Nuclear spins

Begin with a nucleus whose angular momentum operator is $\hbar\vec{I}$. The total spin and its z-component are given by expectation values,

$$\langle\vec{I}\cdot\vec{I}\rangle = I(I+1) \quad \langle I_z\rangle = -I, -I+1, \ldots., I-1, I$$

The nuclear spin *I* may be integral or half-integral. Spin ½ nuclei such as ^{1}H, ^{13}C, ^{19}F, ^{31}P are widely used for chemical identification and MRI (magnetic resonance imaging) but igher spin nuclei are much more common. Examples include spin 3/2 (^{27}Al, ^{63}Cu, ^{65}Cu) and spin 5/2 (^{27}Al). NMR probes the behavior of the nuclear magnetic dipole moment given by,

$$\vec{m} = \gamma_n \hbar \vec{I}$$

γ_n is called the *gyromagnetic ratio* which is determined the nuclear structure. It can be positive or negative. If we place a nucleus in a magnetic field $\vec{B}_0$, which defines our quantization z-axis, then the energy is given by,

$$Energy = -\vec{m}\cdot\vec{B}_0 = -\gamma_n \hbar I_z B_0$$

Since I_z can only change by integral units, the energy levels are evenly spaced,

$$E_n = -\gamma_n \hbar B_0\,(-I, -I+1, \ldots, I-1, I) = \hbar\omega_L\cdot(-I, -I+1, \ldots, I-1, I)$$

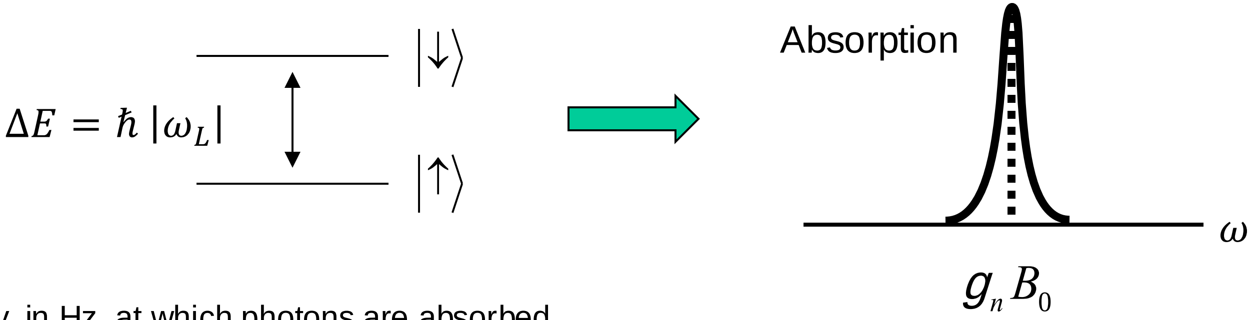
We define the *Larmor frequency* as :

$$\omega_L \equiv -\gamma_n B_0$$

As we'll see, ω_L represents the rate at which the spins precess about a magnetic field B_0 (considered positive.) For most nuclei $\gamma_n > 0$ so the Larmor frequency is *negative* and the precession is *clockwise*. But there are nuclei with $\gamma_n < 0.$ Protons have the largest γ_n of any nucleus and, for a given magnetic field, provide the largest NMR signals.

Larmor frequency

Spin ½ is by far the simplest system to analyze. There are two states, corresponding to I_z = +1/2 and -1/2. If $\gamma_n > 0$ then the I_z = +1/2 state (spin up) will have the lowest energy in a magnetic field. The nucleus can emit and absorb photons equal to the energy difference between the up and down spin states,



$$\Delta E = \hbar\,|\omega_L|$$

The actual frequency, in Hz, at which photons are absorbed and emitted is given by

$$f_L = |\omega_L|/2\pi = \frac{|\gamma_n|}{2\pi}\,B_0$$

The table shows γ_n for some common nuclei. (Not all are spin ½.) Many laboratory superconducting magnets have a maximum B_0 of about 9.4 Tesla, limited by the properties of the superconducting wire from which they are wound. This field corresponds to f_{Larmor} = 400 MHz for protons and about 100 MHz for ^{13}C nuclei, two nuclei that are widely used for chemical identification. For enough money you can get much larger magnetic fields. For example, an 800 MHz proton NMR spectrometer has a maximum field of B_0 = 18.8 T. Since the frequencies encountered in NMR are below 1 GHz , NMR is a radio frequency (RF) spectroscopy.

Nucleus	**$\gamma / 2\pi$ [MHz·T^{-1}]**
^{1}H	42.576
^{2}D	6.53593
^{3}He	-32.434
^{13}C	10.705
^{14}N	3.0766
^{15}N	-4.3156
^{17}O	-5.7716
^{19}F	40.0593
^{31}P	17.235

Density Matrix

Suppose we want to find the expectation value $\langle O\rangle$ of some operator *O*. Expand the wavefunction in a complete set of eigenstates to obtain,

$$|\psi\rangle = \sum_m a_m(t)|m\rangle \quad \rightarrow \quad \langle O\rangle = \langle\psi|O|\psi\rangle = \sum_{m,n} a_n^* a_m \langle n|O|m\rangle$$

Now define the *density operator* ρ as,

$$\rho = \sum_{m,n} a_m a_n^* \, |m\rangle\langle n| \quad \rightarrow \quad \langle m|\rho|n\rangle \; = \rho_{mn} = a_m a_n^*$$

ρ_{mn} is the *density matrix*. ρ is Hermitian since $\rho_{nm}^* = (a_n a_m^*)^* = a_m a_n^* = \rho_{mn}$. We now have,

$$\langle O\rangle = \langle\psi|O|\psi\rangle = \sum_{m,n} a_n^* a_m \langle n|O|m\rangle = \sum_{m,n} \rho_{mn} \langle n|O|m\rangle = \sum_{m,n} \langle n|O|m\rangle\langle m|\rho|n\rangle = \sum_n \langle n|O\rho|n\rangle = \sum_n \langle n|\rho O|n\rangle = Trace(\rho O)$$

Rather than calculating the amplitudes a_m it's often better to use the density matrix and take the trace to find $\langle O\rangle$. To do that we need an equation of motion for the density matrix. Using the Schrodinger equation,

$$|\psi\rangle = \sum_m a_m(t)|m\rangle \qquad i\hbar\frac{\partial|\psi\rangle}{\partial t} = H|\psi\rangle \quad \rightarrow \quad i\hbar\frac{da_k}{dt} = \sum_m a_m(t)\ \langle k|H|m\rangle$$

Using this and taking complex conjugates of both sides we obtain an equation of motion for the density operator,

$$\frac{d\varrho}{dt} = \frac{1}{i\hbar}[H,\rho] = \frac{i}{\hbar}[\rho,H]$$

It looks like the Heisenberg equation of motion but with a minus sign. It's perfectly general so H can depend explicitly on time. We'll now specialize to 2-level systems. Recall that any 2 x 2 matrix *D* can be written as a linear combination of the identity matrix and the 3 Pauli matrices,

$$D = d_0 + \vec{d}\cdot\vec{\sigma} \qquad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

d_0 and $\vec{d}$ are real numbers. Let the Hamiltonian and density operator for a 2-level system be written in this way,

$$H = h_0 + \vec{h} \cdot \vec{\sigma} \qquad\qquad \rho = \rho_0 + \vec{P} \cdot \vec{\sigma}$$

Putting these into the equation of motion for the density operator we get,

$$\frac{d\varrho}{dt} = \frac{1}{i\hbar}[H, \rho] = \frac{1}{i\hbar}\left[\vec{h} \cdot \vec{\sigma}, \vec{P} \cdot \vec{\sigma}\right]$$

To find the commutator we use an identity for Pauli matrices,

$$\overrightarrow{A} \cdot \vec{\sigma}\ \overrightarrow{B} \cdot \vec{\sigma} = \overrightarrow{A} \cdot \vec{B} + i\, \vec{\sigma} \cdot \overrightarrow{A} \,\mathrm{x}\, \vec{B}$$

The equation of motion becomes,

$$\frac{d\varrho}{dt} = \frac{d}{dt}\left(\rho_0 + \vec{P} \cdot \vec{\sigma}\right) = \frac{d\rho_0}{dt} + \frac{d\vec{P}}{dt} \cdot \vec{\sigma} = \frac{1}{i\hbar}[H, \rho] = \frac{1}{i\hbar}\left[\vec{h} \cdot \vec{\sigma}, \vec{P} \cdot \vec{\sigma}\right] = \frac{2}{\hbar}\vec{\sigma} \cdot \overrightarrow{h} \,\mathrm{x}\, \vec{P}$$

Since the Pauli matrix together with the identity matrix form a complete basis set we must have,

$$\frac{d\rho_0}{dt} = 0 \qquad\qquad \frac{d\vec{P}}{dt} = \frac{2}{\hbar}\overrightarrow{h} \,\mathrm{x}\, \vec{P}$$

The vector $\vec{h}$ is related to the Hamiltonian operator *H* by,

$$H = \begin{pmatrix} \langle 1|H|1\rangle & \langle 1|H|0\rangle \\ \langle 0|H|1\rangle & \langle 0|H|0\rangle \end{pmatrix} = h_0 + \vec{h} \cdot \vec{\sigma} = \begin{pmatrix} h_0 + h_z & h_x - ih_y \\ h_x + ih_y & h_0 - h_z \end{pmatrix}$$

For NMR, we'll need, for example, the expectation value of th magnetic moment, $\langle m_x \rangle$ where $m_x = \frac{\hbar}{2}\gamma_n\, \sigma_x$. Using the fact that $Tr\, \sigma_i = 0$, $Tr\, \sigma_i \sigma_j = 2\delta_{ij}$, the expectation value of m_x is given by,

$$\langle m_x \rangle = Tr(m_x \rho) = \frac{\hbar\gamma_n}{2} Tr\left(\sigma_x\left(\rho_0 + \vec{P} \cdot \vec{\sigma}\right)\right) = \gamma_n \hbar\, P_x$$

Going through the same process for $\langle m_y \rangle$ and $\langle m_z \rangle$ leads to $\langle \vec{m} \rangle = \gamma_n \hbar \, \vec{P}$. Using the equation of motion for the density operator we obtain an equation of motion for $\langle \vec{m} \rangle$ in our 2-level system,

$$\frac{d\vec{P}}{dt} = \frac{2}{\hbar} \vec{h} \times \vec{P} \qquad \rightarrow \qquad \frac{d\langle \vec{m} \rangle}{dt} = 2\, \gamma_n \vec{h} \times \langle \vec{m} \rangle$$

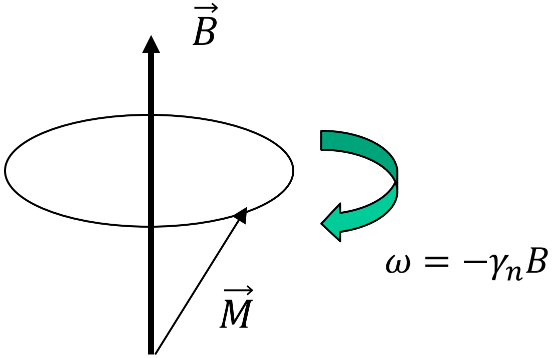
For a spin in a magnetic field $\vec{B}$ the Hamiltonian is given by,

$$H = -\vec{m} \cdot \vec{B} = -\gamma_n \frac{\hbar}{2}\, \vec{\sigma} \cdot \vec{B} \quad \rightarrow \vec{h} = -\gamma_n \frac{\hbar}{2}\, \vec{B}$$

Putting this together we obtain the equation of motion for $\langle \vec{m} \rangle$,

$$\frac{d\langle \vec{m} \rangle}{dt} = \gamma_n \langle \vec{m} \rangle \; x \; \vec{B}$$

This equation of motion corresponds to the precession of the vector $\langle \vec{m} \rangle$ about a magnetic field $\vec{B}$. For most nuclei γ_n is positive so the angular precession frequency $\omega_L = -\gamma_n B$ is negative, corresponding to *clockwise* precession. ω_L is known as the *Larmor frequency.* Despite the fact that the underlying physics is purely quantum mechanical, this result allows us to treat the spin precession classically which is a huge simplification. NMR is a weak probe and we generally require many spins to see a signal. Therefore, we'll generally deal with the macroscopic magnetization vector $\vec{M}$ which is the magnetic moment per unit volume,



$$\vec{M} = \sum_i \vec{m}_i / Vol \quad \rightarrow \quad \frac{d\langle \vec{M} \rangle}{dt} = \gamma_n \langle \vec{M} \rangle \; x \; \vec{B}$$

From here on we'll drop the brackets and assume that $\vec{M}$ represents its own expectation value and treat it as a classical quantity whose equation of motion is,

$$\boxed{\frac{d\,\vec{M}}{dt} = \gamma_n \, \vec{M} \; x \; \hat{B}}$$

Polarizing nuclei

Think of spin ½ nuclei. NMR requires an *imbalance* $(n_\uparrow - n_\downarrow)$ between up and down spins. Otherwise as many spins would absorb energy as those that emit energy. The signal will be proportional to the total magnetizaton,

$$M_0(T) = (n_\uparrow - n_\downarrow)\,|\gamma_n|\hbar\, B_0/2$$

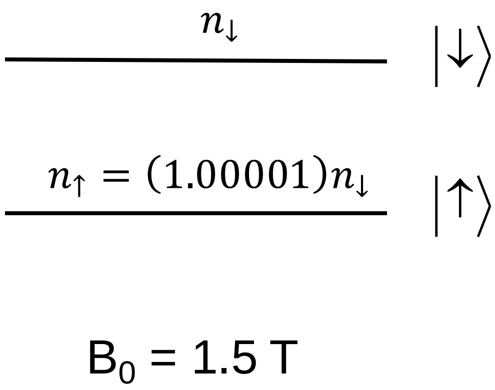
where $n_\uparrow + n_\downarrow = n$, the total number of spins per unit volume. In thermal equilibrium, $n_\downarrow/n_\uparrow = exp(-\hbar|\gamma_n\, B_0|/k_B T)$ so,

$$M_0(T) = N\frac{|\gamma_n|\hbar}{2}\,tanh\left(\frac{\hbar|\gamma_n|\, B_0}{2\, k_B T}\right)$$

The quantity in parentheses is always very small at room temperature. For protons at room temperature in the 1.5 T field that you might find in an MRI machine,

$$\left|\frac{\gamma_n \hbar\, B_0}{2\, k_B T}\right| \approx 10^{-5}$$

The imbalance between up and down spins is therefore also *very small*, as you can see in the figure. To increase $M_0(T)$ we need to either increase the field or lower the temperature. Newer MRI machines work at up to 4 T.



$n_\downarrow$ $|\downarrow\rangle$

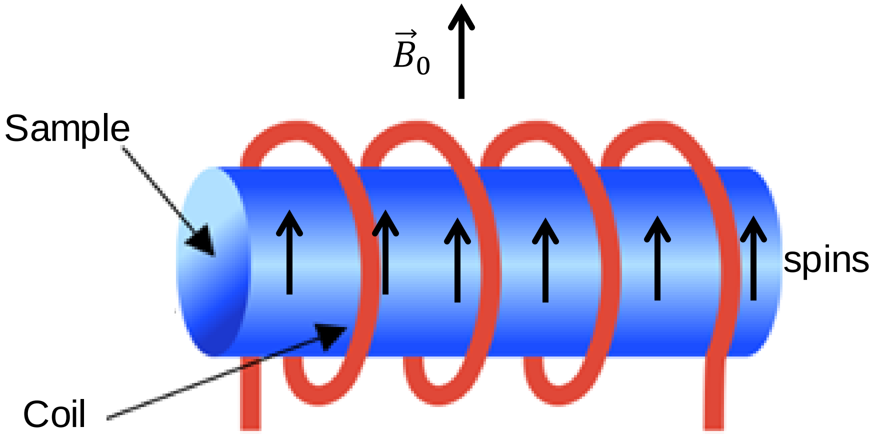
$n_\uparrow = (1.00001)n_\downarrow$ $|\uparrow\rangle$

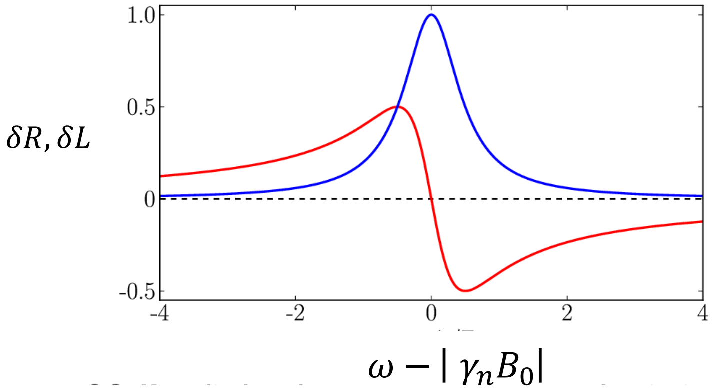
$B_0 = 1.5$ T

In equilibrium $\vec{M}_0$ is oriented along the applied field $\vec{B}_0$. To obtain an NMR signal we'll apply an additional time-dependent magnetic field at the resonant frequency to change the direction of $\vec{M}_0$. This process is easily visualized with classical mechanics but it holds true quantum mechanically.

CW NMR spectroscopy

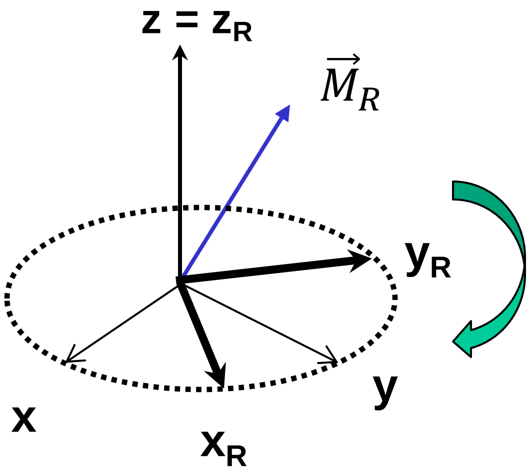
The spectroscopy we first learn about involves exciting a sample with light of a particular frequency and looking for resonant absorption. In NMR this is called continuous wave or CW spectroscopy. The experimental geometry consists of an inductor (coil) of some shape containing the sample of nuclear spins and a static magnetic field $\vec{B}_0$. The coil axis is perpendicular to $\vec{B}_0$. An alternating current at frequency ω (considered positive) is applied to the coil and the amplitude and phase of the voltage across it is monitored as the magnetic field magnitude is varied. When the condition $\omega = |\gamma_n B_0|$ is met the coil will develop an additional change in both its inductance δL and resistance δR that exhibit resonant behavior centered on the Larmor frequency. It's also possible to keep the field fixed and vary the frequency of excitation but that is more difficult to do.





The earliest NMR was CW but since the mid-1960's a much more versatile approach has been used. Short bursts of energy at or near the Larmor frequency are applied to the spins and their subsequent response as a function of *time* is recorded and Fourier transformed. This gives the same spectrum as you would obtain in a CW measurement but it's much faster and permits a much wider range of measurements. This approach is called *Fourier Transform NMR*. The signal is still detected from the voltage across a coil but the mode of excitation and detection involves looking at the spins as a function of time. FT NMR is more demanding of the electronics since amplifiers and detectors must respond to changes on very short time scales.

Rotating Frame



Change of reference frame is essential for understanding NMR. Imagine we step into a frame of reference that rotates about the z-axis (defined by $\vec{B}_0$) at an angular frequency ω_{Rot}. This rotating frame is defined by unit vectors $\hat{x}_R, \hat{y}_R, \hat{z}_R = \hat{z}$. Using a little vector analysis, we find that in the rotating frame $\vec{M}$ obeys,

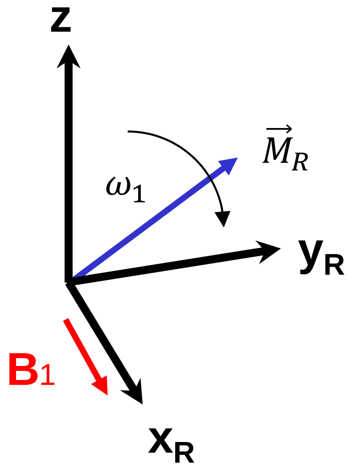
$$\frac{d\,\vec{M}_R}{dt} = \gamma_n \vec{M}_R \; x \left(\vec{B}_0 + \hat{z}\frac{\omega_{Rot}}{\gamma_n} \right)$$

If, for example, we chose $\omega_{Rot} = -\gamma_n B_0 = \omega_L$ then $\vec{M}_R$ is *stationary*,

$$\frac{d\,\vec{M}_R}{dt} = 0 \qquad \omega_R = \omega_L$$

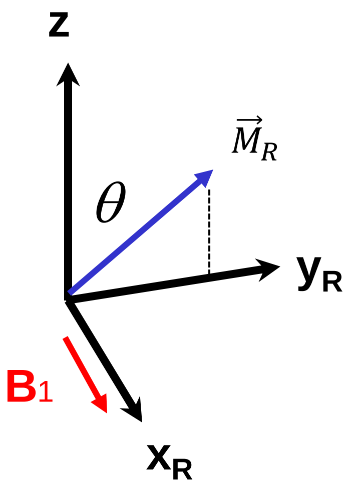
If, on the other hand, we chose $\omega_{Rot} \neq \omega_L$ then in the rotating frame $\vec{M}_R$ precesses at an *offset* frequency $\Omega = \omega_{Rot} - \omega_L$ which can be positive or negative. In FT NMR, Ω is generally *much* less than $|\omega_L|$. This is common is nearly all RF electronics. It means that the signal we detect (explained later) is at a much lower frequency so high precision electronics can be used.

Spins in equilibrium just have a static magnetization $M_0\hat{z}$. To detect a signal we need to generate a changing flux through a coil. If we can tip $\vec{M}_R$ *away* from the z-axis then it will precess at ω_L or, equivalently, at Ω in the rotating frame, producing an oscillating flux along the x-axis and a voltage we can detect. In the rotating frame it's easy to see how to tip $\vec{M}$ away from equilibrium. Set $\omega_{Rot} = \omega_L$ and turn on a magnetic field $\vec{B}_1$ that's *constant* in the rotating frame, say along the $\hat{x}_R$ axis. Now, the only field $\vec{M}_R$ sees is $\vec{B}_1$ so it precesses around it, at frequency, $\omega_1 = -\gamma_n B_1$.



$\gamma_n > 0$

RF pulses



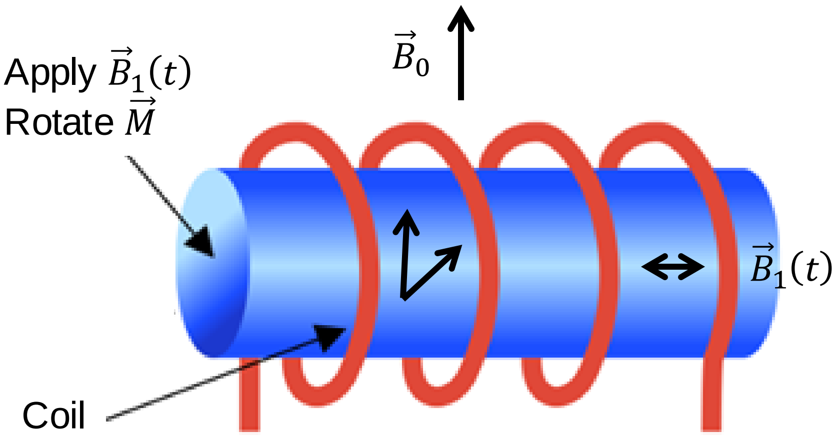
If we apply $\vec{B}_1$ along the x-axis in the rotating frame for a time τ then $\vec{M}_R$ will precess around it by an angle,

$$\theta = \omega_1 \tau = -\gamma_n B_1 \tau$$

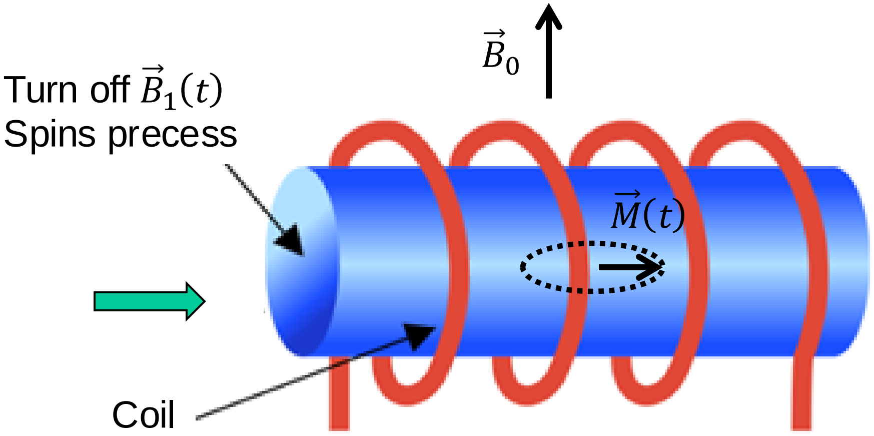
(For $\gamma_n > 0$ that is a clockwise rotation about x_{rot} .) That leaves a *projection* of length $M_0 \sin\theta$ in the x_R , y_R plane. In the *lab* frame, that corresponds to an x-y component of $\vec{M}$ precessing about the z-axis at the Larmor frequency $\omega_L = -\gamma_n B_0$. The signal induced in the coil is proportional to the time rate of change of flux induced by this precessing magnetization moment. Taking the x-axis along the coil, the induced voltage is,

$$V_{coil}(t) = \frac{d\phi_B}{dt} \propto \frac{dM_x}{dt} \propto M_0 \sin\theta \cos(\omega_L t + \phi)$$

This signal is called the free induction decay (FID), although we haven't introduced any decay as yet.



$$I_{coil}(t) \sim \cos\omega_L t$$



$$V_{coil}(t) = \frac{d\phi_B}{dt}$$

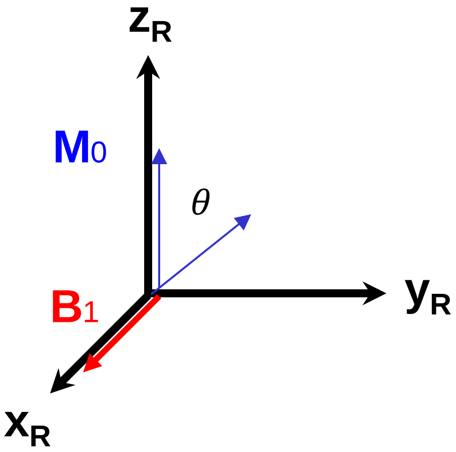
Free induction decay

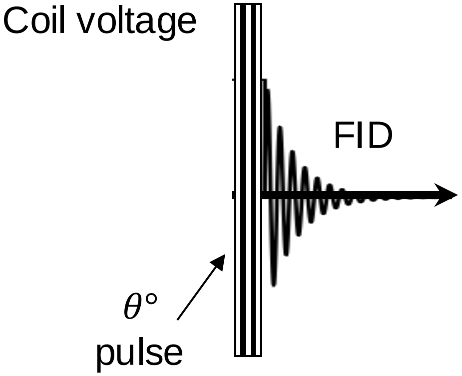
To clarify one thing, recall that we tipped $\vec{M}$ with a field that was *constant* in the frame rotating at ω_L. That can be produced by sending an oscillating current through the coil. The field in the coil is linearly polarized along the coil axis, but that can be written as the sum of two counter-rotating fields,

$$\vec{B}_{1coil}(t) = \vec{B}_+ + \vec{B}_- = 2\,B_1 \cos\omega_L\,t\,\hat{x} = B_1(\cos\omega_L t\,\hat{x} + \sin\omega_L t\,\hat{y}) + B_1(\cos\omega_L t\,\hat{x} - \sin\omega_L t\,\hat{y})$$

$\vec{B}_+$ has magnitude B_1 and is static in a reference frame rotating at ω_L . That's the field that tips tip $\vec{M}$ by θ . Although $\vec{B}_-$ is also present, it rotates in the opposite direction and is ineffective in tipping $\vec{M}$. In effect, the spins choose the field component that precesses along with them and ignore the other component.

The figure shows what happens in the rotating frame if we turn on $\vec{B}_{1coil}(t)$ for time τ and tip $\vec{M}$ by θ. In this case $\theta = 90°$. After the RF pulse, the precessing spins generate a waveform called a **free induction decay (FID)** that oscillates at the Larmor frequency (as seen in the frame of the coil.) The value of the FID right after the RF pulse is proportional to $M_0 \sin\theta$. You'll get the largest FID if $\theta = 90°$ and that's called, appropriately, a $90°$ pulse. **Important: it's only the component of $\vec{M}$ that is perpendicular to the quantization axis that can generate a signal. The M_z component cannot produce a signal.**

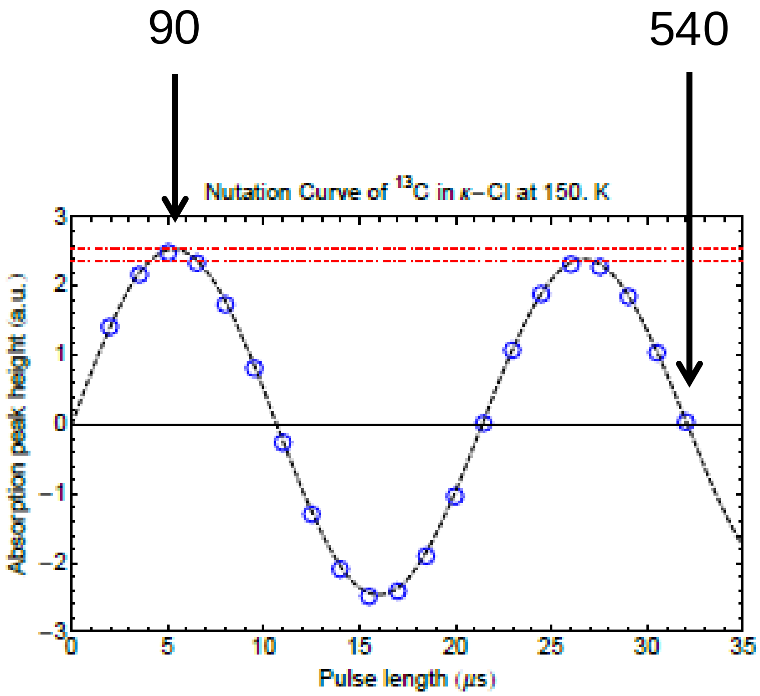




If the magnetic field were perfectly uniform and the spins were entirely isolated from their environment, they would precess forever. (They would eventually radiate energy away, but that's a *very* weak process for a nuclear spin.) But the spins are *not* isolated and they do *not* see in a perfectly uniform magnetic field so the signal decays away in finite time. That's the D part of FID.

Nutation Curve

We don’t know, initially, how long to turn on the RF field to tip the spins by θ. That depends on the precise waveform that reaches the coil, the coil resistance and inductance and other details that are hard to know precisely. Instead, we simply record FIDs as a function of RF pulse length. Their initial value should be a sinusoidal function of θ. The resulting plot of FID size versus pulse length is called a *nutation curve*. The plot below shows one for ^{13}C NMR in an organic solid. Here, the pulse length was increased all the way out to $\theta = \gamma_n B_1 \tau = 540°$.



The nutation curve is usually the first thing to measure once you’ve found the NMR signal. It’s important to know how long to make the pulse for a $90°$ and $180°$ rotation. It’s also a useful diagnostic tool to see if the RF field of the coil is too inhomogeneous, among other things.

Induced signal

The NMR signal comes from the changing flux induced in a coil by the precessing spins. In general, the magnetic field produced by the coil is not uniform nor is the magnetization so we need to take account of that. Suppose the field of the coil is given by,

$$\vec{B}_1(\vec{r}) = I_{coil}\, \vec{b}(\vec{r})$$

where $\vec{b}(\vec{r})$ describes the spatial profile of the coil. Now consider a magnetic moment $\vec{m}$ located at $\vec{r}$. Represent $\vec{m}$ by a current loop of area A carrying a current $I_m = m/A$ with a direction $\hat{n}$ parallel to $\vec{m}$. We now have a transformer in which the current $I_m(t)$ induces a time-changing flux $\Delta\phi_{coil}$,

$$\Delta\phi_{coil} = M_{12} I_m$$

Where M_{12} is the mutual inductance. Now imagine driving a current through the coil and inducing a flux in the current loop,

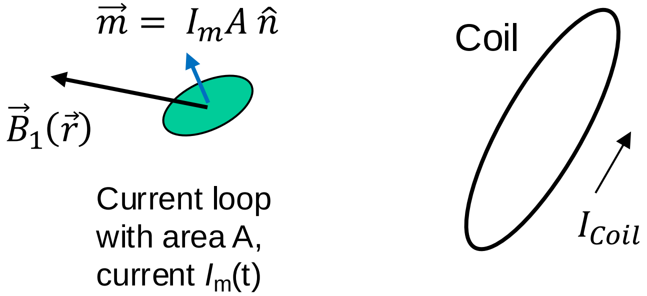
$$\phi_m = M_{21}\, I_{Coil}$$

This flux is much easier to calculate. It's given by,

$$\phi_m = \vec{B}_1(\vec{r}) \cdot \hat{n}\, A = I_{coil}\, \vec{b}(\vec{r}) \cdot \hat{n}\, A = M_{21}\, I_{Coil}$$

But by reciprocity, $M_{21} = M_{21}$ so,

$$\Delta\phi_{coil} = M_{12} I_m = M_{21} I_m = \vec{f}(\vec{r}) \cdot \hat{n}\, A\, I_m = \frac{\vec{B}_1(\vec{r})}{I_{coil}} \cdot \vec{m}\,(\vec{r}, t)$$



Current loop
with area A,
current $I_m(t)$

The total flux induced in the coil is the sum of the contributions from all the moments. The magnetic moment from each little group of spins is $\Delta\vec{m} = \vec{M}(\vec{r}, t)\, dxdydz$. The voltage induced in the coil is the sum of all their flux contributions,

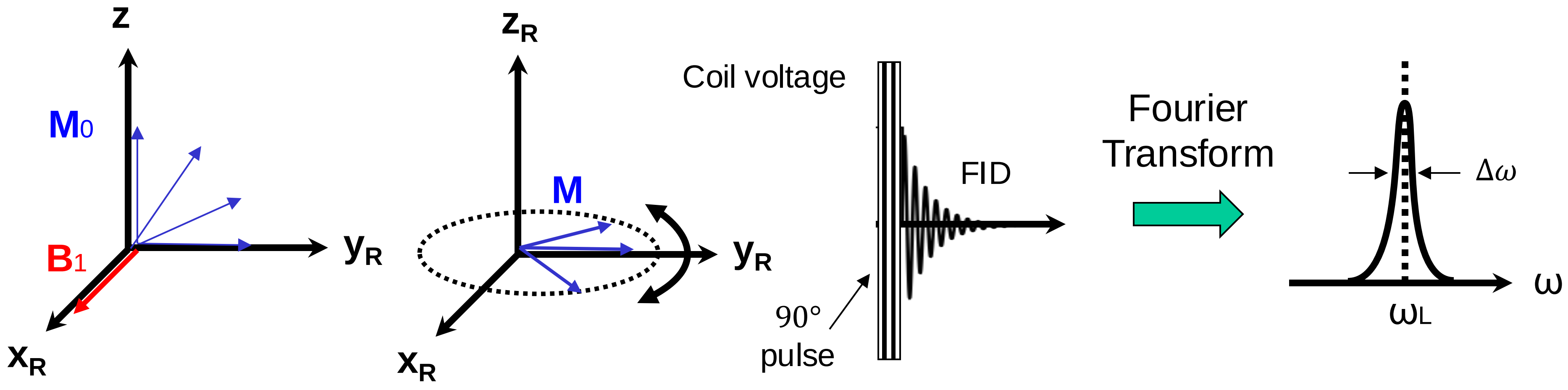
$$V_{coil}(t) = \frac{d}{dt}\int \Delta\phi_{coil}\,(\vec{r}, t)\, dxdydz = \frac{d}{dt}\int \frac{\vec{B}_1(\vec{r})}{I_{coil}} \cdot \vec{M}\big(\vec{R}, t\big)\, dxdydz$$

The integral is over the entire volume of the sample. Often the sample is small enough to fit into a region of the coil where $\vec{B}_1(\vec{r})$ is uniform, in which case everything can be pulled outside the integral.

Inhomogeneous broadening

Suppose now the static field varies by ΔB across the entire sample. Spins in different locations will precess at different rates. In a frame rotating at $\omega_L = -\gamma_n B_0$, spins that see $B = B_0$ just sit still. Those with $B > B_0$ will precess faster and those with $B < B_0$ will precess more slowly. As different spins get out of phase, $\vec{M}$ decreases and eventually vanishes and with it, the signal induced in the coil. The precise time dependence of the FID depends on the magnetic field profile across the sample. In many cases it's approximately exponential with a time constant,

$$T_2^* \approx \frac{2}{\gamma_n \Delta B}$$



How does this dephasing by the inhomogeneous field affect the measured NMR spectrum?

The key feature of FT NMR is that the Fourier transform of the FID is the NMR spectrum.

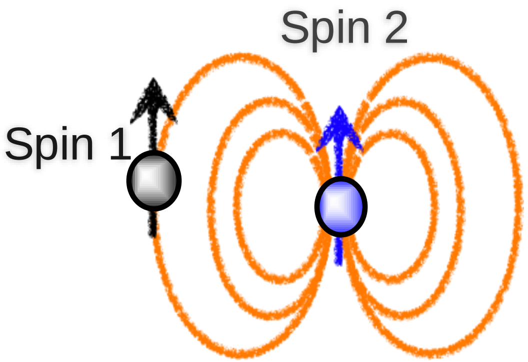
So if the FID decays exponentially with time constant T_2^* then the spectrum will be a Lorentzian, centered at ω_L with a half power width,

$$\Delta\omega = \frac{2}{T_2^*} = \gamma_n \Delta B$$

This is known as *inhomogeneous broadening*. While it does limit spectrum resolution, it's the key to magnetic resonance imaging.

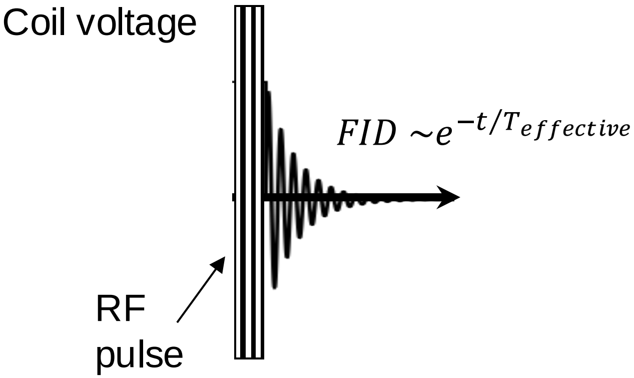
Homogenous broadening

Inhomogeneous broadening is a limitation on high resolution spectroscopy but there are ways to get around it. But even in a perfectly homogeneous magnet the FID will still decay. That comes from, among other things, the fluctuating magnetic fields of nearby spins. In the figure, spin 1 is in the dipole field B_{12} of spin 2. B_{12} is typically a few Gauss in solids or liquids. As spin 1 moves around it samples B_{12} at different locations so it sees a random magnetic field, which causes it to make quantum transitions. The net effect is to change $\vec{M}$ as time goes by. This is know as *spin relaxation*. Or, in terms of the spectrum, it leads to *homogenous* broadening.



B_{12} : dipole field at spin 1 due to spin 2

$$B_{12} \approx \frac{\mu_2}{r_{12}^3} \approx 10^{-4} T$$



In general, both homogeneous and inhomogeneous broadening are present so the FID decays with an effective time constant,

$$\frac{1}{T_{effective}} \approx \frac{1}{T_2} + \frac{1}{T_2^*}$$

$$\Delta\omega = \frac{2}{T_{effective}}$$

In liquids, a phenomenon known as motional narrowing leads to extremely long T_2 's so often $T_2^* \ll T_2$ for many magnets. Inhomogeneous broadening dominates the FID.

In solids, T_2 is usually short so one often has $T_2^* \gg T_2$. The FID is dominated by T_2 and the spectrum can be very broad. It should be remembered that the FID does not always decay exponentially. That's usually the case in liquids but in solids it is often *Gaussian*,

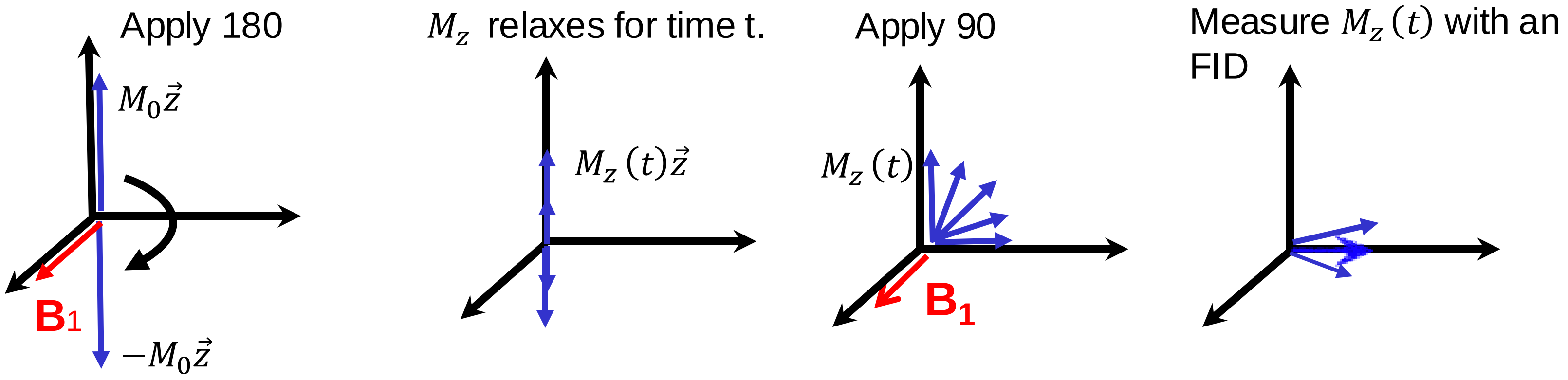
$$e^{-t^2/\alpha}$$

Spin-lattice relaxation

What happens after the FID as decayed away? Somehow the $\vec{M}$ must return to its thermal equilibrium value $M_0\vec{z}$. That process is called *spin-lattice relaxation* and is characterized by a new time constant called T_1. To watch the process, go into the rotating frame. In order to focus on just the T_1 process, send in a $180°$ RF pulse. This sends $\vec{M}$ from $M_0\vec{z}$ to $-M_0\vec{z}$. There is no induced signal afterwards because $\vec{M}$ is entirely along the z-axis. Now wait a time *t*. M_z relaxes back up along the z-axis toward its equilibrium value M_0. To measure M_z at any time, we need to generate a *transverse* component. This is done by applying a $90°$ pulse. The size of the FID is proportional to $M_z(t)$. Often the relaxation back to equilibrium is exponential in which case,

$$M_z(t) = M_0\left(1-2\,e^{-t/T_1}\right)$$

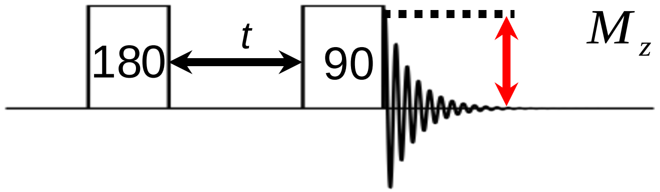
By doing this for many values of *t* you can determine T_1. In solid state NMR T_1 is often the easiest and most important parameter to be measured. For *all* NMR measurements, T_1 limits how fast you can take data. To obtain a good signal to noise ratio you might want to repeat this sequence 100 times and average the results. But you must wait at least 5 T_1 between measurements to make sure the spins are back to equilibrium. For water at room temperature, $T_1 \approx 2.3\ sec$. You can see why a short T_1 can be a real advantage.


Apply 180

M_z relaxes for time t.

Apply 90

Measure $M_z(t)$ with an FID



$$M_z(t) = M_0\left(1-2\,e^{-t/T_1}\right)$$

Bloch Equations

Early in the history of NMR, F. Bloch presented equations for the components of the magnetization that include both spin precession *and* relaxation effects. In the lab (non-rotating) frame, the equations can be written in vector form as,

$$\frac{d\,\vec{M}}{dt} = \gamma_n\,\vec{M}\;x\;\vec{B} - \frac{M_x}{T_2}\hat{x} - \frac{M_y}{T_2}\hat{y} - \frac{M_z - M_0}{T_1}\;\hat{z}$$

The spin precession term is familiar. The other terms account for relaxation.

Longitudinal relaxation: Return to the inversion-recovery sequence.   Before and after the inversion M_x , M_y = 0. Immediately after the inversion (call it t = 0) we have $M_z = -M_0$ and the subsequent value obeys,

$$\frac{d\,M_z}{dt} = -\frac{M_z - M_0}{T_1} \qquad \rightarrow \qquad M_z(t) = M_0\left(1 - 2e^{-t/T_1}\right)$$

Transverse relaxation :   Now imagine performing a 90° pulse in a perfectly uniform magnetic field. After the pulse $M_z = 0$ and $M_x, M_y \neq 0$ The Bloch equations give,

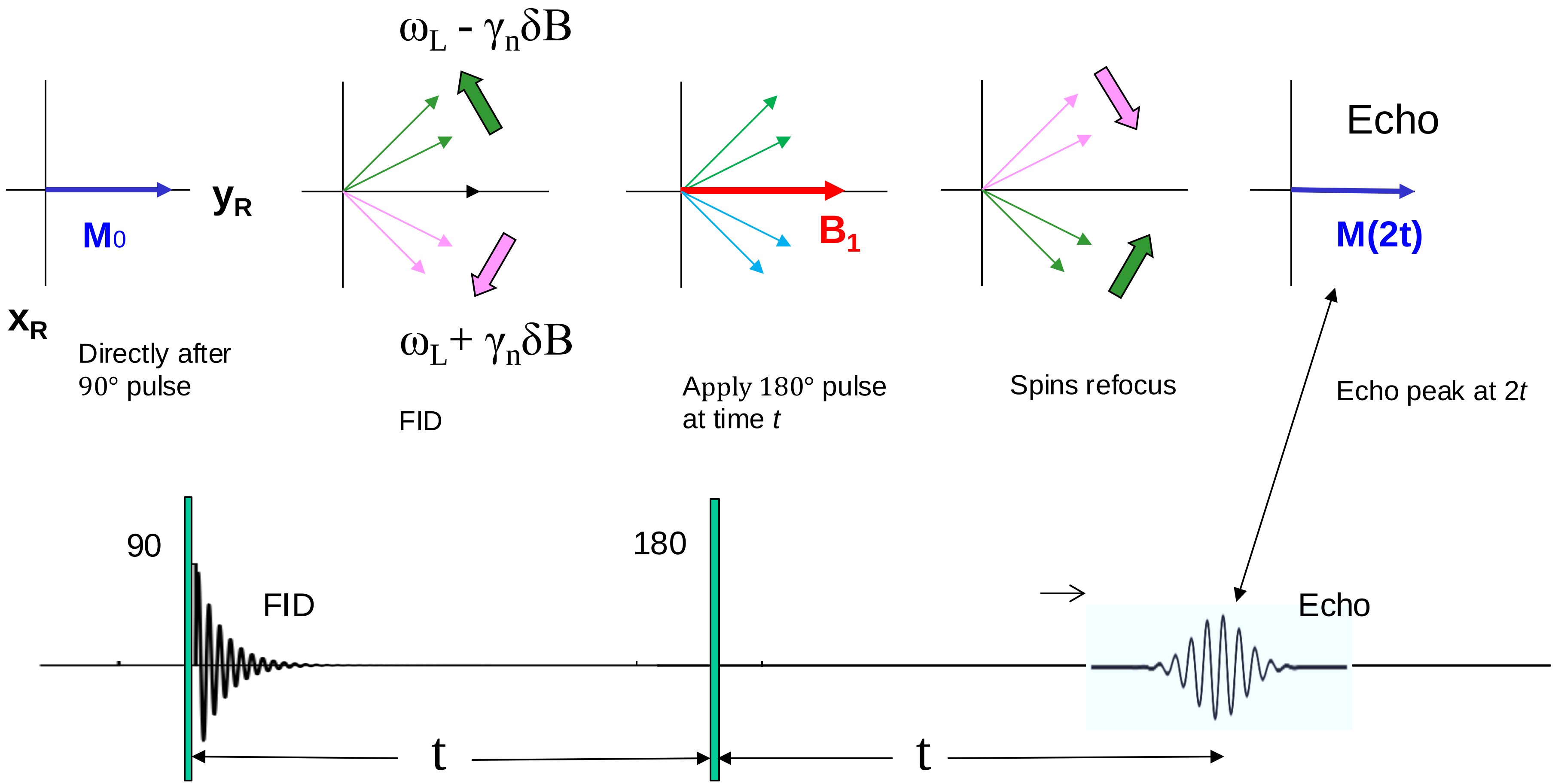
$$\frac{d\,M_x}{dt} = -\frac{M_x}{T_2} \qquad \frac{d\,M_y}{dt} = -\frac{M_y}{T_2}$$

The FID will decay exponentially with time constant T_2. These terms account for homogeneous broadening. In liquids this picture works well. In solids, things are more complicated and the relaxation will not always be exponential.

There is just one value of *B* in these equations. To account for an inhomogeneous magnetic field you would add up contributions to $\vec{M}$ from regions of space having different magnetic field values. Depending on the spatial dependence of the *B* field the FID might decay exponentially but it often has more complicated functional form.

Spin Echo (*E. Hahn, 1950*)

Hahn’s discovery of the spin echo really began the huge field of sophisticated NMR spectroscopy. To understand it, look in the frame rotating at the Larmor frequency and apply a 90° pulse. This leaves $\vec{M}$ lying in the plane, let’s say along the y_R axis. Field inhomogeneity causes the spins to dephase. Wait some time *t* and apply a 180° pulse along the y_R axis. (It could also be along the x_R axis.) In fact you can wait until the FID has *completely vanished* before applying the 180. The 180 pulse rotates the spins around the y_R axis, after which they continue to precess in the *same direction* as before. But now, instead of dephasing, they are *rephasing* and all come together at precisely time 2*t*, producing a *spin echo*. The second half of the echo is equivalent to the original FID. The echo has *refocused* the inhomogeneous broadening and brought the FID back to life! Almost…



$\omega_L - \gamma_n \delta B$

y_R

M_0

x_R

Directly after
90° pulse

$\omega_L + \gamma_n \delta B$

FID

B_1

Apply 180° pulse
at time *t*

Spins refocus

Echo

M(2t)

Echo peak at 2*t*

90

FID

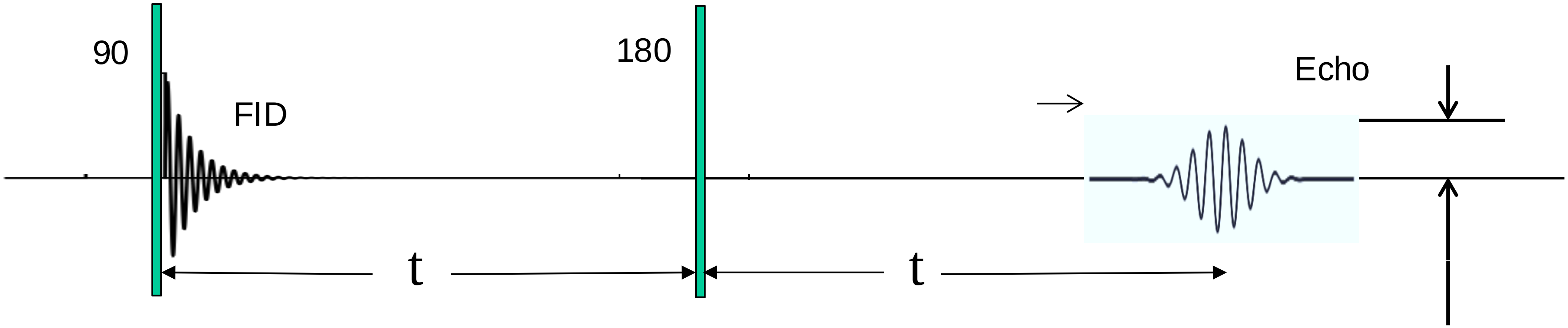
180

Echo

t

t

Spin Echo to measure T_2



$$M(2t) = M_0 e^{-2t/T_2}$$

The echo has refocused the dephasing due to field inhomogeneity. It's as if each spin had a memory of how much it has precessed and the 180 reverses that process. However, dephasing due to the environment (homogeneous broadening) is *random* and cannot be refocused. This random dephasing continuously reduces the magnetic moment so that,

$$Echo\,peak = M(2t) = M_0 e^{-2t/T_2}$$

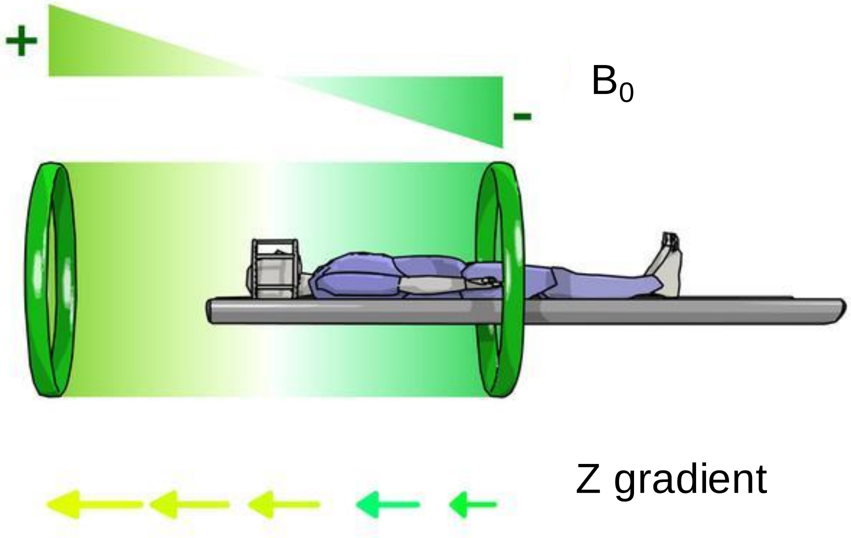
But this is a good thing. It means that even with a highly inhomogeneous magnet, in which $T_2^* \ll T_2$, we can still measure the intrinsic dephasing time T_2. In addition, the second half of the echo is proportional to the true FID. The original FID has the problem that the electronics does not turn off abruptly at the end of the $90°$ pulse. Amplifiers and tuned circuits tend to "ring" for some finite time after a pulse and interfere with the true FID signal. Therefore it's impossible to begin recording the FID at $t = 0$. The echo, on the other hand, is far away from this interference so the peak of the echo represents the true initial value of the FID, aside from the reduction from T_2.

Spin echo to measure diffusion

Along with the intrinsic T_2 dephasing that spins undergo, they can also move around. As they move into regions where the field is different, their precession rates change. This also leads to an irreversible decay of the magnetization and therefore the echo. Suppose, for example, the magnetic field is axially symmetric but has a gradient d*B/dz* along the field direction, z. The figure shows such a gradient in an MIR magnet. It was first shown by Hahn that the spin echo at time 2*t* is reduced by an additional factor (in green),

$$Echo(2t) = M_0\, e^{-2t/T_2}\, exp\left(-\left(\gamma_n \frac{dB}{dz}\right)^2 \frac{2}{3} D t^3\right)$$

where *D* is the diffusion constant of the spin. Notice that the diffusion piece depends on t^3 , not $(2t)^3$. In other words, the diffusion begins anew after each pulse so it depends on the time between pulses, *t,* not the total elapsed time since the 90 degree pulse. Modern methods involve more sophisticated pulse sequences with pulsed *gradients* that can isolate the diffusion contribution.



https://www.imaios.com/de/e-mri/spatial-encoding-in-mri/magnetic-field-gradients

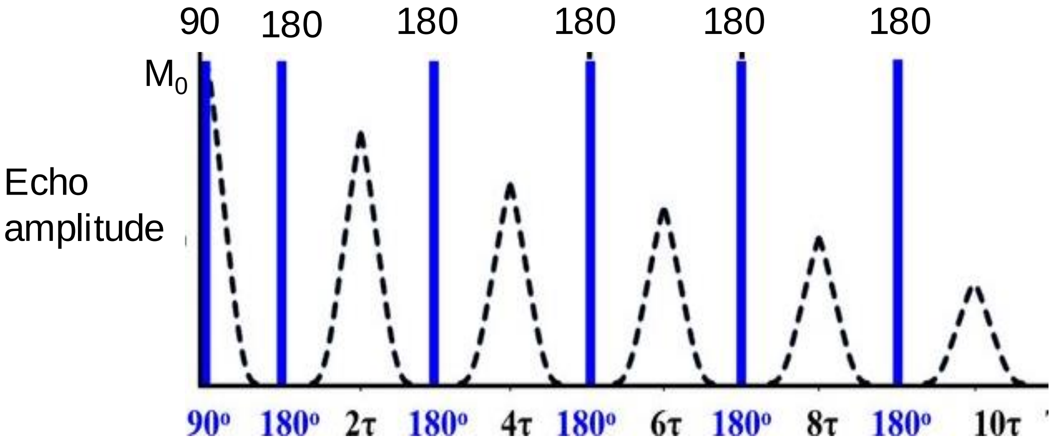
Some diffusion constants

Water at room temp, *D* = 2.3 x 10^{-9} m^2/sec

Glycerol at room temp, *D* = 4 x 10^{-12} m^2/sec

So long as the irreversible effects from T_2 and diffusion have not completely destroyed the magnetization, the dephasing from field inhomogeneity can be refocused repeatedly. The next page shows what is called a Carr-Purcell-Meiboom-Gill (CPMG) sequence.

CPMG sequence



https://www.researchgate.net/publication/339045537_Time Domain_Nuclear_Magnetic_Resonance_Determination_of_Wettability_Alteration_Analysis_for_Low-Salinity_Water/figures?lo=1

The figure shows a $90°$ pulse followed by an equally-spaced train of $180°$ pulses and the ensuing spin echoes.

Each $180°$ pulse refocuses what's left of the magnetization after the previous echo. The first echo after the $90°$ pulse reduces the initial magnetization by,

$$Echo(2\tau) = M_0\, e^{-2\tau/T_2}\, exp\left(-\left(\gamma_n \frac{dB}{dz}\right)^2 \frac{2}{3} D\tau^3\right) = M_0\, \alpha$$

At time $t = 2\tau$ (the peak of the first echo) it's just like the situation at *t* = 0 except that the magnetization has been reduced by α. The N^{th} echo will therefore have height,

$$Echo(t = 2N\tau) = M_0\, \alpha^N \; = \; M_0\, e^{-2N\tau/T_2}\, exp\left(-N\left(\gamma_n \frac{dB}{dz}\right)^2 \frac{2}{3} D\tau^3\right)$$

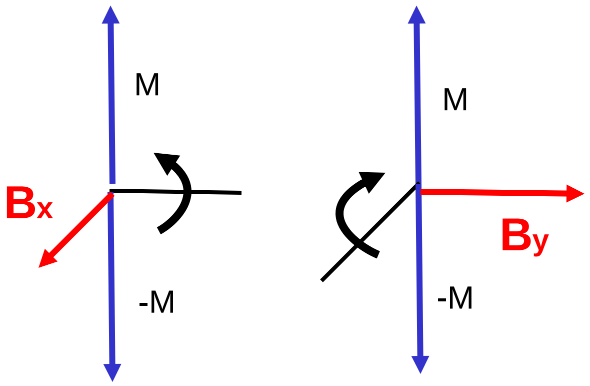
$$= M_0 \;\, e^{-2N\tau/T_2}\, exp\left(-\left(\gamma_n \frac{dB}{dz}\right)^2 \frac{(2N\tau)}{3} D\tau^2\right)$$

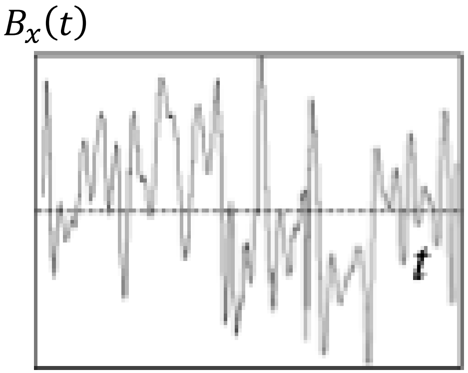
By shortening τ and increasing *N* we can keep $2N\tau$ constant. However, the diffusion term has an additional τ^2 in the exponent so the diffusion part becomes less important relative to the T_2 part. The echo decay is then dominated by T_2.

This figure illustrates the difference between inhomogeneous and homogeneous broadening. Inhomogeneous broadening causes the initial FID and each individual echo to rapidly decay away from its maximum value. But if $T_2 \gg T_2^*$ the echo peak heights decay more slowly, due to homogeneous broadening.

Mechanisms of spin-lattice relaxation

After an RF pulse $\vec{M}$ is no longer in thermal equilibrium. In order to return to equilibrium there must be some way to flip spins. Think of inversion-recovery. We used a magnetic field in the x_R or y_R direction of the rotating frame to rotate $\vec{M}$. That means a field *at the Larmor frequency* in the lab frame. These fields can come from nearby nuclear or electron spins. They *fluctuate* so they don't have a constant frequency. Instead, they have Fourier components ranging from $\omega = 0$ up to very high frequencies but only the components near the Larmor frequency are effective in flipping spins.





The figure shows random fields B_x and B_y with Fourier components at the Larmor frequency. In the rotating frame these components are stationary. Either one can rotate the spin from down to up, thus restoring equilibrium. Since they are random, they average to zero,

$$\langle B_{x,y}(t)\rangle = \frac{1}{2T}\int_{-T}^{T} B_{x,y}(t)\ dt \quad T \to \infty$$

However, the mean-squared values $\langle B_x^2\rangle, \langle B_y^2\rangle \neq 0$. Since they are random functions we can't just expand them in a Fourier series. Instead, look at the *autocorrelation function,*

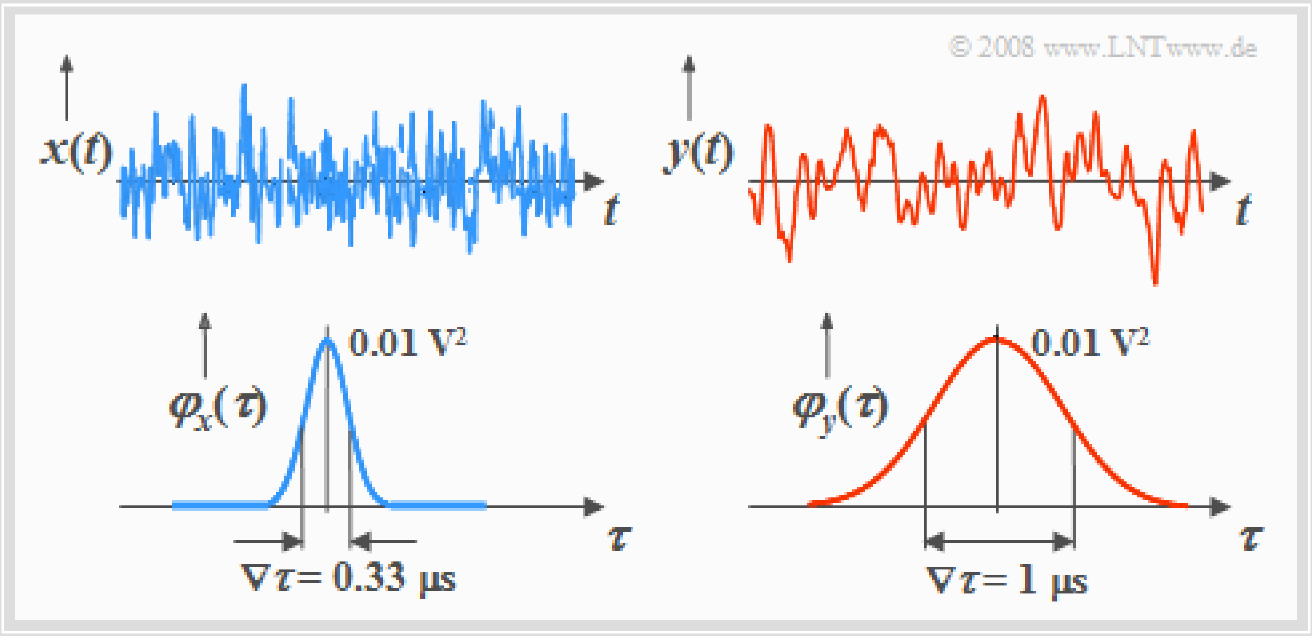
$$\langle B_x(t)B_x(t+\tau)\rangle$$

(and similarly for B_y.) If $\tau = 0$ then this function is just $\langle B_x^2\rangle$. And for $\tau \to \infty$ it will be zero since there can't be any correlation between the field at widely separated times. Since the field is random it shouldn't make any difference if we evaluate the autocorrelation function at τ or $-\tau$. A widely used approximation that satisfies all these criteria is,

$$\langle B_x(t)B_x(t+\tau)\rangle = \langle B_x^2\rangle e^{-|\tau|/\tau_c}$$

where τ_c is the *correlation time*. Correlation functions are the key players when we discuss random processes.

https://en.lntwww.de/Theory_of_Stochastic_Signals/Auto-Correlation_Function



The figure shows two random functions in which x(t) has a smaller correlation time than y(t).

Since we are interested in the Fourier components of the fluctuating fields, we take the Fourier transform of the auto correlation function.

$$J(\omega) = \frac{1}{\langle B_x^2 \rangle} \int_{-\infty}^{\infty} \langle B_x(t) B_x(t+\tau) \rangle \, e^{-i\omega t} \, dt$$

This function is called the *spectral density* or the *power spectrum*. It's the connection to Fourier analysis for random functions. Since we're looking for Fourier components that are stationary in the rotating frame we need to evaluate the spectral density at the Larmor frequency. For two random fields acting on the spin the result is,

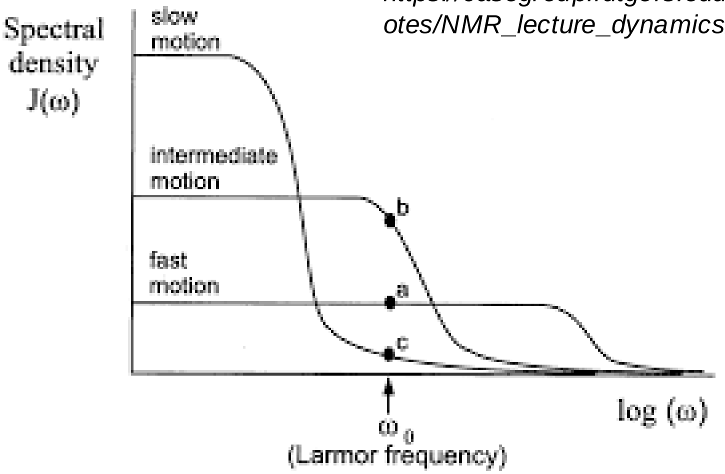
$$\frac{1}{T_1} = \gamma_n^2 \left(\langle B_x^2 \rangle + \langle B_y^2 \rangle \right) J(\omega_L)$$

Using the previous expression for the auto-correlation function we have,

$$\frac{1}{T_1} = \gamma_n^2 \left(\langle B_x^2 \rangle + \langle B_y^2 \rangle \right) J(\omega_L) = \gamma_n^2 \left(\langle B_x^2 \rangle + \langle B_y^2 \rangle \right) \frac{\tau_C}{1 + \omega_L^2 \tau_C^2}$$

The spectral density is shown in the figure. If we fix the Larmor frequency and vary the correlation time, then the spectral density function goes from slow motion (long τ_C) to intermediate, to fast motion (short τ_C). $1/T_1$ will go through a maximum when $\omega_L = 1/\tau_C$. The correlation time generally varies with temperature.

For protons in ordinary water $\tau_C \approx 10^{-11}\ sec$ so that would be considered fast motion for Larmor frequencies $f_L = \omega_L/2\pi$ all the way up to about 10^{10} Hz. On the other hand, spins in solids may have much longer correlation times, in the 10^{-7} sec range.

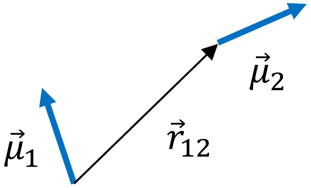


https://casegroup.rutgers.edu/lnotes/NMR_lecture_dynamics.pdf

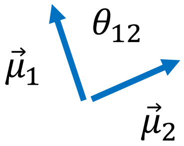
Spin relaxation by dipoles in liquids

The previous example assumed general, random fields, B_x and B_y which lead to relaxation. In real systems like H_2O these come from the dipole fields of the protons. The dipole-dipole interaction is given by,

$$H_{12} = -\vec{\mu}_1 \cdot \vec{B}_{12} = \frac{\mu_0}{4\pi\, r_{12}^3}\{\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \hat{r}_{12})(\vec{\mu}_2 \cdot \hat{r}_{12})\} \qquad \vec{\mu}_i = \gamma_{ni}\vec{I}_i$$



Here $\vec{B}_{12}$ is the field produced by dipole moment of spin 1 at the location of spin 2. The $1/r_{12}^3$ factor means that nearby spins are the most important. Liquids are very complicated so there are many contributions to $1/T_1$, all coming from the dipole interaction:

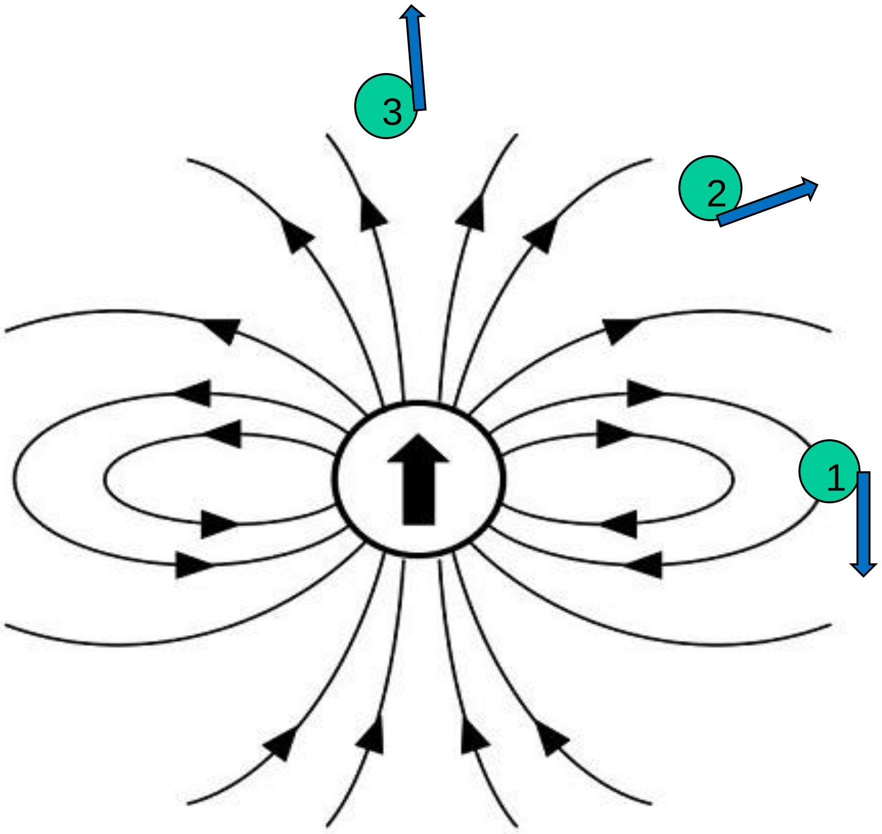


(1) Interaction between spins on the *same* molecule. Here, we assume r_{12} is fixed so just the angle θ_{12} fluctuates. That's equivalent to $\hat{r}_{12}$ diffusing around on the unit sphere. The correlation time and therefore $J(\omega_L)$ depends on the viscosity η of the liquid,

$$\tau_C = \frac{4\pi\eta}{3k_B T} \qquad \sim \ 10^{-10} - 10^{-12}\ sec$$

In a field of B =1 Tesla, the proton Larmor frequency is $|\omega_L| = 1.4\ x\ 10^8$ so usually $|\omega_L \tau_C| \ll 1$ in liquids.

To get a feel for the dipole interactions, consider two protons in a water molecule and suppose the molecule rotates counterclockwise about the proton at the center. If, during this time, the center proton doesn't make a transition, then its dipole field stays *fixed*. As the molecule rotates, the green proton moves from point 1 to 2 to 3. It feels successive magnetic fields shown by the blue arrows. (See M. Levitt, *Spin Dynamics*, pp. 532-533.)



There's another effect. Suppose the static field B_0 is perpendicular to the page. Then the center spin precesses in the plane of the page at ω_L. As seen in the frame rotating at the Larmor frequency, that, together with the molecular rotation at ω_L can rotate the the spin of the green proton and therefore contribute to $1/T_1$. A full quantum treatment takes all these effects into account. All told, for a rotating molecule, T_1 is determined by the spectral density at *both* ω_L and $2\omega_L$,

$$\frac{1}{T_1} = \frac{3}{2}\gamma_n^4\,\hbar^2 I(I+1)\big(J(\omega_L) + 4\,J(2\omega_L)\big)$$

where *I* is the spin. Since $|\omega_L\tau_C| \ll 1$ for typical fields, both spectral densities can be approximated by,

$$J(\omega_L), J(2\omega_L) \propto \tau_C$$

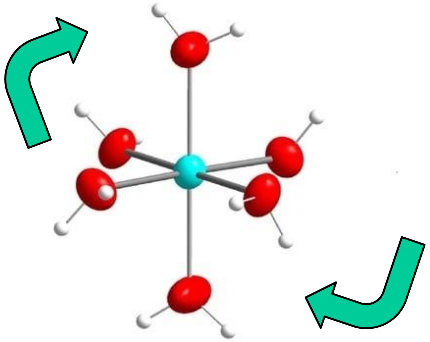
(2) We also need to consider spins on *other* molecules. In that case, it's the translational (rather than rotational) diffusion of these other spins through the dipole field that matters the most. It turns out that both contributions have the same functional form,

$$\frac{1}{T_1} \propto \tau_C \propto \frac{\eta}{T}$$

This proportionality has been verified over several decades for many liquids.

Relaxation by paramagnetic ions

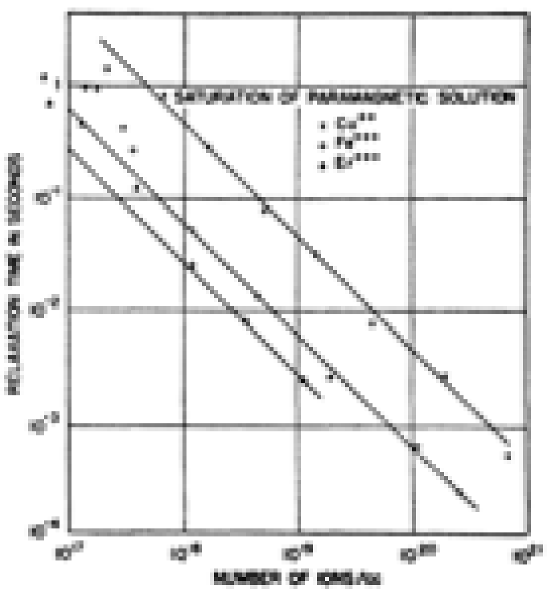
Imagine we now dissolve something like $CuSO_4$ in water. There will now be a concentration of Cu(2+) and SO_4(2-) ions. The ions have unpaired electronic spins so they are paramagnetic and can interact with protons on nearby water molecules. Metallic ions dissolved in water usually form complexes in which 6 water molecules are loosely bound to the metallic ion. The ion Cu(2+) pulls the oxygen end of each H_2O toward it, as shown. (There is some evidence that 5-water complexes also form.) We measure T_1 of the protons, shown as white spheres.



The proton T_1 is now determined by its motion through the dipole field of the *ion*. That's because, for unlike spins, $1/T_1 \propto \gamma_n^2\gamma_e^2$ and the electron gyromagnetic ratio γ_e is 660 times larger than the proton γ_n. We still need to calculate the spectral density of the fluctuating magnetic field seen by the proton. First, we can treat this entire complex as a sphere doing a rotational random walk around the ion at the origin, so the math is pretty much like the case for two protons on the same molecule. The original paper on this subject was written in 1948 by Bloembergen et. al., referred to as BPP. The plot shows their T_1 values for water containing 3 different metallic ions at varying concentrations. The result is,

$$\frac{1}{T_1} \propto \tau_C \propto \frac{\eta}{T} N_{ion}$$

The next refinement is to account for the continual exchange between water molecules in the coordination sphere and those surrounding it. This subject is highly relevant to modern MRI because changes in T_1 can serve as a contrast agent. For an up-to-date reference on the subject see D.A. Faux et. al., *Nuclear spin relaxation in aqueous paramagnetic ion solutions*, Physical Review E, **107**, 054605 (2023).



Proton T_1 in water at 29 MHz. From Bloembergen, Purcell and Pound, *Physical Review* **73**, 679 (1948).

T_2 and motional narrowing

For now, put aside the complications of dipole fields and think back to our discussion of inhomogeneous broadening. After an RF pulse, spins in the x-y plane dephase in an inhomogeneous B_0 field. That's a *static* $(\omega = 0)$ field in the z-direction. Now, imagine we have a random fields with components in the z-direction. As before, relaxation will involve the spectral density but now, it should be evaluated at $\omega = 0$. So one contribution to $1/T_2$ is given by,

$$\frac{1}{T_2} = \gamma_n^2\,(\langle B_z^2\rangle)\,J(\omega = 0) = \gamma_n^2\,\langle B^2\rangle\,\tau_C \qquad \omega = 0\ contribution\ only$$

Next, think of a spin along the x_R direction in the rotating frame. It can be rotated out of the plane by a random field in the y_R direction. The same holds for a spin along y_R and a field along x_R. So the <u>same</u> processes that contributed to $1/T_1$ also contribute to $1/T_2$ except for a factor of ½ due to averaging. The net result is,

$$\frac{1}{T_2} = \gamma_n^2\langle B_z^2\rangle\,J(\omega = 0) + \frac{1}{2}\big(\langle B_x^2\rangle + \langle B_y^2\rangle\big)J(\omega_L) = \gamma_n^2\,\langle B^2\rangle J(\omega = 0) + \frac{1}{2T_1}$$

Therefore, $T_1 > T_2/2$. And in fact, if $\langle B_x^2\rangle = \langle B_y^2\rangle = \langle B_z^2\rangle \equiv \langle B^2\rangle$ and $\omega_L\tau_C \ll 1$ then $T_1 = T_2$. This situation of very rapid motion, is usually encountered in liquid state NMR. The correlation time is very short compared to the period of a Larmor precession so,

$$\frac{1}{T_2} \approx \frac{1}{T_1} = 2\,\gamma_n^2\langle B^2\rangle\,\tau_C \qquad\qquad \omega_L\tau_C \ll 1$$

Since the intrinsic linewidth of the NMR resonance is $\Delta\omega \sim 1/T_2$, a shorter correlation time τ_C leads to a longer T_2 and a *narrower* linewidth. This limit is referred to as *extreme motional narrowing*. It's what makes liquid state NMR lines much sharper than solid state lines. Again, the peculiarities of the dipole field complicate things a bit but the general notion of motional narrowing holds true. The NMR lines in liquids are fantastically sharp, on the order of Hz with Larmor frequencies of order 400 MHz. For more complete discussions, see M. Levitt, *Spin Dynamics* and C. P. Slichter, *Principles of Magnetic Resonance*.

NMR Instrumentation

Quadrature detection

NMR relies heavily on picturing things in a frame rotating at the Larmor frequency. But the precessing spins simply produce an oscillating voltage across the coil. How can we transform this scalar signal into a vector picture of motion in the rotating frame? In order to reduce confusion about (-) signs I'll discuss things using spins with *negative* γ_n. That implies a positive Larmor frequency, $\omega_L = -\gamma_n B_0 > 0$ implying *counterclockwise* precession of spins around the magnetic field.

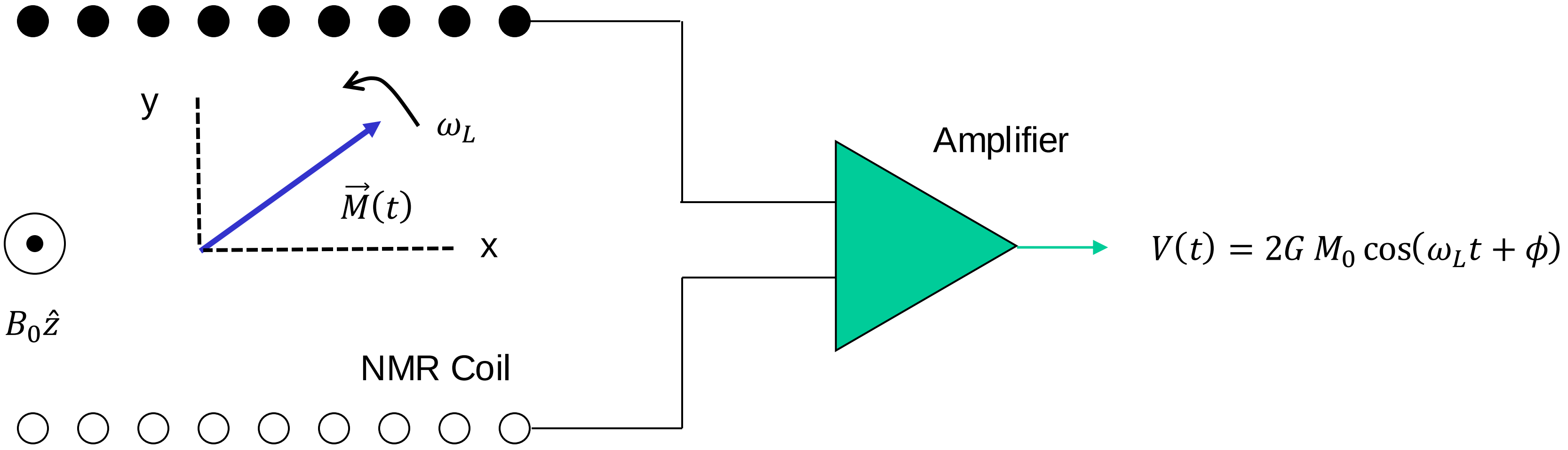
The figure below shows a cutaway of the the NMR coil and spins precessing after a $90°$ pulse. The signal reaching the amplifier is proportional to the time rate of change of flux through the coil,

$$V_{coil}(t) = \frac{d\phi_B}{dt} \propto \frac{dM_x}{dt}$$

This, in turn, induces a voltage across the tuned circuit which then passes through cables and the amplifier chain produce a voltage,

$$V(t) \propto |\omega_L|\, M_0 \cos(\omega_L t + \phi) = 2\, G\, M_0 \cos(\omega_L t + \phi) =$$

where G and ϕ depend on the electronics. (The factor of 2 is just for convenience.) We now will turn it into a snapshot of $\vec{M}(t)$ in the rotating frame. The process is called *quadrature detection.*



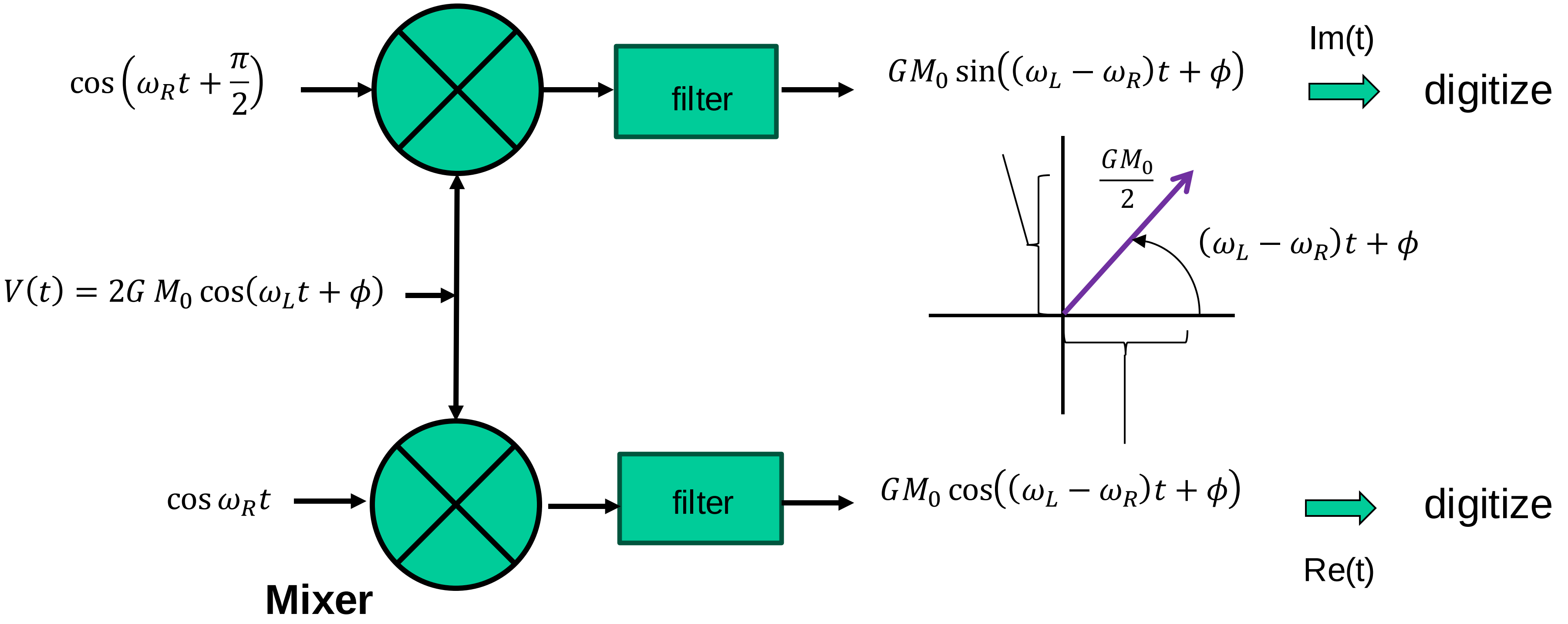
$V(t)$ is first split and separately multiplied by $\cos\omega_R t$ and by $\cos\left(\omega_R t+\frac{\pi}{2}\right)$ where ω_R is called the *reference frequency*. In electronics, multiplication is performed by a *mixer*. Recall that when you multiply two cosines you get sum and difference terms. For example, the bottom channel gives,

$$2G\,M_0\cos(\omega_L t+\phi)\cos\omega_R t = GM_0\cos\big((\omega_L-\omega_R)t+\phi\big)+GM_0\cos\big((\omega_L+\omega_R)t+\phi\big)$$

The reference frequency is chosen to be close to or equal to ω_L . That way $\omega_L-\omega_R$ << ω_R and $\omega_L+\omega_R\approx 2\omega_R$. The mixer outputs are filtered to reject the high frequency $\omega_L+\omega_R$ component but let through the low frequency $\omega_L-\omega_R$ component. This process generates two outputs, 90° out of phase (i.e., in *quadrature*) each proportional to the magnitude of the rotating magnetic moment M_0. We refer to these components as the real and imaginary parts of a *quadrature detector* signal,

$$S(t) = Re(t)+i\,Im(t)$$

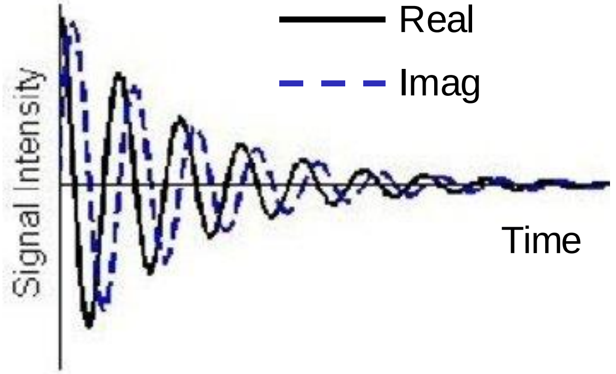
Except for an overall constant and phase, this is a replica of the magnetic moment $\vec{M}(t)$ as measured in a frame of reference rotating at the reference frequency ω_R . The phase ϕ comes from phase shifts in the cables and electronics and can be easily eliminated after the signal is digitized.

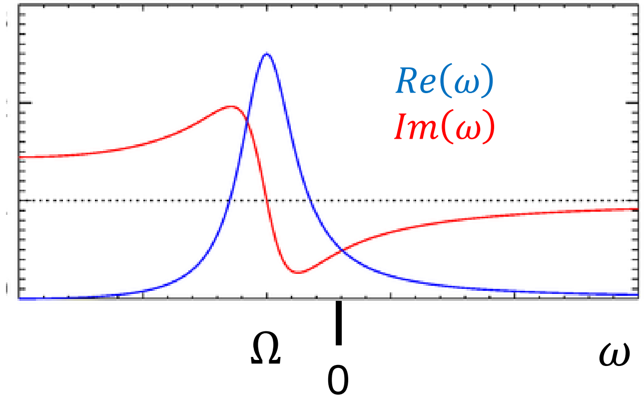


Suppose we have an FID that decays down with a time constant T_2. In a frame rotating at ω_R the magnetic moment would be,

$$M_x = M_0\, e^{-t/T_2} \cos\big((\omega_L - \omega_R)t\big) \qquad M_y = M_0 e^{-t/T_2} \sin\big((\omega_L - \omega_R)t\big)$$

But that's just the same as the signal from our quadrature detector, aside from an overall constant factor and phase shift. It's usual to define $\Omega \equiv \omega_L - \omega_R$ as the *offset frequency*. It's just the frequency at which $\vec{M}$ precesses in the reference frame rotating at ω_R . The real and imaginary parts of the quadrature signal are shown below. There are oscillations at Ω and a decay with time constant T_2 .





The quadrature detector signal, written as a complex number, is now,

$$S(t) = Re(t) + i\, Im(t) = GM_0 e^{-t/T_2} e^{i\Omega t} e^{i\phi}$$

The Fourier transform is given by,

$$S(\omega) = \int_0^\infty e^{-i\omega t}\, GM_0 e^{-t/T_2} e^{i\Omega t} e^{i\phi}\, dt$$

$$S(\omega) = Ge^{i\phi}\left(\frac{M_0 T_2}{1 + \big((\omega - \Omega)\, T_2\big)^{\,2}} + i\frac{M_0 T_2(\Omega - \omega)}{1 + \big((\omega - \Omega)\, T_2\big)^{\,2}}\right)$$

$$S(\omega) = Ge^{i\phi}\big(Re(\omega) + i\, Im(\omega)\big)$$

The $e^{i\phi}$ factor can be eliminated by multiplying $S(\omega)$ by $e^{-i\phi}$. G is just an overall scale factor that's not usually of interest unless you're trying to assess your signal size.

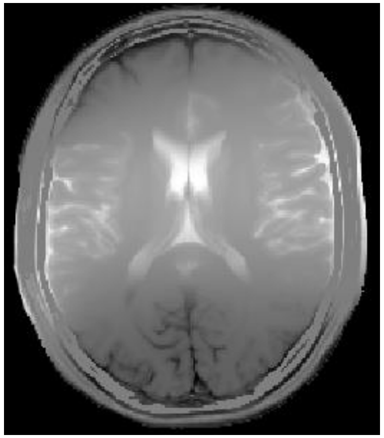
The physically relevant spectrum is $Re(\omega) + i\, Im(\omega)$ which consists of the familiar absorptive and dispersive response functions. I've drawn the spectra for the case in which $\Omega < 0$. This means that $\omega_L < \omega_R$ so the Larmor frequency is *less* than the reference frequency. But we could set the reference frequency so that $\omega_L > \omega_R$, in which case the spectrum would show a peak for $\Omega < 0$.

Often, particularly in MRI work, one just uses the *magnitude* spectrum,

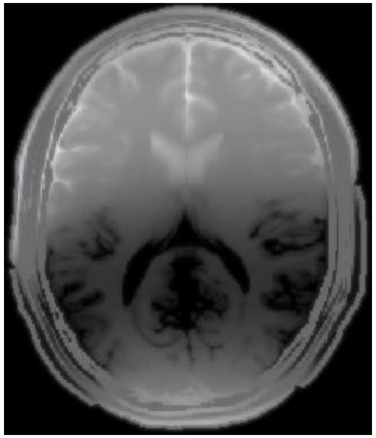
$$Mag(\omega) = \sqrt{Re(\omega)^2 + Im(\omega)^2}$$

The figure below shows MRI images in which each pixel corresponds to a separate NMR spectrum centered on a different Larmor frequency. The figures shown images produced using the real, imaginary and magnitude spectra are used. Most MRI often uses just magnitude spectrum.

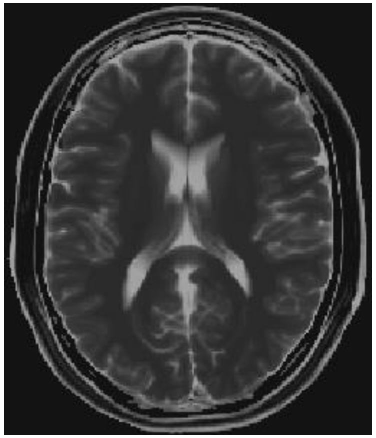
Real



Imag



Mag

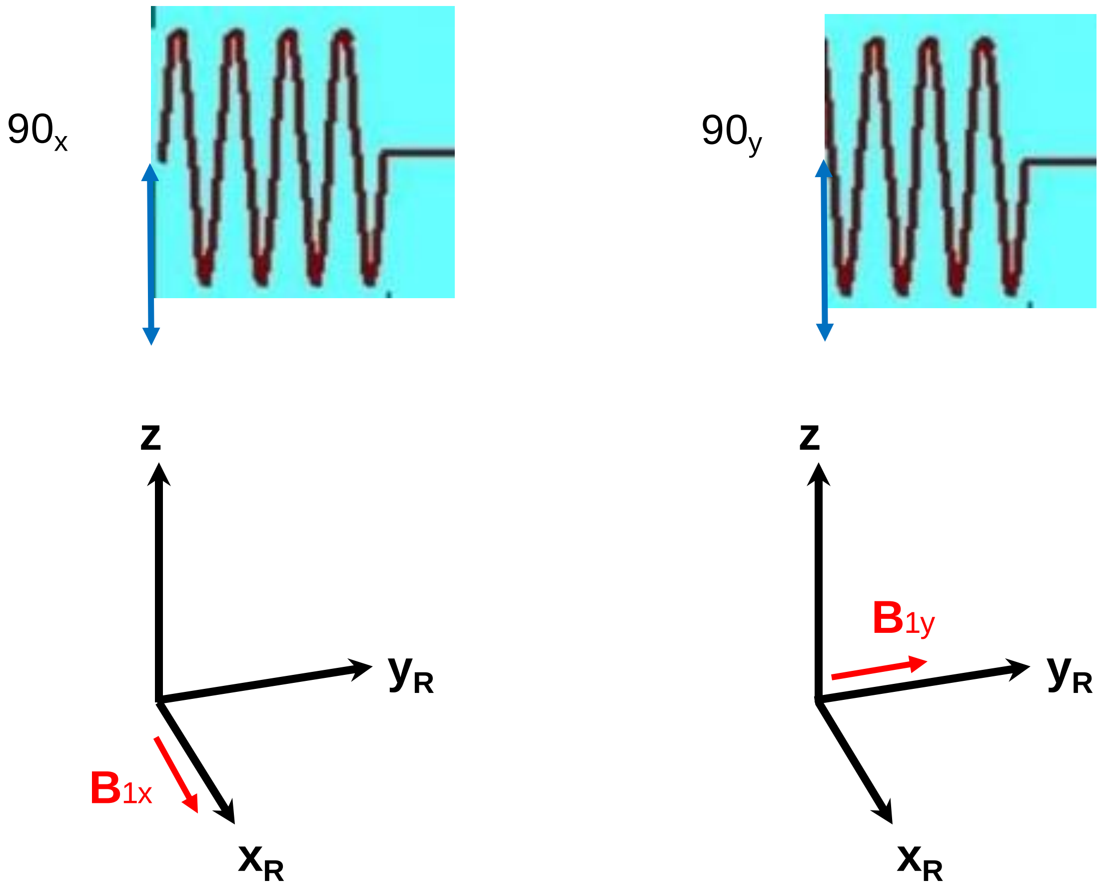


https://mriquestions.com/real-v-imaginary.html#/

Quadrature detection is used throughout RF communications. It's often call *IQ* detection where *I* refers to in-phase (Real) and *Q* to the quadrature phase (Imaginary). Along with the phase separation it has another crucial aspect. It converts the original high frequency signal, whose Larmor frequency could be hundreds of MHz, down to a much lower frequency signal, which could be hundreds of kHz. The lower frequency is much easier and cheaper to digitize precisely.

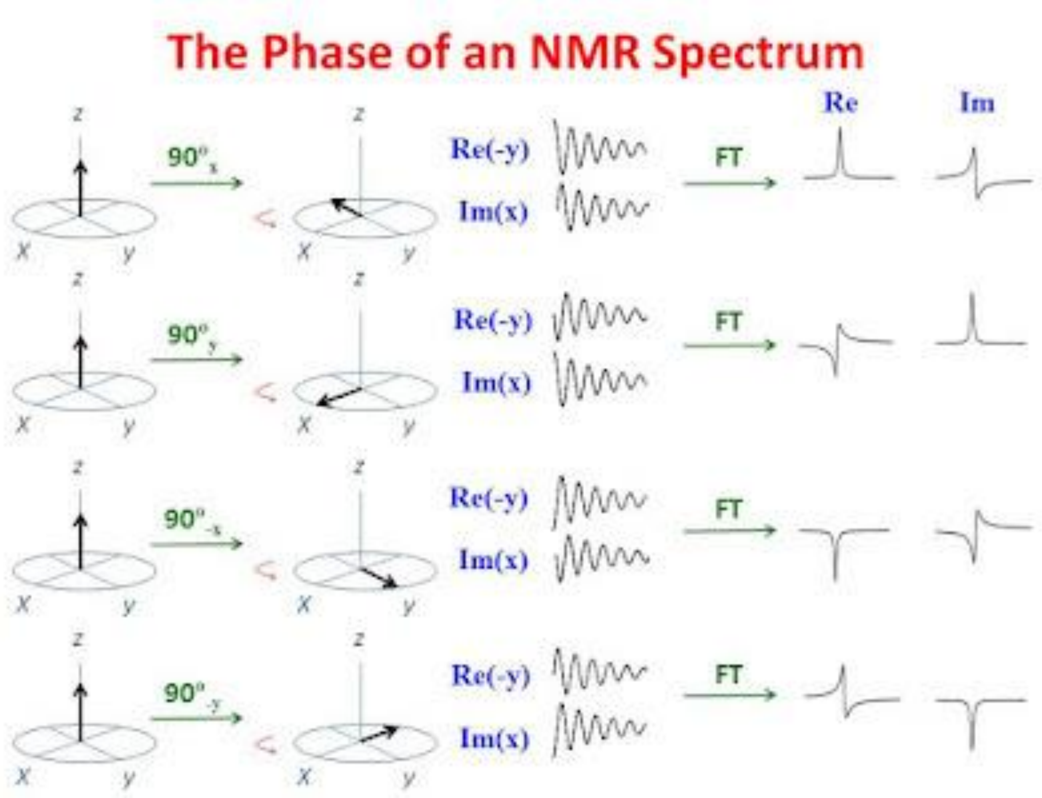
Phase of RF pulses

Throughout FTNMR you'll see pulses referred to as 90_x or 180_y or 90_{-x} , etc. The subscript refers to the axis of the rotating frame along which the B_1 field is applied. Whether it's x, y, -x or –y depends on the *phase* of transmitted RF pulses relative to each other. If we send out the pulse in the left figure we can arbitrarily assign that to the x direction in the rotating frame. If, instead, we sent out a pulse like the one in the right figure, that's 90° out of phase with the left one so it would be along the y axis of the rotating frame. If these pulses were the right length to rotate the magnetization by 90° then we'd call the first one a 90_x and the second one a 90_y, etc.



Phase Cycling

Phase cycling is a way to correct for electronic imbalances in the RF electronics and to focus on particular features of the NMR signal. The figure below shows what happens as we cycle the phase of the applied RF pulses through 90 degrees. Imagine, for variety, the nucleus has $\gamma_n < 0$ so it precesses counterclockwise around the field. (1) After a 90_x pulse, M ends up along the –y axis in the rotating frame. Assume that we've adjusted the overall phase of the received signals so Re(t) corresponds to the –y direction and Im(t) corresponds to the x direction in the rotating frame. Then the two signals and their spectra would look like the first line. (2) Apply a 90_y pulse. Now M ends up initially along the +x direction. The signals and corresponding transforms are shown. (3) Apply a 90-x pulse, etc.



https://u-of-o-nmr-facility.blogspot.com/2010/11/phase-of-nmr-spectrum.html

Now take the averages,

(Re1 + Im2 – Re3 + Im4) / 4 = <Re>

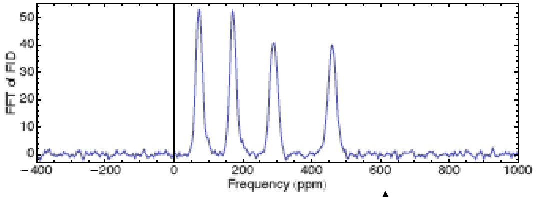
and,

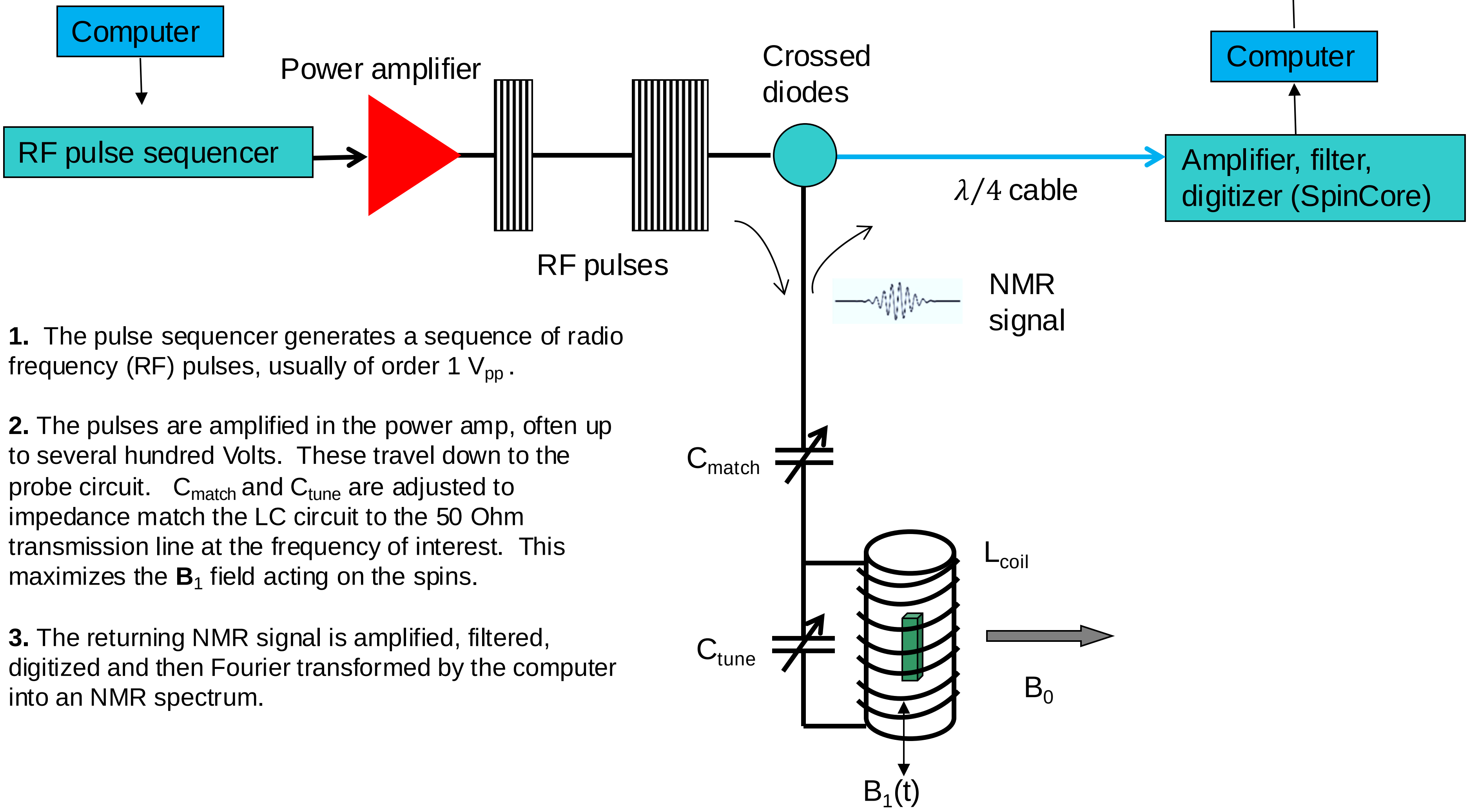
(Im1 – Re2 -Re3 +Re4) / 4 = <Im>

In real spectrometers, the Re and Im channels (i.e., two physically distinct mixers and amplifiers) are not perfectly matched. In addition, transient signals from the transmitter and coil interfere with the FID. By cycling through these 4 phases and averaging them in this way, we subtract away many of these undesirable effects and get a much cleaner representation of desired NMR signal.

The procedure just described is called CYCLOPS. For more elaborate pulse sequences there are more elaborate phase cycling schemes.

Electronics





1. The pulse sequencer generates a sequence of radio frequency (RF) pulses, usually of order 1 V_{pp}.

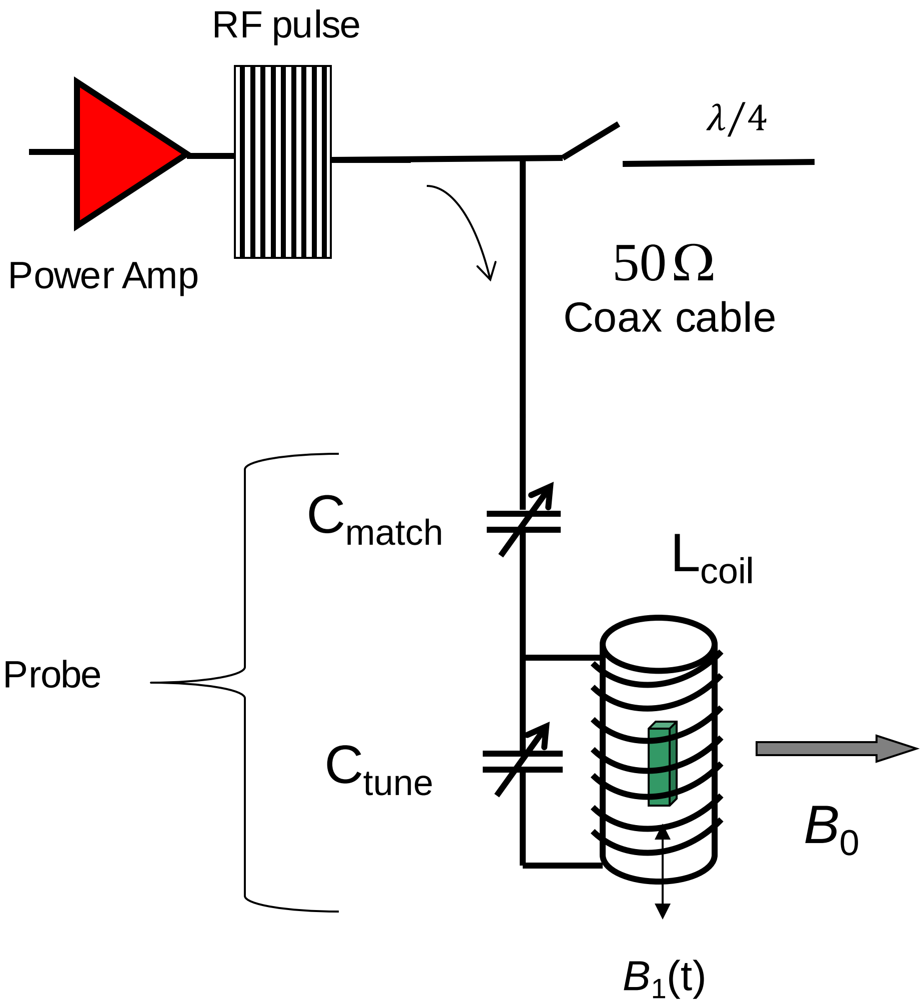
2. The pulses are amplified in the power amp, often up to several hundred Volts. These travel down to the probe circuit. C_{match} and C_{tune} are adjusted to impedance match the LC circuit to the 50 Ohm transmission line at the frequency of interest. This maximizes the $\mathbf{B}_1$ field acting on the spins.

3. The returning NMR signal is amplified, filtered, digitized and then Fourier transformed by the computer into an NMR spectrum.

Transmitting the RF pulse

During the application of the RF pulse, the effective circuit looks like the one shown below. The receiving side appears to be disconnected due to the presence of the quarter wave transmission line and crossed diodes. The RF pulses sent down to the coil are very large, often hundreds of volts. The intent is to create as large a B_1 field as possible and therefore the shortest time for a $90°$ pulse,

$$\gamma_n B_1 \tau_{90} = \frac{\pi}{2}$$

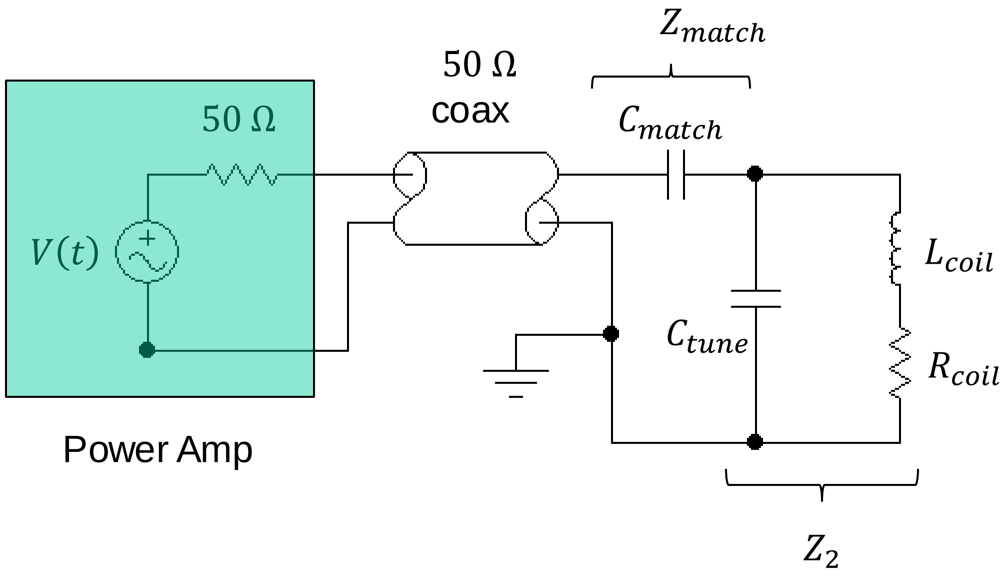


If B_1 is large then during the short time the pulse acts, that part of the Hamiltonian driving the spins,

$$H_1 = -\gamma_n \hbar \vec{B}_1 \cdot \vec{I}$$

dominates things like relaxation and the RF pulse is maximally efficient at rotating the spins. To maximize B_1 it's necessary to make sure no power from the amp is reflected back. That way all of it goes toward generating current in the coil. Since no average power can be dissipated in an ideal inductor or capacitor, all the power must be dissipated in the coil resistance *R*. And since power = I^2R, that leads to the maximum current *I* though *R* and L_{coil} and therefore the maximum B_1 .

The probe circuit consists of L_{coil} , two capacitors, C_{tune} , C_{match} and the internal resistance of the coil. It's connected through a coaxial cable to the power amplifier. Think of the RF pulse as a wave travelling down the coax and encountering the probe circuit. The condition for no reflected wave is $Z_{probe} = Z_{cable}$ where *Z* is the *impedance*. Since $Z_{cable} = 50\ \Omega$ then we must adjust things so the probe also appears like a $50\ \Omega$ resistor. That's called *impedance matching* and is described next.



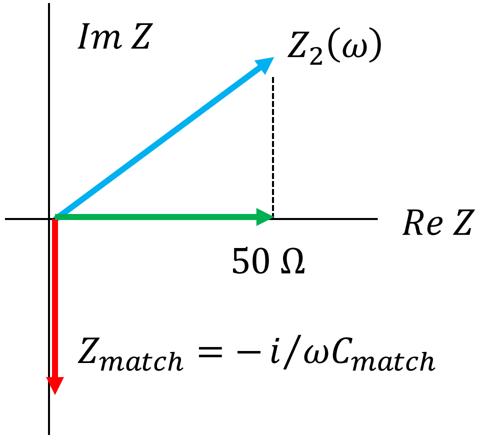
The schematic diagram shows all the circuit elements relevant during the time the RF pulse is transmitted. The goal is to make the impedance of the probe appear to be $50\ \Omega$ at the Larmor frequency. The probe impedance can be written as the sum of two impedance,

$$Z_{probe} = Z_{match} + Z_2$$

In general, the Z’s are complex. For example,

$$Z_{match} = 1/i\omega C_{match}$$

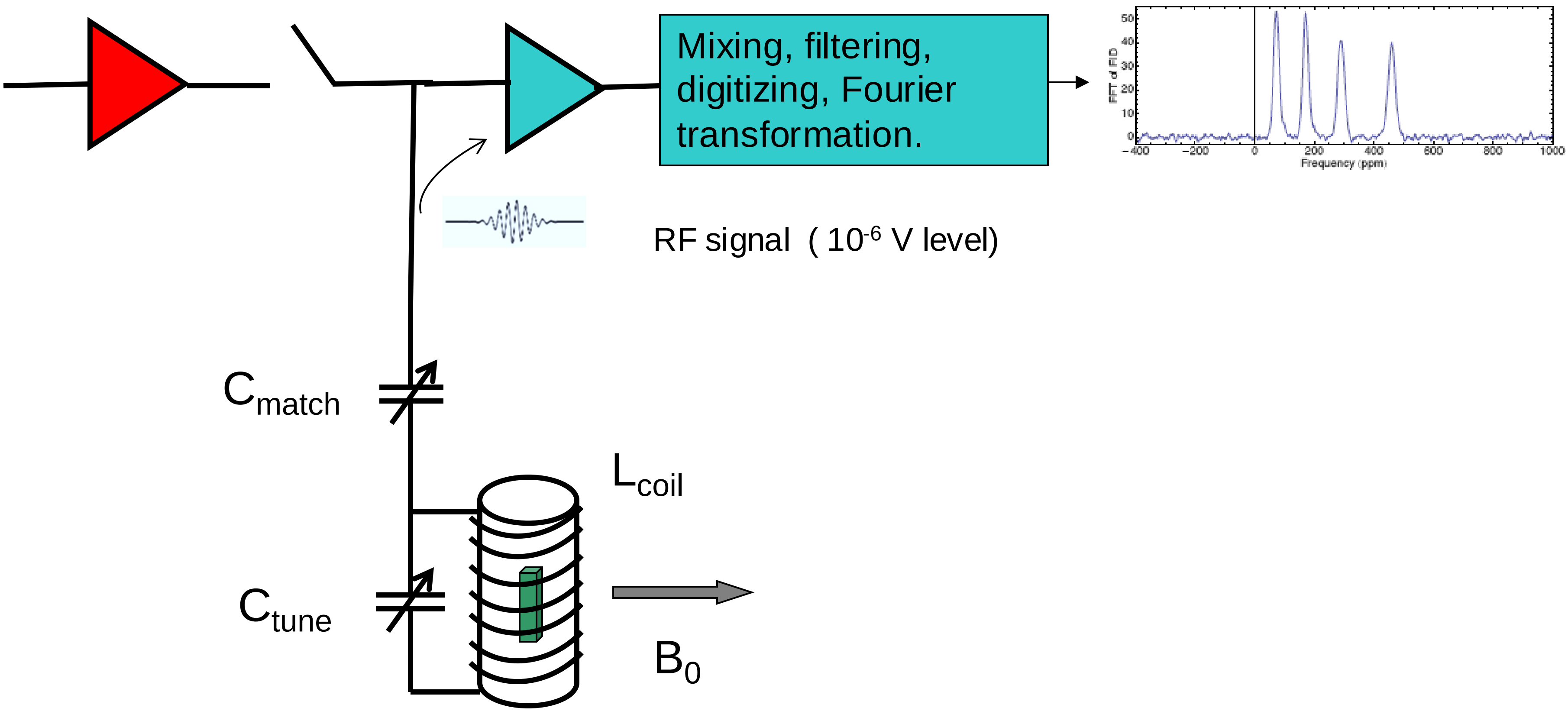
The expression for Z_2 is more complicated but it’s more instructive to just plot Z_{match} and Z_2 in the complex plane. Each will vary with frequency. The goal is to make the sum equal to 50 Ohms at the Larmor frequency. That’s just an arrow along the horizontal axis. We need two capacitors because there are two conditions to satisfy at $\omega = \omega_L$. (1) Im(Z_{probe}) = 0 and (2) Re(Z_{probe}) = $50\ \Omega$.



With only C_{tune} we can certainly satisfy condition (1) so Z_{probe} would be real. However, its value would be $Z_2 = Q^2R_{Coil}$ where Q is the quality factor of the coil. But Q^2R_{Coil} is not necessarily 50 Ohms. With C_{match} added, we vary C_{tune} until $Re(Z_2) = 50$ and use Z_{match} to cancel out the imaginary part. In practice, both capacitors are varied incrementally until a mininum reflection is achieved.

Receiving the NMR signal

After the large RF pulse the crossed diodes turn off and act like open switches. The transmitter is therefore disconnected from the probe. The NMR signal, which is often microvolts in amplitude, travels through coax cables to the low noise preamplifier which has a 50 Ohm input impedance so it matches to the coax cables. After amplification the signal goes through quadrature detection, digitization and Fourier transformation to generate an NMR spectrum.



Low noise preamp

Mixing, filtering, digitizing, Fourier transformation.

RF signal (10^{-6} V level)

Applications of NMR

Chemistry

Medicine (MRI)

Geology

Physics

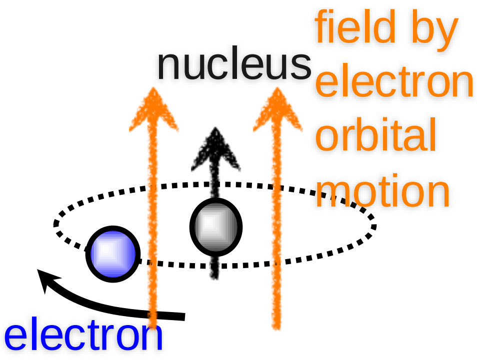
Herbert Gutowsky (U. Illinois)

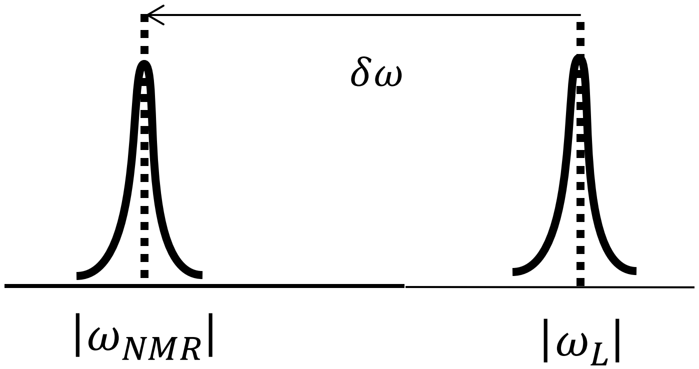
First to apply NMR to the identification of compounds.

Chemical Shift

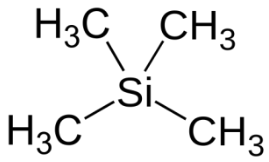
It's only for an isolated spin ½ nucleus that the precession frequency is at exactly $-\gamma_n B_0$. In general the nucleus in a solid, liquid or gas feels the effect of nearby electrons and other nuclei, both of which shift the energy spacing between levels and lead to small shifts $\Delta\omega$ in the NMR absorption frequency. These shifts are fingerprints for molecular structure. For example, the external field B_0 perturbs the orbital motion of nearby electrons. This perturbation, in turn, changes the effective magnetic field seen by the nucleus. B_0 is "shielded" meaning the effective field is *lower* than B_0 by an amount known as the *chemical shift*.

$$B_{nucleus} = B_0\left(1-\sigma_{Chemical}\right) \qquad \omega_{NMR} = \omega_L(1-\sigma_{Chemical})$$





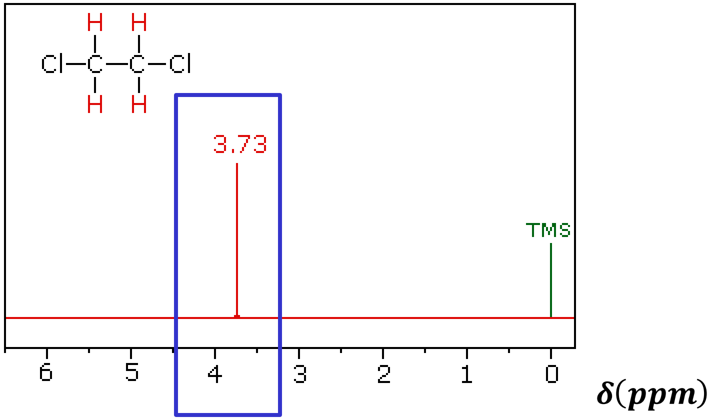
Chemical shifts are tiny and are generally measured in parts per million (ppm). They should be measured relative to an ideal spin ½ nucleus. For ^1H or ^{13}C, a good reference is the corresponding ^1H or ^{13}C resonance absorption line in a material known as TMS, whose structure is shown. The chemical shift is generally shown as dimensionless number, written in parts per million:



$$\delta(ppm) = 10^6\,(\omega_{TMS} - \omega_{NMR})/\omega_{TMS} = 10^6\,(f_{TMS} - f)/f_{TMS}$$

Fine structure of liquid NMR lines

J-coupling gives rise to fine structure in the NMR spectrum. In chemical NMR, the J-coupling comes from an indirect interaction between different spins of the same molecule, mediated by electrons in the chemical bonds. In the first spectrum we see only a single NMR line chemically shifted from TMS by 3.73 ppm. There is no further splitting. In the lower figure, we see two different chemically shifted lines which are further split by J-coupling.

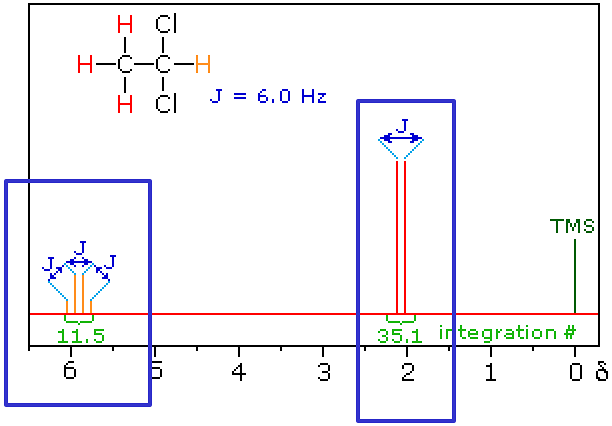


Chemical shift only

$$\delta(ppm) = 10^6\,(f_{TMS} - f_{NMR})/f_{TMS}$$

4 equivalent protons in a molecule give same chemical shift: 1 unsplit NMR line.

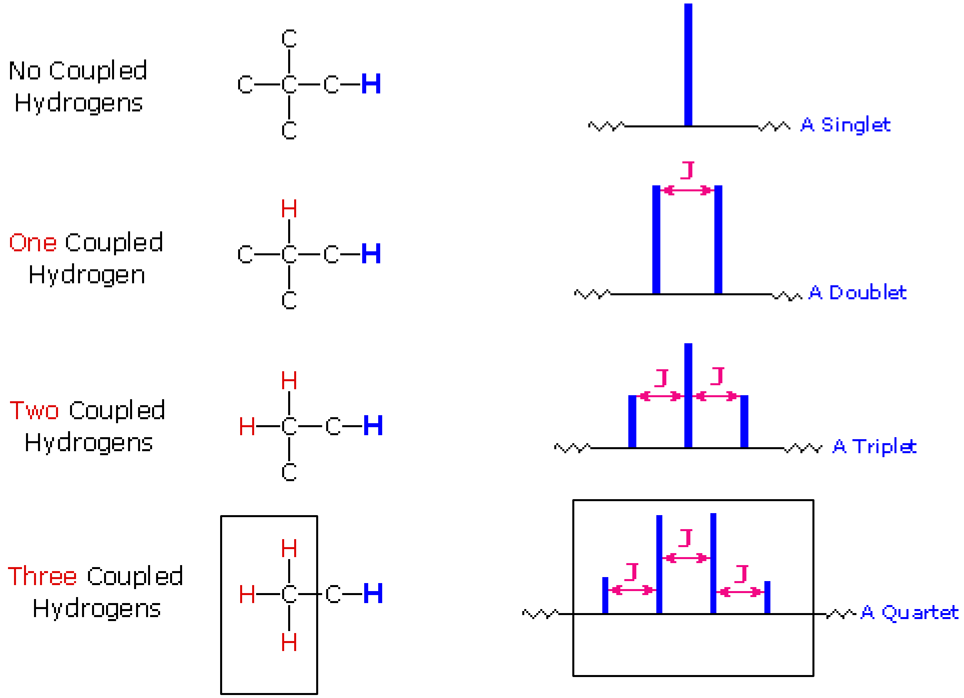
Chemical shifts + J-coupling



We now have 2 inequivalent sets of protons (green and red). The green proton signal is chemically shifted to about 6 ppm and further split into 4 lines by J-coupling to the group of 3 red protons. This group has 4 possible spin states while the green proton line is split into 4.

The red protons are all chemically shifted to about 2.1 ppm but split into 2 lines by J-coupling to the green proton, which has only 2 possible states.

J-coupling (proton NMR)

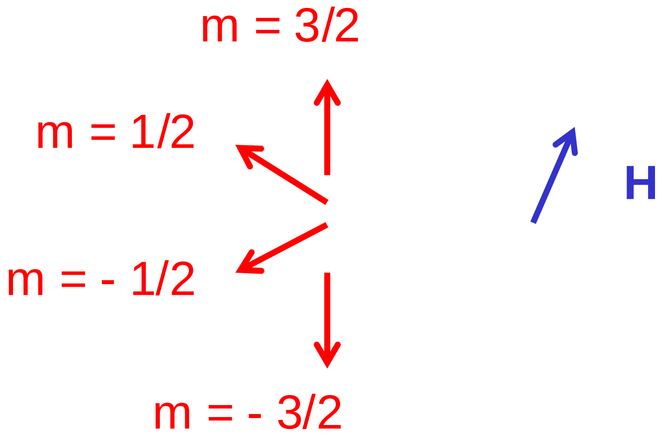


Interaction between nuclear spins, mediated by electrons In chemical bonds.

$$Energy = J\,\vec{I}_1 \cdot \vec{I}_2$$

This is the *J-coupling*.

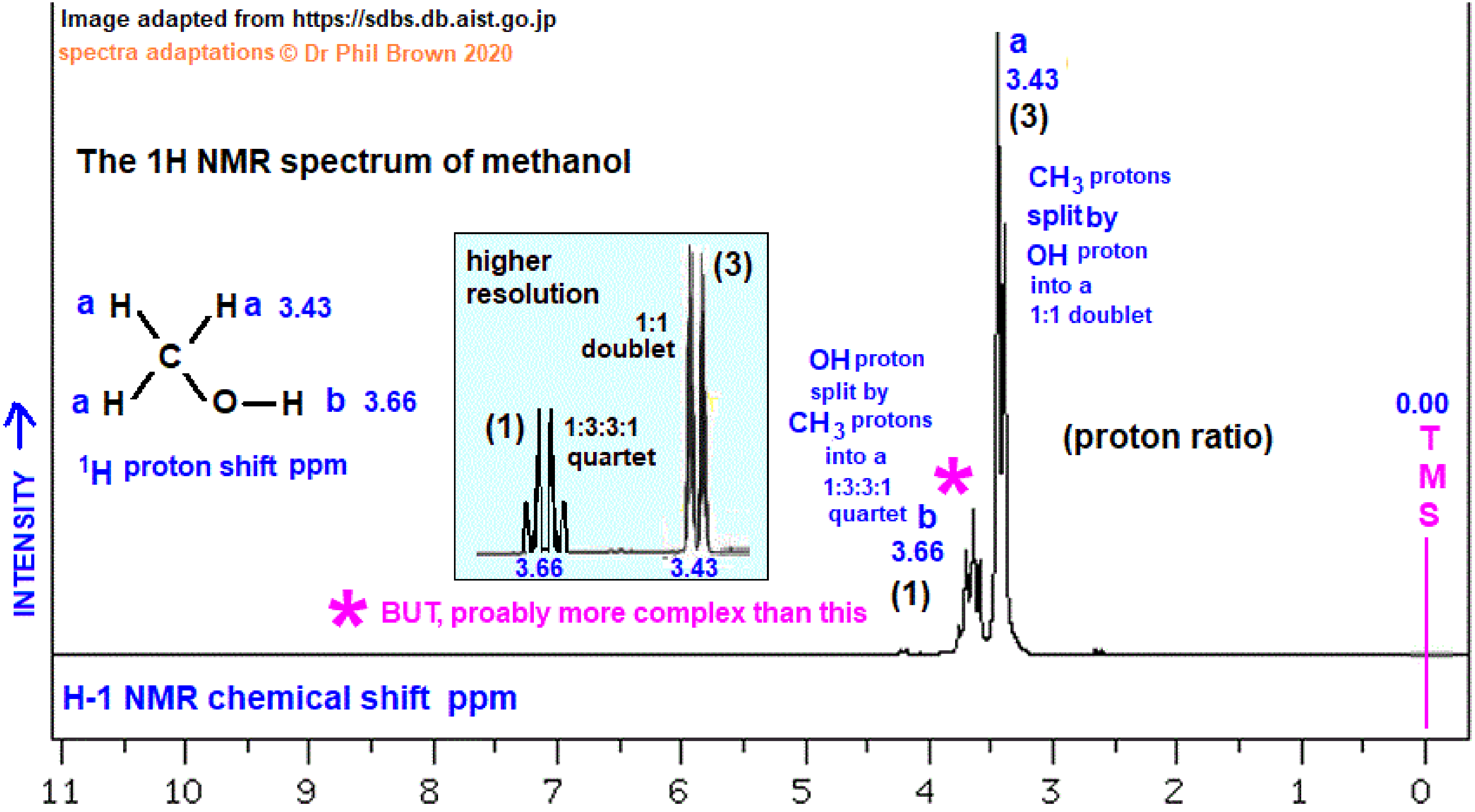
3 coupled, equivalent hydrogens :
Total spin I = 3/2


m = 3/2
m = 1/2
m = - 1/2
m = - 3/2

4 possible states. Like 4 possible “fields” to act on **H.**

1 way to get m = 3/2
3 ways to get m = ½
3 ways to get m = -½
1 ways to get m = - 3/2

Figures from www.chemistry.msu.edu



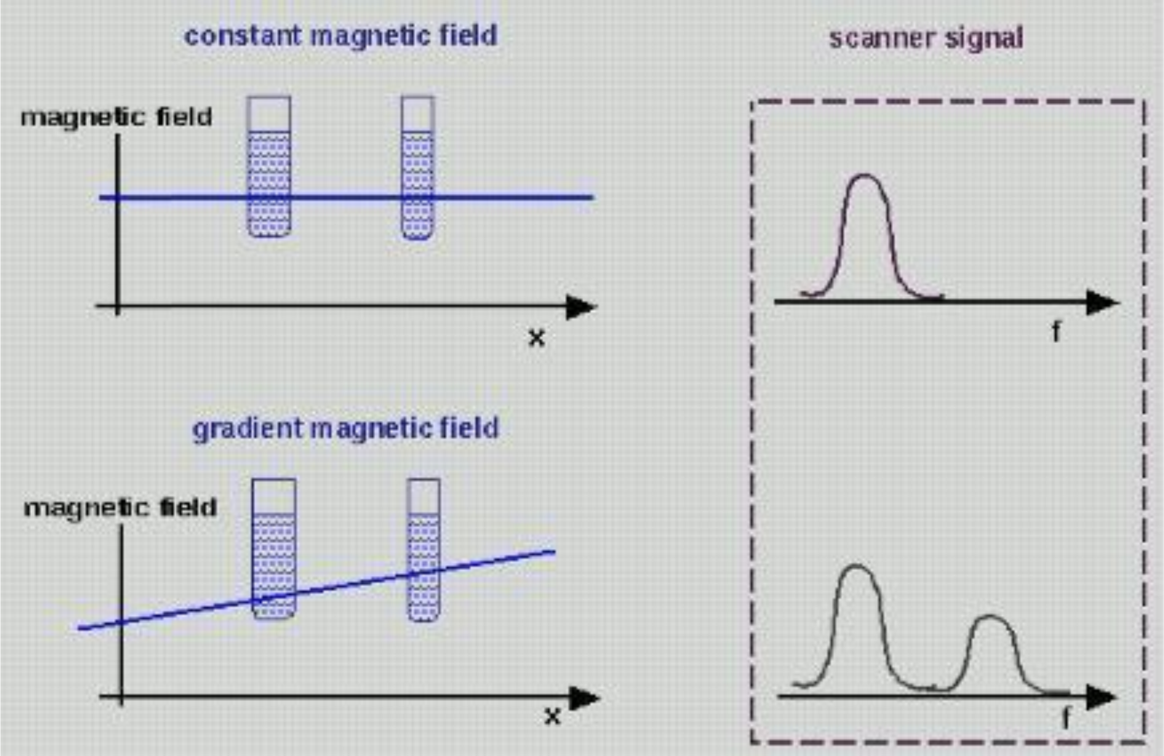
The 1H NMR spectrum of methanol

Image adapted from https://sdbs.db.aist.go.jp

* BUT, proaby more complex than this

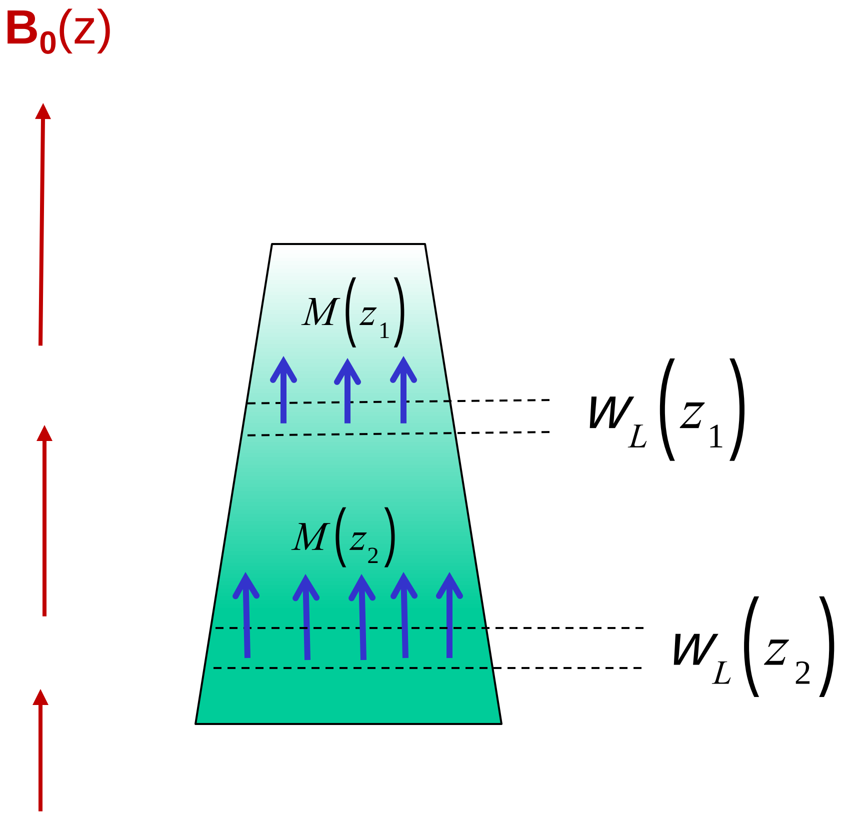
Magnetic Resonance Imaging (MRI)

Spins in different magnetic fields have different Larmor frequencies.



P. Lauterbur, P. Mansfield, Nobel Prize in Medicine, 2003

Controlled field gradients



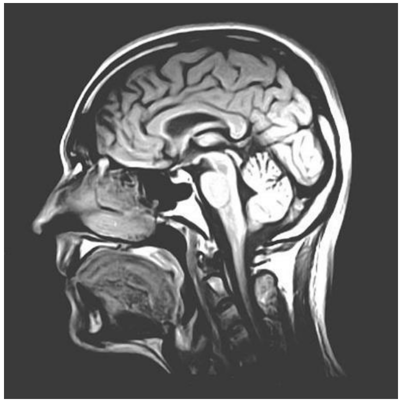
Apply a field *gradient* **:**

$$B = B_0 + G\,z.$$

Larmor frequency depends on z:

$$\omega_L(z) = \gamma_n B_0 + \gamma_n\, Gz$$

Spins in different “z-slices” (1) precess at different rates and (2) respond to different frequencies.

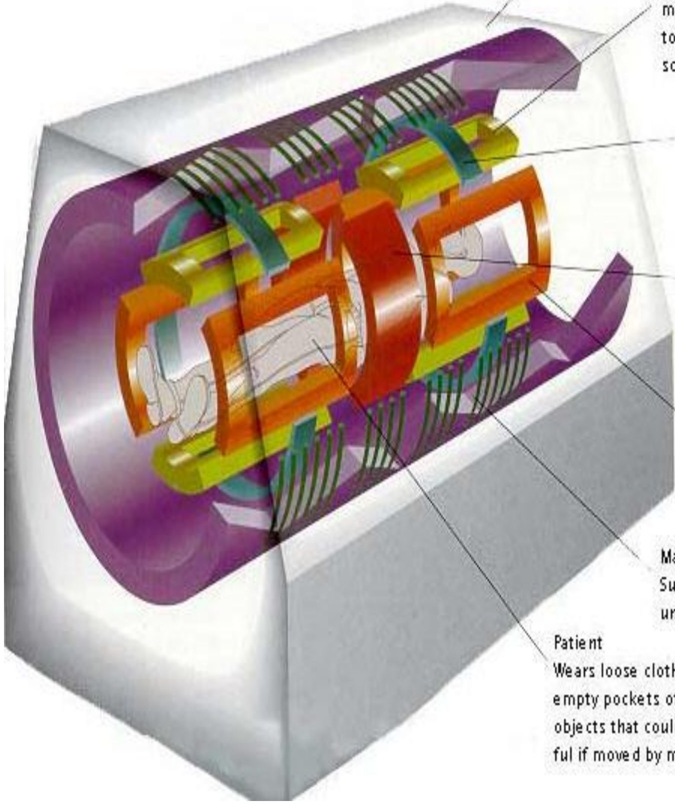


We can measure properties of nuclear spins (M, T_1, T_2) at each location. This is an image…MRI

Liquid helium cooled magnets for MRI

CREATING REFINED ANATOMICAL IMAGES

Within the metallic cocoon of an MRI scanner, the patient is surrounded by four electromagnetic coils and the components of a transciever



Scanner
Uses electromagnets and radio signals to produce cross-sectional images

Y Coil
Creates varying magnetic field from top to bottom across scanning tube

Z Coil
Creates varying magnetic field from head to toe within scanning tube.

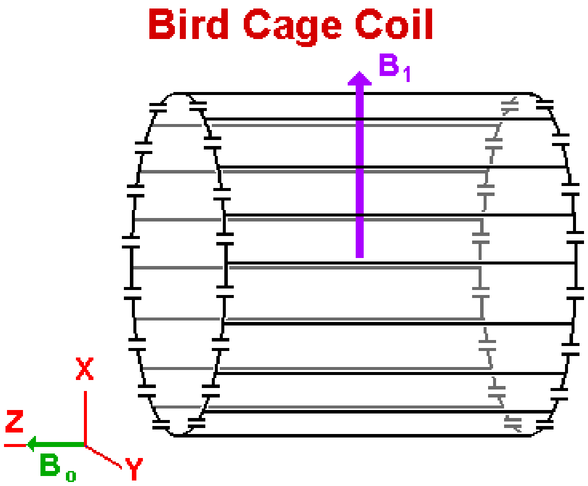
Transciever
Sends radio signals to protons and receives signals from them.

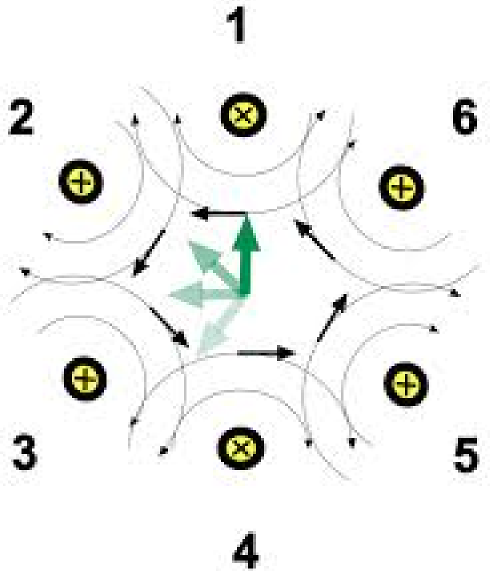
X coil
Creates varying magnetic field from left to right across scanning tuve.

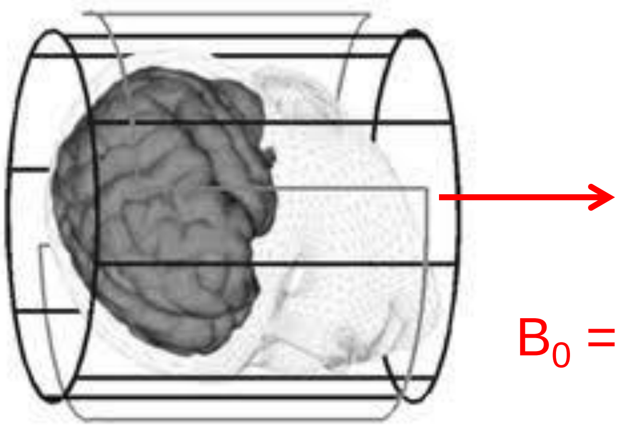
Main Coil
Surrounds patient with uniform magnetic field.

Patient
Wears loose clothing; must empty pockets of metallic objects that could prove harmful if moved by magnetic force

MRI field configuration



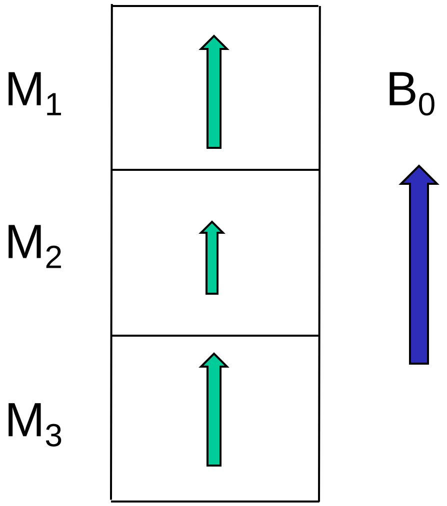




$B_0 = 1.5$ T

Birdcage coil produces $\mathbf{B_1}$**(t)** *perpendicular* to $\mathbf{B_0}$.

Selective Excitation

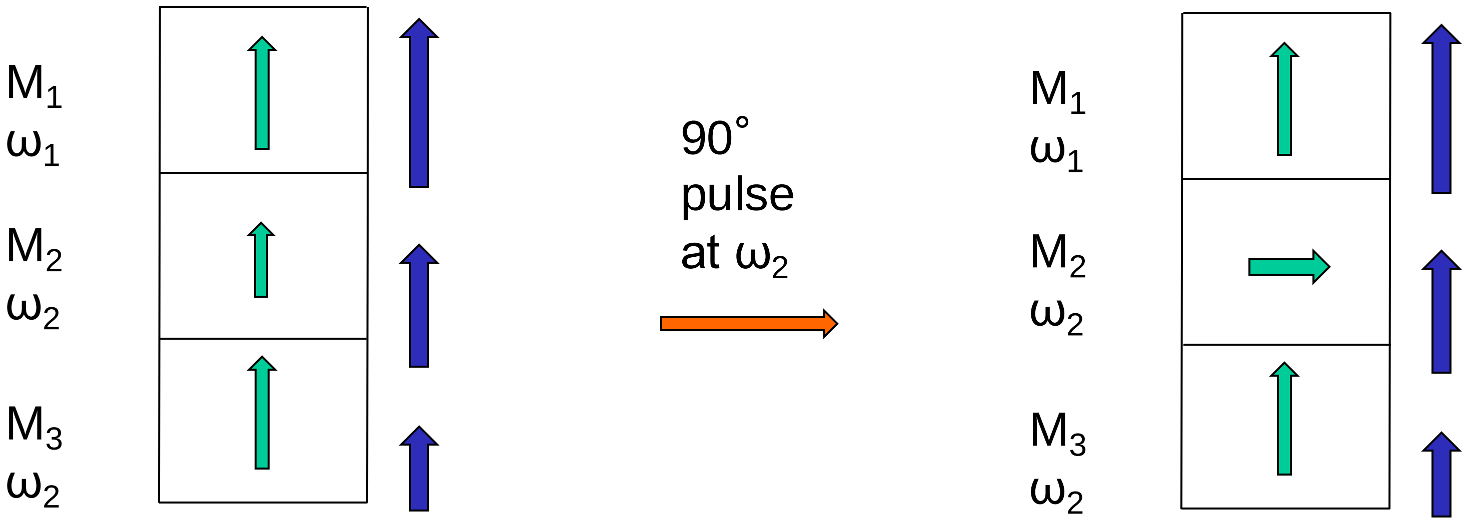


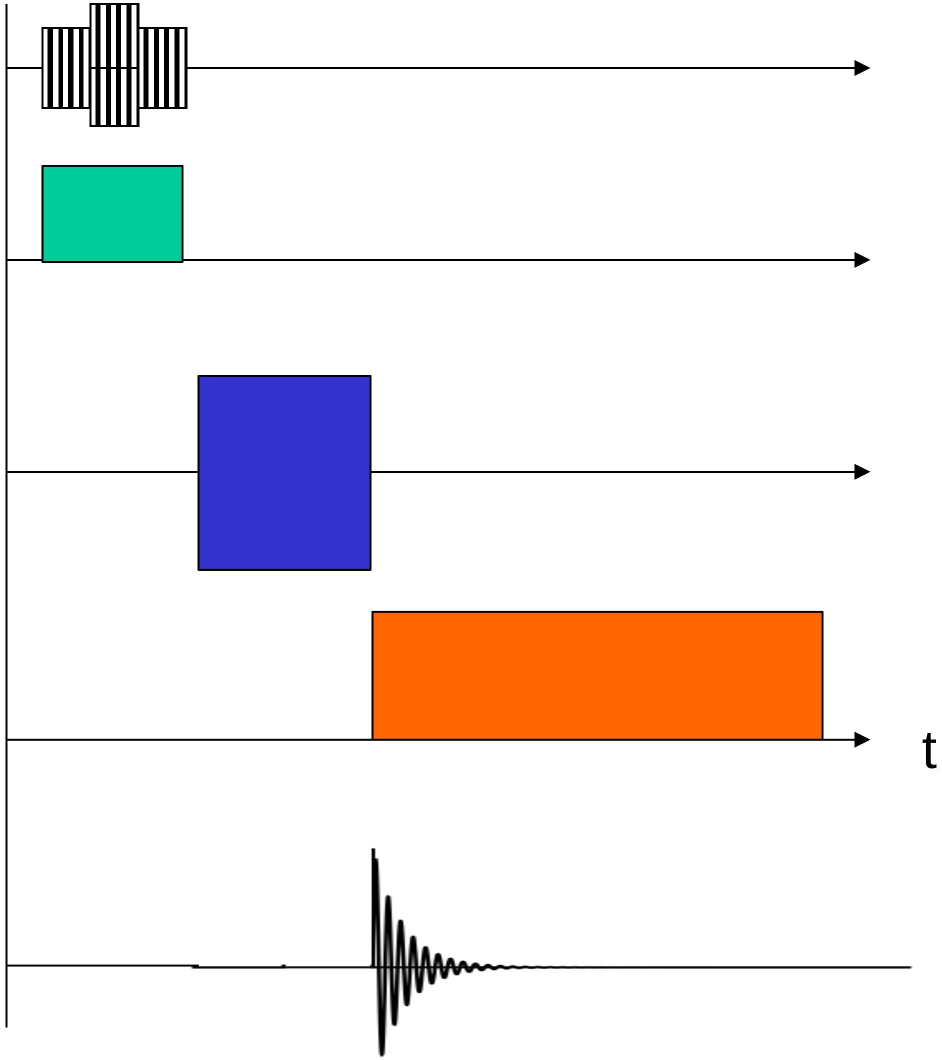
M_i is the nuclear magnetic moment in slice i.

M_i proportional to number of protons, amount of blood, etc.

Magnetic resonance image is a <u>map</u> **of M_i** .

Add a field gradient along z.





Selective 90°
pulse

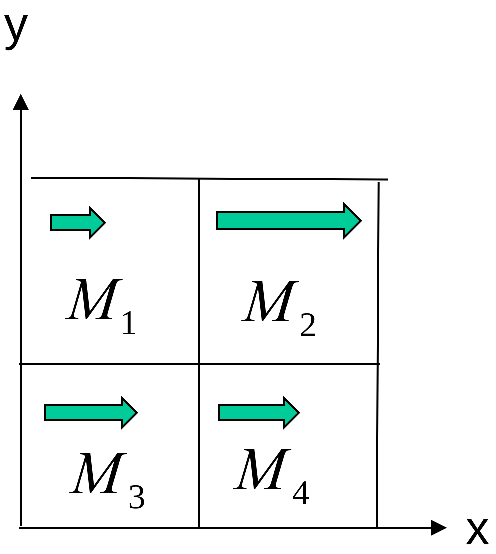
z-gradient (select slice
along z direction)

x-gradient
(phase encoding)

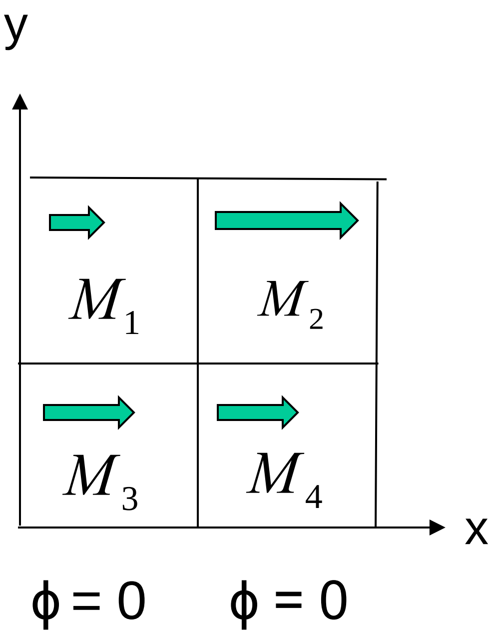
y-gradient
(frequency encoding)

signal

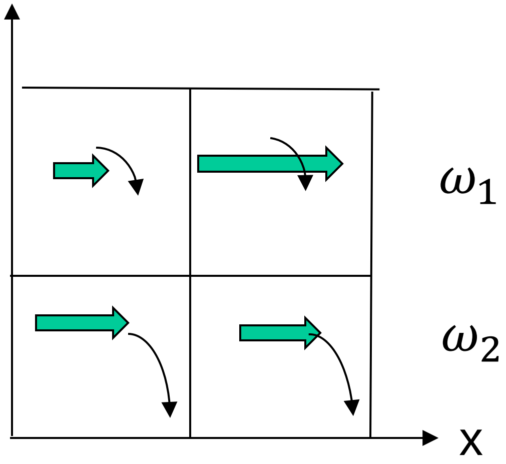
http://www.cis.rit.edu/htbooks/mri/chap-7/chap-7.htm z-slice



Apply x-field gradient.
Phase encoding.

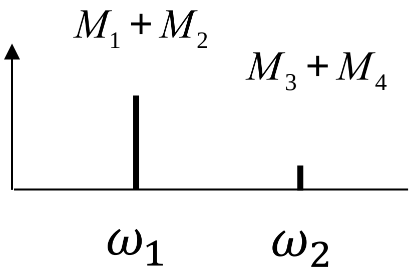


Apply y gradient: M_1, M_2 precess at ω_1, M_3, M_4 precess at ω_2. Record FID.

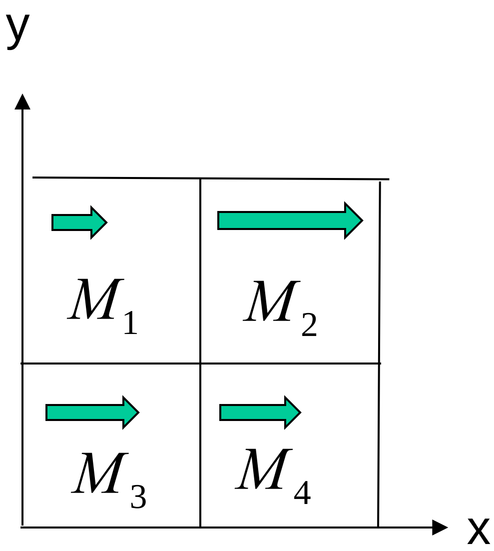


$$FID(t, \Delta\phi = 0) = M_1 e^{i\omega_1 t} + M_2 e^{i\omega_1 t} + M_3 e^{i\omega_2 t} + M_4 e^{i\omega_2 t}$$

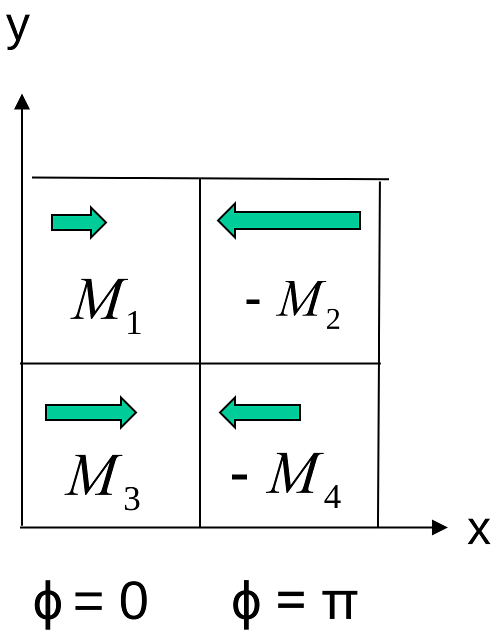
Fourier transform *FID* → Spectrum



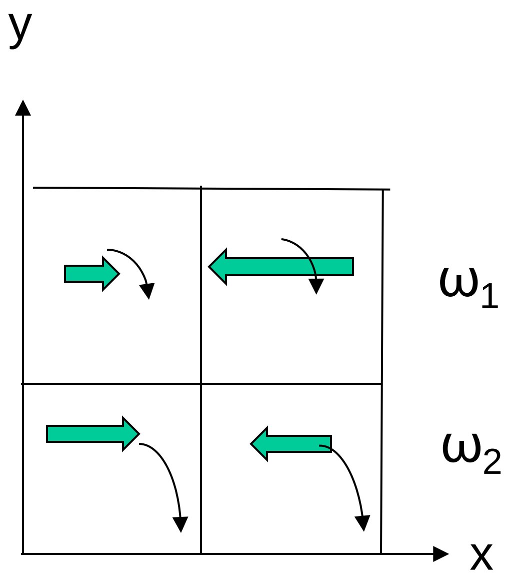
z-slice



Apply x-gradient: Rotate phase of M_2, M_4 by π.

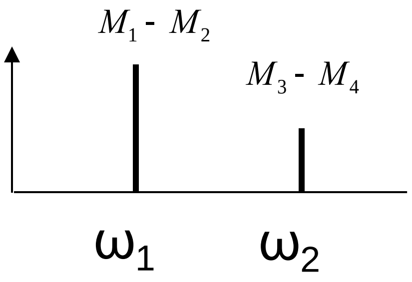


Apply y gradient: M_1, M_2 precess at ω_1, M_3, M_4 precess at ω_2. Record FID.



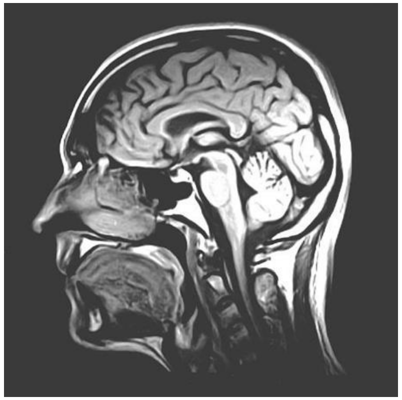
$$FID(t, \Delta\phi = \pi) = M_1 e^{i\omega_1 t} - M_2 e^{i\omega_1 t} + M_3 e^{i\omega_2 t} - M_4 e^{i\omega_2 t}$$

Spectrum



Use spectra for both phases to get M_1, M_2, M_3, M_4 individually. These numbers correspond to the density of spins in each region or “voxel”.

Signal from coil contains information from all the “voxels”. Each voxel contains a group of spins centered at some point (x,y,z).

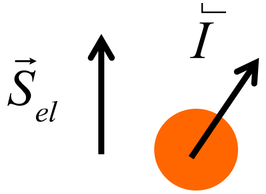


Spins in *oxygenated* and *deoxygenated blood* have different T_2 times.

Functional MRI uses this T_2 difference for contrast.

T_1 in metals

T_1 in metals typically follows a 1/T law, often known as Korringa-like relaxation. It comes from the hyperfine interaction between nuclear spins and the spins of mobile, conduction electrons. The 1/T dependence ultimately comes from the fact that electrons obey Fermi-Dirac statistics so no two can have the same quantum numbers. Therefore the electrons in a metal fill a Fermi sea of states in which only a number proportional to $k_B T$ can participate in interactions.

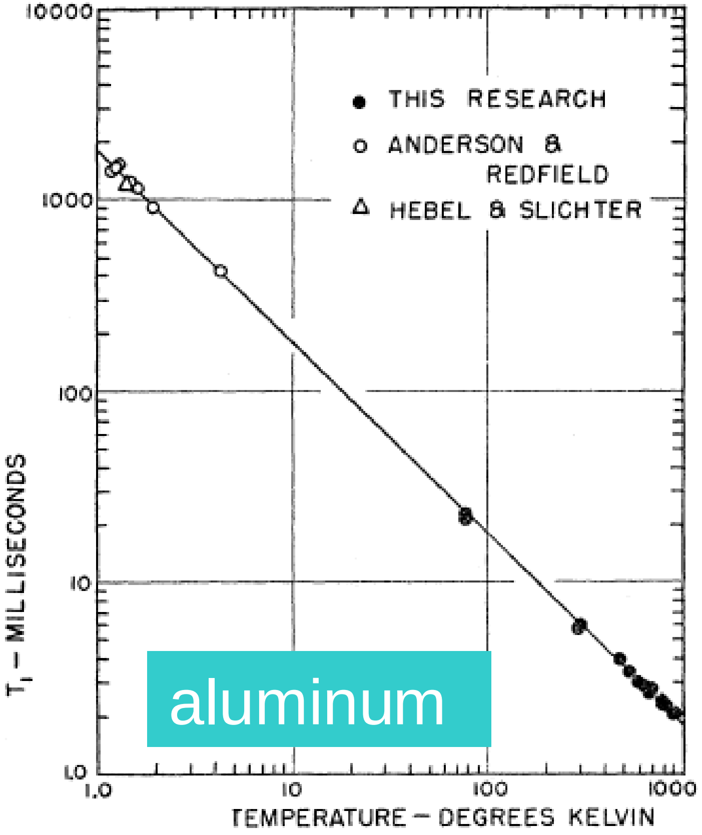


$$H_{hf} = -\gamma_n \gamma_{el} \hbar^2 \frac{8\pi}{3} \vec{I} \cdot \vec{S}_{el} \delta\left(\vec{r}\right)$$

The plot shows that the Korringa law,

$$T_1 \sim \frac{1}{T}$$

holds in aluminum over 3 decades in temperature, all the way from its melting temperature to its superconducting transition temperature (T_C = 1.2 K).

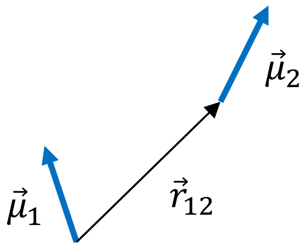


J.J. Spokas and C.P. Slichter, Phys. Rev. ***113****, 1462 (1959)*

T_2 in solids

Things are somewhat easier to understand in solids. For insulators, relaxation will still be determined by the dipole-dipole interaction,

$$H_{12} = -\vec{\mu}_1 \cdot \vec{B}_{12} = \frac{\mu_0}{4\pi\, r_{12}^3}\{\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \hat{r}_{12})(\vec{\mu}_2 \cdot \hat{r}_{12})\} \qquad \vec{\mu}_i = \gamma_{ni}\vec{I}_i$$



But now, the spins are located at fixed positions in a periodic lattice. At low temperatures we can ignore vibrations so all the $\vec{r}_{ij}$ are constant. That gives rise to the so-called *rigid lattice linewidth* for solid NMR resonances. As a rough estimate, we can take, the first term in the dipole field of spin 1 as felt by spin 2,

$$B_{12} \sim \frac{\mu_0}{4\pi}\frac{\mu_1}{r_{12}^3} \rightarrow \delta\omega_{hom} \sim \gamma_n B_{12}$$

For typical atomic spacings of a few Angstroms, B_{12} is a few Gauss (10^{-4} Tesla.) A much more sophisticated calculation, in which we sum over *all* the spins in a cubic lattice with lattice constant *r* gives,

$$\delta\omega_{hom} \approx 2.3\,\frac{\hbar\gamma_n^2}{r^3}\sqrt{I(I+1)}$$

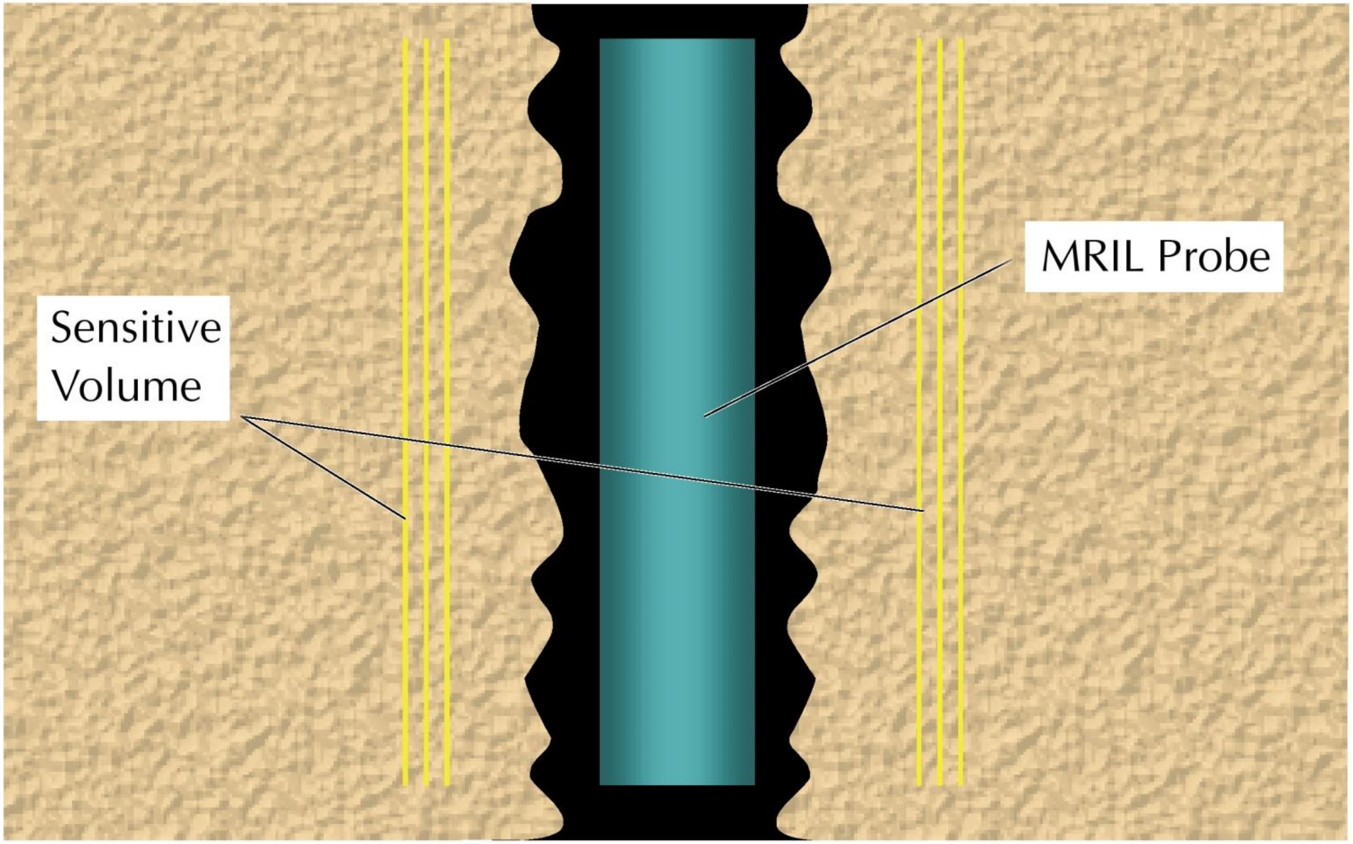
where I is the spin. Unlike a liquid, there is no motional narrowing. T_2 is given by,

$$T_2 \sim \frac{2}{\delta\omega_{hom}}$$

It's approximate because in solids the decay is not usually exponential but is more often Gaussian. But in any case, homogeneous broadening in solids leads to *broad* NMR lines and rapidly decaying FIDs. This puts greater demands on the electronics since things happen faster.

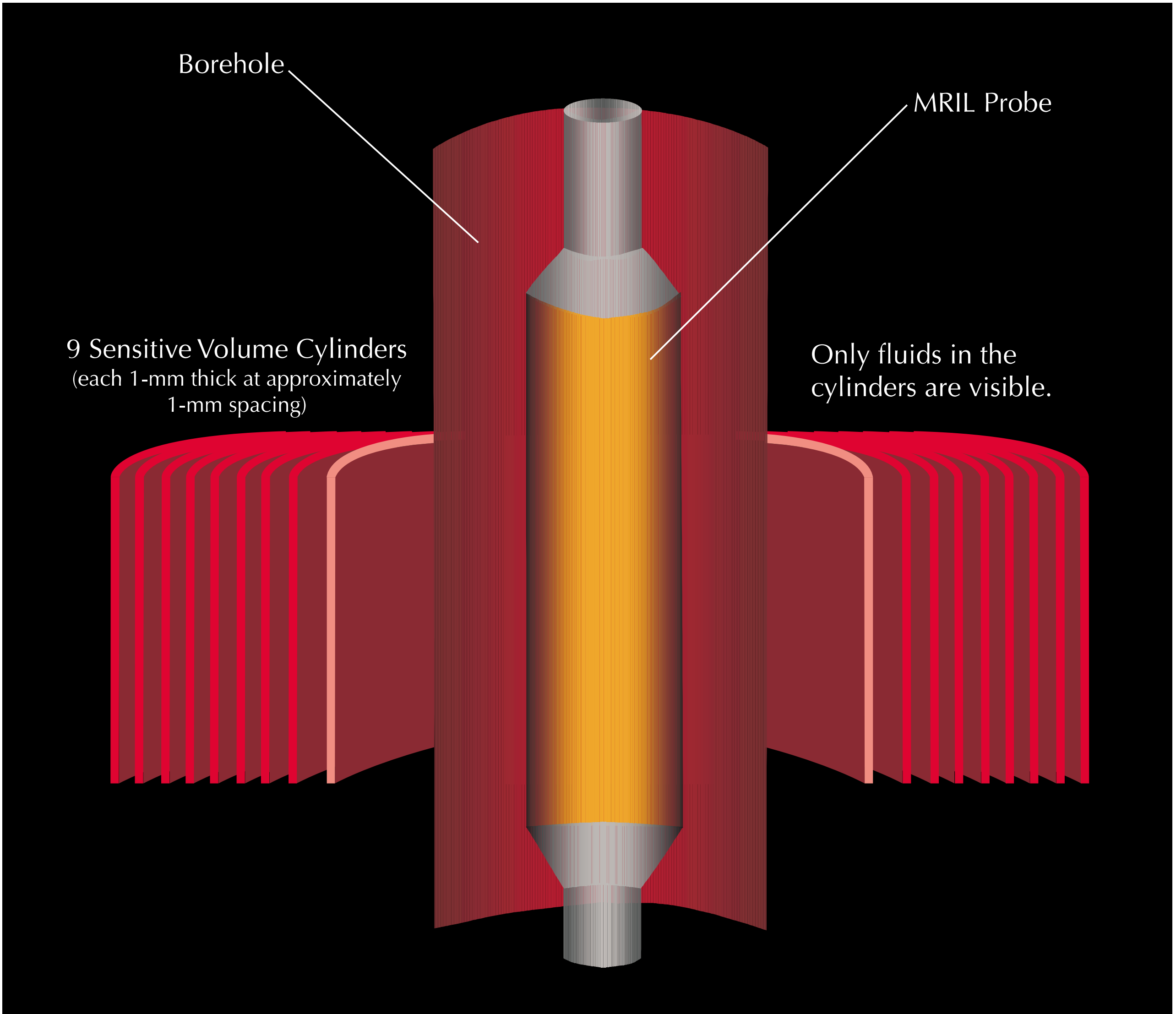
NMR in geology[1]

NMR “well-logging” is widely used to examine the porosity of rocks as well as their oil and water content.

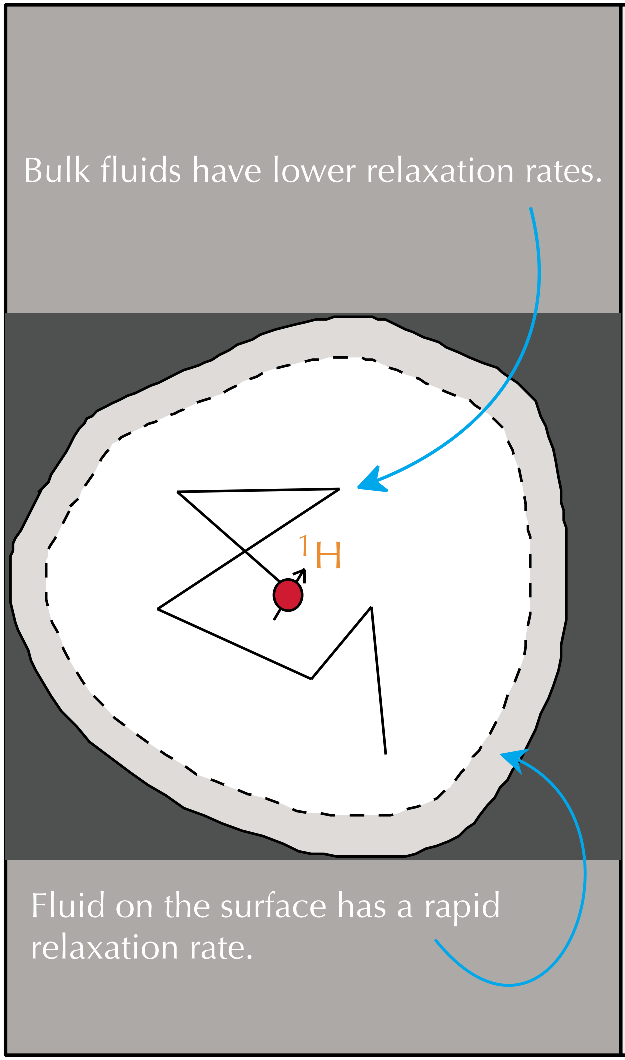


[1] G. *Coates, L. Xiao, M. Prammer,* Haliburton Energy Services

NMR probe generates an inhomogeneous B-field. Cylinders at different radii have different Larmor frequencies and can be separately identified. This is a form of magnetic resonance imaging.



B-fields from permanent magnets are small so Larmor frequencies are typically 600-800 kHz.



Bulk fluids have lower relaxation rates.

Fluid on the surface has a rapid relaxation rate.

Basic Relaxation Mechanisms for Fluids in Rock Pores:

Bulk relaxation for both T_2 and T_1

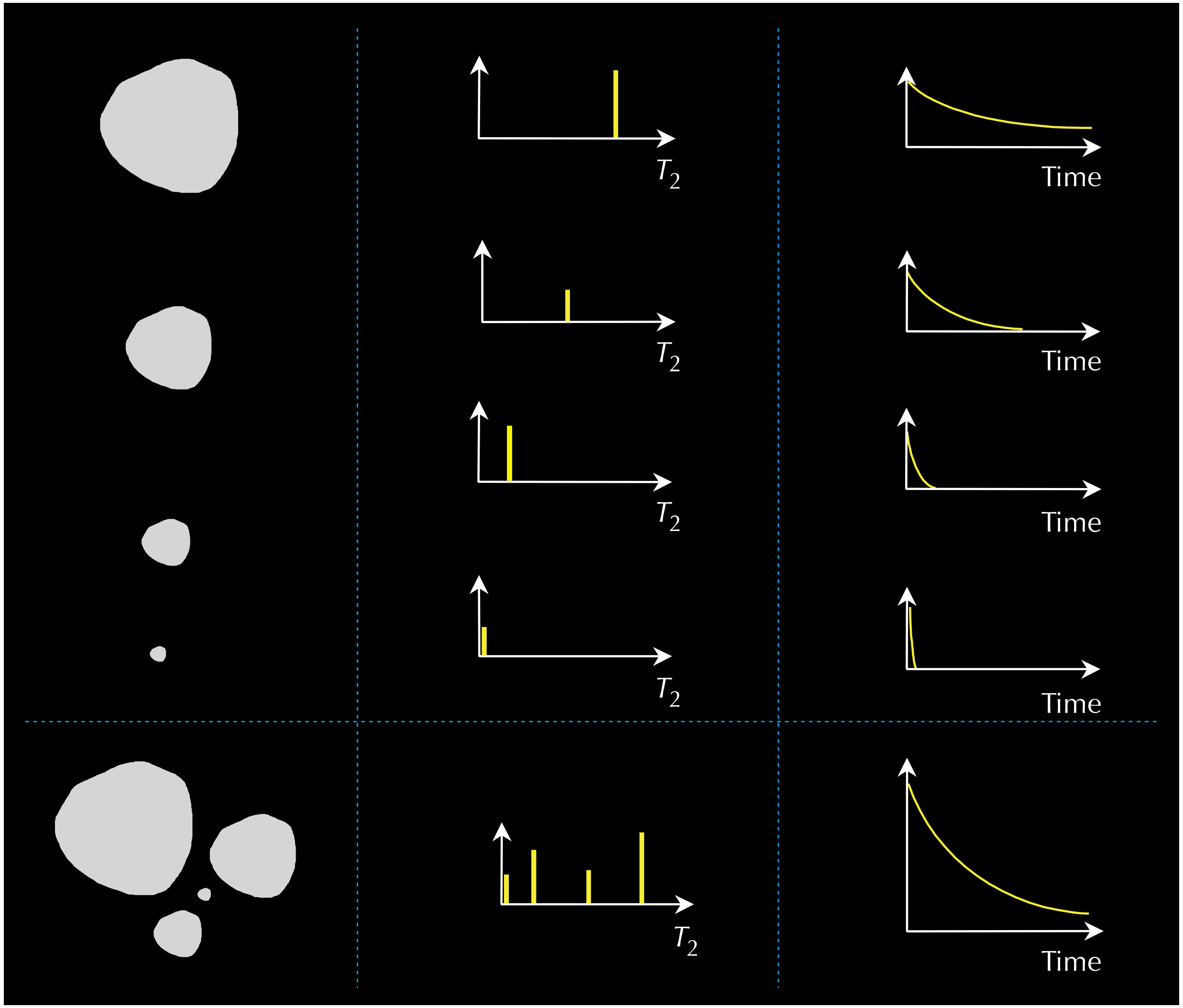
Surface relaxation for both T_2 and T_1

Diffusion relaxation for T_2

$$\frac{1}{T_{2(cpmg)}} = \frac{1}{T_{2,bulk}} + \rho_2 \frac{S}{V} + \frac{D(\gamma\, GTE)^2}{12}$$

$$\frac{1}{T_1} = \frac{1}{T_{1,bulk}} + \rho_1 \frac{S}{V}$$

S/V = surface/volume of pore.



Water in a single pore has a single T_2. With many pore sizes, there is a distribution of T_2 values.

Distribution of T_2 values is used to measure distribution of pore sizes in a rocks saturated with water.