

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:

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

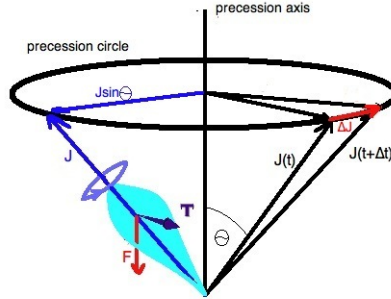


Figure 1: Precession of a Gyroscope in a Gravitational Field.

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

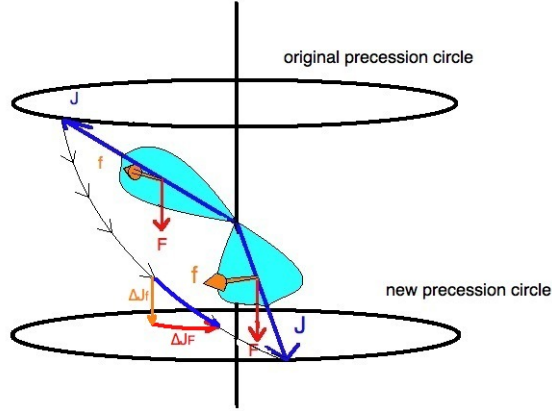


Figure 2: Driving Gyroscope Resonance. A perturbing force, $\vec{f}$ ($f \ll F$), is perpendicular to both $\vec{F}$ and $\vec{J}$ —that is, the turning motion of $\vec{f}$ is in resonance with the original precession of $\vec{J}$ about $\vec{F}$. The new torque due to $\vec{f}$ tips $\vec{J}$ to a new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

radius R , the angular momentum

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

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

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

But for a current loop, $\mu = I \times \text{area} = I \times \pi R^2$, 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 it 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 difference in energy between neighboring **Zeeman levels** is

$$\Delta E = \omega_L \hbar.$$

Precession at ω_L is the classical analogue which derives from the spacing of energy levels defined by $-\vec{\mu} \cdot \vec{B}$. In fact, the explicit solution of the spin- and angular momentum Hamiltonian in a magnetic field implies just that. Assume that the external field points in the $\hat{z}$ direction. For a particle initially polarized in the $\hat{x}$ direction, the *probability* of finding it in the $\pm x$ direction varies sinusoidally with frequency ω_L .

3.1 The Gyromagnetic Ratio and Intrinsic Spin

From the classical argument, Larmor's formula predicts 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 by (unexcited) atomic nuclei, 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

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

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

The reason to go to the trouble of defining γ this way is that it is somewhat independent of our picture of what is really going on between angular momentum and magnetic moment—and the nice, classical pictures of atomic current loops and protons as tiny spinning balls of charge don't work when we talk about magnetic moments on the atomic and smaller scales.

In quantum mechanics, the spin angular momentum of protons, neutrons, and electrons comes in discrete chunks of $\hbar/2$, and orbital angular momentum comes in double-size chunks of $\hbar$. So when we need to describe different experimental precession frequencies, the gyromagnetic ratio gives us a measurable parameter. From our classical analysis, we would predict $\gamma = q/2m$. The Dirac equation for spin-1/2 point particles predicts γ precisely twice that. A more careful QED calculation applies small corrections to this value. The measured proton magnetic moment implies a γ_P of about three times what the classical model would predict. If you believe the Dirac equation, then this implies that the proton is not a point particle, but has some sort of internal structure. For the record, $\gamma_P \approx 2.7 \times 10^8 \text{s}^{-1}\text{T}^{-1}$, so (dividing by 2π to turn ω into f) f corresponds to about 42.29 megacycles per second per Tesla, and $\mu_P = \gamma_P \hbar/2 \approx 1.4 \times 10^{-26} \text{ J/T}$.

4 LF NMR

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 $\vec{B}$.

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 γ_P , from which you get μ_P .

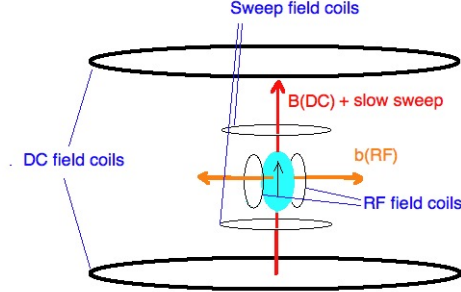


Figure 3: **LF** NMR setup.

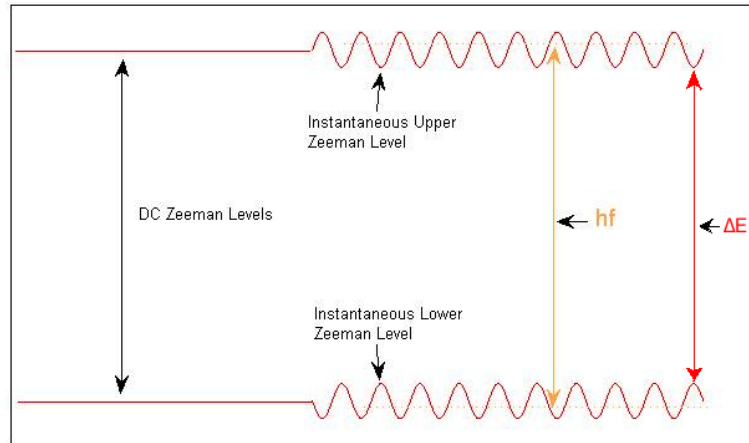


Figure 4: When the modulated Zeeman levels match hf , you get NMR signal.

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

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

(The $\uparrow$ 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

$$M_{eq} = N_{\uparrow} - N_{\downarrow} = N \tanh\left(\frac{\hbar\omega_L}{2k_B T}\right)$$

For $\hbar\omega_L \ll k_B T$,

$$M_{eq} = N \tanh\left(\frac{\hbar\omega_L}{2k_B T}\right) \approx N \frac{\hbar\omega_L}{2k_B T},$$

as you can see by expanding the exponentials to first order. This result is called **Curie's Law** (for 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 .

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

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

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 $\uparrow$ and $\downarrow$. 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 spins 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.

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 is that the quantum mechanical matrix elements for a single spin-flip either way are the same, but that each spin flip probability must also factor in the availability of the energy necessary to make the transition. The fluctuating spin must exchange energy with its “environment,” *e.g.* the electromagnetic field and the electronic magnetic moments in the sample. 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. Thus the

probability for a transition which requires $\Delta\epsilon$ (from a lower energy to a higher energy state) should be proportional to

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

where $\mathcal{W}$ represents the quantum mechanical probability for the transition to go either way regardless of whether the energy is available. Moreover, as long as the heat capacity of the environment is sufficiently huge, this analysis remains true *even if the nuclear spin system is out of equilibrium*.

So you can calculate T_1 in terms of the equilibrium transition rates. Writing plain Γ for $\Gamma_{\uparrow\downarrow}$,

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

and

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

Subtracting the second equation from the first,

$$\frac{d(N_{\uparrow} - N_{\downarrow})}{dt} = -2\Gamma(N_{\uparrow} - N_{\downarrow}) + 2(e^{\frac{\hbar\omega_L}{k_B T}} - 1)N_{\downarrow} \approx -2\Gamma(N_{\uparrow} - N_{\downarrow}) + 2\frac{\hbar\omega_L}{k_B T}N_{\downarrow},$$

which means (writing M for $N_{\uparrow} - N_{\downarrow}$ and M_{eq} for $\frac{\hbar\omega_L}{k_B T}N$),

$$\frac{dM}{M - M_{eq}} = -2\Gamma dt,$$

with the solution

$$M(t) = M_{eq} + (M(0) - M_{eq})e^{-2t\Gamma}.$$

$$\Rightarrow T_1 = 1/2\Gamma$$

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 applied 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. If the passage through resonance is sufficiently quick (that is, if the slowly modulating field B_1 is large enough) so that any given spin has a very small probability of flipping twice, the fractions (just after resonance)/(just before resonance) $N_{\uparrow}(0^+)/N_{\uparrow}(0^-)=N_{\downarrow}(0^+)/N_{\downarrow}(0^-)$ will be the same number, x .

6.3 The Recovery: How Signal Size Depends on Γ

The amount of signal will be proportional to the resultant change in the polarization, which depends on the polarization just before resonance and the flipping fraction x :

$$S \propto M(0^-) - M(0^+) = \{N_{\uparrow}(0^-) - N_{\downarrow}(0^-)\} - \{N_{\uparrow}(0^+) - N_{\downarrow}(0^+)\} = M(0^-)(1 - x).$$

On the other hand, the resonance condition is repeated every half-cycle of B_1 , so using the known relaxation time, we can relate the signal strength to Γ :

$$\begin{aligned} M(0^-) - M_{eq} &= (M(0^+) - M_{eq})e^{-2\Gamma\tau/2} = (xM(0^-) - M_{eq})e^{-2\Gamma\tau/2} \\ \Rightarrow M(0^-) &= M_{eq} \frac{1 - e^{-\Gamma\tau}}{1 - xe^{-\Gamma\tau}}, \\ \Rightarrow S \propto M_{eq}(1 - x) &\frac{1 - e^{-\Gamma\tau}}{1 - xe^{-\Gamma\tau}}. \end{aligned}$$

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 your signal changes with Γ . For large Γ , the exponentials go away, and the signal saturates at its maximum $\propto M_{eq}(1 - x)$. For smaller Γ the signal decreases. For small Γ you can expand the exponentials to get

$$S \propto M_{eq}(1 - x) \frac{\Gamma\tau}{1 - x + x\Gamma\tau} \approx M_{eq}\Gamma\tau.$$

Now it turns out that Γ for pure distilled water *is* very small. You can systematically increase Γ by dissolving some $CuSO_4$ in it. The Cu^{++} ion has a big magnetic moment; interactions between this moment and the proton spins increase the relaxation rate. 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 looks like the one below.

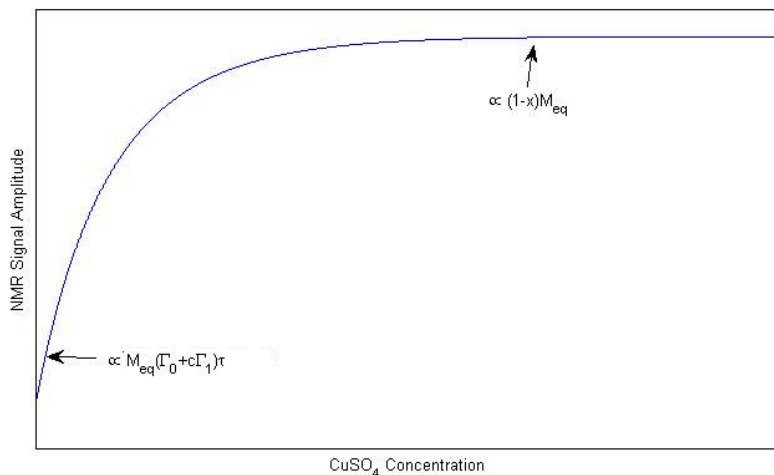


Figure 5: Expected NMR signal strength as a function of the dissolved CuSO_4 concentration.

If you calculate M_{eq} , then by comparing different points on this curve, you can develop a sufficient number of equations to determine the spin-flip parameters Γ_0 and Γ_1 in the model equation for the signal strength. You can then figure out the flipping probability x , and ultimately the instrumental efficiency which turns unitless “signal amplitude” into the voltage you read on your oscilloscope.

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.

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 $\hbar$.

Since the deuteron moment is smaller than the moment of the proton alone, the deuteron gyromagnetic ratio γ_D 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

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

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

$$\begin{aligned} \langle \uparrow \uparrow | \frac{\gamma_P(S_D(S_D + 1) + s_P(s_P + 1) - s_N(s_N + 1)) + \gamma_N(S_D(S_D + 1) + s_N(s_N + 1) - s_P(s_P + 1))}{2S_D(S_D + 1)} M_D | \uparrow \uparrow \rangle \\ \Rightarrow |\vec{\mu}_D| = \frac{(\gamma_P + \gamma_N)}{2} \hbar. \end{aligned}$$

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 .

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 $|\alpha|^2 + |\beta|^2 + |\gamma|^2 = 1$, 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.