Laboratory and Rotating frames

• The coordinate system that we used for the previous example (laboratory frame) is really pathetic. The whole system is spinning at $\omega_o$, which makes any kind of analysis impossible.

• Again, an out-of-date example. It would be like trying to read the label of a record spinning in a turn-table…

• The solution is to take a coordinate system that moves at $\omega_o$. This is like jumping on top of the long play to read the label. What we effectively do is remove the effect of $B_o$. If we take magnetization on the $<xy>$ plane:

![Diagram](image)

• In this coordinate system, $M_{xy}$ does not move if we are at the resonant condition (the $\omega$ of $B_1$ is exactly the frequency of the nuclei, $\omega_o$). If we are slightly off-resonance, the movement of the vectors is still slow with respect to $\omega_o$. 
Chemical shifts

• If each type of nucleus has its characteristic $\omega_o$ at a certain magnetic field, why is NMR useful?

• Depending on the chemical environment we have variations on the magnetic field that the nuclei feels, even for the same type of nuclei. It affects the local magnetic field.

$$B_{\text{eff}} = B_o - B_{\text{loc}} \quad --- \quad B_{\text{eff}} = B_o(1 - \sigma)$$

• $\sigma$ is the magnetic shielding of the nucleus. Factors that affect it include neighboring atoms and groups, etc., etc. The polarization of the bonds to the observed nuclei are important as well.

• As a crude example, ethanol looks like this:
The NMR scale ($\delta$, ppm)

- We can use the frequency scale as it is. The problem is that since $B_{\text{loc}}$ is a lot smaller than $B_o$, the range is very small (hundreds of Hz) and the absolute value is very big (MHz).

- We use a relative scale, and refer all signals in the spectrum to the signal of a particular compound.

\[
\delta = \frac{\omega - \omega_{\text{ref}}}{\omega_{\text{ref}}}
\]

ppm (parts per million)

- The good thing is that since it is a relative scale, the $\delta$ in a 100 MHz magnet (2.35 T) is the same as that obtained for the same sample in a 600 MHz magnet (14.1 T).

- Tetramethyl silane (TMS) is used as reference because it is soluble in most organic solvents, inert, volatile, and has 12 equivalent $^1$Hs and 4 equivalent $^{13}$Cs:

- Other references can be used, such as the residual solvent peak, dioxane for $^{13}$C, etc. What reference we use is not critical, because the instrument (software/hardware) is calibrated internally. Don’t use them if you don’t need to...
Scales for different nuclei

• For protons, ~ 15 ppm:

  - Acids, Aldehydes
  - Amides
  - Aromatics
  - Olefins
  - Aliphatic

  ppm
  15 10 7 5 2 0 TMS

• For carbon, ~ 220 ppm:

  - C=O in ketones
  - Aromatics, conjugated alkenes
  - Olefins
  - Aliphatic CH₃, CH₂, CH
  - C=O of Acids, aldehydes, esters
  - Carbons adjacent to alcohols, ketones

  ppm
  210 150 100 80 50 0 TMS
Chemical shift in the rotating frame

• We will consider only magnetization in the $<xy>$ plane. We start with a signal with an $\omega_o$ equal to the $\omega$ of $B_1$. After some time passes, nothing changes…

• Now, if we are slightly off-resonance ($\omega - \omega_o \neq 0$), the $M_{xy}$ vector will evolve with time. The angle will be proportional to the evolution time and $\omega - \omega_o$ (that’s why we use radians…)

$$\phi = (\omega - \omega_o) \times t$$
Coupling Constants

• The energy levels of a nucleus will be affected by the spin state of nuclei nearby. The two nuclei that show this are said to be *coupled* to each other. This manifests in particular in cases were we have through bond connectivity:

![Diagram showing one-bond and three-bond coupling]

• Energy diagrams. Each spin now has two energy ‘sub-levels’ depending on the state of the spin it is coupled to:

![Energy level diagram]

• The magnitude of the separation is called *coupling constant* \( J \) and has units of Hz.

• Coupling patterns are crucial to identify spin systems in a molecule and to the determination of its chemical structure.
Couplings in the rotating frame

• We will consider an ensemble of spins $I$ coupled to another spin $S$ that is exactly at the resonant condition ($\omega$ of $B_1$ is $\omega_o$), and again, only what goes on in the $<xy>$ plane.

• The situation is analogous to what happened with chemical shift. In this case, since there are two new energy levels for the spin, we get two counter-rotating vectors. Their evolution will depend on the magnitude of $J$, not $\omega_o$:

\[ \phi = \pi \times t \times J \]
NMR Instrumentation

- An NMR machine is basically a big and expensive FM radio.

- **Magnet** - Normally superconducting. Some electromagnets and permanent magnets (EM-360, EM-390) still around.

- **Frequency generator** - Creates the alternating current (at $\omega_o$) that induces $B_1$. Continuous wave or pulsed.

- **Detector** - Subtracts the base frequency (a constant frequency very close to $\omega_o$) to the output frequency. It is lower frequency and much easier to deal with.

- **Recorder** - XY plotter, oscilloscope, computer, etc., etc.
Continuous Wave excitation

- It’s pretty "de mode," and is only useful to obtain 1D spectra.

- The idea behind it is the same as in UV. We scan the frequencies continuously (or sweep the magnetic field, which has the same effect - $\omega = \gamma B$), and record successively how the different components of $M_0$ generate $M_{xy}$ at different frequencies (or magnetic fields).

- We get a time domain effect in the frequency spectrum (the famous "ringing") because we cannot sweep slow enough.
Fourier Transform - Pulsed excitation

• The way every NMR instrument works today.

• The idea behind it is pretty simple. We have two ways of tuning a piano. One involves going key by key on the keyboard and recording each sound (or frequency). The other, kind of brutal for the piano, is to hit it with a sledgehammer and record all sounds at once.

• We then need something that has all frequencies at once. A short pulse of radiofrequency has these characteristics.

• To explain it, we use another black box mathematical tool, the Fourier transform: It is a transformation of information in the time domain to the frequency domain (and vice versa).

\[ S(\omega) = \int_{-\infty}^{\infty} S(t) \, e^{-i\omega t} \, dt \]

\[ S(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} S(\omega) \, e^{i\omega t} \, d\omega \]

• If our data in the time domain is periodical, it basically gives us its frequency components. Extremely useful in NMR, where all the signals are periodical.
Fourier Transform of simple waves

• We can explain (or see) some properties of the FT with simple mathematical functions:

• For \( \cos(\omega \cdot t) \)

• For \( \sin(\omega \cdot t) \)

• The cosines are said to give absorptive lines, while sines give dispersive lines. We’ll refer to these particularly when talking about the phase of the spectrum. It is also important to remember this to understand quadrature detection.
Back to pulses

• Now that we ‘master’ the FT, we can see how pulses work. A radiofrequency pulse is a combination of a wave (cosine) of frequency $\omega_o$ and a step function:

\[
\text{FT: } 1 \text{ at } \omega_o = \pm 1
\]

\[
\text{FT: } \frac{\sin(t_p\omega)}{t_p\omega} \text{ or sinc}(t_p\omega)
\]

• This is the time domain shape of the pulse. To see the frequencies it really carry, we have to analyze it with FT:

• The result is a signal centered at $\omega_o$ which covers a wide range of frequencies in both directions. Depending on the pulse width, we have wider (shorter $t_p$) or narrower (longer $t_p$) ranges. Remember that $f \propto 1 / t$. 
Pulse widths and tip angles

- The pulse width is not only associated with the frequency range (or sweep width), but it also indicates how long the excitation field $B_1$ is on. Therefore, it is the time for which we will have a torque acting on the bulk magnetization $M_o$:

$$\theta_t = \gamma \times t_p \times B_1$$

- As the pulse width for a certain flip angle will depend on the instrument ($B_1$), we will therefore refer to them in terms of the rotation we want to obtain of the magnetization. Thus, we will have $\pi / 4$ (45), $\pi / 2$ (90), $\pi$ (180), etc., etc., pulses.
Some useful pulses

• The most commonly used pulse is the $\pi / 2$, because it puts as much magnetization as possible in the $<xy>$ plane (more signal can be detected by the instrument):

• Also important is the $\pi$ pulse, which has the effect of inverting the populations of the spin system...

• With control of the spectrometer we can basically obtain any pulse width we want and flip angle we want.
Free Induction Decay (FID)

• We forgot about the sample a bit. We are interested in the signal that appears in the receiver coil after putting the bulk magnetization in the $<xy>$ plane ($\pi/2$ pulse).

• We said earlier that the sample will go back to equilibrium ($z$) precessing. In the rotating frame, the frequency of this precession is $\omega - \omega_o$. The relaxation of $M_o$ in the $<xy>$ plane is exponential (more next class). Therefore, the receiver coil detects a decaying cosinusoidal signal (single spin type):
FID (continued)

• In a real sample we have hundreds of spin systems, all with frequencies different to that of $B_1$ (or *carrier frequency*). Since we used a pulse and excited all frequencies in our sample at once, we will see a combination of all of them in the receiver coil, called the *Free Induction Decay* (or *FID*):

![FID Signal](image)

• The FT of this signal gives us the NMR spectrum:

![NMR Spectrum](image)