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 $\omega_0$, 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- Again, an out-of-date example.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 $\omega_0$. This is like jumping on top of the long play to read the label. What we effectively do is remove the effect of $B_0$. If we take magnetization on the $<xy>$ plane:

- 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, $\omega_0$). If we are slightly off-resonance, the movement of the vectors is still slow with respect to $\omega_0$. 
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.

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

• $\sigma$ 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.

$$\delta = \frac{\omega - \omega_{\text{ref}}}{\omega_{\text{ref}}} \quad \text{ppm (parts per million)}$$

- 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
  - Alcohols, protons α to ketones

- 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
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…

![Diagram 1](image1.png)

• 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…)

![Diagram 2](image2.png)

\[ \phi = (\omega - \omega_o) \times t \]
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:

![Energy diagram for one- and three-bond coupling](image)

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

![Energy level diagram](image)

• 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 $\omega_0$), 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 $\omega_0$:

$$\phi = \pi \times t \times J$$
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 $M_o$ 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 sledge hammer 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).

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

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

- 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 $\cos(\omega t)$

• For $\sin(\omega t)$

• 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:

- 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 $M_0$:

\[ \theta_t = \gamma * t_p * B_1 \]

- 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)