Ressonância Magnética Nuclear (RMN)

LEAR USP

V Escola do CBPF

Efeito Zeeman Nuclear - Visão quântica tradicional

Equação de Schrödinger independente do tempo:

$$\mathrm{H}\Psi = E\Psi$$

$$\mathrm{H} = -\vec{\mu}.\vec{B} = -\left(\gamma\hbar I_z\right)B_0$$

$$\mathrm{H}\Psi = E\Psi = -\hbar\left(\gamma B_0\right)I_z\Psi = -\hbar\omega_L I_z\Psi$$

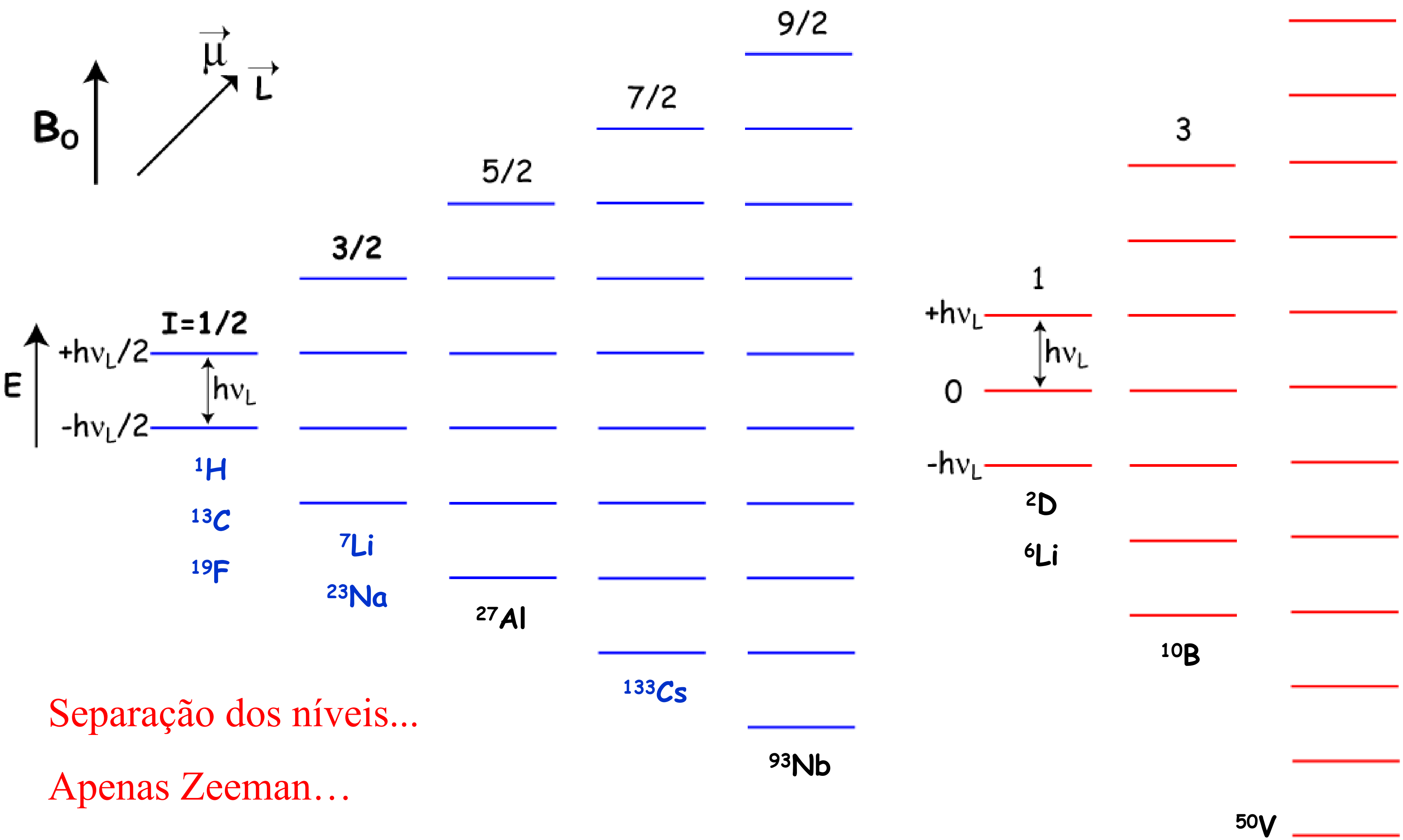
$$I_z\Psi = m\Psi;\;\; m = -I, -I+1, \ldots, +I;\;\; 2I+1 \text{ valores}$$

$$I = 0, 1/2, 1, 3/2, 5/2, 3, 7/2, 4, 9/2, 5, 6$$

Efeito Zeeman: $E_m = -\hbar\omega_L m$

Efeito Zeeman

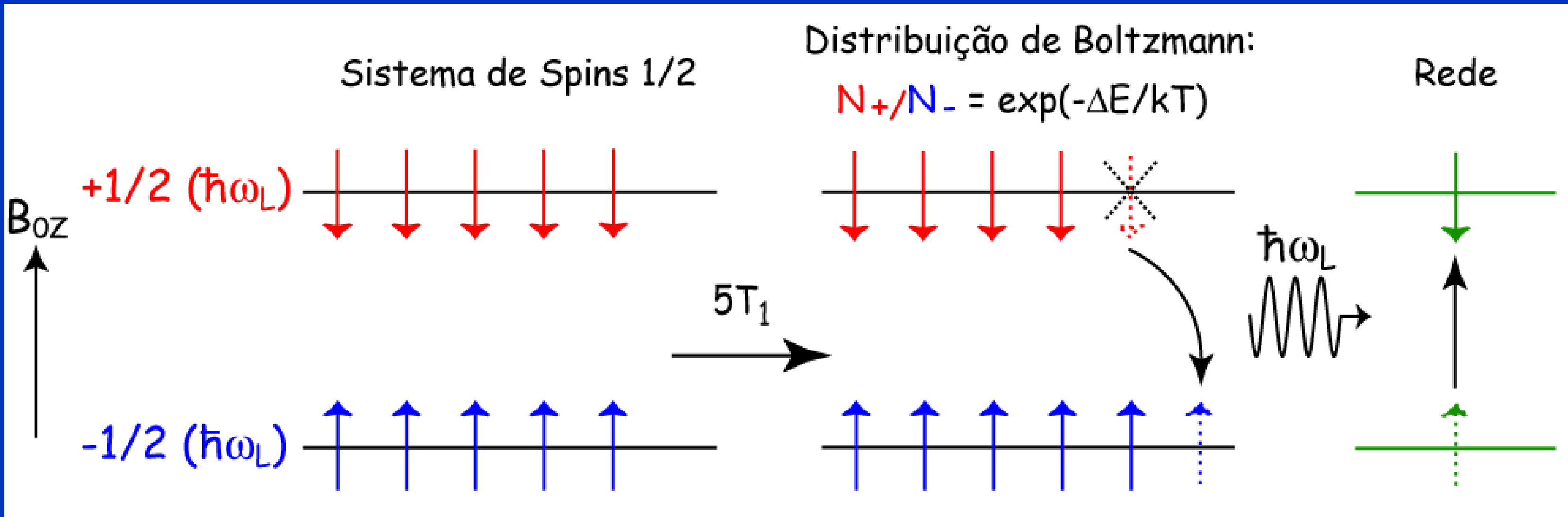
$$\vec{\mu} = \gamma \hbar \vec{I} \quad \Rightarrow \quad |\vec{\mu}| = \gamma \hbar \sqrt{I(I+1)}$$



Separação dos níveis...

Apenas Zeeman…

População dos níveis de energia



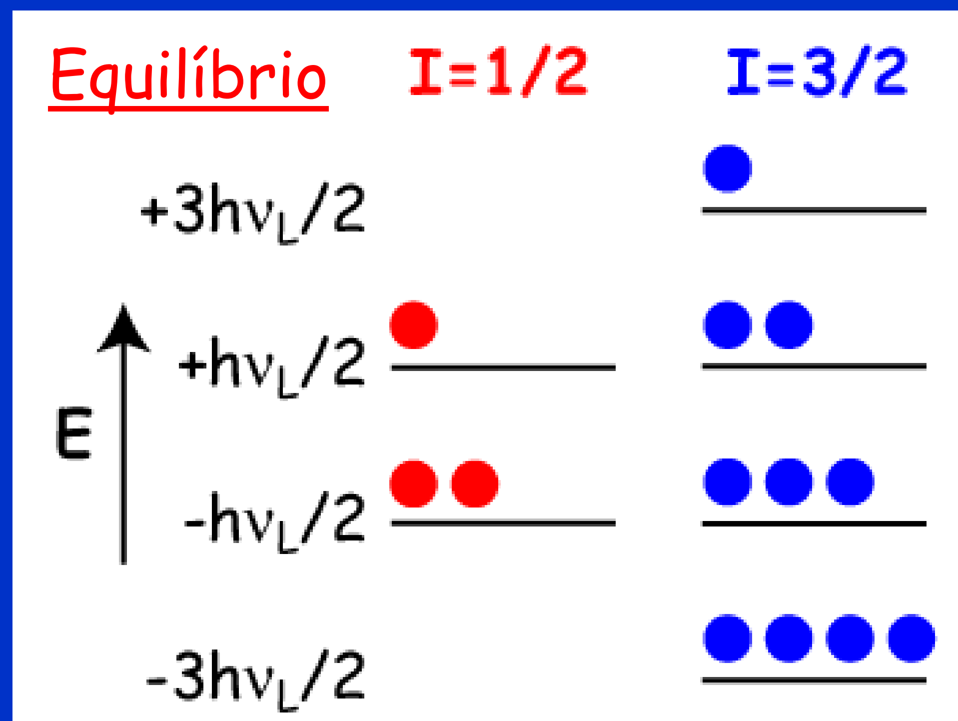
Boltzmann:

$$N_S / N_I = \exp\left(-E/kT\right)$$

$\Delta E \sim 10^{-7}$ eV

$kT \sim 10^{-2}$ eV

$$N_S / N_I = 1 - E/kT$$



Revisão / Mecânica Quântica / NMR (s = ½)

$I_z\Psi = m\Psi \Rightarrow$

Auto funções Ψ: α(−1/2) e β(+1/2)

Auto valores: −1/2 e +1/2

$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$

$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$

$E_{\alpha(-1/2)} = +\hbar\omega_L/2$

$E_{\beta(+1/2)} = -\hbar\omega_L/2$

$I_x\alpha = 1/2\,\beta \qquad I_y\alpha = i/2\,\beta$

$I_x\beta = 1/2\,\alpha \qquad I_y\beta = -i/2\,\alpha$

$I_+ = I_x + iI_y$ e $I_- = I_x - iI_y$

$I_+\alpha = 0 \qquad I_-\alpha = \beta$

$I_+\beta = \alpha \qquad I_-\beta = 0$

$\Rightarrow$ RF...

$\mathrm{H}_{RF} = -\vec{\mu}\cdot\vec{B}_1 =$

$= -\hbar(\gamma B_{1x})I_x$

Valor esperado de um observável: $\langle I_\alpha\rangle = \langle\Psi|I_\alpha|\Psi\rangle$

$\langle I_z\rangle = \langle\alpha|I_z|\alpha\rangle = -1/2$

$\langle I_z\rangle = \langle\beta|I_z|\beta\rangle = +1/2$

$\langle I_x\rangle = \langle\alpha|I_x|\alpha\rangle = 1/2\langle\alpha|\beta\rangle = 0$

$\langle I_x\rangle = \langle\alpha|I_x|\beta\rangle = 1/2\langle\alpha|\alpha\rangle = 1/2$

$$\mathrm{H}\Psi = E\Psi \Rightarrow$$ Valor esperado da energia:

$$\langle \Psi_n | \mathrm{H} | \Psi_n \rangle = E_n \langle \Psi_n | \Psi_n \rangle = E_n$$

$$\langle \Psi_m | \mathrm{H} | \Psi_n \rangle = E_n \langle \Psi_m | \Psi_n \rangle = 0$$

Caso geral:

Rep. op. p/ Matriz quadrada

$$\mathrm{H}_{mn} = \langle \Psi_m | \mathrm{H} | \Psi_n \rangle = \begin{bmatrix} \mathrm{H}_{11} & 0 & \dots & 0 \\ 0 & \mathrm{H}_{22} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \mathrm{H}_{nn} \end{bmatrix} = \begin{bmatrix} E_1 & 0 & \dots & 0 \\ 0 & E_2 & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & E_n \end{bmatrix}$$

Caso spin 1/2:

$$\langle\alpha| \quad \langle\beta|$$

$$\mathrm{H}_{\alpha\beta} = \langle \Psi_\alpha | \mathrm{H} | \Psi_\beta \rangle = \begin{bmatrix} \mathrm{H}_{\alpha\alpha} & 0 \\ 0 & \mathrm{H}_{\beta\beta} \end{bmatrix} = -\frac{\gamma\hbar B_0}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{matrix} |\alpha\rangle \\ |\beta\rangle \end{matrix}$$

Matrizes de Pauli:

$$I_z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad I_x = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad e \quad I_y = \frac{i}{2}\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$$

No caso de sistemas de 2 spins ½:

$$\Psi = \alpha\alpha, \alpha\beta, \beta\alpha, \beta\beta$$

Acoplamentos dipolares.... J

Valores esperados de I_x, I_y e I_z

Valor esperado de um observável: $\langle I_\alpha \rangle = \langle \Psi | I_\alpha | \Psi \rangle$

Evolução temporal do valor esperado:

$$\frac{d}{dt}\langle I_\alpha \rangle = \frac{1}{i\hbar}\langle [I_\alpha, \mathrm{H}] \rangle + \left\langle \frac{\partial I_\alpha}{\partial t} \right\rangle = \frac{1}{i\hbar}\langle [I_\alpha, \mathrm{H}] \rangle$$

Regras de comutação:

$$[I_x, I_z] = -iI_y$$

$$[I_y, I_z] = +iI_x$$

$$\frac{d}{dt}\langle I_x \rangle = \frac{1}{i\hbar}\langle [I_x, (-\gamma\hbar B_0 I_z)] \rangle = \frac{(\gamma B_0)}{i}\langle [I_x, I_z] \rangle = -\omega_L \langle I_y \rangle$$

$$\frac{d}{dt}\langle I_y \rangle = \frac{1}{i\hbar}\langle [I_y, (-\gamma\hbar B_0 I_z)] \rangle = \frac{(\gamma B_0)}{i}\langle [I_y, I_z] \rangle = +\omega_L \langle I_x \rangle$$

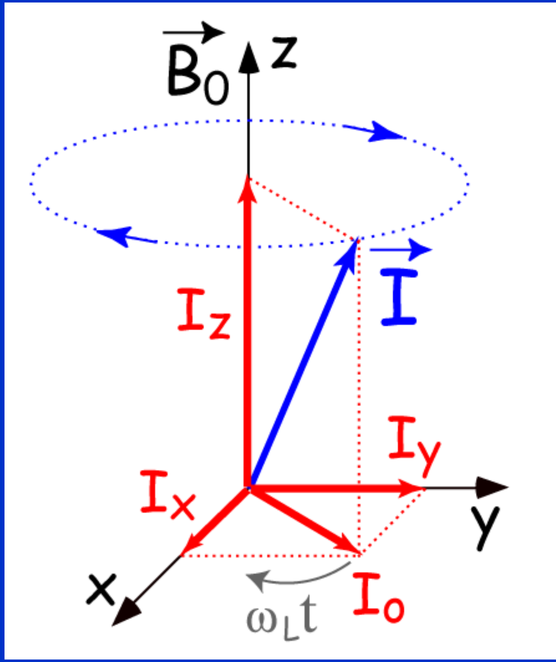
$$\frac{d}{dt}\langle I_z \rangle = \frac{1}{i\hbar}\langle [I_z, (-\gamma\hbar B_0 I_z)] \rangle = \frac{(\gamma B_0)}{i}\langle [I_z, I_z] \rangle = 0$$

Valores esperados de I_x, I_y e I_z

$$\frac{d}{dt}\langle I_z \rangle = 0 \;\Rightarrow\; \langle I_z \rangle = \text{constante!}$$

$$\begin{cases} \dfrac{d}{dt}\langle I_x \rangle = -\omega_L \langle I_y \rangle \\ \dfrac{d}{dt}\langle I_y \rangle = +\omega_L \langle I_x \rangle \end{cases} \Rightarrow \begin{cases} \langle I_x \rangle = I_0 cos(\omega_L t) + I_0 sen(\omega_L t) \\ \langle I_y \rangle = -I_0 sen(\omega_L t) + I_0 cos(\omega_L t) \end{cases}$$

Precessão de Larmor!!!



$$\frac{d}{dt}\langle \vec{I} \rangle = \frac{i}{\hbar}\langle [H,\vec{I}] \rangle = \langle \vec{I} \rangle \wedge (\gamma \vec{B}_0) = \langle \vec{I} \rangle \wedge \vec{\omega}_L$$

$$\frac{d}{dt}\langle \vec{\mu} \rangle = \frac{i}{\hbar}\langle [H,\vec{\mu}] \rangle = \langle \vec{\mu} \rangle \wedge (\gamma \vec{B}_0) = \langle \vec{\mu} \rangle \wedge \vec{\omega}_L$$

Perturbação dependente do tempo: RF

Probabilidade de transição entre dois níveis adjacentes:

$$P_{mn} \propto \left| \left\langle m \middle| H_p(t) \middle| n \right\rangle \right|^2 \delta(\omega - \omega_L)$$

$$\delta(\omega - \omega_L) \Rightarrow \omega = \omega_L$$

$$\left\langle m \middle| H_p(t) \middle| n \right\rangle = \left\langle +1/2 \middle| -\gamma\hbar \vec{I}_\alpha . \vec{B}(t) \middle| -1/2 \right\rangle =$$

$$= a \left\langle +1/2 \middle| I_{+,-} . B_{xy}(t) \middle| -1/2 \right\rangle$$

Campo deve oscilar com $\omega = \omega_L$ (RF) no plano xy !!

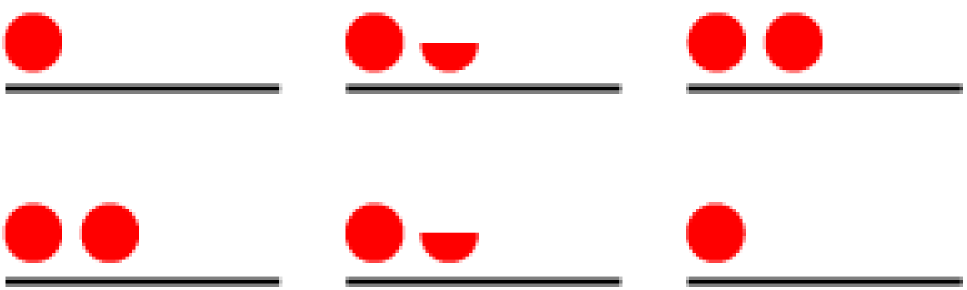
Regra de Seleção: $\Delta m = \pm 1$ (entre níveis adjacentes)

Outras formas de excitar os spins...

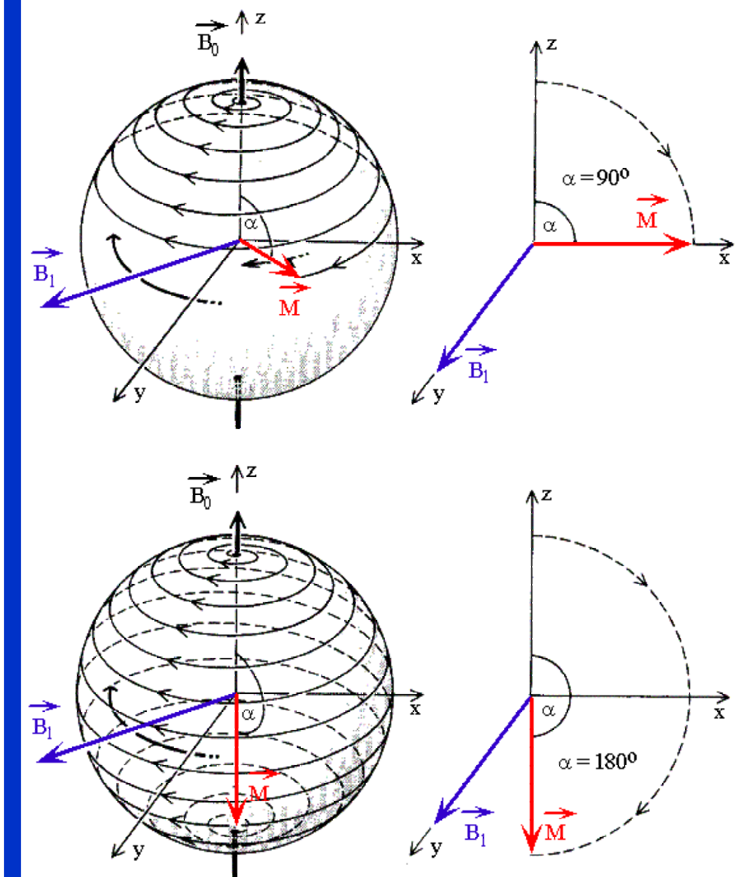
Pulsos de RF de π/2 e π - Spin 1/2

I=1/2

Equilíbrio	π/2	π

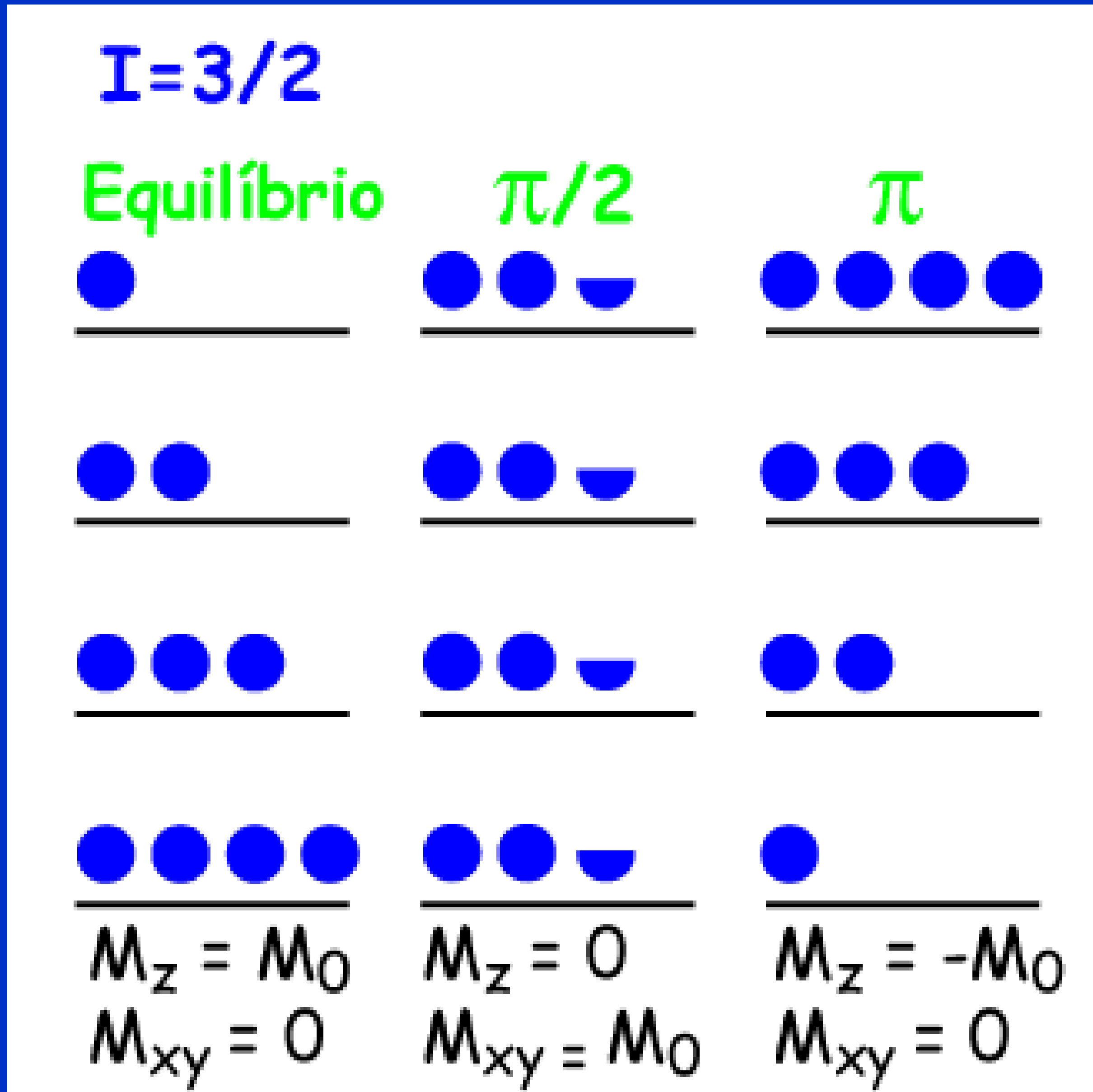


$M_z = M_0$	$M_z = 0$	$M_z = -M_0$
$M_{xy} = 0$	$M_{xy} = M_0$	$M_{xy} = 0$



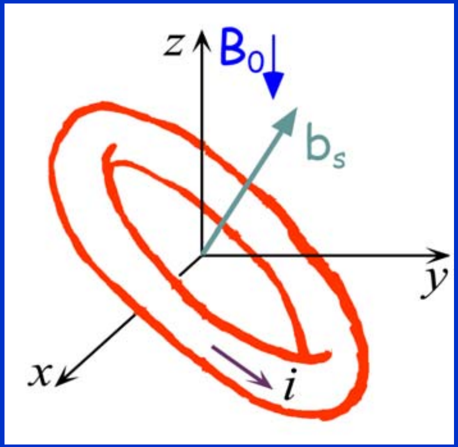
$$\theta = (\gamma B_1)t_p \,,\; B_1 \sim 10\,G \,,\; \gamma B_1 \sim 50\,kHz\,(^1H) \text{ e } t_p \sim 5\,\mu s$$

Pulsos de RF de π/2 e π - Spin 3/2

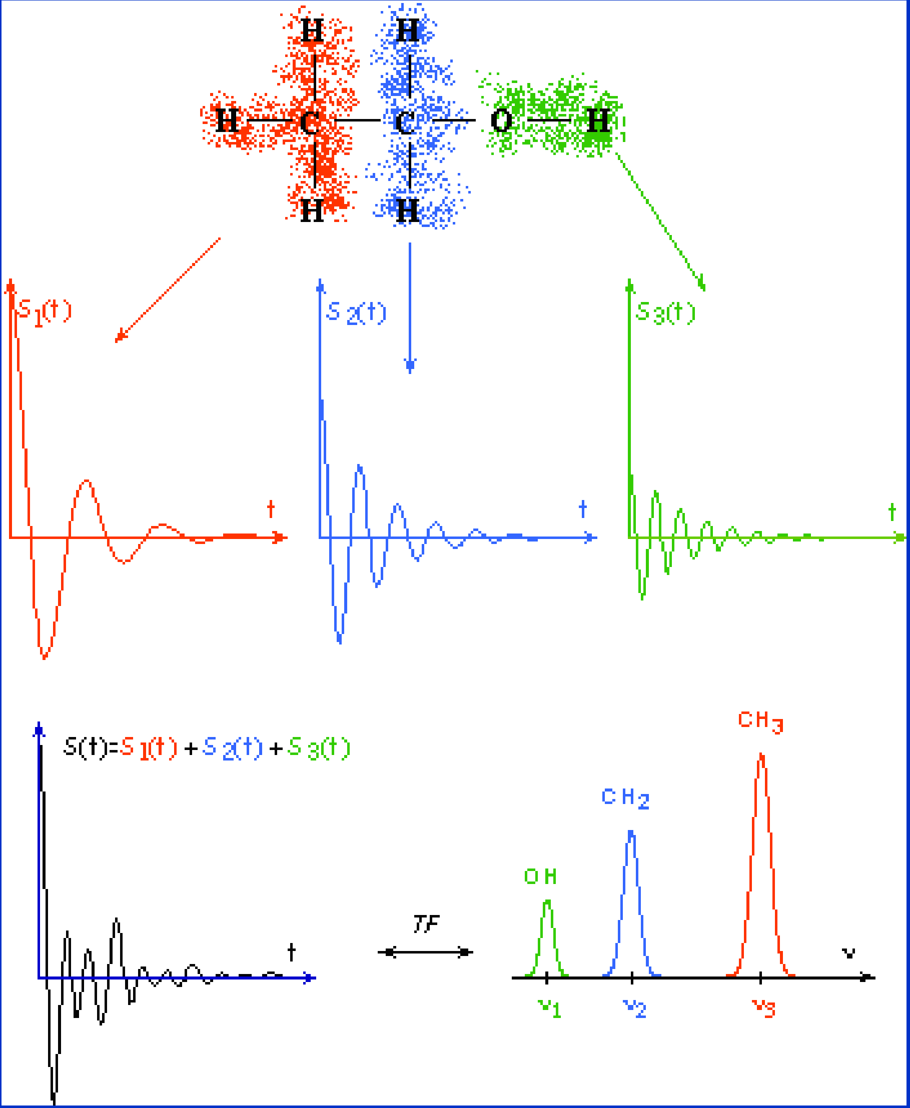


Interações - Deslocamento Químico

CH_3CH_2OH:



A separação entre as linhas é proporcional a B_0

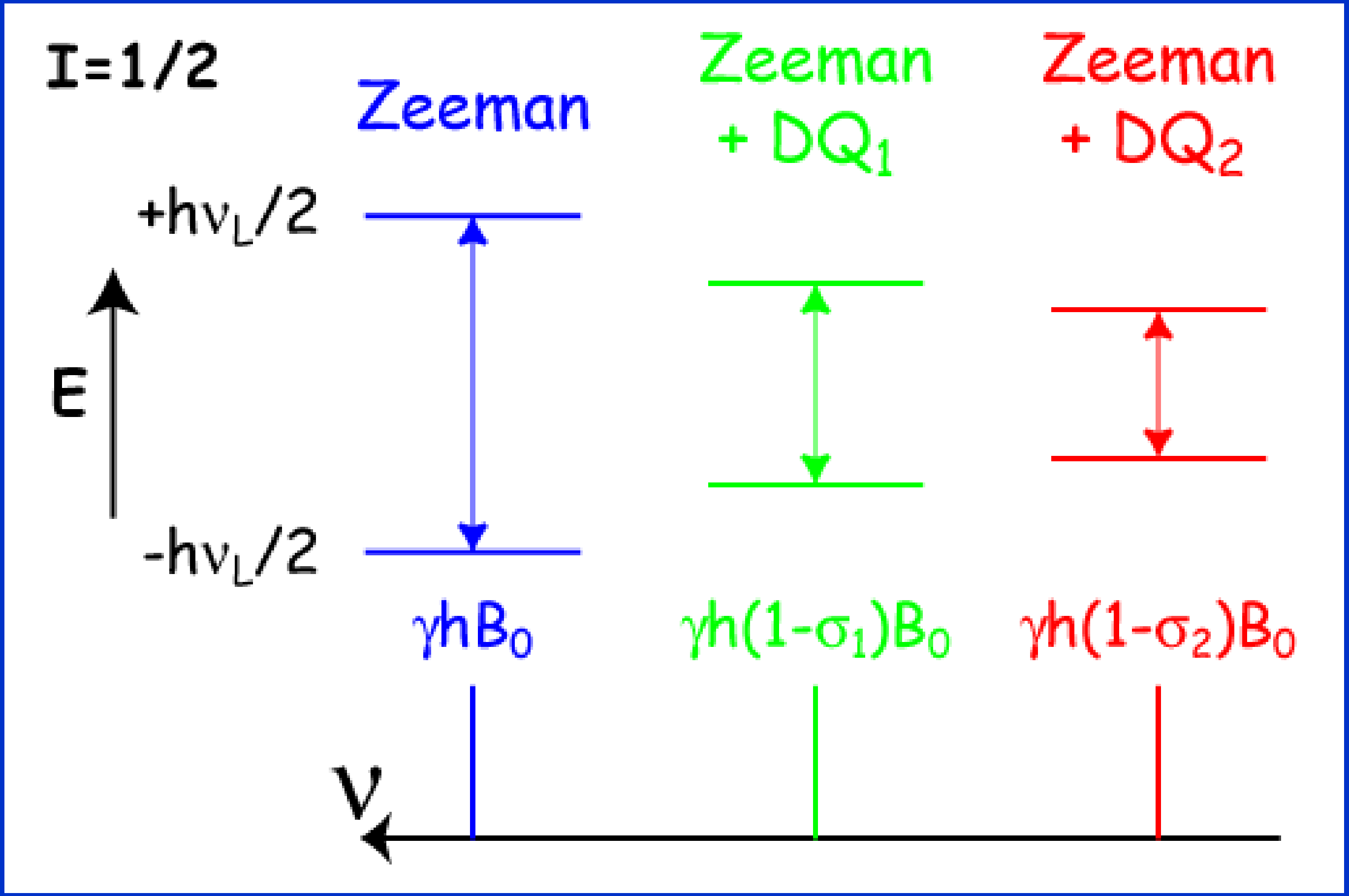


Deslocamento Químico

$$H\Psi = E\Psi$$

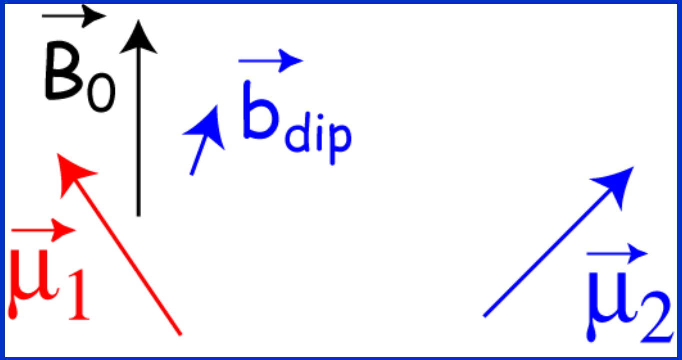
$$H = -\vec{\mu}.\vec{B} = -\left(\gamma\hbar I_z\right)\left(B_0 - \sigma B_0\right)$$

$$H\Psi = E\Psi = -\hbar\left(\gamma B_0\right)\left(1-\sigma\right)I_z\Psi = -\hbar\omega_L\left(1-\sigma\right)I_z\Psi$$



Acoplamento J

Interação Dipolar Magnética:



Interação Dipolar D Direta

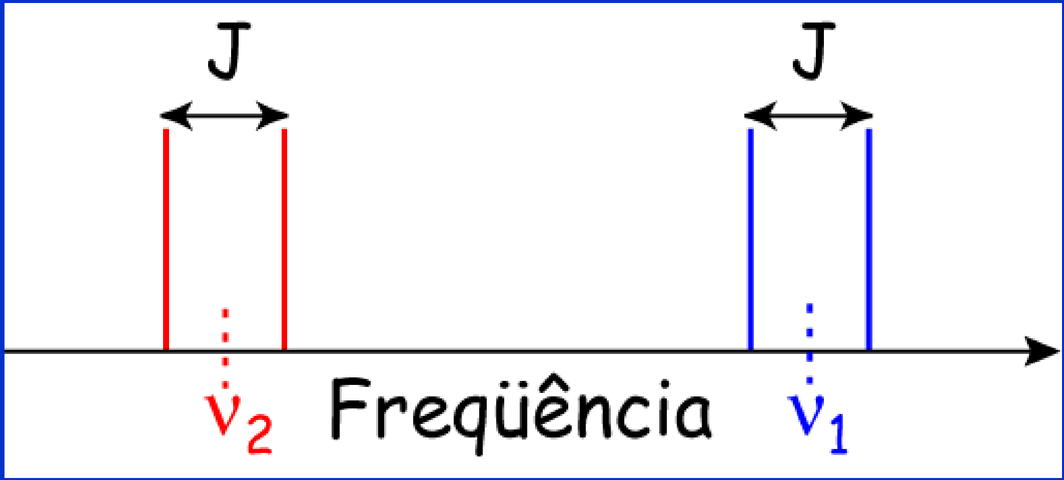
Acoplamento J

Interação Dipolar através dos elétrons:

Orbital ou elétron-núcleo

$$H = -\nu_1 I_{z1} - \nu_2 I_{z2} + J I_{z1} I_{z2}$$

$$\Psi = \alpha\alpha,\ \alpha\beta,\ \beta\alpha,\ \beta\beta$$



Acoplamento J

$$\begin{array}{cccc} \langle\alpha\alpha| & \langle\beta\alpha| & \langle\alpha\beta| & \langle\beta\beta| \end{array}$$

$$I_{z1} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}\begin{matrix} |\alpha\alpha\rangle \\ |\beta\alpha\rangle \\ |\alpha\beta\rangle \\ |\beta\beta\rangle \end{matrix}$$

$$\begin{array}{cccc} \langle\alpha\alpha| & \langle\beta\alpha| & \langle\alpha\beta| & \langle\beta\beta| \end{array}$$

$$I_{z2} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}\begin{matrix} |\alpha\alpha\rangle \\ |\beta\alpha\rangle \\ |\alpha\beta\rangle \\ |\beta\beta\rangle \end{matrix}$$

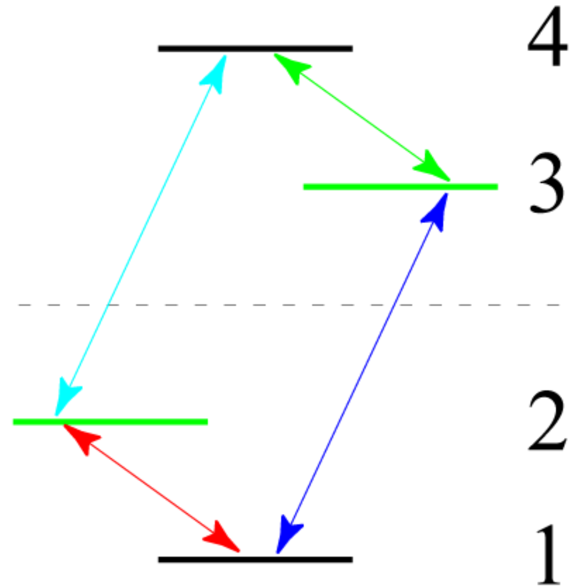
Acoplamento J: $\mathrm{H}_J = -\nu_1 I_{z1} - \nu_2 I_{z2} + J I_{z1} I_{z2}$

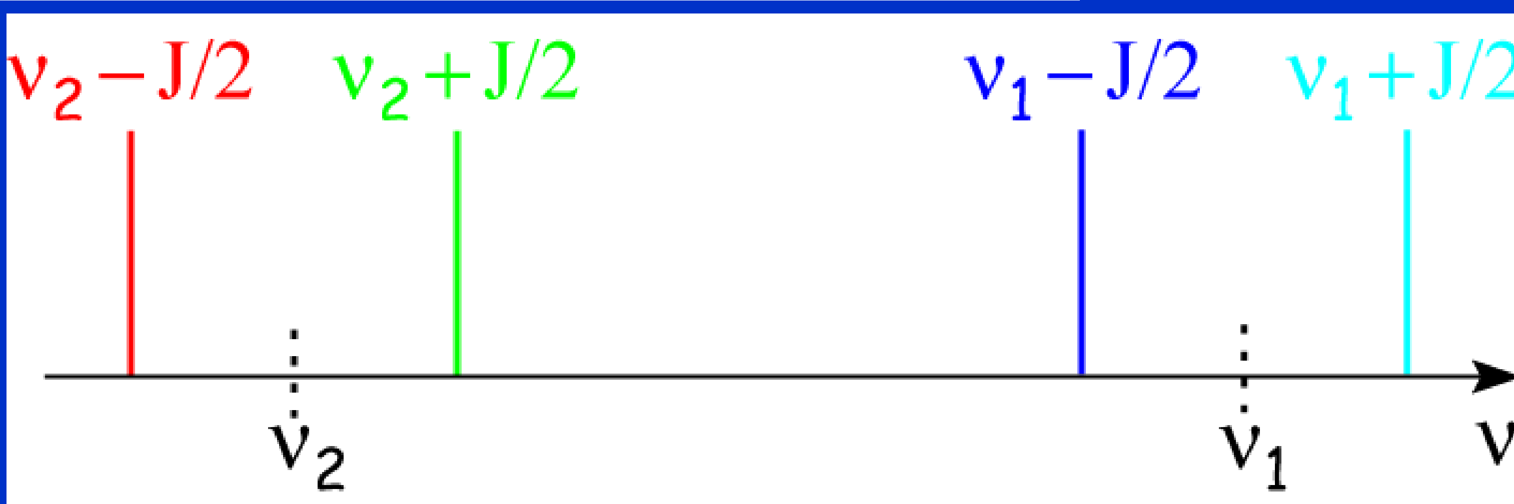
$$\mathrm{H}_{J,mn} = \langle \Psi_m | \mathrm{H}_J | \Psi_n \rangle =$$

$$
\begin{array}{ccccc}
& \langle\alpha\alpha| & \langle\beta\alpha| & \langle\alpha\beta| & \langle\beta\beta| \\
= & \begin{bmatrix}
-\frac{1}{2}(\nu_1+\nu_2)+\frac{J}{4} & 0 & 0 & 0 \\
0 & -\frac{1}{2}(\nu_1-\nu_2)-\frac{J}{4} & \frac{J}{2} & 0 \\
0 & \frac{J}{2} & +\frac{1}{2}(\nu_1-\nu_2)-\frac{J}{4} & 0 \\
0 & 0 & 0 & +\frac{1}{2}(\nu_1+\nu_2)+\frac{J}{4}
\end{bmatrix}
\begin{array}{c} |\alpha\alpha\rangle \\ |\beta\alpha\rangle \\ |\alpha\beta\rangle \\ |\beta\beta\rangle \end{array}
\end{array}
$$

Acoplamento J

Estado	m_t		Freqüências
$\vert\beta\beta\rangle$	-1	4	$+(\nu_1+\nu_2)/2+J/4$
$c\,\vert\alpha\beta\rangle + s\,\vert\beta\alpha\rangle$	0	3	$+(\nu_1-\nu_2)/2-J/4$
$-s\,\vert\alpha\beta\rangle + c\,\vert\beta\alpha\rangle$	0	2	$-(\nu_1-\nu_2)/2-J/4$
$\vert\alpha\alpha\rangle$	1	1	$-(\nu_1+\nu_2)/2+J/4$

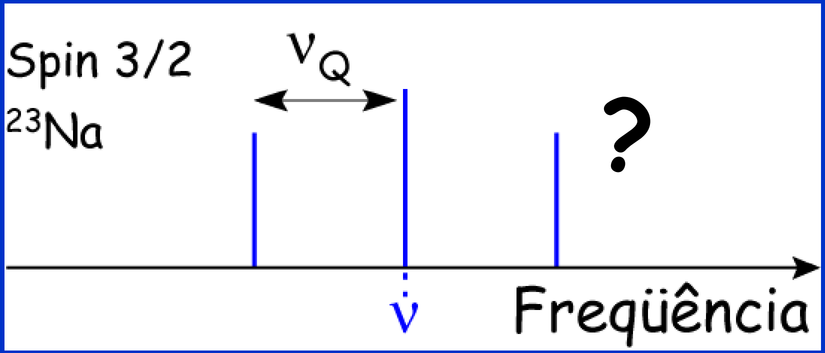




Interação Quadrupolar Elétrica, I = 3/2

$$H_Q = \frac{1}{6}\omega_Q\left[3I_z^2 - I\left(I+1\right)\hat{1}\right]$$

$$\left|+3/2\right\rangle, \left|+1/2\right\rangle, \left|-1/2\right\rangle \text{ e } \left|-3/2\right\rangle$$



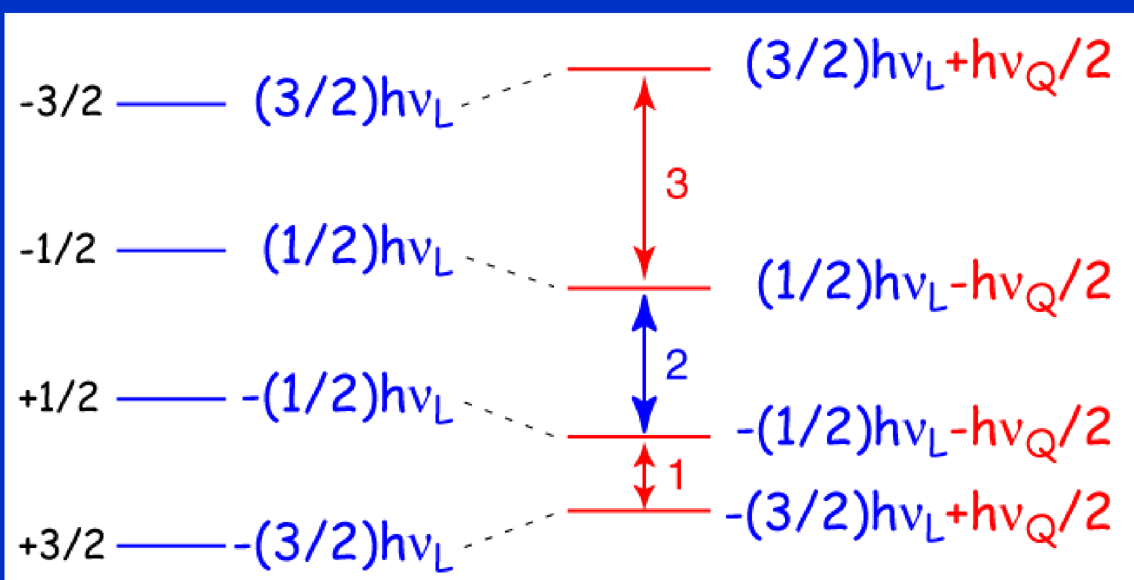
$$\begin{matrix} & \left\langle +3/2\right| & \left\langle +1/2\right| & \left\langle -1/2\right| & \left\langle -3/2\right| & \\ I_z = & \begin{bmatrix} +3/2 & 0 & 0 & 0 \\ 0 & +1/2 & 0 & 0 \\ 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & -3/2 \end{bmatrix} & & & & \begin{matrix} \left|+3/2\right\rangle \\ \left|+1/2\right\rangle \\ \left|-1/2\right\rangle \\ \left|-3/2\right\rangle \end{matrix} \end{matrix}$$

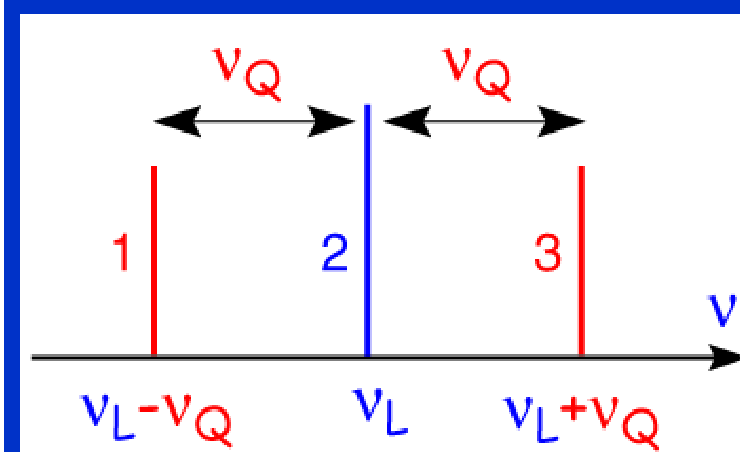
Interação Quadrupolar Elétrica, I = 3/2

$$H_Q = \frac{1}{6}\omega_Q\left[3I_z^2 - I\left(I+1\right)\hat{1}\right] \qquad H = H_Z + H_Q$$

$$\begin{array}{ccccc} & \langle +3/2| & \langle +1/2| & \langle -1/2| & \langle -3/2| \end{array}$$

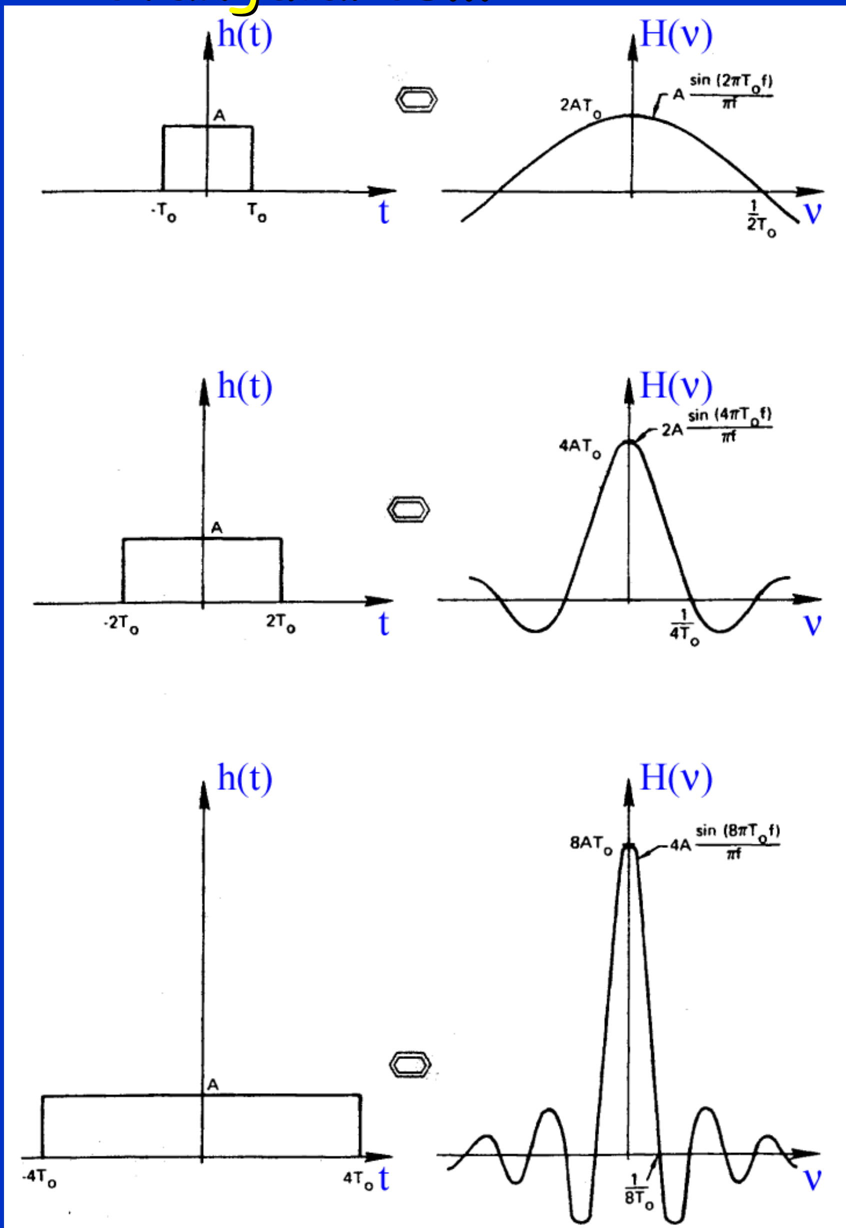
$$H_{Q,mn} = \omega_Q\begin{bmatrix} 1/2 & 0 & 0 & 0 \\ 0 & -1/2 & 0 & 0 \\ 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & 1/2 \end{bmatrix}\begin{array}{c} |+3/2\rangle \\ |+1/2\rangle \\ |-1/2\rangle \\ |-3/2\rangle \end{array}$$



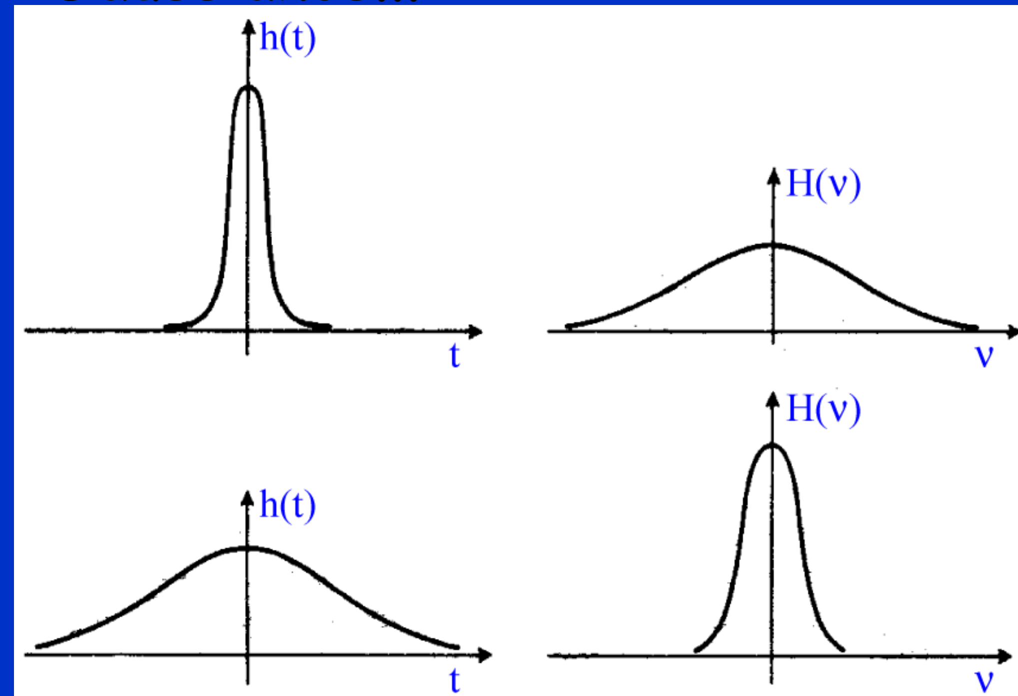


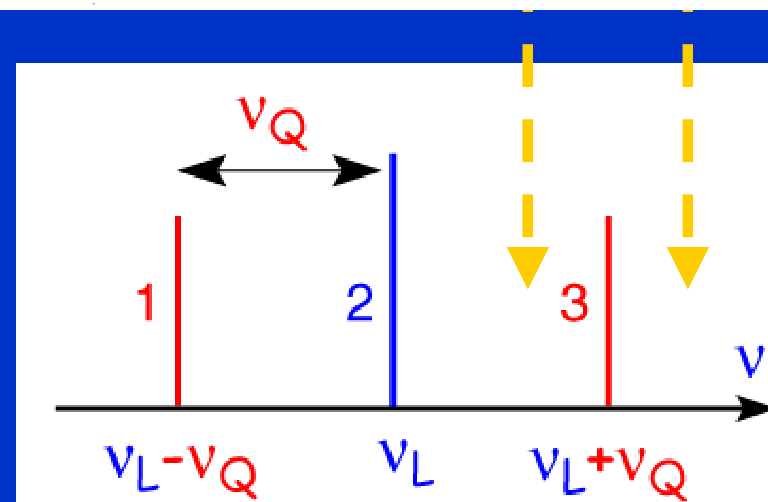
Pulsos de RF Seletivos...

Retangulares...



Gaussianos...





Pulsos de RF de π/2 e π seletivos