

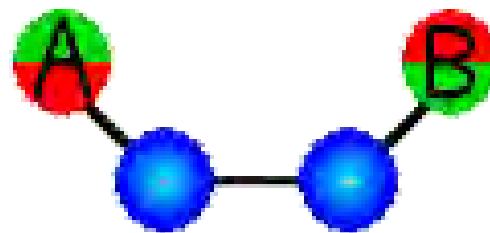
Spectroscopy in Inorganic Chemistry

Nuclear Magnetic Resonance Spectroscopy

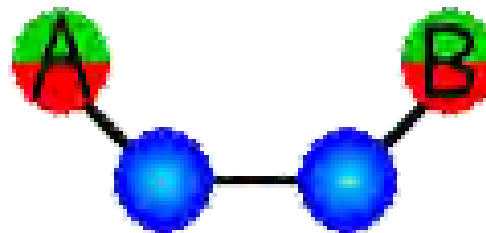
Spin-Spin Coupling

- Nuclei experiencing the same chemical environment or chemical shift are called equivalent. Those nuclei experiencing different environment or having different chemical shifts are nonequivalent. Nuclei which are close to one another exert an influence on each other's effective magnetic field. This effect shows up in the NMR spectrum when the nuclei are nonequivalent. If the distance between non-equivalent nuclei is less than or equal to three bond lengths, this effect is observable. This effect is called spin-spin coupling or J coupling.

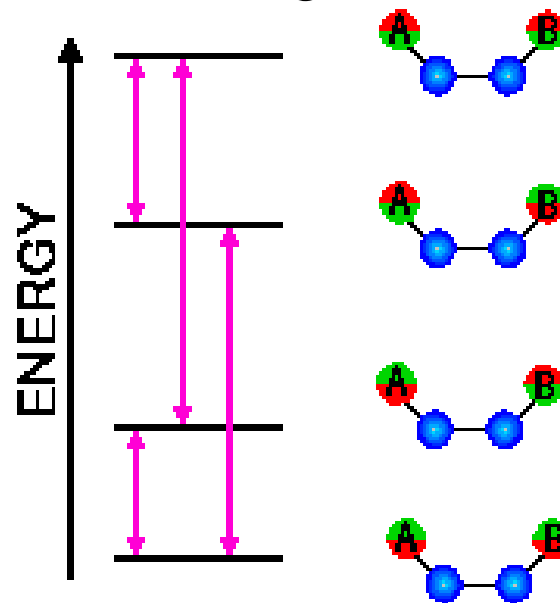
- aligned with the external field such that the fields called spin up



- opposed to the external field such that the fields are called spin down

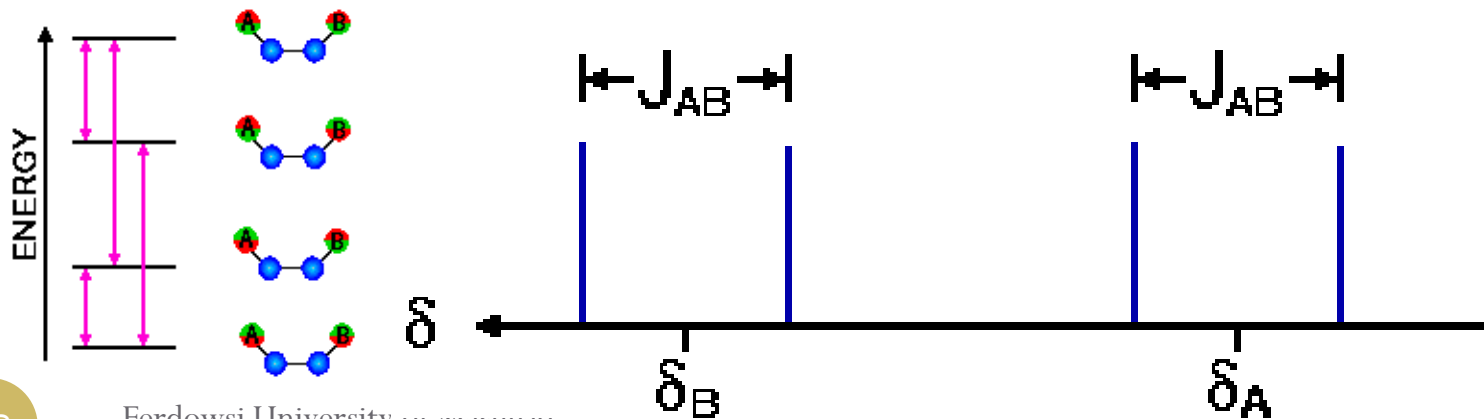


- There are a total of four possible configurations for the two nuclei in a magnetic field.

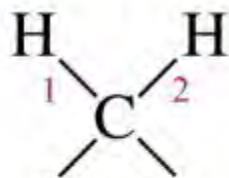


- In NMR, an allowed transition is one where the spin of one nucleus changes from spin up to spin down , or spin down to spin up .

- The NMR spectrum for nuclei A and B reflects the splittings observed in the energy level diagram. The A absorption line is split into 2 absorption lines centered on δ_A , and the B absorption line is split into 2 lines centered on δ_B . The distance between two split absorption lines is called the J coupling constant or the spin-spin splitting constant and is a measure of the magnetic interaction between two nuclei.

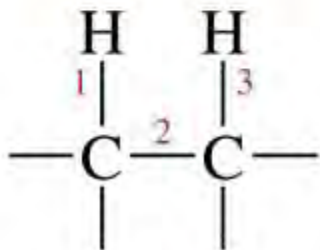


Bonded to the same carbon: two bonds between protons



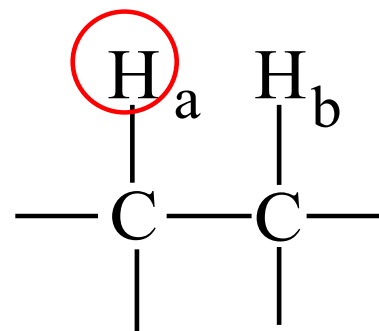
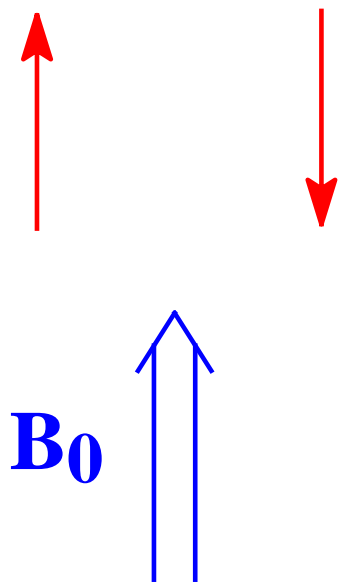
spin-spin splitting is normally observed
(if nonequivalent)

Bonded to adjacent carbons: three bonds between protons



spin-spin splitting is normally observed
(this is the most common case)

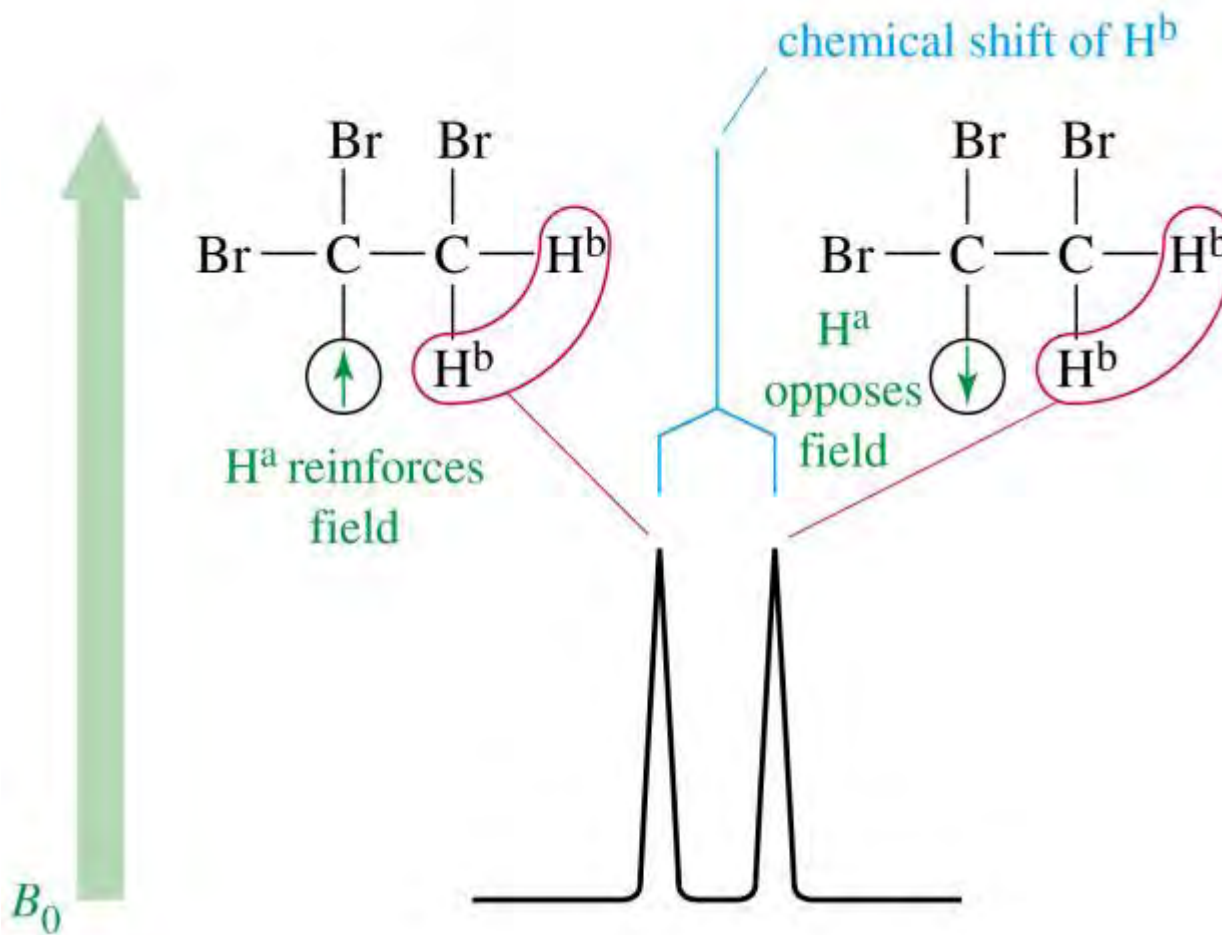
The Doublet in ^1H NMR



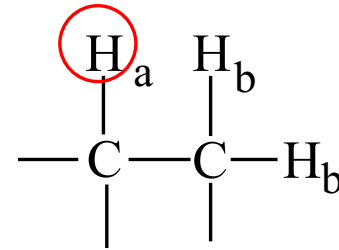
H_a is coupled to H_b

H_b is parallel or anti-parallel to B_0

$\therefore \text{H}_a$ splits into a 1:1 **doublet peak**



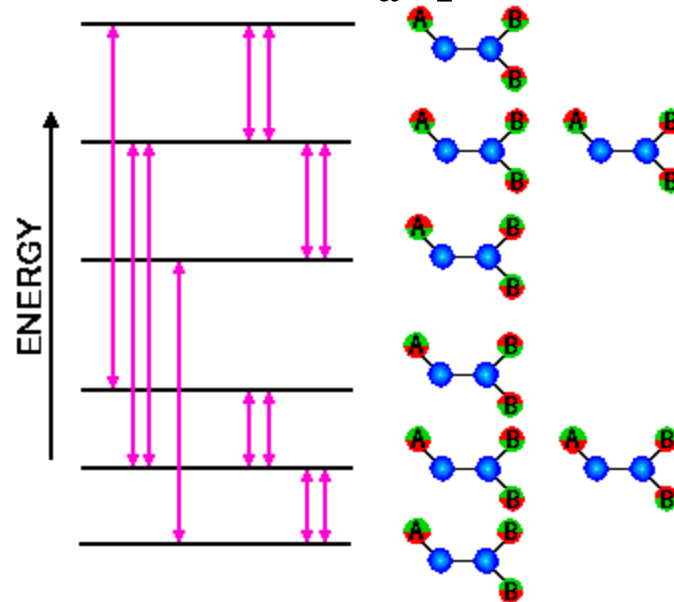
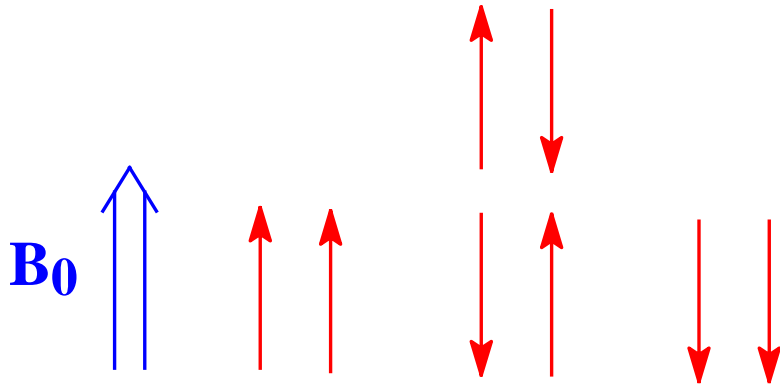
The Triplet in ^1H NMR

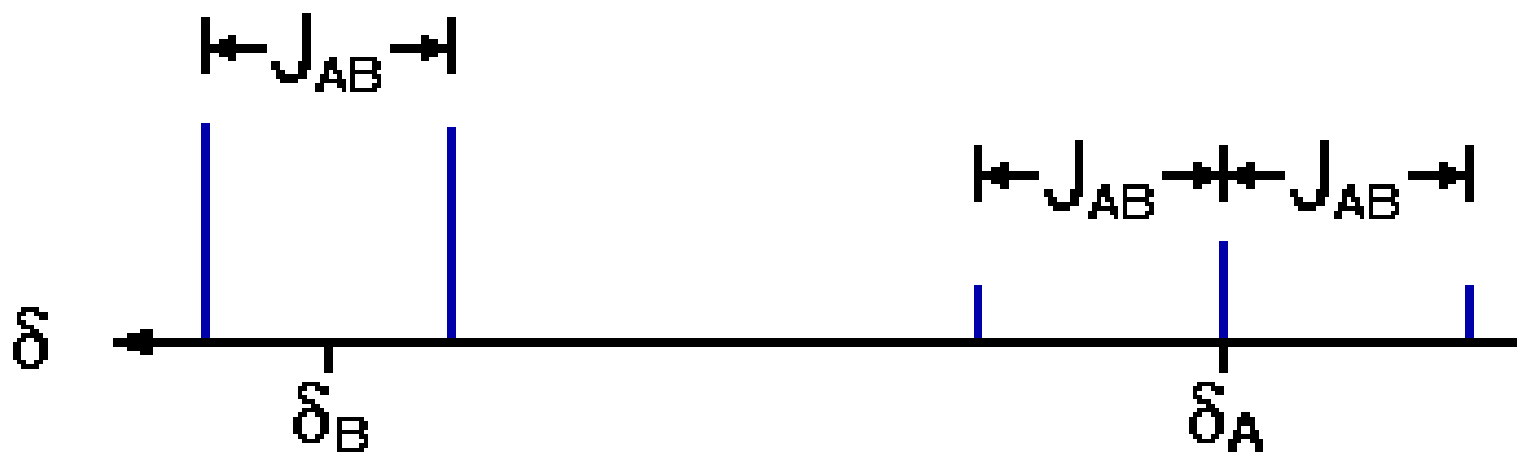
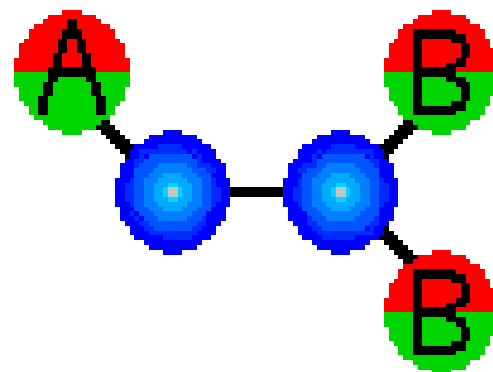
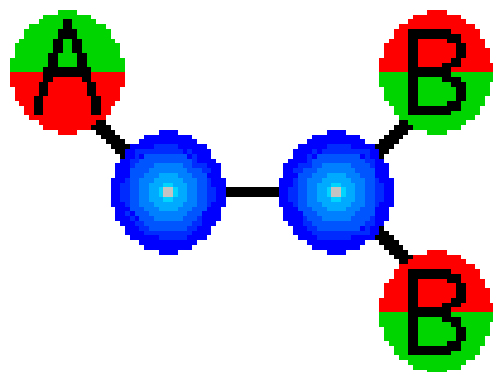


H_a is coupled to H_b and H_b

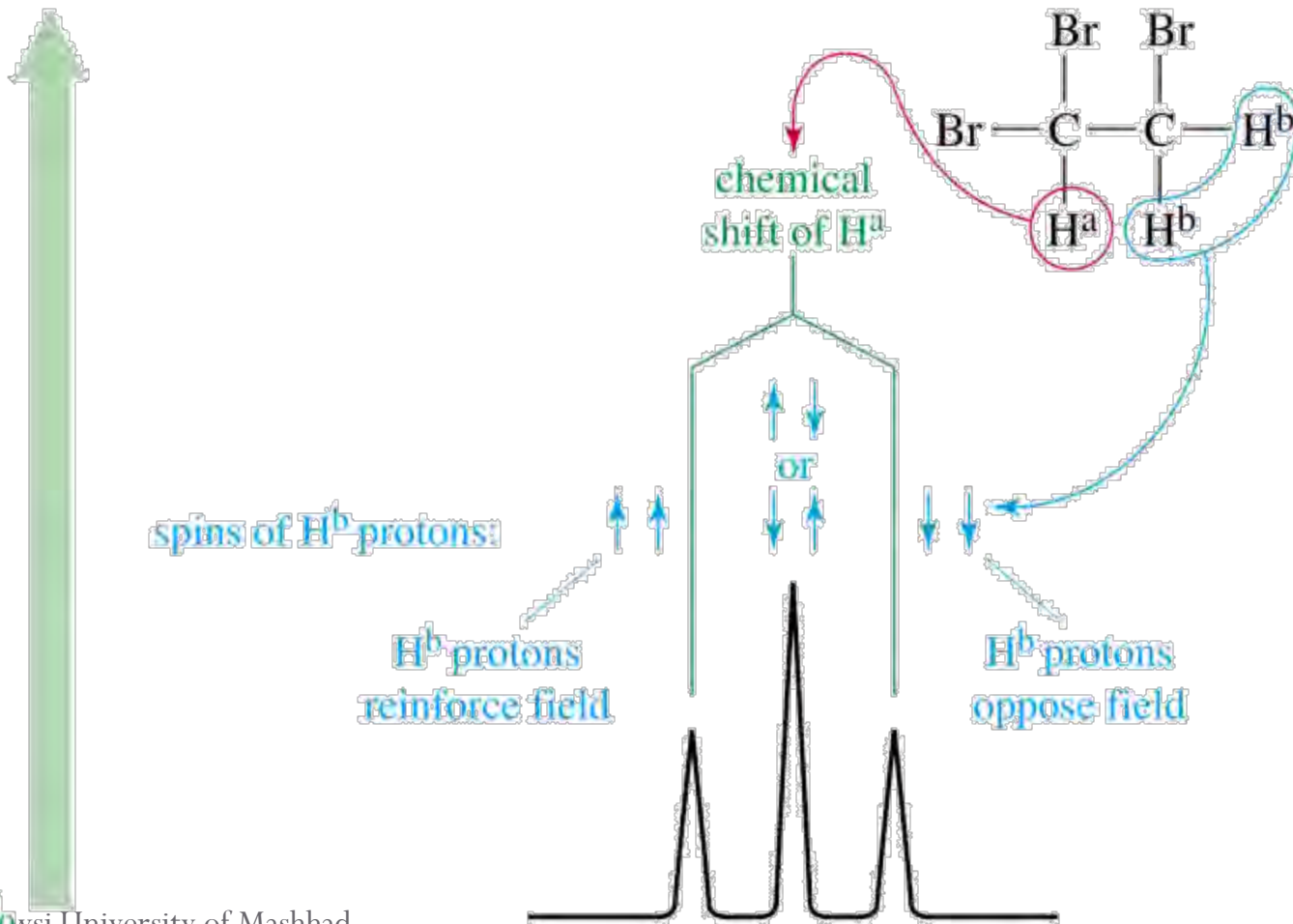
H_b can both be parallel, anti-parallel or one parallel and one anti-parallel

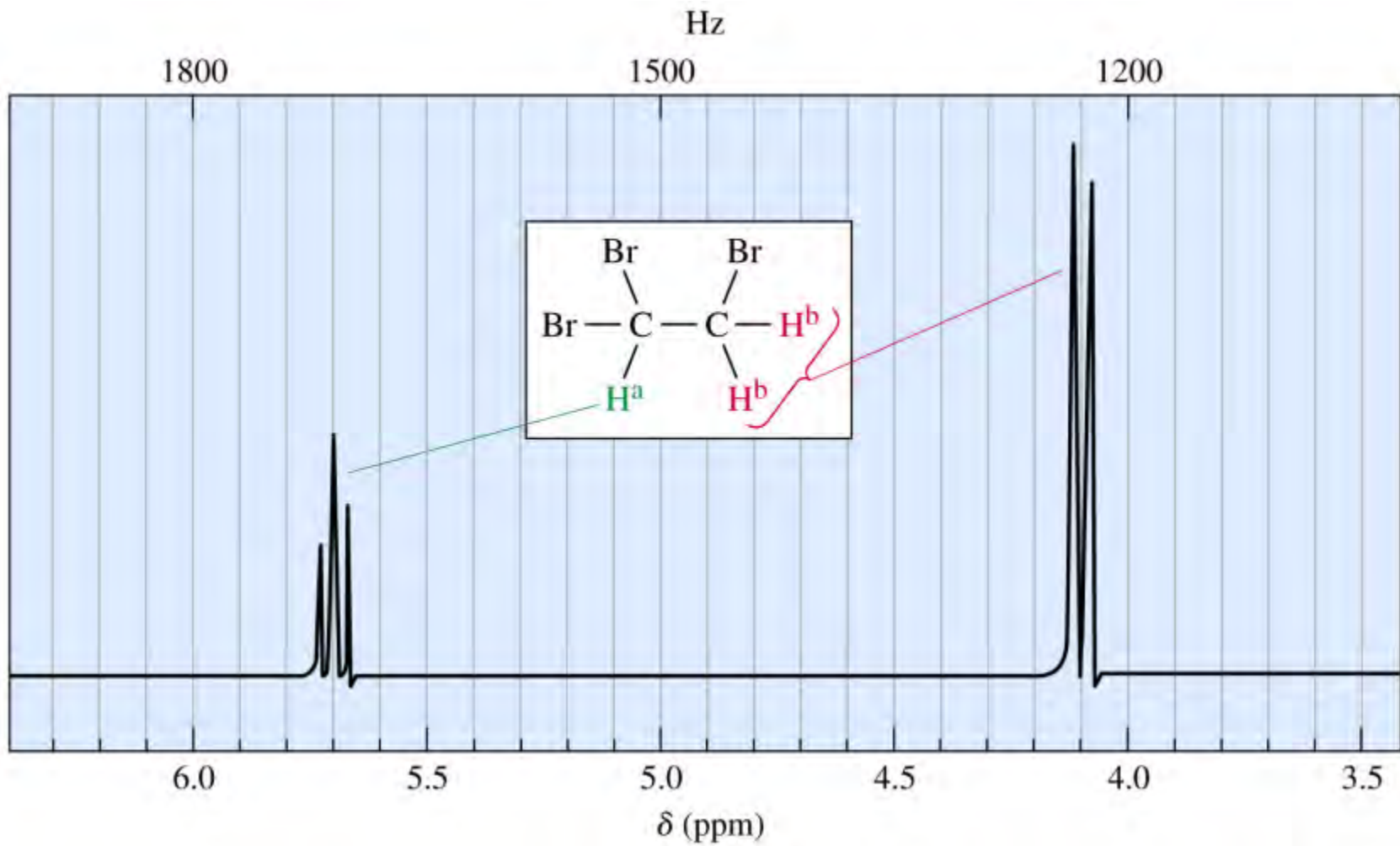
$\therefore \text{H}_a$ splits into a 1:2:1 **triplet** peak



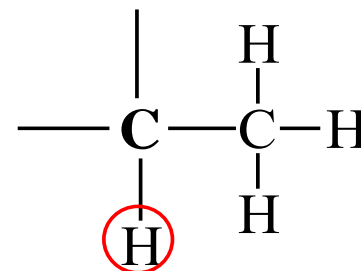
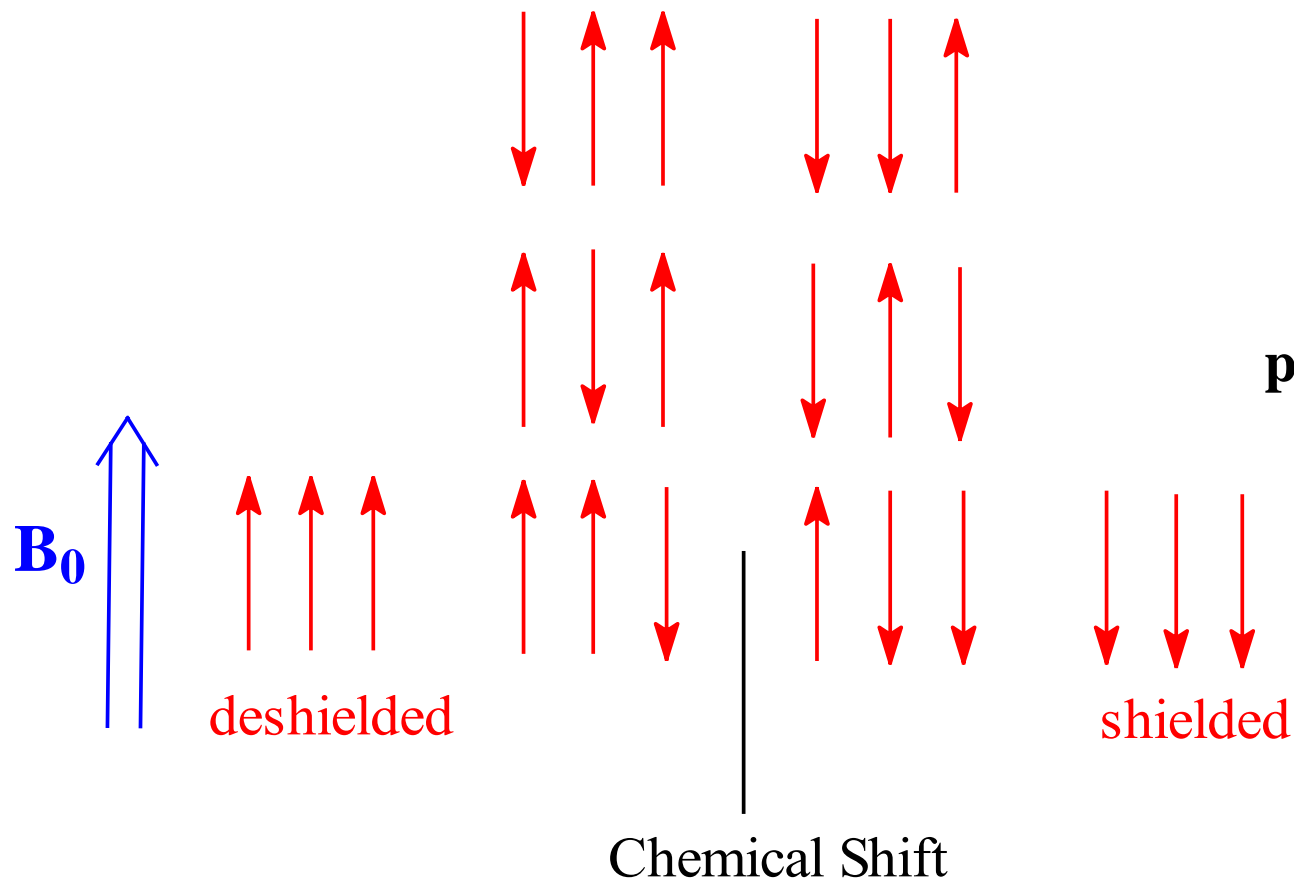


H_a in 1,1,2-Tribromoethane



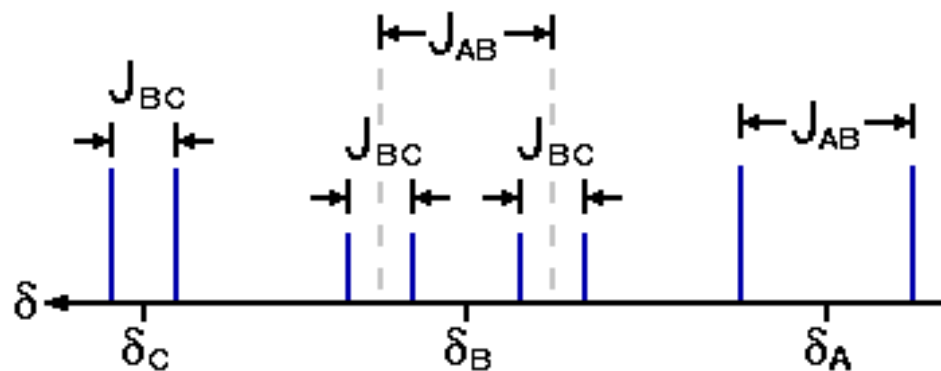
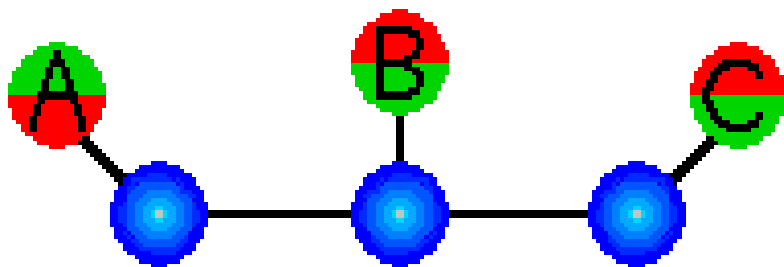


The Quartet in ^1HMR



proton splits into $n+1$
quartet **1:3:3:1**
 $n = \#$ adjacent H's

- When there are two different types of nuclei three bonds away there will be two values of J , one for each pair of nuclei. By now you get the idea of the number of possible configurations and the energy level diagram for these configurations, so we can skip to the spectrum. In the following example J_{AB} is greater J_{BC} .



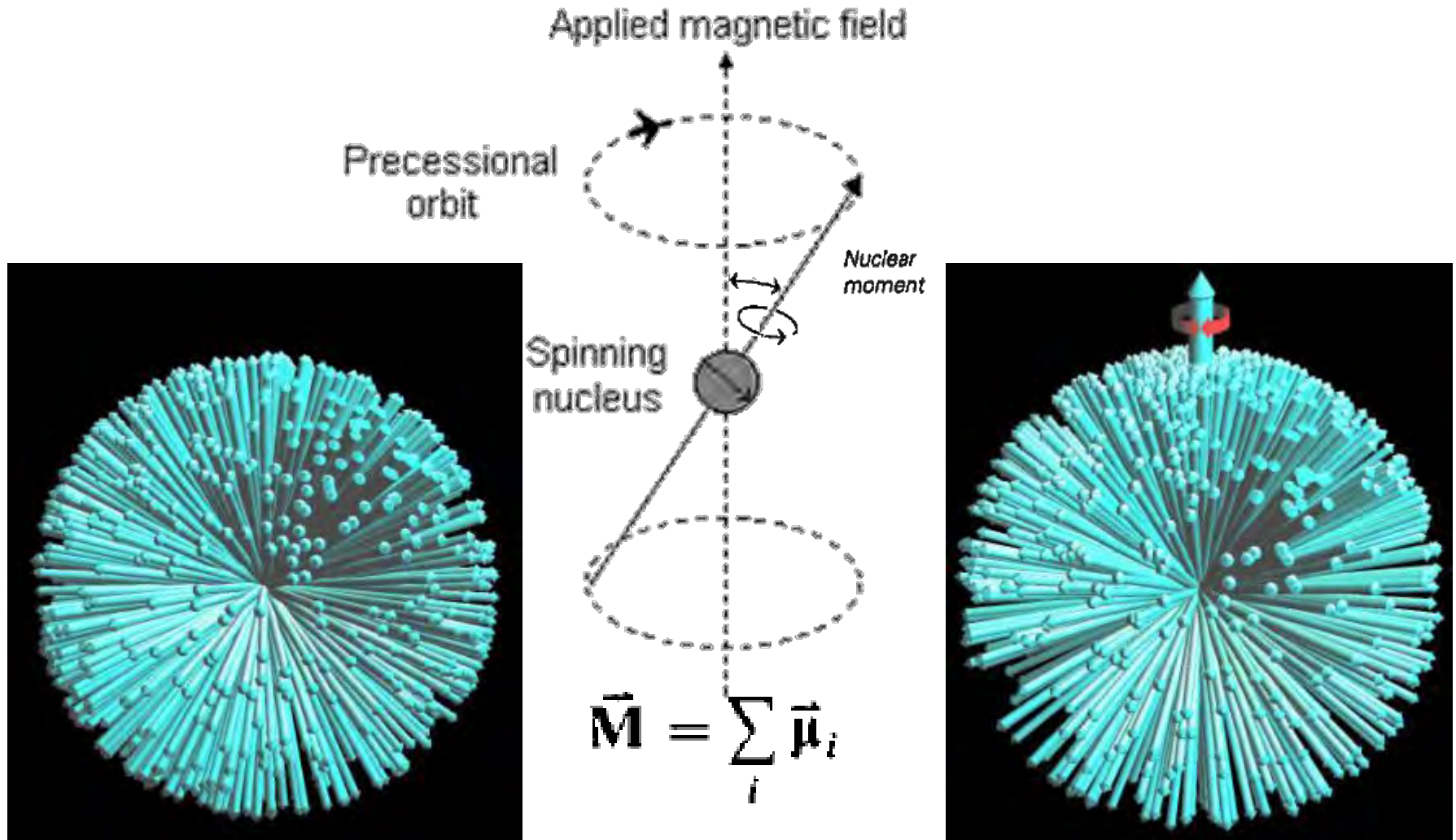
The $N + 1$ Rule

Relative Peak Intensities of Symmetric Multiplets		
Number of Equivalent Protons Causing Splitting	Number of Peaks (multiplicity)	Area Ratios (Pascal's triangle)
0	1 (singlet)	1
1	2 (doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

Spin-Spin Splitting Distance

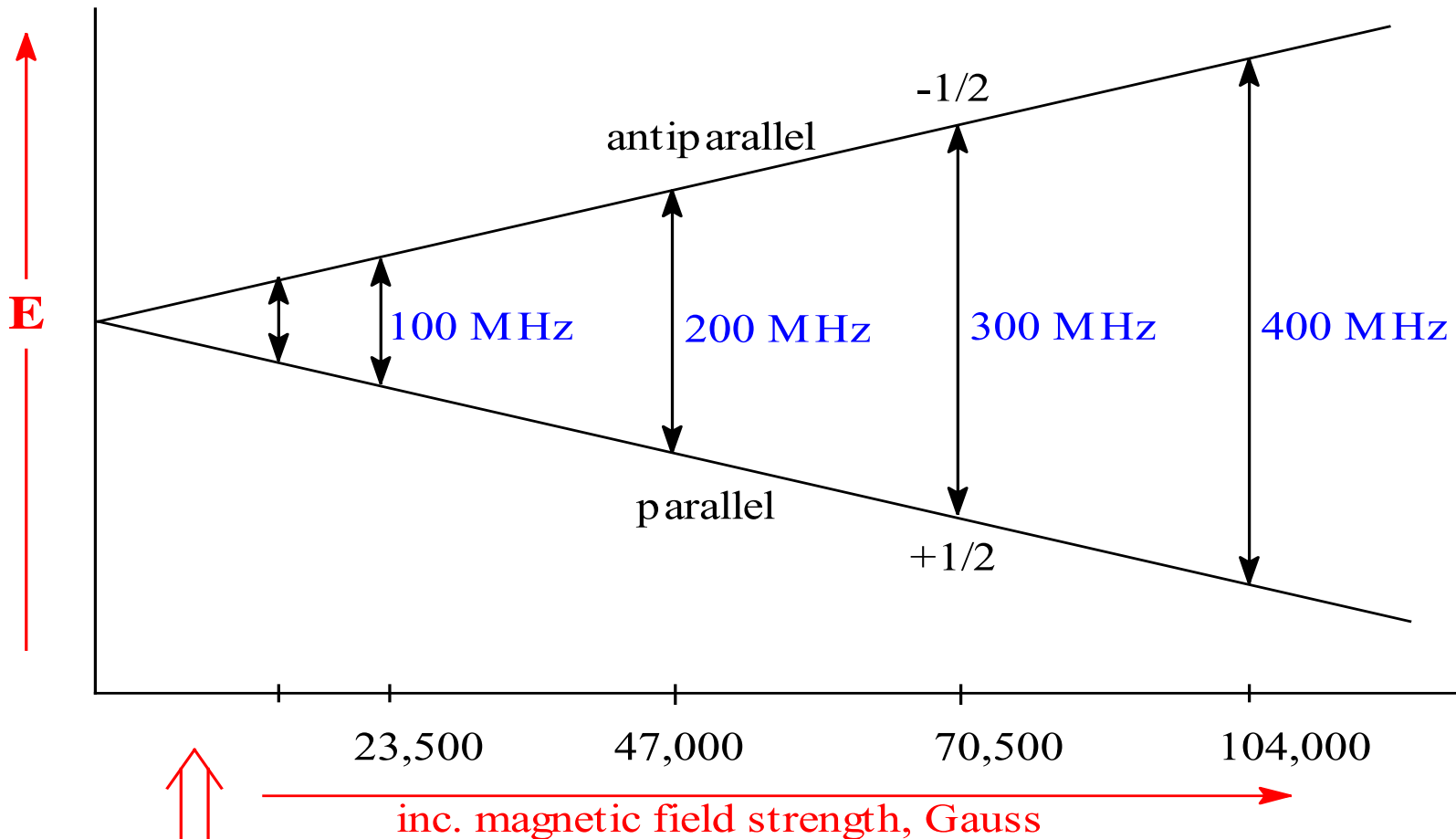
- Equivalent protons do not split each other.
- Protons bonded to the same carbon will split each other if they are nonequivalent.
- Protons on adjacent carbons normally will split each other.
- Protons separated by four or more bonds will rarely split each other.

Magnetization vector



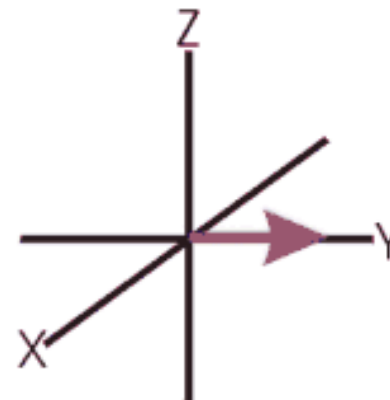
$$-\gamma \vec{H}_0 \times \vec{\mu} \quad \rightarrow \quad \dot{\vec{M}} = -\gamma \vec{H}_0 \times \vec{M}$$

$$|M_0| = \frac{N_0 \mu^2}{3kT} I(I + 1) H_0$$



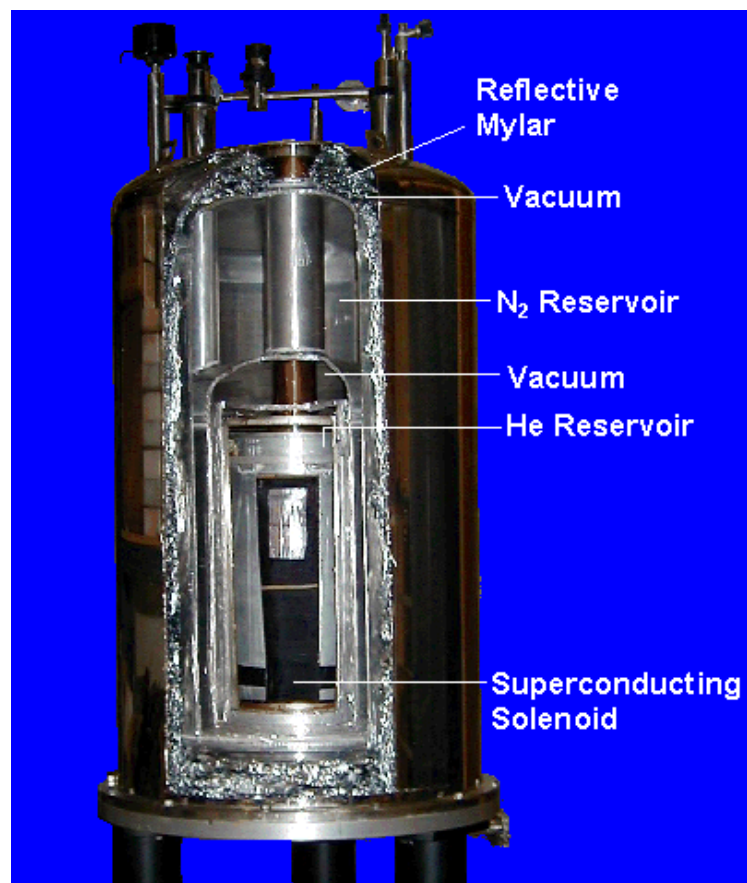
Self study

- **J-Coupling**

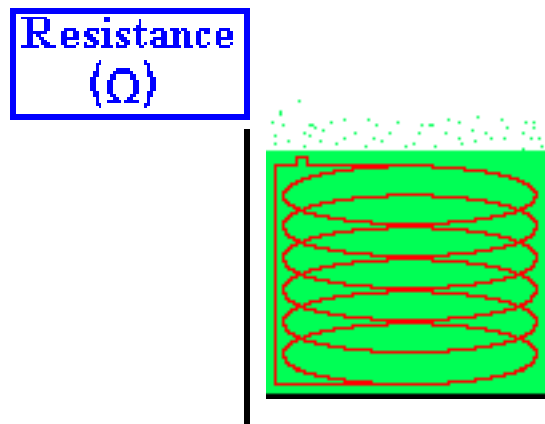


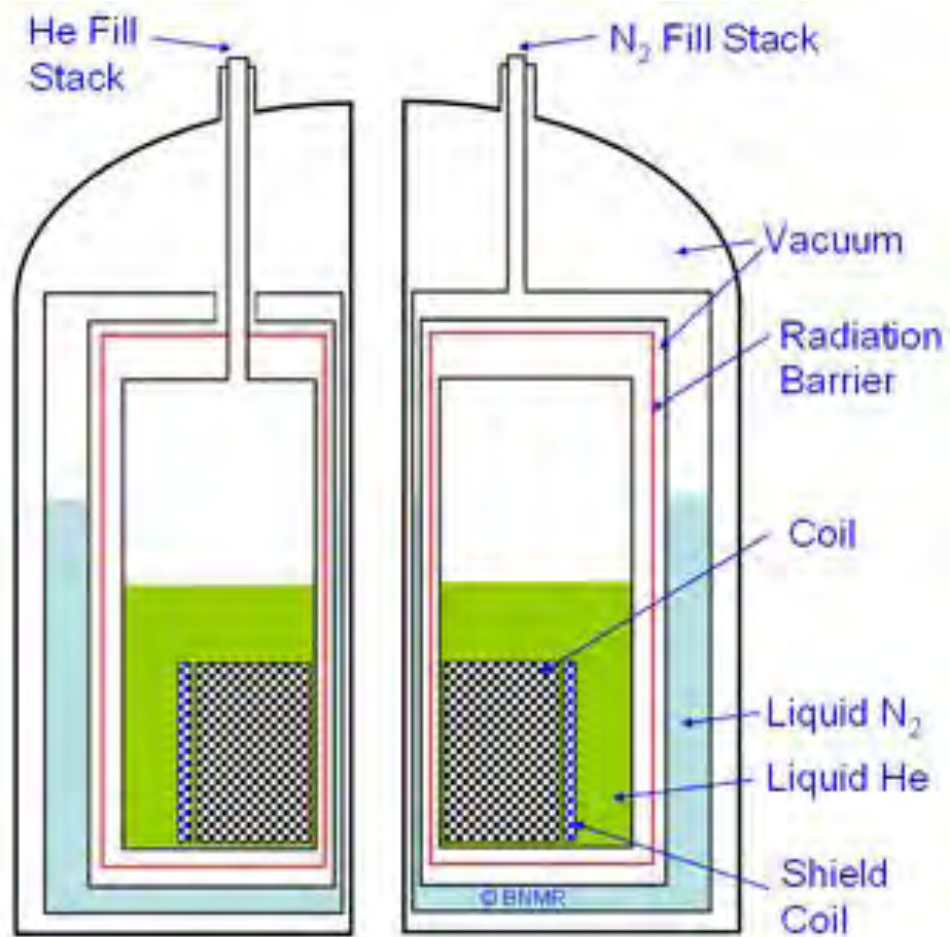
When spin A of a nucleus is coupled to a spin B, it can 'sense' the position of that spin in the B_0 field. If spin B is with the field, spin A resonates at a frequency different from when spin B is against the field. The population of A spins is therefore split into two. The red magnetisation vector represents one of these sub-populations and runs faster than the rotating frame; the blue one represents the other population and runs more slowly. The frequency difference between the vectors is the J-coupling. In $1/J$ seconds, each vector turns 180 degrees and they meet at the -Y axis.

NMR Experiment



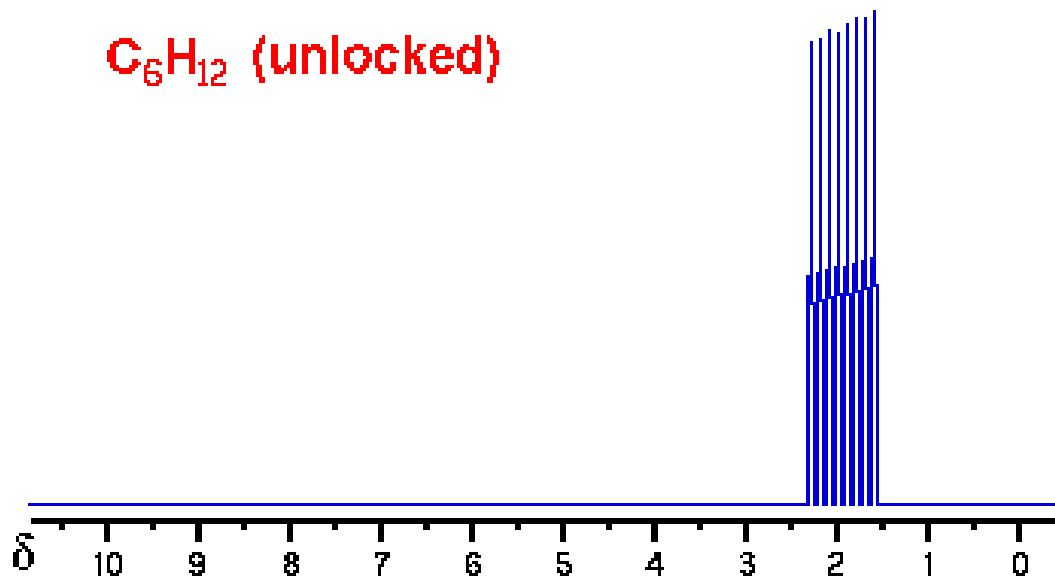
Magnet





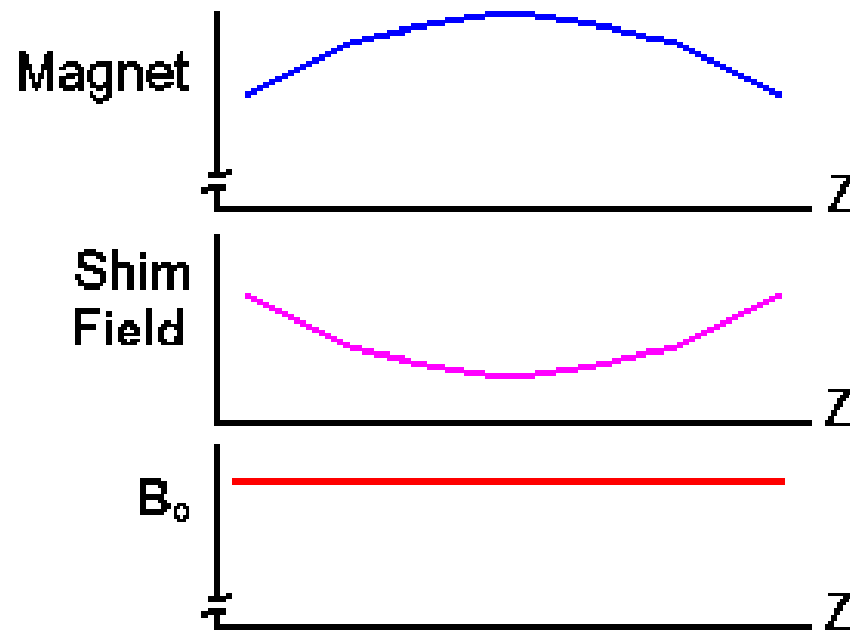
Field Lock

C_6H_{12} (unlocked)

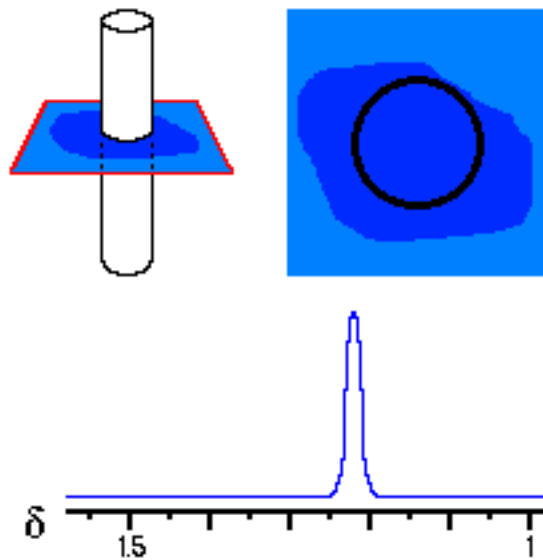


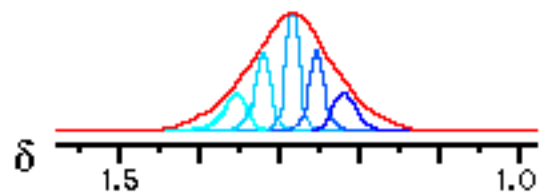
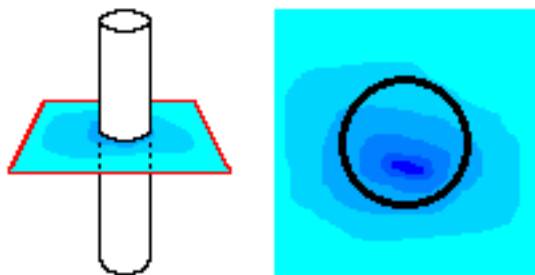
Shim Coils

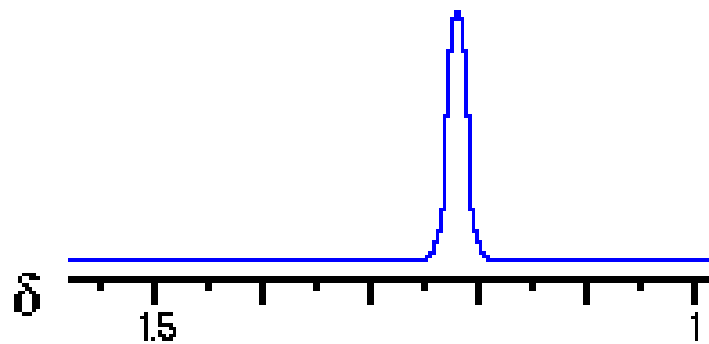
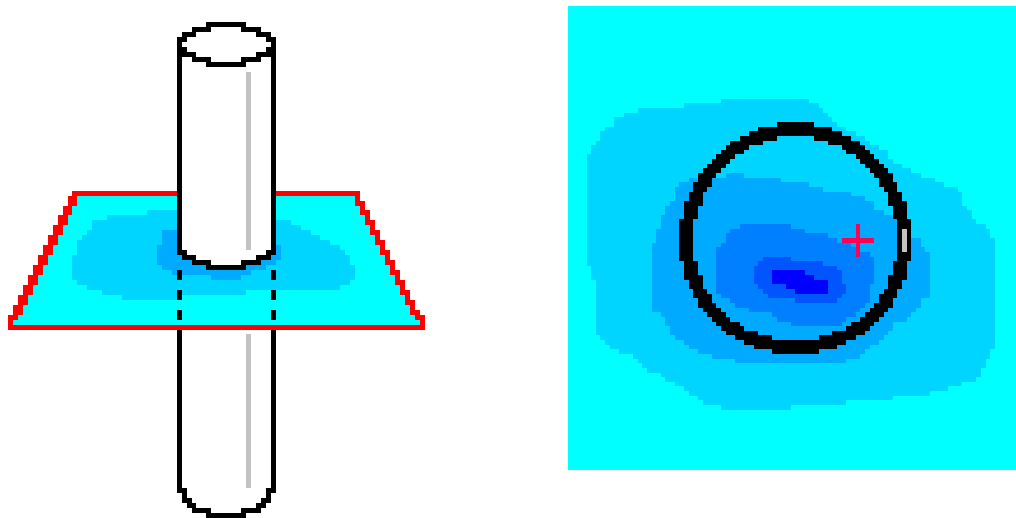
- The purpose of shim coils on a spectrometer is to correct minor spatial inhomogeneities in the B_0 magnetic field

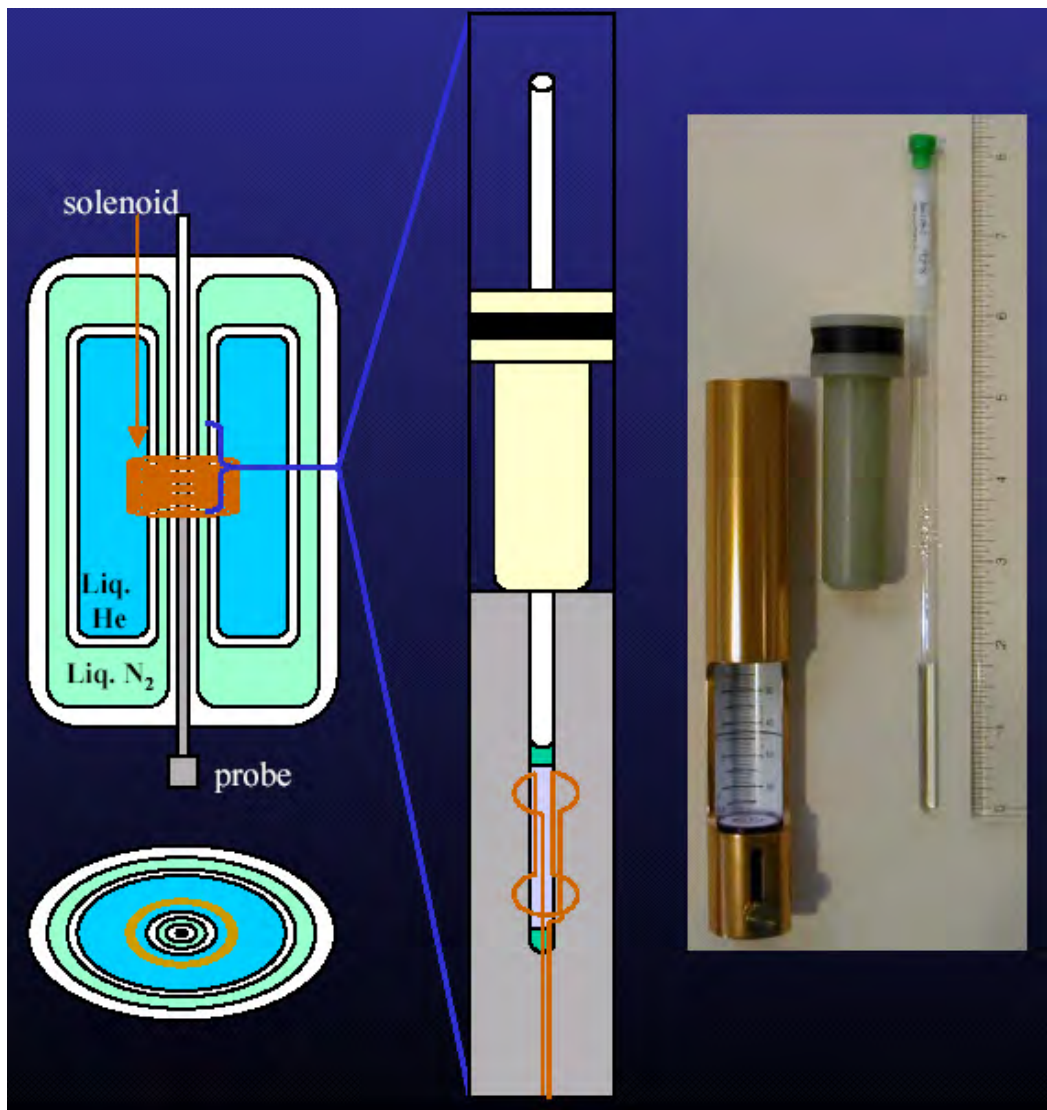
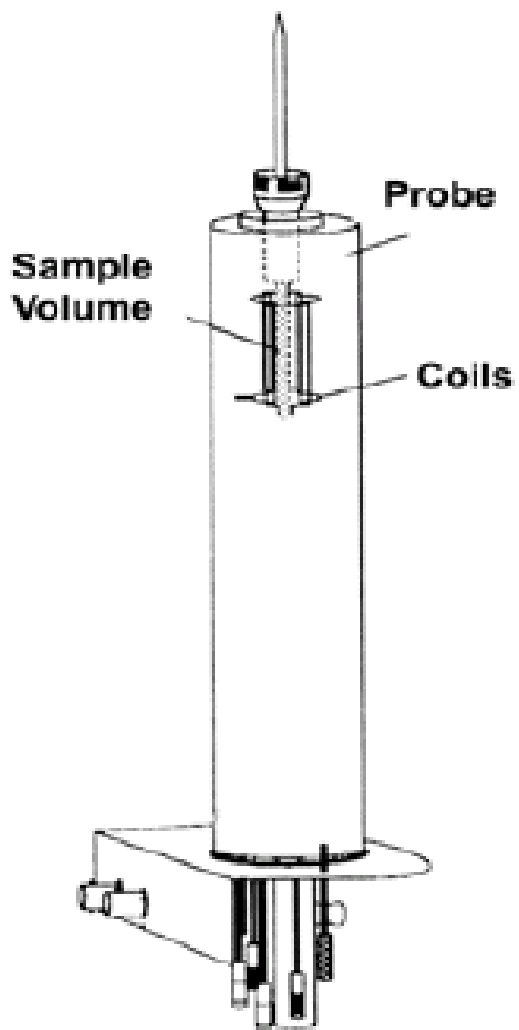


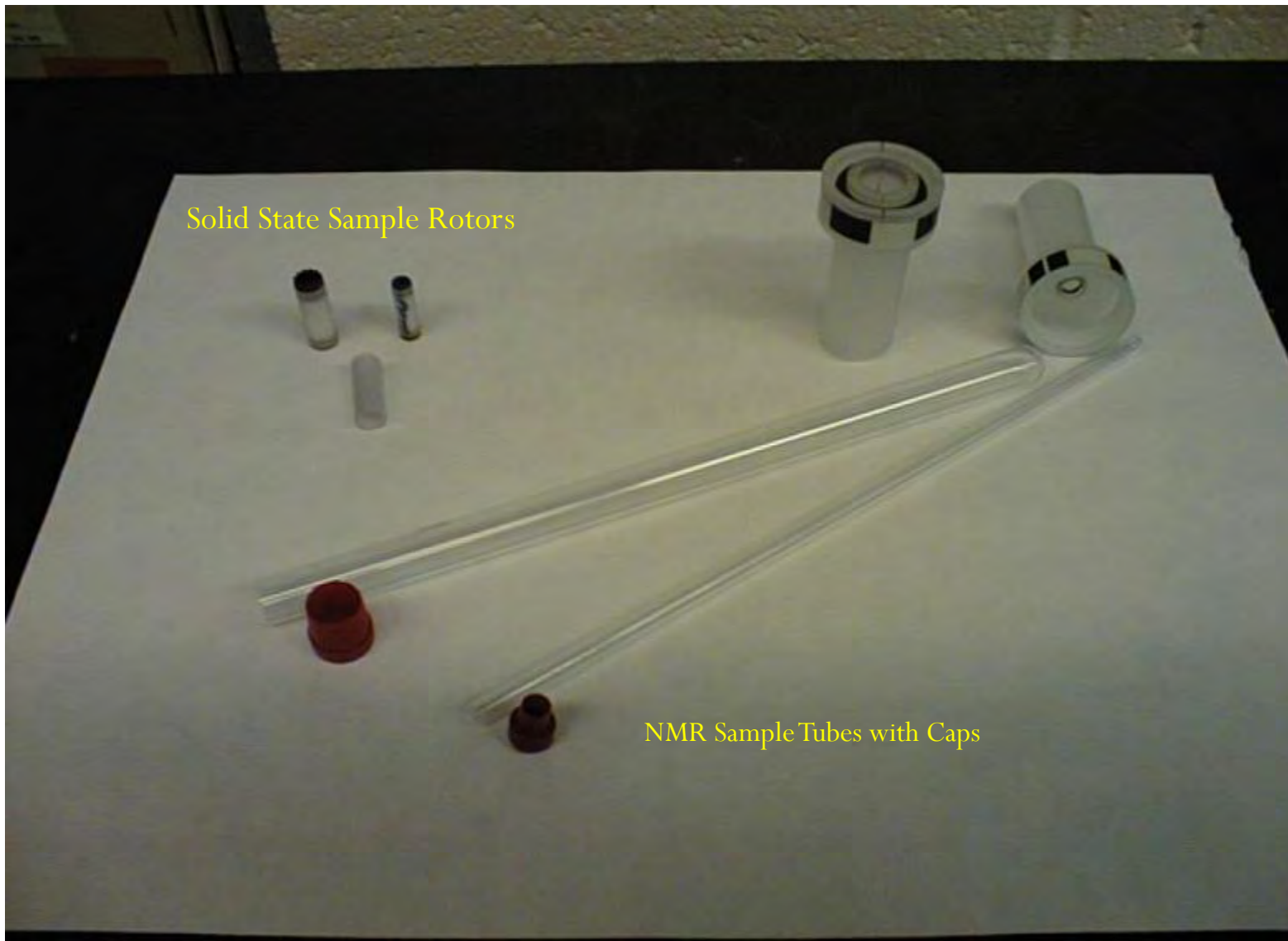
Sample Probe









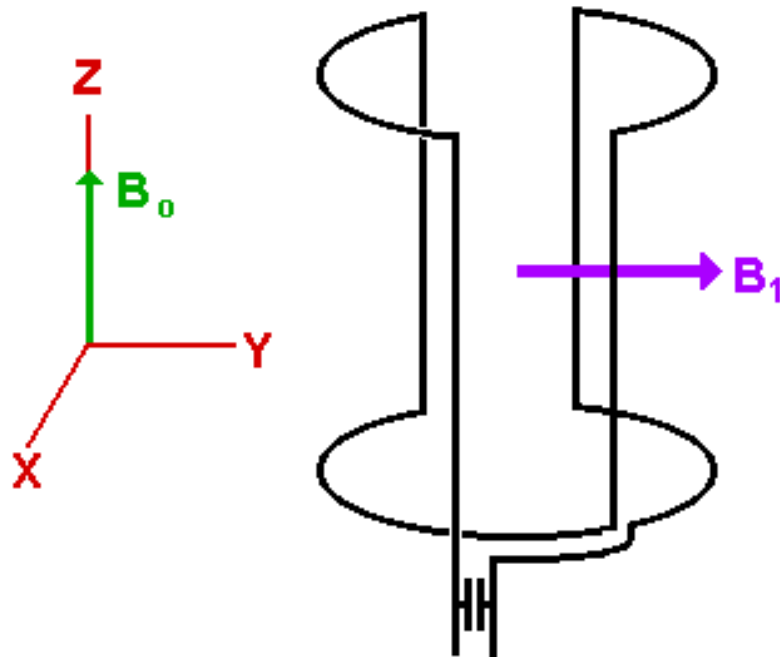


Solid State Sample Rotors

NMR Sample Tubes with Caps

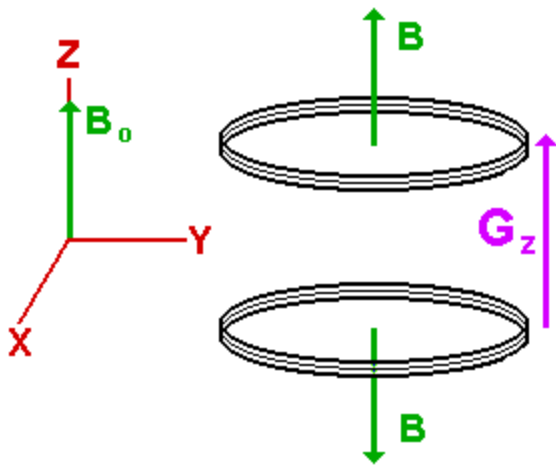
RF Coils

Saddle Coil

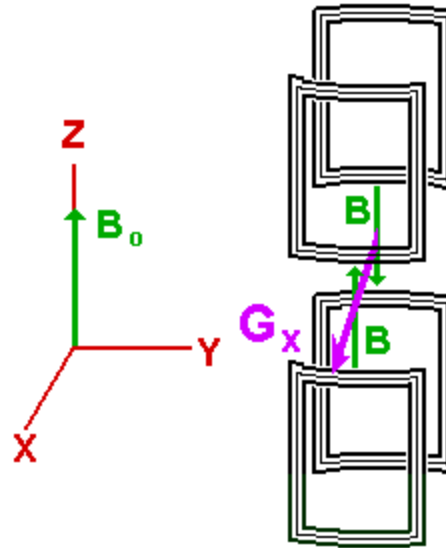


Gradient Coils

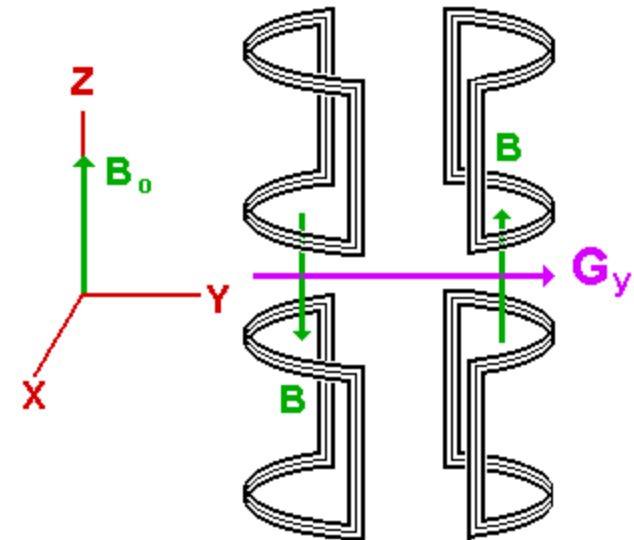
Z Gradient Coil



X Gradient Coil

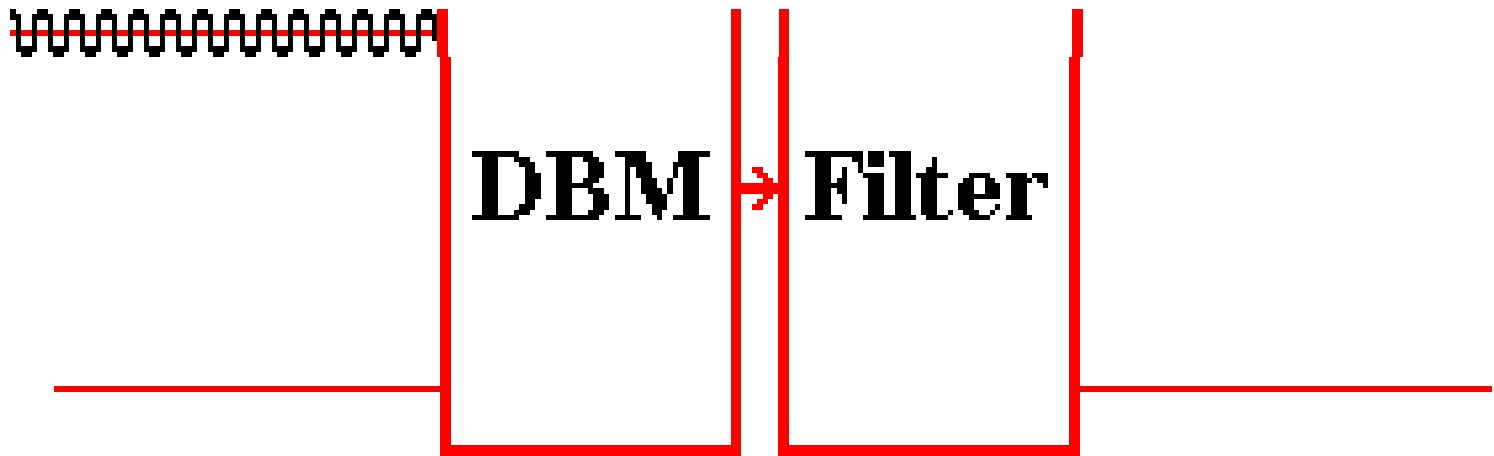


Y Gradient Coil

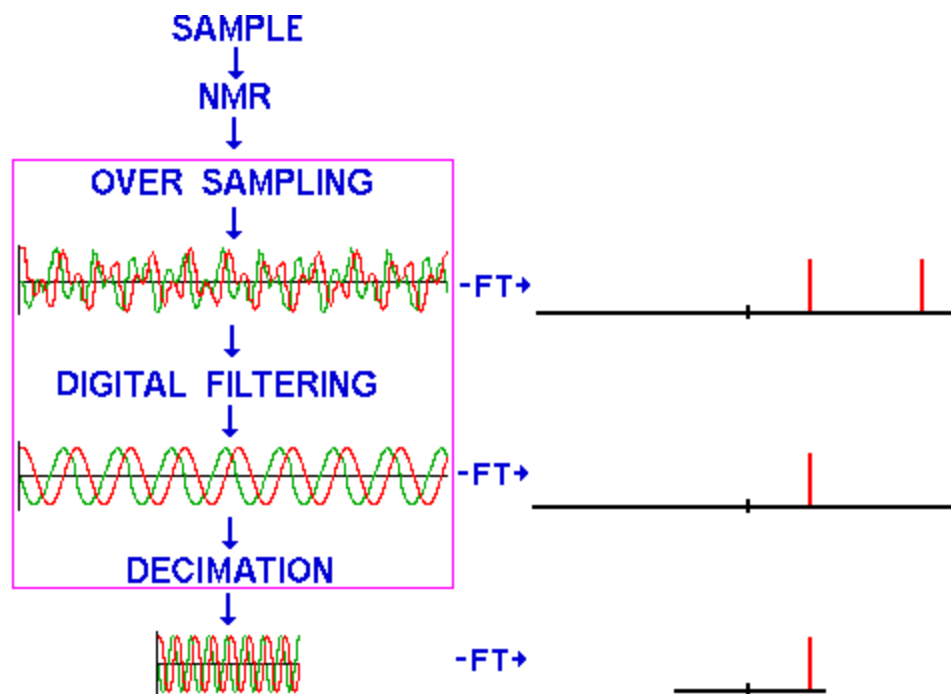


Quadrature Detector

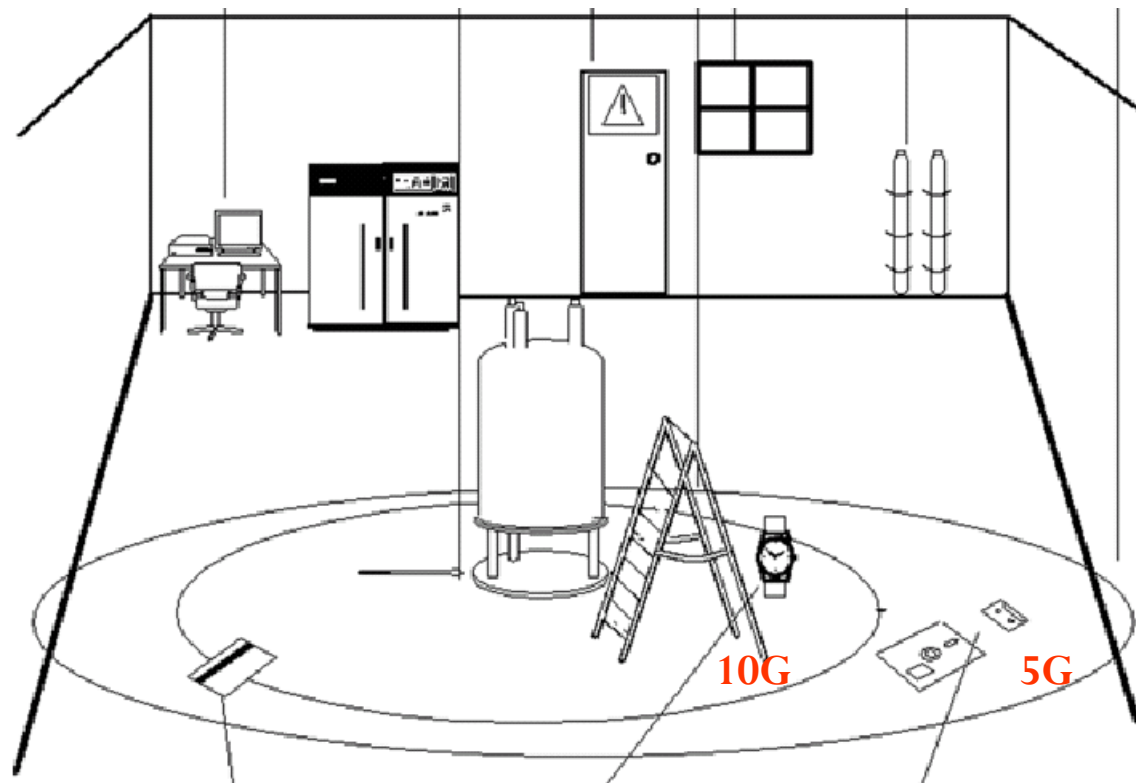
- The quadrature detector is a device which separates out the M_x and M_y signals from the signal from the RF coil.



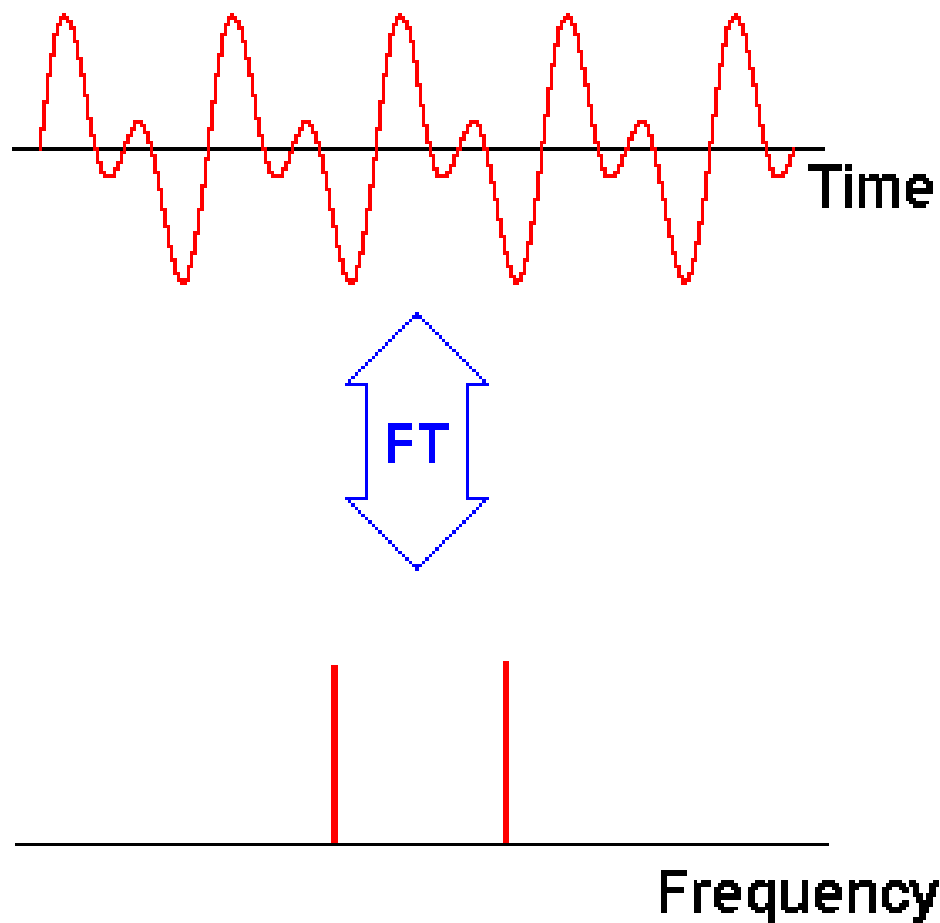
Digital Filtering



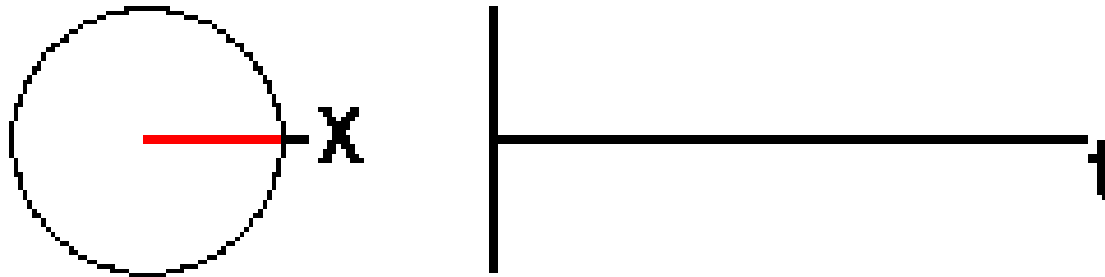
**Safety Precautions:
Very Very
Strong Magnetic Field!**



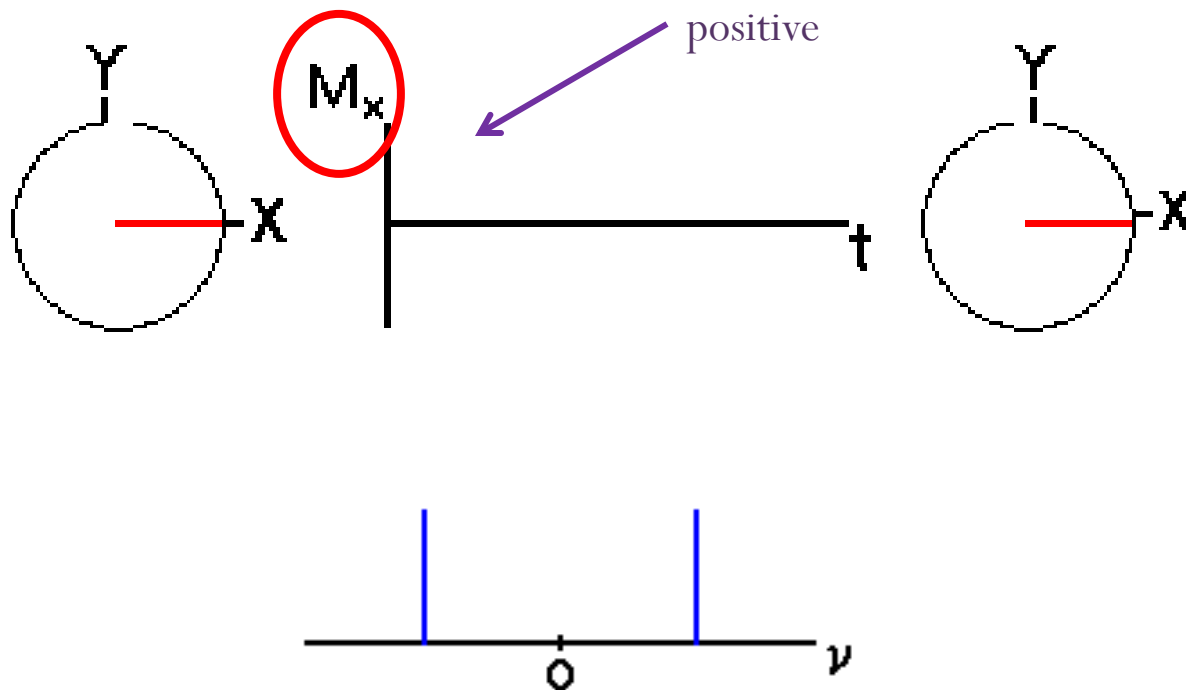
FOURIER TRANSFORMS



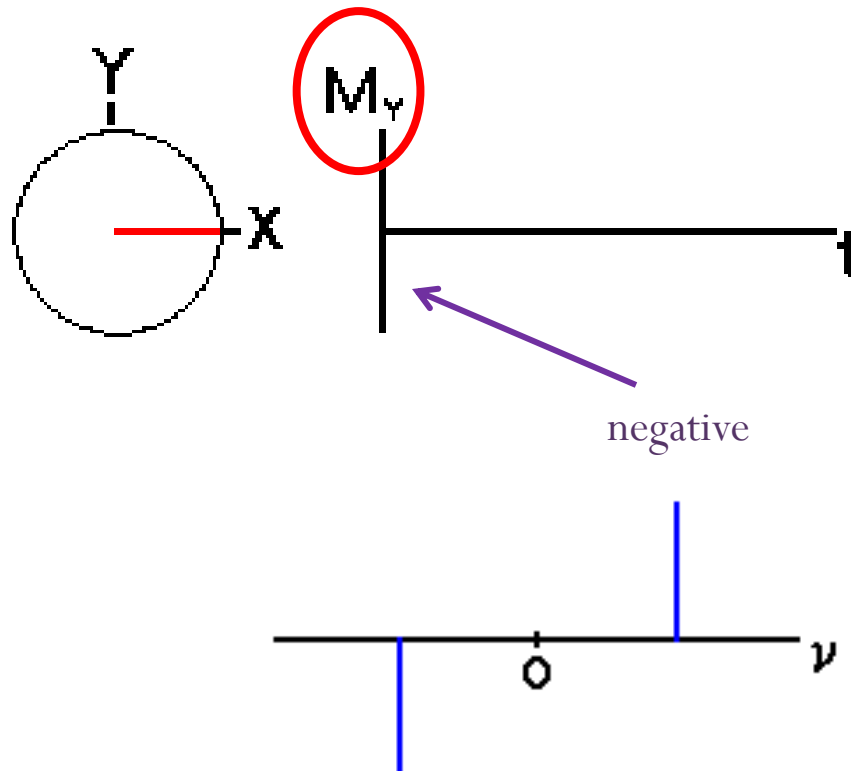
- A magnetization vector, starting at $+x$, is rotating about the Z axis in a clockwise direction. The plot of M_x as a function of time is a cosine wave.



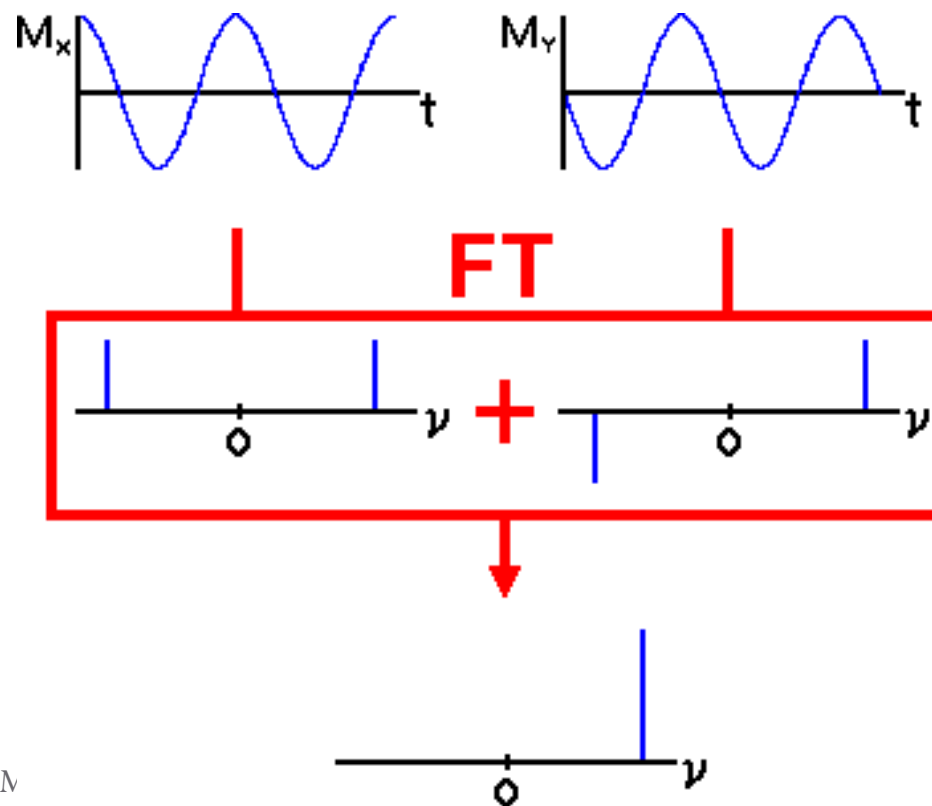
- Fourier transforming this gives peaks at both $+$ and $-$ because the FT can not distinguish between a $+$ and a $-$ rotation of the vector from the data supplied



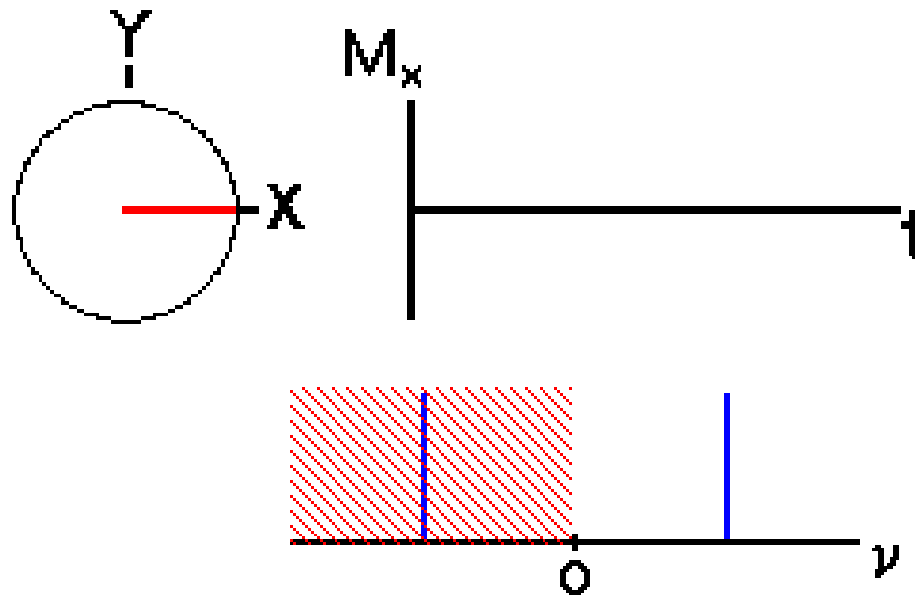
- Fourier transforming this gives peaks at $+$ and $-$ because the FT can not distinguish between a positive vector rotating at $+$ and a negative vector rotating at $-$ from the data supplied.



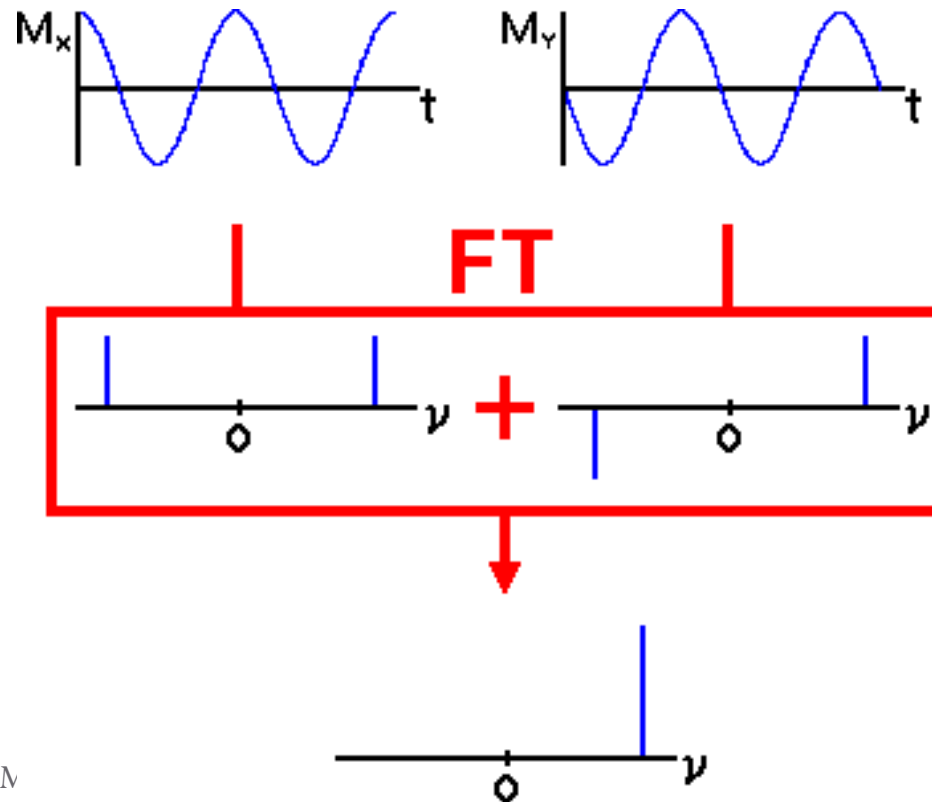
- The solution is to input both the M_x and M_y into the FT. The FT is designed to handle two orthogonal input functions called the real and imaginary components.



- Detecting just the M_x or M_y component for input into the FT is called linear detection. This was the detection scheme on many older NMR spectrometers and some magnetic resonance imagers. It required the computer to discard half of the frequency domain data



- Detection of both M_x and M_y is called quadrature detection and is the method of detection on modern spectrometers and imagers. It is the method of choice since now the FT can distinguish between + and -, and all of the frequency domain data be used.



An FT is defined by the integral

$$f(\omega) = \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} dt = \int_{-\infty}^{+\infty} f(t) [\cos(\omega t) - i \sin(\omega t)] dt$$

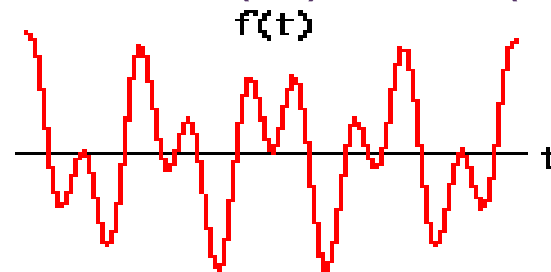
Think of $f(\omega)$ as the overlap of $f(t)$ with a wave of frequency

$$\cdot \quad f(\omega) = \sum_{-\infty}^{+\infty} f(t) [\cos(\omega t) - i \sin(\omega t)]$$

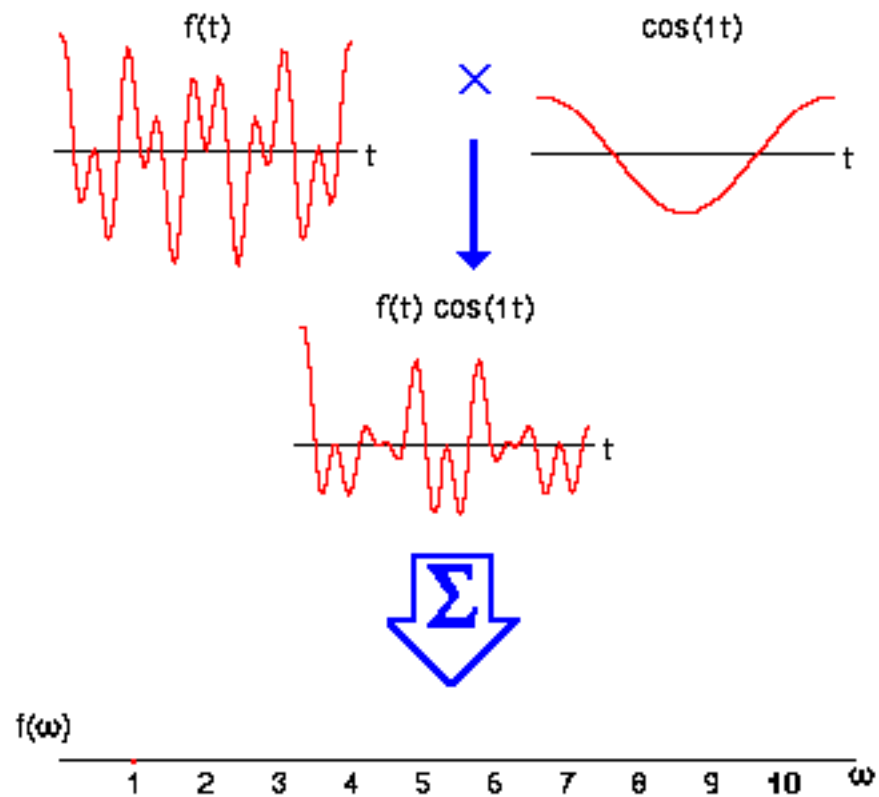
This is easy to picture by looking at the real part of $f(\omega)$ only .

$$f(\omega) = \sum_{-\infty}^{+\infty} f(t) \cos(\omega t)$$

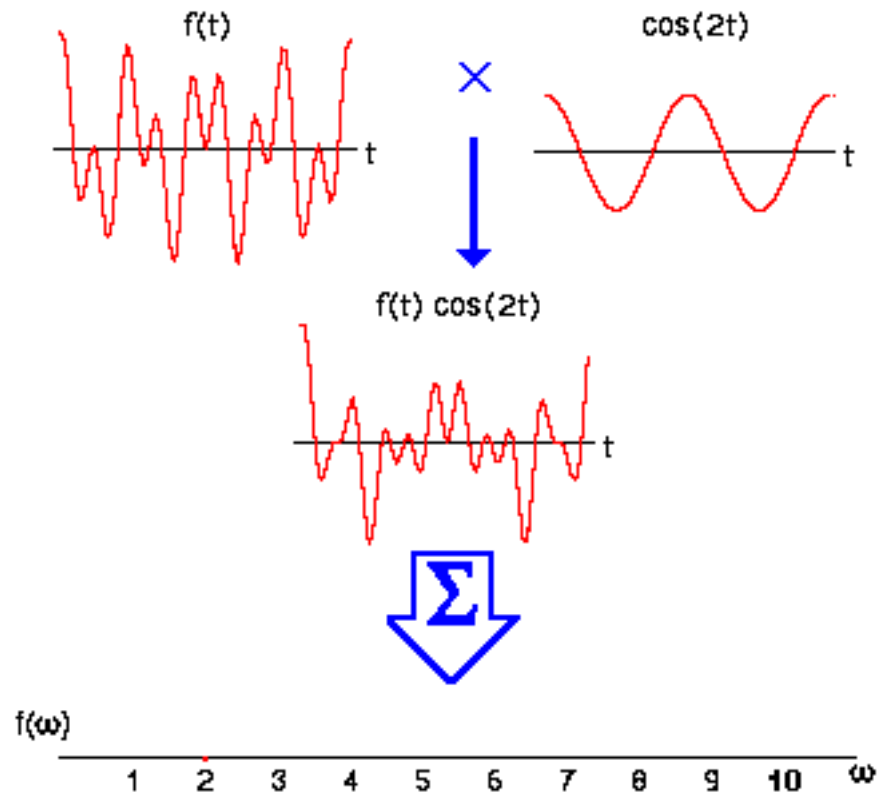
Consider the function of time, $f(t) = \cos(4t) + \cos(9t)$



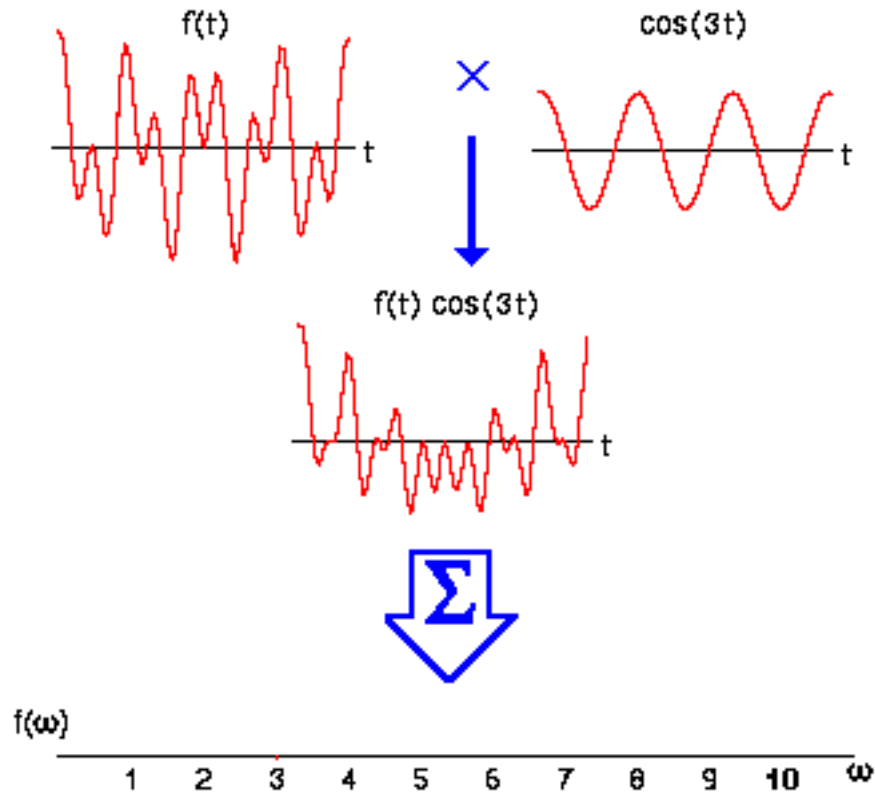
$$\omega = 1$$



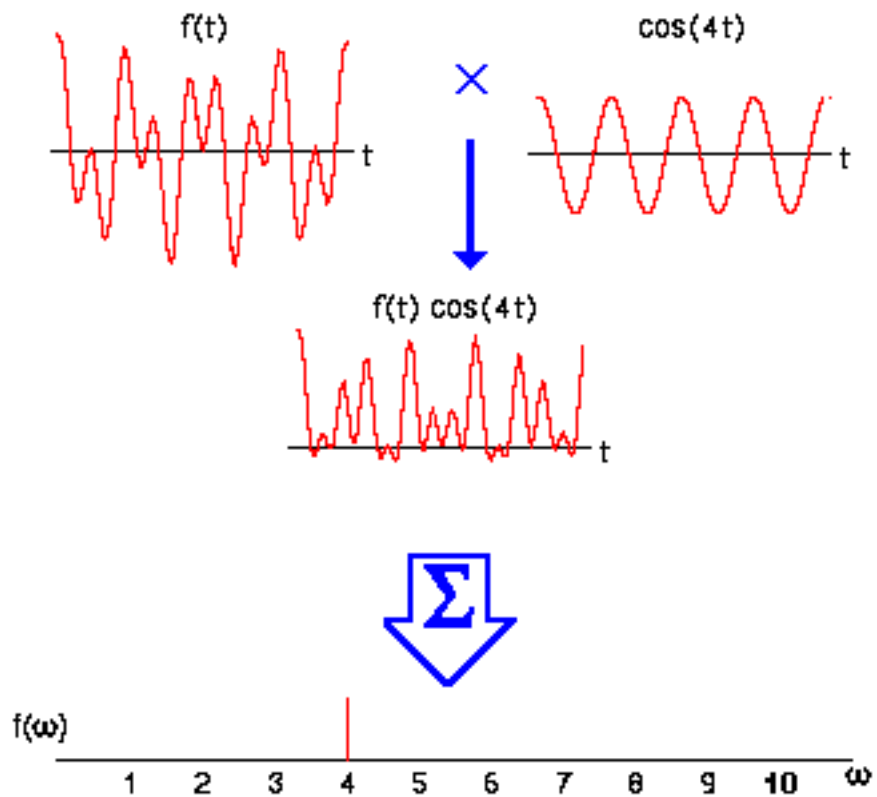
$$\omega = 2$$



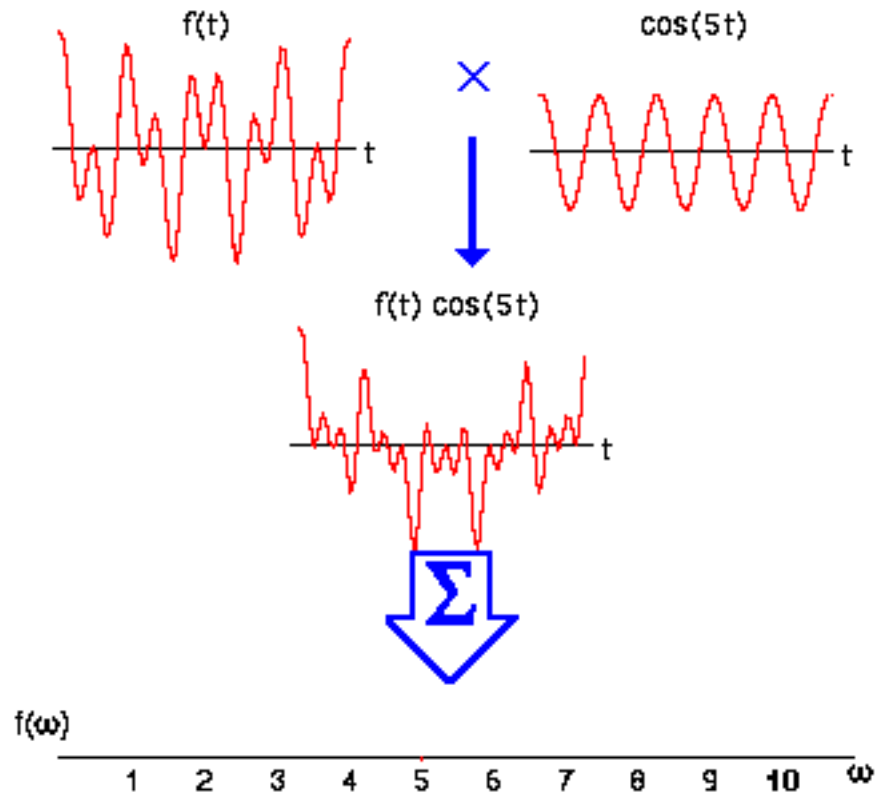
$$\omega = 3$$



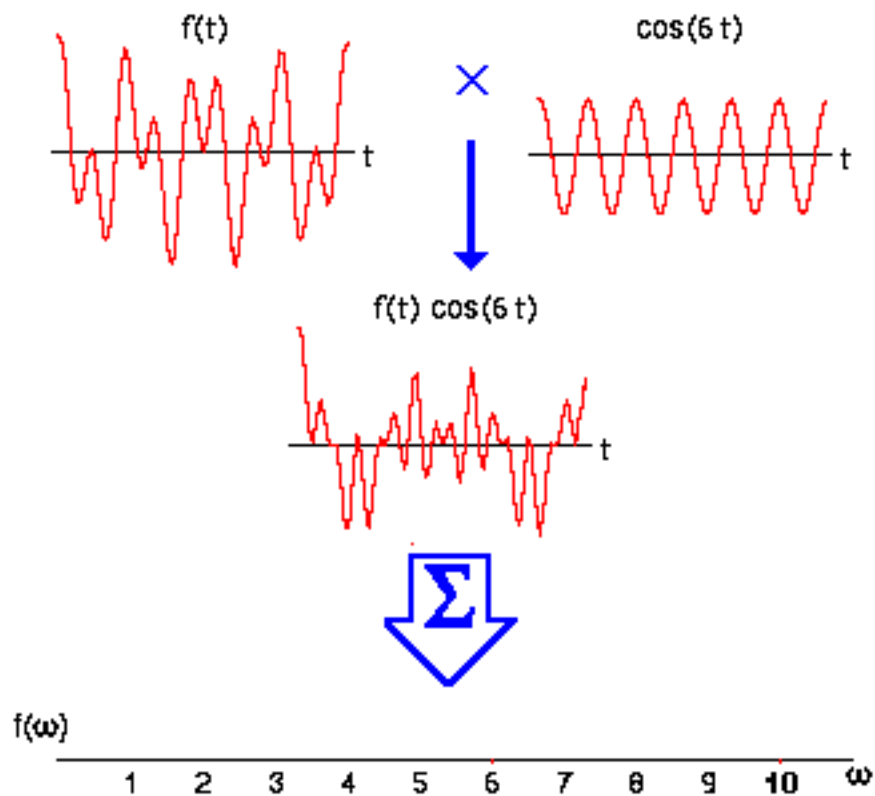
$$\omega = 4$$



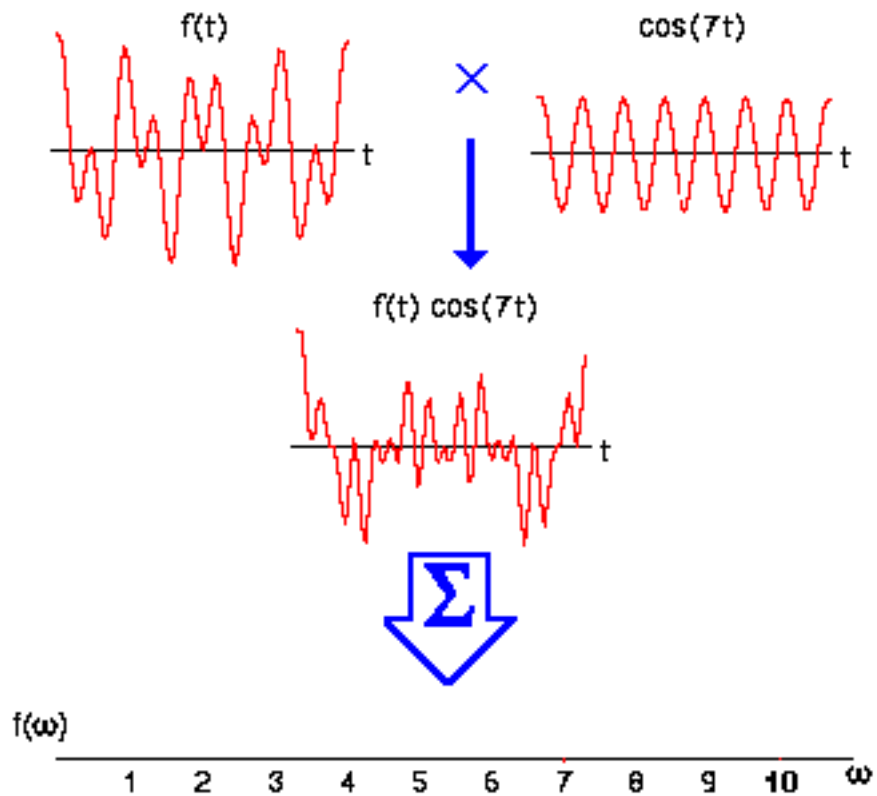
$$\omega = 5$$



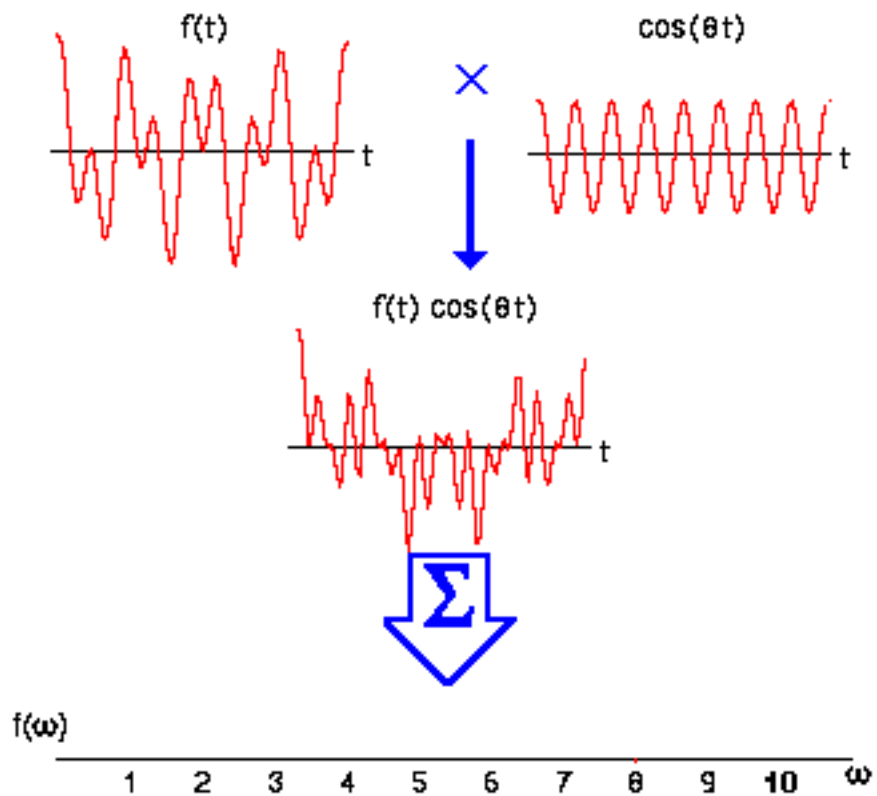
$$\omega = 6$$



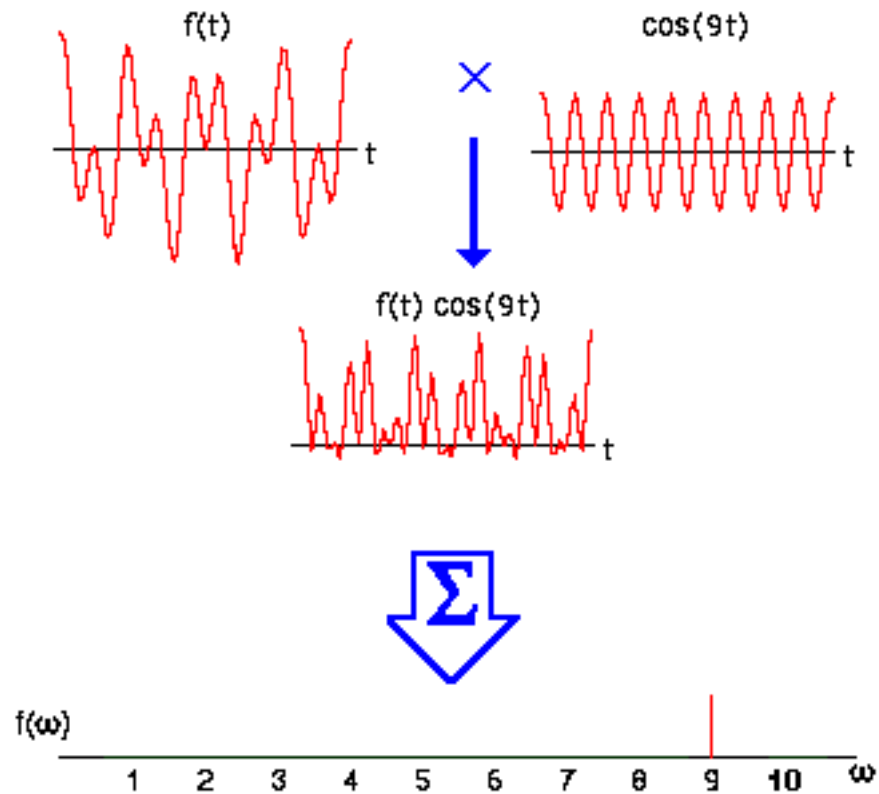
$$\omega = 7$$



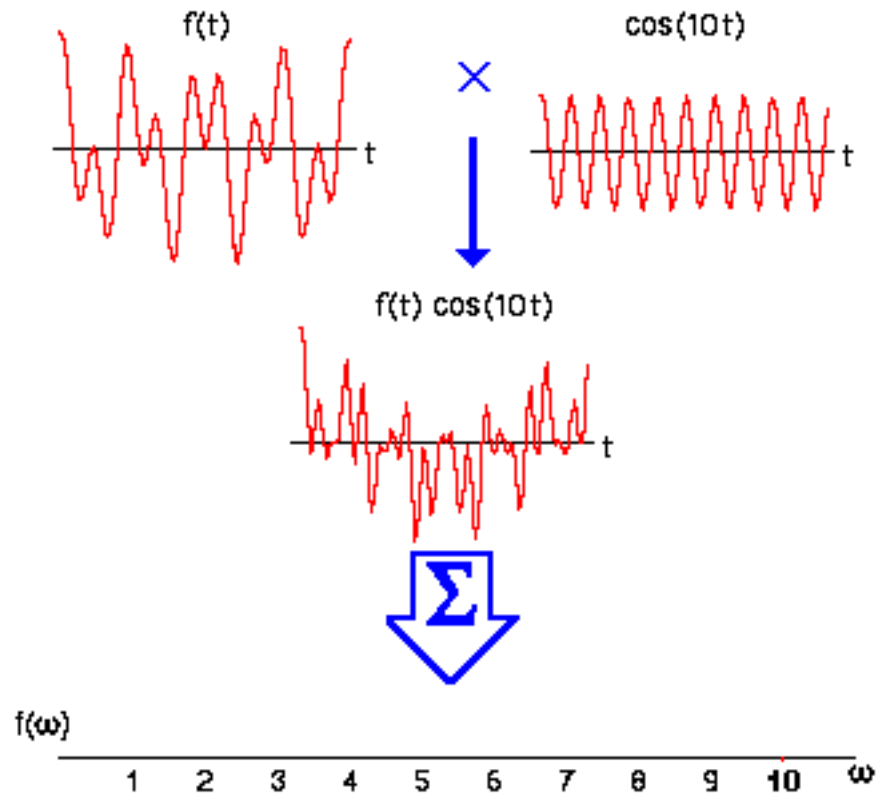
$$\omega = 8$$



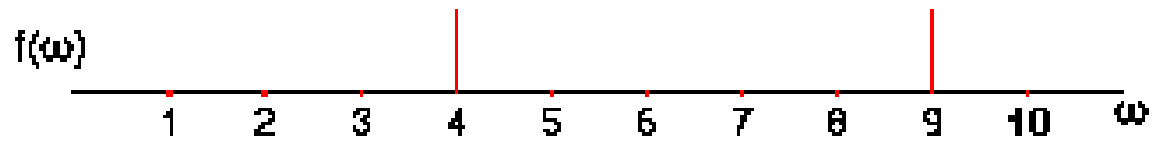
$$\omega = 9$$



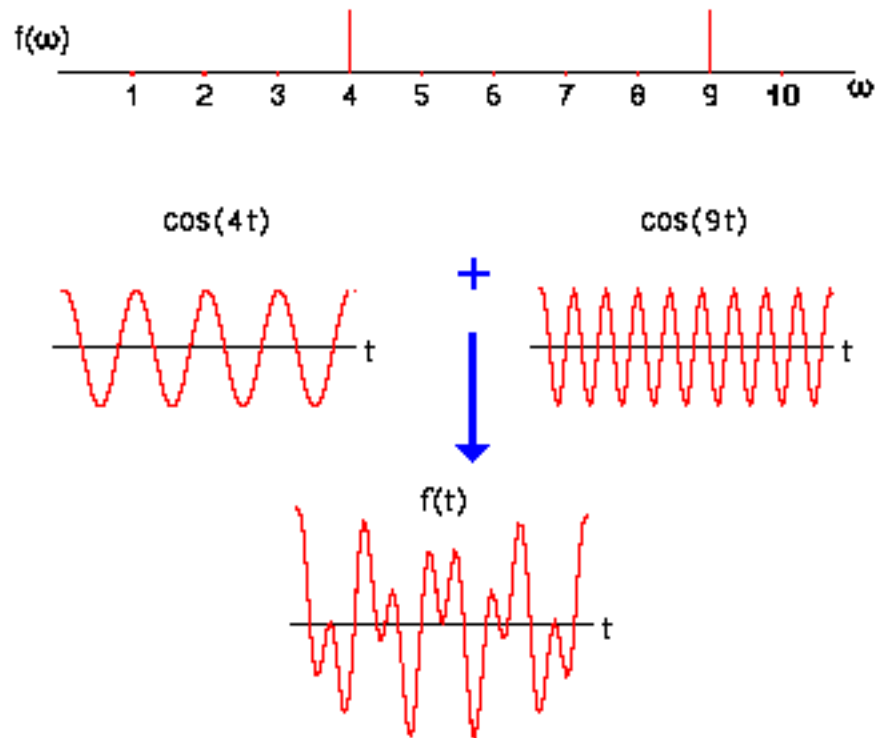
$$\omega = 10$$



$f(\omega)$



- The inverse Fourier transform (IFT) is best depicted as an summation of the time domain spectra of frequencies in $f(\omega)$

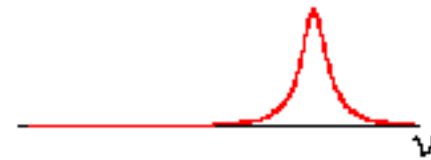
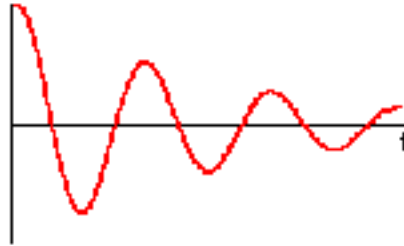


Phase Correction

- The actual FT will make use of an input consisting of a REAL and an IMAGINARY part. You can think of M_x as the REAL input, and M_y as the IMAGINARY input. The resultant output of the FT will therefore have a REAL and an IMAGINARY component, too.

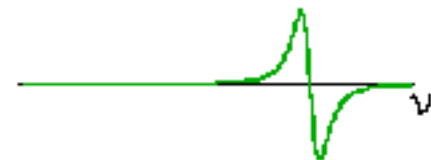
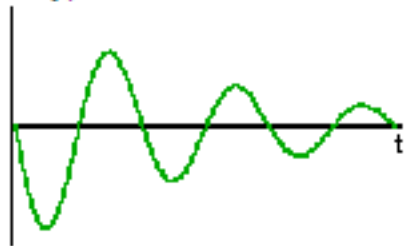
$$f(t) = e^{-at} e^{-i2\pi nt} \blacksquare$$

M_x (Real)



FT

M_y (Imaginary)



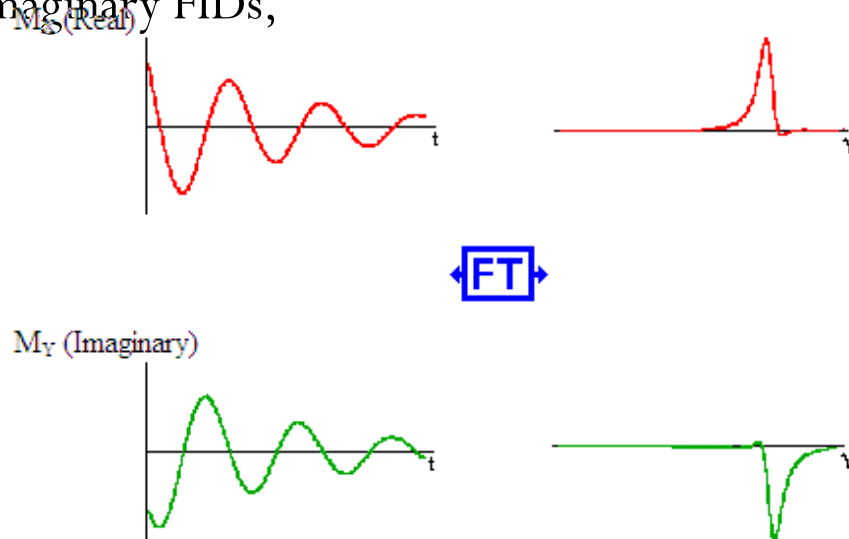
NMR

93/01/20

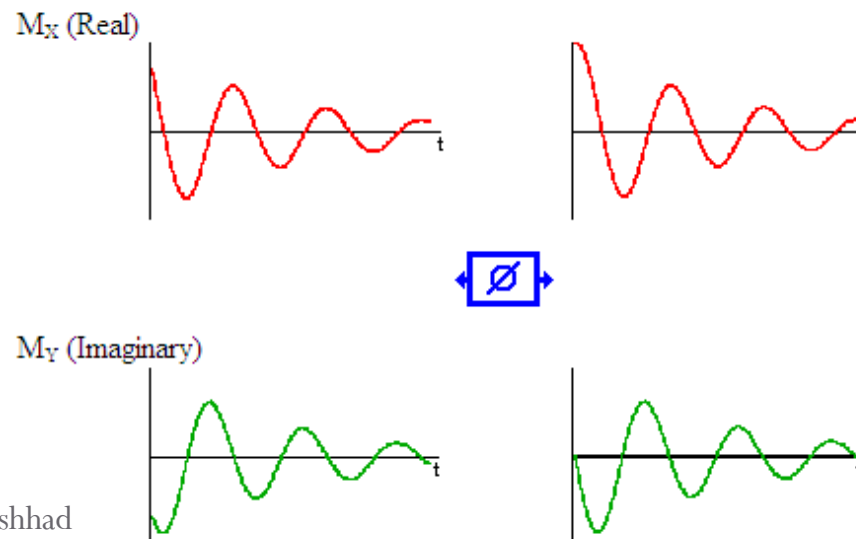
- In an ideal NMR experiment all frequency components contained in the recorded FID have no phase shift. In practice, during a real NMR experiment a phase correction must be applied to either the time or frequency domain spectra to obtain an absorption spectrum as the real output of the FT.

$$\begin{bmatrix} RE'' \\ IM'' \end{bmatrix} = \begin{bmatrix} \cos(\phi) & \sin(\phi) \\ -\sin(\phi) & \cos(\phi) \end{bmatrix} \begin{bmatrix} RE \\ IM \end{bmatrix}$$

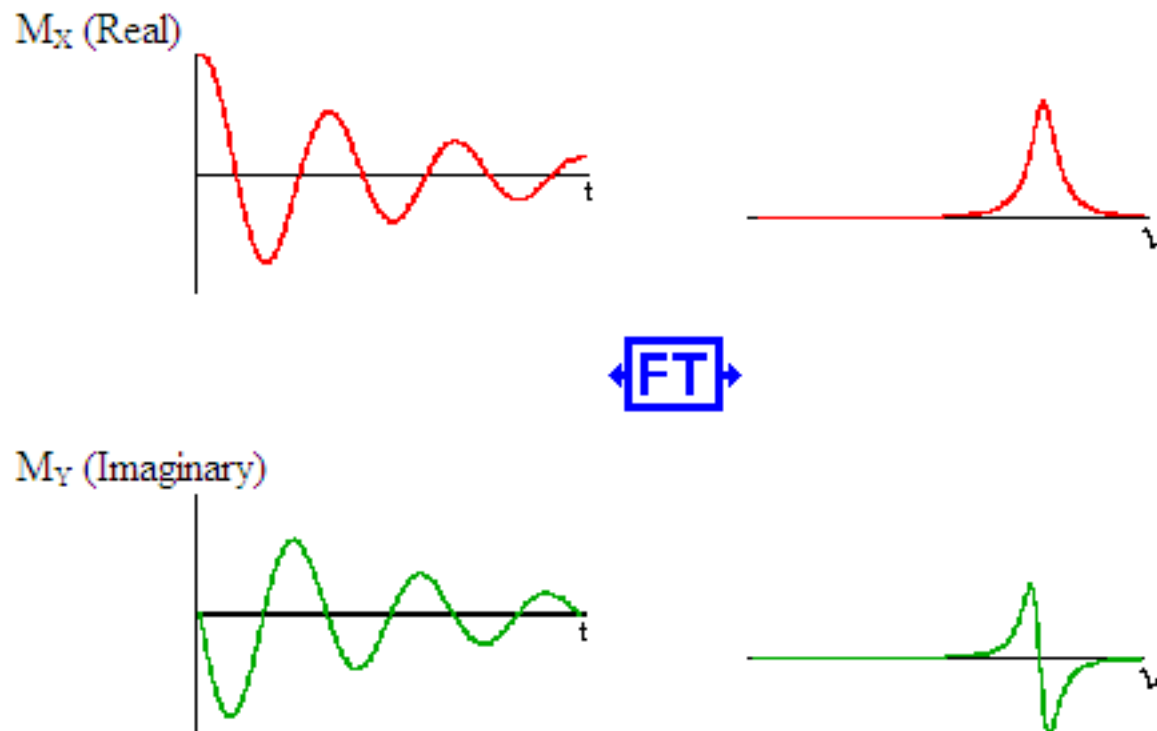
- If the above mentioned FID is recorded such that there is a 45° phase shift in the real and imaginary FIDs,



- the coordinate transformation matrix can be used with $\theta = -45^\circ$. The corrected FIDs look like a cosine function in the real and a sine in the imaginary.



- finally

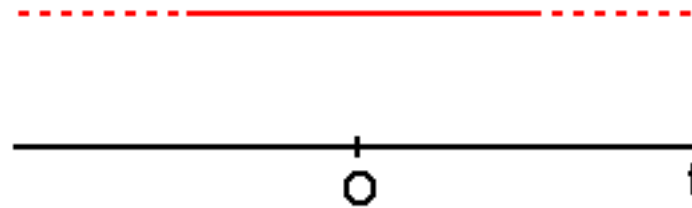


Fourier Pairs

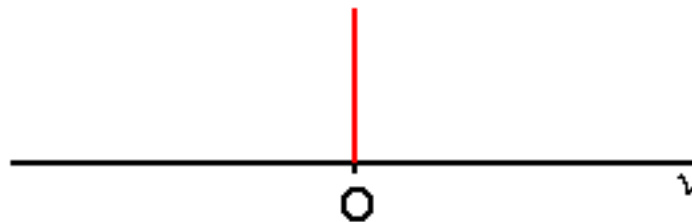
- A Fourier pair is two functions, the frequency domain form and the corresponding time domain form. The amplitude of the Fourier pairs has been neglected since it is not relevant in NMR.

- Constant value at all time

A DC offset or constant value.

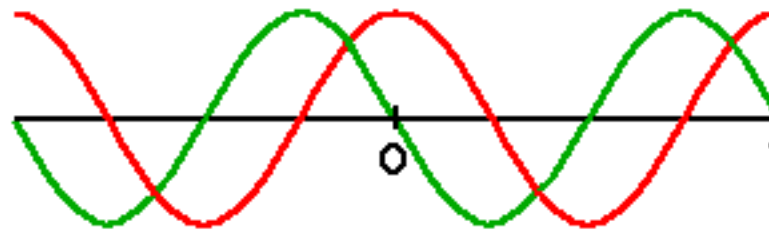


A delta function at zero.



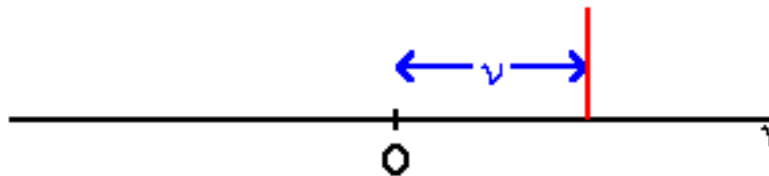
Real: $\cos(2\pi\nu t)$, Imaginary: $-\sin(2\pi\nu t)$

Real: $\cos(2\pi\nu t)$, Imaginary: $-\sin(2\pi\nu t)$



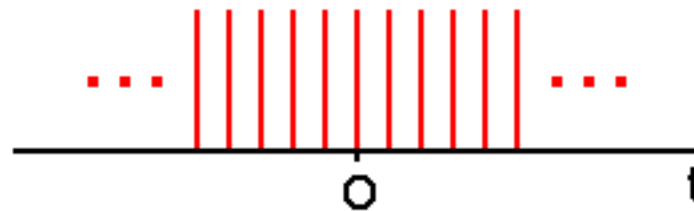
FT

A delta function at ν .



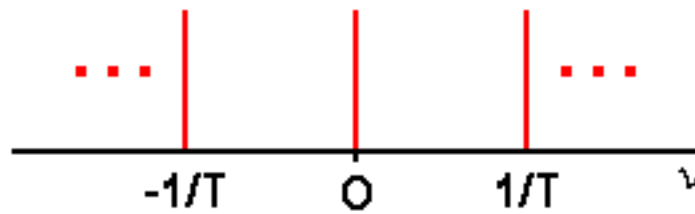
Comb Function (A series of delta functions separated by T.)

Comb Function (A series of delta functions separated by T.)



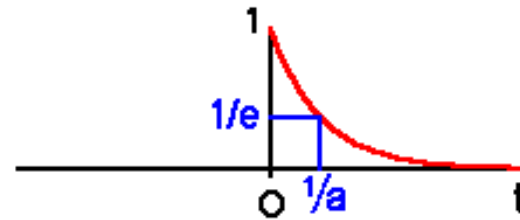
FT

A comb function with separation $1/T$.



$$e^{-at} \text{ for } t > 0$$

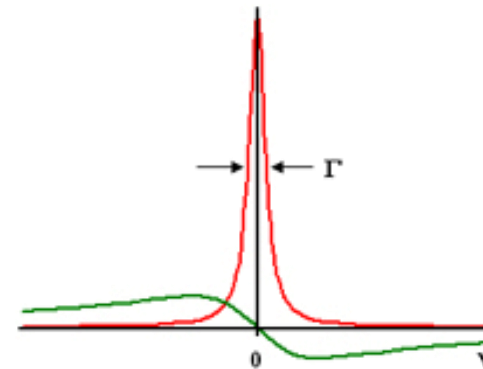
Exponential Decay: e^{-at} for $t > 0$.



Lorentzian

$$\text{RE: } a/(a^2 + 4\pi^2\nu^2)$$

$$\text{IM: } -2\pi\nu/(a^2 + 4\pi^2\nu^2)$$

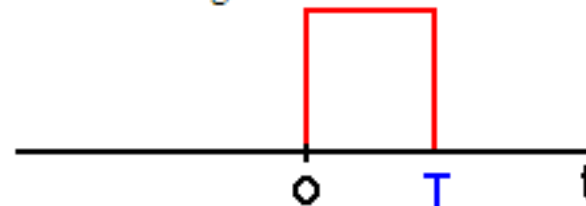


The imaginary component is shown magnified 10x in amplitude. It is worth noting that the width (Γ) of the real Lorentzian peak is related to a by

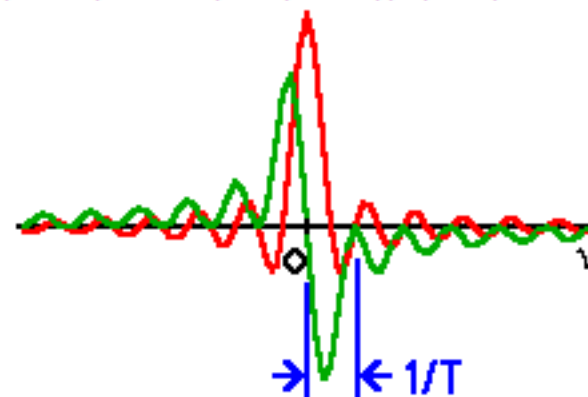
$$\Gamma = a/\pi .$$

A square pulse starting at 0 that is T seconds long.

Rectangular pulse of width T starting at 0.

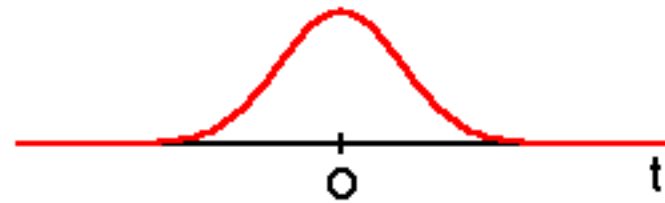


Sinc RE: $(\sin(2\pi\nu t))/(2\pi\nu t)$ IM: $-(\sin^2(2\pi\nu t))/(\pi\nu t)$



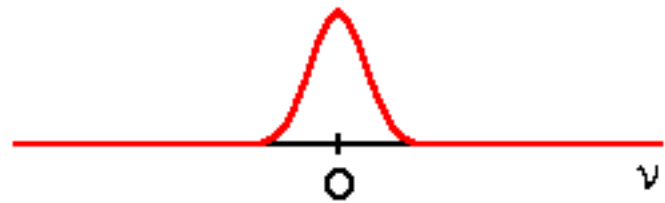
Gaussian: $\exp(-at^2)$

Gaussian: $\exp(-at^2)$



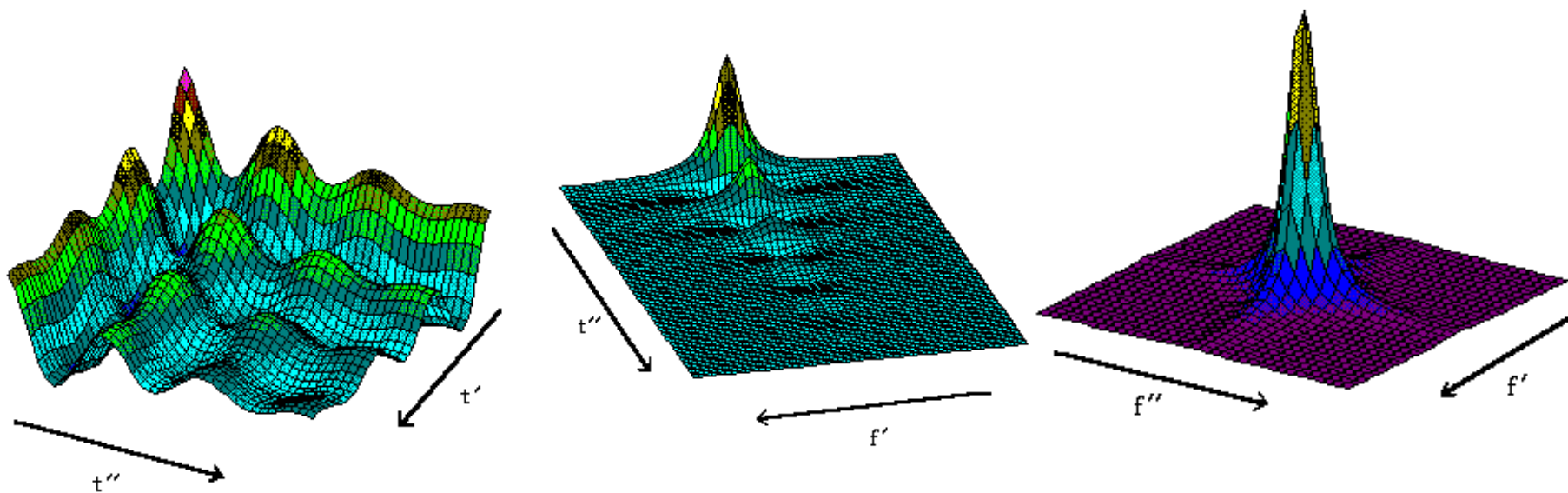
FT

Gaussian: $\exp(-\pi^2\nu^2/a)$



The Two-Dimensional FT

- The two-dimensional Fourier transform (2-DFT) is an FT performed on a two dimensional array of data



Isotope	Abundance (%)	NMR Frequency in 10 Kilogauss Field ^d	Relative ^d Sensitivity (constant H ₀)	Magnetic ^b Moment (μ)	Spin ^c (I)
¹ H	99.9844%	42.577	1.0000	2.7927	1/2
² H (D)	0.0156	6.536	0.0096	0.8574	1
¹⁰ B	18.83	4.575	0.0199	1.8006	3
¹¹ B	81.17	13.660	0.165	2.6880	3/2
¹³ C	1.108	10.705	0.0159	0.7022	1/2
¹⁴ N	99.635	3.076	0.0010	0.4036	1
¹⁵ N	0.365	4.315	0.0010	-0.2830	1/2
¹⁹ F	100.	40.055	0.834	2.6273	1/2
²⁹ Si	4.70	8.460	0.0785	-0.5548	1/2
³¹ P	100.	17.235	0.0664	1.1305	1/2
¹¹⁷ Sn	7.67	15.77	0.0453	-0.9949	1/2
¹¹⁹ Sn	8.68	15.87	0.0518	-1.0409	1/2

SPIN
1/2

Isotope	Nat. Abundance %	Magnetogyric ratio (■) $10^7 \text{ rad T}^{-1} \text{ s}^{-1}$	Relative NMR frequency (MHz)	Rel. Receptivity
^{117}Sn	7.6	-9.578	35.6	$3.5 * 10^{-3}$
^{119}Sn	8.6	-10.021	37.3	$4.5 * 10^{-3}$
^{125}Te	7.0	-8.498	31.5	$2.2 * 10^{-3}$
^{129}Xe	26.4	-7.441	27.8	$5.7 * 10^{-3}$
^{169}Tm	100.0	-2.21	8.3	$5.7 * 10^{-4}$
^{171}Yb	14.3	4.712	17.6	$7.8 * 10^{-4}$
^{183}W	14.4	1.120	4.2	$1.1 * 10^{-5}$
^{187}Os	1.6	0.616	2.3	$2.0 * 10^{-7}$
^{195}Pt	33.8	5.768	21.4	$3.4 * 10^{-3}$
^{199}Hg	16.8	4.8154	17.9	$9.8 * 10^{-4}$
^{203}Tl	29.5	15.436	57.1	$5.7 * 10^{-2}$
^{205}Tl	70.5	15.589	57.6	$1.4 * 10^{-1}$
^{207}Pb	22.6	5.540	20.9	$2.0 * 10^{-3}$

