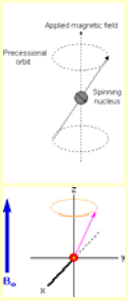
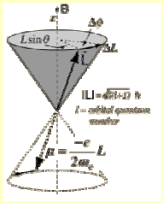
Theory of Magnetic Resonance

Classical Description

- *Spinning particle precesses around an applied magnetic field*

A Spinning Gyroscope in a Gravity Field

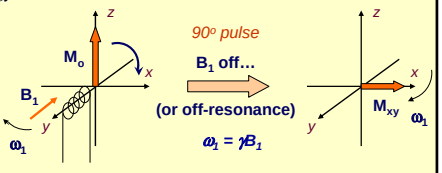




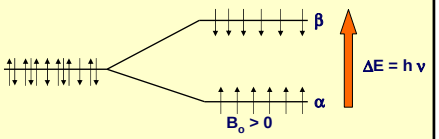
Resonance

Absorption of RF Energy or NMR RF Pulse

Classic View:
- Apply a radio-frequency (RF) pulse a long the y-axis
- RF pulse viewed as a second field (B_1), that the net magnetization (M_o) will precess about with an angular velocity of ω_1
- precession stops when B_1 turned off



Quantum Description:
- enough RF energy has been absorbed, such that the population in α/β are now equal
- No net magnetization along the z-axis



Please Note: A whole variety of pulse widths are possible, not quantized dealing with bulk magnetization

Continuous Wave NMR

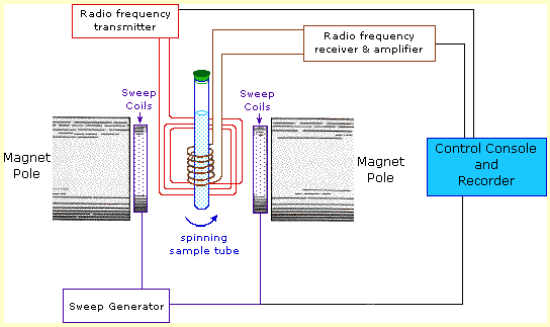
- Continuous wave NMR spectrometers are similar in principle to optical spectrometers.
- The sample is held in a strong magnetic field, and the frequency of the source is slowly scanned
  - in some instruments, the source frequency is held constant, and the field is scanned.

Continuous wave NMR

- In this kind of application, both the magnetic field and the RF excitation signal are continuously on.
  - Either the magnetic field is kept constant and the frequency of the RF excitation is varied,

    OR
  - The magnetic field is varied while keeping the RF input frequency constant.
- Either approach allows you to sweep through the resonance of the sample under investigation.

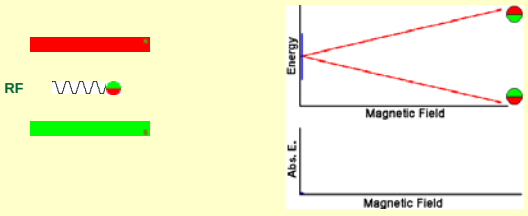
Continuous wave NMR



Continuous wave NMR

Spins Orientation in a Magnetic Field (Energy Levels)

- Transition from the low energy to high energy spin state occurs through an absorption of a photon of radio-frequency (RF) energy



Frequency of absorption: $\nu = \gamma B_o / 2\pi$

Fourier Transform NMR

- 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.

Fourier Transform NMR

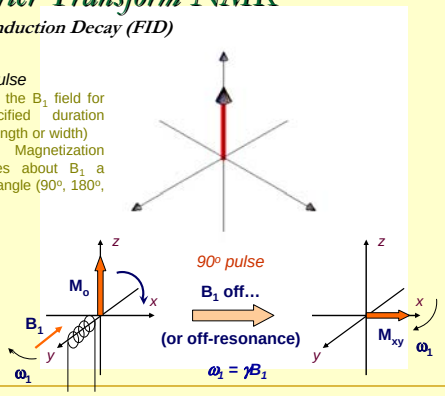
- We are interested in the signal that appears in the receiver coil after putting the bulk magnetization in the **<xy>** plane (**π / 2** pulse).
- The macroscopic magnetization will go back to equilibrium (**z**) precessing. In the rotating frame, the frequency of this precession is **ω – ωo**. The relaxation of **Mo** in the **<xy>** plane is exponential. Therefore, the receiver coil detects a decaying cosinusoidal signal (single spin type)

Fourier Transform NMR

Free Induction Decay (FID)

NMR Pulse

- Applying the B_1 field for a specified duration (Pulse length or width)
- Net Magnetization precesses about B_1 a defined angle (90º, 180º, etc)



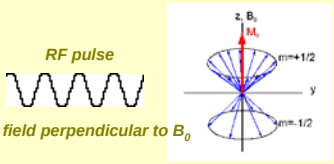
Fourier Transform NMR

Free Induction Decay (FID)

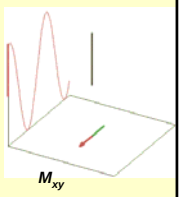
Observe NMR Signal

- Need to perturb system from equilibrium.
  - B_1 field (radio frequency pulse) with $\gamma B_o/2\pi$ frequency
- Net magnetization (M_o) now precesses about B_o *and* B_1
  - M_x and M_y are non-zero
  - M_x and M_y rotate at Larmor frequency
  - System absorbs energy with transitions between aligned and unaligned states
- Precession about B_1 stops when B_1 is turned off

RF pulse



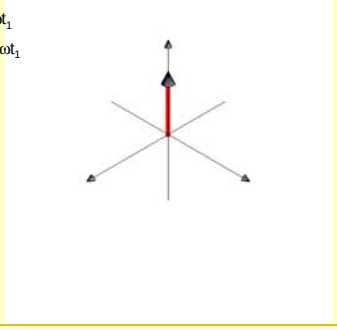
B_1 field perpendicular to B_0



Fourier Transform NMR

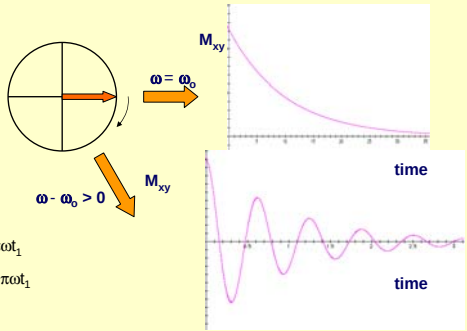
$\upsilon = M\sin 2\pi\omega t_1$

$\upsilon = M\cos 2\pi\omega t_1$



Fourier Transform NMR

Free Induction Decay (FID)



$\upsilon = M\sin 2\pi\omega t_1$

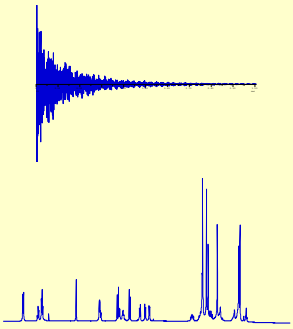
$\upsilon = M\cos 2\pi\omega t_1$

Fourier Transform NMR

Free Induction Decay (FID)

- In a real sample we have hundreds of spin systems, all with frequencies different to that of **B1** (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***)

The FT of this signal gives us the NMR spectrum:



Fourier Transform NMR

- 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*).

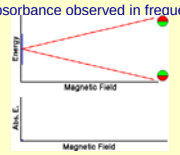
$$S(\omega) = \int S(t)\, e^{-i\omega t}\, dt$$

$$S(t) = {}^{1}/_{2}\,\pi \int S(\omega)\, e^{i\omega t}\, dt$$

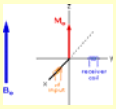
- If our data in the time domain is periodical, it basically gives us its frequency components. Extremely useful in NMR, where all the signals are periodical.

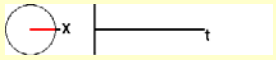
CW vs. FT

Continuous Wave – sweep either magnetic field or frequency until resonance is observed – absorbance observed in frequency domain



Pulse/Fourier Transform – perturb and monitor all resonances at once – absorbance observed in the time domain





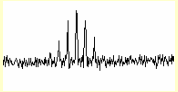
Disadvantages of CW

- **It is time consuming**:
  - The optimum rate of acquiring a spectrum by the CW technique is 1Hz/sec. At this rate, a spectrum having spectral width of 1000 Hz on a 100MHz spectrometer will require 1000seconds or nearly 15 min for a single experiment.
- **Large quantity of sample required**:
  - The normal CW experiment requires about 40 to 50 mg of the sample. Compounds isolated from natural products are obtained in very small quantities and will be difficult to study.
- **Nuclei having low natural abundance cannot be studied**:
  - Nuclei such as 13C, which has a very low natural abundance (only 1.08% of the total population of 12C) cannot be studied by this method. This is so because these nuclei will give very weak signals that cannot be distinguished from the noise generated by the spectrometer.
- **High resolution NMR not possible**:
  - As the magnetic field strength is increased, it becomes difficult to sweep the entire range of resonance thereby making high resolution impossible.

Advantages of FT

- Since all nuclei are excited and observed simultaneously, the pulse can be repeated after each relaxation period (for ^{1}H, about 10 seconds) and the resulting signals added together
- Because we are observing weak radiofrequency signals in a sea of RF noise for dilute samples (or those observed once as in CW NMR) noise becomes an issue
- If several to hundreds of FIDs are added together, signals will tend to constructively add together and become more pronounced;
  - Since noise is random, it will tend to destructively add and become less pronounced
- Signal to noise ratio improves as a function of the square root of the scans (FIDs) performed: S/N = *f* (n)

Signal-to-Noise (S/N) ratios



Measure height

Typical rule of thumb:

Limit of detection, S/N=3

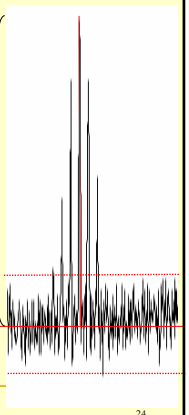
Limit of Quantitation, S/N=10

S/N=6.3/2*0.707

=4.45

So this peak is reliably detectable, but not reliably quantitatable

Noise(rms) is 0.707 x peak to peak

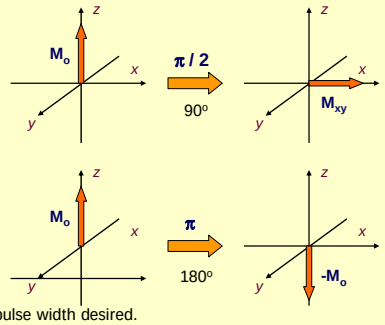


NMR Pulse

Some useful common pulses

90° pulse

Maximizes signal in x,y-plane where NMR signal detected



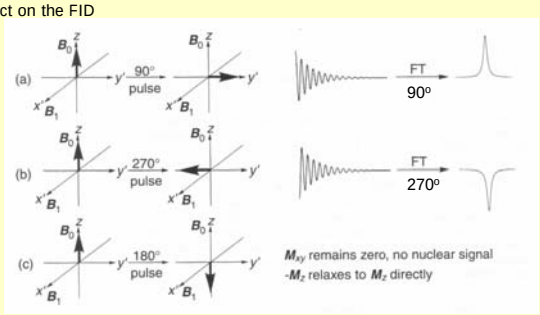
180° pulse

Inverts the spin-population. No NMR signal detected

Can generate just about any pulse width desired.

NMR Pulse

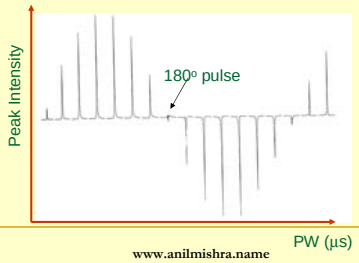
Impact on the FID



NMR Pulse

Measuring an NMR pulse length

a) Vary pulse width (PW) and measure peak intensity
   i. Start with very short (~1μs) PW and properly phased spectra
   ii. Maximum peak intensity at 90° pulse, minimum peak intensity at 180° pulse
b) PW is dependent on power or attenuation of pulse
   i. higher power → shorter pulse length

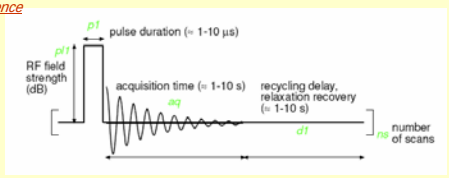


NMR Pulse

NMR pulse sequences

a) composed of a series of RF pulses, delays, gradient pulses and phases
b) in a 1D NMR experiment, the FID acquisition time is the time domain (t_1)
c) more complex NMR experiments will use multiple "time-dimensions" to obtain data and simplify the analysis.
d) Multidimensional NMR experiments may also use multiple nuclei (^2D, ^{13}C,^{15}N) in addition to 1H, but usually detect 1H)

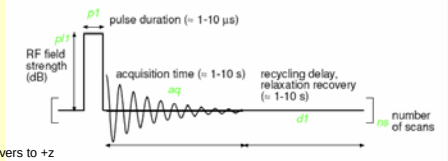
1D NMR Pulse Sequence



1D NMR

- *General summary*

Relaxation – Preparation – Evolution – Mixing – Acquisition



- **Relaxation**
  - signal fully recovers to +z
  - should be > $5T_1$, normally T_1 to $2T_1$ (~1-2 secs.)
- **Preparation**
  - select desired information
- **Evolution**
  - related to coupling constant (~1/2J)
- **Mixing**
  - requires 180 refocusing pulse to phase spectra
  - usually evolution of through space dipole-dipole relaxation (NOE)
- **Acquisition**
  - FID is observed usually with decoupling