now pointing in an orthogonal direction), which will then precess about the  $z$ -axis. The pickup coil will see a signal like that shown in Fig. 4 as the individual magnetic moments  $\vec{\mu}_i$  get out of phase with each other and as the magnetization decays back to its equilibrium state. A pulse which accomplishes this trick is called a “ $\pi/2$  pulse”, and the signal seen as a consequence is called the “free induction decay”. A pulse of a longer duration can flip the net magnetization completely:  $M_z \hat{\mathbf{k}} \rightarrow -M_z \hat{\mathbf{k}}$ ; this type of pulse is called a “ $\pi$  pulse”. Interestingly, the free induction decay signal immediately following a  $\pi$  pulse is *zero* since there is no net transverse component of the magnetization available to induce such a signal.

The real utility of the pulse method comes from using a *sequence* of pulses. By such sequences, one can measure accurately and independently  $T_1$  and  $T_2$ , and also compensate for the effects of field inhomogeneity. The discussion of pulse sequences and their effects are taken up in more detail in the next sections.

## 2 The pulsed NMR experiment

This experiment is performed with the TeachSpin PS1-A pulsed nuclear magnetic resonance (PNMR) spectrometer. This instrument was designed for use in a teaching laboratory. Its modular design separates the basic functions (oscillator and RF amplifier, RF receiver/detector and pulse programmer) of a PNMR system, allowing the experimenter to investigate and understand the function of each module, and how and why the interconnections between the modules are made.

The pulsed NMR technique involves a number of subtle and somewhat complex ideas and methods. One way to learn it is to read through the theory, as laid out here or in the PS1-A manual, and then use the instrument to quickly make the measurements. Another way, perhaps more instructive, is to learn the theory and technique at the same time. In what follows, we will assume that you will proceed along the second way. If, however, you have already read the theory, and would prefer to move directly to the measurement tasks, you can turn to Section 3 (p. 28) for a summary of those.

The instruction manual for the PS1-A gives complete details on the instrument and its operation. Our instructions will focus on the particular operations needed to make the measurements. We will refer to relevant passages in the manual by means of a marginal note ( $\rightarrow$ ). Copies of *Like this.* the manual are available in the lab and online at the course website.

### 2.1 Pulses and Free Induction Decay

We begin by stating a curious mathematical result. Recall that the magnetic moments in our system precess under the influence of the torque from a magnetic field, Eq. 3. This precession occurs with a precession angular frequency  $\omega_0 = \gamma B_0$ . If we were to transform our coordinate system to one which rotated along with this precession, i.e., we translate coordinates  $x$ ,  $y$  and  $z$ , as measured in the fixed lab reference frame to  $x'$ ,  $y'$  and  $z'$  in the rotating frame, where

$$\begin{aligned}x' &= x \cos \omega_0 t - y \sin \omega_0 t, \\y' &= x \sin \omega_0 t + y \cos \omega_0 t, \\z' &= z,\end{aligned}$$

we would find that the magnetic field  $B_0$  *vanishes!* This must be true, since in this rotating frame (at exactly  $\omega_0$ ), we would see *no precession.*

Now consider what would happen if we apply a time-dependent magnetic field  $\vec{B}_1(t)$  which rotates at exactly the frequency  $\omega_0$  and lies in the  $x$ - $y$  plane, e.g.,

$$\vec{B}_1(t) = (B_1 \cos \omega_0 t) \hat{\mathbf{i}} - (B_1 \sin \omega_0 t) \hat{\mathbf{j}}.$$

In the rotating frame,  $\vec{B}_1(t)$  would appear to be a constant. The net effect, as seen from the rotating frame, would be a precession of the moment about an axis lying in the  $x'$ - $y'$  plane at a frequency  $\omega_1$  equal to  $\gamma B_1$ .

Assume, for an illustration, that we have a moment  $\vec{\mu}$  initially pointing along the  $+z'$  (also the  $+z$ ) axis, collinear with  $\vec{B}_0$ , and that we turn on  $\vec{B}_1(t)$  at exactly  $t = 0$ . In the rotating frame,  $\vec{B}_1(t) = B_1 \hat{\mathbf{i}}'$ , where  $\hat{\mathbf{i}}'$  is the unit vector along the rotating  $+x'$  axis. Thus, we would see  $\vec{\mu}$  rotate about the  $+x'$  axis, initially tilting toward the  $+y'$  axis (according to  $\mu \hat{\mathbf{k}}' \times B_1 \hat{\mathbf{i}}'$ ). Now

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pp. 5-7*



imagine that we turn off  $\vec{B}_1(t)$  right at the point where  $\vec{\mu}$  lies along the  $+y'$  axis. In the lab frame, the motion of the tip of the vector corresponding to  $\vec{\mu}$  would look like a spiral ending with the moment lying in the  $x-y$  plane precessing about the  $z$  axis. This motion is shown in Fig. 5 which is taken from the article by Hahn [4].

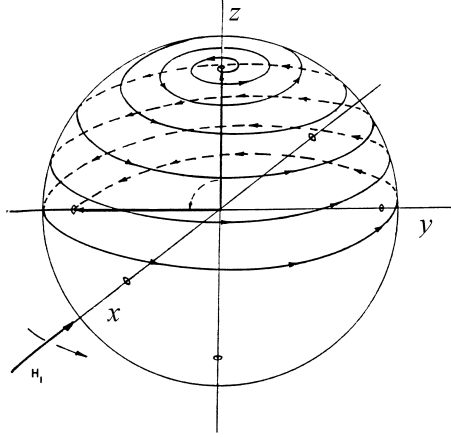


Figure 5: The classical motion of a moment  $\vec{\mu}$  under the influence of a static  $\vec{B}_0$  and rotating  $\vec{B}_1(t)$  field. From Hahn [4].

Now assume that the same time-dependent field (static  $\vec{B}_0$  + rotating  $\vec{B}_1(t)$  for a short time) is applied to a whole collection of moments initially at equilibrium in the static  $\vec{B}_0$  field. The same motion followed by our single moment  $\vec{\mu}$  will now be executed by the net magnetization  $\vec{M}$ , because at equilibrium,  $\vec{M} = M\hat{k}$ . The result?  $\vec{M}$  is tilted into the  $x-y$  plane and precesses about the  $z$ -axis; a pickup coil lying in this plane would detect the induced voltage, following the discussion in Section 1.2. This is the “free induction decay” (FID) signal.

The rotation of  $\vec{M}$  is accomplished by turning the rotating field on and off: a pulse. Since  $\vec{M}$  is rotated by  $90^\circ$ , we call such a pulse a “ $\pi/2$  pulse”. The duration of a  $\pi/2$  pulse is equal to the period of precession  $t_1$  due to  $\vec{B}_1$  divided by 4. From the relation  $\omega_1 = \gamma B_1$ , and because  $\omega_1 = 2\pi f_1 = 2\pi/t_1$ , we obtain the time for the  $\pi/2$  pulse:

$$t_{\pi/2} = \frac{1}{4}t_1 = \frac{\pi}{2\gamma B_1} \quad (13)$$

To create a  $\pi/2$  pulse and to see the resulting signal from a pickup coil, we need the following apparatus:

- A steady magnetic field  $\vec{B}_0$ , here supplied by a permanent magnet.
- A pickup coil, with its axis perpendicular to the direction of  $\vec{B}_0$ , along with electronics to sense the RF signal created by the coil: a receiver and detector circuit.
- An excitation coil to create the rotating  $\vec{B}_1(t)$  field, with its axis also perpendicular to  $\vec{B}_0$ , along with electronics to create an alternating RF current of sufficient strength: an RF oscillator and amplifier. (Note: the excitation coil in our (and most) apparatus actually produces a *linear* oscillating magnetic field. Such a field is equivalent to two counter-rotating fields. The field that rotates in the “wrong” direction only causes a

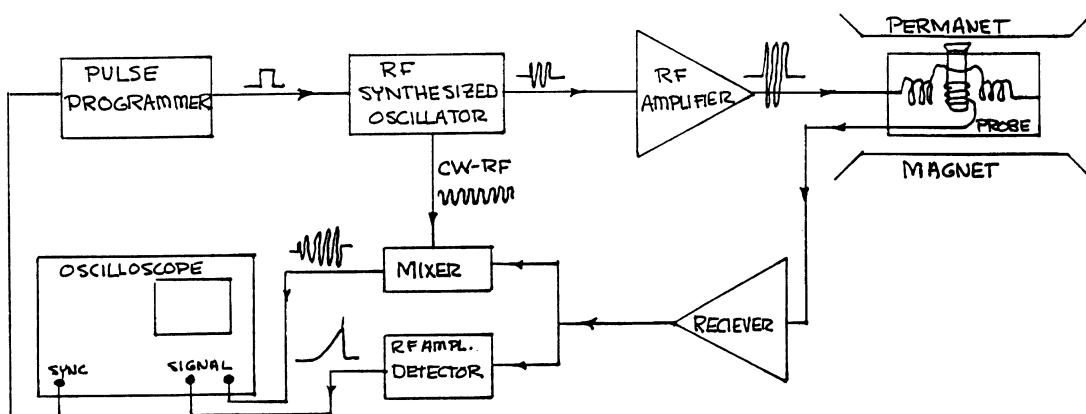


Figure 6: Block diagram of the PS1-A Pulsed NMR apparatus.

negligibly small perturbation to the measured angular rotation frequency—the “Bloch-Siegert shift”).

- Electronics which can allow one to tune the oscillator to the resonant frequency  $f_0$ : a “mixer” circuit which produces a signal showing the difference between the oscillator and receiver signals.
- Electronics which can act as a switch to turn the RF current on and off in a carefully controlled manner: a “pulse programmer”.
- And, finally, a sample containing moments: the protons (hydrogen nuclei) in water and hydrocarbons.

This apparatus is supplied by the PS1-A system, whose block diagram is shown in Fig. 6.

PS1-A  
p. 15

### 2.1.1 Operation of the pulse programmer

You should start by learning to operate the pulse programmer module of the apparatus. The pulse programmer creates logic-level pulses (0-4V) which are used by the other electronics to control the application of the RF pulse and detection of the NMR signal.

The front panel of the pulse programmer is shown in Fig. 7. The programmer creates two types of pulses, called *A* and *B*. To observe free induction decay, you need only use *A* pulses, but we will use the *B* pulses later on, so this exercise will look at both types.

Details of the controls are given in the PS1-A manual, here we give a brief overview of the pulse programmer function.

PS1-A  
pp. 17-20

- Type *A* pulses are controlled by the A-WIDTH knob—to set the pulse duration—and the REPETITION TIME controls—to set how often the pulses occur. The REPETITION TIME controls are operational only when the MODE switch is set to INT (internal). The other settings of the MODE switch allow a pulse to be initiated by an external signal (into EXT START) or by the press of a button (MAN START).

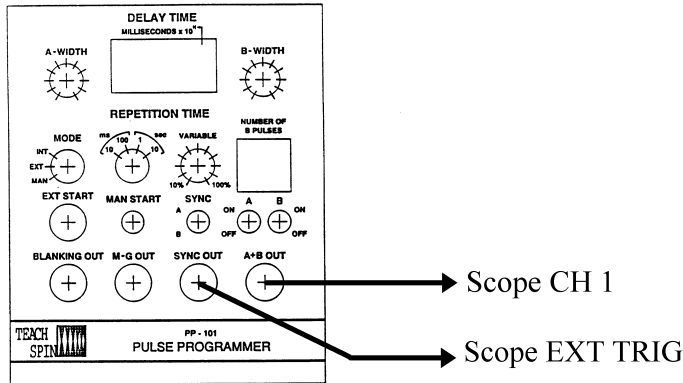


Figure 7: Diagram of connections needed to examine output of the pulse programmer.

- Type *B* pulses are coupled to *A* pulses. They are controlled by the B-WIDTH knob—to set the pulse duration, the NUMBER OF B PULSES thumbwheel switches—to set how many *B* pulses occur, and the DELAY TIME thumbwheel switches—to set how long after the *A* pulses *B* pulses occur and the subsequent time between additional *B* pulses.
- The SYNC OUT connector and SYNC switch allows a very short ( $\approx 0.2 \mu\text{s}$ ) pulse to be used to trigger an oscilloscope at the start of a pulse or pulse sequence. Typically, one connects SYNC OUT to the external trigger input on the scope.
- The BLANKING OUT connector is used to disable the RF detector when the *A* and *B* pulses occur in order to prevent overloading the detector amplifier. The M-G OUT connector sends a signal to the RF oscillator to enable the “Meiboom-Gill” type of multipulse sequence (see Section 2.2.2).

First, we will look at type *A* pulses only. **Disconnect *all* cables from the front panel of the PS1-A except the two cables connected to the magnet and sample holder assembly.** *PS1-A*  
*p. 25* Turn on the power to the PS1-A (the switch is on the back of the case), and turn on the oscilloscope. Connect SYNC OUT to the scope’s EXT TRIG input, and connect A+B OUT to the scope’s CH 1 input. Set the oscilloscope to trigger on “EXT” with a level of +1.4 volts and “NORMAL” triggering mode; set the CH 1 sensitivity to 2V/Div; set the timebase to 20  $\mu\text{s}$ /Div. First, look at *A* pulses only. Set the pulse programmer controls as follows:

A-WIDTH:	half-way (12 o’clock)
MODE:	INT
REPETITION TIME:	10 ms, VARIABLE at 10% ( $\approx 1$ ms)
SYNC:	A
A:	on
B:	off

If all is working correctly, you should see a trace on the oscilloscope similar to that in the lower trace of Fig. 8. Vary the A-WIDTH knob and note what happens. Then turn the A-WIDTH all the way clockwise, and increase the timebase on the scope to 1 ms/Div. You should see multiple pulses, spaced a couple of milliseconds apart. Note the effects when you change the REPETITION TIME controls.

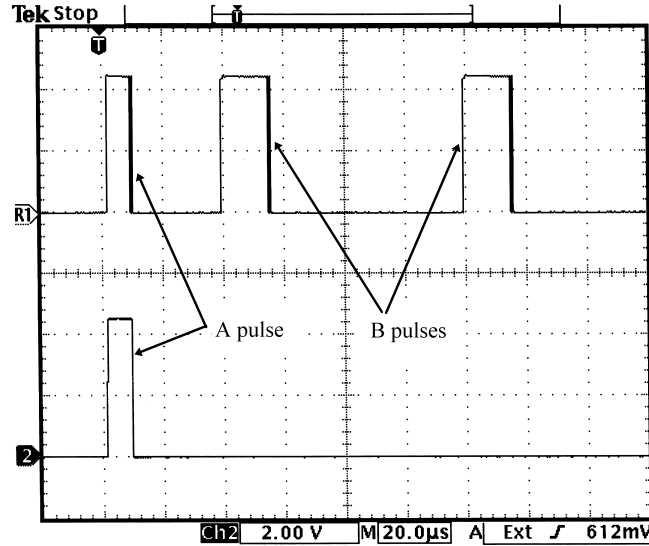


Figure 8: Signals from the pulse programmer. Lower trace: *A* pulse only. Upper trace: a pulse sequence consisting of an *A* pulse followed by two *B* pulses.

Now, we will look at a pulse sequence. Reset the scope timebase to  $20\ \mu\text{s}/\text{Div}$ , and then make *PS1-A*  
*pp. 25-26*

- A-WIDTH: one-quarter-way (9 o'clock)
- B-WIDTH: half-way (12 o'clock)
- REPETITION TIME: 10 ms, VARIABLE at 10%
- NUMBER OF B PULSES: 01
- A: on
- B: on
- DELAY TIME:  $50\ \mu\text{s}$  ( $0.05 \times 10^0$ )

You should see two pulses on the scope, with the second pulse about twice as wide as the first pulse. Now, play around: vary both the A-WIDTH and B-WIDTH knobs and the DELAY TIME settings and note the results.

Next, look at the effect of setting the NUMBER OF B PULSES to a number greater than 1. In *PS1-A*  
*pp. 26-27* particular, pay attention to the effect of the DELAY TIME settings on multiple *B* pulses. It is important to see that the time between the *A* pulse and the first *B* pulse is one-half of the time between subsequent *B* pulses, and that the DELAY TIME setting is equal to the time between the leading edges of the *A* and first *B* pulse. See if you can reproduce the waveform shown in the top trace of Fig. 8. Also explore the REPETITION TIME settings, and expand the timebase to see multiple pictures of multiple pulse sequences.

### 2.1.2 Observation of free induction decay

Once you have thoroughly understood the operation of the pulse programmer, you are ready to observe an actual NMR signal. We will start with the simplest arrangement, a single  $A$  pulse, with the apparatus tuned to produce a  $\pi/2$  pulse in order to observe the free induction decay (FID) signal.

**Exercise 1** Calculate the time needed for a  $\pi/2$  pulse from Eq. (13), given  $\gamma = 2.765 \times 10^4$  rad/s-gauss and the magnetic field  $B_1 \approx 12$  gauss, according to the manufacturer.

PS1-A  
p. 20

**IMPORTANT:** you will need to decrease the pulse repetition rate (increase the repetition time) by quite a bit. If you do not do this, the average power output from the RF amplifier may be too high, which will cause it to overheat and shut itself off. If you suddenly hear the spectrometer unit emit a high-pitched alarm, you should shut the power off (switch on back), increase the pulse repetition time to 0.5–1.0 seconds, and wait 60 seconds before turning the unit back on (so that it can cool off).

The modules on the spectrometer are described here. Set the controls as indicated.

**15 MHz Receiver** This module senses the RF signal produced by the sample-probe coil, amplifies it and rectifies it. The rectified signal is sent to the oscilloscope. The unrectified RF signal is sent to the mixer in order to optimize the oscillator frequency.

PS1-A,  
pp. 22-24

GAIN:	about 30%
BLANKING:	on
TIME CONST:	.01 ms
TUNING:	12 o'clock

**Pulse Programmer** You want to set the controls to make only  $A$  type pulses. Then set the programmer controls:

A-WIDTH:	Set to calculated $t_{\pi/2}$ (use scope)
B-WIDTH:	Fully CCW
NUMBER OF B PULSES:	00
REPETITION TIME:	1 s, VARIABLE at 10-20% ( $\approx 100$ ms)
SYNC:	A
A:	on
B:	off

**15 MHz OSC/AMP/MIXER** This module has three separate circuits in one box. The 15 MHz oscillator is controlled by the FREQUENCY ADJUST knob and the COARSE/FINE switch which changes the significant digit incremented by the knob. The oscillator signal is fed internally to the input of the power amp which is turned on (or “gated”) by the signal going into A+B IN. The output of the power amp, RF OUT is connected to the sample probe excitation coil and delivers an RF power of 150 watts peak power. The M-G IN and M-G switch are used to synchronize the phase of the RF signal with the gating in order to implement the “Meiboom-Gill” type of multipulse sequence, as described in Section 2.2.2. Set the controls as follows:

PS1-A  
p. 20

FREQUENCY:	14.7000
CW-RF:	on
M-G:	on

Now connect the modules together and to the oscilloscope following the diagram shown in Fig. 9. Use the short cables to connect one module to another, and use the long cables to make connections to the oscilloscope. Connect the DETECTOR OUT to CH 1 of the digital oscilloscope, and the MIXER OUT to CH 2. Set the oscilloscope to trigger on "EXT"; set the CH 1 sensitivity to 2V/Div; set the CH 2 sensitivity to 5V/Div; set the timebase to 40–50  $\mu\text{s}/\text{Div}$ .

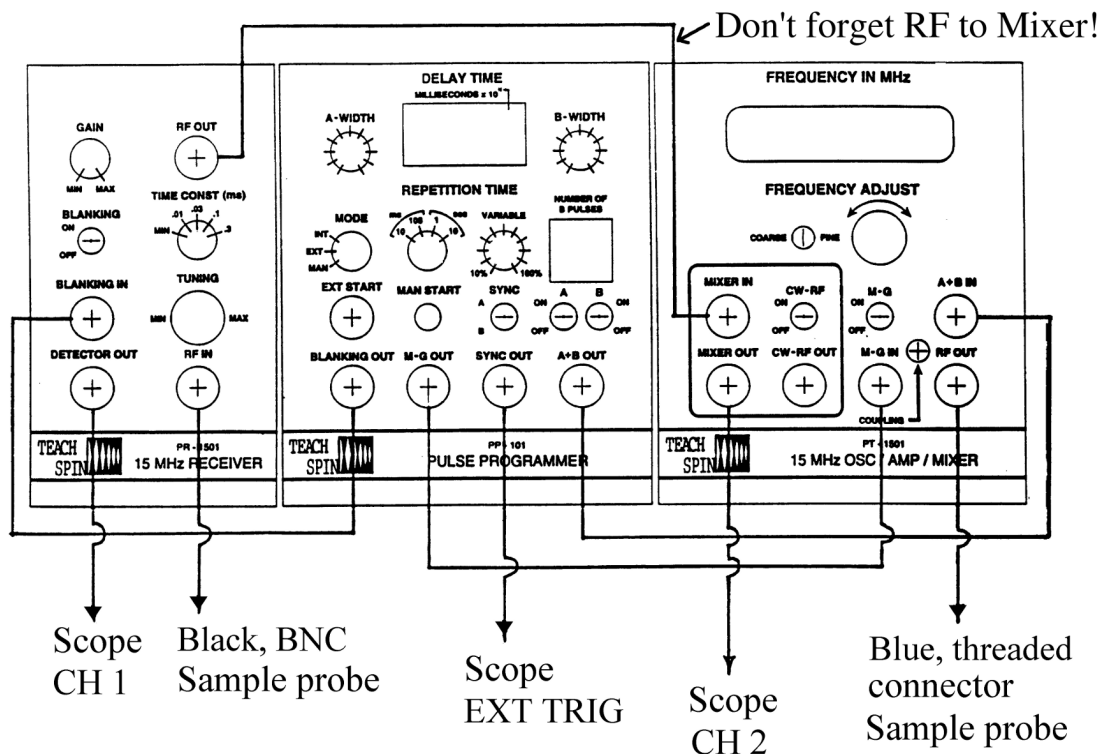


Figure 9: Diagram of connections on the PS1-A spectrometer to make pulsed NMR measurements.

Make sure that the O-ring on the sample vial is 1.5 inches from the bottom and carefully lower the mineral oil sample into the sample holder inside the magnet assembly.

After some adjustment of the oscilloscope, you should observe traces that bear some resemblance to those in Fig. 10. If you don't get anything like Fig. 10 (or anything at all), check the connections on the PS1-A and the switch and knob settings. The CH 1 signal (lower trace) is the free induction decay (FID). This signal is half of the envelope of the RF oscillations generated by the precession of the net magnetization in the  $x$ - $y$  plane. It is the envelope (which represents the magnitude of the net magnetization) and not the individual oscillations that is of interest here. (A rough picture of the RF oscillations can be seen in Fig. 9.2 in the PS1-A manual.) The signal on CH 2 (upper trace) is the mixer output. The oscillations on this signal, also known as "beats", are at the difference frequency between the detected signal (due to the precession of the net magnetization in the  $x$ - $y$  plane) and the frequency of the RF oscillator.

PS1-A  
pp. 22-23

Adjust the frequency on the oscillator to reduce the frequency of the beats on the mixer output

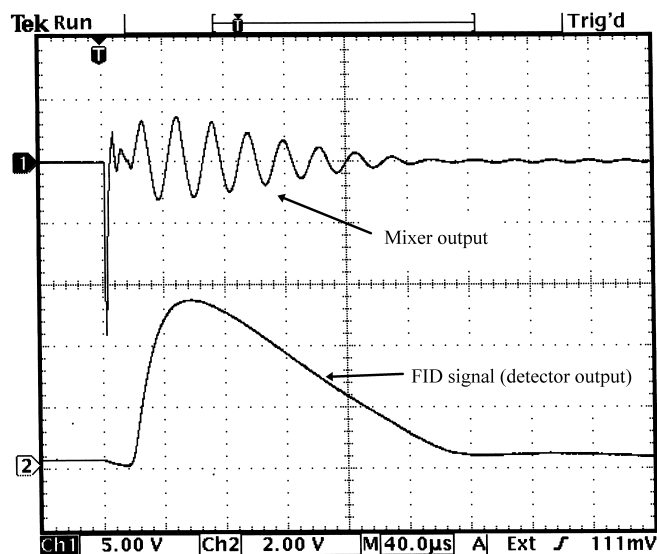


Figure 10: Signals of free induction decay. Upper trace: mixer output showing beats indicating the frequency difference between the resonance frequency and the oscillator frequency. Lower trace: detector output showing the FID signal, which is the positive amplitude envelope of the RF signal obtained from the pick-up coil.

to a minimum. Figure 11 shows a collection of mixer output signals for different oscillator frequencies. The goal of your adjustment is to make the number of oscillations, or zero-crossings, go to zero; the initial bump in the signal is not important. When the beats are at a minimum, you can adjust the TUNING knob to maximize the amplitude of the FID signal.

Finally, pull the sample out of the holder and slide the O-ring down a few millimeters. Then *slowly* lower it back into the sample holder, pressing down so as to scoot the O-ring along the sample vial, while watching the FID signal on the scope. The signal will be strongest when the sample material is centered in the magnetic field. You should try to adjust the position of the O-ring to maximize the FID signal.

**Exercise 2** Now tune the A pulse width to maximize the FID signal in the following manner: turn the A-WIDTH knob completely counterclockwise (the FID signal will diminish), and then slowly turn it clockwise until the FID signal is largest, but before it starts to drop again. (You will see the FID signal vary periodically in intensity as you turn the A width up; this is explained below.) Measure the A pulse width (you will need to move some connections around) and compare it to the width you calculated earlier. No answer the following:

- What value of  $B_1$  would give the measured pulse width?
- What would be the frequency  $f_1 = 1/t_1$  of rotation of this field? See Eq. (13).
- How many rotations about the  $z$  axis would occur between the start and stop of the  $\pi/2$  pulse? See Fig. 5.

The pulse width you have just measured is the pulse width needed for a  $\pi/2$  rotation of the net magnetization  $\vec{M}$ . The decay of the FID signal depends on  $T_2^*$ , as noted in the introduction,

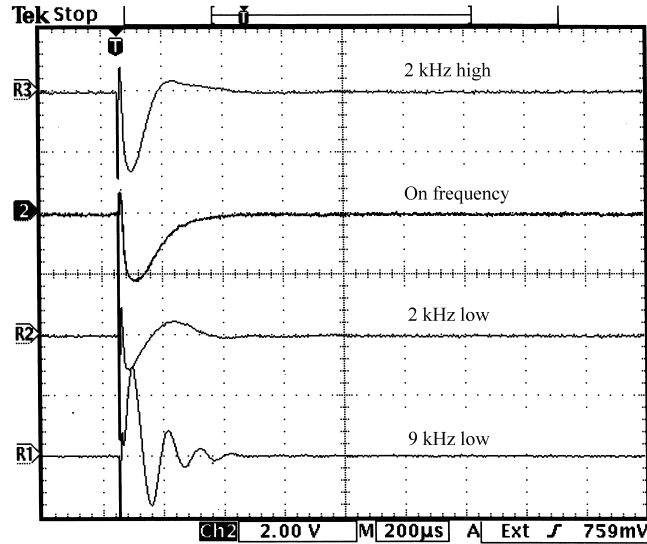


Figure 11: Signals from the mixer output for different oscillator frequencies near resonance. Traces from the bottom, moving up: 9 kHz low (R1), 2 kHz low (R2), on resonance (2), 2 kHz high (R3). (Note: these traces were taken with the M-G switch OFF.)

but is also dependent on the time constant of the detector. You may wish to see what different settings of the TIME CONST switch do to the FID signal. You may also notice that the FID signal does not decay exactly following an exponential curve; this is because the signals from the different precession frequencies mix together, and the resulting signal is more complex than a simple dying-off of the transverse magnetization. As you will see,  $T_2^*$  is *much* shorter than either  $T_2$  or  $T_1$ , indicating that magnetic field inhomogeneity is fairly significant in this apparatus.

Now explore what happens if you *increase* the A pulse width beyond  $t_{\pi/2}$ . You should first see the FID signal decrease, nearly to zero, and then increase again. Measure the pulse widths for the pulse that gives a minimum FID signal and the pulse that gives the following maximum.

**Exercise 3** How are these pulses related to  $t_{\pi/2}$ ? Discuss the relationship between these pulses, the rotation of  $\vec{M}$ , and the resulting FID signal. To help you think about this, remember that the size of the FID signal is proportional to the projection of  $\vec{M}$  onto the  $x$ - $y$  plane.

Technical note: The field of the permanent magnet changes in time (due to changes in the temperature of the magnet) and thus the resonant frequency will change, and beats will reappear on the mixer output signal. You will need to adjust the oscillator frequency from time to time to minimize the beats. It is typical for the resonant frequency to vary in the range of 14.7–14.8 MHz. PS1-A  
p. 16

## 2.2 Pulse sequences and measurements of $T_1$ and $T_2$

Now we will see the real power of the pulsed NMR method in its ability to measure the longitudinal (spin-lattice) relaxation time constant  $T_1$  and the transverse (spin-spin) relaxation time  $T_2$  even when the static magnetic field  $\vec{B}_0$  is not very uniform.



### 2.2.1 Measuring $T_1$ : 2 pulse sequence

The amplitude of the FID signal induced by a  $\pi/2$  pulse is proportional to the initial longitudinal magnetization  $M_z$ . Immediately following a  $\pi/2$  pulse,  $M_z \approx 0$ , which you could confirm by applying another  $\pi/2$  pulse at that time and noting that the FID signal was zero. (Indeed, you will have done this already if you think of what a pulse of  $2 \times t_{\pi/2}$  does!) It takes a while for  $M_z$  to recover its equilibrium value, and if you hit the sample with another  $\pi/2$  pulse before equilibrium has been reestablished, then this second FID signal will be weaker than the first one.

The longitudinal magnetization relaxes according to an exponential function:

$$M_z(t) = M_0 - (M_0 - M_i) e^{-t/T_1}, \quad (14)$$

where  $M_0$  is the equilibrium value of  $M_z$  and  $M_i$  is equal to  $M_z$  at  $t = 0$ . One way of estimating  $T_1$  suggested by Eq. (14) is to decrease the time between successive  $\pi/2$  pulses until you see the FID signal drop by about 1/3 (i.e.,  $1/e$ ) of its “equilibrium” value. You can see this by letting  $M_i = 0$  (what you get after a  $\pi/2$  pulse) in Eq. (14) and calculating  $M_z(t = T_1)$ . Try this: reduce the REPETITION TIME and see how the FID signal behaves. Can you make an estimate of  $T_1$  by this method? (You may find that you cannot make the FID signal reduce by 1/3 if  $T_1$  is too short. Don’t sweat it; this method is merely qualitative.)

A more elegant measurement of  $T_1$  may be accomplished by a two pulse sequence. If one applies a longer pulse—a  $\pi$  pulse—the net magnetization  $\vec{M}$  can be *inverted*:  $M_0 \rightarrow -M_0$ . The decay of  $M_z$  can be tracked by applying subsequent  $\pi/2$  pulses at varying intervals after the  $\pi$  pulse, since the FID signal is proportional to  $M_z$  at any time. Of particular interest is the point at which  $M_z$  momentarily vanishes, or “crosses zero” in its decay from a net negative value to the equilibrium positive value.

This pulse sequence is illustrated in Fig. 12, which is taken from reference [5]. In the figure, we see that a  $\pi$  pulse initially inverts the magnetization, and that a  $\pi/2$  pulse interrogates the magnetization at a time interval “TI” later.

Since the zero crossing point is easily found, we will use this method to measure  $T_1$  for our samples. The spectrometer should already be configured to observe FID pulses (see Section 2.1.2 for settings and Fig. 9 for connections). The strategy is to set up the *A* pulse so that it rotates the net magnetization by  $\pi$ , and then a single *B* pulse so that it rotates the net magnetization by  $\pi/2$ .

Set the REPETITION TIME to allow for a comfortably long recovery time, say 1 sec,  $\approx 20\%$  (assuming you are looking at the mineral oil sample). Start with the *A* pulse only (*B* off) and adjust the A-WIDTH, oscillator FREQUENCY and receiver TUNING to maximize the FID signal and minimize the beats on the mixer output. Next, increase the *A* pulse width to *minimize the FID signal*. This is the pulse width that rotates the net magnetization by  $\pi$ . (As an option you can measure the  $\pi/2$  and  $\pi$  pulse widths to check the ratio.)

NOTE: The minimization of the FID signal with a  $\pi$  pulse is more sensitive to both the pulse width and the tuning of the oscillator to resonance than the maximum which you see with a  $\pi/2$  pulse. You may find that it is hard to make the FID signal completely disappear as you turn the A-WIDTH knob back and forth. This is OK; just try to make the signal as small as possible

Now turn off the *A* switch, turn on the *B* switch and set the NUMBER OF B PULSES to 01.

PS1-A  
pp. 31-33

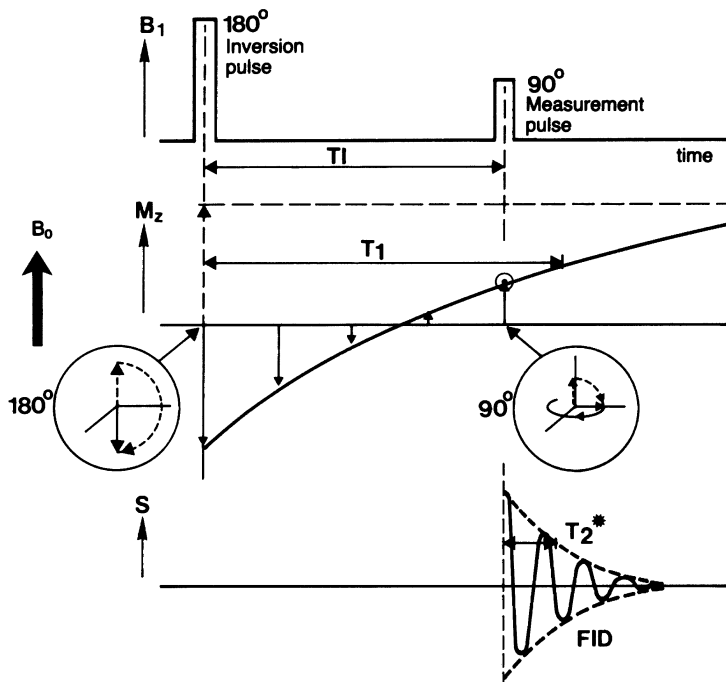


Figure 12: Two pulse sequence showing inversion recovery of  $M_z$ . The FID signal produced by the  $\pi/2$  ( $90^\circ$ ) pulse has an initial amplitude related to the value of  $M_z$  at the end of the interval  $T_I$ . Taken from reference [5].

Switch SYNC to B. Adjust the  $B$  pulse width, starting from fully counterclockwise, to maximize the FID signal (mark on knob should be just below 9 o'clock position). The  $B$  pulse is now rotating the net magnetization by  $\pi/2$ . If this  $B$  pulse comes close in time (relative to  $T_1$ ) after the  $\pi$  pulse (A), the net magnetization will be rotated by  $3\pi/2$  or  $270^\circ$ . Set the DELAY TIME to  $30 \mu\text{s}$  ( $0.03 \times 10^0 \text{ ms}$ ), turn on both A and B switches, set SYNC to A, and confirm that you get a healthy FID signal.

Now set the DELAY TIME between the A and B pulses to several milliseconds. There should now be two bumps on the scope trace, the first one being a weak transient from the  $\pi$  pulse, the second one being the stronger FID signal. As the delay time is increased (millisecond intervals are handy) the amplitude of the FID signal should decrease until at some delay time, it goes away (almost) completely, as shown in Fig. 13. At this point in time, there is no net magnetization, hence no FID signal; in the language of Eq. (10),  $N_+ = N_-$  for a brief moment. You will notice that if you keep increasing the delay time, the FID signal reappears, indicating that  $M_z$  has gone from net negative value to a net positive value, as indicated in Fig. 12.

The delay time for  $M_z$  to decay to 0, may be used to calculate  $T_1$ . Since  $M_z = 0$  is halfway between  $M_z = -M_0$  and  $M_z = +M_0$ , the zero-crossing time interval is equal to the “half-life” of the exponential decay. You can use this fact to calculate  $T_1$ . If you want to work it out, let  $M_i = -M_0$  and  $M_z(t) = 0$  in Eq. (14) and find  $T_1$  in terms of  $t$ . You should find that  $T_1$  is equal to the zero crossing time divided by  $\ln(2)$ .

Big instrumentation hint: For samples of long  $T_1$  you will find that in order to see both the A and B pulse responses you will need to increase the Time/Div setting on the oscilloscope so

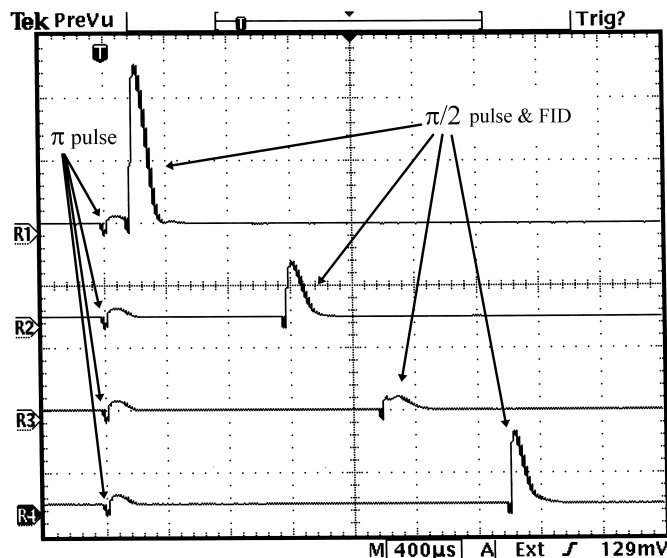


Figure 13: Oscilloscope traces showing zero-crossing method of determining  $T_1$ . The  $\pi$  pulse occurs at the trigger point (T), and the FID signal from the  $\pi/2$  pulse first diminishes as the delay time increases (traces R1 and R2), nearly vanishing at the delay time in the third trace from the top (R3), and then recovers at a later delay time (R4). Sample:  $\text{H}_2\text{O} + \text{CuSO}_4$ ; zero crossing at  $\approx 1.8$  ms,  $T_1 \approx 2.6$  ms.

much that it becomes hard to see the pulses because they become proportionately narrower. But since you are only looking for the DELAY TIME setting which minimizes the FID signal from the  $B$  pulse you can simply switch the SYNC to B, allowing you to view only the FID signal with a comfortable Time/Div setting.

Be careful about repetition times: make sure they are not too short! To see why, try reducing the repetition time to about  $2T_1$  and remeasure  $T_1$  with the shortened repetition time. It will be noticeably shorter. Why is this so?

### 2.2.2 Measuring $T_2$ : spin echoes & a multipulse sequence

You may have noticed, while adjusting the controls to set up the  $\pi$ - $\pi/2$  pulse sequence in the previous exercise, that you saw an additional bump in the scope trace at twice the delay time. This curious artifact was also noticed by Erwin Hahn in 1949 (when he was still a graduate student). Hahn realized that the signal must be due to a “rephasing” of the transverse components of the magnetic moments in the sample, leading to a nonzero transverse magnetization and subsequent FID signal. He called this process a “spin echo” [6]. In this exercise you will learn how to create a spin echo and how to use it to make a good measurement of the spin-spin relaxation time constant  $T_2$ .

Although a variety of pulse sequences can produce an echo signal, the strongest echo is produced by a  $\pi/2$ - $\pi$  pulse sequence. It is also easiest to understand how the transverse rephasing is caused by this particular sequence, which is illustrated in Fig. 14. The pulse sequence and resulting detector signal are shown at the top of the figure. A  $90^\circ$  ( $\pi/2$ ) pulse tips the net magnetization into the  $x$ - $y$  plane, creating the FID signal. This signal decays mainly due to

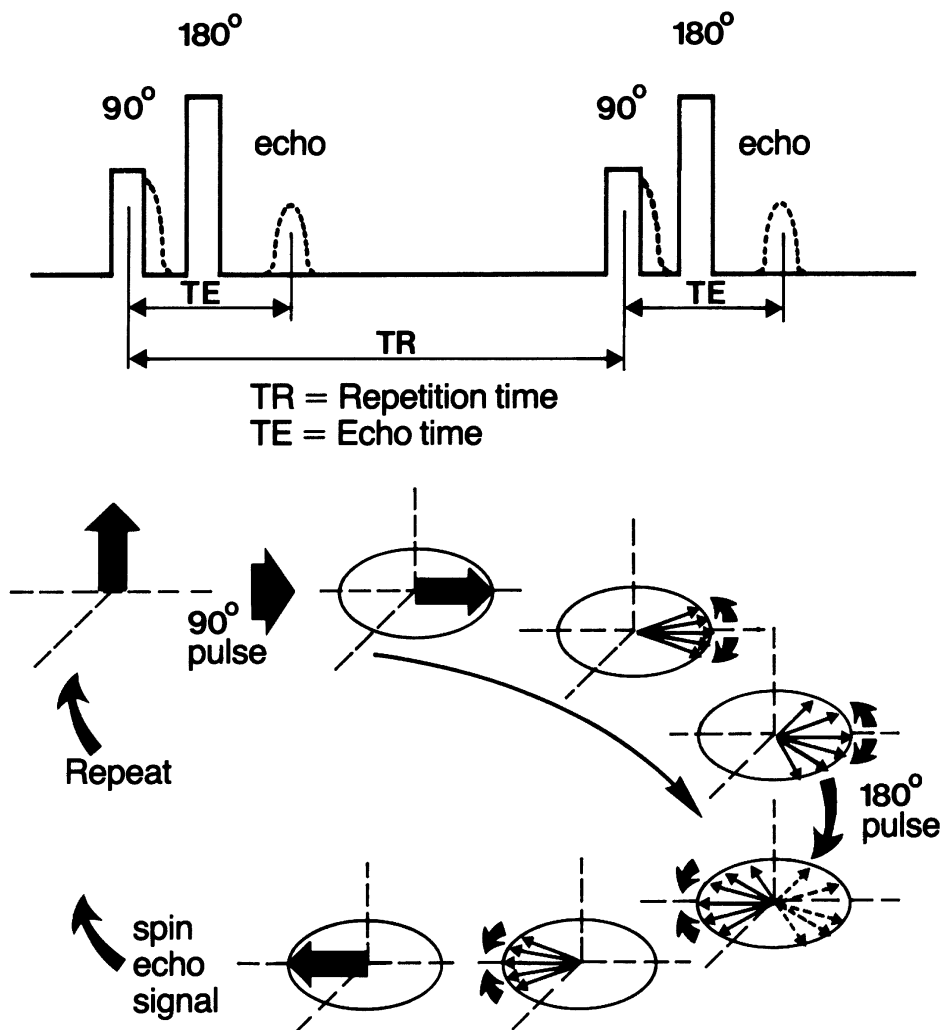


Figure 14: Illustration of how a spin echo is created by a  $\pi/2-\pi$  pulse sequence. From reference [5].

dephasing of the moments as they precess at different rates in a nonuniform  $\vec{B}_0$  field. The lower part of the figure shows this dephasing *from the point of view of the rotating reference frame*. In this frame we see that some moments lag behind the group, while others lead. A  $180^\circ$  ( $\pi$ ) pulse is applied at time  $\tau$  after the  $\pi/2$  pulse. This pulse effectively “flips the pancake” of the collection of dephased magnetic moments about an axis in the  $x$ - $y$  plane. The overall precession of the group continues in the same direction, but now those moments which had lagged the group now lead the group, and vice versa. At time  $2\tau$  (TE in the figure) all of the moments come back into phase, and we see a recovery of the FID signal.

Hahn nicely illustrates the formation of the echo by means of an analogy [4, p. 8]:

Let a team of runners with different but constant running speeds start off at a time  $t = 0$  as they would do at a track meet... At some time  $T$  these runners would be distributed around the race track in apparently random positions. The referee fires his gun at a time  $t = \tau > T$ , and by previous arrangement the racers quickly turn about-face and run in the opposite direction with their original speeds. Obviously, at a time  $t = 2\tau$ , the runners will return together precisely at the starting line.

Before worrying about  $T_2$  and its relationship to spin echoes, first set up the spectrometer so that you can see an echo. The spectrometer should already be configured to observe FID pulses (see Section 2.1.2 for settings and Fig. 9 for connections).

Now you want to set the  $A$  pulse so that it rotates the net magnetization by  $\pi/2$  and then make a single  $B$  pulse so that it rotates the net magnetization by  $\pi$ . Start with just the  $A$  pulse ( $B$  pulses turned off) and adjust the electronics (A-WIDTH, TUNING and FREQUENCY) to maximize the FID signal. Set the repetition time to 1 sec, 30% (again, assuming mineral oil as a sample; with other samples you may need a longer time for full recovery of  $M_z$ ) and make sure that the M-G switch is on. Next, turn on the  $B$  pulses and set the NUMBER OF B PULSES to 01 and the DELAY TIME to 2.5 ms. Finally, adjust the B-WIDTH (starting from fully counterclockwise) to maximize spin echo which occurs at twice the delay time. You should get a scope display similar to that in Fig. 15. PS1-A  
pp. 33

Now note what happens when you increase the delay time. The reduction in the magnitude of the echo signal is due to a loss of “phase memory” among the magnetic moments. This in turn is due to variations in the local magnetic field of each moment *over time*; it does *not* depend on the static variation in the applied  $\vec{B}_0$  field that is responsible for the comparatively short FID decay time. In other words, the reduction in the spin echo amplitude follows  $T_2$ , not  $T_2^*$ . Hahn explains [4, p. 9]:

The decay of the echo may be understood in terms of the race track analogy if it is assumed now that the runners become fatigued after the start of the race. For this reason they may change their speeds erratically or even drop out of the race completely. Consequently, following the second gun shot (the second pulse) some of the racers may return together at the starting line, but not all of them.

In terms of the analogy,  $T_2^*$  depends on the inherent differences in base speeds among the runners; in terms of our collection of moments this is like the different precession speeds of the spins in different parts of the sample. However,  $T_2$  depends on the *changing* of each runner’s speed over time; similarly, each moment will change its precession speed as it feels the fluctuating effects of neighboring moments, diffusing molecules, etc.

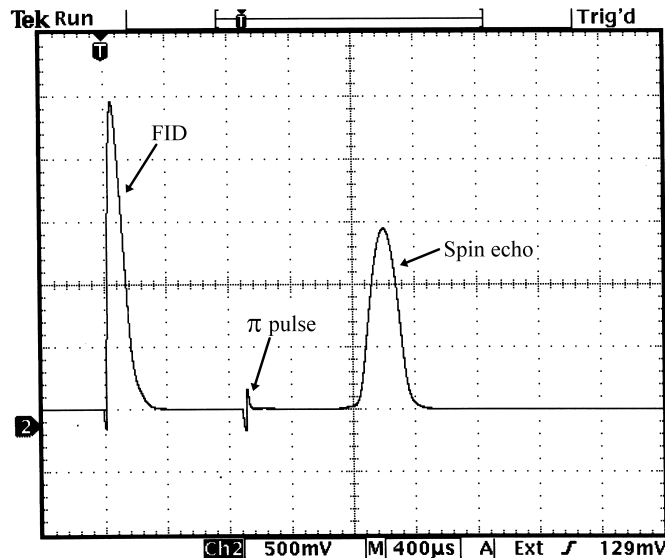


Figure 15: Oscilloscope trace showing one spin echo. The small transient between the initial FID signal and the echo is from the  $\pi$  pulse. Note that the initial FID signal is larger in magnitude than the echo, indicating loss of phase memory among the spins. Sample:  $\text{H}_2\text{O} + \text{CuSO}_4$ .

So, a way to measure  $T_2$  is to track the peak height of the spin echo as a function of the delay time. For example, you could look for the change in delay time which reduces the echo by  $1/2$ , and thus obtain the “half life” of the spin echo.

Unfortunately, this method is still beset by the effects of a non-homogeneous  $\vec{B}_0$  field. If the molecules in the sample (typically a liquid) can diffuse easily to other parts, then the precession speeds of the moments in those molecules will change as they move into regions of different static field. The dephasing of the moments will occur more quickly than it would if the field were uniform.

Hahn was aware of the effects of diffusion in a nonuniform field, and developed a theoretical expression for the amplitude of a spin echo which depended on  $T_2$  as well as the diffusion constant and magnetic field gradient. Later, Carr and Purcell discovered that the effects of diffusion could be minimized if one used a *multipulse* sequence, wherein many successive  $\pi$  pulses followed after the initial  $\pi/2$  pulse [7]. The result of such a sequence is a single scope trace showing many spin echoes. In effect, each echo is like a “start pulse” for the later  $\pi$  pulse that creates a subsequent echo. The decay of the echo amplitudes follows an exponential curve, of time constant  $T_2$  as long as the echo spacing is sufficiently close together relative to the diffusion time. A diagram showing the method of the multipulse sequence is given in Fig. 16 and an example of the scope trace with multiple echoes is shown in Fig. 17.

Use the multipulse sequence method to measure  $T_2$  for the samples. The instrument should already be set up to look at a single spin echo. All you need to do is increase the NUMBER OF B PULSES. Note the effect; you should get a picture like Fig. 17. With more B pulses it may now be easier to optimize the echo signals by fine tuning the A and B pulse widths; do this, and strive for maximum echo amplitudes and minimum between-echo “glitches” (short pulses).

As the NUMBER OF B PULSES is increased, the sweep speed of the scope (time per division) must be reduced to display all the echoes. But as the sweep speed is reduced, so is the sampling

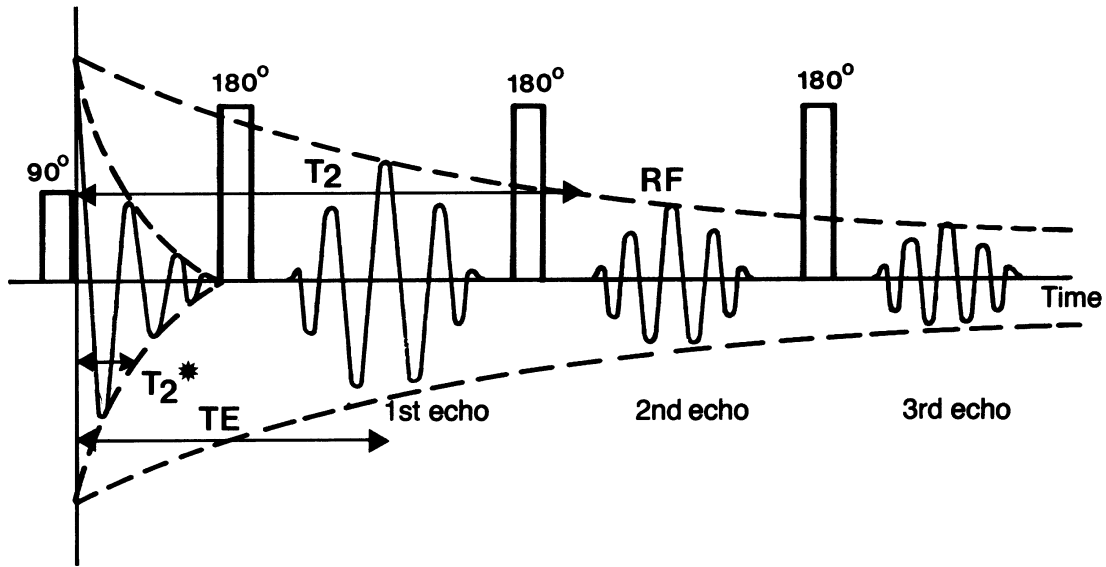


Figure 16: Multipulse spin echo sequence. Later  $180^\circ$  ( $\pi$ ) pulses refocus the spins to produce additional spin echoes following on the first echo. The envelope of the decay follows an exponential in terms of  $T_2$ . From reference [5].

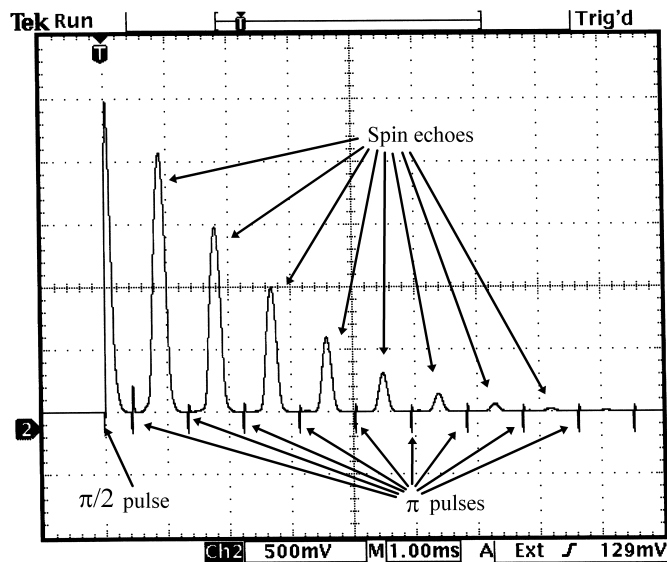


Figure 17: Oscilloscope trace showing many spin echoes. The small transients between the peaks are from the  $\pi$  pulses.  $T_2$  can be measured from the decay of the envelope of the peaks; here we see a half-life time of  $\approx 2.2$  ms, so  $T_2 \approx 3.2$  ms. Sample:  $H_2O + CuSO_4$ .

rate (indicated at the top of the scope screen). If the sampling rate is too low, the echo signals will not be captured accurately. Check this out on the scope with 3 or 4 echoes and the DELAY TIME set to several milliseconds. Reduce the sweep speed of the scope to 25 ms/Div or slower and observe how the amplitude of the echoes is no longer accurately captured. You can work around this limitation by using the scope's "Peak Detect" feature. With this feature, only the most extreme voltage at each pixel time is recorded. The Peak Detect mode is available under the scope's "Acquire" menu.

Also, you may need to increase the repetition time to allow the system to come to equilibrium between pulse sequences. As pointed out in the PS1-A manual, "...each pulse sequence must wait at least 3  $T_1$  (preferably 6–10  $T_1$ 's) before repeating the pulse train." If the repetition time is too short, the FID and echo signals will be reduced. Once you have selected the number of  $B$  pulses for your  $T_2$  measurement, adjust the repetition time so that a slight variation in this time does not affect the amplitude of the echoes. For samples with a very long  $T_1$ , you may get better results by using manual triggering of the pulse sequence. You can do this by setting the MODE switch to MAN, and then firing the sequence with the MAN START button. The scope will hold the most recent waveform indefinitely. PS1-A  
p. 29

Once a satisfactory spin echo sequence has been acquired, time and voltage measurements need to be taken of the maxima of the echoes to map out the envelope. This is most easily accomplished using the paired cursors on the scope (activate the "Cursor" menu for this option) which allow for both time and voltage measurements. It is useful to record the  $\Delta V$  and  $\Delta t$  measurements as well as the absolute values at each echo maximum.

## 2.3 Experiments

Now that you know how to operate the spectrometer and measure  $T_1$  and  $T_2$  accurately, you need to carry out some investigations. Here are some possibilities. You are required to do the first experiment at least two more, but you may do them all.

### *Required Experiment 1: Characteristics of different materials*

Measure  $T_1$  and  $T_2$  for the following materials: mineral oil, Vaseline, glycerine, water, and ethyl alcohol (ethanol). Note: some samples have very long time constants, so you will need to keep a watch on the pulse repetition time and, in the case of  $T_2$ , the number of pulses and associated delay time. If your multipulse envelope does not follow an exponential curve, you have work to do. (Reduce the delay time and increase the number of  $B$  pulses.)

For very long  $T_2$  measurements, you may not be able to see a full half-life ( $T_{1/2}$ ) of decay in the spin-echo envelope. In this case, the best you can do is to measure the initial slope and amplitude of the signal, and from this, estimate  $T_2$  by a linear approximation. Note that the equation  $V(t) = V_0 e^{-t/T_2}$  may be expanded to first order in  $t/T_2$  (when  $t \ll T_2$ ) as  $V(t) \approx V_0(1 - t/T_2)$ . Thus, if you measure the initial height of a peak pattern (to get  $V_0$ ) and then the change of that height over a known time, to get the slope  $\Delta V/\Delta t$ , you can get  $T_2 \approx -V_0/(\Delta V/\Delta t)$ . Caution! This approximation only works if  $\Delta t \ll T_{1/2}$ .

Once you have measured  $T_1$  and  $T_2$  for a variety of materials, compare these results to each other, both across the samples and within each sample. Theory says that low viscosity liquids should have long time constants, with  $T_1 \approx T_2$ . It also says that as the viscosity increases, the



time constants should become shorter, and that  $T_1$  will become noticeably longer than  $T_2$ . Do you see this behavior? Discuss it in your report.

Finally, you may compare your measurements to those others have done and published by looking around online. You may also find that your values do not match such “literature” values. This is typical. Viscosity is highly dependent on temperature and the specific make-up of the sample. See what happens if you warm up the mineral oil by holding it in your hand for a few minutes (or warm it with a hair dryer).

### ***Experiment 2: Effect of doping with paramagnetic ions***

If you have done the continuous NMR experiment, you will be familiar with the idea behind this experiment, but you get much better results with the pulsed technique. There is a jar with a saturated  $\text{CuSO}_4$  solution available, as well as sample vials and deionized water. You want to make up a set of samples with different concentrations. The concentrations should be “logarithmic”, that is, varying by a power from one to the other. For example, with a power of 2, starting with 1/4 mixture (one part  $\text{CuSO}_4$  solution to 3 parts water), the next would be  $1/16 = 1/4^2$ , then  $1/64 = 1/4^3$ , then  $1/256 = 1/4^4$ , etc.

Here is a practical way to do this: Use a dropper to put 2 drops of the  $\text{CuSO}_4$  solution into a clean plastic cup, and then add 6 drops of pure water (1/4 mixture). Use another dropper to put 4 drops of the mixture into a vial, and set it aside. Then put 2 drops of the mixture into another cup, and mix it with 6 drops of water, use 4 drops for the next vial, and 2 drops for the next dilution, etc., until you have 6-8 different dilutions.

Measure  $T_2$  for the samples. Plot your results using log-log scales, comparing concentration to  $T_2$ . If you have done your work carefully, your  $T_2$  measurements should appear to lie on a straight line in the log-log plot. Compare your results to those given by Hahn [6, p. 586].

You may also measure  $T_1$  for the samples, but it takes longer than measuring  $T_2$ , especially for the high dilutions.

See [https://en.wikipedia.org/wiki/Solubility\\_table](https://en.wikipedia.org/wiki/Solubility_table) for a good chart. At 20° C, the solubility of copper sulfate is 32 grams per 100 ml. With this information you can determine the concentration of  $\text{Cu}^{++}$  ions in your samples.

### ***Experiment 3: Effect of diffusion on spin echo signal***

As discussed above, diffusion of spins in a magnetic field gradient will affect the spin-echo amplitude. Hahn [6], and later, Carr and Purcell [7], derived an expression for the decay envelope which included the diffusion effects. It has this form:

$$M_{\text{peak}}(t) = M_i \exp(-t/T_2) \exp(-Kt^3/n^2), \quad (15)$$

where  $M_{\text{peak}}(t)$  is the amplitude of the echo peak at time  $t$ ,  $M_i$  is the amplitude of the initial  $\pi/2$ -pulse response,  $K$  is a function of the diffusion constant and field gradient, and  $n$  is the number of intervening  $\pi$  pulses between the time of the initial  $\pi/2$  pulse and the echo at time  $t$ . As shown by Carr and Purcell

$$K = \frac{\gamma^2 \left( \frac{\partial B_0}{\partial z} \right)^2 D}{12}, \quad (16)$$

where  $\gamma$  is as defined in Eqs. (1) and (2),  $\partial B_0/\partial z$  is the gradient of the static field along the field direction, and  $D$  is the diffusion constant of the sample material. As is evident from Eq. (15), if  $T_2^3 \gg K$  and  $n = 1$ , the decay of the echo envelope should follow a form proportional to  $e^{-Kt^3}$ . But if we increase the number of  $\pi$  pulses while making the time between them shorter, that is increase  $n$ , we can reduce the effect of the  $e^{-Kt^3}$  factor.

In this exercise you want to test Eq. (15) and then use it to make an estimate of the “self-diffusion” of water. Make a sample of pure water in a clean vial. Use mineral oil to tune up the instrument and set up a spin-echo pulse sequence.

Replace the mineral-oil sample with the water sample, and set the repeat time to a long value—typically 10 seconds or so. Make sure that the repeat time is long enough so that it does not affect the height of the initial FID signal. (Note: if you need a longer time than available on the pulse programmer, you may use the external trigger input and a separate function generator. Ask for help to set this up.)

Start by setting up a spin-echo sequence with 99 B-pulses and make the delay time very short: about 1.0–1.5 ms. From this signal estimate  $T_2$  using the linear approximation method described in the instructions for Experiment 1.

Then, watch what happens when you increase the delay time as you decrease the total number of pulses, while keeping the total pulse sequence time the same, i.e.,

$$(\text{DELAY TIME}) \times (\text{NUMBER OF B PULSES}) = \text{constant.}$$

Take some scope-screen pictures to illustrate the trend.

Finally, reduce the number of B-pulses to 1, and measure the height of the echo as a function of delay time until it vanishes. It is good to get a lot of points here in order to see the shape: use steps of 1 or 2 ms in delay time to get about 30 data points. Use the cursors on the scope to measure the echo pulse amplitude.

If you use the newer TDS 3012 or MSO 2024 (color screen) oscilloscope, you can obtain a picture of the pulse-height envelope that shows the  $e^{-Kt^3}$  form to best effect. Use the infinite persistence feature of the scope (available under the “Display” menu button on the TDS 3012 or the “Acquire” button, then Waveform Display on the MSO 2024)—this feature holds all previous waveforms indefinitely. With NUMBER OF B PULSES set to 1, make a succession of traces by advancing the DELAY TIME between each pulse sequence. They should be about 10 seconds apart, enough time to operate the delay time buttons with some practice. The scope will simply add all of the signal traces to the display, and you can print or save the final picture.

To analyze the data set, plot the echo-pulse time (which is twice the delay time) versus echo-pulse height. Notice the “S” shape to the curve: it is not a simple exponential! Use a computer to create a fit to a function based on Eq. (15), for example with LMfit and Python. When you run your fit the function, fix  $T_2$  to the value obtained in the first step with 99 closely-spaced B-pulses, and let the fitting routine find best values of  $M_i$  and  $K$ . (Advice: you will need a starting value for both of these parameters.  $M_i$  can be estimated by the height of the first echo-pulse.  $K$  can be estimated by solving  $e^{-K\tau^3} = 1/2$  where  $\tau$  is the time for the echo height to have dropped to 1/2 of  $M_i$ .)

After obtaining a value for  $K$ , use Eq. (16) to calculate a value for the diffusion constant  $D$ . To do this you need an estimate of the field gradient along the z-direction. Look back at Eq. (12). When  $T_2$  is long, the FID width is given by the static field’s variation across the sample  $\Delta B_0$ . So a crude estimate may be obtained from the width of an echo pulse and the size of the sample:

roughly, the inner diameter of the sample vial. Use this information to obtain  $D$ . Compare your result to the one given by Hahn in [6].

#### ***Experiment 4: The Meiboom-Gill multipulse sequence***

The Carr-Purcell multipulse method of obtaining  $T_2$  suffers from a systematic experimental error: if the width and field strength of the  $\pi$  pulses are not exactly right, then the phase error from each pulse will accumulate, leading to a decay of the echo envelope that is too rapid. To wit: if the  $\pi$  pulses produce, say, a rotation of  $198^\circ$  per pulse (rather than the expected  $180^\circ$ ), then after, say, 5 such pulses, the effective rotation would accumulate to a tilting of the “pancake” by  $90^\circ$  ( $5 \times 18^\circ$ ) out of the  $x$ - $y$  plane, and at the echo the moments would be spread out across an arc that intersects the  $z$  axis. This would reduce the magnitude of the echo by about half what it would have been without the error. Further echos may show the signal disappearing and then reappearing; indeed if the error is very large you may see the echo envelope oscillate in amplitude. (The spin dynamics are fairly complicated, so this description is oversimplified.)

Meiboom and Gill discovered a way to correct for this accumulated error by a simple trick. They found that by shifting the phase of the RF signal by  $90^\circ$  for the first  $\pi/2$  pulse relative to the phase of the RF signal for the subsequent  $\pi$  pulses, that the phase error of two successive  $\pi$  pulses could be made to cancel, and thus, over many pulses, there would be no accumulated error. In effect, the  $90^\circ$  phase shift causes the first  $\pi/2$  rotation of  $\vec{M}$  to be about the  $y'$  axis (in the rotating frame of reference), but the following  $\pi$  rotations will be about the  $x'$  axis [8]. The key to the error correction is that the spins evolve so that the tilt of the “pancake” is reversed from its initial (incorrect) angle at the moment that the B pulse is applied, so that the subsequent pulse flips the pancake back to lie in the  $x$ - $y$  plane.

As noted, the PS1-A has a provision for implementing (or not) the Meiboom-Gill phase shift on the first pulse. You can study the effect of this by setting up a long multipulse sequence and then noting how the spin echo envelope depends on the setting of the M-G switch and the B-WIDTH position.

To study this effect, choose the glycerin sample. It (typically) has a longer  $T_2$  than mineral oil, but not so long that it is difficult to use. Set up a multi-pulse sequence to make spin echoes in the usual way. Use about 5–10 B pulses.

Then flip the M-G switch off. You will probably see a sudden drop in the spin-echo envelope. Notice how tricky it is to set the B-WIDTH to make a strong envelope. Even a slight error makes the spin echos drop quickly. In particular, you can see a very interesting modulation of the echo envelope with the M-G switch off and the B-WIDTH set notably low.

Now focus on the first four echoes. With the M-G switch on and the B-WIDTH optimized to make the strongest echoes, set the DELAY TIME so that they drop in amplitude very little. Now adjust the B-WIDTH so that you force a significant error, and notice how the second and fourth echoes resist dropping in amplitude, but the first and third echoes can change a lot. The Meiboom-Gill correction is applied every other echo.

The *VPython Simulation of Pulsed NMR* linked on the course webpage has an option to simulate the Meiboom-Gill correction. You may find it helpful to study to understand the process.

Take a few pictures of the scope screens for the different settings to include with your discussion. In your notebook explain the error and envelope modulation in terms of the effect of accumulated

phase errors.

### ***3 A Summary of Tasks for the Prepared Student***

If you have read through the write-up and feel that you know the theoretical underpinnings well enough, you may want to follow the list below as you do the lab.

1. Learn how to use the pulse programmer. You should know how to set up single pulse sequences, double pulse sequences, and multipulse sequences, with various repetition times, delay times, and  $A$  and  $B$  pulse widths.
2. Set up the instrument to observe free induction decay (FID) by means of a  $\pi/2$  pulse applied to a mineral oil sample. Study the effect of varying the  $A$  pulse width. Compare the actual pulse widths to those expected from manufacturer specifications, and compare the widths of  $\pi/2$ ,  $\pi$  and  $3\pi/2$  pulses to each other.
3. Study the effect of shortening the pulse repetition time on the FID signal. Use this effect to estimate (crudely) the longitudinal relaxation time  $T_1$ .
4. Set up a  $\pi$ - $\pi/2$  pulse sequence to make an accurate measurement of  $T_1$  by means of the zero-crossing method. Measure  $T_1$  for mineral oil.
5. Set up the instrument to observe spin echoes using the  $\pi/2$ - $\pi$  pulse sequence. Then use the multipulse sequence with many more  $\pi$  pulses to display the envelope of the echo amplitudes. Use this to obtain an accurate measurement of  $T_2$  for mineral oil.
6. Carry out the first and at least two other experiments in Section 2.3. Make sure you obtain representative printouts of the oscilloscope displays along with your hand-written data.

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