

The following pages include background information about the technique of NMR and a write-up for the CW NMR setup at the back-wall of the lab.

Contact the instructor if you need a pdf version of the write-up for the teachspin pulsed NMR experiment.

CW Nuclear Magnetic Resonance

PURPOSE: To learn radio-frequency electronic and lock-in amplifier techniques, to understand the physical basis of nuclear magnetic resonance (NMR), to observe it using continuous wave (CW) techniques, and to measure the ratio of the magnetic moment of hydrogen to that of fluorine.

APPARATUS: Createch Model 1020 NMR Oscillator; 20-30 VDC Power Supply; 12-inch Magnion Electromagnet with HS1050B Power Supply; Hewlett-Packard 5313A Universal Counter; Tektronix RM503 Oscilloscope; Keithley 810 Phase Shifter; 60 Hz Modulation Panel; SRS Model 510 Lock-In Amplifier; Omega Chart Recorder

INTRODUCTION: Nuclear Magnetic Resonance (NMR) is of particular interest at Rutgers because two Rutgers professors, Henry Torrey and Herman Carr, were early pioneers in its discovery and early development (see the first reading listed at the end of this write-up).

NMR is a technique for observing the Zeeman Effect in nuclei. Classically a proton -- the hydrogen nucleus -- can be thought of as a rotating ball of charge. The angular momentum \mathbf{S} due to the rotation is called the spin and its observable component S_z has a magnitude $h/4\pi$ where h is Planck's constant. A rotating charge generates a magnetic field and thus the nucleus acts like a small magnet with magnetic moment μ . When a magnetic field \mathbf{B} (whose direction is defined to be the z -axis) is applied, the magnetic moment can align itself either parallel or antiparallel to the field with an energy $E = -\mu \cdot \mathbf{B} = \pm \mu B$. Then the up and down alignments of the nucleus have an energy difference $\Delta E = 2\mu B$. This magnetic field dependent splitting of energy levels between up and down spins is the **Zeeman effect**. To induce nuclear resonance, an alternating magnetic field, frequency ν , is applied to the sample. When the energy $h\nu$ of the photons in the alternating field exactly equals $2\mu B$ they can be absorbed by the nucleus and cause it to flip from down to up -- NMR. Experimentally one detects NMR by observing this absorption of energy by the flipping nuclei.

In the classical picture of the nucleus (ref. 1) one would expect the spatial distribution of the mass M and the charge e to be the same and the angular momentum \mathbf{S} should be related to μ by the equation

$$\mu = \frac{e}{2M} S_z,$$

or

$$\mu = \frac{eh}{8\pi M}.$$

The quantity $\mu_N = eh/4\pi M$ is called the nuclear magneton (in analogy to the

Bohr magneton for electrons) and has magnitude 0.50508×10^{-26} J/T. Thus in the classical picture, one would expect the proton magnetic moment to be one-half nuclear magneton. However, experimentally we find that the magnetic moment is much larger: $\mu_p = 2.7928\mu_N$. It is not really surprising that the classical prediction is wrong since we know the proton is not a ball of charge but rather three quarks bound together. Reference 2 gives a more thorough discussion of magnetic resonance from both a classical and quantum mechanical point of view.

From the equations above we can easily calculate the frequency ν of the alternating magnetic field needed to induce resonance in a given magnetic field.

$$h\nu = 2\mu B = 5.5856\mu_N B = 2.8212 \times 10^{-26} B \text{ Joules}$$

or

$$\frac{\nu}{B} \equiv \frac{\gamma}{2\pi} = [42.577 \text{ MHz/T for protons}]. \quad (1)$$

γ is called the gyromagnetic ratio and its numerical value will be different for various nuclei. Note that for two nuclei, x and y,

$$\frac{\gamma_x}{\gamma_y} = \frac{\mu_x}{\mu_y} \quad (2)$$

Equation (1) leads to one of the most frequent experimental uses of CW NMR. By measuring the NMR frequency of a proton sample in a magnetic field, which can be done with high accuracy, you can accurately determine the value of the magnetic field. In fact, the electromagnet you will be using in this experiment has been calibrated using proton NMR.

In this experiment you will study two nuclei ^{19}F and ^1H . ^{19}F is a much more complicated nucleus than the proton. It consists of 10 neutrons and 9 protons. According to nuclear shell theory (see Williams, ref. 3 for a complete discussion of nuclear shell theory), the neutrons and the protons form pairs, with their magnetic moments in opposite directions, and the nuclear magnetic moment arises from the last unpaired nucleon. Thus the ^{19}F magnetic moment arises from the single unpaired proton. In the shell model the "magic numbers" for filled shells are 2, 8, 20, Hence the ninth proton goes into the third shell, which the shell model predicts (see Fig. 8.6 of Williams) has three energy levels -- $1d_{3/2}$, $2s_{1/2}$ and $1d_{5/2}$. (d denotes orbital angular momentum $\ell = 2$, s denotes $\ell = 0$, the fractions 1/2 etc. denote the total angular momentum j where $\vec{j} = \vec{\ell} + \vec{s}$.) Unlike the atomic shell theory, the nuclear shell model is not an exact theory and the ordering of the energy levels is somewhat flexible. Normally, of the three energy levels, the $1d_{5/2}$ state is lowest, but in some nuclei the $2s_{1/2}$ state is lower. The predicted magnetic moment depends strongly on which level is lowest and can be

calculated from:

$$\mu = \mu_N \left[jg_L \pm \frac{j}{2\ell + 1} (g_S - g_L) \right] \quad (3)$$

where

μ_N is the nuclear magneton

$g_L = 1$ for the proton, 0 for the neutron

$g_S = +5.58$ for the proton, -3.83 for the neutron

ℓ is the orbital and j the total angular momentum of the lowest energy level (i.e. in this case of the $1d_{5/2}$ or $2s_{1/2}$ states)

\pm use $+$ if $j = \ell + 1/2$ and $-$ if $j = \ell - 1/2$.

In this experiment you will observe the NMR of both ^1H and ^{19}F nuclei using an NMR probe containing both a hydrocarbon sample (a pink pencil eraser) and fluorocarbon sample (TeflonTM). This will allow you, using Eq. (2), to accurately obtain the ratio of magnetic moments and compare your result with the predictions given above to see which state is lowest. (You will not be able to obtain the absolute value of the proton magnetic moment because the magnetic field is calibrated using proton NMR.) Accepted values for the nuclear magnetic moment of various nuclei can be found in ref. 4.

EXPERIMENTAL CONSIDERATIONS:

A. Observing NMR. There are two different, commonly used techniques for observing NMR: pulsed NMR and continuous wave (CW) NMR. [Alternating waves with frequencies in the Megahertz range are called, in the common jargon, rf (radio-frequency) fields.] In pulsed NMR a short intense rf pulse disturbs the nuclear magnetization from its equilibrium orientation and the transient behavior of the magnetization as it returns to equilibrium is observed. In CW NMR the energy absorbed from a continuous low level rf field is observed as the frequency is slowly changed. Resonance shows up as an increase in absorbed energy. [Experimentally it is easier to keep the rf frequency fixed and slowly sweep the magnetic field through resonance.] The two techniques are complimentary and contain the same information; the CW NMR signal is the Fourier transform of the pulsed NMR signal. However, because of the development of highly advanced digital (pulse) electronics, pulsed NMR is much more frequently used, e.g. for magnetic resonance imaging.

The CW NMR spectrometer you will use is described in detail in ref. 5. The operating principle is that the sample is placed inside a small wire coil, inductance L , which is in parallel with a variable capacitor whose capacitance can be adjusted between about 100 pF to 30 pF. This LC circuit forms the heart of a rf oscillator that operates at the resonant frequency ν of the LC circuit:

$$\nu = \frac{1}{2\pi} \frac{1}{\sqrt{LC}}$$

The spectrometer circuitry supplies a fixed amount of energy to sustain the oscillation and provides an output proportional level of oscillation. At magnetic resonance,

$$\nu = \frac{2\mu B}{h},$$

the sample absorbs rf energy and decreases the level of oscillation. This is the NMR signal that you observe. In principle, one could detect NMR by observing the level of oscillation as the magnetic field is slowly swept upward through the resonance condition, but in practice it is more convenient to superimpose a small AC (60Hz) magnetic field (~ 2 G; 1 Tesla = 10^4 Gauss) on the slowly increasing DC magnetic field. This modulation has the effect of repeatedly sweeping through the NMR signal when the DC field approaches resonance. If the modulation width is greater than the width of the NMR signal then it can then be clearly observed on the oscilloscope as the DC field sweeps as a slowly moving signal (blip). Using modulation also reduces the need for a highly stable DC magnetic field and allows us to use lock-in detection techniques, discussed below, to increase the signal-to-noise of the NMR signal. The use of modulation to enhance a signal is widely used in many types of spectroscopies and is called modulation spectroscopy.

B. Lock-in Detection. The lock-in amplifier is an instrument that allows one to detect an AC signal even in the presence of noise voltages as much as a million times larger. To function it depends on the fact that the frequency of the noise that one wants to eliminate is different from that of the signal. For a noisy signal if you were to simply measure the average signal voltage, the noise would obscure the signal. The lock-in functions by only measuring voltages whose frequencies are very close to that of the signal and thus can be thought of as an amplifier whose gain is large only near the signal frequency.

In simplest form a lock-in amplifier consists of a high gain AC amplifier followed by phase sensitive detector (PSD), a low pass filter, and a high gain DC amplifier followed by another low pass filter. The phase sensitive detector works by multiplying the signal voltage by a sinusoidal reference voltage. [For this experiment the 60 Hz reference voltage comes for the power lines and is used to drive a set of coils on the electromagnet that produce the AC modulation of the magnetic field.] Mathematically, if the reference and signal voltages are

$$\begin{aligned} V_{ref} &= V_r \sin(\omega_r t + \theta_r) \\ V_{sig} &= V_s \sin(\omega_s t + \theta_s)' \end{aligned}$$

then the PSD output is

$$V_{psd} = V_s V_r \sin(\omega_s t + \theta_s) \sin(\omega_r t + \theta_r)$$

or

$$V_{psd} = 1/2 V_s V_r \cos[(\omega_s - \omega_r)t + \theta_s - \theta_r] - \\ 1/2 V_s V_r \cos[(\omega_s + \omega_r)t + \theta_s + \theta_r]$$

The PSD output consists of two AC signals, one at the difference frequency ($\omega_s - \omega_r$) and the other at the sum frequency ($\omega_s + \omega_r$). When this voltage is passed through a low pass filter the sum frequency is removed, as is the difference frequency unless ω_s is close to ω_r . [What we mean by “close” depends on the characteristics of the low pass filter.] If ω_s equals ω_r the output signal is

$$V_{psd} = 1/2 V_s V_r \cos[\theta_s - \theta_r] \quad (4)$$

This is a DC signal that is proportional to the signal V_s that you want to study. Note that the signal also depends on the phase difference between the signal and reference voltages -- hence the name phase sensitive detector. For some applications this phase sensitivity is very useful, but you will not be utilizing it for this experiment; you will simply adjust the reference phase to make the output of the phase sensitive detector a maximum.

The important thing to notice from Eq. (4) is that the PSD in conjunction with the low pass filter has eliminated all noise voltages except those with a frequency close to the signal frequency. What we mean by “close” depends on the characteristics of the low pass filter. For the lock-in we will be using there are two low pass filters -- pre and post -- before and after the output amplifier. Each can be thought of as a simple RC filter with a time constant Γ that can be adjusted to suit the particular experiment. Each attenuates the signal outside the pass band of the filter at a rate 6 dB/octave. When both filters are used with the same setting (say $\Gamma = 1$ second) the attenuation rate is 12 dB/oct. [When the settings are different the attenuation rate is more complicated.] The effective noise band width (ENBW) of the filter is defined as the band width of a perfect square filter (infinite attenuation - ∞ dB/octave - outside the pass band) that passes the same amount of noise as the actual filter. For the filters in the lock-in you will be using,

<u>Slope</u>	<u>ENBW (Hz) for time constant Γ (s)</u>
6 dB/oct	$1/(4\Gamma)$
12 dB/oct	$1/(8\Gamma)$

For this experiment you will be using a time constant of 1 s for both filters, which gives an ENBW of 0.125 Hz. Thus the lock-in will be sensitive only to

noise within ± 0.062 Hz of the 60 Hz; it is functioning as an amplifier that has large gain only in the narrow band 60.000 ± 0.062 Hz.

In principle you could reduce the noise further by using a larger Γ ; the lock-in you will use allows time Γ 's of up to 100 s. But the drawback is that to avoid distortion, you must make changes in the system at a rate slow compared to Γ . As a rule of thumb, to avoid distorting the signal you should sweep the DC field through the resonance signal no faster than about 100 time constants. For $\Gamma = 1$ s this is a couple of minutes, but for $\Gamma = 100$ s the sweep would take several hours!

The lock-in amplifier is discussed in greater detail in ref. 6. However, we need to discuss one further aspect of lock-in detection. The NMR signal S depends on the total magnetic field $B = B_o + B_m$, where B_o is the slowly swept DC field and B_m is the 60 Hz modulation field, $B_m = B_1 \cos \omega t$. Since $B_1 \ll B_o$, we can expand $S(B)$ in a Taylor series:

$$S(B) = S(B_o) + \frac{dS}{dB} B_m + \frac{1}{2} \frac{d^2 S}{dB^2} B_m^2$$

$$S(B) = S(B_o) + \frac{dS}{dB} B_1 \cos \omega t + \frac{1}{2} \frac{d^2 S}{dB^2} B_1^2 \frac{1}{2} (1 - \cos 2\omega t)$$

Thus the NMR signal has a DC component plus components at angular frequency ω , 2ω , **If we use the lock in to detect the ω component we detect the magnetic field derivative of the NMR signal.** If $S(B)$ has a Gaussian lineshape, then the lock-in output will be the derivative of a Gaussian, which has a positive peak, passes through zero at exact resonance followed by a negative peak as the DC field is sweeps beyond resonance. The lock-in is also able to detect the second harmonic signal, in which case the signal is the second field derivative of the NMR absorption.

One caution is necessary. The size of the signal is proportional to B_1 . So it is tempting to increase B_1 as much as possible to get a better signal-to-noise. But in order to get a signal that is an accurate derivative, it is necessary to keep B_1 small compared to the linewidth. If you over modulate, the lineshape will be distorted or the line broadened. This may or may not be a problem, depending on what information you are trying to extract from the signal. [Note that to observe the signal on the oscilloscope you want the modulation to be large compared to the linewidth.]

Also note that, in general, it is a very bad idea to choose a 60 Hz modulation frequency because most experiments suffer from moderate to severe 60 Hz noise due to stray magnetic fields etc. from the 60 Hz power lines. By choosing 60 Hz you would be maximizing the interference from this noise. In fact, most lock-ins have band-stop filters to reject 60 Hz and 120 Hz noise. You

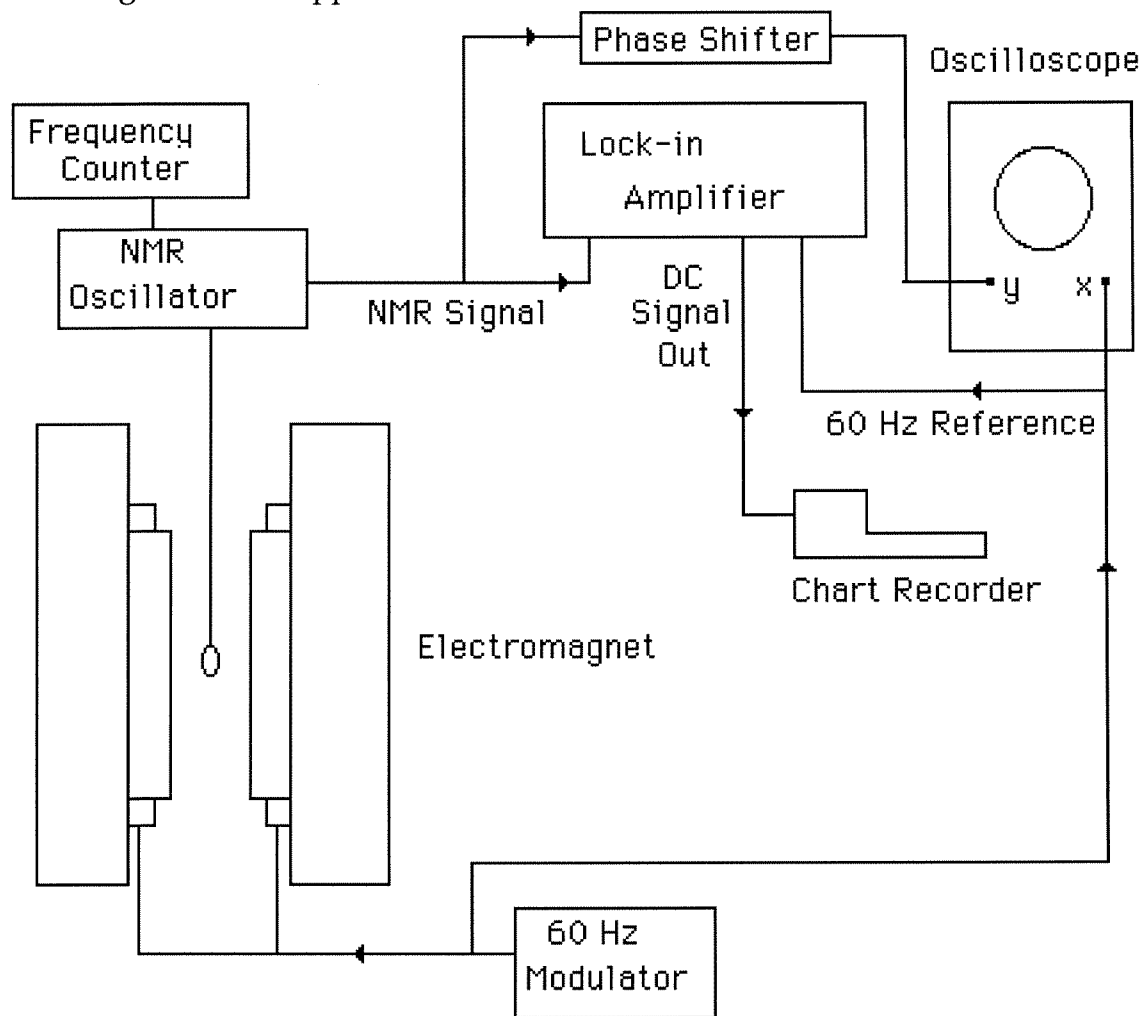
would normally use a different frequency like 37 Hz that is not a multiple or sub-multiple of 60 Hz. However, in this experiment the 60 Hz noise is extremely small and the NMR signal is quite strong. We have used 60 Hz as a convenience because we can directly use the 60 Hz AC from the power line for the modulation without needing an extra power oscillator.

WIGGLES: When you observe the proton NMR on the oscilloscope, you will observe an interesting phenomenon which can easily be understood with a classical picture of NMR. When in thermal equilibrium in a magnetic field, the magnetization $\vec{M} = \sum \vec{\mu}_i$ of a sample is aligned parallel to the field. For NMR the rf coil is aligned so that its rf field is perpendicular to the large DC field and thus is perpendicular \vec{M} . The magnetic field exerts a torque on \vec{M} given by $\vec{M} \times \vec{B}$. In equilibrium there is no torque since the two vectors are parallel. But the rf field is perpendicular to \vec{M} and causes it to precess in a plane perpendicular to the rf field. For CW NMR the rf field is very weak and the precession is counterbalanced by the relaxation of the magnetization back to its equilibrium orientation. This relaxation is described by the spin-lattice relaxation time T_1 . The net effect is that during passage through resonance \vec{M} tilts only slightly away from \vec{B}_0 . On the other hand, for pulsed NMR the rf field is intense and applied for a short time compared to T_1 . The effect is to strongly rotate \vec{M} away from \vec{B}_0 . In fact the usual pulsed NMR arrangement is for the pulse length to be chosen so that after the pulse \vec{M} ends up perpendicular to \vec{B}_0 . \vec{M} then precesses around \vec{B}_0 and induces a large signal in the rf coil which is the NMR signal. This signal decays away with a time T_2 that is shorter than T_1 . T_2 arises because B_0 is not uniform across the sample. This means the individual moments precess at slightly different rates and soon get out of phase and cancel out each others' induced voltages. T_2 is called the spin-spin relaxation time.

When you observe the proton NMR on the oscilloscope you are not quite doing pure CW NMR, but rather a mixture of CW and pulsed NMR. The reason is that the modulation sweeps through the NMR condition in a time shorter than T_1 and thus acts like we have applied a weak rf pulse. **After** the modulation carries the system through resonance the magnetization ends up tipped somewhat away from \vec{B}_0 and as it precesses a voltage is induced in the coil, which dies away in a time T_2 . The frequency of this signal corresponds to the resonance frequency of the spins in a magnetic field greater (or less) than the frequency of the rf field produced by the oscillator. The two rf signals -- one from the oscillator and one from the precessing magnetization -- then beat together to form the characteristic beat pattern called wiggles that exponentially dies away (time T_2). The number of wiggles that you observe depends on the uniformity of the DC magnetic field (and the size of the sample).

EQUIPMENT:

NMR spectrometer: The spectrometer circuitry is discussed in ref. 6. The block diagram of the apparatus is shown below:



Electromagnet: The Magnion electromagnet is extremely easy to operate.

- When operating at high fields (greater than 4000 G) it is necessary to turn on the water cooling for the coils. The water valve is mounted on the wall and needs to be only opened a small amount. **Do not exceed 10 PSI water pressure.**
- To generate a magnetic field, turn on the power switch; there will be a 30-second wait before the system is ready to run.
- Next to reach a desired field simply set the five field switches to the desired value in kG, turn the Mode Selector switch to "field set" and press the on switch. The red light will come on. The current will slowly increase until the field reaches the desired value.
- The meter on the front panel displays the difference between the actual magnetic field (as measured by a rotating coil in the magnet gap) and the

field you set on the front panel switches. The full scale reading of this meter can be adjusted to be ± 10 G, 100 G, 1 kG or 10 kG. Note that the rate at which the current increases depends on this range setting. For most rapid operation start with the range at 10kG and decrease the range as the field deviation decreases.

- To sweep the magnetic field up or down set the Mode Selector switch to sweep, adjust the sweep rate, and choose the type of sweep (sawtooth, triangle etc.). Press the up, down, or stop buttons to control the direction of the sweep. The adjustable red needles on the Field Deviation meter act as limit switches to control the range of the sweep.
- The power supply is completely self protected with an automatic shut down. To shut down simply turn off the power supply at any time -- even at maximum field -- and the supply will shut itself down.
- **Be sure to turn the cooling water off** after shutting down the magnet.

EXPERIMENTAL PROCEDURE:

RF techniques

1. First examine the NMR probe. Note that it consists of a coil in the form of a single layer solenoid of about 15 turns. An empirical formula for the self inductance of such a coil is

$$L = 0.395N^2 \frac{r^2}{9r + 10\ell},$$

where L is in μH , r is the radius of the solenoid in cm, ℓ is the length in cm and N is the number of turns. [Note that when $\ell \gg r$, this equation reduces to the inductance of a long solenoid, $\mu_0 N^2 \pi r^2 / \ell$.] Measure the relevant dimensions of the coil and calculate L . Use the LC meter to measure the actual inductance and compare. When measuring such a small L , the inductance of the leads is very important. Twist the leads together to reduce the inductance and measure L first with the ends of the leads shorted together and then with the ends attached to the coil. Subtract these two readings to get L . Also use the LC meter to measure the input capacitance to the NMR oscillator to verify that it varies between about 50 to 150 pF.

2. Calculate the range of frequencies over which the LC circuit should oscillate. Measure the actual frequency and compare. It may be less because the oscillator may not oscillate for the entire range of C .

Observation of the proton NMR signal

1. Be sure the NMR probe is in the center of the magnet gap. Turn the 60 Hz modulation amplitude to its maximum. Measure the rf frequency and use Eq. (1) to calculate the resonance field for protons. Turn on the electromagnet and adjust the field to this value. If the magnet is accurately calibrated, you should see the NMR signal on the oscilloscope. In practice, the calibration may be off by a few Gauss. Adjust the magnetic field so that the NMR signal is at the center of the oscilloscope. Notice that you see two NMR signals - one for when the 60 Hz modulation sweeps upward through the NMR and another as it sweeps back down. You will want to adjust the Keithley phase

shifter (which changes the phase of the 60 Hz signal driving the x-axis of the oscilloscope) so that the two NMR peaks coincide at the center.

2. Observe the wiggles on the NMR signal when the field setting is slightly off resonance. Move the probe away from the center of the magnet and notice how the number wiggles that can be observed decrease due to the reduced uniformity of the magnetic field. Return the probe to the center of the magnet.

3. Observe the NMR signal for the full range of possible rf frequencies and prepare a calibration graph for the magnet plotting the difference between the actual (NMR) field and the field setting on the dials on the front of the power supply versus the field setting.

4. Now search for the fluorine NMR of the Teflon sample. This resonance is much broader and weaker than the proton NMR and you will need to search carefully. To search, use Eq. (3) to predict the magnetic moment for the $2s_{1/2}$ and $1d_{5/2}$ states. Then calculate the gyromagnetic ratio, Eq. (1), for each of these states, calculate the resonance field for the value of ν you are using, and search over a range of magnetic fields near the predicted field. Note that the shell model is not exact, so the actual resonant field may differ by as much as 5% from the prediction. Also note that the nuclear ground state is either $2s_{1/2}$ or $1d_{5/2}$. So you will see the F resonance at one of the predicted fields but not both!

5. When you found the fluorine NMR, determine the ratio μ_F/μ_H and compare with the accepted value, ref. 4. Note to get a more accurate value for the ratio you should avoid the uncertainty in the calibration of the magnetic field by first finding the fluorine NMR, noting the value of γ , then **keeping the magnetic field fixed, vary γ until you find the proton NMR.** From Eqs. (1) and (2) we see the ratio of magnetic moments equals the ratio of resonant frequencies.

6. Now record the proton and fluorine NMR signals using the lock-in amplifier. For the proton NMR the following lock-in settings are appropriate:

Bandpass filter: in [This filter eliminates signals outside a band of $\pm 10\%$ of the reference (60 Hz) frequency. For this experiment it has little effect.]

Line: out [This is a 60 Hz band-stop (notch) filter.]

2XLine: in [This is a 120 Hz band-stop filter.]

Sensitivity: 20mv [This setting depends on how large the signal is.]

Time Constant:

Pre: 1s [Low pass filter]

Post: 1s [Low pass filter]

Reference:

f [Detects the 60 Hz (f) or 120 Hz signal (2f).]

~ [Sine wave 60 Hz reference input]

The reference section of the lock-in (right hand side) gives the characteristics

of the reference signal you are inputting. If you select Hz, the display should read 60.0 Hz. If you press Hz again the display reads the phase difference between the signal you are detecting and the reference signal, $\theta_s - \theta_r$, Eq. (3). This phase should be adjusted to be about 90° . The exact setting isn't crucial; once you see a NMR signal you can adjust the phase for a maximum signal. You expect the phase to be about 90° because the current in an inductor (the modulation coils that produce the modulated magnetic field) lags the applied voltage (the reference voltage) by 90° .

The lock-in output signal appears on the analog meter and the LED display on the front panel of the lock-in as well as output connector which is attached to a chart recorder to give a permanent record.

Adjust the modulation amplitude to a small value so that the NMR signal can barely be seen on the oscilloscope. Adjust the lock-in gain or the chart recorder gain so that the signal is almost full scale on the chart paper. Record the signal on the chart recorder as you slowly sweep from several Gauss below the signal to several Gauss above. Be sure to add magnetic field markers to the chart recording so that you can measure the linewidth in Gauss. To add markers use the switch attached to the chart recorder by the long cable to momentarily short the input when the field deviation meter on the power supply indicates zero deviation from the field dial settings on the power supply. Use a fast enough chart speed so that the NMR signal is spread out over 2 or 3 inches

For your report carefully measure from the chart paper the signal [dS/dB] as a function of magnetic field. Enter this data into a spreadsheet and fit it as best you can to (the derivative of) a Gaussian lineshape:

$$S(B) = S_0 e^{-\delta B^2 / \Delta B^2},$$

where δB is the deviation of the magnetic field from resonance, and the peak signal height S_0 and the linewidth ΔB are adjustable parameters. Make a plot showing your data and the theoretical lineshape.

Now repeat for the fluorine resonance. This is a weaker signal and you will have to make careful adjustments to get adequate signal-to-noise. You can increase the modulation amplitude somewhat since the fluorine resonance is considerably broader than for protons. You should sweep over a range of at least 20 G. Determine the ratio of the fluorine to the hydrogen linewidths.

6. For the hydrogen resonance set the reference to 2f and record the NMR signal. Be sure to remove the 2XLine filter!

REPORT: Your report should include:

- the measurements and calculations you made in the section on rf techniques
- the field calibration curve from step 3
- your predictions for the gyromagnetic ratio of fluorine for the two possible

ground states of the nucleus and your conclusion about the actual ground state based on the observed NMR signal.

- your experimental value for μ_F/μ_H , an estimate of your error, and a comparison of your results with the accepted ratio.
- your lock-in data for the proton and fluorine resonances.
- a graph comparing your proton lock-in signal with the theoretical signal for a Gaussian lineshape. Discuss why the observed signal might deviate from a Gaussian lineshape.

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For a system of independent, non-interacting particles, which has two energy levels (splitting of the ground state in B), the probability that the energy level $E(m_j)$ is occupied is given by Maxwell-Boltzmann statistics (the system is in thermal equilibrium with the environment):

$$P[E(m_j)] \propto \exp \left[- \frac{E(m_j)}{k_B T} \right]$$

This system can absorb e.-m. radiation because of a difference in occupation numbers for these two levels:

$$\begin{aligned} \frac{N(m_j)}{N(m'_j)} &= \frac{N P[E(m_j)]}{N P[E(m'_j)]} = \exp \left[- \frac{E(m_j) - E(m'_j)}{k_B T} \right] = \\ &= \left[\text{a proton at } 300 \text{ K in a } 0.5\text{-T field, } \mu_{H_1} = \frac{5.59 + 0.5 \times 10^{-26}}{2} \text{ J/T} \approx \right. \\ &\quad \left. \approx 1.41 \times 10^{-26} \text{ J/T} \right. \\ \text{splitting } \pm \mu_{H_1} B, \quad \Delta = 2\mu_{H_1} B \\ \left. \exp \left[- \frac{\mu_{H_1} B}{k_B T} \right] \approx 1 + \frac{2\mu_{H_1} B}{k_B T} = \underline{1 + 3.4 \times 10^{-6}} \right] \end{aligned}$$

This small, but finite, excess of population in the lower energy state causes a net absorption of energy from the radio-frequency field in NMR.

The transition probabilities, $W(m_j \rightarrow m_{j-1})$ and $W(m_{j-1} \rightarrow m_j)$, are equal. The power radiated per unit volume of sample, due to stimulated emission, is $N(m_{j-1}) h\nu W(m_{j-1} \rightarrow m_j)$, and the power absorbed, due to stimulation absorption, $N(m_j) h\nu W(m_j \rightarrow m_{j-1})$

The net power absorbed per unit volume: $P(t) = [N(m_j) - N(m_{j-1})] h\nu W(m_j \rightarrow m_{j-1})$
 Spontaneous emission is small at rf frequencies ($\sim 10^3$) &