RMN de Sólidos: Teoria, Experimentos e Simulações Computacionais

Jair C. C. Freitas, Wanderlã L. Scopel, Daniel F. Cipriano, Thierry R. Lopes

Departamento de Física - UFES

Programa

- **Revisão sobre fundamentos de RMN.**
- **Interações de spin nuclear.**
- **Técnicas de alta resolução em sólidos.**
- **Descrição teórica de experimentos de RMN em sólidos.**
- **Práticas experimentais e computacionais em RMN em sólidos.**

Equipe

Departamento de Física - UFES

Dr. Jair C. C. Freitas: fundamentos teóricos e aplicações de RMN de sólidos.

Dr. Wanderlã L. Scopel: métodos computacionais para cálculos de parâmetros espectrais em RMN.

MSc. Daniel F. Cipriano: práticas experimentais em RMN de sólidos.

MSc. Thierry R. Lopes: processamento e simulações de espectros de RMN de sólidos.

Agenda – 29 e 30/08/2016

Segunda-feira, 08:30-12:30: Fundamentos de RMN, interações de spin nuclear, técnicas de alta resolução em sólidos.

Segunda-feira, 14:00-15:30: Descrição teórica de experimentos de RMN em sólidos.
(Parte expositiva; responsável - Jair)

Segunda-feira, 15:30-18:00: Práticas experimentais em RMN de sólidos.
(Parte prática; responsável - Daniel)

Terça-feira, 08:30-10:30: Métodos teóricos e estratégias computacionais para cálculos de parâmetros espectrais em RMN de sólidos.
(Parte expositiva; responsável - Wanderlã)

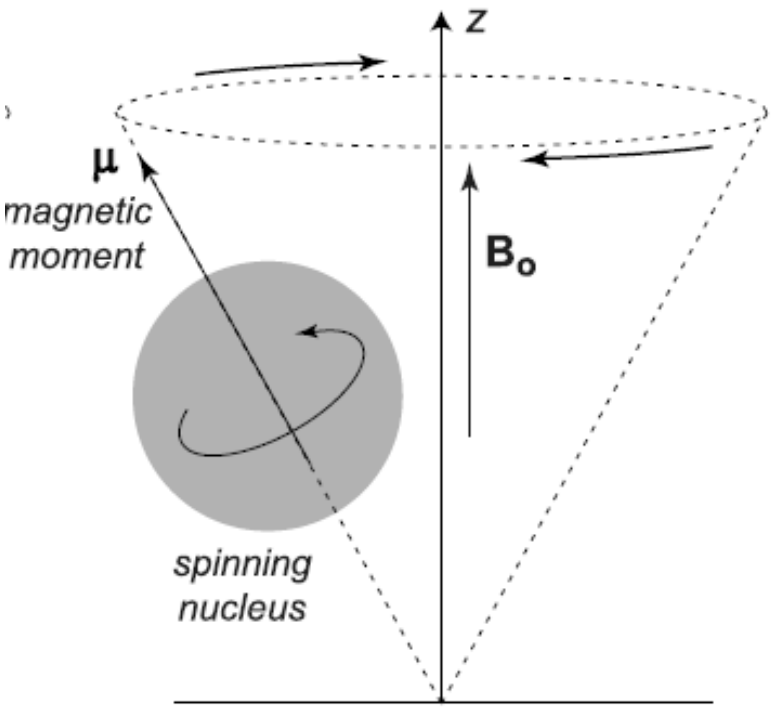
Terça-feira, 10:30-12:30: Processamento e simulações de espectros de RMN de sólidos.
(Parte prática; responsável - Thierry)

Fundamentos teóricos e aplicações de RMN de sólidos

Jair C. C. Freitas

Fundamentos de RMN

Precessão de Larmor:



Frequência de Larmor:

$$\omega_L = \gamma B_0$$ (~10^7 rad/s)

$$f_L = \gamma B_0 / 2\pi$$ (~MHz)

↓

Radiofrequência (RF)

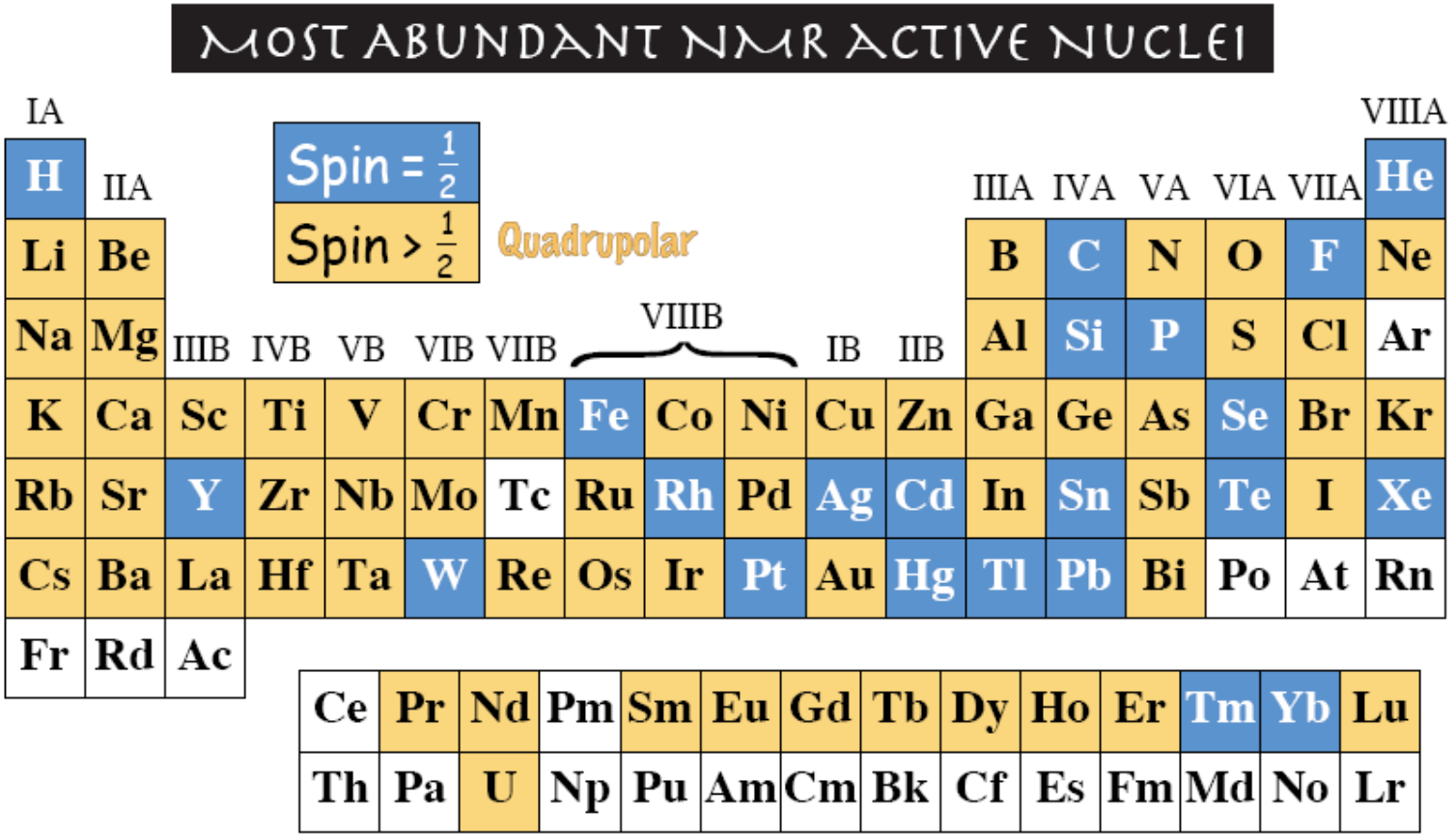
Fundamentos de RMN

Nuclide	*Natural abundance* (%)	*Nuclear spin*	*Larmor frequency* [a] (MHz)	*Sensitivity* [b]
^{1}H	99.99	1/2	100.000	1.000
^{13}C	1.07	1/2	25.145	1.70×10^{-4}
^{14}N	99.632	1	7.226	1.00×10^{-3}
^{17}O	0.038	5/2	13.556	1.11×10^{-5}
^{23}Na	100	3/2	26.452	9.27×10^{-2}
^{27}Al	100	5/2	26.057	0.207
^{29}Si	4.683	1/2	19.867	3.68×10^{-4}
^{31}P	100	1/2	40.481	6.65×10^{-2}
^{33}S	0.76	3/2	7.676	1.72×10^{-5}
^{39}K	93.258	3/2	4.666	4.76×10^{-4}
^{43}Ca	0.135	7/2	6.730	8.68×10^{-6}
^{129}Xe	26.44	1/2	27.810	5.72×10^{-3}

[a] Corresponding to the magnetic field of 2.35 T of a 100 MHz NMR spectrometer.
[b] Relative to ^{1}H.

Harris et al., *Pure Appl. Chem.* 2001;73(11):1795-1818

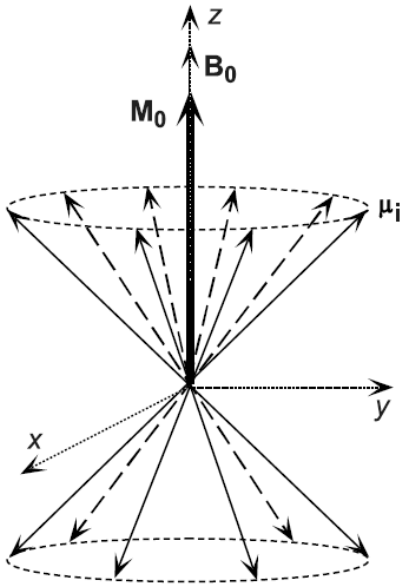
Fundamentos de RMN

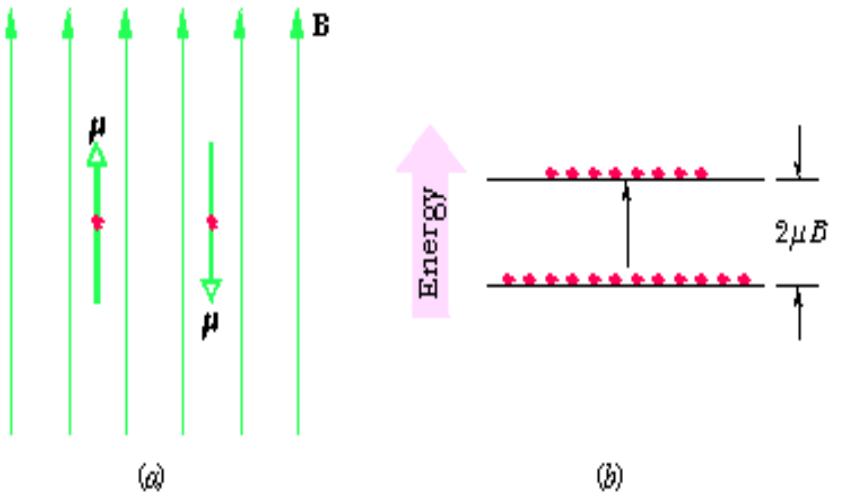


http://www.grandinetti.org/Research/NMR

Generalidades sobre RMN

Paramagnetismo nuclear:





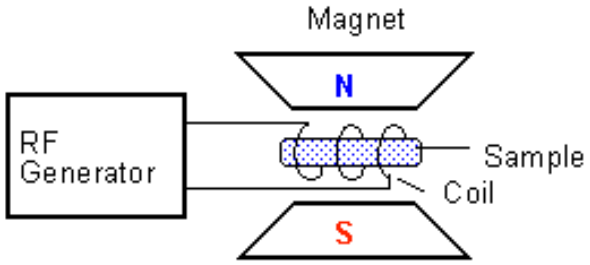
$$E = -\vec{\mu} \cdot \vec{B}_0 = -\gamma m \hbar B_0 = -m \hbar \omega_L$$

$$\mathrm{M}_0 = \frac{N \mu^2 B_0}{3kT}$$

$$\frac{n_-}{n_+} = \mathrm{e}^{(-\hbar\omega_L / kT)}$$

Generalidades sobre RMN

$$B_0 \sim 1\text{T} \Rightarrow \begin{cases} f_L \sim 43\ \text{MHz} \ (^1\text{H}) \\ f_L \sim 28\ \text{GHz} \ (\text{elétron}) \end{cases}$$



Campo de RF: $B_1 \sim 10\text{G} = 10^{-3}\text{T}$

Campo da Terra: $B_T \sim 10^{-5}\text{T}$

$$\vec{B}_0 = B_0 \hat{z}$$

$$\vec{B}_1 = (2B_1 \cos \omega t)\hat{x}$$

Pulsos de RF

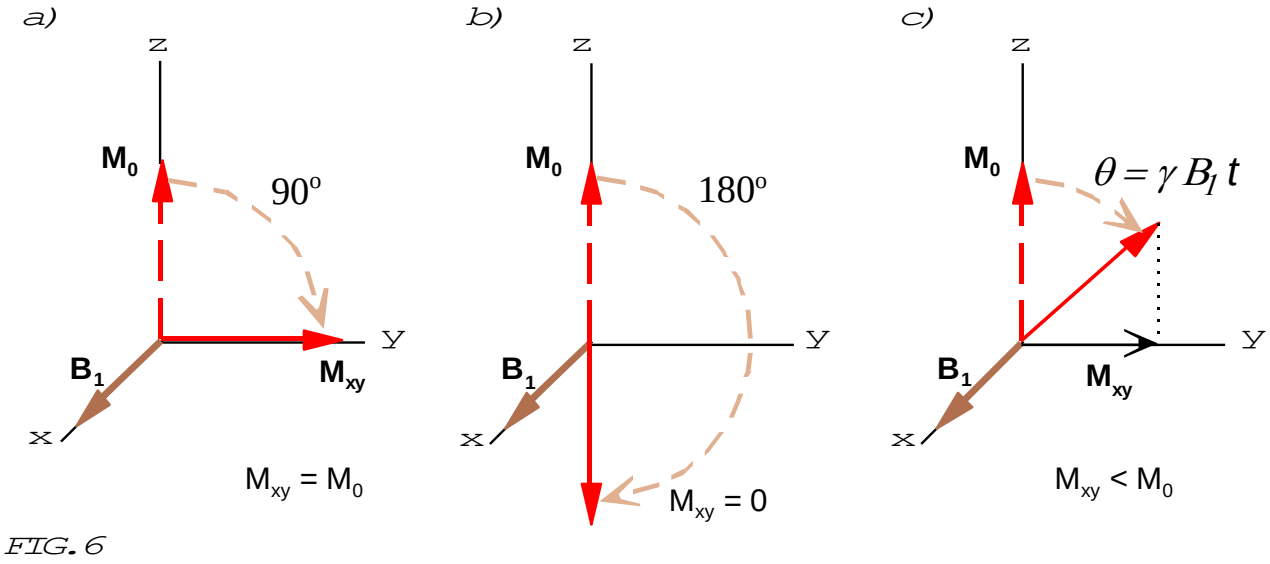
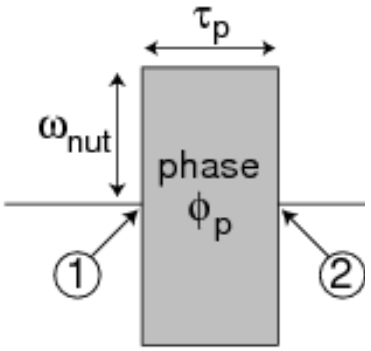


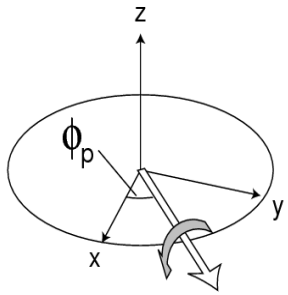
FIG. 6

Pulso $\pi/2$ | Pulso π | Pulso θ

Controle

- Duração (~ μs)
- Amplitude (~ 10^2 kHz)
- Fase (0, 90°, 180°, 270°)



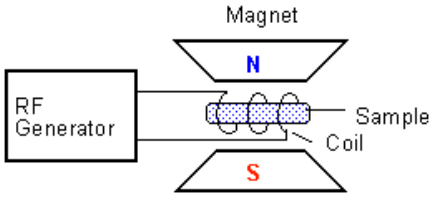


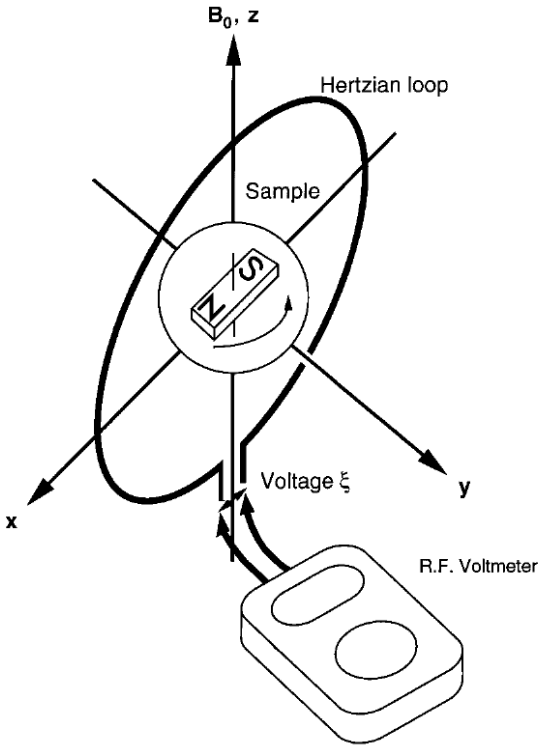
Detecção do sinal de RMN

Bobina posicionada ao longo do eixo *x* (Lab.):

$$S(t) = -\frac{d\phi_B}{dt} \propto \mu_0 \omega_L M_0 \cos \omega_L t$$

$$S_{\max} = S(0) \propto \frac{\mu_0 N \gamma^3 I(I+1)\hbar^2 B_0{}^2}{3kT}$$

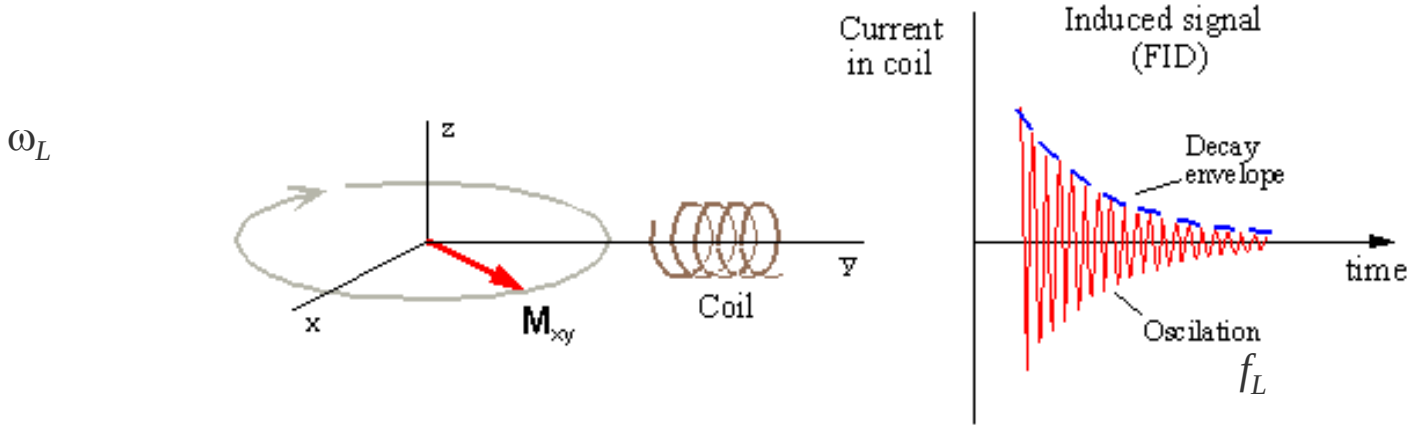




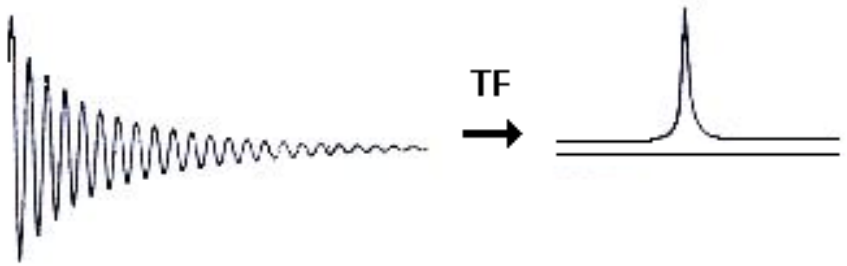
Hoult & Bhakar (1997)

Detecção do sinal de RMN

FID = decaimeno livre de indução

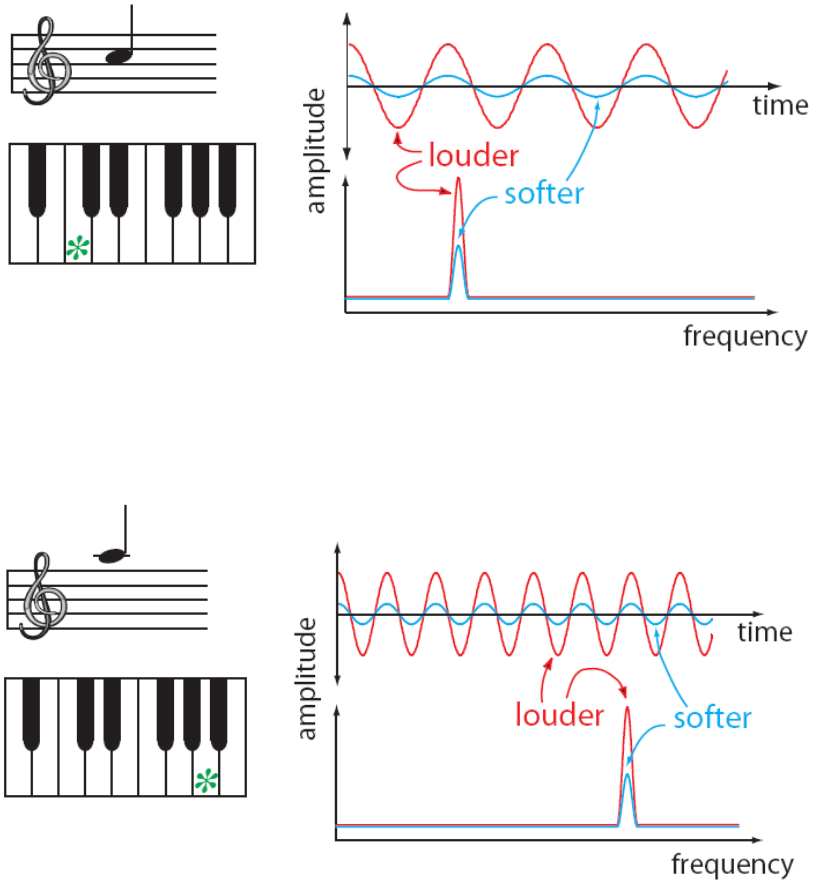


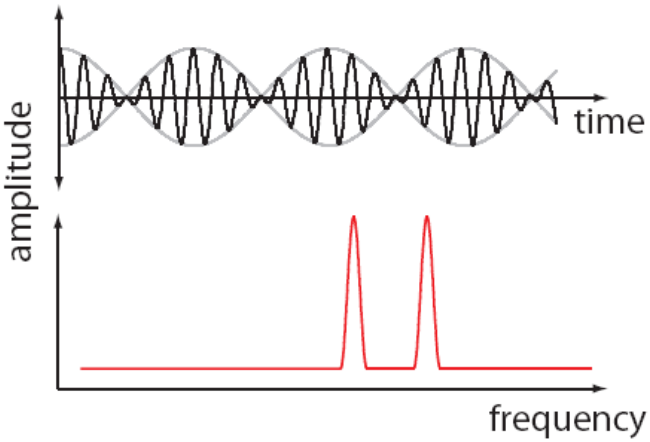
Transformada de Fourier (FT)



FID Espectro

Método da transformada de Fourier

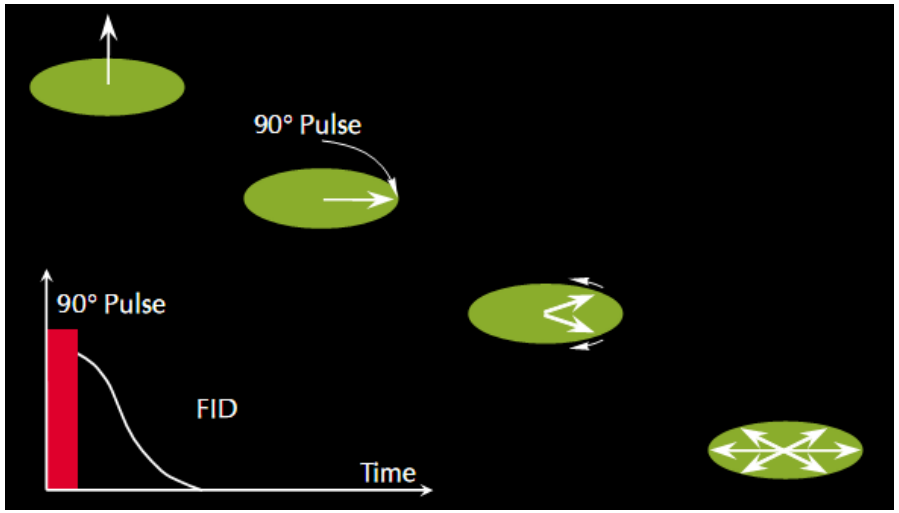




http://grandinetti.org/Teaching/Chem824/Notes

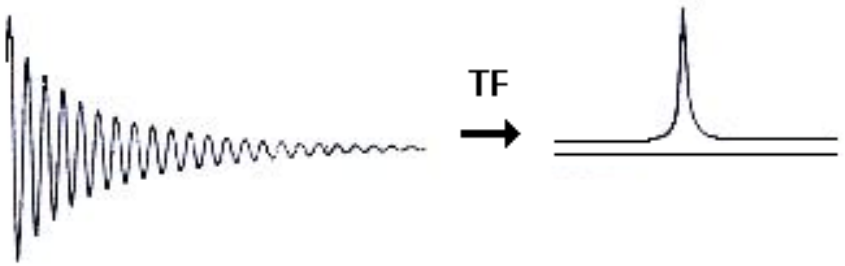
Um experimento simples de RMN (1D)

Experimento de excitação com pulso único ou decaimento de Bloch:



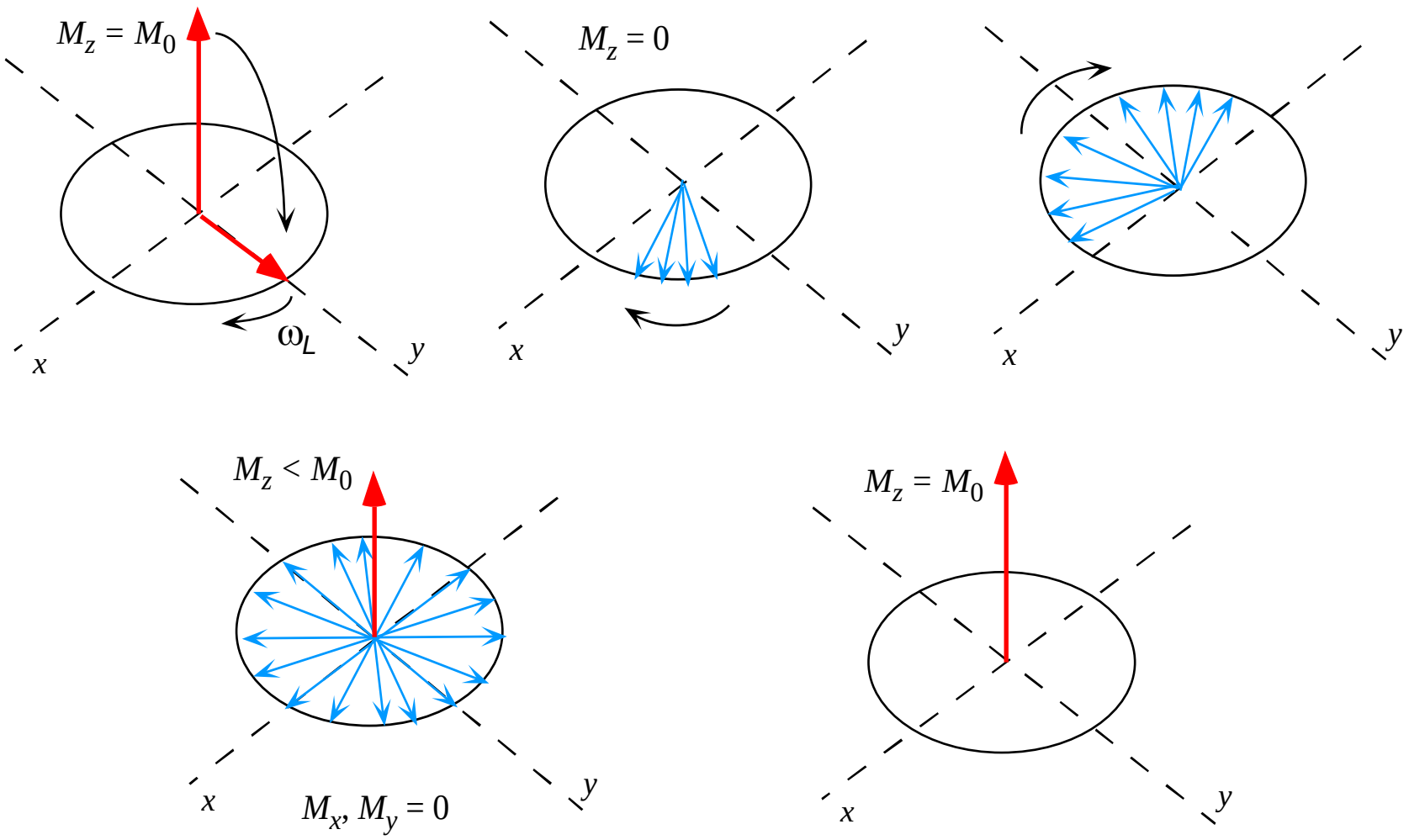
Sinal detectado com frequência:
$\Delta f = f_L - f_{RF}$ (áudio)

Sinal em ressonância: $\Delta f = 0$



FID Espectro

Relaxação do sistema de spins



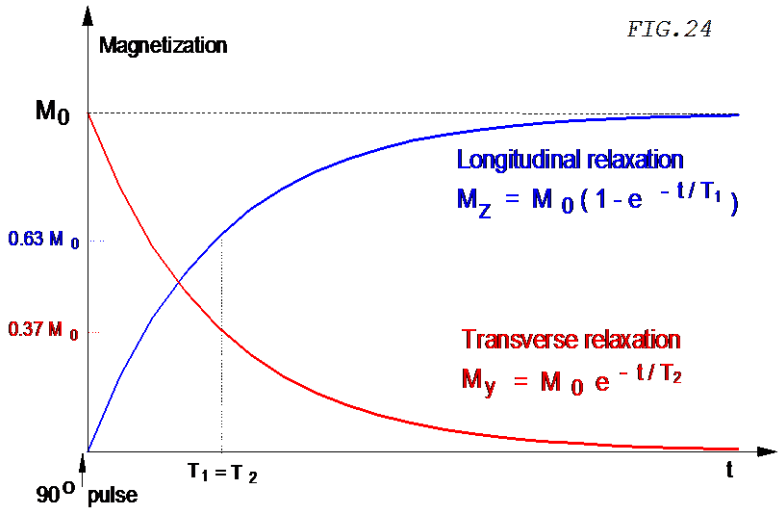
Relaxação do sistema de spins

- Relaxação longitudinal (T_1):
  - Trocas de energia entre spins e "rede".
  - Existência de campos flutuantes com freqüências ~ ω_L.
  - Restauração do equilíbrio térmico.
- Relaxação transversal (T_2):
  - Perda de coerência entre os spins no plano transversal.
  - Distribuições de freqüências de precessão.
  - Interações entre os spins.

Líquidos: $T_1 \approx T_2$

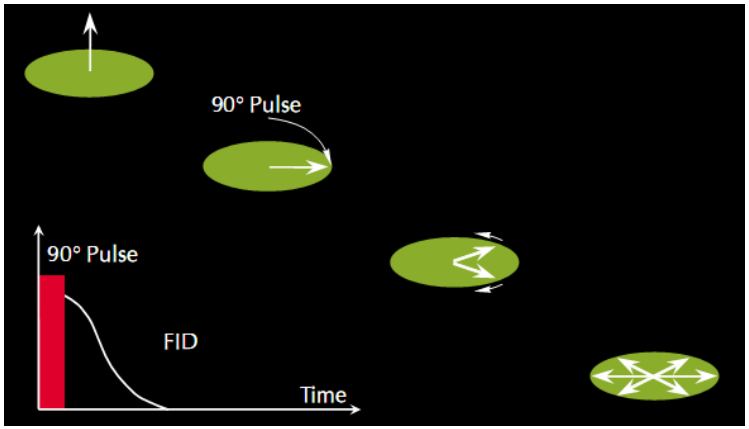
Sólidos: $T_1 >> T_2$

$T_1 \geq T_2$



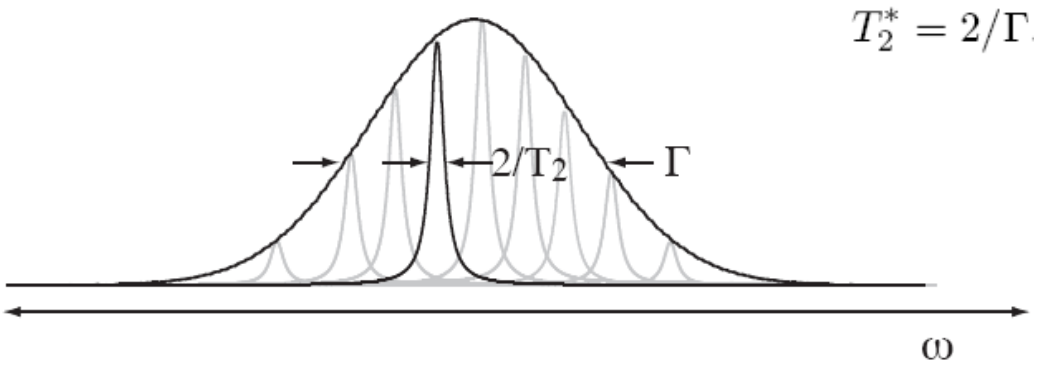
Relaxação transversal

- Inomogeneidade do campo magnético:



$$\omega_L(\mathbf{r}) = \gamma B_0(\mathbf{r}) \qquad \Omega(\mathbf{r}) = \omega_L(\mathbf{r}) - \omega_{RF}$$

$$S_{\text{total}}(t) = \int\int\int \rho(\mathbf{r}) e^{i\Omega(\mathbf{r})t} \cdot e^{-t/T_2} dV$$

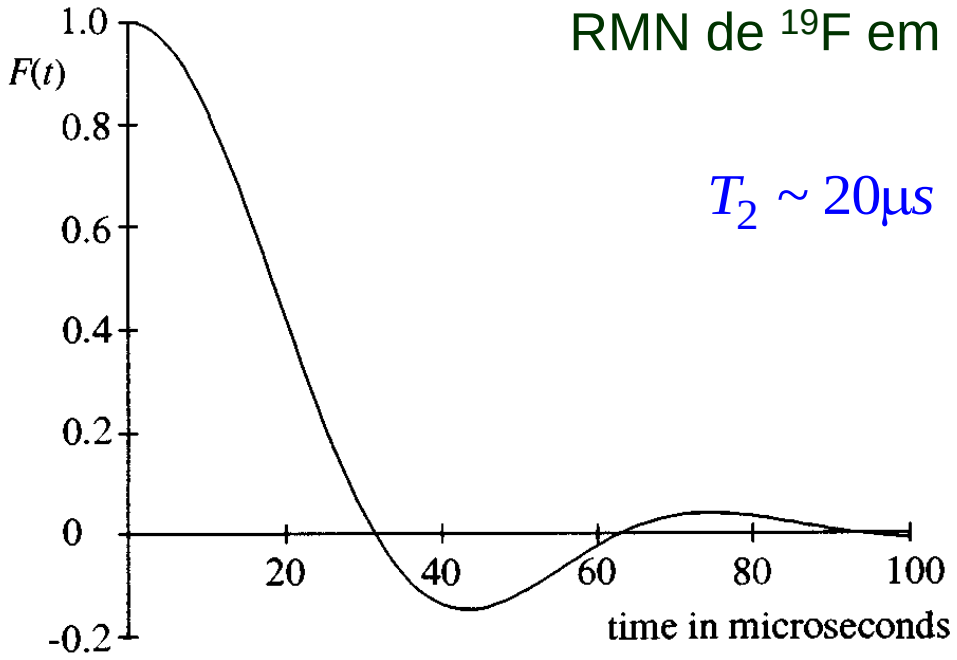


$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma \Delta B_0$$

http://grandinetti.org/Teaching/Chem824/Notes

Relaxação transversal

- Relaxação transversal em sólidos:



RMN de ^{19}F em CaF_2

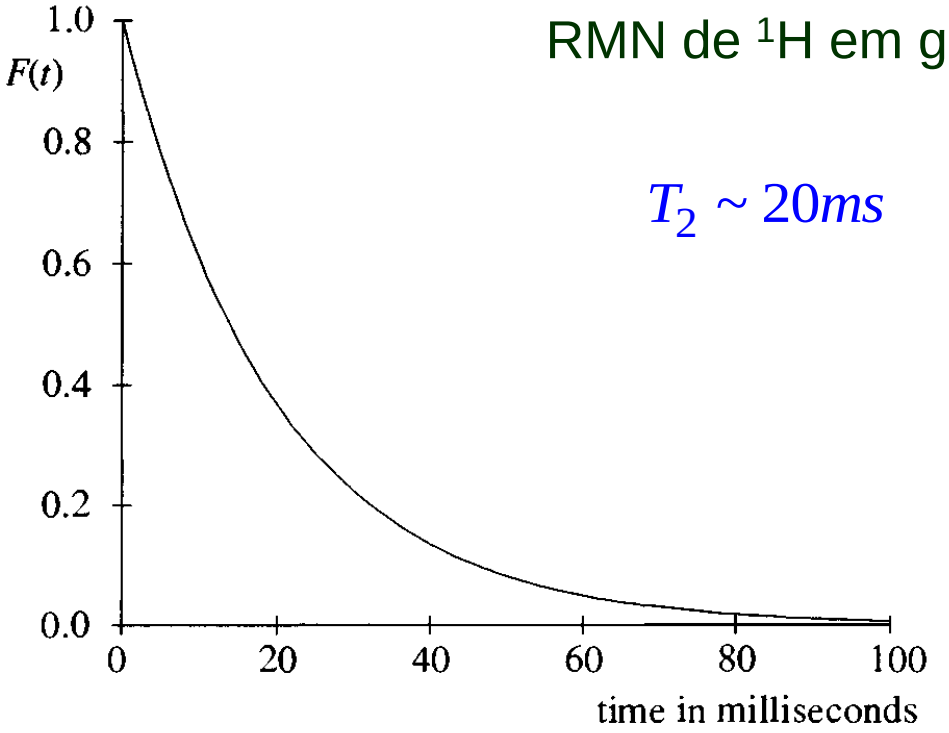
$T_2 \sim 20\mu s$

Figure 4.2 FID of calcium fluoride.

"NMR and relaxation", Cowan. Cambridge University Press, 1997.

Relaxação transversal

- Relaxação transversal em líquidos:



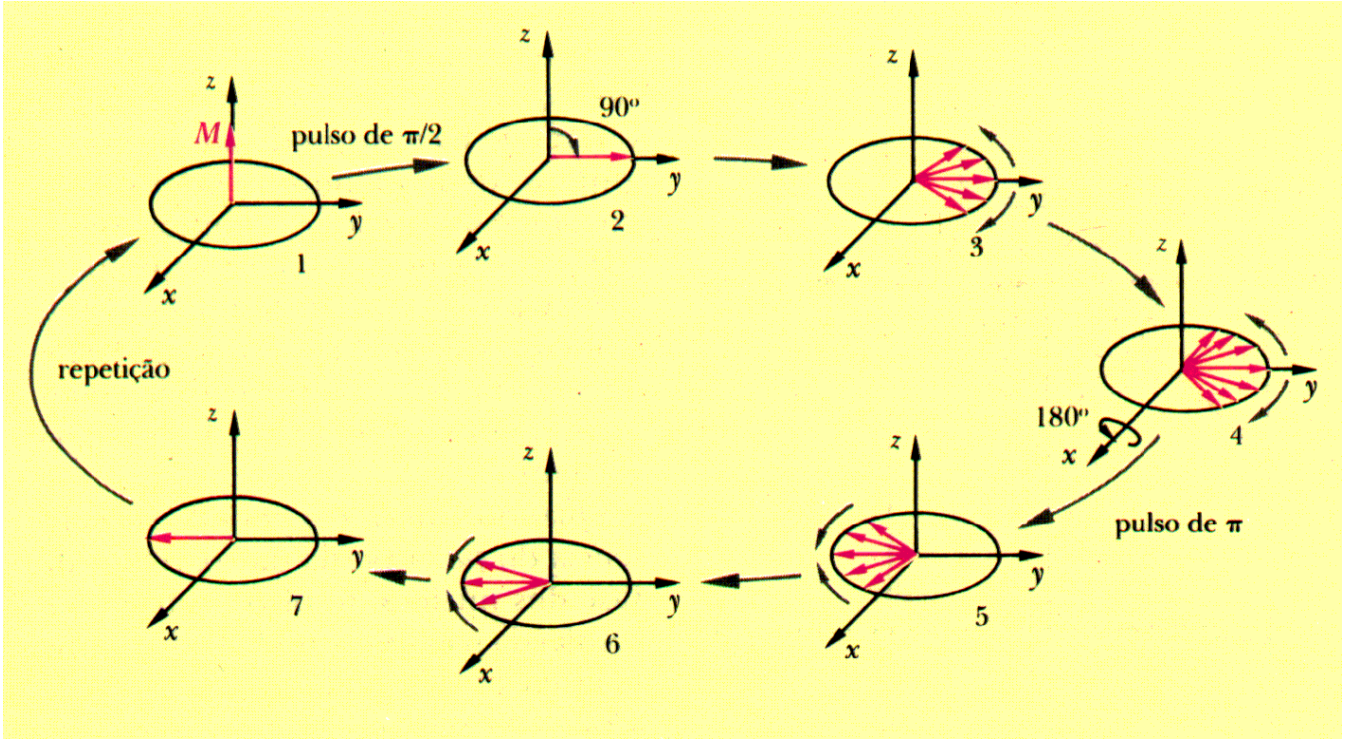
RMN de ^{1}H em glicerol

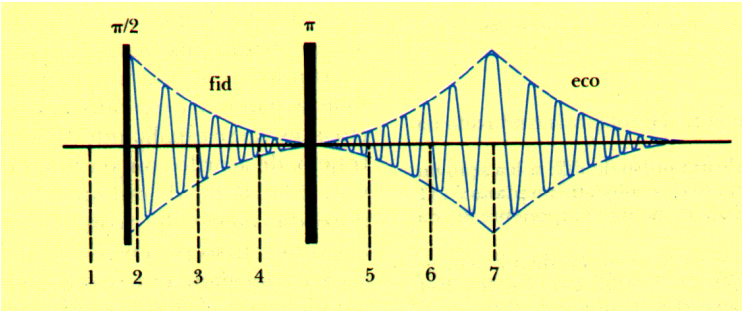
$T_2 \sim 20ms$

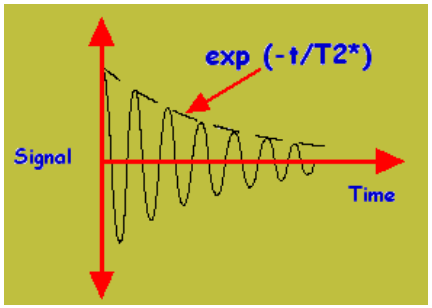
Figure 4.3 Proton transverse relaxation in glycerol.

"NMR and relaxation", Cowan. Cambridge University Press, 1997.

Técnica dos ecos de spin ("spin-echoes")

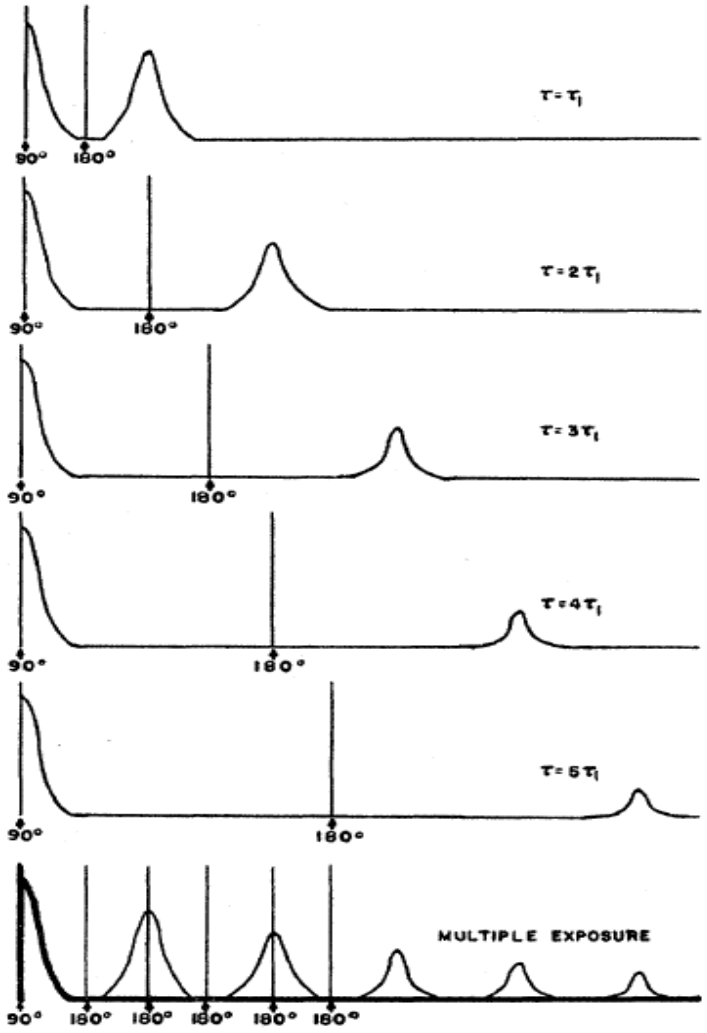






Hahn (1950)

Medida de T_2: sequência spin-eco



Amplitudes dos ecos de spin:

Sem difusão:

$$A(2\tau) = A(0)e^{-2\tau/T_2}$$

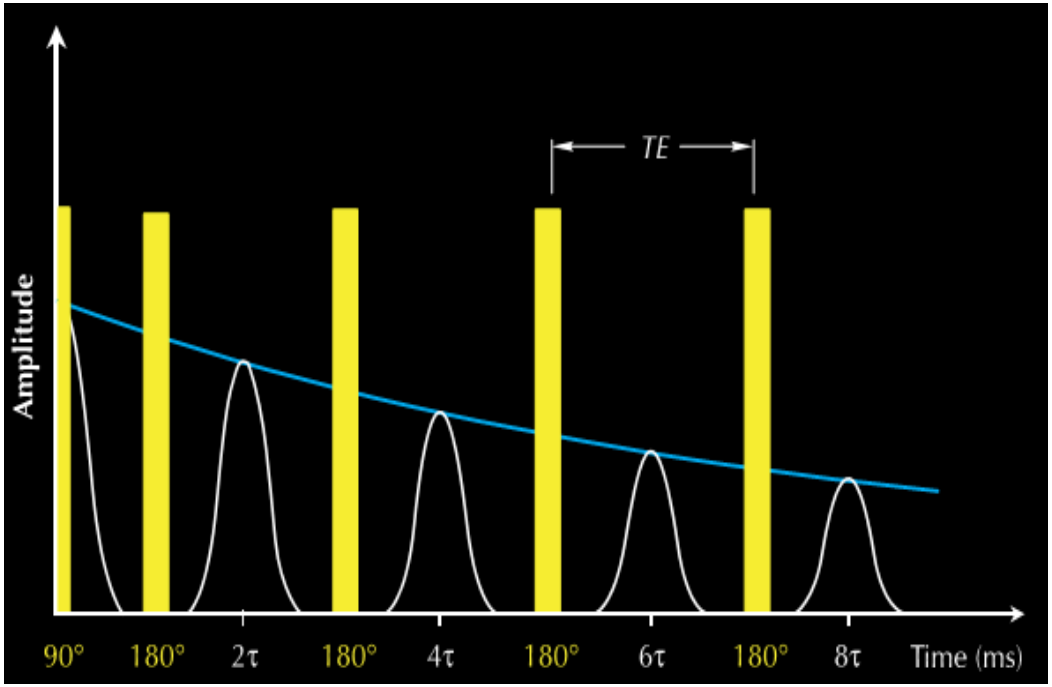
Com difusão:

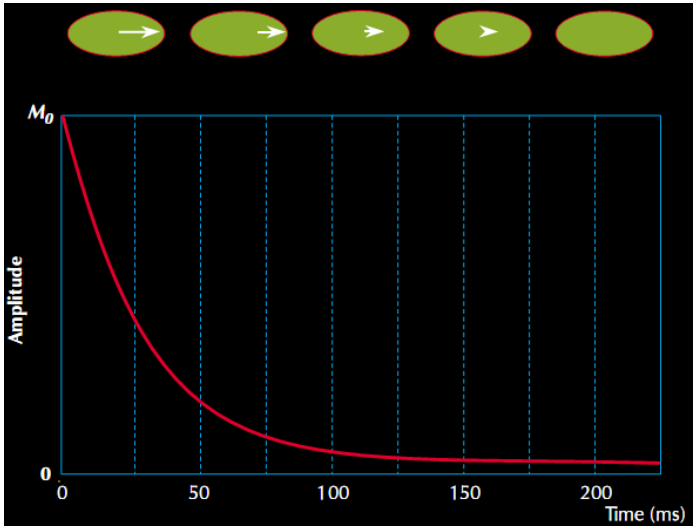
$$A(2\tau) = A(0)e^{-2\tau/T_2}e^{-\gamma^2\left(\frac{\partial B}{\partial z}\right)^2 D\frac{2\tau^3}{3}}$$

Carr & Purcell (1954)

Sequência CPMG

Sequência CPMG:





Carr & Purcell (1954); Meiboom & Gill (1958)

Sequência CPMG

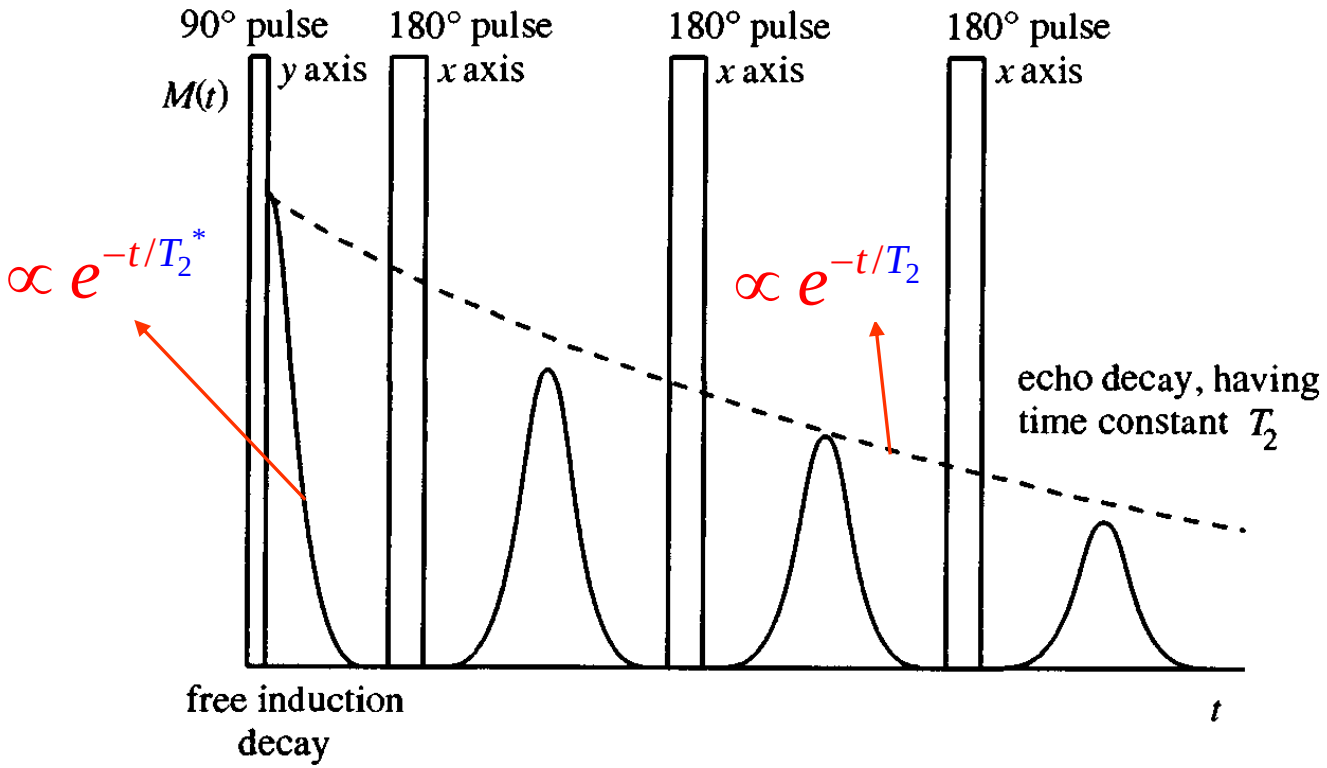


Figure 4.13 Carr–Purcell–Meiboom–Gill sequence.

"NMR and relaxation", Cowan. Cambridge University Press, 1997.

Sequência CPMG

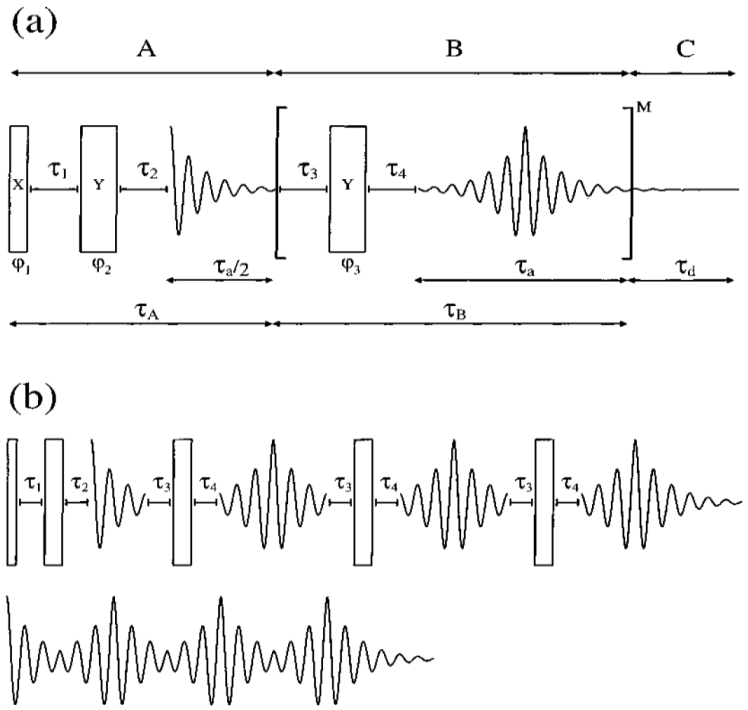
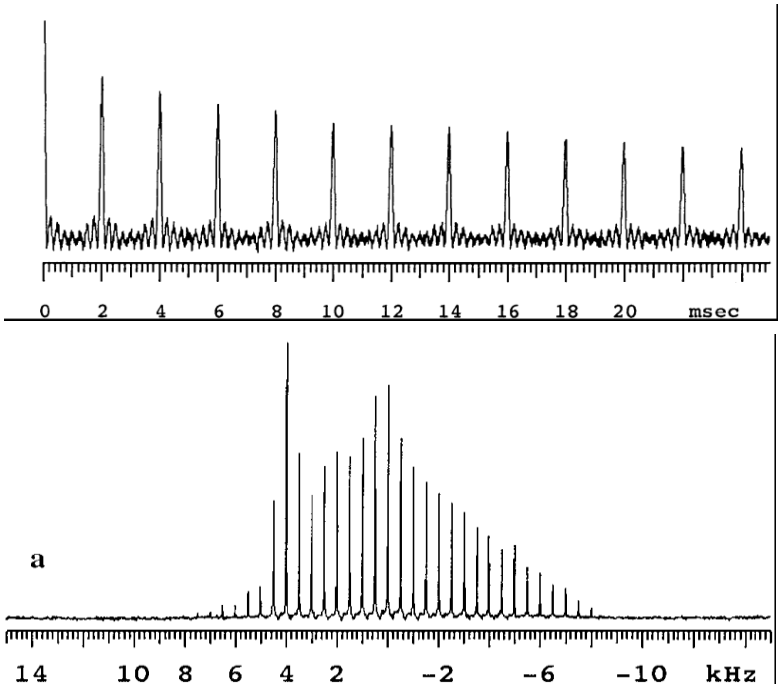


Figure 1. Quadrupolar CPMG (QCPMG) pulse sequence for sensitivity-enhanced quadrupolar-echo (QE) solid-state NMR of half-integer quadrupolar nuclei: (a) timing scheme of the pulse sequence; (b) relation between the pulse sequence timing t and the timing t_2 of the free induction decay (see text). Shaded and open bars correspond to selective (central transition) $\pi/2$ and π pulses, respectively. The phases ϕ_1, ϕ_2, ϕ_3, and the receiver reference phase ϕ_{rec} are cycled (see Table 2) to select the $p = 0 \rightarrow \pm 1 \rightarrow \mp 1 \rightarrow \pm 1$ etc. coherence transfer pathways.

Larsen et al., *J. Phys. Chem. A* 101 (1997) 8597

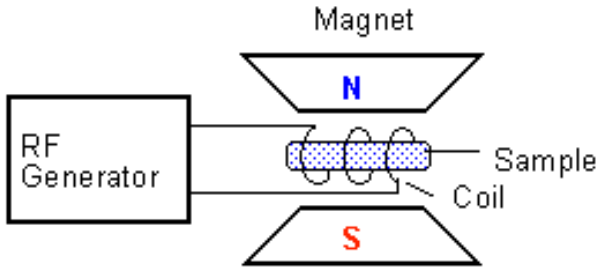
RMN de ^{25}Mg – $Mg(OAc)_2 \cdot 4H_2O$



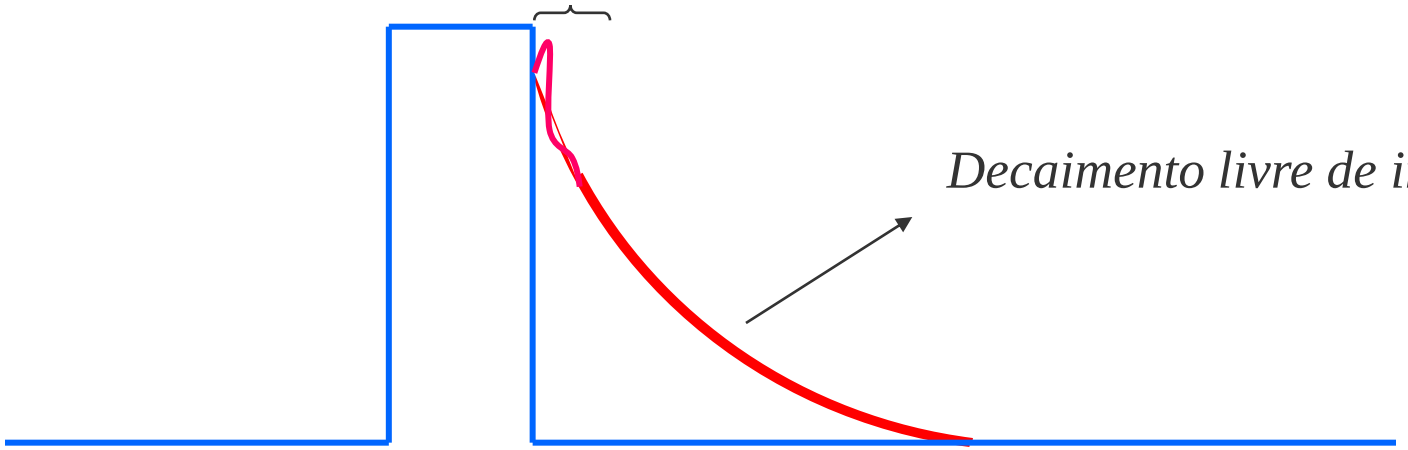
Ellis et al., *J. Magn. Reson.* 151 (2001) 48

Problemas com “tempo morto”

Experimento de **pulso simples**:



Região “corrompida”

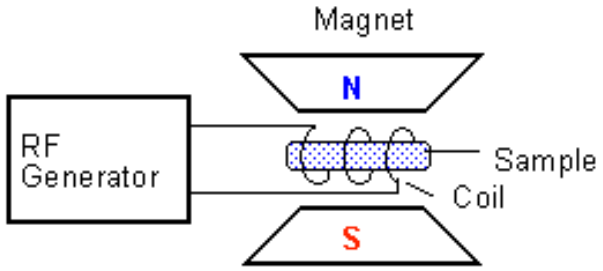


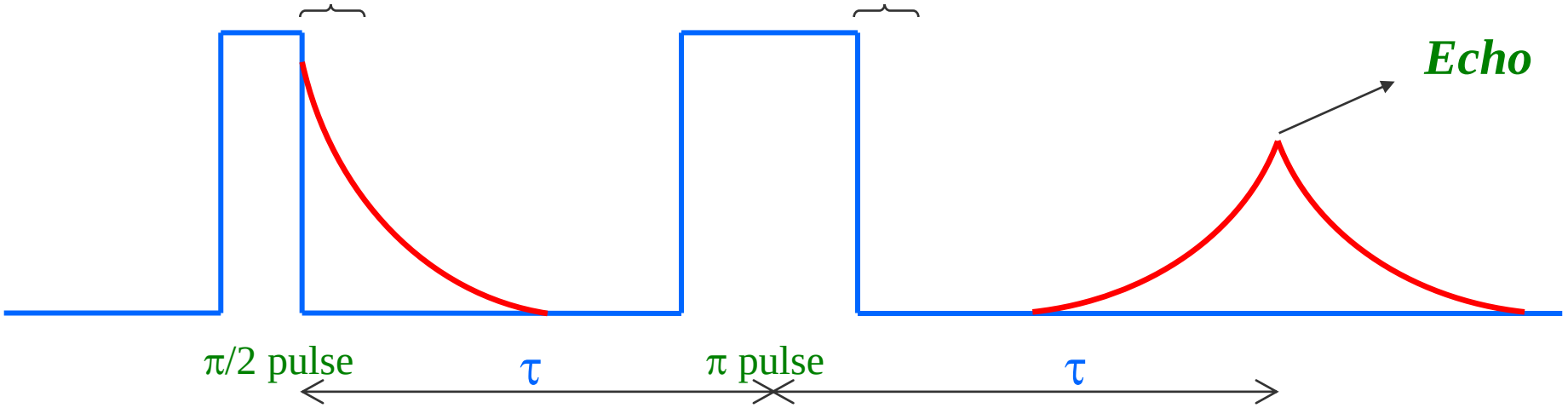
Decaimento livre de indução (***FID***)

$\pi/2$ pulse

Problemas com “tempo morto”

Experimento de **spin-eco**:

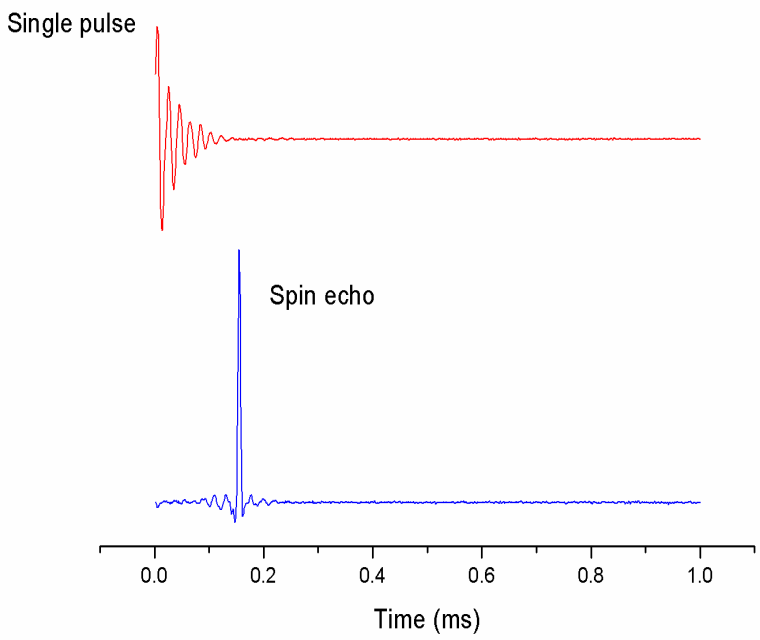


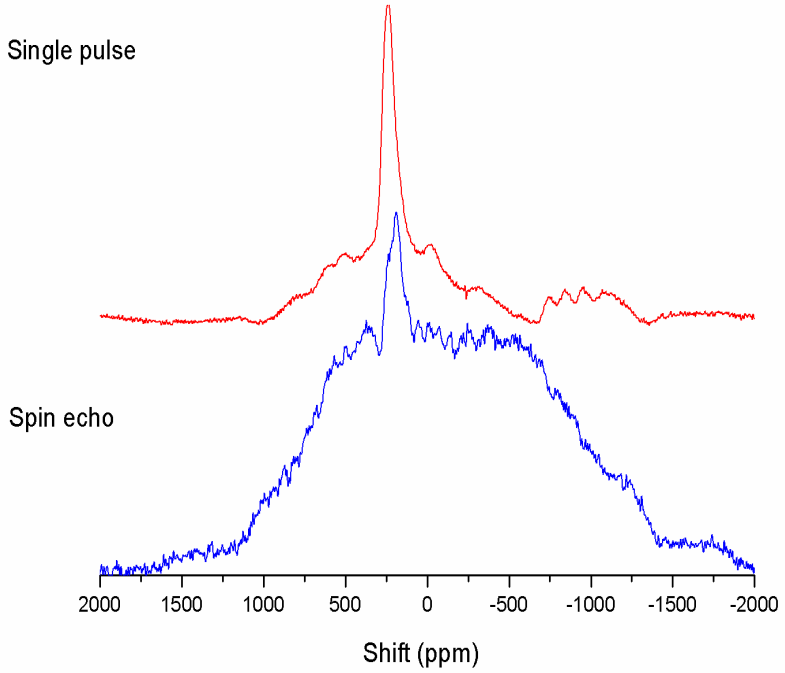


Problemas com “tempo morto”

Comparação – registro de “linhas largas”:

Experimentos de RMN de ^{51}V – V_2O_5 :

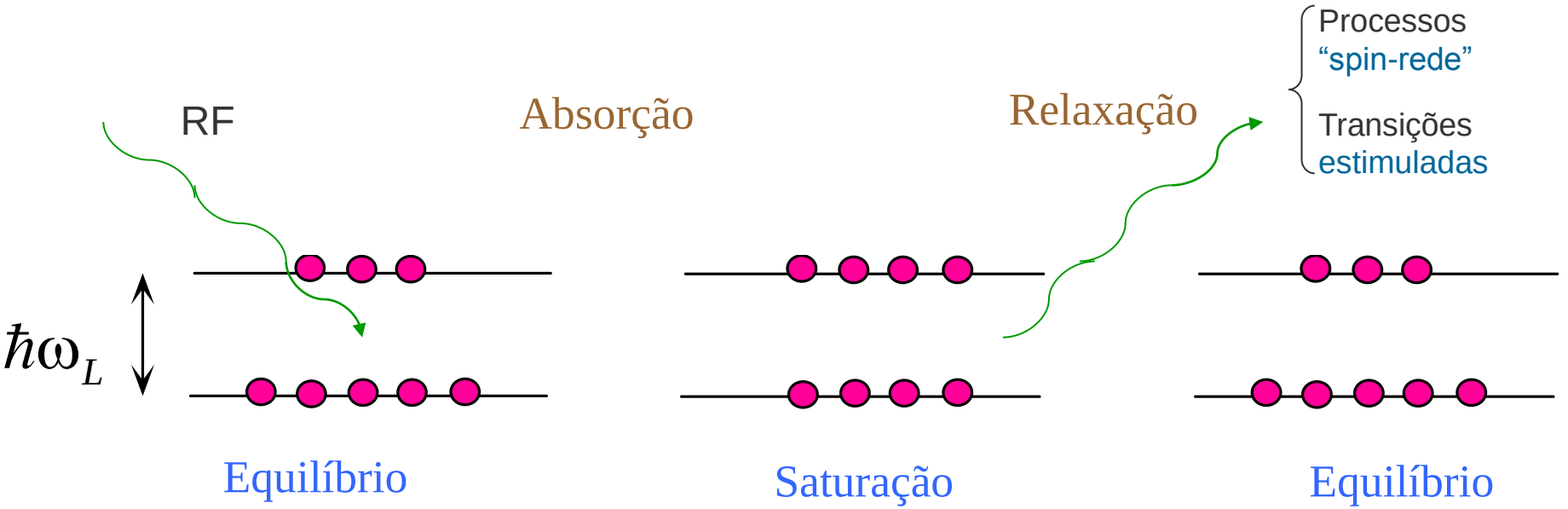


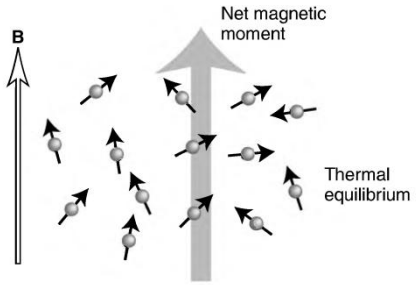


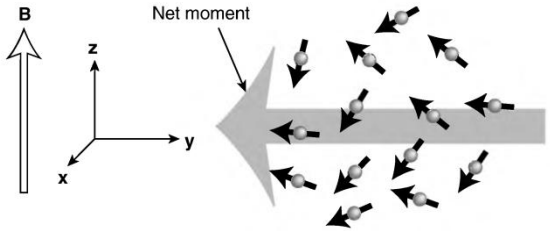
Domínio do tempo

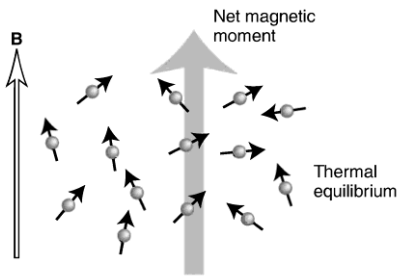
Espectros

Relaxação longitudinal



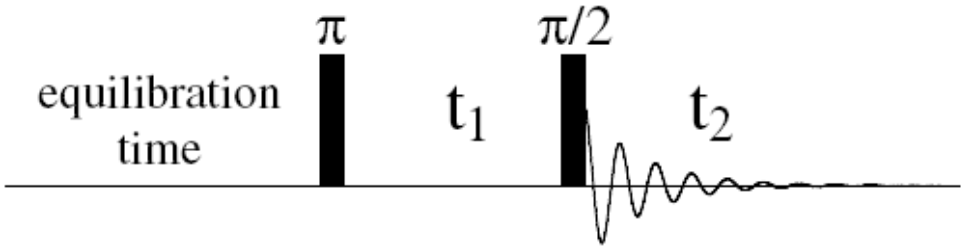


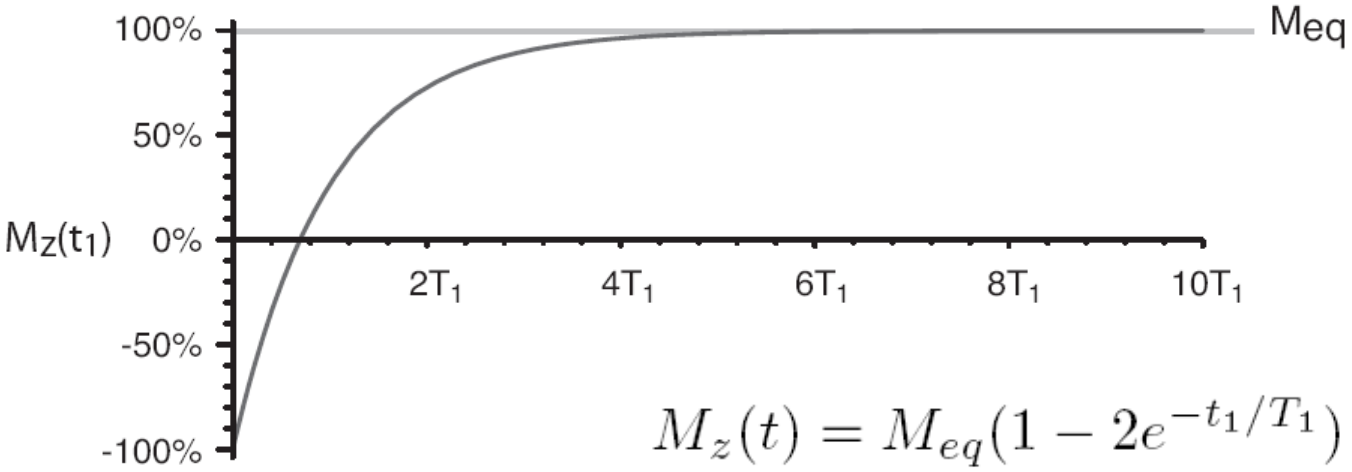




"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Medida de T_1: sequência inversão-recuperação

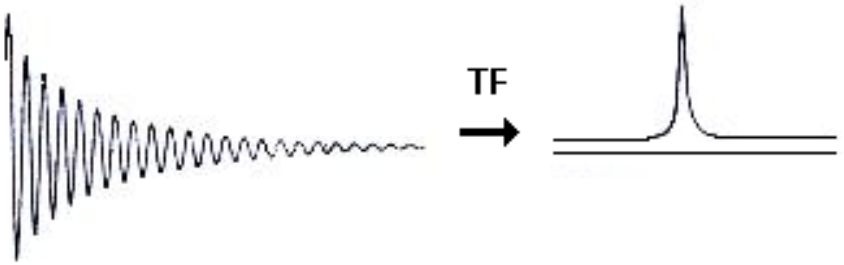




$$M_z(t) = M_{eq}(1 - 2e^{-t_1/T_1})$$

http://grandinetti.org/Teaching/Chem824/Notes

Interações de spin nuclear



$$f_L = \gamma B_0 / 2\pi$$

- Núcleo atômico *isolado*: medida de f_L fornece B_0 ou γ.
- Núcleo atômico na *matéria*: espectros de RMN (contendo vários valores ou distribuições de f_L) fornecem informações sobre a estrutura da matéria.

Interações de spin nuclear

Materiais isolantes e diamagnéticos:

- Deslocamento químico: Termo isotrópico + parte anisotrópica
- Interação dipolar direta: Homonuclear ou heteronuclear.
- Acoplamento escalar *(J)*: Termo isotrópico.
- Interação quadrupolar: $I > 1/2$.

Interações de spin nuclear

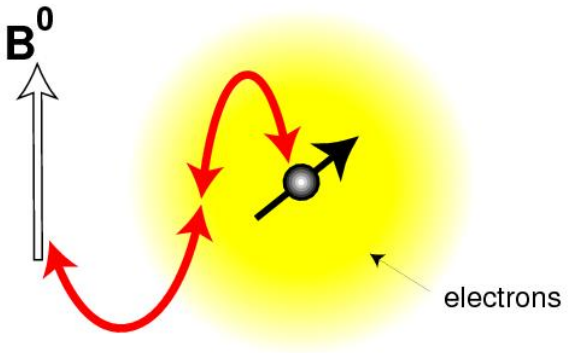
Materiais isolantes e diamagnéticos:

- Hamiltoniano contendo diferentes interações:

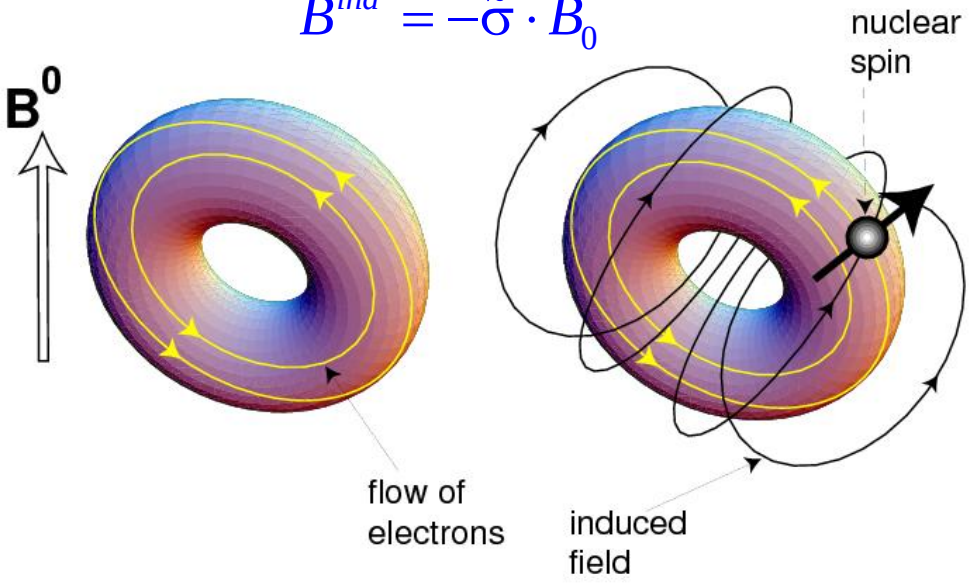
$$H_{spin} = \underbrace{H_0 + H_{RF}}_{H_{ext}} + \underbrace{H_{DQ} + H_{dip} + H_J + H_Q}_{H_{int}}$$

$$H_{ext} = -\vec{\mu} \cdot \vec{B}_0 - \vec{\mu} \cdot \vec{B}_1(t)$$

Deslocamento químico ("chemical shift")



$$\vec{B}^{ind} = -\tilde{\sigma} \cdot \vec{B}_0$$



Em líquidos:

$$\omega = \gamma B_{loc} = \gamma(1-\sigma_{iso})B_0$$

$$\delta = (f_{obs} - f_{ref}) / f_{ref}$$

ppm TMS

$$\delta = \frac{f_{obs} - f_{ref}}{f_{ref}} = \frac{\sigma_{ref} - \sigma_{obs}}{1-\sigma_{ref}} \cong \sigma_{ref} - \sigma_{obs}$$

"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

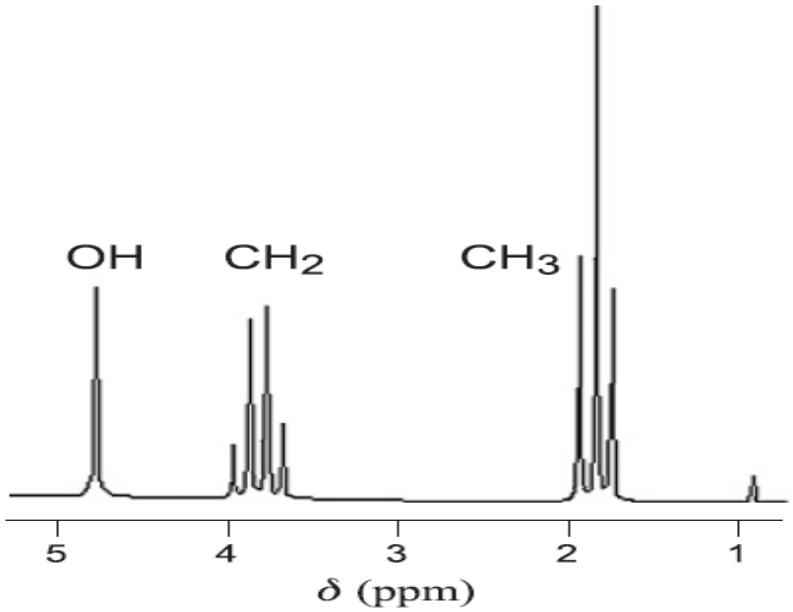
Deslocamento químico em líquidos

Packard et al. (1951)

$$\vec{B}_{loc} = (1-\sigma_{iso})\vec{B}_0$$

$$f_{obs} = \frac{\gamma B_{loc}}{2\pi} = f_L(1-\sigma_{iso})$$

$$\delta = \frac{f_{obs} - f_{ref}}{f_{ref}}$$



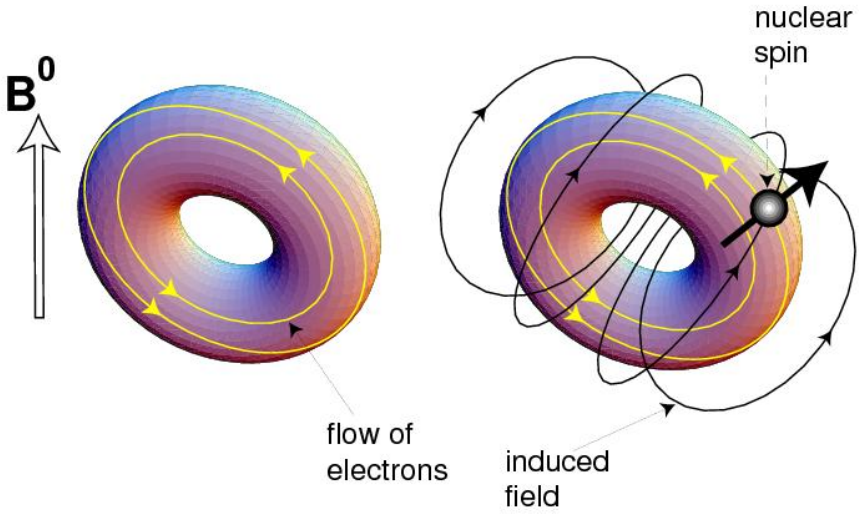
Valores típicos (^{1}H):

f_{ref} ~ 400MHz (TMS)

$f_{obs} - f_{ref}$ ~ 400-4000 Hz

$\delta \sim 10^{-6}$: partes por milhão (ppm)

Deslocamento químico em sólidos



$$\vec{B}^{ind} = -\tilde{\sigma} \cdot \vec{B}_0$$

$$\begin{pmatrix} B_x^{ind} \\ B_y^{ind} \\ B_z^{ind} \end{pmatrix} = - \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix}$$

$\tilde{\sigma}$: tensor de blindagem ("*shielding*")

$$\vec{B}^{loc} = \vec{B}_0 + \vec{B}^{ind} = (1 - \tilde{\sigma}) \cdot \vec{B}_0$$

$$H_{DQ} = -\vec{\mu} \cdot \vec{B}^{ind} = \gamma \hbar \vec{I} \cdot \tilde{\sigma} \cdot \vec{B}_0$$

"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Deslocamento químico em sólidos

Sistema de laboratório: $\tilde{\sigma}^{SLAB} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$ $|\sigma_{ZZ} - \sigma_{iso}| \geq |\sigma_{XX} - \sigma_{iso}| \geq |\sigma_{YY} - \sigma_{iso}|$

Sistema de eixos principais:
(fixo com relação ao cristal) $\tilde{\sigma}^{SEP} = \begin{pmatrix} \sigma_{XX} & 0 & 0 \\ 0 & \sigma_{YY} & 0 \\ 0 & 0 & \sigma_{ZZ} \end{pmatrix}$

Deslocamento químico isotrópico: $\sigma_{iso} = \frac{1}{3}(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ})$

Constante de anisotropia: $|\zeta| = |\sigma_{ZZ} - \sigma_{iso}|$

"Span": $\Omega = \sigma_{33} - \sigma_{11}$
$(\sigma_{33} \geq \sigma_{22} \geq \sigma_{11})$

Parâmetro de assimetria: $\eta = \frac{\sigma_{YY} - \sigma_{XX}}{\zeta}$ $0 \leq \eta \leq 1$

Harris et al., *Pure Appl Chem.* 2008;80:59-84

Deslocamento químico em sólidos

Campo magnético local:

$$\vec{B}^{loc} = \vec{B}_0 + \vec{B}^{ind} = (1-\tilde{\sigma}) \cdot \vec{B}_0$$

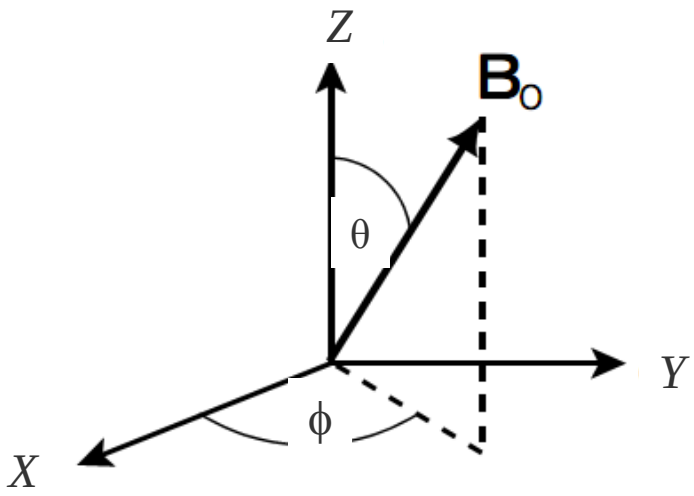
Campo magnético externo intenso:

$$B_0 >> B^{ind} \Rightarrow \vec{B}^{loc} \parallel \vec{B}_0$$

$$B^{loc} \cong (1-\sigma_{zz}) B_0$$

SLAB

$$\sigma_{zz} = \sigma_{iso} + \frac{\zeta}{2}\left[(3\cos^2\theta - 1) + \eta \,\mathrm{sen}^2\theta \cos 2\phi\right]$$

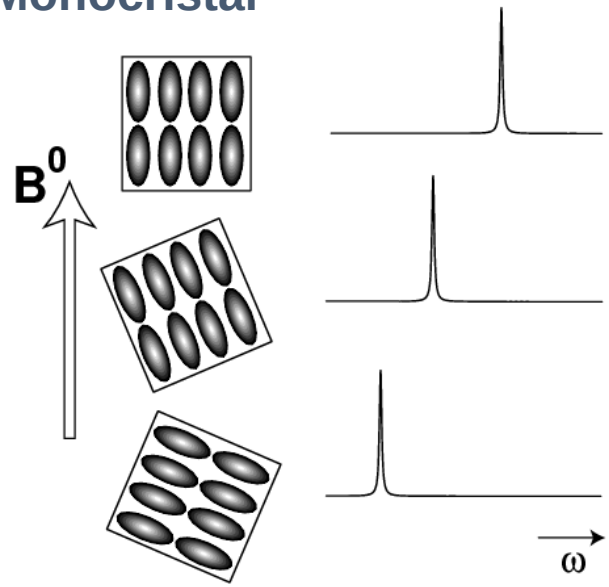


Deslocamento químico em sólidos

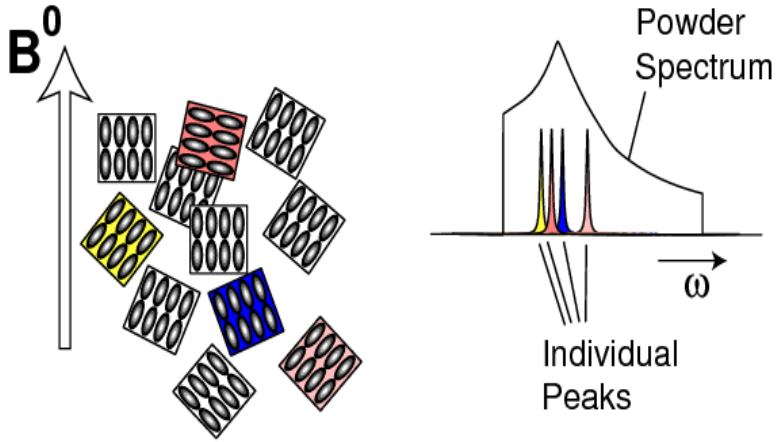
Frequência dependente da orientação molecular: ***Alargamento inomogêneo***

$$\omega(\theta,\phi) = \omega_L - \omega_L \left\{ \sigma_{iso} + \frac{\zeta}{2}\left[(3\cos^2\theta - 1) + \eta \,\mathrm{sen}^2\theta \cos 2\phi \right] \right\}$$

Monocristal



Sólido policristalino ou pó

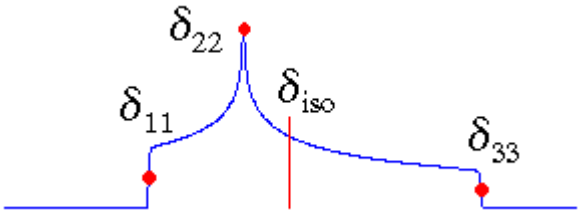


"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Deslocamento químico em sólidos

Tensor de anisotropia de deslocamento químico (CSA):

$$\delta_{jj} = \sigma_{ref} - \sigma_{jj}$$

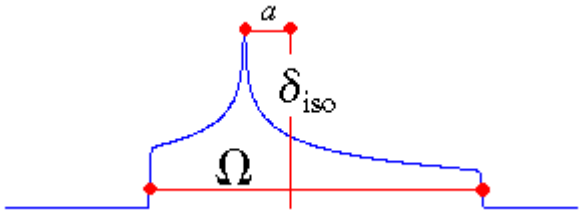


Notação de Herzfeld-Berger:

$$\delta_{11} \geq \delta_{22} \geq \delta_{33}$$

$$\delta_{iso} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33})$$

$$\Omega = \delta_{11} - \delta_{33} \qquad \kappa = \frac{3(\delta_{22} - \delta_{iso})}{\Omega}$$

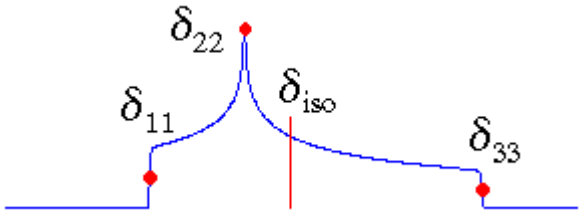


http://anorganik.uni-tuebingen.de/klaus/nmr/index.php?p=conventions/csa/csa

Deslocamento químico em sólidos

Tensor de anisotropia de deslocamento químico (CSA):

$$\delta_{jj} = \sigma_{ref} - \sigma_{jj}$$



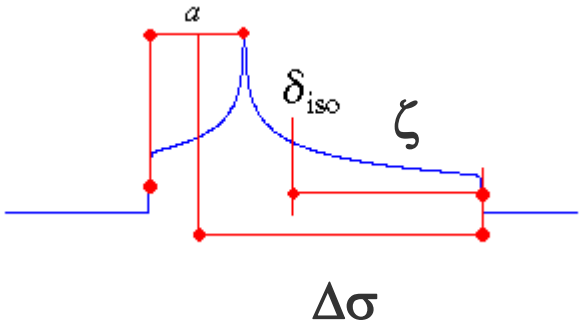
Notação de Haeberlen:

$$\left|\delta_{ZZ} - \delta_{iso}\right| \geq \left|\delta_{XX} - \delta_{iso}\right| \geq \left|\delta_{YY} - \delta_{iso}\right|$$

$$\delta_{iso} = \frac{1}{3}(\delta_{XX} + \delta_{YY} + \delta_{ZZ})$$

$$\zeta = \delta_{ZZ} - \delta_{iso} \qquad \Delta\sigma = \delta_{ZZ} - \frac{\delta_{XX} + \delta_{YY}}{2}$$

$$\eta = \frac{\delta_{YY} - \delta_{XX}}{\zeta} \qquad 0 \leq \eta \leq 1$$



Uso mais frequente (IUPAC, DMFIT, SIMPSON, ...)

http://anorganik.uni-tuebingen.de/klaus/nmr/index.php?p=conventions/csa/csa

Deslocamento químico em sólidos

Exemplos de espectros de pó:

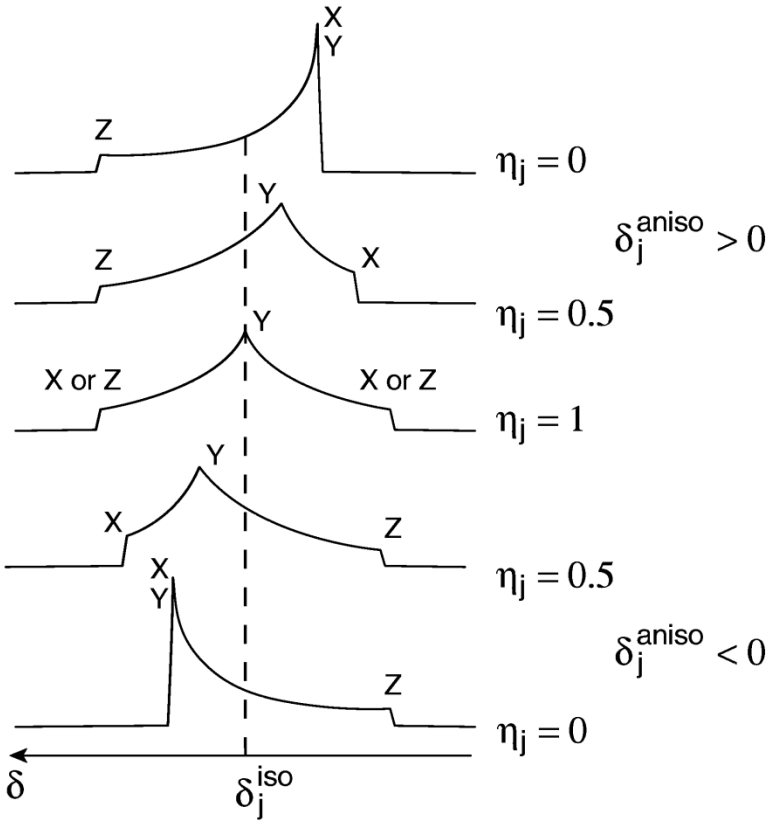


Figure 9.11
Powder pattern lineshapes for a single molecular site with CSA. All patterns belong to sites with the same magnitude of CSA $|\delta_j^{aniso}|$. The CSA is positive for the upper two patterns, and negative for the lower two. The sign of the CSA may be chosen arbitrarily in the case of maximum biaxiality ($\eta_j = 1$). The dashed line shows the position of the isotropic chemical shift δ_j^{iso}.

"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Deslocamento químico em sólidos

Exemplos de espectros de pó:

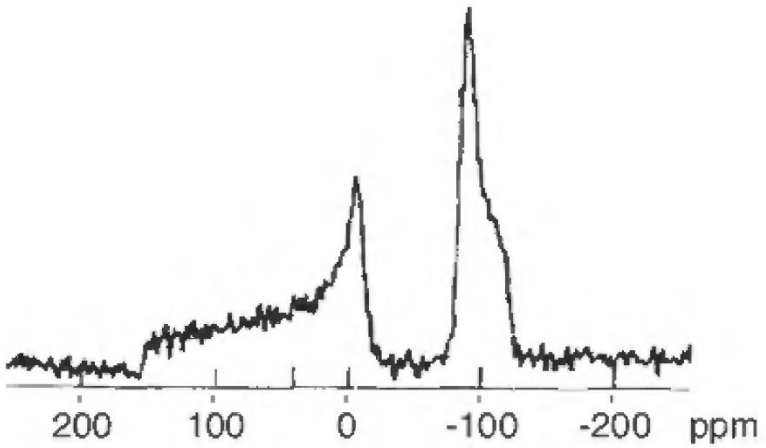
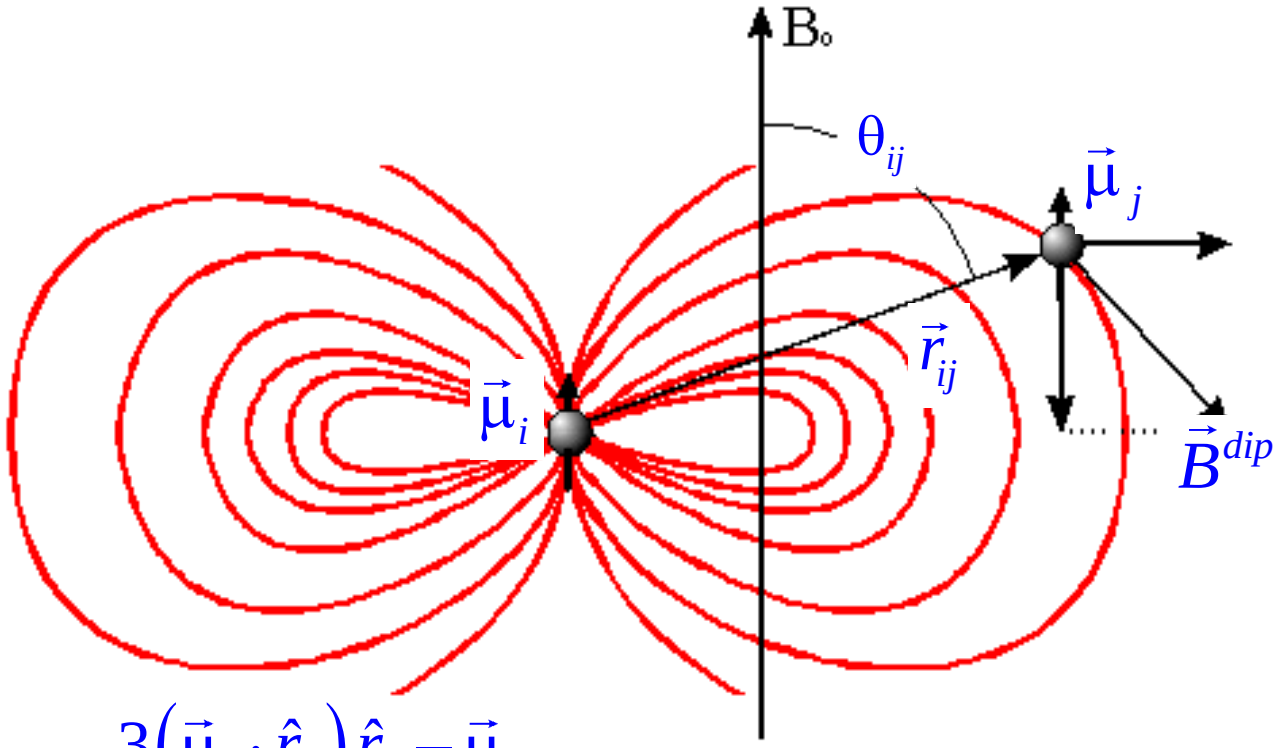


Figure 9.12 Experimental ^{1}H-decoupled ^{13}C spectrum for frozen acetic anhydride. The spectrum displays a powder pattern for each of the two chemically distinct ^{13}C sites. Both CSA tensors are almost uniaxial $\eta_j \cong 0$, but the sign and magnitude of the CSA are different. Reused from A. Pines, M. G. Gibby and J. S. Waugh, *J. Chem. Phys.* **59**, 569–590 (1973). Copyright 1973, American Institute of Physics.

"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

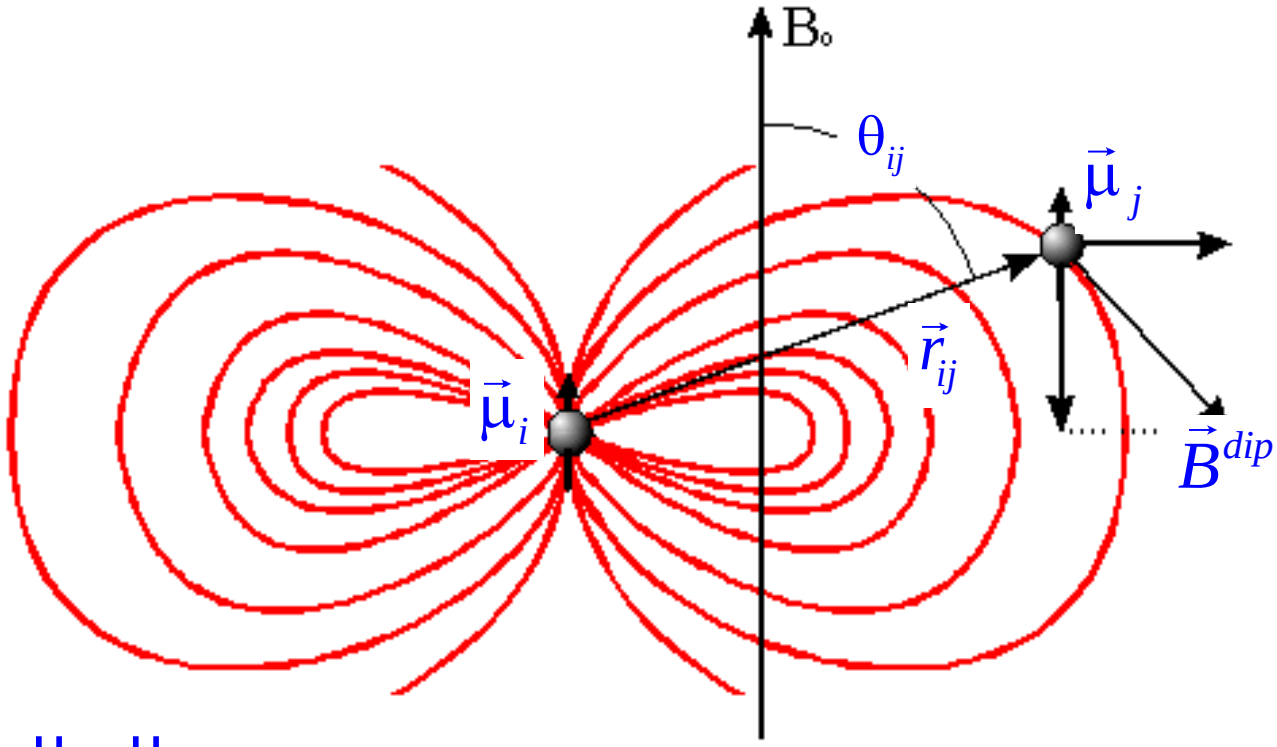
Interação dipolar internuclear



$$\vec{B}^{dip} = \frac{\mu_0}{4\pi} \frac{3\left(\vec{\mu}_i \cdot \hat{r}_{ij}\right)\hat{r}_{ij} - \vec{\mu}_i}{r_{ij}^3}$$

Interação através do espaço

Interação dipolar internuclear



$$B_z^{dip} \cong \frac{\mu_0}{4\pi}\frac{\mu}{r_{ij}^3}(3\cos^2\theta_{ij} - 1)$$

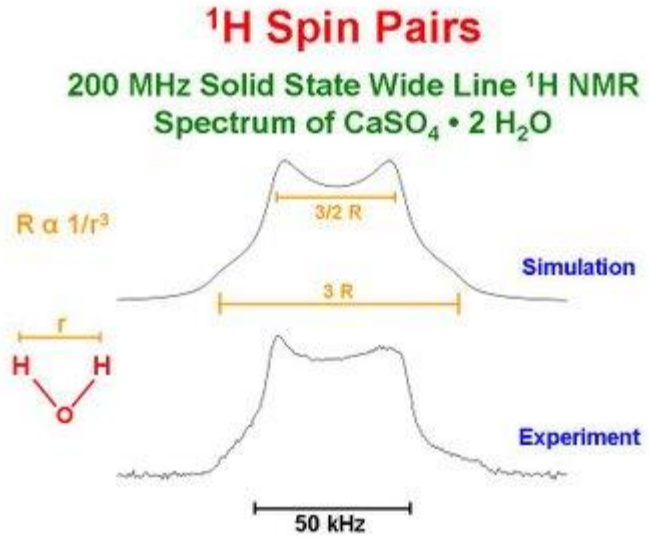
Interação através do espaço

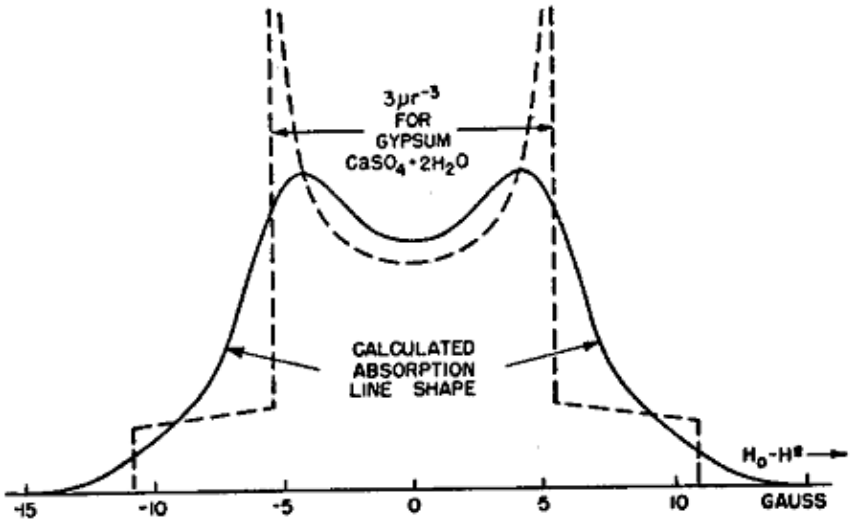
Interação dipolar em sólidos

Frequência dependente da orientação molecular (caso homonuclear):

$$\omega(\theta) = \omega_L \pm 3d\,\frac{3\cos^2\theta - 1}{4} \qquad d = \frac{\mu_0}{4\pi}\,\frac{\gamma^2\hbar}{r^3}$$

Dubleto de Pake

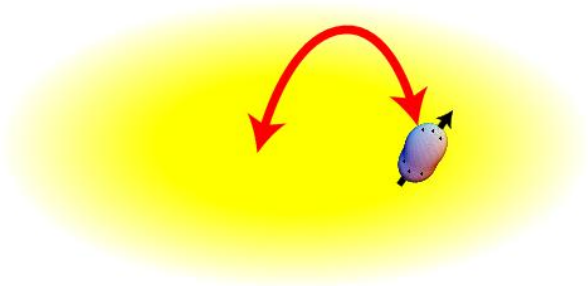


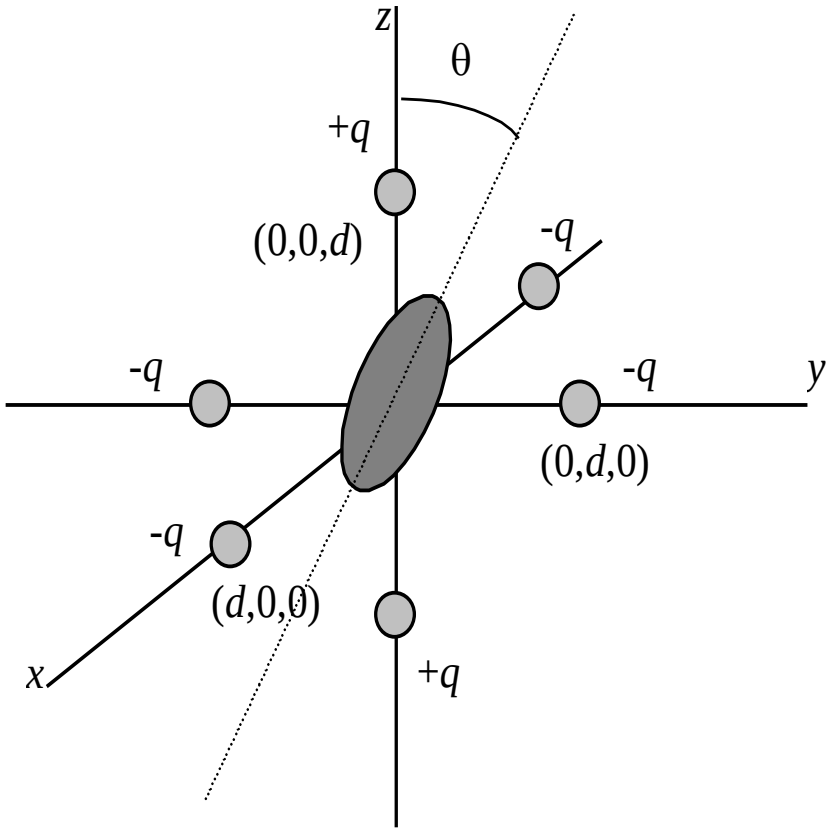


http://u-of-o-nmr-facility.blogspot.com/2008_10_01_archive.html

G. E. Pake, *J. Chem. Phys.* 1948;16:327-336.

Interação quadrupolar elétrica





Núcleos quadrupolares (I > ½):

^{2}H, ^{23}Na, ^{25}Mg, ^{27}Al, ^{35}Cl, ^{55}Mn, ...

Gradiente de campo elétrico (EFG):

$$V_{\alpha\beta} = \left(\frac{\partial^2 V}{\partial x_\alpha \partial x_\beta}\right)_0$$

"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Tensor gradiente de campo elétrico (EFG)

Sistema de laboratório: $\tilde{V}^{SLAB} = \begin{pmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{pmatrix}$

$|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$

Sistema de eixos principais:
(fixo com relação ao cristal)

$$\tilde{V}^{SEP} = \begin{pmatrix} V_{XX} & 0 & 0 \\ 0 & V_{YY} & 0 \\ 0 & 0 & V_{ZZ} \end{pmatrix}$$

Contribuição isotrópica nula
(equação de Laplace):

$$Tr(\tilde{V}) = V_{XX} + V_{YY} + V_{ZZ} = \nabla^2 V = 0$$

Anisotropia do EFG: $eq = V_{ZZ}$

Parâmetro de assimetria: $\eta_Q = \dfrac{V_{XX} - V_{YY}}{V_{ZZ}}$ $\quad 0 \leq \eta \leq 1$

Harris et al., *Pure Appl Chem.* 2008;80:59-84

Interação quadrupolar elétrica

Caso de simetria axial: $\eta_Q = 0$ $\qquad \omega_Q = \dfrac{3e^2qQ}{2I(2I-1)\hbar}$

Correções de primeira e segunda ordens na energia:

$$E_m^{(1)} = \frac{1}{4}\hbar\omega_Q(3\cos^2\theta - 1)\left[m^2 - \frac{1}{3}I(I+1)\right]$$

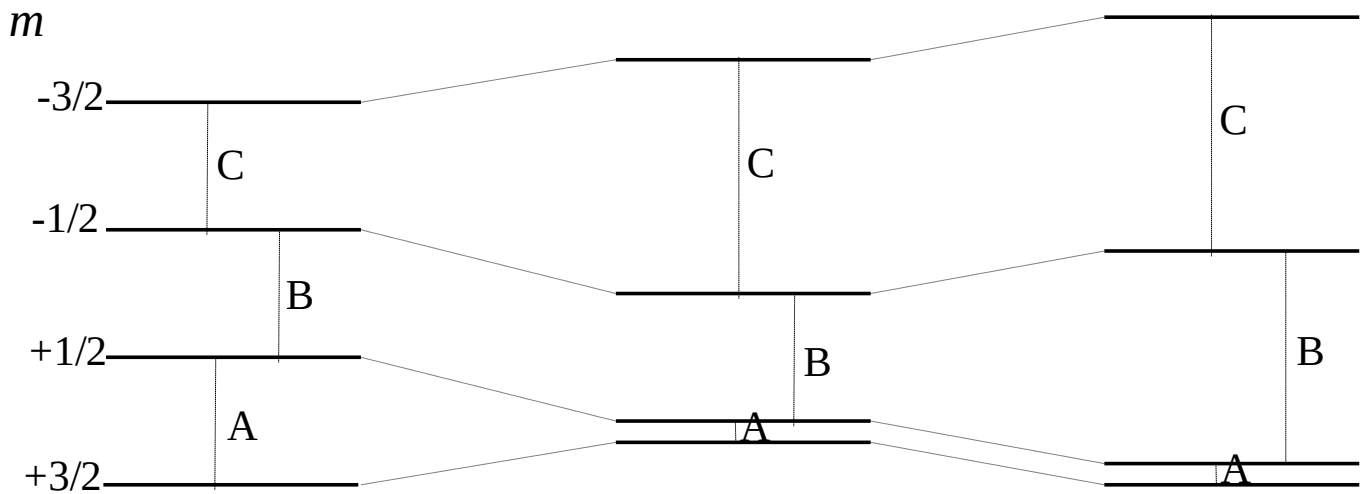
$$E_m^{(2)} = -\hbar\left(\frac{\omega_Q^{\,2}}{12\omega_L}\right)m\left\{\frac{3}{2}\cos^2\theta(1-\cos^2\theta)[8m^2 - 4I(I+1)+1] + \frac{3}{8}(1-\cos^2\theta)[-2m^2 + 2I(I+1) - 1]\right\}$$

Correções de primeira e segunda ordens nas frequências:

$$\omega_m^{(0)} = \omega_L \qquad \omega_m^{(1)} = -\omega_Q\left(m - \frac{1}{2}\right)\frac{3\cos^2\theta - 1}{2} \qquad \omega_{1/2}^{(2)} = -\frac{\omega_Q^{\,2}}{12\omega_L}\left[I(I+1) - \frac{3}{4}\right](1-\cos^2\theta)(9\cos^2\theta - 1)$$

Interação quadrupolar elétrica

Correções de primeira e segunda ordens – caso de simetria axial:

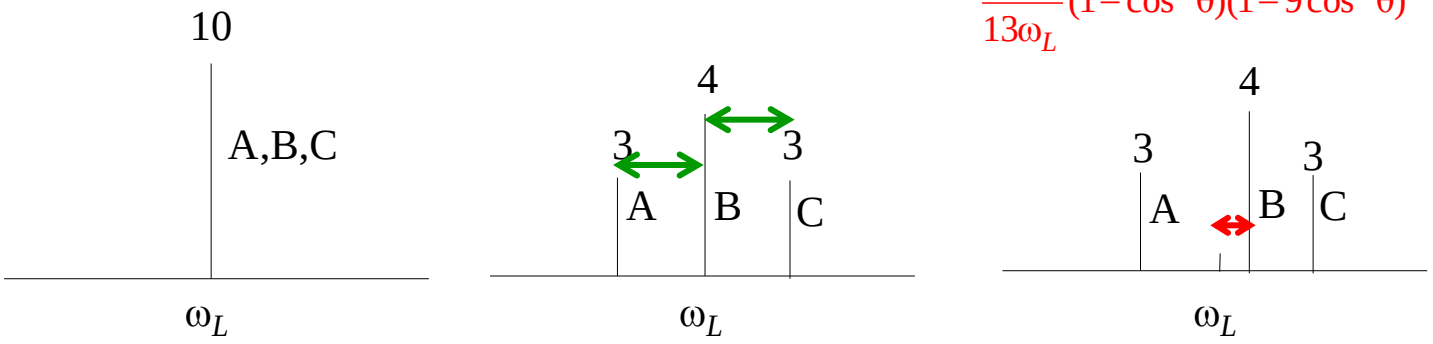


$I = 3/2$

$\eta_Q = 0$

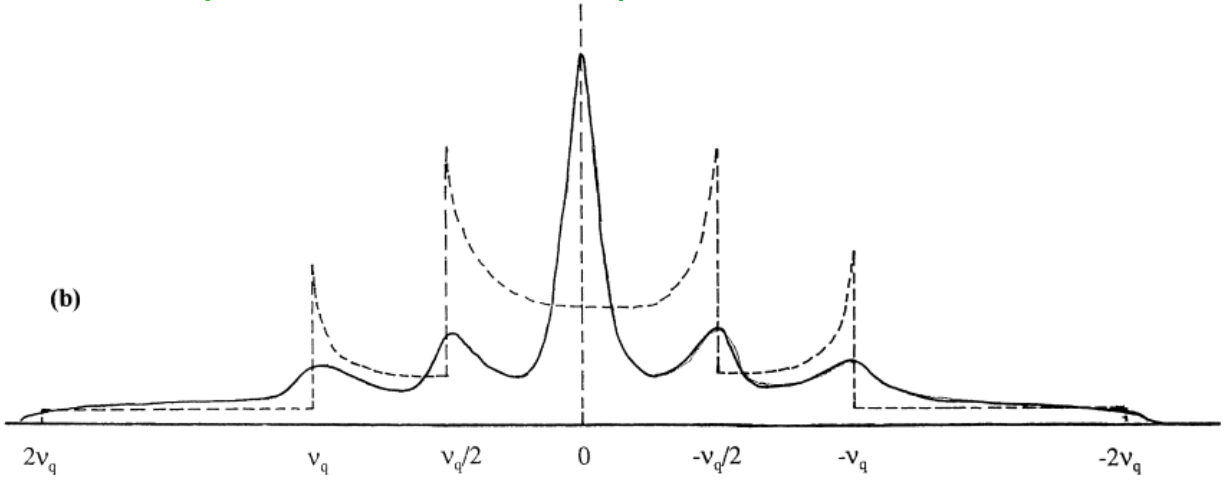
$\omega_Q(3\cos^2\theta - 1)$

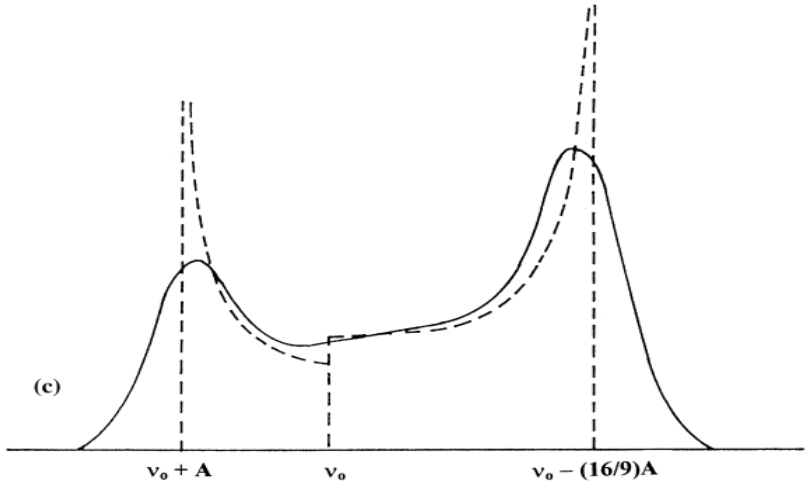
$\frac{3\omega_Q{}^2}{13\omega_L}(1-\cos^2\theta)(1-9\cos^2\theta)$



Interação quadrupolar elétrica

Espectros de pó – núcleos com spin semi-inteiro:





1ª ordem:

$$\nu_q = \frac{3e^2qQ}{2I(2I-1)h}$$

2ª ordem – transição central:

$$A = \left[I(I+1) - 3/4\right]\frac{\nu_q^{\,2}}{\nu_0}$$

Smith & van Eck, *Prog. Nucl. Magn. Reson. Spectr.* 1999;34:159-201

Interação quadrupolar elétrica

Espectros de pó – exemplos:

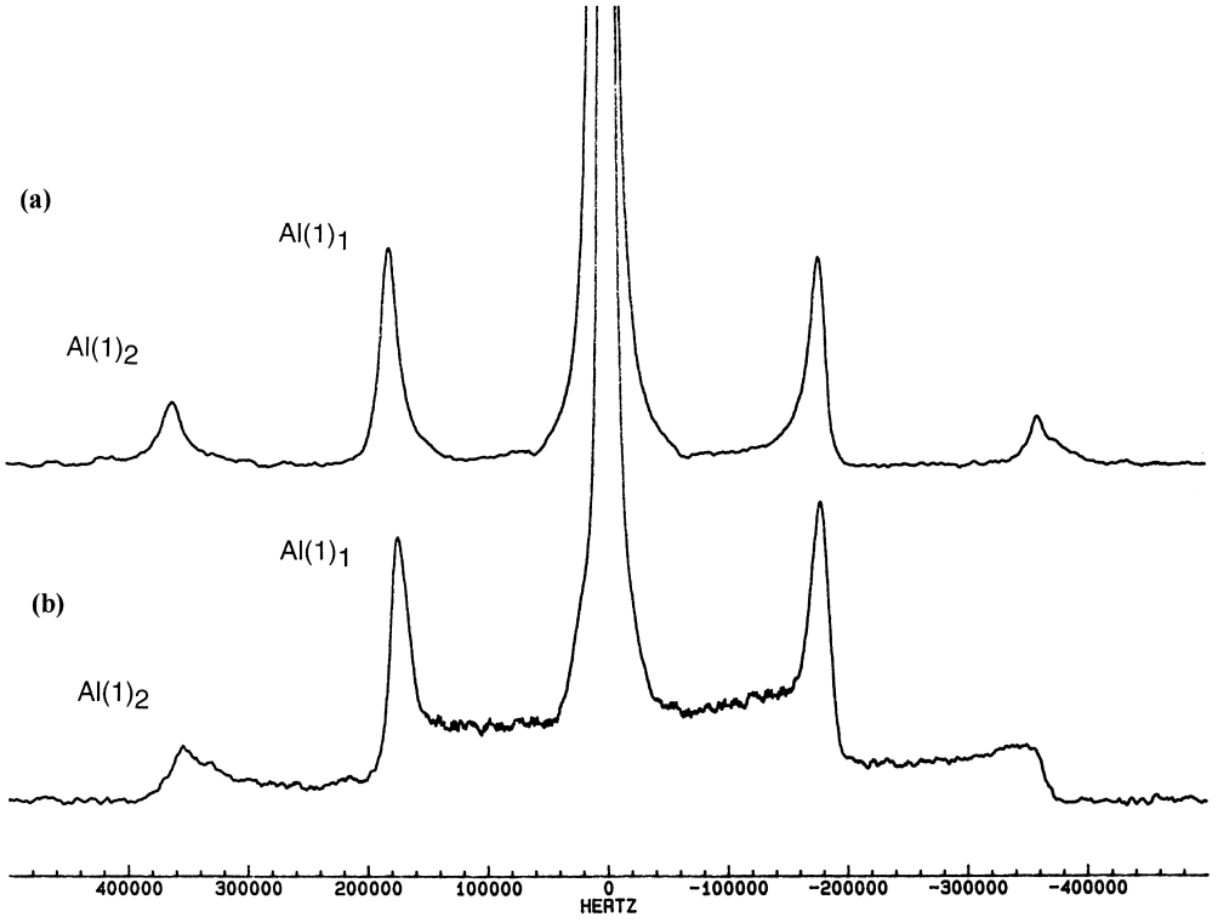
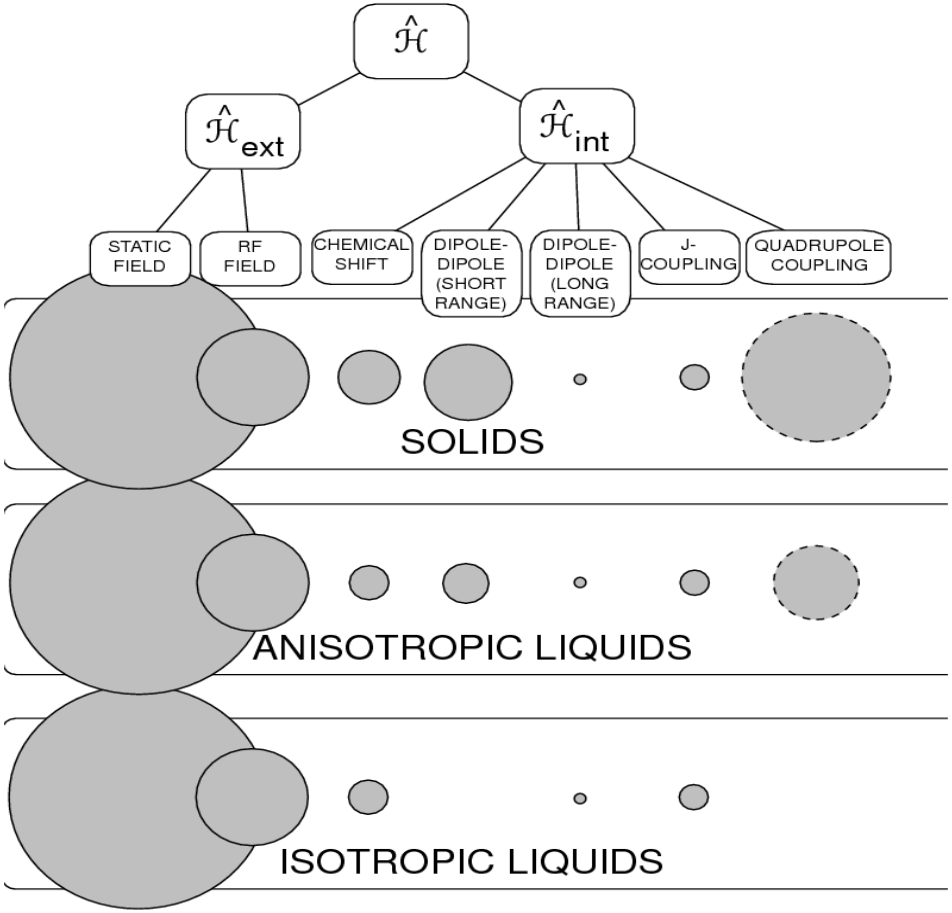


Fig. 8. Static ^{27}Al NMR spectra from α-Al_2O_3 using (a) single pulse and (b) spin-echo acquisition.

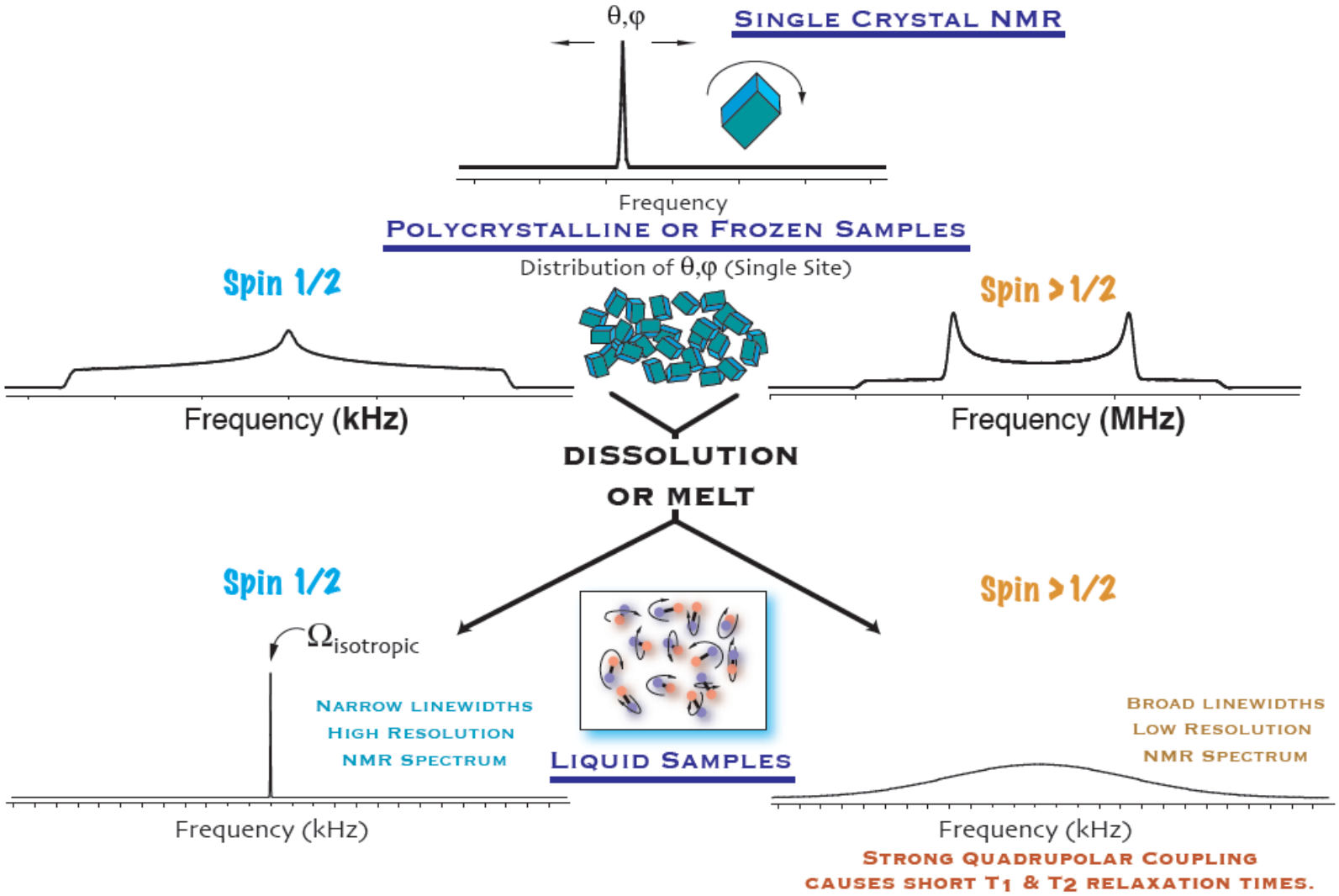
Smith & van Eck, *Prog. Nucl. Magn. Reson. Spectr.* 1999;34:159-201

Interações de spin nuclear: resumo



"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Interações de spin nuclear: resumo

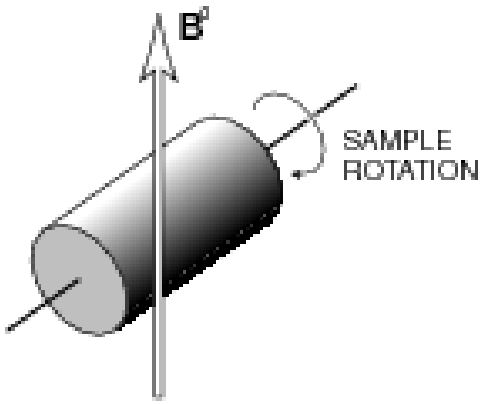


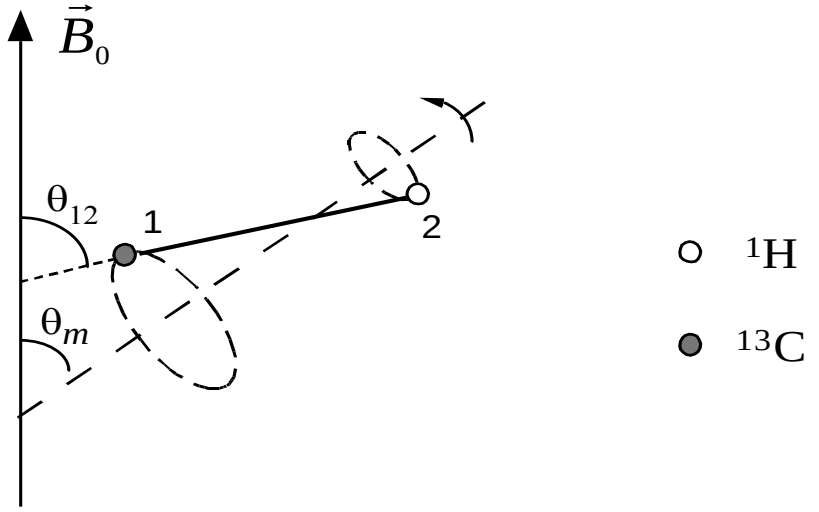
http://www.grandinetti.org/Research/NMR

RMN em sólidos policristalinos

- Alargamento inomogêneo: interações anisotrópicas.
- Algumas técnicas de alta resolução:
  - Desacoplamento dipolar .
  - Rotação em torno do ângulo mágico (MAS).
  - Polarização cruzada (CP).
- Objetivo: obtenção de espectros em sólidos com resolução similar à de líquidos, permitindo a medida de deslocamentos químicos isotrópicos.

Rotação em torno do ângulo mágico (MAS)





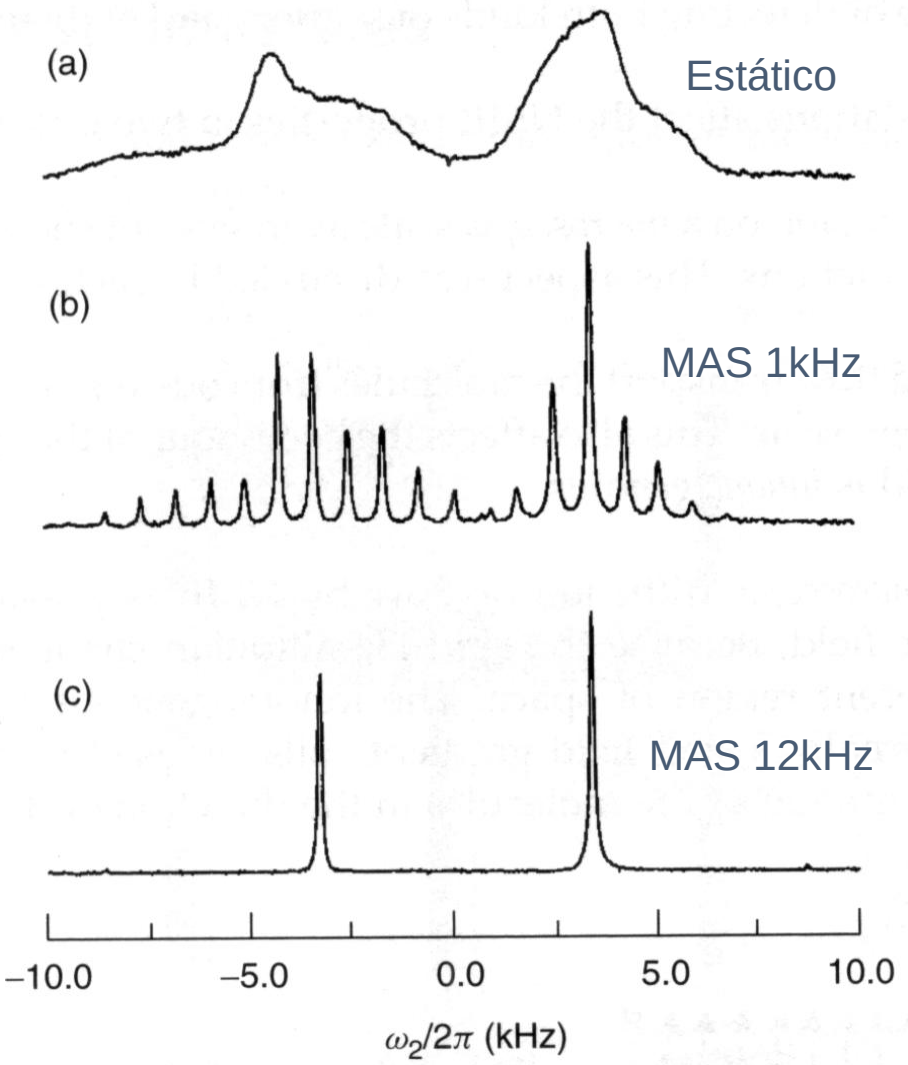
$$\left\langle 3\cos^2\theta_{12} - 1 \right\rangle \propto 3\cos^2\theta_m - 1 = 0$$

$$\theta_m = \cos^{-1}(1/\sqrt{3}) = 54,74^o$$

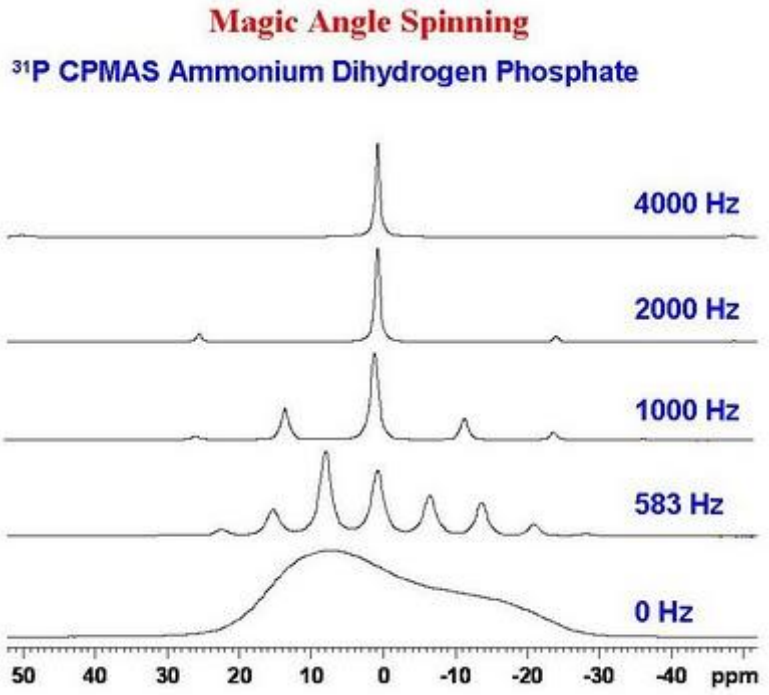
Andrew, *Nature* 1958;182:1659.
Lowe, *Phys. Rev. Lett.* 1959;2:285.

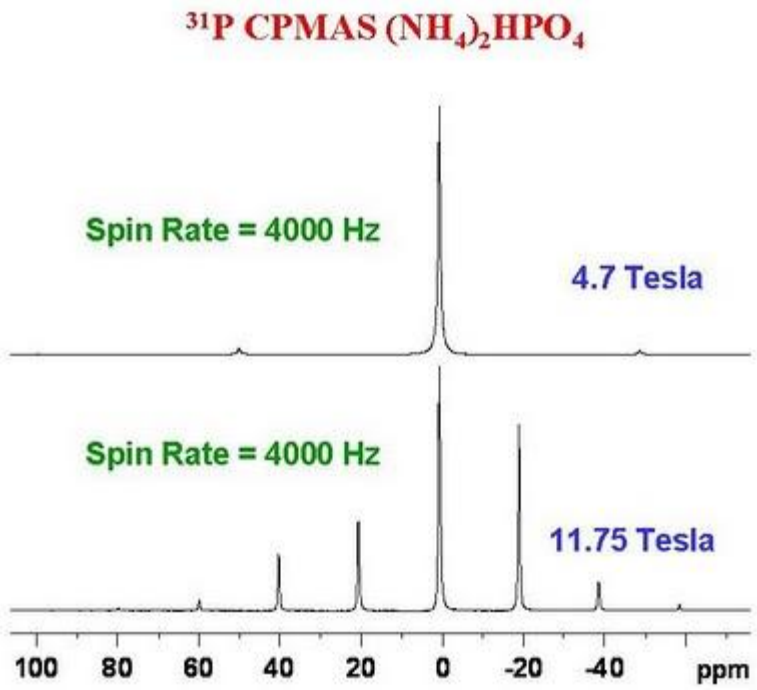
Rotação em torno do ângulo mágico (MAS)

RMN de ^{13}C (glicina)



MAS e bandas laterais (ssb)





http://u-of-o-nmr-facility.blogspot.com/

Ecos rotacionais e bandas laterais (ssb)

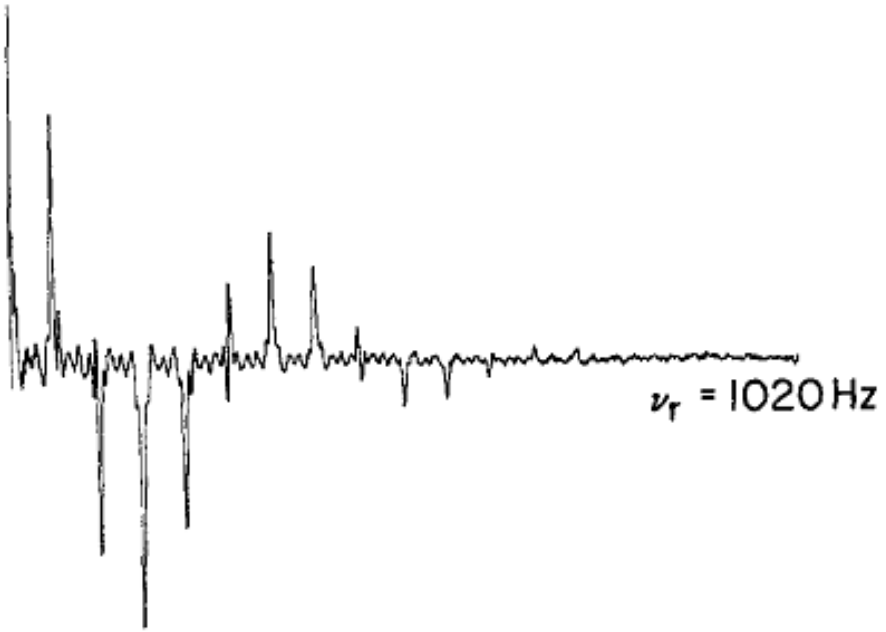
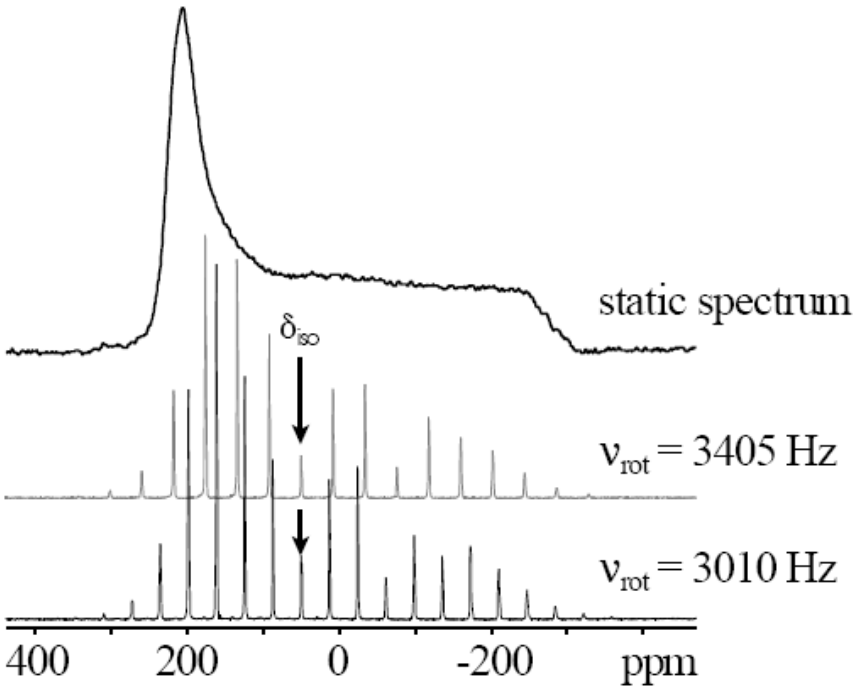
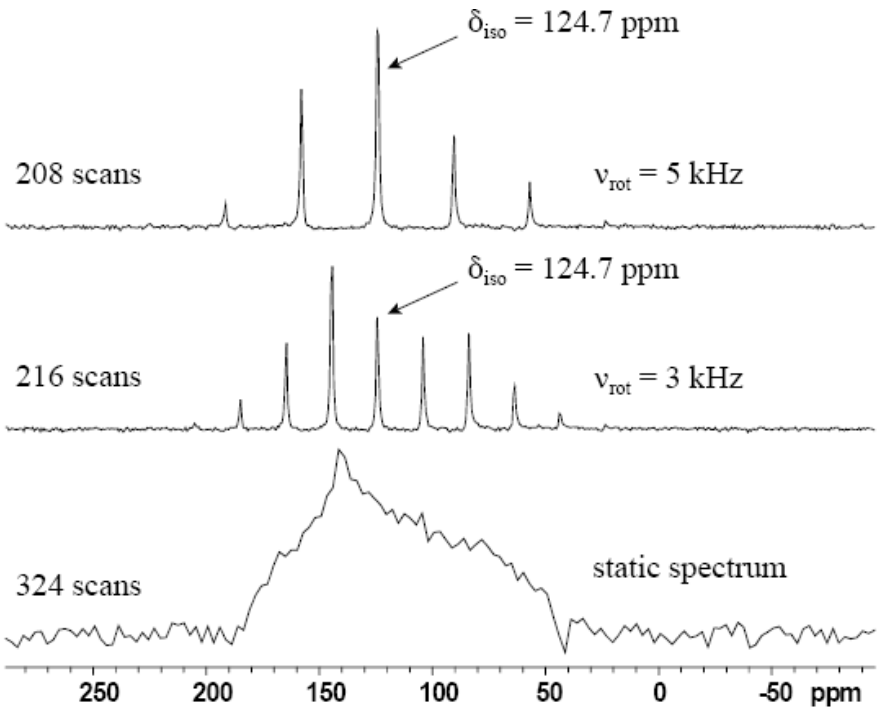


FIG. 1. FID of ^{31}P in powdered barium diethyl phosphate, spinning at $\nu_r = 1020$ Hz. The FID takes the form of a train of rotational spin echoes, spaced by $1/\omega_r = 0.98$ msec. The echo envelope shows an oscillation of period 6.0 msec, because the isotropic chemical shift is off the spectrometer reference frequency by 167 Hz.

Maricq & Waugh, J. Chem. Phys. 1979;70:3300

Ecos rotacionais e bandas laterais (ssb)

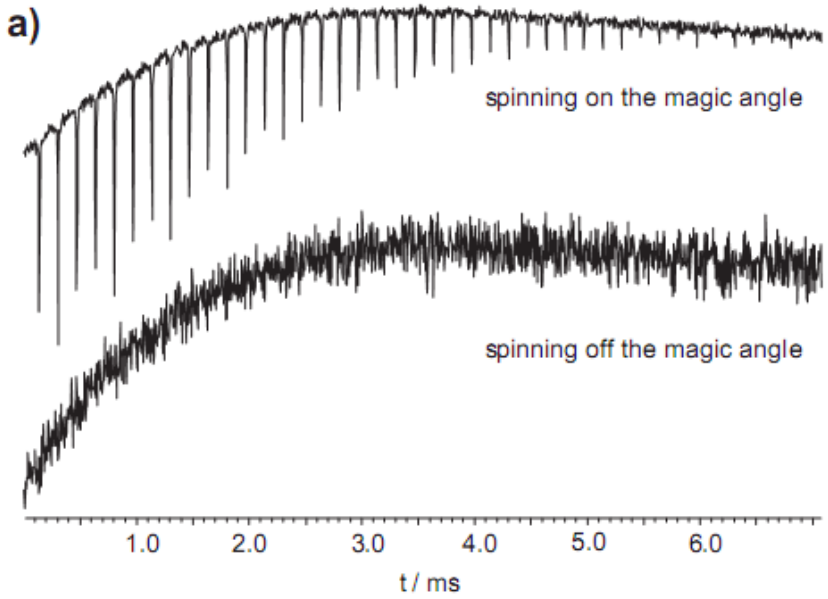




Remoção das bandas laterais: altas frequências de rotação ou técnicas especiais (TOSS).

Ecos rotacionais e bandas laterais (ssb)

Ajuste do ângulo mágico:



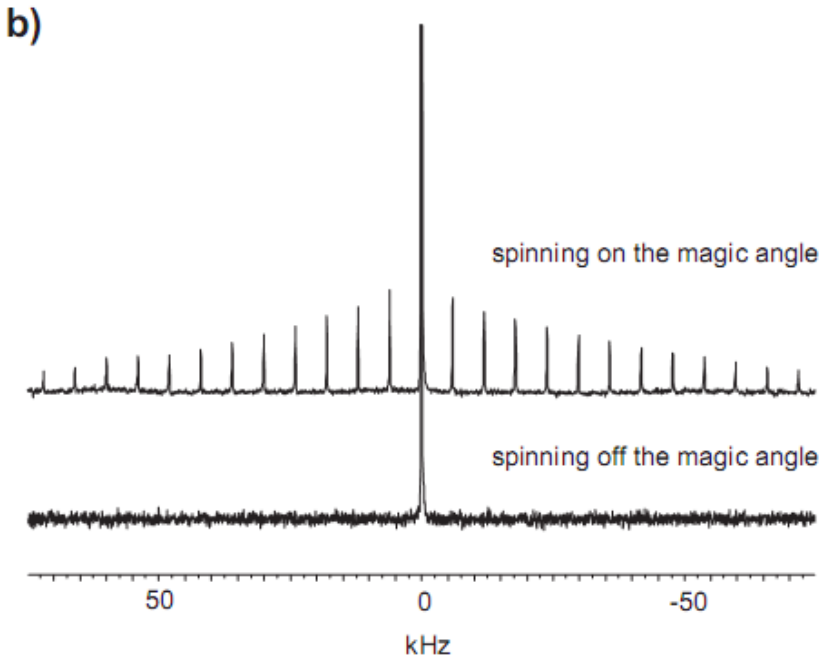


Figure 11: (a) The ^{79}Br NMR FID in polycrystalline KBr both on and off the magic angle and (b) the corresponding ^{79}Br MAS NMR spectra. The spinning frequency for both spectra is 6000 Hz. In both cases, 16 transients were acquired. $B_0 = 4.7$ T.

Bryce et al., Can. J. Anal. Sci. Spectr. 2001;46:46.

Supressão de bandas laterais (TOSS)

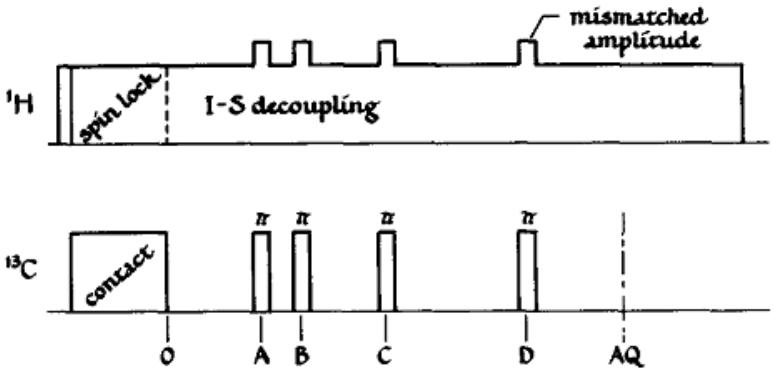


FIG. 10. Pulse sequence which produces spin echoes at arbitrary times in rotating solids. For times A, B, C, D, and AQ see Table II.

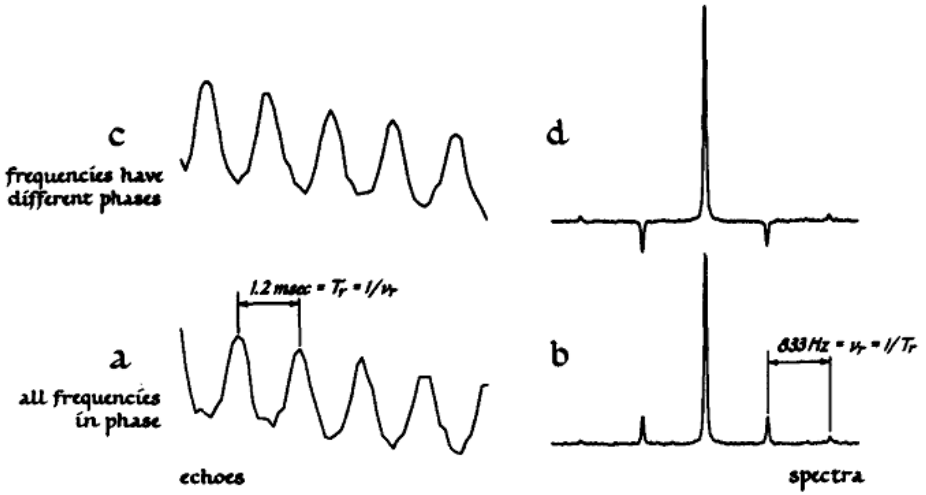


FIG. 2. Echoes and spectra: (a) Beginning of an ordinary fid; (b) Fourier transform of a; (c) Beginning of a train of supplementary echoes; (d) Transform of c.

Dixon, J. Chem . Phys. 1982;77:1800.

Supressão de bandas laterais (TOSS)

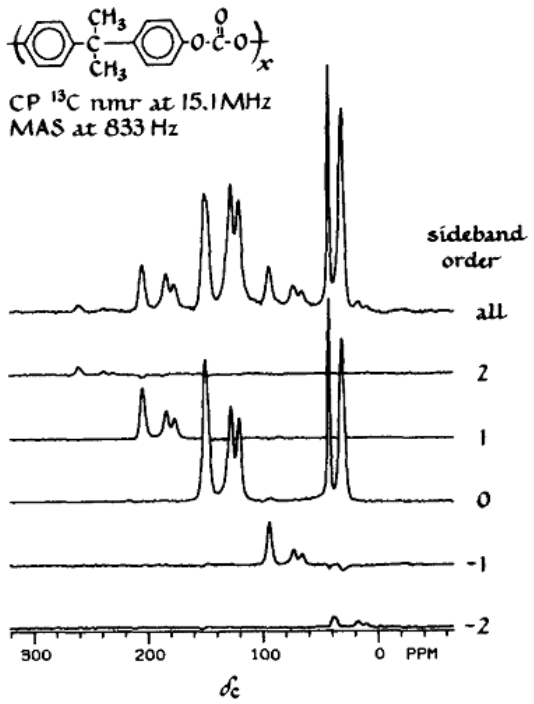


FIG. 1. Polycarbonate spectrum. Top curve—ordinary cross polarization experiment, 65 000 acquisitions. Lower curves—separated spectrum reconstructed from a total of 65 000 echoes.

Dixon, J. Chem . Phys. 1982;77:1800.

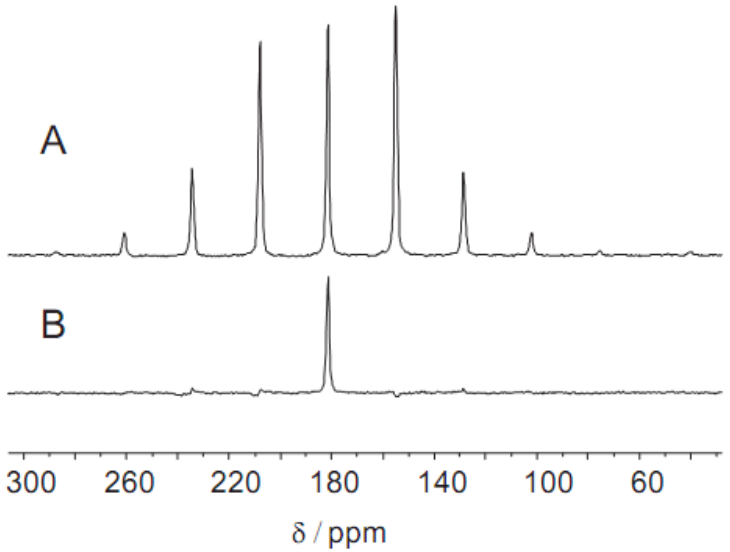
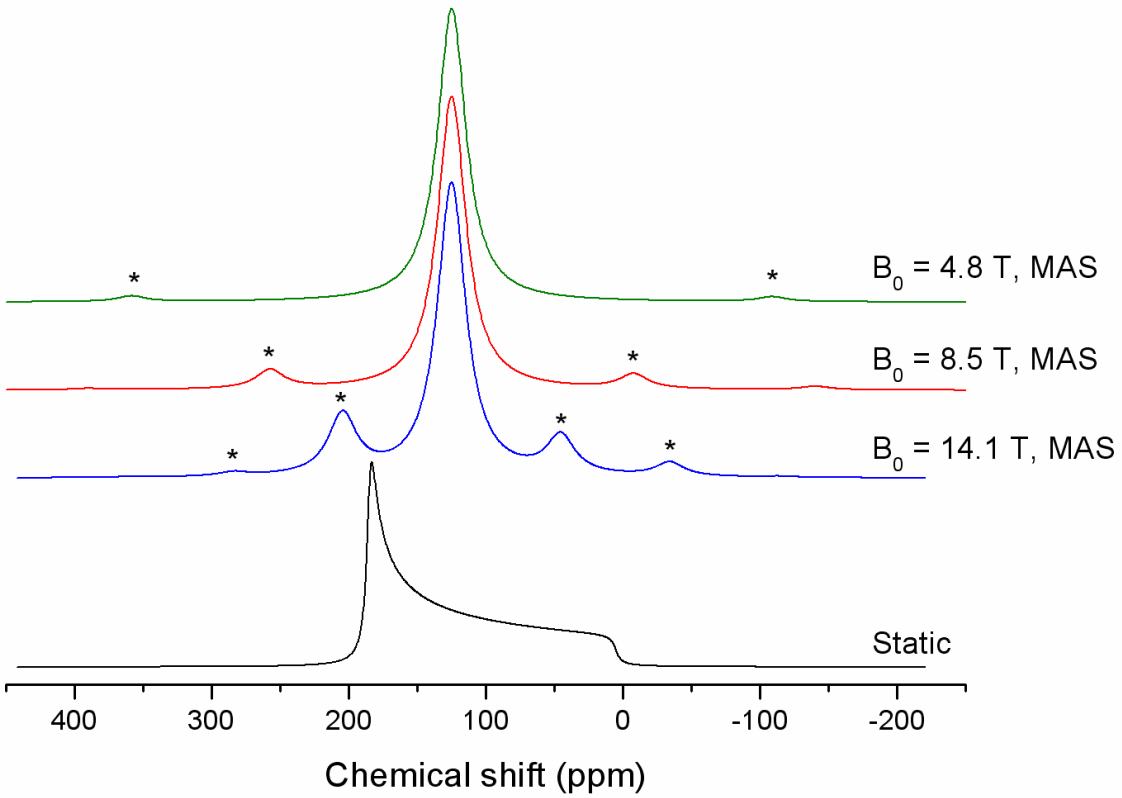


Figure 9: Carbon-13 CP/MAS spectra of singly-labelled (99%) phenylacetic-*carboxy*-^{13}C acid (B_0 = 4.7 T, ν_L = 50.3 MHz, ν_{rot} = 1.339 kHz) acquired with high-power proton decoupling. In spectrum A, a standard CP pulse program was used. The isotropic peak is at 181 ppm. In spectrum B, the TOSS sequence has been used to suppress the spinning sidebands; only the isotropic peak remains. One drawback of the TOSS sequence is the loss of intensity relative to the standard CP/MAS spectrum. Number of acquisitions: 64 (trace A); 128 (trace B).

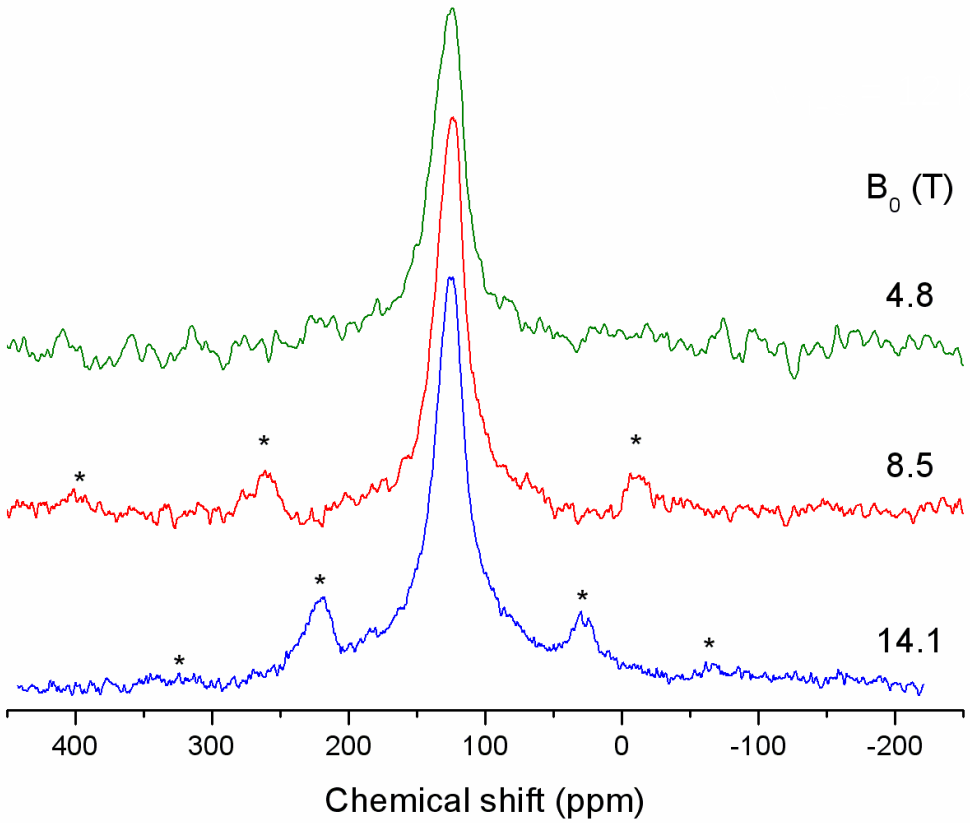
Bryce et al., Can. J. Anal. Sci. Spectr. 2001;46:46.

MAS e efeitos de CSA: importância da magnitude de B_0



Freitas et al. *Chem. Phys. Carbon*, vol. 31, p. 85-170; CRC Press: Boca Raton, U.S.A., 2012.

MAS e efeitos de CSA: importância da magnitude de B_0



Freitas et al. *Chem. Phys. Carbon*, vol. 31, p. 85-170; CRC Press: Boca Raton, U.S.A., 2012.

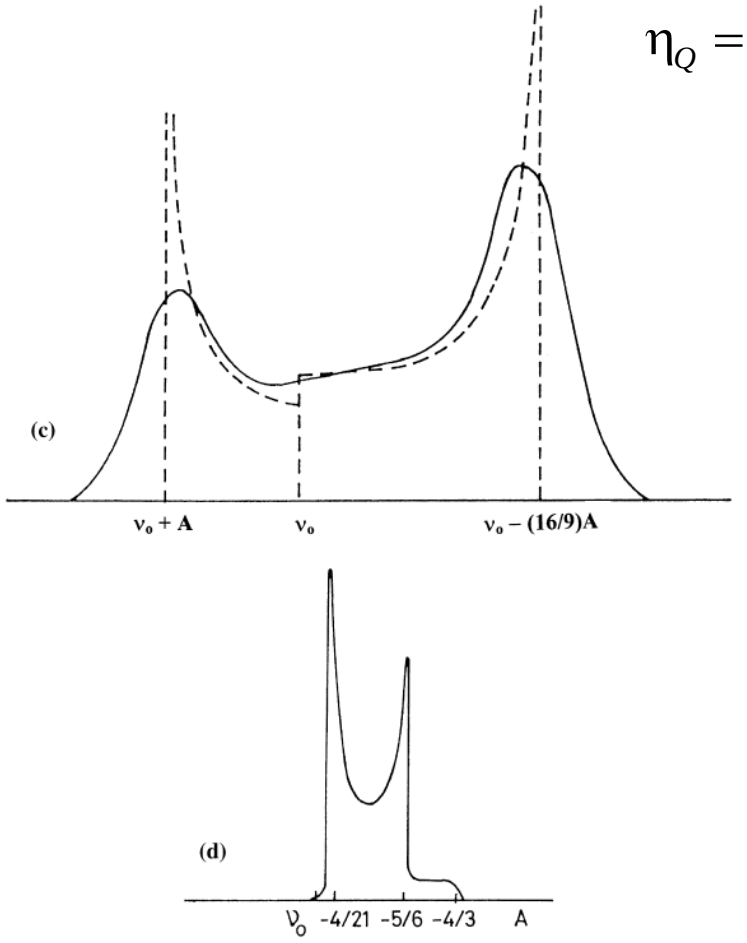
MAS e efeitos de CSA: importância da magnitude de B_0

Magnetic field (T)	^{1}H NMR frequency (MHz)	^{13}C NMR frequency (MHz)	Δf_{CSA} (kHz)
2.35	100	25.2	5
4.70	200	50.3	10
7.05	300	75.4	15
9.39	400	100.6	20
11.74	500	125.8	25
14.09	600	150.9	30
16.44	700	176.1	35
18.79	800	201.2	40
21.14	900	226.4	45

Freitas et al. *Chem. Phys. Carbon*, vol. 31, p. 85-170; CRC Press: Boca Raton, U.S.A., 2012.

MAS e efeitos quadrupolares

Espectros de pó – núcleos com spin semi-inteiro:



$\eta_Q = 0$

2ª ordem – transição central:

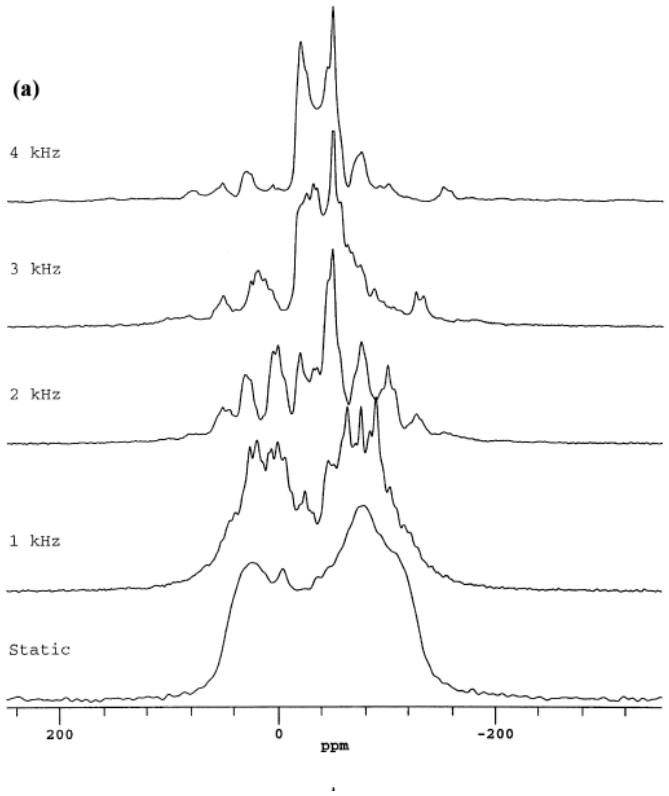
$$\nu_Q = \frac{3e^2qQ}{2I(2I-1)h}$$

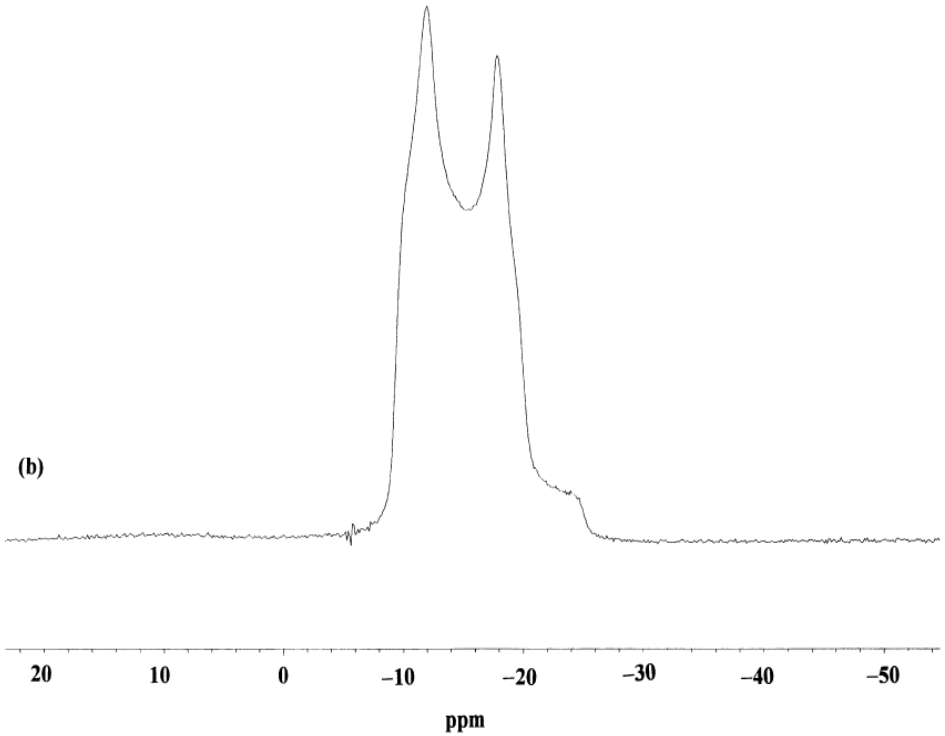
$$A = \left[I(I+1) - 3/4\right]\frac{\nu_Q^{\,2}}{\nu_0}$$

Smith & van Eck, Prog. Nucl. Magn. Reson. Spectr. 1999;34:159-201

MAS e efeitos quadrupolares

RMN de ^{23}Na com MAS em $NaAlSi_3O_8$:





Smith & van Eck, Prog. Nucl. Magn. Reson. Spectr. 1999;34:159-201

MAS e efeitos quadrupolares

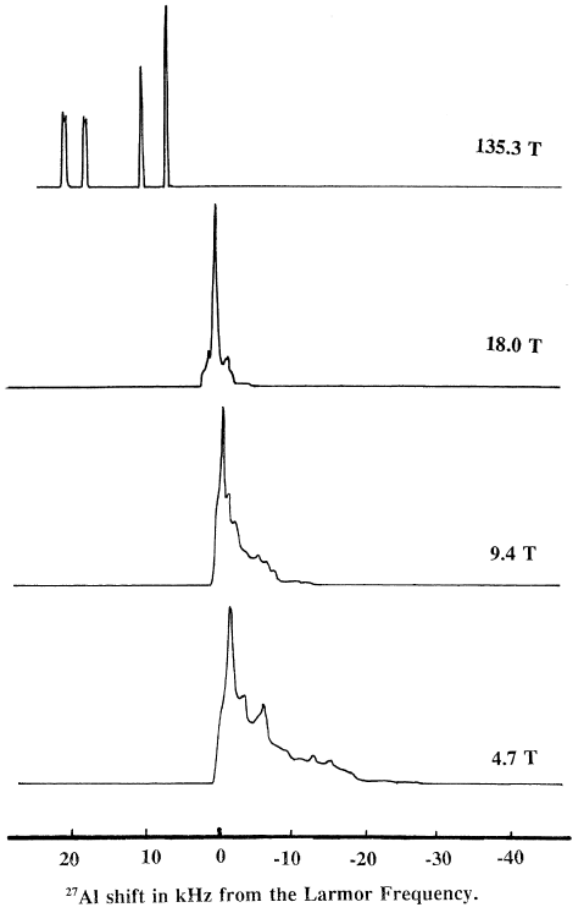


Fig. 7. Simulations of the ^{27}Al MAS centreband of kyanite (Al_2SiO_5) as a function of the applied magnetic field.

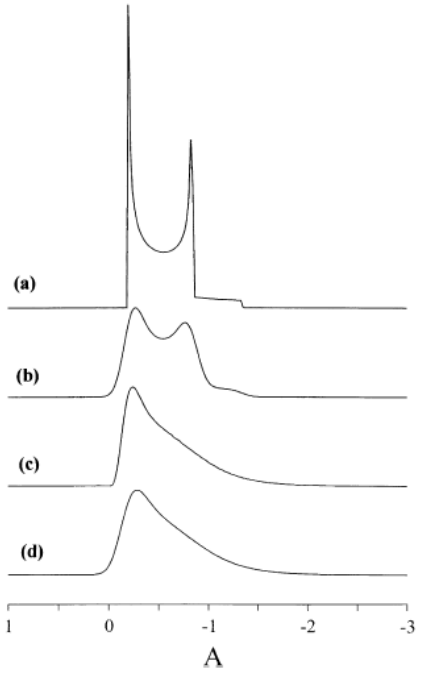
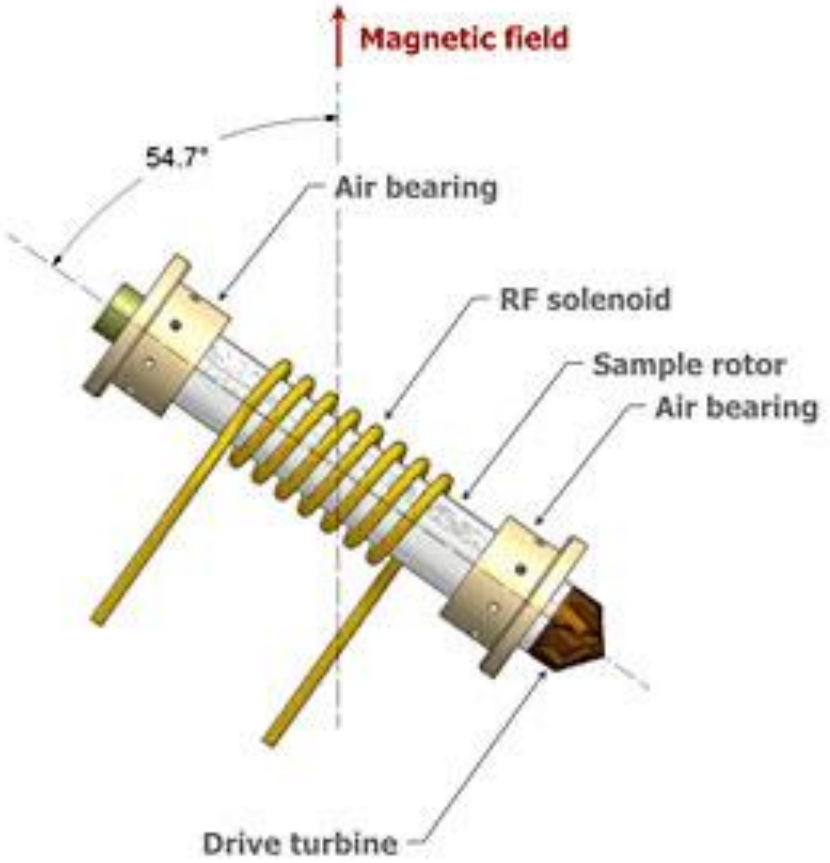


Fig. 14. The effect of a distribution in the isotropic chemical shift and the quadrupole coupling constant on the central transition MAS lineshape. For these simulations the average C_q is 2 MHz, $\eta_q = 0$ and the isotropic chemical is 0 ppm. The Larmor frequency is 80 MHz so $A = 2343.8$ Hz. (a) No distribution, (b) Gaussian distribution of the isotropic chemical shift of FWHM = 400 Hz (5 ppm) or 0.17 A, (c) Gaussian distribution of FWHM = 0.8 MHz and (d) Gaussian distribution of both the isotropic chemical shift and C_q which are the same as in (b) and (c). ($A = (I(I+1) - 3/4)\nu_q^2/\nu_0$).

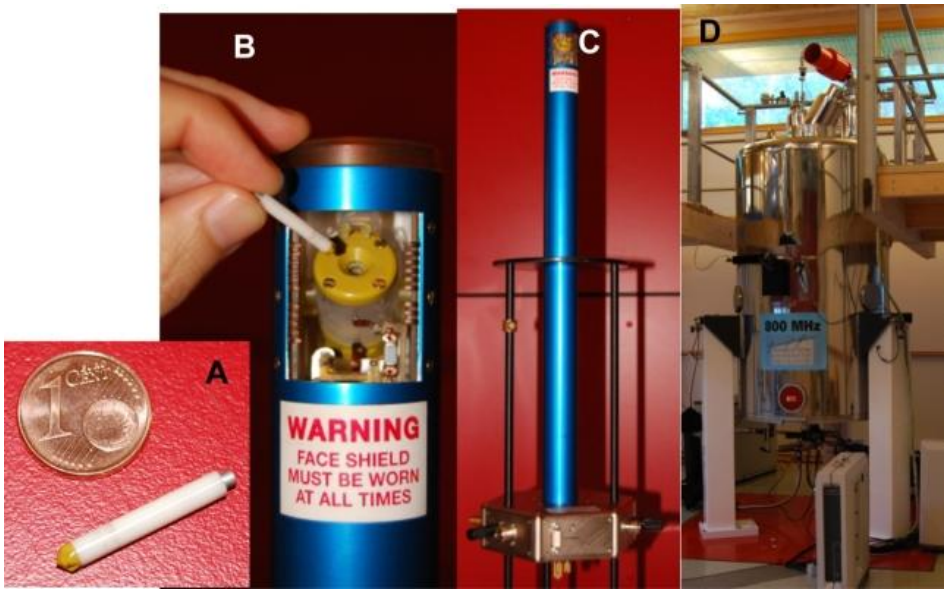
Smith & van Eck, Prog. Nucl. Magn. Reson. Spectr. 1999;34:159-201

Sondas e rotores para experimentos com MAS



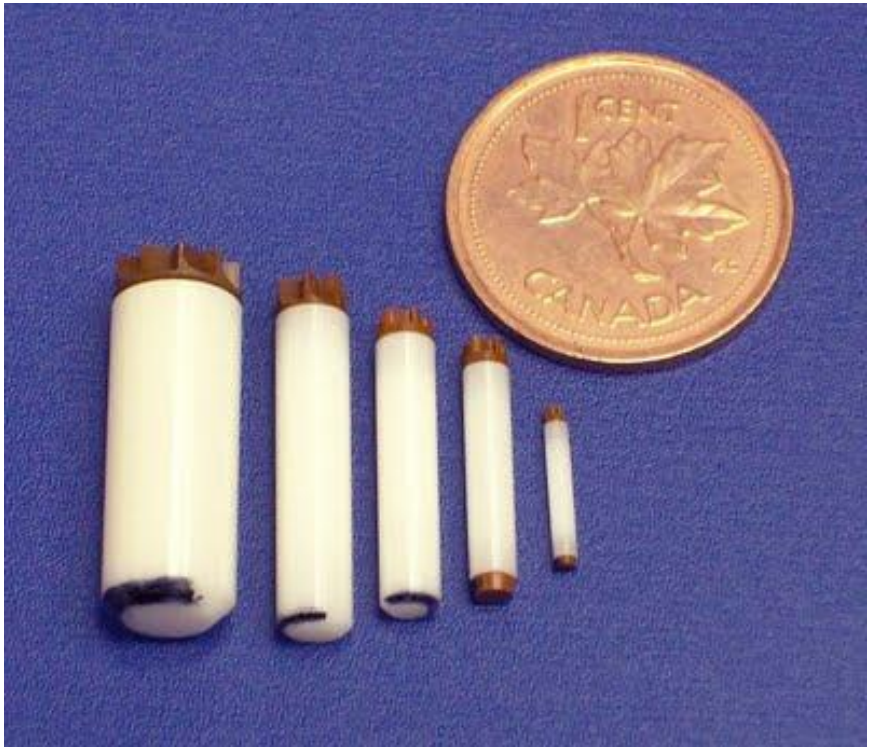
http://www.magnet.fsu.edu/education/tutorials/tools/probes/magicangle.html

Sondas e rotores para experimentos com MAS



- Rotores menores:
  - ✓ Frequências de MAS maiores.
    - 7mm: f_{MAS} < 8 kHz.
    - 2,5mm: f_{MAS} < 35 kHz.
  - ✓ Menor sensibilidade.

Sondas e rotores para experimentos com MAS

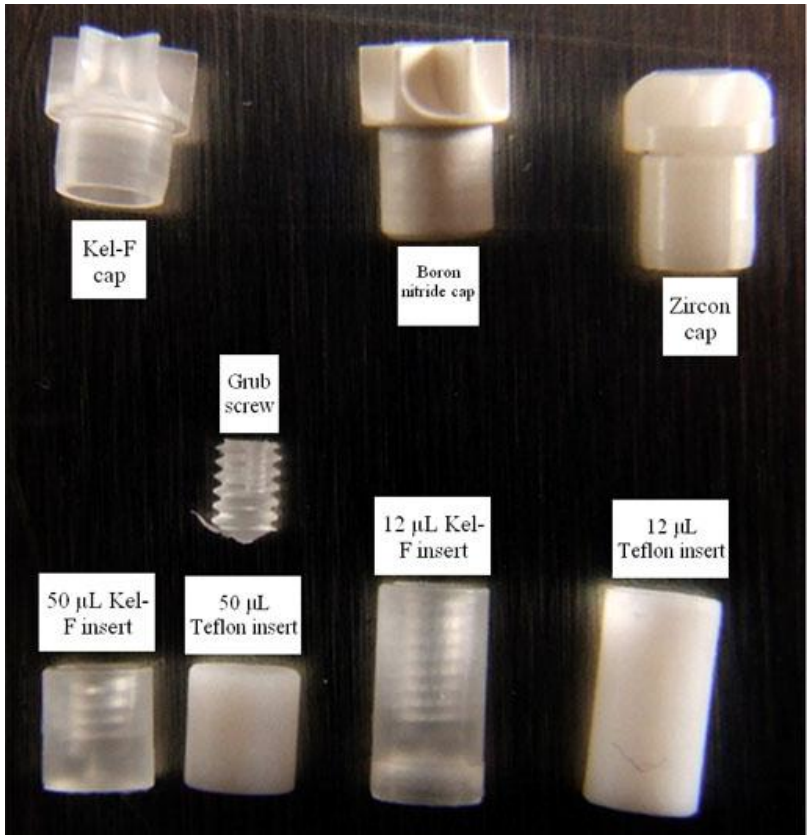


ϕ (mm): 7,0 4,0 3,2 2,5 1,3

$\nu_{rot}^{máx.}$ (kHz): 8 18 23 35 70

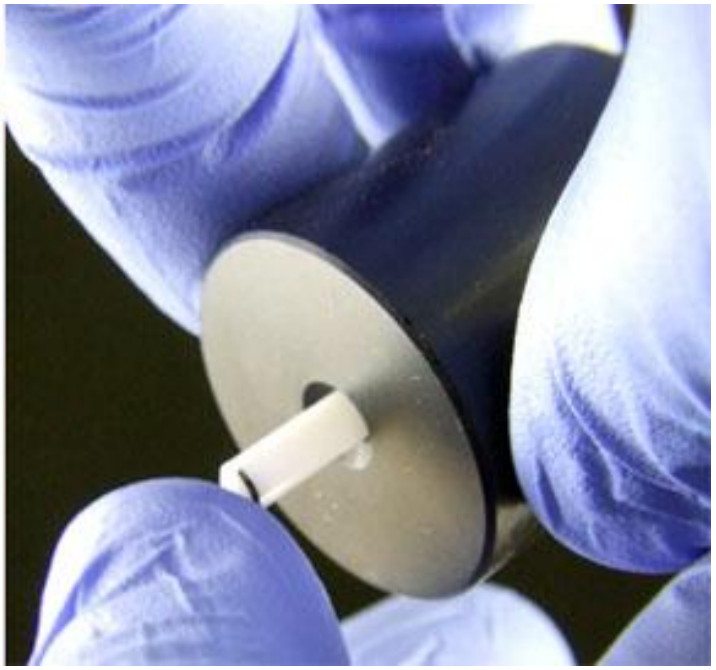
http://u-of-o-nmr-facility.blogspot.com/2008/04/how-much-sample-do-i-need-to-get-solid.html

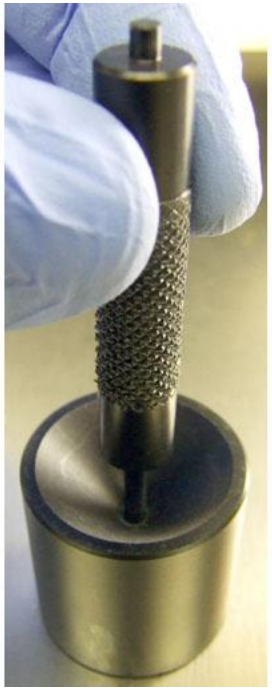
Sondas e rotores para experimentos com MAS



http://chem.ch.huji.ac.il/nmr/preparation/preparation.html

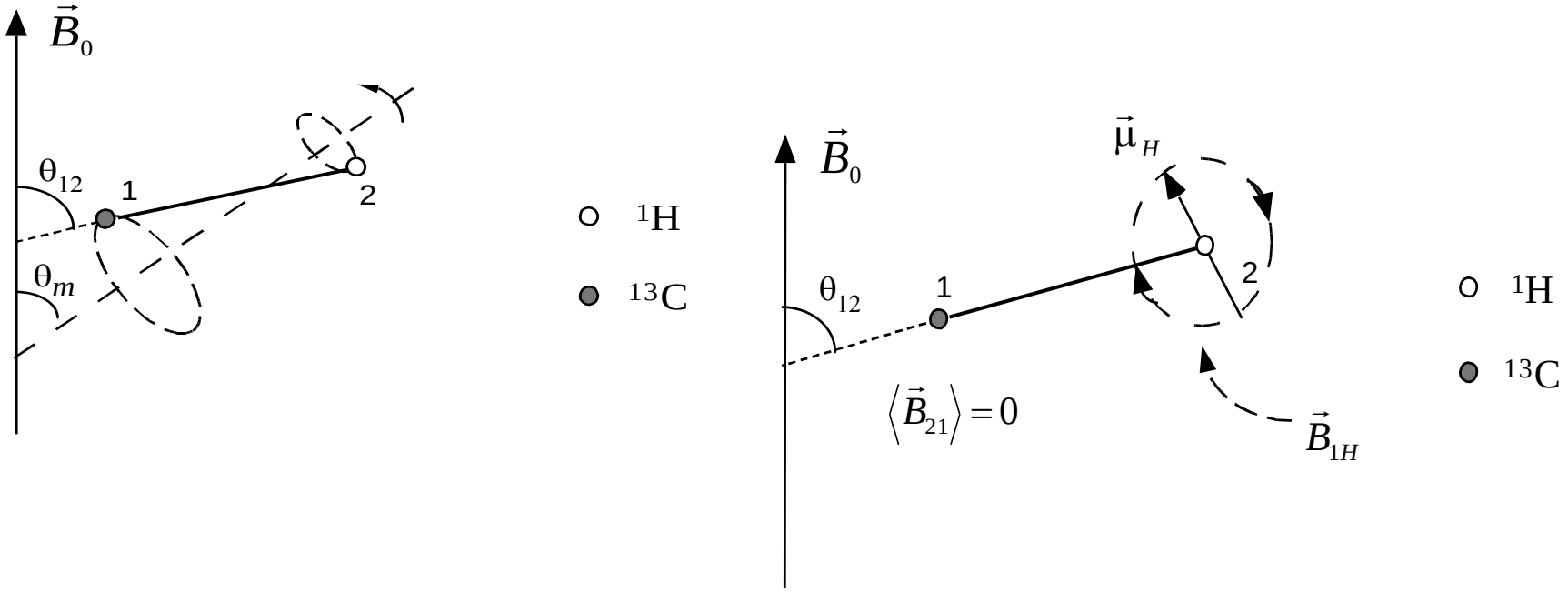
Sondas e rotores para experimentos com MAS





http://chem.ch.huji.ac.il/nmr/preparation/preparation.html

Desacoplamento dipolar heteronuclear



Ressonância dupla:

- Excitação de ^{1}H (f_{1H}) e de ^{13}C (f_{13C}).
- Detecção de ^{13}C (f_{13C}).

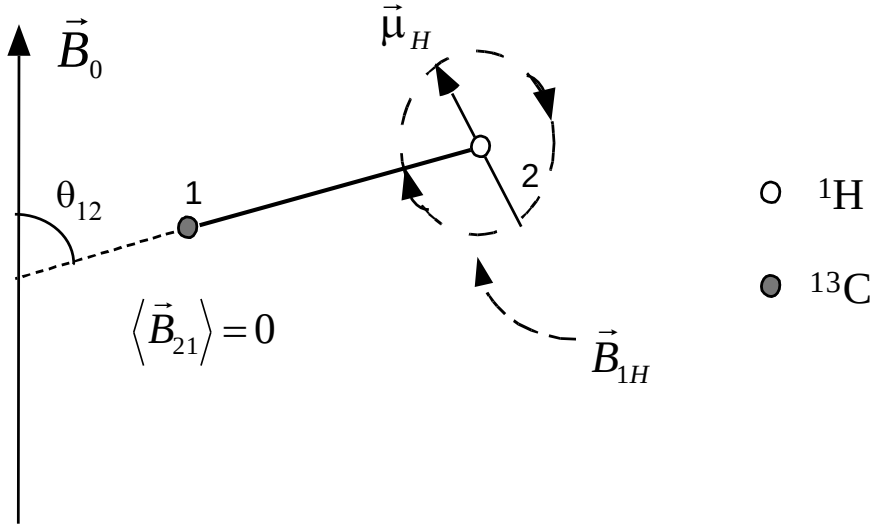
Desacoplamento dipolar heteronuclear

Eficiência do desacoplamento:

$$\gamma_H B_{1H} / 2\pi > \Delta f_{dip}$$

$$\Delta f_{dip} \sim d = \frac{\mu_0}{8\pi^2} \frac{\gamma_I \gamma_S \hbar}{r^3}$$

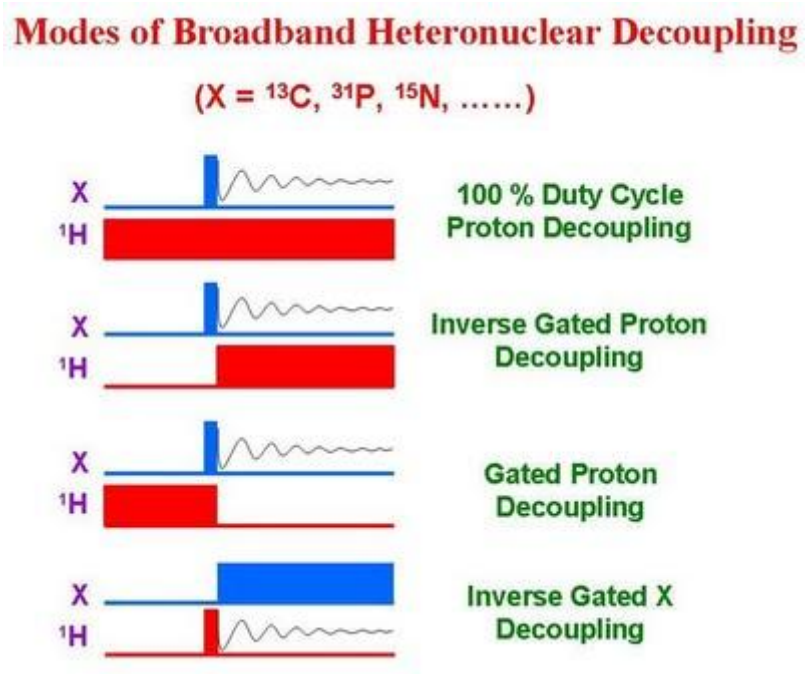
(alargamento devido ao acoplamento dipolar)



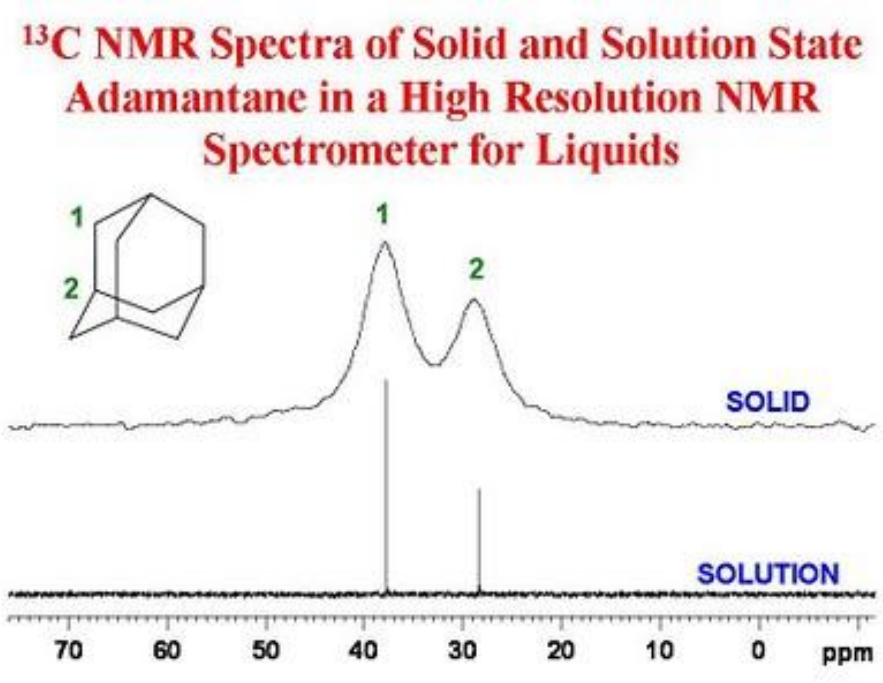
Par ^{1}H-^{13}C em grupo CH (ligação simples):

$$\Delta f_{dip} \sim 70 \text{ kHz}$$

Desacoplamento dipolar heteronuclear



Espectros de RMN de ^{13}C com desacoplamento de ^{1}H:



http://u-of-o-nmr-facility.blogspot.com/

Desacoplamento dipolar heteronuclear

Problemas com aquecimento da amostra:

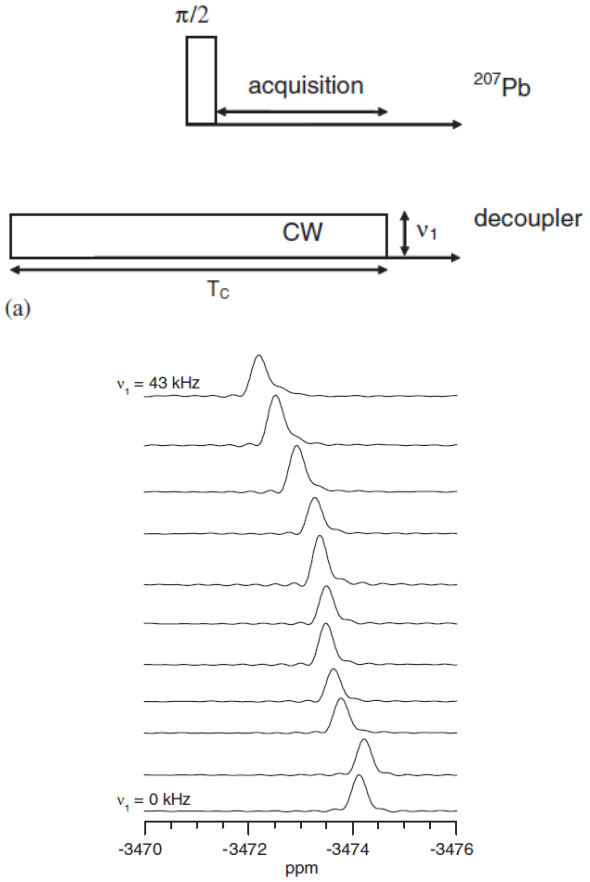


Fig. 2. ^{207}Pb one-pulse MAS NMR spectra of $Pb(NO_3)_2$ hydrated with 1% water with varying levels of CW irradiation (see Fig. 1a) at 500 MHz and using a duty cycle of 1%. The chemical shift increased according to 0.753 ppm/K, thus expressing the temperature increase due RF losses and dissipation as heat.

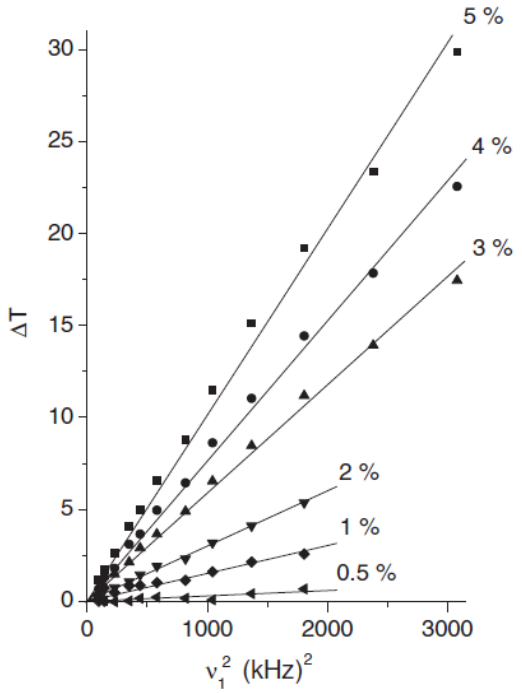


Fig. 3. Dependence of the temperature increase in $Pb(NO_3)_2$ hydrated with 1% water with the square of the CW level (ν_1) at several duty cycles (indicated in % on the plot). The monotonous dependence with the duty cycle and the quadratic dependence with the CW level established that the temperature rise was indeed associated with the conversion of RF energy into heat.

de Lacaillerie et al., Solid State Nucl. Magn. Reson. 2005;28:225.

Desacoplamento dipolar heteronuclear

Outras sequências de desacoplamento combinadas com MAS:

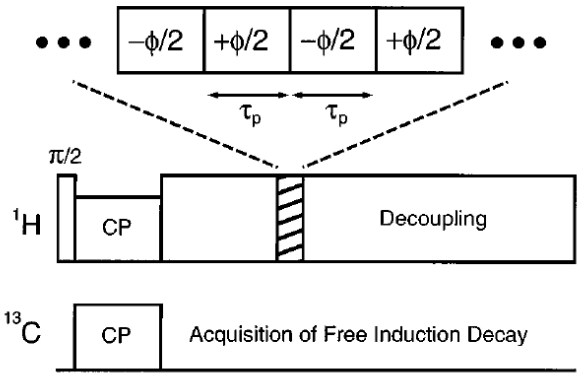


FIG. 1. Pulse sequence for the CPMAS experiment with the addition of phase modulated TPPM decoupling on the ^{1}H channel. A small hatched region of the decoupling period is expanded in order to illustrate the rapid alternation of the phase of the rf excitation between two values $-\phi/2$ and $+\phi/2$ with overall period $2\tau_p$, which is carried out throughout the acquisition of the FID.

TPPM = two pulse phase-modulation

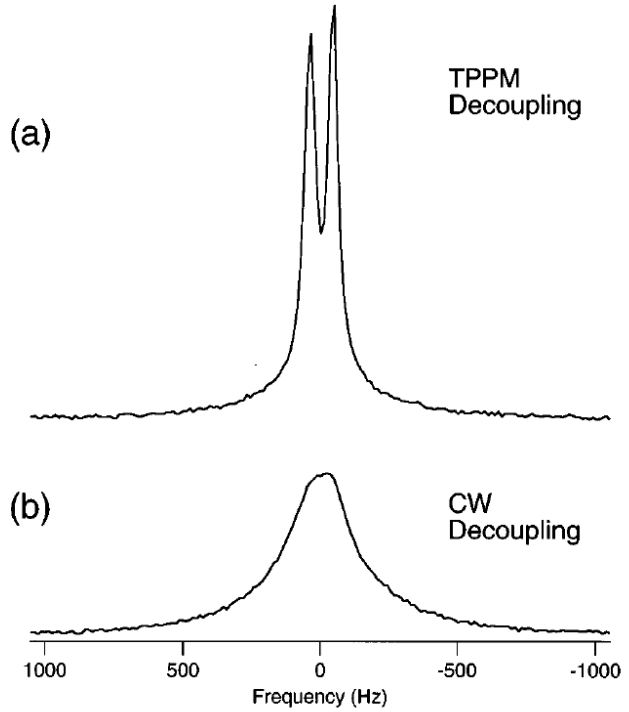


FIG. 3. The centerband of the CPMAS spectra of calcium formate at 10.7 kHz spinning frequency with (a) TPPM and (b) CW decoupling using the parameters: ϕ=75°, τ_p=7.5 μs. An rf field strength of 62.5 kHz (4.0 μs $\pi/2$ pulse length) was applied. The nonequivalent formate ions are separated by 80 Hz.

Bennett et al., J. Chem. Phys. 1995;103:6951.

Desacoplamento dipolar homonuclear

Espectroscopia com sequência de múltiplos pulsos combinada com rotação (CRAMPS):

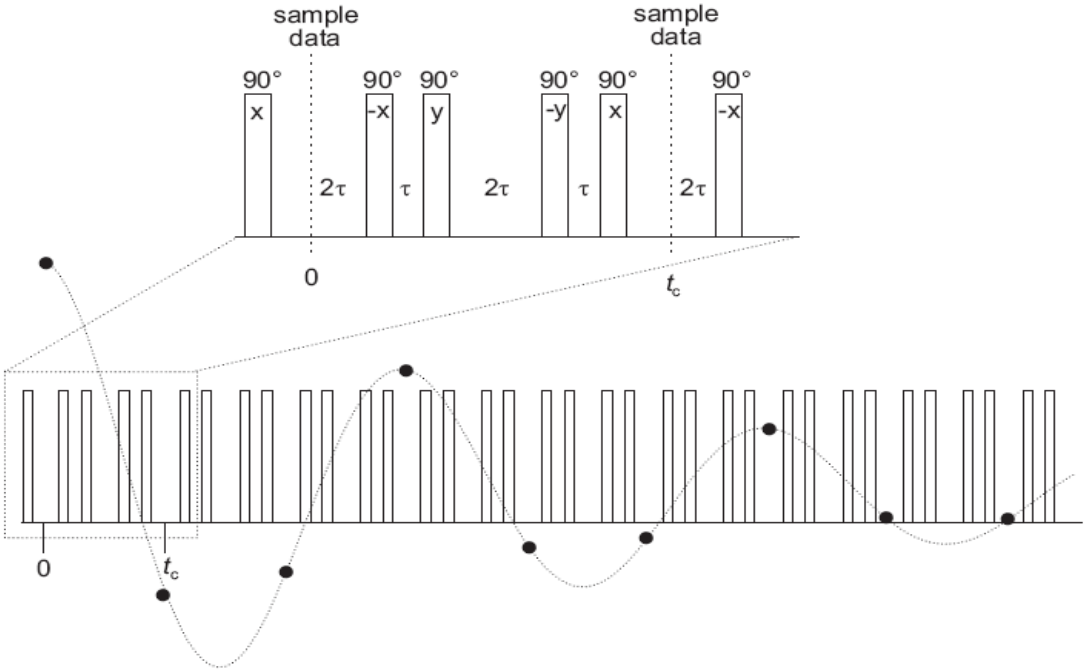


Figure 14: The WAHUHA pulse sequence for the CRAMPS experiment and the timing for data acquisition. The expanded region shows the details of the phase cycling and data sampling.

Bryce et al., Can. J. Anal. Sci. Spectr. 2001;46:46.

MAS e desacoplamento dipolar homonuclear

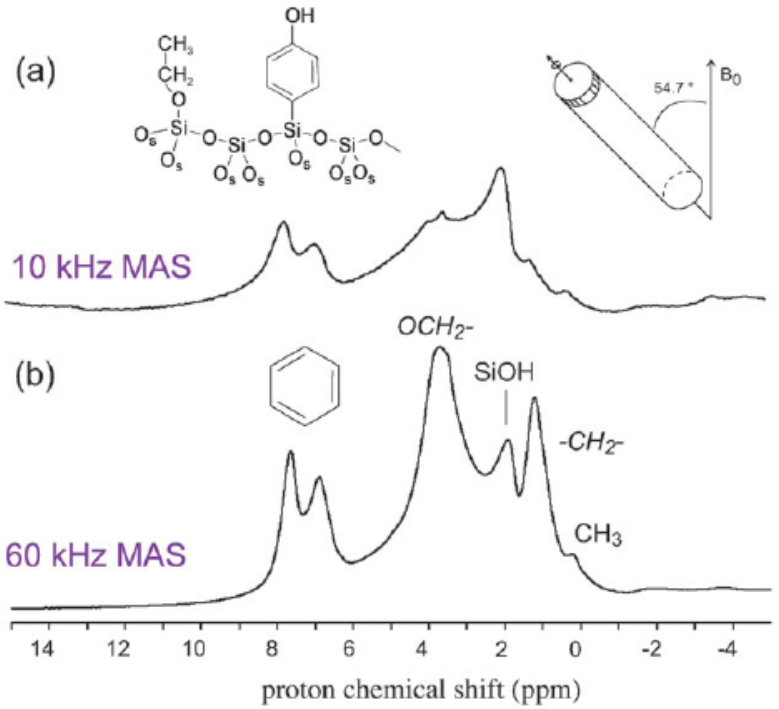


Fig. 1 One-dimensional ^{1}H spectra of an organic compound grafted inside the mesopores of a silica matrix, at 10 kHz (a) and 60 kHz MAS frequencies (resonances corresponding to surfactant chains are also observed). A total of 64 transients were recorded at a ^{1}H frequency of 900 MHz. The spectra were recorded using a 1.3 mm CPMAS probe (sample volume of 2 µL) on a Bruker Avance III spectrometer. (In collaboration with Dr C. Copéret and D. Gajan.)

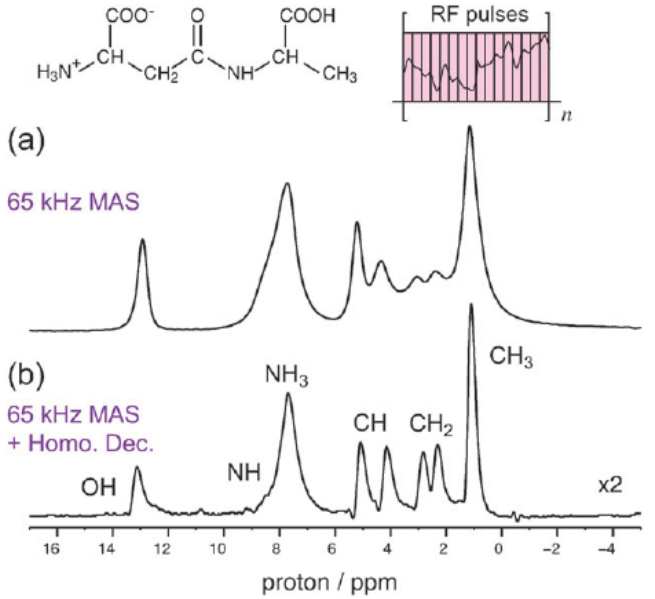
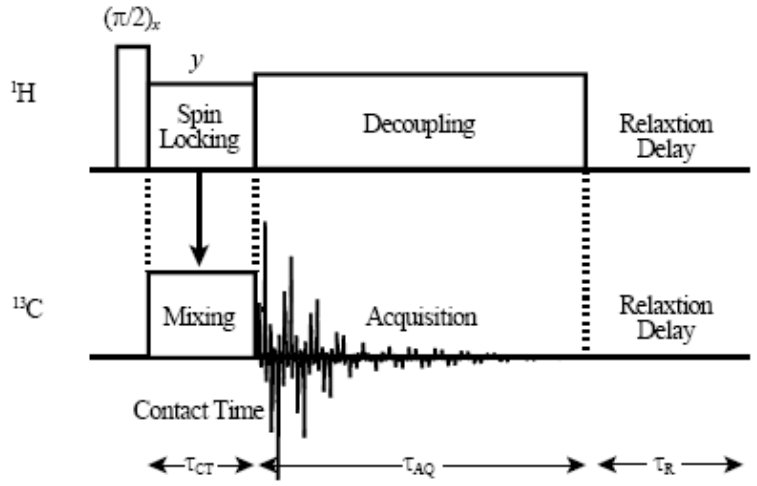


Fig. 2 One-dimensional ^{1}H spectra of the dipeptide b-L-Asp-L-Ala under MAS at 65 kHz. (a) MAS spectrum (2 transients). (b) Homonuclear-decoupled spectrum using the windowed eDUMBO-1_{22} sequence during direct acquisition (16 transients). eDUMBO-1_{22} was implemented with an RF pulse amplitude of 170 kHz. The homonuclear-decoupled spectrum shows a highly linear scaling factor (0.58) across the entire ^{1}H chemical shift range (as evaluated from the comparison between the decoupled and the MAS-only spectra). We note that windowed decoupling during acquisition compromises the overall spectral sensitivity. Reprinted from *Chem. Phys. Lett.*, 2009, **469**, E. Salager, R. S. Stein, S. Steuernagel, A. Lesage, B. Elena and L. Emsley. Enhanced sensitivity in high-resolution ^{1}H solid-state NMR spectroscopy with DUMBO dipolar decoupling under ultra-fast MAS, 336–341. Copyright 2009, with permission from Elsevier.[27]

Lesage, Phys. Chem. Chem. Phys. 2009;11:6876-6891

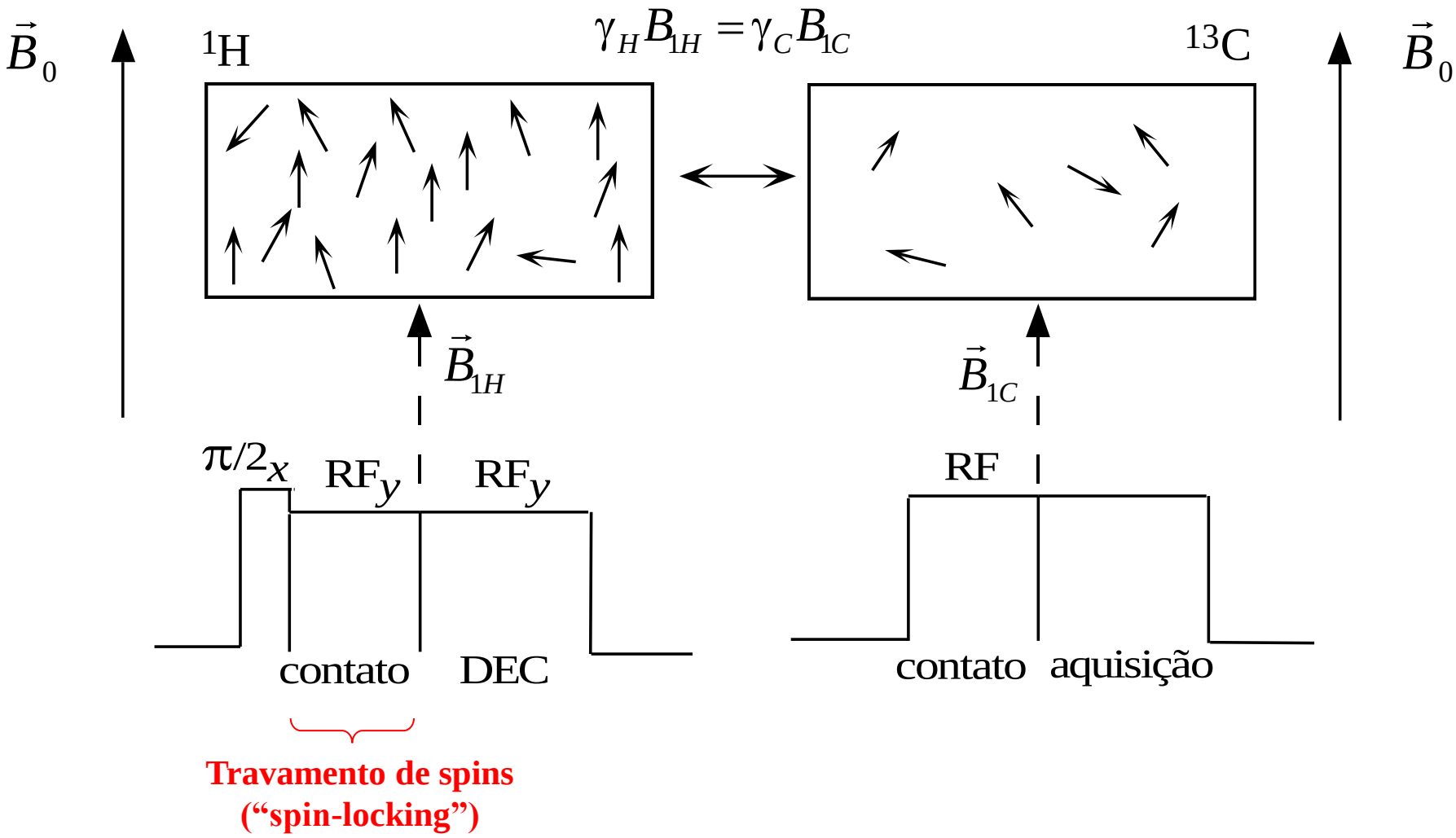
Polarização cruzada (CP)



Ressonância dupla:

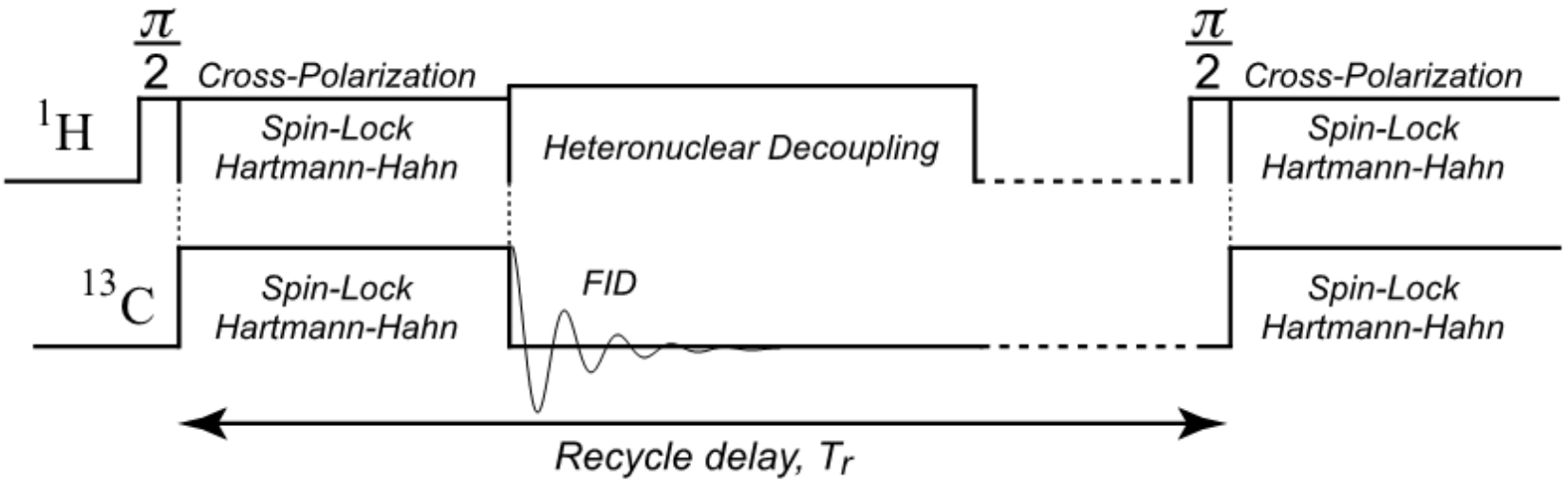
- Excitação de ^{1}H (f_{1H}) e de ^{13}C (f_{13C}).
- Detecção de ^{13}C (f_{13C}).
- Aumento do sinal de ^{13}C por um fator de no máximo $\gamma(^{1}H) / \gamma(^{13}C) \sim 4$ (por "contato").
- Redução no tempo de repetição: $T_1(^{1}H) < T_1(^{13}C)$.
- Detecção seletiva de grupos hidrogenados ("edição de espectros").

Polarização cruzada (CP)



Experimento CP/MAS

Espectroscopia de alta resolução em sólidos por RMN:



Condição de Hartmann-Hahn:

$$\gamma_H B_{1H} = \gamma_C B_{1C}$$

Schaefer & Stejskal, J. Am. Chem. Soc. 1976;98:1031

Experimento CP/MAS

Ajuste da condição de Hartmann-Hahn:

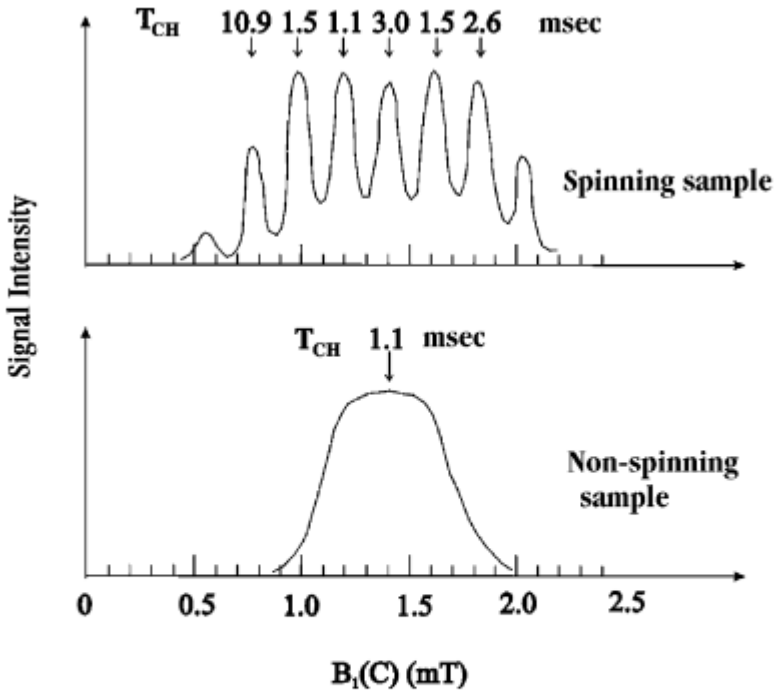


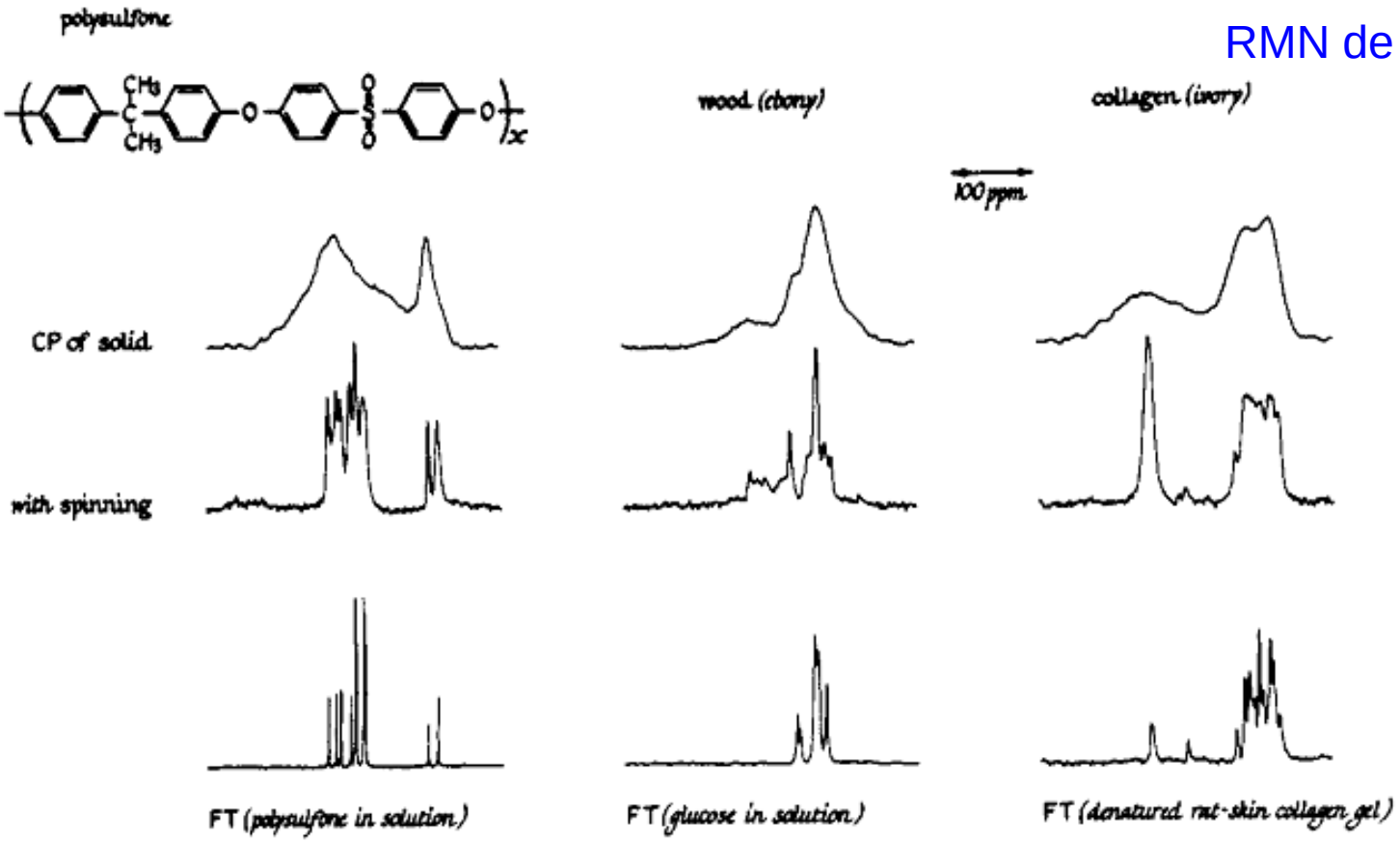
Fig. 3. Hartmann–Hahn (Ha–Ha) condition affected by fast sample rotation. The lower part of the figure shows that Ha–Ha is stable in a wide range of rf fields when samples are not spun. Upper part of the figure reports fluctuations of the Ha–Ha condition when a fast rotation is applied on the sample (from Ref. [47]).

Conte et al., Prog. Nucl. Magn. Reson. Spectr. 2004;44:215.

Experimento CP/MAS

Espectroscopia de alta resolução em sólidos por RMN:

RMN de ^{13}C



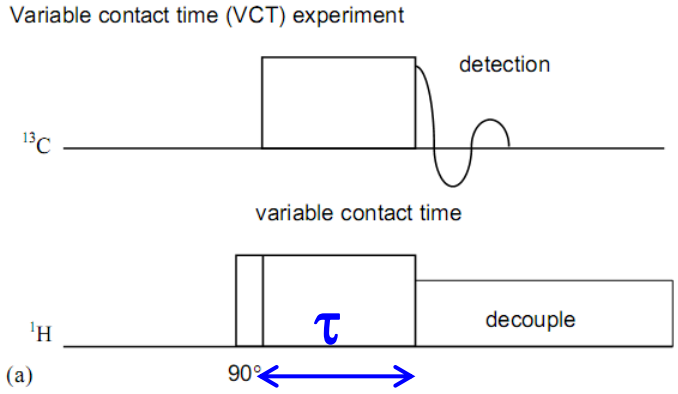
Schaefer & Stejskal, J. Am. Chem. Soc. 1976;98:1031

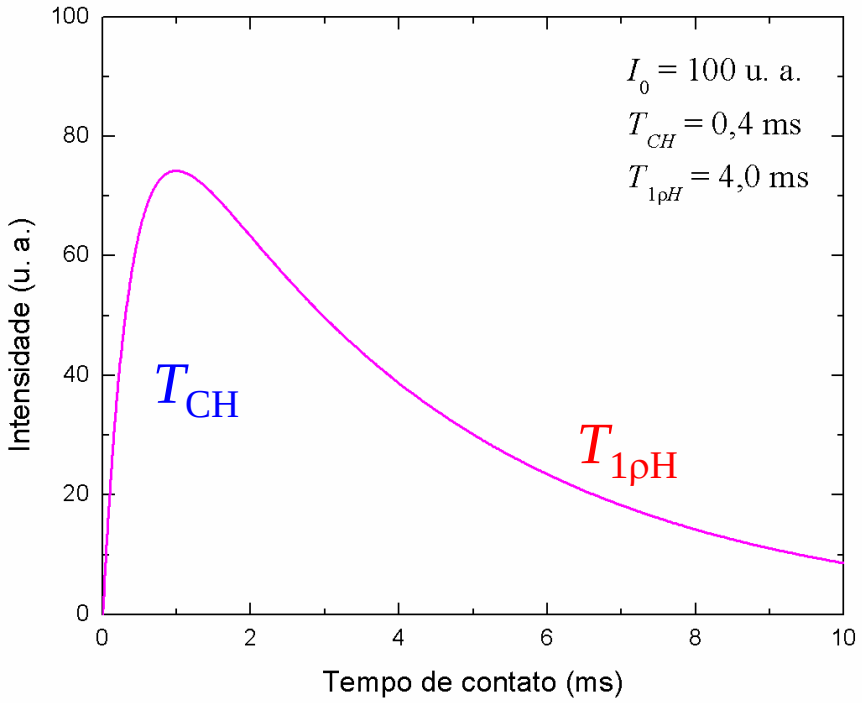
Experimento CP/MAS

Dinâmica do processo de CP:

$^{1}H \rightarrow {}^{13}C$

$$\alpha = 1 - T_{CH} / T_{1\rho H} \qquad I(\tau) = I_0 \left(\frac{1}{\alpha}\right)\left[1 - \exp\left(\frac{-\alpha\tau}{T_{CH}}\right)\right]\left(\exp\frac{-\tau}{T_{1\rho H}}\right)$$





Experimento CP/MAS

Dinâmica do processo de CP:

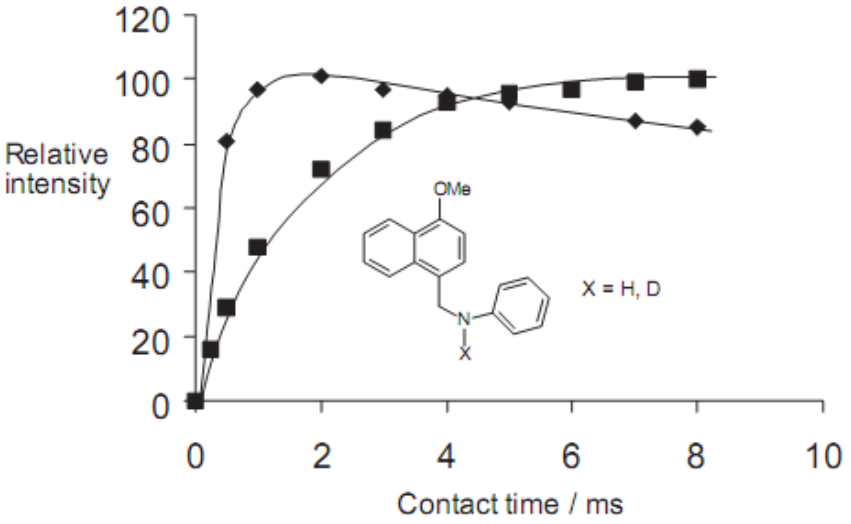


Figure 6: Plots of the ^{15}N isotropic signal intensity as a function of contact time (CP from protons) for MAS samples of normal (♦) and *N*-deuterated (■) 1-methoxy-4-(*N*-phenylamino-methyl) naphthalene.

Bryce et al., Can. J. Anal. Sci. Spectr. 2001;46:46.

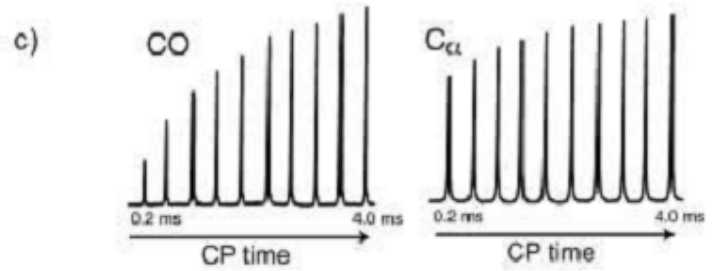


Figure 11. Hartmann–Hahn CP: a) The energy differences between the transitions of the *I* and the *S* spins can be made equal in a doubly rotating frame when the nutation frequencies on both spins are equal. b) Pulse sequence for CP of ^{13}C (*S*) nuclei by protons (*I*) with detection of the ^{13}C magnetization. c) Solid-state ^{13}C NMR spectra (125 MHz) of uniformly ^{13}C-labeled (10 %) glycine powder acquired by using the pulse sequence in b) as a function of the CP time. Because of the directly bonded H_α protons, the $^{13}C_\alpha$ nuclei are polarized more rapidly than the unprotonated carbonyl carbon nuclei.

Jerschow et al., Angew Chem. Int. Ed. 2002;41:3096.

Experimento CP/MAS

Dinâmica do processo de CP:

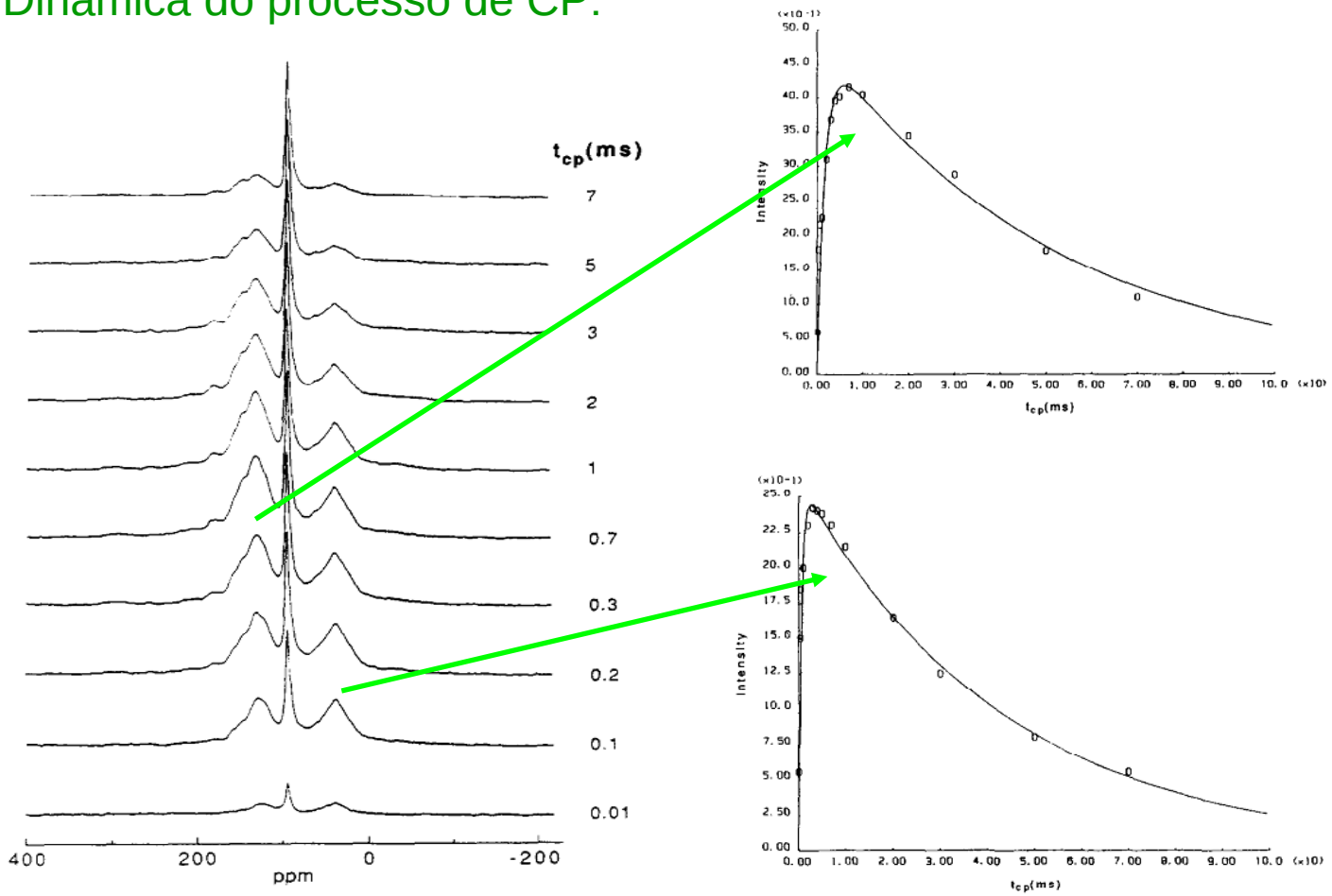


Figure 8 Variable-contact-time ^{13}C CP–MAS spectra of coal 801 as a function of CP contact time t_{CP}; repetition delay 0.7 s

$$T_{CH}^{arom} = 0,19\ ms$$

$$T_{1\rho H}^{arom} = 5,3\ ms$$

$$T_{CH}^{alif} = 0,053\ ms$$

$$T_{1\rho H}^{alif} = 4,5\ ms$$

Pan & Maciel, Fuel 1993;72:451

Experimento CP/MAS

Problemas para análise quantitativa:

CP (polarização cruzada) *versus*

SPE (polarização direta com pulso simples)

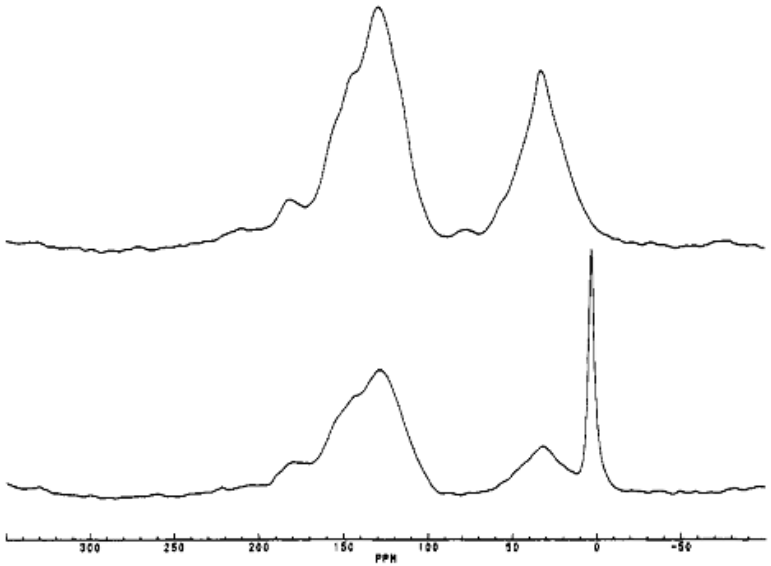


Figure 3. Comparison of 25-MHz spectra of North Dakota lignite obtained by (a, upper) CP with a contact time of 1 ms and (b, lower) SPE.

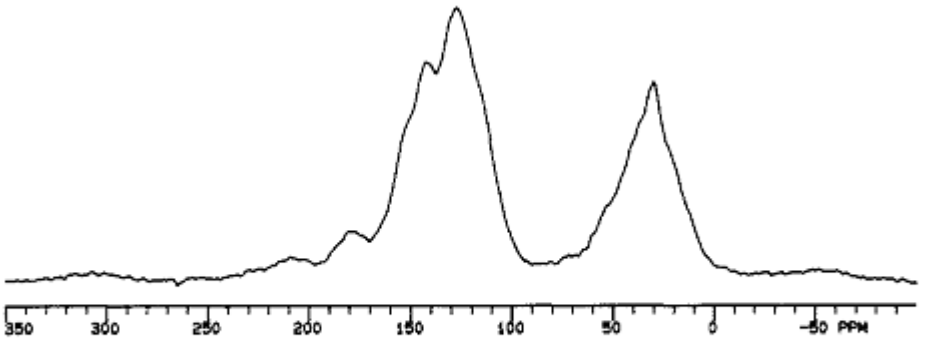


Figure 4. 75-MHz spectrum of North Dakota lignite obtained by CP with a contact time of 0.7 ms.

Franz et al., Energy Fuels 1992;6:598.

Experimento CP/MAS

Problemas para análise quantitativa:

CP (polarização cruzada) *versus*

SPE (polarização direta com pulso simples)

Table I. Aromaticity Values Derived from CP Spectra of the Argonne Coals[a]

sample	% dmmf C	aromaticity (total sp^2 carbon) 75 MHz	25 MHz this study	25 MHz ref 7	25 MHz ref 8
North Dakota lignite	73	0.67	0.67	0.66	0.70
Wyodak subbit.	75	0.54	0.63	0.63	0.65
Illinois No. 6	80	0.73	0.72	0.72	0.72
Pittsburgh No. 8	83	0.79	0.72	0.72	0.74
Blind Canyon	81	0.67	0.63	0.65	0.67
Lewis-Stockton	84	0.77	0.71	0.75	0.75
Upper Freeport	88	0.78	0.80	0.81	0.82
Pocahontas	91	0.86	0.86	0.86	0.86

[a] At low field, values from fitting aromatic carbon band to two components for T_{CH} and $T_{1\rho}$ which gave much better fits.

Table II. Aromaticity Values Derived from SPE Spectra of the Argonne Coals

sample	% dmmf C	aromaticity (all sp^2 carbon) 75 MHz	25 MHz this study	25 MHz ref 8[a]	% of C obsd at 25 MHz[d]
North Dakota lignite	73	0.77	0.76	0.74	95
Wyodak subbit.	75	0.76	0.75	0.66	95
Illinois No. 6	80	0.72	0.75	0.72	85
			0.75[b,c]		100[b]
Pittsburgh No. 8	83	0.75	0.75	0.75	90
Blind Canyon	81	0.67	0.67	0.68	75
Lewis-Stockton	84	0.77	0.78	0.71	75
Upper Freeport	88	0.80	0.81	0.83	75
			0.84[c]		90[c]
Pocahontas	91	0.89	0.90	0.89	90

[a] Initial samples. [b] = 100 s delay. [c] After demineralization. [d] This study; ±5%.

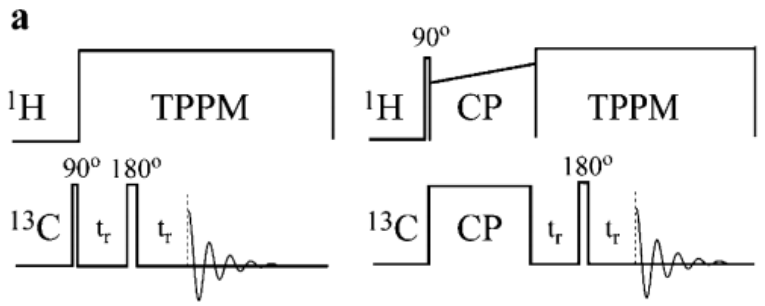
Franz et al., Energy Fuels 1992;6:598.

Experimento CP/MAS

Problemas para análise quantitativa:

CP (polarização cruzada) *versus*

SPE (polarização direta com pulso simples)



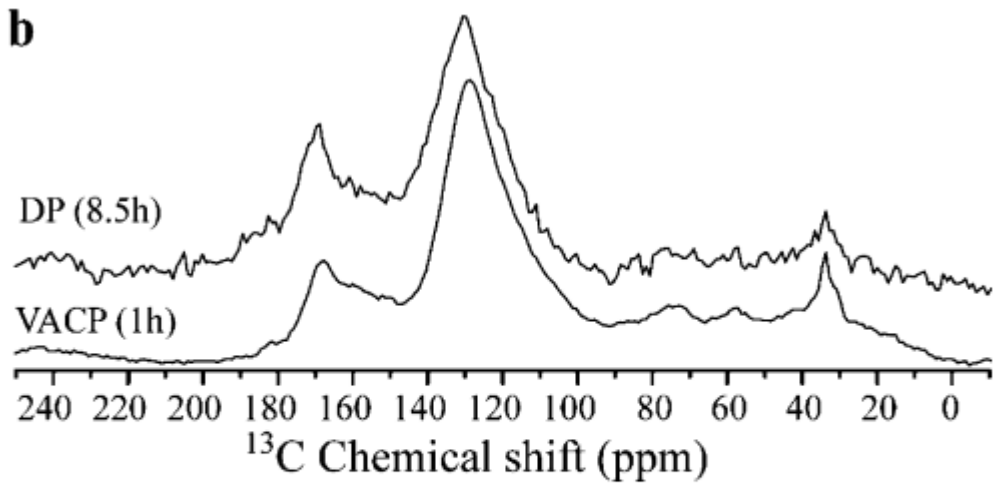
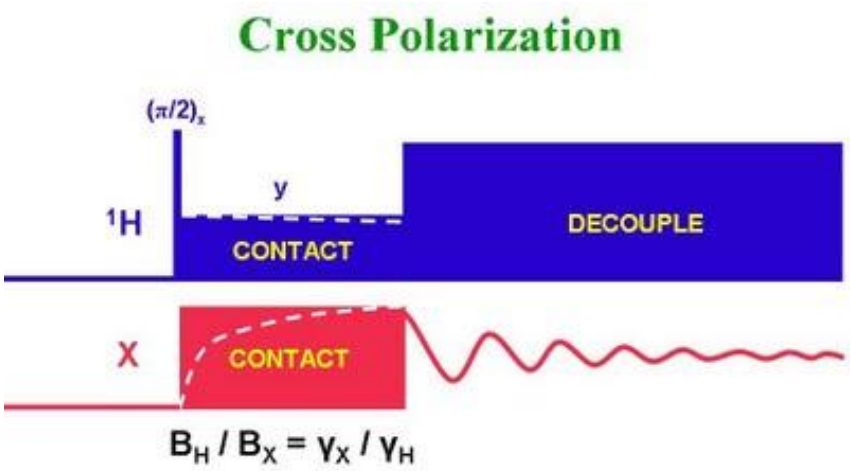


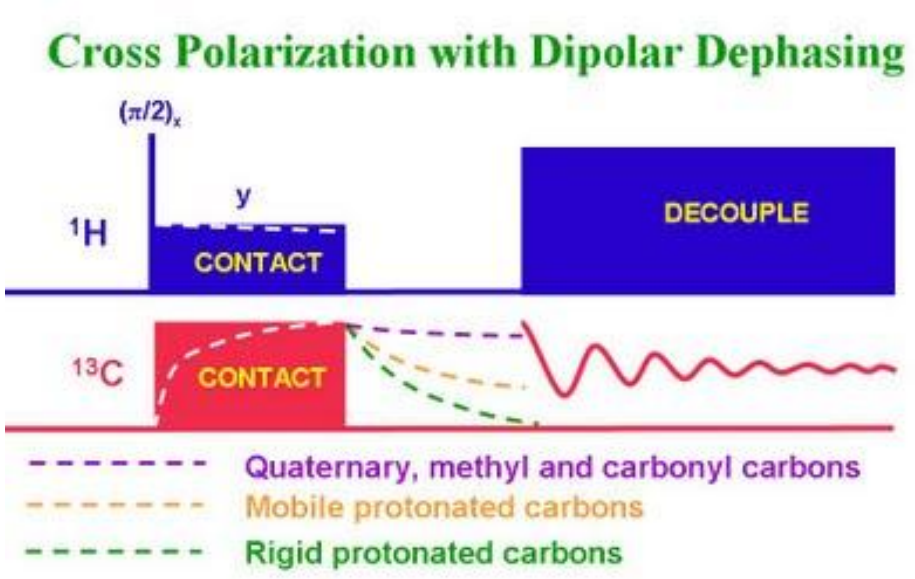
Fig. 1 DP/MAS (*left*) and CP/MAS (*right*) pulse sequences with Hahn echo acquisition (**a**); DP/MAS (12 kHz; 1,024 scans) and VACP/MAS (12 kHz; 8,192 scans) spectra of a HA sample extracted from an area rich in BC (**b**)

Novotny et al., Naturwissenschaften 2006;93:447

Polarização cruzada (CP) com defasamento dipolar



Opella & Frey, J. Am. Chem. Soc. 1979;101:5854



http://u-of-o-nmr-facility.blogspot.com

Polarização cruzada (CP) com defasamento dipolar

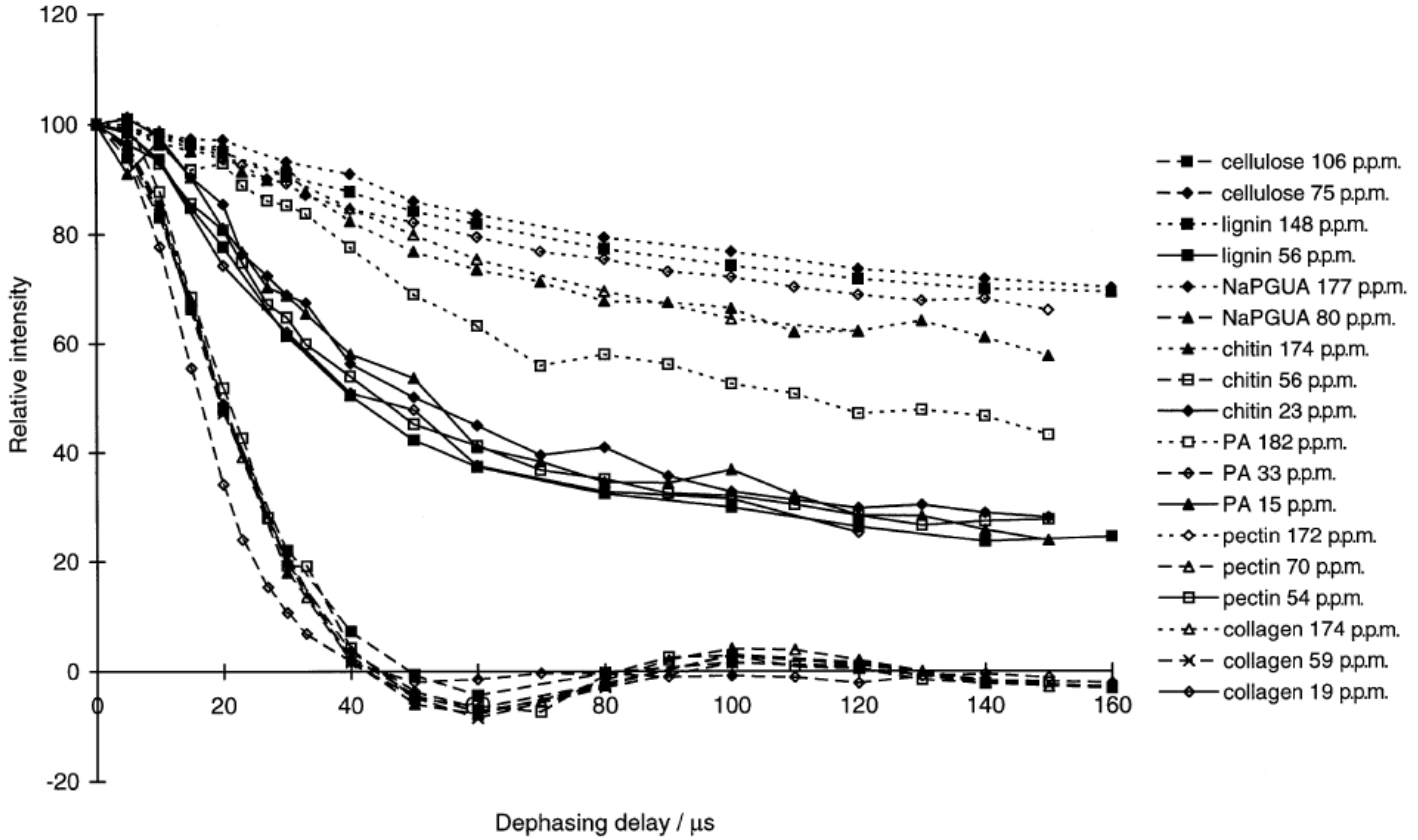


Figure 2 Plot of I/I_0 (signal intensity relative to zero dipolar dephasing delay resonance intensity) against dipolar dephasing delay for a selection of model system resonances; curves for non-protonated ^{13}C resonances represented by short dashes, curves for non-methyl protonated ^{13}C resonances represented by long dashes, curves for methyl ^{13}C resonances represented by solid lines. NaPGUA, sodium polygalacturonate; PA, palmitic acid.

Smernik & Oades, Eur. J. Soil Sci. 2001;52:103.

Edição espectral

Combinações de CP, defasamento dipolar, inversão-recuperação, etc.

RMN de ^{13}C em carvão mineral

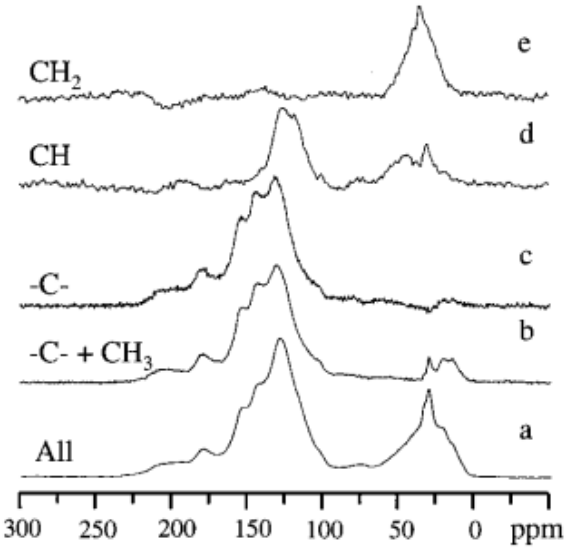


Figure 1. The five experimental ^{13}C CP/MAS spectral editing spectra obtained on PSOC-1488 (~260 mg). (a) The spectrum containing all the carbons, (b) C + CH_3 only spectrum, (c) C only spectrum, (d) CH only spectrum, and (e) CH_2 only spectrum. The accumulation numbers are (a) 20,000, (b) 20,000, (c) 40,000, (d) 20,000 for both the (+) and the (−) sequences (d) and 20,000 for both the (+) and the (−) sequences (e). The so-called (+) and (−) sequences are detailed in ref 13.

Hu et al., Energy Fuels 2001;15:14

Edição espectral

Combinações de CP, defasamento dipolar, inversão-recuperação, etc.

RMN de ^{13}C em carbono amorfo

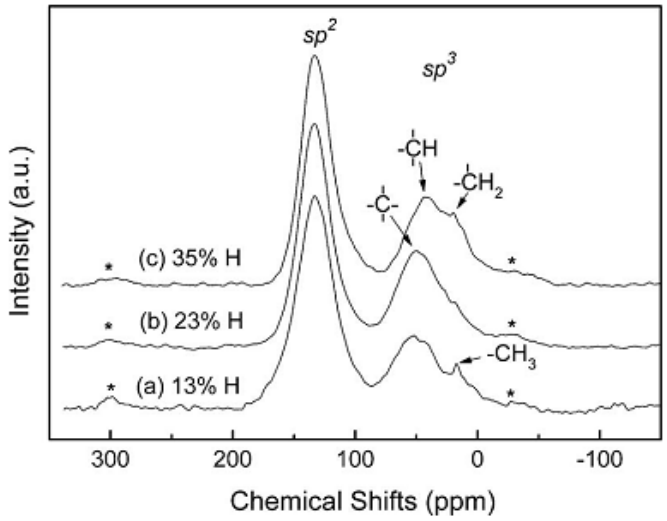


FIG. 1. ^{13}C SP-MAS NMR spectra with dipolar decoupling of (a) H13, (b) H23, and (c) H35 samples at 12.0 kHz. The locations of the various chemical shifts of the groups comprising the sp^3 region, as determined by spectral editing methods, are indicated by arrows. Asterisks indicate spinning sidebands.

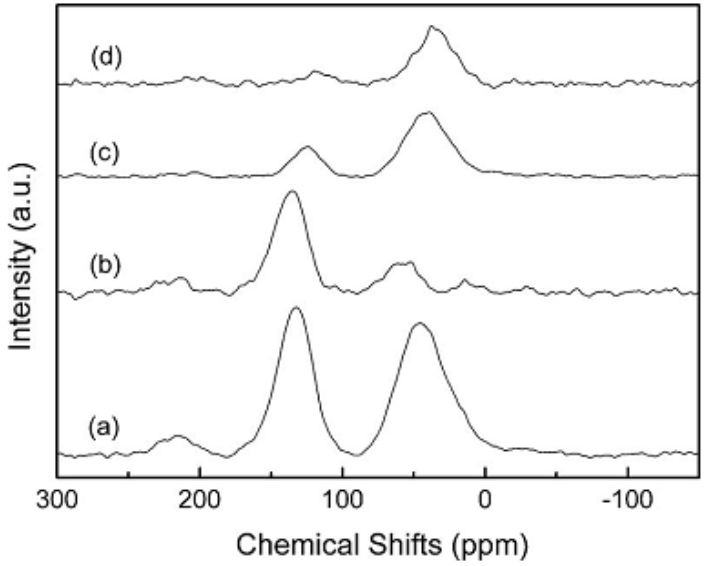
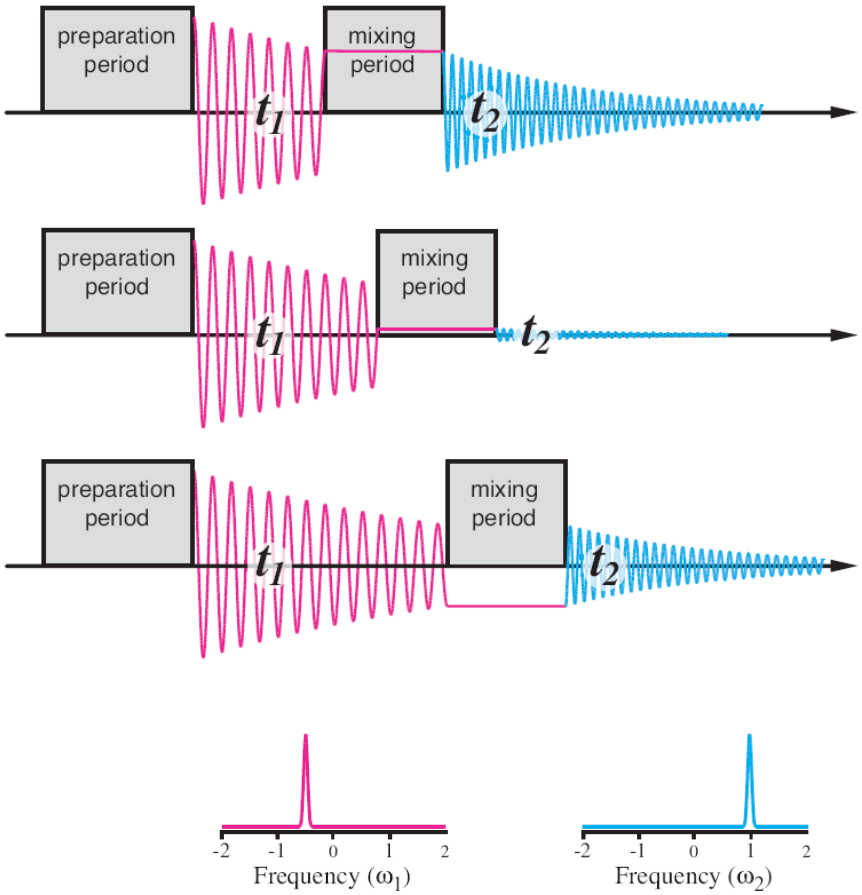
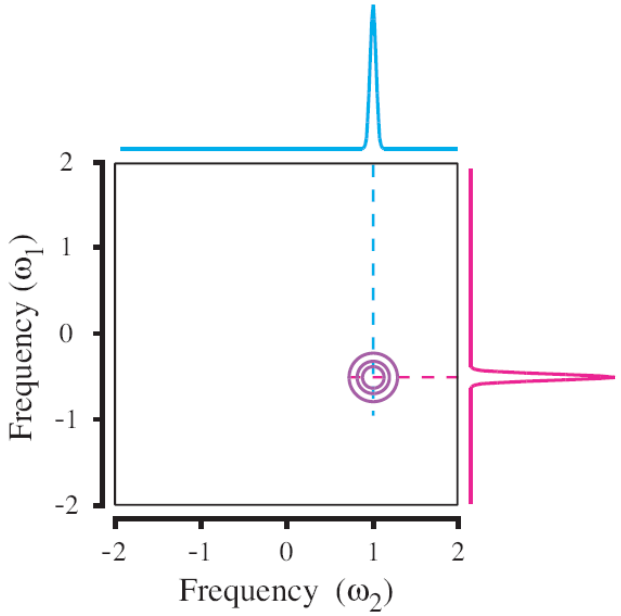


FIG. 2. ^{13}C CP-MAS NMR subspectra of H23 sample obtained from spectral editing techniques: (a) spectrum from long CP, (b) spectrum obtained by subtracting a scaled short CP spectrum from a long CP spectrum, (c) spectrum obtained by subtracting a scaled long CP spectrum with depolarization from a short CP spectrum, and (d) spectrum obtained from short CP with PI.

Cho et al., J. Appl. Phys. 2008;104:013531

RMN multidimensional





Espectros 2D de correlação

http://grandinetti.org/Teaching/Chem824/Notes

Métodos de RMN 2D em sólidos

Correlação heteronuclear (HETCOR):

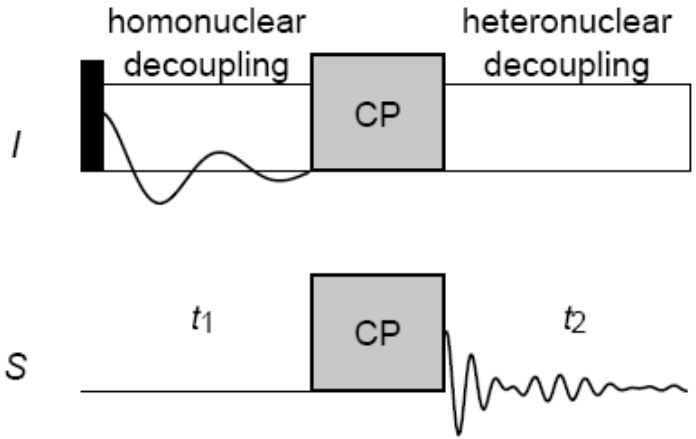


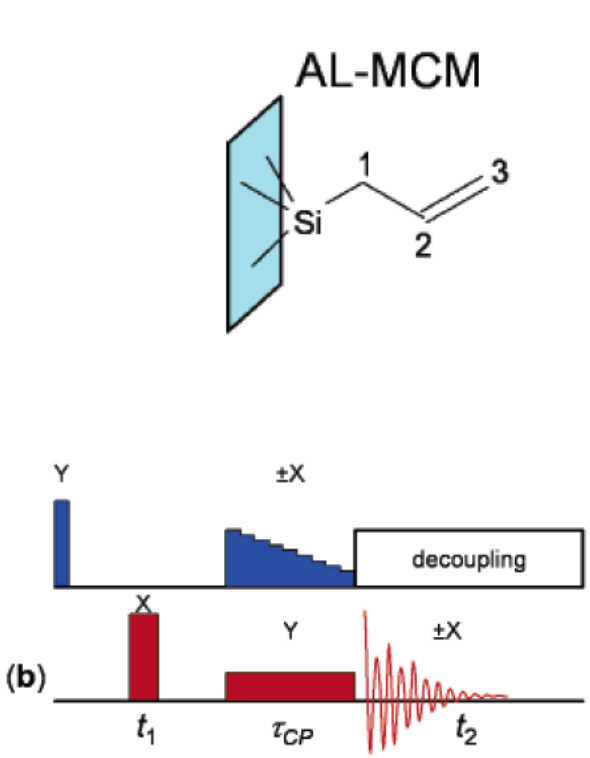
Figure 17. Principle of the HETCOR experiment: The pulse sequence is identical to that of the WISE experiment, except for the incorporation of homonuclear dipolar decoupling in the indirect dimension. Heteronuclear decoupling of the *S* spins can also be incorporated into the indirect dimension.

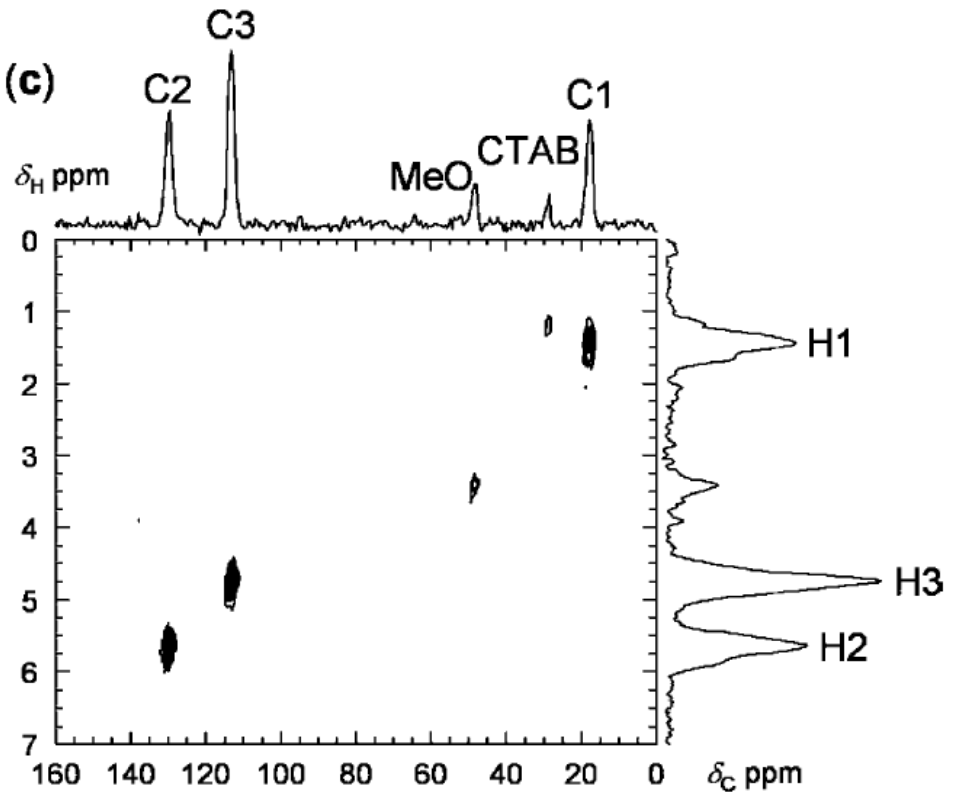
WISE = “wideline separation”

Jerschow et al., Angew Chem. Int. Ed. 2002;41:3096.

Métodos de RMN 2D em sólidos

Correlação heteronuclear (HETCOR):

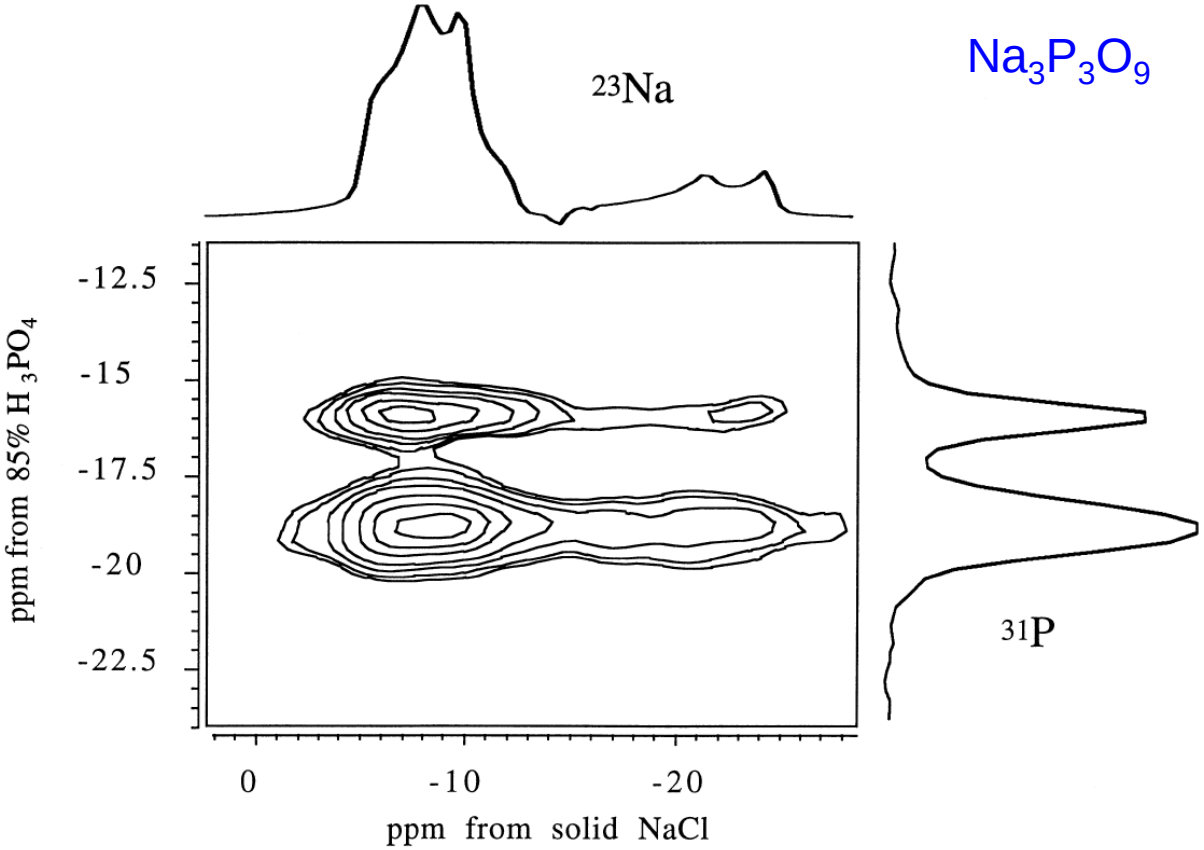




Trebosc et al., J. Am. Chem. Soc. 2005;127:7587.

Métodos de RMN 2D em sólidos

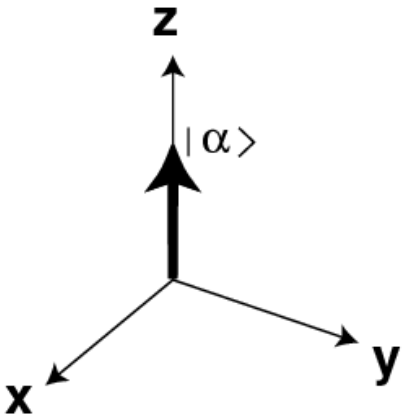
Correlação heteronuclear (HETCOR):

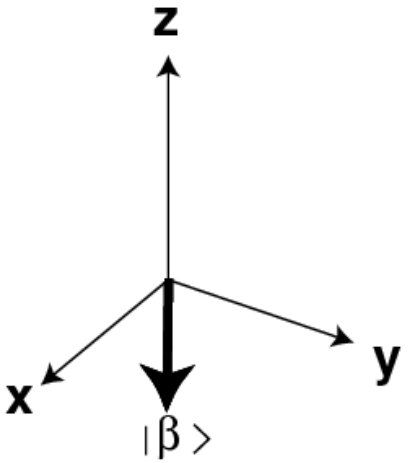


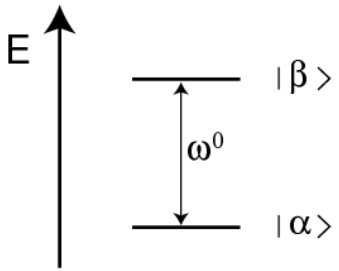
Wang et al., J. Magn. Reson. 1997;125:364.

Dinâmica de spins em experimentos de RMN

Partícula com spin 1/2 em um campo magnético:







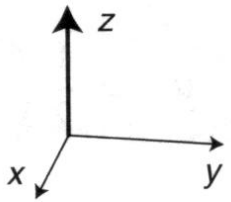
$$I_z|\alpha\rangle = +\tfrac{1}{2}|\alpha\rangle \qquad I_z|\beta\rangle = -\tfrac{1}{2}|\beta\rangle$$

"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

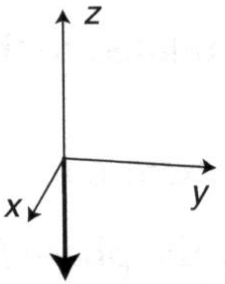
Dinâmica de spins em experimentos de RMN

Partícula com spin 1/2 em um campo magnético:

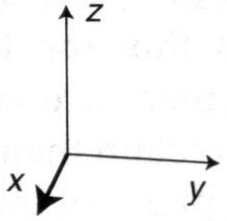
$$|\alpha> = \begin{pmatrix}1\\0\end{pmatrix} =$$



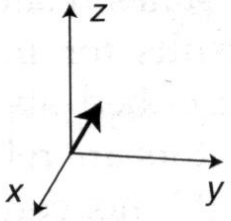
$$|\beta> = \begin{pmatrix}0\\1\end{pmatrix} =$$



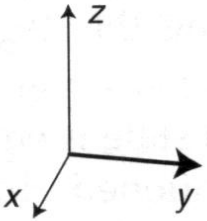
$$|+x> = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} =$$



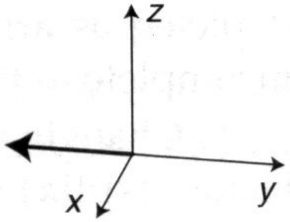
$$|-x> = \frac{1}{\sqrt{2}}\begin{pmatrix}-i\\+i\end{pmatrix} =$$



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



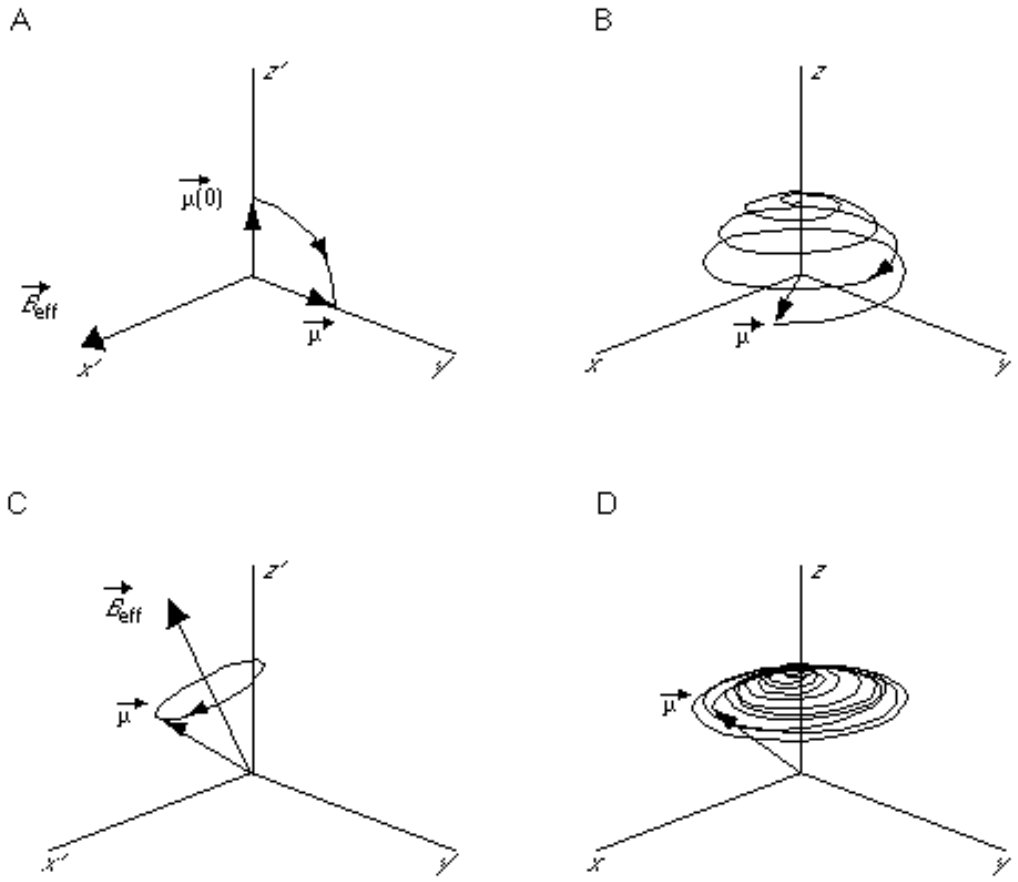
$$|-y> = \frac{1}{2}\begin{pmatrix}1+i\\1-i\end{pmatrix} =$$



"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Dinâmica de spins em experimentos de RMN

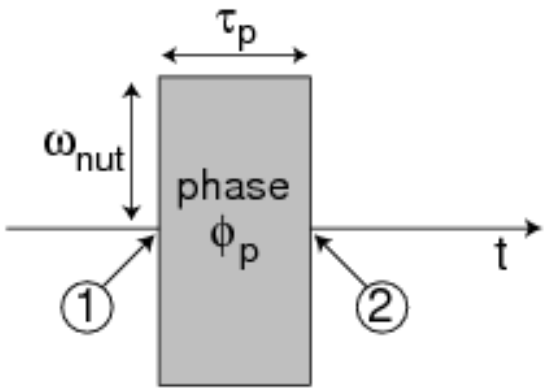
Pulsos de RF – descrição no sistema girante de coordenadas:

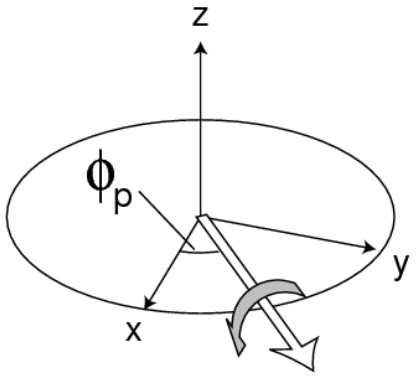


http://www.currentprotocols.com/protocol/mib0102

Dinâmica de spins em experimentos de RMN

Pulsos de RF – matrizes de rotação:





$$\left|\psi\right\rangle_2 = R_{\phi_P}(\theta)\left|\psi\right\rangle_1$$

$$R_{\phi_P}(\theta) = \begin{pmatrix} \cos\tfrac{1}{2}\theta & -i\,\mathrm{sen}\,\tfrac{1}{2}\theta\, e^{-i\phi_P} \\ -i\,\mathrm{sen}\,\tfrac{1}{2}\theta\, e^{-i\phi_P} & \cos\tfrac{1}{2}\theta \end{pmatrix}$$

$$\theta = \gamma B_1 t_P$$

(ângulo de nutação)

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

(frequência de nutação)

"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Dinâmica de spins em experimentos de RMN

Pulsos de RF – matrizes de rotação:

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

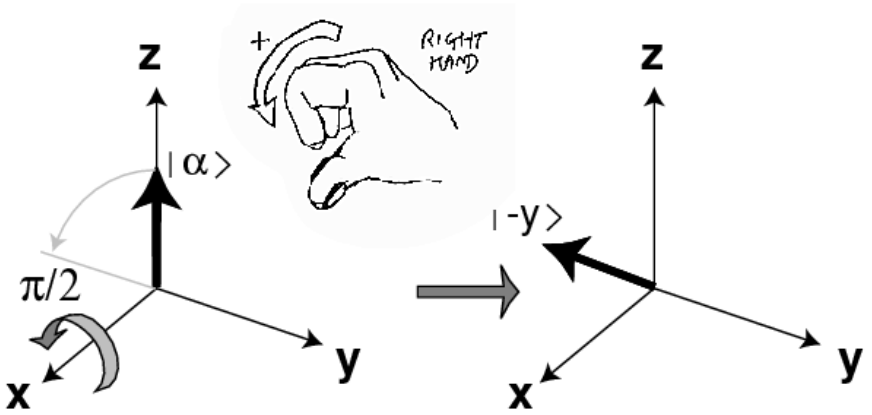
$$\theta = \gamma B_1 t_P$$

(ângulo de nutação)

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

***Exemplo* 1**:

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



"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Dinâmica de spins em experimentos de RMN

Pulsos de RF – matrizes de rotação:

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

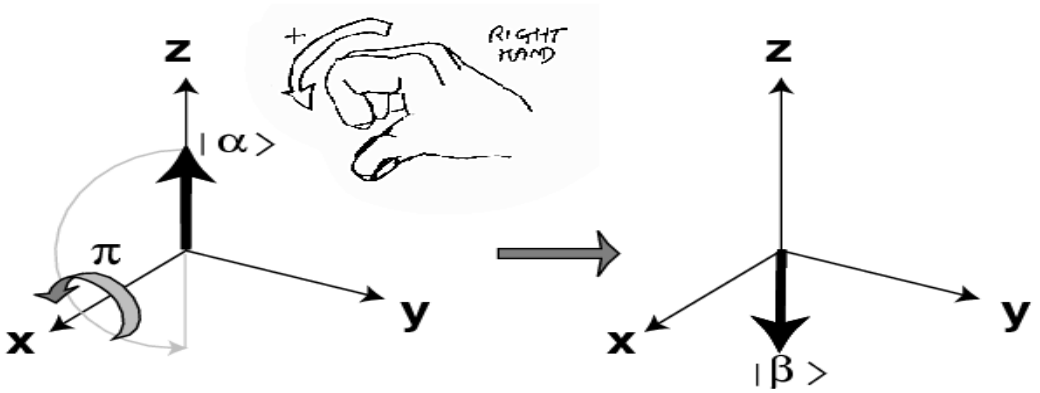
$$\theta = \gamma B_1 t_P$$

(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:

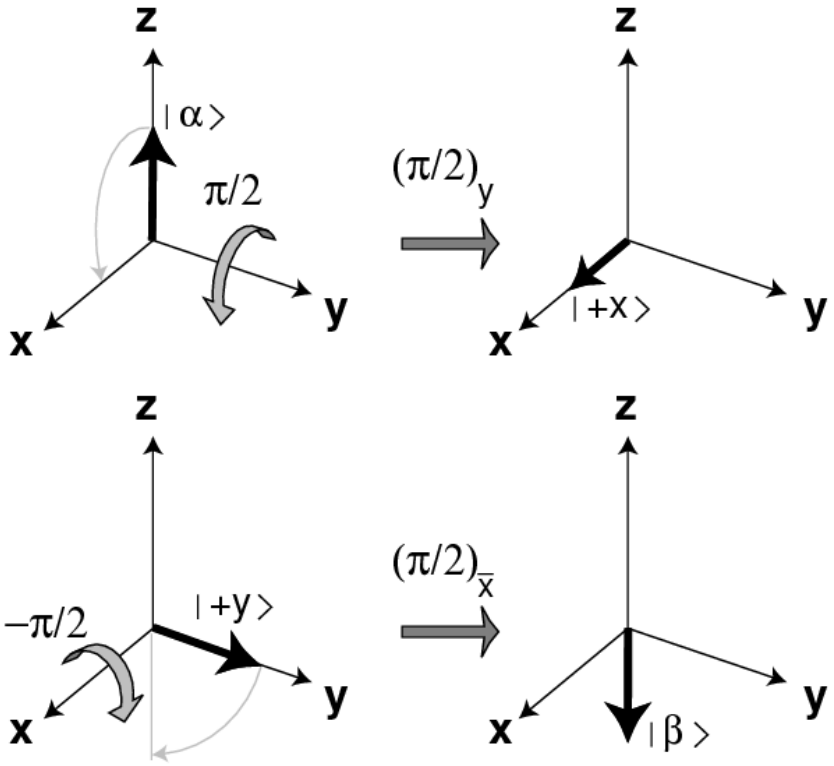
Pulso π na direção *x* atuando sobre estado inicial com spin na direção *z*:



"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Dinâmica de spins em experimentos de RMN

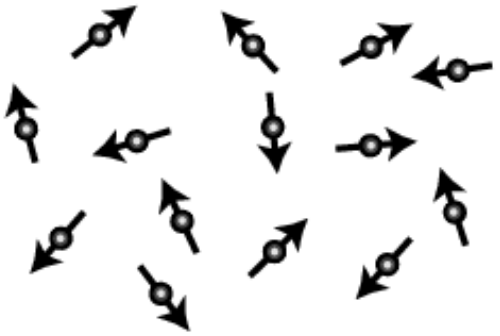
Pulsos de RF – matrizes de rotação:



"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Dinâmica de spins em experimentos de RMN

"Ensemble" de partículas com spin 1/2 em um campo magnético:



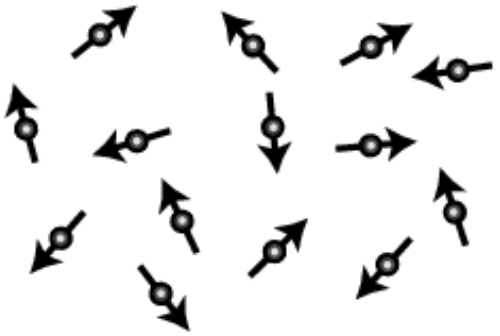
Estado de um spin: $|\psi\rangle = \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}$

Matriz densidade para um spin: $|\psi\rangle\langle\psi| = \begin{pmatrix} c_\alpha c_\alpha^* & c_\alpha c_\beta^* \\ c_\beta c_\alpha^* & c_\beta c_\beta^* \end{pmatrix}$

"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Dinâmica de spins em experimentos de RMN

"Ensemble" de partículas com spin 1/2 em um campo magnético:



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: $$\langle A \rangle = \mathrm{Tr}\{\rho A\}$$

"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Dinâmica de spins em experimentos de RMN

Formalismo do operador densidade:

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

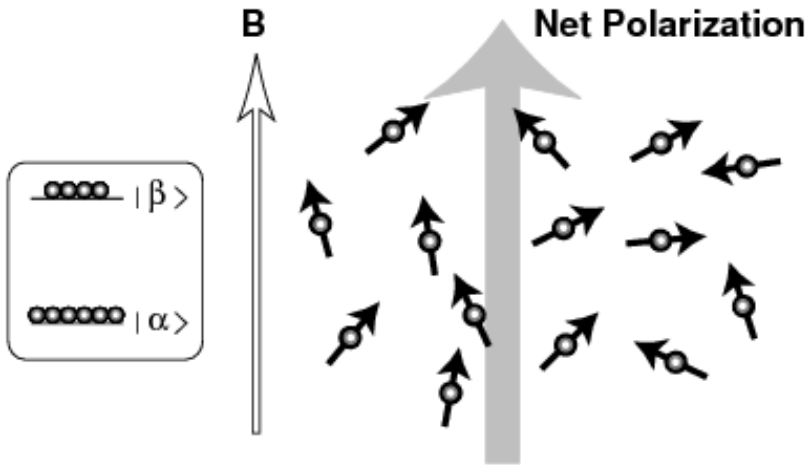
Populações: $\rho_{\boxed{\alpha}} \quad \rho_{\boxed{\beta}} \quad \rho_{\boxed{\alpha}} + \rho_{\boxed{\beta}} = 1$

Coerências: $\rho_{\boxed{+}} \quad \rho_{\boxed{-}} \quad \rho_{\boxed{+}} = \rho_{\boxed{-}}^{*}$

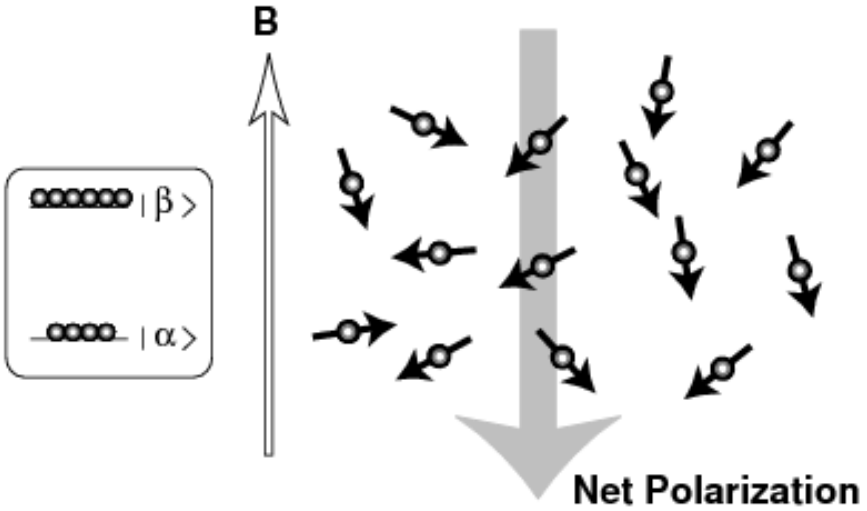
"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Dinâmica de spins em experimentos de RMN

Interpretação física das populações:



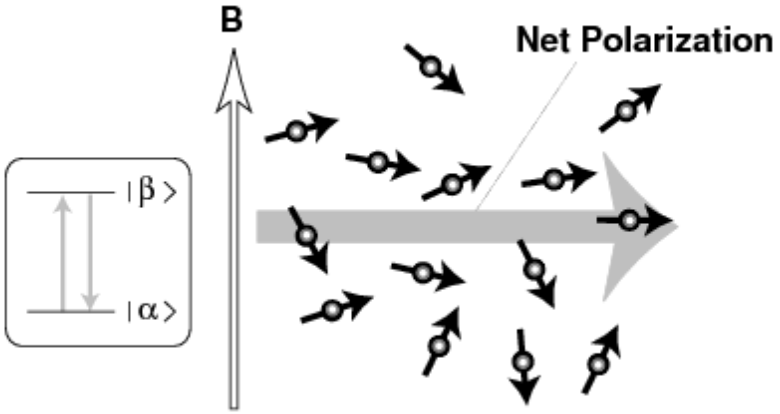
$$|\alpha\rangle\langle\alpha| = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \qquad |\beta\rangle\langle\beta| = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$



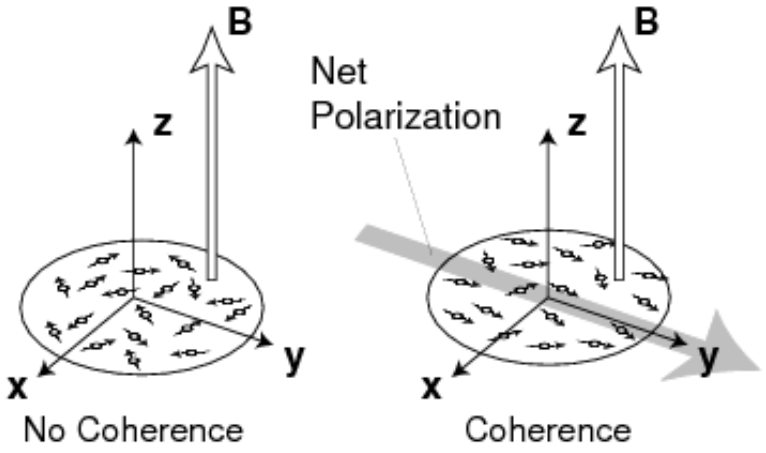
"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Dinâmica de spins em experimentos de RMN

Interpretação física das coerências:



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



"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Dinâmica de spins em experimentos de RMN

Operador densidade – equilíbrio térmico:

$$\rho_{eq} = \frac{e^{-H/kT}}{Z} \qquad \rho_{eq} \cong \frac{1}{Z} - \underbrace{\frac{1}{Z}\frac{H}{kT}}_{\text{Desvio}} \qquad U\rho_{eq}U^{\dagger} \cong \frac{1}{Z} - \frac{1}{Z}\frac{1}{kT}UHU^{\dagger}$$

$$\rho_{eq} = \begin{pmatrix} \frac{1}{2}+\frac{1}{4}\varepsilon & 0 \\ 0 & \frac{1}{2}-\frac{1}{4}\varepsilon \end{pmatrix} = \tfrac{1}{2}\mathbf{1} + \tfrac{1}{4}\mathbf{I}_z \qquad \varepsilon = \frac{\hbar\gamma B_0}{kT} \approx 10^{-4}$$

Magnetização:

$$\begin{cases} \rho_{\boxed{\alpha}} = \frac{1}{2}+\frac{1}{4}\varepsilon M_z & \rho_{\boxed{\beta}} = \frac{1}{2}-\frac{1}{4}\varepsilon M_z \\ \rho_{\boxed{+}} = \frac{1}{4}\varepsilon(M_x - iM_y) & \rho_{\boxed{-}} = \frac{1}{4}\varepsilon(M_x + iM_y) \end{cases}$$

Dinâmica de spins em experimentos de RMN

Evolução temporal do operador densidade – equação de Liouville-von Neumann:

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

Para Hamiltoniano independente do tempo: $\rho(t) = e^{-(i/\hbar)\mathcal{H}t}\,\rho(0)\,e^{(i/\hbar)\mathcal{H}t}$

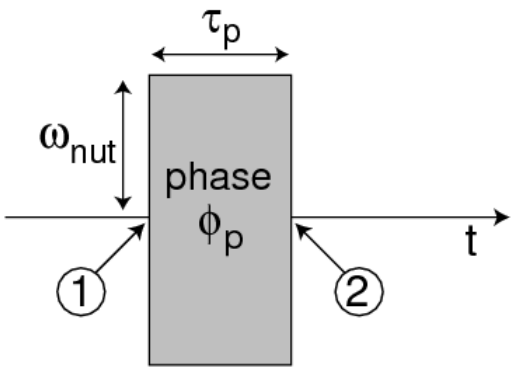
Passagem para o sistema girante de coordenadas:

$$\rho^{Rot} = e^{-i\Omega t I_z}\,\rho^{Lab}\,e^{i\Omega t I_z} \qquad \mathcal{H}_{eff} = -\hbar(\omega_L - \Omega)I_z - \hbar\omega_1 I_x$$

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

Dinâmica de spins em experimentos de RMN

Atuação de pulsos de RF:



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

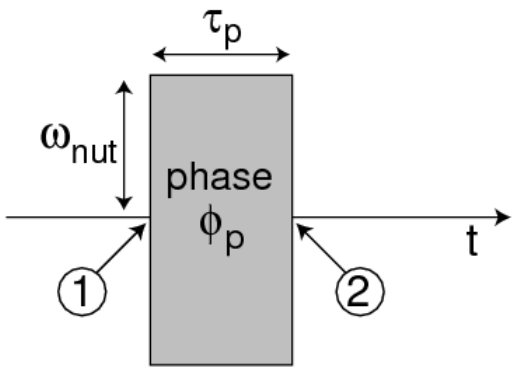
$$\rho(t_p) = R_x(-\theta_p)\rho_0 R_x(\theta_p)$$

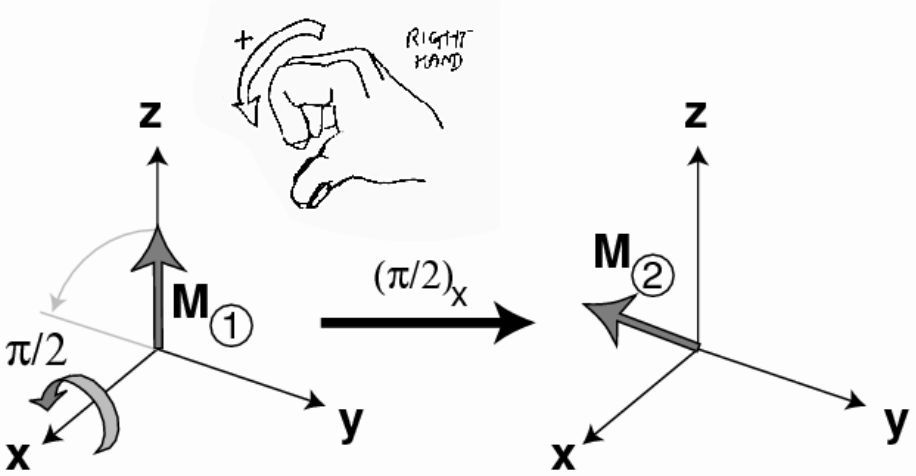
$$R_x(\theta_p) = \begin{bmatrix} \cos(\theta_p/2) & -i\sin(\theta_p/2) \\ -i\sin(\theta_p/2) & \cos(\theta_p/2) \end{bmatrix}$$

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

Dinâmica de spins em experimentos de RMN

Atuação de pulsos de RF:

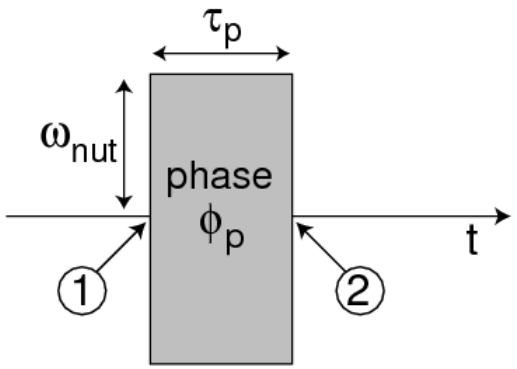


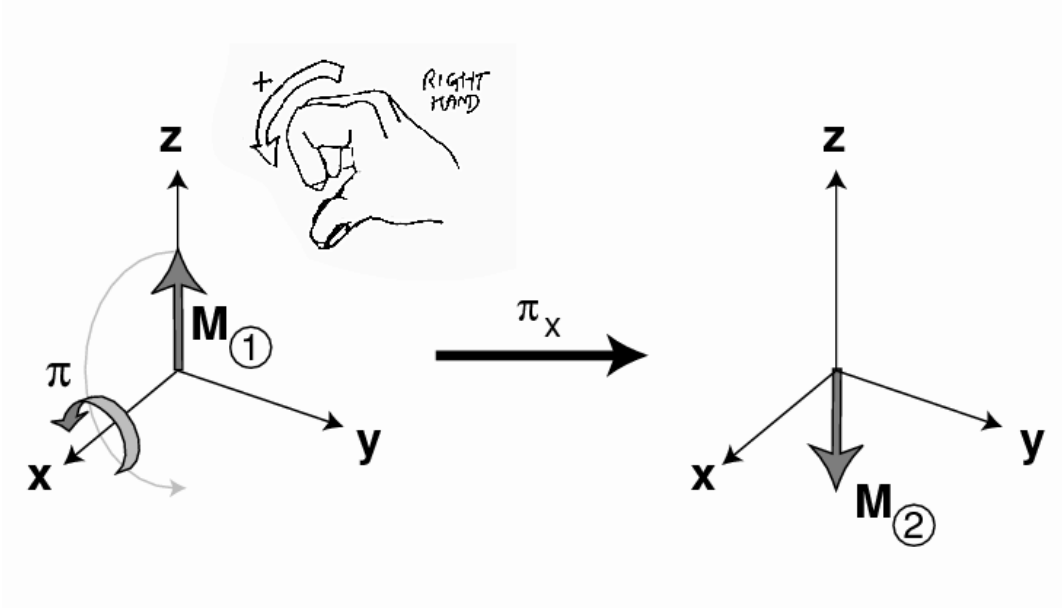


$$\rho_1 = \begin{pmatrix} \frac{1}{2}+\frac{1}{4}\varepsilon & 0 \\ 0 & \frac{1}{2}-\frac{1}{4}\varepsilon \end{pmatrix} \xrightarrow{(\pi/2)_x} \rho_2 = \begin{pmatrix} \frac{1}{2} & -\frac{1}{4i}\varepsilon \\ \frac{1}{4i}\varepsilon & \frac{1}{2} \end{pmatrix}$$

Dinâmica de spins em experimentos de RMN

Atuação de pulsos de RF:





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

Dinâmica de spins em experimentos de RMN

Evolução livre:

Hamiltoniano no sistema girante de coordenadas: $H_Z = -\hbar(\omega_L - \Omega) I_z$

Evolução do operador densidade: $\rho(\tau) = e^{i(\omega_L - \Omega)\tau I_z} \rho(t_p) e^{-i(\omega_L - \Omega)\tau I_z}$

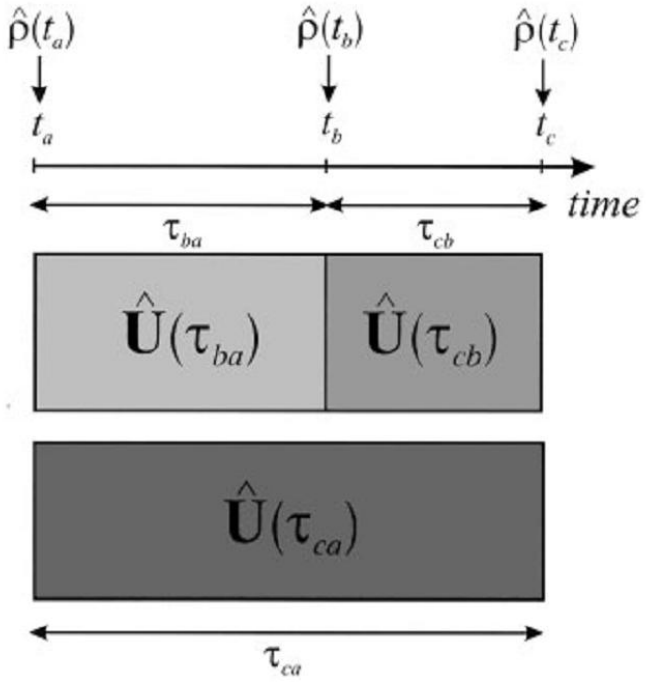
Evolução após pulso $(\pi/2)_{-x}$:

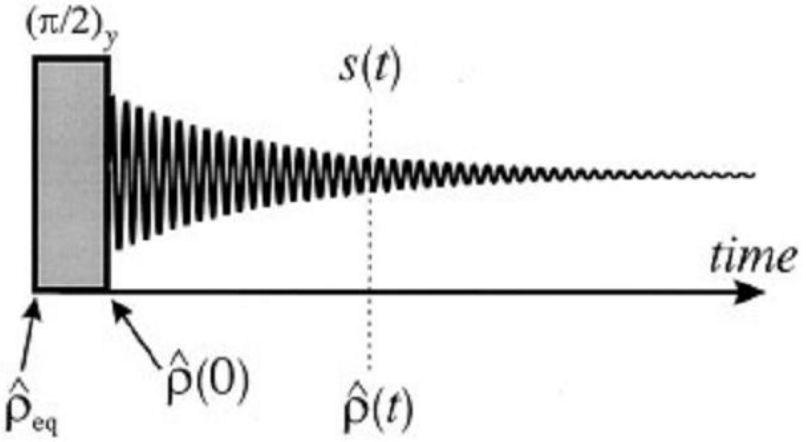
$$\Delta\rho(\tau) = e^{i(\omega_L - \Omega)\tau I_z} \left(\frac{\hbar\omega_L}{2k_B T} I_y \right) e^{-i(\omega_L - \Omega)\tau I_z}$$

$$= \frac{\hbar\omega_L}{2k_B T} \left[I_y \cos(\omega_L - \Omega)\tau + I_x \sin(\omega_L - \Omega)\tau \right]$$

Dinâmica de spins em experimentos de RMN

Uso de propagadores e álgebra matricial:





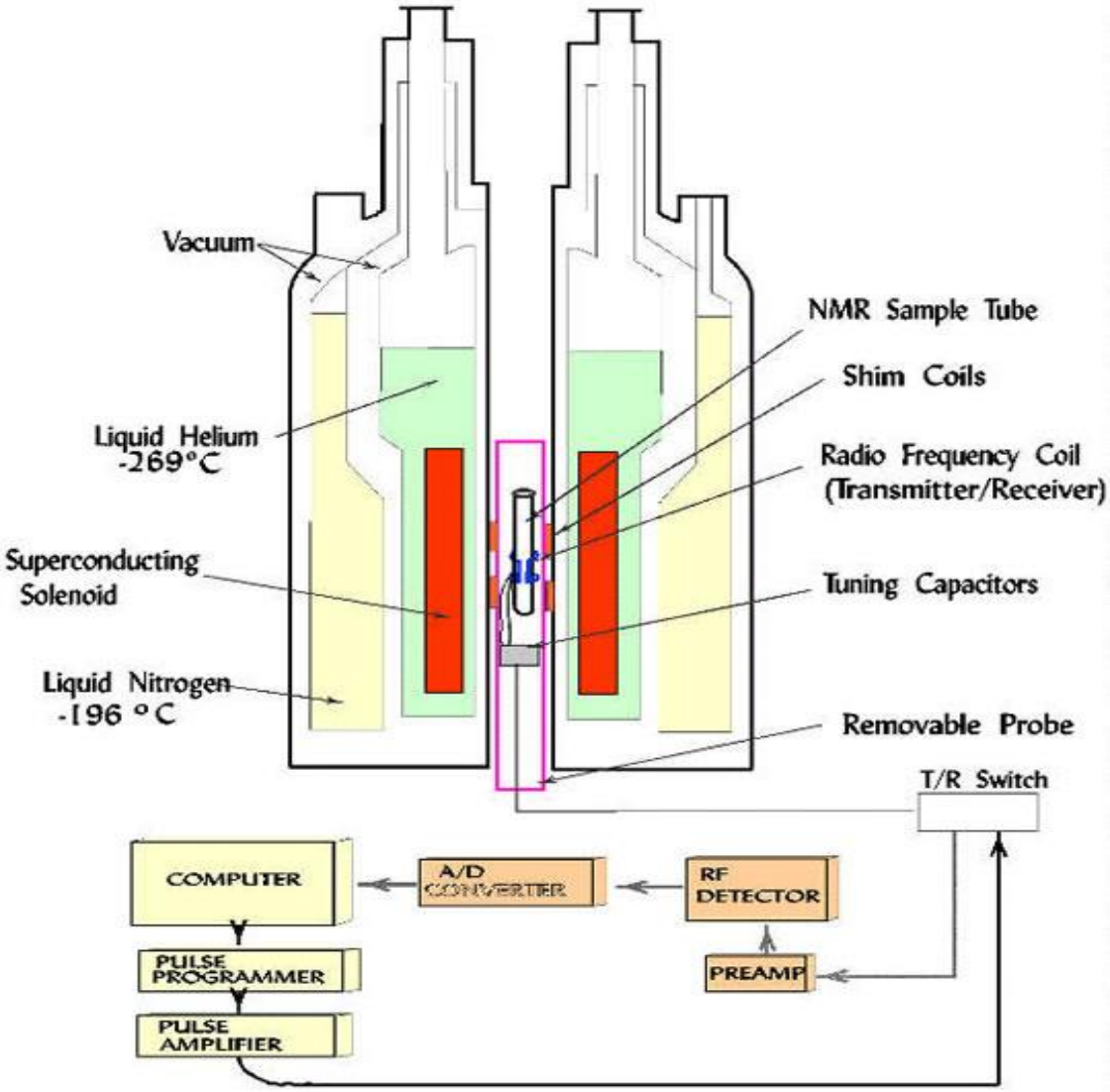
M. Edén, Concepts Magn. Reson. 2003;17A:117

Métodos computacionais em RMN de sólidos

Diferentes tipos de programas e abordagens:

- Cálculos de primeiros princípios / DFT:
  - Quantum ESPRESSO, CASTEP, VASP, Wien2k, Gaussian, ...
- Simulações de dinâmica de spins:
  - SIMPSON, SPINEVOLUTION, MathNMR, GAMMA, ...
- Simulações espectrais:
  - DMFIT, Wsolids, QuadFit, QUEST,...
- Processamento de sinais e espectros:
  - ACD/NMR Processor, MestReNova, TopSpin, VNMRJ, Spinsights, ...

Espectrômetro de RMN



Magnetos supercondutores

Espectrômetros: frequências e campos magnéticos

B_0 (T)	f_L (^{1}H) (MHz)	f_L (^{13}C) (MHz)
2.35	100	25.2
4.70	200	50.3
7.05	300	75.4
9.39	400	100.6
11.74	500	125.8
14.09	600	150.9
16.44	700	176.1
18.79	800	201.2
21.14	900	226.4

Sonda de RF (“probe”)

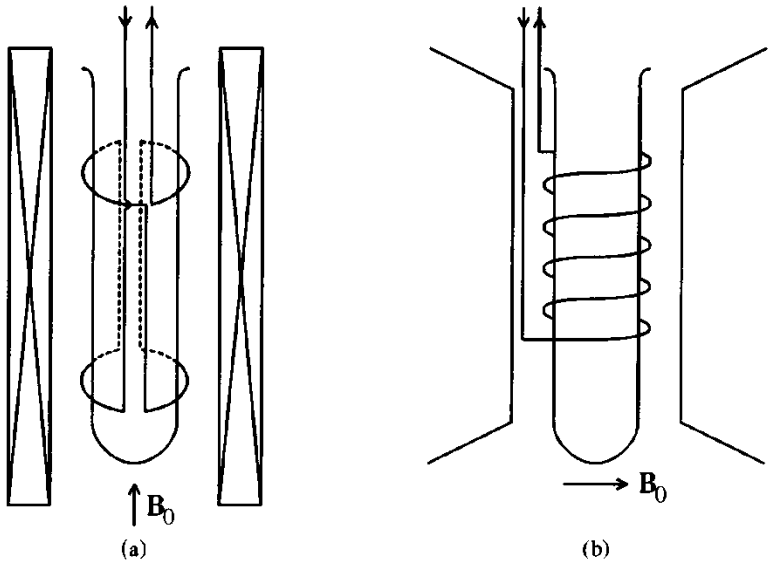
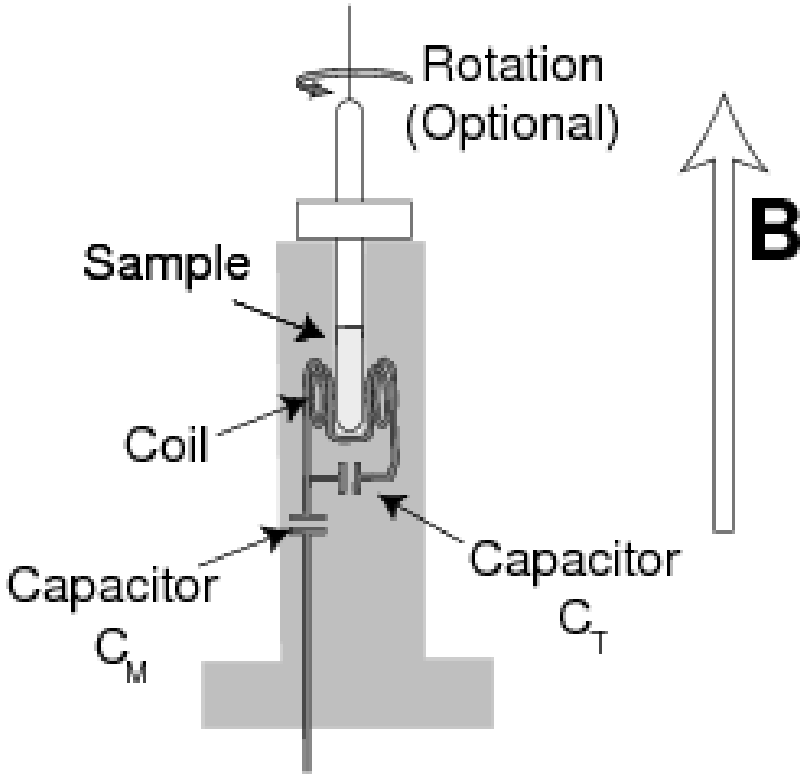


Figure 3.7 Sample coil configuration for use in superconducting solenoids and iron core electromagnets: (a) superconducting solenoid; (b) iron core electromagnet.

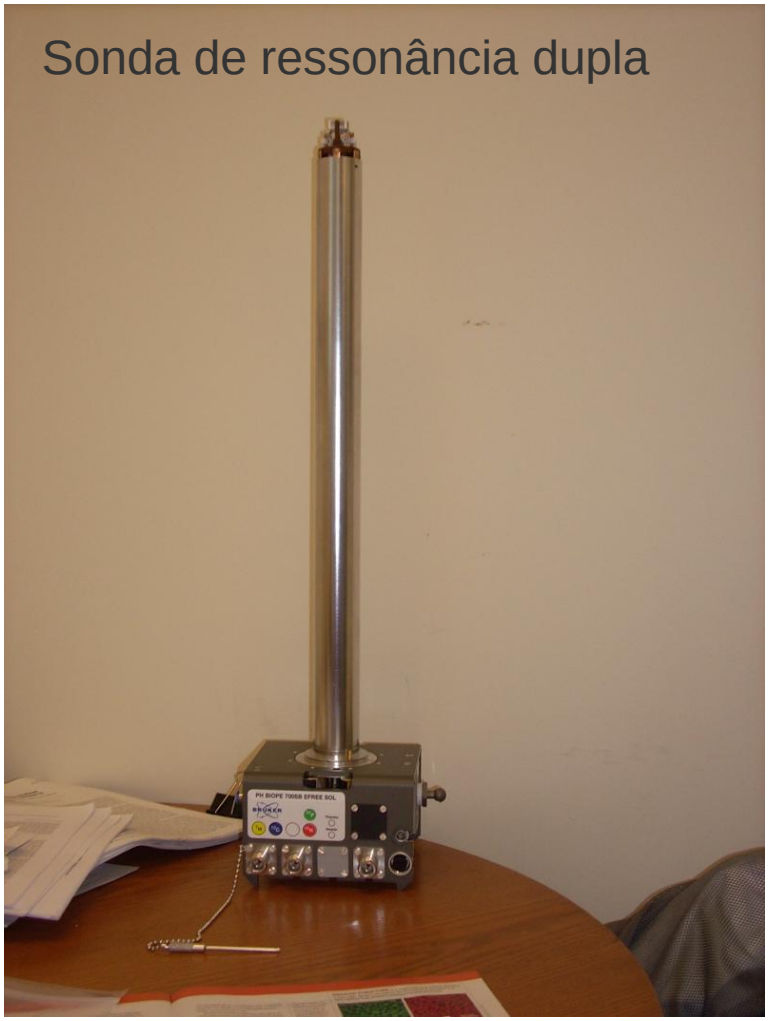
“NMR and relaxation”, Cowan. Cambridge University Press, 1997.

Sonda de RF (“probe”)



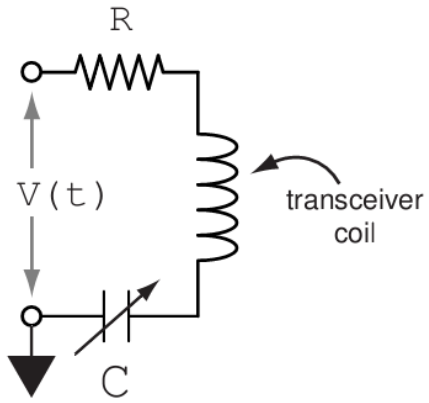
“Spin dynamics”, M. H. Levitt. John Wiley & Sons, 2002.

Sonda de RF (“probe”)

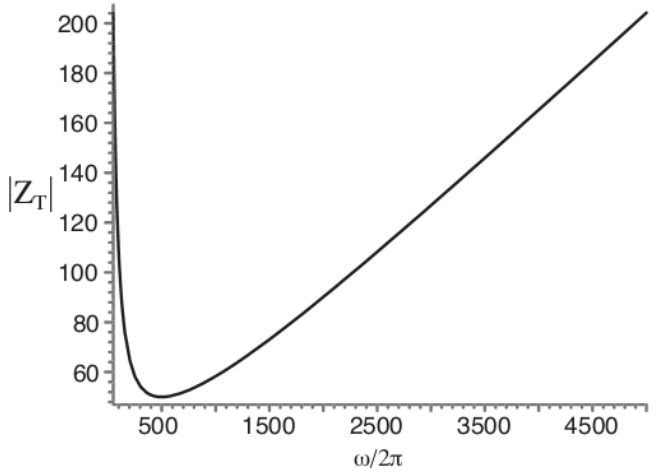


Sonda de RF (“probe”)

Circuito RLC:



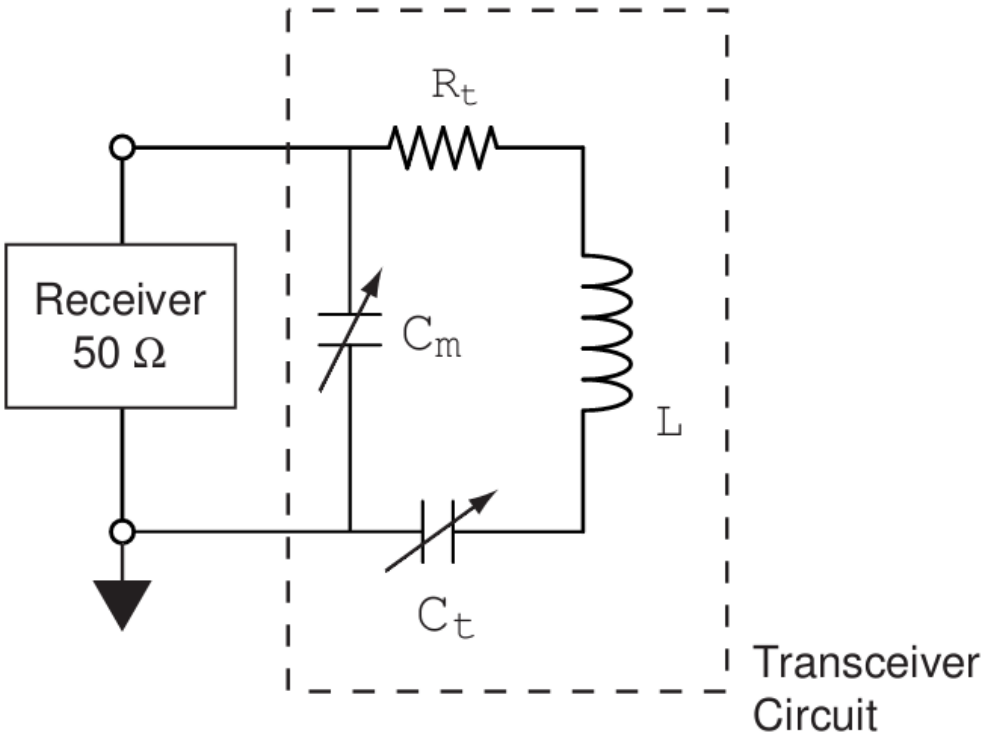
$$\omega_0 = 1/\sqrt{LC}$$ (ressonância elétrica)



http://grandinetti.org/Teaching/Chem824/Notes

Sonda de RF (“probe”)

Sonda sintonizável (circuito “tanque”):



$$\frac{1}{Z_T} = i\omega C_m + \frac{1}{R_t + i\left(\omega L - \frac{1}{\omega C_t}\right)}$$

http://grandinetti.org/Teaching/Chem824/Notes

Sonda de RF (“probe”)

Sonda de dupla ressonância:

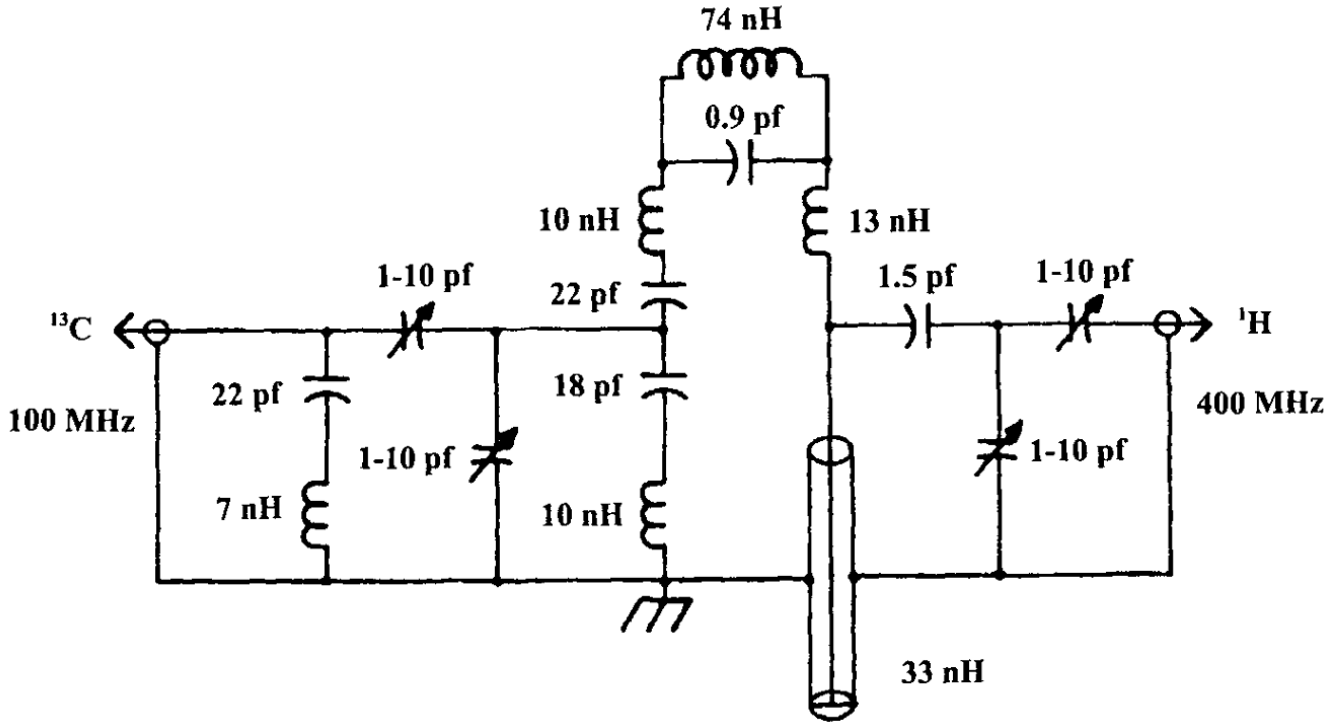
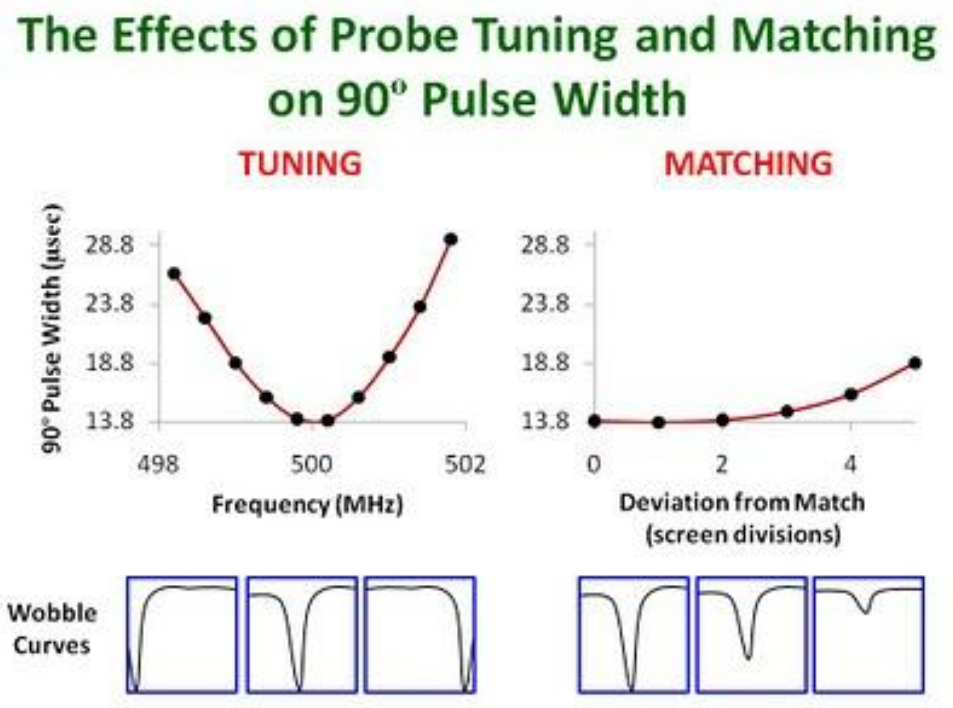


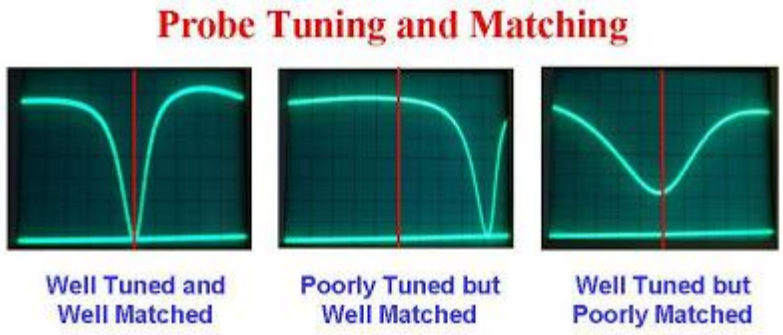
Figure 3.6. Typical circuit of a doubly resonant probe from Doty *et al.* (1988) with permission of the copyright owner.

“Multinuclear solid-state NMR of inorganic materials”, Mackenzie & Smith. Pergamon, 2002.

Sonda de RF (“probe”)

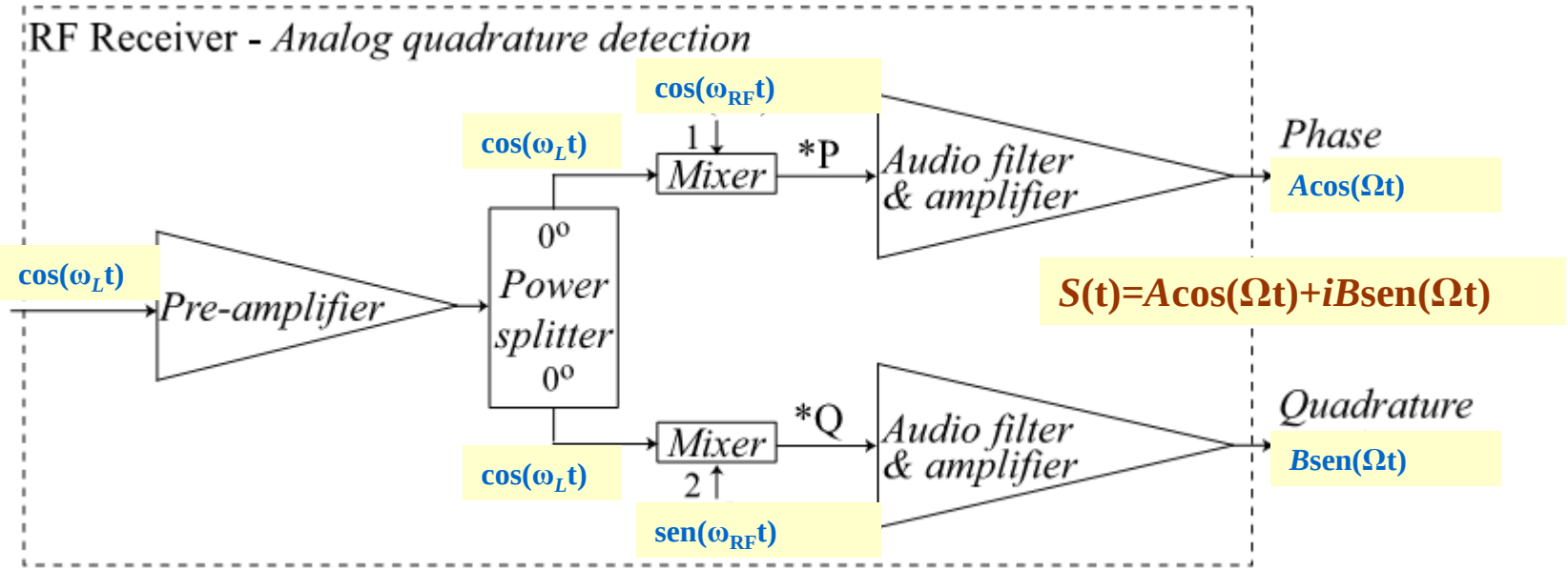
Sintonia:





http://u-of-o-nmr-facility.blogspot.com

Detecção em fase e quadratura

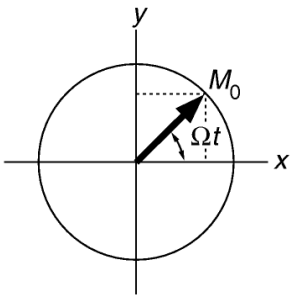


"NMR Quantum Information Processing", Oliveira et al. Elsevier, 2007.

Detecção em fase e quadratura

Sinal de RMN típico:

$$S(t) = S_0\left[(\cos\Omega t) + i(\text{sen}\,\Omega t)\right]e^{-\lambda t} = S_0 e^{i\Omega t}e^{-\lambda t}$$

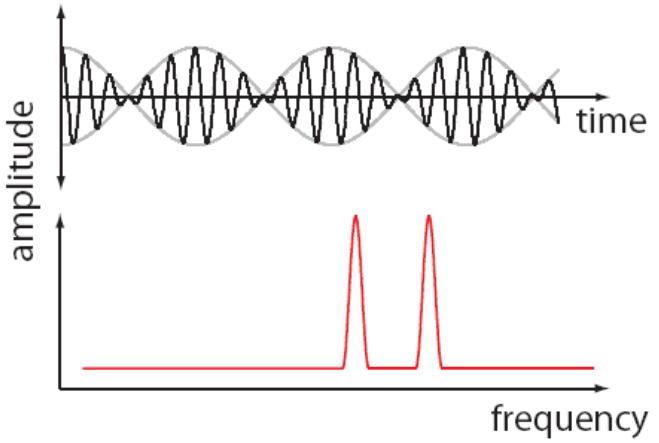


$$\Omega = \omega_L - \omega_{RF}$$

"Understanding NMR spectroscopy", J. Keeler. Wiley , 2005.

$$F(\omega) = \int_{-\infty}^{+\infty} S(t)e^{-i\omega t}dt$$

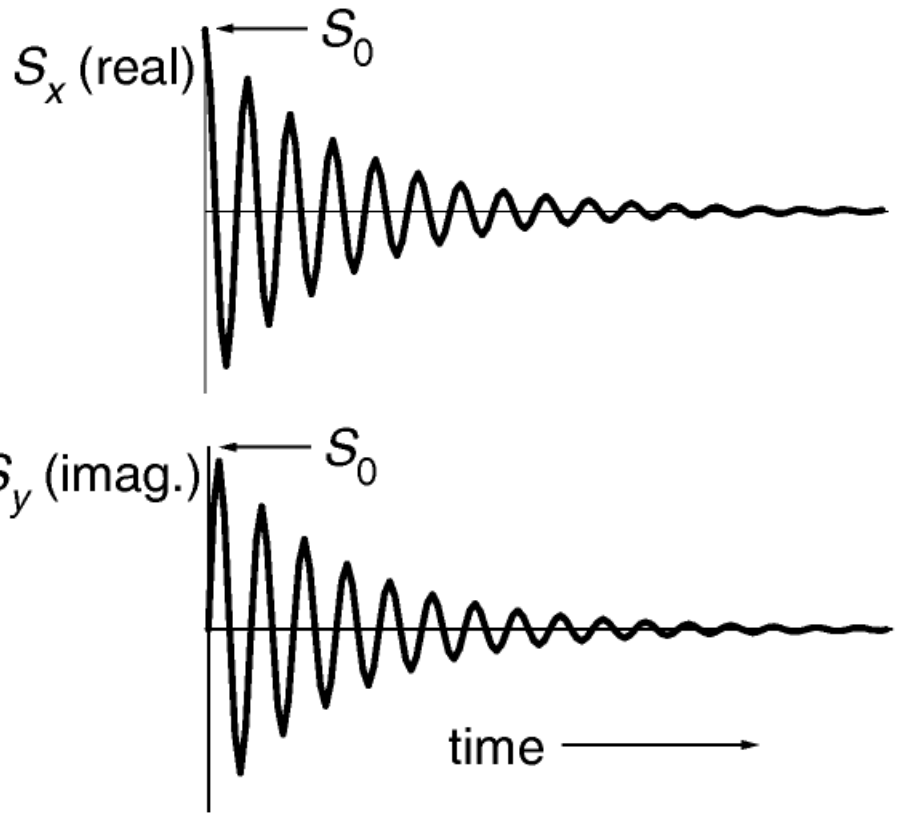
$$S(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} F(\omega)e^{i\omega t}d\omega$$

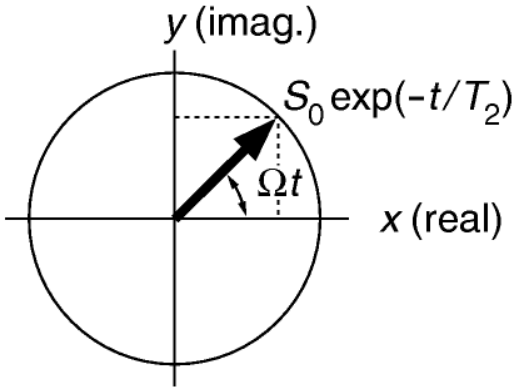


http://grandinetti.org/Teaching/Chem824/Notes

Detecção em fase e quadratura

$$S(t) = S_0\left[(\cos\Omega t) + i(\text{sen}\,\Omega t)\right]e^{-\lambda t} = S_0 e^{i\Omega t}e^{-\lambda t}$$





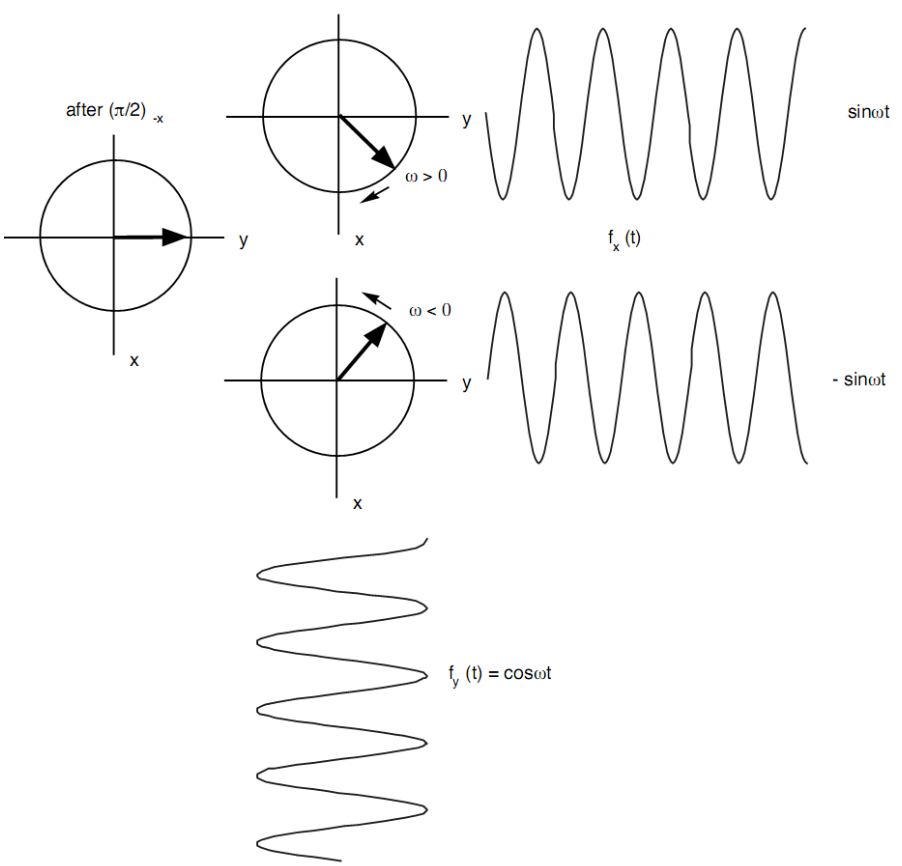
$$\lambda = 1/T_2 \qquad \Omega = \omega_L - \omega_{RF}$$

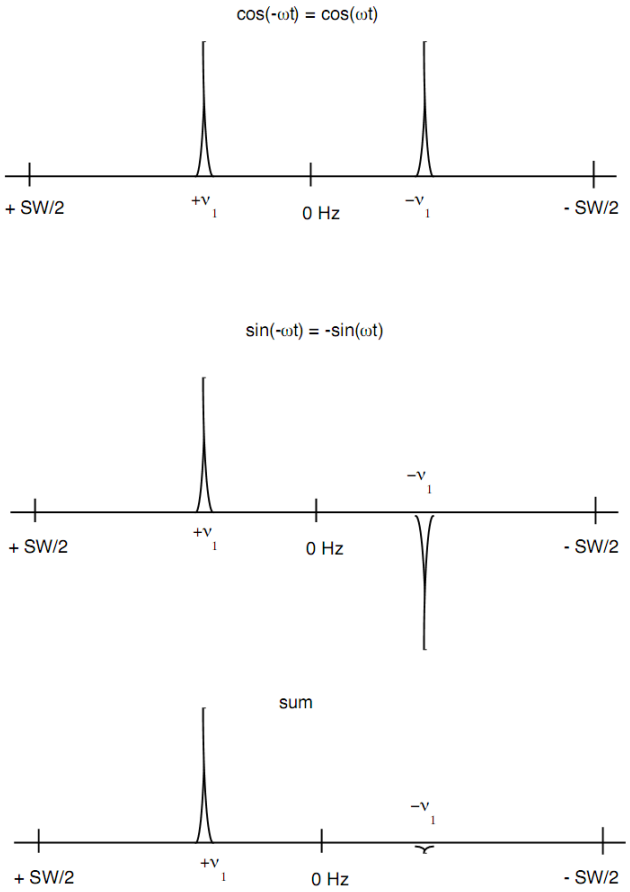
Decaimento (relaxação)

Offset

"Understanding NMR spectroscopy", J. Keeler. Wiley , 2005.

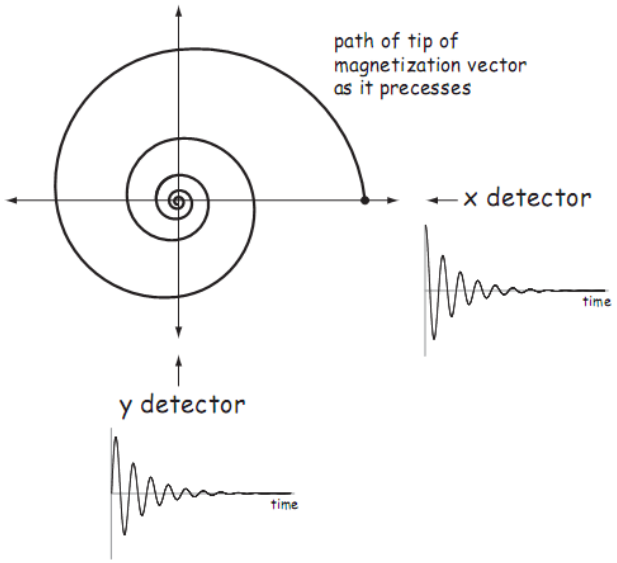
Detecção em fase e quadratura





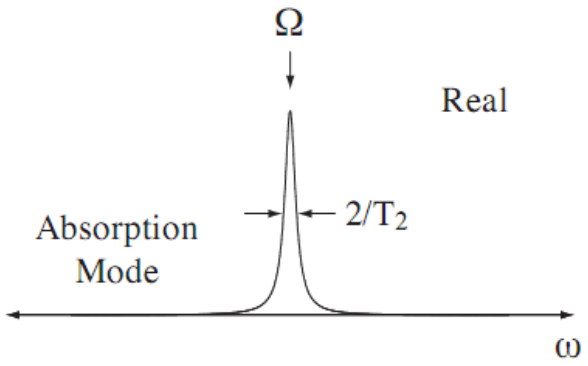
http://www.analytik.ethz.ch/praktika/phys_anal/nmr/ft-nmr.pdf

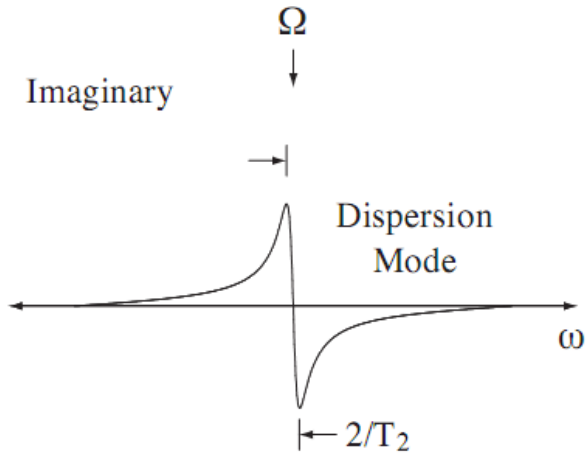
Ajuste de fase



$$A(\omega) = \frac{\lambda}{\lambda^2 + \omega^2}; \qquad \text{Absorption Mode Lineshape}$$

$$D(\omega) = \frac{\omega}{\lambda^2 + \omega^2}; \qquad \text{Dispersion Mode Lineshape}$$

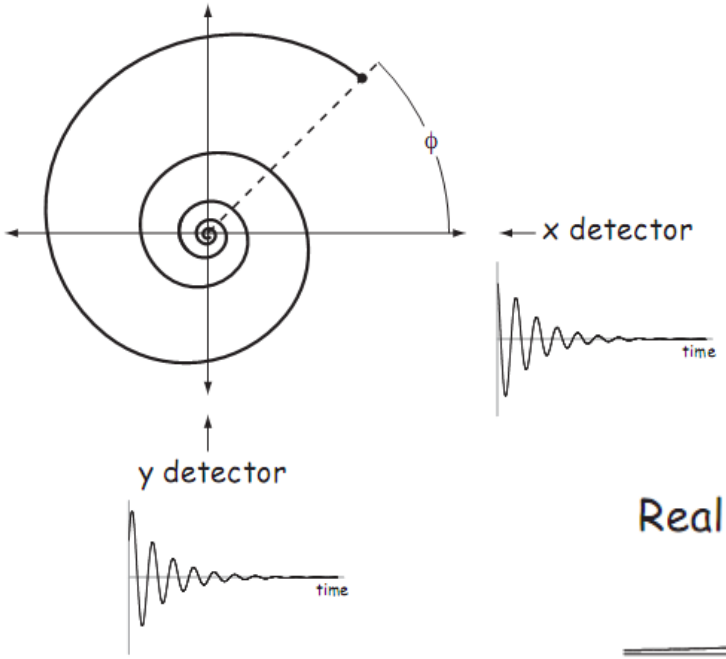


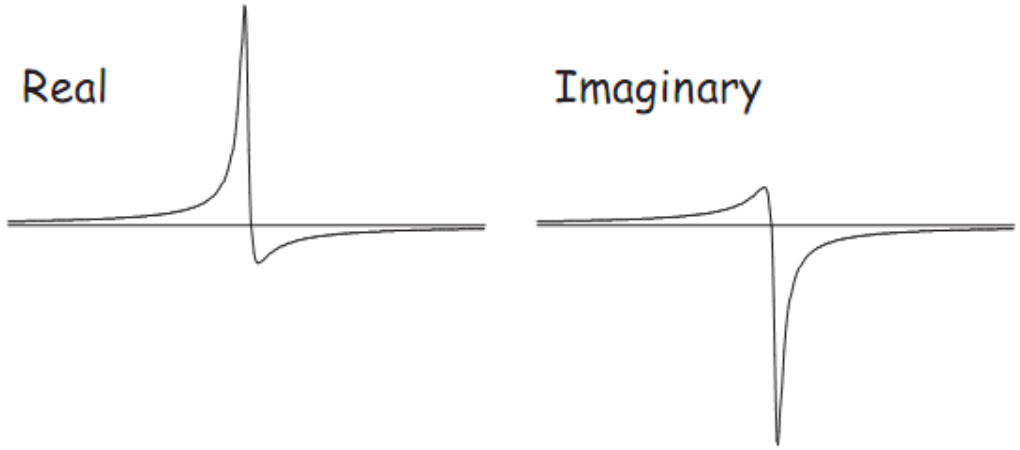


http://grandinetti.org/Teaching/Chem824/Notes

Ajuste de fase

Erro de fase:



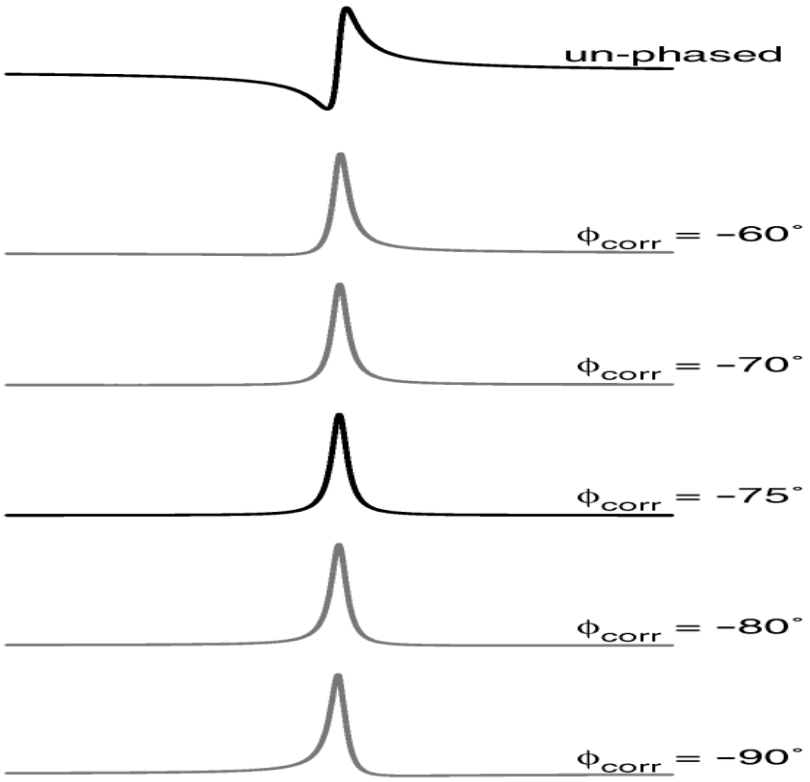


http://grandinetti.org/Teaching/Chem824/Notes

Ajuste de fase

Correção de fase de ordem 0:

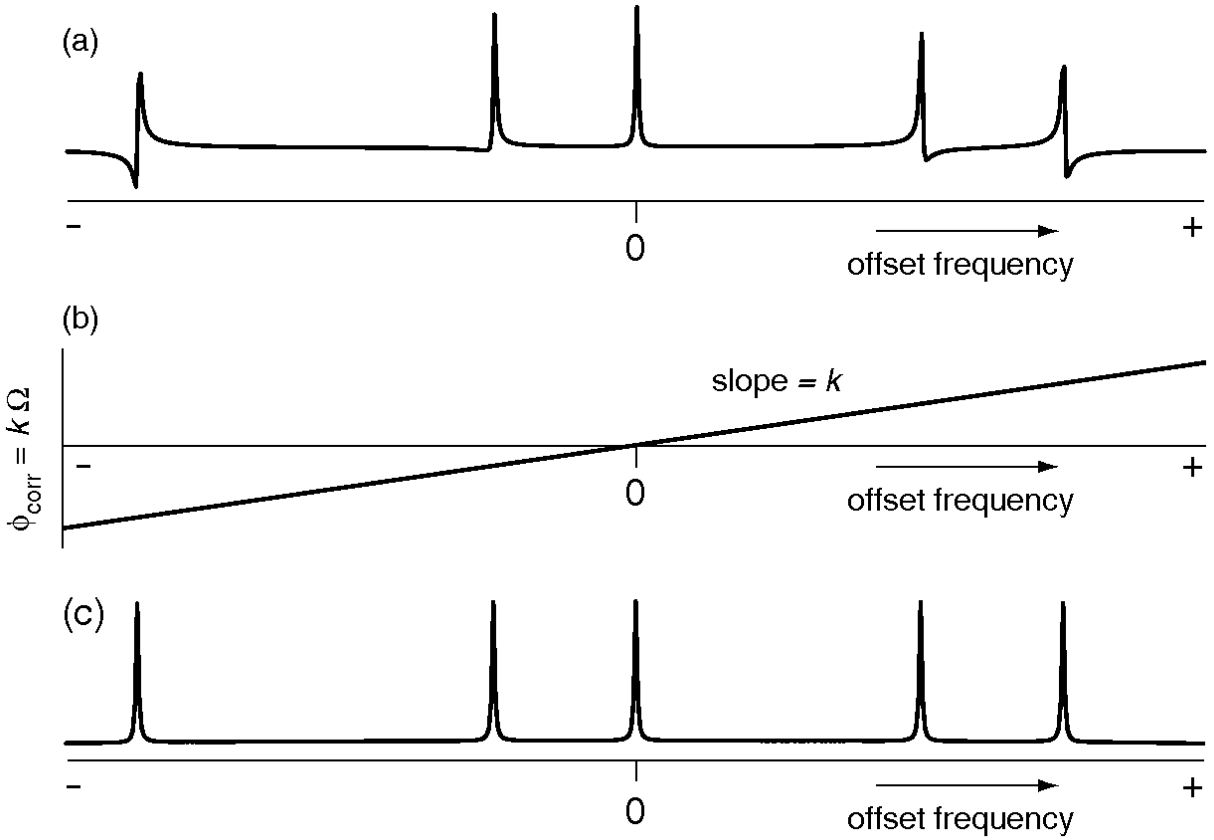
$$S'(\omega) = S(\omega)e^{-i\phi_0}$$



"Understanding NMR spectroscopy", J. Keeler. Wiley, 2005.

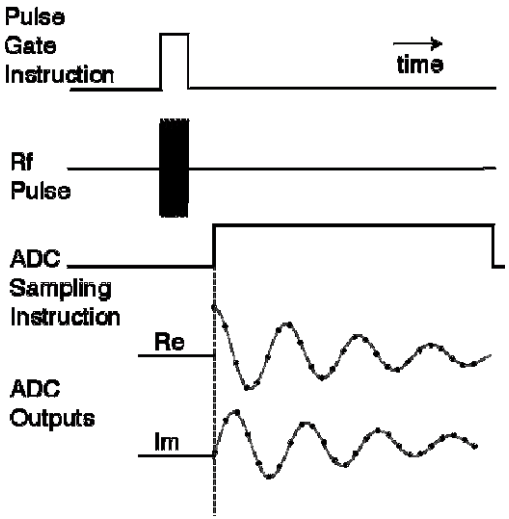
Ajuste de fase

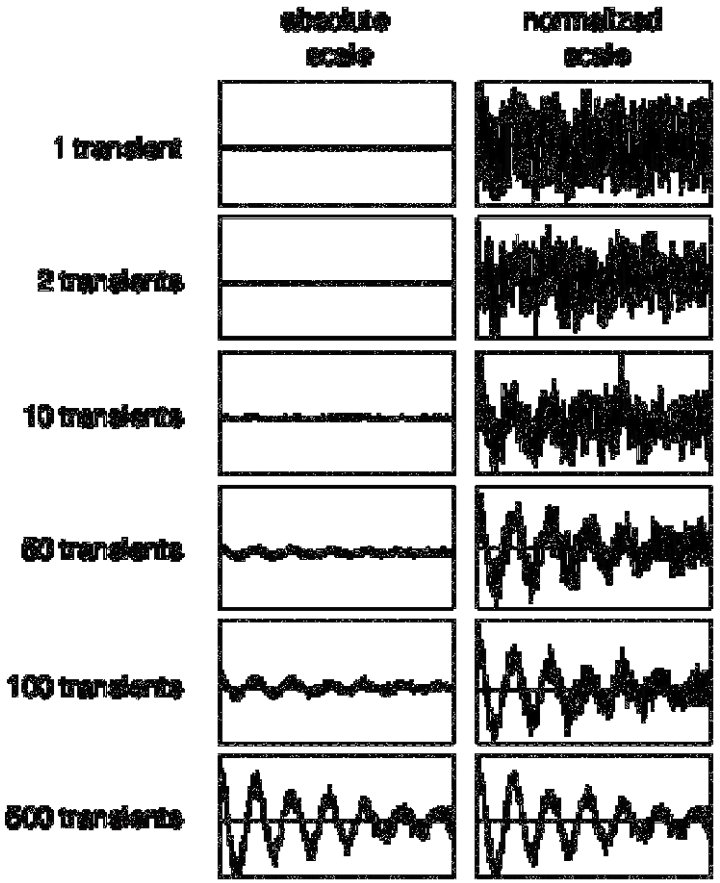
Correção de fase de primeira ordem:



"Understanding NMR spectroscopy", J. Keeler. Wiley, 2005.

Acumulação de transientes





Aumento na relação sinal/ruído:

$$\frac{S}{N} \propto \sqrt{\text{nº de transientes}}$$

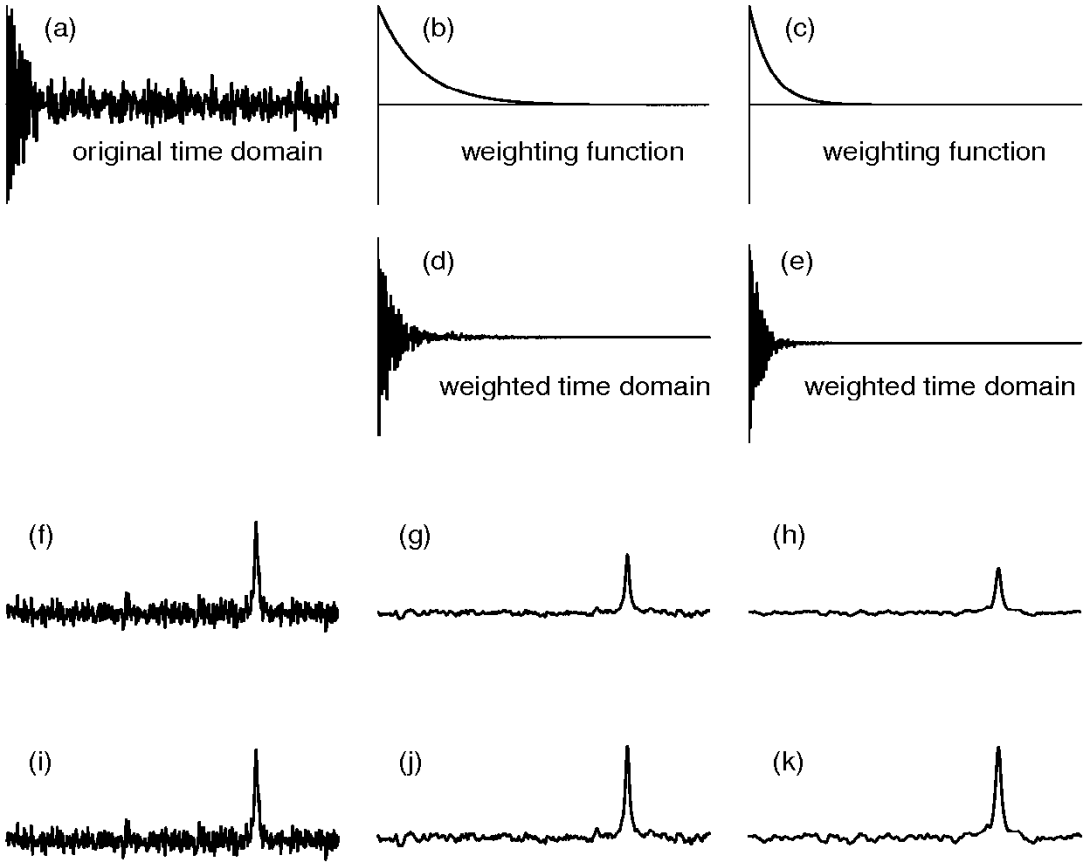
Intervalo entre transientes:

$$t_r > 5T_1$$

"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Processamento de FIDs e espectros

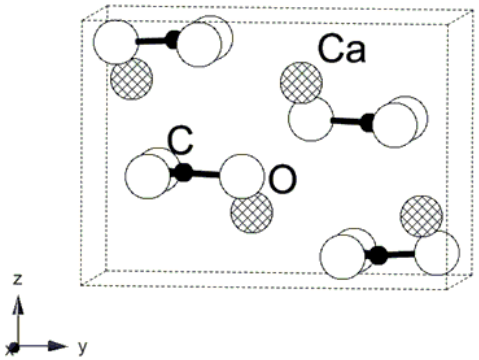
Apodização (funções “janela”):



“Understanding NMR spectroscopy”, J. Keeler. Wiley, 2005.

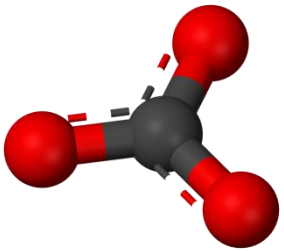
Práticas experimentais e computacionais

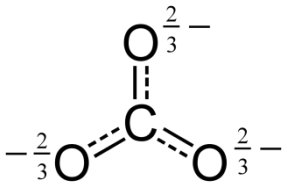
Material para RMN de ^{13}C – Aragonita ($CaCO_3$):



Célula unitária
(Estrutura ortorrômbica)

Xy & Poduska, *Phys. Chem. Chem. Phys.* 2014;16:17634



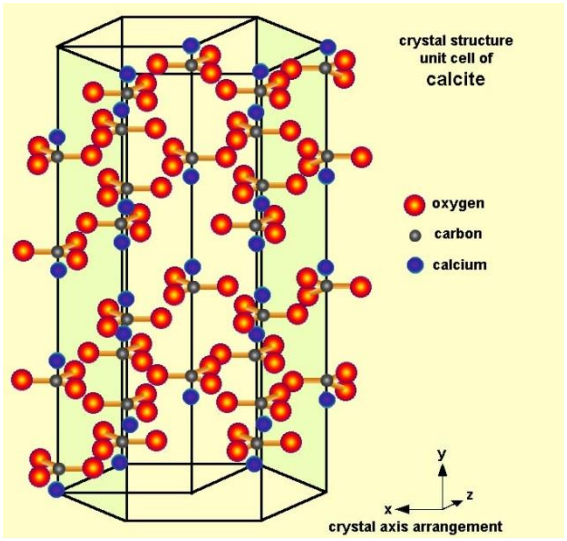


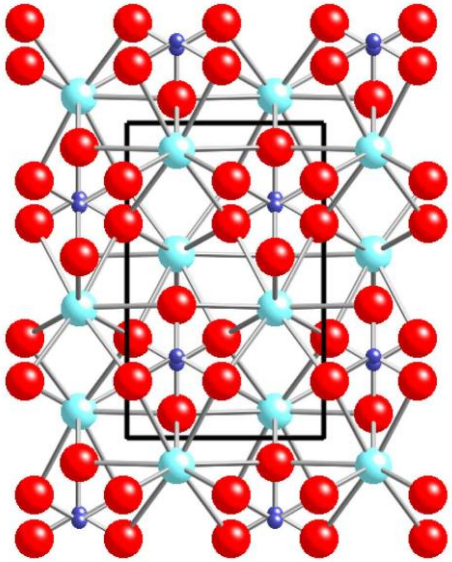
https://en.wikipedia.org/wiki/Carbonate

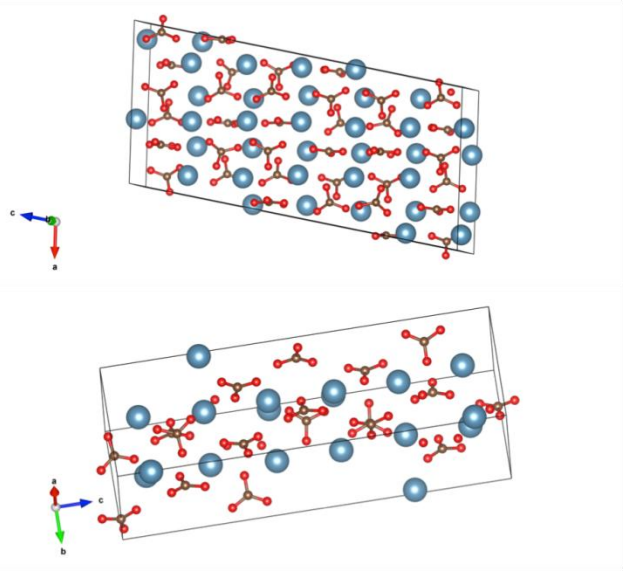
https://en.wikipedia.org/wiki/Aragonite

Práticas experimentais e computacionais

$CaCO_3$ – Polimorfos:







Calcita
(Romboédrica)

http://geologycafe.com/class/chapter3.html

Aragonita
(Ortorrômbica)

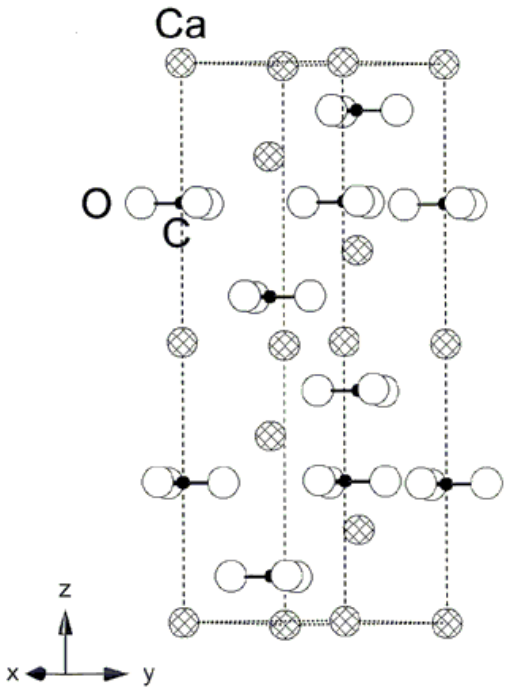
http://geology.byu.edu/Displays/minerals/aragonite-32

Vaterita
(Hexagonal)

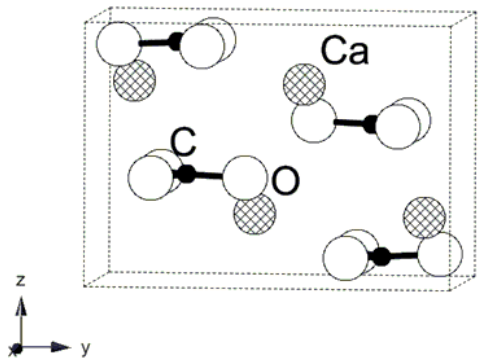
https://crystallography365.files.wordpress.com/2014/11/vaterite_two.png

Práticas experimentais e computacionais

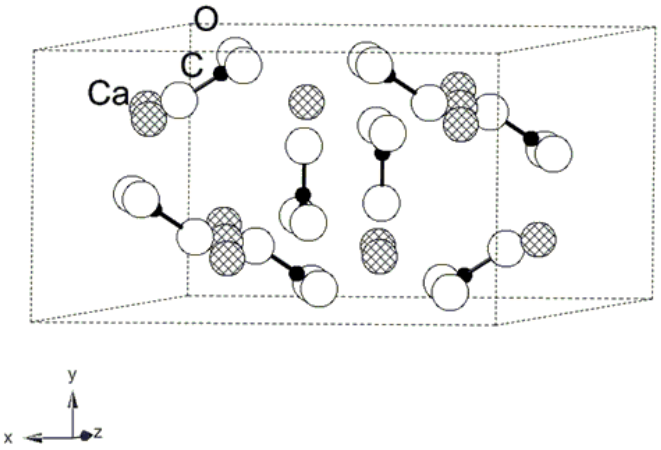
$CaCO_3$ – Polimorfos:



Calcita
(Romboédrica)



Aragonita
(Ortorrômbica)



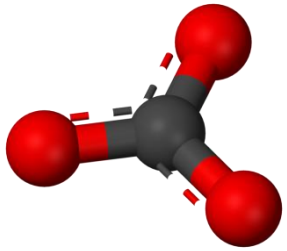
Vaterita
(Hexagonal)

Xy & Poduska, *Phys. Chem. Chem. Phys.* 2014;16:17634

Práticas experimentais e computacionais

Material para RMN de ^{13}C – Aragonita ($CaCO_3$):

- Vantagens:
  - Presença somente de elementos químicos com núcleos ativos para RMN pouco abundantes (^{13}C, ^{43}Ca, ^{17}O) – interação dipolar heteronuclear desprezível.
  - Núcleo ^{13}C com spin = 1/2 – interação quadrupolar ausente.
  - Existência de apenas um sítio quimicamente distinto para ^{13}C.



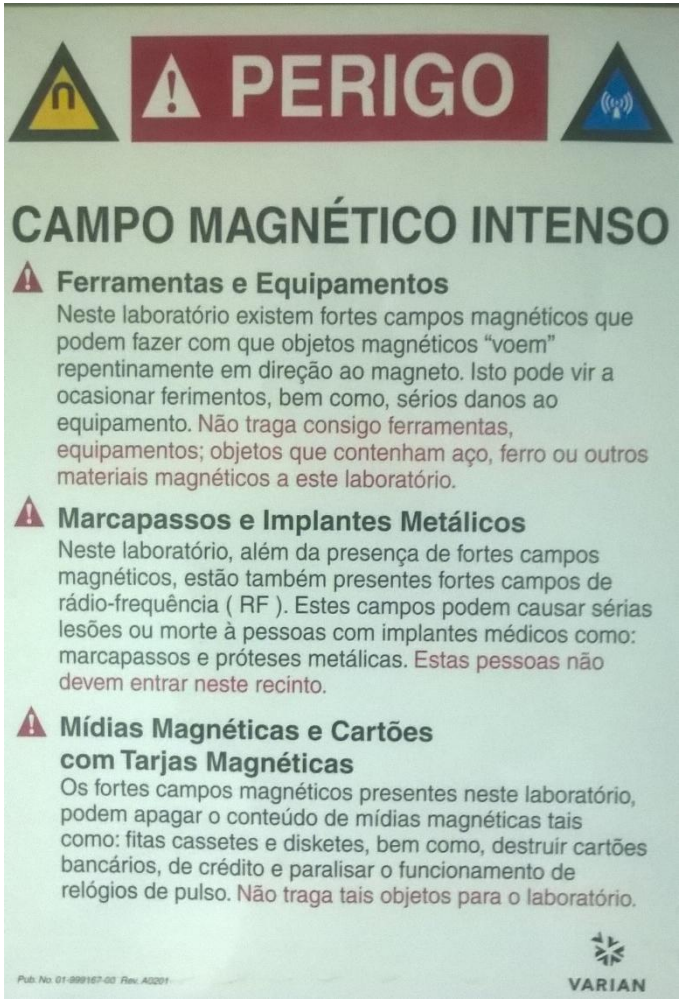
- Desvantagens:
  - Não é a fase mais estável (e frequente) do composto $CaCO_3$.
  - Tempo de relaxação longitudinal longo ($T_1 \sim 10^2$ s).

Práticas experimentais em RMN de sólidos

Daniel F. Cipriano

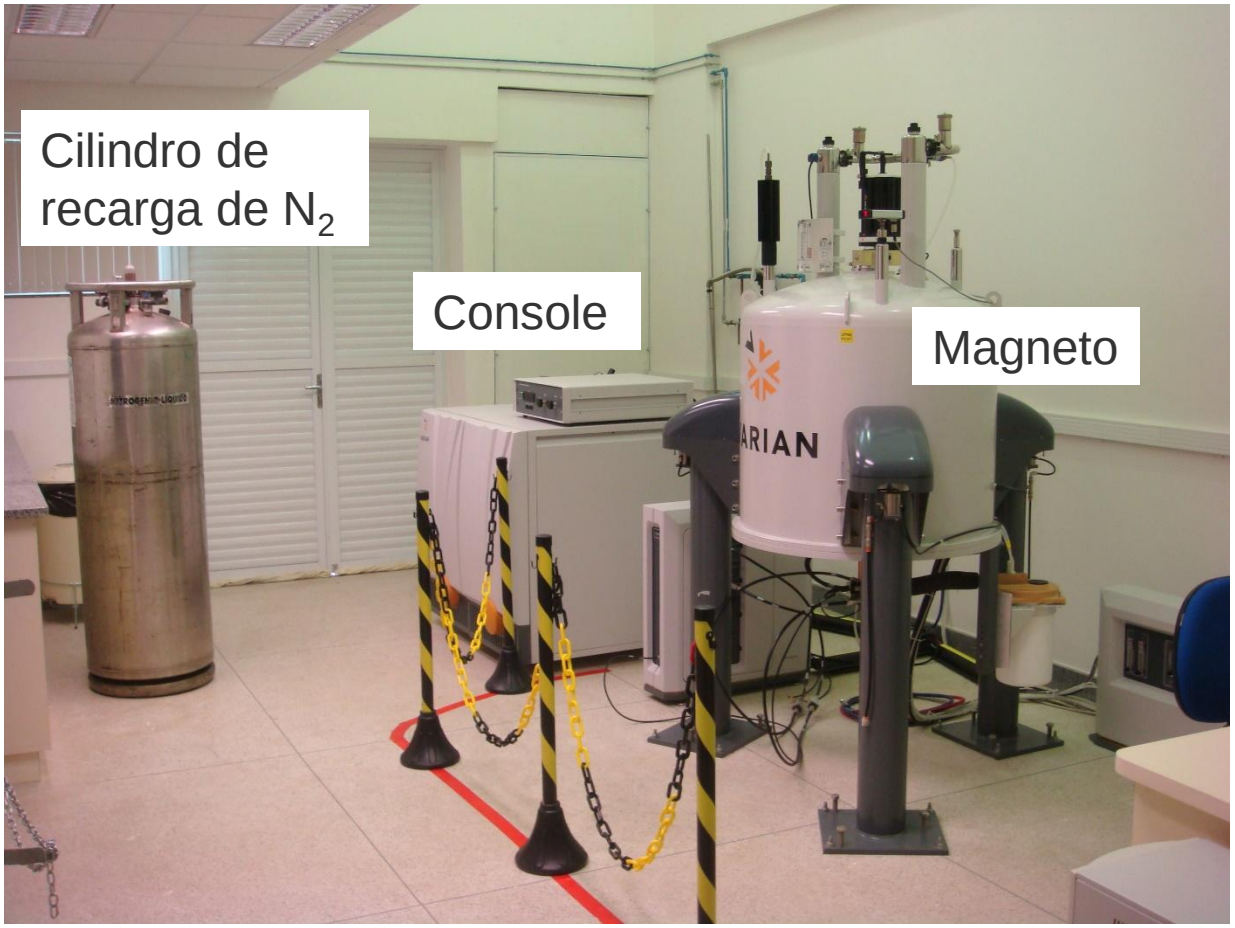
Práticas experimentais em RMN de sólidos

Cuidados iniciais...



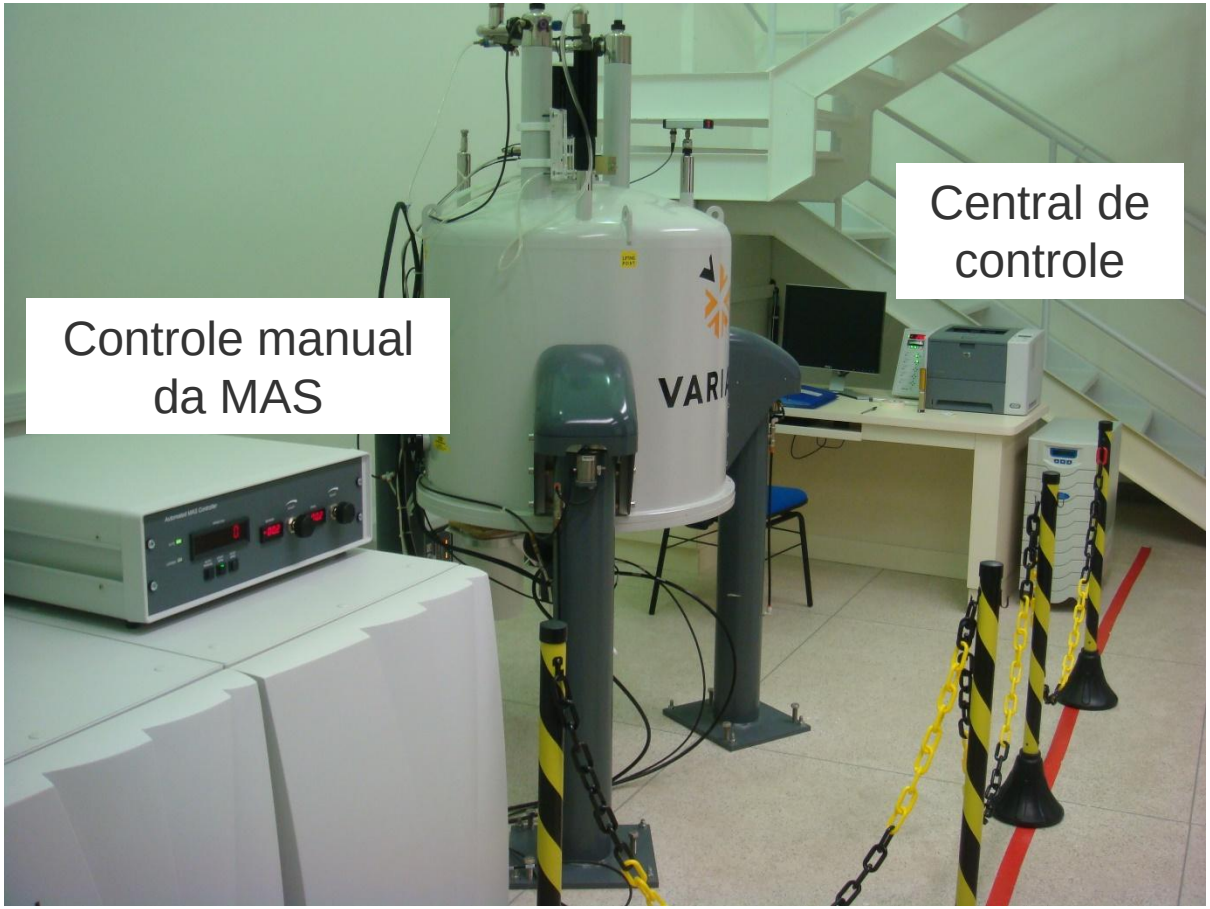
Práticas experimentais em RMN de sólidos

Equipamento:



Práticas experimentais em RMN de sólidos

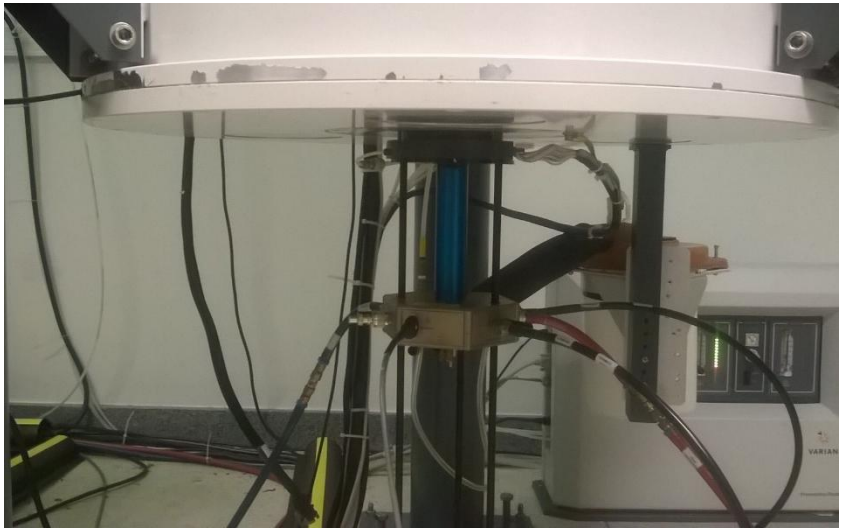
Equipamento:



Práticas experimentais em RMN de sólidos

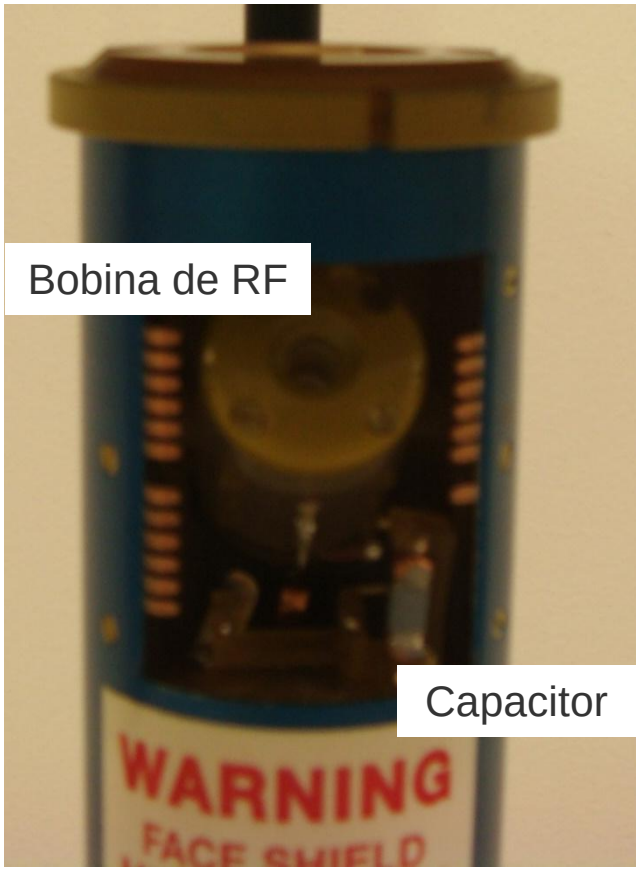
Equipamento:

Sonda em operação

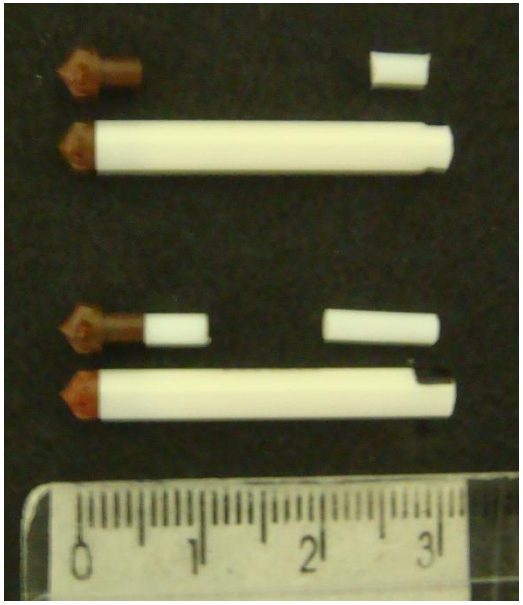


Práticas experimentais em RMN de sólidos

Sonda para experimentos com MAS:

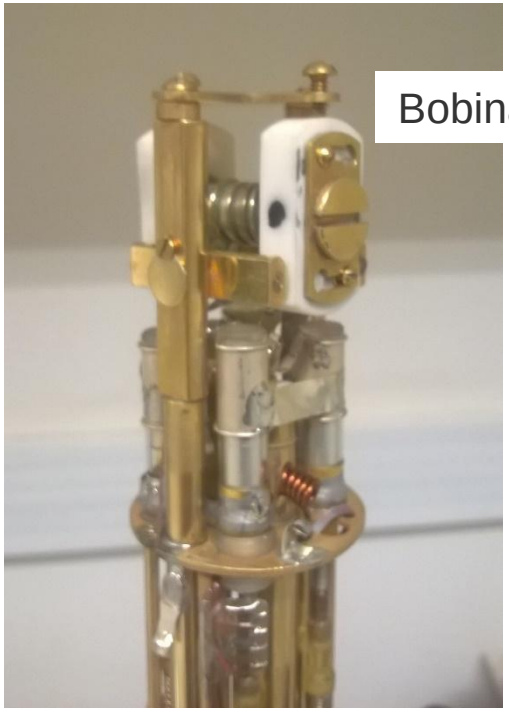


Rotor



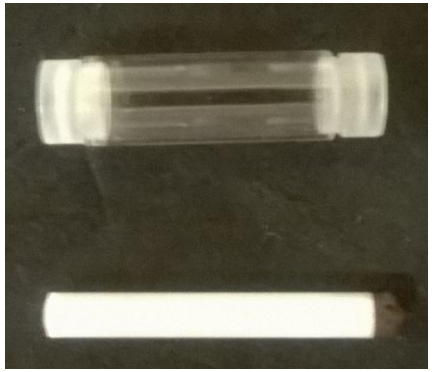
Práticas experimentais em RMN de sólidos

Sonda para experimentos com amostra estática:



Bobina de RF

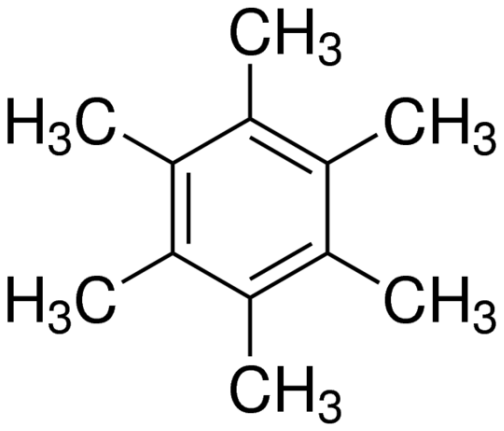
Porta-amostra



Práticas experimentais em RMN de sólidos

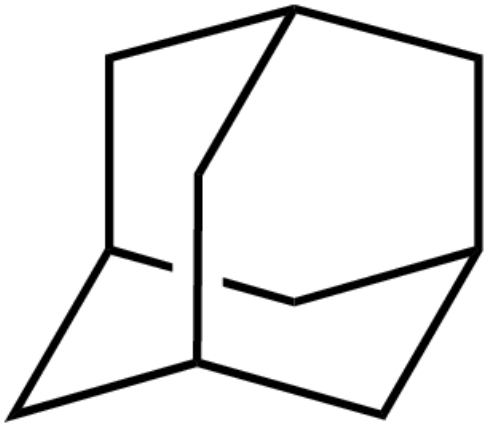
Referências secundárias para deslocamento químico – RMN de ^{13}C:

Hexamethylbenzeno (HMB)



δ (^{13}C) = 17,3 ppm

Adamantano



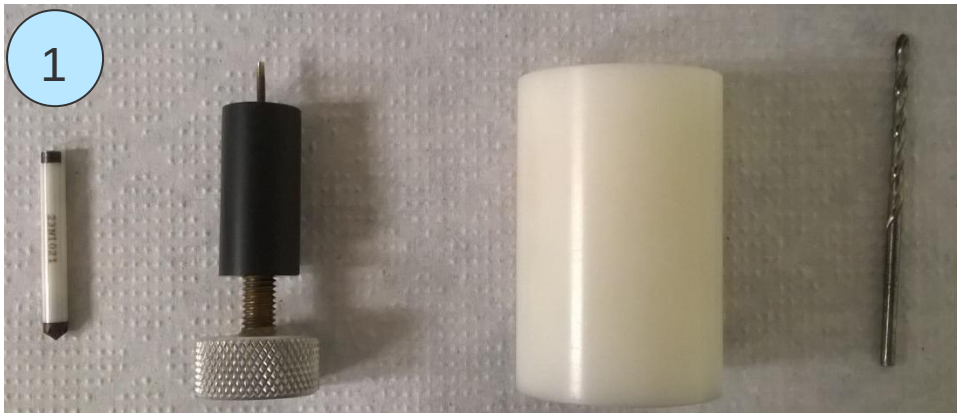
δ (^{13}C) = 38,5 ppm

http://www.sigmaaldrich.com

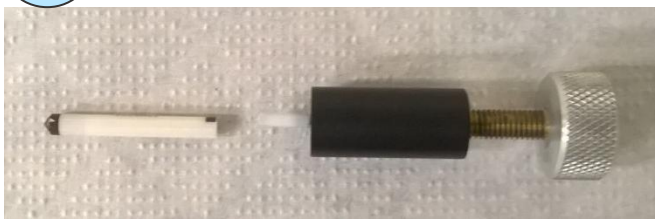
Práticas experimentais em RMN de sólidos

Empacotamento da amostra:

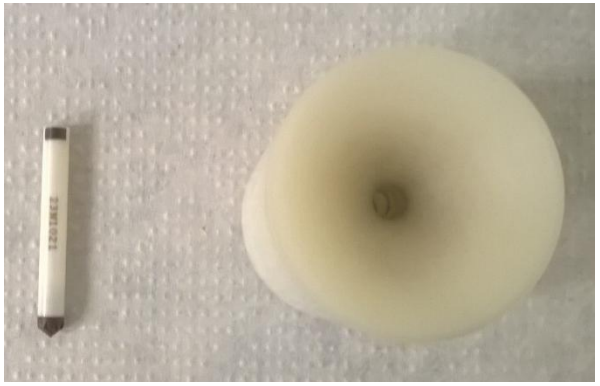
1



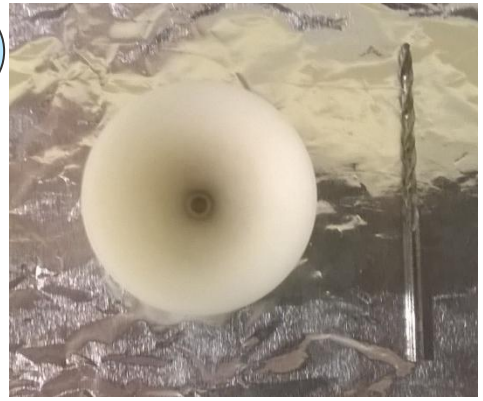
2



3

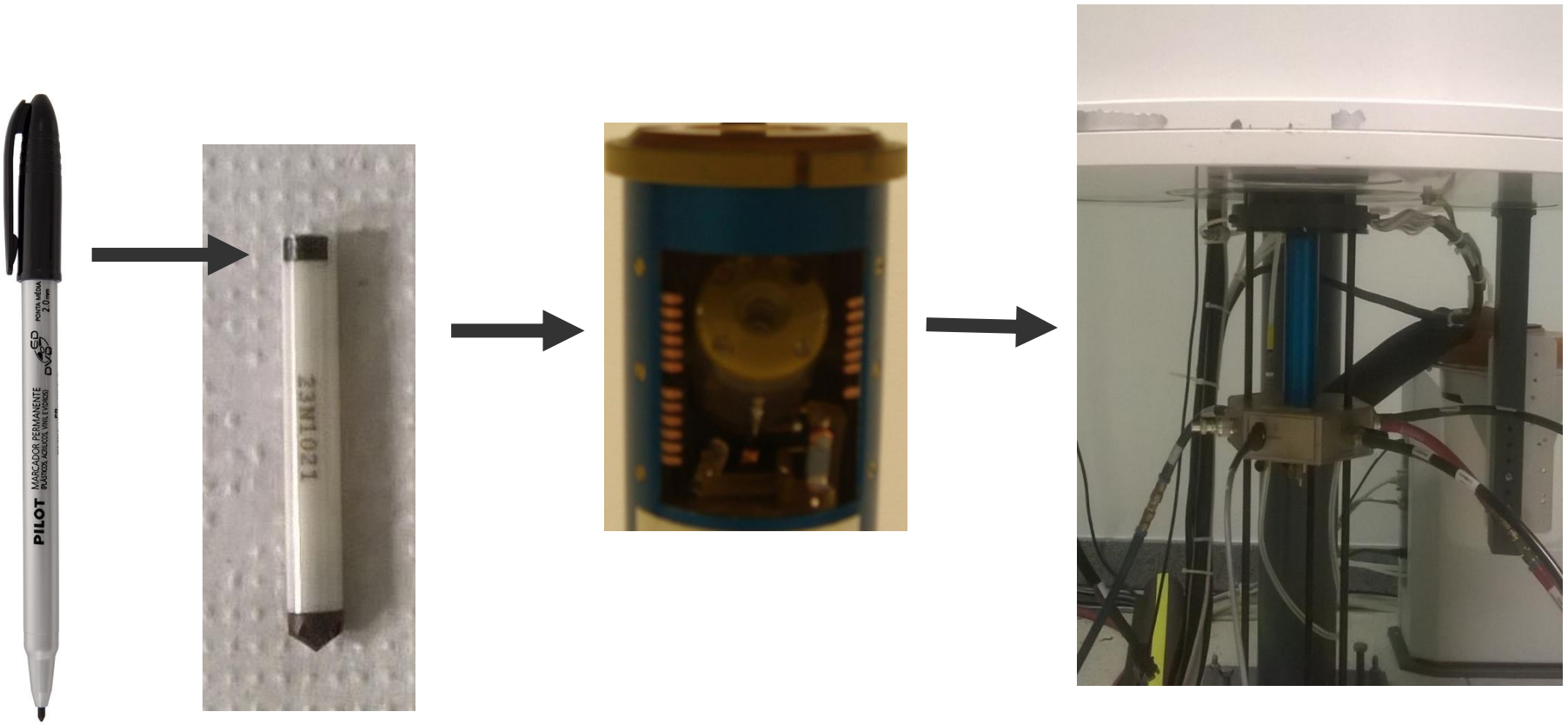


4



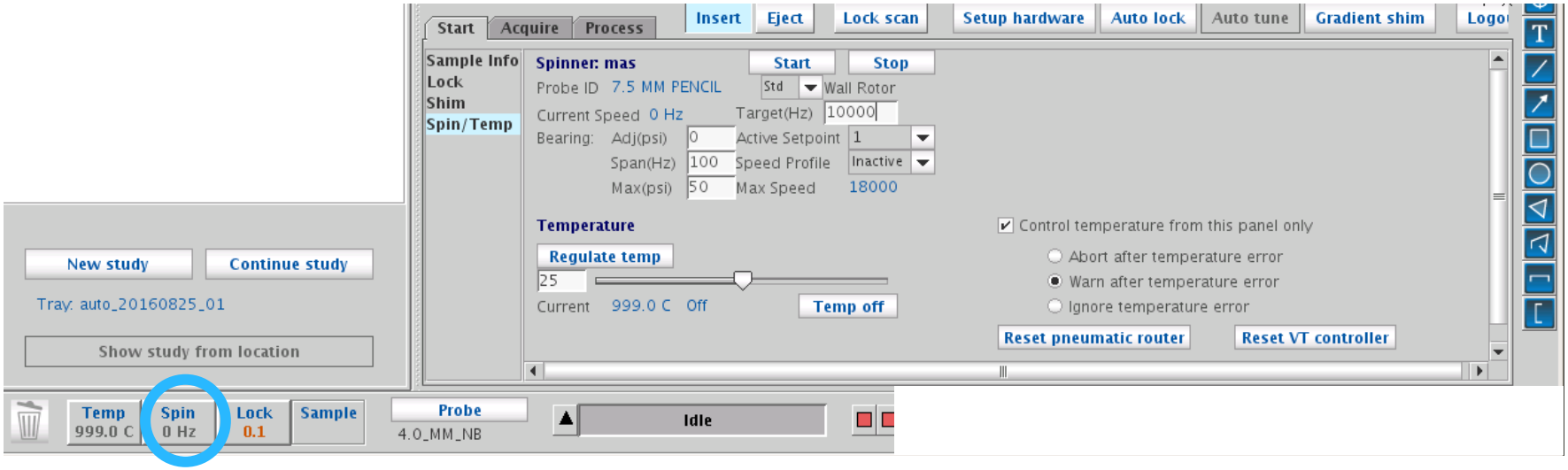
Práticas experimentais em RMN de sólidos

Posicionamento do rotor na sonda:



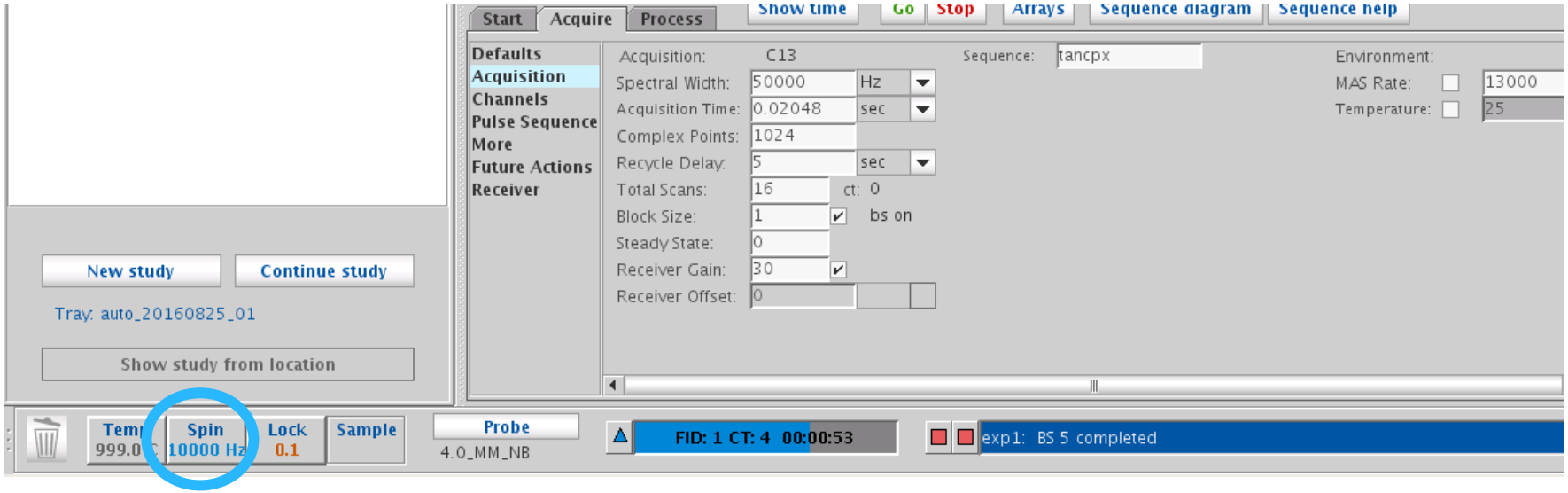
Práticas experimentais em RMN de sólidos

Ajuste da frequência de MAS:



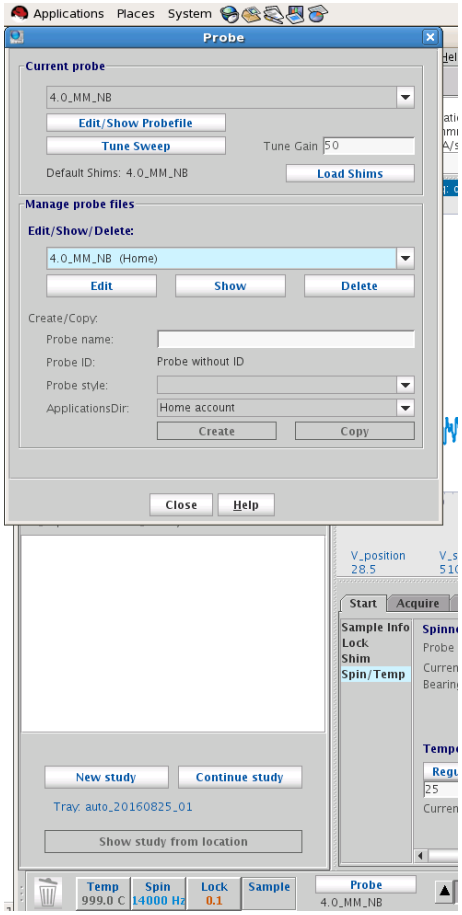
Práticas experimentais em RMN de sólidos

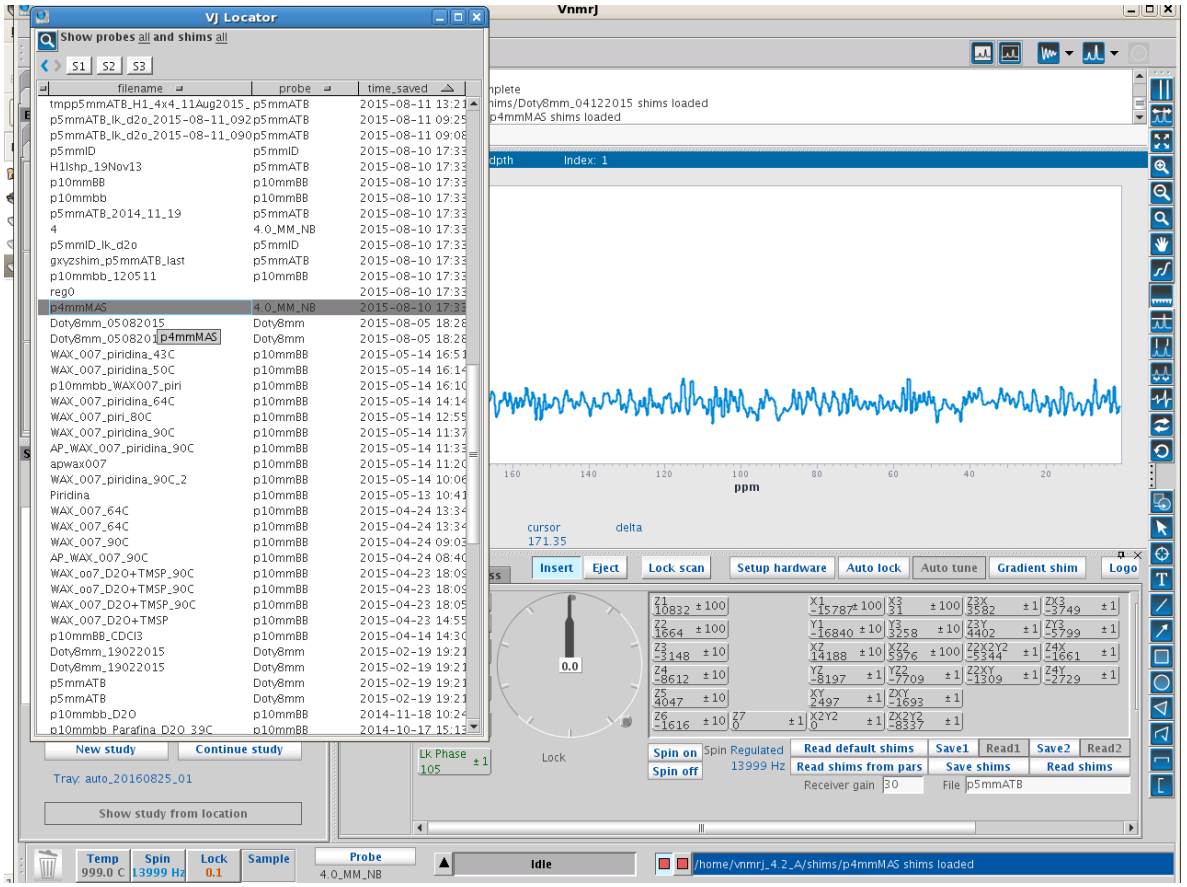
Ajuste da frequência de MAS:



Práticas experimentais em RMN de sólidos

Escolha do arquivo de *shimming*:

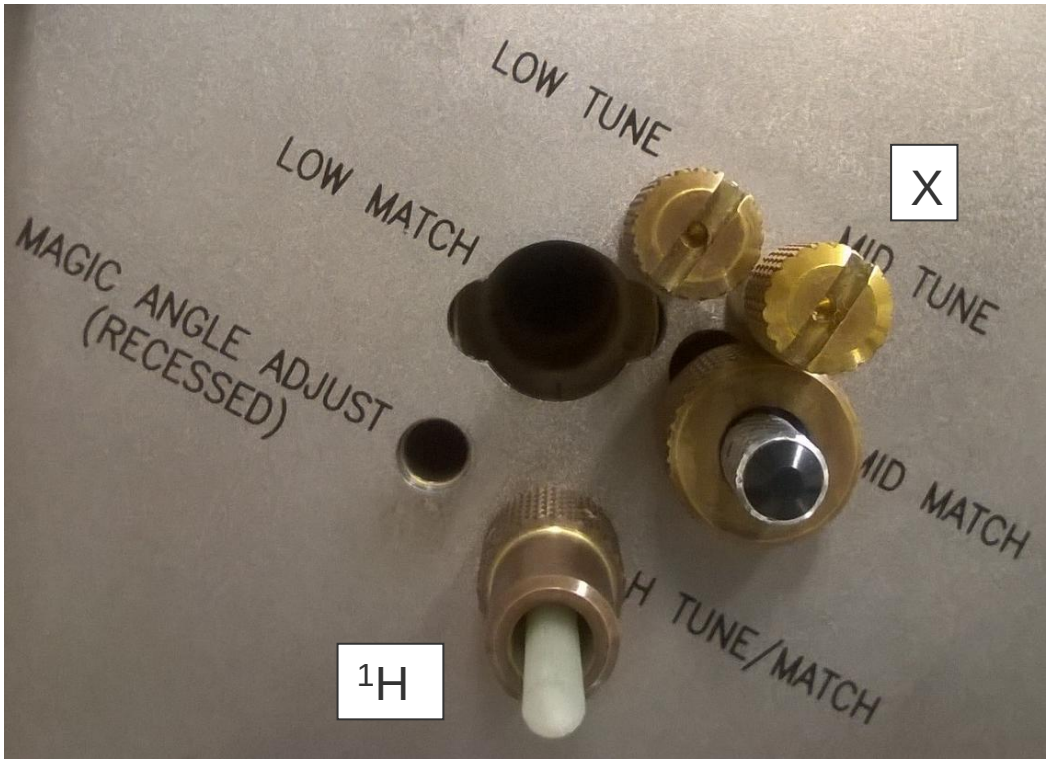




Práticas experimentais em RMN de sólidos

Sintonia:

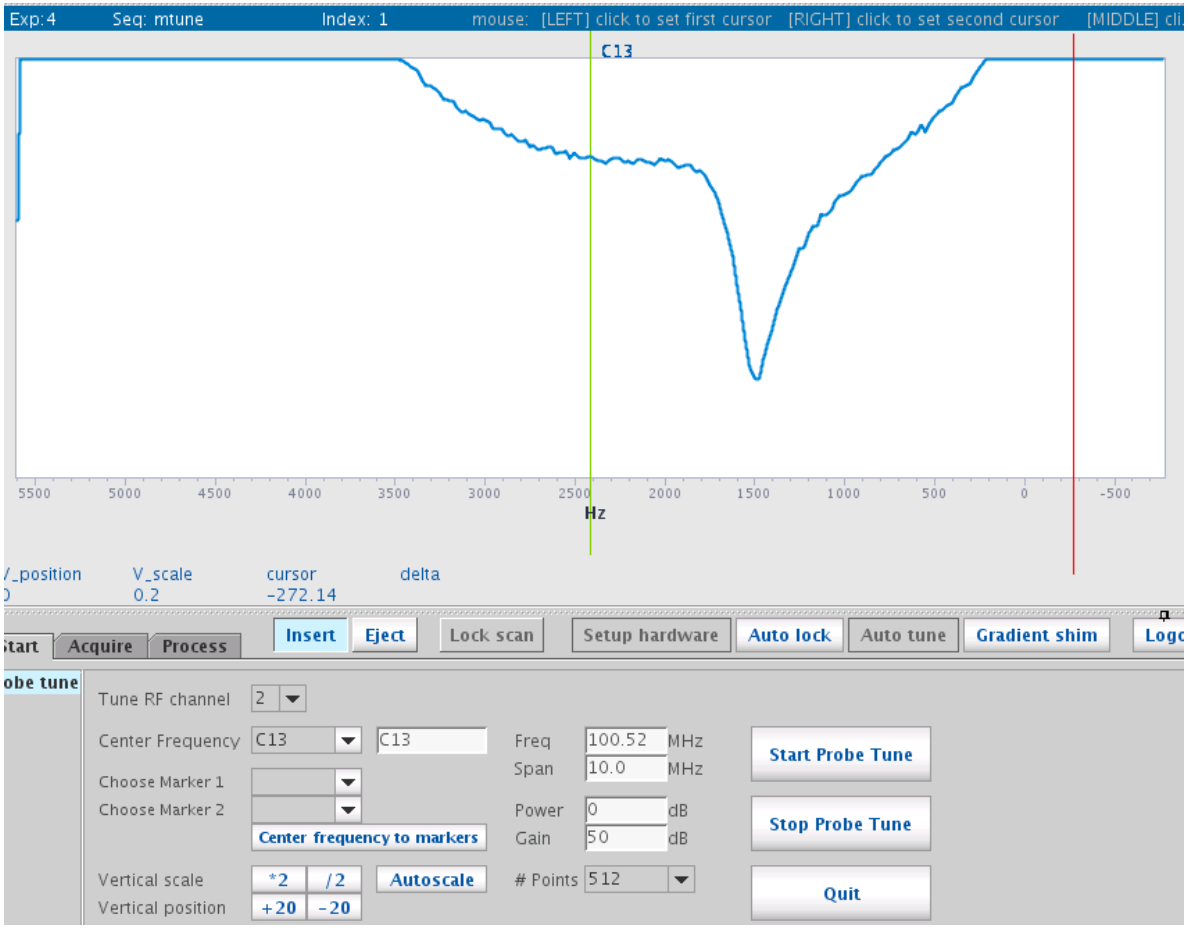
Sonda MAS



Sonda ESTÁTICA

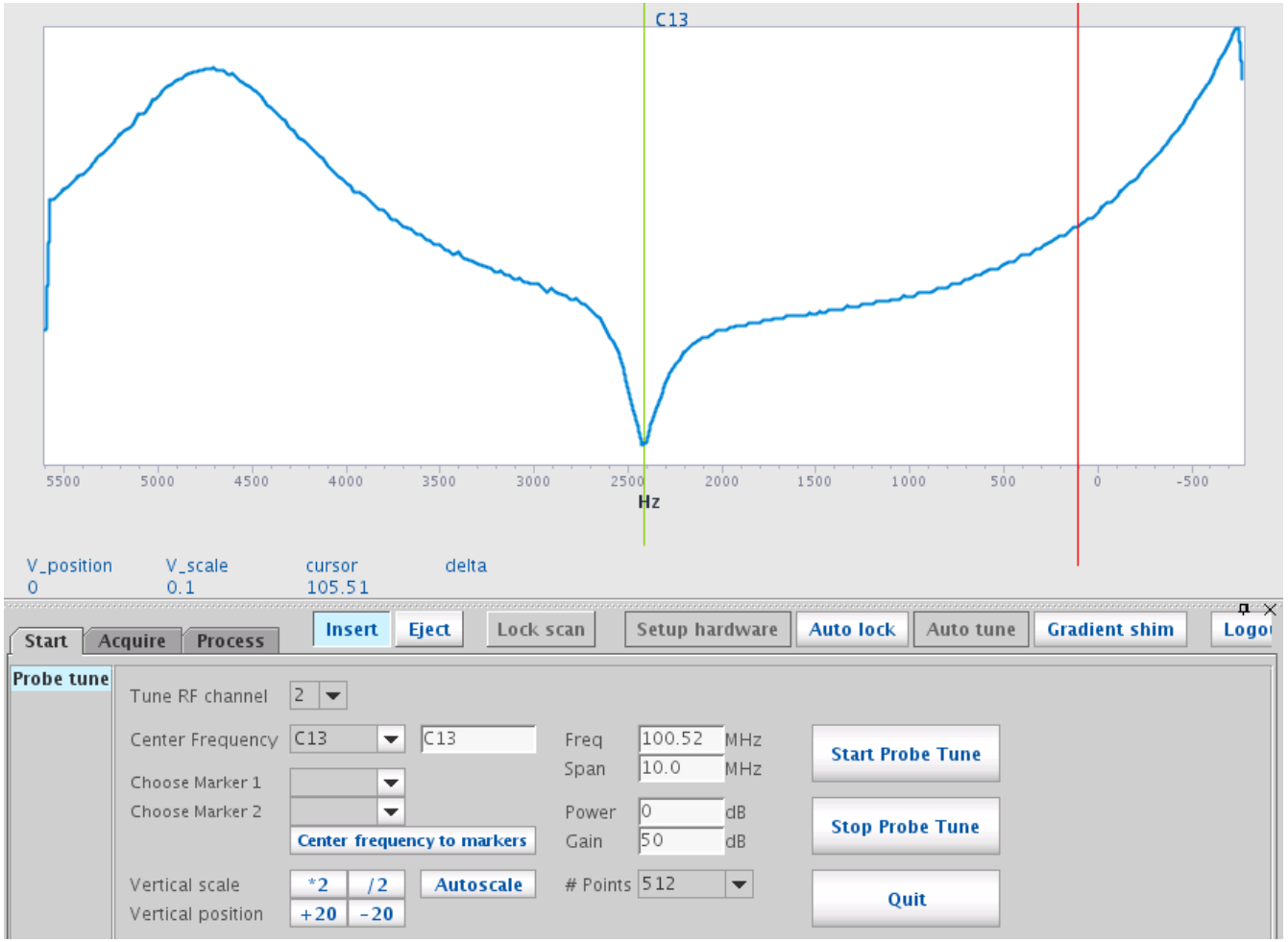
Práticas experimentais em RMN de sólidos

Sintonia:



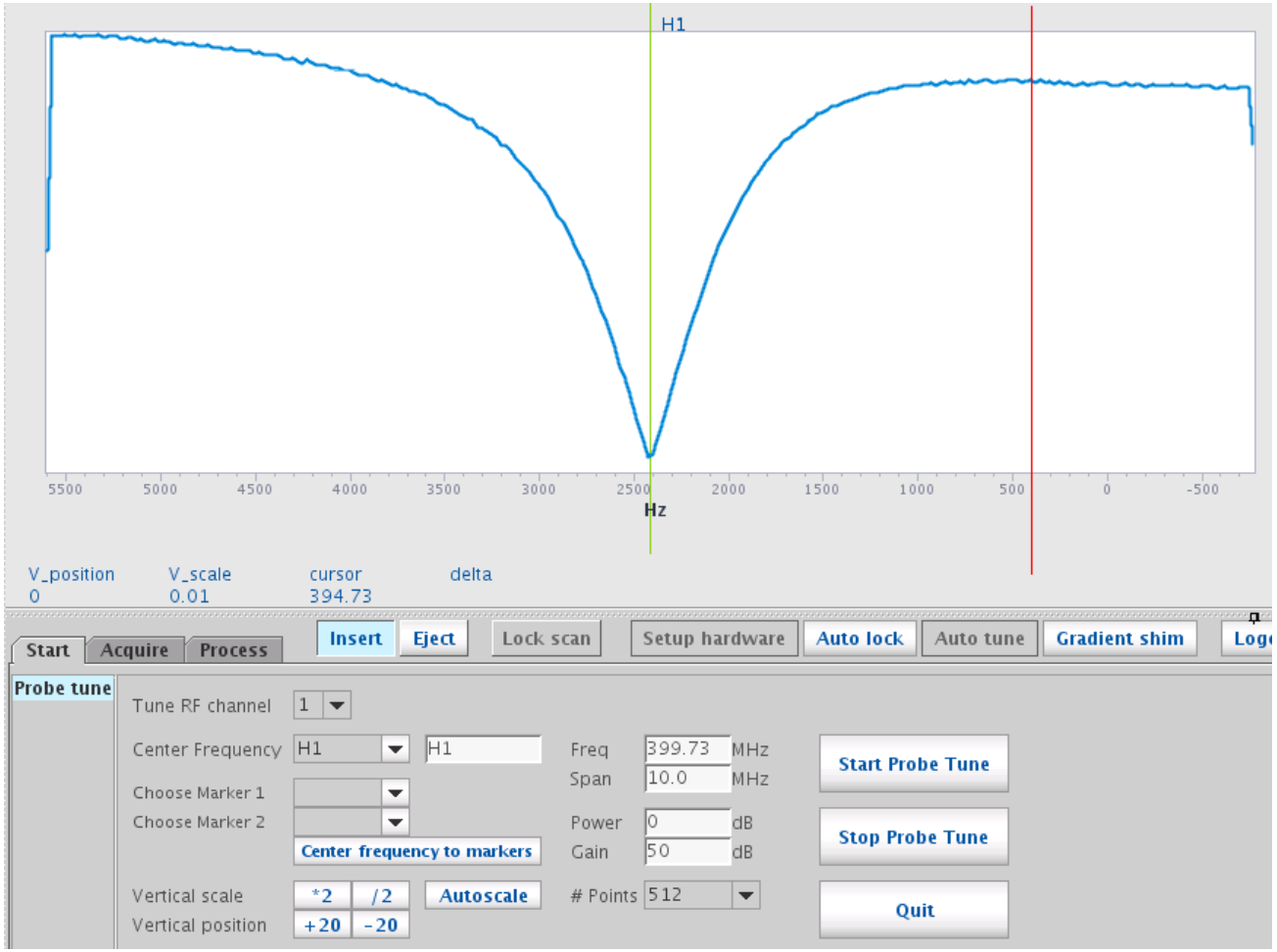
Práticas experimentais em RMN de sólidos

Sintonia:



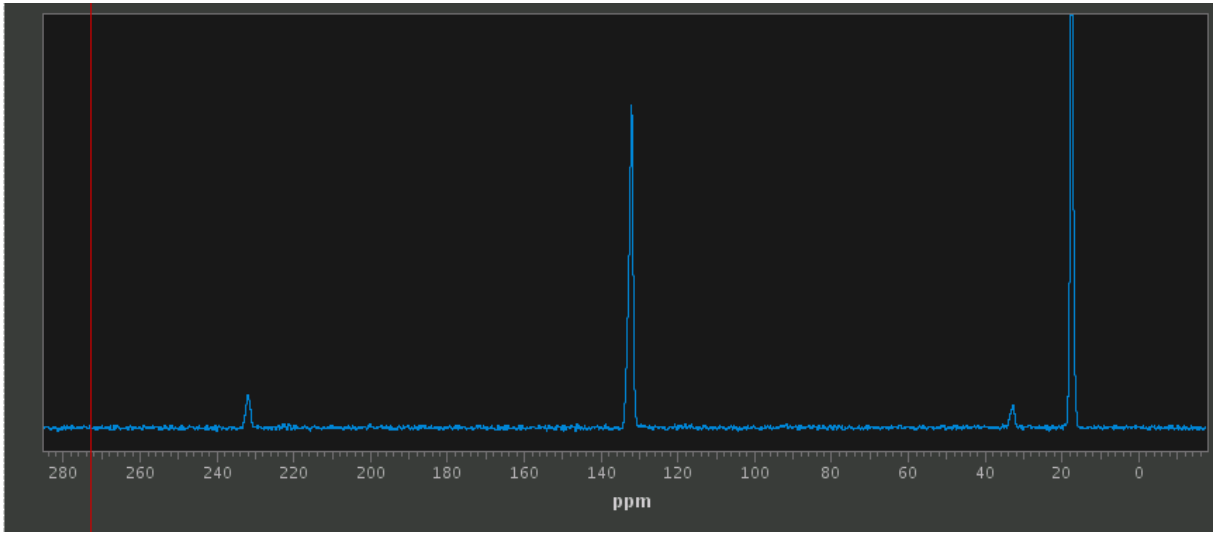
Práticas experimentais em RMN de sólidos

Sintonia:

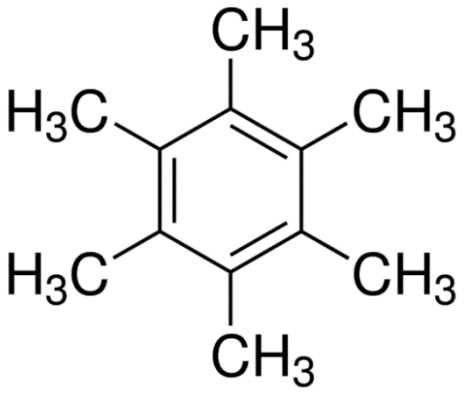


Práticas experimentais em RMN de sólidos

Referência da escala de deslocamentos químicos:



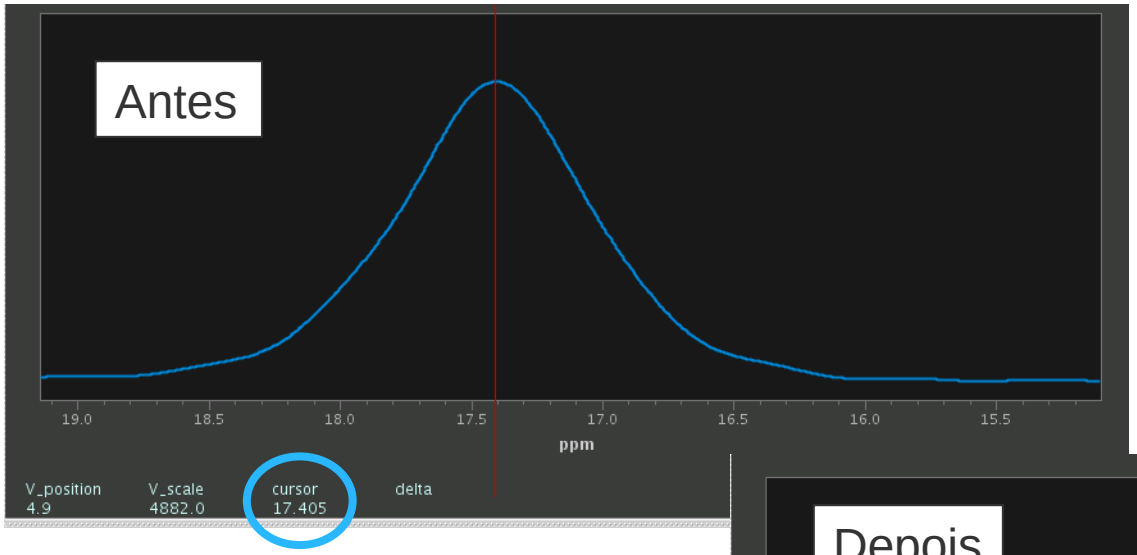
HMB



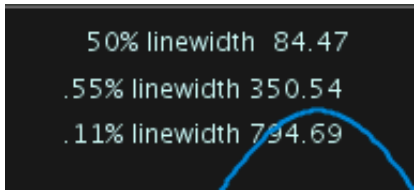
http://www.sigmaaldrich.com

Práticas experimentais em RMN de sólidos

Referência da escala de deslocamentos químicos:



Largura a meia altura



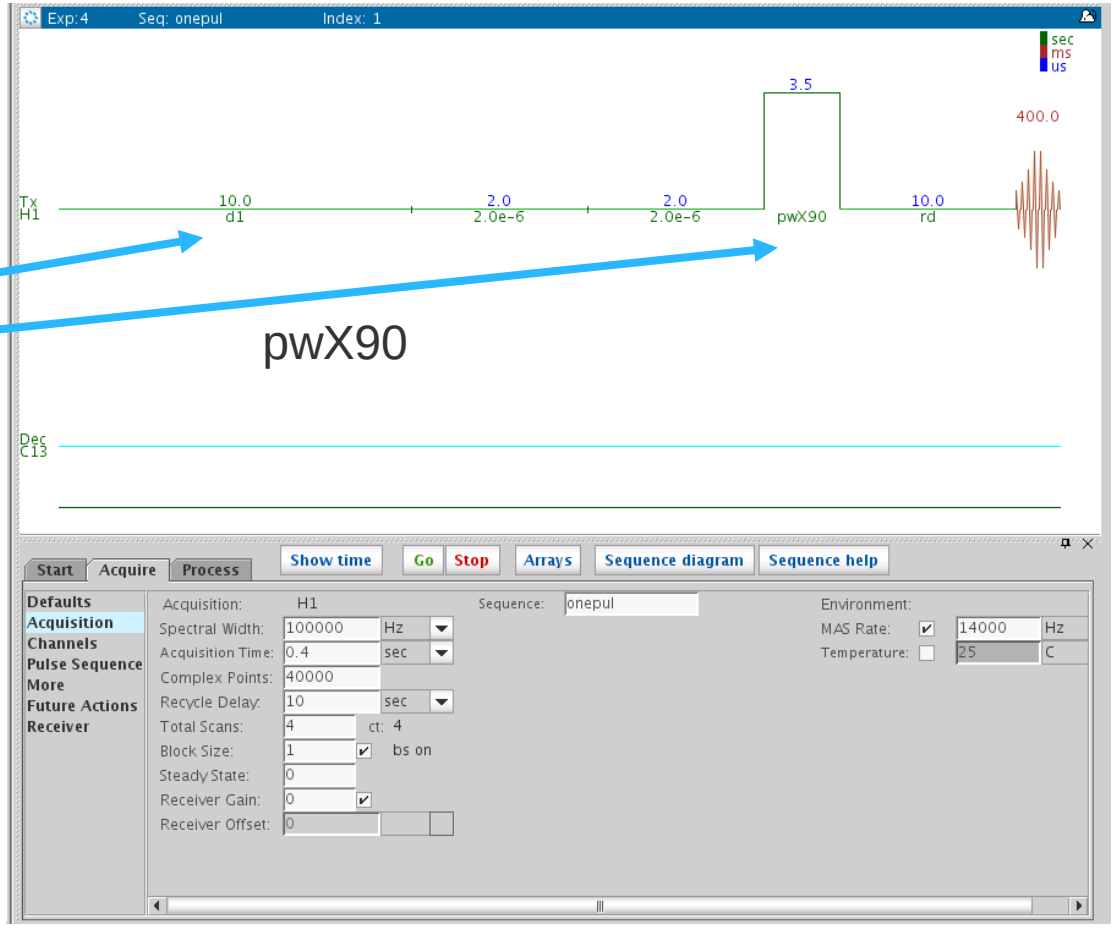
Práticas experimentais em RMN de sólidos

Experimento de excitação com pulso único (SPE):

Parâmetros a serem ajustados.

d1

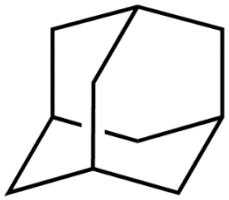
pwX90

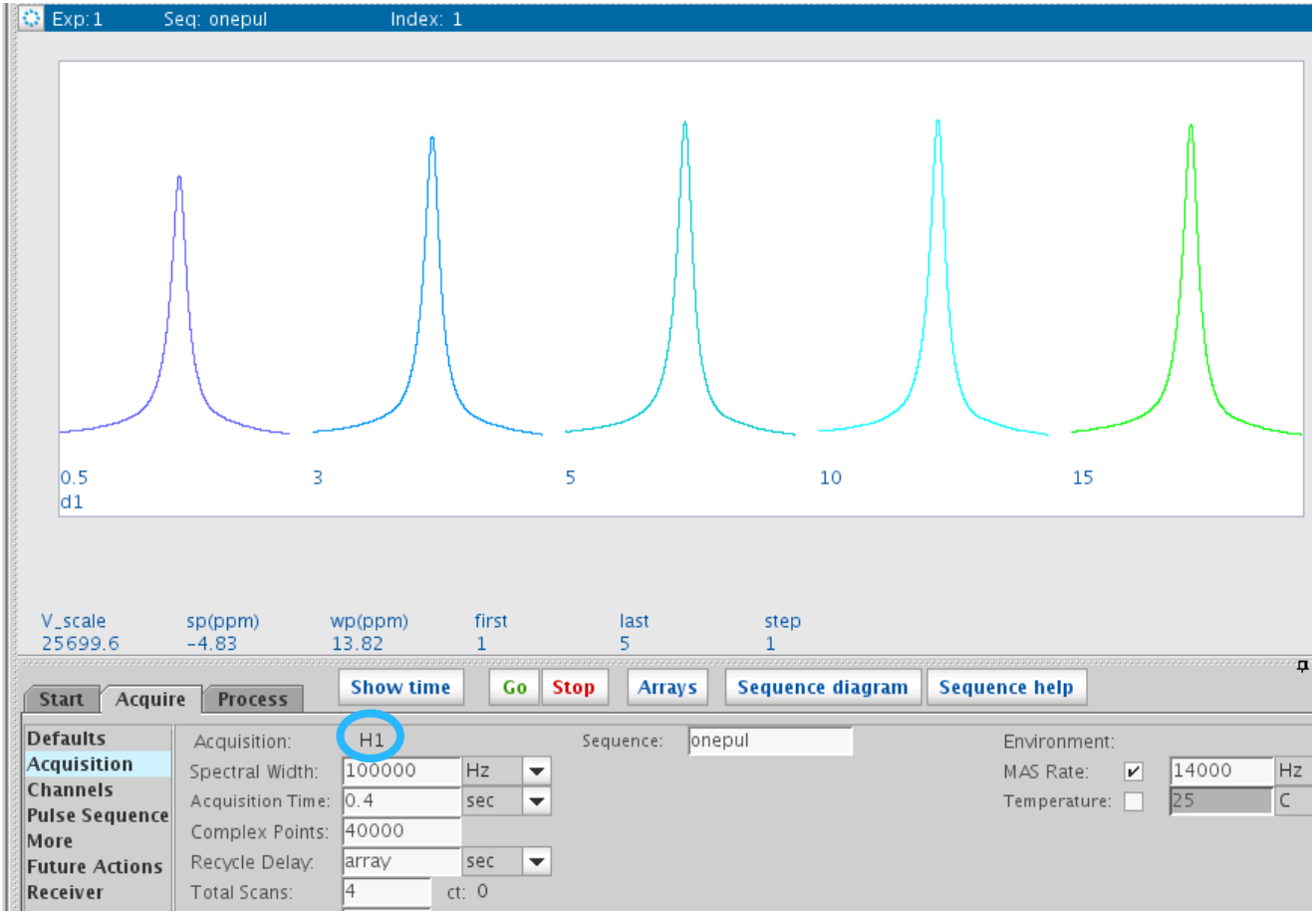


Práticas experimentais em RMN de sólidos

Variação do tempo de repetição (*array* de d1):

Adamantano

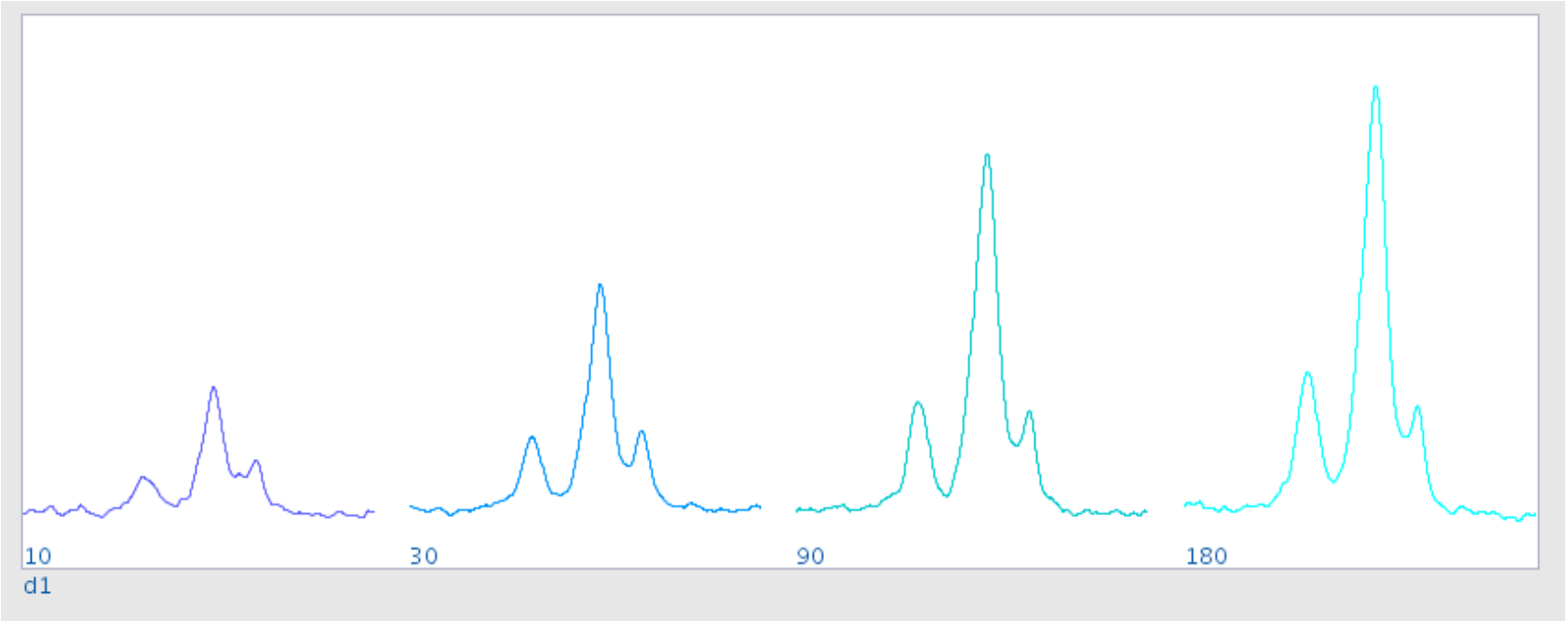




Práticas experimentais em RMN de sólidos

Variação do tempo de repetição (*array* de d1):

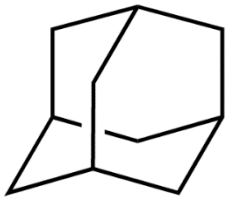
RMN de ^{13}C - resina fenólica

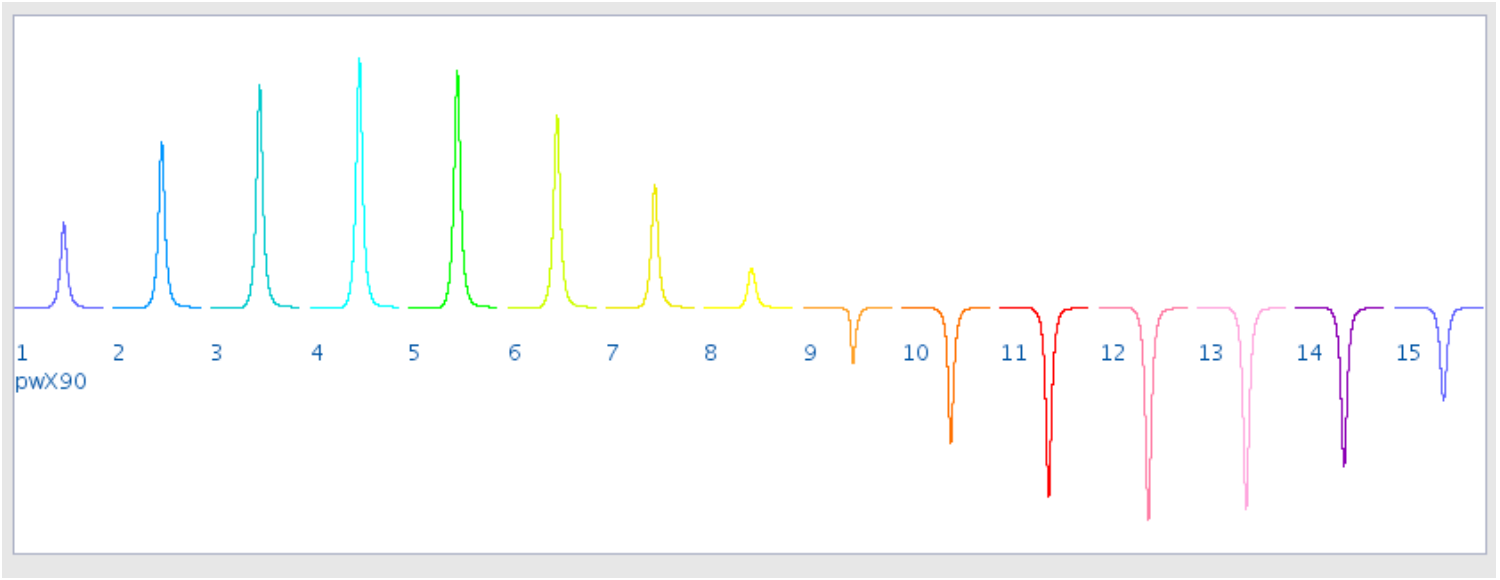


Práticas experimentais em RMN de sólidos

Variação do tempo de duração do pulso de excitação (*array* de pwX90):

Adamantano

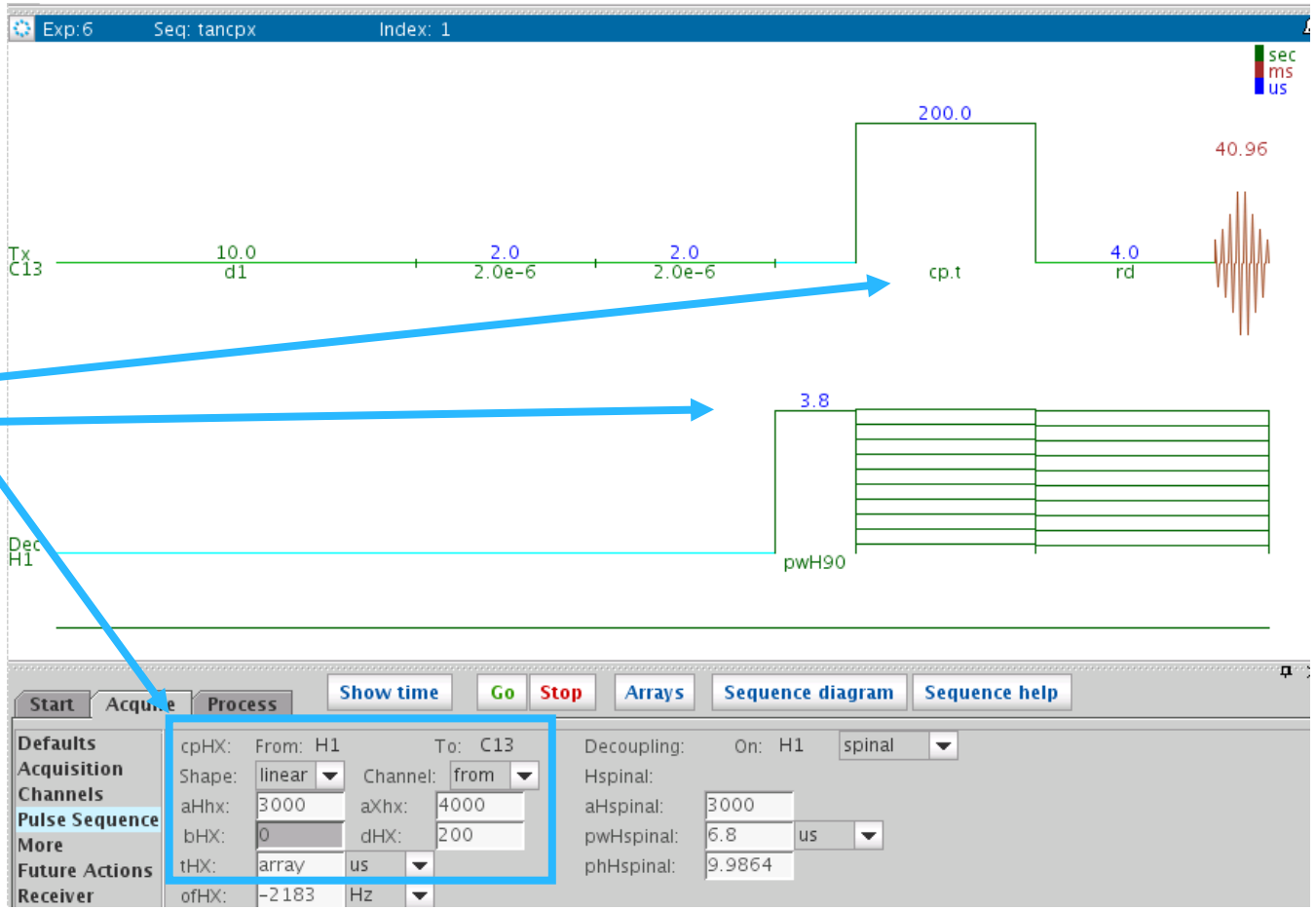




Práticas experimentais em RMN de sólidos

Experimento de polarização cruzada (CP):

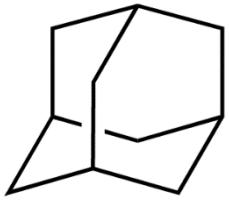
Parâmetros a serem ajustados.

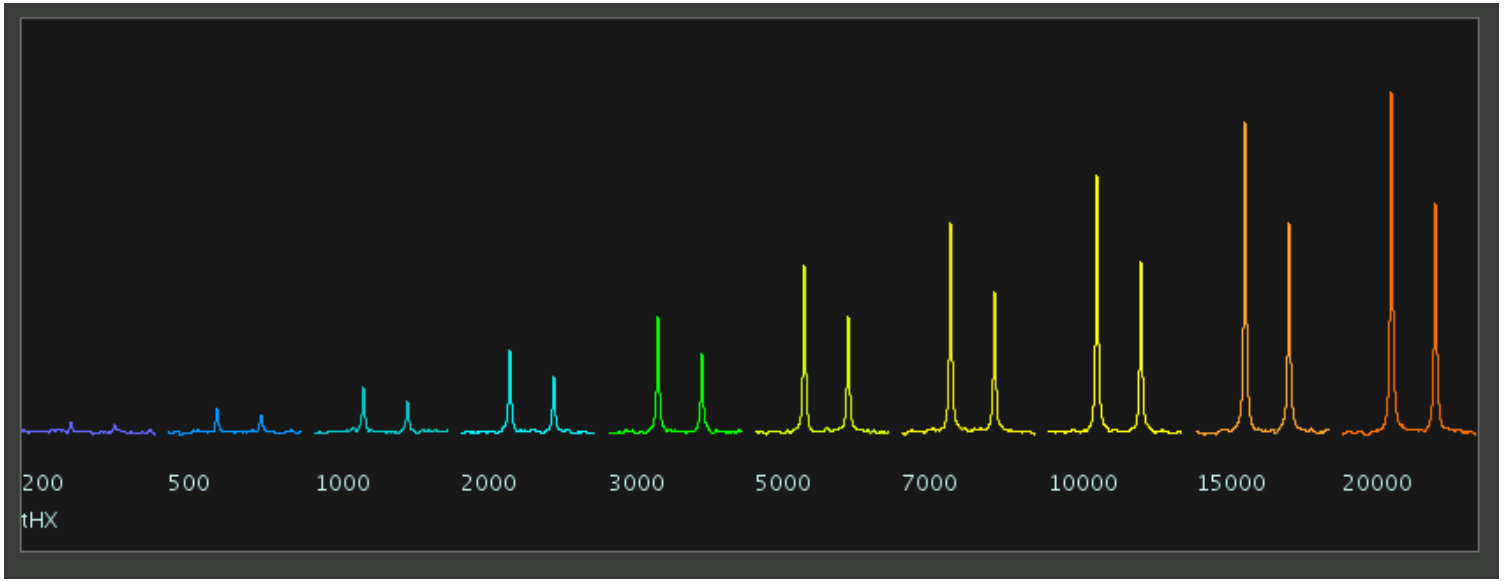


Práticas experimentais em RMN de sólidos

Variação do tempo de contato (*array* de tHX):

Adamantano

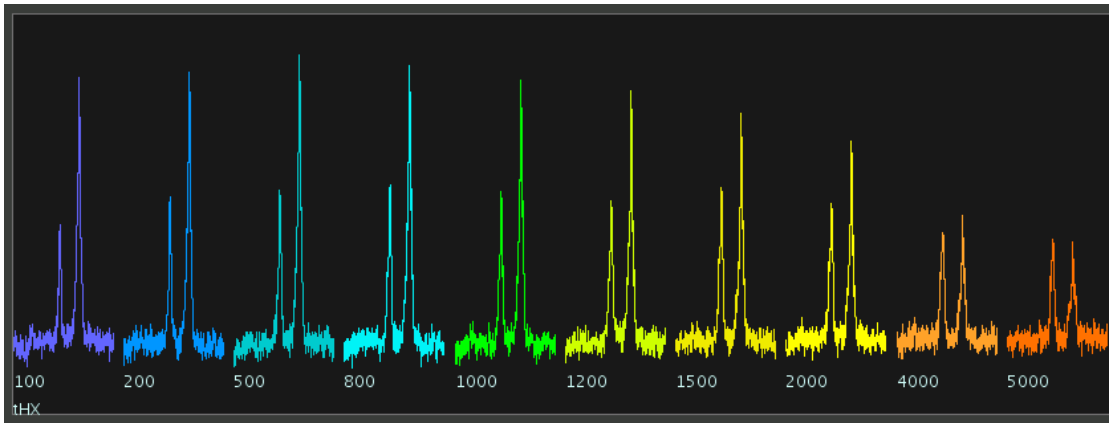




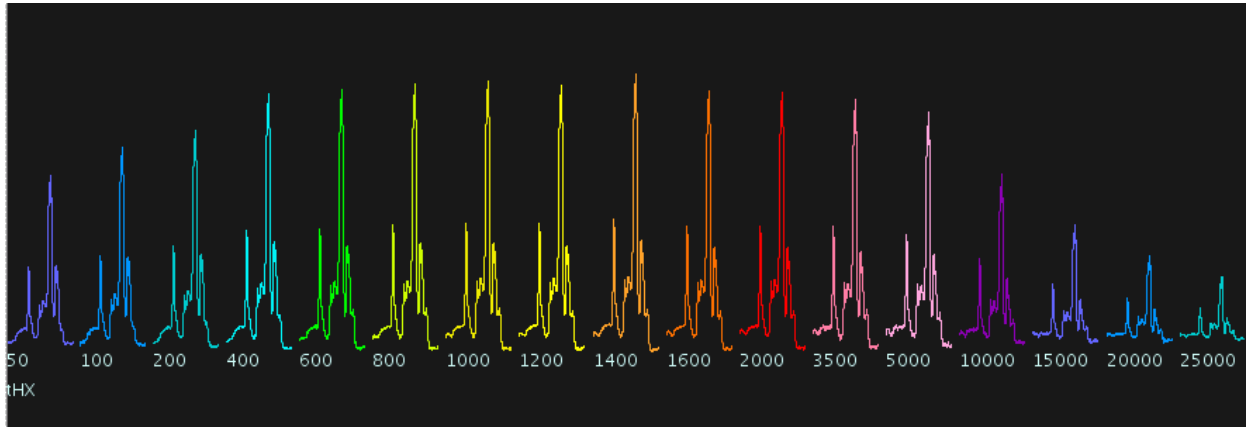
Práticas experimentais em RMN de sólidos

Variação do tempo de contato (*array* de tHX):

Asfalteno

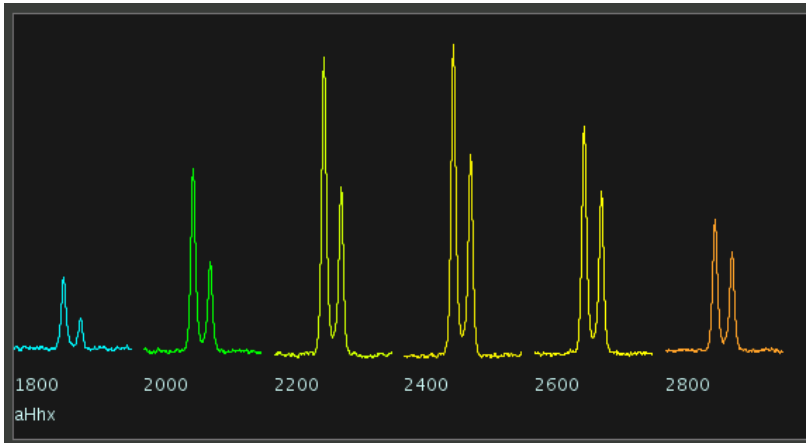


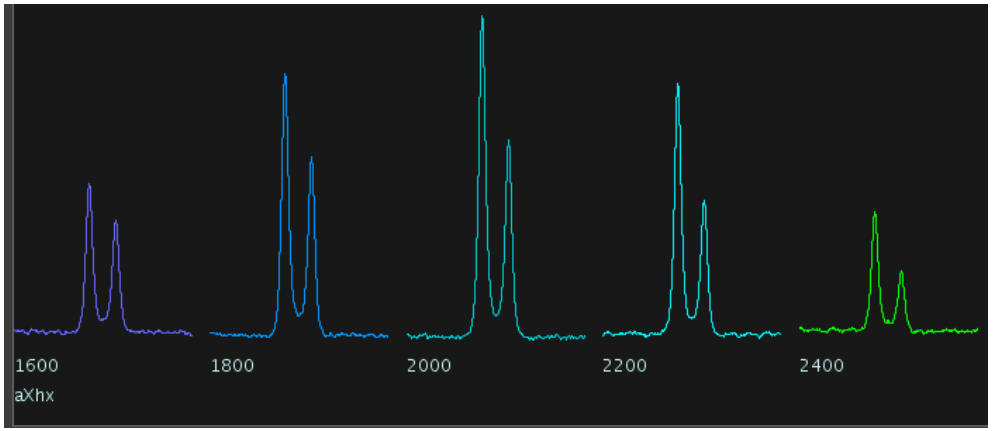
Madeira de pinho



Práticas experimentais em RMN de sólidos

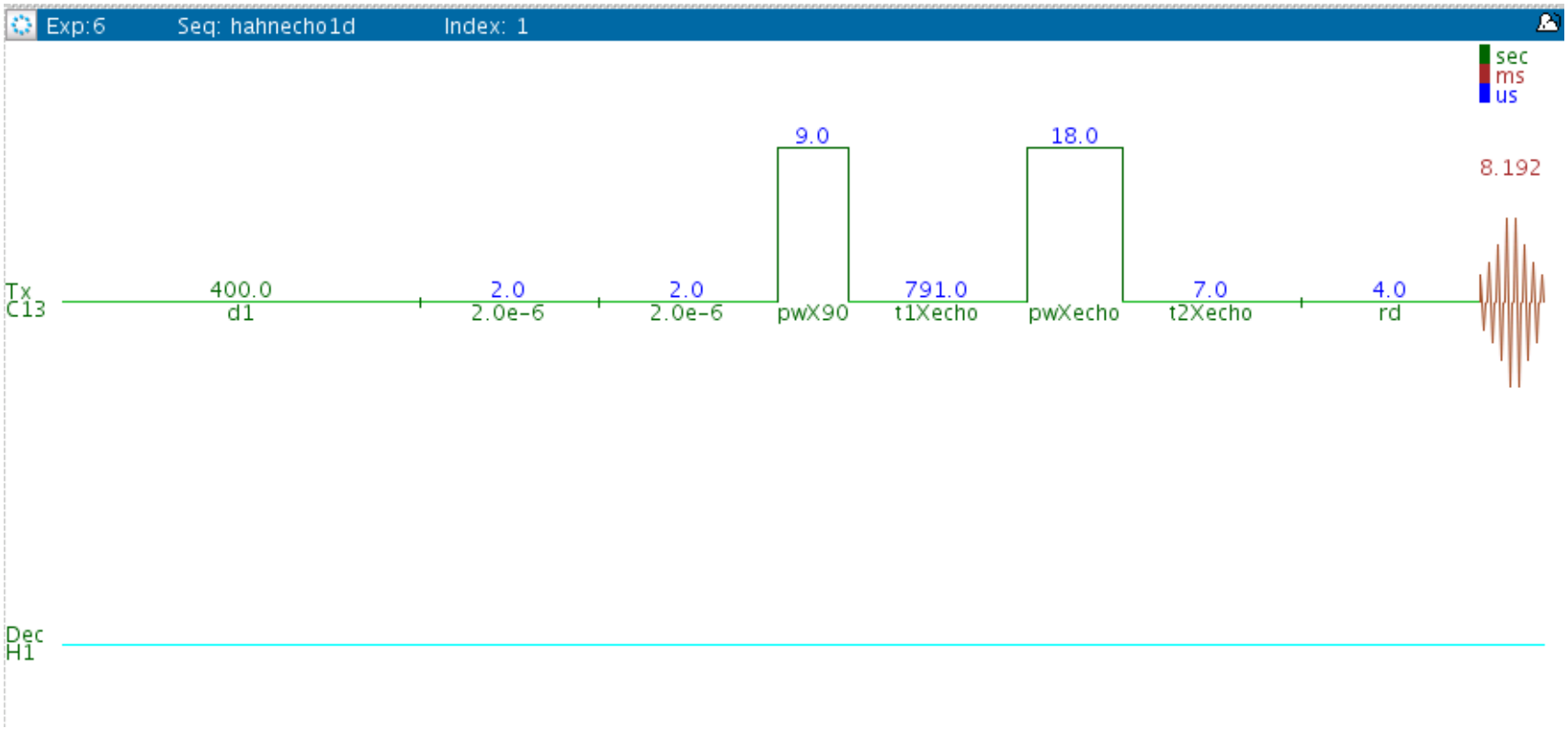
Ajuste da condição de Hartmann-Hahn (*array* de aHhx e/ou aXhx):





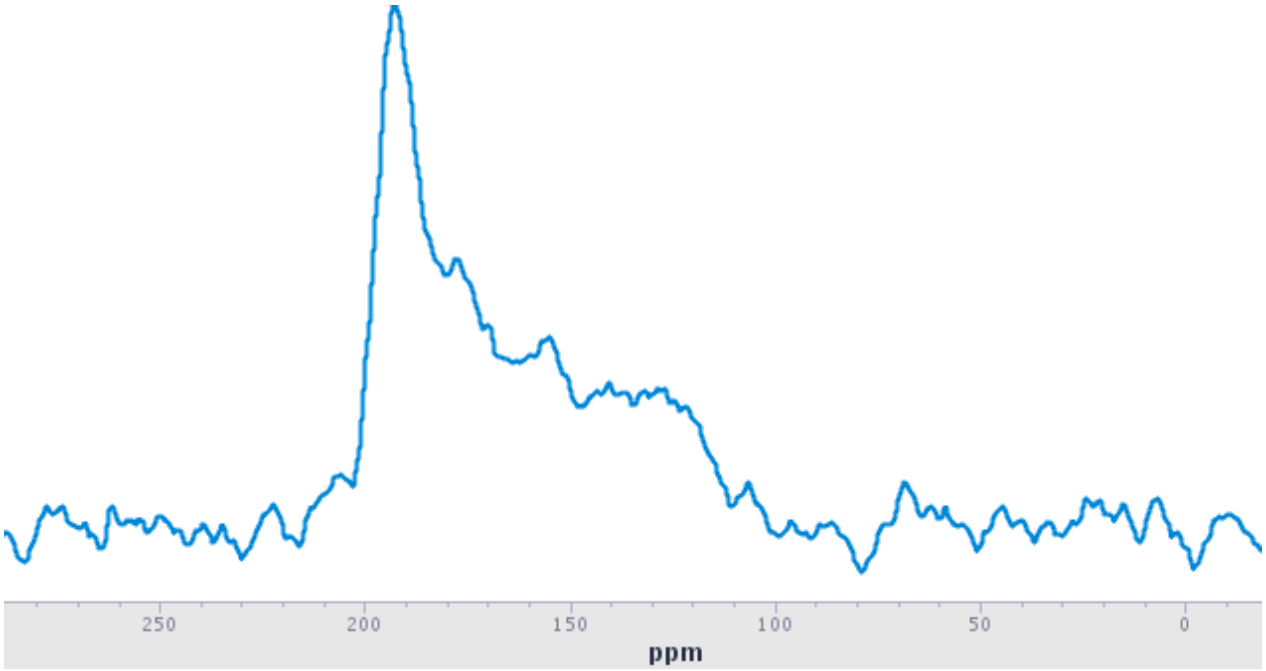
Práticas experimentais em RMN de sólidos

Experimento de spin-eco:



Práticas experimentais em RMN de sólidos

Experimento de spin-eco – RMN de ^{13}C em $CaCO_3$ com amostra estática:



Métodos computacionais para cálculos de parâmetros espectrais em RMN

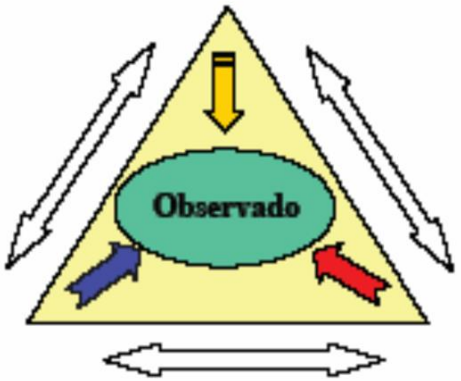
Wanderlã L. Scopel

Sumário

- Introdução
- Teoria do Funcional Densidade (DFT)
- Aplicações
- Método GIPAW
- Simulação do tensor de blindagem magnética (RMN)

Experimento, Teoria e Simulação

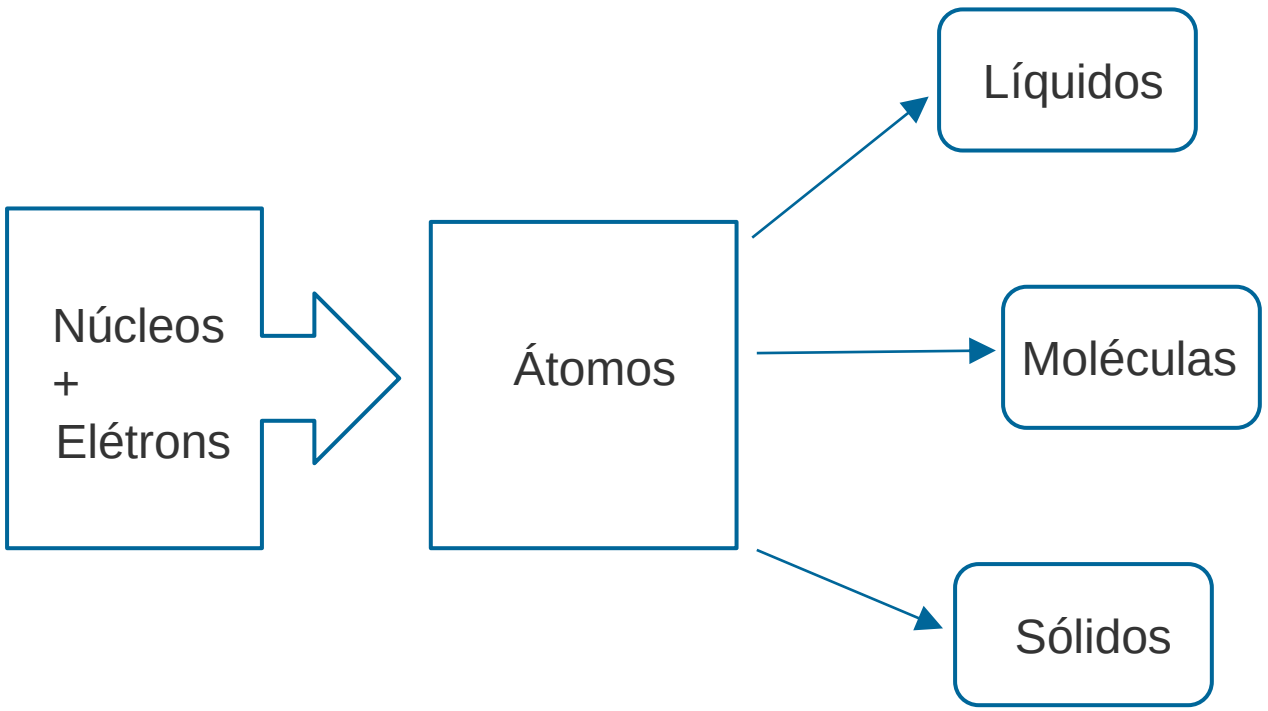
Experimento: Resultado observado de fatos Naturais.



Teoria: Modelo para descrever os fatos experimentais. Em geral só se conhece soluções para casos especiais e aproximações.

Simulação: Resolve *exatamente* o modelo, e testa teorias.

Materiais



E. Schroedinger (1926)

Second Series *December, 1926* *Vol. 28, No. 6*

THE

PHYSICAL REVIEW

AN UNDULATORY THEORY OF THE MECHANICS OF ATOMS AND MOLECULES

By E. Schrödinger

Abstract

The paper gives an account of the author's work on a new form of quantum theory. §1. The Hamiltonian analogy between mechanics and optics. §2. The analogy is to be extended to include real "physical" or "undulatory" mechanics instead of mere geometrical mechanics. §3. The significance of wave-length; macro-mechanical and micro-mechanical problems. §4. The wave-equation and its application to the hydrogen atom. §5. The intrinsic reason for the appearance of discrete characteristic frequencies. §6. Other problems; intensity of emitted light. §7. The wave-equation derived from a Hamiltonian variation-principle; generalization to an arbitrary conservative system. §8. The wave-function physically means and determines a continuous distribution of electricity in space, the fluctuations of which determine the radiation by the laws of ordinary electrodynamics. §9. Non-conservative systems. Theory of dispersion and scattering and of the "transitions" between the "stationary states." §10. The question of relativity and the action of a magnetic field. Incompleteness of that part of the theory.

Formulação Moderna: DFT iniciou-se com P. Hohenberg e W. Kohn (1964)

PHYSICAL REVIEW VOLUME 136, NUMBER 3B 9 NOVEMEBR 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†
École Normale Superieure, Paris, France
AND
W. KOHN‡
École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France
and
University of California at San Diego, La Jolla, California

(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E\equiv\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$, $\tilde{n}/n_0<<1$, and (2) $n(\mathbf{r})=\varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0\to\infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

Avanço com W. Kohn e L. J. Sham (1965)

PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

W. KOHN AND L. J. SHAM
University of California, San Diego, La Jolla, California
(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

Ideia Fundamental da DFT

- O estado de energia fundamental, função de onda, e todos os outros observáveis são determinados unicamente pela densidade de probabilidade total do elétron: ρ(x,y,z).
- Esta densidade (ρ(x,y,z)) é função somente 3 variáveis, e não 3N!

Então o que é densidade? É uma função positiva tal que:

$$\int n(\vec{r}) d^3 r = N$$

Note que conhecendo a função de onda podemos escrever a densidade:

$$n(\vec{r}) = N \int |\Psi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)|^2 d^3 r_2 \ldots d^3 r_N$$

Teoria do Funcional Densidade (DFT)

P. Hohenberg e W. Kohn, Phys. Rev **136**, 864B (1964) -

W. Kohn e L. J. Sham, Phys. Rev. **140**, 1133A (1965) -

Antes de Kohn: Função de onda $\Psi(\mathbf{r}_1 \ldots \mathbf{r}_N)$ era a entidade fundamental. $\Psi \rightarrow E_o$

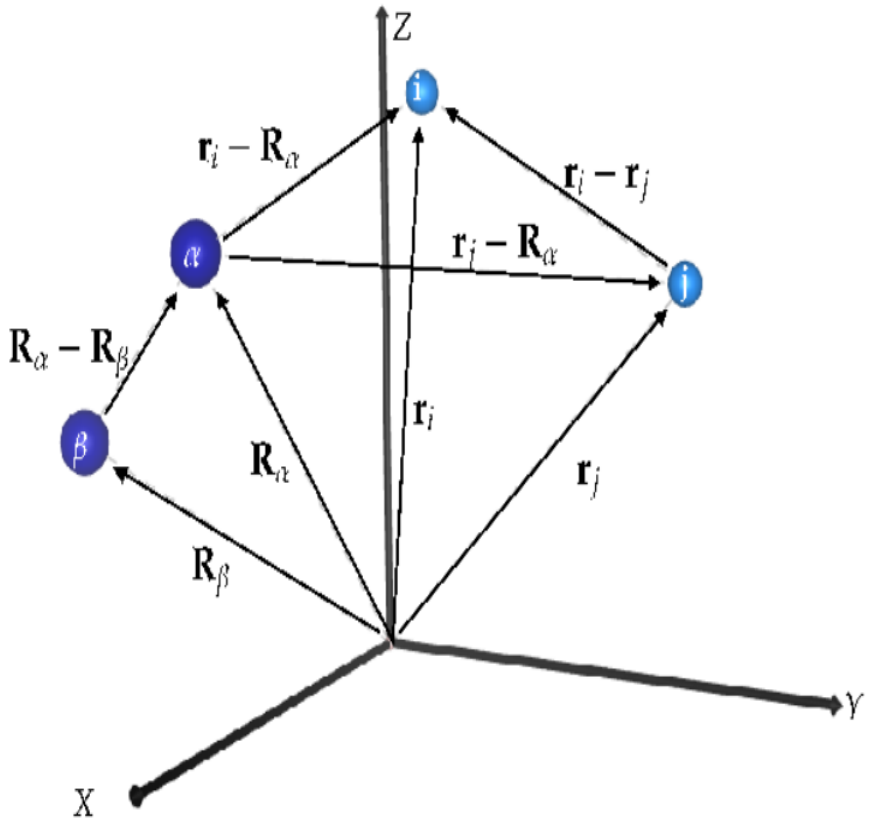
Depois de Kohn: Densidade eletrônica $n(\mathbf{r})$ é a entidade fundamental! $n \rightarrow \Psi, E_o$

Problema de muitos elétrons interagentes é mapeado **exatamente** (em princípio) no problema de um elétron sob a ação de um potencial efetivo (porém desconhecido).

- A Teoria do Funcional Densidade está alicerçada em dois teoremas propostos por Hohenberg e Kohn.
  - O potencial externo sentido pelos elétrons é um funcional único da densidade eletrônica [$n(\mathbf{r})$].
  - A energia do estado fundamental $E_0[n(\mathbf{r})]$ é mínima para a densidade $n(\mathbf{r})$ exata.

P. Hohenberg e W. Kohn, Phys. Rev. 136, B864 (1964)

Sistema com muitos corpos interagentes



Szabo, A. & Ostlund, N. S. Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory

Sistema com elétrons e núcleos

$$\hat{H}\Psi(\{\mathbf{r_i}\};\{\mathbf{R}_\alpha\}) = E\Psi(\{\mathbf{r_i}\};\{\mathbf{R}_\alpha\})$$

Coordenadas nucleares

Acopladas

Coordenadas eletrônicas

Hamiltoniano:

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{NN} + \hat{V}_{Ne}$$

$$\hat{T}_e = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2$$

$$\hat{T}_N = -\frac{1}{2}\sum_{\alpha=1}^{M}\frac{1}{M_\alpha}\nabla_\alpha^2$$

$$\hat{V}_{ee} = \frac{1}{2}\sum_{j\neq i}^{N}\sum_{i=1}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{V}_{Ne} = -\sum_{i=1}^{N}\sum_{\alpha=1}^{M}\frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|}$$

$$\hat{V}_{NN} = \frac{1}{2}\sum_{\alpha\neq\beta}^{M}\sum_{\beta=1}^{M}\frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}$$

Sistema com N elétrons

$$\hat{H}\Psi(\vec{r}_1,\ldots,\vec{r}_N) = E\Psi(\vec{r}_1,\ldots,\vec{r}_N)$$

- Considerando a aproximação de Born-Oppenheimer, onde os núcleos estão estáticos, isto é, contribuindo somente para a energia potencial.

$$\hat{H}_{ele} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \frac{1}{2}\sum_{j\neq i}^{N}\sum_{i=1}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} - \frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{M}\frac{Z_\alpha}{|\mathbf{r}_i-\mathbf{R}_\alpha|}$$

Energia cinética dos elétrons

Energia potencial elétrons-elétrons

Energia potencial elétrons-núcleos

Equações de Kohn-Sham

- Energia Total:

$$E_v[\rho] = T_s[\rho] + E_{\mathsf{H}}[\rho] + E_{\mathsf{XC}}[\rho] + \langle \rho(\mathbf{r}) v_{\mathsf{ne}}(\mathbf{r}) \rangle$$

O termo exato Exc é desconhecido!

- A densidade do estado fundamental deve satisfazer o princípio estacionário como requerido pelo princípio variacional

$$\delta \{ E_v[\rho] - \mu \left[\langle \rho(\mathbf{r}) \rangle - N \right] \} = 0$$

$$\frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{\mathsf{H}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{\mathsf{XC}}[\rho]}{\delta \rho(\mathbf{r})} + v_{\mathsf{ne}}(\mathbf{r}) = \mu$$

Kohn & Sham, *Phys. Rev.* **140**, A1133 (1965).

Esquema baseado no Orbital-Kohn-Sham (KS)

- Equação de KS: $\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}^{\text{KS}}(\mathbf{r})\right)\psi_{i,k} = \epsilon_{i,k}\,\psi_{i,k}$

- Potencial Efetivo KS: $v_{\text{eff}}^{\text{KS}}(\mathbf{r}) = v_{\text{ne}}(\mathbf{r}) + \frac{\delta E_{\text{H}}[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}$

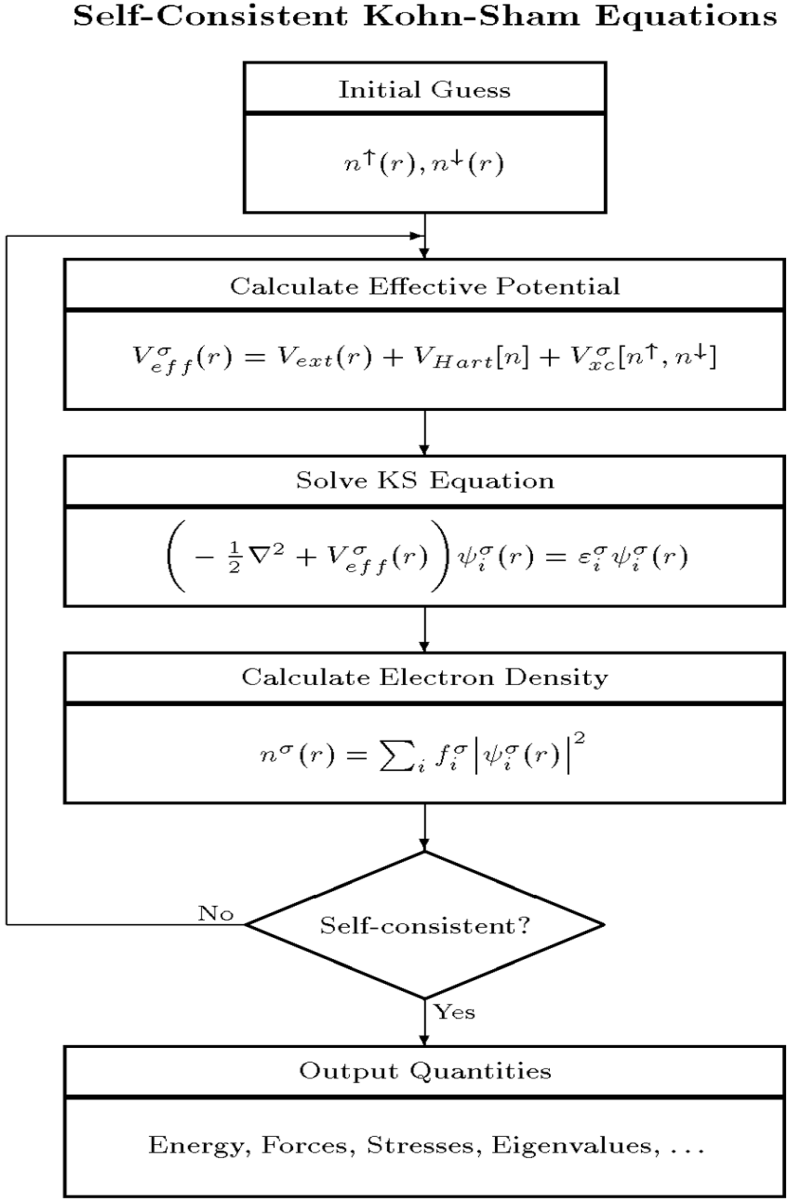
Potencial External

Potencial de Hartree

Potencial de Troca-Correlação

Kohn & Sham, *Phys. Rev.* **140**, A1133 (1965).

Resolvendo as equações de **Kohn-Sham**

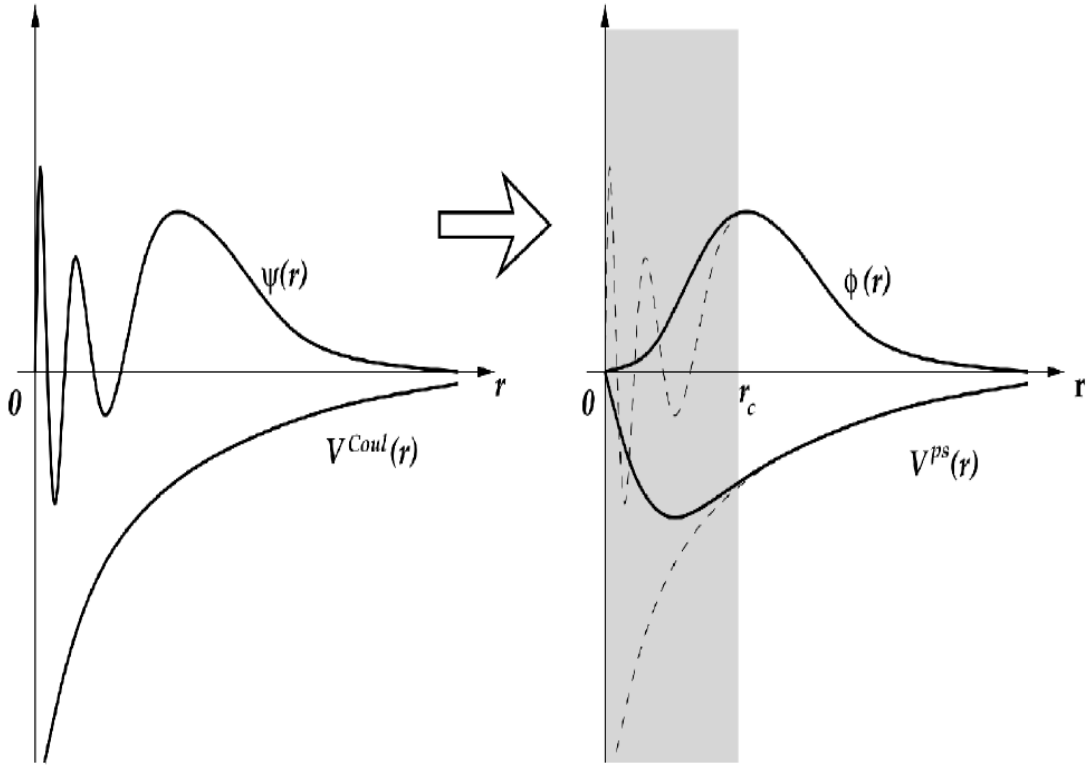


Escolha de um conjunto de bases

- Ondas planas e funções de bases relacionadas
  - Ondas planas (PW)
  - Linearized (Augment planes waves) (L) APW's
  - Linearized (Muffin-tin orbitals) (L) MTO's
  - Projector augment waves PAW's

- Localized Orbitals
  - Atomic orbitals (LCAO's)
  - Gaussian Orbitals

Aproximação do Pseudopotencial



Kaxiras, E. *Atomic and Electronic Structure of Solids* (Cambridge University Press, New York, 2003). ISBN: 978-0-521-52339-4.

Visão Global da DFT

- Exchange-correlation functionals
  - Local-density approximation (LDA)
  - Generalized Gradient approximation (GGA); metal-GGA.
  - Hybrid-functionals (HSE06)
- Limitaçãoes da DFT
  - Valores do Band-gap
  - correlação eletrônica forte
  - Van der Waals

Propriedades

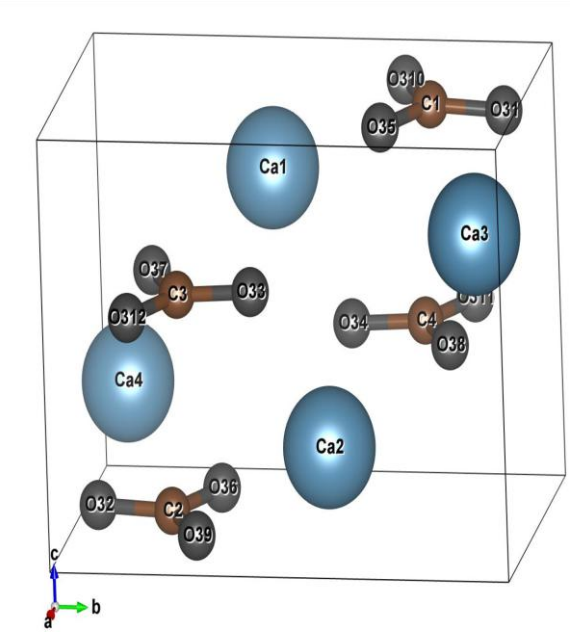
- Propriedades Estruturais:
  - Parâmetros de rede; número de coordenação; comprimento de ligação; função de distribuição de pares
- Defeitos:
  - Vacâncias, interstícios, impurezas substitucionais
- Propriedades eletrônicas:
  - Estrutura de bandas, densidade de estados, bandgap
- Propriedades magnéticas:
  - Momento magnético, energia anisotrópica magnética
- Estrutura hiperfina:
  - Deslocamento químico, campo magnético hiperfino

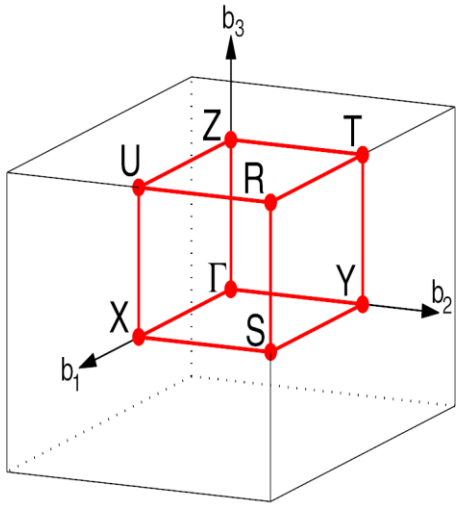
Códigos Computacionais

- Quantum ESPRESSO - http://www.quantum-espresso.org
- vasp code - The Vienna Ab initio Simulation Package - https://www.vasp.at
- Wien2k - http://www.wien2k.at/
- CASTEP - http://www.castep.org/
- Siesta - http://departments.icmab.es/leem/siesta/

Prática Computacional

Rede Ortorombica
a=4.962Å;
b=5.739Å;
c=7.970Å
c/a=1.606
α=90.000°
β=90.000°
γ=90.000°

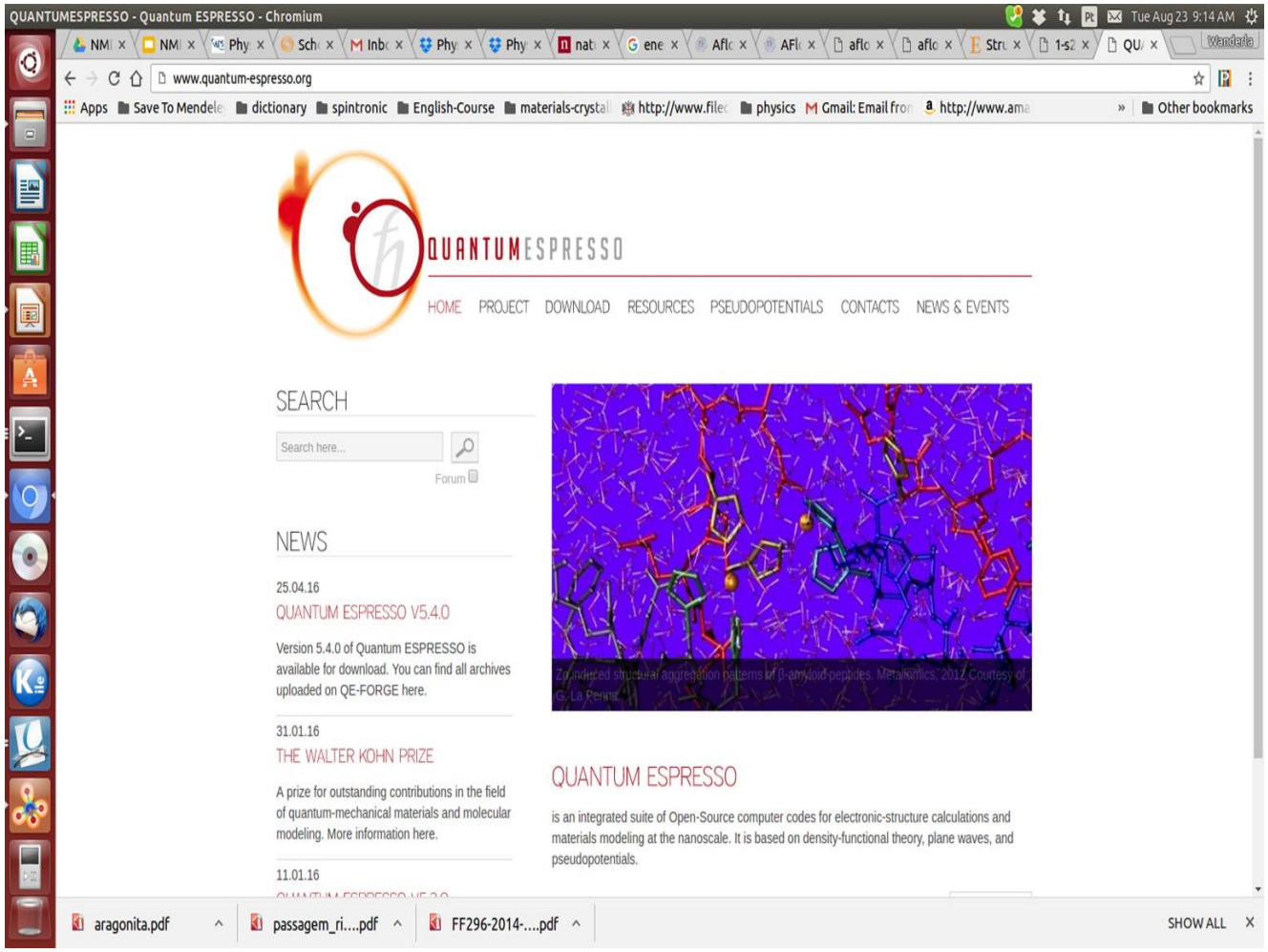




ORC path: Γ-X-S-Y-Γ-Z-U-R-T-Z|Y-T|U-X|S-R

J. Balmain, B. Hannoyer, E. Lopez, J. Biomed. Mater. Res. 48 (1999) 749

Quantum ESPRESSO



Arquivos iniciais

- Estrutura Cristalina em coordenadas cartesianas (xyz)
- Vetores primitivos
- Pseudopotencial (gipaw) -http://www.quantum-espresso.org/pseudopotentials/

Otimização da Estrutura

Arquivo de entrada CaCO3.in

```
&CONTROL
  calculation='vc-relax'
  restart_mode='from_scratch'
  nstep=150
  tstress= .true.
  tprnfor= .true.
  prefix='CaCO3'
  etot_conv_thr = 1.0D-5
  forc_conv_thr = 1.0D-3
  pseudo_dir = '/home/wlscopel/pseudo/'
  outdir='./data/'
/
&SYSTEM
  ibrav     = 0
  nat       = 20
  ntyp      = 3
  ecutwfc   = 100
! ecutrho   = 560
  occupations='smearing'
  nspin=1
  spline_ps=.true.
  degauss=0.01
! london=.true.
! london_s6 = 0.5
/
&ELECTRONS
  electron_maxstep=300
  conv_thr = 1.0D-10
  diagonalization='david'
  mixing_mode = 'plain'
  mixing_beta = 0.3
/
&IONS
  ion_dynamics='bfgs'
/
&CELL
/
ATOMIC_SPECIES
Ca 20.00 Ca.pbe-mt_gipaw.UPF
C  12.00 C.pbe-mt_gipaw.UPF
O  16.00 O.pbe-tm-gipaw.UPF
```

```
ATOMIC_POSITIONS {angstrom}
Ca      1.240350     3.306346     4.360982
Ca      3.721050     4.660754     1.379418
Ca      3.721050     7.289896     4.249618
Ca      1.240350     0.677204     1.490782
 C      1.240350     6.072524     5.245577
 C      3.721050     1.894576     0.494822
 C      3.721050     2.088974     3.365022
 C      1.240350     5.878127     2.375377
 O      1.240350     7.349650     5.188173
 O      3.721050     0.617450     0.552226
 O      3.721050     3.366100     3.422426
 O      1.240350     4.601000     2.317974
 O      2.349719     5.425595     5.245577
 O      2.611681     2.541505     0.494822
 O      2.611681     1.442045     3.365022
 O      2.349719     6.525055     2.375377
 O      4.830419     2.541505     0.494822
 O      0.130981     5.425595     5.245577
 O      0.130981     6.525055     2.375377
 O      4.830419     1.442045     3.365022
CELL_PARAMETERS {angstrom}
  4.9614000320         0.0000000000         0.0000000000
  0.0000000000         7.9671001434         0.0000000000
  0.0000000000         0.0000000000         5.7403998375
K_POINTS {automatic}
 5 5 5 0 0 0
~
```

Arquivo de saída do programa CaCO3.out

```
     Final enthalpy=    -443.3493901596 Ry
Begin final coordinates
     new unit-cell volume =   1605.79526 a.u.^3 (   237.95430 Ang^3 )

CELL_PARAMETERS (angstrom)
   5.031828091   0.000000000   0.000000000
   0.000000000   8.078297857   0.000000000
   0.000000000   0.000000000   5.853935170

ATOMIC_POSITIONS (angstrom)
Ca       1.257957015   3.356370618   4.444288794
Ca       3.773871044   4.721927093   1.409646542
Ca       3.773871044   7.395519474   4.336614210
Ca       1.257957015   0.682778238   1.517321126
C        1.257957015   6.158925017   5.352751455
C        3.773871044   1.919372694   0.501182862
C        3.773871044   2.119776162   3.428150530
C        1.257957015   5.958522564   2.425783787
O        1.257957015   7.456526957   5.290862850
O        3.773871044   0.621770755   0.563071466
O        3.773871044   3.417378101   3.490839134
O        1.257957015   4.660919611   2.363896202
O        2.387224530   5.498348889   5.339915265
O        2.644603528   2.579948822   0.514019051
O        2.644603528   1.459200034   3.440986719
O        2.387224530   6.619097678   2.412947597
O        4.903138559   2.579948822   0.514019051
O        0.128689499   5.498348889   5.339915265
O        0.128689499   6.619097678   2.412947597
O        4.903138559   1.459200034   3.440986719
End final coordinates



     A final scf calculation at the relaxed structure.
     The G-vectors are recalculated for the final unit cell
     Results may differ from those at the preceding step.

     Parallelization info
     --------------------
     sticks:   dense  smooth     PW     G-vecs:    dense   smooth      PW
     Min         231     231     62                10843    10843    1520
     Max         232     232     63                10846    10846    1523
     Sum        4621    4621   1249              216883   216883   30413
```

```
     ewald contribution            =    -257.59596211 Ry
     smearing contrib. (-TS)       =       0.00000000 Ry

     convergence has been achieved in  17 iterations

     Forces acting on atoms (Ry/au):

     atom    1 type  1   force =     0.00000000   -0.00007501    0.00010042
     atom    2 type  1   force =     0.00000000    0.00007501   -0.00010042
     atom    3 type  1   force =     0.00000000   -0.00007501   -0.00010042
     atom    4 type  1   force =     0.00000000    0.00007501    0.00010042
     atom    5 type  2   force =     0.00000000   -0.00000439    0.00016954
     atom    6 type  2   force =     0.00000000    0.00000439   -0.00016954
     atom    7 type  2   force =     0.00000000   -0.00000439   -0.00016954
     atom    8 type  2   force =     0.00000000    0.00000439    0.00016954
     atom    9 type  3   force =     0.00000000   -0.00031239   -0.00018590
     atom   10 type  3   force =     0.00000000    0.00031239    0.00018590
     atom   11 type  3   force =     0.00000000   -0.00031239    0.00018590
     atom   12 type  3   force =     0.00000000    0.00031239   -0.00018590
     atom   13 type  3   force =    -0.00021652   -0.00009372   -0.00015547
     atom   14 type  3   force =     0.00021652    0.00009372    0.00015547
     atom   15 type  3   force =     0.00021652   -0.00009372    0.00015547
     atom   16 type  3   force =    -0.00021652    0.00009372   -0.00015547
     atom   17 type  3   force =    -0.00021652    0.00009372    0.00015547
     atom   18 type  3   force =     0.00021652   -0.00009372   -0.00015547
     atom   19 type  3   force =     0.00021652    0.00009372   -0.00015547
     atom   20 type  3   force =    -0.00021652   -0.00009372    0.00015547

     Total force =     0.001160     Total SCF correction =     0.000001


     entering subroutine stress ...

          total   stress  (Ry/bohr**3)                   (kbar)     P=    0.05
     0.00000191   0.00000000   0.00000000         0.28      0.00      0.00
     0.00000000  -0.00000030   0.00000000         0.00     -0.04      0.00
     0.00000000   0.00000000  -0.00000052         0.00      0.00     -0.08


     Writing output data file CaCO3.save

     init_run     :     27.61s CPU     28.50s WALL (       2 calls)
     electrons    :  10140.39s CPU  11230.80s WALL (      13 calls)
     update_pot   :     29.97s CPU     31.02s WALL (      11 calls)
     forces       :     39.01s CPU     41.50s WALL (      13 calls)
```

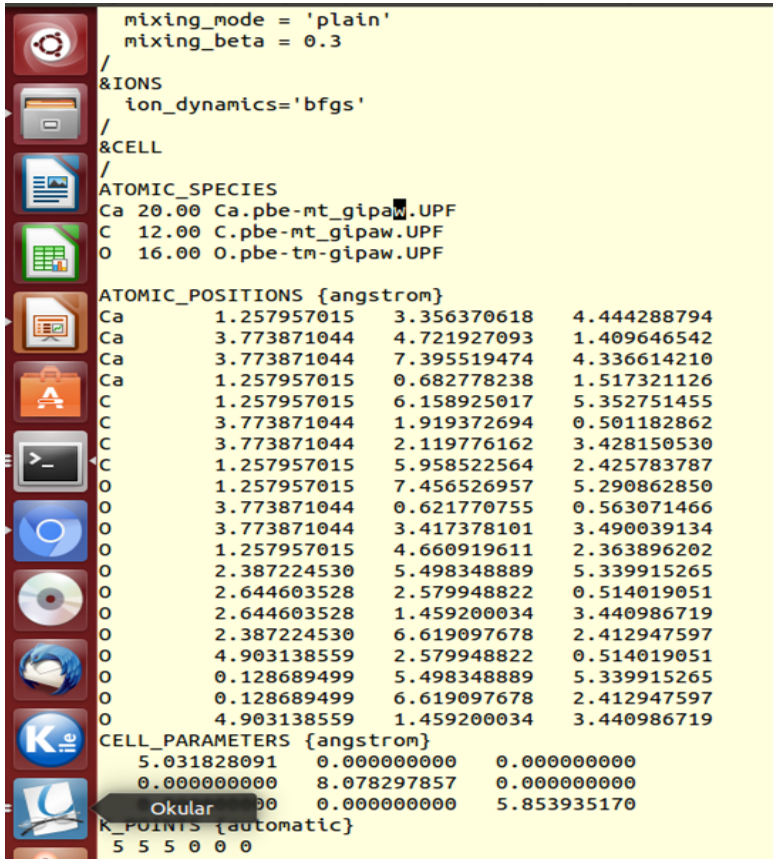
```
     update_pot   :     29.97s CPU     31.02s WALL (      11 calls)
     forces       :     39.01s CPU     41.50s WALL (      13 calls)
     stress       :     61.40s CPU     63.17s WALL (      13 calls)

     Called by init_run:
     wfcinit      :     24.47s CPU     25.32s WALL (       2 calls)
     potinit      :      1.43s CPU      1.43s WALL (       2 calls)

     Called by electrons:
     c_bands      :   9007.09s CPU   9969.45s WALL (     188 calls)
     sum_band     :   1101.89s CPU   1225.39s WALL (     188 calls)
     v_of_rho     :     13.31s CPU     14.89s WALL (     195 calls)
     mix_rho      :     14.96s CPU     17.17s WALL (     188 calls)

     Called by c_bands:
     init_us_2    :     23.42s CPU     23.71s WALL (   10908 calls)
     cegterg      :   8905.57s CPU   9862.07s WALL (    5103 calls)

     Called by sum_band:

     Called by *egterg:
     h_psi        :   6309.91s CPU   6990.02s WALL (   23851 calls)
     g_psi        :     17.51s CPU     17.78s WALL (   18694 calls)
     cdiaghg      :    915.18s CPU   1009.13s WALL (   23311 calls)

     Called by h_psi:
     add_vuspsi   :     58.48s CPU     59.59s WALL (   23851 calls)

     General routines
     calbec       :    290.02s CPU    313.85s WALL (   25606 calls)
     fft          :     24.21s CPU     25.95s WALL (    2480 calls)
     fftw         :   6992.98s CPU   7764.07s WALL ( 2024546 calls)
     davcio       :      0.02s CPU      0.35s WALL (      54 calls)

     Parallel routines
     fft_scatter  :   6053.56s CPU   6773.80s WALL ( 2027026 calls)

     PWSCF        :    2h51m CPU       3h10m WALL


    This run was terminated on:  10:12:43   7Apr2016
=------------------------------------------------------------------------------
   JOB DONE.
=------------------------------------------------------------------------------
```

Cálculo auto-consistente

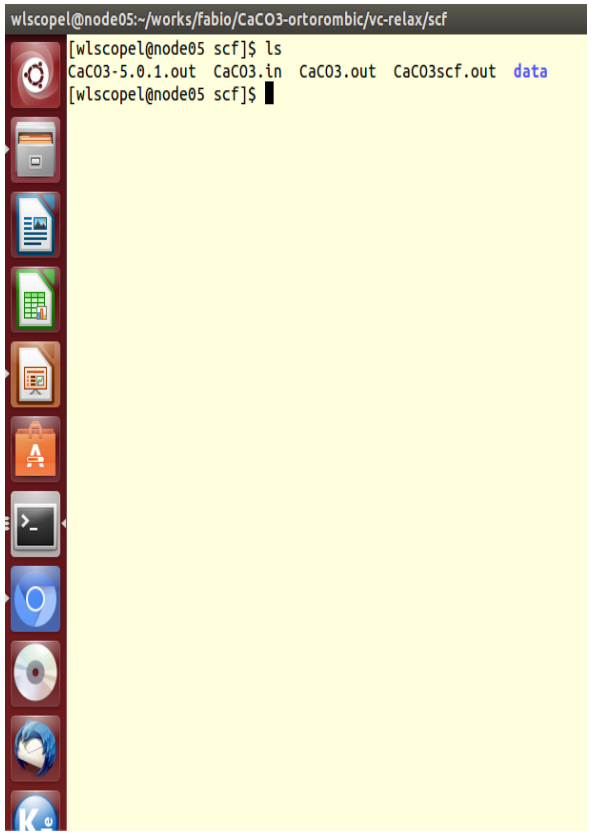
Arquivo de entrada CaCO3-scf.in

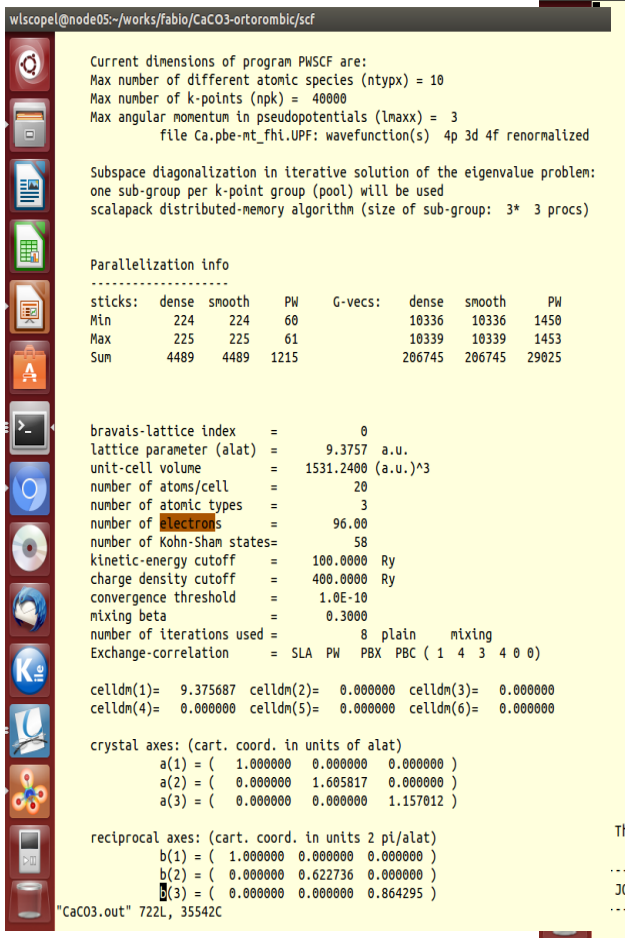
```
&CONTROL
  calculation='scf'
  restart_mode='from_scratch'
  nstep=150
  tstress= .true.
  tprnfor= .true.
  prefix='CaCO3'
  etot_conv_thr = 1.0D-5
  forc_conv_thr = 1.0D-3
  pseudo_dir = '/home/wlscopel/pseudo/'
  outdir='./data/'
/
&SYSTEM
  ibrav     = 0
  nat       = 20
  ntyp      = 3
  ecutwfc   = 100
! ecutrho   = 560
  occupations='smearing'
  nspin=1
  spline_ps=.true.
  degauss=0.01
! london=.true.
! london_s6 = 0.5
/
&ELECTRONS
  electron_maxstep=300
  conv_thr = 1.0D-10
  diagonalization='david'
```

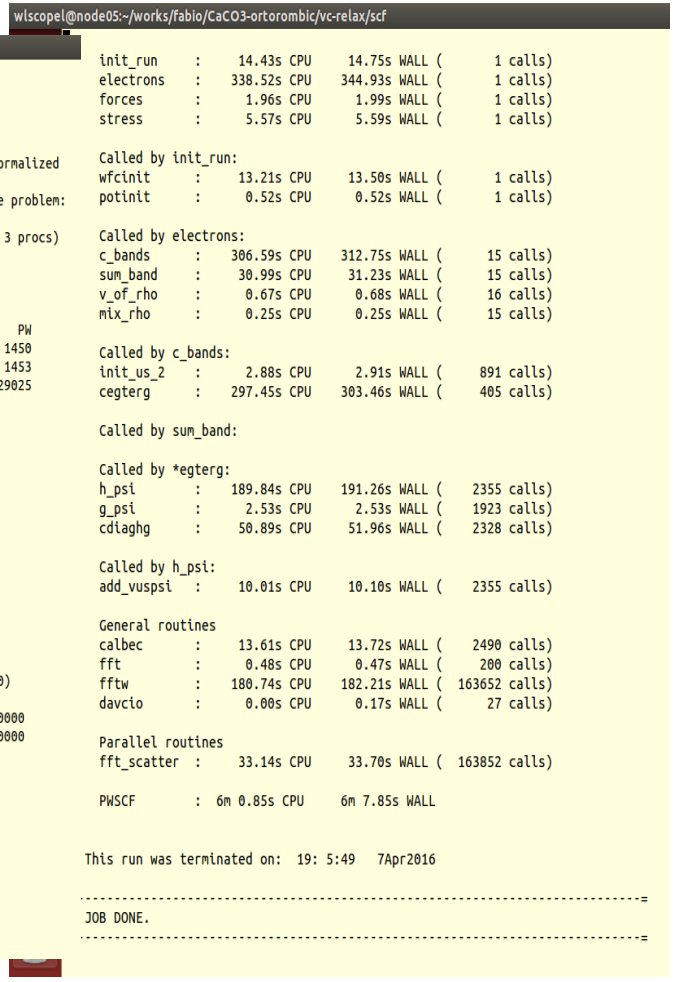
```
  mixing_mode = 'plain'
  mixing_beta = 0.3
/
&IONS
  ion_dynamics='bfgs'
/
&CELL
/
ATOMIC_SPECIES
Ca 20.00 Ca.pbe-mt_gipaw.UPF
C  12.00 C.pbe-mt_gipaw.UPF
O  16.00 O.pbe-tm-gipaw.UPF

ATOMIC_POSITIONS {angstrom}
Ca        1.257957015   3.356370618   4.444288794
Ca        3.773871044   4.721927093   1.409646542
Ca        3.773871044   7.395519474   4.336614210
Ca        1.257957015   0.682778238   1.517321126
C         1.257957015   6.158925017   5.352751455
C         3.773871044   1.919372694   0.501182862
C         3.773871044   2.119776162   3.428150530
C         1.257957015   5.958522564   2.425783787
O         1.257957015   7.456526957   5.290862850
O         3.773871044   0.621770755   0.563071466
O         3.773871044   3.417378101   3.490039134
O         1.257957015   4.660919611   2.363896202
O         2.387224530   5.498348889   5.339915265
O         2.644603528   2.579948822   0.514019051
O         2.644603528   1.459200034   3.440986719
O         2.387224530   6.619097678   2.412947597
O         4.903138559   2.579948822   0.514019051
O         0.128689499   5.498348889   5.339915265
O         0.128689499   6.619097678   2.412947597
O         4.903138559   1.459200034   3.440986719
CELL_PARAMETERS {angstrom}
   5.031828091   0.000000000   0.000000000
   0.000000000   8.078297857   0.000000000
   0.000000000   0.000000000   5.853935170
K_POINTS {automatic}
 5 5 5 0 0 0
```



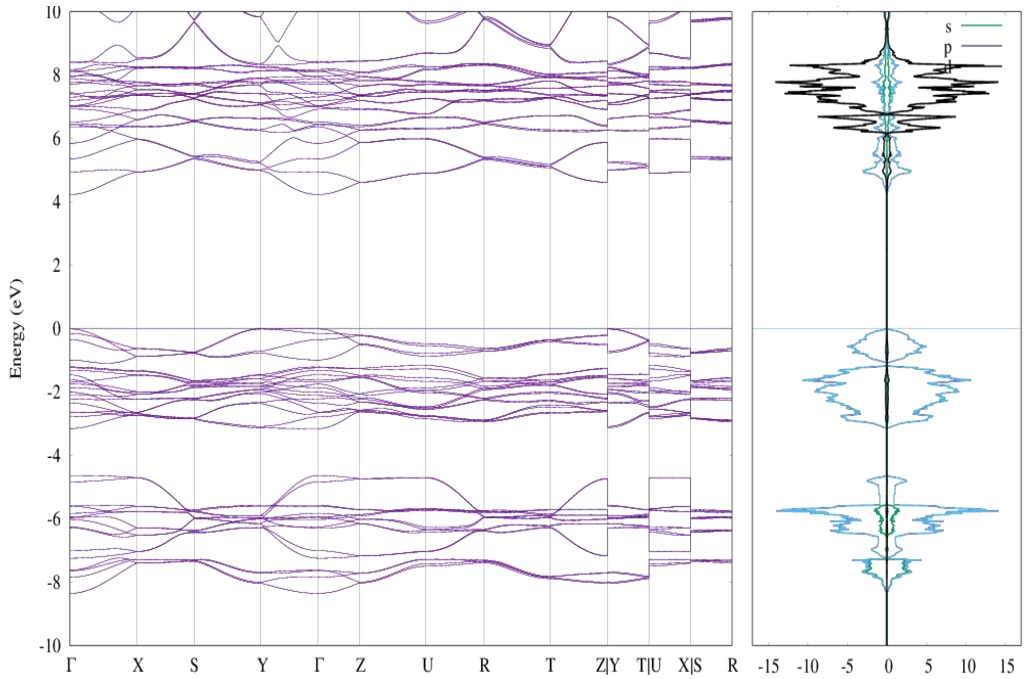
Arquivos de saída do cálculo de campo auto-consistente (scf)

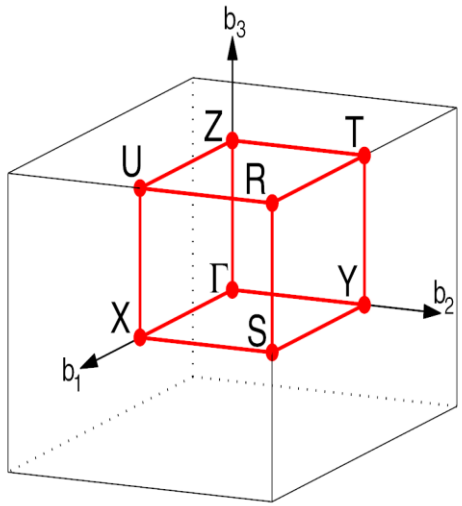






Propriedades Eletrônicas

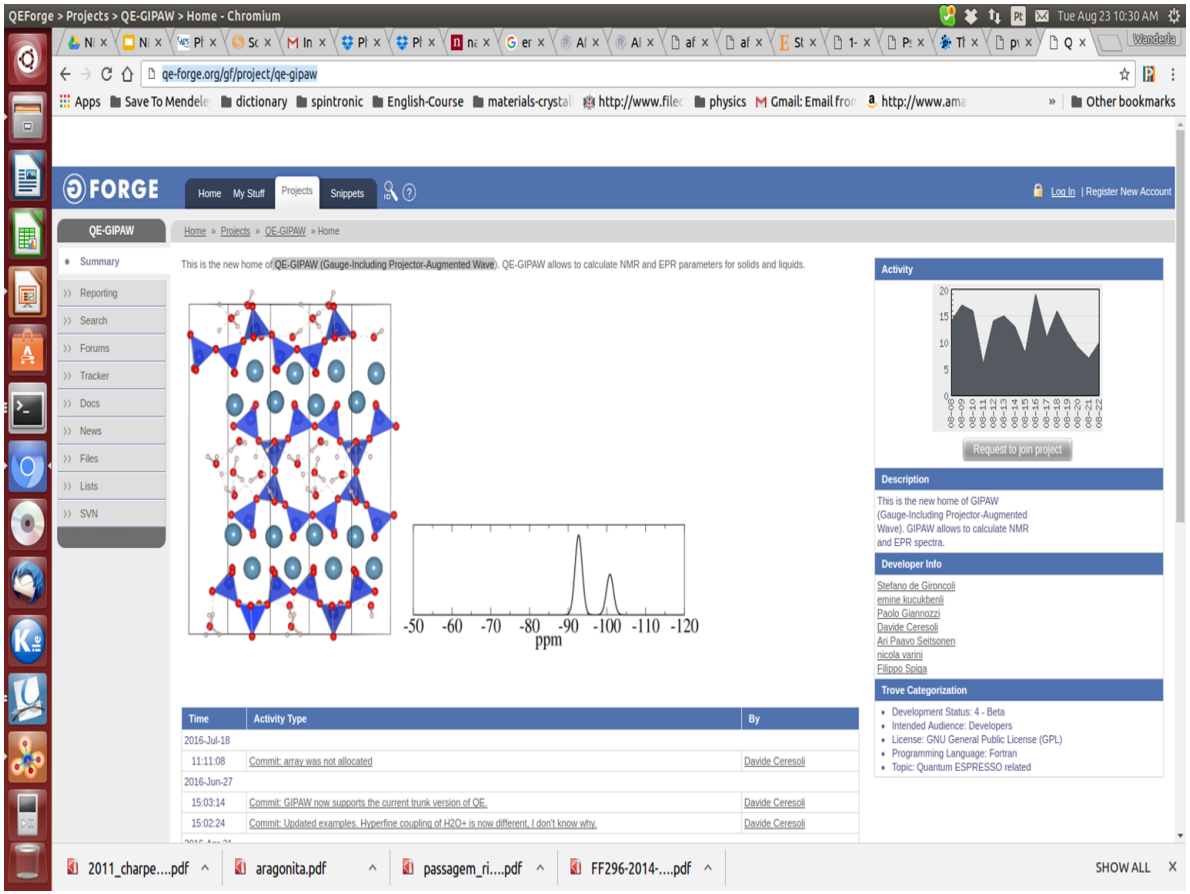




ORC path: Γ-X-S-Y-Γ-Z-U-R-T-Z|Y-T|U-X|S-R

NMR - Método -GIPAW (Gauge-Including Projector-Augmented Wave)

http://qe-forge.org/gf/project/qe-gipaw



Método GIPAW

Tensor de blindagem magnética-- resposta do sistema na presença de um campo magnético uniforme.

$$\vec{B}_{ind}(r) = -\sigma(r) \cdot \vec{B}_0$$

Campo Magnético induzido

Campo Magnético externo

C.J. Pickard, F. Mauri, Phys. Ver. B 63 (2001) 245101 (a thorough technical description and derivation of the DFT-GIPAW theory).

$$\vec{j}^{(1)}(r) = -\sum_{j}^{occ}(\phi_j^{(0)}(r)\vec{\nabla}\phi_j^{(1)}(r) + \phi_j^{(1)}(r)\vec{\nabla}\phi_j^{(0)}(r)) - \frac{1}{c}n_0(r)\vec{A}(r)$$

$$= \vec{j}_p^{(1)}(r) + \vec{j}_d^{(1)}(r)$$

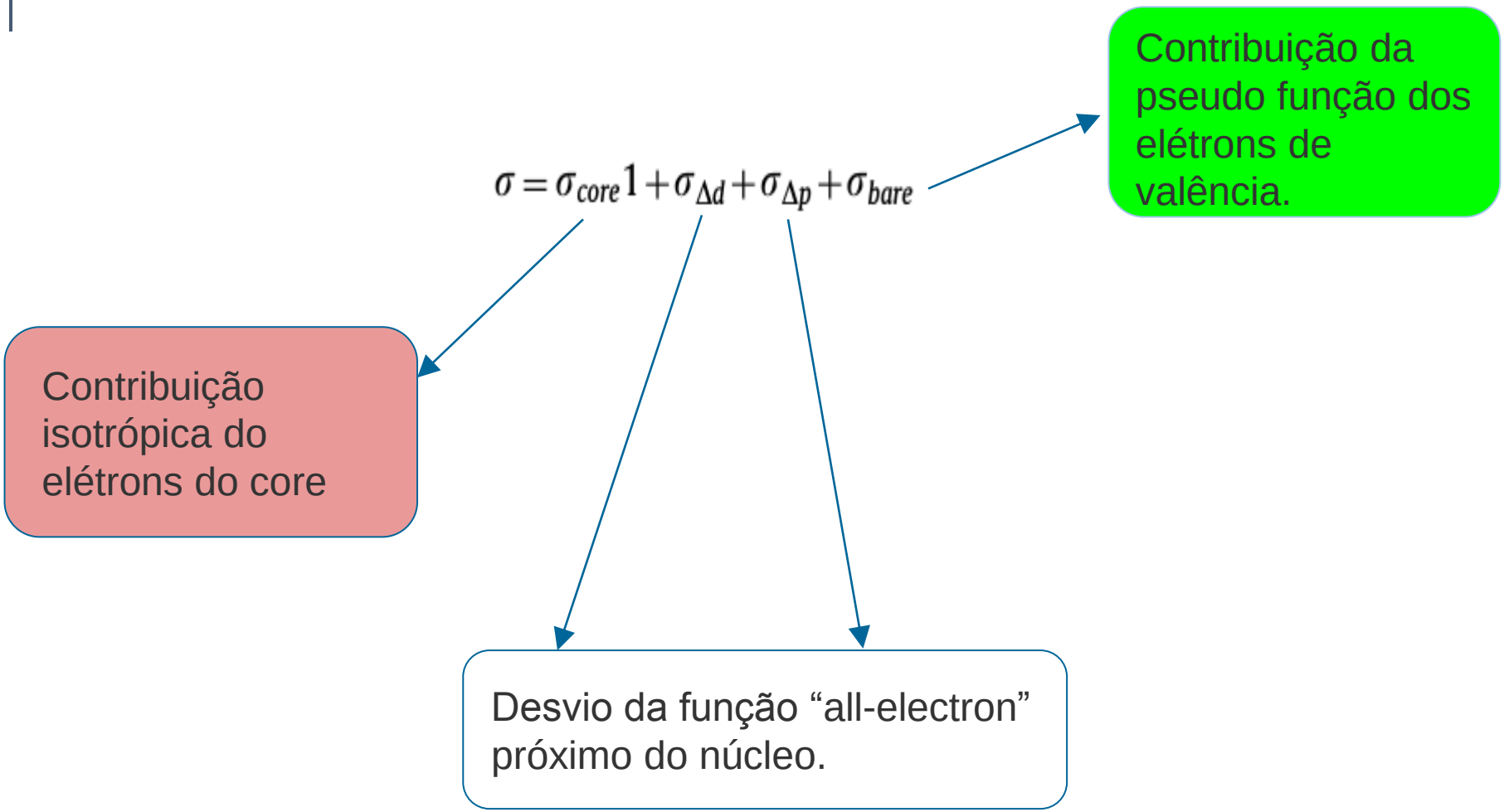
$n_0(r)$ → Densidade de carga não perturbada

$\phi_j^{(0)}(r)$ → Orbital de kohn-sham não perturbado

$\phi_j^{(1)}(r)$ → Orbitais de kohn-sham perturbados

$$\vec{A}(r) = \frac{1}{2}\vec{B}_0 \times (r - r_o)$$ (Potencial Vetor)

$$\vec{B}_{ind}(r) = \frac{1}{c}\int dr' \vec{j}^{(1)}(r') \times \frac{r - r'}{|r - r'|^3}$$ (Lei de Biot-Savart)


$\sigma = \sigma_{core}1 + \sigma_{\Delta d} + \sigma_{\Delta p} + \sigma_{bare}$
Contribuição da pseudo função dos elétrons de valência.
Contribuição isotrópica do elétrons do core
Desvio da função “all-electron” próximo do núcleo.

Arquivo de entrada NMR-QE-GIPAW

Pwscf

wlscopel@node05:~/works/fabio/CaCO3-ortorombic/nmr-ort

```
&inputgipaw
        job = 'nmr'
        prefix = 'CaCO3'
        tmp_dir = './data/'
        isolve = 0
        iverbosity = 1
        q_gipaw = 0.01
        conv_threshold =1.0d-12
        spline_ps = .true.
        use_nmr_macroscopic_shape = .false.
/
```

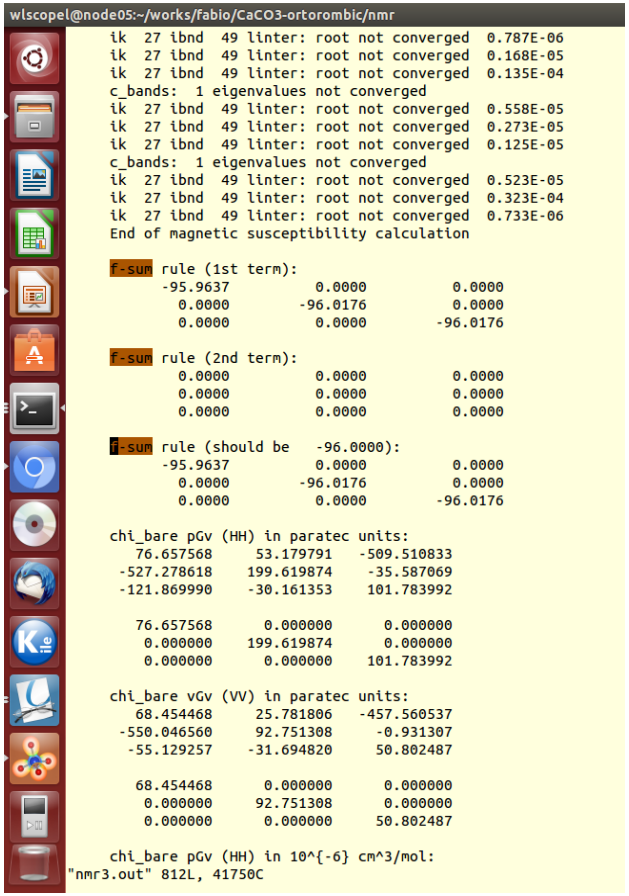
CaCO3-scf.out

wlscopel@node05:~/works/fabio/CaCO3-ortorombic/scf

```
     Current dimensions of program PWSCF are:
     Max number of different atomic species (ntypx) = 10
     Max number of k-points (npk) =  40000
     Max angular momentum in pseudopotentials (lmaxx) =  3
              file Ca.pbe-mt_fhi.UPF: wavefunction(s)  4p 3d 4f renormalized

     Subspace diagonalization in iterative solution of the eigenvalue problem:
     one sub-group per k-point group (pool) will be used
     scalapack distributed-memory algorithm (size of sub-group:  3*  3 procs)


     Parallelization info
     --------------------
     sticks:   dense  smooth     PW    G-vecs:    dense   smooth      PW
     Min         224     224     60                10336    10336    1450
     Max         225     225     61                10339    10339    1453
     Sum        4489    4489   1215               206745   206745   29025



     bravais-lattice index     =            0
     lattice parameter (alat)  =       9.3757  a.u.
     unit-cell volume          =    1531.2400 (a.u.)^3
     number of atoms/cell      =           20
     number of atomic types    =            3
     number of electrons       =        96.00
     number of Kohn-Sham states=           58
     kinetic-energy cutoff     =     100.0000  Ry
     charge density cutoff     =     400.0000  Ry
     convergence threshold     =      1.0E-10
     mixing beta               =       0.3000
     number of iterations used =            8  plain     mixing
     Exchange-correlation      =  SLA  PW   PBX  PBC ( 1  4  3  4 0 0)

     celldm(1)=   9.375687  celldm(2)=   0.000000  celldm(3)=   0.000000
     celldm(4)=   0.000000  celldm(5)=   0.000000  celldm(6)=   0.000000

     crystal axes: (cart. coord. in units of alat)
               a(1) = (   1.000000   0.000000   0.000000 )
               a(2) = (   0.000000   1.605817   0.000000 )
               a(3) = (   0.000000   0.000000   1.157012 )

     reciprocal axes: (cart. coord. in units 2 pi/alat)
               b(1) = (  1.000000  0.000000  0.000000 )
               b(2) = (  0.000000  0.622736  0.000000 )
               b(3) = (  0.000000  0.000000  0.864295 )
"CaCO3.out" 722L, 35542C
```

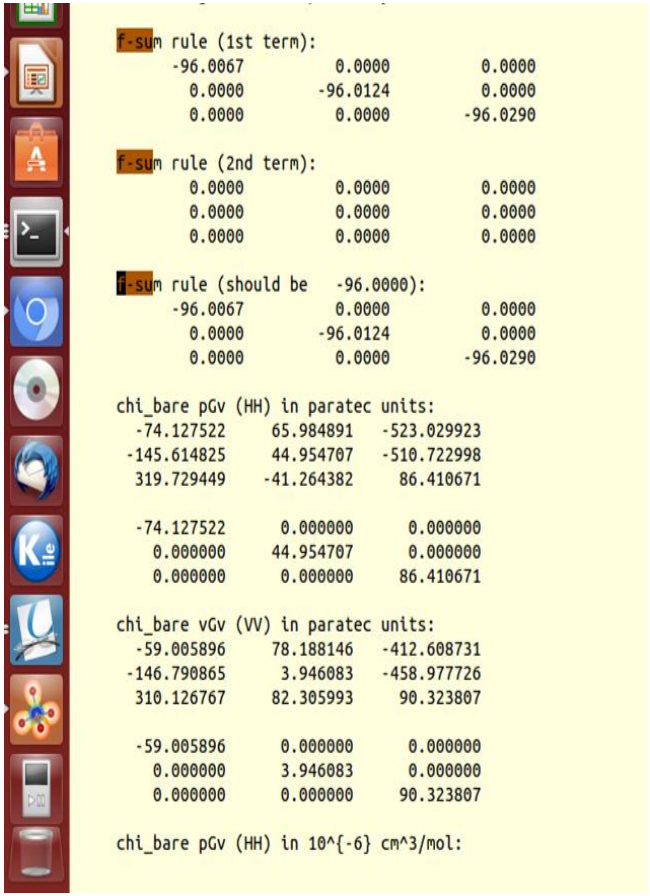
Saída do cálculo de NMR

Malha - 2x2x2

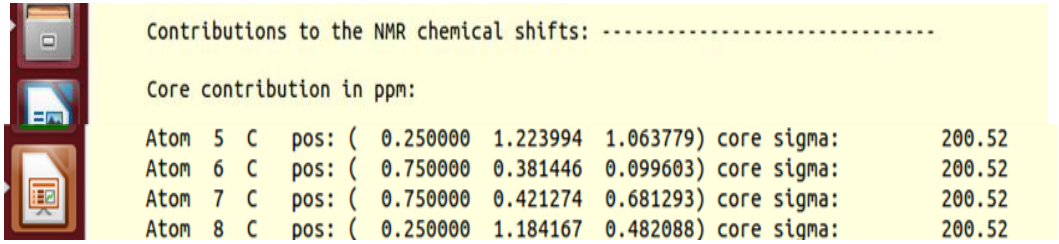


```
wlscopel@node05:~/works/fabio/CaCO3-ortorombic/nmr
     ik  27 ibnd  49 linter: root not converged  0.787E-06
     ik  27 ibnd  49 linter: root not converged  0.168E-05
     ik  27 ibnd  49 linter: root not converged  0.135E-04
     c_bands:  1 eigenvalues not converged
     ik  27 ibnd  49 linter: root not converged  0.558E-05
     ik  27 ibnd  49 linter: root not converged  0.273E-05
     ik  27 ibnd  49 linter: root not converged  0.125E-05
     c_bands:  1 eigenvalues not converged
     ik  27 ibnd  49 linter: root not converged  0.523E-05
     ik  27 ibnd  49 linter: root not converged  0.323E-04
     ik  27 ibnd  49 linter: root not converged  0.733E-06
     End of magnetic susceptibility calculation

     f-sum rule (1st term):
           -95.9637          0.0000          0.0000
             0.0000        -96.0176          0.0000
             0.0000          0.0000        -96.0176

     f-sum rule (2nd term):
             0.0000          0.0000          0.0000
             0.0000          0.0000          0.0000
             0.0000          0.0000          0.0000

     f-sum rule (should be   -96.0000):
           -95.9637          0.0000          0.0000
             0.0000        -96.0176          0.0000
             0.0000          0.0000        -96.0176

     chi_bare pGv (HH) in paratec units:
        76.657568     53.179791   -509.510833
      -527.278618    199.619874    -35.587069
      -121.869990    -30.161353    101.783992

        76.657568      0.000000      0.000000
         0.000000    199.619874      0.000000
         0.000000      0.000000    101.783992

     chi_bare vGv (VV) in paratec units:
        68.454468     25.781806   -457.560537
      -550.046560     92.751308     -0.931307
       -55.129257    -31.694820     50.802487

        68.454468      0.000000      0.000000
         0.000000     92.751308      0.000000
         0.000000      0.000000     50.802487

     chi_bare pGv (HH) in 10^{-6} cm^3/mol:
"nmr3.out" 812L, 41750C
```

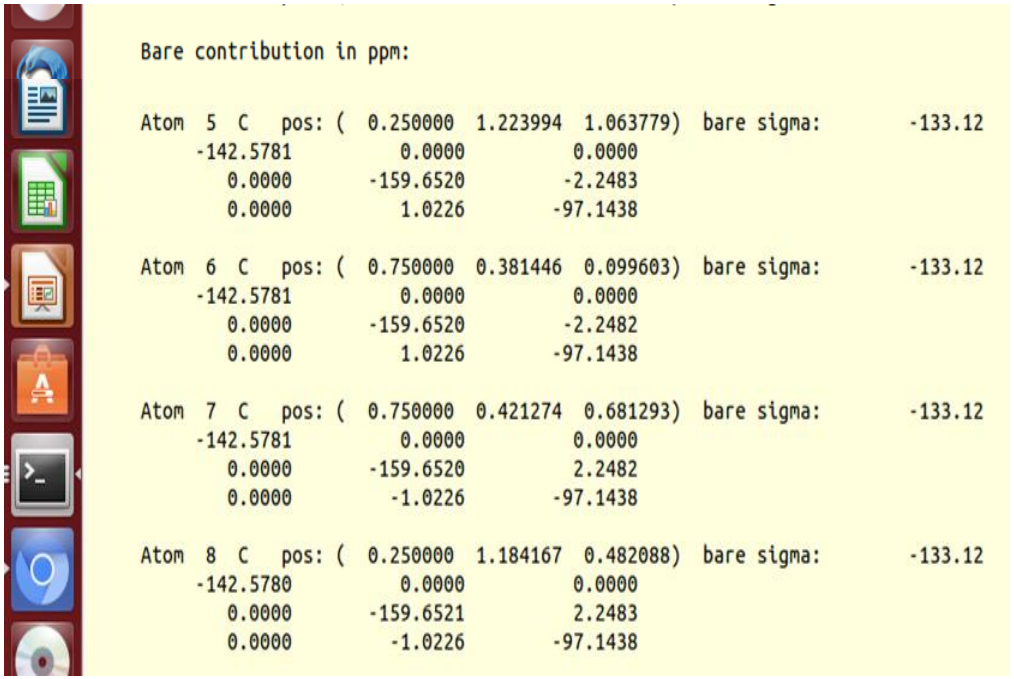
Malha - 5x5x5



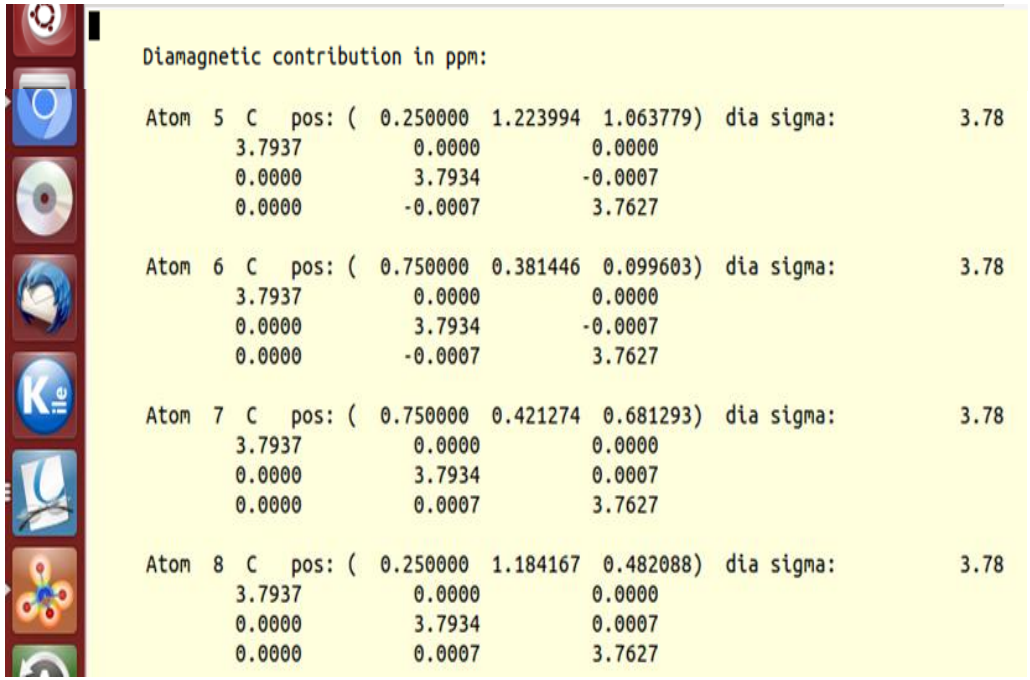
```
     f-sum rule (1st term):
           -96.0067          0.0000          0.0000
             0.0000        -96.0124          0.0000
             0.0000          0.0000        -96.0290

     f-sum rule (2nd term):
             0.0000          0.0000          0.0000
             0.0000          0.0000          0.0000
             0.0000          0.0000          0.0000

     f-sum rule (should be   -96.0000):
           -96.0067          0.0000          0.0000
             0.0000        -96.0124          0.0000
             0.0000          0.0000        -96.0290

     chi_bare pGv (HH) in paratec units:
       -74.127522     65.984891   -523.029923
      -145.614825     44.954707   -510.722998
       319.729449    -41.264382     86.410671

       -74.127522      0.000000      0.000000
         0.000000     44.954707      0.000000
         0.000000      0.000000     86.410671

     chi_bare vGv (VV) in paratec units:
       -59.005896     78.188146   -412.608731
      -146.790865      3.946083   -458.977726
       310.126767     82.305993     90.323807

       -59.005896      0.000000      0.000000
         0.000000      3.946083      0.000000
         0.000000      0.000000     90.323807

     chi_bare pGv (HH) in 10^{-6} cm^3/mol:
```



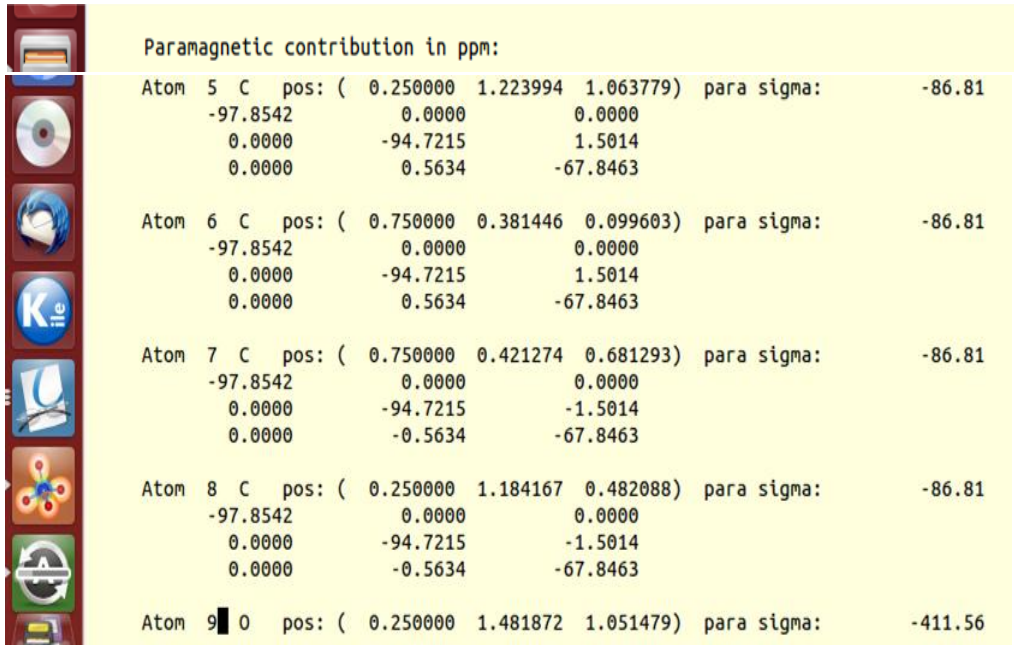
```
Contributions to the NMR chemical shifts: -----------------------------

Core contribution in ppm:

Atom  5  C   pos: (  0.250000  1.223994  1.063779) core sigma:         200.52
Atom  6  C   pos: (  0.750000  0.381446  0.099603) core sigma:         200.52
Atom  7  C   pos: (  0.750000  0.421274  0.681293) core sigma:         200.52
Atom  8  C   pos: (  0.250000  1.184167  0.482088) core sigma:         200.52
```



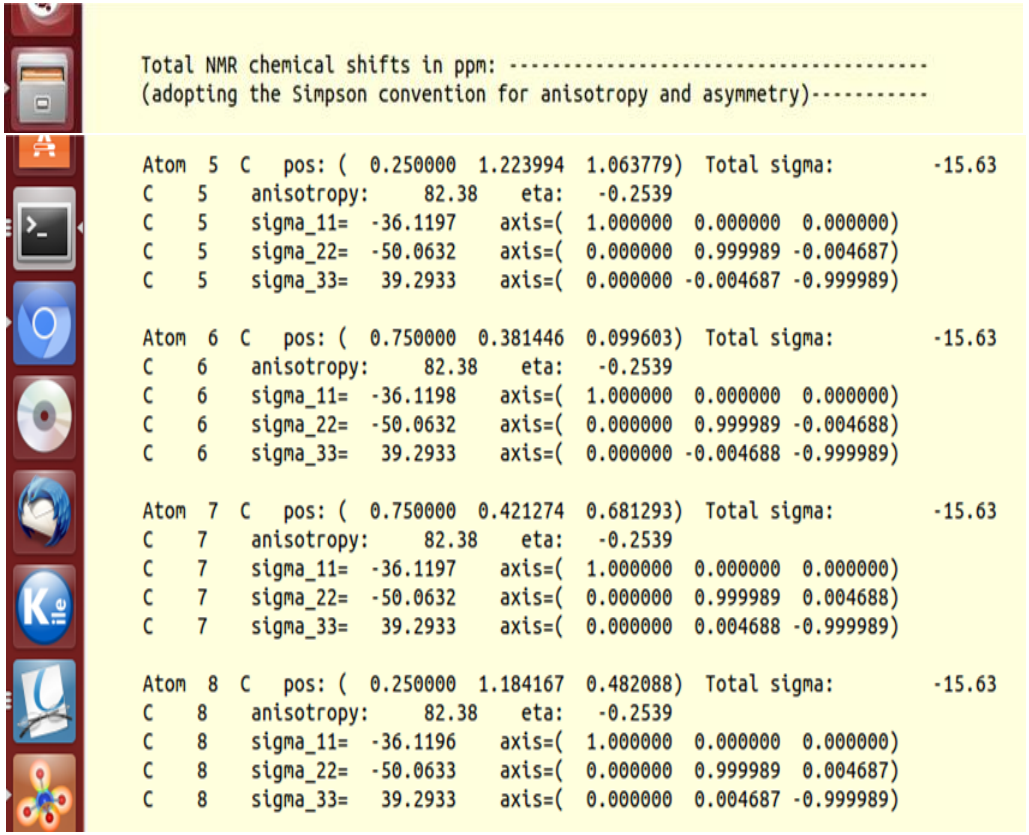
```
Bare contribution in ppm:

Atom  5  C   pos: (  0.250000  1.223994  1.063779)  bare sigma:        -133.12
     -142.5781         0.0000         0.0000
        0.0000      -159.6520        -2.2483
        0.0000         1.0226       -97.1438

Atom  6  C   pos: (  0.750000  0.381446  0.099603)  bare sigma:        -133.12
     -142.5781         0.0000         0.0000
        0.0000      -159.6520        -2.2482
        0.0000         1.0226       -97.1438

Atom  7  C   pos: (  0.750000  0.421274  0.681293)  bare sigma:        -133.12
     -142.5781         0.0000         0.0000
        0.0000      -159.6520         2.2482
        0.0000        -1.0226       -97.1438

Atom  8  C   pos: (  0.250000  1.184167  0.482088)  bare sigma:        -133.12
     -142.5780         0.0000         0.0000
        0.0000      -159.6521         2.2483
        0.0000        -1.0226       -97.1438
```



```
Diamagnetic contribution in ppm:

Atom  5  C   pos: (  0.250000  1.223994  1.063779)  dia sigma:          3.78
       3.7937          0.0000          0.0000
       0.0000          3.7934         -0.0007
       0.0000         -0.0007          3.7627

Atom  6  C   pos: (  0.750000  0.381446  0.099603)  dia sigma:          3.78
       3.7937          0.0000          0.0000
       0.0000          3.7934         -0.0007
       0.0000         -0.0007          3.7627

Atom  7  C   pos: (  0.750000  0.421274  0.681293)  dia sigma:          3.78
       3.7937          0.0000          0.0000
       0.0000          3.7934          0.0007
       0.0000          0.0007          3.7627

Atom  8  C   pos: (  0.250000  1.184167  0.482088)  dia sigma:          3.78
       3.7937          0.0000          0.0000
       0.0000          3.7934          0.0007
       0.0000          0.0007          3.7627
```



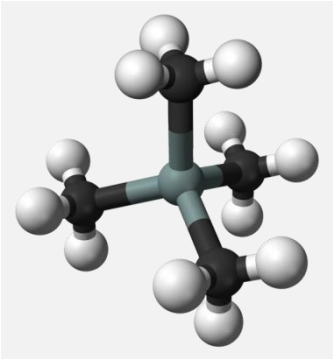
```
Paramagnetic contribution in ppm:
Atom  5  C   pos: (  0.250000  1.223994  1.063779)  para sigma:        -86.81
      -97.8542          0.0000          0.0000
        0.0000        -94.7215          1.5014
        0.0000          0.5634        -67.8463

Atom  6  C   pos: (  0.750000  0.381446  0.099603)  para sigma:        -86.81
      -97.8542          0.0000          0.0000
        0.0000        -94.7215          1.5014
        0.0000          0.5634        -67.8463

Atom  7  C   pos: (  0.750000  0.421274  0.681293)  para sigma:        -86.81
      -97.8542          0.0000          0.0000
        0.0000        -94.7215         -1.5014
        0.0000         -0.5634        -67.8463

Atom  8  C   pos: (  0.250000  1.184167  0.482088)  para sigma:        -86.81
      -97.8542          0.0000          0.0000
        0.0000        -94.7215         -1.5014
        0.0000         -0.5634        -67.8463

Atom  9  O   pos: (  0.250000  1.481872  1.051479)  para sigma:       -411.56
```

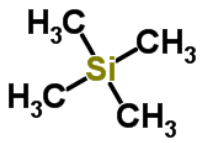


```
Total NMR chemical shifts in ppm: ------------------------------------
(adopting the Simpson convention for anisotropy and asymmetry)----------

Atom  5  C   pos: (  0.250000  1.223994  1.063779)  Total sigma:        -15.63
C    5    anisotropy:     82.38    eta:   -0.2539
C    5    sigma_11=  -36.1197    axis=(  1.000000  0.000000  0.000000)
C    5    sigma_22=  -50.0632    axis=(  0.000000  0.999989 -0.004687)
C    5    sigma_33=   39.2933    axis=(  0.000000 -0.004687 -0.999989)

Atom  6  C   pos: (  0.750000  0.381446  0.099603)  Total sigma:        -15.63
C    6    anisotropy:     82.38    eta:   -0.2539
C    6    sigma_11=  -36.1198    axis=(  1.000000  0.000000  0.000000)
C    6    sigma_22=  -50.0632    axis=(  0.000000  0.999989 -0.004688)
C    6    sigma_33=   39.2933    axis=(  0.000000 -0.004688 -0.999989)

Atom  7  C   pos: (  0.750000  0.421274  0.681293)  Total sigma:        -15.63
C    7    anisotropy:     82.38    eta:   -0.2539
C    7    sigma_11=  -36.1197    axis=(  1.000000  0.000000  0.000000)
C    7    sigma_22=  -50.0632    axis=(  0.000000  0.999989  0.004688)
C    7    sigma_33=   39.2933    axis=(  0.000000  0.004688 -0.999989)

Atom  8  C   pos: (  0.250000  1.184167  0.482088)  Total sigma:        -15.63
C    8    anisotropy:     82.38    eta:   -0.2539
C    8    sigma_11=  -36.1196    axis=(  1.000000  0.000000  0.000000)
C    8    sigma_22=  -50.0633    axis=(  0.000000  0.999989  0.004687)
C    8    sigma_33=   39.2933    axis=(  0.000000  0.004687 -0.999989)
```

Cálculos de deslocamento químico em sólidos

Referência comum para experimentos de RMN de ^{1}H, ^{13}C e ^{29}Si: Tetrametilsilano (TMS)

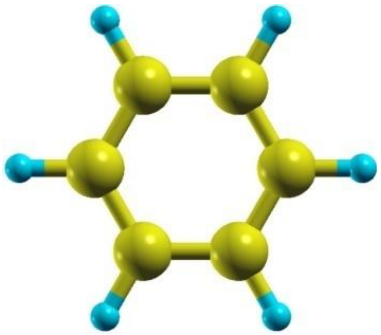




$$\delta_{\text{Calc./TMS}} = \sigma^{(iso)}_{\text{TMS}} - \sigma_{\text{Calc.}}$$

Valor calculado: $\sigma^{(iso)}_{\text{TMS}} = 177,5 \text{ ppm}$

Referência intermediária comumente usada em cálculos de RMN de ^{13}C: Benzeno



$$\delta_{\text{Calc./TMS}} = \sigma^{(iso)}_{\text{Benzene}} - \sigma_{\text{Calc.}} + \delta_{\text{Benzene/TMS}}$$

Valor calculado: $\sigma^{(iso)}_{\text{Benzene}} = 38,8 \text{ ppm}$

Valor experimental: $\delta_{\text{Benzene/TMS}} = 126,9 \text{ ppm}$

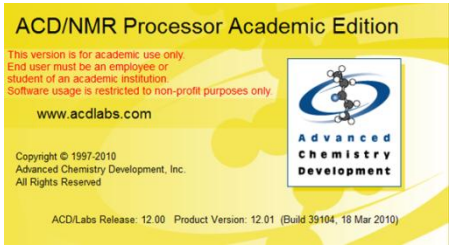
RMN de ^{13}C em $CaCO_3$ - Parâmetros espectrais

Fase	δ_{iso} (ppm)	Ω (ppm)	ζ (ppm)	η	*Ref.*
n.i.	n.d.	76,0	-50,7	0	Pines et al., J. Chem. Phys. 1971;54:5438
Calcita	n.d.	75,0	-50,0	0	Lauterbur, PRL 1958;1:343
Calcita	167,9	n.d.	n.d.	n.d.	Papenguth et al., Amer. Miner. 1989;74:1152
Calcita	165,7	76,1	-47,1	0,04	Feng et al., Amer. Miner. 2006;91:957
Calcita	168,2	n.d.	n.d.	n.d.	Nebel et al., Inorg. Chem. 2008;47:7874
Calcita	168,9	80,7	-51,9	0,11	**Experimental (este trabalho)**
Vaterita	168,7	n.d.	n.d.	n.d.	Papenguth et al., Amer. Miner. 1989;74:1152
Vaterita	170,1; 169,1	n.d.	n.d.	n.d.	Nebel et al., Inorg. Chem. 2008;47:7874
Vaterita	170,0	78,0	-46,8	0,33	Bryce et al., JACS 2008;130:9282
Aragonita	169,9	n.d.	n.d.	n.d.	Papenguth et al., Amer. Miner. 1989;74:1152
Aragonita	170,5	n.d.	n.d.	n.d.	Nebel et al., Inorg. Chem. 2008;47:7874
Aragonita	171,4	83,8	-53,7	0,12	**Experimental (este trabalho)**
Aragonita	175,7	74,0	-46,2	0,20	**Cálculo DFT (este trabalho)**

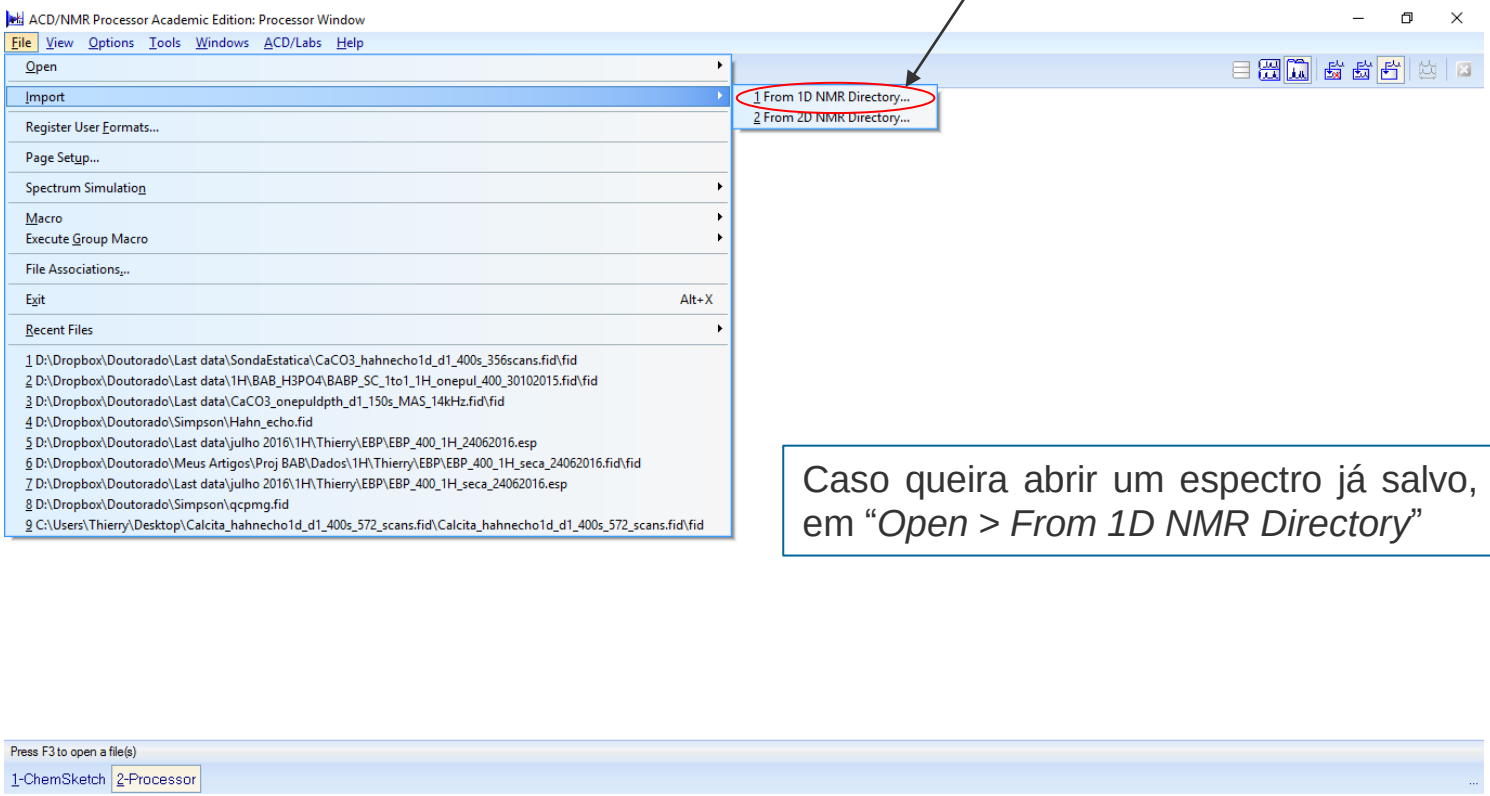
Processamento e simulações de espectros de RMN de sólidos

Thierry R. Lopes

Processamento dos espectros de RMN

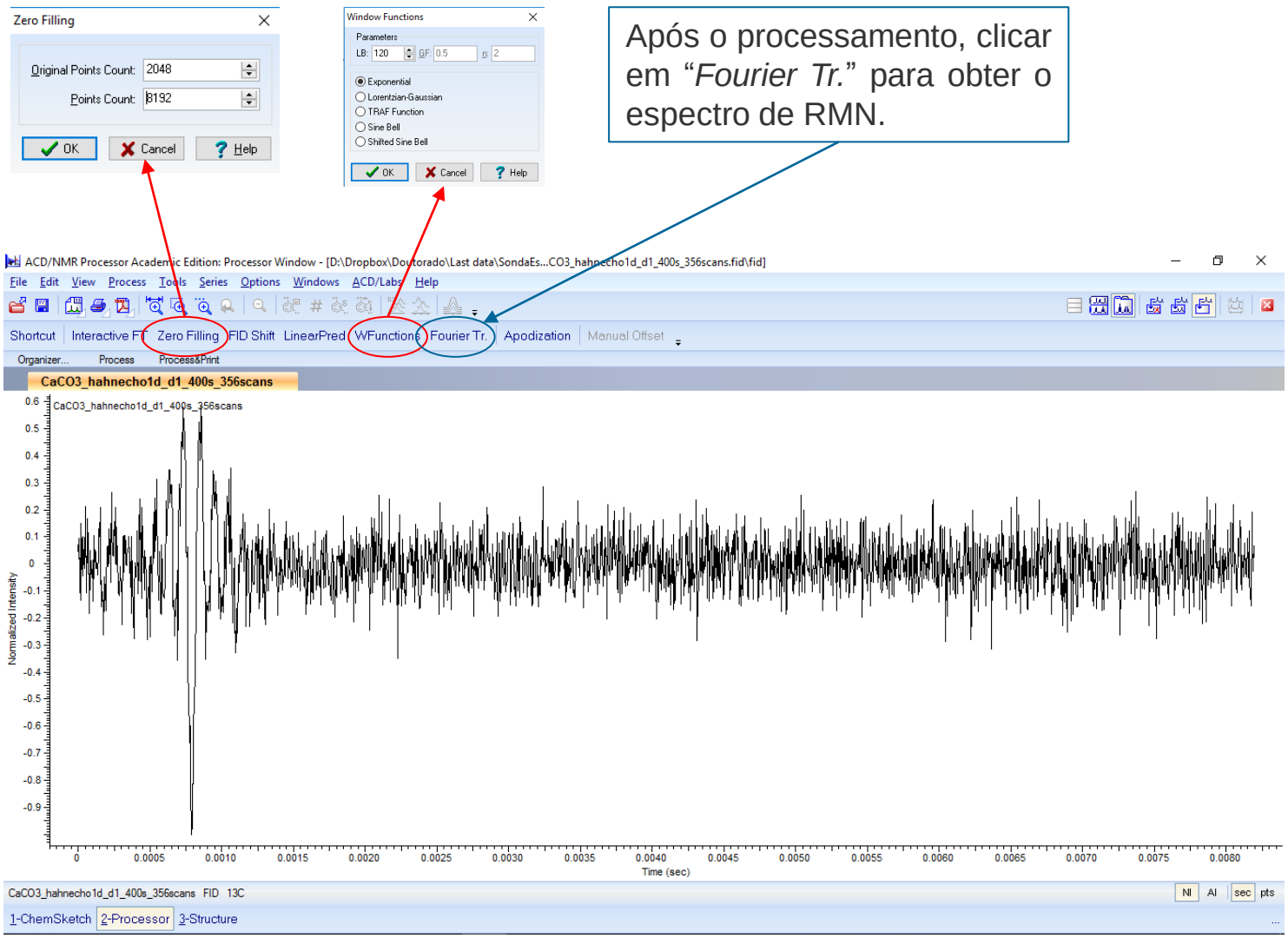


Para importar o arquivo *.FID direto do espectrômetro para o ACD/NMR processor, clicar em "*Import > From 1D NMR Directory*"

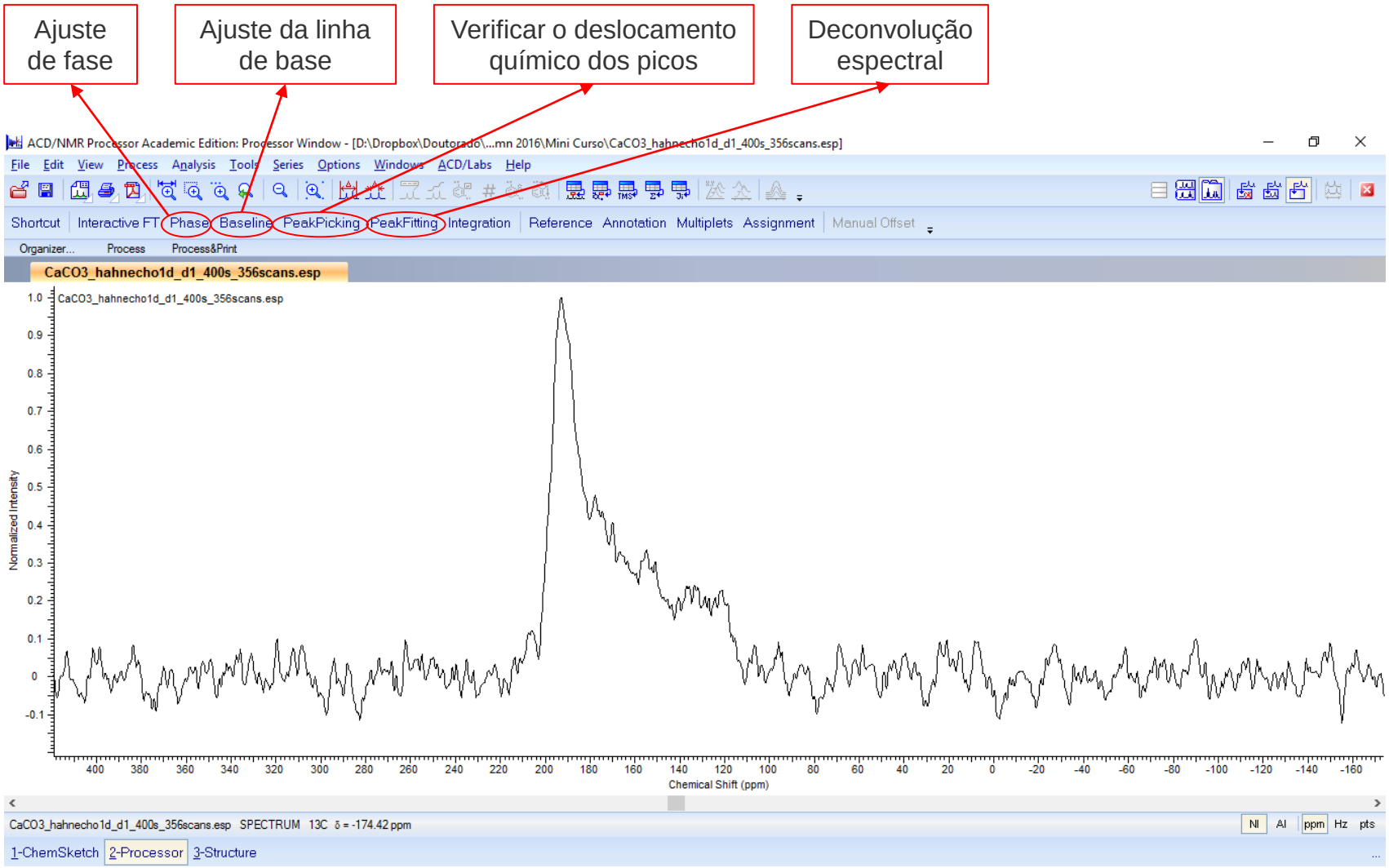


Caso queira abrir um espectro já salvo, clicar em "*Open > From 1D NMR Directory*"

Processamento dos espectros de RMN



Processamento dos espectros de RMN

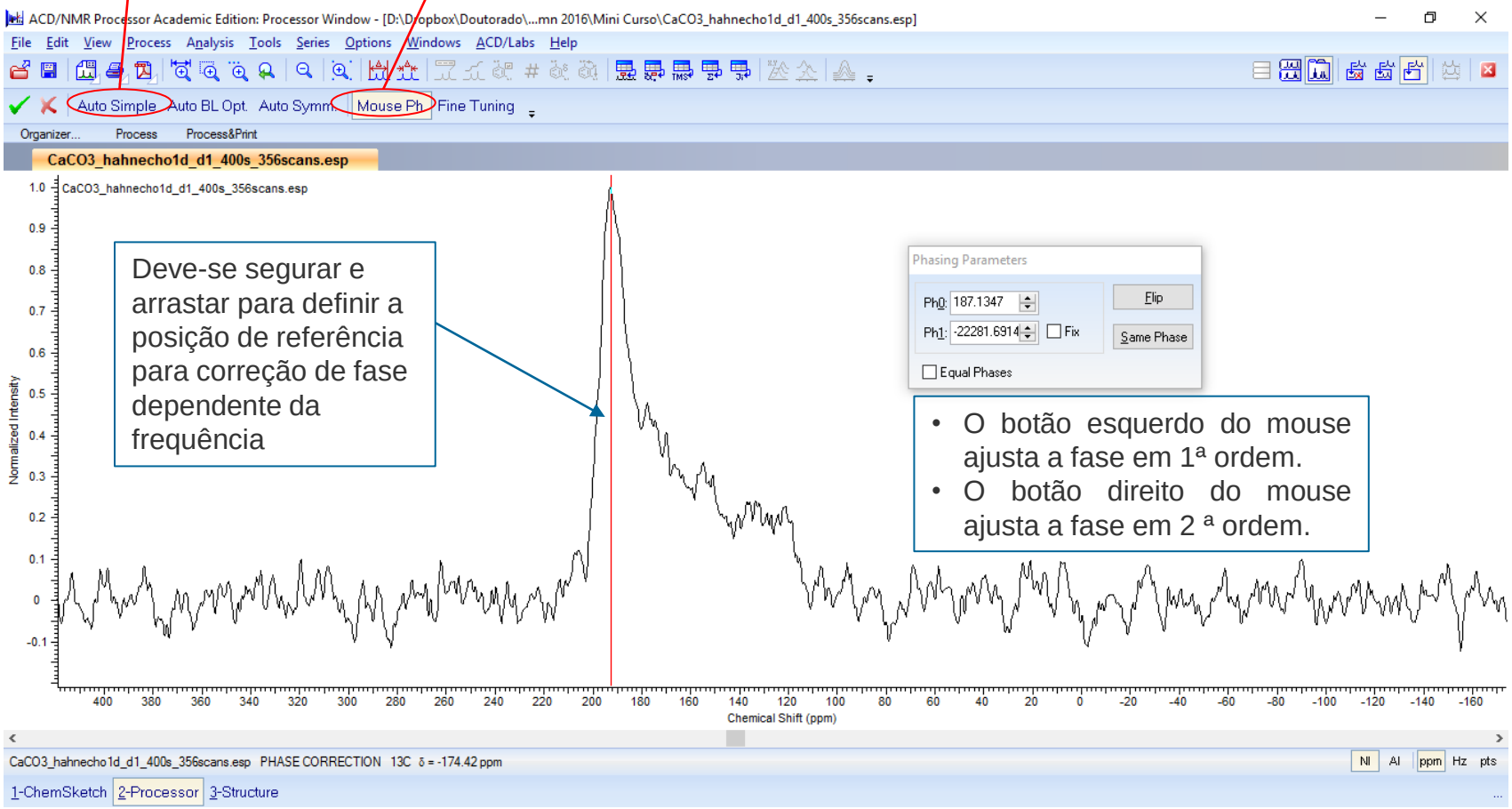


Processamento dos espectros de RMN

Ajuste de Fase

Ajuste de fase automático

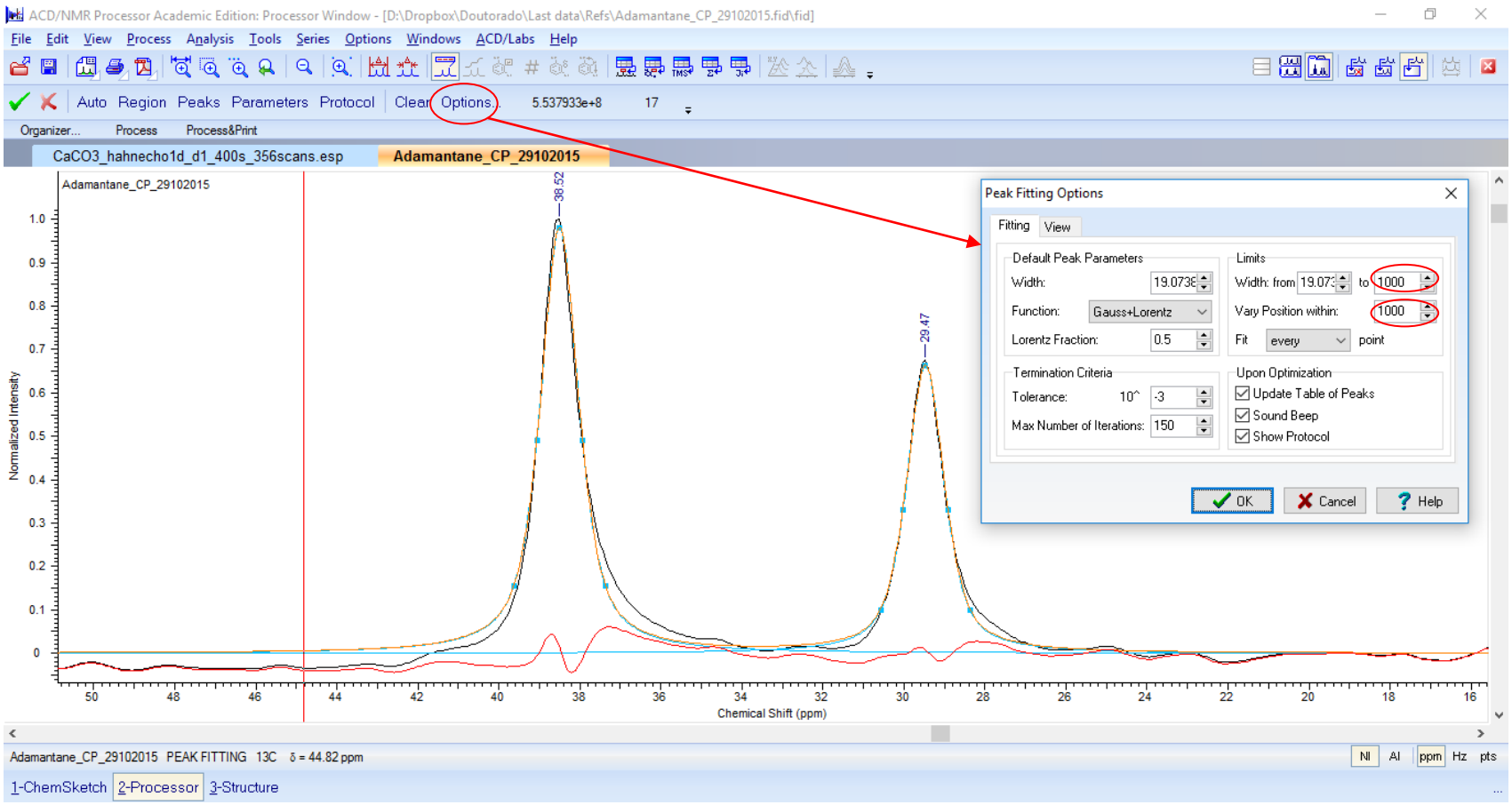
Ajuste de fase com o mouse



Processamento dos espectros de RMN

Deconvolução espectral

Após definir os deslocamentos dos picos em "*PeakPicking*", clicar em "*PeakFitting*"

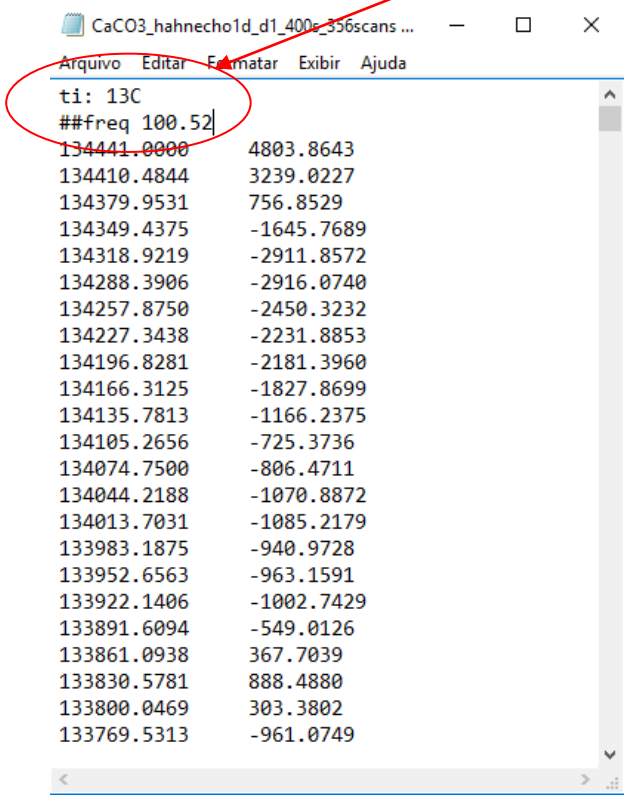


Processamento dos espectros de RMN

Exportar em Hz para usar o programa DMFIT.

Simulação dos espectros de RMN

Antes de abrir o arquivo no DMFIT, deve-se inserir manualmente a informação do núcleo e da frequência de ressonância (em MHz), como mostra a figura.



MAGNETIC RESONANCE IN CHEMISTRY
Magn. Reson. Chem. 2002; **40**: 70–76

MRC

Modelling one- and two-dimensional solid-state NMR spectra†

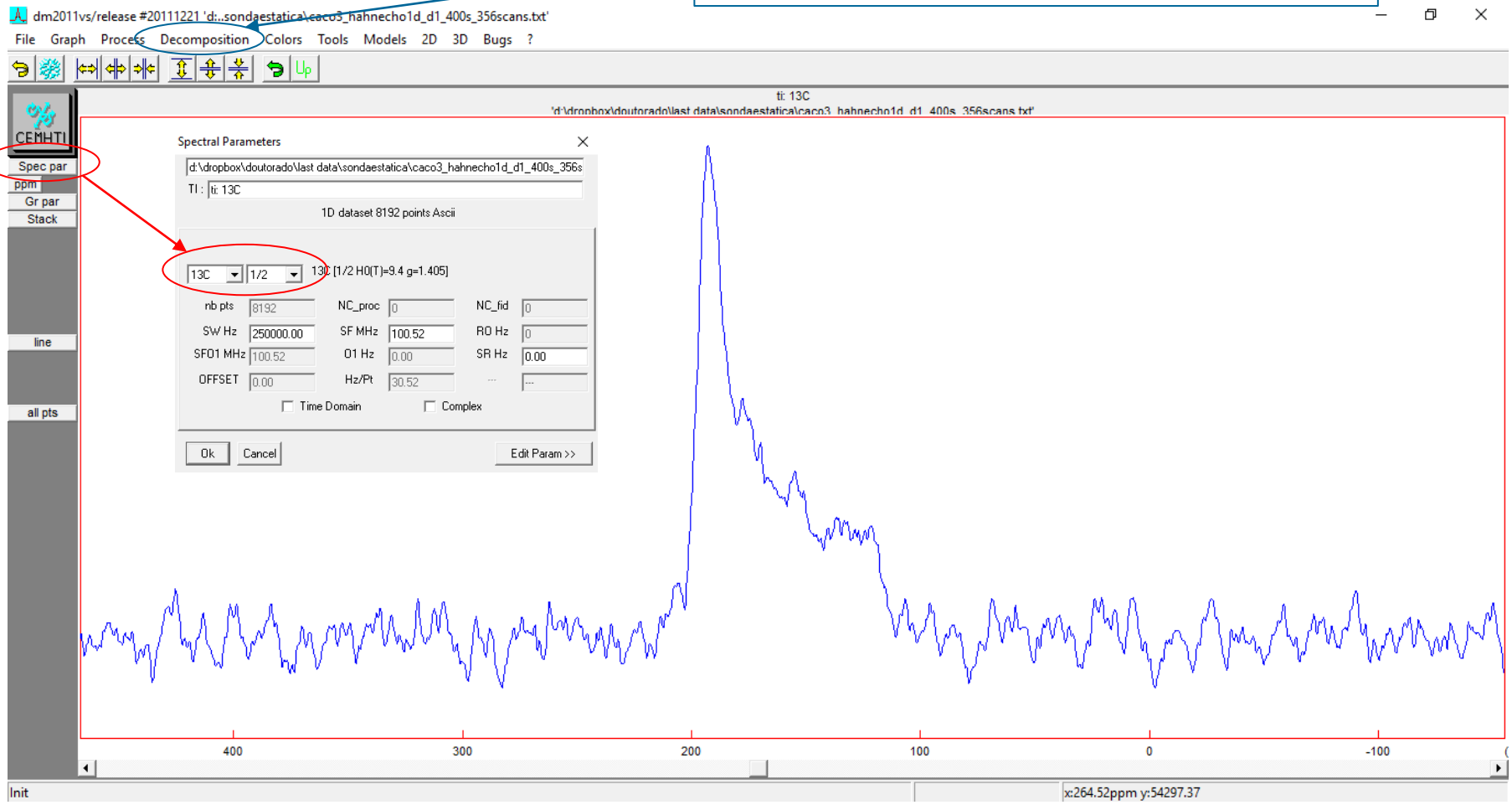
Dominique Massiot,[1]* Franck Fayon,[1] Mickael Capron,[1] Ian King,[1,2] Stéphanie Le Calvé,[1] Bruno Alonso,[1] Jean-Olivier Durand,[3] Bruno Bujoli,[4] Zhehong Gan[5] and Gina Hoatson[6]

[1] Centre de Recherche sur les Matériaux à Haute Température, CRMHT-CNRS, 1D avenue de la Recherche Scientifique, 45071 Orléans cedex 2, France
[2] Department of Chemistry, University of Durham, Durham, UK
[3] Laboratoire de Chimie Moléculaire et Organisation du Solide, UMR 5637, Case 007, Université Montpellier 2, Place Eugène Bataillon, 34095 Montpellier cedex 05, France
[4] Laboratoire de Synthèse Organique, UMR CNRS 6513, 2 Rue de la Houssinière, BP 92208, 44322 Nantes cedex 03, France
[5] Center of Interdisciplinary Magnetic Resonance, NHMFL, Tallahassee, Florida 32310, USA
[6] College of William & Mary, Department of Physics, Box 8795, Williamsburg, Virginia 23187-8795, USA

FIT Dmfit

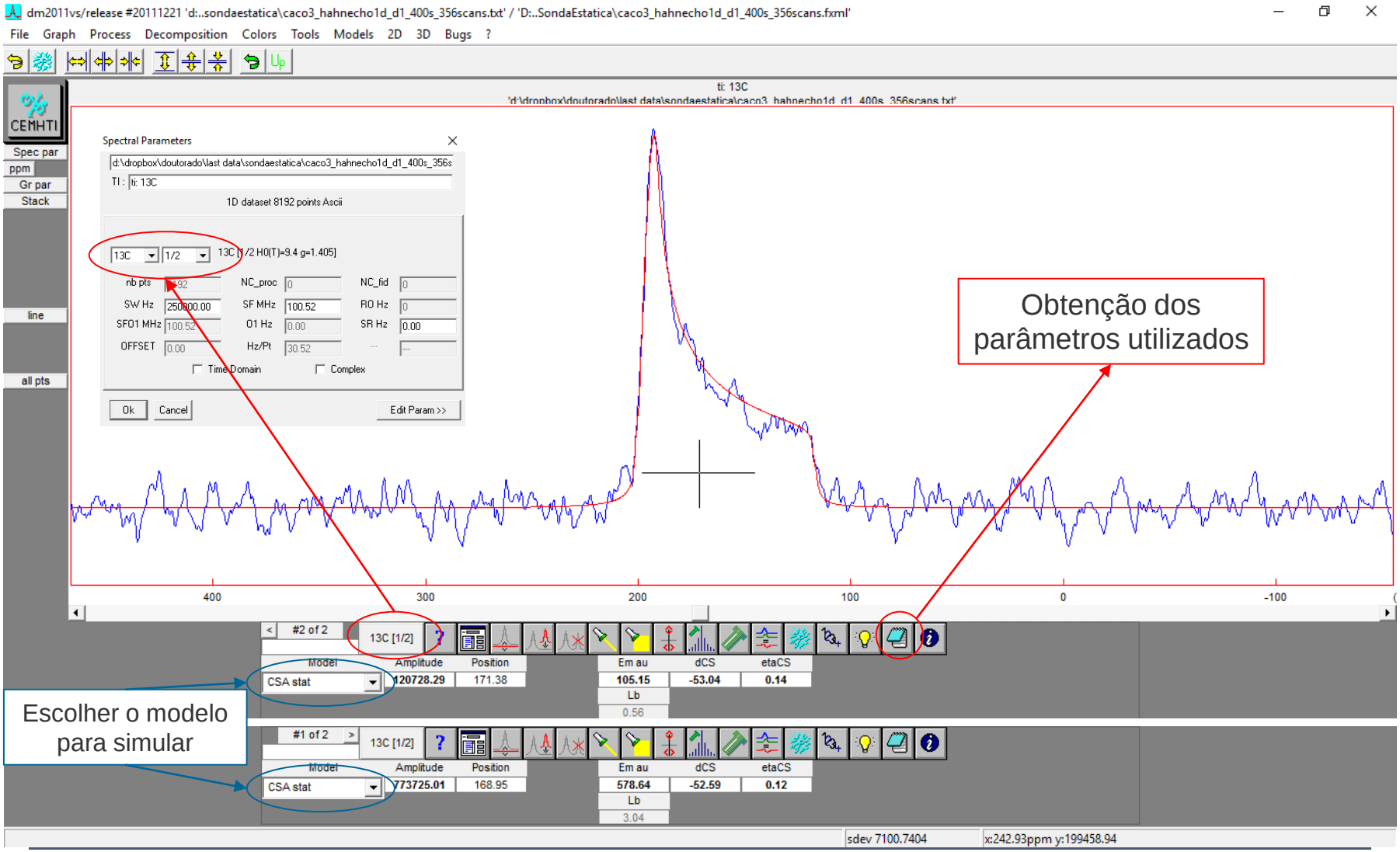
Simulação dos espectros de RMN

Após definir o núcleo em "*Spectral Parameters*", clicar em *"Decomposition"* e depois *"New Fit"*.



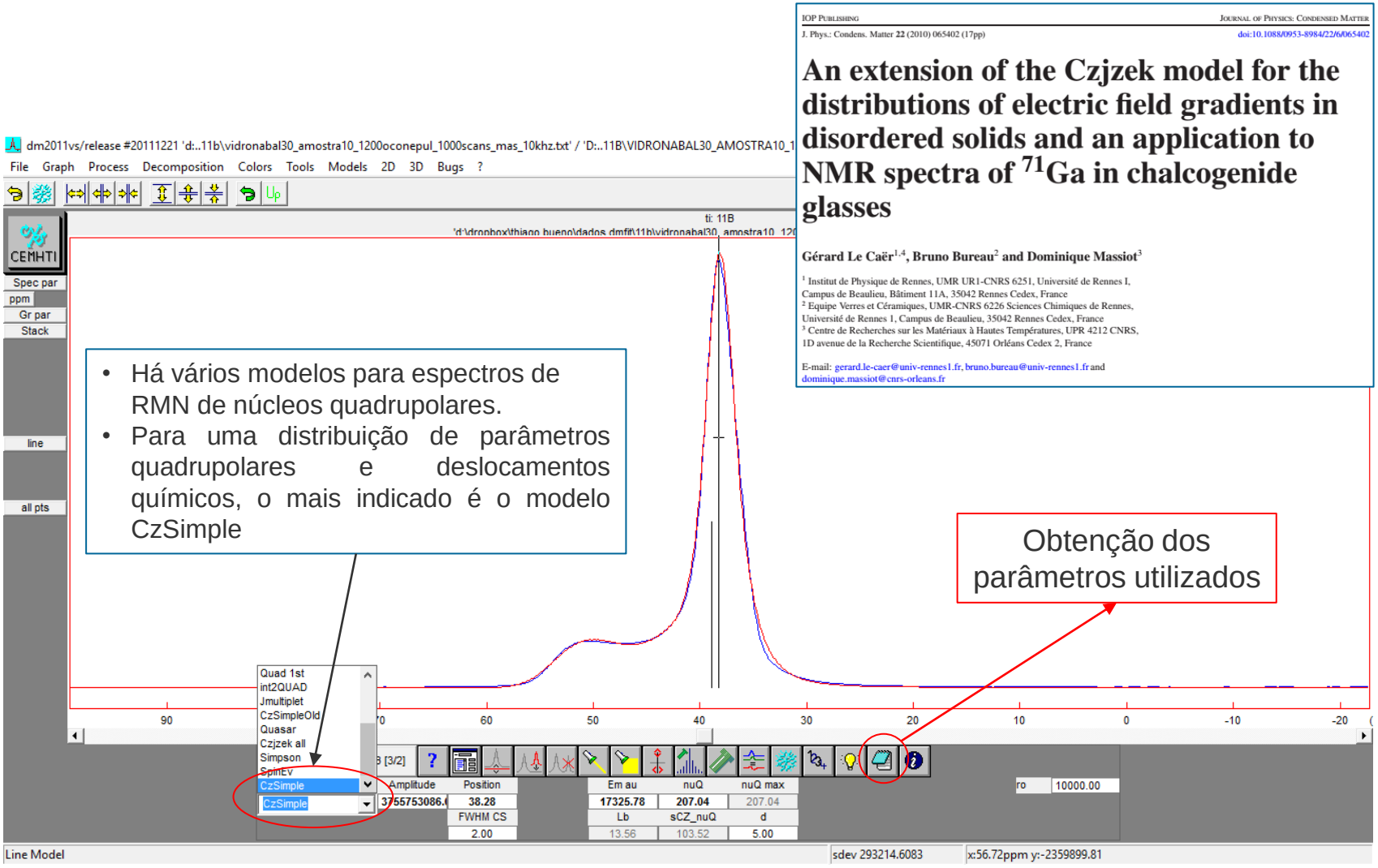
Simulação dos espectros de RMN

Padrão de pó - CSA



Simulação dos espectros de RMN

Núcleos quadrupolares



- Há vários modelos para espectros de RMN de núcleos quadrupolares.
- Para uma distribuição de parâmetros quadrupolares e deslocamentos químicos, o mais indicado é o modelo CzSimple

Obtenção dos parâmetros utilizados

IOP Publishing — Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **22** (2010) 065402 (17pp) doi:10.1088/0953-8984/22/6/065402

An extension of the Czjzek model for the distributions of electric field gradients in disordered solids and an application to NMR spectra of ^{71}Ga in chalcogenide glasses

Gérard Le Caër[1,4], Bruno Bureau[2] and Dominique Massiot[3]

[1] Institut de Physique de Rennes, UMR UR1-CNRS 6251, Université de Rennes I, Campus de Beaulieu, Bâtiment 11A, 35042 Rennes Cedex, France
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[3] Centre de Recherches sur les Matériaux à Hautes Températures, UPR 4212 CNRS, 1D avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France

E-mail: gerard.le-caer@univ-rennes1.fr, bruno.bureau@univ-rennes1.fr and dominique.massiot@cnrs-orleans.fr

Bibliografia recomendada

- Fundamentos de RMN:
  - "**Spin Dynamics**", M. H. Levitt. John Wiley & Sons, 2002.
  - "**Principles of nuclear magnetic resonance in one and two dimensions**", R. R. Ernst, G. Bodenhausen, A. Wokaun. Oxford, 1987.
  - "**Ressonância magnética nuclear: fundamentos, métodos e aplicações**", V. M. S. Gil, C. F. G. C. Geraldes. Fundação Calouste Gulbekian, 1987.

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  - "**NMR techniques and applications in geochemistry and soil chemistry**", M. A. Wilson, Oxford, 1987.
  - "**Solid-state nuclear magnetic resonance (NMR) methods applied to the study of carbon materials**", J. C. C. Freitas, A. G. Cunha, F. G. Emmerich. In: Radovic LR (ed.), *Chemistry and Physics of Carbon*, vol. 31, Boca Raton; CRC Press; 2012, p. 85-170.

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  - M. Bak, J. T. Rasmussen, N. C. Nielsen. SIMPSON: A general simulation program for solid-state NMR spectroscopy. *J. Magn. Reson.* 2000;147:296.
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  - T. F. Kemp, M. E. Smith. QuadFit - A new cross-platform computer program for simulation of NMR line shapes from solids with distributions of interaction parameters. *Solid State Nucl. Magn. Reson.* 2009;35:243-252.

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  - "**Density-Funcional Theory of atoms and molecules**", Robert G. Parr and Weitao Yang, Oxford University Press, Oxford, 1989.
  - "**Atomic and electronic structure of solids"**, E. Kaxiras, Cambridge University Press, New York, 2003.
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Bibliografia recomendada

- Métodos computacionais – cálculos de parâmetros espectrais de RMN por métodos baseados em DFT:

  - F. Mauri, B. G. Pfrommer, S. G. Louie. *Ab initio* theory of NMR chemical shifts in solids and liquids. *Phys. Rev. Lett.* 1996;77:5300-5303.
  - C. Bonhomme et al. First-principles calculation of NMR parameters using the gauge including projector augmented wave method: A chemist's point of view. *Chem. Rev.* 2012;112:5733-5779.
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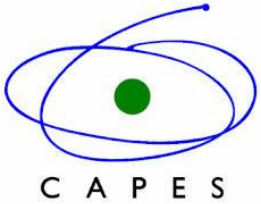
Agradecimentos

UFES

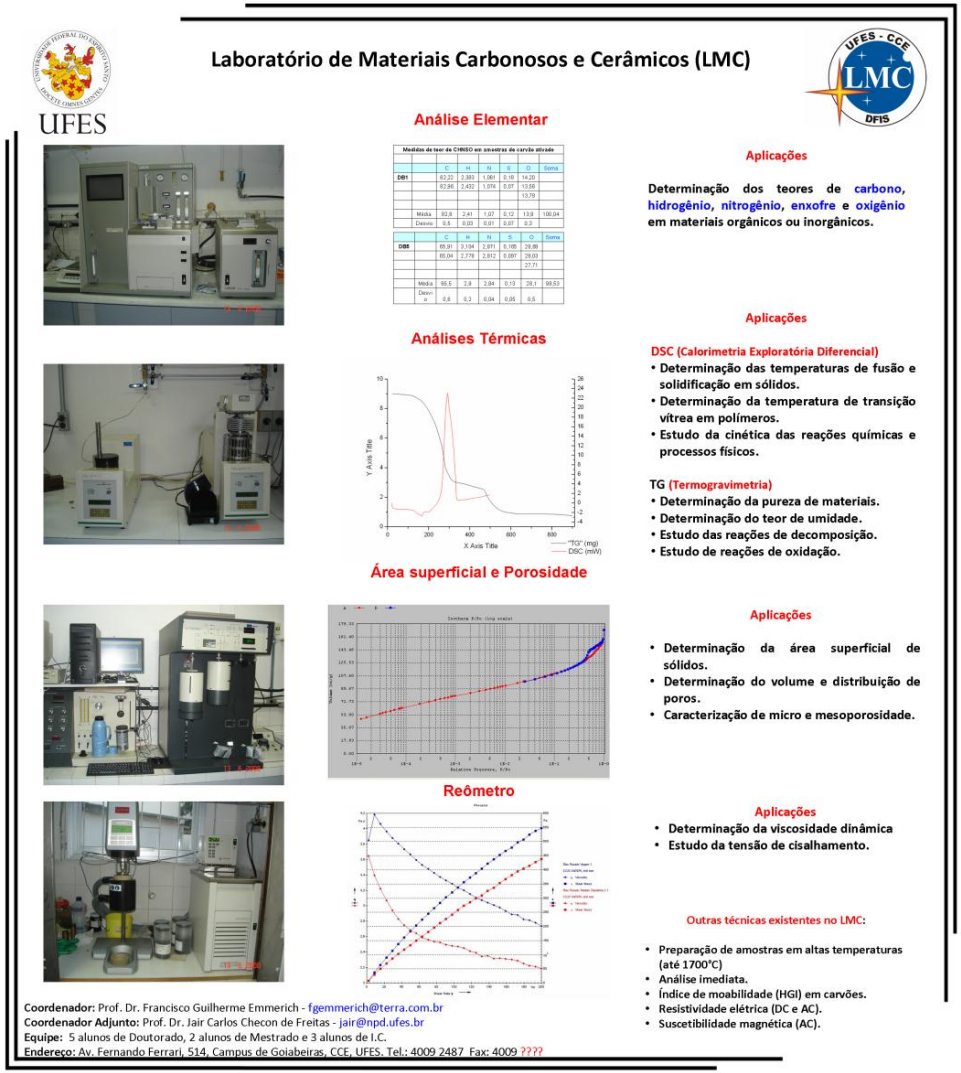
ASSOCIAÇÃO DE USUÁRIOS DE RESSONÂNCIA MAGNÉTICA NUCLEAR

Schlumberger



FINEP

Contato: dúvidas, comentários, sugestões, etc.



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