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),…

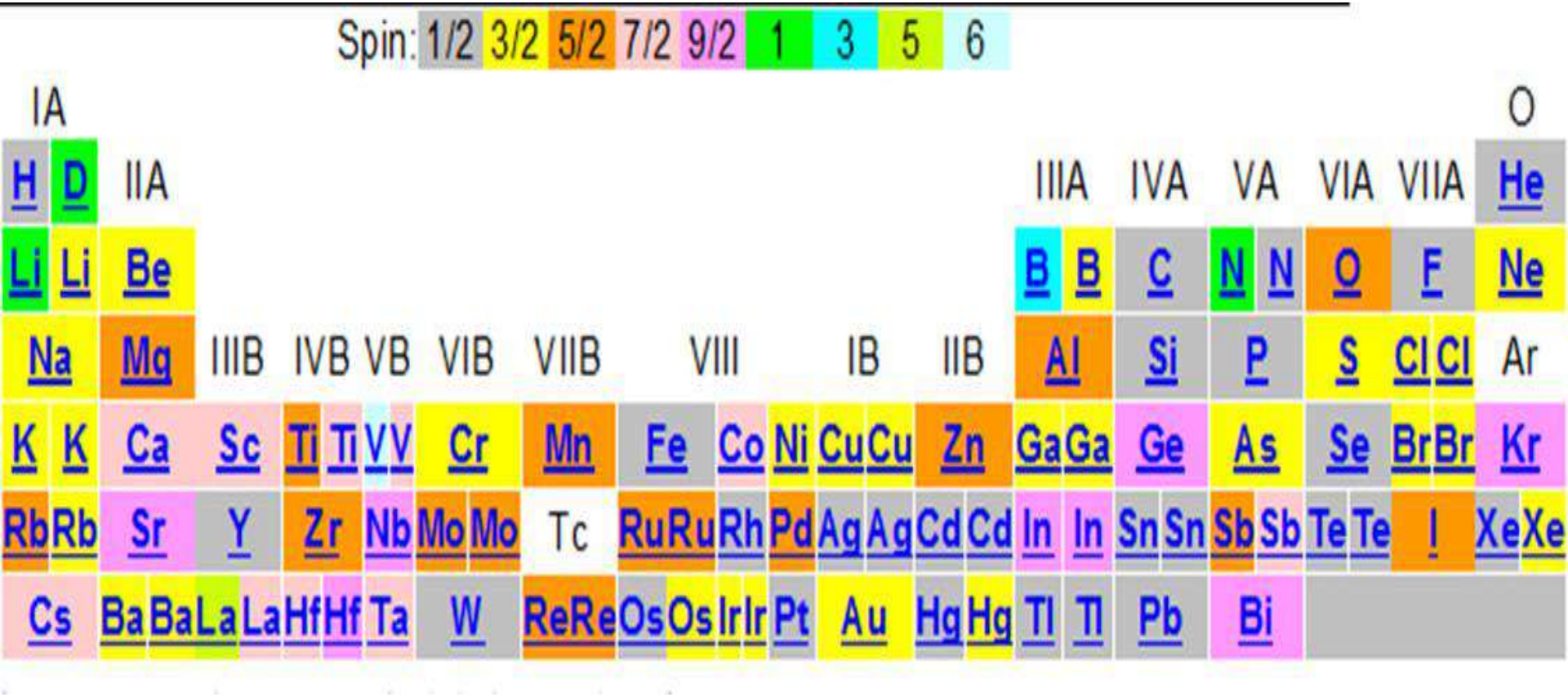
5/2 : ^{17}O, ^{27}Al, …..

$\vec{I}$ = dimensionless vector

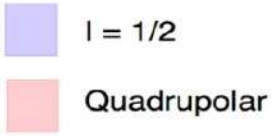
$\mathcal{M} = \hbar \vec{I}$ = angular momentum

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

γ = gyromagnetic ratio


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

The Periodic Table of the Elements



1 H Hydrogen 1.00794																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012182											5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050											13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

- Zeeman interaction

Zeeman interaction : $\hat{H}_Z$

The energy of a magnetic dipole μ in a magnetic field with induction 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 are therefore $2I + 1$ accessible energy levels

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

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

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

$$\omega_0 = \gamma B_0$$

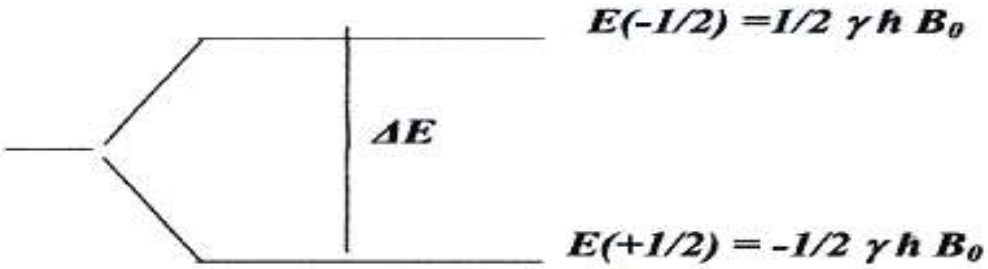
where ω_0 is the angular frequency.

SPIN ½

$$\vec{\mu} = \gamma h \vec{I}$$

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

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



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

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

SPIN > ½

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

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

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

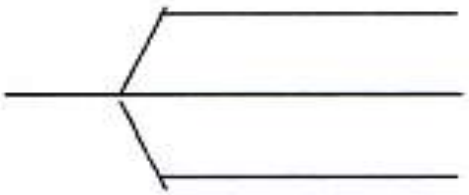
Examples spin I> ½

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

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

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

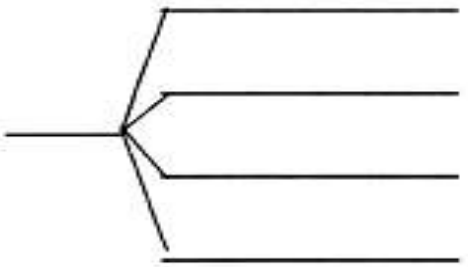
B=0	*B=B₀*	*Levels*	*Energies*
		-1	$+\gamma \hbar B_0$
		0	0
		+1	$-\gamma \hbar B_0$



The three equidistant Zeeman energy levels of an isolated 1 spin

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

B=0	*B=B₀*	*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

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

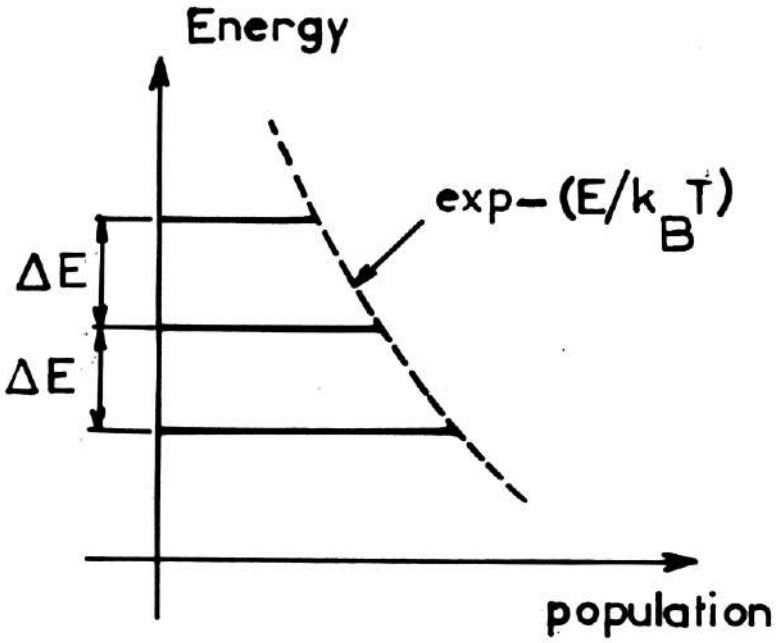
$k_B T \sim 10^{-21}$ j

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

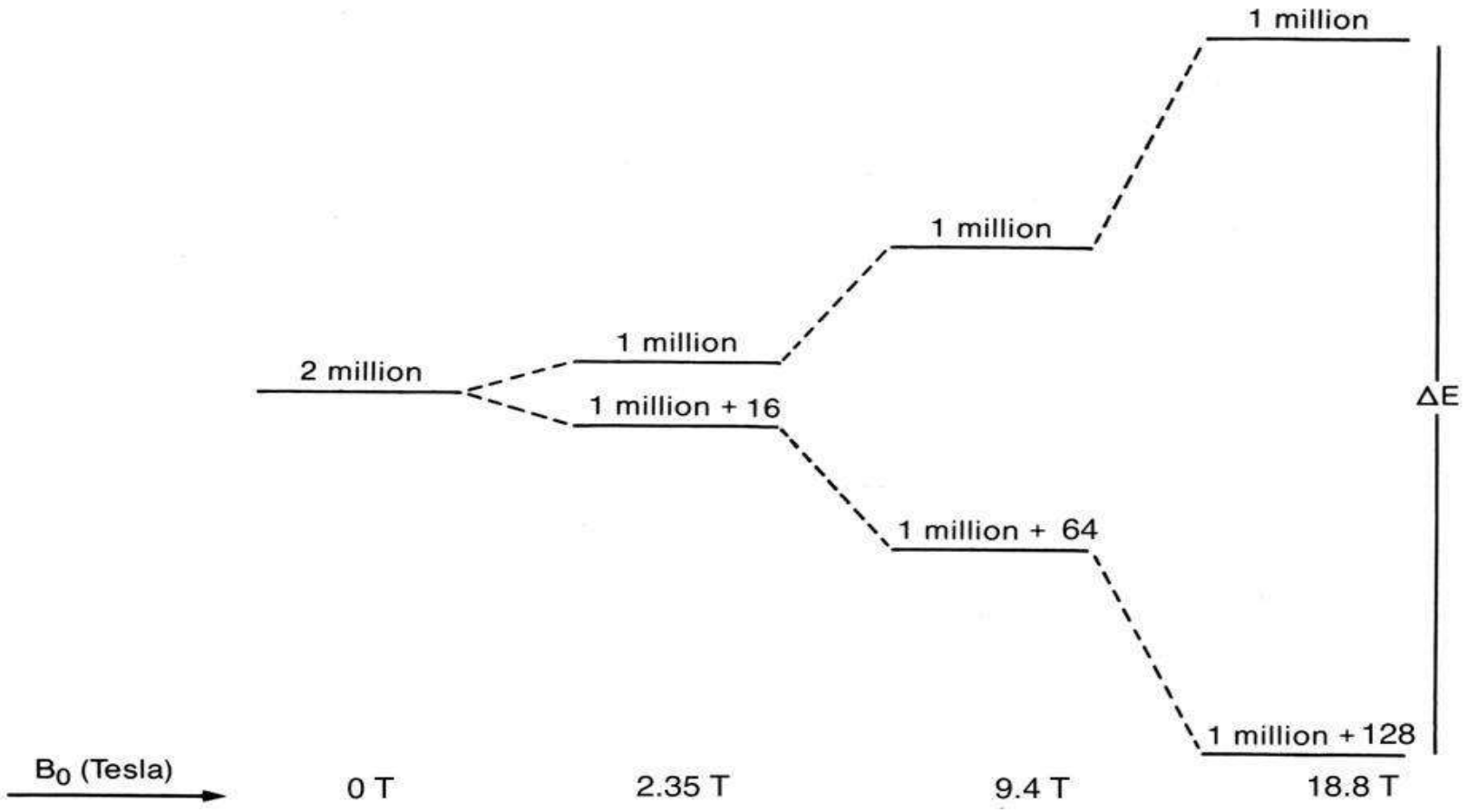
$h\nu_{OPT.} \sim 6.6 \times 10^{-34}$ j.s $\times 10^{15}$ $s^{-1} = 6.10^{-19}$ j

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

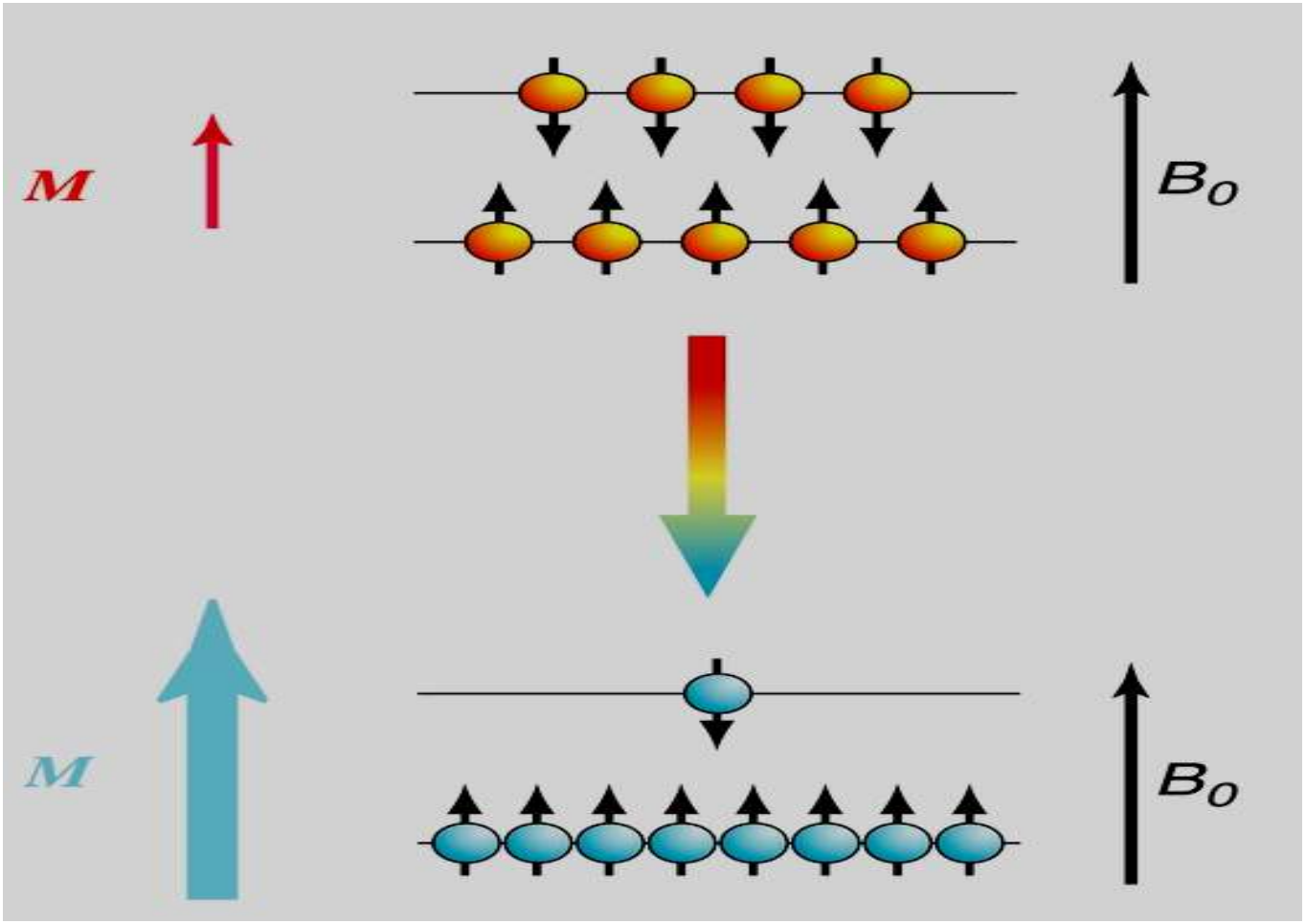
$\Delta E_{OPT.} >> k_B T$



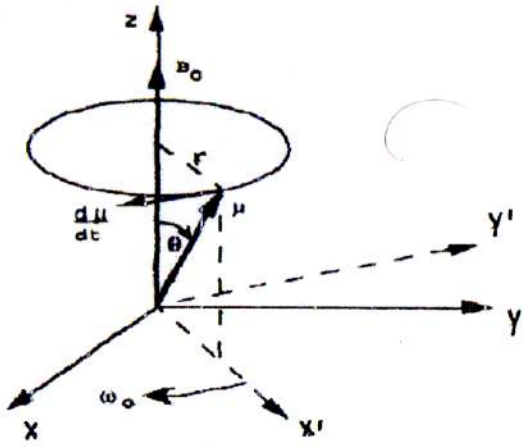
Distribution of the spins ½ assuming that we have two millions of spins. Of course generally there are more numerous



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

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

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

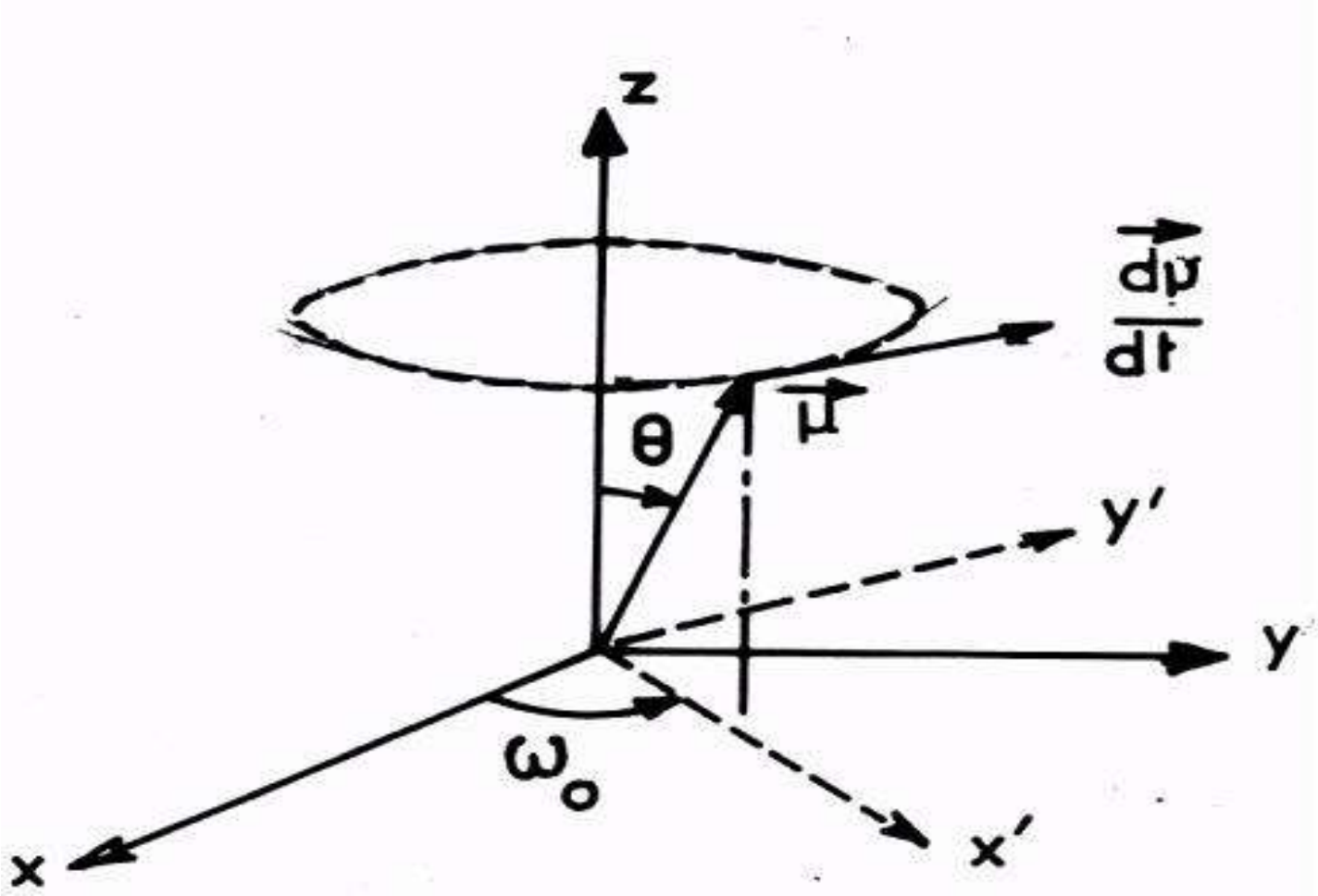
$\Rightarrow$ Precession of $\vec{\mu}$ around B_0

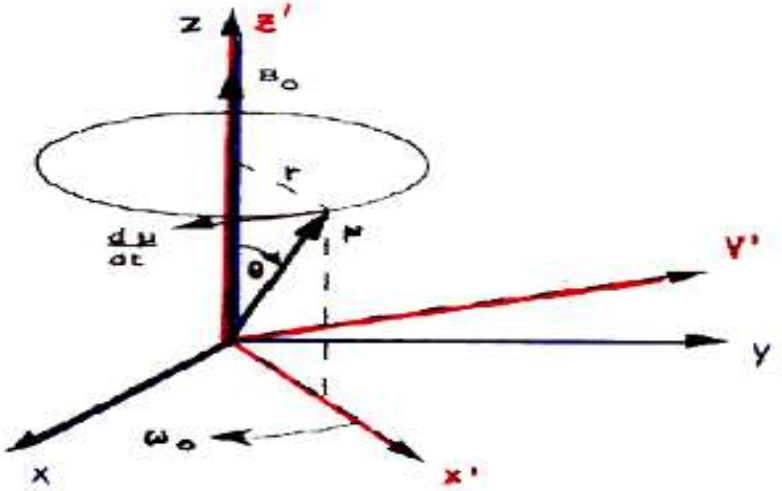
<u>Period of precession:</u>

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

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

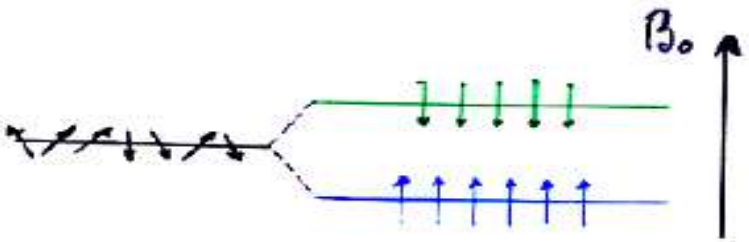
Precession of the magnetic moment around the magnetic field B_0

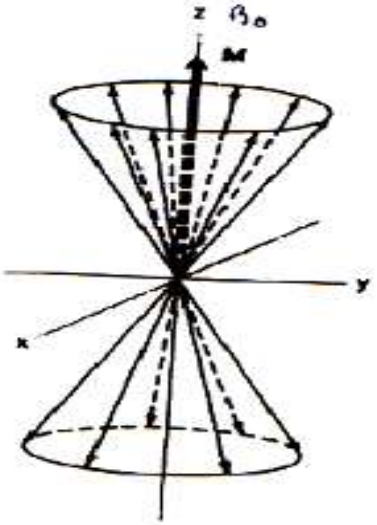




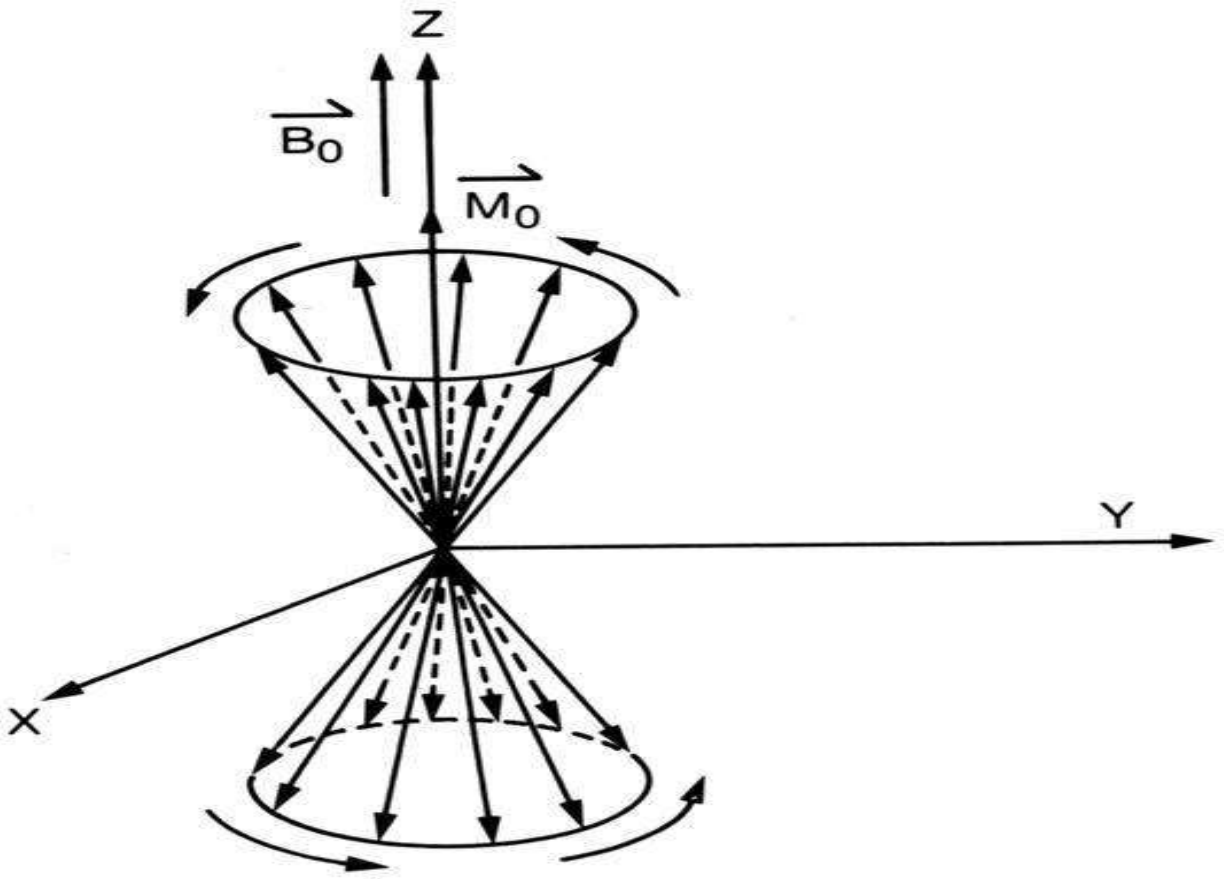
LABORATORY FRAME

ROTATING FRAME



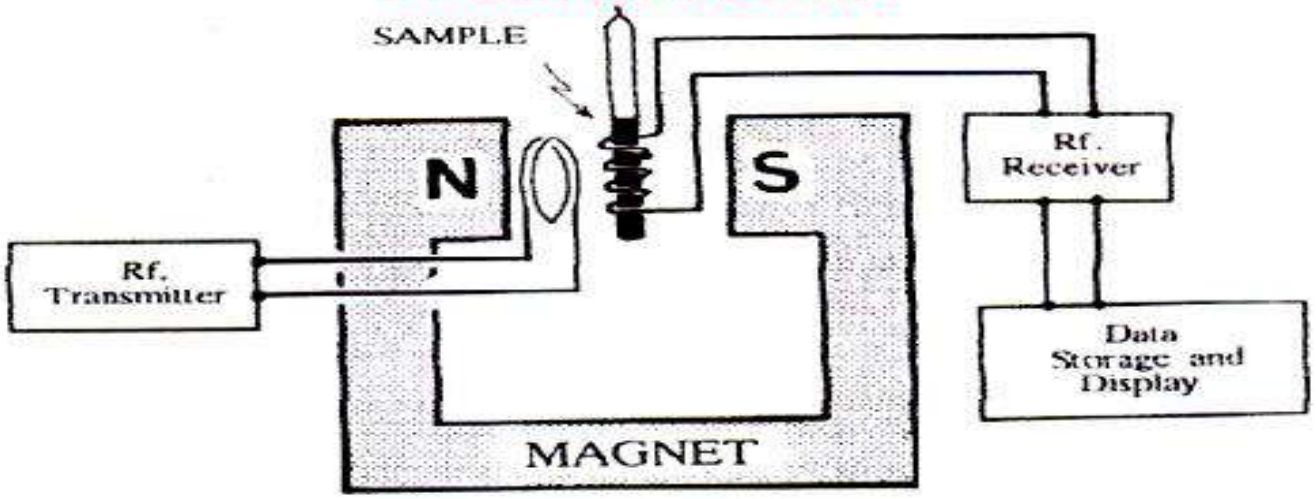


Orientation and precession of nuclear spins (I = 1/2) at thermal equilibrium in a stationary magnetic field Bo that defines the z-axis. In reality, the angle between the vectors and the z-axis is much smaller than is shown for illustrative purposes



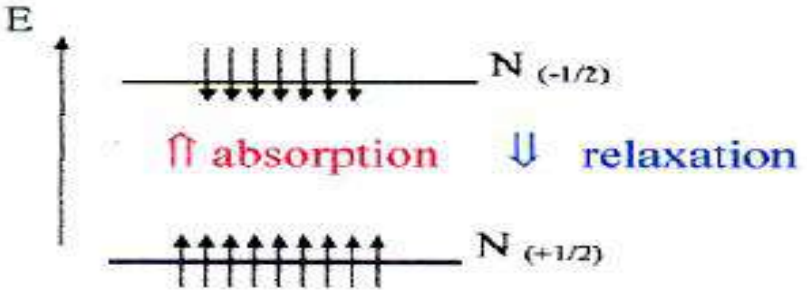
- Spectrometer

Continuous wave NMR



Schematic diagram indicating the basic components of an NMR spectrometer

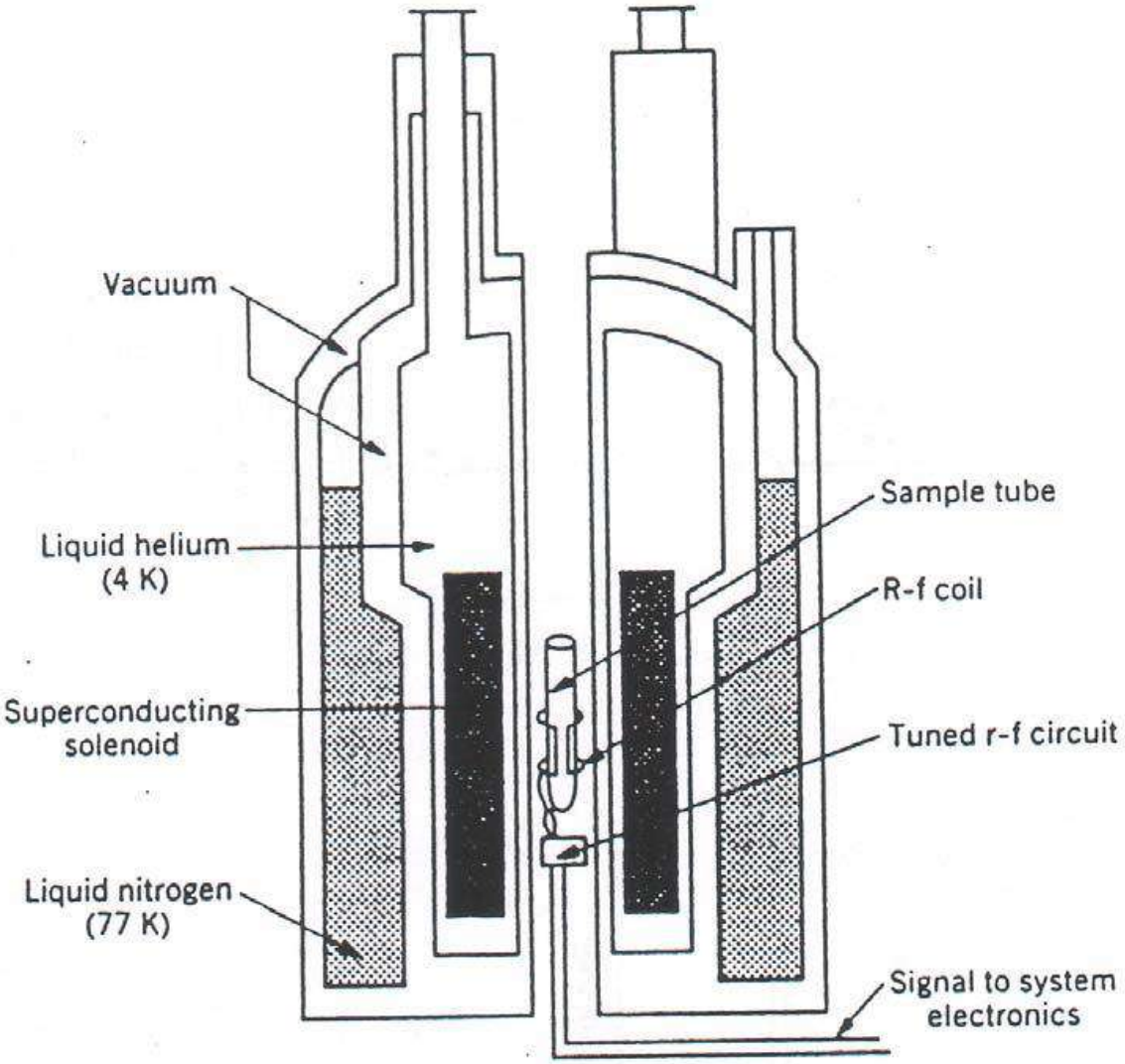
$\omega_0 = \gamma B_0$. Generally ω_0 is fixed and we scan B_0.



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

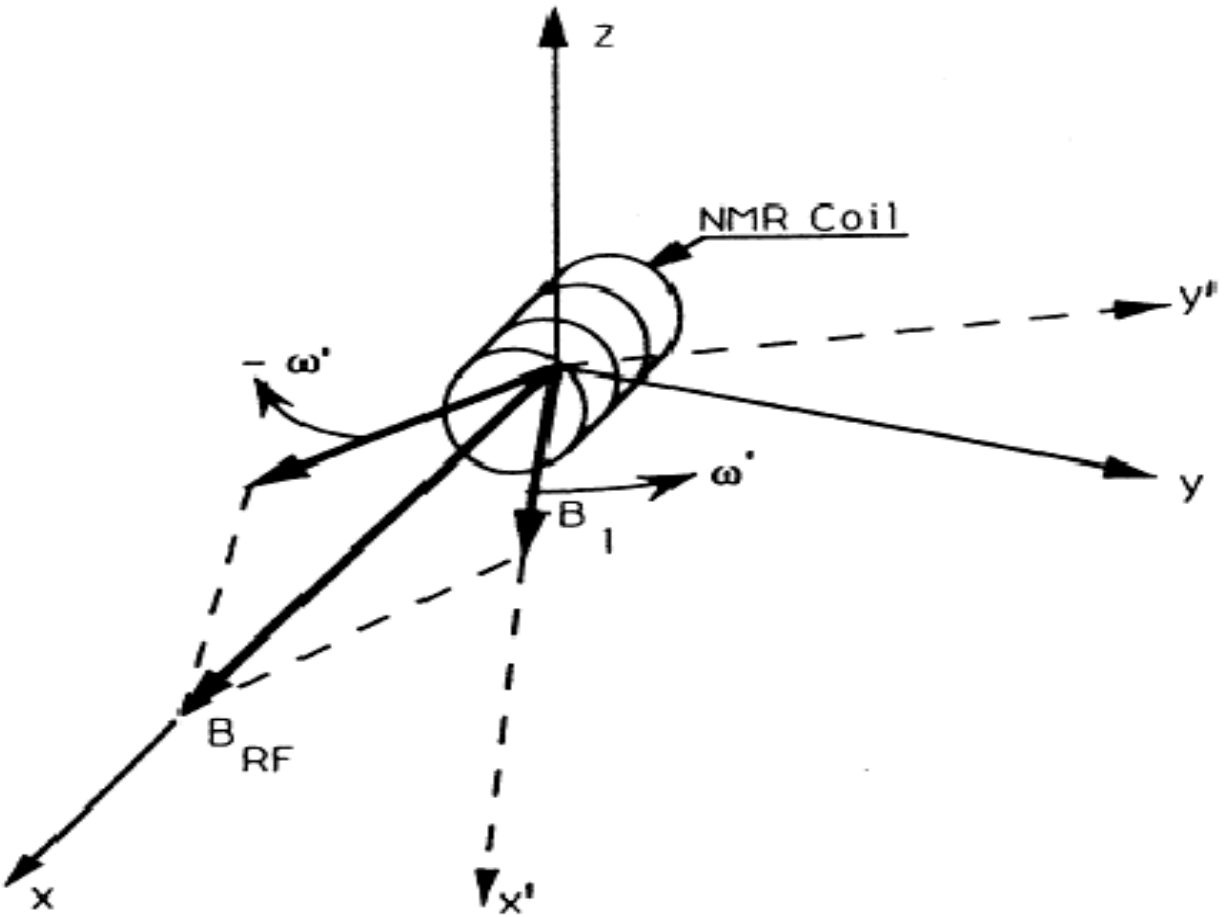
Phenomenon of saturation due to a strong absorption: $N_{(+1/2)} - N_{(-1/2)}$
$\Rightarrow$ S =0

Superconducting magnet



- NMR experiment

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



Interaction with the radiofrequency Field $\vec{B}_{RF}$

A radiofrequency field $\vec{B}_{RF}$ is applied $\perp B_0$ 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 $\pm \omega'$. The component with the velocity $-\omega'$ has a negligible effect.

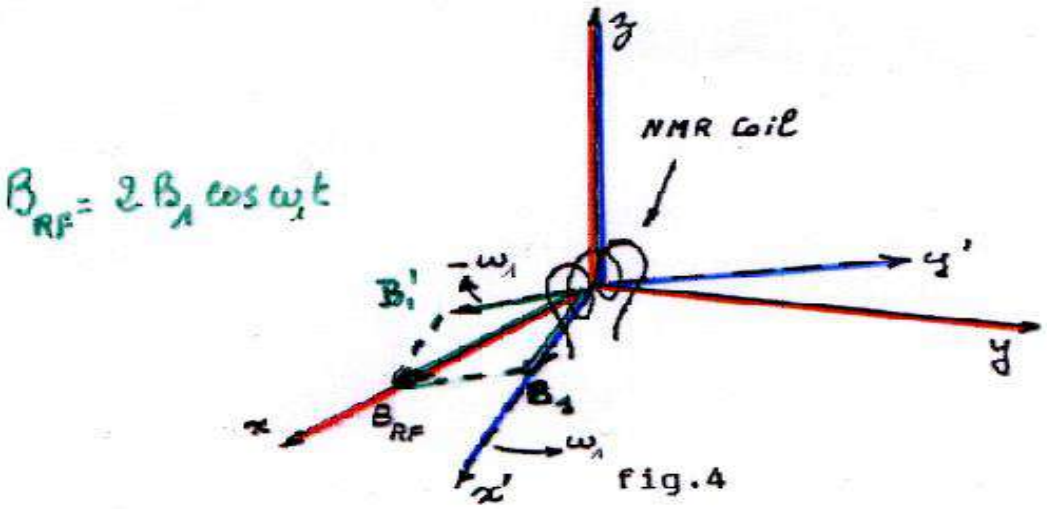
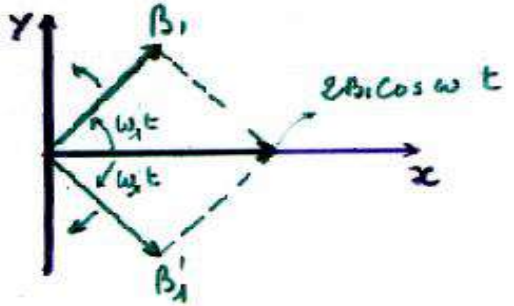


fig.4



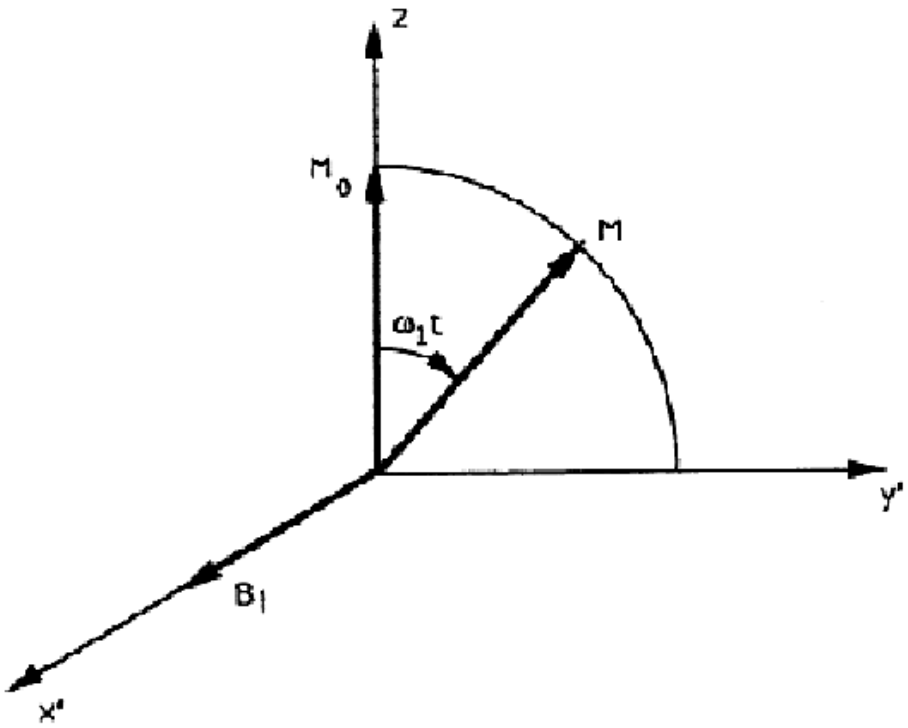
Pulsed NMR

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

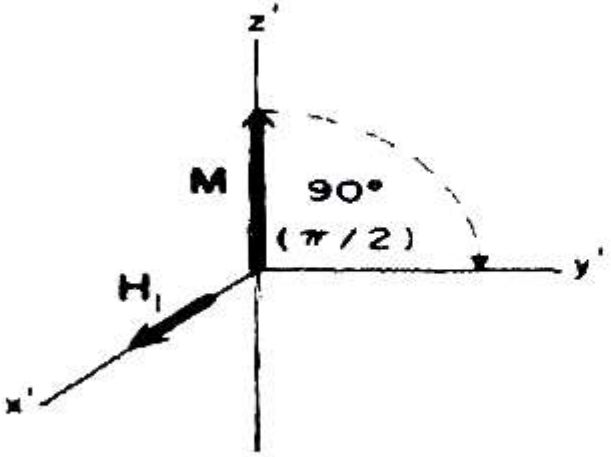
$$\omega_1 = \gamma B_1$$

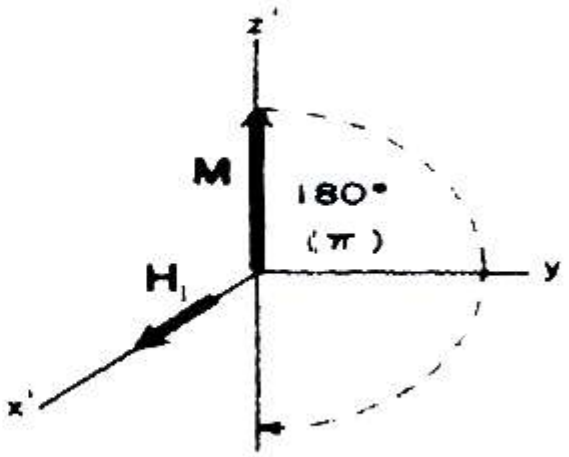
at a rate proportional to the RF intensity.

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

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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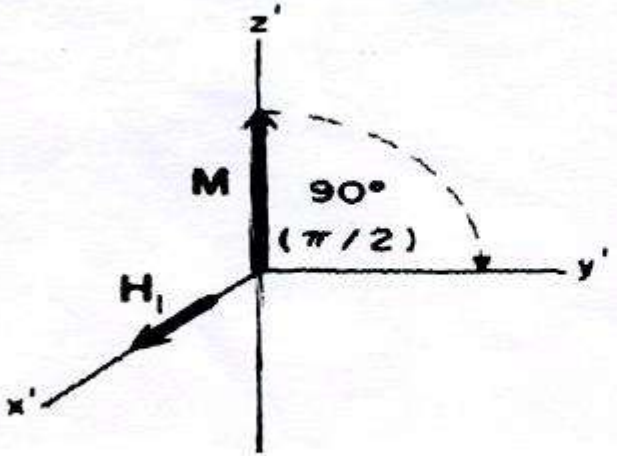
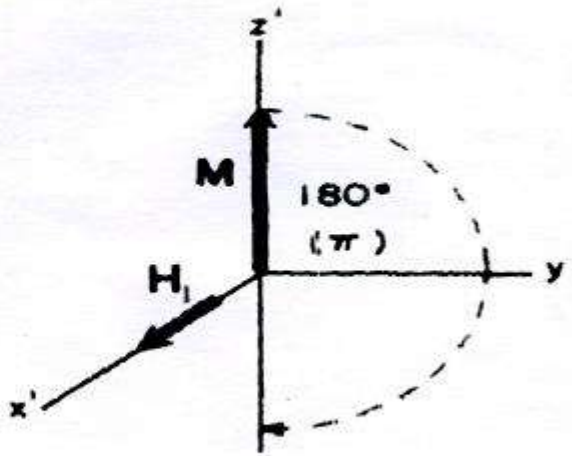
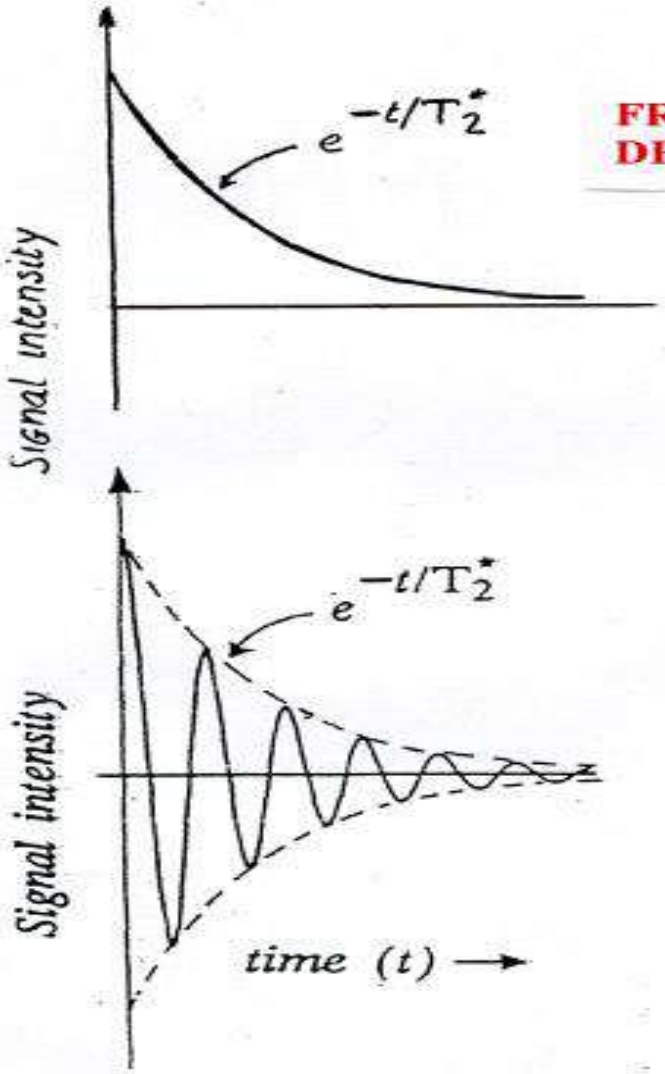
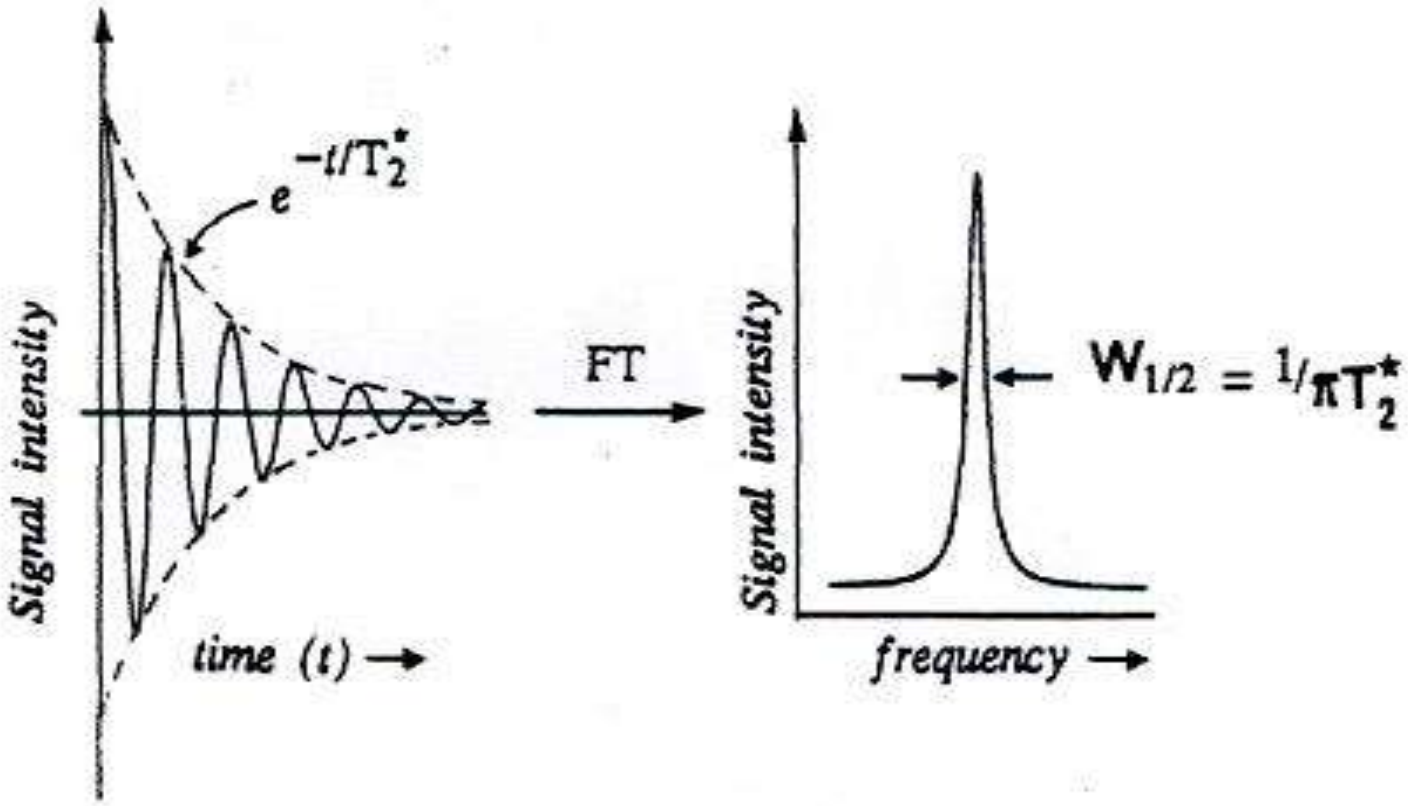




FREE INDUCTION DECAY (FID)



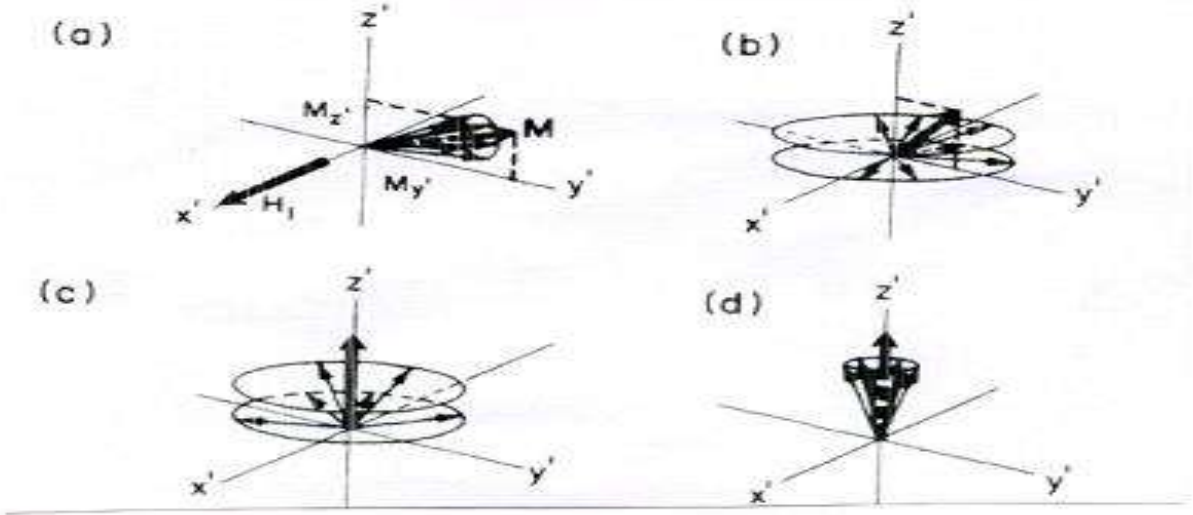
Generally the system contains several nuclei of the same species that differ in Larmor frequency because of various perturbations (chemical shifts, spin-spin coupling, etc.). Then they are precessing at a frequency different from that of the rotating frame, and interference effects can occur (beatings).



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

- **Relaxation**

Pulsed NMR- Relaxation



The system evolves under two relaxation mechanisms:

- For a set of spins coupled by interactions, as in a solid, the system can tend very rapidly towards an internal quasi-equilibrium with a time constant, **T_2, named spin-spin relaxation time.** During T_2 there is disappearance of the transversal magnetization by dispersion of the spins in the XOY plane.
- For such a set of spins in contact with the lattice, there is a **spin-lattice relaxation** characterized by the time **T_1,** and then restoration of the magnetization M_0 along B_0.

Generally, and specially for solids, $T_2 << T_1$

Bloch's equations: $dM_Z/dt = -(M_Z - M_0)/T_1$

$dM_X/dt = -M_X/T_2$ $\quad dM_Y/dt = -M_Y/T_2$

The magnitude of the relaxation time depends highly on:

- the type of nuclei (nuclei with spin 1/2 and low magnetogyric ratio have usually long relaxation time whereas nuclei with spin>1/2 have very short relaxation time)
- other factors like the physical state (solid or liquid state), the viscosity of the solution, the temperature ... etc.

In other words the relaxation time depends on the motion of the molecule.

Definitions:

The correlation time -τc (Tau-c): represents the time it takes for a molecule to reorient by 1 degree ("tumbling time").

The spectral density - J(w): describes the ranges of frequency motion that are present. Not all molecules tumbles at a unique rate: molecules tumbles, collide, change direction... at a range of rates up to the maximum rate of (1/ τc).

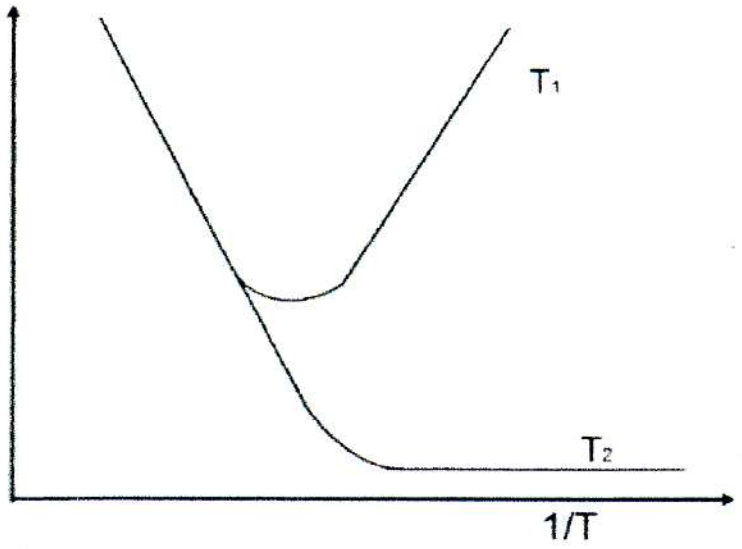
There are several relaxation mechanisms:

Interaction	**Range of interaction (Hz)**	**relevant parameters**
1- Dipolar coupling	10^4 - 10^5	- abundance of magnetically active nuclei -size of the magnetogyric ratio
2- Quadrupolar coupling	10^6 - 10^9	- size of quadrupolar coupling constant - electric field gradient at the nucleus
3- Paramagnetic	10^7 -10^8	concentration of paramagnetic impurities
4- Scalar coupling	10 - 10^3	size of the scalar coupling constants
5-Chemical Shift Anisotropy (CSA)	10 - 10^4	- size of the chemical shift anisotropy - symmetry at the nuclear site
6- Spin rotation		

Relaxation spin-lattice: transfert of energy from the system of spins to an acceptor of the lattice: rotations, translations, vibrations fluctuating in the domain of larmor frequencies

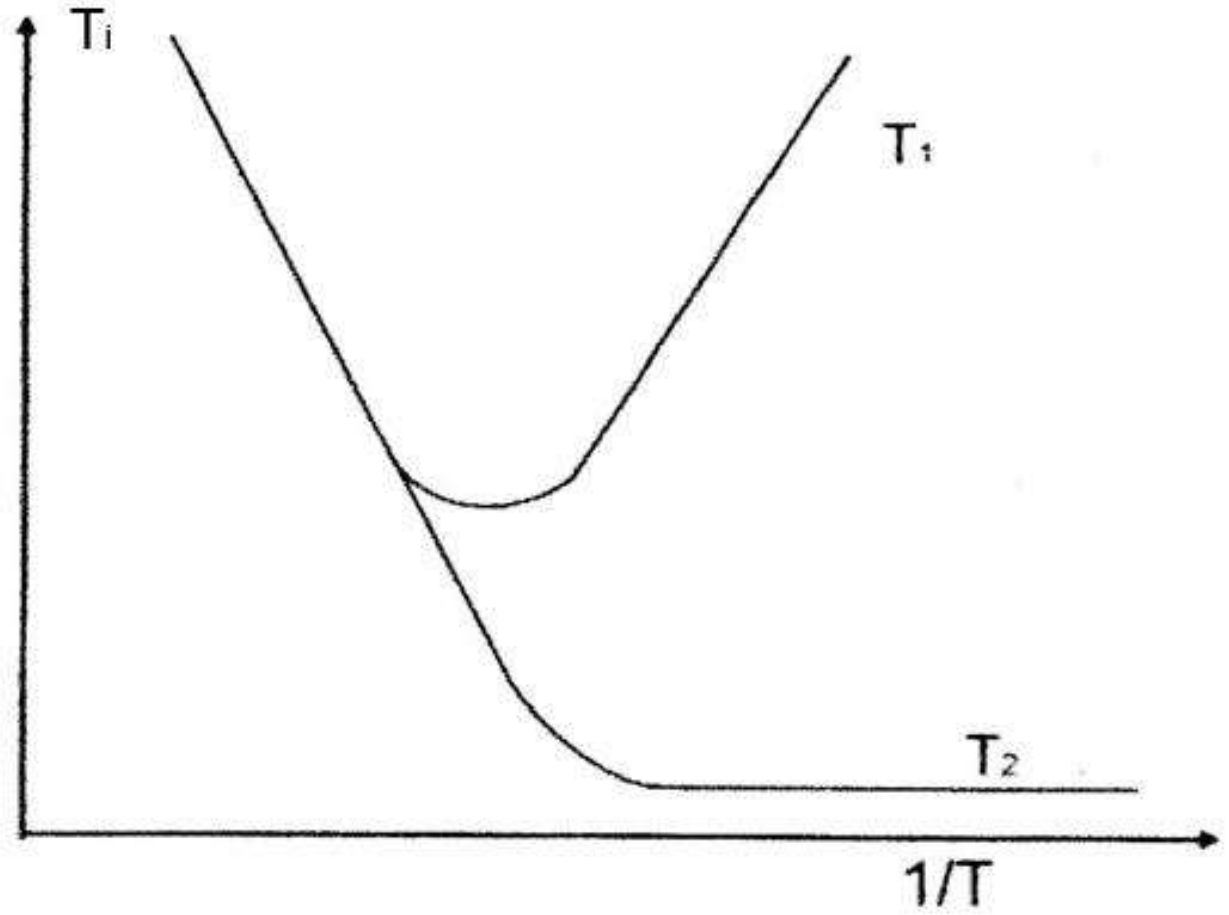
Relaxation spin-spin: destruction of the component MXY after a pulse.

Liquids: generally $T_1 = T_2$
Solids: Often $T_1 >> T_2$

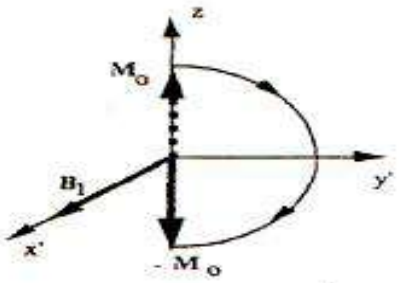


Variation of T_1 and T_2 against 1/T.

Generally: In liquids $T_1 = T_2$; in solids $T_1 >> T_2$

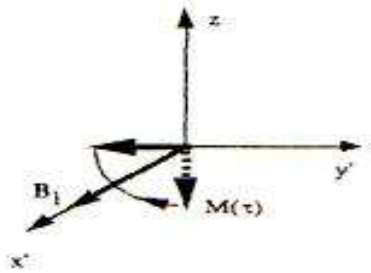


Measurement of T_1 with 180°, τ, 90° sequences



$t = 0+ \varepsilon$

Figure (a)



$t = \tau$

Figure (b)

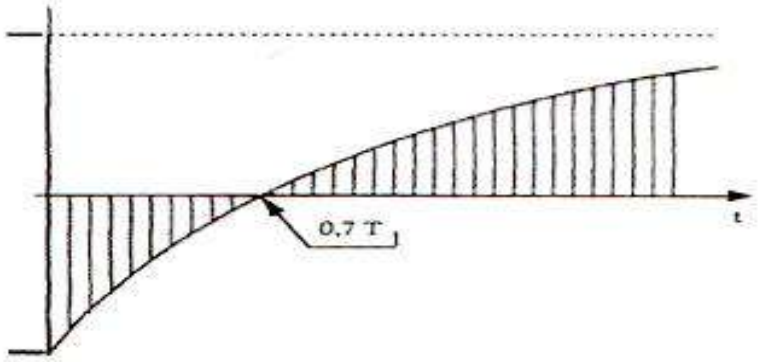


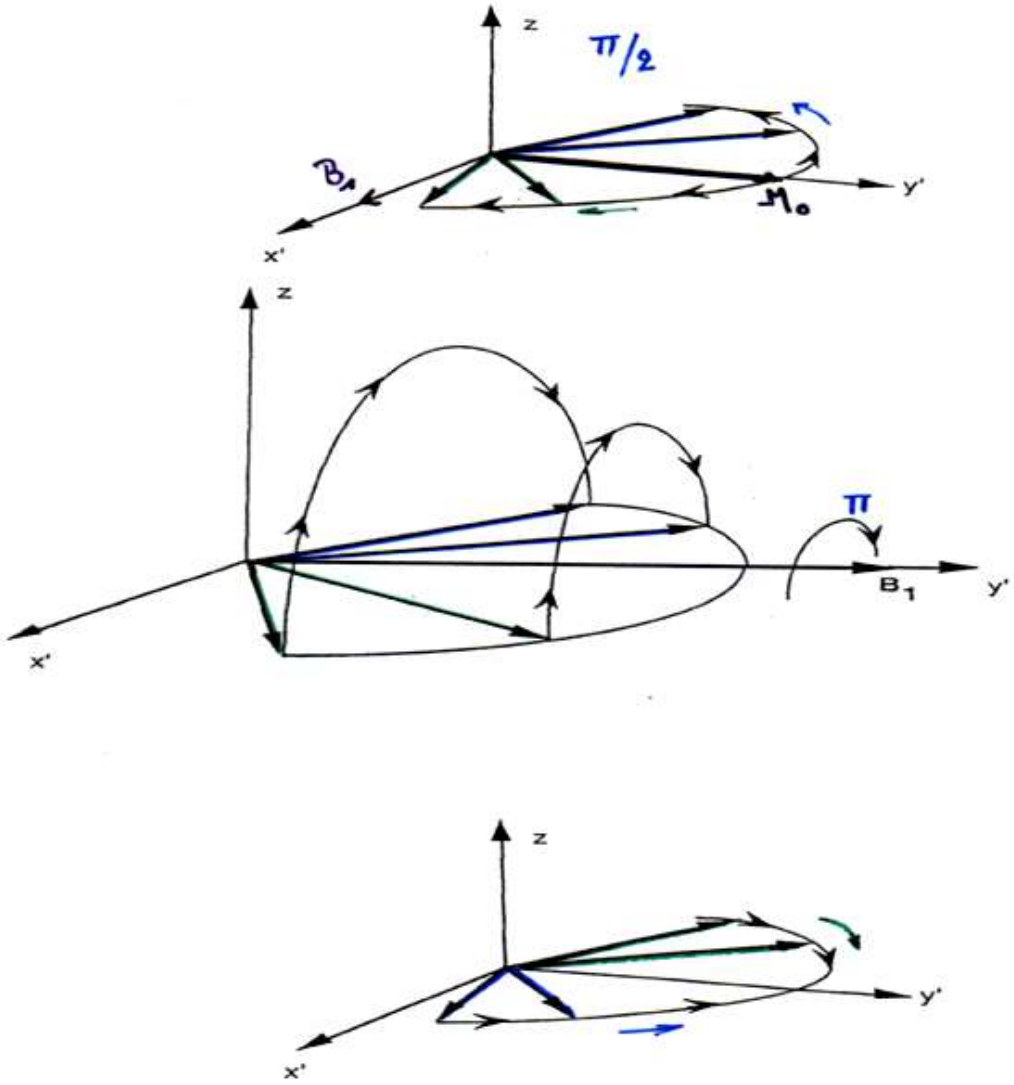
Figure (c)

a) M is inverted by a 180° pulse at time 0; b) After a time τ a 90° rotates M to the Y' (or –Y') axis. c) the amplitude of the FID after the 90°pulse, which is proportional to the amplitude of M at time τ, is plotted as a function of τ.

$$dM_z/dt = -(M_z - M_0)/T_1 \quad \Rightarrow \quad M_z = M_0(1 - 2\exp - t/T_1)$$

- Hahn Spin-echo

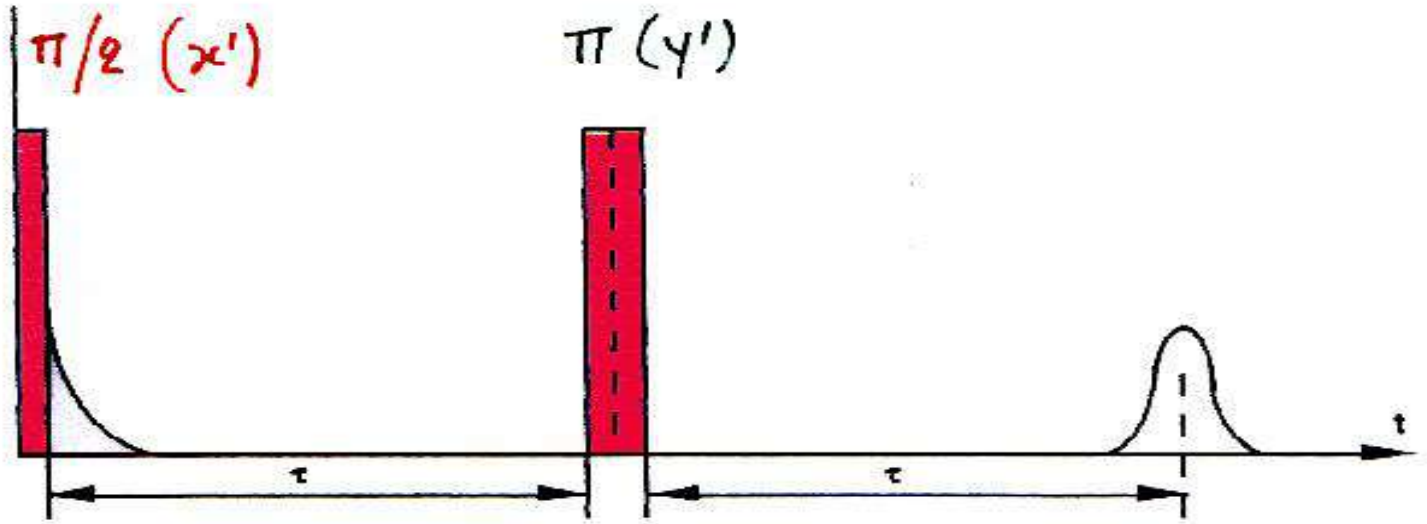
Hahn spin-echo experiment



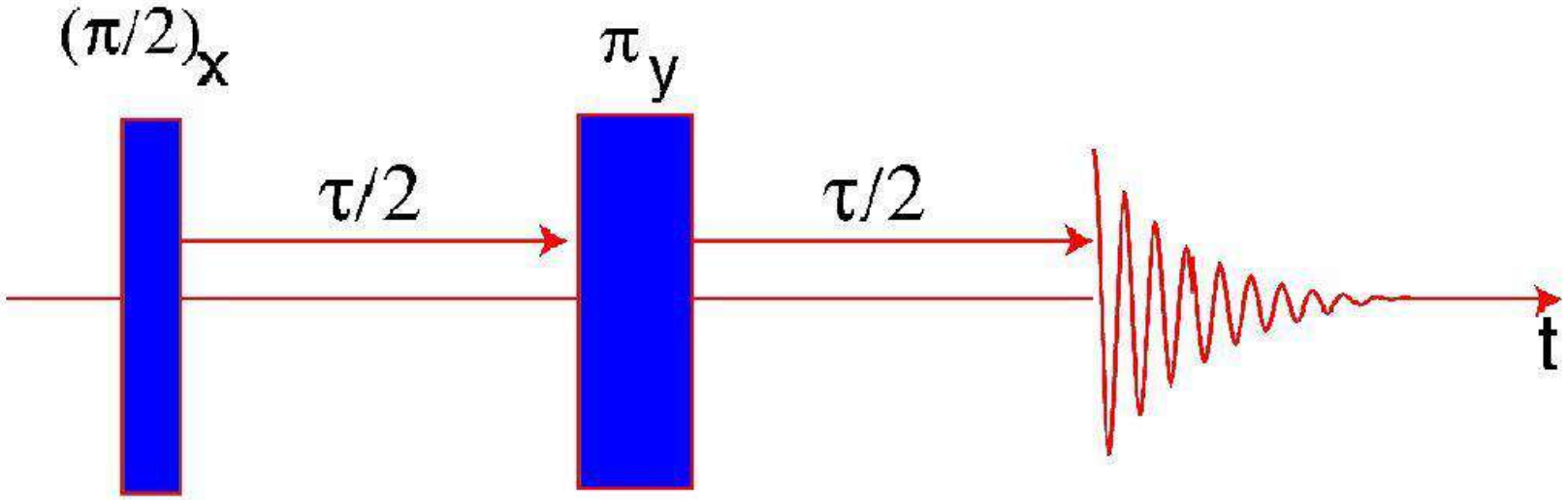
Hahn spin-echo experiment

The distribution of the spin in the X'OY' plan after a pulse $\pi/2$ is due to the spin-spin interactions but also to the inhomogeneity of B_0. The spin-echo experiment overcomes the inhomogeneity problem. In addition it is used for several applications of NMR.

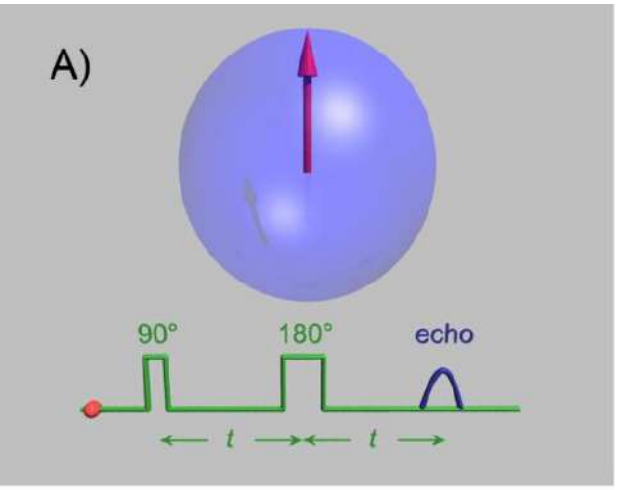
90°, τ, 180° sequence , and observation at time 2τ of a free induction "echo".

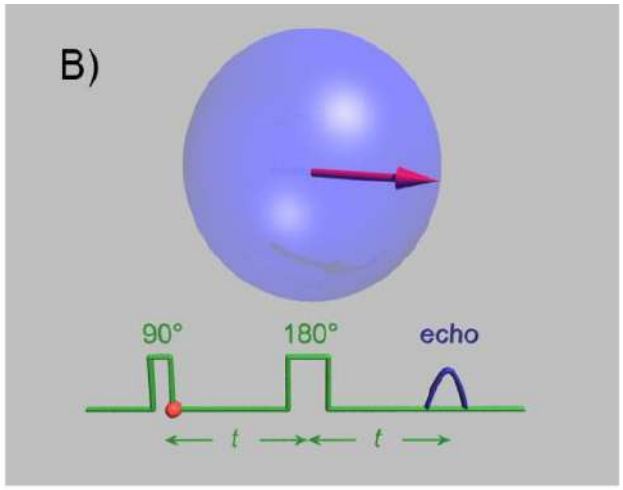


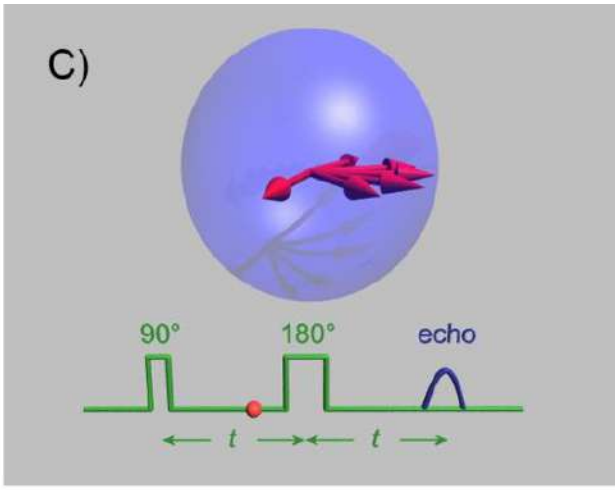
Spin-echo experiment

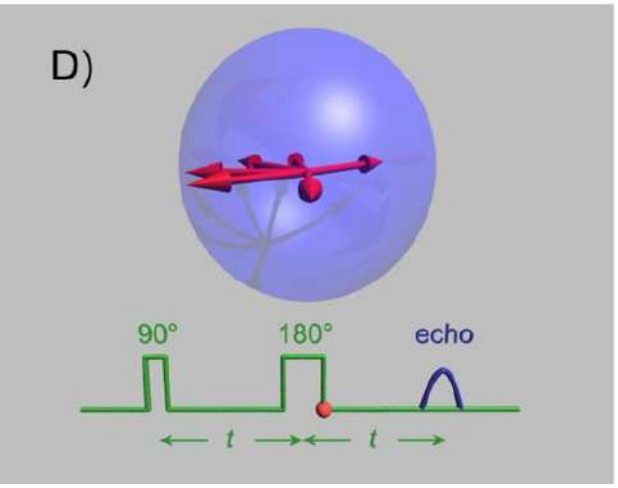


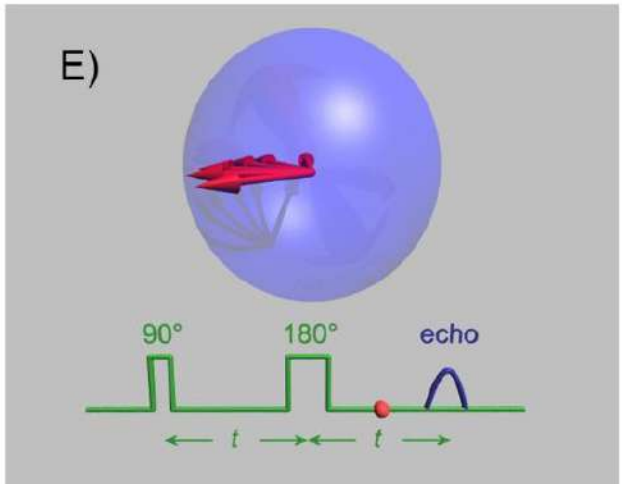
Spin-echo experiment

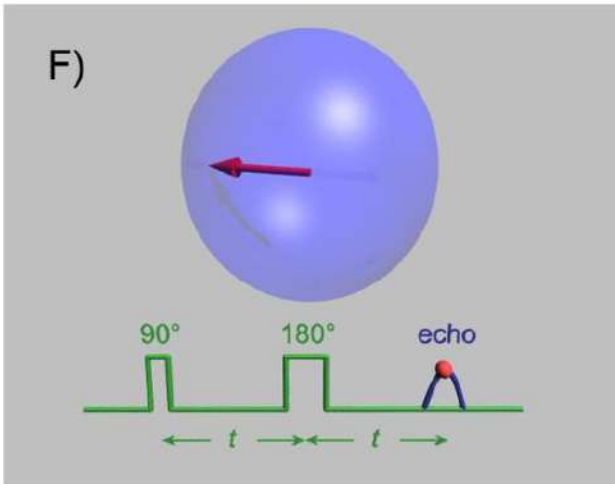












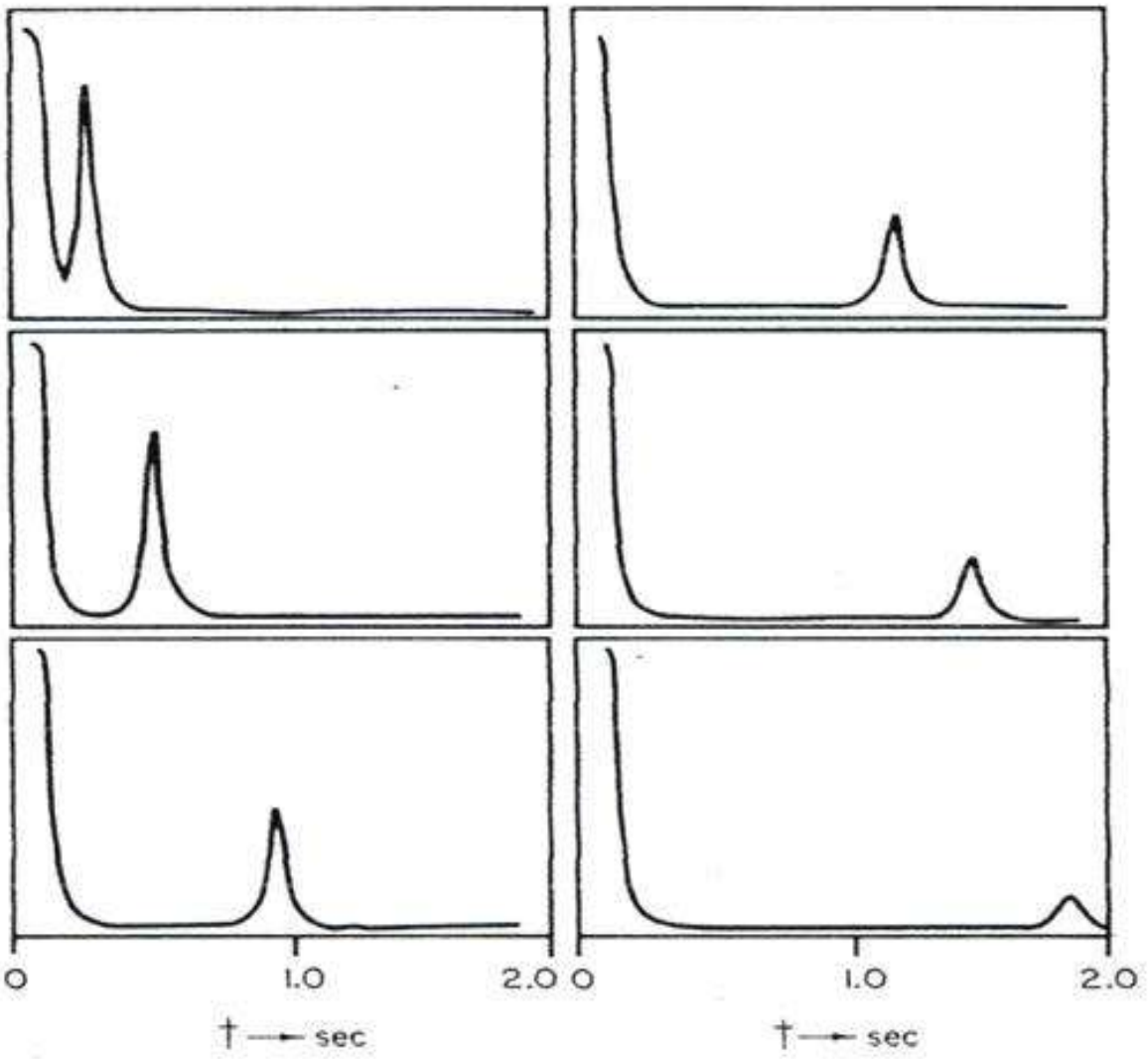
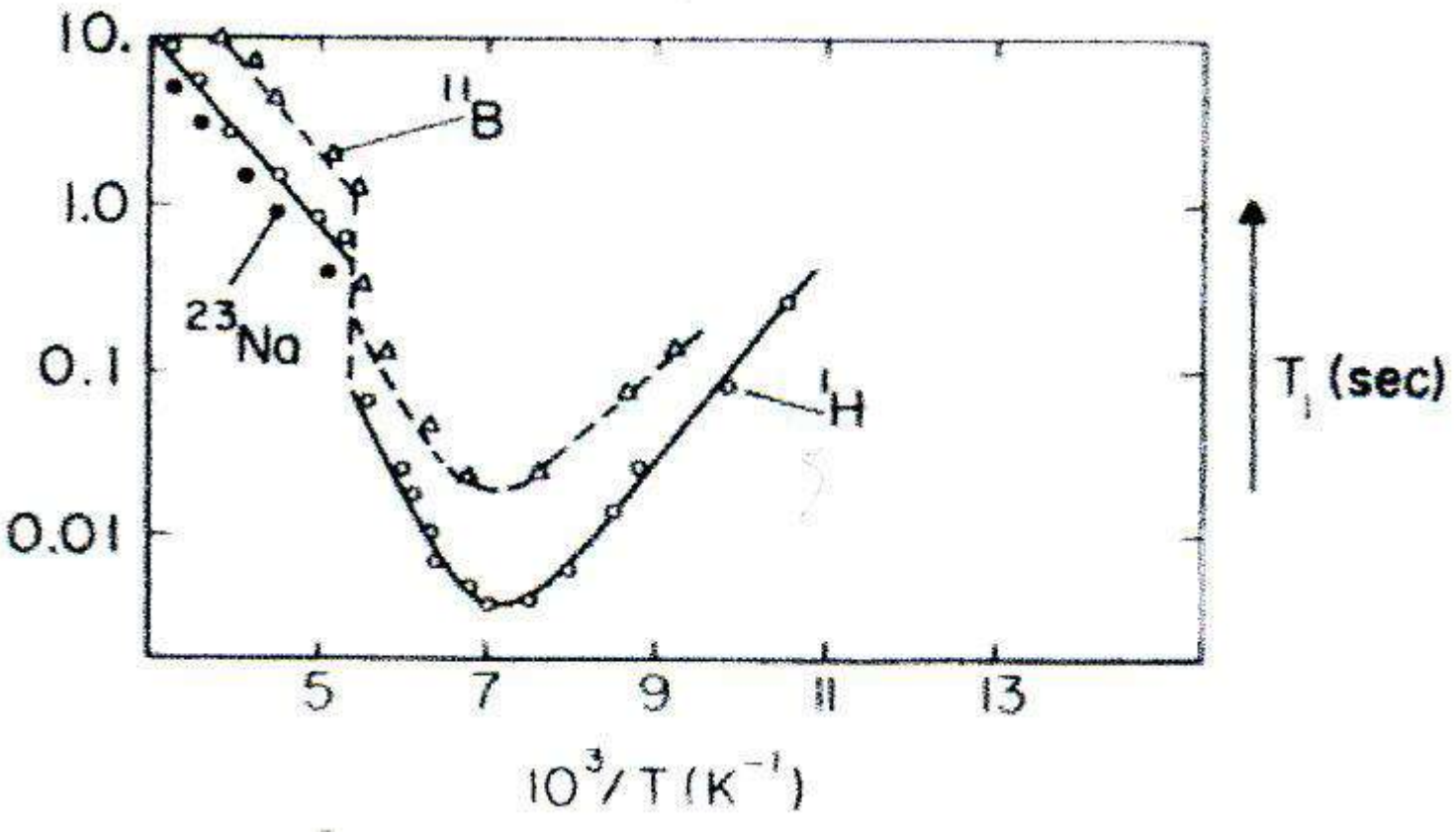
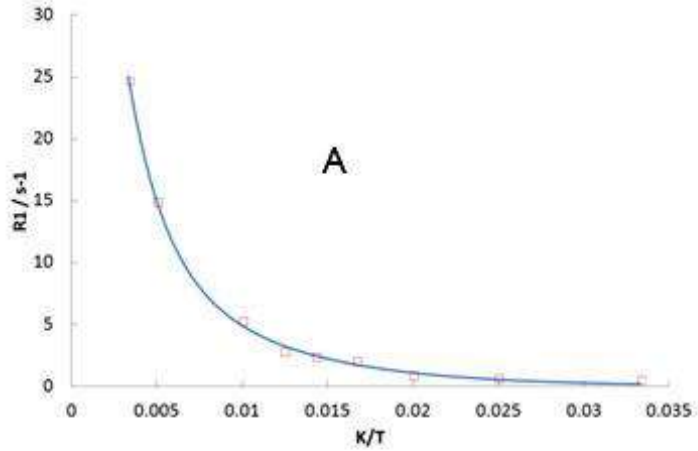


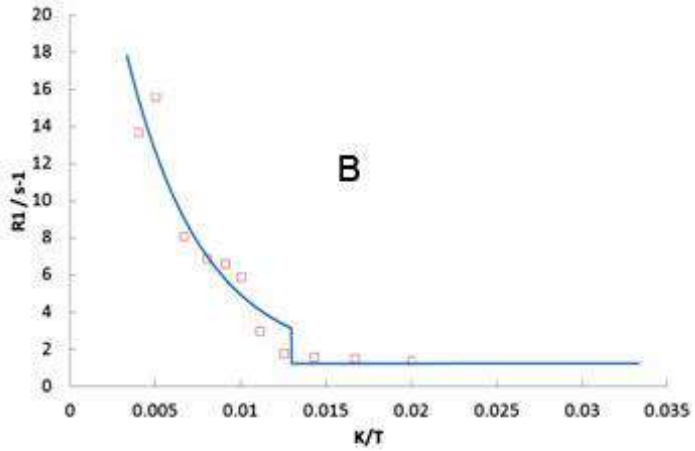
Figure 2.5. A typical Hahn spin-echo experiment, consisting of six 90°, τ, 180° sequences, with τ varying from 0.1–1 sec. Note that the amplitude of the echo decreases as τ increases. In this experiment the echoes are positive, rather than negative as expected, since a diode detector was used, which measures only amplitude, not phase of the signal. (See Chapter 3 for further details on detectors.)

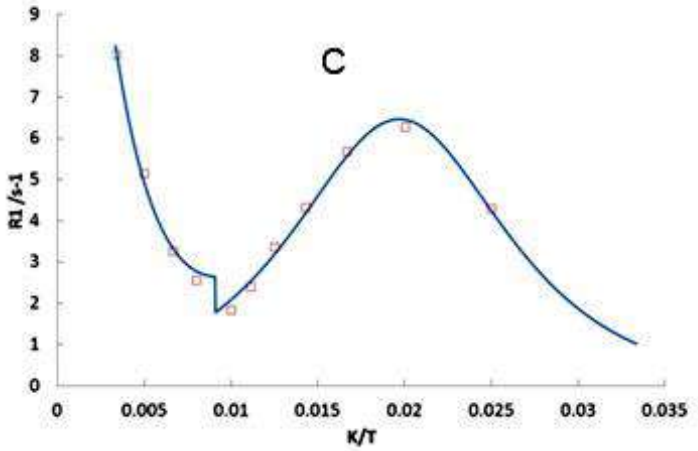
Spin-lattice T_1 in $NaBH_4$ *vs* 1/T showing a phase transition at about 190°K

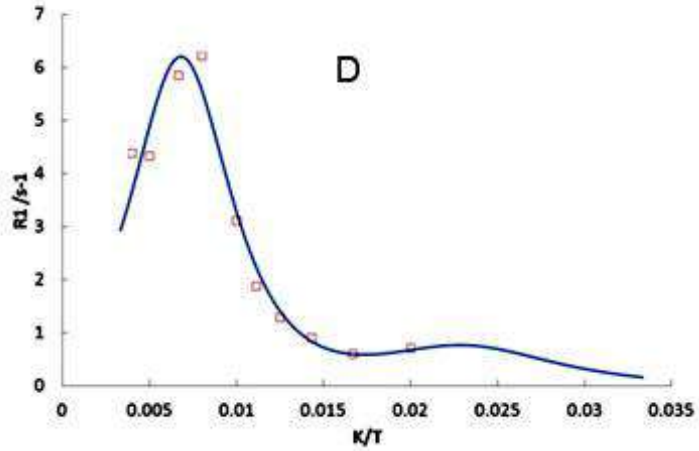


Relaxation rate R1 *versus* T-1. A- SBA-80: spin-rotation;
B- Zeolite Omega:spin-rotation + dipolar contribution (cut-off 77K)
C- Zeolite ZSM5: spin-rotation + dipolar contribution (cut-off 110K) ;
D- Zeolite Rho: two dipolar contributions



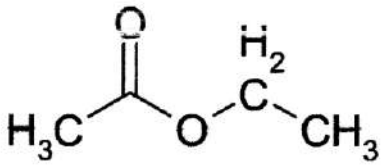


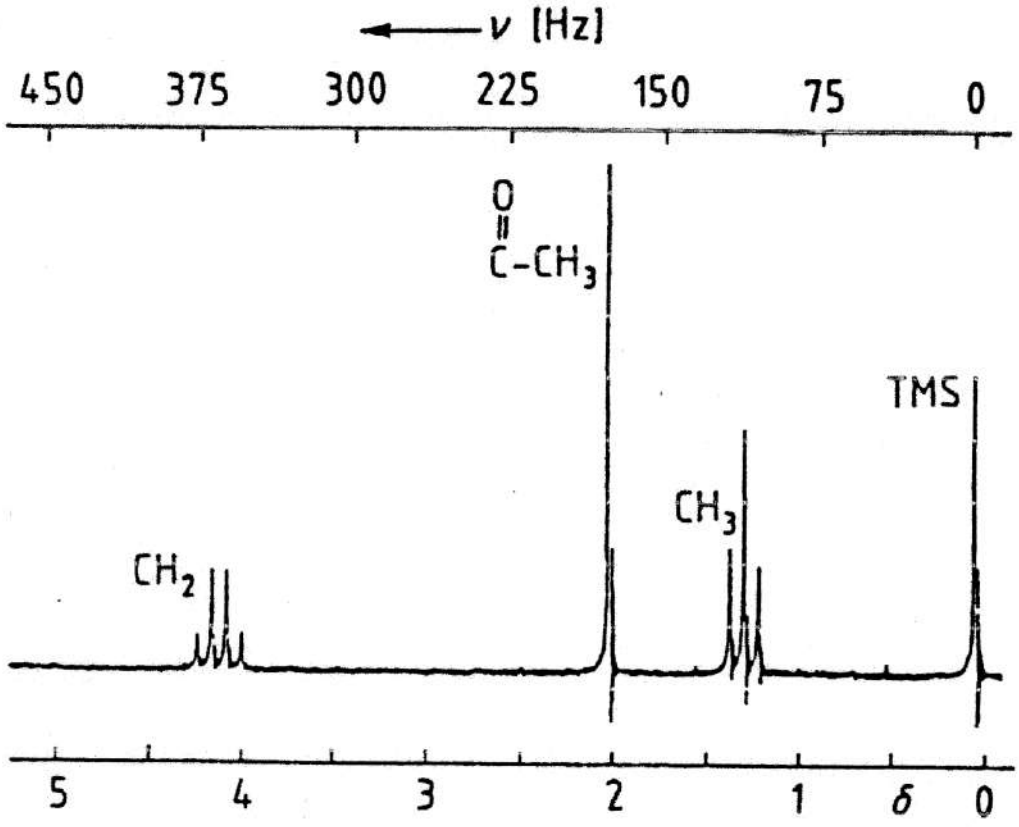




- End of the first lecture

Ethyl acetate





We consider a system of three axis rotating about B_0 in the same direction in which the nuclear moments process (rotating frame) with a velocity ω'.
The classical relationship

$$d\vec{\mu}/dt = \gamma \vec{\mu} \wedge \vec{B}_0$$

is valid provided the Coriolis force is added:

$$(d\vec{\mu}/dt)_{LF} = (d\vec{\mu}/dt)_{RF} + \vec{\omega}' \wedge \vec{\mu}$$

$$(d\vec{\mu}/dt)_{RF} = \gamma \vec{\mu} \wedge \vec{B}_0 - \vec{\omega}' \wedge \vec{\mu}$$

$$= \gamma \vec{\mu} \wedge [\vec{B}_0 - \vec{\omega}'/\gamma]$$

$$(d\vec{\mu}/dt)_{RF} = \gamma \vec{\mu} \wedge \vec{B}_e \quad \text{with } B_e = B_0 - \omega'/\gamma$$

$$\text{If } \omega' = \omega_0 \Rightarrow B_e = 0$$

In the rotating frame $(d\vec{\mu}/dt)_{RF} = 0$ and $\vec{\mu}$ is fixed.

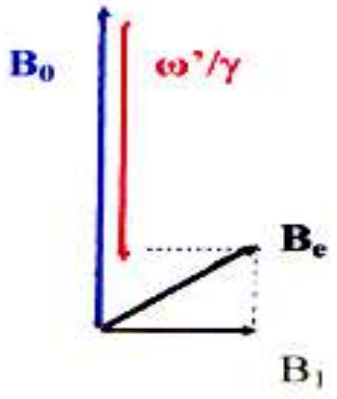
So, with the addition of B_1 along OX', rotating with a velocity ω_1, the previous equation

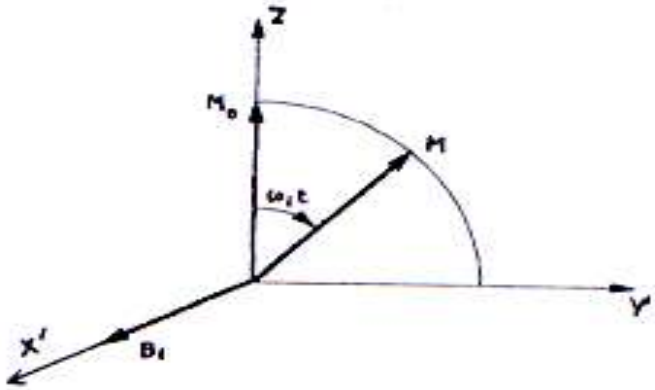
$$(d\vec{\mu}/dt)_{RF} = \gamma \vec{\mu} \wedge \vec{B_e} \quad \text{with } B_e = B_0 - \omega'/\gamma$$

characterizing the variation of $(d\vec{\mu}/dt)_{RF}$ in a frame rotating with a velocity ω' keep the same form but with

$$\vec{B_e} = (B_0 - \omega'/\gamma).\vec{k} + B_1.\vec{i}$$

$$B_e = [(B_0 - \omega'/\gamma)^2 + B_1^2|^{1/2}$$

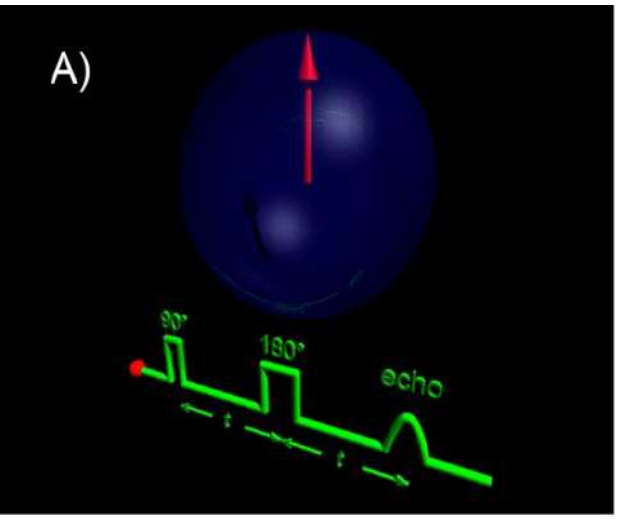


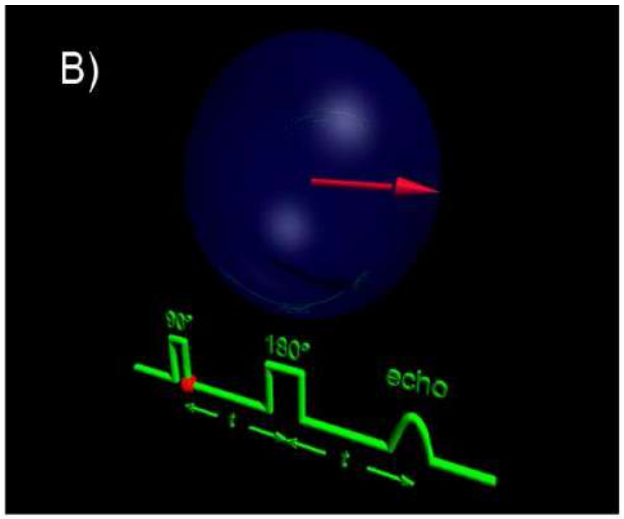


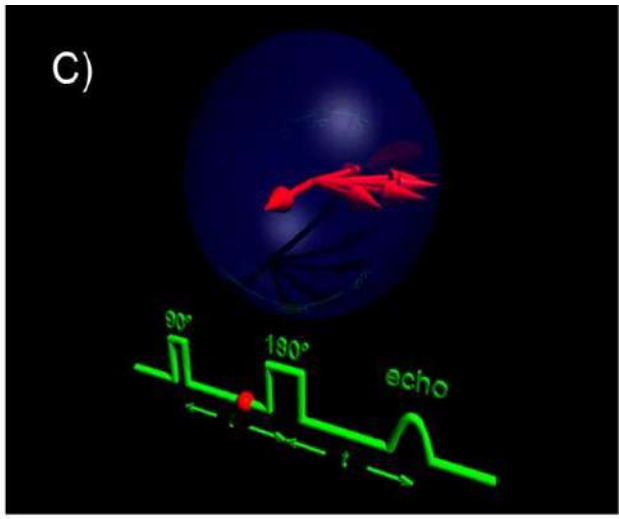
If $\omega' = \omega_0 \quad \Rightarrow \quad B_e = B_1$

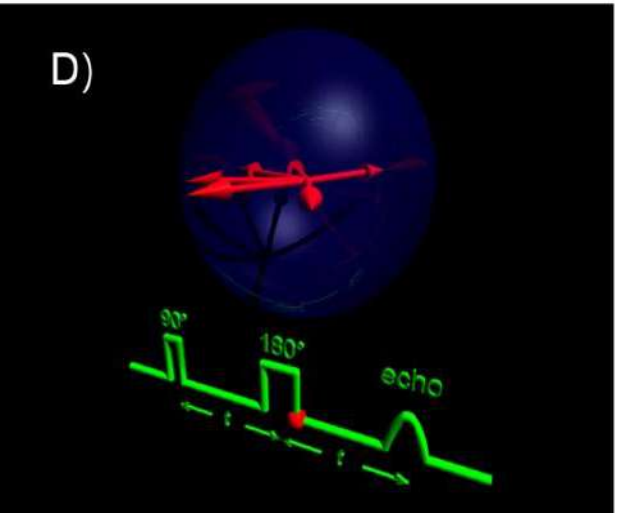
In the rotating frame with a velocity ω_0 there is a precession of the spins around OX' (B_1) with a velocity ω_1.

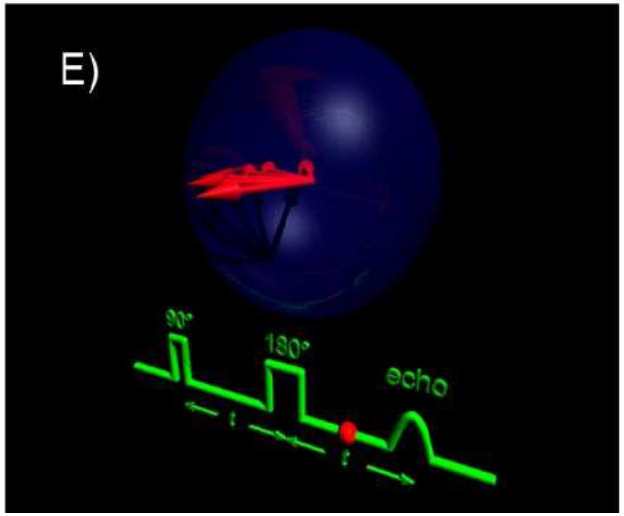
Spin-echo experiment

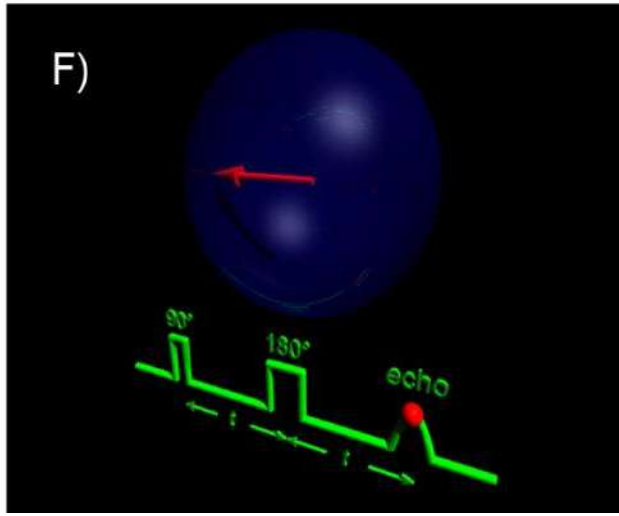












Interactions of nuclear spins in a solid

-:-:-:-:-:-:-:-

$\hat{H}_Z$ = Zeeman effect $\hat{H}_{RF}$ = RF field $\hat{H}_{CS}$ = Chemical shift $\hat{H}_J$ = JJ coupling $\hat{H}_D$ = Dipole interactions $\hat{H}_Q$ = Quadrupole coupling $\hat{H}_{ij}$ = Unpaired electron	$\hat{H}_X = \vec{A}\ \overline{T_X}\ \vec{B}$ $\overline{T_X}$=second rank tensor

$\hat{H}_Z >>$ other interactions

Very often some effects are masked by the others.
For example $\hat{H}_D >> \hat{H}_J$

$\hat{H}_X$ = K (spin factor) [space factor f(θ)]

θ = angle between an axis of the system and B_0