

Métodos de RMN no estado sólido

Jair C. C. Freitas

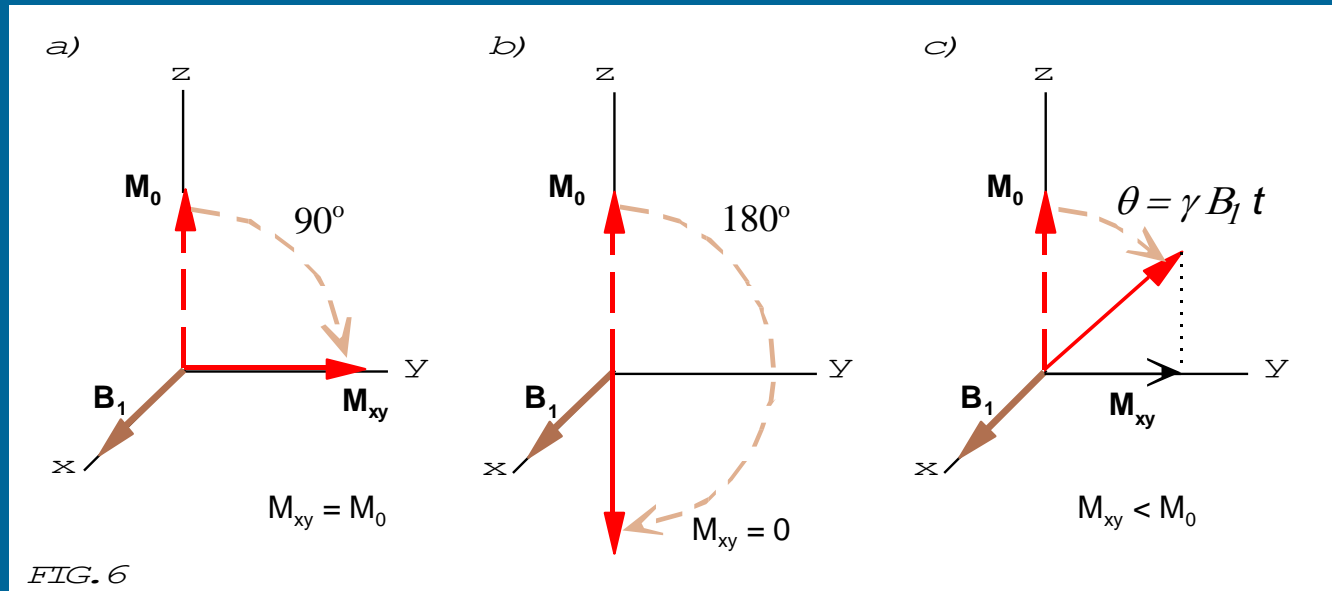
Programa de Pós-graduação em Física – UFES

Programa de Pós-graduação em Química - UFES

Sumário

- Fundamentos de RMN:
 - Descrição quântica:
 - Vetores de estado.
 - Pulsos de RF e matrizes de rotação.
 - Operador densidade: populações e coerências.
 - Evolução temporal.

Pulsos de RF



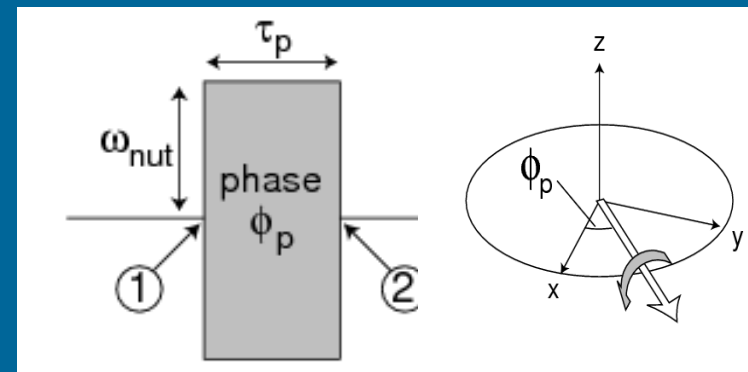
Pulso $\pi/2$

Pulso π

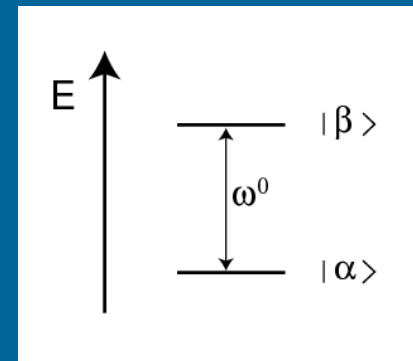
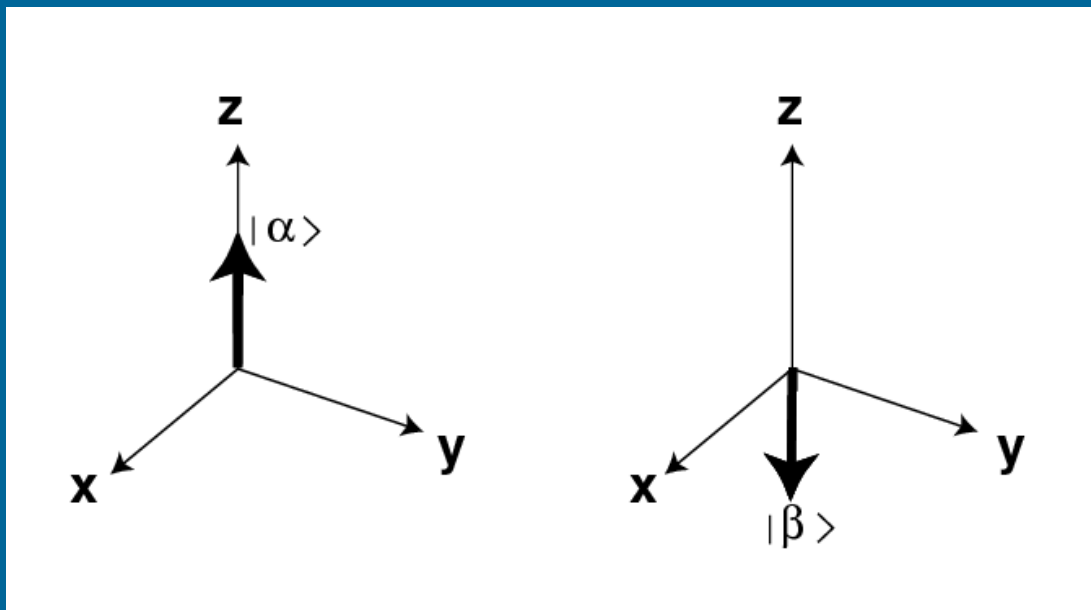
Pulso θ

Controle {

- Duração ($\sim \mu\text{s}$)
- Amplitude ($\sim 10^2 \text{ kHz}$)
- Fase ($0, 90^\circ, 180^\circ, 270^\circ$)



Spin 1/2 em um campo magnético

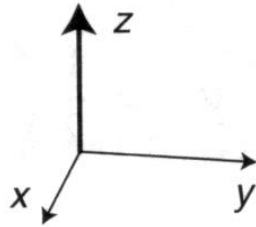


$$I_z |\alpha\rangle = +\frac{1}{2} |\alpha\rangle$$

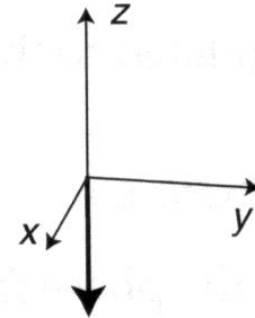
$$I_z |\beta\rangle = -\frac{1}{2} |\beta\rangle$$

Alguns vetores de estado

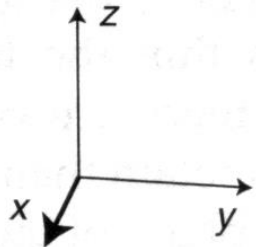
$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} =$$



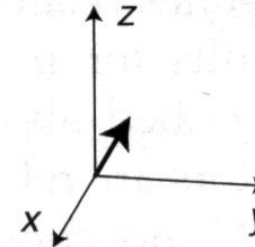
$$|\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} =$$



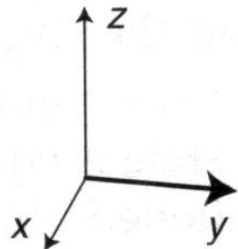
$$|+x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} =$$



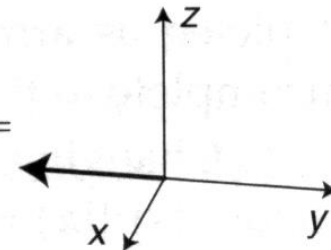
$$|-x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} -i \\ +i \end{pmatrix} =$$



$$|+y\rangle = \frac{1}{2} \begin{pmatrix} 1-i \\ 1+i \end{pmatrix} =$$

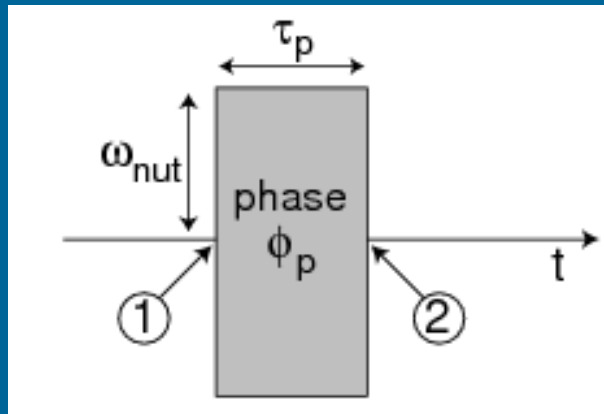


$$|-y\rangle = \frac{1}{2} \begin{pmatrix} 1+i \\ 1-i \end{pmatrix} =$$



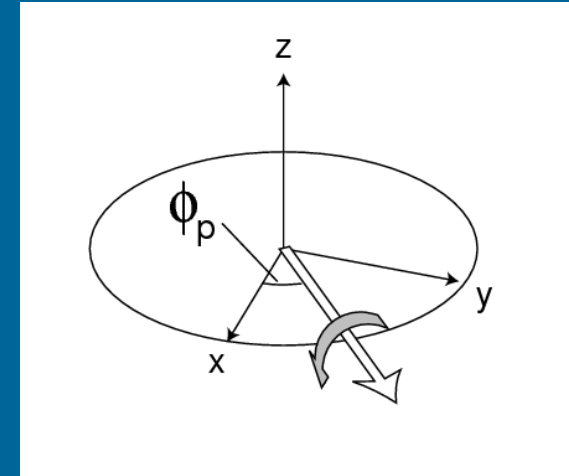
Pulsos de RF: matrizes de rotação

Solução da equação de Shrödinger no sistema girante de coordenadas:



$$|\psi\rangle_2 = R_{\phi_p}(\theta) |\psi\rangle_1$$

$$R_{\phi_p}(\theta) = \begin{pmatrix} \cos \frac{1}{2} \theta & -i \sin \frac{1}{2} \theta e^{-i\phi_p} \\ -i \sin \frac{1}{2} \theta e^{i\phi_p} & \cos \frac{1}{2} \theta \end{pmatrix}$$



$$\theta = \gamma B_1 t_p$$

(ângulo de nutação)

$$\omega_{\text{nut}} = \gamma B_1$$

(frequência de nutação)

Pulsos de RF: matrizes de rotação

$$R_x(\theta) = \begin{pmatrix} \cos \frac{1}{2} \theta & -i \sin \frac{1}{2} \theta \\ -i \sin \frac{1}{2} \theta & \cos \frac{1}{2} \theta \end{pmatrix}$$

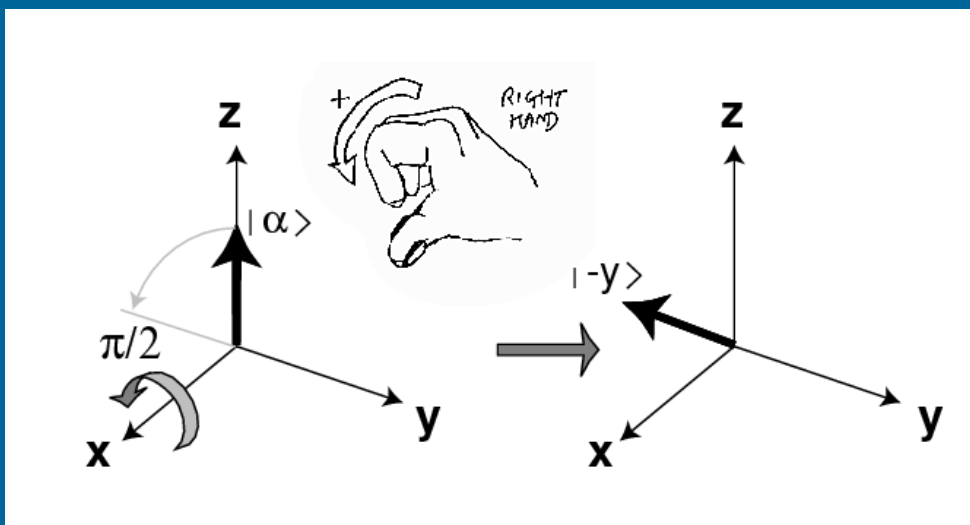
$$\theta = \gamma B_1 t_P$$

(ângulo de nutação)

$$R_x(\pi/2) |\alpha\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \\ -i & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} = e^{-i\pi/4} |-y\rangle$$

Exemplo 1:

Pulso $\pi/2$ na direção x atuando sobre estado inicial com spin na direção z :



Pulsos de RF: matrizes de rotação

$$R_x(\theta) = \begin{pmatrix} \cos \frac{1}{2} \theta & -i \sin \frac{1}{2} \theta \\ -i \sin \frac{1}{2} \theta & \cos \frac{1}{2} \theta \end{pmatrix}$$

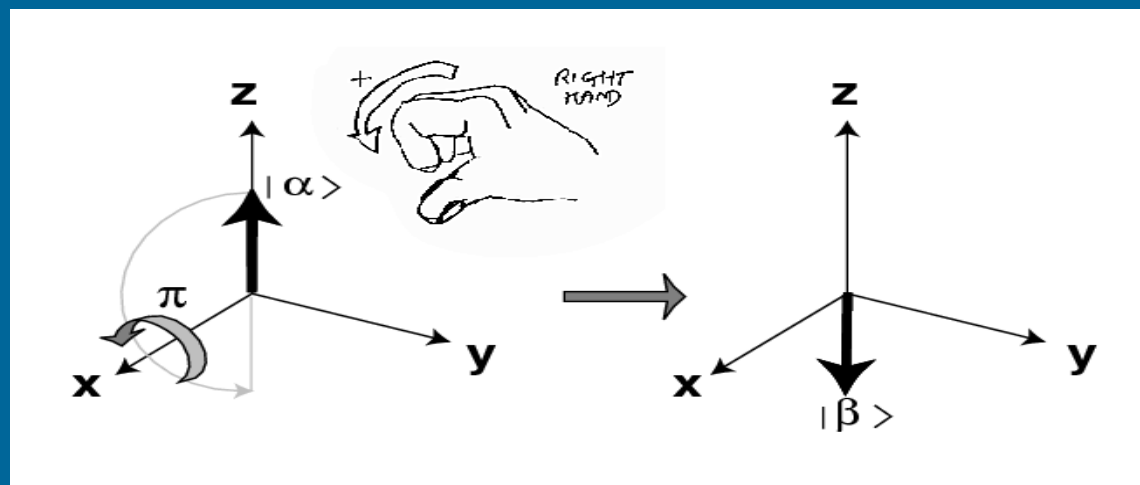
$$\theta = \gamma B_1 t_P$$

(ângulo de nutação)

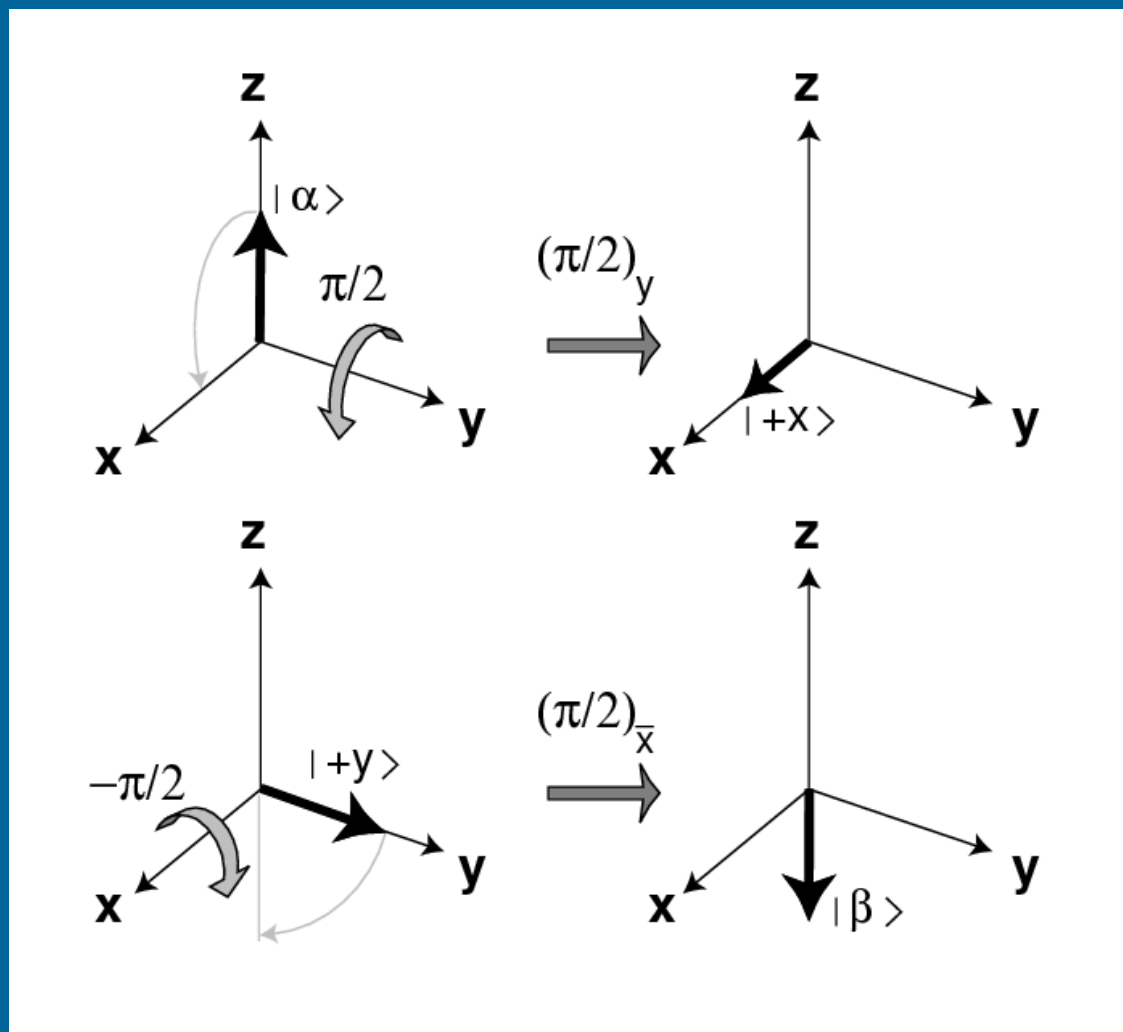
$$R_x(\pi) |\alpha\rangle = \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = -i \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -i |\beta\rangle$$

Exemplo 2:

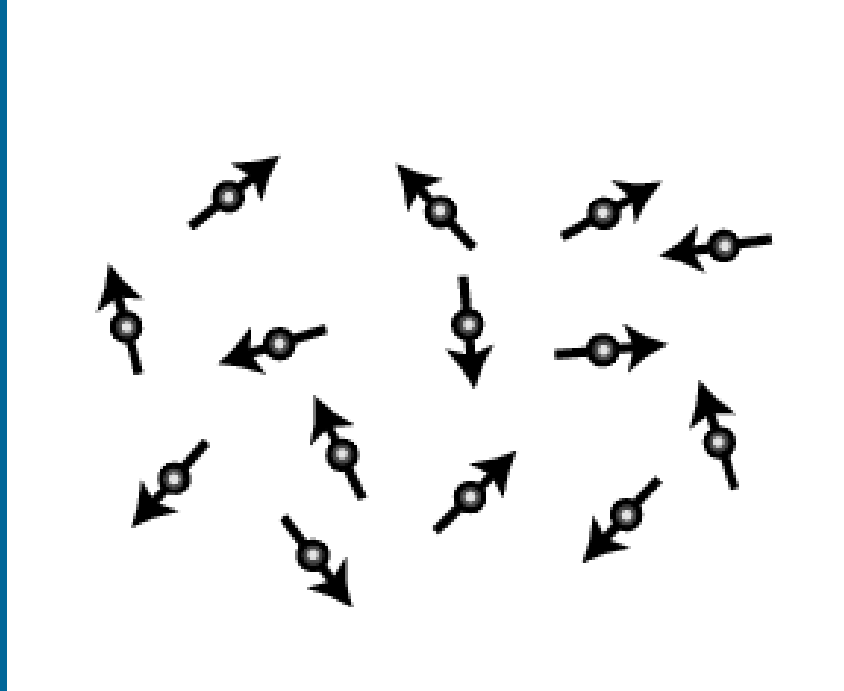
Pulso π na direção x atuando sobre estado inicial com spin na direção z :



Outros exemplos



“Ensemble” de spins $\frac{1}{2}$

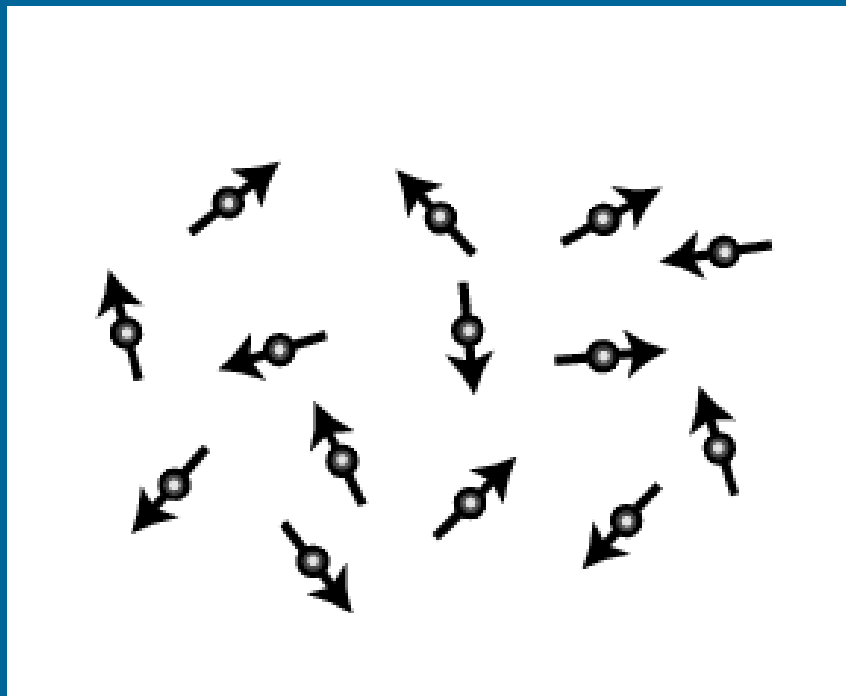


Estado de um spin: $|\psi\rangle = \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}$

Matriz densidade para um spin:

$$|\psi\rangle\langle\psi| = \begin{pmatrix} c_\alpha c_\alpha^* & c_\alpha c_\beta^* \\ c_\beta c_\alpha^* & c_\beta c_\beta^* \end{pmatrix}$$

“Ensemble” de spins $\frac{1}{2}$



Matriz densidade para o ensemble:

$$\rho = \begin{pmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{pmatrix} = \begin{pmatrix} \overline{c_{\alpha} c_{\alpha}^*} & \overline{c_{\alpha} c_{\beta}^*} \\ \overline{c_{\beta} c_{\alpha}^*} & \overline{c_{\beta} c_{\beta}^*} \end{pmatrix}$$

Cálculos de valores médios para o ensemble: $\langle A \rangle = \text{Tr} \{ \rho A \}$

Populações e coerências

$$\rho = \begin{pmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{pmatrix} = \begin{pmatrix} \rho_{\boxed{\alpha}} & \rho_{\boxed{+}} \\ \rho_{\boxed{-}} & \rho_{\boxed{\beta}} \end{pmatrix}$$

Populações:

$$\rho_{\boxed{\alpha}}$$

$$\rho_{\boxed{\beta}}$$

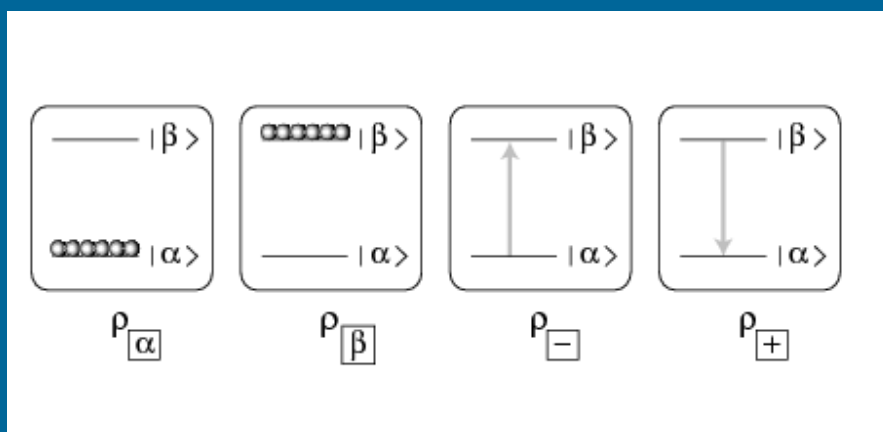
$$\rho_{\boxed{\alpha}} + \rho_{\boxed{\beta}} = 1$$

Coerências:

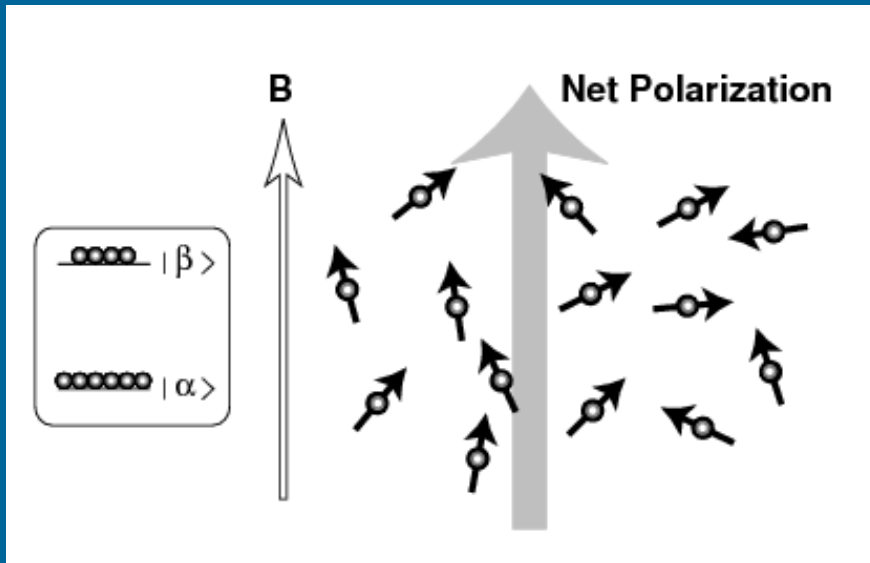
$$\rho_{\boxed{+}}$$

$$\rho_{\boxed{-}}$$

$$\rho_{\boxed{+}} = \rho_{\boxed{-}}^*$$

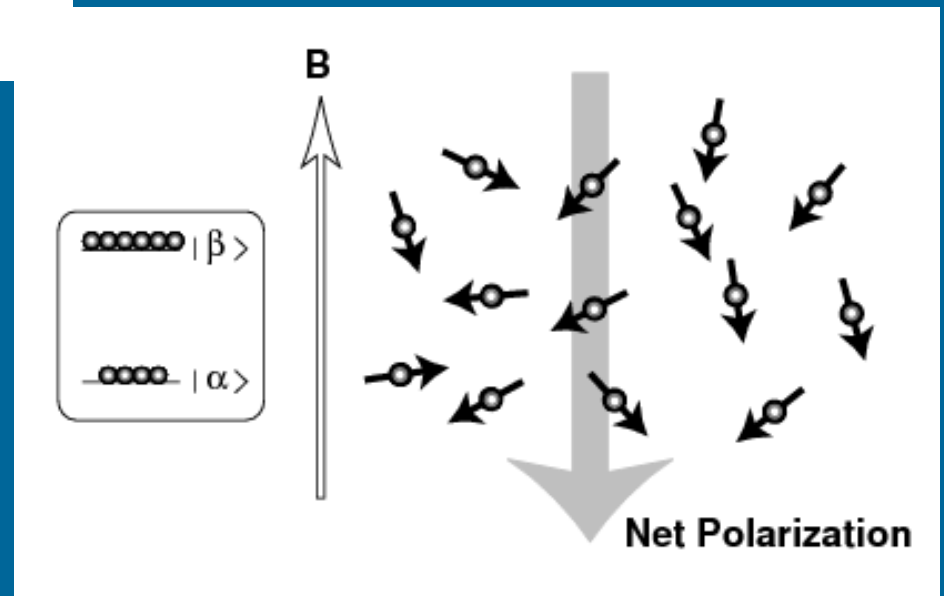


Interpretação física das populações

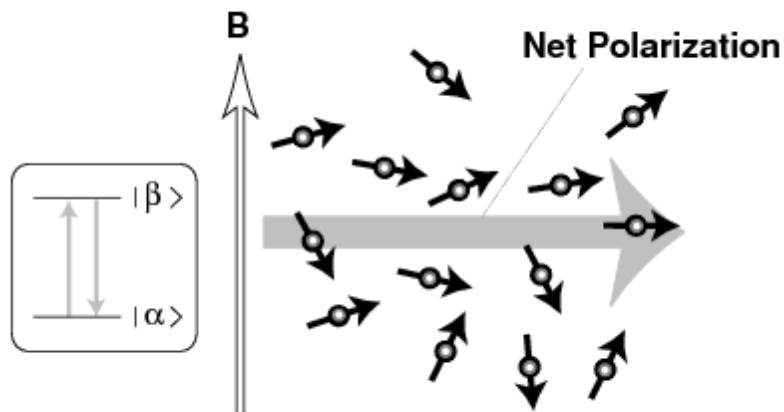


$$|\alpha\rangle\langle\alpha| = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

$$|\beta\rangle\langle\beta| = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

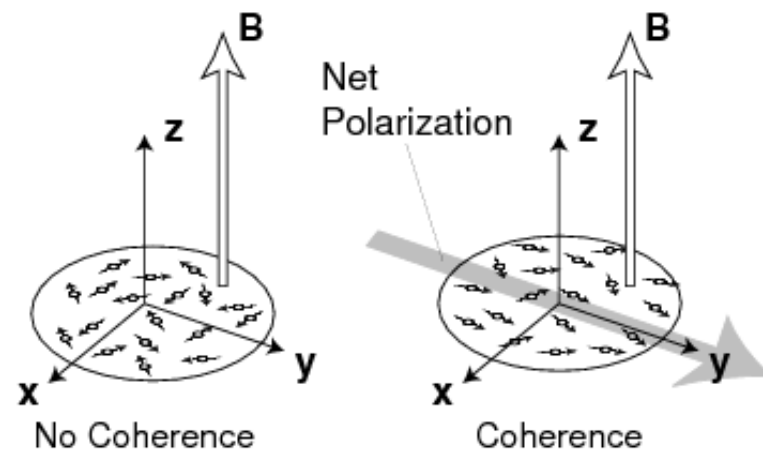


Interpretação física das coerências



$$|x\rangle\langle x| = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

$$|y\rangle\langle y| = \frac{1}{2} \begin{pmatrix} 1 & i \\ -i & 1 \end{pmatrix}$$



Equilíbrio térmico

$$\rho_{\text{eq}} = \frac{e^{-H/kT}}{Z}$$

$$\rho_{\text{eq}} \cong \frac{1}{Z} - \underbrace{\frac{1}{Z} \frac{H}{kT}}_{\text{Desvio}}$$

$$U\rho_{\text{eq}}U^\dagger \cong \frac{1}{Z} - \frac{1}{Z} \frac{1}{kT} UHU^\dagger$$

$$\rho_{\text{eq}} = \begin{pmatrix} \frac{1}{2} + \frac{1}{4}\varepsilon & 0 \\ 0 & \frac{1}{2} - \frac{1}{4}\varepsilon \end{pmatrix} = \frac{1}{2}\mathbf{1} + \frac{1}{2}\varepsilon\mathbf{I}_z$$

$$\varepsilon = \frac{\hbar\gamma B_0}{kT} \approx 10^{-4}$$

Magnetização:

$$\rho_{\boxed{\alpha}} = \frac{1}{2} + \frac{1}{4}\varepsilon M_z$$

$$\rho_{\boxed{\beta}} = \frac{1}{2} - \frac{1}{4}\varepsilon M_z$$

$$\rho_{\boxed{+}} = \frac{1}{4}\varepsilon(M_x - iM_y)$$

$$\rho_{\boxed{-}} = \frac{1}{4}\varepsilon(M_x + iM_y)$$

Evolução temporal

Equação de Liouville-von Neumann:

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, \mathcal{H}]$$

Para Hamiltoniano independente do tempo:

$$\rho(t) = e^{-(i/\hbar)\mathcal{H}t} \rho(0) e^{(i/\hbar)\mathcal{H}t}$$

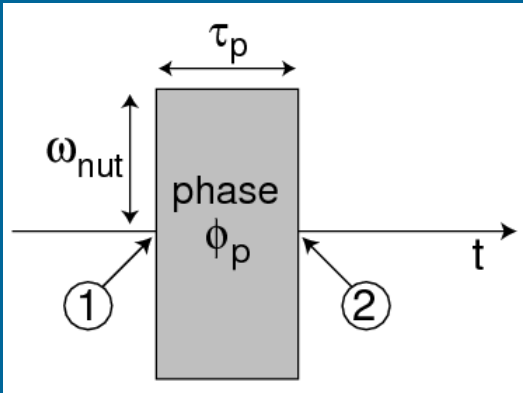
Passagem para o sistema girante de coordenadas:

$$\rho^{Rot} = e^{-i\Omega t I_z} \rho^{Lab} e^{i\Omega t I_z}$$

$$\mathcal{H}_{eff} = -\hbar(\omega_L - \Omega)I_z - \hbar\omega_1 I_x$$

Próximo à condição de ressonância: $\mathcal{H}_{eff} \cong -\hbar\omega_1 I_x$

Atuação de pulsos de RF



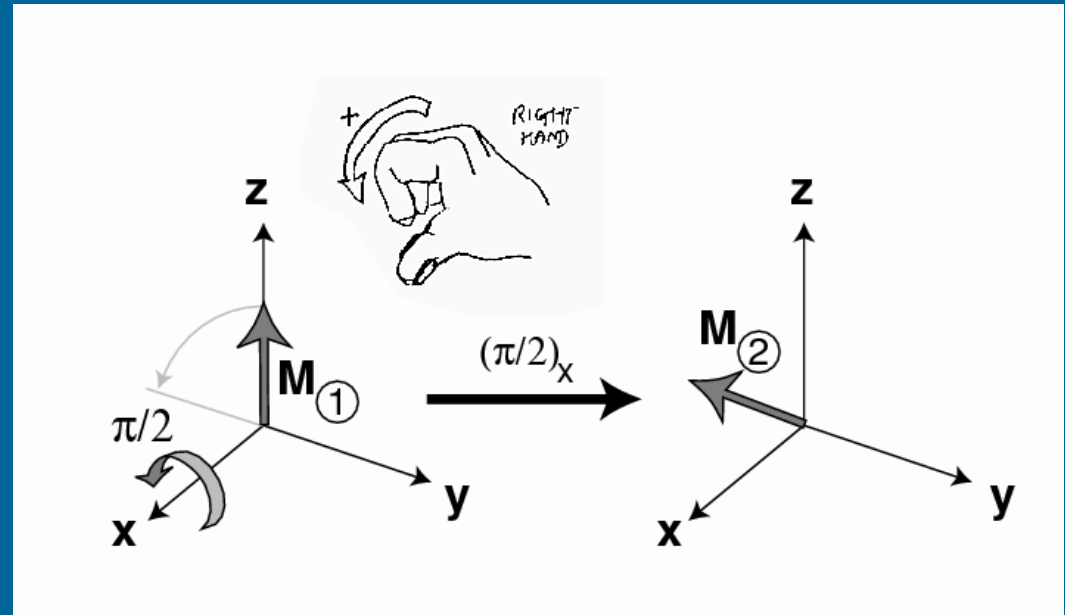
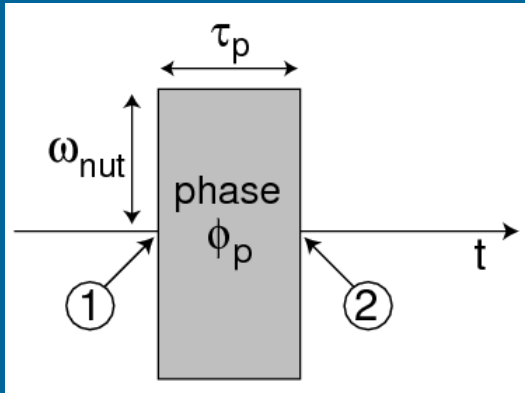
$$U = e^{-(i/\hbar)\mathcal{H}_{\text{eff}}t_p} = e^{i\omega_1 t_p I_x} = R_x(-\theta_p)$$

$$\rho(t_p) = R_x(-\theta_p)\rho_0 R_x(\theta_p)$$

$$R_x(\theta_p) = \begin{bmatrix} \cos(\theta_p/2) & -i \sin(\theta_p/2) \\ -i \sin(\theta_p/2) & \cos(\theta_p/2) \end{bmatrix}$$

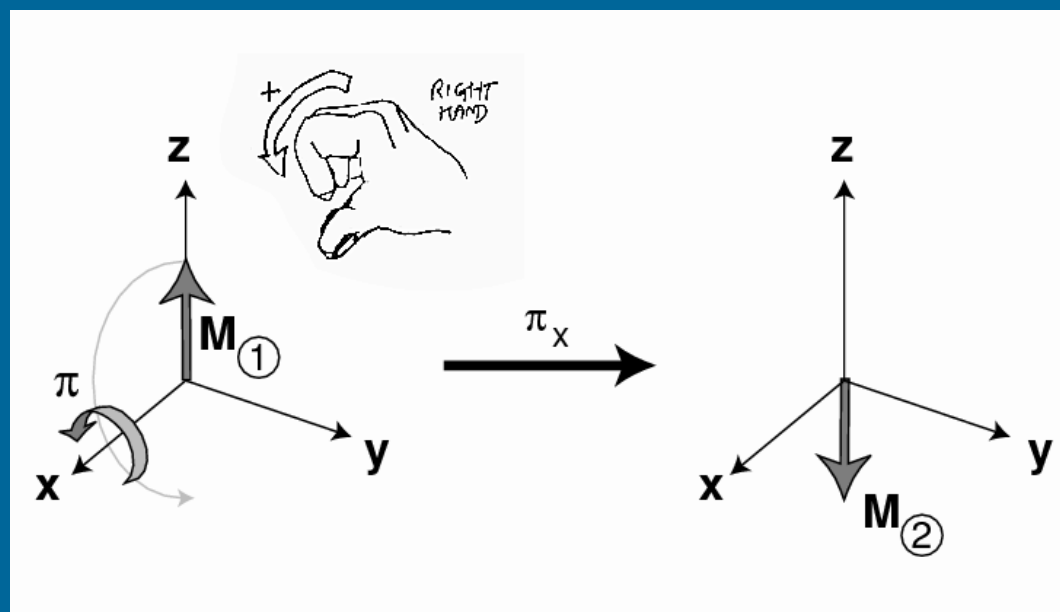
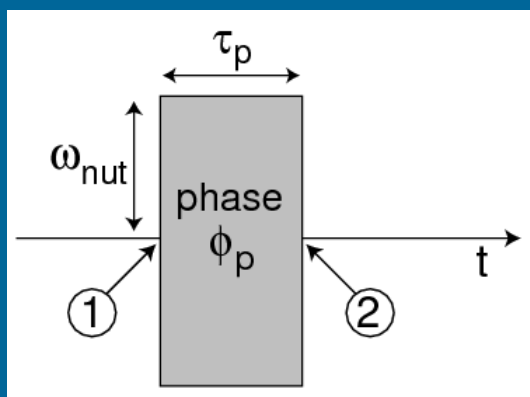
$$R_{\phi_p}(\theta_p) = \begin{bmatrix} \cos(\theta_p/2) & -i \sin(\theta_p/2)e^{-i\phi_p} \\ -i \sin(\theta_p/2)e^{i\phi_p} & \cos(\theta_p/2) \end{bmatrix}$$

Atuação de pulsos de RF



$$\rho_1 = \begin{pmatrix} \frac{1}{2} + \frac{1}{4}\epsilon & 0 \\ 0 & \frac{1}{2} - \frac{1}{4}\epsilon \end{pmatrix} \xrightarrow{(\pi/2)_x} \rho_2 = \begin{pmatrix} \frac{1}{2} & -\frac{1}{4i}\epsilon \\ \frac{1}{4i}\epsilon & \frac{1}{2} \end{pmatrix}$$

Atuação de pulsos de RF



$$\rho_1 = \begin{pmatrix} \frac{1}{2} + \frac{1}{4}\epsilon & 0 \\ 0 & \frac{1}{2} - \frac{1}{4}\epsilon \end{pmatrix} \xrightarrow{(\pi)_x} \rho_2 = \begin{pmatrix} \frac{1}{2} - \frac{1}{4}\epsilon & 0 \\ 0 & \frac{1}{2} + \frac{1}{4}\epsilon \end{pmatrix}$$

Evolução livre

Hamiltoniano no sistema girante de coordenadas:

$$H_Z = -\hbar(\omega_L - \Omega)I_z$$

Evolução do operador densidade:

$$\rho(\tau) = e^{i(\omega_L - \Omega)\tau I_z} \rho(t_p) e^{-i(\omega_L - \Omega)\tau I_z}$$

Evolução após pulso $(\pi/2)_{-x}$:

$$\begin{aligned} \Delta\rho(\tau) &= e^{i(\omega_L - \Omega)\tau I_z} \left(\frac{\hbar\omega_L}{2k_B T} I_y \right) e^{-i(\omega_L - \Omega)\tau I_z} \\ &= \frac{\hbar\omega_L}{2k_B T} [I_y \cos(\omega_L - \Omega)\tau + I_x \sin(\omega_L - \Omega)\tau] \end{aligned}$$

Bibliografia recomendada

➤ Fundamentos de RMN:

- “Spin dynamics”, M. H. Levitt. John Wiley & Sons, 2002.
- “Principles of magnetic resonance”, C. P. Slichter. Springer, 1996.
- “Ressonância magnética nuclear: fundamentos, métodos e aplicações”, V. M. S. Gil, C. F. G. C. Geraldes. Fundação Calouste Gulbekian, 1987.
- “Nuclear magnetic resonance for the people”, P. J. Grandinetti (notas de aula), disponível em <http://grandinetti.org/Teaching/Chem824/Notes>.