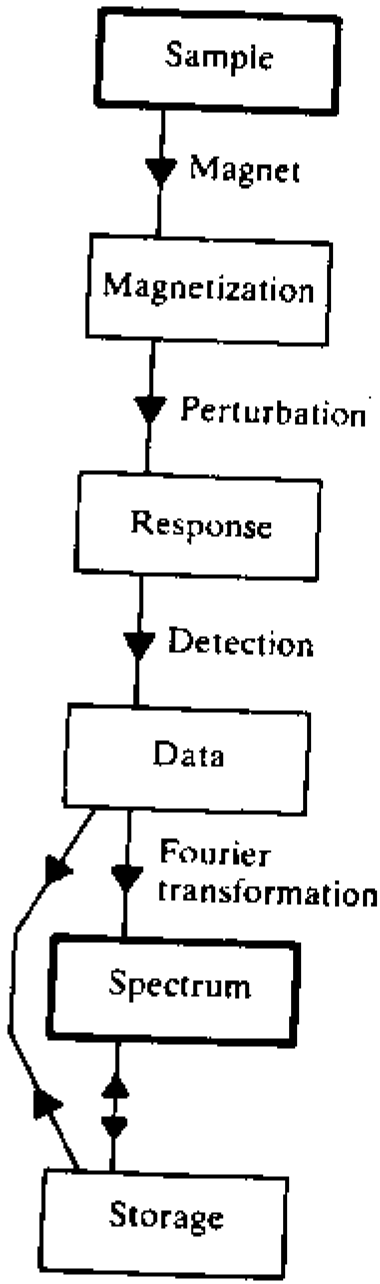
CHEM / BCMB 4190/6190/8189

Introductory NMR

Lectures 1 and 2


Sample
Magnet
Magnetization
Perturbation
Response
Detection
Data
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transformation
Spectrum
Storage

Nuclear Magnetism:

NMR is a manifestation of nuclear spin angular momentum (**P**).

$$\mathbf{P} = \hbar\sqrt{I\,(I+1)}$$

I = angular momentum quantum number
$\hbar$ = Planck's constant/ 2_

Possible Values of I:

1. I=0, mass number (A) and atomic number (Z) are even.
2. I= half-integral value, A is odd.
3. I= integral value, A is even and Z is odd.

For NMR:

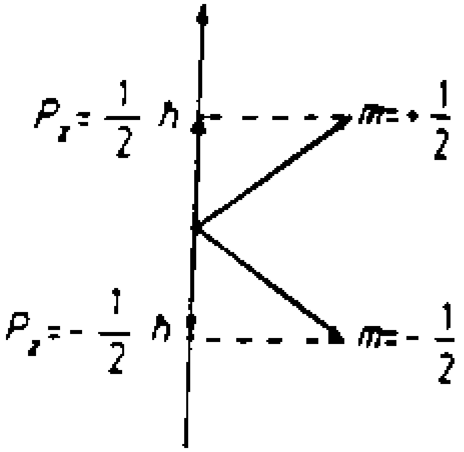
- I=0 are NMR-inactive
- I > 1/2, nuclei possess electric quadrupole moment due to non-spherical nuclear charge distribution. The lifetime of the magnetic states for quadrupoles in solution are much shorter than for I=1/2. This results in line broadening and they can be more difficult to study.
- I= 1/2 include ^{1}H, ^{13}C, ^{15}N and ^{31}P.

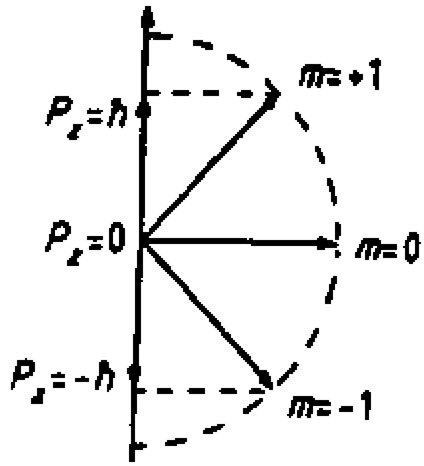
Due to restrictions of quantum mechanics only one of the three Cartesian coordinates can be specified.

$$P_z = \hbar m$$

m = (-I, -I +1, ..., I-1, I) - magnetic quantum number.

I_z has 2I+1 values of m. This behavior is called directional quantization.





Nuclei with non-zero spin angular momentum also possess nuclear magnetic moment:

$$\mu = \gamma \mathbf{P}$$

– γ in part determines the receptivity of a nucleus in NMR spectroscopy. It is a constant for a given nuclide and it is referred to as the gyromagnetic ratio.

- μ and **P** are usually in the same direction but one important exception is ^{15}N.

Therefore:

$$\mu_z = m\gamma\hbar$$

More Quantitatively:

$$\mu = g\,\frac{ehI}{4\pi Mc}$$

M = mass
e = charge uniformly spread over the surface
c = speed of light.

** No simple model can predict or explain the actual magnetic moments of nuclei**

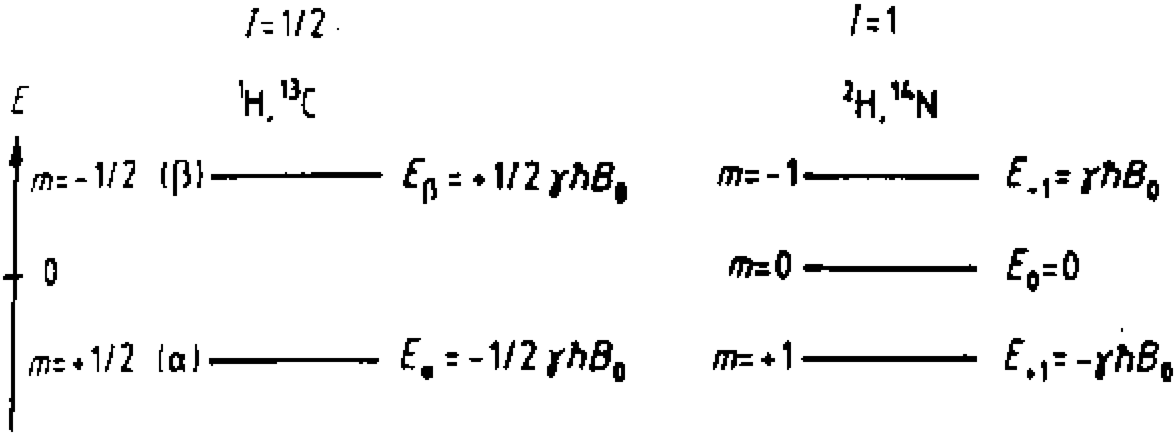
In absence of an external magnetic field:
2I + 1 states of m are equivalent

In presence of an external magnetic field, the spin states of a nucleus have energies given by:

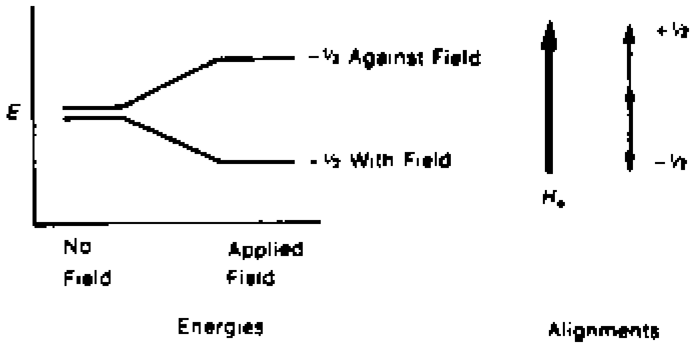
$$E = \mu_z B_0 = -I_z \gamma \hbar B_0$$

B_0 = static magnetic field strength

The projection of angular momentum of the nuclei onto the z-axis of the laboratory frame results in 2I + 1 equally spaced energy levels, which are referred to as the Zeeman levels or Zeeman States.



For I_z = 1/2 we have m = +1/2 and m = - 1/2 in which μ_z is either parallel or anti-parallel to the field direction.



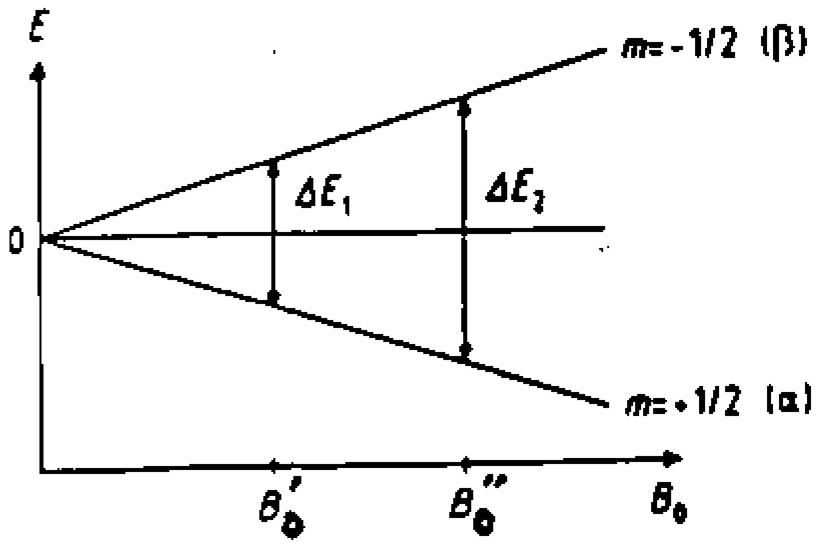
In quantum mechanics:

m = +1/2 = spin function α

m = -1/2 = spin function β

Since we are restricted to single quantum transitions:

$$\Delta m = \pm 1$$



$$\Delta E = \gamma \hbar B_0$$

What Effects ΔE and why is this important?

- gyromagnetic ratio
- strength of static magnetic field

At equilibrium the energy states are not equally populated and the relative populations is given by the Boltzmann distribution.

$$\frac{N_m}{N} = \exp\left(\frac{-E_m}{k_B T}\right) \Big/ \sum_{m=-I}^{I} \exp\left(\frac{-E_m}{k_B T}\right)$$

In our case, $E_m = -m\hbar\gamma B_O$

$$= \exp\left(\frac{m\hbar\gamma B_0}{k_B T}\right) \Big/ \sum_{m=-I}^{I} \exp\left(\frac{m\hbar\gamma B_0}{k_B T}\right)$$

Since $m\hbar\gamma B_O$ << kbT the exponential can be expanded to first order using Taylor series.

$$\approx \left(1 + \frac{m\hbar\gamma B_0}{k_B T}\right) \Big/ \sum_{m=-I}^{I} \left(1 + \frac{m\hbar\gamma B_0}{k_B T}\right)$$

$$\approx \left(1 + \frac{m\hbar\gamma B_0}{k_B T}\right) \Big/ (2I + 1),$$

- $\exp(-E/k\,T) \approx 1 - E/k\,T$
- denominator sums to $\approx 2I + 1$

The book gives an example for I=1/2

$$\frac{N_\beta}{N_\alpha} = e^{-\Delta E/k_b T} \cong 1 - \Delta E/k_b T = 1 - \gamma\hbar B_0/k_b T$$

k: Boltzmann constant (1.3805×10^{-16} erg K^{-1})
T: temperature (K)
$\hbar$: Plank constant (1.0546×10^{-27}erg S)
B_0: magnetic field strength
(Tesla, T; 100 MHz <=> 2.35 T)
γ: gyromagnetic ratio (10^7 Hz T^{-1})

e.g.

At T = 300K and B_0 = 5.875 T (250 MHz),

^{1}H:

$$\frac{N_\beta}{N_\alpha} = 1 - \frac{26.7519 \times 10^7 \times 1.0546 \times 10^{-27} \times 5.875}{1.3805 \times 10^{-16} \times 300}$$

$$\boxed{N_\beta \approx (1 - 0.00004)\, N_\alpha = 0.99996\, N_\alpha}$$

For B_0 = 18.8 T (800 MHz),

$$\boxed{N_\beta \approx 0.99987\, N_\alpha}$$

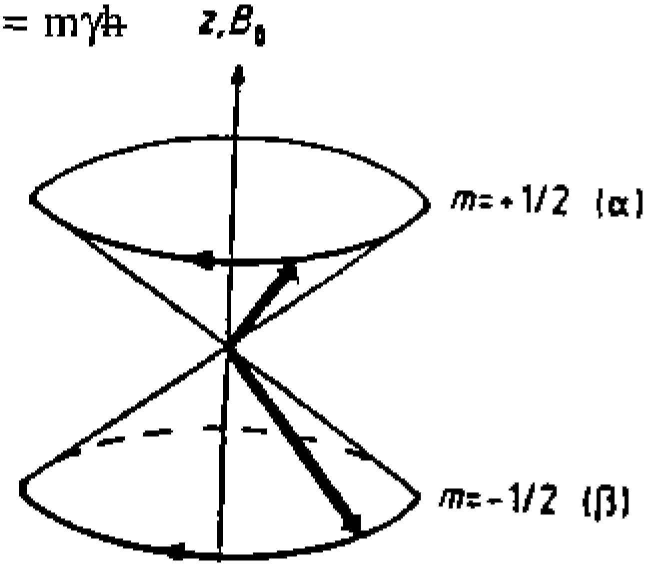
In classical representation the nuclear dipoles precess about the magnetic field direction with Larmor Frequency:

$$\omega_0 = \gamma B_0 \quad \text{(Radians/sec)}$$

$$\upsilon = \omega_0 / 2\pi = \gamma B_0 / 2\pi \quad \text{(Hertz or cycles/sec)}$$

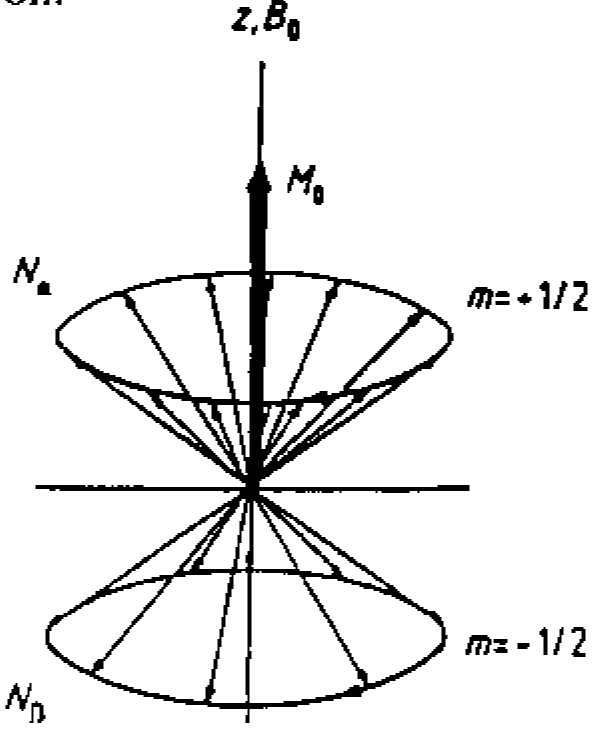
The z-component is given by the magnetic moment:

$$\mu_z = \gamma P_z = m\gamma\hbar$$



When m = +/- 1/2; The nuclear dipoles precess around a double cone with a half-angle of the cone is 54.7°.

Due to the differences in populations of the energy states there is macroscopic magnetization along the magnetic field direction.



For a macroscopic sample,

The x and y components are random and sum to zero so:

$$M_0 = \gamma\hbar \sum_{m=-I}^{I} mN_m$$

but we know that:

$$N_m = N \exp(m\hbar\gamma B_0/k_bT)/ \sum \exp(m\hbar\gamma B_0/k_bT)$$

Doing the math:

$$M_0 = N\gamma^2\hbar^2 B_0 I(I+1)/(3k_bT)$$

So the macroscopic magnetization (M_0) depends on:

- B_0
- I
- γ^2
- 1/T

What happens in NMR:

To induce NMR transitions a radiofrequency pulse is applied to the sample. The pulse is generated by a linear alternating electromagnetic field (B_1) along a transverse axis. This results in M_0 being rotated into the XY plane.

Resonance Condition:

$$h\,\upsilon_1 = \Delta E$$

Absorption: Lower energy ⇒ higher enrgy

Emission: Higher energy ⇒ Lower energy

Saturation: Equal number of emissions to absorption.

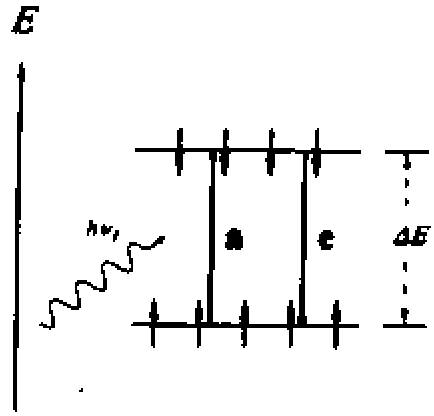


Figure 1-6.

Larmor frequency : $\upsilon_1 = \upsilon_L = |\gamma/2\pi|\,B_0$

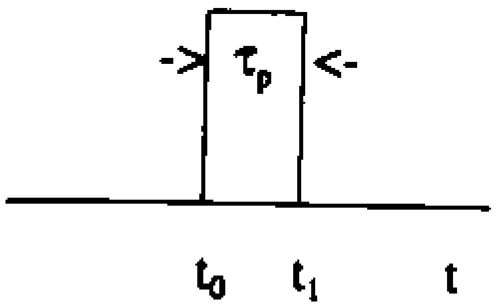
At 11.7T: for ^1H $\gamma = 2.675 \times 10^8$ $\upsilon_0 = 500$ MHz

For ^{13}C $\gamma = 0.6726 \times 10^8$ $\upsilon_0 = 125$ MHz

B_0 (T)	Resonance frequencies (MHz)	
	^1H	^{13}C
1.41	60	15.1
1.88	80	20.1
2.11	90	22.63
2.35	100	25.15
4.70	200	50.3
5.87	250	62.9
7.05	300	75.4
9.40	400	100.6
11.74	500	125.7
14.09	600	150.9
17.62	750	188.2
18.79	800	201.2

Pulsed NMR:

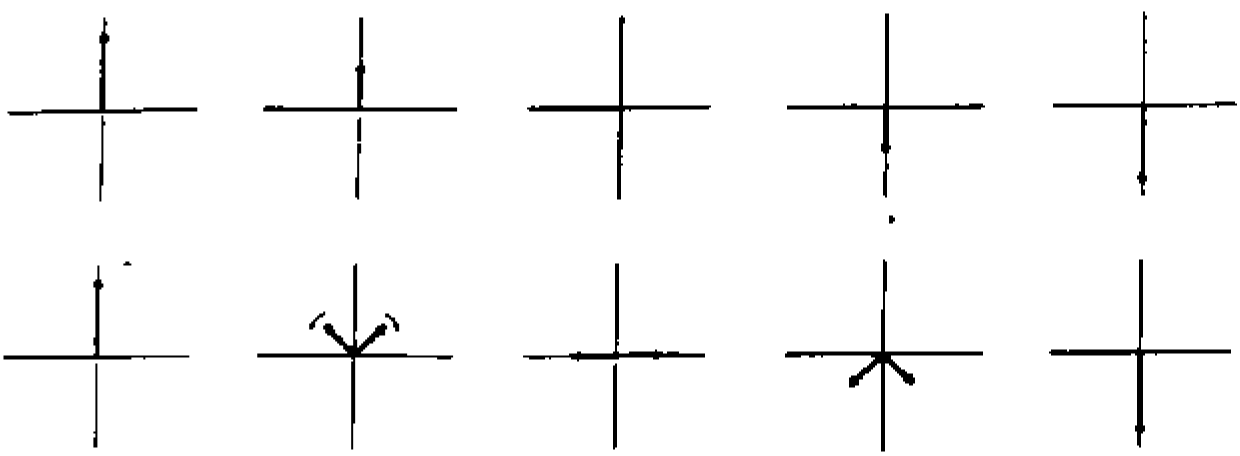
All nuclei are excited simultaneously by a radiofrequency pulse.



Pulse angle is proportional to the pulse width (duration) and pulse power (Magnitude of B_1 field).

The coil is arranged so that this field is perpendicular to the applied field (in the x-y plane)

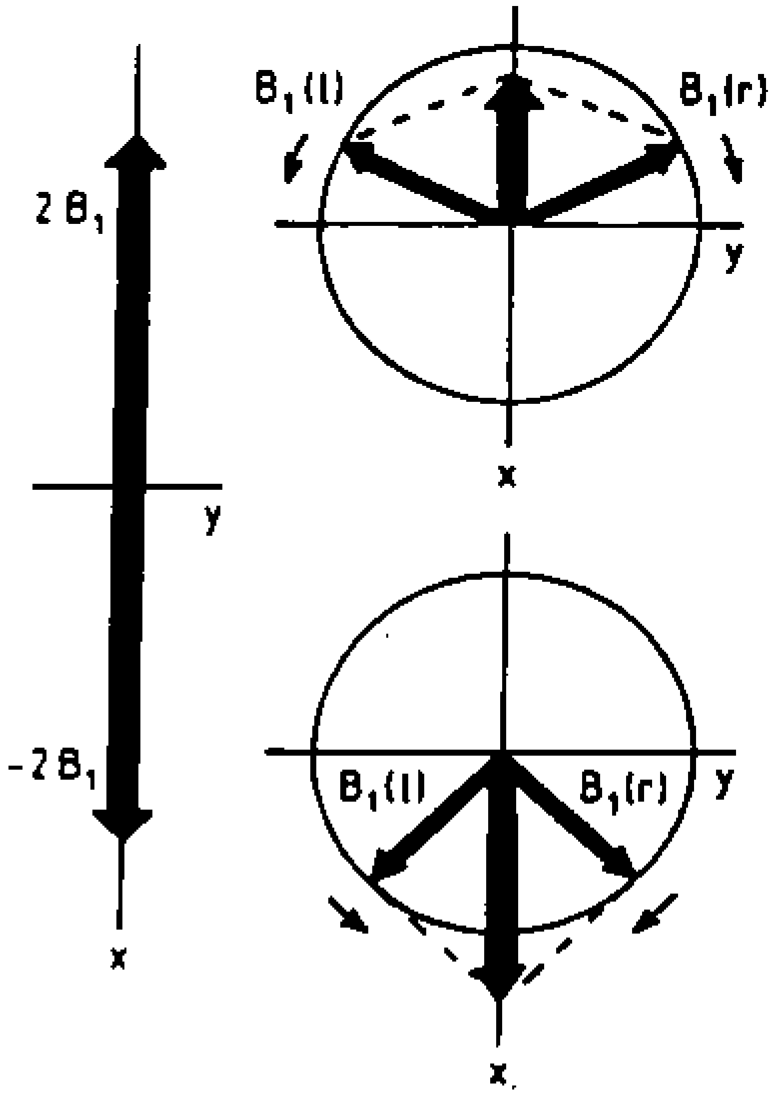
The oscillating magnetic field is equivalent to two counter-rotating magnetization vectors.



We can use this pair of counter-rotating vectors as an equivalent representation of the *rf* signal.

We will represent the *rf* along the x-direction as two vectors with the same magnitude (B_1)

- one vector rotates clockwise B_1 (r)
- one vector rotates c-clockwise B_1 (l)



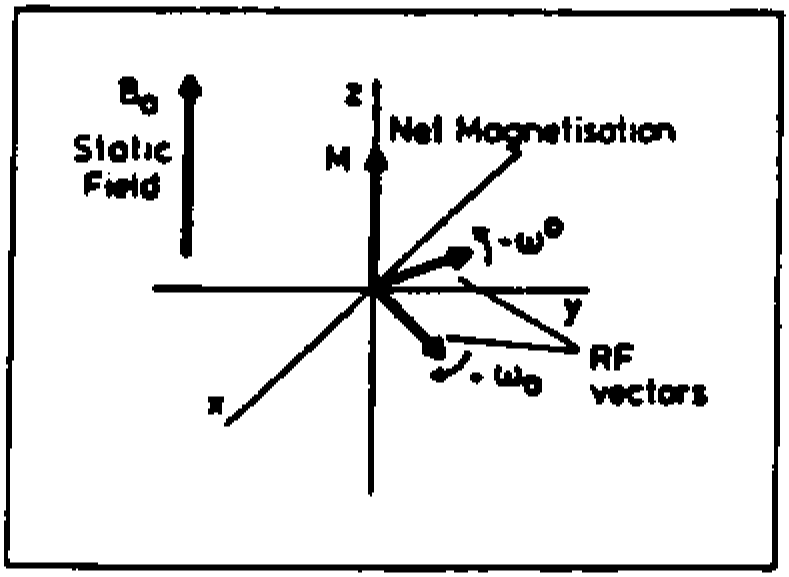
Only one of the two components is capable of interacting with the precessing nuclear dipoles (B_1).

The sample magnetization is static along the z-axis.

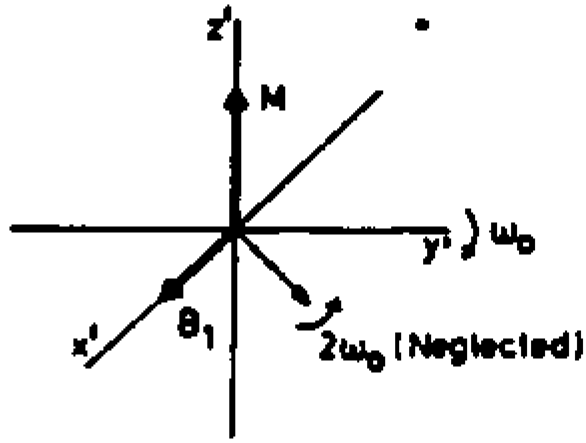
What happens when the *rf* magnetization (which is moving) interacts with the sample magnetization?

The Rotating Frame:

- Experimentally, detected signal is subtracted from the carrier frequency. We chose a set of coordinates that rotate along with the nuclear precession.



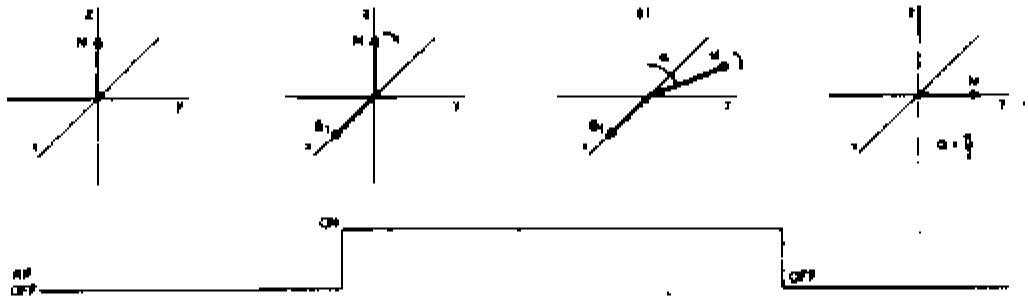
LAB FRAME



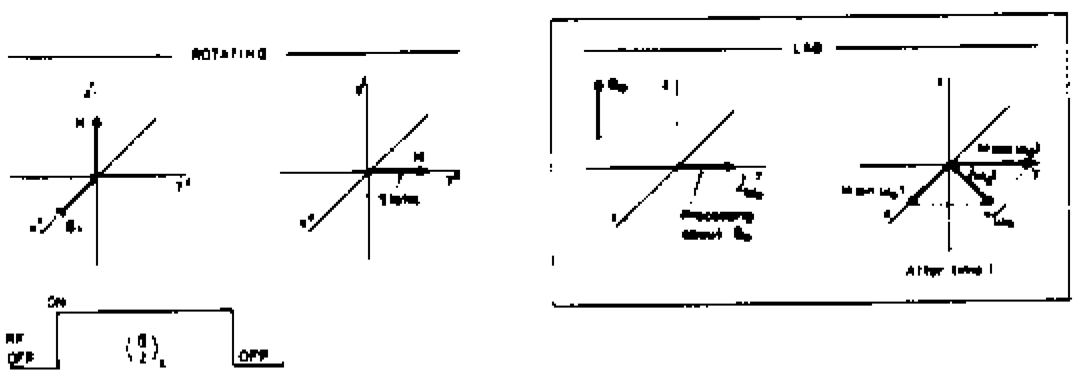
ROTATING FRAME

How can we use this to look at *rf* pulses(B_1)?

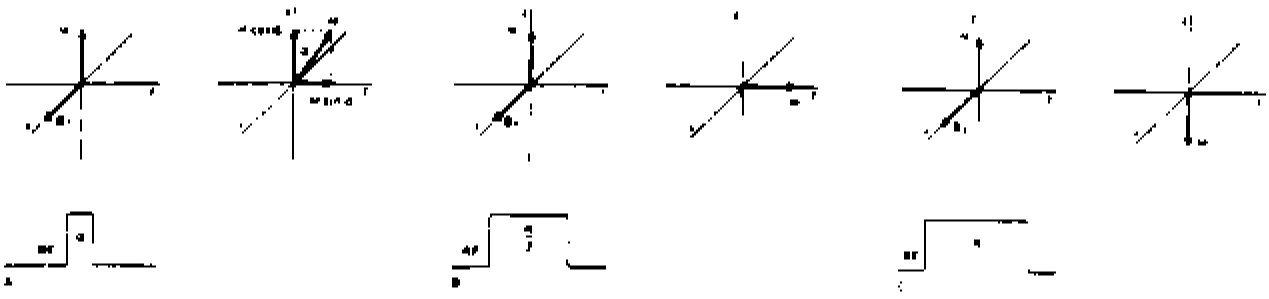
- In the rotating frame B_1 is at right angles to M.
- The net result is to produce a torque acting around B_1 at a speed depending on the field strength.

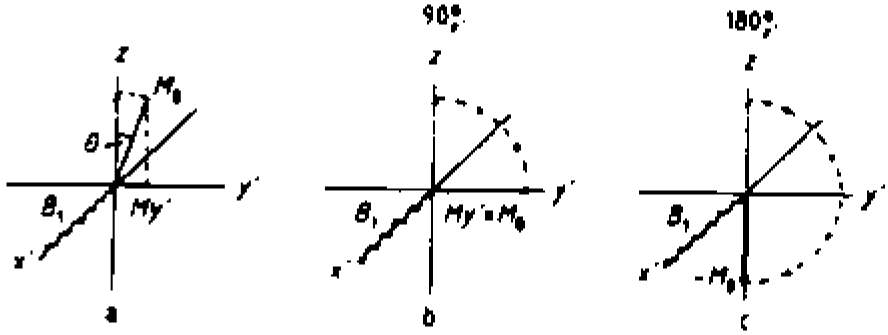


How does this look in our two frames of reference?

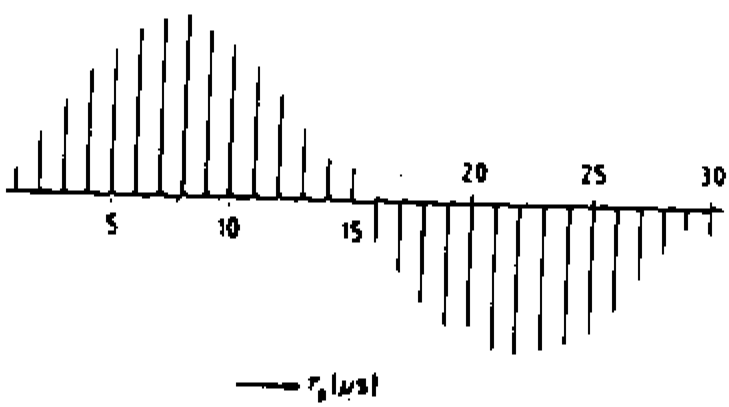


What happens to M as we increase the leng h of the pulse?





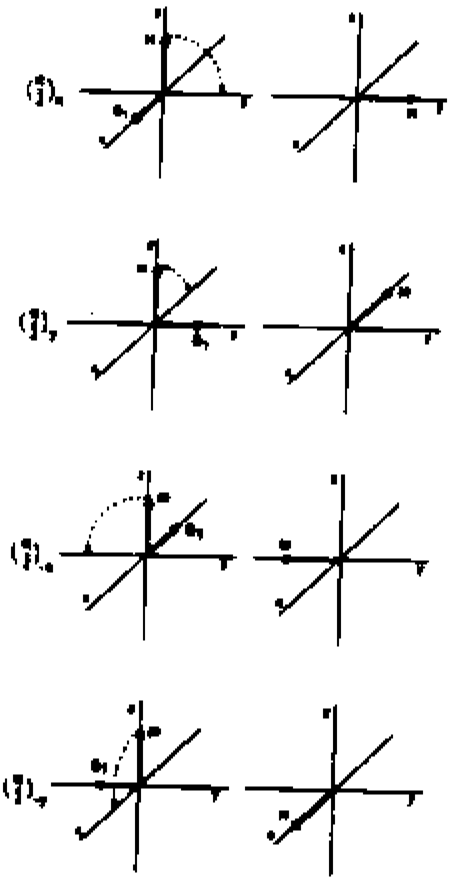
How does this effect the NMR signal?



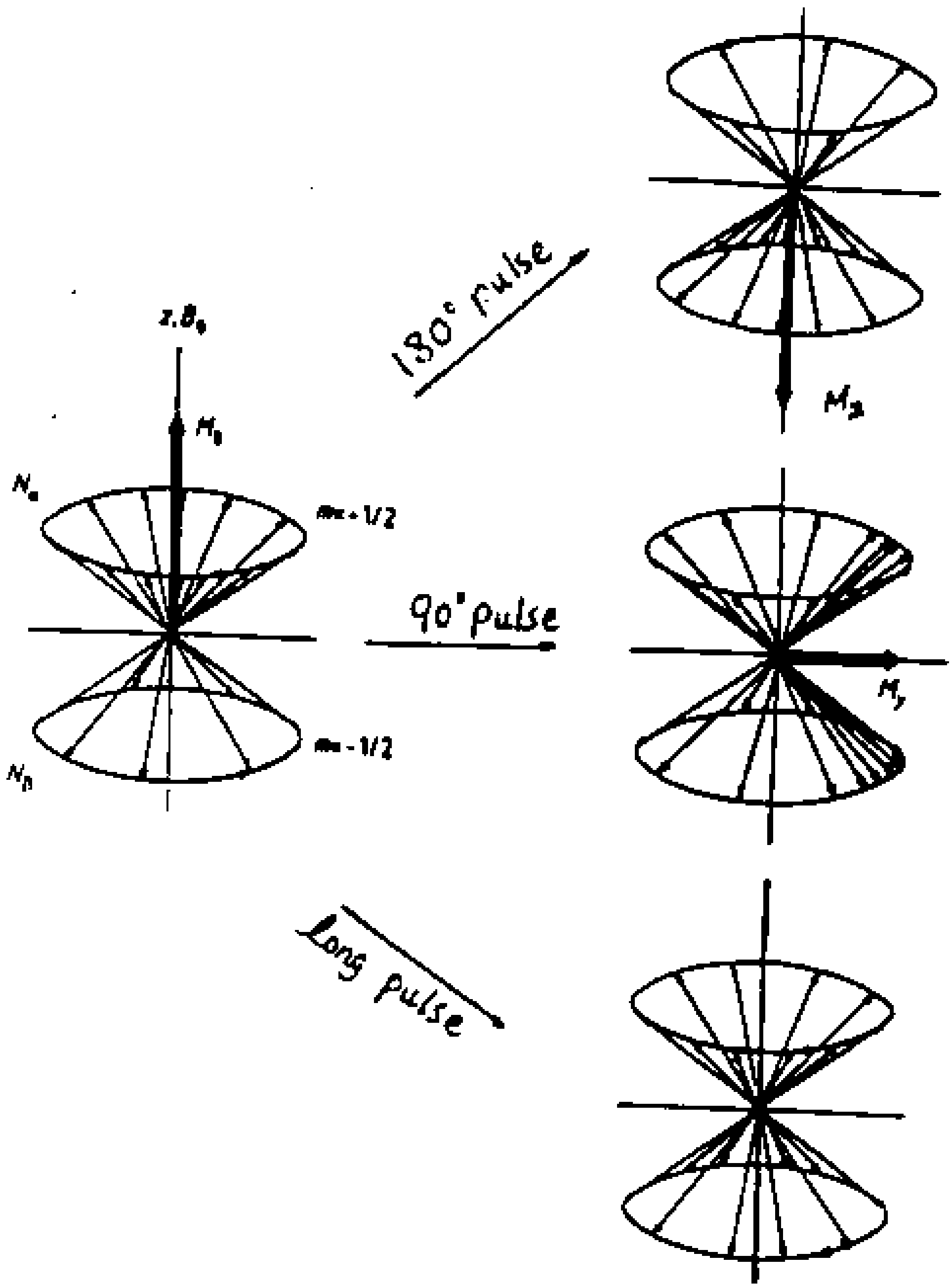
Our receiver is oriented with its axis along the y-direction.

θ = pulse angle or pulse flip-angle.

Four common pulses and their phases (φ):



Pictorial representation of phase coherence:



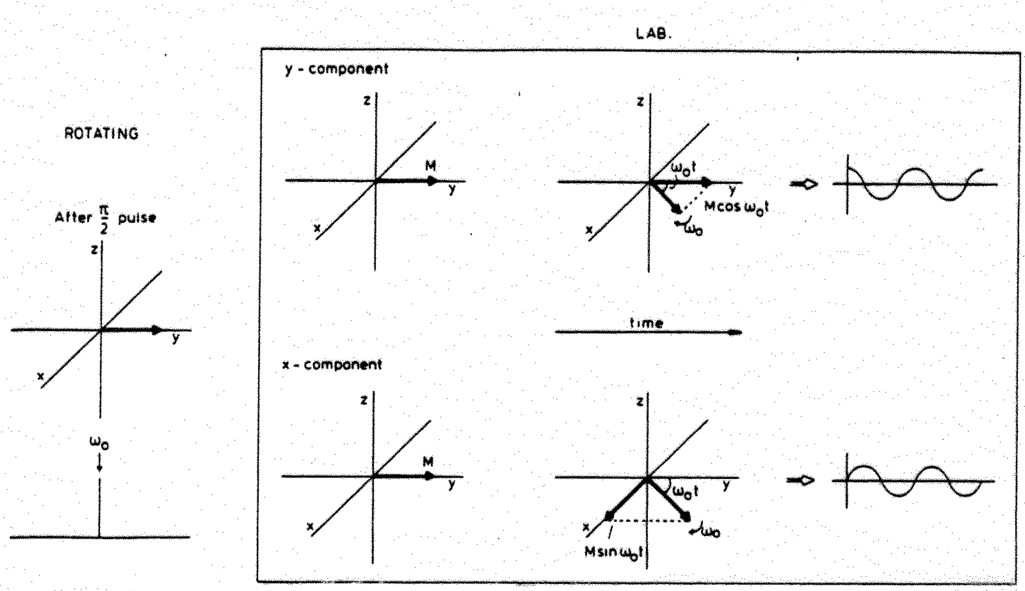


Figure 4.13 A closer look at the sample magnetisation in the lab. frame after a $(\pi/2)_x$ pulse reveals *two rf* signals, differing only in phase (by 90°).

Figure 4.14 The same as 4.13, but after a $(\pi/2)_y$ pulse.