Mecânica Quântica – Operador densidade

Estados de base: $\left\{ \left| u_n \right\rangle \right\} \; , \; \left\langle u_m \middle| u_n \right\rangle = \delta_{m,n}$

$$\left| \Psi(t) \right\rangle = \sum_n c_n(t) \left| u_n \right\rangle \; , \; \sum_n \left| c_n(t) \right|^2 = 1$$

Projeção:

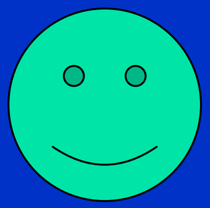
$$\left\langle u_p \middle| \Psi(t) \right\rangle = c_p \left\langle u_p \middle| u_p \right\rangle = c_p \quad \text{ou} \quad \left\langle \Psi(t) \middle| u_p \right\rangle = c_p^* \left\langle u_p \middle| u_p \right\rangle = c_p^*$$

Representação Matricial:

$$\left\langle u_n \middle| A \middle| u_p \right\rangle = A_{np} \quad \left\langle A \right\rangle(t) = \left\langle \Psi(t) \middle| A \middle| \Psi(t) \right\rangle = \underbrace{\sum_{np} c_n^* c_p A_{np}}$$

Equação de Schrödinger:

$$i\hbar \frac{d}{dt} \left| \Psi(t) \right\rangle = \mathrm{H}(t) \left| \Psi(t) \right\rangle$$



Operador e Matriz Densidade

$$c_n^*(t)\,c_p(t) = \left[\langle u_p|\Psi(t)\rangle\right]\left[\langle\Psi(t)|u_n\rangle\right] = \langle u_p|\underbrace{\Psi(t)\rangle\langle\Psi(t)}|u_n\rangle$$

$$= \langle u_p|\rho(t)|u_n\rangle = \rho_{pn}(t)$$

$$\sum_n |c_n(t)|^2 = \sum_n \rho_{nn}(t) = Tr\rho(t) = 1$$

$$\langle A\rangle(t) = Tr\{\rho(t)A\}$$

Equação de Liouville - von Neumann:

$$\frac{d}{dt}\rho(t) = \frac{1}{i\hbar}\left[\mathrm{H}(t),\rho(t)\right]$$

Evolução temporal do operador densidade

Se H é independente do tempo:

$$\frac{d}{dt}\rho(t) = \frac{1}{i\hbar}\left[\mathrm{H}(t), \rho(t)\right]$$

Equação de Liouville - von Neumann

$$\rho(t) = e^{-i\mathrm{H}t}\rho(0)e^{+i\mathrm{H}t} \quad , \quad U(t) = e^{-i\mathrm{H}t}$$

$$\rho(t) = e^{-i\mathrm{H}_n t_n} \ldots \underbrace{\left\{ \underbrace{e^{-i\mathrm{H}_3 t_3} \left[\underbrace{e^{-i\mathrm{H}_2 t_2} \left(\underbrace{e^{-i\mathrm{H}_1 t_1}\rho(0)e^{+i\mathrm{H}_1 t_1}}_{evento\ 1} \right) e^{+i\mathrm{H}_2 t_2}}_{evento\ 2} \right] e^{+i\mathrm{H}_3 t_3}}_{evento\ 3} \right\} \ldots e^{+i\mathrm{H}_n t_n}}_{n\text{-ésimo evento}}$$

Estado Puro vs. Estado Misto

Estado Puro:

$$\left|\Psi\right\rangle = \sum_n c_n \left|u_n\right\rangle \;\Rightarrow\; E_n$$

RMN: Mistura Estatística de Estados

$$\left|\Psi_1\right\rangle, \left|\Psi_2\right\rangle, \ldots, \left|\Psi_k\right\rangle \;\Rightarrow\; p_1, p_2, \ldots, p_k \Rightarrow E_1, E_2, \ldots, E_k$$

$$p_1 + p_2 + \ldots + p_k = 1$$

Populações e Coerências - Estado Misto

Qual é o significado físico dos elementos de matriz ρ_{np} em uma base: $\left\{\left|u_n\right\rangle\right\}$?

$$\rho_{nn} = \sum_k p_k \left[\rho_k\right]_{nn} = \sum_k p_k \left|c_n^{(k)}\right|^2 \Rightarrow \text{ População do estado } \left|u_n\right\rangle$$

$$\rho_{np} = \sum_k p_k c_n^{(k)} c_p^{(k)*}$$

$$c_n^{(k)} c_p^{(k)*} \Rightarrow \text{ Efeitos de Interferência entre os estados } \left|u_n\right\rangle \text{ e } \left|u_p\right\rangle$$

$$\rho_{np} \neq 0 \Rightarrow \text{ Coerência entre os estados } \left|u_n\right\rangle \text{ e } \left|u_p\right\rangle$$

Sistema em equilíbrio térmico

Estatística: $\rho = \dfrac{e^{-\mathrm{H}/kT}}{Z}, \quad Z = Tr\left\{ e^{-\mathrm{H}/kT} \right\}, \quad Tr\,\rho = 1$

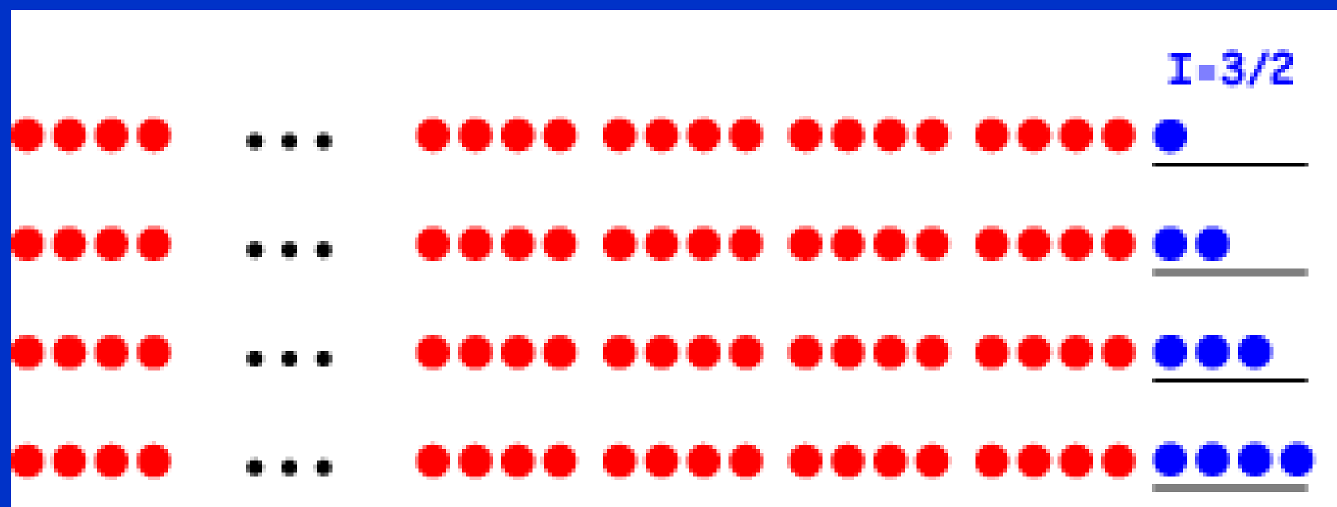
$$\rho_{nn} = \frac{1}{Z}\left\langle u_n \middle| e^{-\mathrm{H}/kT} \middle| u_n \right\rangle = \left\langle u_n \middle| u_n \right\rangle . \frac{e^{-E_n/kT}}{Z} = \frac{e^{-E_n/kT}}{Z}$$

(Populações...)

$$\rho_{np} = \frac{1}{Z}\left\langle u_n \middle| e^{-\mathrm{H}/kT} \middle| u_p \right\rangle = \left\langle u_n \middle| u_p \right\rangle = 0$$

(Coerências...)

$$\rho_{nn} \approx \left(\hat{1} + \frac{n\hbar\omega_L}{kT} I_z + \ldots \right)$$



Sistema em equilíbrio térmico: Zeeman

$$\mathrm{H} = -\gamma\hbar I_z B_0 = \hbar\omega_L I_z$$

$$\left|\mathrm{H}/kT\right| = \left|\hbar\omega_L I_z / kT\right| \ll 1$$

$$\rho = \frac{e^{-\mathrm{H}/kT}}{Z} \approx \left(\hat{1} + \frac{\hbar\omega_L I_z}{kT} + \ldots\right) \qquad \frac{d}{dt}\rho(t) = \frac{1}{i\hbar}\left[\mathrm{H}(t), \rho(t)\right]$$

Operador densidade parcial:

$$\Delta\rho \approx \frac{\hbar\omega_L}{kT} I_z = \alpha I_z \Rightarrow \boxed{\Delta\rho(0) = I_z} \;\; *$$

<u>Spin 3/2:</u> $\Delta\rho(0) = I_z = \begin{pmatrix} 3/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \\ 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & -3/2 \end{pmatrix}$

Sistema girante de coordenadas - Zeeman

Sistema Laboratório:

$$\rho(t) = e^{-i\omega_L t I_z} I_\alpha e^{i\omega_L t I_z} \quad , \; I_\alpha = I_x, \; I_y \; \text{ou} \; I_z$$

Sistema Girante:

$$\rho_R(t) = e^{i\omega_R t I_z} \rho(t) e^{-i\omega_R t I_z} =$$

$$= e^{i\omega_R t I_z} \left(e^{-i\omega_L t I_z} I_\alpha e^{i\omega_L t I_z} \right) e^{-i\omega_R t I_z} =$$

$$= e^{i(\omega_R - \omega_L) t I_z} I_\alpha e^{-i(\omega_R - \omega_L) t I_z} = I_\alpha$$

Efeito do campo de radiofreqüência

$$B_1(t) = B_1 \cos(\omega_{RF} t + \phi)$$

$$\mathrm{H}_{RF} = -\gamma \hbar I_\alpha B_{1\alpha}$$

$$e^{-i(\gamma B_{1\alpha}) I_\alpha t} I_{\alpha'} e^{i(\gamma B_{1\alpha}) I_\alpha t} = e^{i\gamma B_{1\alpha} t} I_{\alpha'} = e^{i\beta_\alpha} I_{\alpha'}$$

$$\rho(t) = e^{-i\hbar(\gamma B_{1\alpha}) I_x t} I_z e^{i\hbar(\gamma B_{1\alpha}) I_\alpha t} = e^{i\gamma B_{1\alpha} t} I_z$$

$$\rho_{\pi/2,x}(t) = e^{i(\pi/2)_x} I_z = I_z \cos(\pi/2) - I_y sen(\pi/2) = I_y$$

$$\rho_{\pi,y}(t) = e^{i(\pi)_y} I_z = I_z \cos(\pi) + I_x sen(\pi) = -I_z$$

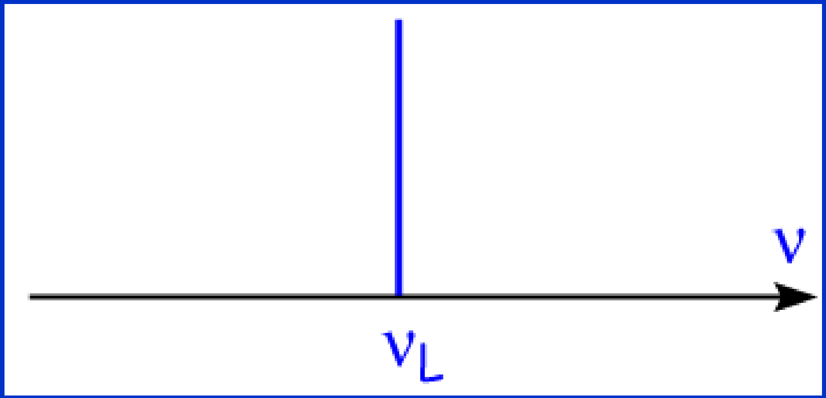
Sinal de RMN - Zeeman

$$\rho(t) = e^{-i(\gamma B_0) I_z t} I_x e^{i(\gamma B_0) I_z t} = e^{i\gamma B_0 t} I_x =$$

$$= I_x \cos(\omega_L t) + I_y sen(\omega_L t)$$

$$\vec{\mu} = \gamma \hbar \vec{I} \;\; \Rightarrow \;\; \vec{M} = \sum_i \langle \vec{\mu}_i \rangle$$

$$\langle M_{xy}(t) \rangle = \langle M_{xy,0} \rangle \exp(i\omega_L t)$$



Sinal de RMN – Quadrupolar – pulsos não seletivos

LEAR USP

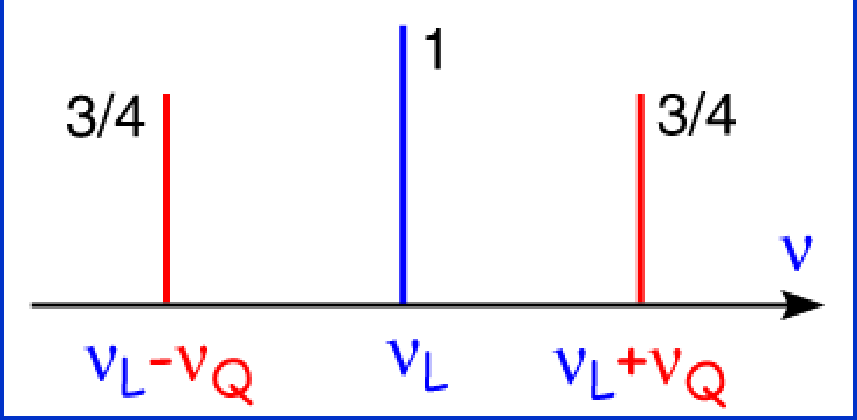
V Escola do CBPF

$$H_Q = \frac{1}{6}\omega_Q\left[3I_z^2 - I(I+1)\hat{1}\right] = \omega_Q\begin{bmatrix} 1/2 & 0 & 0 & 0 \\ 0 & -1/2 & 0 & 0 \\ 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & 1/2 \end{bmatrix}$$

$$\rho(t) = e^{-i\omega_Q t} I_x e^{i\omega_Q t} = \begin{bmatrix} 0 & \sqrt{3/4}e^{-i\omega_Q t} & 0 & 0 \\ \sqrt{3/4}e^{i\omega_Q t} & 0 & 1 & 0 \\ 0 & 1 & 0 & \sqrt{3/4}e^{i\omega_Q t} \\ 0 & 0 & \sqrt{3/4}e^{-i\omega_Q t} & 0 \end{bmatrix}$$

$$\left\langle I_x(t) + iI_y(t)\right\rangle = Tr\left[\rho(t)\left(I_x + iI_y\right)\right] = 3\cos\left(\omega_Q t\right) + 2\cos\left(0.t\right)$$

FID



TF

Sinal de RMN – Quadrupolar – pulsos seletivos

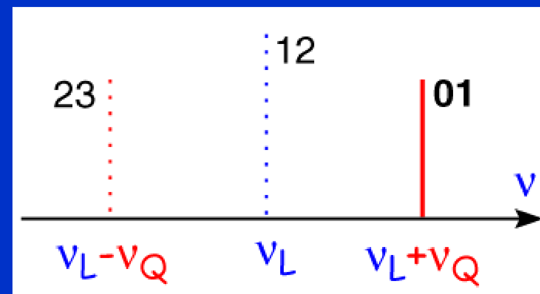
$$P_\alpha^{01}(\theta)=\begin{pmatrix} \cos\left(\frac{\sqrt{3}\theta}{2}\right)e^{2i\omega_q t_p} & isen\left(\frac{\sqrt{3}\theta}{2}\right)e^{-i\left(2\omega_q t_p+\frac{\pi}{2}\alpha\right)} & 0 & 0 \\ isen\left(\frac{\sqrt{3}\theta}{2}\right)e^{-i\left(2\omega_q t_p-\frac{\pi}{2}\alpha\right)} & \cos\left(\frac{\sqrt{3}\theta}{2}\right)e^{2i\omega_q t_p} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & e^{-i4\omega_q t_p} \end{pmatrix}$$

$$P_\alpha^{12}(\theta)=\begin{pmatrix} e^{-i\omega_q t_p} & 0 & 0 & 0 \\ 0 & \cos\left(\frac{\theta}{2}\right)e^{i\omega_q t_p} & isen\left(\frac{\theta}{2}\right)e^{-i\left(\omega_q t_p+\frac{\pi}{2}\alpha\right)} & 0 \\ 0 & isen\left(\frac{\theta}{2}\right)e^{-i\left(\omega_q t_p-\frac{\pi}{2}\alpha\right)} & \cos\left(\frac{\theta}{2}\right)e^{i\omega_q t_p} & 0 \\ 0 & 0 & 0 & e^{-i\omega_q t_p} \end{pmatrix}$$

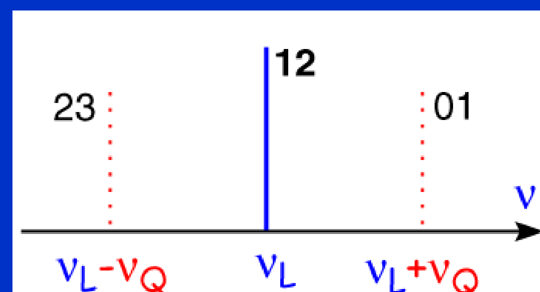
$$P_\alpha^{23}(\theta)=\begin{pmatrix} e^{-2i\omega_q t_p} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos\left(\frac{\sqrt{3}\theta}{2}\right)e^{2i\omega_q t_p} & isen\left(\frac{\sqrt{3}\theta}{2}\right)e^{-i\left(2\omega_q t_p+\frac{\pi}{2}\alpha\right)} \\ 0 & 0 & isen\left(\frac{\sqrt{3}\theta}{2}\right)e^{-i\left(2\omega_q t_p-\frac{\pi}{2}\alpha\right)} & \cos\left(\frac{\sqrt{3}\theta}{2}\right)e^{2i\omega_q t_p} \end{pmatrix}$$

Sinal de RMN – Quadrupolar – pulsos seletivos

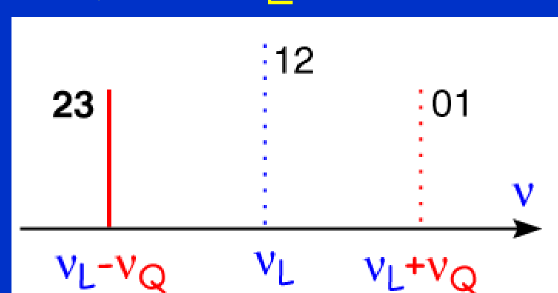
$$P_y^{01} \Rightarrow \left\langle I_x(t) + iI_y(t) \right\rangle = Tr\left[\rho(t)\left(I_x + iI_y\right)\right] = \sqrt{3/4}\,e^{+i\omega_Q t}$$



$$P_y^{12} \Rightarrow \left\langle I_x(t) + iI_y(t) \right\rangle = Tr\left[\rho(t)\left(I_x + iI_y\right)\right] = 1$$



$$P_y^{23} \Rightarrow \left\langle I_x(t) + iI_y(t) \right\rangle = Tr\left[\rho(t)\left(I_x + iI_y\right)\right] = \sqrt{3/4}\,e^{-i\omega_Q t}$$



RMN - Manipulação dos Spins Nucleares

- Mecânica Quântica
- Espectrômetro de RMN
- Química
- Física do problema...

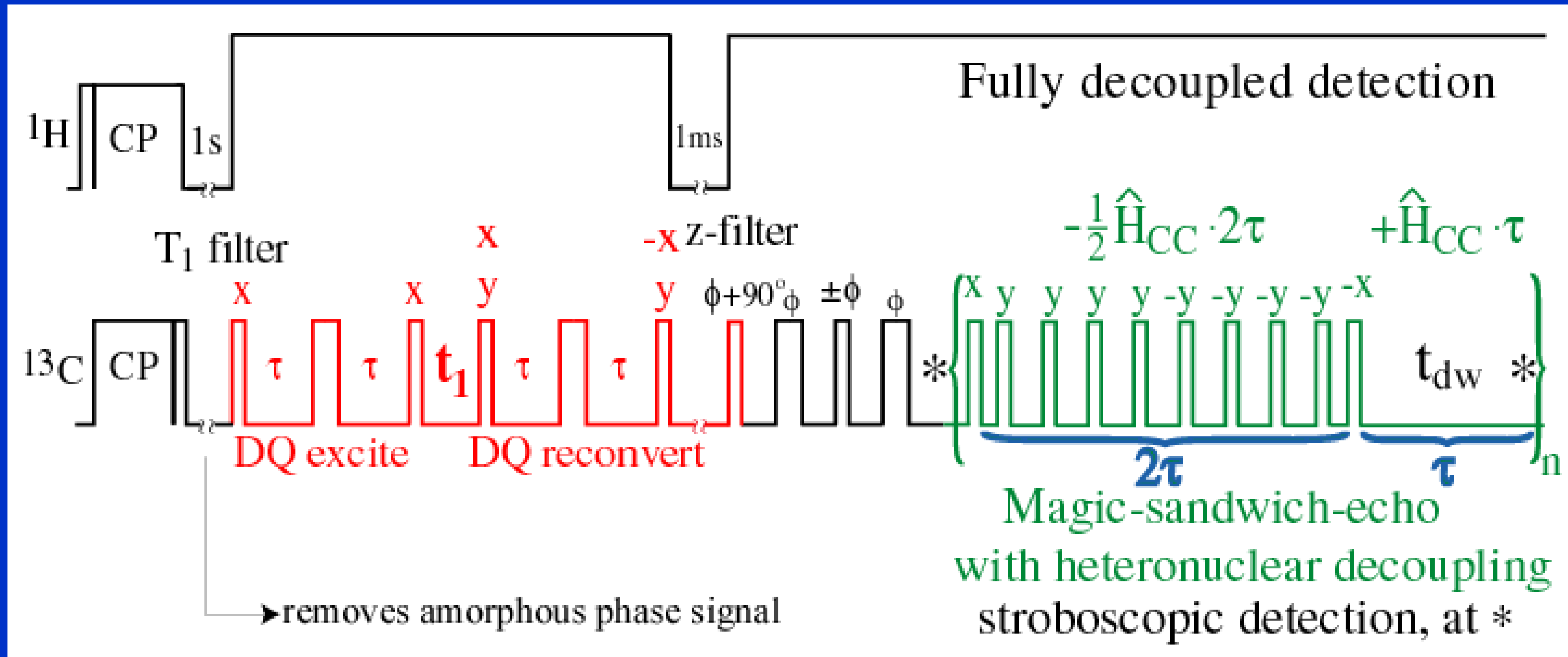
- Pulsos de RF
- Tripla ressonância
- Campos magnéticos
- Rotação da amostra
- Manipulação química
- Temperatura

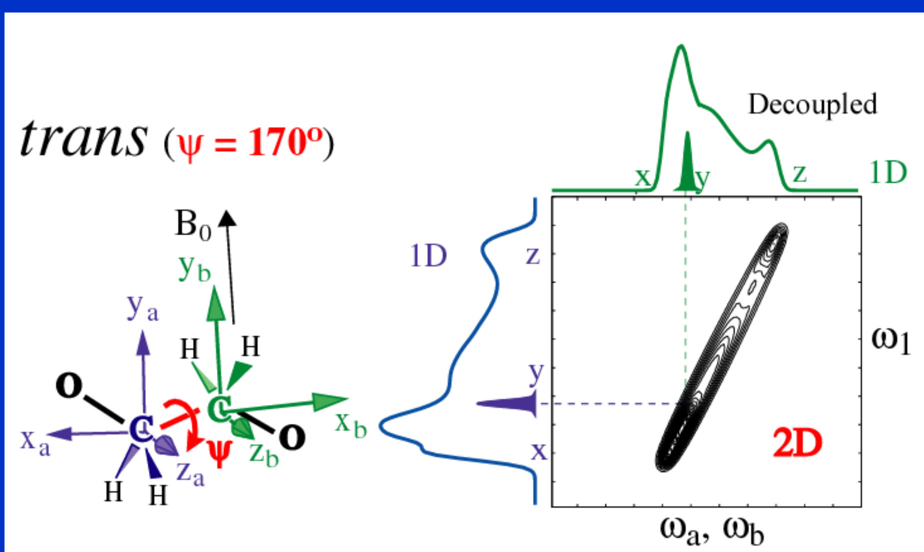
Estudos de conformação por RMN molecular...

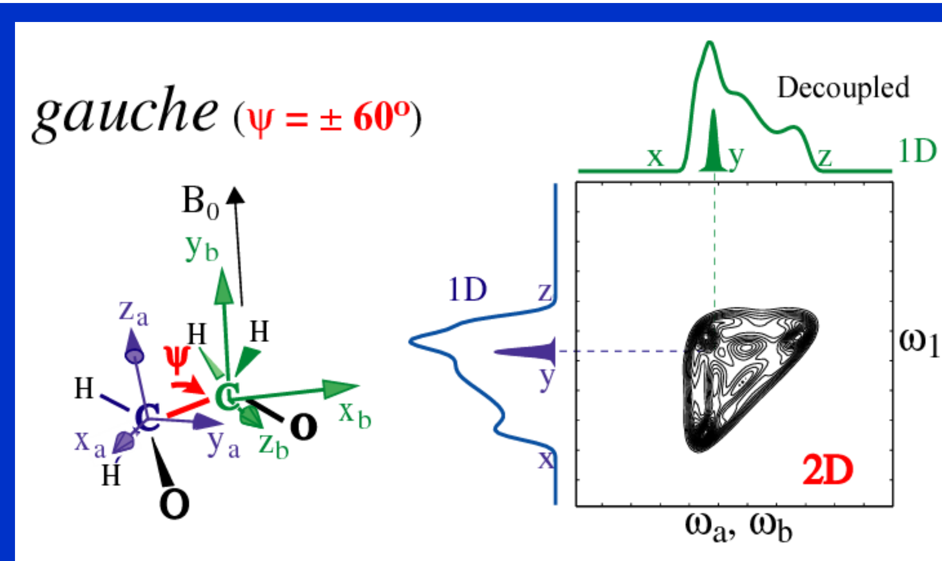
Double-

-Quantum

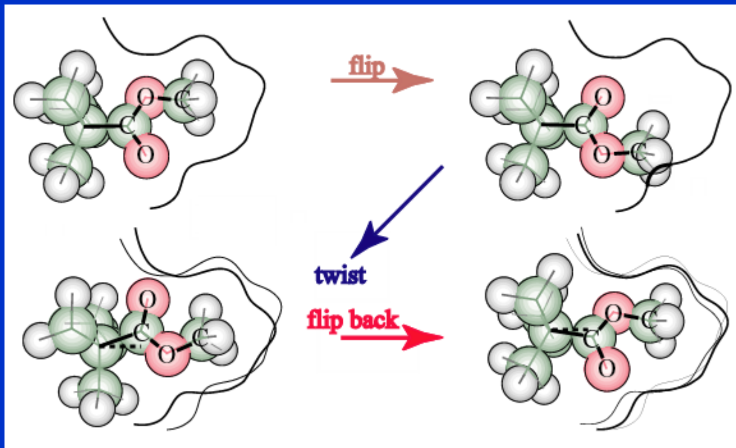
NMR

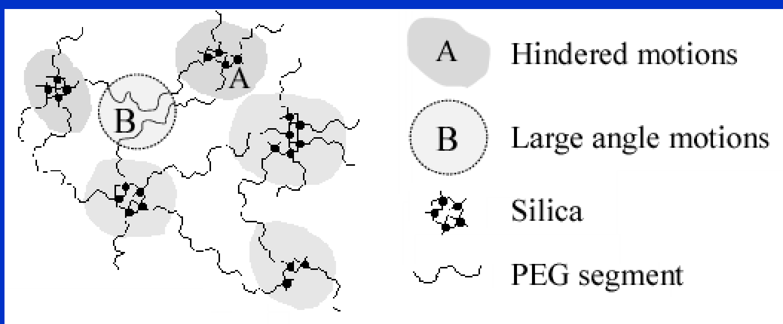


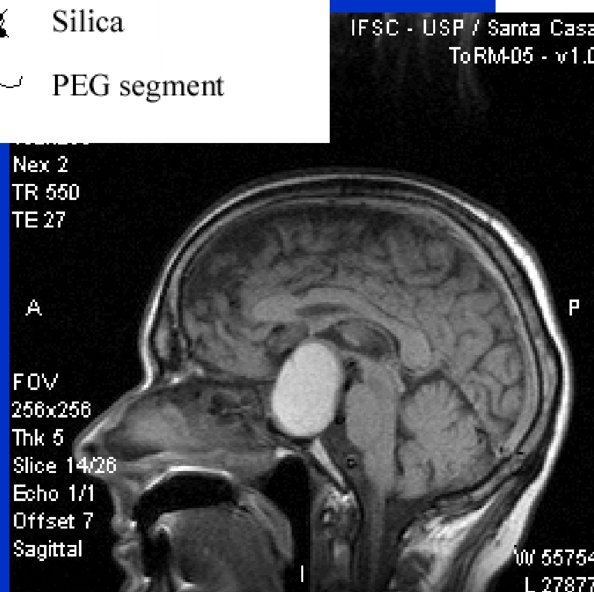


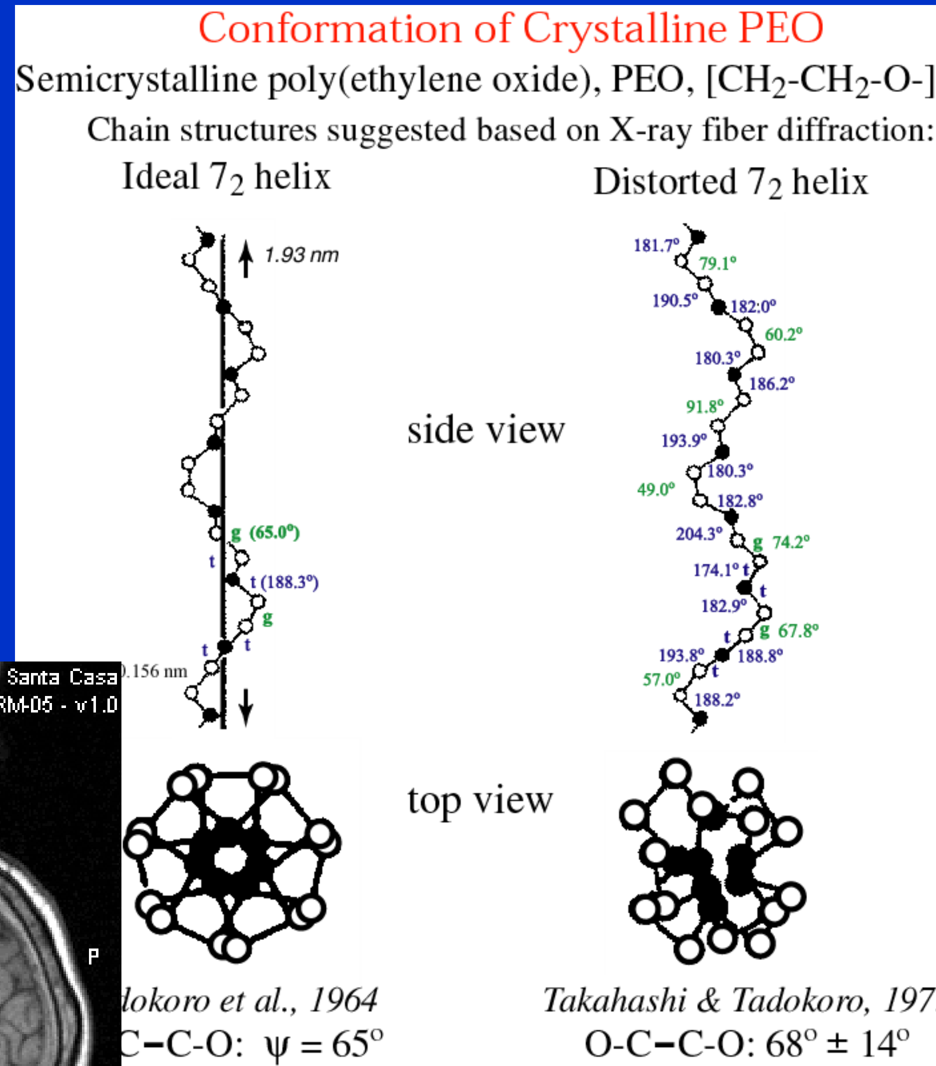


Exemplos... RMN...









Matrizes exponenciais - Diagonalização

Sendo D diagonal:
$$e^{D} = \sum_{N=0}^{\infty} \frac{D^N}{N!} = \begin{bmatrix} e^{D_{11}} & 0 & \dots & 0 \\ 0 & e^{D_{22}} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & e^{D_{ii}} \end{bmatrix}$$

Sendo A não Diagonal → *diagonalizar* A:

$$\left(R_D^{-1} A R_D\right)_{mn} = \delta_{mn} a_n \Rightarrow e^{R_D^{-1} A R_D} = \begin{bmatrix} e^{a_{11}} & 0 & \dots & 0 \\ 0 & e^{a_{22}} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & e^{a_{ii}} \end{bmatrix}$$

$$e^{R_D^{-1} A R_D} = R_D^{-1} e^{A} R_D \Rightarrow$$

$$e^{A} = R_D \left[R_D^{-1} e^{A} R_D \right] R_D^{-1} = R_D \begin{bmatrix} e^{a_{11}} & 0 & \dots & 0 \\ 0 & e^{a_{22}} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & e^{a_{ii}} \end{bmatrix} R_D^{-1}$$