

Pulsed Nuclear Magnetic Resonance

Experiment NMR

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References

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Introduction

To observe nuclear magnetic resonance, the sample nuclei are first aligned in a strong magnetic field. In this experiment, you will learn the techniques used in a pulsed nuclear magnetic resonance apparatus (a) to perturb the nuclei out of alignment with the field and (b) to measure the small return signal as the misaligned nuclei precess in the field.

Because the return signal carries information about the nuclear environment, the technique has become widely used for material analysis. Initially, you will study the behavior of hydrogen nuclei in glycerine because the signal is easy to find and interpret. Samples involving other nuclei and other nuclear environments can also be investigated.

Theory

Recall that the hydrogen nucleus consists of a single proton and no neutrons. The precession of a bare proton in a magnetic field is a simple consequence of the proton's intrinsic angular momentum and associated magnetic dipole moment. A classical analogy would be a gyroscope having a bar magnet along its rotational axis. Having a magnetic moment, the proton experiences a torque in a static magnetic field. Having angular momentum, it responds to the torque by precessing about the field direction. This behavior is called *Larmor precession*.

The model of a proton as a spinning positive charge predicts a proton magnetic dipole moment $\boldsymbol{\mu}$ that is aligned with and proportional to its spin angular momentum \mathbf{s}

$$\boldsymbol{\mu} = \gamma \mathbf{s} \quad (1)$$

where γ , called the gyromagnetic ratio, would depend on how the mass and charge is distributed within the proton. Determined by various magnetic resonance experiments to better than 1 ppm, to four figures $\gamma = 2.675 \times 10^8$ rad/(sec Tesla).

Note that different nuclei will have different spin angular momentum, different magnetic moments, and different gyromagnetic ratios. The gyromagnetic ratio given above is only for the hydrogen nucleus. In NMR, the word proton generally only refers to the nucleus of the

^1H hydrogen isotope (a bare proton), not protons in other nuclei. For example, the nucleus of ^{16}O has eight protons, but no nuclear spin or magnetic dipole moment. While it is possible to study NMR in other nuclei, such measurements require different experimental settings and can not be performed at the same time that protons are under investigation.

Exercise 1 Show that the classical value for the proton gyromagnetic ratio (the ratio of the classical magnetic moment to the classical angular momentum) is $e/2m$ (a) assuming the proton is a point particle of mass m and charge e moving at constant speed in a circular orbit, and (b) assuming the proton is a solid sphere with a uniform mass and charge density rotating at a constant angular velocity. (c) Using the proton mass $m = 1.67 \times 10^{-27}$ kg, and charge $e = 1.60 \times 10^{-19}$, find the ratio of the true gyromagnetic ratio of the proton given above to this classical value (called the proton g -factor). (d) Why might different nuclei be expected to have different gyromagnetic ratios?

The proton has two energy eigenstates in a magnetic field \mathbf{B}_0 : spin-up and spin-down. The eigenenergies are governed by the Hamiltonian

$$\mathcal{H} = -\boldsymbol{\mu} \cdot \mathbf{B}_0 \quad (2)$$

Defining the z -axis along \mathbf{B}_0

$$\mathbf{B}_0 = B_0 \hat{\mathbf{z}} \quad (3)$$

and with $\boldsymbol{\mu} = \gamma \mathbf{s}$, the Hamiltonian becomes

$$\mathcal{H} = -\gamma B_0 s_z \quad (4)$$

where $s_z = \mathbf{s} \cdot \hat{\mathbf{z}}$ is the z -component of the spin. Since s_z has eigenvalues $\hbar/2$ for the spin-up state and $-\hbar/2$ for the spin-down state, \mathcal{H} has eigenenergies

$$E_{\pm} = \mp \frac{\hbar \omega_0}{2} \quad (5)$$

where $\omega_0 = \gamma B_0$ is called the Larmor frequency.

NMR signals arise from the collective behavior of a large number of nuclei in a macroscopic sample. The net nuclear angular momentum \mathbf{L} is the sum of the individual spin angular momenta

$$\mathbf{L} = \sum \mathbf{s} \quad (6)$$

The net dipole moment becomes

$$\begin{aligned} \mathbf{P} &= \sum \boldsymbol{\mu} \\ &= \sum \gamma \mathbf{s} \\ &= \gamma \mathbf{L} \end{aligned} \quad (7)$$

The dipole moment per unit volume is called the *magnetization* and is given the symbol \mathbf{M} . Depending on experimental conditions \mathbf{M} may vary at different points within a sample. Here we will assume \mathbf{M} is uniform throughout the sample volume V so that $\mathbf{M} = \mathbf{P}/V$. (However, keep in mind there may be effects associated with a non-uniform sample magnetization.) In the jargon of NMR, it is more common to refer to the sample magnetization rather than the dipole moment, and we will adopt this language in this writeup. In most instances, the term magnetization and dipole moment can be substituted for one another without confusion.

It is important to note that Eqs. 6 and 7 are vector sums, so if the individual proton moments are randomly oriented—as is often the case in the absence of any applied magnetic field—the net angular momentum (and net dipole moment) will sum to zero. In a magnetic field, however, a sample of protons at an absolute temperature T will come to thermal equilibrium with more spins in the lower energy (spin-up) state. The ratio of the number of protons in the higher energy state N_- to the lower energy state N_+ is given by the

Boltzmann factor:

$$\frac{N_-}{N_+} = e^{-\Delta E/kT} \quad (8)$$

where k is Boltzmann's constant and $\Delta E = \hbar\omega_0$ is the energy difference between the spin-up and spin-down states.

The excess of spin-up states results in a net equilibrium magnetization \mathbf{M}_0 in the direction of \mathbf{B}_0 . That is, $\mathbf{M}_0 = M_0\hat{\mathbf{z}}$, where

$$M_0 = \mu(N_+ - N_-)/V \quad (9)$$

and $\mu = \gamma\hbar/2$ is the magnitude of the z -component of an individual proton magnetic moment. M_0 can be calculated from the Boltzmann factor with $(N_+ + N_-)/V$ being the density of protons in the sample.

Exercise 2 (a) Give an expression for the fraction $(N_+ - N_-)/(N_+ + N_-)$ of aligned protons in the weak field or high temperature limit: $kT \gg \hbar\omega_0$. (b) Calculate the value of M_0 for water at room temperature in a 2 kG field. (c) Why must you determine the density of hydrogen atoms in the sample, but not include any protons inside the water's oxygen nuclei? (d) The dipole moment of a simple wire loop of area A carrying a current I is $P = IA$. So how big is the dipole moment of a 1 cm³ sample of water in a 2 kG field? Express your answer in SI units and also as the current needed in a 1 cm² loop that would give it the same dipole moment.

We will later show how the nuclear magnetization \mathbf{M} can be turned away from its equilibrium alignment with the z -axis. For the present discussion we assume the configuration shown in Fig. 1 has been achieved and \mathbf{M} (and \mathbf{L}) make a non-zero angle with the z -axis. The resulting torque $\boldsymbol{\tau} = \mathbf{M} \times \mathbf{B}_0$ causes the angular momentum \mathbf{L} to change $\boldsymbol{\tau} = d\mathbf{L}/dt$.

$$\frac{d\mathbf{L}}{dt} = \mathbf{M} \times \mathbf{B}_0 \quad (10)$$

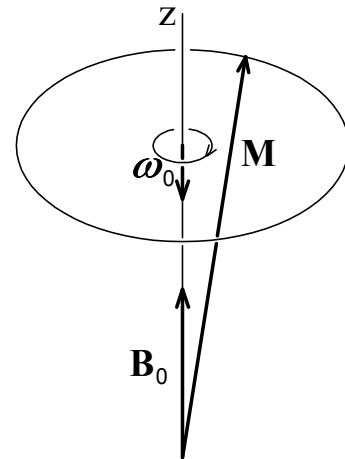


Figure 1: The magnetization \mathbf{M} precesses clockwise about an external field \mathbf{B}_0 .

Differentiating Eq. 7 and substituting for $d\mathbf{L}/dt$, this equation can be rewritten

$$\frac{d\mathbf{M}}{dt} = \gamma\mathbf{M} \times \mathbf{B}_0 \quad (11)$$

With $\mathbf{B}_0 = B_0\hat{\mathbf{z}}$ and $\omega_0 = \gamma B_0$ this equation further simplifies to

$$\frac{d\mathbf{M}}{dt} = \omega_0\mathbf{M} \times \hat{\mathbf{z}} \quad (12)$$

By components

$$\begin{aligned} \frac{dM_z}{dt} &= 0 \\ \frac{dM_x}{dt} &= \omega_0 M_y \\ \frac{dM_y}{dt} &= -\omega_0 M_x \end{aligned} \quad (13)$$

These are the equations for the clockwise precession of \mathbf{M} on a cone that maintains a constant polar angle with the z -axis. This behavior is called Larmor precession and the precession frequency ω_0 is called the Larmor frequency.

As \mathbf{M} precesses, its dipole field precesses with it. The precession can be detected by the

alternating voltage it induces in a receiver coil surrounding the sample. The voltage arises from Faraday's law $V = -d\phi/dt$ and thus the coil axis is oriented perpendicular to \mathbf{B}_0 to maximize the change in the magnetic flux ϕ through the coil as \mathbf{M} precesses.

To get a precession and an induced coil voltage (signal), \mathbf{M} must make a non-zero angle with \mathbf{B}_0 , i.e., the z -axis. So we define the *transverse magnetization* \mathbf{M}_r

$$\mathbf{M}_r = M_x \hat{\mathbf{x}} + M_y \hat{\mathbf{y}} \quad (14)$$

and the longitudinal magnetization

$$\mathbf{M}_z = M_z \hat{\mathbf{z}} \quad (15)$$

The amplitude of the precession-induced coil signal is proportional to the magnitude M_r of \mathbf{M}_r and is independent of M_z . Note that M_r is zero or positive, while M_z can be positive, negative, or zero.

In thermal equilibrium, the magnetization is entirely longitudinal: $\mathbf{M}_0 = M_0 \hat{\mathbf{z}}$ or $M_z = M_0$ and $M_r = 0$. With no transverse magnetization, there is no precession and no induced coil voltage. To observe Larmor precession we need a way to create transverse magnetization. We will show how an oscillating magnetic field \mathbf{B}_1 can rotate the equilibrium longitudinal magnetization away from the z -axis so that precessional motion will occur. To this end, the protons are placed inside a coil oriented with its axis perpendicular to \mathbf{B}_0 . The coil axis will be taken to define the laboratory x -direction. In our apparatus, the same receiver coil used to pick up the Larmor precession is also used to generate the \mathbf{B}_1 field.

\mathbf{B}_1 is produced by applying an alternating voltage to the coil at a frequency ω near the Larmor frequency ω_0 causing an alternating current to flow in the coil. Near the coil center, a linearly polarized magnetic field is created which oscillates back and forth along the coil

axis. Choosing an arbitrary initial phase and taking the amplitude of this field as $2B_1$, \mathbf{B}_1 can be written

$$\mathbf{B}_1 = 2B_1 \cos \omega t \hat{\mathbf{x}} \quad (16)$$

\mathbf{B}_1 can be decomposed into two counter-rotating circularly polarized components each with half the amplitude of the total oscillating field.

$$\begin{aligned} \mathbf{B}_1 = & B_1 (\cos \omega t \hat{\mathbf{x}} - \sin \omega t \hat{\mathbf{y}}) \\ & + B_1 (\cos \omega t \hat{\mathbf{x}} + \sin \omega t \hat{\mathbf{y}}) \end{aligned} \quad (17)$$

The first component rotating in the same sense as the Larmor precession will be responsible for changing the magnetization and the second component rotating in the opposite sense has little effect. Neglecting this counter-rotating component is called the rotating-wave approximation and allows us to rewrite the \mathbf{B}_1 field as

$$\mathbf{B}_1 = B_1 (\cos \omega t \hat{\mathbf{x}} - \sin \omega t \hat{\mathbf{y}}) \quad (18)$$

The equation of motion for the magnetization \mathbf{M} is still given by Eq. 11

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} \quad (19)$$

with the replacement of \mathbf{B}_0 by \mathbf{B} , the vector sum of \mathbf{B}_0 and the rotating field \mathbf{B}_1 given by Eq. 18.

However, it will be mathematically convenient to work in a frame rotating clockwise about the z -axis at the frequency ω . In this frame, the unit vectors are time dependent

$$\begin{aligned} \hat{\mathbf{x}}' &= \cos \omega t \hat{\mathbf{x}} - \sin \omega t \hat{\mathbf{y}} \\ \hat{\mathbf{y}}' &= \sin \omega t \hat{\mathbf{x}} + \cos \omega t \hat{\mathbf{y}} \\ \hat{\mathbf{z}}' &= \hat{\mathbf{z}} \end{aligned} \quad (20)$$

and the \mathbf{B}_1 field is constant

$$\mathbf{B}_1 = B_1 \hat{\mathbf{x}}' \quad (21)$$

The \mathbf{B}_0 field—lying along the rotation axis—is the same in both the laboratory and rotating frames.

A time dependent vector \mathbf{A} in the laboratory frame could be expressed

$$\mathbf{A} = A_x \hat{\mathbf{x}} + A_y \hat{\mathbf{y}} + A_z \hat{\mathbf{z}} \quad (22)$$

where A_x , A_y , and A_z are functions of time. This same vector in a rotating reference frame would be expressed

$$\mathbf{A} = A'_x \hat{\mathbf{x}}' + A'_y \hat{\mathbf{y}}' + A'_z \hat{\mathbf{z}}' \quad (23)$$

where A'_x , A'_y , and A'_z are new functions of time determined by A_x , A_y and A_z and the unit vector transformations describing the rotating frame.

Differentiating Eq. 23 gives

$$\begin{aligned} \frac{d\mathbf{A}}{dt} = & \frac{dA'_x}{dt} \hat{\mathbf{x}}' + \frac{dA'_y}{dt} \hat{\mathbf{y}}' + \frac{dA'_z}{dt} \hat{\mathbf{z}}' \quad (24) \\ & + A'_x \frac{d\hat{\mathbf{x}}'}{dt} + A'_y \frac{d\hat{\mathbf{y}}'}{dt} + A'_z \frac{d\hat{\mathbf{z}}'}{dt} \end{aligned} \quad (25)$$

The first three terms give the time derivative of \mathbf{A} as it would appear in the rotating frame and will be written $(d\mathbf{A}/dt)'$. The final three terms are equal to the expression $\boldsymbol{\omega} \times \mathbf{A}$ where $\boldsymbol{\omega}$ is the vector angular velocity of the rotating frame.

$$\frac{d\mathbf{A}}{dt} = \left(\frac{d\mathbf{A}}{dt} \right)' + \boldsymbol{\omega} \times \mathbf{A} \quad (26)$$

For a frame rotating clockwise about the z -axis at a frequency ω the transformation is given by Eqs. 26 with $\boldsymbol{\omega} = -\omega \hat{\mathbf{z}}$.

Eq. 19 then becomes

$$\left(\frac{d\mathbf{M}}{dt} \right)' + \boldsymbol{\omega} \times \mathbf{M} = \gamma \mathbf{M} \times (\mathbf{B}_0 + \mathbf{B}_1) \quad (27)$$

or

$$\left(\frac{d\mathbf{M}}{dt} \right)' = \gamma \mathbf{M} \times \left(\mathbf{B}_0 + \frac{\boldsymbol{\omega}}{\gamma} + \mathbf{B}_1 \right) \quad (28)$$

With $\mathbf{B}_0 = B_0 \hat{\mathbf{z}}$ and $\boldsymbol{\omega} = -\omega \hat{\mathbf{z}}$ we can define an effective field along the z -axis

$$\mathbf{B}'_0 = B'_0 \hat{\mathbf{z}} \quad (29)$$

where

$$B'_0 = B_0 - \frac{\omega}{\gamma} \quad (30)$$

With $\mathbf{B}_1 = B_1 \hat{\mathbf{x}}'$, the total effective field in the rotating frame becomes

$$\mathbf{B}' = B'_0 \hat{\mathbf{z}} + B_1 \hat{\mathbf{x}}' \quad (31)$$

The “on resonance” condition is $\omega = \omega_0 = \gamma B_0$, and is achieved by adjusting either the static field strength B_0 (thereby changing the Larmor frequency ω_0) or the frequency ω of the voltage applied to the coil. On resonance, the effective field along the z -axis is zero ($B'_0 = 0$) and the net effective field lies entirely along the rotating x -axis. ($\mathbf{B}' = B_1 \hat{\mathbf{x}}'$).

But on resonance or not, the net effective field \mathbf{B}' is a constant, and the equation of motion for \mathbf{M} in the rotating frame becomes

$$\left(\frac{d\mathbf{M}}{dt} \right)' = \gamma \mathbf{M} \times \mathbf{B}' \quad (32)$$

This equation is analogous to Eq. 11, and its solution is also analogous. \mathbf{M} precesses clockwise about the effective field at a frequency $\omega' = \gamma B'$ where B' is the magnitude of \mathbf{B}' . ω' is called the Rabi frequency in analogy with the first treatment of this effect in atomic physics by I.I. Rabi.

On or near the resonance condition, $B_1 \gg B'_0$, the net effective field lies along or nearly along the rotating x' -axis. Then, if \mathbf{B}_1 is pulsed on and off just long enough to cause 1/4 of a Rabi cycle, \mathbf{M} will Rabi-precess to the rotating y' -axis. This kind of pulse is called a 90° or $\pi/2$ pulse. After the $\pi/2$ pulse ends, it should be clear that in the laboratory frame the magnetization will lie in the xy -plane and it will be Larmor-precessing flat

out like one blade of a propeller. Were \mathbf{B}_1 left on for a longer time, \mathbf{M} would Rabi-precess further than 90° and the Larmor precession cone would start to close around the negative z -axis. If the \mathbf{B}_1 field is pulsed on just long enough to cause $1/2$ of a full precession cycle, (such a pulse is called a 180° or π pulse) the magnetization becomes inverted and points against the external magnetic field.

Relaxation

Relaxation in NMR refers to processes that restore the equilibrium magnetization after a perturbation, such as an \mathbf{B}_1 pulse, has created a non-equilibrium population of nuclear spin states. The breadth of possible relaxation studies and the wealth of information regarding the nuclear environment and the nuclear motion that becomes available through those studies is why NMR has become such an important analytical technique. The sections to follow focus on a small subset of those studies which highlight the most general features of relaxation.

Free Induction Decay

Figure 2a shows the magnetization \mathbf{M} (solid arrow) immediately following a $\pi/2$ -pulse. The pulse has Rabi-precessed the equilibrium magnetization (dashed arrow) to the y' -axis. At the end of the \mathbf{B}_1 pulse, the now transverse magnetization induces an observable Larmor precession signal.

After the $\pi/2$ -pulse, the relaxation of the transverse and longitudinal magnetization from their perturbed values $M_r = M_0$ and $M_z = 0$ back to their equilibrium values of $M_r = 0$ and $M_z = M_0$, respectively, can occur on quite different time scales.

Figures 2b and c show a case where the transverse magnetization (and thus the signal)

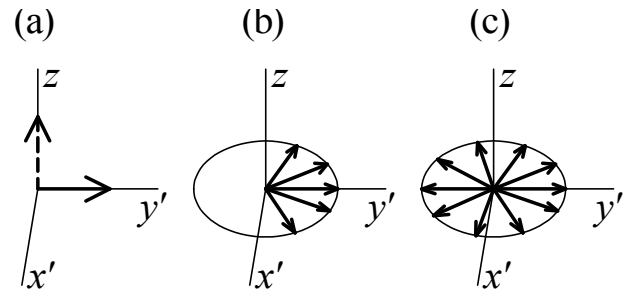


Figure 2: (a) Immediately following a $\pi/2$ pulse, the individual spins—originally aligned along the z -axis—are Rabi-precessed to the rotating y' -axis. (b) Afterward, different individual spins Larmor precess slightly faster or slower than the average Larmor frequency and get somewhat ahead of or behind the y' -axis. (c) Ultimately, the spins spread out over the entire xy -plane.

decays away quickly, before there is any significant change in the longitudinal magnetization. As in our apparatus, this is often the case, and is a result of the inhomogeneities in the \mathbf{B}_0 field. Spins in different parts of the sample experience slightly different \mathbf{B}_0 field strengths and thus precess at slightly different Larmor frequencies. As shown in Fig. 2b, the individual dipole moments begin to spread out in the xy -plane. In Figs. 2b and c, the x' - and y' -axes rotate at the average Larmor frequency, corresponding to the average \mathbf{B}_0 field strength. Some spins precess at this frequency and stay aligned with the y' -axis. However, those spins in regions of higher field strength precess faster than the average and get ahead of the y' -axis, and those in lower fields fall behind. The vector sum of the individual spins, and therefore the net transverse magnetization, decreases. As the spins completely spread out over the xy -plane as in Fig. 2c, the transverse magnetization, and therefore the signal, decays to zero. The decay of the transverse magnetization is called free induction decay (FID). We will also refer to the signal picked up by the

receiver coil as a FID.

The relaxation of the transverse magnetization M_r from an initial value M_i to its equilibrium value of zero is often modeled by an exponential

$$M_r(t) = M_i e^{-t/T_2^*} \quad (33)$$

where T_2^* is called the transverse relaxation time. While most real FID signals decay non-exponentially, the concept of a time constant associated with the decay of transverse magnetization is nonetheless useful.

Inhomogeneities in the \mathbf{B}_0 field are not the only reason the spins fan out. There are also randomly fluctuating magnetic fields from other sources in the sample, e.g., the dipole field of one proton moving past another. These random fields vary over the sample volume and thus also cause proton precession rates to vary. Were the \mathbf{B}_0 field perfectly uniform, the random fields (and other processes) would become the dominant source for the decay of the FID. The decay of transverse magnetization would then occur on a longer time scale, called the spin-spin relaxation time, and given the symbol T_2 . The *spin echo* (described later) is an interesting phenomenon which largely cancels the effect of field inhomogeneities and makes measurements of T_2 possible even when T_2^* is much shorter.

Thus, any transverse magnetization decays to zero as the individual spins fan out. What happens to longitudinal magnetization M_z after it is perturbed from equilibrium? Recall (Eq. 9) that the value of M_z is directly proportional to the difference between the populations of protons in the spin-up and spin-down states. Also recall that these states differ in energy by the amount $\hbar\omega_0$. In a sample, individual spins make transitions from spin-up to spin-down and vice versa, absorbing and releasing energy depending on the transition direction. At equilibrium, although the pop-

ulations of the two states are unequal (more spins are in the lower energy spin-down state), the transition rates in the two directions are equal and there is no net energy transfer into or out of the spin degrees of freedom.

If the longitudinal magnetization M_z is not at its equilibrium value M_0 , the transition rates in the two directions will not be equal, and there will be a net energy transfer into or out of the spin degrees of freedom. For isolated spins spontaneous photon emission and stimulated emission and absorption from the background radiation field would reestablish the Boltzmann populations, though it might take quite some time to come to equilibrium. In a real sample, the spins are not isolated. While stimulated emission and absorption are still the major mechanisms by which transitions occur, the radiation field experienced by the spins includes contributions from the motion of the electrons and nuclei in the sample. In effect, the spins exchange energy with the electrons and other nuclei causing the transition rates to be much higher than for isolated spins and the approach to equilibrium is much faster.

An exponential approach to equilibrium is often a satisfactory model. If the initial perturbed longitudinal magnetization is taken as M_i , $M_z(t)$ would be expressed

$$M_z(t) = M_0 + (M_i - M_0)e^{-t/T_1} \quad (34)$$

where T_1 is called the longitudinal relaxation time. T_1 is also called the spin-lattice relaxation time in reference to NMR in solids where the constituents of the lattice (nuclei and electrons) provide for the exchange of energy necessary for the relaxation process.

Spin Echo

The basic spin echo technique, used to measure the spin-spin relaxation time T_2 , is to apply a $\pi/2$ -pulse, wait a bit, and then apply

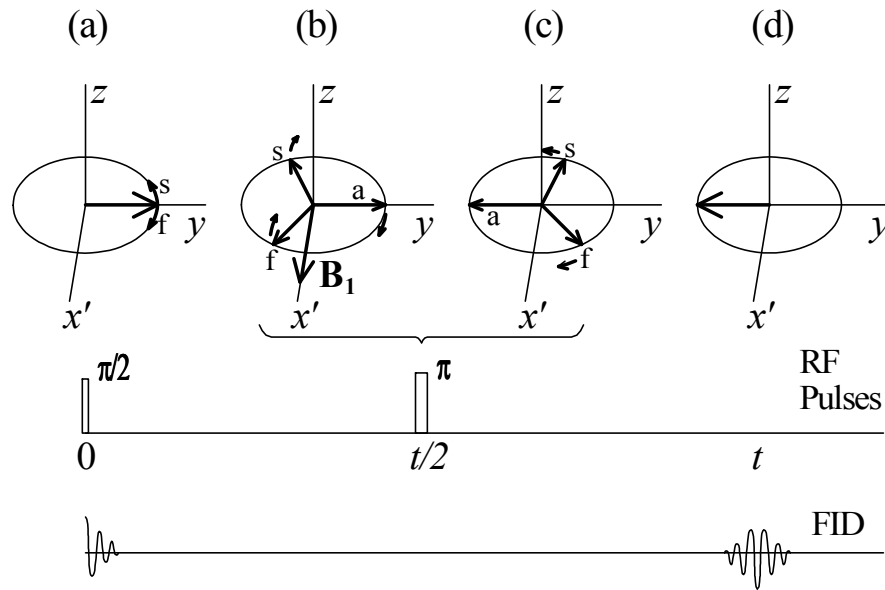


Figure 3: The $\pi/2 - \pi$ spin echo sequence.

a π -pulse, as illustrated in Fig. 3. In (a) the magnetization \mathbf{M} is shown already rotated to the y' -axis by an initial $\pi/2$ -pulse. With no field inhomogeneities and no T_2 processes, all spins would precess at the same rate and there would be no decay of the transverse magnetization. If we now allow for field inhomogeneities, then some spins will precess faster than average and some slower. As in Fig. 2, the spins eventually fan out into a uniform pancake covering the xy -plane and the FID decays to zero. Figure 3b shows the situation at some time $t/2$ when the spins are completely fanned out, though in the figure only three spins are shown. One spin is precessing at the average Larmor frequency, another is precessing faster than the average, and the third is precessing slower.

Figure 3b also shows the application of a second \mathbf{B}_1 pulse, this one a π -pulse. The π -pulse flips the pancake of spins over, 180° about the x' -axis. The three illustrated spins end up as shown in Fig. 3c. The proton that

was ahead is now behind the average and the proton that was behind is now ahead. In addition to no T_2 processes, let's also temporarily assume that the spins don't move around within the field during the pulse sequence. A spin in a stronger-than-average field stays in that field, continually precessing at a constant, faster-than-average rate from the beginning of the $\pi/2$ -pulse to well after the end of the π -pulse. Similarly, a spin in a lower-than-average field continually precesses at a constant, slower-than-average rate. The faster precessing proton in Fig. 3c, now behind, begins to catch up to the average. The slower, now ahead, begins to lose ground to the average. If it took a time $t/2$ to get to the configuration in Fig. 3b/c, then after an additional time $t/2$ (i.e., at the time t), the three spins (in fact, all the spins) would be realigned along the $-y'$ -axis as shown in Fig. 3d. The transverse magnetization created by the original $\pi/2$ -pulse would be completely restored and the amplitude of the FID would be as

large as it was at Fig. 3a. This is the echo FID. Afterward, the spins again fan out and again the FID decays away.

The magnetization at t (Fig. 3d) will be smaller than the original magnetization because spins don't only fan out due to the \mathbf{B}_0 field inhomogeneities. As mentioned previously, the spin-spin relaxation time T_2 arises because there are other random fields in the sample which make individual spins precess at different rates. For liquids, the diffusion of protons within the sample provides an additional reason the spin echo signal will be smaller than the original FID. During the interval from the initial $\pi/2$ -pulse to the appearance of the echo, the spins move within the sample. Consequently, if there is any inhomogeneity in the \mathbf{B}_0 -field, all spins will not precess at the same rate for the whole time t as was assumed, and the echo will not reconstitute perfectly.

The amplitude of the echo pulse, as a function of the time t when it is made to appear, decays according to the relation

$$M(t) = M_0 \exp \left[- \left(\frac{t}{T_2} + \frac{\gamma^2 G^2 D t^3}{12} \right) \right] \quad (35)$$

The first term in the exponential describes the spin-spin relaxation processes. The second term arises from the diffusive motion. G is the \mathbf{B}_0 -field gradient, i.e. the maximum rate of change of \mathbf{B}_0 with position (units of G are thus Tesla per meter) and D is the diffusion coefficient which has units of square meters per second.

Equation 35 illustrates how spin echo measurements provide information about parameters of physical interest by unmasking the effects of field inhomogeneities responsible for the quick and relatively uninteresting T_2^* decay of the FID. Fits to the data can be used to determine T_2 as well as the diffusion constant D (under the right conditions such as a

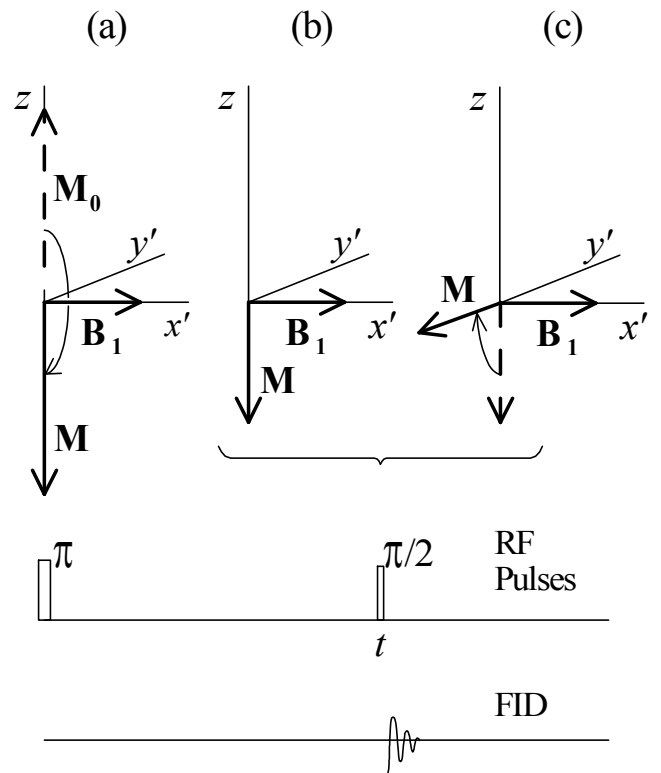


Figure 4: The π - $\pi/2$ inversion recovery sequence.

known field gradient and sufficiently long T_2). Whereas the T_2^* decay of the FID depends on the field inhomogeneity over the whole length of the sample, field inhomogeneity in the diffusion term involves the smaller distances spins diffuse during the measurement time t .

Inversion Recovery

We next consider the inversion recovery sequence used to measure T_1 and illustrated in Fig. 4. Recall that T_1 gives the time scale for relaxation of longitudinal magnetization toward the equilibrium value M_0 . The inversion recovery sequence starts with a π -pulse applied to a sample initially aligned in the z -direction. In Fig. 4a, the initial magnetization (dashed arrow) is inverted by the π -

pulse, and ends up pointing along the negative z -axis: $M_z = -M_0$. In Fig. 4b, the inverted \mathbf{M} becomes smaller as it relaxes back toward equilibrium. \mathbf{M} continues shrinking, passes through zero, and then increases until it reaches the equilibrium value M_0 .

An exponential decay of the longitudinal magnetization from a perfectly inverted value $M_z = -M_0$ to the equilibrium value $M_z = M_0$ is modeled

$$M_z(t) = M_0 \left(1 - 2e^{-t/T_1}\right) \quad (36)$$

Because the perturbed magnetization has no component in the xy -plane after it is inverted by the π -pulse (nor while it is relaxing toward equilibrium), there is no transverse magnetization to produce a FID. To observe the changing $M_z(t)$, the magnetization is precessed over to the xy -plane by applying a second pulse, this time a $\pi/2$ -pulse, at the desired observation time t . This is illustrated in Fig 4b. The FID will decay with the T_2^* time constant, but its initial size will be proportional to $M_z(t)$. By varying the time t at which the second $\pi/2$ pulse is applied, the behavior of $M_z(t)$ can be measured.

Exercise 3 *Make a plot of $M_z(t)$ (assuming exponential decay) and describe what effect the second $\pi/2$ -pulse will have on \mathbf{M} if it is applied at $t = 0$, $t = T_1 \ln 2$, and $t = \infty$?*

Spectral Density Function

An important concept in NMR relates to the intensity of the random electromagnetic fields experienced by spins in different frequency intervals. This spectral density function is strongly related to the motion of the spins and therefore depends indirectly on the temperature and (for liquid samples) the viscosity of the sample. At low temperatures and high viscosities the mean time t_c between molecular

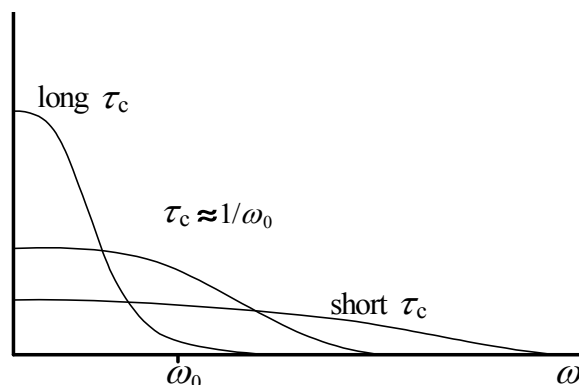


Figure 5: The spectral density function changes as the mean time between collisions τ_c changes.

collisions is long and the spectrum is dominated by low frequency fluctuations. At high temperatures and low viscosities, t_c is short and the spectrum spreads out to higher frequencies. Figure 5 shows how the frequency distribution spreads out as the collision time decreases.

Recall that the \mathbf{B}_1 -field must oscillate near the resonant frequency ω_0 to cause a Rabi-precession of \mathbf{M} away from its equilibrium alignment with the z -axis, and thus effect a change in the relative populations of the two spin states. So, too, must the random fields have intensities in the frequency interval near ω_0 to stimulate transitions and reestablish the equilibrium longitudinal magnetization $M_z = M_0$. Thus at low temperatures (long t_c) where low frequencies dominate the spectrum, T_1 is long. While at very high temperatures (short t_c) the spectrum is spread so thin that again the intensity near ω_0 is small and T_1 is long. At intermediate collision times one expects to find a minimum in T_1 . Theory predicts the shortest T_1 when t_c is of order $1/\omega_0$.

T_2 is also affected by these “resonant” field fluctuations but in addition, field fluctuations along the z -axis at any frequency will cause the individual spins to fan out; just as they

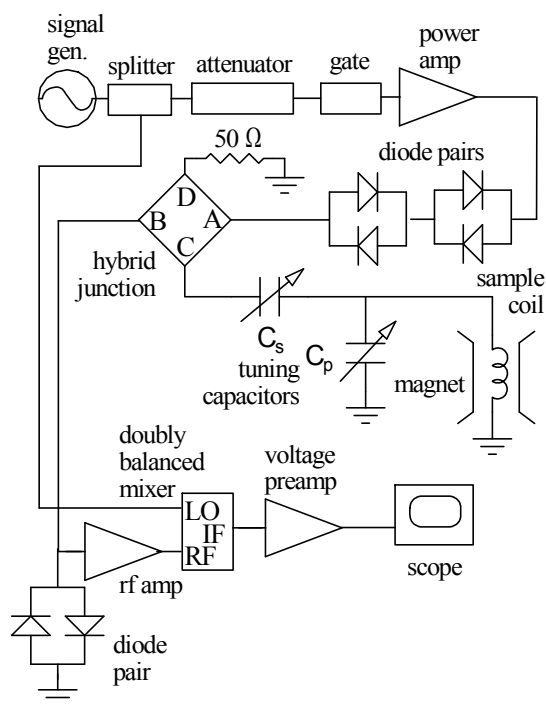


Figure 6: Schematic of our pulsed NMR apparatus.

fan out due to field inhomogeneities. It is these fluctuations that can cause T_2 to be appreciably shorter than T_1 .

Besides varying the sample temperature or viscosity to influence the relaxation times, adding small amounts of paramagnetic ions to the sample will change the amplitude of the frequency fluctuations. These ions have large magnetic moments, which when whizzing by the protons, cause very large fluctuations. Their importance can be investigated by varying the concentration of the ions.

Apparatus

A schematic of the experimental apparatus is shown in Fig. 6.

The RF signal generator should be set to produce a 9.5 MHz, continuous RF signal at

an amplitude of 10 dBm¹ (0.707 V_{rms}, 2.00 V_{pp}). This value is chosen because the 50-50 splitter reduces the voltage at its two outputs by 3 dB and 7 dBm is the recommended amplitude for the local oscillator (LO) input of the *doubly balance mixer*.

This RF is reduced another 10 dB by the attenuator to about -3 dBm so that it will be at the appropriate level before being fed to the RF gate. The gating signal for the RF gate is not shown in the schematic. It is derived from a TTL circuit in a separate interface box which is driven by timing signals from a National Instruments 6601 timer/counter board inside the computer. The output of the RF gate then consists of short RF pulses whose amplitude and frequency are set by the signal generator amplitude and attenuator settings and whose durations are set by the computer generated gating signal.

The gated RF pulses are amplified to about 50 V_{rms} by the power amplifier. However, the RF gate is not perfect and even while the computer gating signal is off, a small amount of RF still passes through. After amplification, this gate-off RF signal has an amplitude around 1 V and is largely eliminated by the two sets of diode pairs.

The pulsed RF is delivered to the coil through a *hybrid junction* which when properly balanced, sends half the incident power to the coil and half to the 50 Ω terminator. The receiver circuitry (RF amplifier and doubly balanced mixer) thus sees very little of the transmitter power driving the \mathbf{B}_1 -field.

The coil is part of a tank circuit with variable capacitors which must be properly tuned. Tuning must cancel the inductive reactance of the coil to produce the largest sample coil cur-

¹dBm is a unit of absolute power and is defined by the expression $10 \log_{10}(V^2/V_0^2)$ where $V_0 = \sqrt{0.05} = 0.224$ volts is the rms voltage across a $R = 50 \Omega$ resistor that will dissipate energy at a rate of $V_0^2/R = 1$ mW.

rent and match the tank circuit impedance to $50\ \Omega$ for proper operation of the hybrid junction.

The hybrid junction also routes the FID to the receiver circuitry. The first component of the receiver is a low noise RF amplifier protected from large signals by a diode pair to ground. The amplified RF signal is frequency “mixed” with a small signal leaked continuously from the signal generator. The frequency of the signal at the mixer output will be the difference between the FID frequency (at the Larmor frequency ω_0) and the signal generator frequency ω . The \mathbf{B}_0 field strength will be adjusted so that the “beat” frequency $\omega - \omega_0$ is around 1 kHz.

The signal from the mixer is filtered and amplified by a voltage preamp before being measured with a digital oscilloscope.

Experiment

The magnet is field regulated using a Hall probe attached to one pole face. The instructor will show you how to bring up the magnet. Remember to open the cooling water supply and drain line. While it is important to have the water running while the magnet supply is on it is even more important to **turn off the water lines when the magnet supply is turned off**. If the water is left running for more than a few hours while the supply is not running, humidity in the air will condense all over the internal cooled parts of the supply. If you think the water has been left on for more than a few hours with the supply off, do not turn the supply back on without first asking an instructor to check it for condensation.

Tuning the tank circuit

Make sure the RF power amplifier is off or that its output is temporarily discon-

nected. If the gate signal from the computer stays high (as it may when starting or shutting down the computer), the high (50 W) power from its output will be on continuously instead of only for short bursts and the components downstream will fry in no time at all.

Check the sample coil and remove any sample vial that may have been left in it from the previous experimenters. It is easily pushed out the top of the mounting tube with a pencil inserted from the coil end at the bottom. Do not try to push it out the bottom of the tube. Replace the coil near the center of the magnet.

Set the signal generator for a 10 dBm output ($0.7\ V_{\text{RMS}}$, $2\ V_{\text{PP}}$) and a frequency of 9.5 MHz. This signal goes to the splitter which provides two equal RF voltages of 7 dBm amplitude at its outputs.

Temporarily disconnect one of the 7 dBm continuous signals from the splitter, say the one that normally goes to the LO input of the doubly balanced mixer, and connect it instead to the hybrid junction “A” input. Disconnect the “B” output from the RF amp and monitor it with an oscilloscope. Be sure to use a BNC tee and $50\ \Omega$ terminator at the scope input. Get a clear stable trace showing the 9.5 MHz waveform. The basic idea in tuning the tank circuit capacitors is that when the impedance of the branch connected to the “C” output matches the $50\ \Omega$ impedance attached to the “D” output, the “B” output will be as small as possible. When the “C” and “D” outputs are not balanced, more of the “A” input will pass through to the “B” output.

Adjust the series capacitor knob for a minimum signal on the scope and note its amplitude. Next adjust the backmost knob for the parallel capacitors² by about 1/20 of a turn

²The parallel capacitors are two capacitors in series that are in parallel with the coil (go to ground). The series capacitor is a single capacitor in series with the coil.

at first (you may need to go in even smaller steps as you get close to the correct setting) and note whether you are turning the knob clockwise or counterclockwise. Either is OK at first. Because your hand on this knob seems to significantly affect the tuning, don't worry about how it affects the scope signal, but move your hand away and then again adjust the series capacitance for a minimum on the scope. If the voltage at the minimum goes down after adjusting the series capacitance, you are changing the parallel capacitance in the correct direction. If it goes up, you are going the wrong way; change the parallel capacitance in the opposite direction. Continue this two-step procedure until the scope signal becomes fairly non-sinusoidal and has an amplitude under 50 mV. The perfectly balanced circuit would show a doubled frequency around 19 MHz.

Check with the instructor if this tuning process is taking more than 15 minutes or so.

When balanced, note how the balance is affected when you move the sample coil a few centimeters farther or closer to the pole faces. The balancing is important, but getting it perfect is not critical.

When you are finished tuning, return the 7 dBm splitter output to the "LO" input of the mixer and the "B" output to the RF amp.

Learning the NMR pulse sequencer

Temporarily, rout the gating signal from the computer interface to an oscilloscope input and rout the trigger signal from the computer interface to the oscilloscope trigger source. Launch the NMR pulser program and viewing the gating pulses on the scope, learn how to externally trigger the scope and see the gating pulses. Also learn how to operate the program to produce gating pulse-pairs. You can adjust the width of each pulse, the separation between them, and the pulse sequence repeti-

tion rate. The separation between the start of the (first) A -pulse and the start of the (second) B -pulse is labeled T_d . Between the start of one A -pulse and the next is the repeat time T_r . Try turning the A - and B -pulses on and off by clicking on the appropriate buttons. The trigger output can be offset relative to end of the A - or B -pulse or to the temporal position of a spin echo with the pretrigger control. Leave it set to zero. Play around with the buttons and controls to get familiar with their workings. Check that the gating pulse durations and the separations between them agree with the values as specified on the program control panel. Check with an instructor if they don't.

Creating the RF pulses

Now, reconnect the gating signal from the computer interface to the gating input on the RF gate and rout the pulsed RF from the output of the RF gate to the input of the RF power amplifier. Disconnect the output from the power amplifier and turn it on. The power level meter on the front panel should barely move because it measures average output power (into a $50\ \Omega$ load) and is only on for short pulsed periods. **If you ever see the amplifier output meter rise above zero while the output is connected to anything, turn it off immediately. Something will likely be cooking.**

Look at the amplified RF pulses using a $10\times$ scope probe. (The pulse amplitude is too big for a direct connection.) Pull off the $10\times$ probe's clip lead and push the straight tip end into the BNC jack. The fit is a bit loose. Just rest the probe on the bench top with the tip connected. Don't bother connecting the probe's ground connection. Look at the RF pulses straight out of the power amplifier and then after the diode pair. Figure out how to see what the diodes do and report on it.

Set the pulser program for A -pulses only (turn B off). Make the A -pulse width $8\ \mu\text{s}$, and set the repetition time to 250 ms. Rout the amplified RF pulses from the power amplifier through the series diodes to the hybrid junction “A” terminal and rout the “B” terminal to the diode-protected input of the RF signal amplifier (not the power amplifier). Connect the output of the RF signal amplifier to the RF input of the mixer. The mixer’s LO (local oscillator) input is taken from one of the two RF splitter outputs driven directly by the function generator. The mixer’s IF (intermediate frequency) output is then routed to the voltage preamp input. View the output from the preamp on the scope. Start with this preamp set to AC coupling, high-pass filtering to 100 Hz, low-pass filtering to 10 kHz, and gain to 1000. Set the scope to a time base around 2 msec/div and the gain to around 50 mV/div. You are now ready to find a resonance.

Finding the FID

Now it’s time to adjust the B_0 field strength to find the free induction decay. Put the glycerine sample into the sample coil (from the top) taking care to get the 5 mm or so of glycerine centered in the 1 cm coil. You can put a small piece of tape on the sample if it slides around too easily in the coil.

Make sure the screw marked **LOCK** located below the coarse dial on the magnet power supply is loosened. Then slowly vary the magnetic field around 2-2.5 kG until you see a FID. Keep your eye on the scope because a damped beat frequency signal from the FID will appear at resonance. Once you have a signal, finger tighten the coarse control locking screw and adjust the fine control to get the FID beat frequency around 1 kHz. Check that its locking mechanism—a sliding lever at the base of

the dial—is also loose (pushed left) during adjustments.

If the B_0 field varies—even by a little—the FID frequency varies by a lot. If your FID frequency is not very stable, the problem may lie with the potentiometers connected to the fine and coarse adjustment knobs. They may be a little noisy (have a varying resistance) depending on where they are set and whether they are locked in position. We have found less problems when the coarse control knob is in the locked position. The fine control knob can be left in the unlocked position. If the FID frequency is still unstable, try finding a better spot for the potentiometers—moving both dials to keep the beat frequency around 1 kHz. Remember to unlock both before making adjustments and to lock down the coarse control afterward.

Another cause of field instability seems to be associated with the cooling water. We have found that changing a dirty filter in the water line often improves the magnet stability.

Adjust the preamp gain and filter settings and watch how the FID changes as the filter settings change and as the FID beat frequency changes by varying the magnetic field fine control. Report on your observations and describe the issues associated with the preamp settings and the FID beat frequency.

The FID decays with the time constant T_2^* , and will vary if the sample is moved around in the field. Move the sample up/down, back/forth, and left/right trying to find the most uniform field region characterized by the longest decay.

Measurements

In general, pulse sequences should not be repeated at intervals faster than $5T_1$. It takes at least this long for the sample to return to thermal equilibrium after being perturbed.

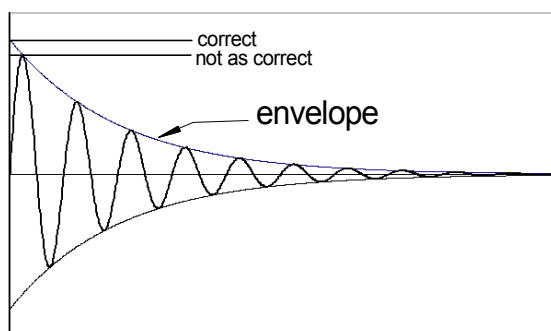


Figure 7: The “size” of the FID should be chosen as the amplitude at the start of the envelope, not as the amplitude at the first maximum.

With only A -pulses on, vary T_a to find pulses which rotate the magnetization by $\pi/2$, π , $3\pi/2$, 2π , and $5\pi/2$. The $\pi/2$ -pulse is at the first maximum in the FID signal. The π -pulse is at the first minimum, etc. Use the duration of the A -pulses relative to the rotation of the magnetization they cause to determine the Rabi frequency and then use it to estimate the amplitude of your \mathbf{B}_1 -field. You can assume you are exactly on resonance (where $\omega' = \gamma B_1$) for the calculation.

Applying $\pi/2$ A -pulses, adjust the \mathbf{B}_0 -field slightly and notice the change in frequency of the detected signal. Describe how the signal changes as you go through the zero beat frequency.

Note that the oscilloscope can be used in a **Measure|Average** mode to get a smoother trace from which to take measurements. For this to work, however, the FID signal must be quite stable. For example, if the magnet is the least bit unstable, the FIDs will have slightly different oscillation patterns and averaging may wash out the signal rather than improve it.

The true transverse magnetization \mathbf{M}_r oscillates at the Larmor frequency with an envelope that decays quickly due to field inhomogeneities, and the quantity of general inter-

est is the starting amplitude of the envelope. The signal you see on the oscilloscope is at a much lower beat frequency around 1 kHz rather than at the Larmor frequency, but it should have an envelope proportional to that of \mathbf{M}_r . Consequently, the starting amplitude of the oscilloscope envelope should provide the desired measure, but the only way to get it is to extrapolate back to its starting point and there is no easy way to do this reliably. Thus it is tempting to use the amplitude at the first oscillation maximum as a measure of the desired quantity. (See Fig. 7.) Even though the envelope will have already decayed somewhat by the time the first oscillation in the signal reaches a maximum, this need not be a problem because the amplitude at this first maximum would also be proportional to the starting amplitude of the envelope. However, it may be problematic because the proportionality constant will depend on the beat frequency and the initial phase of \mathbf{M}_r and these may vary during your investigations. For example, the beat frequency will vary if the magnet is even a little unstable. And for the inversion recovery measurements for T_1 , the signal inverts (its phase changes by π) as the magnetization passes through zero at the crossover time. Consequently, rather than use the amplitude at the first oscillation as a measure of the signal’s amplitude, it is better to make an “eyeball” estimate extrapolating the envelope back to the start of the signal as best you can.

T_2^*

Look at the FID envelope for a $\pi/2$ -pulse. Does it appear exponential? Make a rough estimate of T_2^* . Estimate the dimensions of your sample and assuming T_2^* is entirely due to \mathbf{B}_0 -field inhomogeneities, estimate the gradient of the \mathbf{B}_0 -field. For the estimate, you may assume T_2^* represents the time for protons at one

end of the sample to make one more Larmor precession than those at the other end.

T_1

Set the A -pulse to a π -pulse by adjusting T_a . Then turn the A -pulse off and set the B -pulse to a $\pi/2$ -pulse. Then turn the A -pulse back on. Starting at T_d small, as you increase T_d , you should see the FID decrease in size until it is nearly zero as M_z increases from around $-M_0$ towards zero, and then it will increase again as M_z increases to its equilibrium value M_0 . The point where the signal goes to zero, the crossover, occurs at $t = 0.693T_1$. Measuring the amplitude of the FID as a function of T_d . Check if your decay is exponential by computer fitting the amplitude of the FID as a function of $t = T_d$ in Eq. 34 with M_0 , M_i and T_1 as fitting parameters. Do not fit to Eq. 36, which is Eq. 34 with $M_i = -M_0$. The fitted value for M_i should come out close to $-M_0$, but if the A -pulse is not a good π -pulse, the longitudinal magnetization following this pulse will not be perfectly inverted and M_i will be smaller (in magnitude) than M_0 . Fitting the data to a formula with M_i fixed at $-M_0$ can then lead to systematic errors in the fitted T_1 .

For the fit, you must treat the FID amplitude as negative for signals before the crossover and positive for those afterward. Near the crossover you may want to throw out data points as it may be difficult to determine their correct sign. Does the fitted time constant agree with the crossover time? Determine the uncertainty in the fitted time constant.

T_2

Set up the necessary A - and B -pulse widths and find the spin echo. Measure the FID amplitude of the echo as a function of T_d .

Perform a fit to Eq. 35 with $t = 2T_d$ (why $t = 2T_d$, not $t = T_d$?) and determine a value and uncertainty for T_2 . Perform fits both with and without the t^3 term in the exponential. Can you see the effects of diffusion and field inhomogeneities? Why would the effects of diffusion be difficult or impossible to measure if T_2 is too short? Comment on the relative sizes of T_2^* , T_2 and T_1 . What should be their predicted ordering and why?

CHECKPOINT: Measurements for the glycerine sample and the determinations of its T_2^* , T_1 , and T_2 should be complete.

Distilled Water

Change to the distilled water sample. Push the glycerine sample vial out of the sample holder with a pencil eraser from the bottom so the vial comes out the top of the mounting tube. Then push the distilled water vial in from the top of the tube so the liquid inside is in the center of the coil.

The time constants T_1 and T_2 for distilled water will be much longer—on the order of seconds. This means data acquisition for inversion recovery and echo sequences will take much longer. (Recall that T_r needs to be at least $5T_1$ to let the spins reestablish equilibrium populations.) For long T_1 , the oscilloscope trigger must be set for normal (not auto) so the FIDs will not disappear between pulses.

A good way to determine how big T_r needs to be is to measure the zero-crossing time for the inversion recovery sequence, increasing T_r until the crossover time stops changing. This also lets you check the $T_r > 5T_1$ rule of thumb. Report on the results of this experiment and the validity of this rule.

Because of the long T_2 , the spin echo measurement in distilled water clearly shows the

the effect of diffusion. Unfortunately, the field gradient G is not well determined in the present apparatus. So use your measurements and the fitted coefficient of the t^3 term (in the argument of the exponential) with the known value of D (about 2.3×10^{-9} m²/s at 25°C) to determine G and compare with the cruder determination based on T_2^* .

Another sequence that is sometimes used to measure long T_1 's is to apply a single A -pulse repeatedly at fixed time intervals T_r . This one pulse (with its repeat time T_r) is then used for both preparation and probing. For an A -pulse that causes a precession through an angle θ ($\theta = \pi/2$ is typically used) the steady state amplitude of the magnetization immediately following each A -pulse can be shown to be:

$$M = M_0 \sin \theta \cdot \frac{1 - \exp(-T_r/T_1)}{1 - \cos \theta \exp(-T_r/T_1)} \quad (37)$$

(You might want to try to derive this equation yourself.)

To use Eq. 37, measure the size of the FID using a $\pi/2$ A -pulse (leave the B -pulse off) as you vary the pulse repeat time T_r . Start off by fitting your results to Eq. 37 with M_0 and T_1 as fit parameters but with θ fixed at the nominal value of $\pi/2$ (1.57). The reason that fitting θ is problematic should become clearer if you try the fit with θ still fixed but off the nominal value (at, say, 1.47 and 1.67). What happens to T_1 for these conditions? What happens to T_1 if you let θ be a third fitting parameter? Is the fitted value of θ reasonable? Discuss the results.

Special projects

There are many studies that can be performed with this apparatus. Here are three you might consider.

1. Measure the gyromagnetic ratio of the ¹⁹F (fluorine) nucleus in the liquid Fluor-

inert (perfluorotributylamine or FC-43) or in the solid teflon (tetrafluoroethylene). Only try the solid sample after finding a FID with the liquid. The solid has short T_1 and T_2 and the amplifier high pass filtering may need to be set higher to see the weak FID. The Fluorinert FID should show a beating pattern. Learn enough about chemical shifts to relate them to the (at least two) Larmor frequencies that must be present in the sample in order to create a beating FID. (See auxiliary material for chemical shifts in FC-43.) How can you determine the very small difference in the two Larmor frequencies from the beat pattern? Express the difference in ppm of the mean Larmor frequency.

2. Add small amounts of CuSO₄ (copper sulfate) to distilled water samples to determine how the time constants depend on the concentrations of paramagnetic ions.
3. Make mixtures with varying ratios of glycerine and water, which changes the viscosity of the mixture. Measure how the time constants depend on the viscosity.