Os experimentos de Purcell & Bloch

O experimento Ressonância Magnética Nuclear - Onda Contínua (CW)

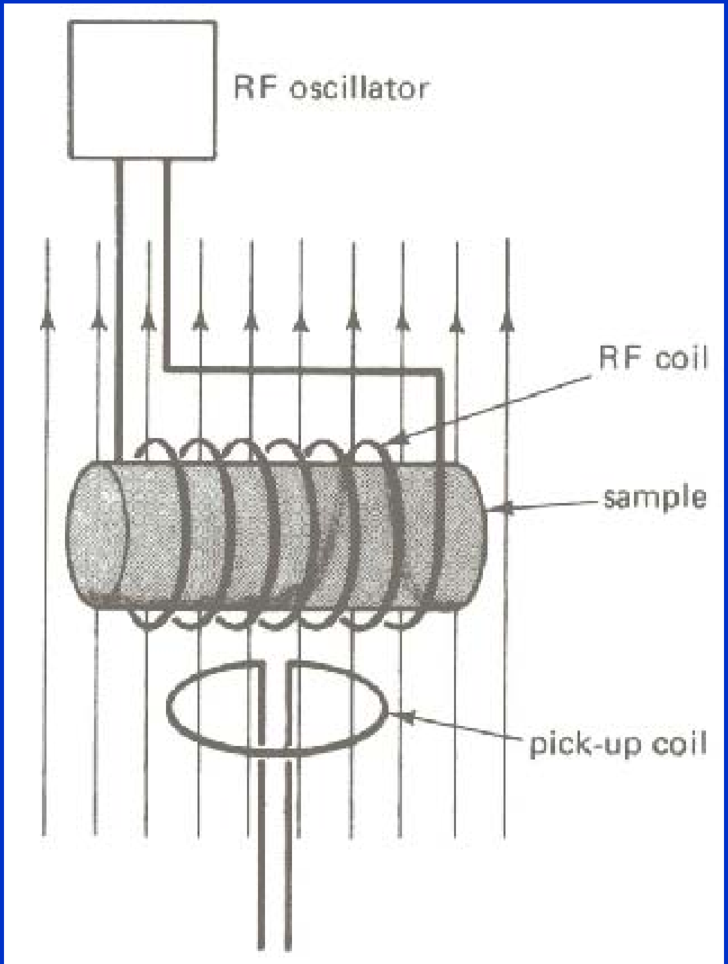
E.M Purcell**, H.C Torrey, and R.V. Pound, Physical Review 69, 37 (1946) - **Nobel 1952

Massachusetts Institute of Technology, Cambridge - USA

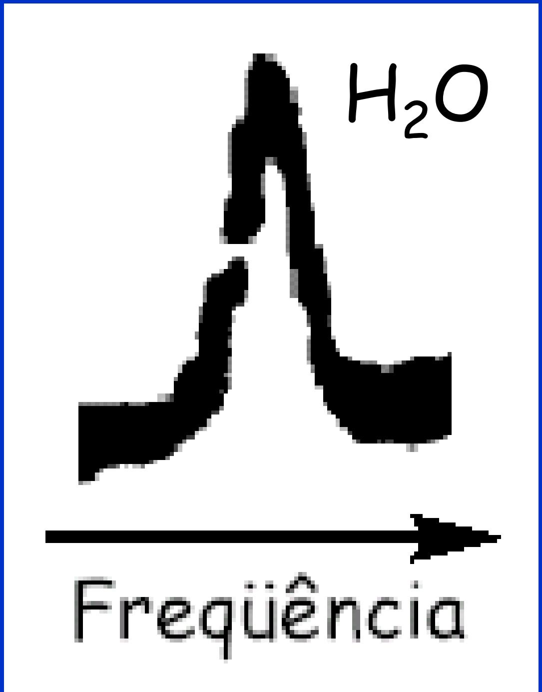
O experimento Ressonância Magnética Nuclear - Pulsada

F. Bloch**, W.W. Hansen, M Packard,, Physical Review 69, 127 (1946) - **Nobel 1952

Stanford University, California - USA



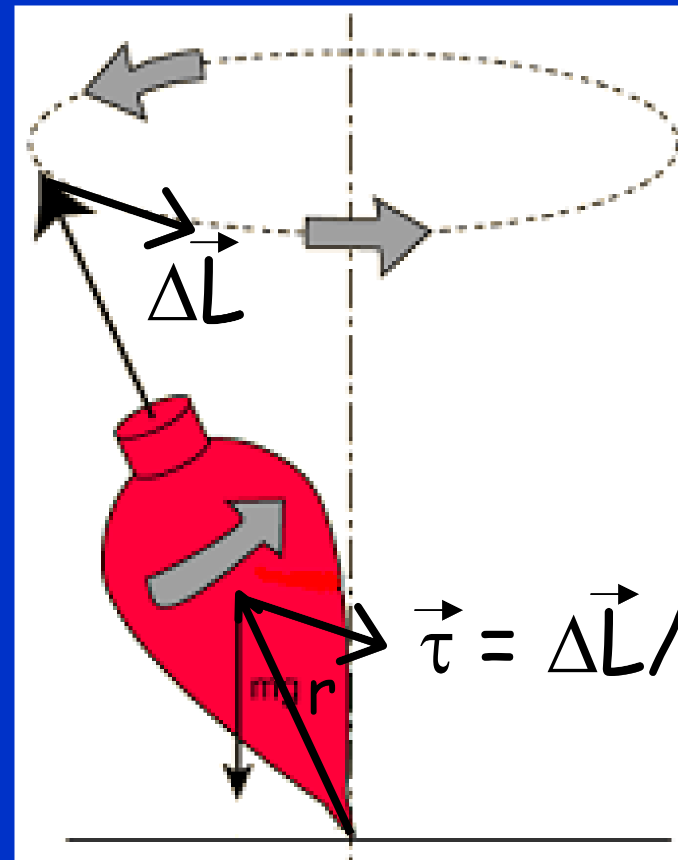
Experimentos realizados sem feixes moleculares !!!



Giroscópio

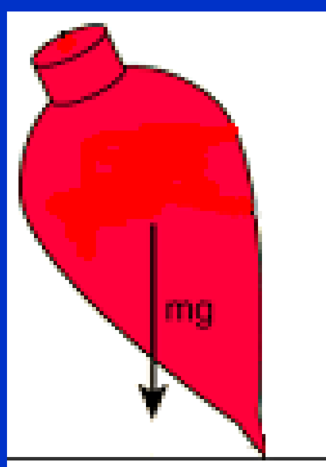
Com rotação

$\vec{L} = I\,\vec{\omega}$



$\vec{\tau} = \Delta\vec{L}/\Delta t$

Sem rotação



Cai !

Movimento de Precessão !

f ~ 1 Hz

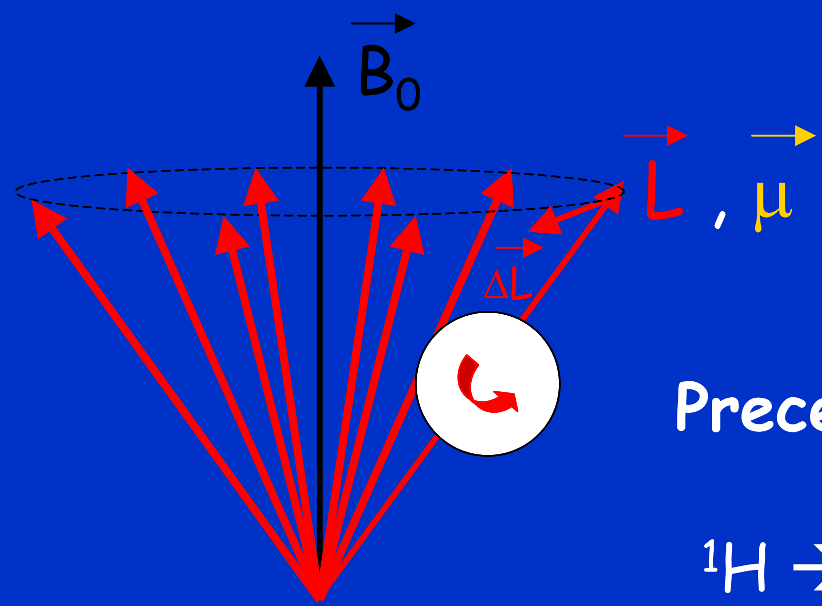
***** Lembrando: $|\tau| = rF = I\alpha = I\Delta\omega/\Delta t = \Delta L/\Delta t$

Aspectos “Clássicos” da RMN

Núcleo atômico:

momento angular (spin): $\vec{L}$

momento magnético: $\vec{\mu}$



Precessão: $\omega_L = \gamma B_0$

$^{1}H \rightarrow$ 42,58 MHz/Tesla

$^{13}C \rightarrow$ 10,71 MHz/Tesla

Propriedades Físicas dos Spins Nucleares

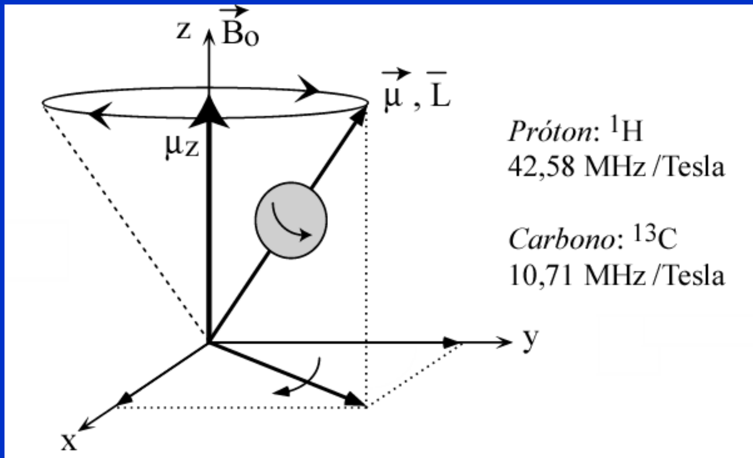
Núcleos com spin ½

Isótopo	Spin	Abundância natural (%)	Freqüência de Larmor (MHz), 10 T
^{1}H	1/2	99,98	425,75
^{13}C	1/2	1,108	104,07

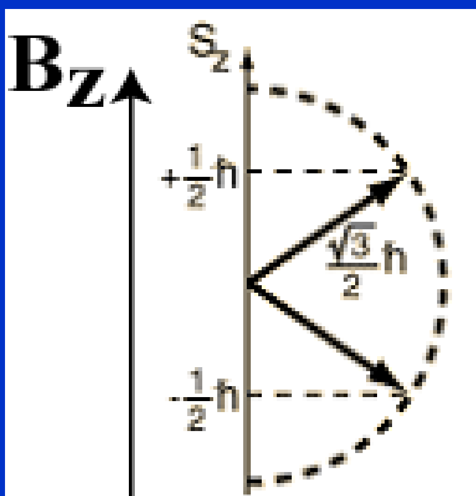
Núcleos com spin > ½

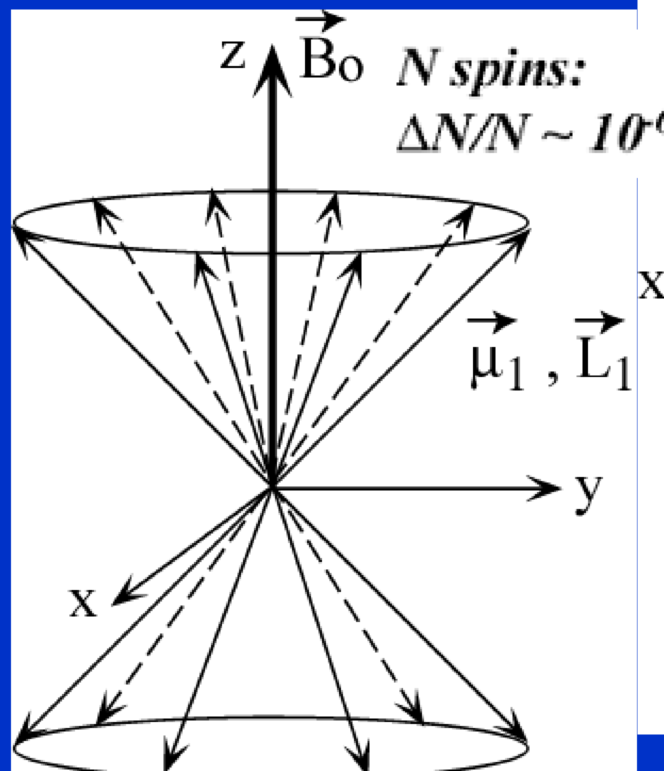
Isótopo	Spin	Abundância natural (%)	Freqüência de Larmor (MHz), 10 T	Mom. de quadrupolo elétrico (10^{-28} m^2)
^{7}Li	3/2	92,58	165,45	-4,0 10^{-2}
^{23}Na	3/2	100	112,60	0,1
^{133}Cs	7/2	100	56,05	-3,0 10^{-3}

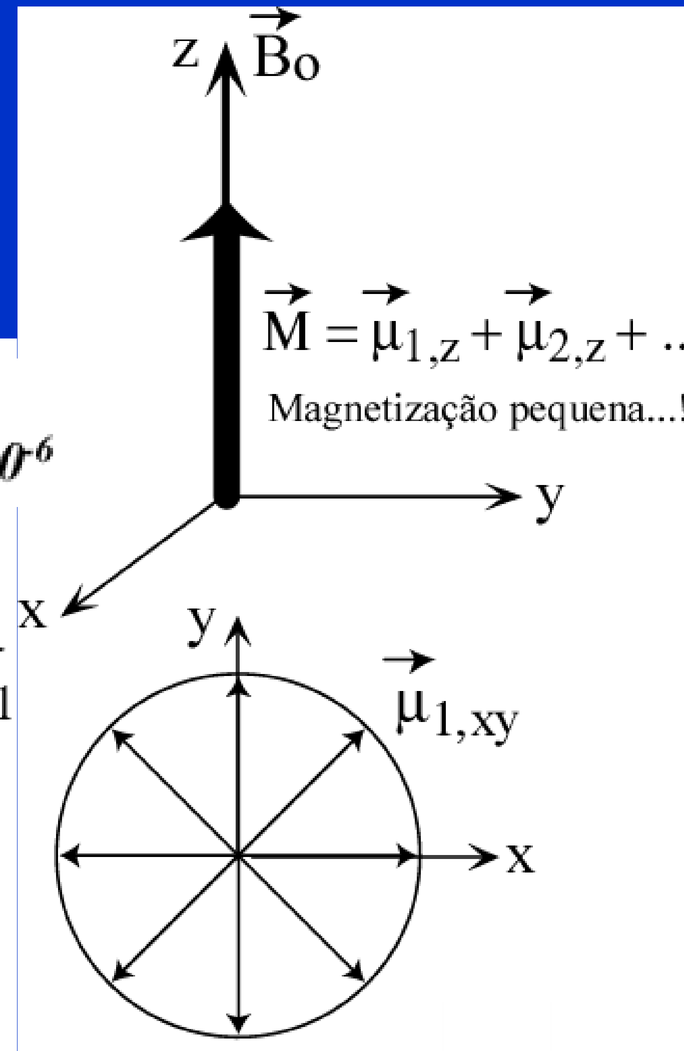
Aspectos "Clássicos" da RMN



Spin ½





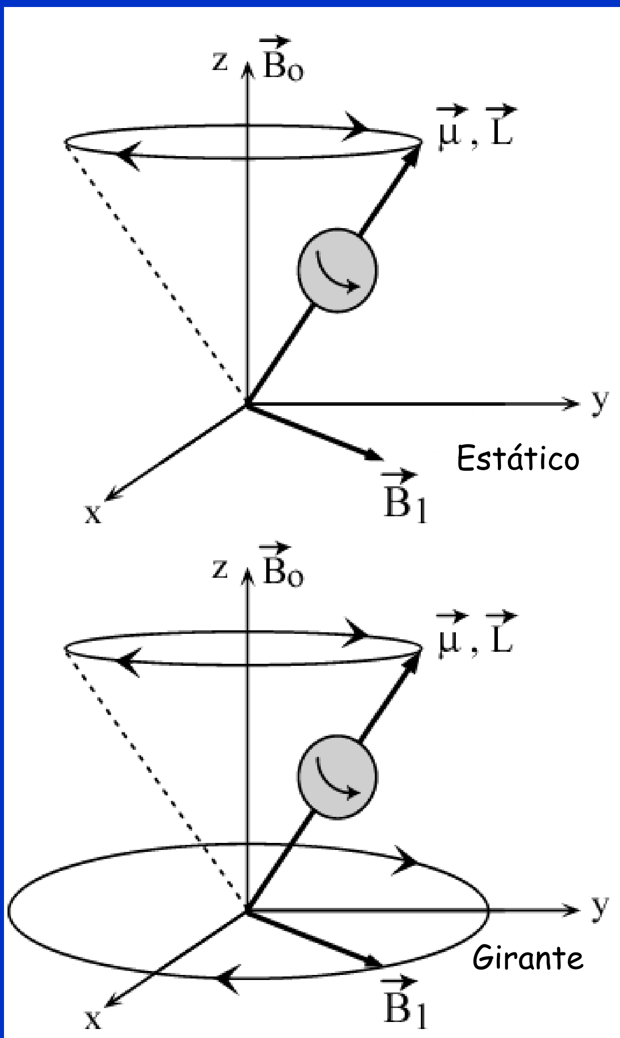


$$E = -\vec{\mu}.\vec{B} = -\gamma\hbar I_Z B_Z$$

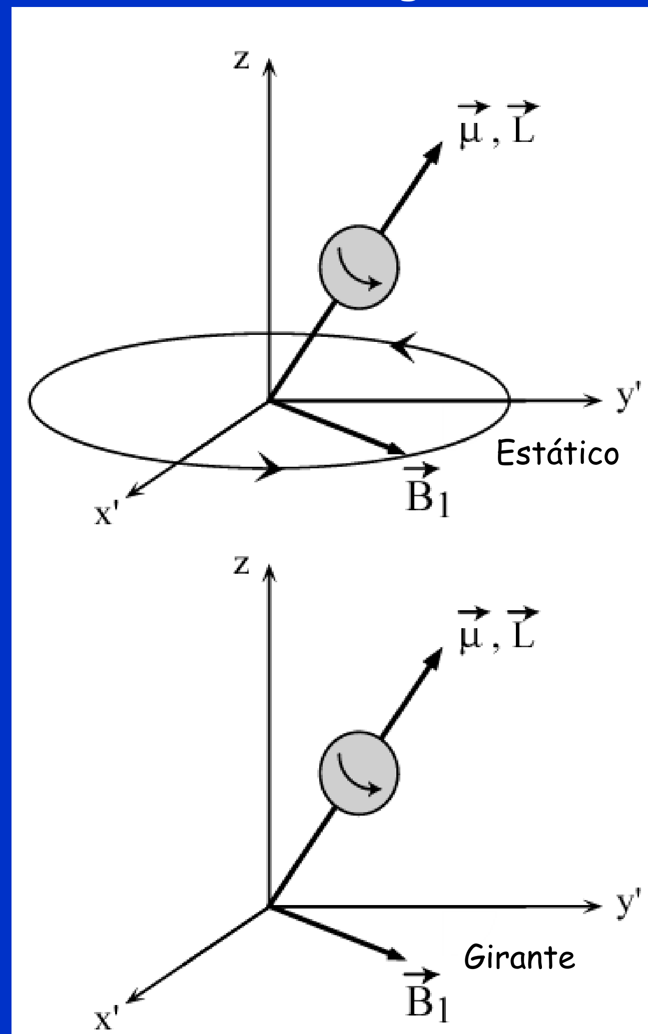
$$= \pm\frac{1}{2}\hbar\left(\gamma B_Z\right) = \pm\frac{1}{2}\hbar\omega_L$$

Excitação dos spins - Pulsos de RF

Referencial de laboratório



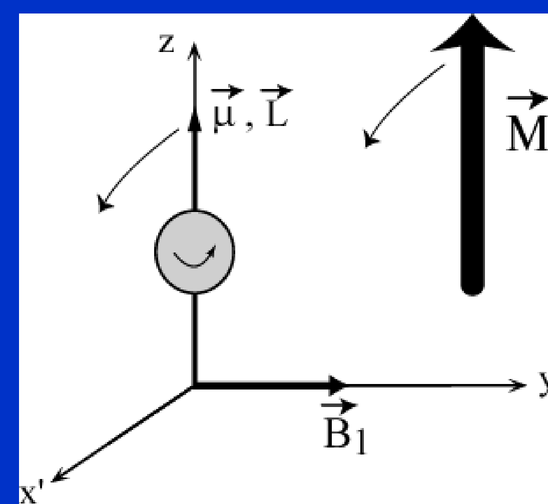
Referencial girante



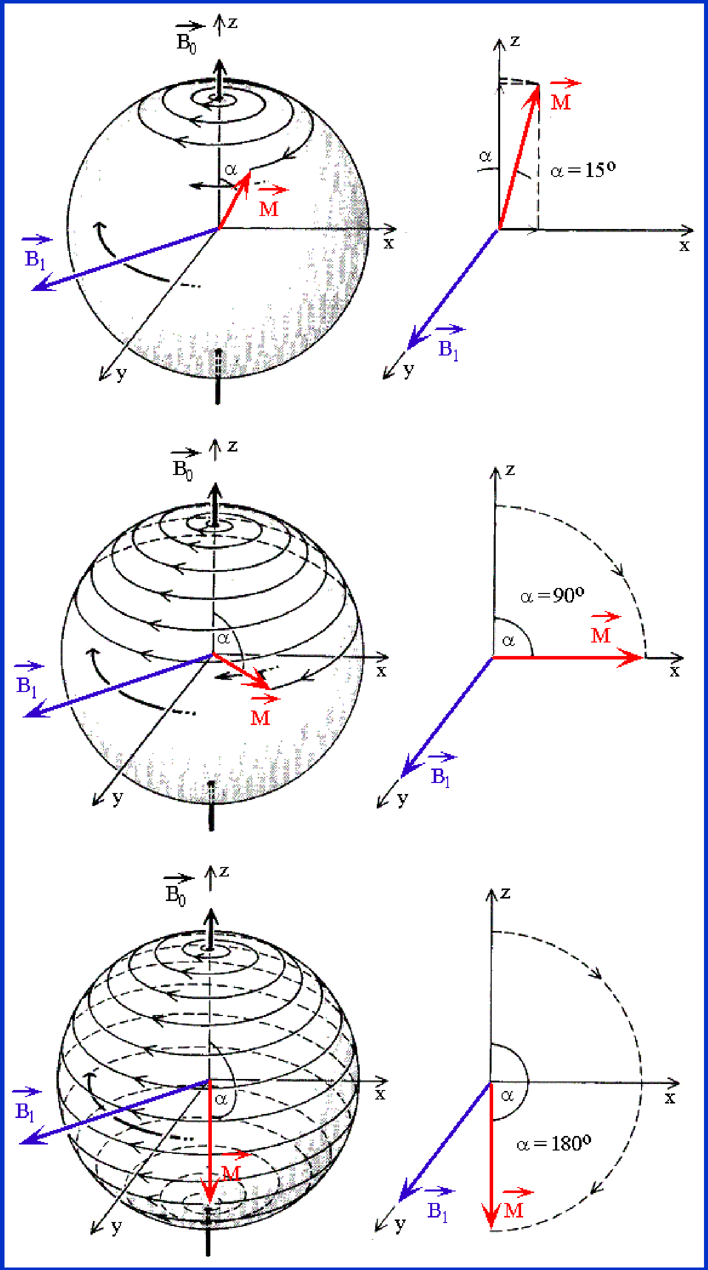
Ressonância Magnética Nuclear !

Movimento de Precessão do spin em torno de B_1:

$$\nu_{Larmor} = \nu_L = \gamma B_1$$



Pulsos de RF



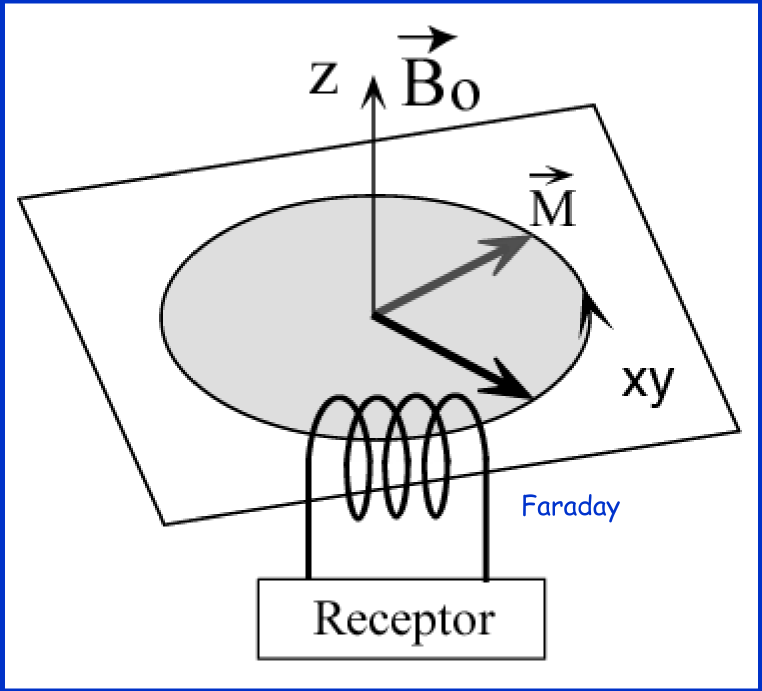
Pulso de RF de 15^0

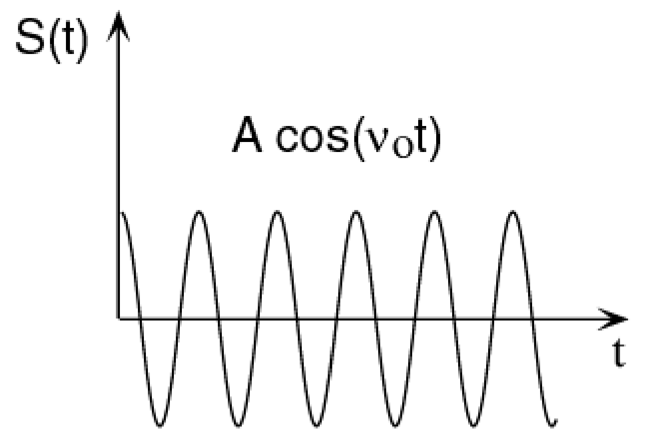
Pulso de RF de 90^0

Pulso de RF de 180^0

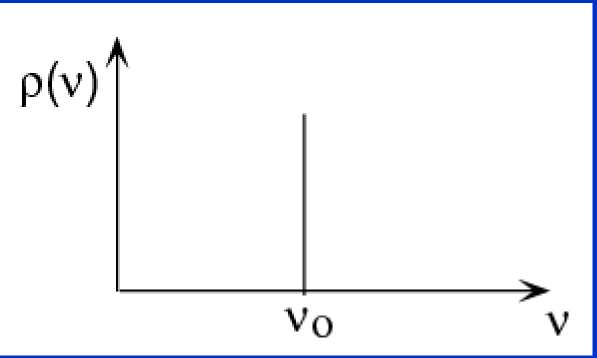
Fases da RF: x, y, -x e -y

Deteção do Sinal de RMN

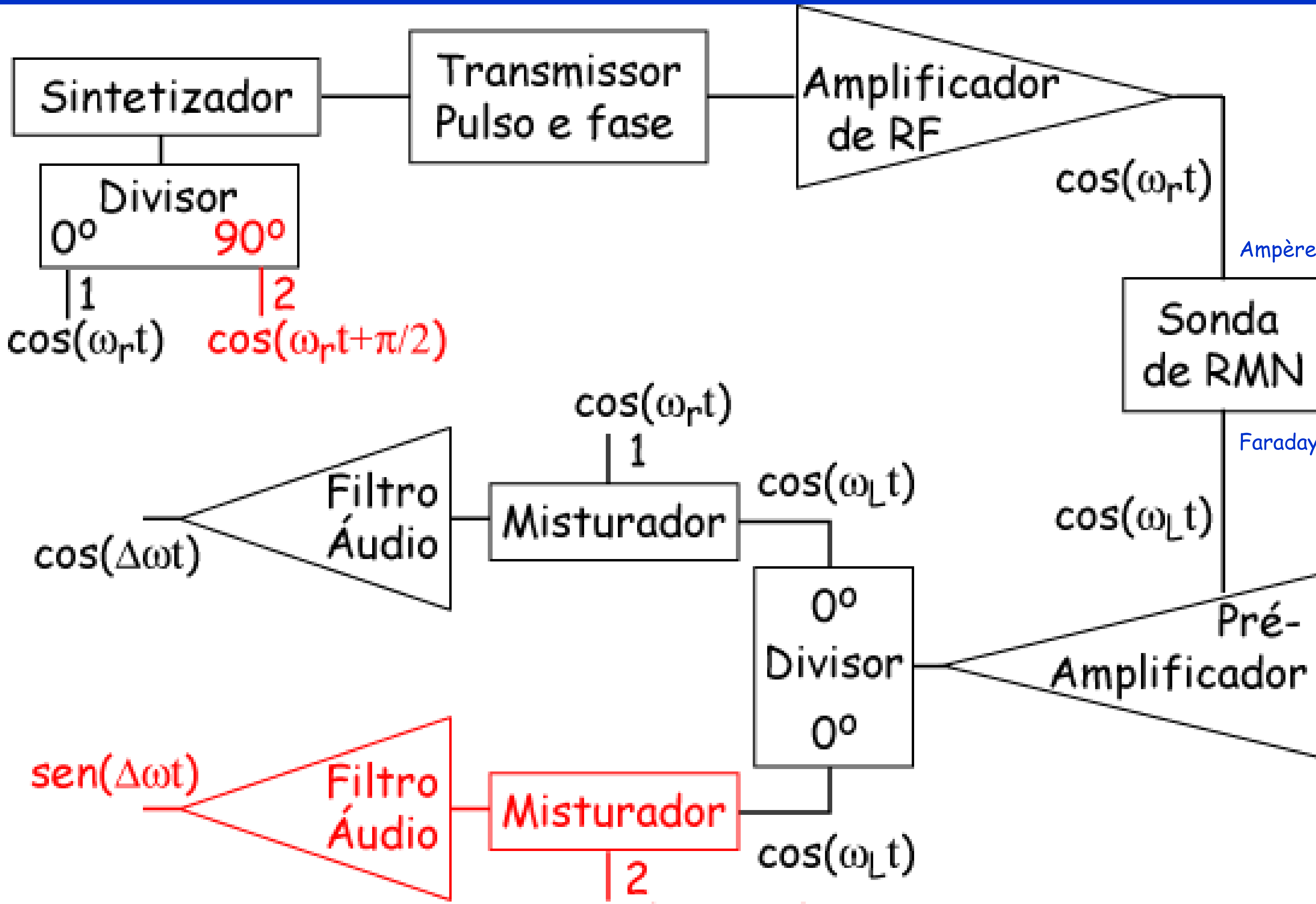




TF



Espectrômetro de RMN



$S(t) = \cos(\Delta\omega t) + i\,sen(\Delta\omega t)$

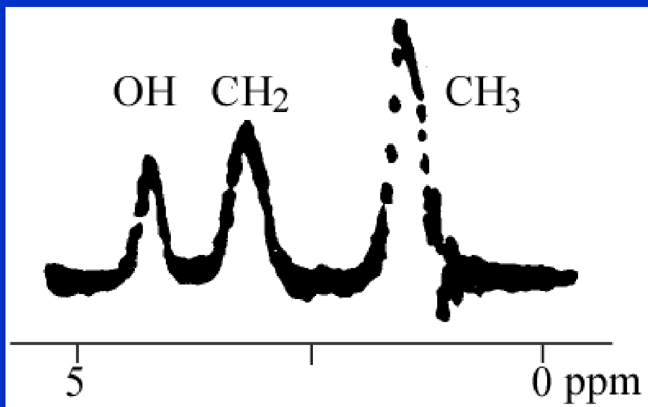
Interações do Spin - Deslocamento Químico

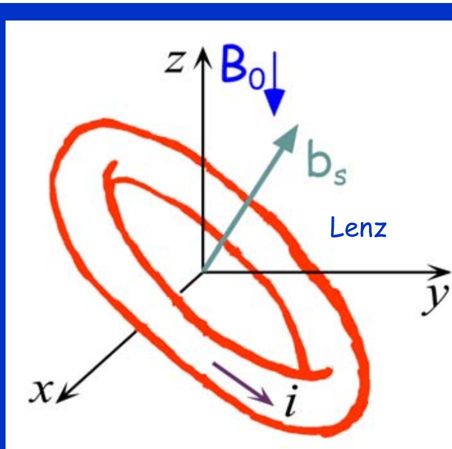
CHEMICAL EFFECTS ON NUCLEAR INDUCTION SIGNALS FROM ORGANIC COMPOUNDS

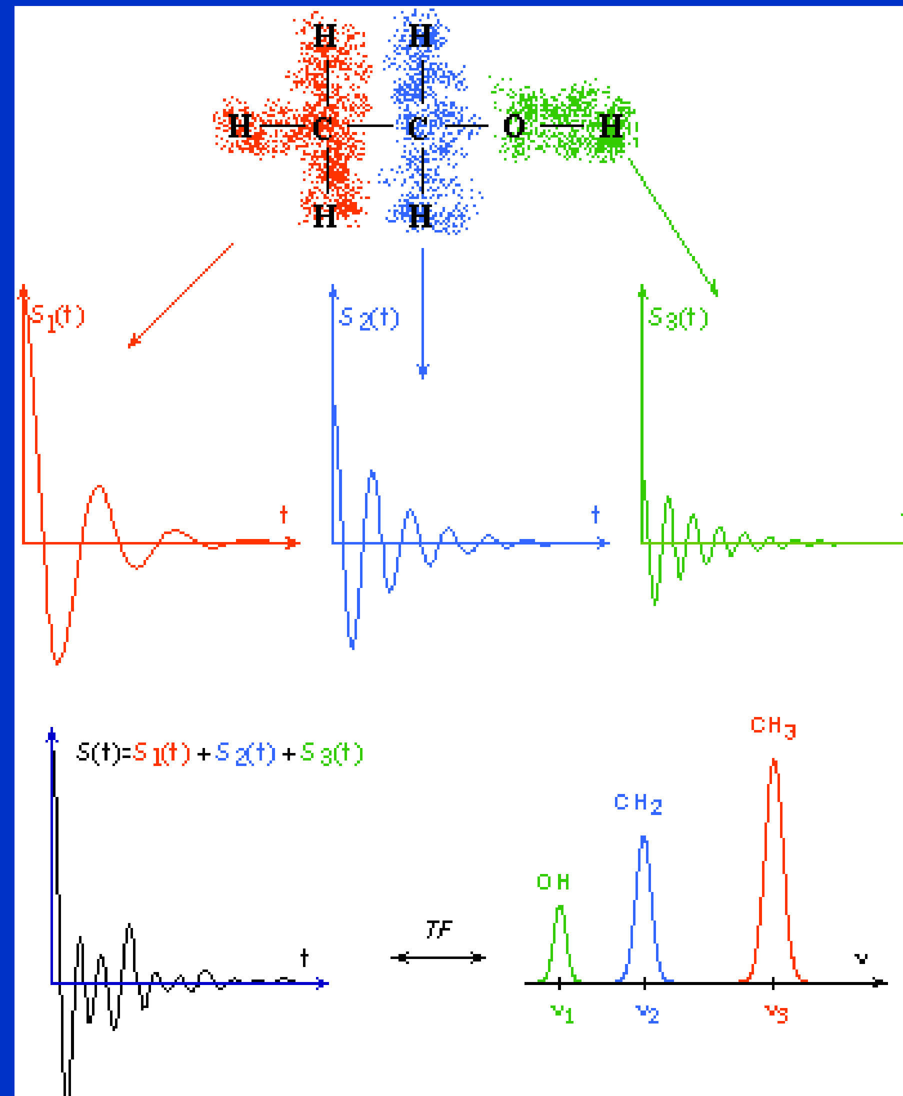
ARNOLD JT, DHARMATTI SS, **PACKARD ME**

JOURNAL OF CHEMICAL PHYSICS, 19 (4): 507-507 1951

CH_3CH_2OH:







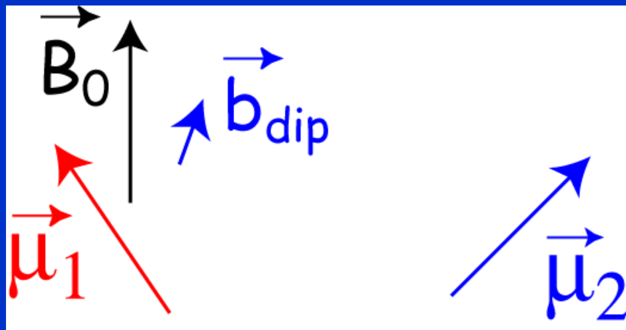
A separação entre as linhas é proporcional a B_0

Deslocamento Químico Isotrópico do ^1H (0-12 ppm)

Type of Proton	Structure	Chemical Shift, ppm
Cyclopropane	C_3H_6	0.2
Primary	R-C**H**$_3$	0.9
Secondary	R$_2$-C**H**$_2$	1.3
Tertiary	R$_3$-C-**H**	1.5
Vinylic	C=C-**H**	4.6-5.9
Acetylenic	triple bond,CC-**H**	2-3
Aromatic	Ar-**H**	6-8.5
Benzylic	Ar-C-**H**	2.2-3
Allylic	C=C-C**H**$_3$	1.7
Fluorides	**H**-C-F	4-4.5
Chlorides	**H**-C-Cl	3-4
Bromides	**H**-C-Br	2.5-4
Iodides	**H**-C-I	2-4
Alcohols	**H**-C-OH	3.4-4
Ethers	**H**-C-OR	3.3-4
Esters	RCOO-C-**H**	3.7-4.1
Esters	**H**-C-COOR	2-2.2
Acids	**H**-C-COOH	2-2.6
Carbonyl Compounds	**H**-C-C=O	2-2.7
Aldehydic	R-(**H**-)C=O	9-10
Hydroxylic	R-C-O**H**	1-5.5
Phenolic	Ar-O**H**	4-12
Enolic	C=C-O**H**	15-17
Carboxylic	RCOO**H**	10.5-12
Amino	RN**H**$_2$	1-5

Outras Interações Importantes do Spin Nuclear

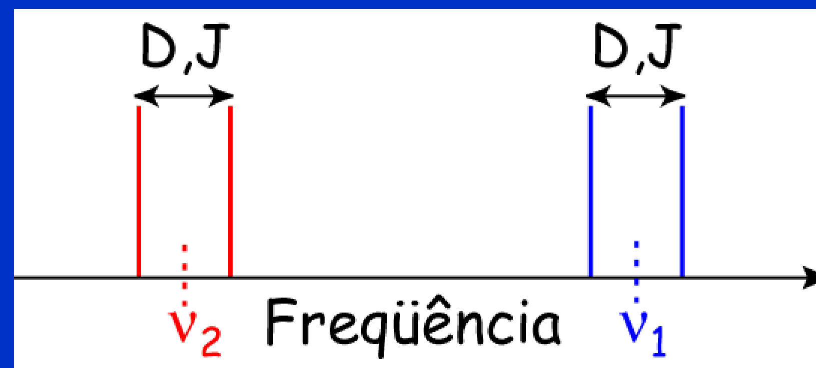
Interação Dipolar Magnética:



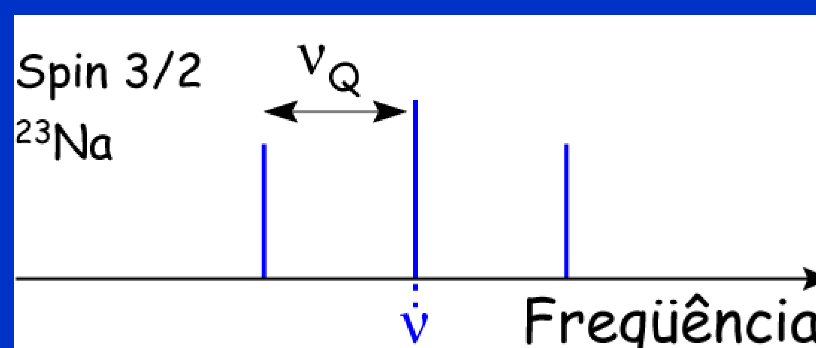
Interação Dipolar D Direta

Acoplamento J

Interação Dipolar através dos elétrons: orbital ou elétron-núcleo



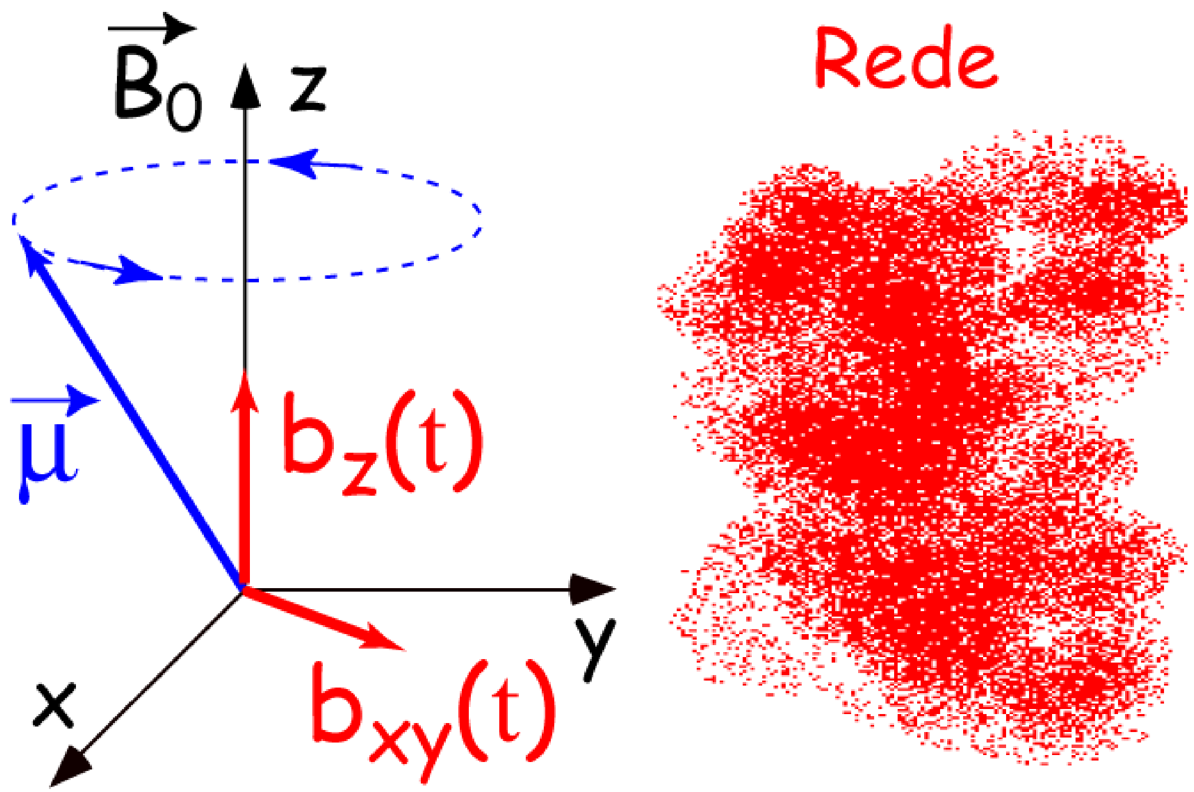
Interação Quadrupolar Elétrica:



Intervalos típicos das intensidades das interações de spin nuclear

Interação	Intervalo de intensidades (Hz)
Zeeman	**10^6-10^9**
Acoplamento J	0-10^2
Deslocamento Químico	0-10^3
Dipolar Magnética Direta, D	0-10^4
Quadrupolar Elétrica	0-10^6

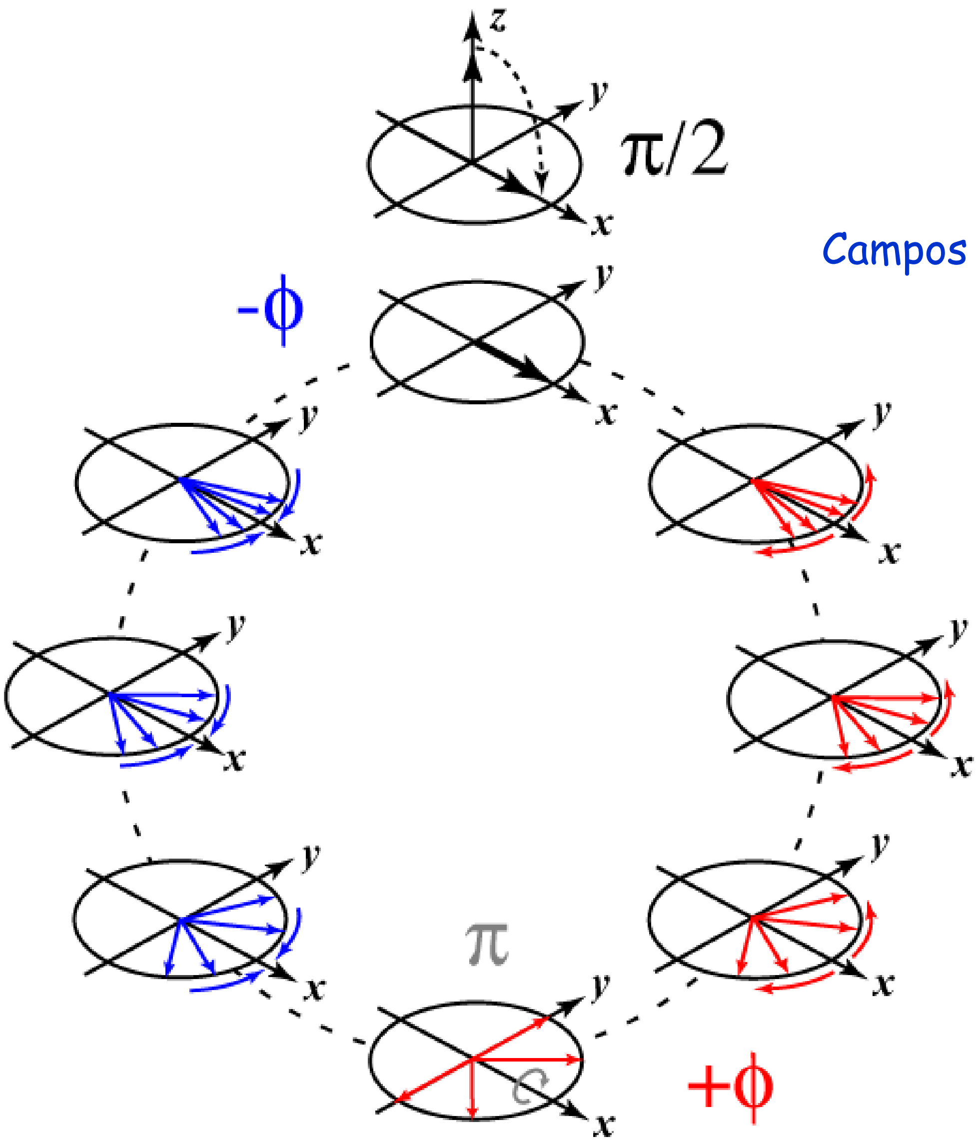
Relaxação Magnética Nuclear / Descoerência



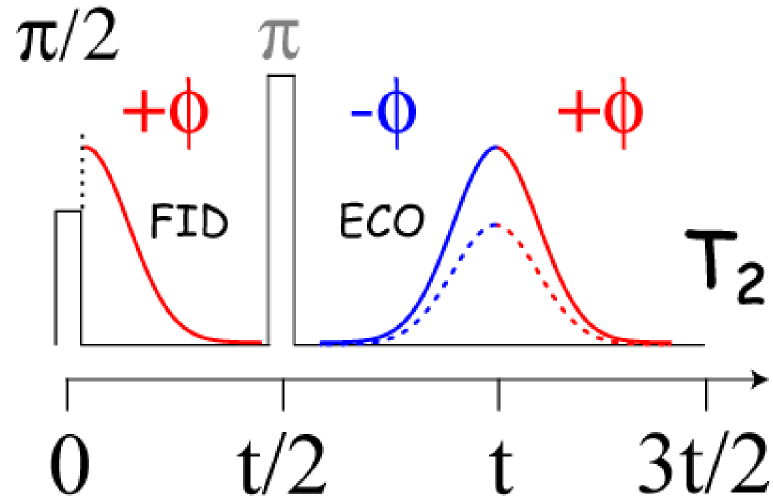
T_2	Relaxação Transversal	Relaxação Longitudinal	T_1
$b_z \approx cte$	$b_z(t)$	$b_{xy}(t)$	$\nu_{xy} \approx \nu_L$
b_z osc.			$\nu_{xy} \neq\neq \nu_L$

Relaxação Transversal - T_2

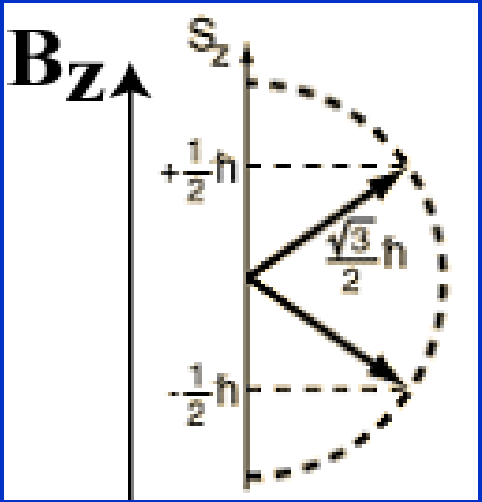
Eco de spin (Hahn):

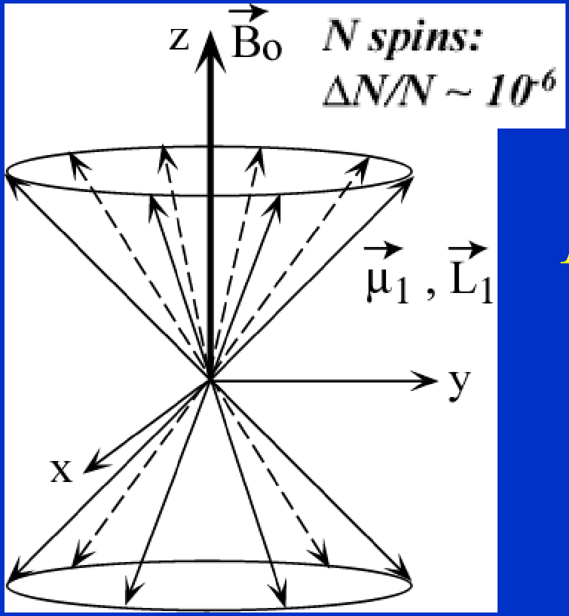


Campos locais na direção *z*



Relaxação Longitudinal - T_1





$$E = -\vec{\mu}.\vec{B} = -\gamma\hbar I_Z B_Z$$

$$= \pm\frac{1}{2}\hbar\left(\gamma B_Z\right) = \pm\frac{1}{2}\hbar\omega_L$$

Campos locais no plano transversal