NMR of Solids

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- Generalities

I = nuclear spin = quantum number

A Atomic weight	odd		even	
Z Atomic number	even	odd	odd	even
I	1/2, 3/2, 5/2, …..		1, 2, 3,…	0

I= 1/2 : ^{1}H, ^{3}He, ^{13}C, ^{15}N, ^{29}Si, ^{31}P, ^{109}Ag, ^{129}Xe, ^{195}Pt, ...

3/2 : ^{7}Li, ^{9}Be, ^{131}Xe, ...

1 : ^{14}N, D(^{2}H),...

5/2 : ^{17}O, ^{27}Al, ...

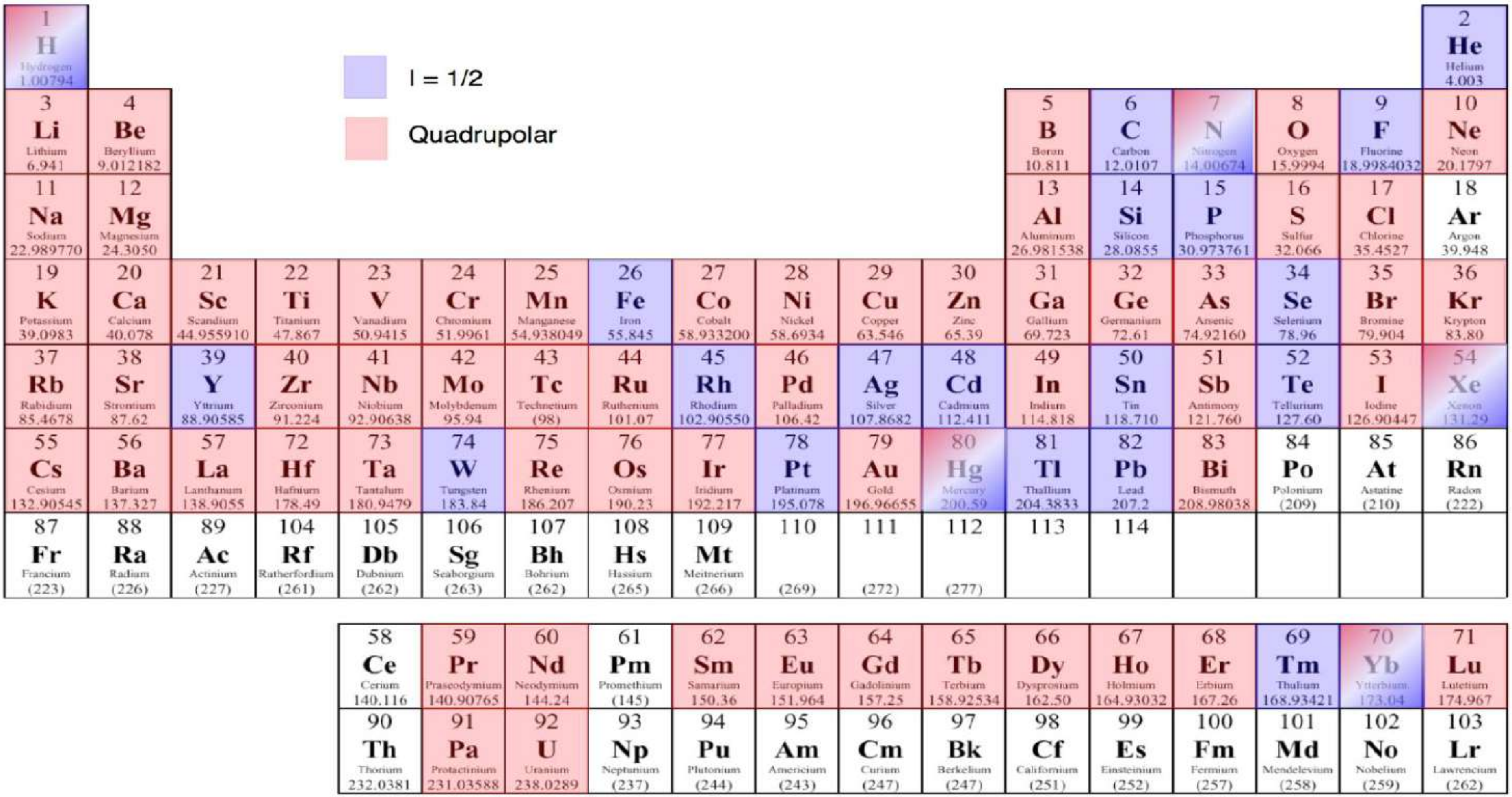
$\vec{I}$ = dimensionless vector

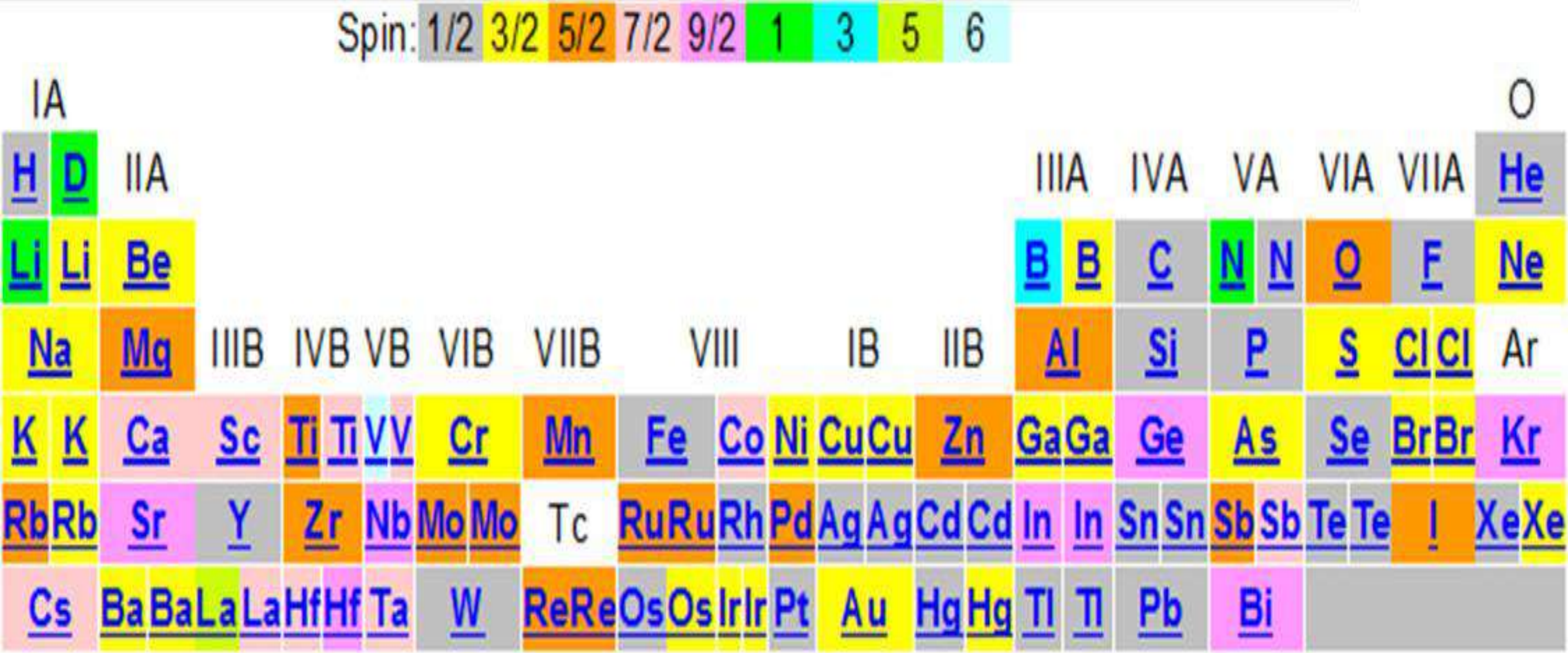
$\mathcal{M} = \hbar \vec{I}$ = angular momentum

$\vec{\mu}$ = magnetic moment = $\gamma \hbar \vec{I}$

γ = gyromagnetic ratio

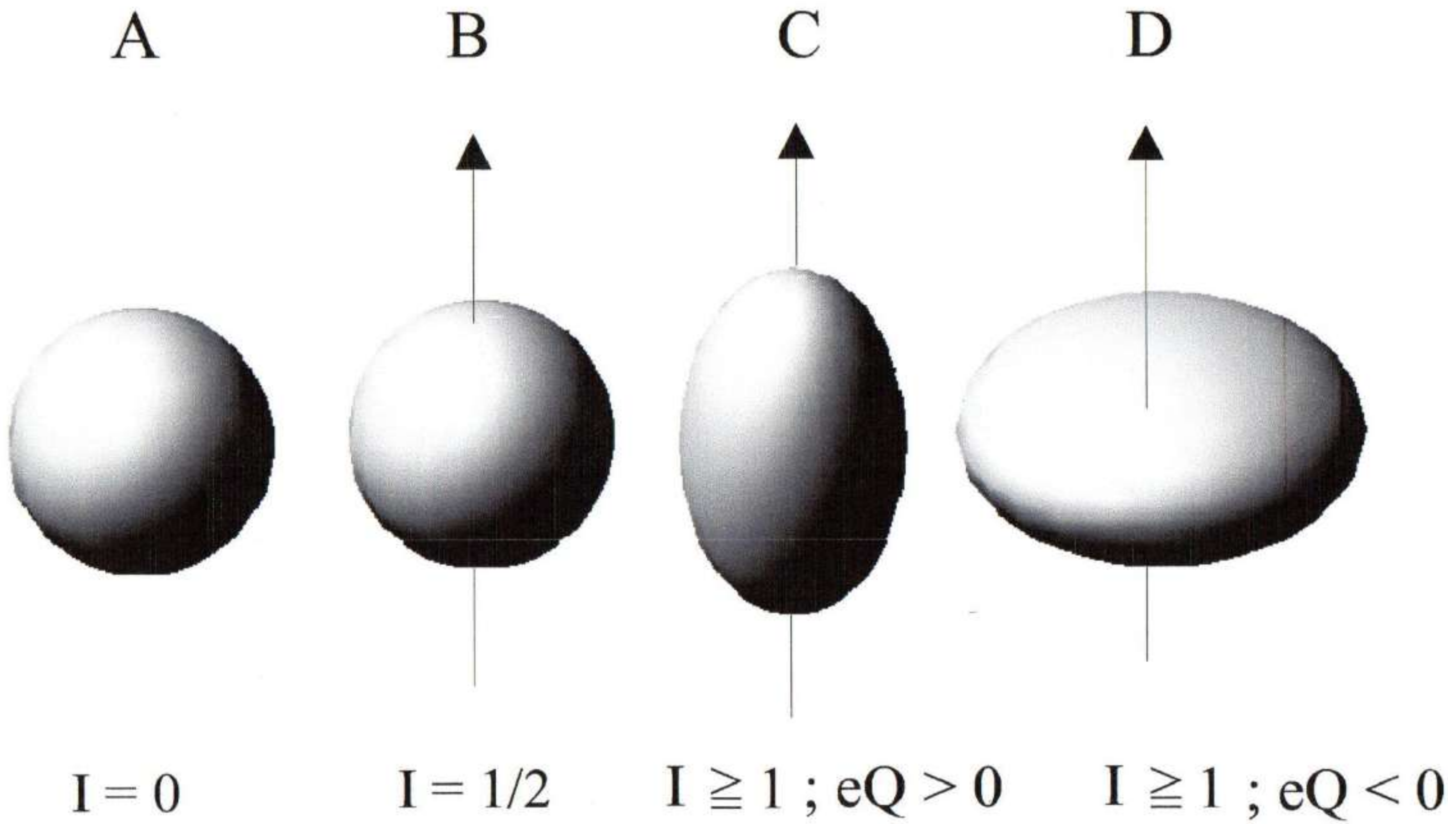
The Periodic Table of the Elements




Spin: 1/2 3/2 5/2 7/2 9/2 1 3 5 6
IA
O
H D IIA
IIIA IVA VA VIA VIIA He
Li Li Be
B B C N N O F Ne
Na Mg IIIB IVB VB VIB VIIB VIII IB IIB Al Si P S Cl Cl Ar
K K Ca Sc Ti Ti V V Cr Mn Fe Co Ni Cu Cu Zn Ga Ga Ge As Se Br Br Kr
Rb Rb Sr Y Zr Nb Mo Mo Tc Ru Ru Rh Pd Ag Ag Cd Cd In In Sn Sn Sb Sb Te Te I Xe Xe
Cs Ba Ba La La Hf Hf Ta W Re Re Os Os Ir Ir Pt Au Hg Hg Tl Tl Pb Bi

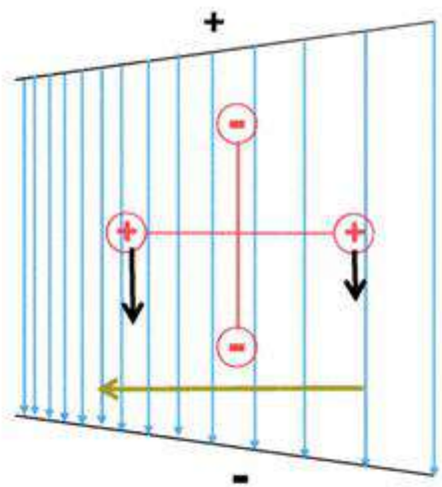
Nuclear electric quadrupole moment:

non-spherical distribution of nuclear charge



$eQ \sim 10^{-25}$ to 10^{-30} m^2

The physical picture



This quadrupole moment interacts with local electric field gradients created by the bonding environment of the nuclei.

-> probe of local symmetry

- Zeeman interaction

Zeeman interaction : $\hat{H}_Z$

The energy of a magnetic dipole μ in a magnetic field with inductio[n]
B_0 along the axis OZ is

$$E = -\mu . B_0 = -\gamma \hbar B_0 . I = -\gamma \hbar B_0 I_z$$

The corresponding Hamiltonian operator is of the same form:

$$\hat{H}_Z = -\gamma \hbar B_0 \hat{I}_Z$$

Being proportional to $\hat{I}_Z$, it allows $2I + 1$ eigenvalues. There ar[e]
therefore $2I + 1$ accessible energy levels

$$E_m = -\gamma \hbar B_0 m \qquad (m = -I, -I+1, \ldots, I)$$

The energy gap ΔE between two consecutive levels being constant, proportional to B_0,

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

we observe a single-line spectrum at frequency ν

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

$$\omega_0 = \gamma B_0$$

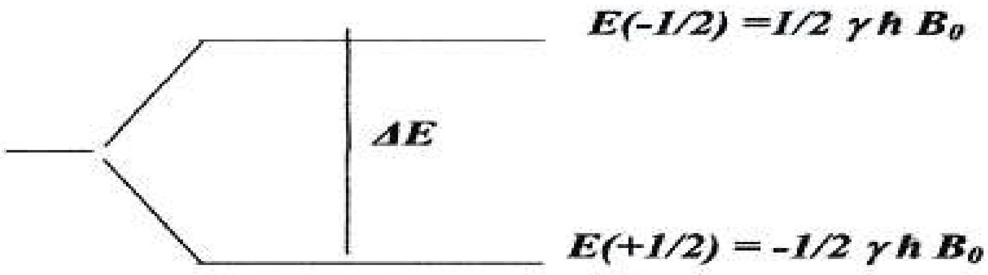
where ω_0 is the angular frequency.

SPIN ½

$$\vec{\mu} = \gamma\hbar\,\vec{I}$$

$$E = -\vec{\mu}\,.\,\vec{B_0} = -\,\gamma\hbar\vec{B_0}\,.\,\vec{I} = -\,\gamma\hbar\,B_0\,I_z$$

$$E_m = -\gamma\hbar\,B_0\,m \qquad (m = -1/2, +1/2))$$



$$\Delta E = h\,\nu_0 = \gamma\hbar\,B_0$$

$$2\pi\,\nu_0 = \omega_0 = \gamma\,B_0$$

SPIN > ½

$I \;\rightarrow\; 2I + 1$ energy levels $\rightarrow\; 2I$ intervals

$$\Delta E = (\,2I\;\gamma\hbar\,B_0)/\,2I = \gamma\hbar\,B_0 = h\,\nu_0$$

$$2\pi\,\nu_0 = \omega_0 = \gamma\,B_0$$

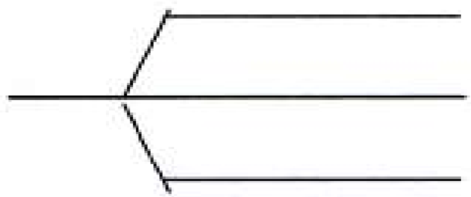
Examples spin I> ½

$\vec{M} = \hbar \vec{I}$ = *angular momentum*

$M_Z = I\hbar, (I-1)\hbar, \ldots\ldots, (I-n)\hbar, \ldots\ldots, -I\hbar$

Spin I = 1 (D, ^{14}N, ...)

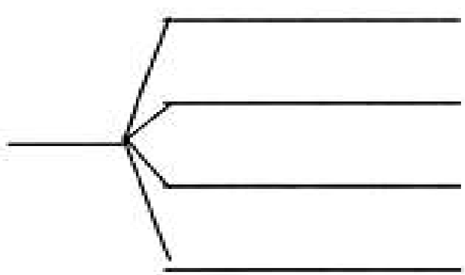
B=0	$B=B_0$	*Levels*	*Energies*
		-1	$+\gamma\hbar B_0$
		0	0
		+1	$-\gamma\hbar B_0$



The three equidistant Zeeman energy levels of an isolated 1 spin

Spin I = 3/2 (^7Li, ^{131}Xe, ...)

B=0	$B=B_0$	*Levels*	*Energies*
		-3/2	$3/2\ \gamma\hbar B_0$
		-1/2	$1/2\ \gamma\hbar B_0$
		+1/2	$-1/2\ \gamma\hbar B_0$
		+3/2	$-3/2\ \gamma\hbar B_0$



Populations of levels

$N_{m+1}/ N_m = \exp(-\Delta E/k_B T)$

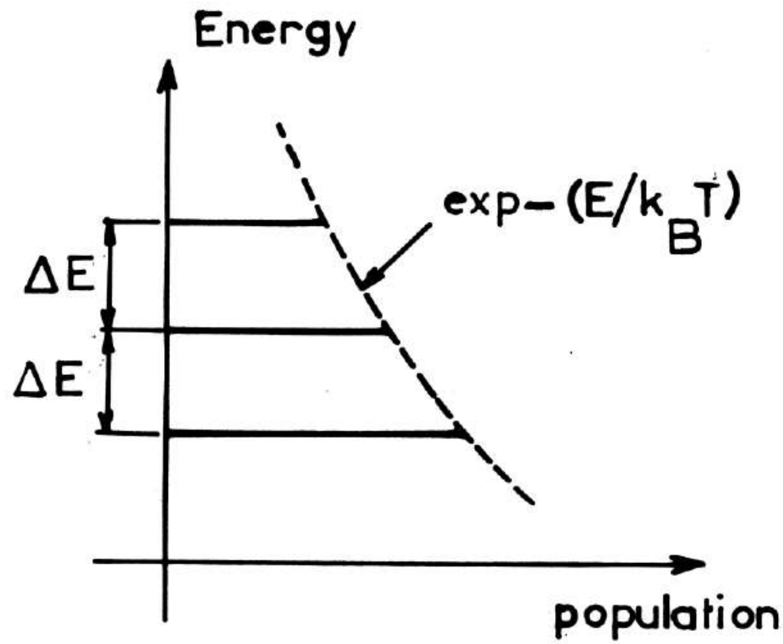
$k_B T \sim 10^{-21}$ j

$h\nu_{NMR} \sim 6.6 \times 10^{-34}$ j.s $\times 10^{6}$ s^{-1} =
6.10^{-28} j

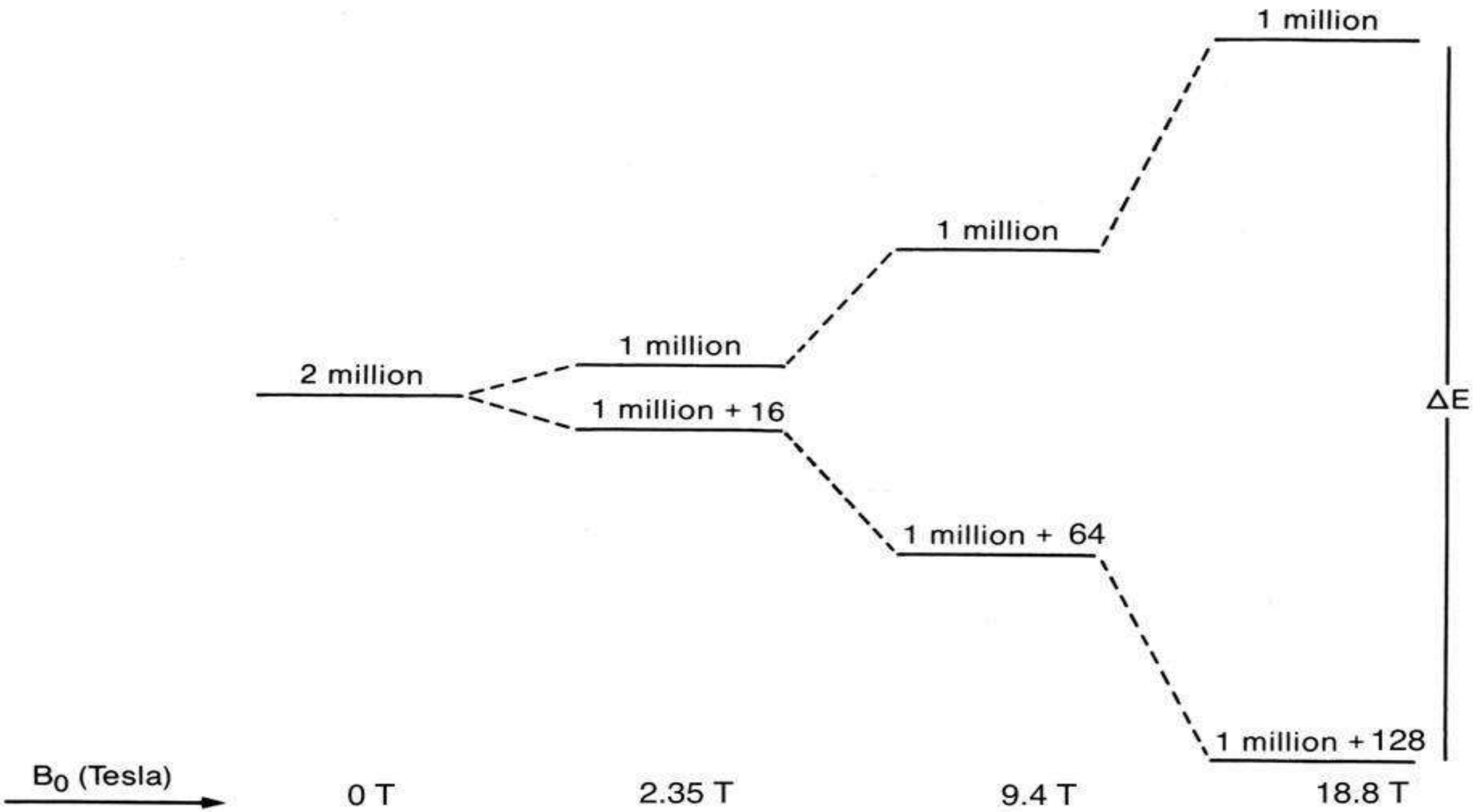
$h\nu_{OPT.} \sim 6.6 \times 10^{-34}$ j.s $\times 10^{15}$ s^{-1} =
6.10^{-19} j

$\Delta E_{NMR} \ll k_B T$

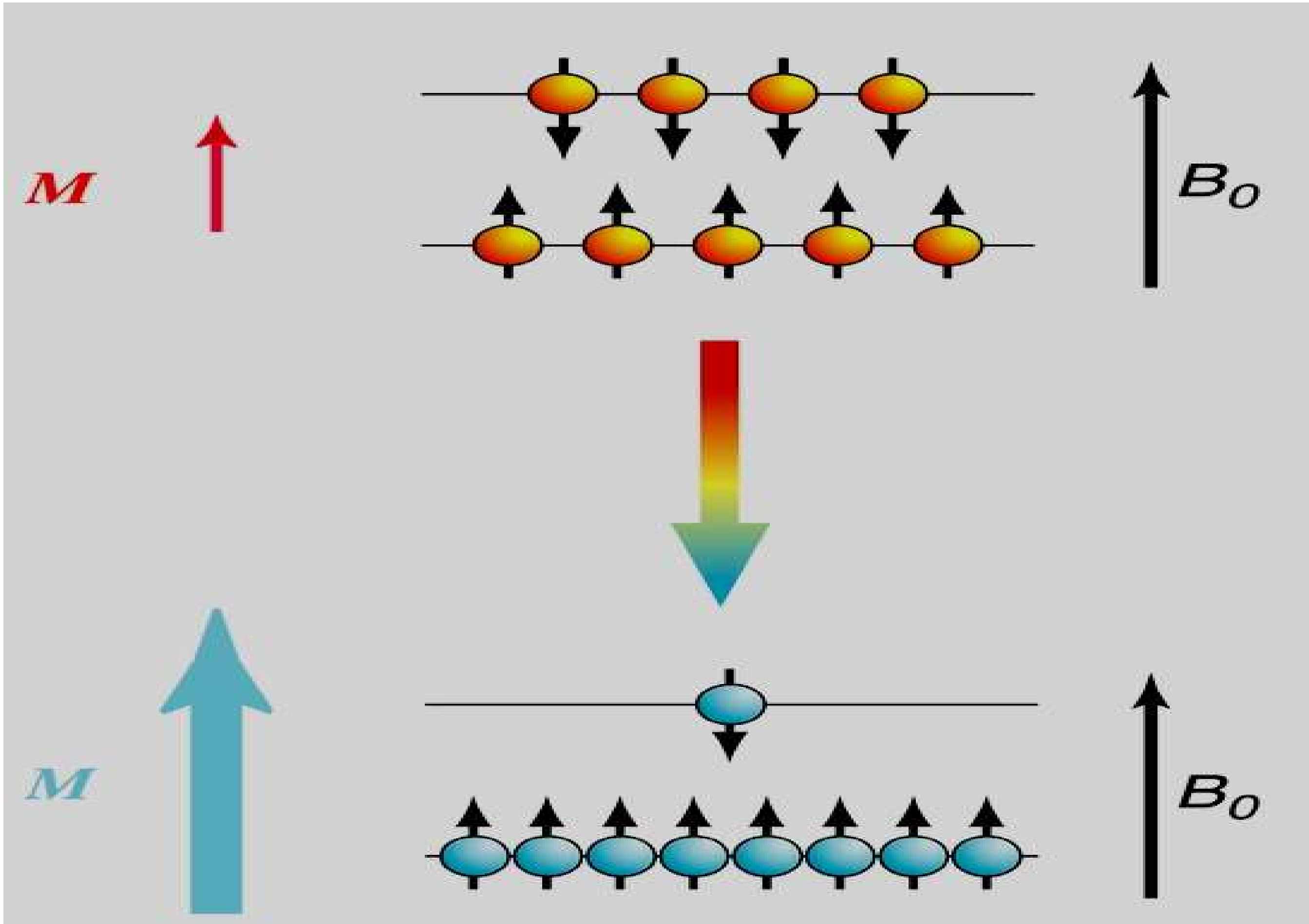
$\Delta E_{OPT.} \gg k_B T$



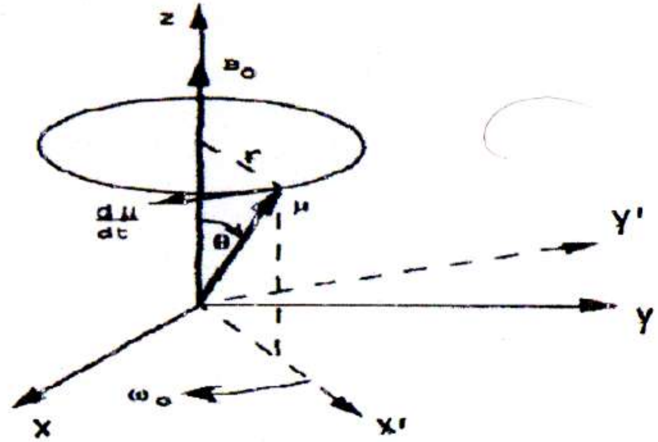
Distribution of the spins ½ assuming that we have two millions of spins. Of course generally there are more numerous



Normal polarization



Hyperpolarization



The torque exerted on a magnetic moment $\vec{\mu}$ by a magnetic field is

$$\vec{C} = \vec{\mu} \wedge \vec{B_0}$$

It equals the rate of change of angular momentum

$$\hbar\, d\vec{I}/dt = \vec{C} = \vec{\mu} \wedge \vec{B_0}$$

$$d\vec{\mu}/dt = \hbar\, \gamma\, d\vec{I}/dt = \gamma\, \vec{\mu} \wedge \vec{B_0}$$

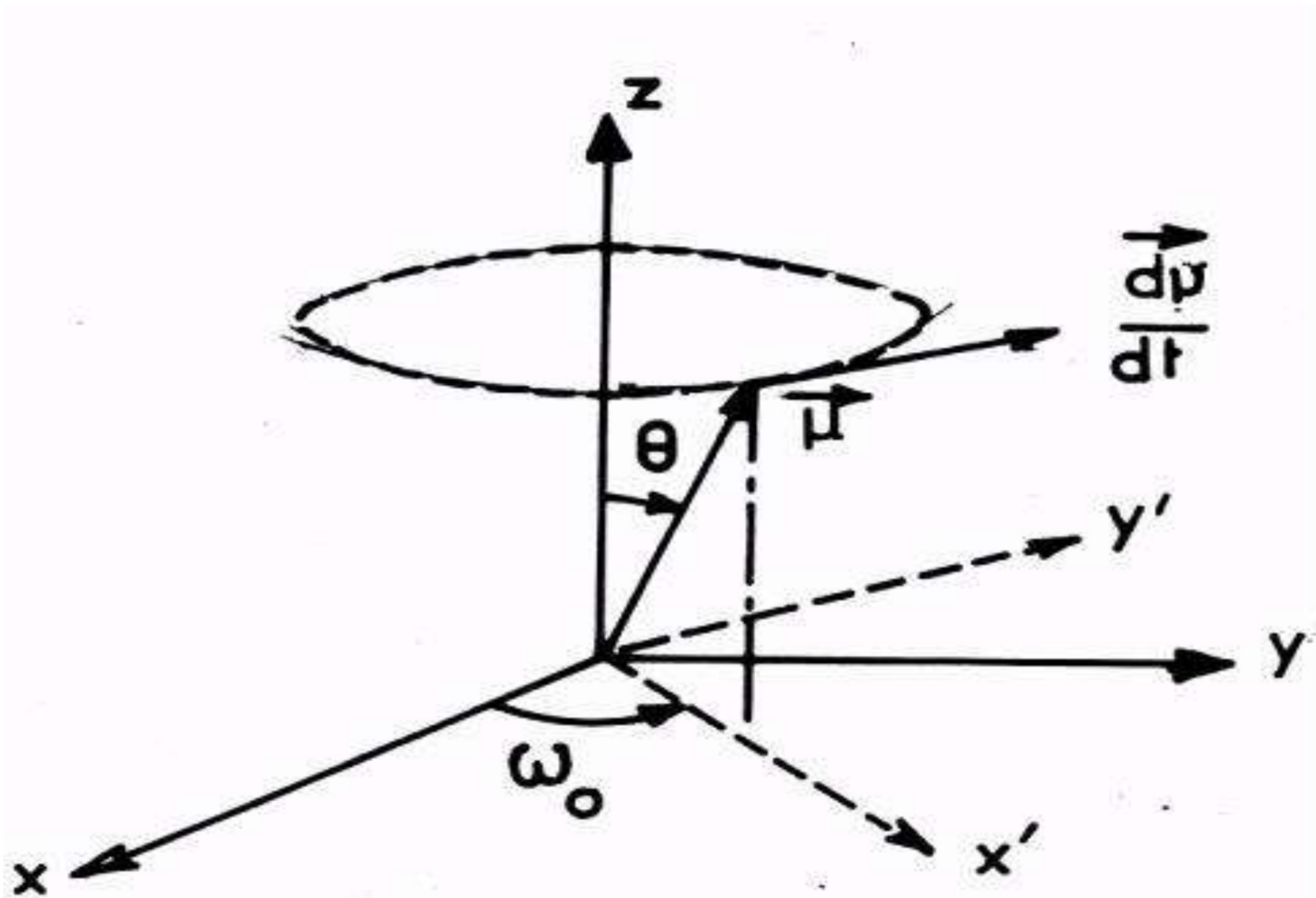
$\Rightarrow$ Precession of $\vec{\mu}$ around B_0

<u>Period of precession:</u>

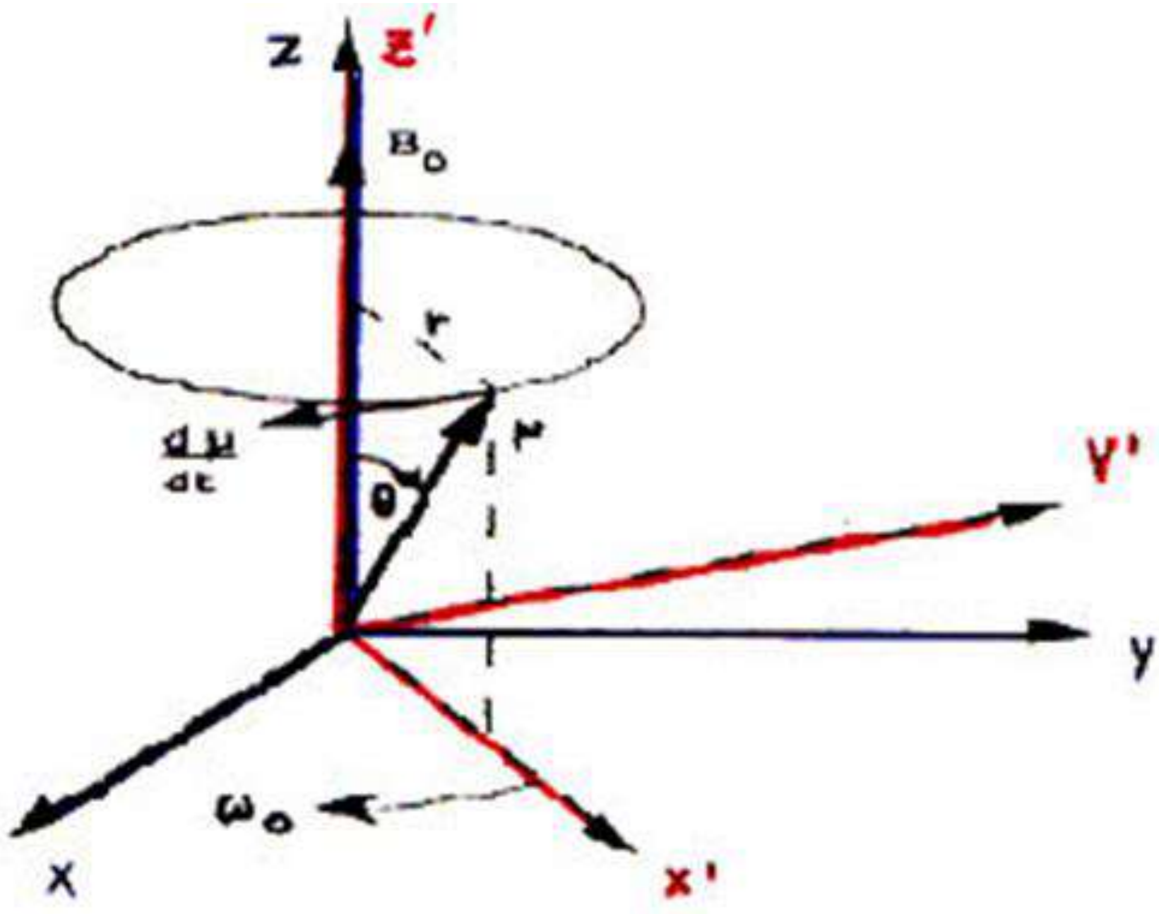
$T_0 = 2\pi r \,/\, d\mu/dt$ with $r = \mu \sin\theta$ and $d\mu/dt = \gamma\, \mu\, B_0 \sin\theta$

$\Rightarrow T_0 = 2\pi / \gamma B_0$ $\Rightarrow$ $\omega_0 = \gamma B_0$ **Larmor frequency**

Precession of the magnetic moment around the magnetic field B_0

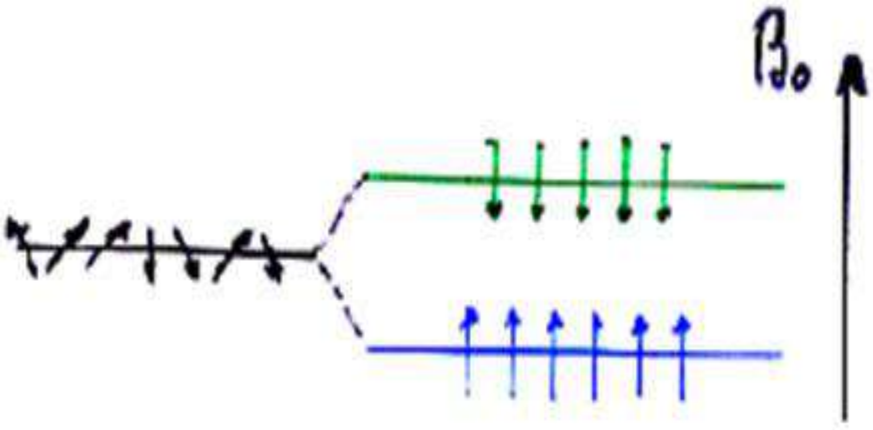


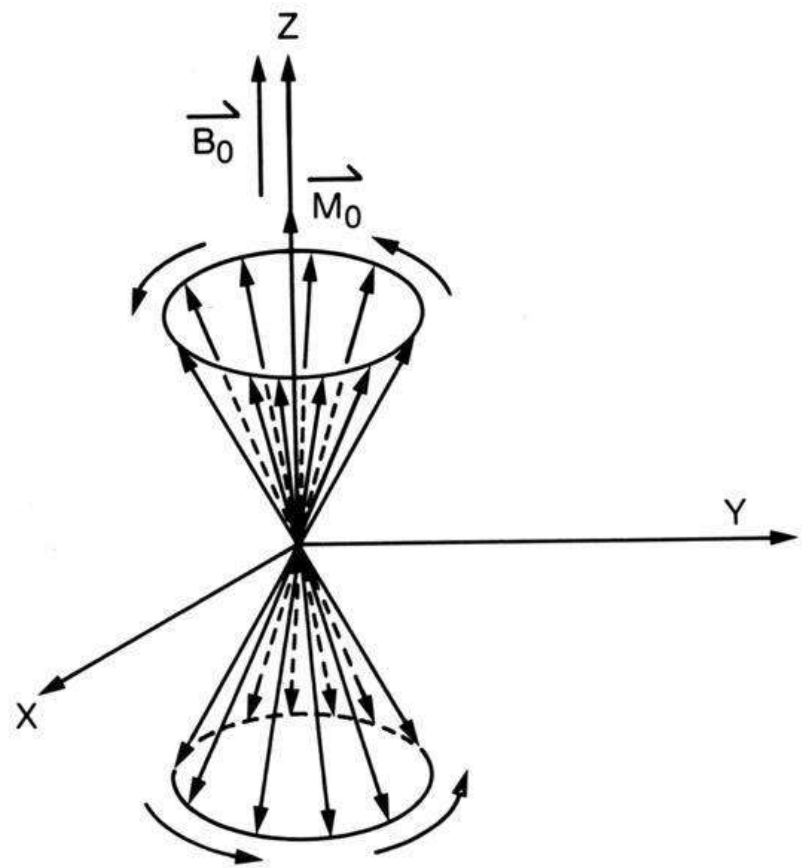
Laboratory frame and rotating frame



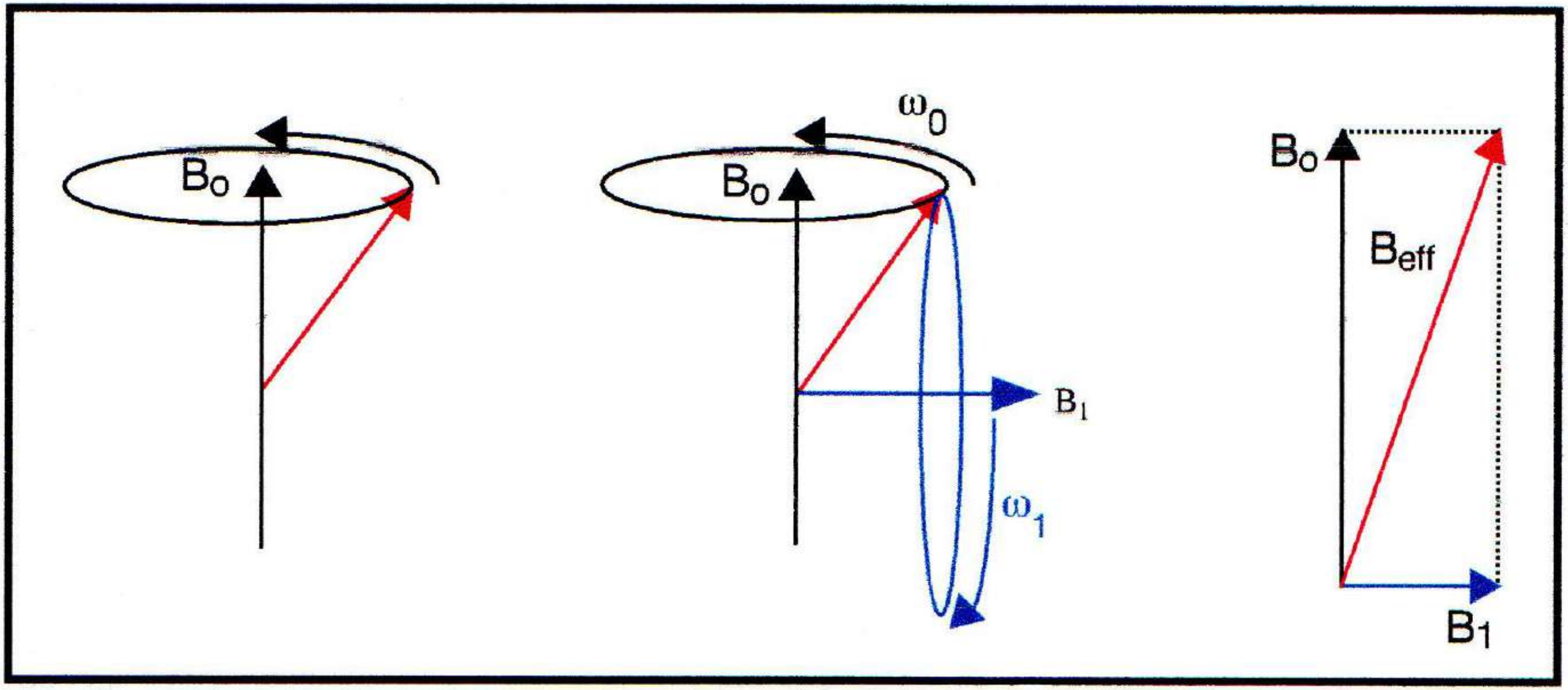
Orientation and precession of nuclear spins (I = 1/2) at thermal equilibrium in a stationary magnetic field Bo that defines the z-axis. In reality, the angle between the vectors and the z-axis is much smaller than is shown for illustrative purposes

Spins 1/2

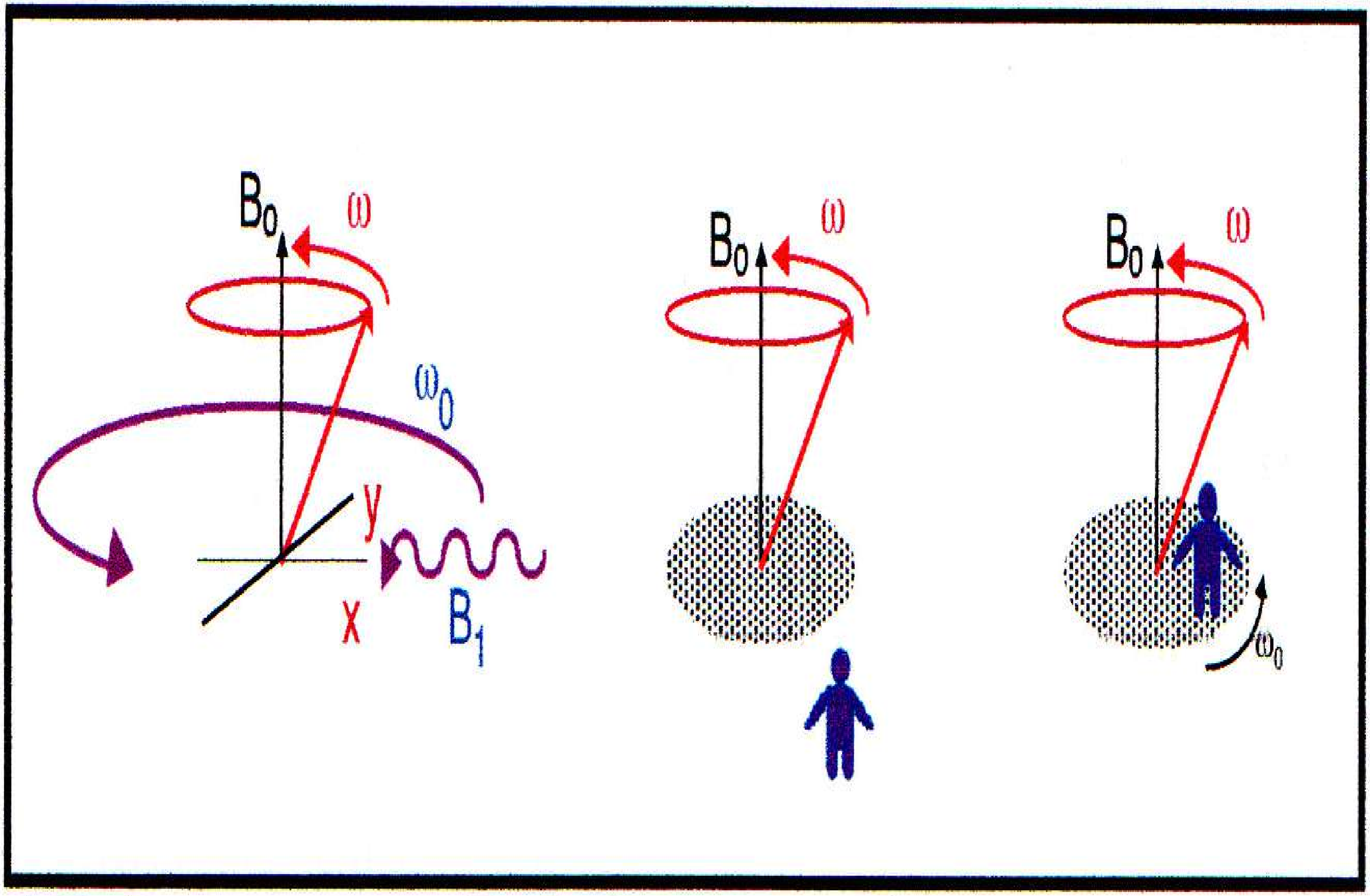




During the NMR experiment we use B_0 and B_1

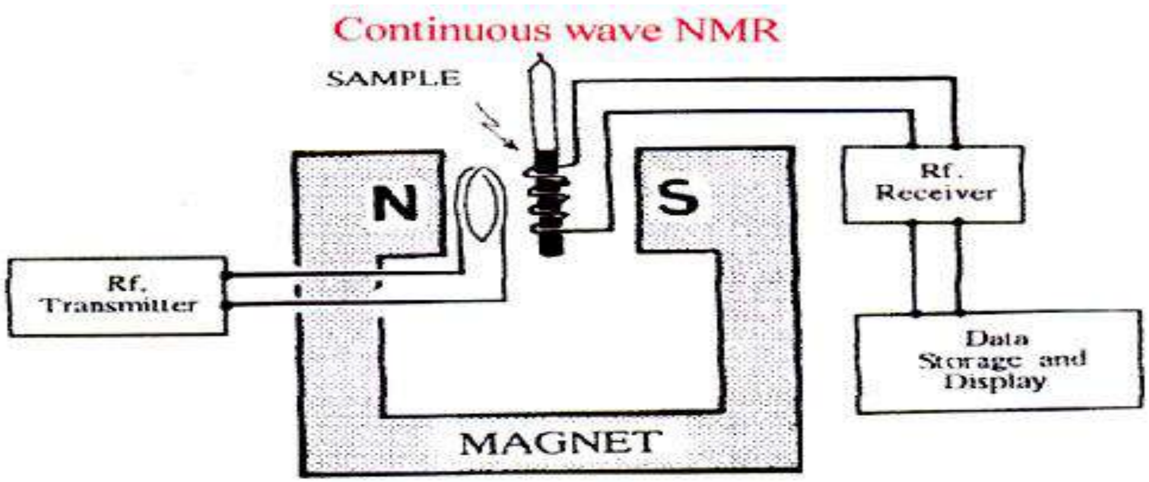


Laboratory and rotating frames



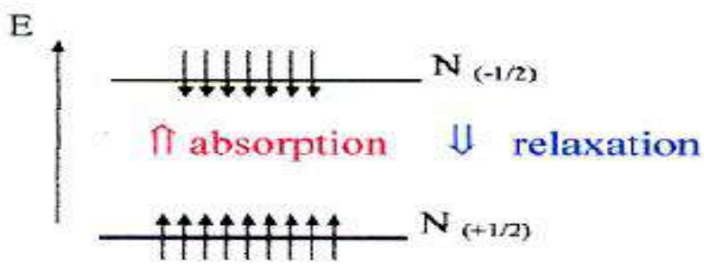
- Spectrometer

Electro- magnet up to 100 MhZ for protons (2.34 T)



Schematic diagram indicating the basic components of an NMR spectrometer

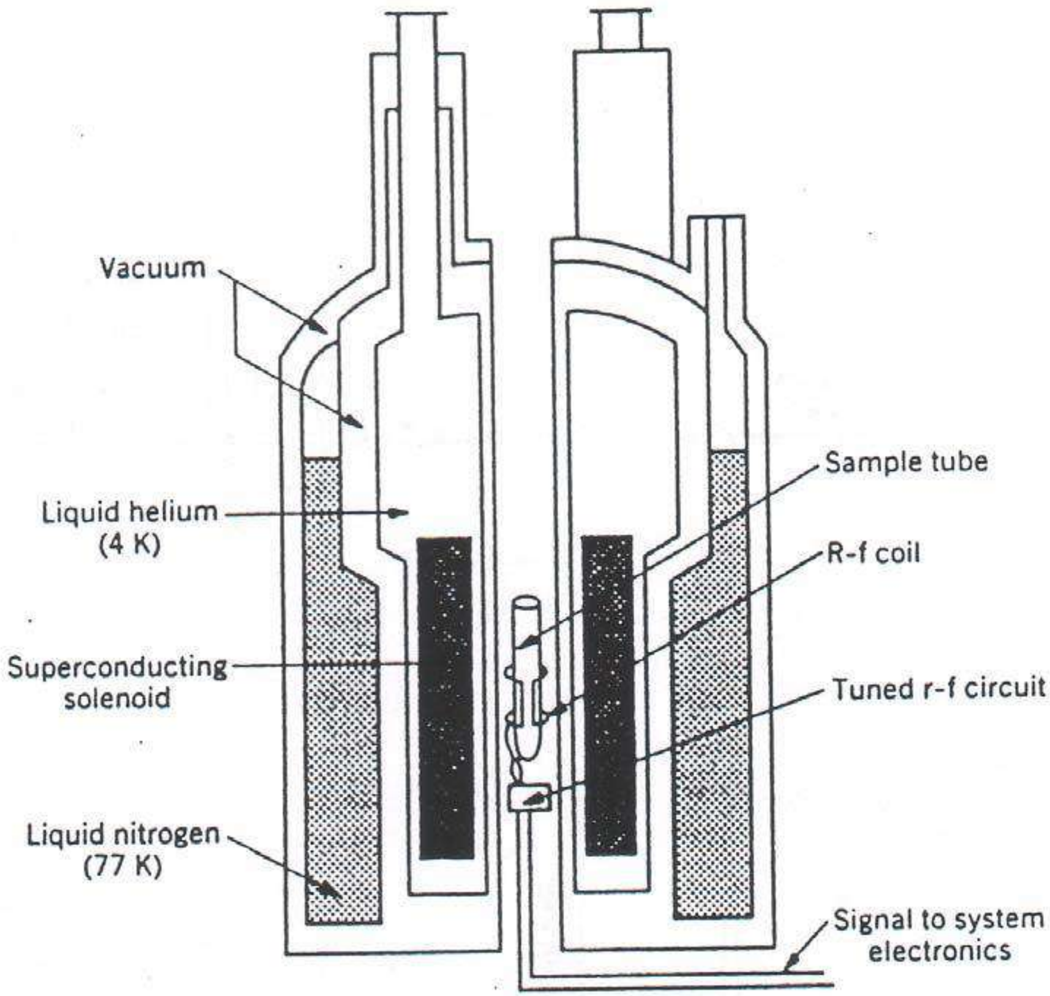
$\omega_0 = \gamma B_0$. Generally ω_0 is fixed and we scan B_0.



Signal intensity proportional to $N_{(+1/2)} - N_{(-1/2)}$ (very small). For example for protons, 300K, B_0= 0,95 tesla, $N_{(+1/2)}/N_{(-1/2)}$=1.0000066.

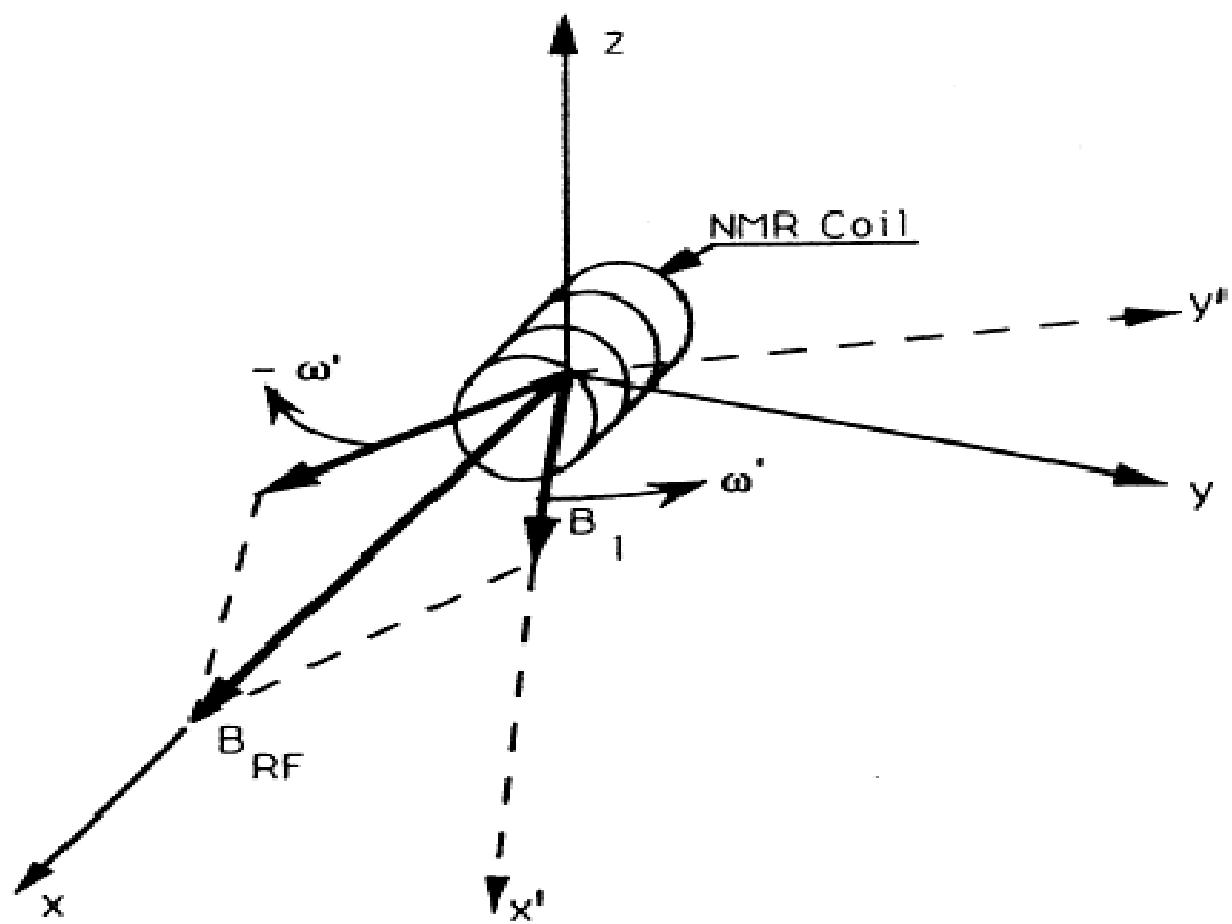
Phenomenon of saturation due to a strong absorption: $N_{(+1/2)} - N_{(-1/2)}$ $\Rightarrow$ S =0

Superconducting magnet
now up to about 23 teslas



- NMR experiment

Decomposition of the radiofrequency field in two components with two opposite angular velocity.



Interaction with the radiofrequency Field $\overrightarrow{B_{RF}}$

A radiofrequency field $\overrightarrow{B_{RF}}$ is applied ⊥ B_0 along OX of the lab. Frame.

$$B_{RF} = 2\,B_1 \cos \omega_1\, t$$

This rf field can be split into two rotating components of fixed amplitude and with angular velocities of ± ω '. The component with the velocity -ω ' has a negligible effect.

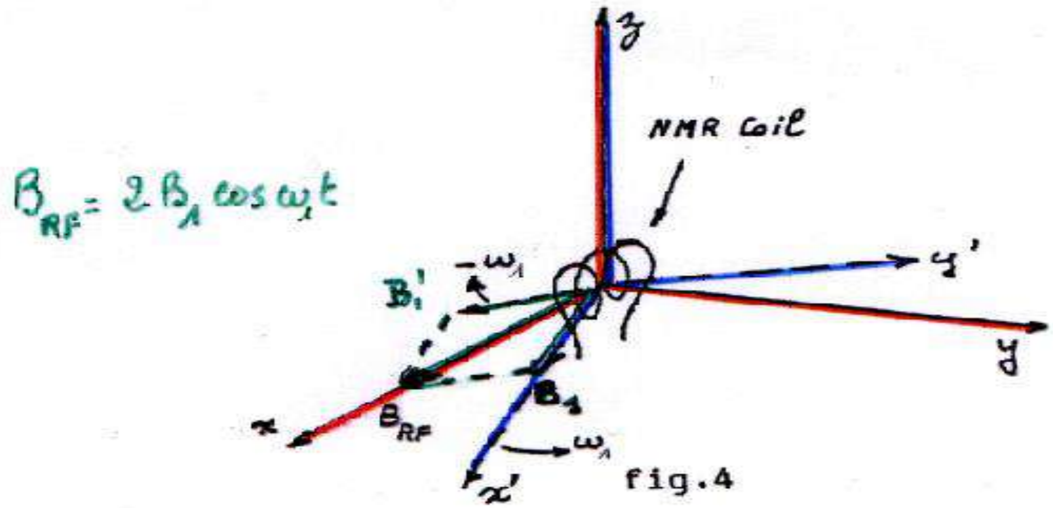
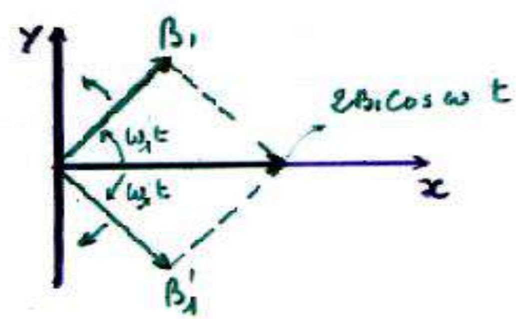


fig.4



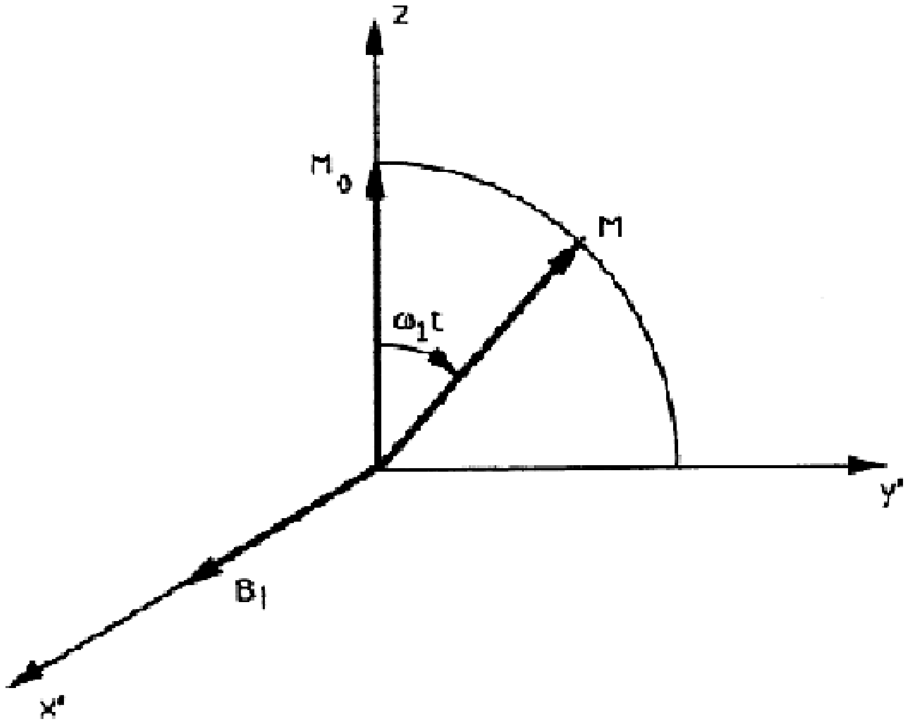
Pulsed NMR

A high power radiofrequency field B_1 is applied to the sample for a short time (about microsecond). During this pulse the magnetization rotates in the rotating frame according to the equation

$$\omega_1 = \gamma B_1$$

at a rate proportional to the RF intensity

$$\theta = \omega_1 t_p = \gamma B_1 t_p$$



Pulsed NMR

This method does not give the NMR signal directly. A high power B_{RF} is applied to the sample for about one microsecond. During this pulse the magnetization rotates in the rotating frame according to equation

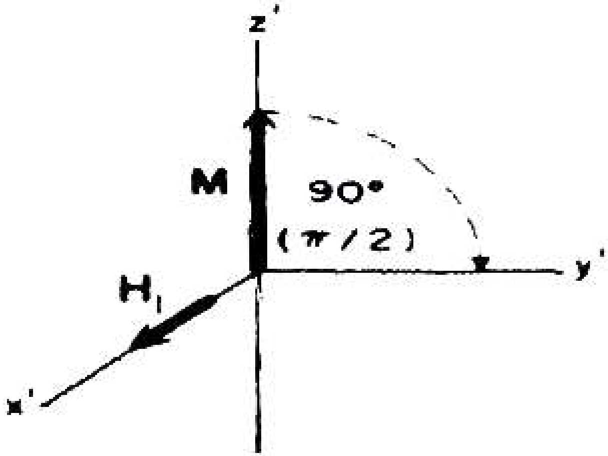
$$\omega_1 = \gamma B_1$$

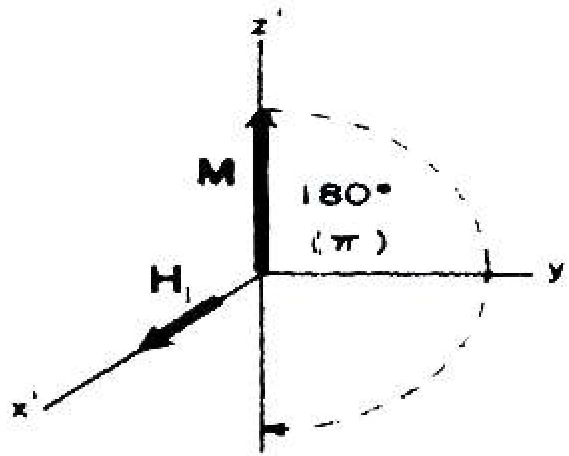
at a rate proportional to the RF intensity.

$$\theta = \omega_1\ t_p = \gamma B_1\ t_p$$

We will use very often $\theta=\pi/2$ **and** $\theta=\pi$

If $\theta=\pi/2$, $\vec{M_0}$ will be directed along Y'. It then induces a current in the receiver coil which is in the X0Y plane. This current is at the origin of the NMR signal. After this period the system evolves under the effect of relaxation.





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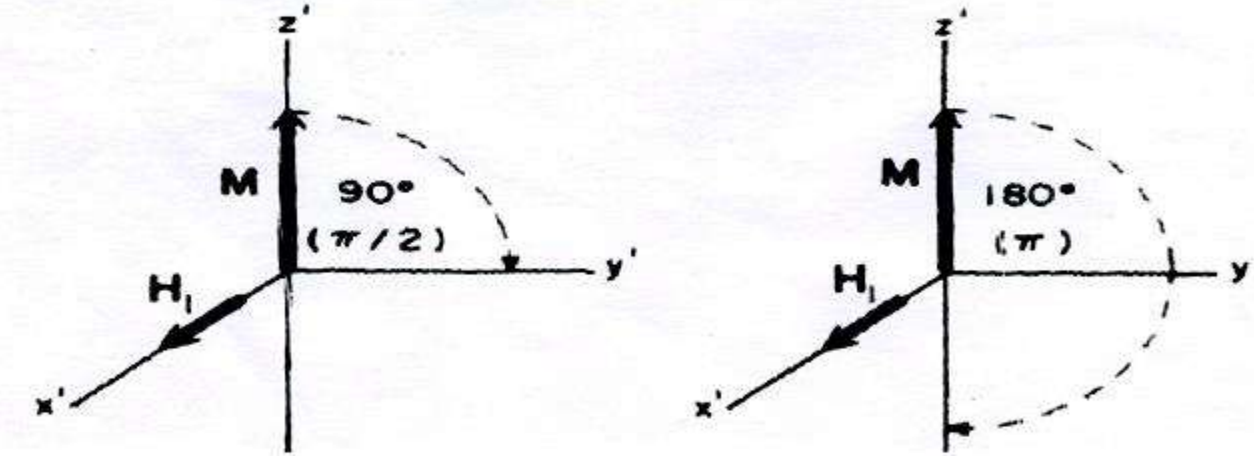
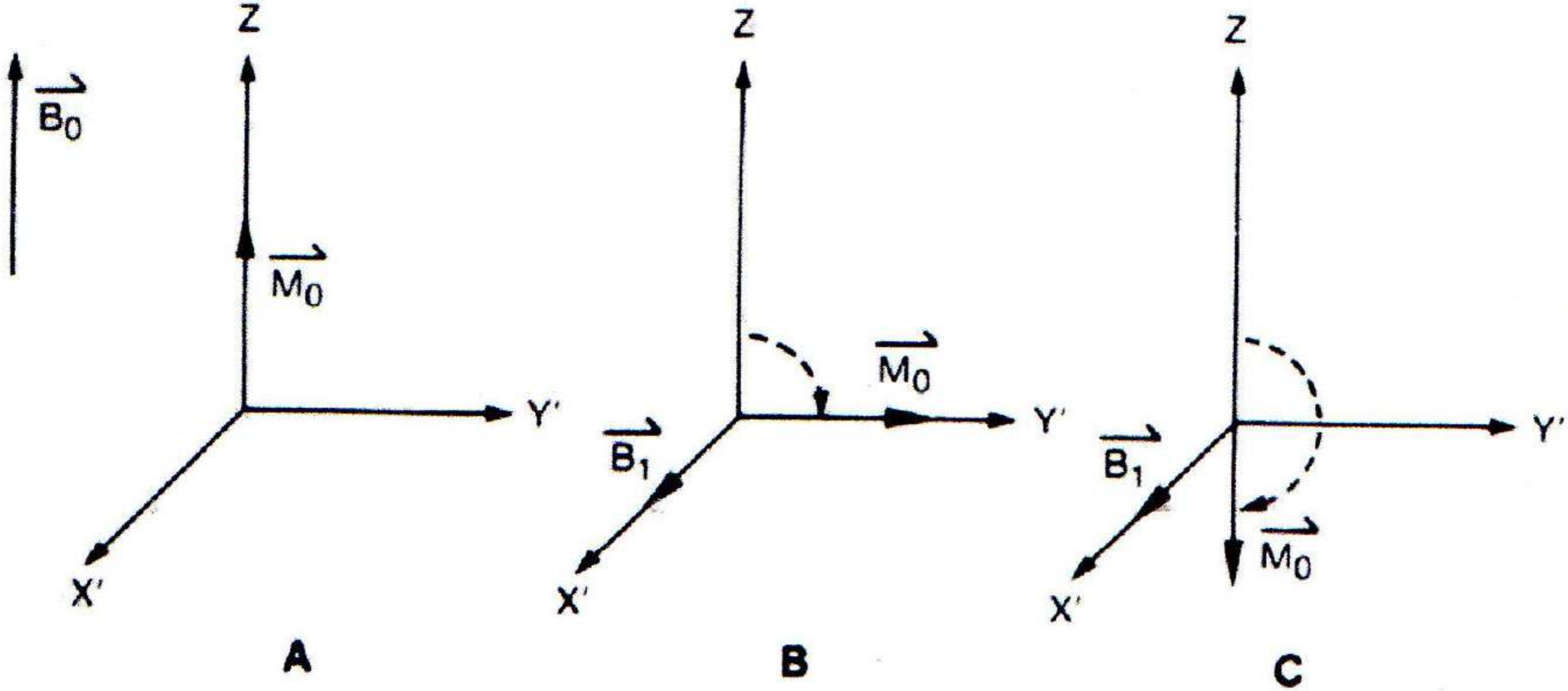
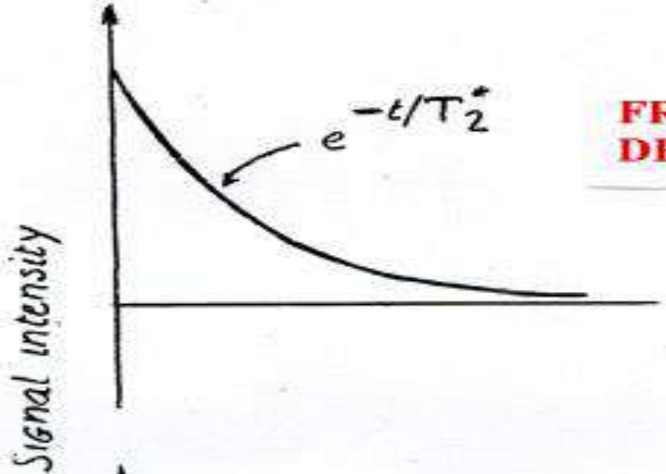
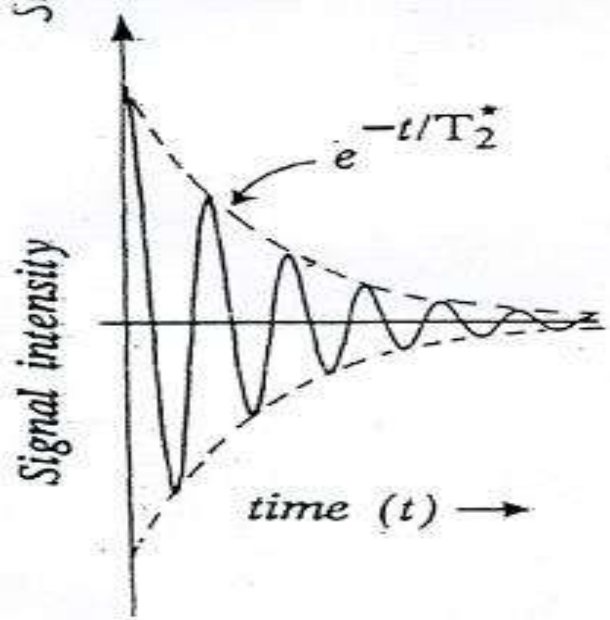


Pulses $\pi/2$ and π

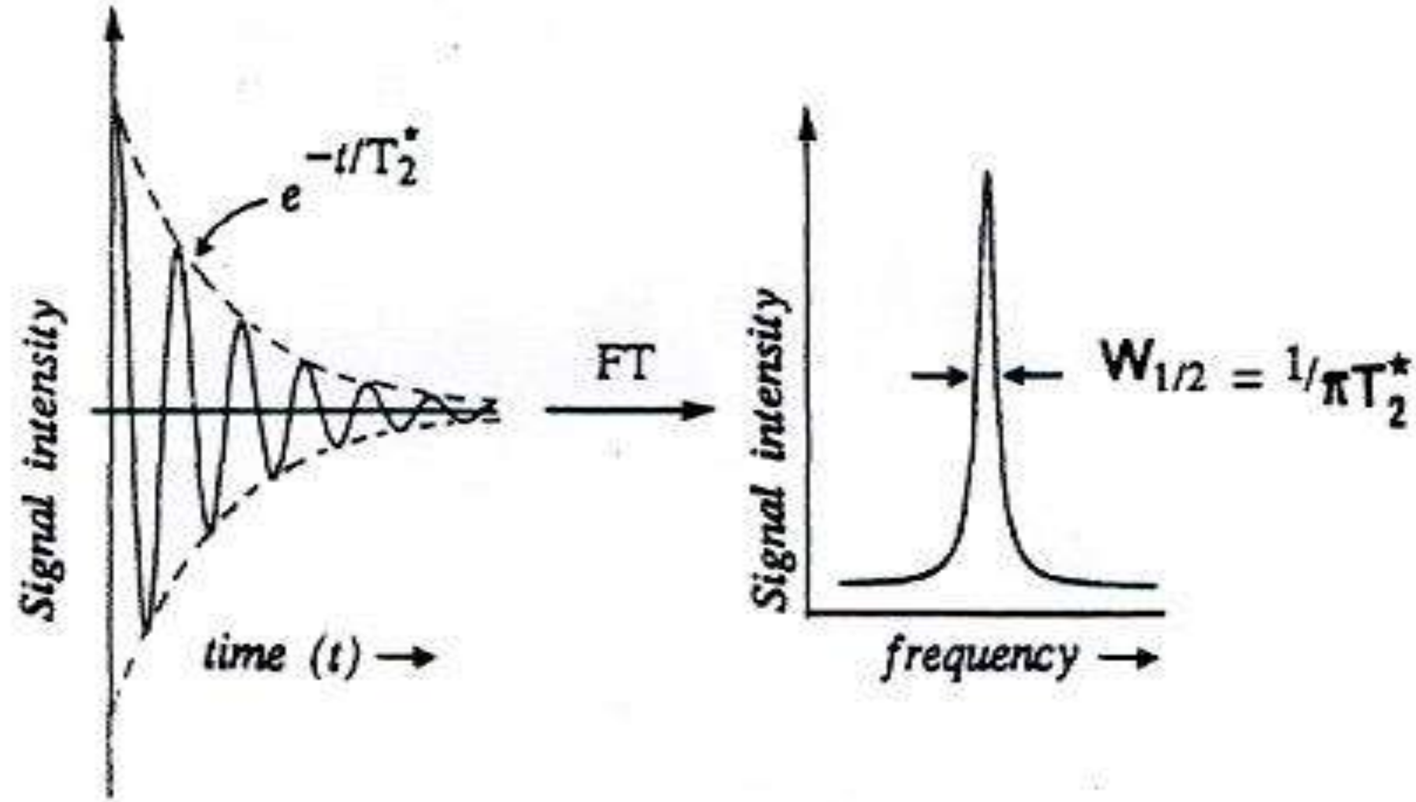


FREE INDUCTION DECAY (FID)





Generally the system contains several nuclei of the same species that differ in Larmor frequency because of various perturbations (chemical shifts, spin-spin coupling, etc.). Then they are precessing at a frequency different from that of the rotating frame, and interference effects can occur (beatings).



Fourier transformation of an FID which decays exponentially with a time constant of T_2^* s gives rise to a Lorentzian lineshape whose width at half-height is $1/\pi T_2^*$ Hz

Free induction decay (FID) and Fourier transform