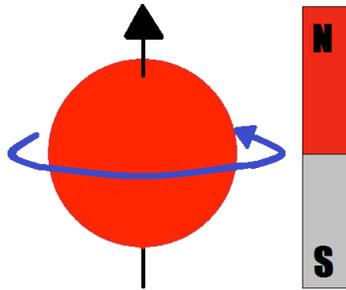


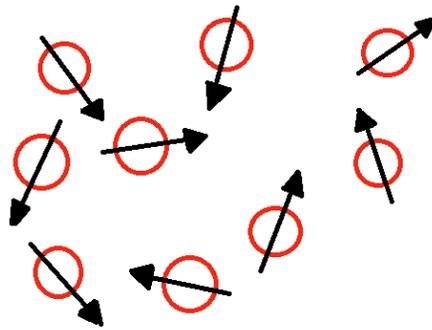
## NMR SPECTROSCOPY

This section will discuss the basics of NMR (nuclear magnetic resonance) spectroscopy. Most of the section will discuss mainly  $^1\text{H}$  or 'proton' spectroscopy but the most popular nuclei in NMR are  $^{13}\text{C}$ ,  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{14}\text{N}$ ,  $^{17}\text{O}$ ,  $^{31}\text{P}$ . These are nuclei of particular interest because they have  $\frac{1}{2}$  spin states. Nuclei with spin, or an angular momentum, have an associated magnetic moment. To fully understand what is happening it is important to understand 2 basic concepts: **1) Electric currents have associated magnetic fields.** This can be seen in simple experiments where an insulated copper wire is wound around a nail and current applied. This creates an electromagnet. **2) Magnetic fields can generate currents.** This can be seen in simple machine like an electric generator or a car's alternator.

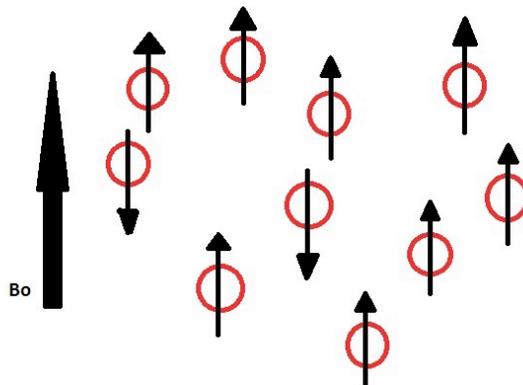
With that first concept in mind, it is seen that a spinning nucleus creates a magnetic field, like a bar magnet



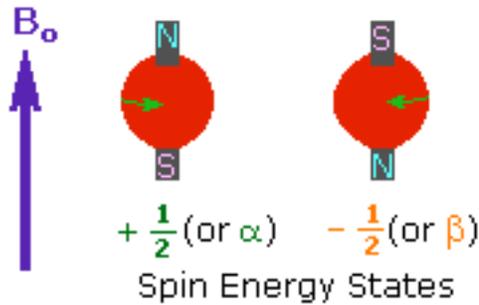
In nature these nuclei are oriented in a random fashion, pointing in all different directions.



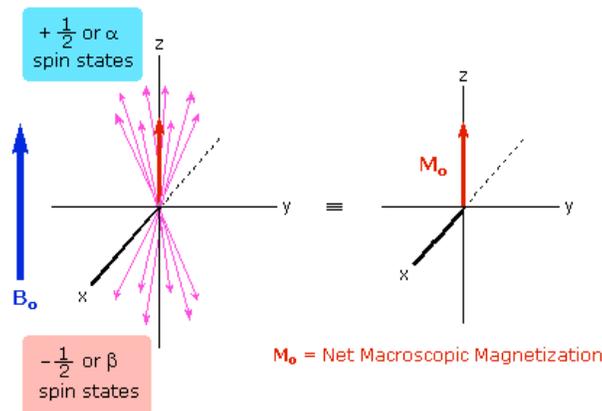
Once placed in a strong applied magnetic field they align with the external field.



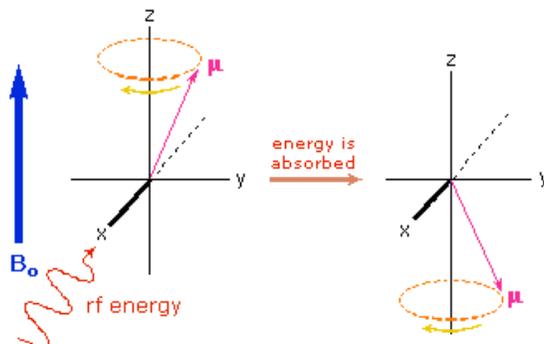
You will notice that they are not all pointed in the same direction. There are 2 basic orientations, the Alpha and Beta. The Alpha which aligns ‘with’ the field (north of the nucleus to south of the field and vice versa) is the low energy orientation. The Beta orientation has the north poles and south poles facing. This, as expected, is the high energy orientation. Predictably the Alpha orientation represents the large majority of the nuclei but there are always some that are in the Beta. (to note: The external field ( $B_0$ ) arrow points from N to S)



The Larmor or precessional frequency in NMR refers to the rate of precession of the magnetic moment of the proton around the external magnetic field. The frequency of precession is related to the strength of the magnetic field,  $B_0$ . While we discuss the direction of the magnetic moment of a nucleus as a single direction it is actually the net of the precession of the nucleus. Think of the nucleus as a spinning top while spinning along an axis has a precession about it.



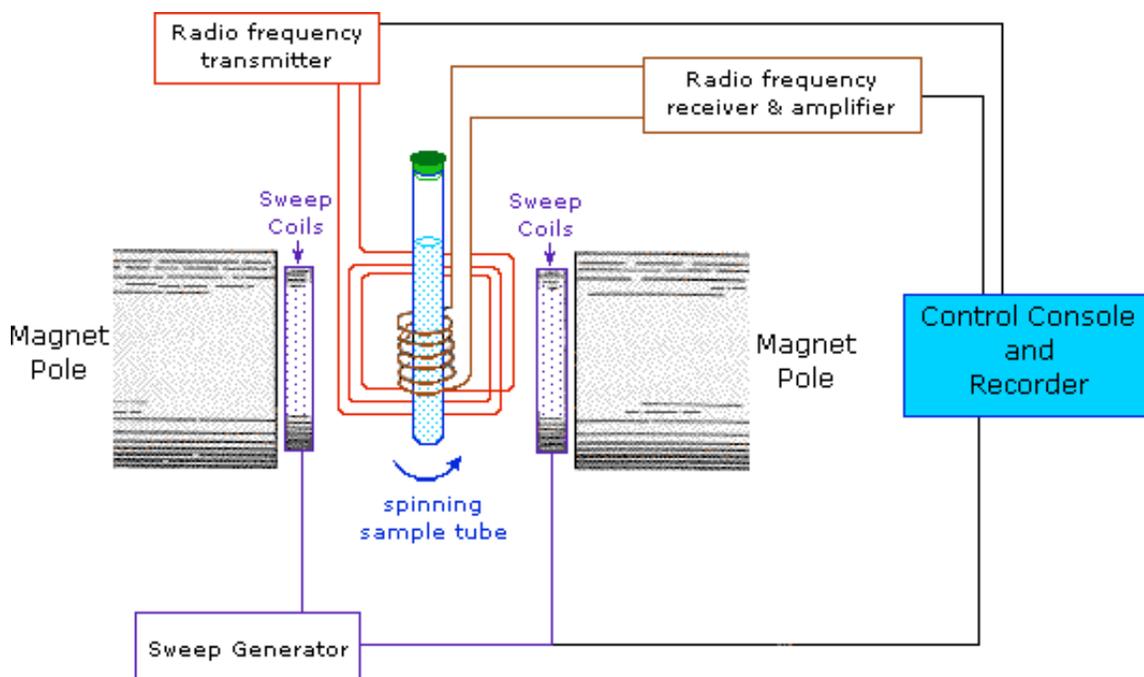
The Larmor frequency refers to the radio frequency needed to flip that precession to the Beta position from the Alpha.



The video below illustrates the precession phenomena in the physical environment

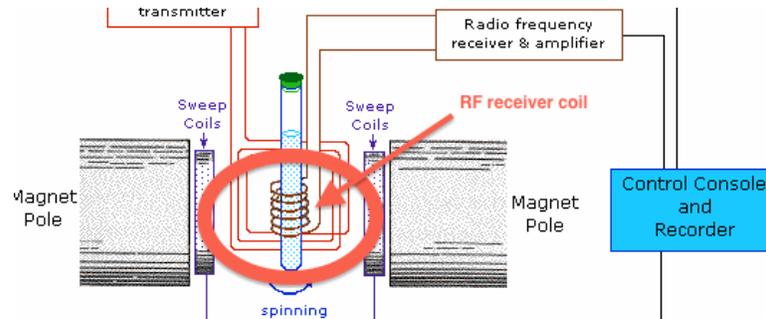
<https://www.youtube.com/watch?v=7aRKAXD4dAg>

Inside an NMR instrument the sample is exposed to a very strong magnetic field, typically 1 to 20 Tesla. By comparison a refrigerator magnet is approximately 5 mT (milli Tesla) and about 0.3T for a strong neodymium magnet. Within the NMR tube the samples nuclei align with the field in either the Alpha (typical) or Beta orientation. The NMR tube ( a long thin tube) sits inside an area surrounded by the large magnet, a radio frequency transmitter and a coil to receive radio frequency signals (more on why that is important later).

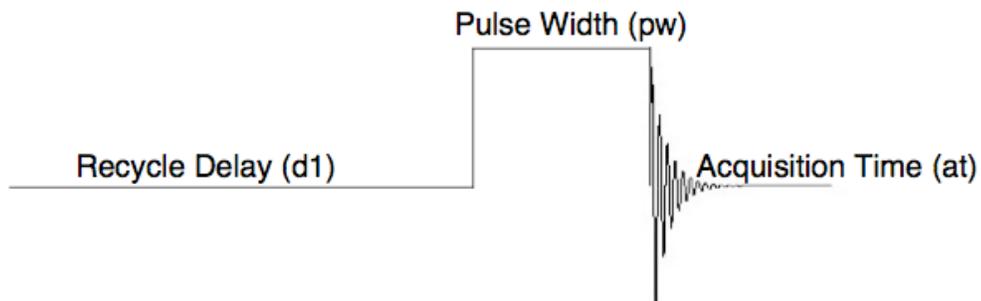


NMR spectroscopy works by applying a radio frequency to the sample, specific to the nuclei of interest. The energy from the radio frequency pulse is enough to flip the nuclei from its Alpha position to the Beta. (remember the beta is the high energy orientation). The analysis part of the instrument is to “listen” to the nuclei “relax” back to its Alpha

position. As you will recall from the first paragraph, the second concept we need to remember is that “magnetic fields can generate currents”. As the spinning nuclei generates a magnetic field (albeit small), the “flipping back” generates a small amount of current within the receiver coil surrounding the sample tube.



The signal created is called an FID (free induction decay).



The frequency is determined by the equation below where  $\Delta E$  is the radio frequency,  $I$  is the spin state, and  $B_x$  is the external magnetic field applied.

$$\Delta E = \frac{\mu \cdot B_x}{I}$$

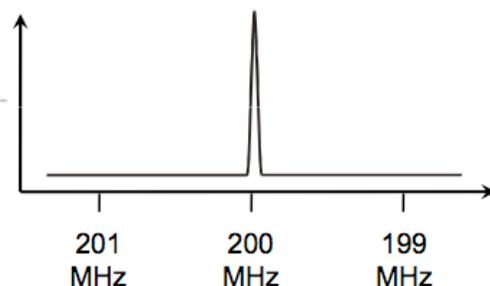
- $\Delta E$  : radio frequency applied
- $\mu$  : magnetic moment of particular nuclei
- $B_x$  : external magnetic field
- $I$  : spin state (1/2)

### **CHEMICAL SHIFT:**

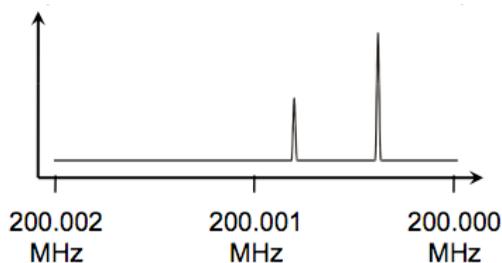
Spectrometers are typically named by frequency: 400 MHz, 300 MHz etc. This is a generic name for the radio frequency to ‘flip’ a proton under the applied magnetic field of

that NMR magnet. The higher the frequency the spectrometer means the higher the magnetic field applied to the nuclei. This is intuitive as a stronger magnetic field applied to the 'tiny bar magnet' of a nucleus means the more energy (higher frequency) needed to be applied to "flip" the nucleus.

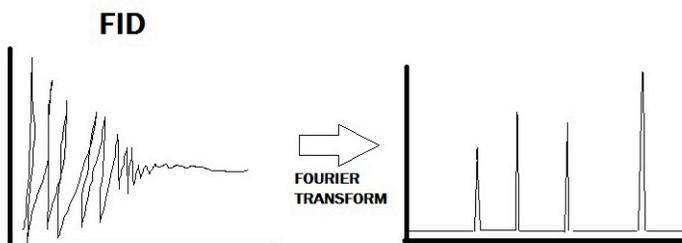
If all protons wobbled at the same frequency then NMR would be of no use; as there would be one peak for all the protons in the molecule.



But not all protons within a molecule are the same so they have different frequencies due to their molecular environment (more on that later). If we look closer we see the difference.

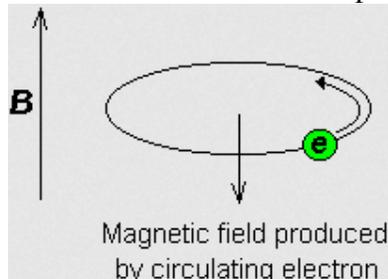


All distinct protons in a molecule have a distinct frequency. The same way each tone bar on a xylophone has its own distinct frequency. We could strike each bar of a xylophone individually to see the associated frequency. An alternative means of acquiring the same information is to strike all the bars simultaneously, and to subject the complex collection of frequencies produced to mathematical analysis. The FID we see is all the frequencies of the protons simultaneously along a time scale. We subject that information to Fourier Transform and get the typical "baseline with peaks" spectrum we are used to looking at with NMR.

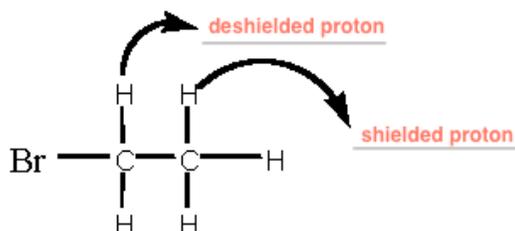


Why does each equivalent proton have a different frequency?

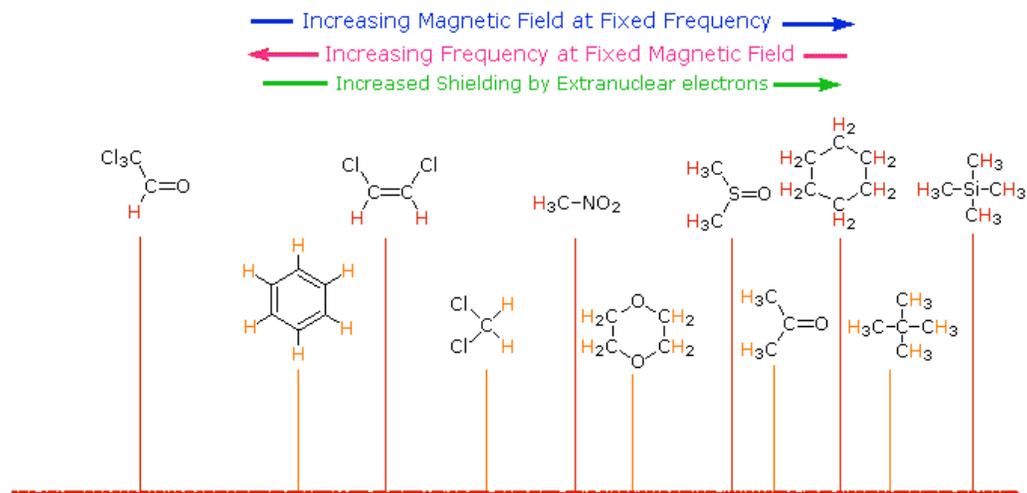
The reason is that the applied magnetic field also produces a circulation of the e- (electron) cloud as well. This circulation creates an OPPOSING magnetic field. This begins the phenomenon of “shielded” and “deshielded” protons.



If the particular proton is adjacent to an electron withdrawing group, like a Halogen or Oxygen, that proton becomes “deshielded”. Conversely a proton that has no electron withdrawing group close by is considered “shielded”.



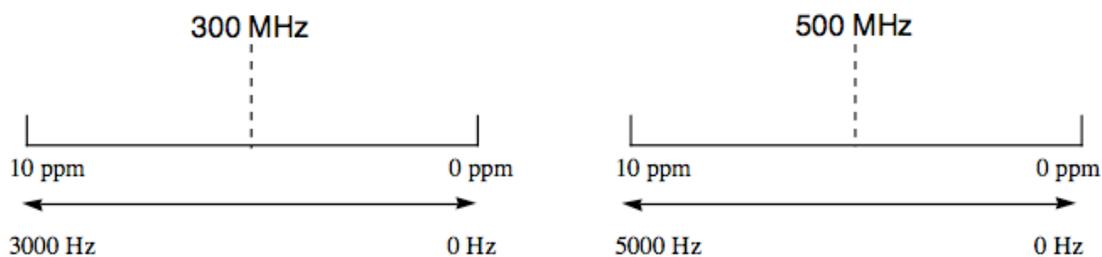
A “shielded” proton is less susceptible to the applied magnetic field from the NMR because of the opposing field induced from the electron cloud. Thus it takes less energy, and by proxy lower frequency, to flip that proton. A “deshielded” proton, one that has had its electron cloud slightly withdrawn by an adjacent group is MORE exposed to the applied magnetic field from the NMR. Therefore it will take more energy, and by proxy a higher frequency, to flip the proton. The scale of higher and lower frequencies is plotted along a linear graph in typical NMR spectrum.



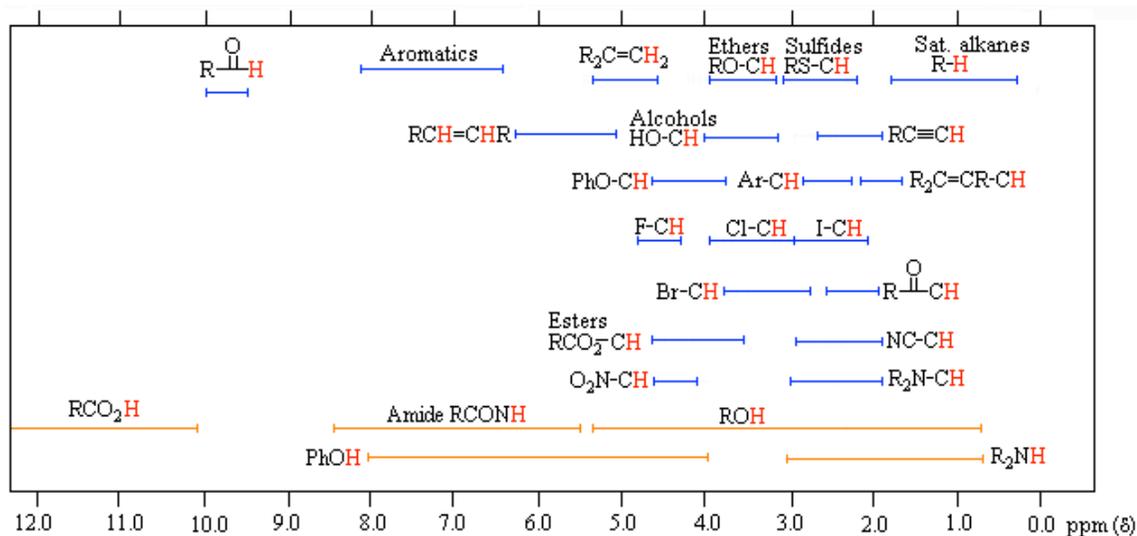
<sup>1</sup>H NMR Resonance Signals for some Different Compounds

Because not every spectrometer has the same Larmor frequency, the scale for each proton is used. A generic term called “ppm”, short for parts per million is the unit. Here is an illustration of the ppm scale for each spectrometer frequency and the equation used to determine ppm scale.

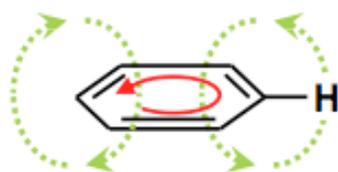
$$\text{Chemical shift in ppm} = \frac{\text{peak position in Hz (relative to TMS)}}{\text{spectrometer frequency in MHz}}$$



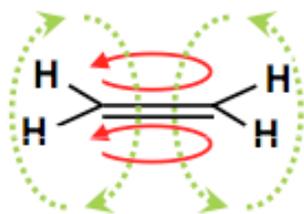
Here is a scale of the important functional groups and their associated ppm ranges.



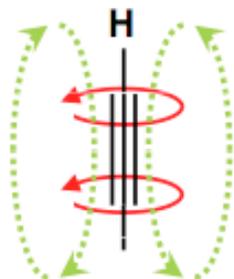
There are a few functional groups that have a more complicated de-shielding by the nature of their groups structure.



"Ring current"  
*reinforces* applied  $B_0$  field; **deshields** aromatic protons ( $\delta = 6.5-8.5$  ppm).



Induced current is less effective in olefins, still **deshields**, but less ( $\delta = 4-6$  ppm).



Acetylene protons  
are **shielded**  
( $\delta = 1.5-3$  ppm).

**TMS – tetra methyl silane** is a standard usually used in proton spectroscopy as a 0ppm molecule. It is a symmetrical molecule with all 12 equivalent protons and no electron withdrawing groups.

