NMR I: LF NMR

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1 Introduction

This document does not tell you how to make the experiment go, how to operate the actual equipment. For those instructions, consult the NMR manual and your TA. The presentation here is a bit deeper. The first few sections set up some basic ideas of NMR, and the rest present effects you can measure in the LF apparatus, and some ways to think about their physical implications.

2 What is Nuclear Magnetic Resonance?

2.1 Precession and Resonance: a Classical Example

From your study of oscillators, you should be familiar with the idea of **resonance**. Whenever a system has a characteristic frequency at which it oscillates, vibrates, swings or spins, it responds readily to an external drive at that same frequency.

You should also be aware of the phenomenon of **precession** of angular momentum. Consider a supported gyroscope, spinning very fast about its axis with angular momentum $\vec{J}$. The gyroscope is subject to its own weight $\vec{F}$ through the center of mass at $\vec{x}$, and so $\vec{F}$ induces a torque about the pivot point:

$$\vec{\tau} = \vec{x} \times \vec{F} = \frac{d\vec{J}}{dt}.$$

In $\vec{J}$ space, $\vec{J}$ will precess in a cone of half-angle θ about the direction of $\vec{F}$, and the tip of $\vec{J}$ traces out a circle in a plane perpendicular to $\vec{F}$. The circumference of this circle in $\vec{J}$ space is

$$2\pi J \sin\theta,$$

and the angular precession frequency is 2π times the quotient of the J-speed by the J-circumference:

$$\omega = 2\pi \times \frac{xF\sin\theta}{2\pi J\sin\theta} = \frac{xF}{J}.$$

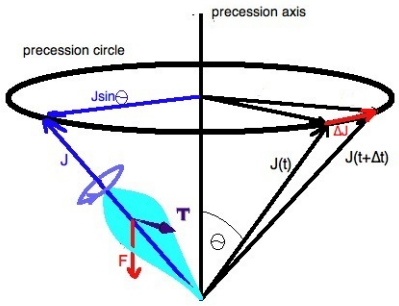

Figure 1: Precession of a Gyroscope in a Gravitational Field.

The most important point here is that the angular precession frequency is independent of the angle between $\vec{F}$ and $\vec{J}$. ω defines a resonance frequency for the system.

Imagine applying, at the top's center of mass, a moving force $\vec{f}$ that is perpendicular to both $\vec{J}$ and $\vec{F}$. To turn $\vec{J}$ efficiently over a period of time, $\vec{f}$ must follow $\vec{J}$ in direction. Thus "on-resonance," the new torque due to $\vec{f}$ must turn around with the same precession frequency ω. On the other hand, when $\vec{f}$ doesn't follow $\vec{J}$ around at the same relative angle, it is less efficient at turning the gyroscope over. In that case, $\vec{f}$ is "out of resonance" with the precession.

With $\vec{f}$ added to $\vec{F}$, the total motion is a more complicated combination, but notice that ΔJ per unit time is a sum of two perpendicular terms, one due to the torque exerted by the static $\vec{F}$, and the other due to the oscillating $\vec{f}$.

2.2 Torque on a Magnetic Moment: Current Loops Precess!

From your introductory physics courses, you know that a magnetic moment $\vec{\mu}$ placed in a magnetic field $\vec{B}$ experiences a torque, $\vec{\mu} \times \vec{B}$. This torque tends to align the magnetic moment along the direction of the magnetic field, and leads to a magnetic potential energy

$$U = -\vec{\mu} \cdot \vec{B}.$$

Classically, there is a relationship between the magnetic moment of a current loop and the angular momentum due to the mass of the charge circulating around the loop. For a single electron of charge q, mass m, speed v, taking time t to complete a loop of radius

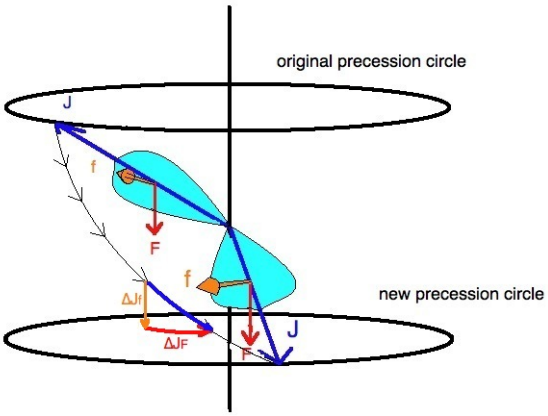

Figure 2: Driving Gyroscope Resonance. A perturbing force, $\vec{f}$ ($f \ll F$), is perpendicular to both $\vec{F}$ and $\vec{J}$–that is, the turning motion of $\vec{f}$ is in resonance with the original precession of $\vec{J}$ about $\vec{F}$. The new torque due to $\vec{f}$ tips $\vec{J}$ to a new precession circle without changing the precession frequency about $\vec{F}$.

R, the angular momentum

$$J = mvR = \frac{2\pi m R^2}{t}.$$

This corresponds to a current $I = q/t$, so

$$J = \frac{2\pi R^2 m I}{q}.$$

But for a current loop, $\mu = I\times$ area$= I \times \pi R^2$, so that

$$\mu = \frac{q}{2m} J.$$

The magnetic moment is proportional to the angular momentum. Putting our current loop in a magnetic field, this means that

$$\vec{\tau} = \frac{d\vec{J}}{dt} = \vec{\mu} \times \vec{B} = \frac{q}{2m} \vec{J} \times \vec{B}!$$

So the current loop will precess with the **Larmor frequency**

$$\omega_L = \frac{q}{2m} B.$$

Since the magnetic moment carries its own magnetic field, you could hope to detect its precession from its effects on a stationary pickup coil. This is the basic idea of NMR.

2.3 Magnetic Resonance

The analogue of driving the gyroscope around with a time-dependent force $\vec{f}$ is driving the magnetic moment between adjacent energy levels with a time-dependent magnetic field $\vec{b}$. Recall that the driving force $\vec{f}$ is perpendicular to the gyroscope's weight $\vec{F}$, and changes direction so that it is always perpendicular to the angular momentum vector $\vec{J}$. Likewise, the driving field for the magnetic moment is made with a $\vec{b}$ that is perpendicular to the static magnetic field $\vec{B}$, and moves around so that is is always perpendicular to the precessing $\vec{\mu}$.

3 Enter Quantum Mechanics

Quantum mechanically, we expect angular momentum states spaced by $\hbar$, a quantum of angular momentum. The spin angular momentum of protons, neutrons, and electrons comes in discrete chunks of $\hbar/2$, with only two possible z components: $+\hbar/2$ ("up", or"$|\uparrow\rangle$") or $-\hbar/2$ ("down", or "$|\downarrow\rangle$"). The angular momentum of a photon comes in double-size chunks of $\hbar$. The difference in energy between neighboring **Zeeman levels** of a magnetic moment in a magnetic field is

$$\Delta E = 2\mu B.$$

Precession at ω_L is the classical analogue which derives from the spacing of energy levels

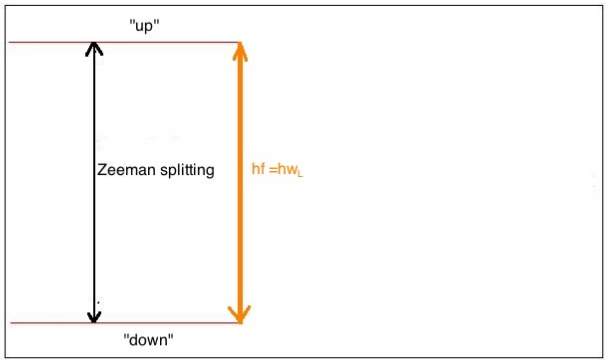

Figure 3: Zeeman splitting schematic.

defined by $-\vec{\mu}\cdot\vec{B}$. Absorbing a photon at the right frequency $\omega = 2\mu B/\hbar$ induces a transition between adjacent energy levels. In fact, $\omega = \omega_L$.

3.1 The Gyromagnetic Ratio and Intrinsic Spin

From the classical argument about current loops, we get the remarkable result that any magnetic moment composed of a particular kind of charge (proton, electron, etc.) will precess with the same frequency per unit field $\omega_L = q/2m$. However for intrinsic spin, the kind of angular momentum carried, for example, by (unexcited) protons; this isn't so.

There is a more general way to think about ω_L. We know that the magnetic moment $\vec{\mu}$ will precess in its cone about $\vec{B}$. In a time Δt, the angular momentum $\vec{J}$ changes by

$$\Delta J = \omega_L J \sin\theta \Delta t.$$

But this is also

$$\tau \Delta t = \mu \sin\theta B \Delta t.$$

So in general, without specifying exactly how angular momentum and magnetic moment are connected, we can define

$$\omega_L = \frac{\mu}{J} B.$$

The field-independent part of this formula

$$\gamma = \mu/J = \omega_L/B,$$

is called the **gyromagnetic ratio** of the object.

Like all photons, the one which flips the proton spin carries angular momentum $\hbar$. It must also carry energy $2\mu_P B = \hbar\gamma_P B = \hbar\omega_L$. So γ_P represents both the Larmor frequency per Tesla, and the angular frequency of the resonance photon per Tesla. Moreover, so long as both spin and orbital angular momenta differences are quantized in units of $\hbar$, this identification will hold for any isolated magnetic moment whatsoever.

We go to the trouble of defining γ because it is allows us to depend less on our classical picture of what is really going on between angular momentum and magnetic moment–we retain only upon the notion that the magnetic moment is proportional to the angular momentum. And the full classical picture is wrong: the Dirac equation for spin-1/2 point particles predicts $\gamma = q/m$, precisely *twice* the classical value, and is pretty close to the experimental truth. The measured proton magnetic moment implies a γ_P of about *three times* what the classical model would predict. The measured neutron moment is not zero, as the Dirac equation implies it ought to be. So if you believe the Dirac equation, nucleons cannot be point particles, and must have some sort of internal structure.

4 LF NMR

The main goal of the LF experiment is to measure these nucleonic γ's. Here's a schematic of how you find the resonance frequencies.

In what follows, $\vec{B}$ refers to a static field with a small, 60Hz ripple field added to it: $\vec{B} = \vec{B}_{DC} + \vec{B}_1 \cos(120\pi t)$. The quickly oscillating perturbation field which drives the resonance is $\vec{b}$, and f is the frequency at which $\vec{b}$ oscillates (in cycles per second). At the beginning of each cycle, the sample is polarized: a majority of the spins in the sample are parallel to $\vec{B}$.

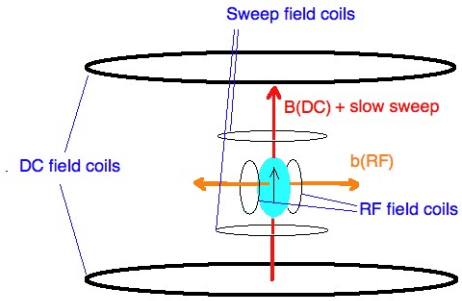

Figure 4: **LF** NMR setup.

As the magnetic field is modulated, so is the Zeeman level difference: $\Delta E = (2\mu_P(B_0 + B_1 \cos(120\pi t))$. Resonance occurs when this energy difference coincides with the quantum hf of the perturbing $\vec{b}$ field. In the classical picture, at resonance, the $\vec{b}$ field is turning spins over efficiently, and these are changing the magnetic response of the pickup coil. In quantum mechanical terms, the $\vec{b}$ field induces a dipole transition from the up to the down state, absorbing extra energy from the RF field. In either case, at resonance, the effect is to induce an extra EMF in the same coil that is producing the $\vec{b}$ field. For a given DC magnet current, your goal is to set the frequency of the $\vec{b}$ field so that the peaks of extra EMF happen precisely half a modulation cycle apart. When that is happening, hf corresponds to the Zeeman splitting $2\mu_P B_{DC}$ defined by the DC field. If you have done a good field-versus-current calibration, you can then use this information to extract μ_P. In practice, it is best to find the resonance frequency as a function of B_{DC} and then fit this to a straight line. The slope of the frequency versus field plot will be $\gamma_P/2\pi$, from which you get μ_P. For the record, $\mu_P = \gamma_P \hbar/2 \approx 1.4 \times 10^{-26}$ J/T, $\gamma_P \approx 2.7 \times 10^8 \mathrm{s}^{-1}\mathrm{T}^{-1}$, and so (dividing by 2π to turn ω into f) f/B corresponds to about 42.29 megacycles per second per Tesla.

The energy levels are never quite perfectly defined–there are inhomogeneities in the $\vec{B}$

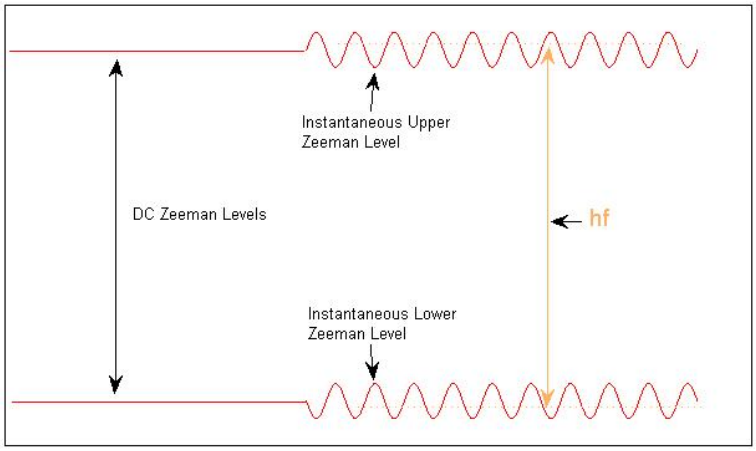

Figure 5: When the modulated Zeeman levels match hf, you get NMR signal.

field as well as sample-dependent factors which tend to spread them out a bit. So instead of seeing an infinitely sharp spike in the EMF, the resonance occurs over a small range of fields. There are also some fine oscillations in the signal. These happen because, in the passage through resonance, the collection of spins develops a transverse component. The oscillations are beats between the instantaneous Larmor frequency of this transverse component (which changes with $\vec{B}$) and the fixed frequency f which has been used to demodulate the coil EMF to make it more visible on the oscilloscope screen.[1]

5 Curie's Law Magnetization and Signal Size

The laws of quantum mechanics are microscopically reversible, which implies that the RF field will flip any isolated proton $\uparrow \rightarrow \downarrow$ and $\downarrow \rightarrow \uparrow$ equally well. So to see any proton signal at all, you have to have a disproportionation between spins aligned with and against $\vec{B_{DC}}$. The better polarized your sample, bigger your signal from spin flips. Ideas from statistical mechanics allow you to predict just how the polarization depends on $\vec{B}_{DC}$ and the temperature of the sample.

Given the energy difference between neighboring angular momentum states, $\Delta E = \hbar\omega_L$, the relative populations of these states at thermal equilibrium will be

$$\frac{N_\downarrow}{N_\uparrow} = e^{\frac{-\hbar\omega_L}{k_B T}}.$$

[1] To understand these oscillations–their amplitude and decay–requires a bit more care than I can put in here. Look for **NMR II: TF NMR**.

(The ↑ state is the one pointed along $\vec{B}$.) Here we are applying **Boltzmann's Law**. This statistical mechanical result does *not* mean that individual spins remain in the same state. Rather, it means that because of the availability of thermal energy $\hbar\omega_L$ at this temperature, the rates of transition $\mathbf{R}_{\uparrow\downarrow}$ and $\mathbf{R}_{\downarrow\uparrow}$ are balanced for this population ratio. For more about this, see the next section.)

The magnetization M_{eq} is the equilibrium population difference

$$M_{eq} = N_\uparrow - N_\downarrow = N \tanh(\frac{\hbar\omega_L}{2k_BT})$$

For $\hbar\omega_L \ll k_BT$,

$$M_{eq} = N \tanh(\frac{\hbar\omega_L}{2k_BT}) \approx N\frac{\hbar\omega_L}{k_BT},$$

as you can see by expanding the exponentials to first order. This result is called **Curie's Law** (for S=$\frac{1}{2}$ paramagnets)[2]. The higher the DC field (so the higher ω_L) and the lower the temperature, the larger the NMR signal corresponding to transitions between the two levels. Moreover, the larger the energy level difference, the more energy will be required to flip the spins, and hence the larger the resonance EMF. This is easily seen from the classical picture: a larger energy level splitting corresponds to a larger ω_L, which means a larger rate of change of magnetic flux. Taken together, these two factors suggest that the NMR signal strength $S \propto B_{DC}^2$. What you actually see will be modulated by the intrinsic frequency response of your detection electronics. But within the pass band of your probe, you should see that a bigger B_{DC} yields a larger NMR signal. You might even consider using the theoretical dependence $S \propto B_{DC}^2$ dependence to map out the relative efficiency of the detection electronics as a function of ω_L.

6 The LF Relaxation Time T_1

A magnetized sample tends to demagnetize when the DC field is turned off. This is because the ever present thermal fluctuations will tend to redistribute the spins according to Boltzmann's Law for the new energy level structure where there is no energy difference between ↑ and ↓. On the other hand, if the thermal equilibrium belongs to a magnetized state, then the fluctuations tend to restore that equilibrium. After your sample of protons passes through resonance, the magnetization takes a certain amount of time to recover. The amount that you recover between successive pulses will also determine your signal strength. One way to characterize the strength of the fluctuations is the **longitudinal relaxation time**, T_1. The stronger the fluctuations, the shorter T_1, the quicker the recovery, and the larger the signal tends to be.

[2]Named for Pierre Curie, rather than his more famous wife.

6.1 How T_1 Depends on the Fluctuations

Begin with the two fluctuation-induced transition probabilities per spin per unit time $\Gamma_{\downarrow\uparrow}$ and $\Gamma_{\uparrow\downarrow}$, denoting the probability per unit time of a single spin in either state to flip to the other state. The total rate of transition from down to up will be

$$\mathbf{R}_{\downarrow\uparrow} = N_{\downarrow}\Gamma_{\downarrow\uparrow}$$

and the total rate at which spins flip the other way will be

$$\mathbf{R}_{\uparrow\downarrow} = N_{\uparrow}\Gamma_{\uparrow\downarrow}.$$

At equilibrium, the difference of the transition rates will be zero:

$$\mathbf{R}_{\uparrow\downarrow} - \mathbf{R}_{\downarrow\uparrow} = N_{\uparrow}\Gamma_{\uparrow\downarrow} - N_{\downarrow}\Gamma_{\downarrow\uparrow} = 0,$$

which means that in thermal equilibrium

$$\frac{\Gamma_{\downarrow\uparrow}}{\Gamma_{\uparrow\downarrow}} = \frac{N_{\uparrow}}{N_{\downarrow}} = e^{\frac{E_{\downarrow}-E_{\uparrow}}{k_B T}} = e^{\frac{\hbar\omega_L}{k_B T}}.$$

In thermal equilibrium, the ratio of the transition probabilities depends on the thermal population of the states, and the tendency for a single spin to go from the higher energy state to the lower energy state is greater. This might sound paradoxical–after all, aren't the laws of nature supposed to be irreversible? The answer has to do with the conservation of energy. The fluctuating spin must exchange energy with its "environment," *e.g.* the electromagnetic field and the electronic magnetic moments in the sample. So while the quantum mechanical matrix elements for a single spin-flip either way are the same, each spin flip probability must also factor in the availability of the energy necessary to make the transition. Thus the probablity of a transition involving a change in energy $\Delta\epsilon$ should look like

$$\Gamma_{\Delta\epsilon} \propto \mathcal{W} e^{\frac{-\Delta\epsilon}{k_B T}},$$

where $\mathcal{W}$ represents the quantum mechanical probability for the transition to go either way regardless of whether the energy is available.

If the environment is always at a temperature T regardless of what the spins are doing (that is, if the environment has a comparatively huge heat capacity), then the ratio of the rates for the out-of-equilibrium case will be the same as for the equilibrium case, and the transition rates will work the same way. Consider an out-of-equilibrium situation, with $N_{\uparrow} = N_{\uparrow eq} + \Delta N_{\uparrow}$, $N_{\downarrow} = N_{\downarrow eq} + \Delta N_{\downarrow}$, and $\Delta M = M - M_{eq} = \Delta N_{\uparrow} - \Delta N_{\downarrow}$. Writing plain Γ for $\Gamma_{\uparrow\downarrow}$,

$$\frac{d(N_{\uparrow eq} + \Delta N_{\uparrow})}{dt} = -\Gamma(N_{\uparrow eq} + \Delta N_{\uparrow}) + e^{\frac{\hbar\omega_L}{k_B T}}\Gamma(N_{\downarrow eq} + \Delta N_{\downarrow}),$$

and

$$\frac{d(N_{\downarrow eq} + \Delta N_{\downarrow})}{dt} = -e^{\frac{\hbar\omega_L}{k_B T}}\Gamma(N_{\downarrow eq} + \Delta N_{\downarrow}) + \Gamma(N_{\uparrow eq} + \Delta N_{\uparrow}).$$

Since these transition rates are precisely those that preserve equilibrium, the equilibrium parts of both equations already balance, leaving the out of equilibrium portions,

$$\frac{d\Delta N_\uparrow}{dt} = -\Gamma \Delta N_\uparrow + e^{\frac{\hbar\omega_L}{k_B T}} \Gamma \Delta N_\downarrow,$$

and

$$\frac{d\Delta N_\downarrow}{dt} = -e^{\frac{\hbar\omega_L}{k_B T}} \Gamma \Delta N_\downarrow + \Gamma \Delta N_\uparrow.$$

The total number of spins is constant, so that $\Delta N_\downarrow = -\Delta N_\uparrow$. Putting in this information, and then subtracting the second rate equation from the first,

$$\frac{d\Delta M}{dt} = -\Gamma(1 + e^{\frac{\hbar\omega_L}{k_B T}})\Delta M,$$

that is,

$$\Delta M(t) = \Delta M(0) e^{-t/T_1},$$

with

$$T_1 = \frac{1}{\Gamma(1 + e^{\frac{\hbar\omega_L}{k_B T}})} \approx \frac{1}{2\Gamma}$$

for protons at room temperature.

6.2 The Passage through Resonance

The discussion above is valid far from resonance, when the RF field has little chance of flipping a spin and the overwhelming majority of the spin flips are due to thermal relaxation. At resonance the situation is different: there will be extra transitions induced by the RF field. You can account for this situation by adding an induced transition term to the rate equations:

$$\frac{dN_\uparrow}{dt} = -\Gamma N_\uparrow + e^{\frac{\hbar\omega_L}{k_B T}} \Gamma N_\downarrow + \Gamma_{RF} N_\downarrow,$$

and

$$\frac{dN_\downarrow}{dt} = -e^{\frac{\hbar\omega_L}{k_B T}} \Gamma N_\downarrow + \Gamma N_\uparrow + \Gamma_{RF} N_\uparrow.$$

The same term is added to both equations, with no relative temperature factor. This is right, because the RF $\vec{b}$ field is *not* thermalized with the environment–it supplies or absorbs energy with equal probability Γ_{RF} per spin per unit time. As the instantaneous Zeeman splitting ΔE passes through the hf of the appied RF $\vec{b}$ field, Γ_{RF} gets very big compared to Γ, and spins will flip $\uparrow$ to $\downarrow$ and $\downarrow$ to $\uparrow$ with equal probability per spin per unit time. In terms of detailed balance, the equality of the transition rates (both equal the same Γ_{RF}) means that, as long as the RF is on, the spins think they're in contact with a thermal bath at $T \to \infty$. So while the system is at resonance,

$$\frac{dN_\uparrow}{dt} \approx \Gamma_{RF} N_\downarrow,$$

$$\frac{dN_\downarrow}{dt} \approx \Gamma_{RF} N_\uparrow,$$

so that when the system is on resonance, the magnetization relaxes toward zero, with a rate that depends on the power of the applied field:

$$\frac{dM}{dt} \approx -\Gamma_{RF} M \rightarrow M(t) \approx M_0 e^{-\Gamma_{RF} t}.$$

6.3 The Recovery: How Signal Size Depends on Γ

So in this experiment, the modulating field brings the sample in and out of resonance. We can use the ideas developed above to see the effects of different relaxation rates on the signal you can observe. Call the time just before resonance 0^-, and the time just after resonance 0^+. Let the time during which the sample dwells at resonance be t_{res}. Then the difference between the magnetization just before resonance and just after is:

$$S \propto M(0^-) - M(0^+) = M(0^-)(1 - e^{-\Gamma_{RF} t_{res}}) \equiv x M(0^-)$$

(so x stands for the fractional difference in the magnetization). But the resonance condition is repeated every half-period τ of B_1, so using the known relaxation time,

$$M(0^-) - M_{eq} = (M(0^+) - M_{eq}) e^{-2\Gamma\tau} = ((1-x)M(0^-) - M_{eq}) e^{-2\Gamma\tau},$$

and insisting that everything be self-consistent,

$$\Rightarrow M(0^-) = M_{eq} \frac{1 - e^{-2\Gamma\tau}}{1 - (1-x)e^{-2\Gamma\tau}},$$

gives:

$$\Rightarrow S \propto x M_{eq} \frac{1 - e^{-2\Gamma\tau}}{1 - (1-x)e^{-2\Gamma\tau}}.$$

This expression leaves out the connection between the signal you see, in volts, and the magnetization–that is, it ignores an overall multiplicative factor related to the efficiency of the coil and the electronics behind it.

6.4 Things You Can Measure: the Relaxation Saturation Effect

Consider how this signal changes with x, the size of the RF, and $2\Gamma\tau$, the relaxation exponent. For very small RF fields, that is $x \rightarrow 0$, the signal becomes independent of the relaxation rate:

$$S \propto x M_{eq}.$$

That is, if very few spins are flipped, the system is always near thermal equilibrium. On the other hand, for very large RF fields, $x \rightarrow 1$, and the signal strength depends fairly simply on the relaxation:

$$S \propto M_{eq}(1 - e^{-2\Gamma\tau}).$$

What is happening is that, when the RF is large enough to flip most of the spins, a small value of $2\Gamma\tau$ means that the sample remains far out of thermal equilibrium between resonances, leaving fewer spins to flip. On the other hand, a sample with a large $2\Gamma\tau$ will regain its polarization before the next resonance.

You can and should test these ideas by comparing the signal for small and large RF amplitudes applied to both pure distilled water, and water with copper sulfate dissolved in it. It turns out that $2\Gamma\tau$ for pure distilled water is relatively small. The Cu^{++} ion has a big magnetic moment. When $CuSO_4$ is dissolved in the water, interactions between this moment and the proton spins increase the relaxation rate.

You can be quantitative about this effect. If the rate of depolarization of the proton spins is proportional to the rate at which each given proton encounters a dissolved Cu^{++} ion, then the change in Γ should be proportional to the $CuSO_4$ concentration. That is,

$$\Gamma = \Gamma_0 + c\Gamma_1,$$

where Γ_0 is the relaxation rate for pure water, Γ_1 is the additional relaxation rate per mole of dissolved $CuSO_4$, and c is the molarity of the solution. Putting this all together, a plot of NMR signal strength versus $CuSO_4$ concentration (with all else kept constant) looks like the one below. The effect should be more pronounced for high RF power, and should go away as the RF power gets smaller. In practice, the signal strength reaches its plateau very quickly, so that to really see the effect requires making some fairly dilute solutions.

7 Other Nuclei

Having found μ for the proton, you are supposed to find μ for ^{19}F and for the deuteron. Each of these experiments tells you something interesting about nuclear structure.

7.1 Fluorine

μ for the fluorine nucleus is quite close to μ for the proton. According to the shell model of nuclear structure, the two kinds of nucleons occupy orbitals in opposite-spin pairs. In this description, ^{19}F has one spare "valence" proton mostly outside an otherwise closed shell–and so the magnetic properties of the ^{19}F nucleus should closely resemble those of a single proton. You can probably find the Fluorine resonance from a sample of Teflon (a "perfluorinated hydrocarbon") by setting up on the proton resonance and then adjusting the field downward a little bit.

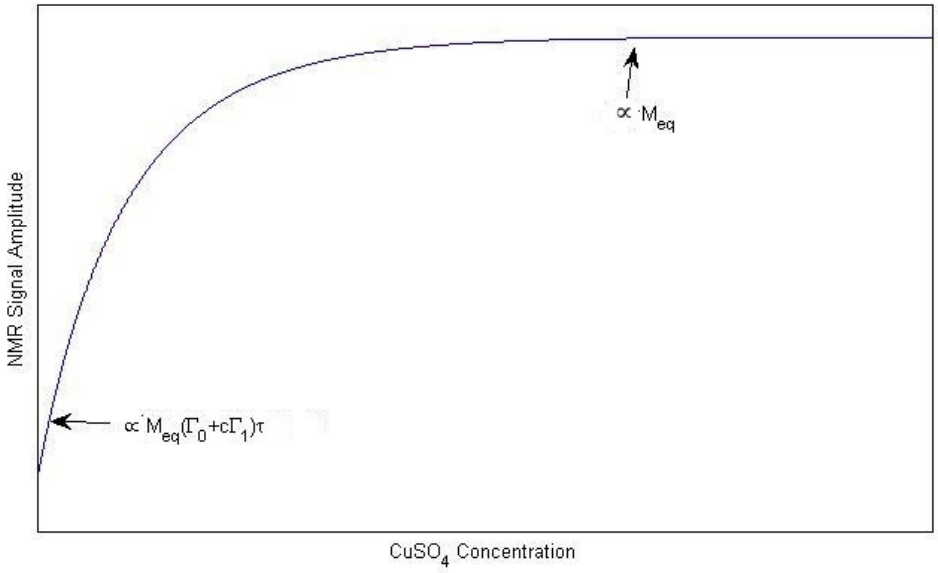

Figure 6: Expected NMR signal strength as a function of the dissolved $CuSO_4$ concentration (High RF power).

7.2 The Deuteron

μ for the deuteron is about a sixth of the proton μ. This implies that the neutron, while electrically neutral, also possesses a magnetic moment, and that in deuterium this moment is oriented opposite to the proton moment. This is a predicted consequence of the isospin theory of nucleons. The proton and neutron are actually different isospin=1/2 states of the "nucleon"; "proton" and "neutron" are "isospin up" ($|I\uparrow\rangle$) and "isospin down" ($|I\downarrow\rangle$) states of the nucleon, respectively. The proton+neutron state of two nucleons of the deuteron can either be

$$\frac{|I_1\uparrow\rangle|I_2\downarrow\rangle + |I_1\downarrow\rangle|I_2\uparrow\rangle}{\sqrt{2}}$$

($I_{total} = 1$), symmetric under exchange of isospin labels, or it can be the isospin singlet

$$\frac{|I_1\uparrow\rangle|I_2\downarrow\rangle - |I_1\downarrow\rangle|I_2\uparrow\rangle}{\sqrt{2}}$$

($I_{total} = 0$), antisymmetric under isospin exchange. Since the nucleon is a fermion, the total wave function

$$|\psi(1,2)\rangle = |I(1,2)\rangle|S(1,2)\rangle|\vec{r}(1,2)\rangle$$

has to be antisymmetric under the exchange $1 \leftrightarrow 2$. Hence either all three factors are antisymmetric, or only one is. Well, it turns out that the ground state of the deuteron is

mostly an orbital angular momentum=0 (symmetric), which is nice for binding with the strong nuclear force, and an isospin singlet (antisymmetric, which prevents excursions into unstable biproton states). Therefore the intrinsic spins of the proton and neutron are, for the most part, aligned: the deuteron has total intrinsic spin of $\hbar$. This leads to a slight difference in the interpretation of the deuteron resonance frequency. The induced transitions we have been discussing conserve angular momentum. The photons of the RF field–indeed, any photons–carry angular momentum $\hbar$. This is enough to flip the $\hbar/2$ proton between the two possible"down" and "up" states, but a spin $\hbar$ particle like the deuteron will have *three* possible projections of the angular momentum on the direction of the DC field: $-\hbar$, 0, and $+\hbar$. Hence the resonance frequency in the case of spin-$\hbar$ deuterons corresponds to just $f = \Delta E/h = \mu B/h$, and not $2\mu B/h$, as it does for spin-$\hbar/2$ protons. But γ_D is still ω_L/B.

For the record, $\gamma_D/2\pi \approx 6.54 \times 10^6 \mathrm{s}^{-1}\mathrm{T}^{-1}$. This means that, compared to the proton signal, the deuteron signal will be *small*: remember, both the polarization and the power absorbed at resonance are proportional to γ. If the deuteron is spin-1, but its moment is smaller than the moment of the proton alone, then the neutron gyromagnetic ratio γ_N must be negative. Suppose that you have measured the deuteron's magnetic moment, μ_D. Having already measured γ_P for the proton, and assuming the deuteron is $|\vec{S}| = \hbar$, you can use the **Landé g formula** to figure out the neutron's γ_N.

There is an easy quasi-classical way to understand the Landé formula. Consider two strongly coupled spins, $\vec{s}_P$ and $\vec{s}_N$, which add up to deuteron spin $\vec{S}_D$, in the $|\vec{s}_P\vec{s}_N\vec{S}_D M_D\rangle$ representation. In combining the spins, the z-components must add: $M_D = m_P + m_N$. The big idea is that the individual magnetic moments are slaved to the total spin, so that only their projections onto the total spin matter:

$$\vec{\mu}_D = \frac{(\vec{\mu}_P \cdot \vec{S}_D + \vec{\mu}_N \cdot \vec{S}_D)}{|\vec{S}_D|^2}\vec{S}_D,$$

which means that

$$\vec{\mu}_D = \frac{(\gamma_P\vec{s}_P \cdot \vec{S}_D + \gamma_N\vec{s}_N \cdot \vec{S}_D)}{|\vec{S}_D|^2}\vec{S}_D.$$

Note that

$$|S_D|^2 = (\vec{s}_P + \vec{s}_N)\cdot(\vec{s}_P + \vec{s}_N) = |s_P|^2 + |s_N|^2 + 2\vec{s}_P \cdot \vec{s}_N,$$

$$\vec{s_P} \cdot \vec{S_D} = |s_P|^2 + \vec{s}_P \cdot \vec{s}_N = \frac{|S_D|^2 + |s_P|^2 - |s_N|^2}{2},$$

and

$$\vec{s_N} \cdot \vec{S_D} = |s_N|^2 + \vec{s}_N \cdot \vec{s}_P = \frac{|S_D|^2 + |s_N|^2 - |s_P|^2}{2},$$

so that

$$\vec{\mu}_D = \frac{\gamma_P(|S_D|^2 + |s_P|^2 - |s_N|^2) + \gamma_N(|S_D|^2 + |s_N|^2 - |s_P|^2)}{2|\vec{S}_D|^2}\vec{S}_D.$$

The reason for that bit of algebra is that now we can evaluate $(\vec{\mu}_D)_z \propto (\vec{S}_D)_z$ using the s_P^2, s_N^2, and S_D^2 and $(S_D)_z$ operators, which are all diagonal in a $|\vec{s}_P\vec{s}_N\vec{S}_D M_D\rangle$ state. To get $|\vec{\mu}|$, evaluate $\vec{\mu}_z$ as an operator in the top ($M_D = 1$) state, which is simply $|\uparrow_P\uparrow_N\rangle$:

$$|\vec{\mu}| = \langle\uparrow\uparrow|(\vec{\mu}_D)_z|\uparrow\uparrow\rangle$$

which is

$$\langle\uparrow\uparrow|\frac{\gamma_P(S_D(S_D+1)+s_P(s_P+1)-s_N(s_N+1))+\gamma_N(S_D(S_D+1)+s_N(s_N+1)-s_P(s_P+1))}{2S_D(S_D+1)}M_D|\uparrow\uparrow\rangle$$

$$\Rightarrow |\vec{\mu}_D| = \frac{(\gamma_P+\gamma_N)}{2}\hbar.$$

Well, *that* makes sense: the proton and neutron contribute equally and with the same sign to the total angular momentum, so the net gyromagnetic ratio must be the average. Since you already know μ_P, you can use this result to get a reasonable estimate for μ_N. I will leave it to you to calculate γ_N in terms of what you have measured. For the record, $\gamma_N/2\pi \approx -29.2 \times 10^6 \mathrm{s}^{-1}\mathrm{T}^{-1}$

Extra Credit

The value you get for μ_N is only approximate, because the nucleon-nucleon interaction mixes states of different orbital angular momentum. Using the nominal μ_N of $-9.66 \times 10^{-27} J/T$ in place of your estimate, you can recalculate $\langle|\mu_D|\rangle$ for both the $l = 0$, $s = 1$, $J = 1$, $M_J = 1$, and the nearest state with the same parity, $l = 2$, $s = 1$, $J = 1$, $M_J = 1$ to estimate the relative proportions of the two in the true deuteron ground state. Here are the complications:

- In the $l = 2$, $s = 1$ calculation, the orbital motion of the proton/neutron pair contributes to the magnetic moment as well, with the *orbital gyromagnetic ratio* of $\gamma_O = \frac{e}{2M_P}$. That is, $\vec{\mu}_D = \gamma_O\vec{l} + \gamma_N\vec{s}_N + \gamma_P\vec{s}_P$.
- To get the expectation value of $\vec{\mu}_D$ in this state, you must figure out how to rewrite $\vec{l}\cdot\vec{J}$ in terms of operators which are diagonal in the $|ls; JM_J\rangle$ basis.
- To take the expectation value, you will have to construct the top $M = 1$ state of the $|l = 2, s = 1; J = 1M_J\rangle$ set. The easiest way is to recognize that

  $$|21;11\rangle = \alpha|22\rangle|1{-}1\rangle + \beta|21\rangle|10\rangle + \gamma|20\rangle|11\rangle$$

  and the fact that the total raising operator $J_+ = L_+ + S_+$ on this state must give zero. This yields proportionalities amongst the Clebsch-Gordon coefficients α, β, γ, and since you also know that $|\alpha|^2 + |\beta|^2 + |\gamma|^2 = 0$, you will have enough information to determine them all. For the general calculation of Clebsch-Gordon coefficients, see R. Shankar, *Principles of Quantum Mechanics*, chapter 14. For an interesting point of view on this standard calculation, see vol. 3 of R. P. Feynman, *The Feynman Lectures on Physics* chapter 18.