

# NUCLEAR MAGNETIC RESONANCE

## OBJECTIVES

1. To observe NMR (nuclear magnetic resonance) for protons and for fluorine nuclei in a magnetic field and to determine their  $g$ -factors.
2. To investigate the NMR relaxation lifetimes.

## REFERENCES

Melissinos, Chapter 7 and particularly Section 7.4. Also review the Zeeman effect, if you have already done that experiment.

## THEORETICAL BACKGROUND

Nuclear magnetic resonance can be modeled two apparently different (although equivalent) ways: A classical model of magnetic moments precessing in a magnetic field, or a quantum model of “spin flips” between two different energy levels. For this experiment, it will be easiest to think about what’s going on in terms of spin flips. In Physics 342, for pulsed NMR, a precession model will be more useful.

Electrons and protons are spin-1/2 particles, with spin quantum number  $m = \pm 1/2$ . Because of their spin, they have a magnetic moment  $\vec{\mu}$ . If placed in an external magnetic field  $B_0$ , the two spin states will have different energies. This is just the Zeeman effect, but a more physical picture is to think of a proton (or electron) as a little compass needle. The lowest energy state – usually called “spin up,” is when the spin (the compass needle, the magnetic moment) is aligned with the magnetic field. The “spin down” state, with the spin anti-aligned with the field, is a higher energy state. That is, you have to put energy into a compass needle to turn it against the field. This is shown in Figure 1. For protons the lower energy state is  $m = +1/2$ , (electrons – because the negative charge reverses the sign of the magnetic moment – have  $m = -1/2$  as the lower energy state).

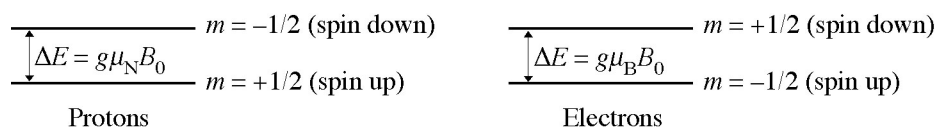


Figure 1: The two energy states represent the spin aligned with or opposite to the external magnetic field.

**Energies:** The energy of a classical magnetic moment  $\vec{\mu}$  in a magnetic field  $\vec{B}_0$  is  $E = -\vec{\mu} \cdot \vec{B}_0$ . The quantized energy levels, for a particle with magnetic quantum number  $m$ , are

$$E_m = \begin{cases} -mg\mu_N B_0 & \text{protons} \\ mg\mu_B B_0 & \text{electrons} \end{cases} \quad (1)$$

The constant  $\mu_B$  is the **Bohr magneton**, which you also meet in the Zeeman effect. It is, more or less, the inherent strength of the electron magnetic dipole moment in that an electron with 1 unit of orbital angular momentum ( $L = \hbar$ ) would have magnetic moment  $\mu = \mu_B$ . The accepted value, to three significant figures, is  $\mu_B = 9.27 \times 10^{-24}$  J/T. Similarly,  $\mu_N$  is the **nuclear magneton**. It is, more or less, the inherent strength of the proton magnetic dipole moment in that a proton with 1 unit of orbital angular momentum ( $L = \hbar$ ) would have magnetic moment  $\mu = \mu_N$ . The accepted value, to three significant figures, is  $\mu_N = 5.05 \times 10^{-27}$  J/T. The nuclear magneton is much smaller than the Bohr magneton, and a more detailed analysis shows that the ratio is the same as the ratio of electron and proton masses:  $\mu_N/\mu_B = m_e/m_p = 1/1836$ . The large difference between  $\mu_N$  and  $\mu_B$  has experimental consequences.

More interesting in Equation (1) is the “g-factor.” An orbiting point charge has  $g = 1$ , so you don’t see g-factors in our Zeeman experiment (but you do in the optical pumping experiment). But not all magnetic moments are due to orbital angular momentum. Spin is an inherently quantum effect with no classical limit (i.e., there’s no “limit of large quantum numbers” when spin is always 1/2). The relativistic quantum mechanics invented by Dirac predicts that the g-factor associated with the spin of a point charge is  $g = 2$ . Later, in the 1950s, the invention of quantum electrodynamics (by Feynman and others) found that there are slight corrections to the electron g-factor. Today, the electron g-factor is the most precisely predicted (from theory) and precisely measured physical constant. It is  $g_{\text{elec}} = 2.0023193043622 \pm 0.0000000000015$ . For our purposes, however, we can assume  $g_{\text{elec}} = 2.00$ .

The proton, however, is not a point charge; it is a composite particle made of three quarks, each of which has a spin. A complete theory of quantum chromodynamics would predict the g-factor of the proton on the basis of its quark structure – a prediction that would certainly lead to a Nobel Prize. But it hasn’t been done, so today the proton g-factor is known only from empirical measurements, such as the one you’re about to do. The accepted value is  $g_{\text{proton}} = 5.5857$ . The fact that the g-factor is not 2 is telling us something about the structure of the proton.

**Transitions:** The energy difference between the two states – spin up ( $m = +1/2$ ) and spin down ( $m = -1/2$ ) – is

$$\Delta E = g\mu_N B_0 \quad (2)$$

If you measure  $\Delta E$  for several different values of  $B_0$ , you can use your results to determine the proton g-factor. To do so, you are going to cause spin flips by irradiating a sample of protons with photons whose energy is tuned to  $E_{\text{photon}} = hf = \Delta E_{\text{proton}}$ . That is, the photons have to be *resonant* with the transition energy to cause a spin flip, and that is the origin of the term nuclear magnetic *resonance*.

Figure 2 illustrates the idea. If we illuminate the sample with photons whose energy is *not*  $\Delta E_{\text{proton}}$ , nothing happens; they pass right through. But at resonance, where the energies match,

the photons cause quantum jumps. An upward transition is **absorption**, which you'll recall from Modern Physics. The photon disappears, and its energy is transferred to the proton.

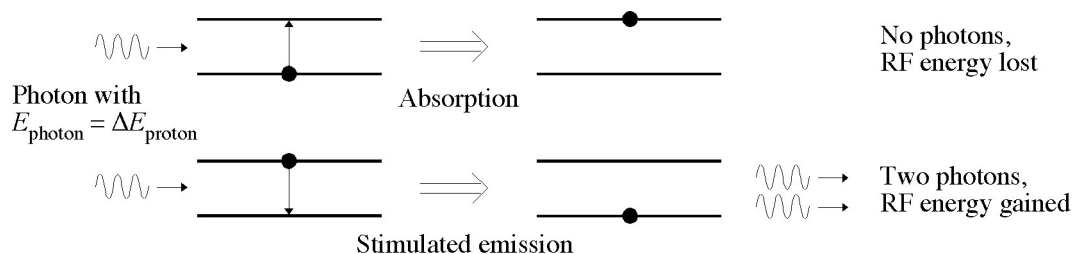


Figure 2: A photon whose energy matches the transition energy – a resonance – can cause a quantum jump between the two states. These quantum jumps represent a spin flip in the magnetic field. An upward quantum jump is an absorption process in which a photon is lost. A downward quantum jump is stimulated emission in which photon is gained.

You learned in Modern Physics about spontaneous emission, where a system undergoes a quantum jump to a lower level by emitting a photon. In principle, a proton in the higher energy level could spontaneously emit a photon, but in practice it will never happen. In quantum mechanics you can show that the probability of spontaneous emission scales like  $f^3$ , where  $f$  is the photon frequency. The photon frequency you'll be using is about 7 orders of magnitude smaller than the frequencies of visible light ( $\sim 10^7$  Hz compared to  $\sim 10^{14}$  Hz), so the probability of spontaneous emission is a factor  $\sim 10^{21}$  less. On average, it would take nearly 1 million years before a spin-down proton would spontaneously flip and emit a photon!

The downward transition important to us is not spontaneous emission but **stimulated emission** in which the system is *driven* in the downward direction by the external photons. It is stimulated emission, not spontaneous emission, that is the inverse process of absorption. In stimulated emission (which you'll recall is essential to the operation of lasers), an incoming photon forces a proton in the upper state to jump to the lower state, emitting a photon. This emitted photon has exactly the same energy as the incoming photon, so one incoming photon becomes two outgoing photons.

We just noted that the frequency will be  $\sim 10^7$  Hz, or roughly 10 MHz. Frequencies in the range 1 MHz to 1000 MHz are used in radio and telecommunications, and historically they are called **RF**, for *radio frequencies*. We're not used to thinking of such low frequencies in terms of photons, primarily because low-frequency detectors are rarely sensitive at the photon level. Magnetic resonance is an exception, and it does help us realize that *all* electromagnetic radiation, regardless of frequency, is quantized.

Three questions arise: (1) How do we generate low-frequency photons? (2) how do we achieve resonance? and (3) how do we *know* if we're in resonance? The first is an experimental detail that will be described below. In this experiment, you will be able to vary both the photon energy (the RF frequency) and the difference in proton energy levels (by changing the magnetic field

$B_0$ ), and either can be used to bring the system into resonance. But by far the most important of these three questions is the third: It's easy to say that spin flips are occurring at resonance, but we'll never know unless something *detectable* is associated with the spin flips. What we're going to detect – with a very clever experimental arrangement – is the loss of RF photons at resonance.

**Populations:** Suppose *all* the protons were in the lower-energy spin-up state. Off resonance, all the incoming RF photons pass through the sample with no loss. On resonance, every quantum jump (i.e., every spin flip) absorbs a photon, so photons are disappearing. Physically, *electromagnetic energy is being lost*. If we can detect the loss of RF energy, we'll know we're on resonance.

But consider a different situation. Suppose there were equal numbers of spin-up and spin-down protons. Being on resonance would cause spin flips, but now there would be an equal number of absorptions (up transitions) and stimulated emissions (down transitions). Every absorption destroys a photon, but every emission creates a new one. Although we would be on resonance, with spin flips occurring, there would be *no loss of electromagnetic energy*.

So which is it? The question “In equilibrium, how many particles are in each state of a quantum system?” is a question addressed in thermodynamics. If you've had PHYS 301, hopefully you'll remember the *Boltzmann factor*, which tells us that the equilibrium population in a state of energy  $E$  is

$$N \propto e^{-E/kT}$$

where  $T$  is the absolute temperature and  $k$  is Boltzmann's constant. We can avoid knowing the proportionality constant by taking ratios. In particular, consider the ratio of the population of spin-down (higher energy) protons to spin-up (lower energy protons):

$$\frac{N_-}{N_+} = \frac{e^{-E_-/kT}}{e^{-E_+/kT}} = e^{-\Delta E_{\text{proton}}/kT} = e^{-g\mu_N B_0/kT} \quad (3)$$

where  $\Delta E_{\text{proton}}$  was found in Equation (2). A very useful thing to learn is that  $kT \approx 1/40$  eV at room temperature. The excited states of atoms are  $\gg 1/40$  eV, so in atoms  $e^{-E/kT} \approx 0$ . Thus in Modern Physics you learned that room-temperature atoms are all in the ground state, none in excited states. This experiment runs under the opposite extreme:  $\Delta E_{\text{protons}} \ll 1/40$  eV. That is, the energy separation between spin-up and spin-down protons is very, very small in comparison with the size of room temperature thermal fluctuations. Consequently, Equation (3) tells us that  $N_- \approx N_+$ ; the two states are almost equally populated at room temperature, hence upward and downward transitions are balanced at resonance and there is almost no loss of electromagnetic energy.

But “almost zero” isn't “exactly zero,” and it's the very, very slight difference between upward and downward transitions, leading to a very small energy loss, that we're going to detect. As part

of your lab report, should finish the calculation to show that  $N_- / N_+ \approx 0.999998$ , differing from exactly 1 by only about 2 parts in a million. But, with an appropriate detector, that's enough net loss of RF energy to detect.

**Detection:** The detector you'll use is called a **marginal oscillator**. It is an  $LC$  oscillator, like you studied in Electronics, that, as its name implies, is barely able to sustain an oscillation. Any resistance added to the circuit, which causes energy loss, is enough to cause the oscillation amplitude to decrease rapidly until the oscillations fail.

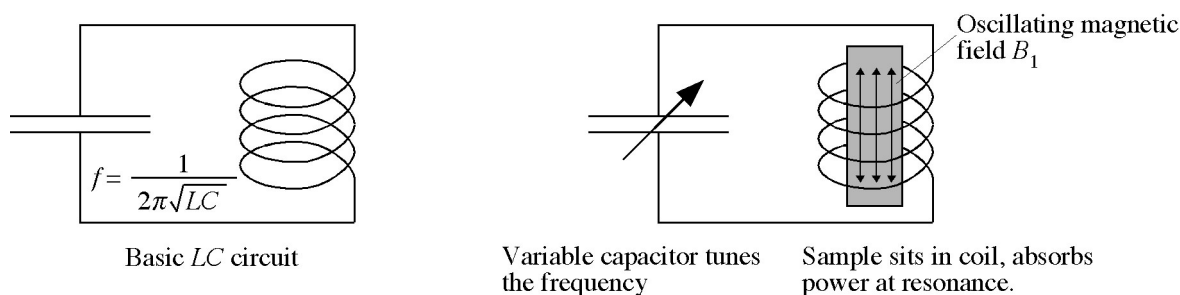


Figure 3: The marginal oscillator is an  $LC$  circuit with a variable capacitor to change the frequency. The sample sits inside the coil, bathed in RF photons.

As Figure 3 shows, the sample sits inside the coil of the oscillator. Because the coil is a solenoid, its magnetic field, called  $B_1$ , oscillates along the coil direction. This oscillation establishes the polarization of the RF photons. You can think of the sample as sitting inside a “bath” of RF photons being created by the coil. At resonance, the very small net absorption of RF photons by the sample is a loss of energy. Dissipation of energy is what resistors do, so as far as the circuit is concerned, the sample – at resonance – is an *effective resistance*. Consequently, the circuit's oscillation amplitude decreases – a detectable response!

Thus the basic procedure will be to observe the amplitude of the oscillations while changing either the magnetic field (tuning  $\Delta E_{\text{protons}}$ ) or the oscillation frequency (tuning  $E_{\text{photons}}$ ). A sudden loss of amplitude indicates that magnetic resonance has been found and that the protons (or electrons) are undergoing spin flips in the magnetic field.

**Modulations:** But it's not quite that easy. If you were to tune the system to resonance, you would be driving the protons back and forth between the two states with rapid spin flips. This totally overwhelms the thermal effects that make for the slight population difference, and very quickly you would force the populations of the two states to become equal. (We say that you **saturate** the transition, and it is no longer in thermal equilibrium.) With equal populations, there is no longer any energy loss and thus no effect on the marginal oscillator. The very process of finding the resonance destroys the signal!

The solution – a common experimental technique – is not to stay on resonance but to keep passing back and forth across resonance, a process called **modulation**. We're going to do so by adding a small *modulation field*  $B_{\text{mod}}$  to the external field  $B_0$ , making the net field

$$B_{\text{ext}} = B_0 + B_{\text{mod}} \cos(2\pi f_{\text{mod}} t) \quad (4)$$

with a modulation frequency  $f_{\text{mod}} \approx 30$  Hz. If you look back at Figure 2, imagine the two energy levels bouncing toward and away from each other very slightly at the modulation frequency.

Figure 4 shows what happens:

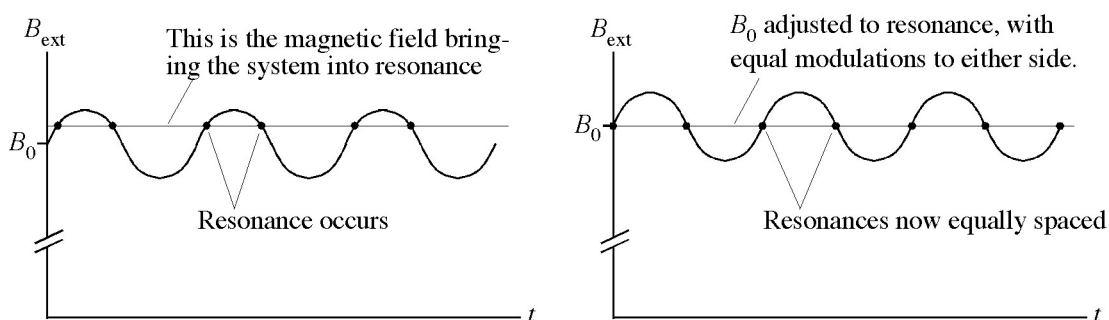


Figure 4: Modulation causes the system to pass through resonance twice per period.

The modulations in the figure are greatly exaggerated. In practice,  $B_0 \approx 3000$  gauss while  $B_{\text{mod}} \approx$  few gauss, so the magnetic field changes on the order of one part in a thousand. The “broken axis” implies that we’re looking at a magnified view of the modulations. If  $B_0$  is *close* (within a few gauss) to the value that causes magnetic resonance, the modulations will cause resonance to occur twice per period and you will see a resonance signal. (Of course, you won’t have a signal at all until you get to within a few gauss of resonance.) What you’ll then want to do is adjust  $B_0$  to produce *equally spaced resonances*. Equal spacing tells you that  $B_0$  is the correct value for resonance and that you would stay on resonance if you turned off the modulations – although doing so immediately makes the signal go away for the reasons just noted.

**Relaxation:** Why  $f_{\text{mod}} \approx 30$  Hz? The exact value isn’t at all critical, but if it is too fast the signal diminishes. Each time you pass through resonance, the spin flips drive the system out of thermal equilibrium. To continue seeing a signal, you have to allow the system to return to thermal equilibrium before you again pass through equilibrium. The time it takes a system to come to thermal equilibrium with its surroundings is called the **relaxation time**. Relaxation to equilibrium occurs via interactions with the environment – interactions with what in thermodynamics is called a *heat bath*.

Protons, your first sample, interact magnetically with other magnetic moments in the sample. These magnetic interactions with the environment can cause spin flips, eventually establishing a thermal equilibrium in which the protons are distributed between the two states in accordance with the Boltzmann factor. Much of NMR is done using solid samples, so the environment is a *lattice* of nuclei and their electrons. The interaction of the protons with the magnetic moments of

the lattice nuclei is called the **spin-lattice interaction**, and the strength of these spin-lattice interactions determines how quickly a disturbed spin system returns to equilibrium.

For historical reasons, the interaction of the spins of the sample with the magnetic moments of the environment is always called the spin-lattice interaction, even if the environment is a liquid – as it will be in your study of NMR in the protons of water. The relaxation time due to the spin-lattice interaction is called  $T2^*$ . The approach to equilibrium is exponential with time constant  $T2^*$ , rather like charging a capacitor that exponentially approaches the fully charged state with time constant  $\tau = RC$ . There's no strict answer to "When is the system back in equilibrium?" but a reasonable rule-of-thumb is after  $\approx 5$  time constants since  $e^{-5} = 0.006$  means that the all populations are within 1% of equilibrium values after 5 time constants. So we need to wait  $\approx 5T2^*$  after each resonance crossing before doing it again.

For pure water,  $T2^* \approx 3$  s, so we would need to wait  $\approx 15$  s between resonance crossings to study NMR in pure water. Now in practice there are other factors reducing the relaxation time – inhomogeneity of  $B_0$  for one thing. But in order to shorten  $T2^*$  our sample will be water with a small amount of dissolved copper sulfate, which is why the water is blue. The copper nuclei have a magnetic moment, and the protons interact magnetically with the copper much more strongly than they interact with other protons, thus decreasing  $T2^*$ . The exact value of  $T2^*$  depends on the strength of the solution, but  $T2^* \approx 1$  ms is typical for solutions used in NMR. Thus the sample is pretty much back in equilibrium  $\approx 5$  ms after a resonance crossing. Since the modulation makes two crossings per cycle, the sample will have sufficient time to return to thermal equilibrium if  $f_{\text{mod}} < 100$  Hz (a 10 ms period). Then each crossing is an independent measurement, not disturbed by anything that happened during the last resonance crossing.

Note: You'll measure  $T2^*$  in several samples if you take PHYS 342 and do the pulsed NMR experiment.  $T2^*$  is one of the most important quantities measured in medical resonance imaging (MRI) because it allows different tissues to be differentiated.

**Signal:** The marginal oscillator oscillates at  $f \approx 10$  MHz, the RF frequency, and its amplitude dips every time the modulation takes the sample through resonance. It's possible but not very practical to observe the oscillations. What we want to see is not the oscillations themselves but the dip in amplitude, and a good way of doing so is with a *rectifier circuit*. Rectifier circuits, which you studied in Electronics, use diodes and capacitors to turn AC to DC. They are how the audio-frequency amplitude in AM (amplitude-modulated) radio is pulled off from the RF carrier frequency. Figure 5 shows how the signal you see on the scope is derived from the oscillator.

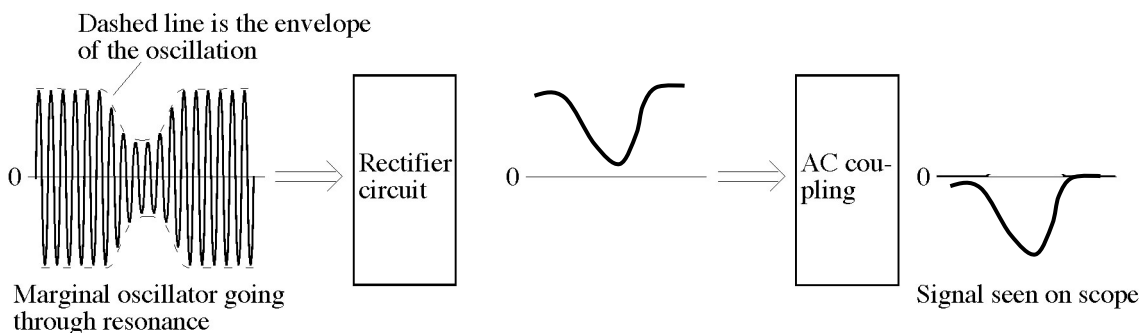


Figure 5: The signal is rectified on the negative side so the dip is a rise, then AC-coupled (through a capacitor) out to make a pulse (an inverted dip) whenever you pass through resonance. In reality, there are *many* more oscillations across the dip than are shown here.

If you compare Figures 4 and 5, you should see a series of pulses on the scope, one for each pass through resonance, and you'll need to adjust either  $B_0$  or the RF frequency  $f$  to get the pulses equally spaced.

Note that if two different nuclei are measured in *exactly the same* field, the ratio of resonance frequencies is  $f_1/f_2 = g_1/g_2$ . This permits very accurate determinations of unknown magnetic moments relative to known ones if frequencies can be accurately measured. You'll see this when you measure the g-factor of the fluorine nucleus.

## NMR PROCEDURE

Figure 6 shows a block diagram of the experiment. Take a moment to familiarize yourself with the arrangement in the lab. This experiment involves three magnetic fields ( $B_0$ ,  $B_1$ , and  $B_{\text{mod}}$ ) and two frequencies ( $f_{\text{RF}}$  and  $f_{\text{mod}}$ ). **It is essential that you know what these represent, how they're generated, and which pieces of the experiment control them.** You won't get far without knowing this. Be prepared to explain the setup in the lab to your instructor.

Classically, the coil in the marginal oscillator produces an oscillating magnetic field  $B_1$ . Notice that it is perpendicular to  $B_0$ . In terms of photons, this means that photons at frequency  $f_{\text{RF}}$  are generated with the magnetic polarization perpendicular to  $B_0$ . This is required by quantum-mechanical selection rules for the spin-flip transition. (It's the same reason the two  $\Delta M = \pm 1$  frequencies you saw in the Zeeman effect were polarized perpendicular to  $B_0$ .) Think of the sample in the coil as being in a sea of photons with the correct polarization.

The first thing to do is determine the magnetic field at the sample position as a function of the current applied to the electromagnet. We need this information since we cannot put both the Hall probe and the sample simultaneously at the center of the magnet. Turn on the current to the magnet – perhaps a couple of amps. **VERY CAREFULLY** insert the Hall probe into the sample



chamber, positioning it so that the end of the probe is about the middle of the pole pieces. Rotate the probe until you get the maximum reading and clamp it in place. Now you can adjust the current and measure the magnetic field. Note that the frequencies available from the oscillator range from about 16 MHz to 19 MHz so there is a limited range of magnetic fields you would be interested in. What are these fields? Well, since you will be using protons it is useful to combine Equation (2), the resonance condition  $E_{\text{photon}} = hf_{\text{RF}} = \Delta E_{\text{proton}}$ , and the known values of various constants to derive a formula that relates the RF frequency  $f_{\text{RF}}$  (in MHz) at resonance for protons to the magnetic field  $B_0$  (in gauss). Without such a formula, you'll have no idea where to start searching for a resonance.

Now that you know the magnetic fields for a number of currents, you can start searching for the NMR signal.

Referring again to figure 6, remove the Hall probe and insert the small tube of “blue water” into the coil that’s sitting between the magnet pole tips.

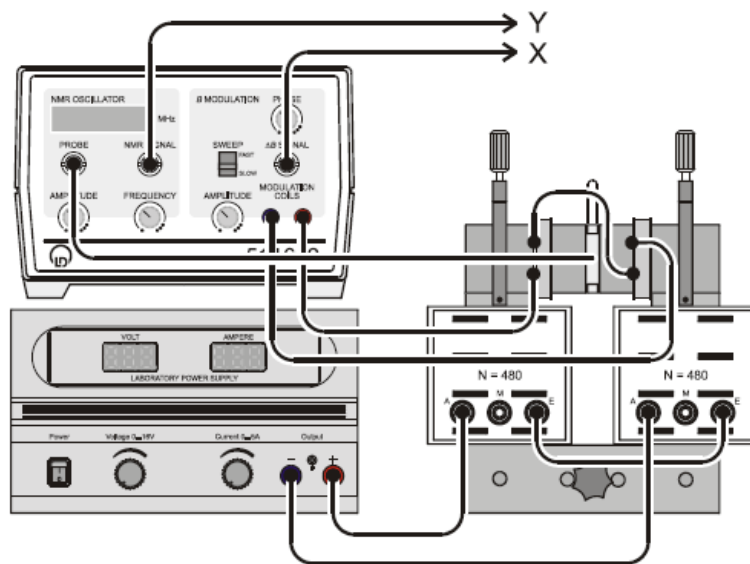


Figure 6: Experimental arrangement – taken from Leybold Physics Website. (This is just suggestive the actual connections are slightly different than this.)

Put the output from the NMR SIGNAL to Channel 1 and the  $\Delta B$  SIGNAL to Channel 2 on the oscilloscope. Set the scope to trigger on Channel 2 (the modulation signal), set the modulation frequency to “fast”, and adjust the scope time base to see  $\approx 2$  full cycles of the modulation.

Using your earlier calculation for guidance, find the NMR signal for protons in a field of  $\approx 4000$  G. Use the Fine Adjust on the magnet power supply to get equal spacings between the peaks.

The signal is inherently noisy. Once you have a signal, you can greatly improve the signal-to-noise ratio by using “Averaging” on the scope. However, the more you average, the longer the scope takes to respond, and you can pass right over a signal without the scope having time to display it. So it’s best to have averaging off while searching for a signal.

Vary the amplitude of the modulation current and the RF amplitude to optimize the signal.

You will notice that the NMR signal for water is not a simple absorption feature. Rather, it is an oscillation that dies away. Also, the frequency varies – the signal is “chirped”. Why is this? You can find a good discussion in Melissinos, but a brief explanation goes like this: imagine first that you can bring the sample to resonance and then switch the RF signal off. Even though the signal is off, the magnetic moments are still precessing about the field  $B_0$ , giving a time-varying field in the probe coil. This varying field creates a time varying current and if you could see it directly this would be a very high frequency oscillatory output which would die away as the magnetic moments interact with the atoms around them and with each other. However, remember that the magnetic field is changing so that the precessional frequency is changing and that we are continuously irradiating the sample with a fixed frequency. Now, the output that we see is the mixture of these two close frequencies, leading to beats, and over time the frequency difference increases, leading to an increase in the beat frequency.

We can use these “wiggles” in the NMR signal to determine the lifetime of the NMR signal, as discussed below.

## **What to Measure?**

### **Protons**

Devise and carry out a series of measurements by which you (a) test whether or not Equation (2) is valid and (b) if it is, determine the proton  $g$ -factor. Compare your result to the accepted value.

Remember the wiggles from above? You can use those to find the lifetime of the NMR response. What you need to do is measure the amplitude of the oscillatory signal as a function of time. Assuming an exponential decay in the signal, you can make a log amplitude vs time plot and fit a straight line to extract the lifetime. You can get some hints here in Melissinos.

### **Fluorine**

The approximate  $g$ -factor of fluorine nuclei is 5.25. This is close enough to the  $g$ -factor of protons that you can see a fluorine resonance in this apparatus. (The resonances of nearly all other nuclei don’t fall within the tuning range of our marginal oscillator.) Replace the water with

the solid sample of Polytetrafluoroethylene (PTFE). The goal is to determine the fluorine  $g$ -factor by measuring the NMR frequency of the fluorine. You should be able to show (and should do so in your report) that if  $B_0$  remains constant, the ratio of the  $g$ -factors of two different nuclei is the same as the ratio of their resonance frequencies. The fluorine resonance is weak and a little harder to find. To find it the first time:

- Find the proton resonance at a frequency near  $\approx 17.5$  MHz. Record the specific frequency.
- Use the approximate  $g$ -factor to *predict* the approximate resonance frequency of fluorine nuclei in the same field.
- Insert the fluorine sample. **Leaving the field unchanged**, vary the frequency to find the fluorine resonance.

Now that you have found the fluorine resonance you can find it again for various magnetic field strengths and, using the same procedure you developed for the protons, find the  $g$ -factor for fluorine.

### Fluorine signal linewidth

You will have noticed that as you change the frequency of the oscillator the position of the resonance changes. Thus, by adjusting the frequency and noting the position of the resonance you can convert the horizontal (time) scale on the oscilloscope to one of frequency – not absolute frequency but change in frequency. Once you have this then you can measure the width of the resonance line. You should find it to be of order 10 kHz.

### REPORT:

The background section of this write-up is long. Please don't try to reproduce all of it in your report! You do need a summary of important ideas, but think about how to convey the essential physics and the essential experimental details to a reader in just a couple of pages.

Note that:

- You're asked on page 5 to complete the calculation of the population ratio.
- You're asked on page 9 to derive an equation for the resonance frequency in which plugging in  $B_0$  in gauss gives  $f_{\text{RF}}$  in MHz.
- You're asked on page 11 to prove that the ratio of resonance frequencies equals the ratio of  $g$ -factors if the magnetic field is unchanged.

All these should be woven into your report in a natural and seamless way, not merely stuck on like you were doing a homework problem.