NMR Spectroscopy vs. MRI:

The applied magnetic field is **same everywhere in sample.**

Field at the nucleus is **reduced** because of **electron density**
so each chemically distinct H has a slightly different resonant frequency
i.e., **CHEMICAL SHIFT**
For MRI (magnetic resonance imaging):

Applied field is deliberately made to vary across the sample.

Frequency set to ONLY MEASURE WATER

Then, protons in different parts of sample will resonate at different frequency

Only because of POSITION;

NOT because of different chemical shift

MRI Detects primarily two things:
(1) amount of water at different positions

(2) and direction of diffusion (more difficult)
Using color to indicate frequency in different parts of the sample

Protons in different places absorb different frequencies.

Field increasing in \( x \)
Resonant frequency \( V_f \) increasing in \( x \)

Field increasing in \( z \)
Resonant frequency \( V_f \) increasing in \( z \)

red is low frequency (because low field)
blue is high frequency (because high field)
Consider a 10 x 10 x 10 inch "Beaker" of water with "Rose", "Jaw", and "Tumor". A bubble of air is located at:

\[
\begin{align*}
    x &= 5 \\
    y &= 9 \\
    z &= 1
\end{align*}
\]

Take 3 spectra with magnetic field gradient along x, y, or z.

Remember, \( \nu_r \) is proportional to magnetic field strength.

\[
\begin{align*}
    B_0 & \quad \nu_r \\
    x \Rightarrow & \quad x \Rightarrow \\
    y \Rightarrow & \quad y \Rightarrow \\
    z \Rightarrow & \quad z \Rightarrow
\end{align*}
\]
Now we return to NMR and learn the reality at 300K:

Boltzmann:

Ratio of spin up/spin down:

\[
\frac{N_2}{N_1} = e^{-\frac{\Delta E}{k_B T}}
\]

Divide energy by Planck’s constant x speed of light in cm/sec

\[\Delta E = h\nu\]

At room temperature only 0.01 % more in lowest state than in highest state.

(about the ratio of the atmospheric pressure between the floor and ceiling in this room!)
Einstein pointed out that excitation is **stimulated** from the high state to low state at same rate as excitation upwards. (predicted LASERS 60 years before they could be created)

Resonant frequency is RADIO FREQUENCY; Wavlength is ~ ½ meter, so **Entire sample literally feels oscillating magnetic field.**

At room temperature only 0.01 % more in lowest state than in highest state
Quantum Concept: Superposition.
A molecule may be “in” more than one state at once!

Although there are two quantum “energy levels”: spin up and spin down, there is a continuous mixture. The spins are all in superposition states.

\[ \Psi_{total} = c_{up} \Psi_{up} e^{-i\frac{2\pi E_{up}}{\hbar} \text{time}} + c_{down} \Psi_{down} e^{-i\frac{2\pi E_{down}}{\hbar} \text{time}} \]

\( \Psi_{up} \) and \( \Psi_{down} \) are “orbitals” i.e., wavefunctions for the nuclear spin.

If the temperature = 1 billion K, the SAME would be said of the 1s and 2p orbitals of the H atom

\[ \Psi_{total} = c_{1s} \Psi_{1s} e^{-i\frac{2\pi E_{1s}}{\hbar} \times \text{time}} + c_{2p} \Psi_{2p} e^{-i\frac{2\pi E_{2p}}{\hbar} \times \text{time}} \]

The electron density would oscillate back and forth, and would be in RESONANCE with high frequency light.
**Quantum Concept: Superposition.**

A molecule may be “in” more than one state at once!

Although there are two quantum “energy levels”: spin up and spin down, there is a continuous mixture. The spins are all in superposition states.

\[
\Psi_{total} = c_{up} \Psi_{up} e^{-i \frac{2\pi E_{up}}{h} \text{time}} + c_{down} \Psi_{down} e^{-i \frac{2\pi E_{down}}{h} \text{time}}
\]

\(\Psi_{up}\) and \(\Psi_{down}\) are “orbitals” i.e., wavefunctions for the nuclear spin.

The Time Dependent Schrodinger Equation says that the individual parts oscillate at a frequency given by their energy/Planck’s constant & cause **precession**.

The squares of the coefficients gives probability to observe in the up or down state i.e., \(c_{up}^2 + c_{down}^2 = 1\).

The lines pointing in all directions give an idea of the proportion of spin up and spin down for each of the spins.

The relative signs of \(c_{up}\) and \(c_{down}\) give **direction**.
Each spin precessing.

Tipping because the applied pulse can only interact with those individual spins that are in phase with the pulse—a small percentage of the many spins.

The whole magnet will tip by an angle proportional to how long the pulse is on.

http://en.wikipedia.org/wiki/Spin_echo
very short pulse contains many frequencies

**Intense pulse of radio freq.**
in coil perpendicular changes ratio of up/down from .9999 to 1.0
Causes **coherent motion** of the 0.0001 excess spin up.
So sample magnet points horizontally. Creates signal in receiver coil (not shown).

Entropy makes sample return to most probable state (Boltzmann distribution). Time to do so is called the $T_1$ relaxation time. (1$^{st}$ order rate constant is $1/T_1$)

Fourier transform of these oscillations give the entire NMR spectrum

Another very important relaxation is the called the $T_2$ relaxation time which comes from the dephasing of the individual spins due to collisions. The ordering caused by the pulse causing the net dipole of the spins to add up to a vector pointing in the $y$ direction initially, and direction rotating at a frequency given by ($E_{up}$-$E_{down}$)/$h$ is ruined by the thermal motion. But the energy is not lost so quickly. The phase information is not lost! A second pulse twice as long as the first will reverse the phases and therefore the direction of rotation. Those vectors that lagged behind will be leading the pack, and all will reach the “finish line” simultaneously. Almost all the signal comes back for a brief time. This is called a **“SPIN ECHO”**. Please go to: http://en.wikipedia.org/wiki/Spin_echo for nice visual demos.
http://en.wikipedia.org/wiki/Spin_echo
This is the **Fourier Transform** of the “free induction decay” from Figure 14.5

These are amounts and frequencies that when summed give the free induction decay from the short intense pulse of radio frequency.