

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 “ π -pulse” (180 degrees) or sideways with a “ $\pi/2$ -pulse” (90 degrees). With 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 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 semi-classical 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 γ 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 γ 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”):

$$\gamma = \frac{g\mu_n}{\hbar} = \frac{ge}{2m_p}, \tag{2}$$

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 to \vec{B}_0

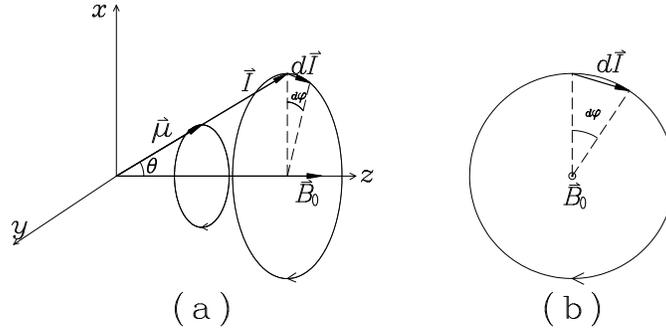


Figure 1: (a) Vectors defined in semiclassical picture of NMR. (b) Tip of angular momentum vector \vec{I} , viewed opposite to \vec{B}_0 .

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

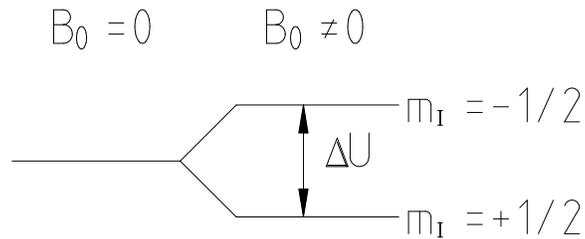


Figure 2: Splitting of nuclear energy levels due to applied magnetic field.

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

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

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 along

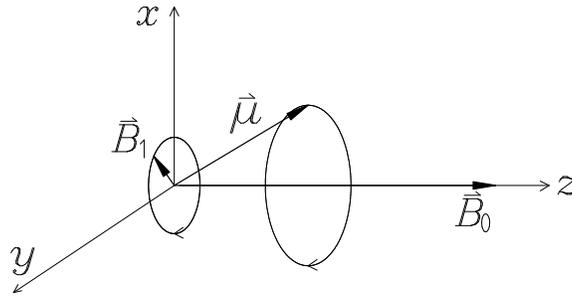


Figure 3: The RF \vec{B}_1 field rotates with the precessing $\vec{\mu}$ in the semiclassical picture.

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 ω_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 μ_z , μ_x and μ_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 ω_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 $+x$ 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 ω_0 , and calculate the rate of change of the flux, $d\Phi/dt$ from this.)

As the moments precess, the induced voltage oscillates at the Larmor frequency (ν_{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

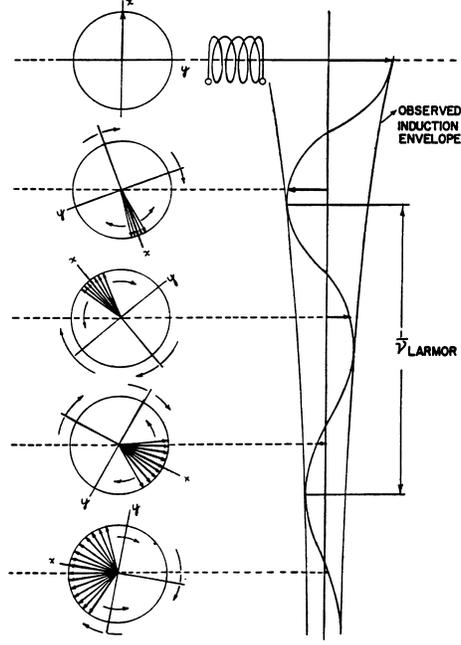


Figure 4: Induction signal measured by a pickup coil in the transverse plane following orientation of moments along the x -axis. Taken from the article by Hahn [4].

relaxation time T_2^* defined as

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

where ΔB_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 $\Delta\omega_{eff} \sim 1/T_2^*$.

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, γ , 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° . If this pulse is applied to a sample initially at equilibrium with a net magnetization $\vec{M} = M_z \hat{k}$, then \vec{M} will become $M_z \hat{i}$ (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: $M_z \hat{k} \rightarrow -M_z \hat{k}$; this type of pulse is called a “ π pulse”. Interestingly, the free induction decay signal immediately following a π 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 found in the theoretical introduction to the pulsed NMR experiment write-up.

References

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- [2] Melissinos, A. C., *Experiments in Modern Physics*, Academic Press, San Diego, 1966, pages 340–374.
- [3] Slichter, C. P., *Principles of Magnetic Resonance, 3rd Ed.*, Springer-Verlag, Berlin, 1990.
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2 The continuous-wave NMR experiment

In this experiment you will be looking for the magnetic resonance condition for protons (also known as ^1H nuclei) and for fluorine (^{19}F) nuclei. As discussed previously, our apparatus brings the sample into resonance by adding a small sweep magnetic field to the steady state field, B_0 . A diagram of the apparatus is shown in Fig. 5. The sweep field has a triangular waveform (frequency ≈ 80 Hz) as

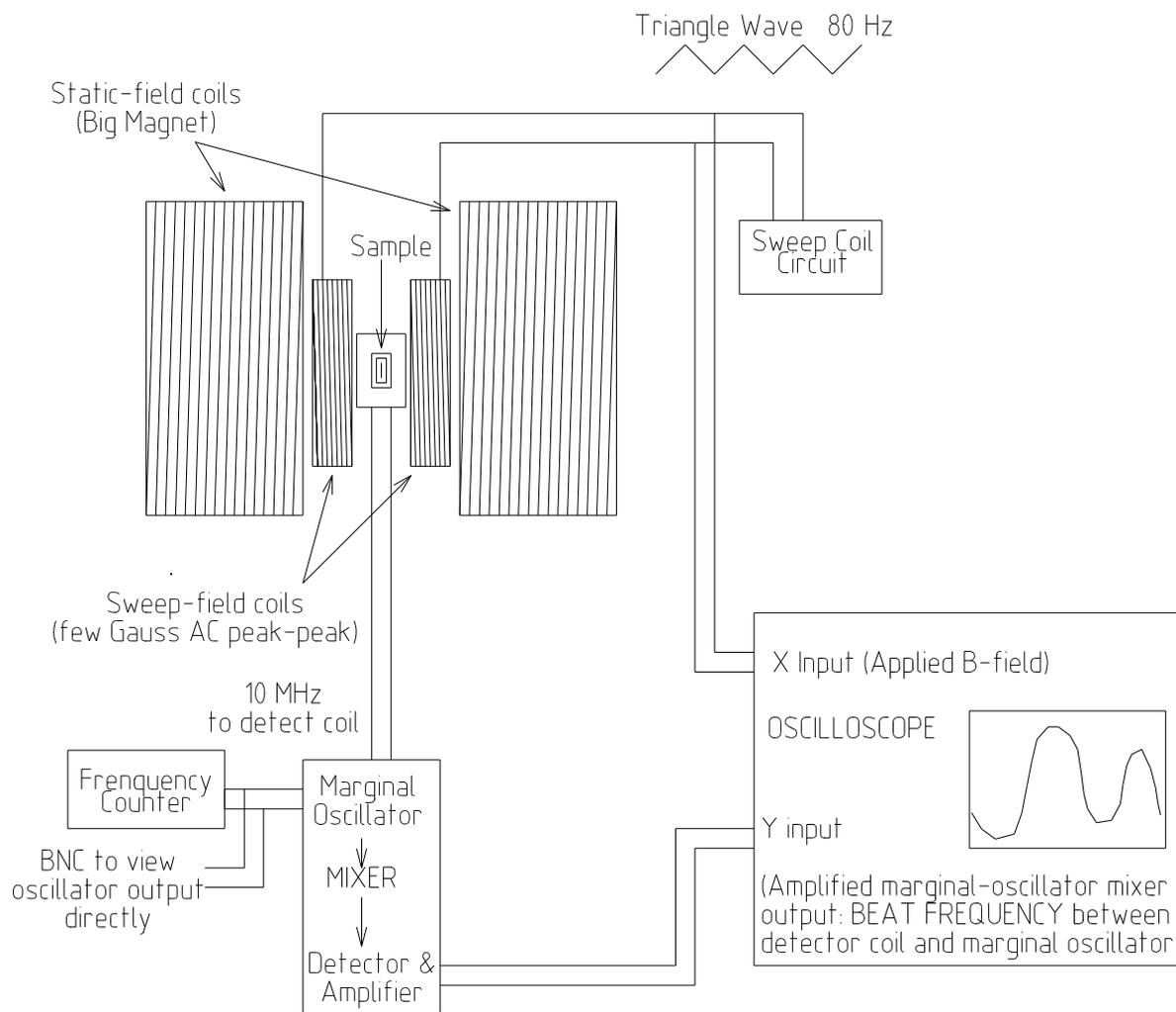


Figure 5: The continuous-wave NMR (CWNMR) apparatus.

shown in Fig. 6, is symmetric about zero, and has a magnitude of several gauss peak to peak (which is very small compared to the steady state field generated by the electromagnet). Figure 6 also shows the resonance signal as the sample passes through the resonance condition on both sides of the triangular waveform. A more detailed picture of the resonance signal is shown in Fig. 7, which was acquired using the averaging feature of the digital oscilloscope. It is a signal similar to this that you will be looking for, first with the X-Y analog scope, and later with the digital scope. A gaussmeter is used to provide an independent measure of magnetic field strength. The gaussmeter probe is attached to the shaft holding the NMR head, and the sensing region of the probe is right at the tip, which has been positioned as close to the sample as possible. The gaussmeter is capable

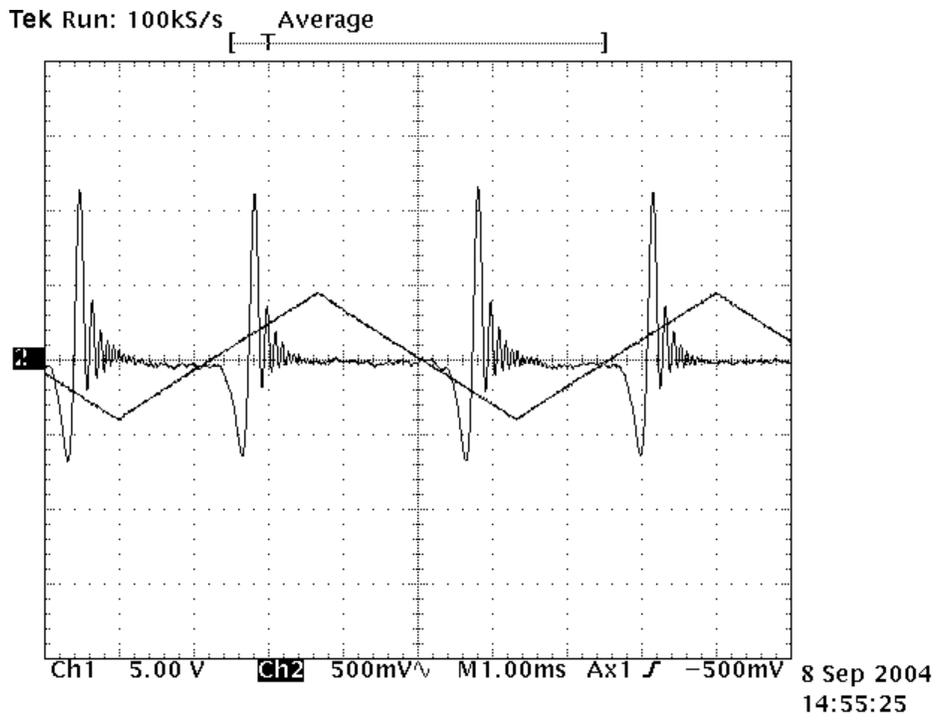


Figure 6: Resonance signal compared to field sweep drive.

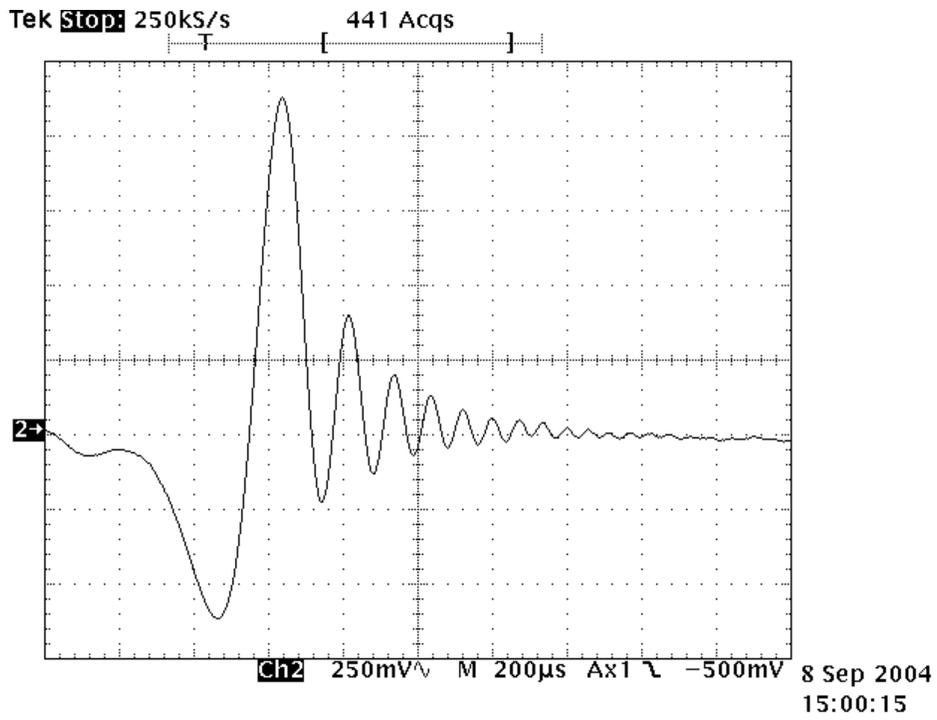


Figure 7: Closeup of resonance signal.

of measuring either AC or DC fields, and you will find specifications for this device available in the lab or on the class web site. This gaussmeter uses the Hall effect to measure the magnetic field, but almost all Hall effect based gaussmeters are factory calibrated against NMR standards.

2.1 Procedure

The sample of choice for seeing your first resonance is $\text{H}_2\text{O} + \text{CuSO}_4$ as it has a strong, easily observed signal. The main effect of CuSO_4 in solution is to shorten the relaxation time, as discussed below. The CuSO_4 ions do not appreciably shift the resonance conditions (frequency or magnetic field) for the protons in the H_2O molecules.

1. As a precaution, remove watches, credit cards, computer disks, or any other magnetically sensitive material from your clothes and body, and set them aside on a table. *Don't forget to pick them up when you are done!*
2. Turn on the cooling water for the magnet and plug in the circulating pump (or turn on the power strip that the pump may already be plugged into). The TA or Professor will assist you with this.
3. Place the $\text{H}_2\text{O} + \text{CuSO}_4$ sample in the “NMR head” and position the NMR oscillator/detector box so the head is approximately centered in all directions between the electromagnet pole pieces.
4. Check that the magnet current is set to 0 (current adjust control on front of magnet power supply should be set to 0), and turn on the supply by pushing the black button. You should hear a click and see the power light come on. (Note: the *only* controls you will use on the magnet current supply are the on/off buttons and the current adjust knob.)
5. Turn on the rest of the electronics: both oscilloscopes, the gaussmeter, the HP frequency counter, the EG&G 5113 pre-amplifier, the Exact model 7050 function generator and the RF oscillator/detector box that has the NMR head on it.
6. After the scopes have warmed up, look at the trace produced by the output of the Exact function generator on the digital scope. It should be set to make a triangle wave of about 80 Hz with an amplitude of about 8 volts peak-to-peak, similar to triangle wave seen in Fig. 6.
7. On the analog oscilloscope in the instrument rack, you should see a horizontal trace centered on the screen. With both inputs set to 1V/div, you should see a line that is about 8 divisions wide. Adjust the trace position controls to center this line.
8. Set the EG&G preamplifier so that it has a gain of 10 and a filter bandwidth of 3 Hz to 300 kHz. You may want to change these settings as you start to make measurements, but these are a good place to start.
9. Adjust the frequency of the RF oscillator to about 9.4 MHz which is near the “50” mark on the large dial. If you do not see noise wiggles on the scope screen and/or if the HP frequency counter is not responding, adjust the Oscillator Current Control (small knob below and left of the frequency control) in order to bring the circuit into oscillation. Please ask for help if you cannot get it to work (the batteries may be dead).

10. Once you see evidence that the oscillator is working, steadily increase the magnet current. When you get close to 35 amps slow down your adjustment: you are looking for the resonance signal to pass by on the analog scope “X-Y” display. After finding the resonance (at about 36 amps or 2.19 kG), adjust the magnet current so that the two resonance bumps are symmetrically located on the X-Y display.
11. Carefully move the NMR head around in the gap between the magnet pole pieces to find the position where the resonance signal reaches a maximum. You are looking for the strongest signal with the most “wiggles”. It may be necessary to shim the oscillator box on the bottom with some foam strips to keep it in the optimum tilt position.
12. Adjust the Oscillator Current Control to optimize the combination of signal amplitude and background noise. Note that turning this knob clockwise increases the signal (and noise!) amplitude. If this knob is turned too far in either direction, the oscillator circuit may shut down, as noted by a flat line on the scope screen, or it may latch-up into spontaneous oscillation, which will look like an excessively large signal. Ideally, you want the oscillator current drive to be just a little above the lowest value needed to see the noise plus NMR resonance signal.

Observe how the position of the resonance signals on the X-Y display is shifted by changing either the oscillator frequency or the magnetic field. For this part of the experiment, the gaussmeter is set up to measure only the static field B_0 . To associate a resonant frequency with a particular gaussmeter reading, the resonance must occur at the zero crossing of the sweep field. This condition is met when the two resonance signals are symmetrically located on the X-Y display.

NOTE: It is common for the signal to drift, especially when the equipment is just turned on, until the temperature of both the oscillator circuit and magnet coil stabilizes.

The signal “wiggles” or “ringing” that one sees as the sample goes through resonance are the beats between signals at the (fixed) frequency of the oscillator, f_{osc} , and the signal at the frequency of precession, f_{prec} , of the net magnetic moment of the protons in the total magnetic field, which is the static field plus the sweep field. If resonance occurs as the sweep field crosses zero, then right at resonance we have the condition

$$f_{\text{prec}} = f_{\text{osc}} = \gamma B_0 . \quad (13)$$

As the sweep field changes from zero, f_{prec} changes as

$$f_{\text{prec}} = \gamma[B_0 + B_{\text{sweep}}(t)] . \quad (14)$$

The oscillator has a detection system which outputs the difference or “beat” frequency between the fixed oscillator frequency and the changing precession frequency. The “beat” signal observed on the scope is in the audio frequency range, and you can see the beat frequency increase as the sweep field moves further away from zero.

Note: the EG&G PAR 5113 preamplifier has been added to the electronics in to filter out some of the noise on the NMR oscillator output. To give a cleaner signal you can raise the low pass frequency up to 1 kHz, and drop the high pass frequency down to 10 kHz if you need to. In order to avoid overloading the preamp input, it is necessary to attenuate the oscillator signal by sending it through the 1:4 attenuator box before connecting it to the preamp. Once you have found the resonance, you may want to adjust the preamp settings to give a clean signal on the scopes.

Exercise I: Measurement of γ for protons in water.

The gyromagnetic ratio γ is defined as the proportionality constant between the magnetic moment $\vec{\mu}$ and the angular momentum \vec{I} of the nucleus, $\vec{\mu} = \gamma\vec{I}$. As shown in section 1.1, γ can also be expressed as

$$\gamma = \frac{2\pi f_{\text{resonance}}}{B_0},$$

where B_0 is the value of the steady state field at resonance and $f_{\text{resonance}}$ is the resonant frequency.

Place the $\text{H}_2\text{O} + \text{CuSO}_4$ sample in the NMR head and center the head between the pole pieces so as to obtain the strongest resonance signal. For a series of B_0 -values between approximately 1.9 and 2.6 kilogauss, measure the frequency and magnetic field at which resonance occurs. It is important that the resonance be symmetrically centered on the horizontal trace, and this is most easily accomplished by first centering the trace on the scope screen, making sure you can see both ends of the trace, and then centering the “bat-wings” of the resonance on the screen itself.

As there are typically fluctuations due to noise in both the frequency and magnetic field readings, take at least 5 independent readings of each and compute the average. A good strategy is to hold the frequency steady and recenter the resonance with the current control for each reading. Plot the averages of resonant frequency vs. magnetic field, and from the slope of this graph, derive a value for γ_{proton} . Compare your value to the accepted value given Eq. 9. Also, calculate the g factor for the proton according to Eq. (2).

You should be able to measure over the whole range of the RF oscillator: from about 6.4 MHz up to a little over 12 MHz. The relationship is linear, so 10 to 15 data points (with their uncertainty) is sufficient. You will need to adjust the RF Oscillator Current Control as you go to optimize the signal. Notice how the control also affects the oscillator frequency.

When you are above 10 MHz the magnet current will be rather large (> 40 amps). Do NOT leave the current at such high values for an extended period of time, and when you are not making measurements turn the current down to zero. If the current supply gets too hot it will shut itself off.

Exercise II: Precise measurement of magnetic fields.

In terms of a bona fide measurement, exercise I is something of a ruse: the γ for protons is extremely well known. In fact, gaussmeters are typically calibrated *against NMR resonances*, since frequency is easy to measure to a high accuracy, all protons are exactly alike, and the response of Hall probes varies with temperature and construction which makes them unsuitable as a primary standard. In effect, exercise I should be better thought of as a measurement of the accuracy of the gaussmeter. In this exercise we’ll use the sensitivity of the NMR resonance to study the magnetic field and its variation between the pole pieces of the magnet.

Adjust the magnet current to a value of 36–38 amps, and allow it to stabilize for a minute or so. Using the $\text{H}_2\text{O} + \text{CuSO}_4$ sample, find the frequency at which resonance occurs in different regions between the pole pieces. The field values may be calculated from

$$\text{magnetic field} = \frac{f_{\text{resonance}}(\text{MHz})}{4.2577 \text{ MHz/kilogauss}}.$$

Another effect should be obvious as you move the sample around—the shortened relaxation time and diminished magnitude of the resonance signal. These effects are due to the increasing inhomogeneity

of the magnetic field as you move the sample away from the center of the gap between the pole pieces. When B_0 is not uniform over the sample volume, different parts of the sample go through the resonance condition for different values of the sweep field. The signals from these various resonances tend to cancel each other out, thus shortening the observed relaxation time and diminishing the signal magnitude.

Estimate the variation in B_0 from the center of the gap between the pole pieces to positions on either side of the center, both along the axis of the magnet (shift the head from side to side) and perpendicular to the axis (shift the head forward and back) by noting the change in resonant frequency at these non-optimum positions. You will see two effects: (1) the resonance position will shift slightly on the scope screen and (2) when the head is near the edges of the pole pieces the resonance will vanish suddenly as the field becomes highly nonuniform.

Also keep an eye on the gaussmeter as you move the head around. Does the gaussmeter follow what you measure from the resonance shift? Try to estimate how much B_0 changes over the extent of the sample itself.

Then, measure the magnitude of the sweep field produced by the Exact function generator and the sweep coils mounted on the NMR head by noting how much frequency shift is needed to move the resonance from one side of the trace to the other side of the trace. (It takes a steady hand to control the resonance position with the RF frequency control knob!). In your report, estimate these variations in both relative (percent) and absolute (e.g., kilogauss or tesla) units.

Don't sweat too much over these measurements. You only need to give a rough calculation for each part, not a full uncertainty analysis.

Exercise III: Measurement of γ for ^{19}F nuclei

In order to measure γ for fluorine nucleus ^{19}F , repeat Exercise I with a twist: instead of comparing the resonance frequency to the magnetic field measured by the gaussmeter, compare the frequency of the fluorine resonance to the the frequency of the proton resonance at the same magnet current. Then use the ratio of these frequencies, and the known value of γ for the proton to obtain γ for ^{19}F .

Specifically, make the following measurements. For a series of different magnet currents (i.e., different field strengths), tune the oscillator to center the resonance on the X-Y display for the $\text{H}_2\text{O}+\text{CuSO}_4$ sample. Then, without changing the magnet current, replace the sample with the perfluoropolyether oil sample (a high-quality lubricant containing fluorine) and re-tune the oscillator to center its resonance on the X-Y display. *Be careful when changing the sample in the oscillator probe while the magnet is on. Remove watches and jewelry from the hand you use to reach into the magnet gap.*

Hint: at a given field strength, the fluorine resonance frequency is about 94% of the proton resonance frequency.

Plot the resonance frequency of the proton versus the resonance frequency of the fluorine, fit the result to a line, and use the fit to calculate γ and g of the fluorine in terms of the known values for the proton. The accepted value of g for ^{19}F is +5.2952. However, fluorine is known to be susceptible to relatively large "chemical shifts:" the actual resonant frequency depends on the particular electron environment that the fluorine atom resides in. Based on the accepted value of g and your measurement, how much (if any) chemical shift do you see?

Finally, see if you can find the resonance of the Teflon sample. Teflon (polytetrafluoroethylene) is a polymer containing long chains of carbon atoms with two fluorine atoms bonded to each carbon atom. The signal from the Teflon sample is considerably smaller than that from the proton sample, so you will have to look for it very carefully. You may also be able to see a chemical shift between Teflon and fluorinated oil.

Exercise IV : Effect of paramagnetic ion concentration on T_2^* of protons in water

Relaxation, in general, means the return of a system to an equilibrium condition after an external stimulus has been applied to the system. In this experiment, relaxation means the re-establishment of the net magnetization of the sample parallel to \vec{B}_0 (equilibrium condition) after the sample has gone through resonance (external stimulus). If the sample goes through the resonance condition again before it has had sufficient time to relax, the resonance signal will be reduced in amplitude. Why this is so is more readily understood after doing the pulsed NMR experiment, where the relationship between observed signal strength and relaxation time can be investigated in detail.

In this exercise you will qualitatively investigate the relationship between the relaxation time of a sample of water with varying concentrations of copper sulfate in solution. CuSO_4 ions have large magnetic moments due to the unpaired electron spins in the copper atoms. These magnetic moments perturb the local field seen by individual protons with the result that the equilibrium configuration is recovered more rapidly (T_1 is shorter), and the resonance signal decays more rapidly (T_2 is also shorter) than in the absence of the CuSO_4 ions. Thus T_2^* is shorter and we see a stronger resonance signal since the oscillator can continuously put energy into the sample.

Distilled water, saturated CuSO_4 solution and vials are available in the lab for making up samples. Start by putting some distilled water into a vial and sealing the top with a piece of masking tape. Do not overfill the vial—notice how the pre-made samples have about 1 cm depth of liquid. Note how weak the resonance signal is: in fact you may not see it at all. This is because protons in pure water have a T_1 relaxation time on the order of a second or more, while we are sweeping through the resonance condition at approximately 160 Hz (i.e., $2 \times f_{\text{sweep}}$). Now make up a sample with half pure water and half saturated CuSO_4 solution, again to a depth of about one centimeter, sealing the top with masking tape. Note the dramatically shorter T_1 relaxation time as evidenced by the strong signal every time the sample goes through resonance.

To make a quantitative estimate of T_2^* , it is convenient to capture the resonance signal on the digital scope, similar to that shown in Fig. 7. Ask for help if you have trouble configuring the scope to capture this signal. Once you have the resonance signal displayed on the scope, you can use the averaging feature to eliminate some of the noise on the signal. After capturing a satisfactory waveform, print it out by pressing the **HARDCOPY** button on the scope, and from this copy, estimate the relaxation time T_2^* of the sample, where the envelope of the signal decays approximately as e^{-t/T_2^*} .

Repeat the scope grabs for several samples of varying concentrations of copper sulfate in solution, starting with the saturated solution, and then diluting it by a factor of 2 until your signal is indistinguishable from that of pure water. The easiest way to do this is to use two eyedroppers, one with saturated CuSO_4 and one with pure water. For each sample you want to have the same overall volume because the signal strength depends on the size of your sample. About 4 drops in a vial gives a depth of about 1 cm. You can mix the pure water and the saturated solution in a small plastic cup and then transfer a few drops into a vial.

Your goal in these measurements is to see the number of wiggles (as the trace decays) increase as the concentration of CuSO_4 decreases. Unfortunately, because of the inhomogeneity of the magnetic field, the effect is fairly weak: the observed relaxation time is shorter than that due to just the interactions between the spins themselves and any other magnetic moments in the sample environment.

The limitations of this apparatus do not allow one to separate out the contribution to the relaxation time due to inhomogeneities in the external field, but you will see how this can readily be done using the more sophisticated pulsed NMR technique.

2.2 Shut Down

After you have made your measurements on the various solutions, please empty and rinse out the vials for use by the next group of students.

Then in this order:

- Turn off the electronics,
- *Turn off the NMR oscillator box, as the batteries will run down overnight.*
- Turn the magnet current to zero *before* turning off the magnet power supply.
- Close the Supply and Return valves for the cooling water.
- Unplug the circulating pump.

Prepared by J. Stoltenberg, D. Pengra, R. Van Dyck and O. Vilches

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