# NMR I: LF NMR

Ben Nachumi

January 29, 2013

## 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, 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 $\theta$ 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 simply the quotient of the $J$-circumference by the $J$-speed:

$$\omega = 2\pi \times \frac{2\pi J \sin\theta}{xF \sin\theta} = \frac{4\pi^2 J}{xF}.$$

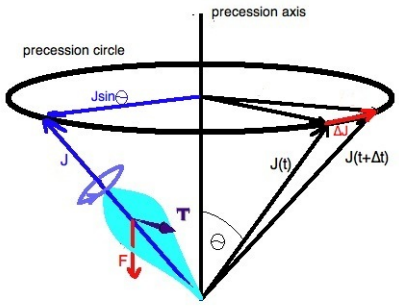


Figure 1: Precession of a Gyroscope in a Gravitational Field.

The most important point here is that the angular precession frequency is independent of the angle between $\vec{F}$ and $\vec{J}$. $\omega$ 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 $\omega$. 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 $\Delta J$ 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

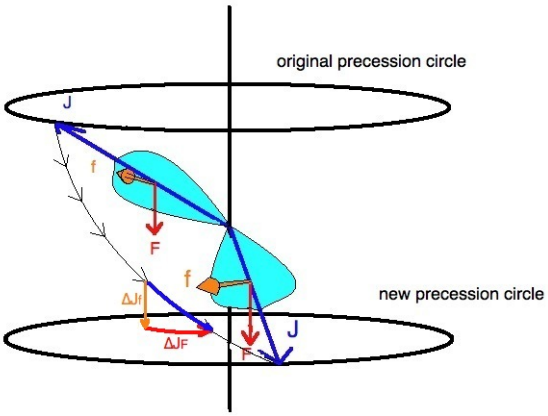


Figure 2: Driving Gyroscope Resonance. A perturbing force, $\vec{f}$ ($f \ll F$), is perpendicular to both $\vec{F}$ and $\vec{J}$–that is, the turning motion of $\vec{f}$ is in resonance with the original precession of $\vec{J}$ about $\vec{F}$. The new torque due to $\vec{f}$ tips $\vec{J}$ to a new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

radius $R$, the angular momentum

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

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

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

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

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

In words, 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 difference in energy between neighboring **Zeeman levels** is

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

Precession at $\omega_L$ 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 $\omega_L$.

### 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 $\omega_L$. We know that the magnetic moment $\vec{\mu}$ will precess in its cone about $\vec{B}$. In a time $\Delta t$, 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 $\gamma$ 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 $\gamma$ precisely twice that. A more careful QED calculation applies small corrections to this value. The measured proton magnetic moment implies a $\gamma_P$ of about five and a half times what the classical model would predict.

## 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 $\vec{B}$.

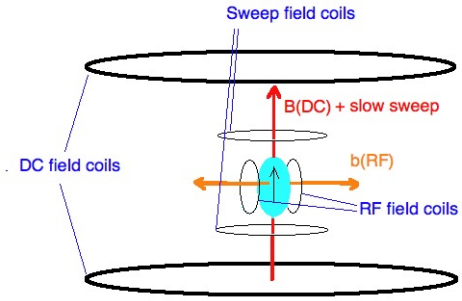


Figure 3: **LF** NMR setup.

As the magnetic field is modulated, so is the Zeeman level difference: $\Delta\mathcal{E} = (2\mu(B_0 + B_1\cos(120\pi t))$. Resonance occurs when this energy difference coincides with the quantum $hf$ of the perturbing $\vec{b}$ field. In the classical picture, the $\vec{b}$ field is turning spins over efficiently. In quantum mechanical terms, the electromagnetic field induces a dipole transition, and the spin can absorb a photon from the electromagnetic field. In either case, at resonance, the flipping spins will 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 $2\mu B_{DC}$ defined by the DC field. If you have done a good field-versus-current calibration, you can then use this information to extract $\mu$. 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 $2\mu$.

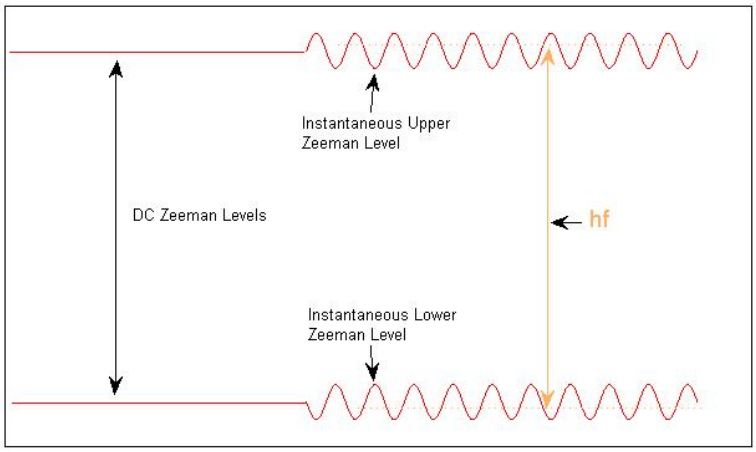


Figure 4: When the modulated Zeeman levels match $hf$, you get NMR signal.

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 are beats between the instantaneous Larmor frequency of the flipped spins (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. The oscillations die away as the spin system returns to equilibrium.

## 5 Longitudinal Polarization 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 $\Delta E = \hbar\omega_L$ at this temperature, the rates of transition $\mathbf{R}_{\uparrow\to\downarrow}$ and $\mathbf{R}_{\downarrow\to\uparrow}$ are balanced for this population ratio.

The total magnetic moment due to polarization between these two levels will be proportional to the fractional population difference

$$\frac{\Delta N}{N} = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} = \tanh(\frac{\hbar\omega_L}{2k_B T})$$

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

$$\tanh(\frac{\hbar\omega_L}{k_B T}) \approx \frac{\hbar\omega_L}{2k_B T},$$

as you can see by expanding the exponentials to first order. This result is called **Curie's Law** (for paramagnets). The higher the polarizing field (so the higher $\omega_L$) 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 $\omega_L$, which means a larger rate of change of magnetic flux.

Taken together, these two factors suggest that the NMR signal strength $S \propto B_{DC}^2$.

## 6 The LF Relaxation Time $T_1$

A polarized sample tends to depolarize when the polarizing 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 ↓.

The **principle of detailed balance** says that the difference of the average transition rates $\mathbf{R}_{\uparrow\to\downarrow}$ and $\mathbf{R}_{\downarrow\to\uparrow}$ can only depend on the population difference:

$$\mathbf{R}_{\uparrow\to\downarrow} - \mathbf{R}_{\downarrow\to\uparrow} = \Gamma \times (N_\uparrow - N_\downarrow),$$

with $\Gamma$ standing for the *normalized* transition rate for an individual nucleus. This normalized rate is itself a sum of products: how often the nucleus interacts with a factor in its environment, multiplied by the probability of a spin flip from each such interaction:

$$\Gamma = \Gamma_0 + \Gamma_1 + \ldots$$

In equilibrium, the net rate of transition is zero:

$$\mathbf{R}_{\uparrow\to\downarrow} - \mathbf{R}_{\downarrow\to\uparrow} = \Gamma \times ((N_\uparrow - N_\uparrow(eq)) - (N_\downarrow - N_\downarrow(eq)),$$

that is,

$$\frac{\mathbf{d}\Delta M}{\mathbf{d}t} = -\Gamma\Delta M,$$

where $\Delta M$ stands for the deviation from the equilibrium magnetization. So if we take an initially polarized sample out of equlibrium by shutting off the polarizing field, the net magnetization ought to decay like

$$M(t) = M_0 e^{-t\Gamma} = M_0 e^{-\frac{t}{T_1}}.$$

This last equation defines the **LF relaxation time** $T_1$: it is simply the inverse of $\Gamma$. $T_1$ is the "characteristic time" that a sample of spins takes to return to equilibrium. The *same* $T_1$ describes the recovery of polarization equilibrium after your sample pops through resonance at $t = 0^+$:

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

As $\Delta\mathcal{E}$ passes through resonance, the $\vec{b}$ field will flip ↑ to ↓ and ↓ to ↑ with equal probability. The fractions of each spin (just after resonance)/(just before resonance) $n_\uparrow(0^+)/n_\uparrow(0^-)$=$n_\downarrow(0^+)/n_\downarrow(0^-)$ will be the same number, $x$, which depends on the amplitude of the $\vec{b}$ field. The amount of signal you see will be proportional to the number of spins flipped, or

$$S \propto M(0^-) - M(0^+) = M(0^-)(1 - x).$$

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

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

and

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

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.

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

$$S \propto M_{eq}\frac{\Gamma\tau/2}{1-x+x\Gamma\tau/2},$$

and for *very* small $\Gamma$,

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

Now you may have noticed that the signal from distilled water is small. It turns out that $\Gamma$ for pure distilled water is very small. You can systematically increase $\Gamma$ 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 $\Gamma$ should be proportional to the $CuSO_4$ concentration. That is,

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

where $\Gamma_0$ is the relaxation rate for pure water, $\Gamma_1$ 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.

After all of this, what information should you get? Well, since you can calculate $M_{eq}$ from Curie's Law, you can extract $(1-x)\times$ the unknown coil/electronics efficiency factor from the region where the curve saturates. The signal for zero concentration divided by the signal for saturation should be $\Gamma_0\tau/2$, and $\tau/2$ is just a half-cycle, 1/120s, so now you know $\Gamma_0$. You can now fit the low-concentration data (approximately a line) to extract $\Gamma_1$.

You can also measure the effect of the RF power on the signal strength. To do this, you will have to change the amplitude of $\vec{b}$. Thinking quantum-mechanically, you know that a flipping spin gets an energy of $\Delta E$ from the RF field, so if the time of passage through resonance is the same, then the probability of a spin flip ought to be proportional to the RF power. But the power in an electromagnetic wave is proportional to the square of the amplitude, so you expect $1-x \propto |\vec{b}|^2$.

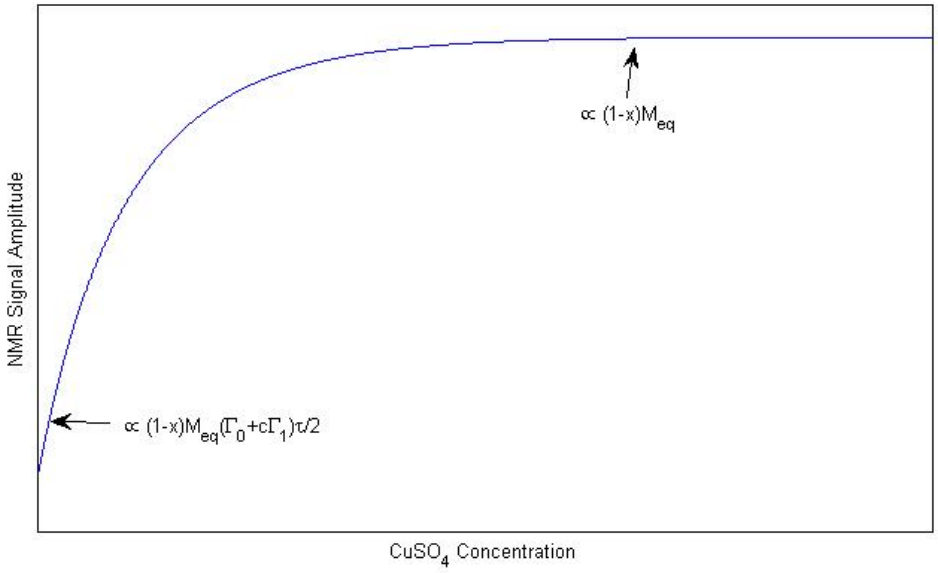


Figure 5: Expected NMR signal strength as a function of the dissolved $CuSO_4$ concentration.

# 7 Other Nuclei

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

## 7.1 Fluorine

$\mu$ for the fluorine nucleus is quite close to $\mu$ 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

$\mu$ for the deuteron is about a sixth of the proton $\mu$. 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 $\gamma_D$ must be negative. Suppose that you have measured the deuteron's magnetic moment, $\mu_D$. Having already measured $\gamma_P$ for the proton, and assuming the deuteron is $|\vec{S}| = \hbar$, you can use the **Landé g formula** to figure out the neutron's $\gamma_N$.

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

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

and

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

so that

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

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 $|\uparrow_P\uparrow_N\rangle$:

$$\langle(\vec{\mu}_D)_z\rangle = \Big\langle \frac{\gamma_P(S_D(S_D+1) - s_N(s_N+1)) + \gamma_N(S_D(S_D+1) - s_P(s_P+1))}{2S_D(S_D+1)} M_D \Big\rangle \Rightarrow |\vec{\mu}_D| = \frac{5}{8}(\gamma_P+\gamma_N)\hbar.$$