

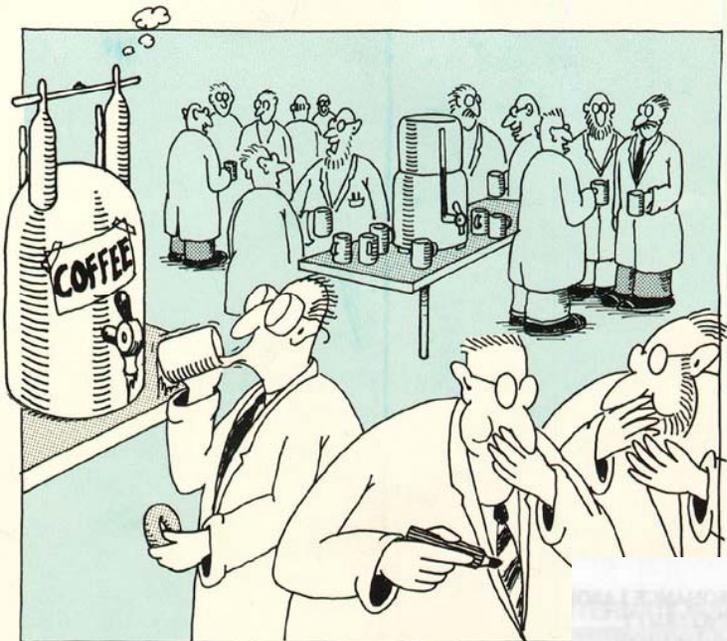
A Ressonância Magnética Nuclear (RMN) e suas aplicações



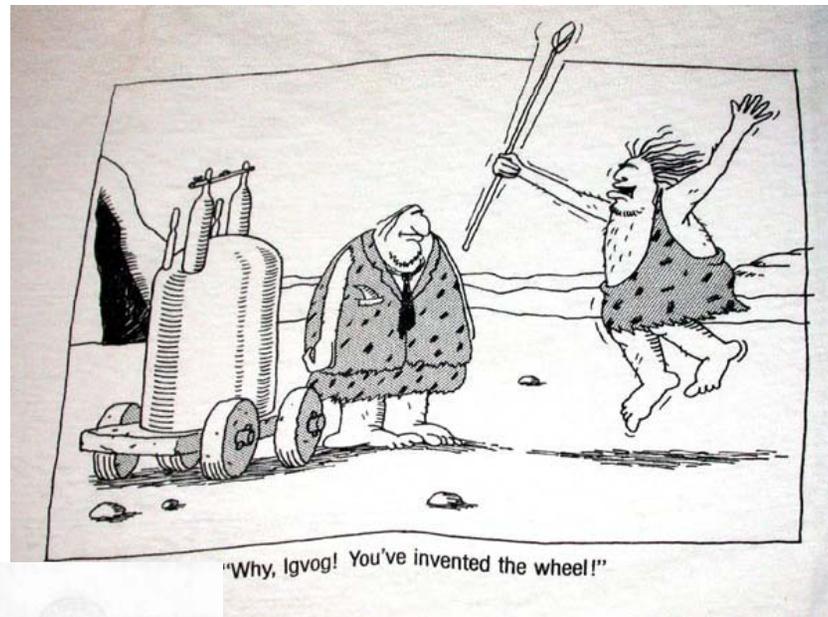
Eduardo Ribeiro de Azevedo



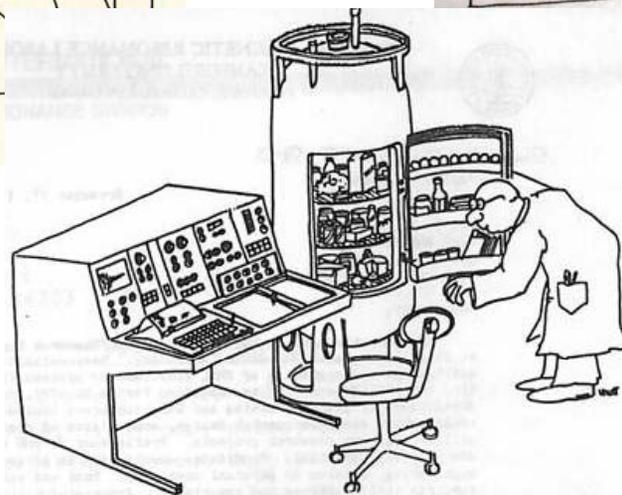
Universidade de São Paulo - USP
Instituto de Física de São Carlos - IFSC



NMR practical jokes.



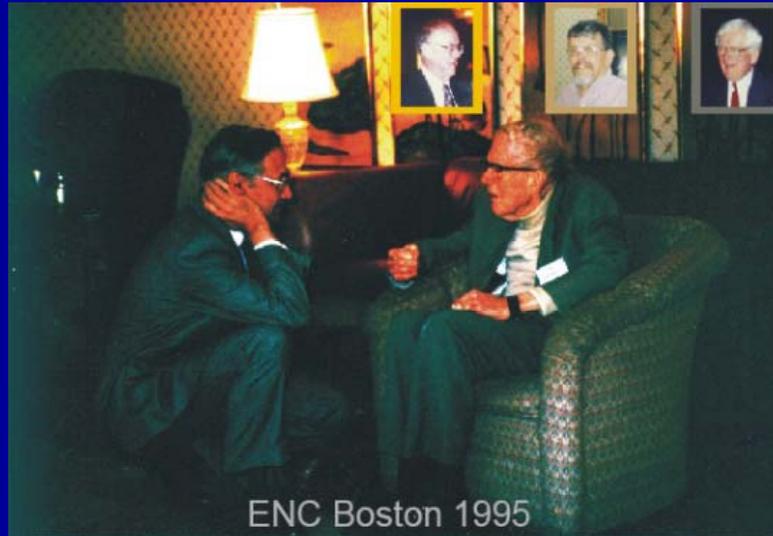
"Why, Igvog! You've invented the wheel!"



Uma breve visão dos 50 anos de história da RMN



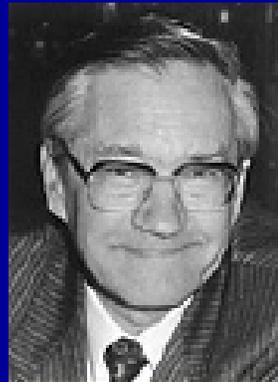
Felix Bloch
1905-1983
Nobel em Física
(1952)



ENC Boston 1995



Edward Mills Purcell
1912-1997
Nobel em Física
(1952)



Richard Ernst
1933
Nobel em Química
(1991)



Paul Lauterbur
1929-2007
Nobel em Medicina
(2003)



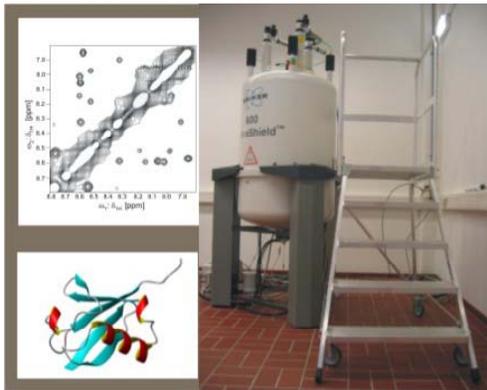
Sir Peter Mansfield
1933
Nobel em Medicina
(2003)



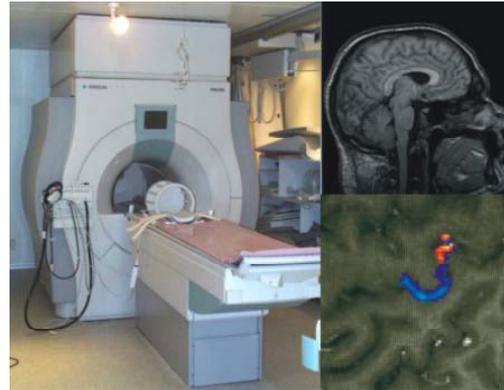
Kurt Wüthrich
1938
Nobel em Química
(2002)

As muitas faces da Ressonância Magnética Nuclear

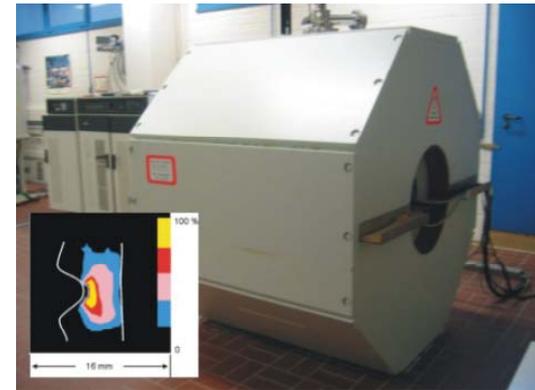
Química e Física:
Espectroscopia de RMN



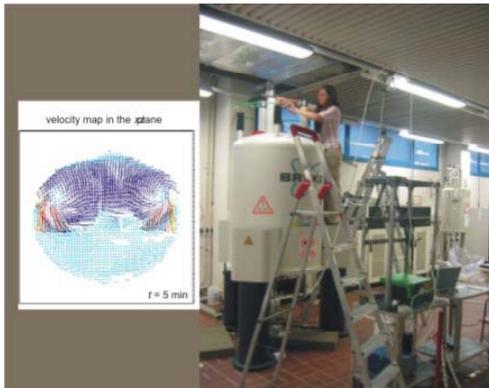
Medicina:
Imagens por RMN



Ciências dos Materiais:
Imagens por RMN



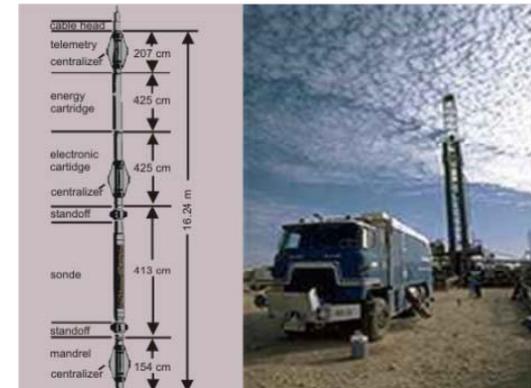
Engenharia Química:
Imagens de fluxo



Controle de Qualidade:
Relaxação por RMN

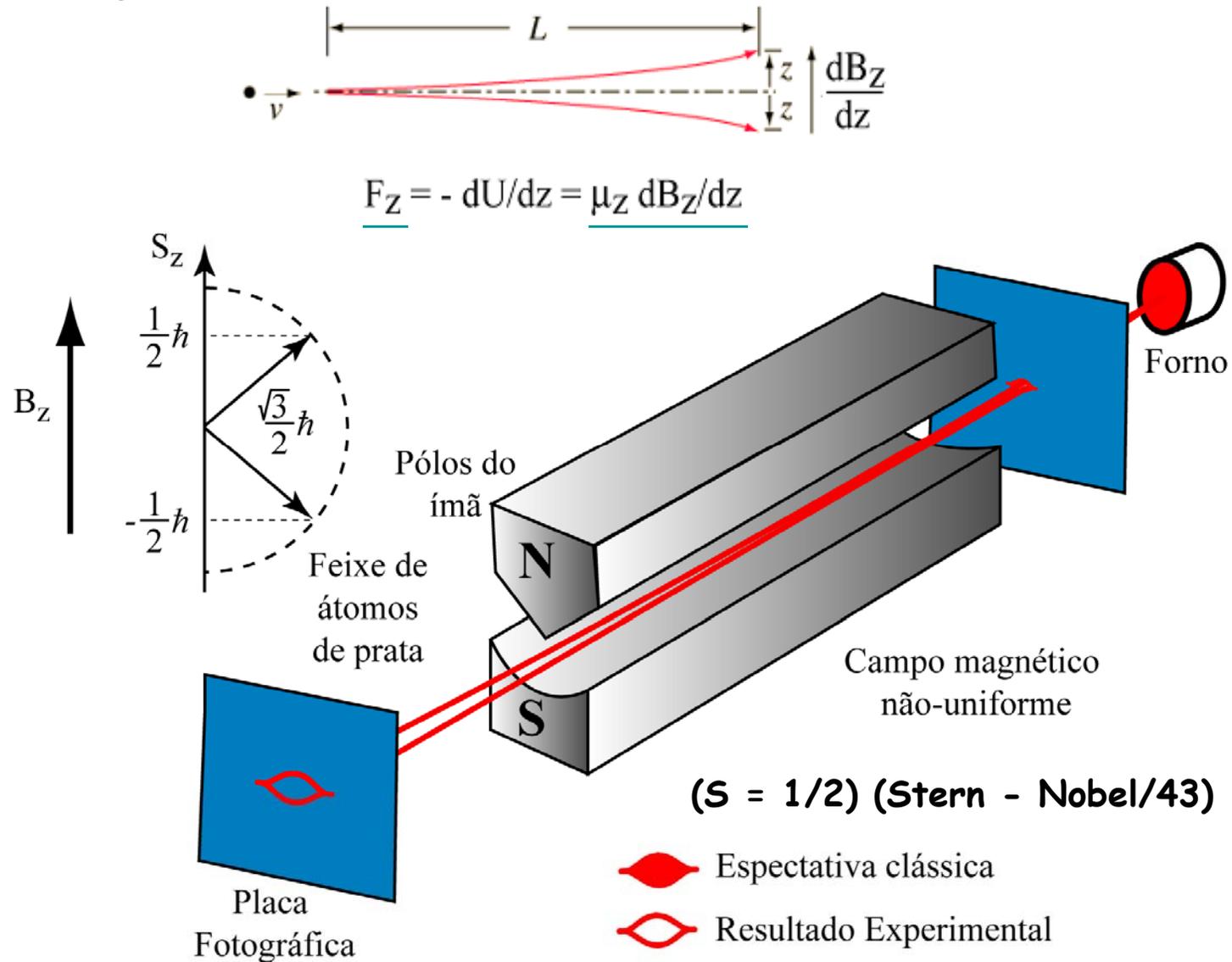


Indústria do Petróleo:
Relaxação por RMN



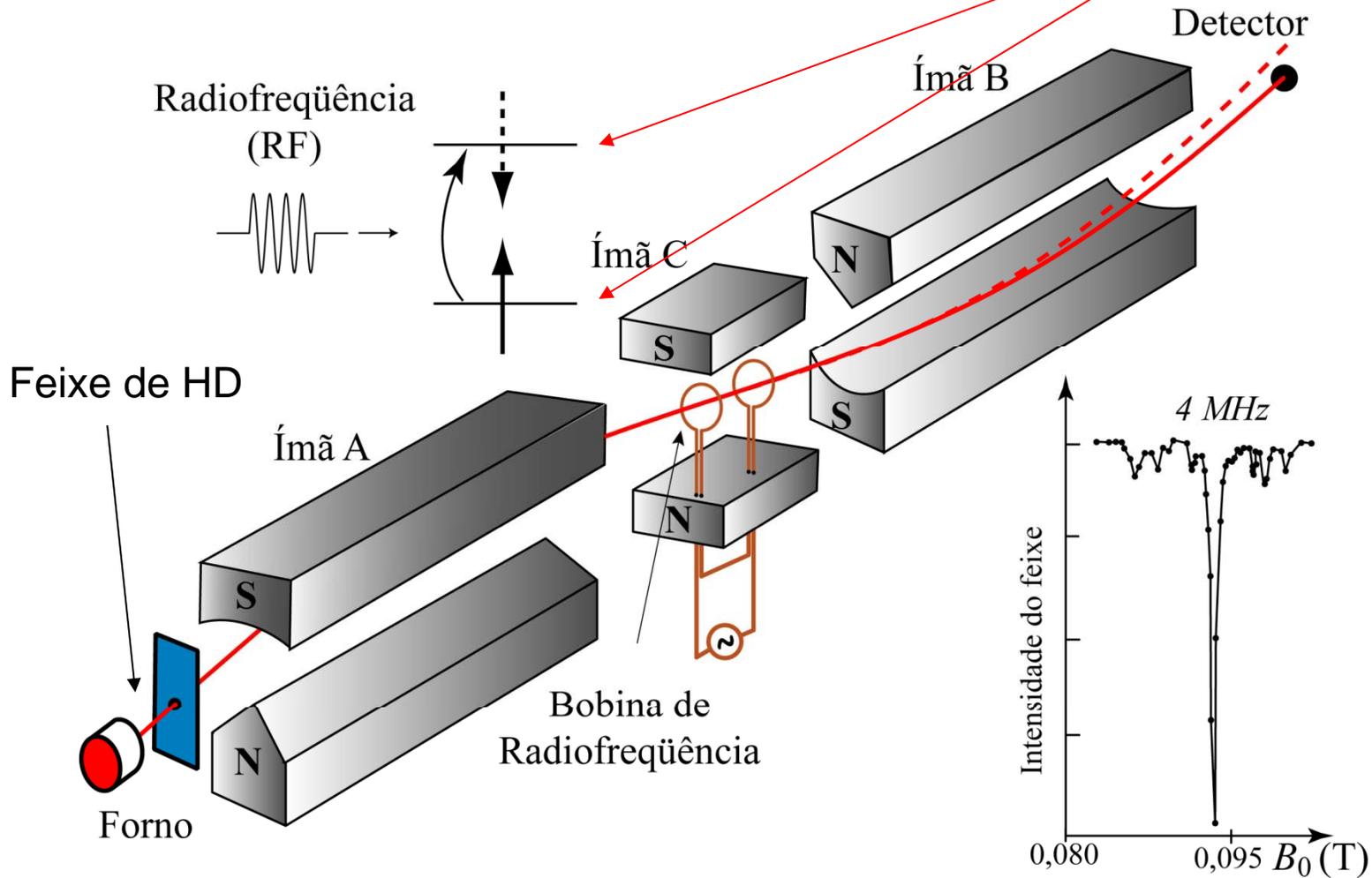
Os experimentos precursores da RMN

A detecção do spin eletrônico: O Experimento de Stern-Gerlach



A detecção do spin nuclear: O Experimento de Rabi-Cohen

$$E = -\vec{\mu} \cdot \vec{B} = \mu_z B_z = -\gamma \hbar I_z B_z = \pm \frac{1}{2} \hbar (\gamma B_z) = \pm \frac{1}{2} \hbar \omega_L$$



O Fenômeno Básico da RMN

A origem do Spin Nuclear e a A RMN

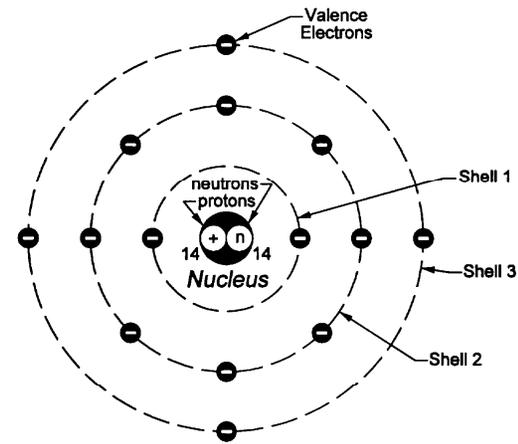
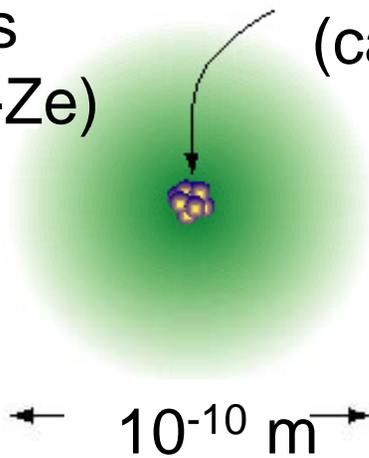
Spin:

- O Spin é um momentum angular, propriedade fundamental de elétrons e núcleos como massa, carga.
- No caso de partículas como elétrons, prótons e neutrons, denominamos spin uma propriedade intrínseca, vale $\frac{1}{2}$ e não tem análogo clássico.
- O que chamamos de spin nuclear é uma propriedades que está associada à combinação de todos os momentos angulares das partículas dentro do núcleo sejam eles de origem intrínseca ou orbital (movimento nuclear).
- O Spin está diretamente associado ao magnetismo da partícula através de uma relação de com o momento magnético. No caso de núcleos no seu estado fundamental, existe uma relação de proporcionalidade entre o spin nuclear e o momento magnético.
- O spin nuclear pode ser inteiro ou semi-inteiro e o seu valor depende se o número de massa do núcleo é par ou ímpar.
- Núcleos que possuem $I > 1/2$ possuem uma propriedade denominada momento de quadrupolo elétrico, que afeta de forma importante suas características para RMN.

O modelo de camadas atômico

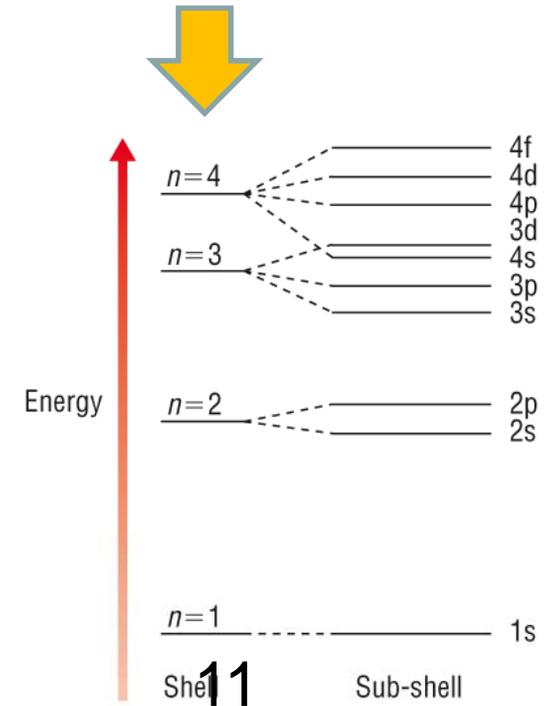
Elétrons (carga $-Ze$)

Núcleo (carga $+Ze$)

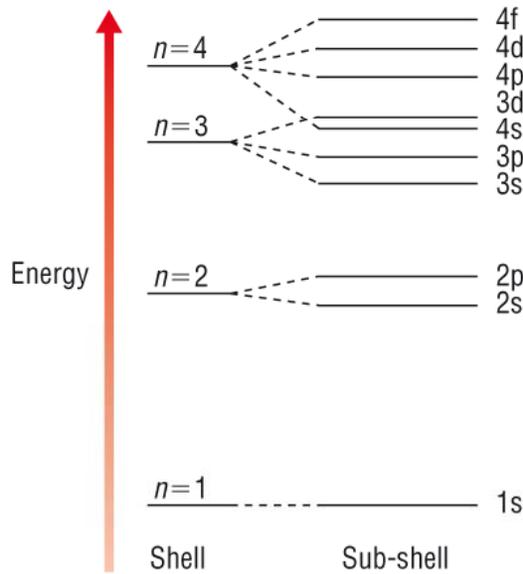


$$V(r)$$

$$\left[\underbrace{\sum_{i=1}^Z \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right)}_{e-n} + \underbrace{\sum_{i>j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{e-e} \right] \psi = E\psi.$$



Regras de Hund

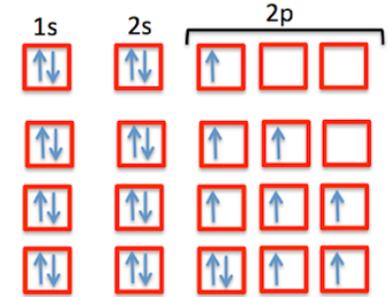


+

Forma fraca do princípio de exclusão de Pauli

=

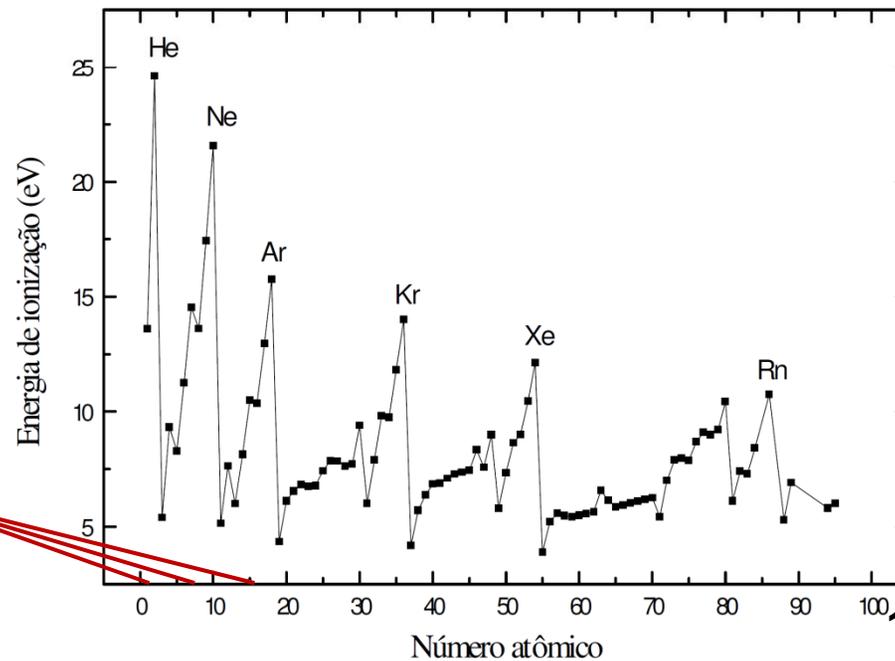
Boron (5 electrons)
 $1s^2 2s^2 2p^1$
Carbon (6 electrons)
 $1s^2 2s^2 2p^2$
Nitrogen (7 electrons)
 $1s^2 2s^2 2p^3$
Oxygen (8 electrons)
 $1s^2 2s^2 2p^4$



Hund's Rule

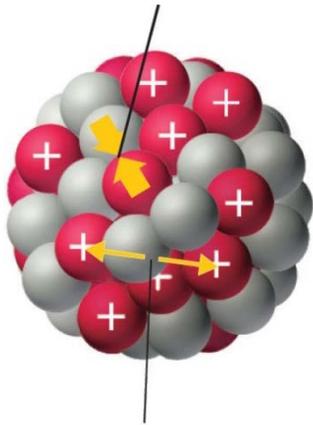


Números mágicos atômicos



O núcleo atômico

Interação forte (força forte) e de curto alcance entre prótons e neutrons (nucleons)



~~Interação eletrostática entre prótons (muito mais fraca que a interação forte a ponto de poder ser ignorada)~~



$V(r)$



$V(r)\psi = E\psi$

M = massa atômica
 Z = número atômico

M X Z

Núcleons:

Z prótons
 N ($M-Z$) nêutrons

Energias permitidas para os nucleons

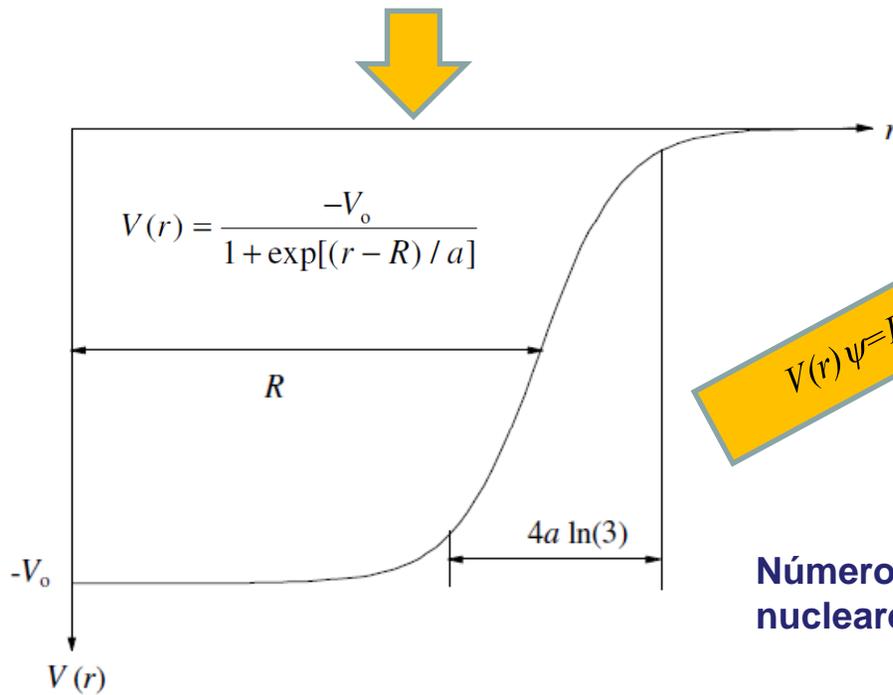


Problema: a forma de $V(r)$ é desconhecida



O modelo de camadas e o spin nuclear

Uma aproximação para o potencial de um nucleon (próton ou neutron) dentro do núcleo



$V(r)\psi = E\psi$

Números mágicos nucleares

$R = 1,25A^{1/3} F, a = 0,525 F$ e $V_0 \sim 50 \text{ MeV}$

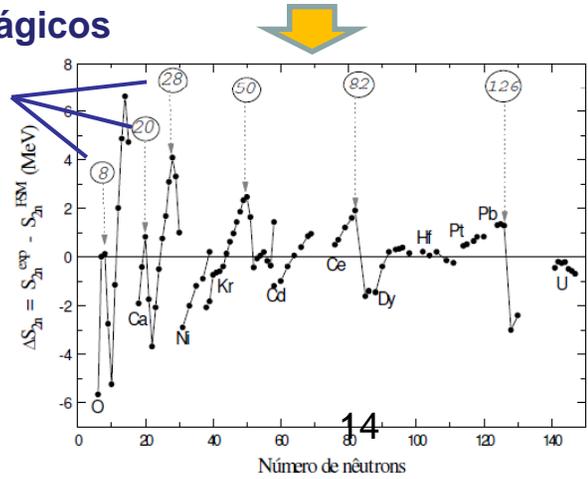
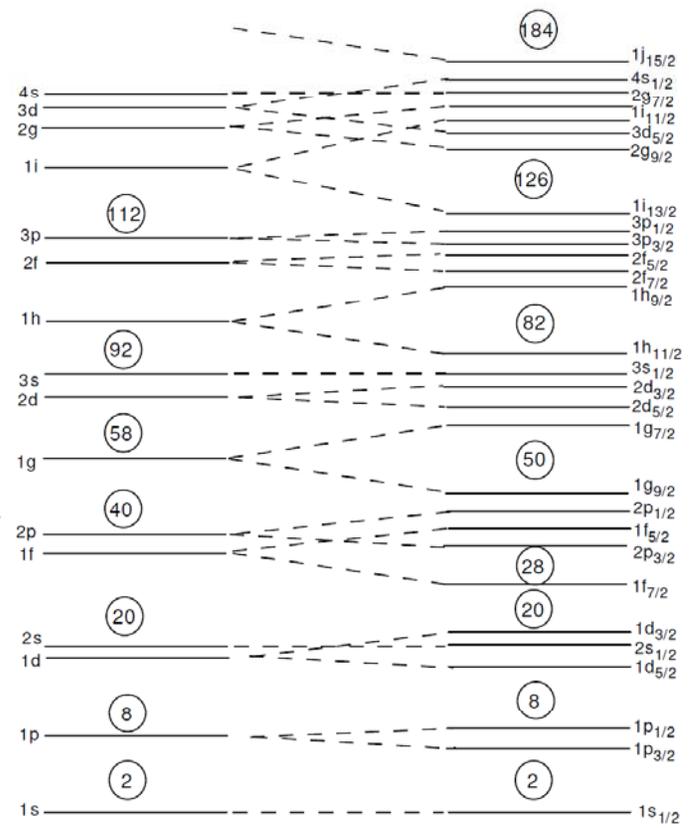
Raio do núcleo (1F = 10-15m)

Espessura da superfície nuclear

Energia de ligação dos nucleons

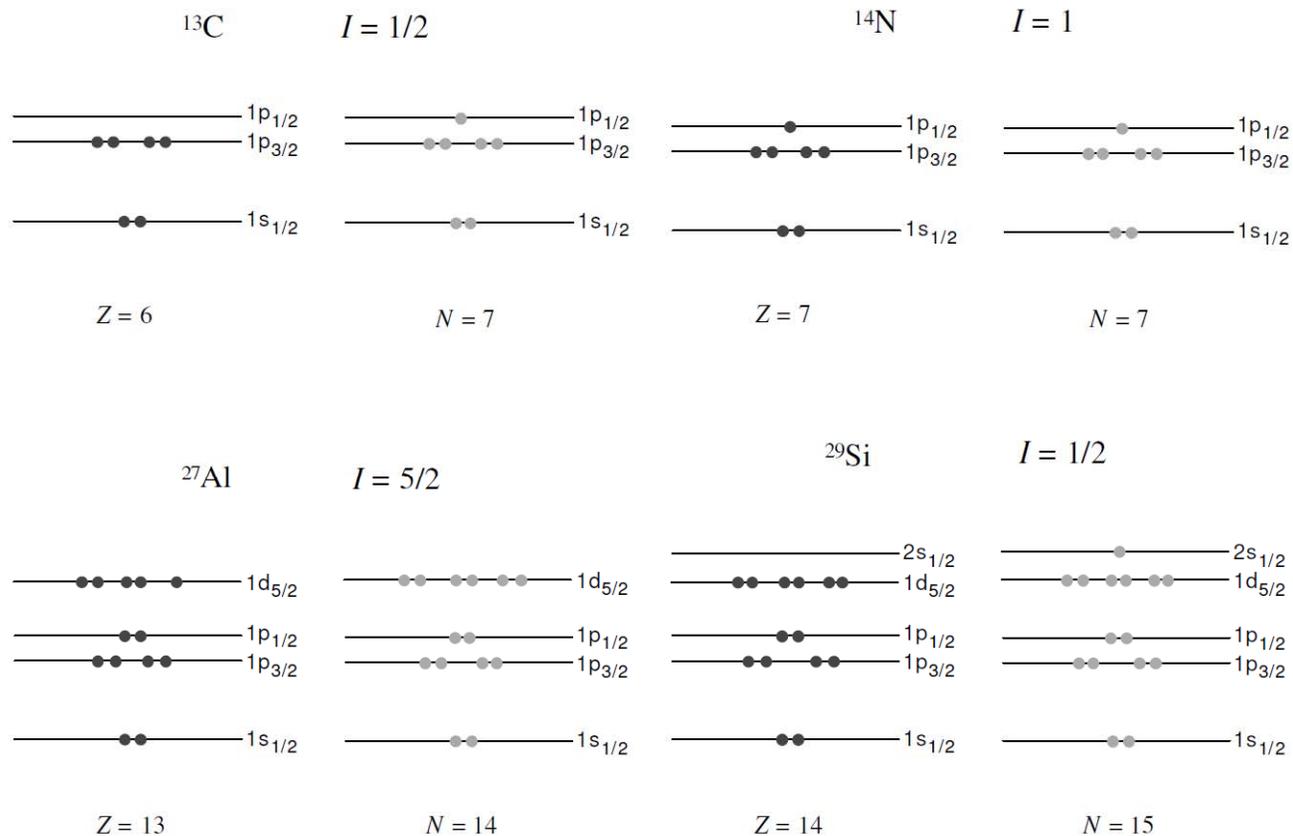
Sem interação spin-órbita

Com interação spin-órbita



Número quântico associado ao módulo do Momentum angular total da camada

O modelo de camadas e o spin nuclear



<i>Z</i> prótons	<i>N</i> nêutrons	<i>M</i>	Spin nuclear <i>I</i>	Exemplos
Par	Par	Par	Zero	$^{12}\text{C}_6$ e $^{16}\text{O}_8$
Par	Ímpar	Ímpar	Semi-inteiro	$^{13}\text{C}_6$ e $^{17}\text{O}_8$
Ímpar	Par	Ímpar	Semi-inteiro	$^{19}\text{F}_9$ e $^{31}\text{P}_{15}$
Ímpar	Ímpar	Par	Inteiro	$^{25}\text{Mg}_{12}$ e $^{14}\text{N}_7$

A Tabela Periódica da RMN

IA																			VIIIA
H	IIA											IIIA	IVA	VA	VIA	VIIA			He
Li	Be											B	C	N	O	F			Ne
Na	Mg	IIIB	IVB	VB	VIB	VII B	VIII B			IB	IIB	Al	Si	P	S	Cl			Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br			Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I			Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At			Rn
Fr	Rd	Ac																	
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

Spin = $\frac{1}{2}$
Spin > $\frac{1}{2}$

Quadrupolar

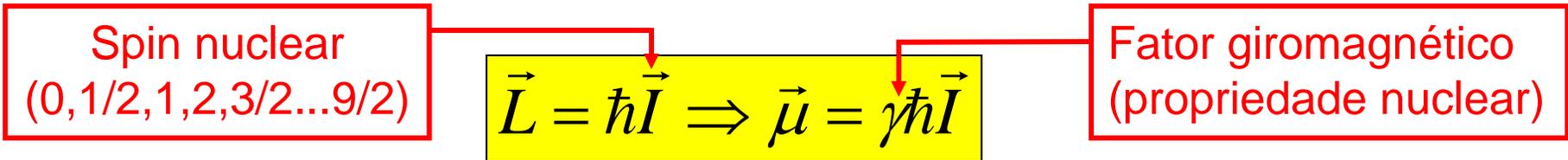
<http://grandinetti.org/Research/NMRMethods/index.html>

O núcleo atômico e o spin nuclear

M = massa atômica Z = número atômico M X_Z	<u>Núcleons:</u> Z prótons N ($M-Z$) nêutrons
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<i>Exemplo:</i> $^{27}Al_{13}$	13 prótons 14 nêutrons
--------------------------------	---------------------------

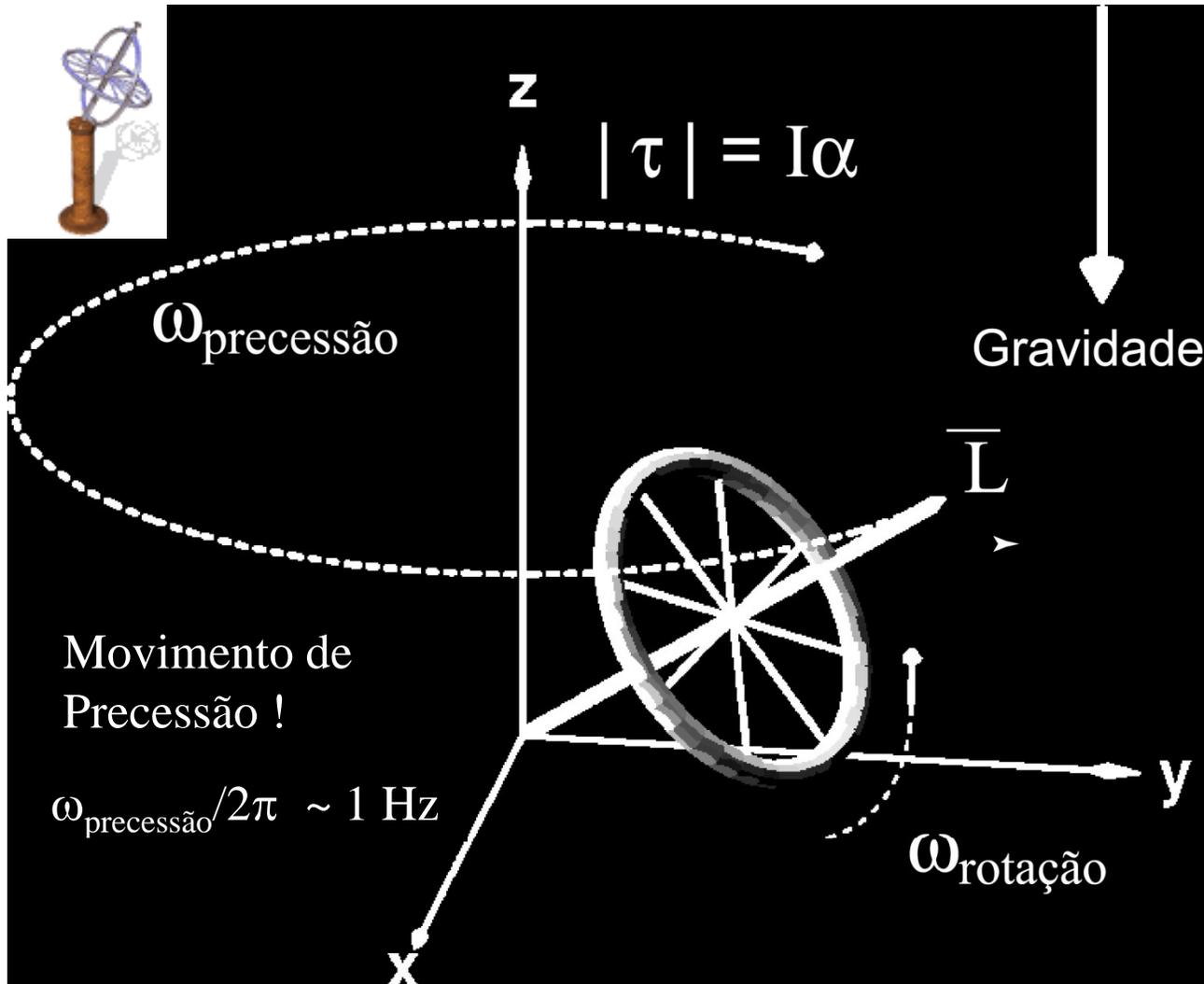
Momento angular total = soma das contribuições das partículas que o constituem



$$L_z = -I\hbar, -(I + 1)\hbar, \dots, I\hbar$$

Z prótons	N nêutrons	M	Spin nuclear I	Exemplos
Par	Par	Par	Zero	$^{12}C_6$ e $^{16}O_8$
Par	Ímpar	Ímpar	Semi-inteiro	$^{13}C_6$ e $^{17}O_8$
Ímpar	Par	Ímpar	Semi-inteiro	$^{19}F_9$ e $^{31}P_{15}$
Ímpar	Ímpar	Par	Inteiro	2H_1 e $^{14}N_7$

Precessão

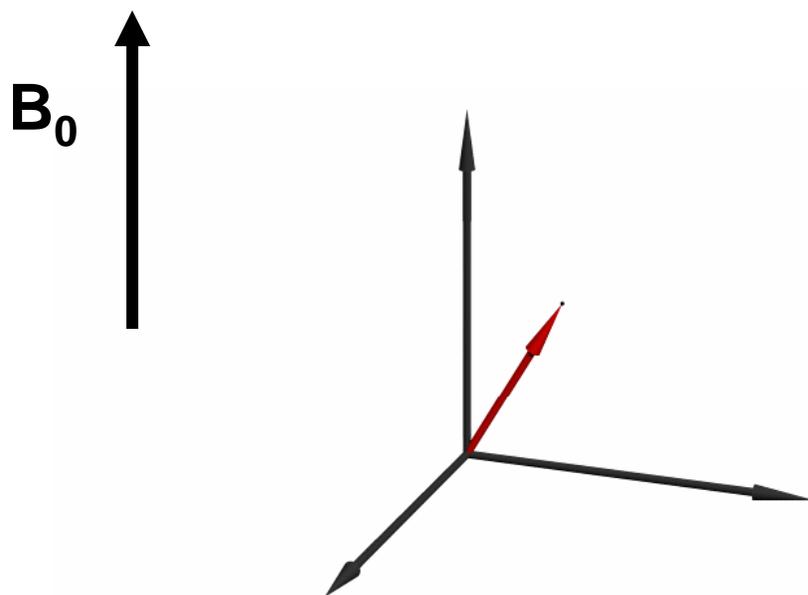


Princípios de RMN – Visão Clássica

Núcleo atômico:

momento angular (spin): $\hbar\vec{I}$

momento magnético: $\vec{\mu} = \gamma\hbar\vec{I}$



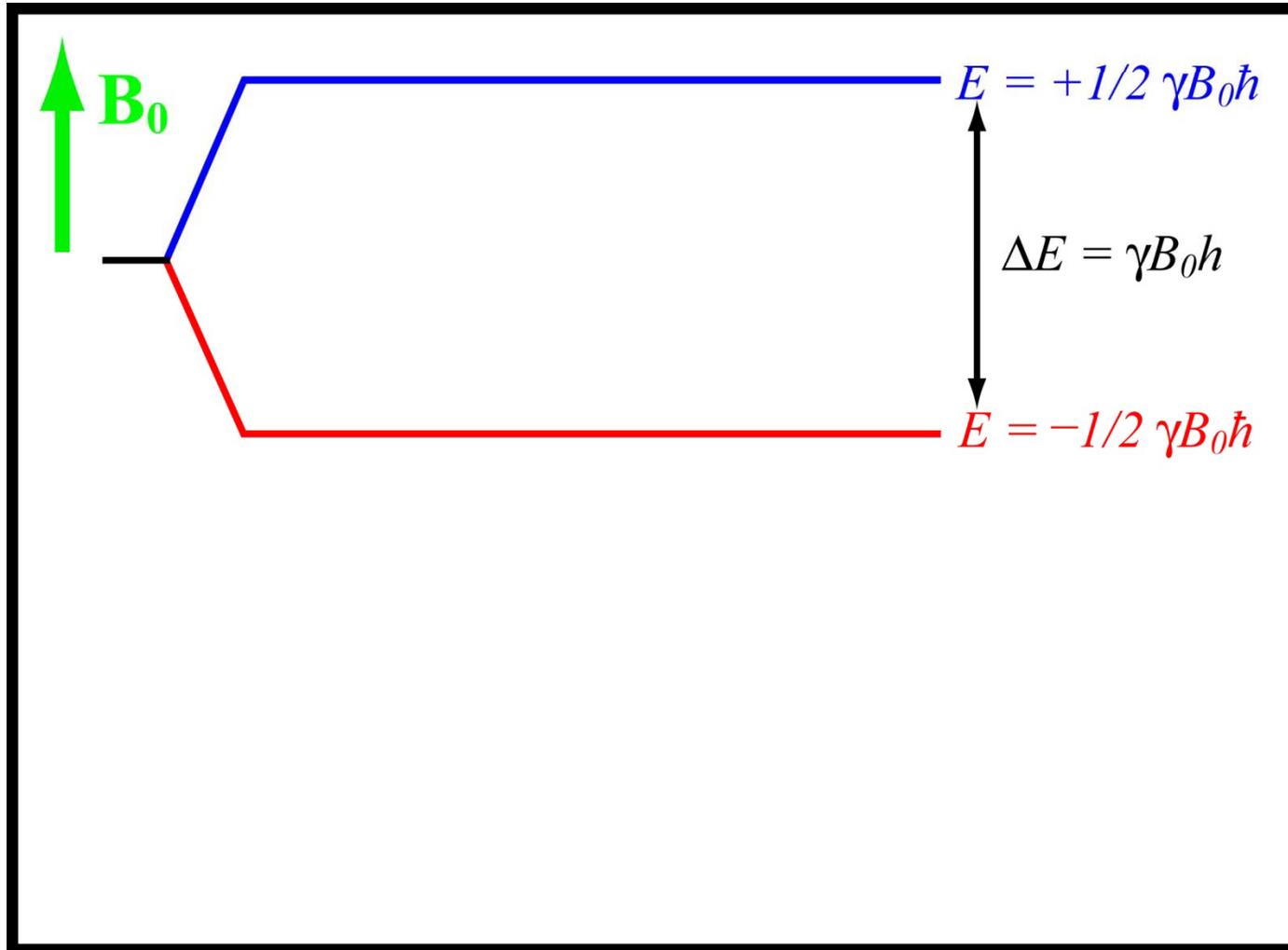
Frequência de Larmor

Precessão: $\omega_0 = \gamma B_0$

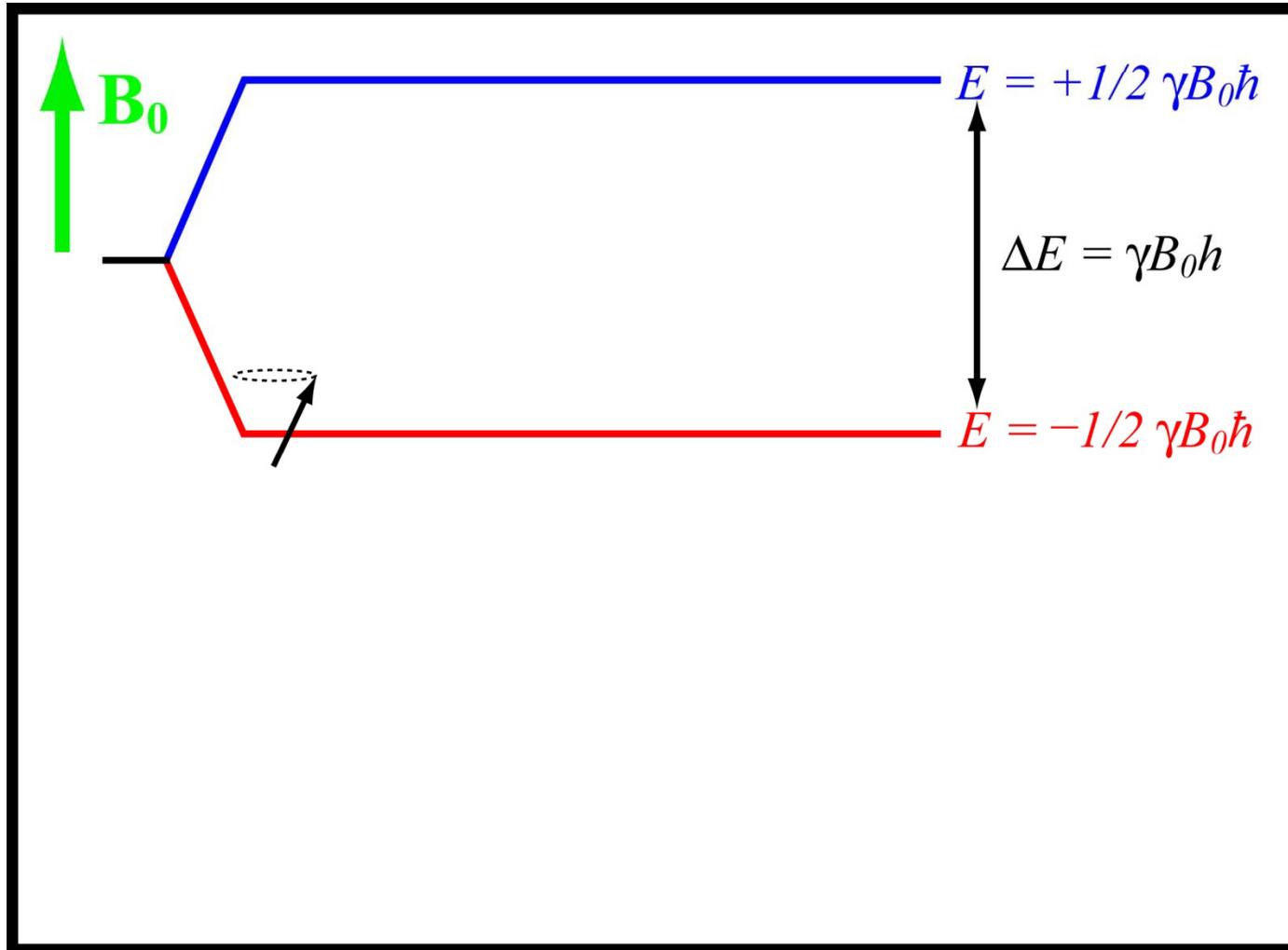
$^1\text{H} \rightarrow \gamma = 42,58 \text{ MHz/Tesla}$

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

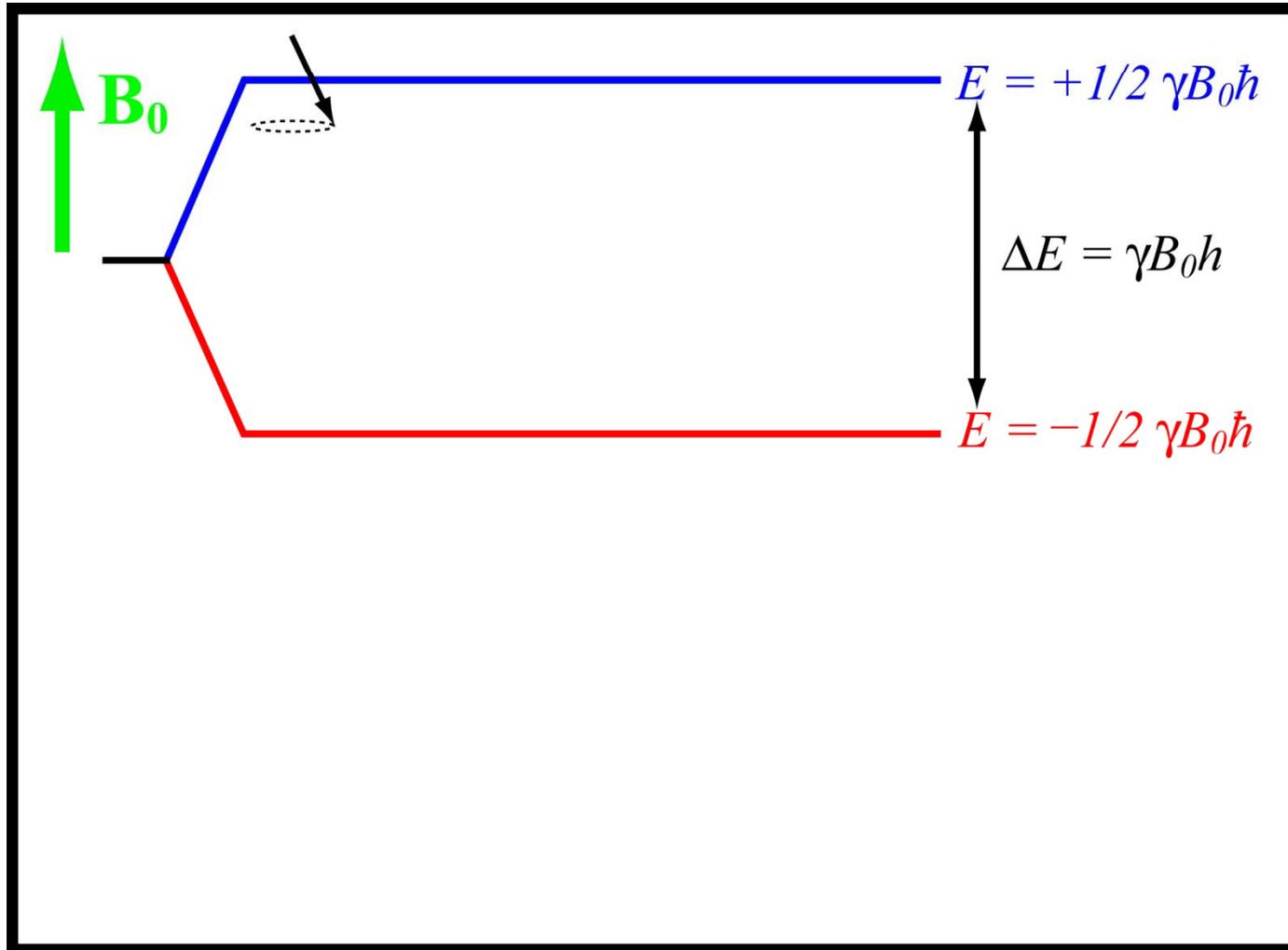
Estados de Spin ($I=1/2$)



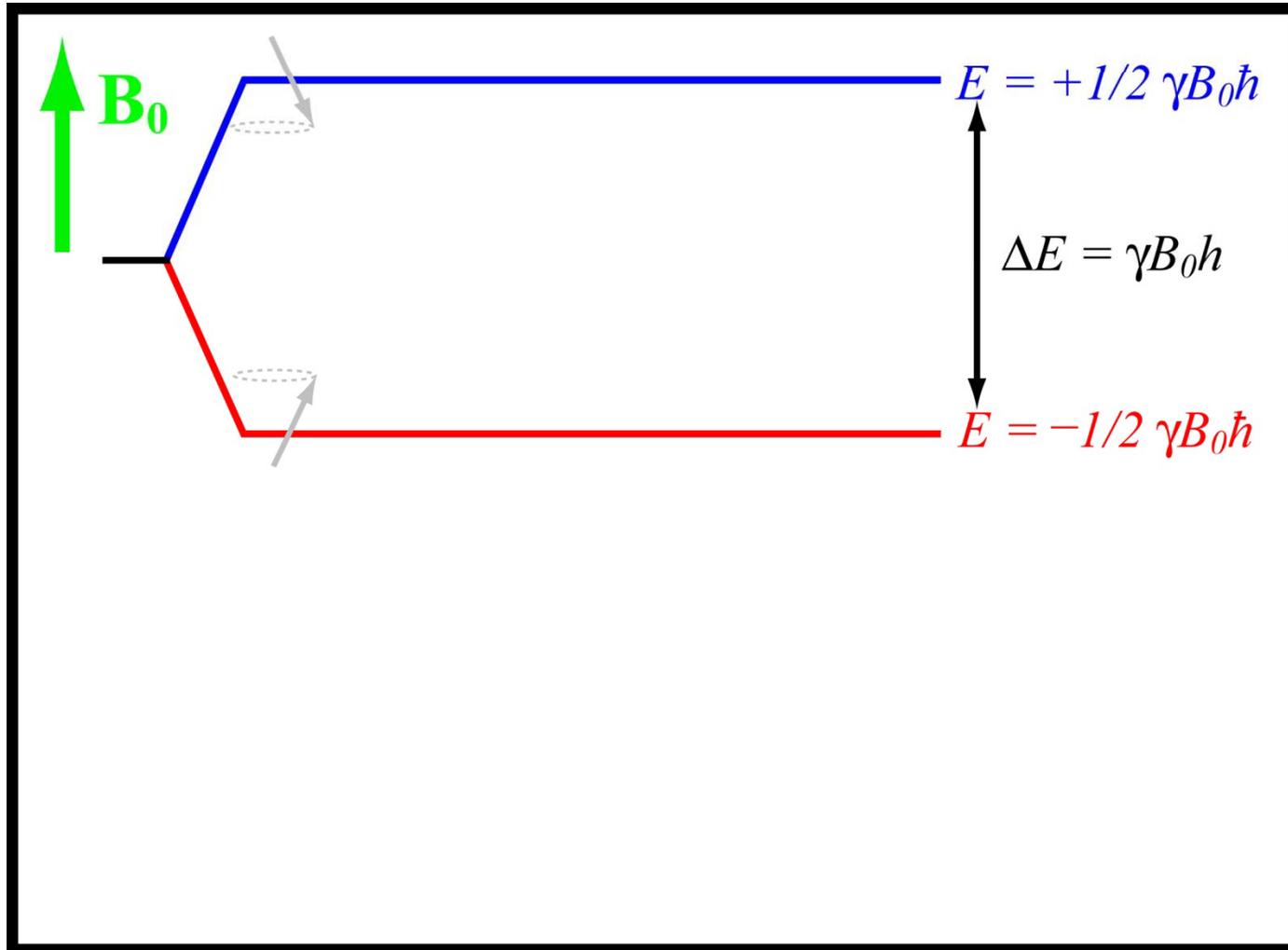
Estados de Spin ($I=1/2$)



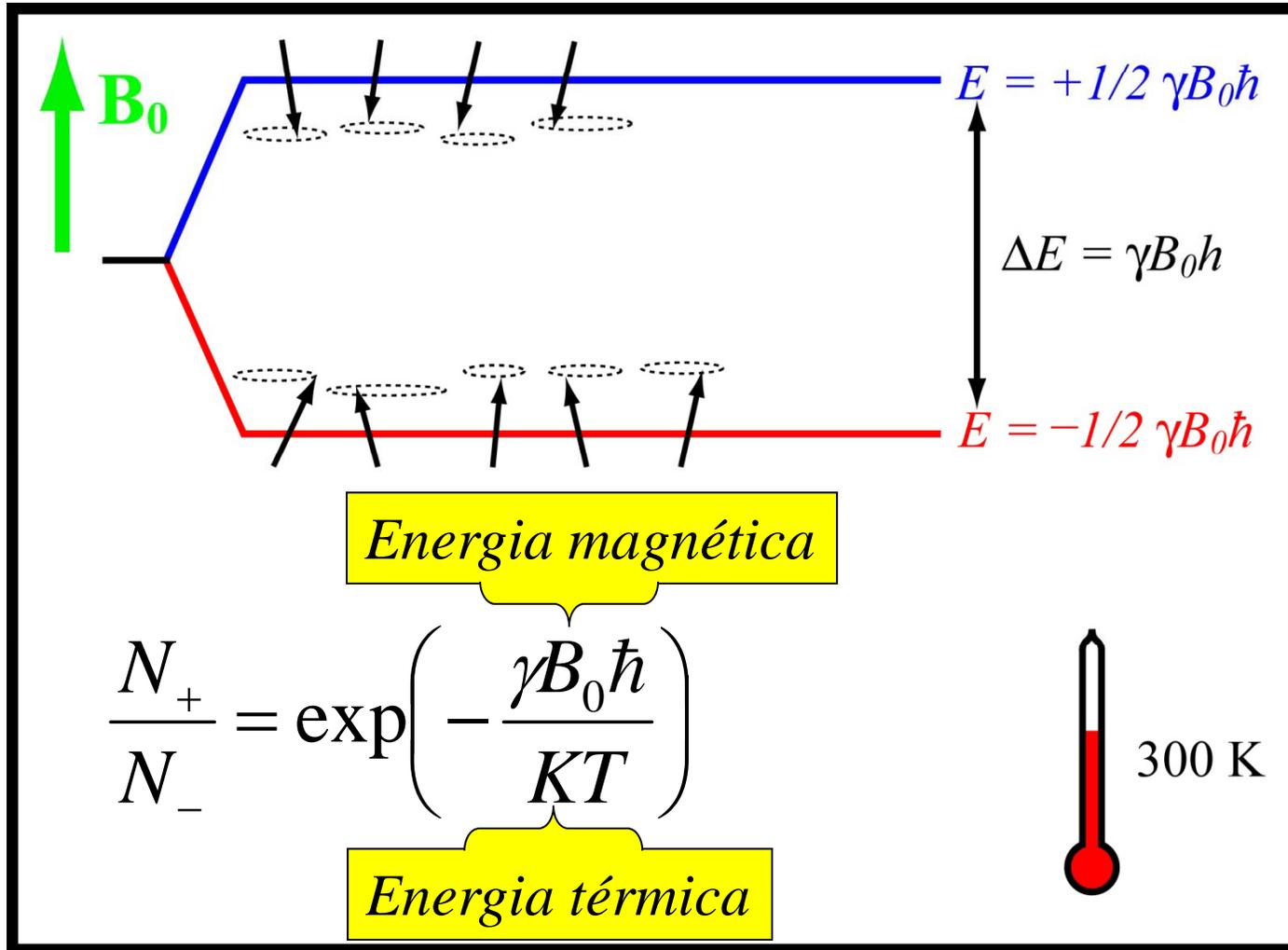
Estados de Spin ($I=1/2$)



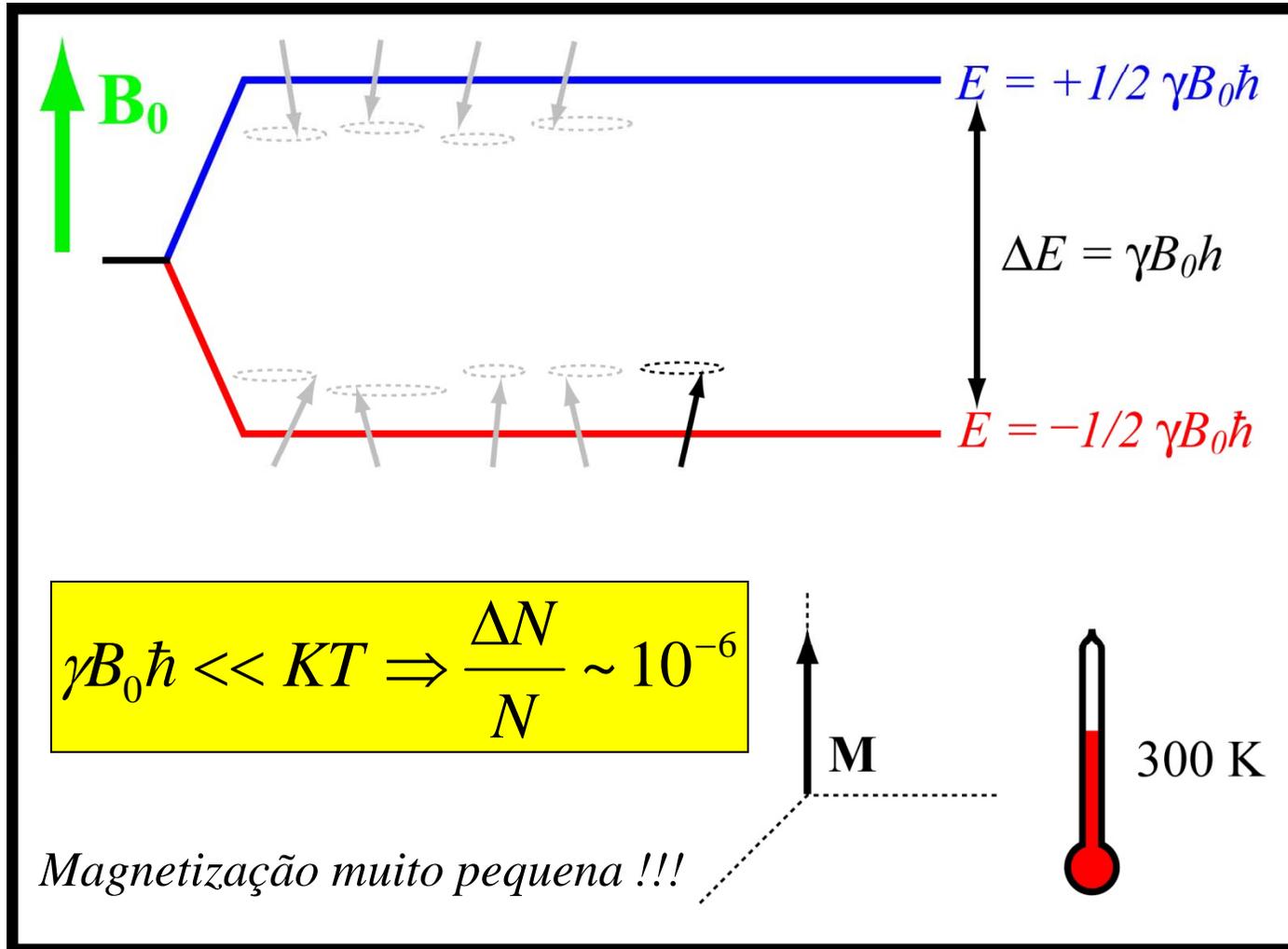
Estados de Spin ($I=1/2$)



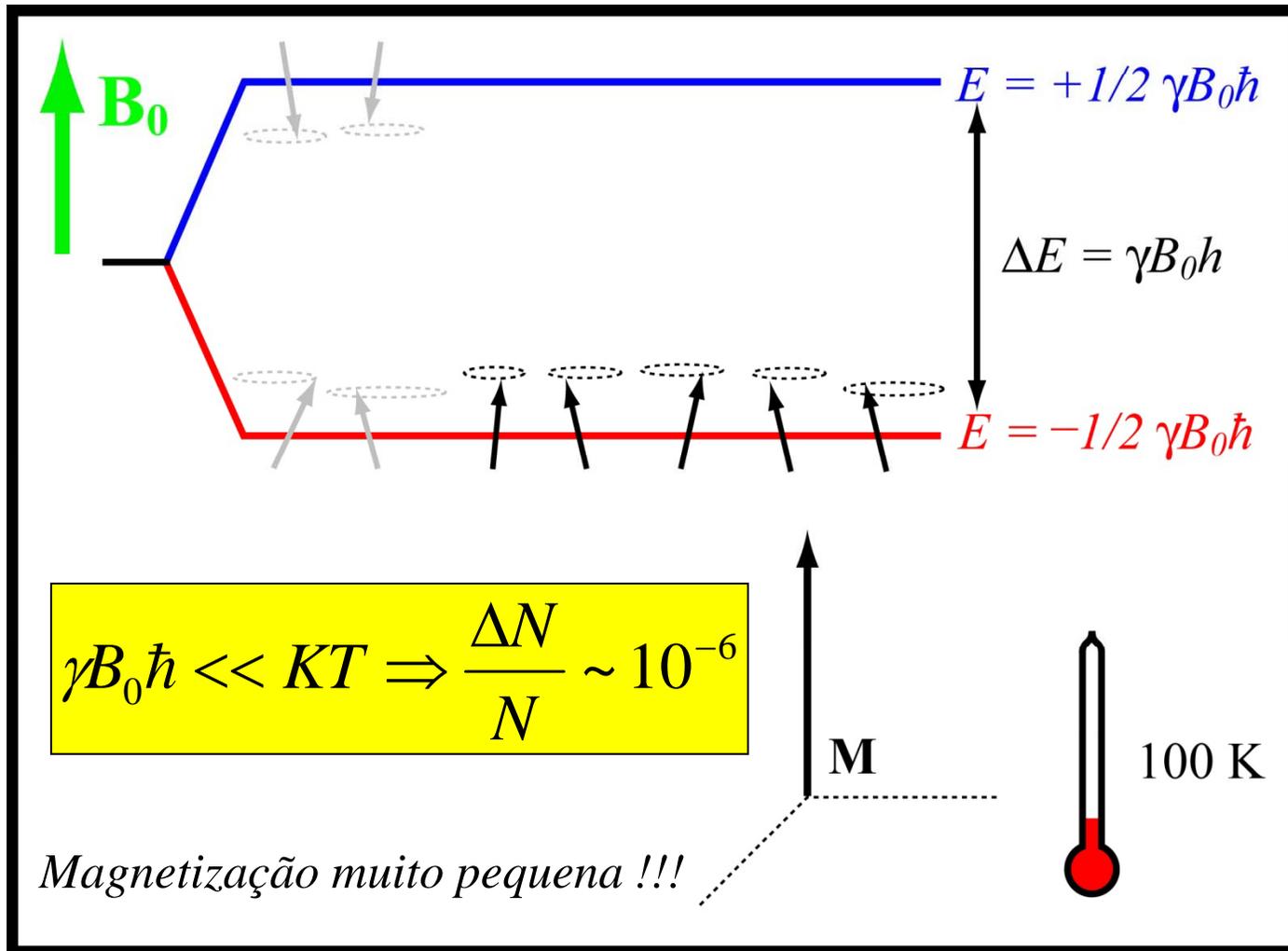
Equilíbrio Térmico ($I=1/2$)



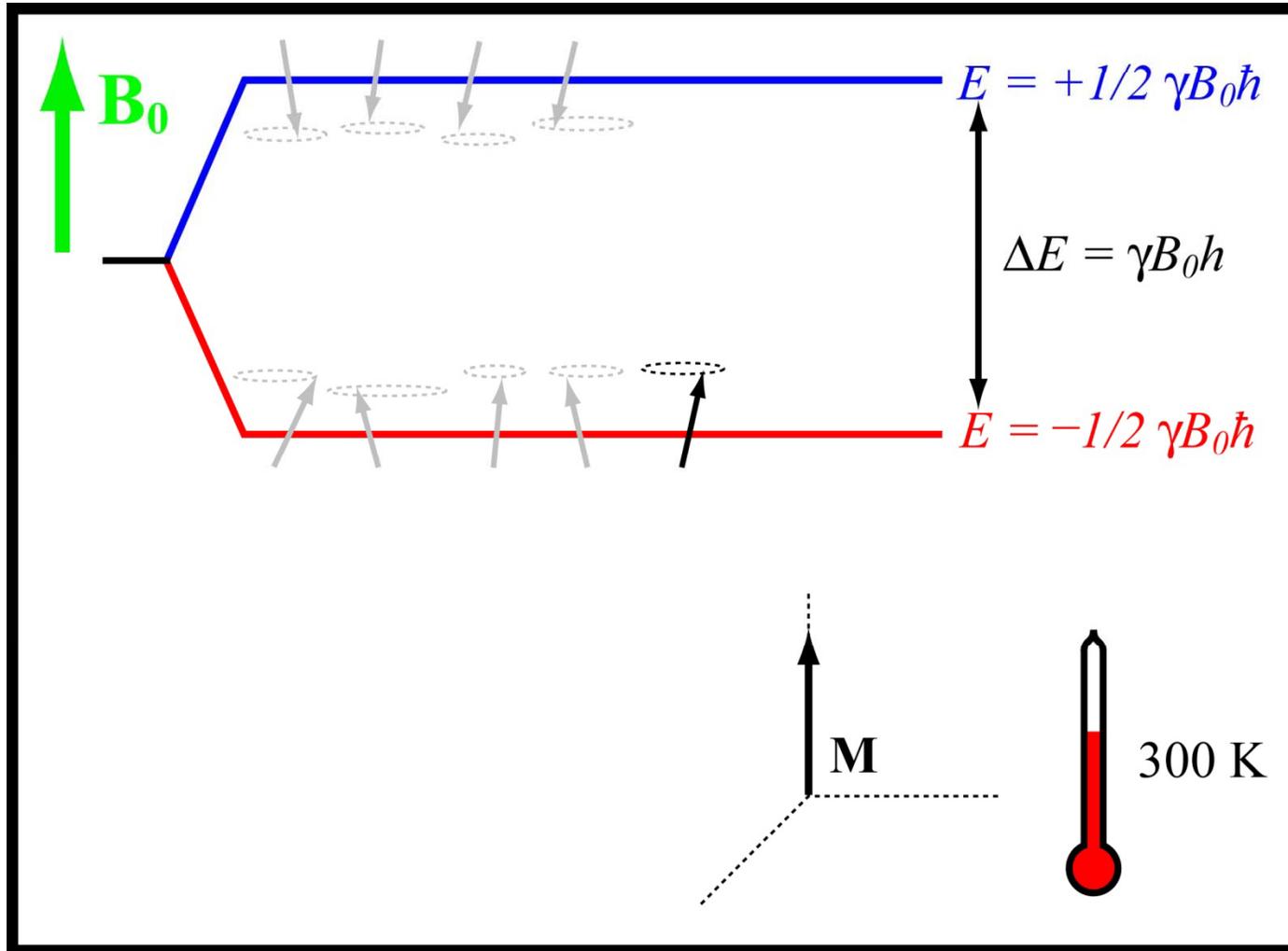
Equilíbrio Térmico ($I=1/2$)



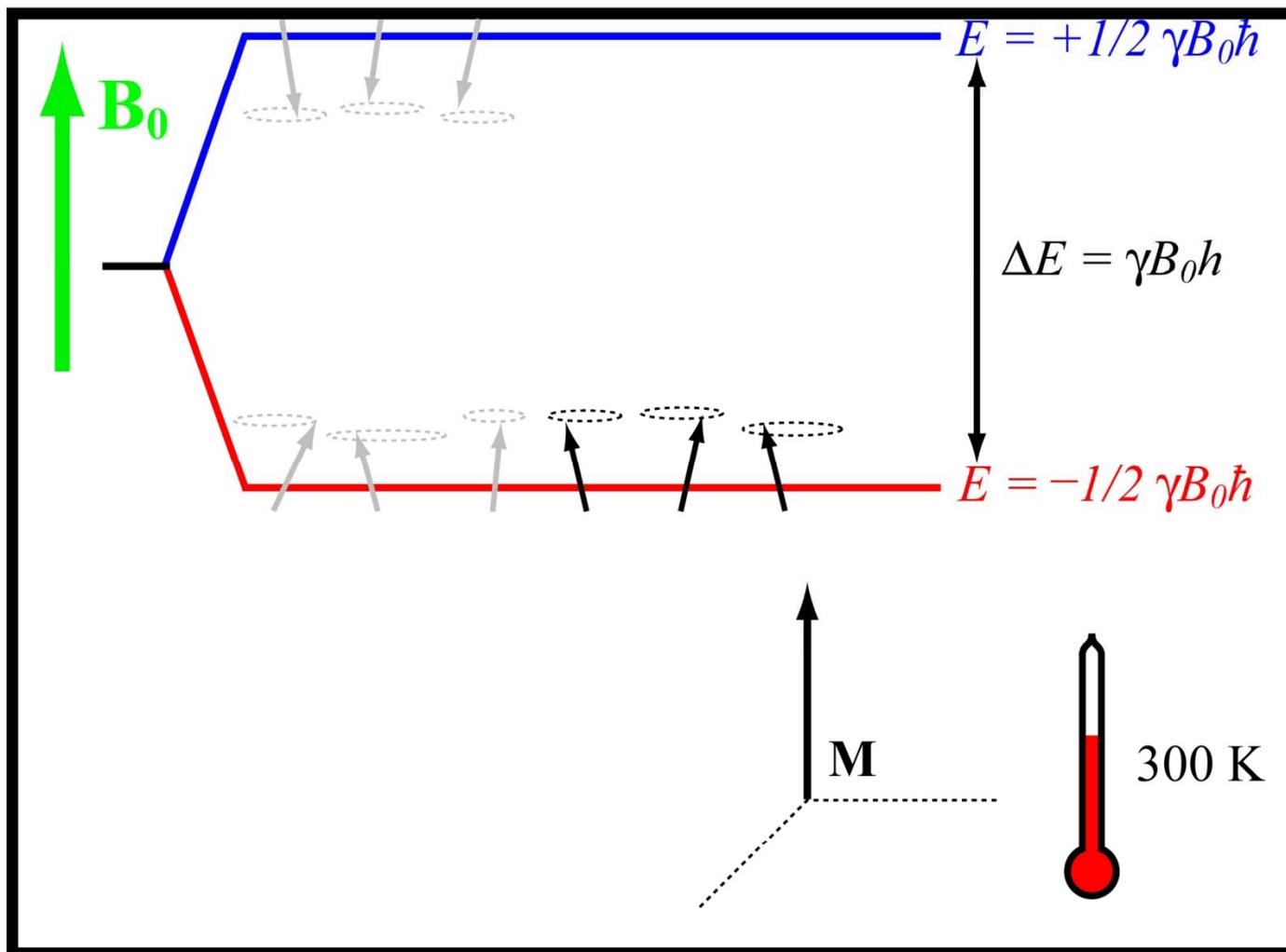
Equilíbrio Térmico ($I=1/2$)



Equilíbrio Térmico ($I=1/2$)



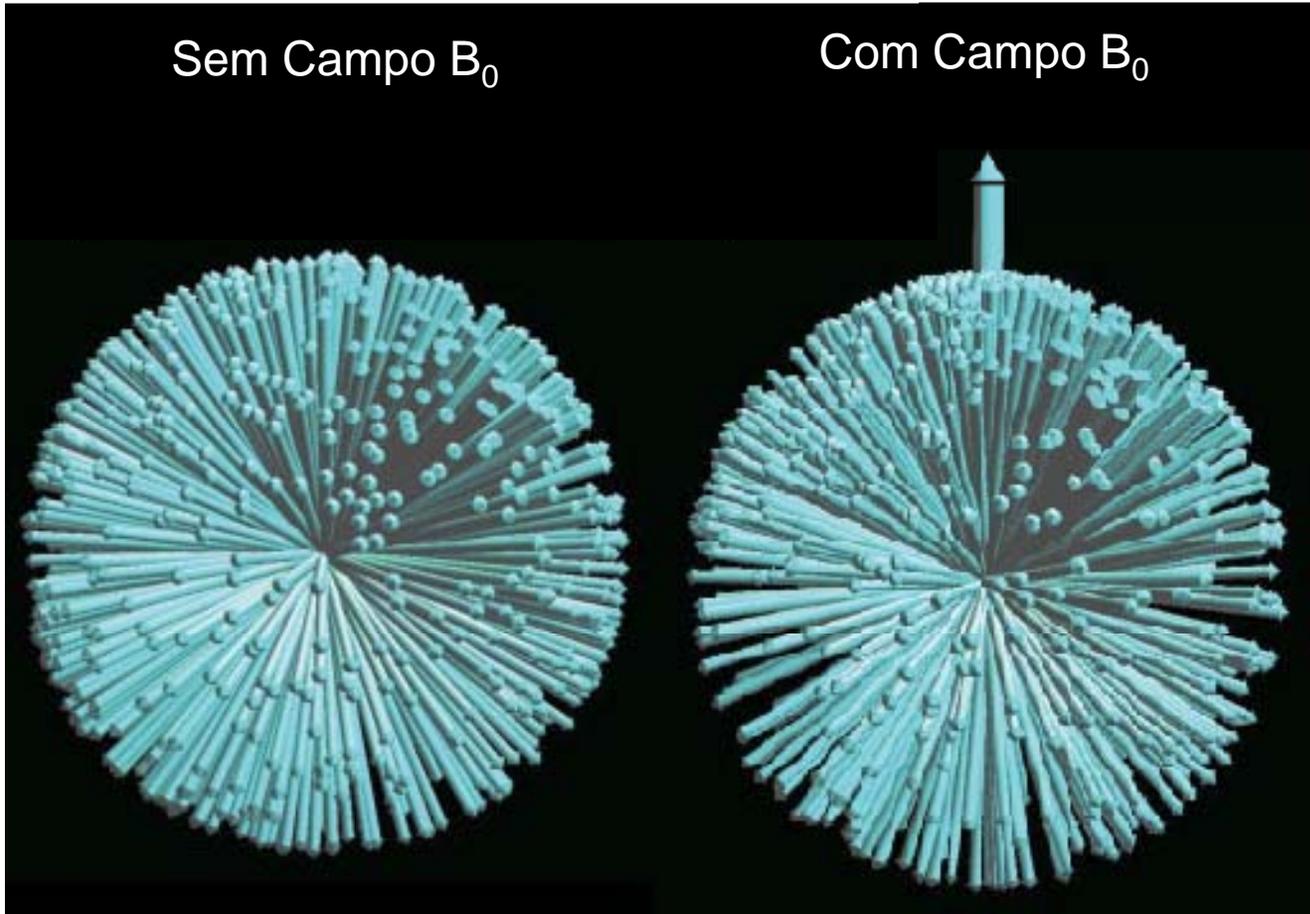
Equilíbrio Térmico ($I=1/2$)



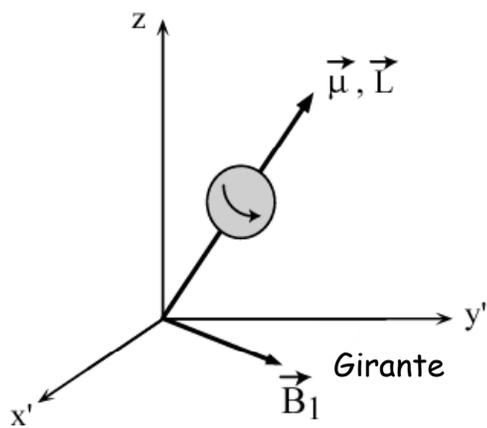
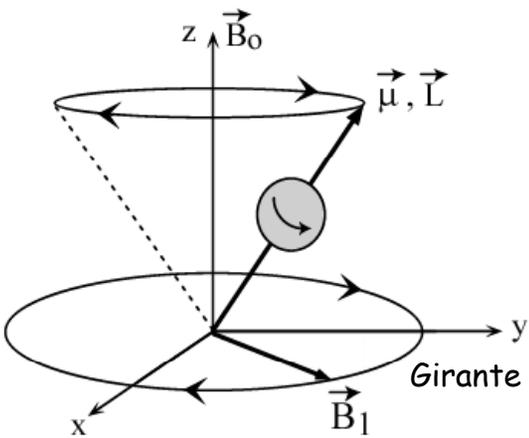
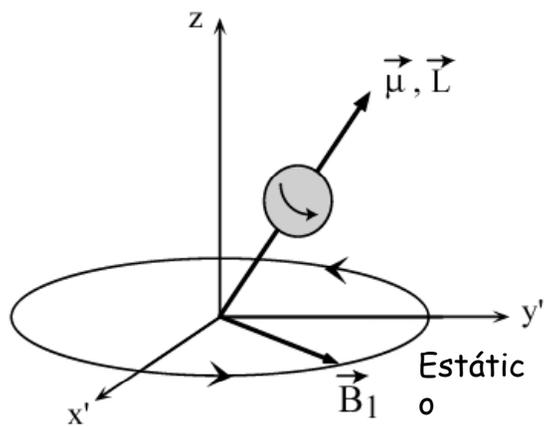
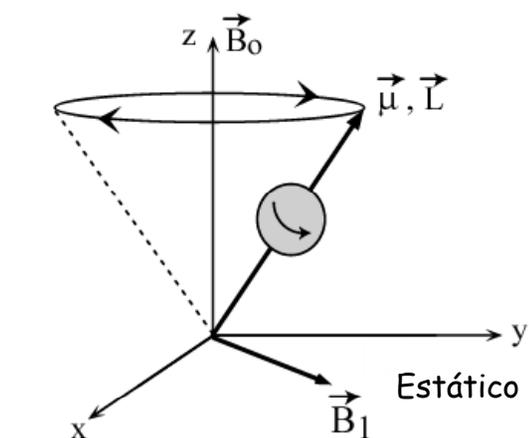
Equilíbrio Térmico – Visão Pictórica

Sem Campo B_0

Com Campo B_0



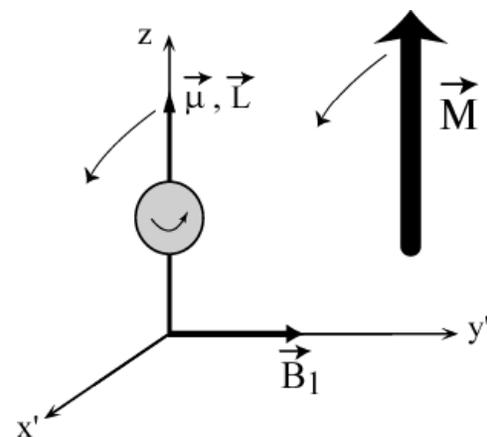
Excitação dos Momentos Magnéticos Nucleares



Ressonância Magnética Nuclear !

Movimento de Precessão do spin em torno de B_1 :

$$v_{\text{Larmor}} = v_L = \gamma B_1$$

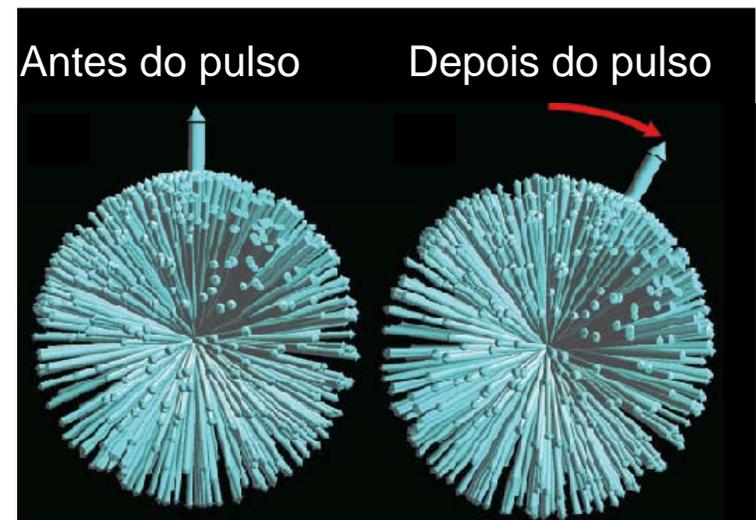
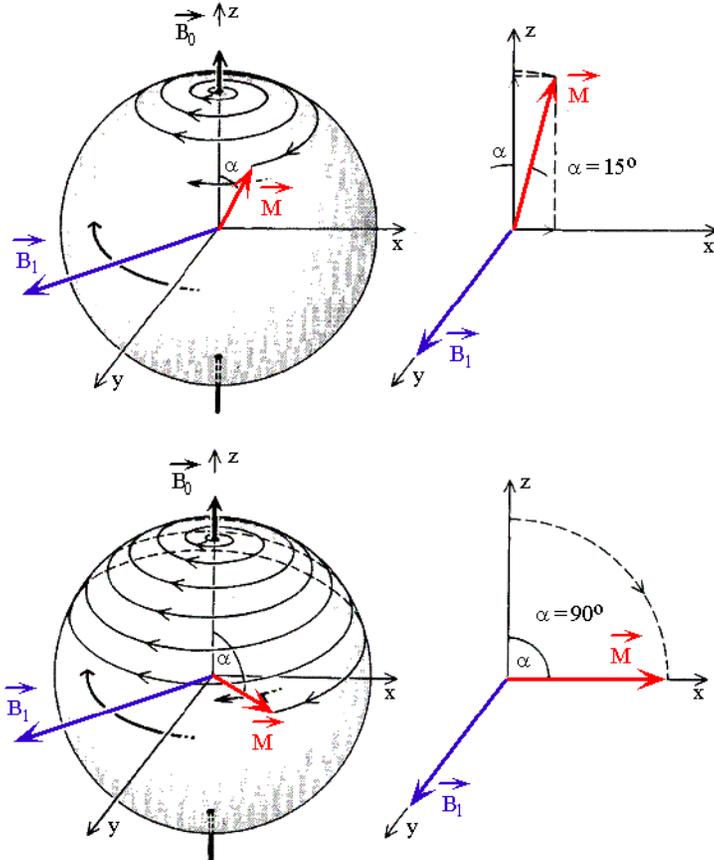


Excitação dos Momentos Magnéticos Nucleares

Visão Clássica

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

➤ Pulsos Radiofrequencia $\theta = -\gamma B_{rf}t$

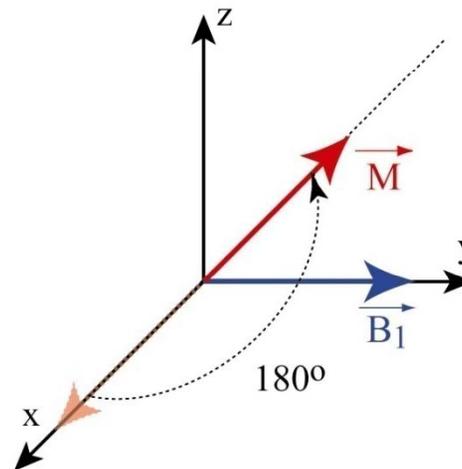
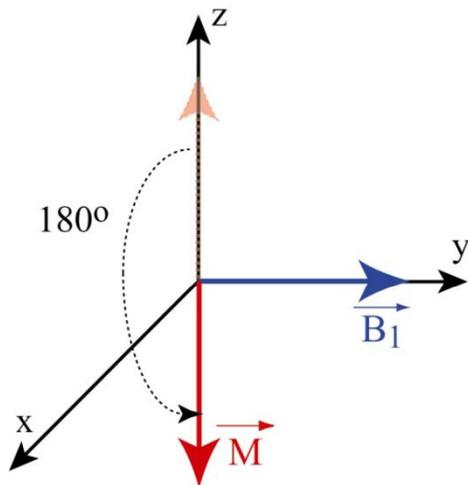
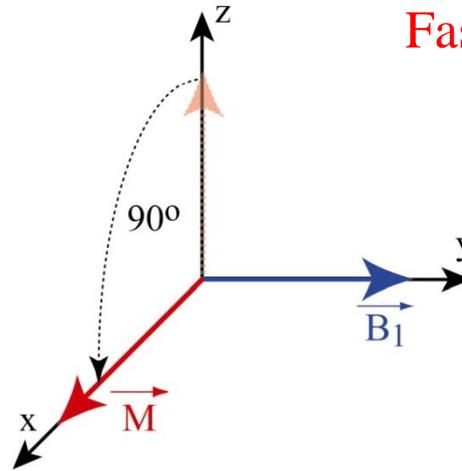
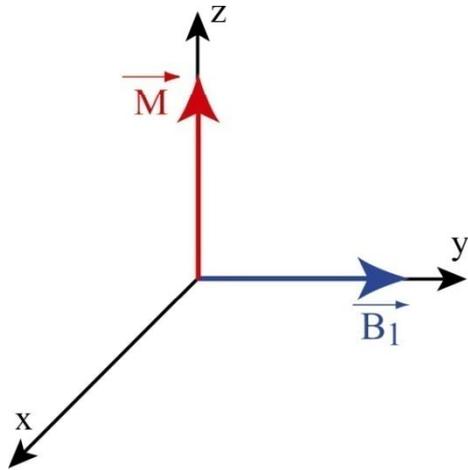


Ressonância: $\omega_{RF} = \omega_0 = \gamma B_0$

$$\alpha = \omega_1 t_p = \gamma B_1 t_p$$

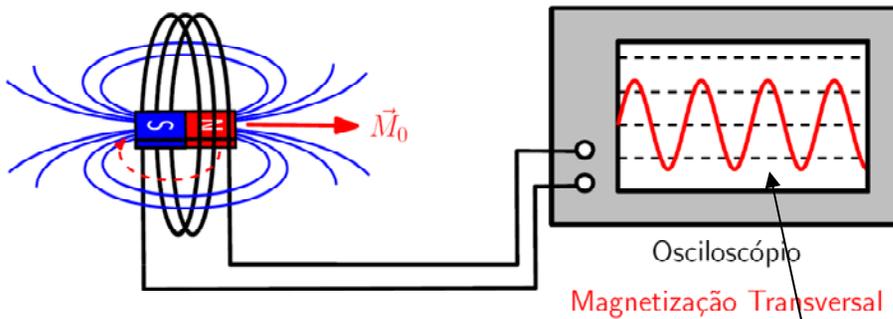
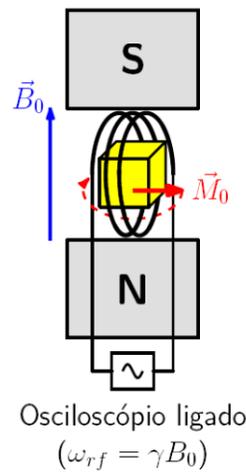
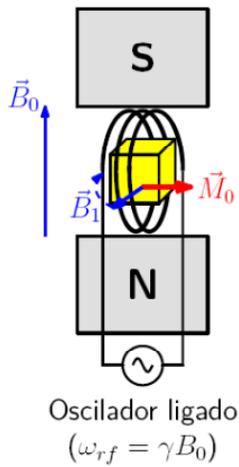
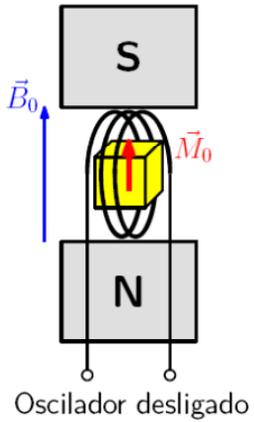
Ginástica com os Spins com pulsos de RF

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



Equilíbrio térmico

Pulso de $\pi/2$ Força eletromotriz induzida

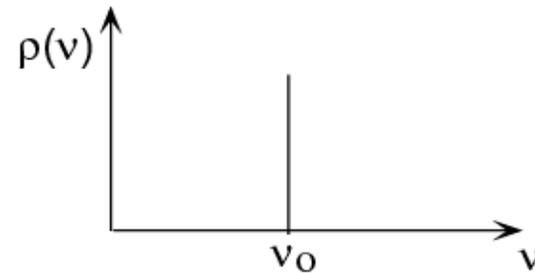


$$\varepsilon = - \frac{d\Phi_B}{dt}$$

$$\omega_0 = \gamma B_0$$

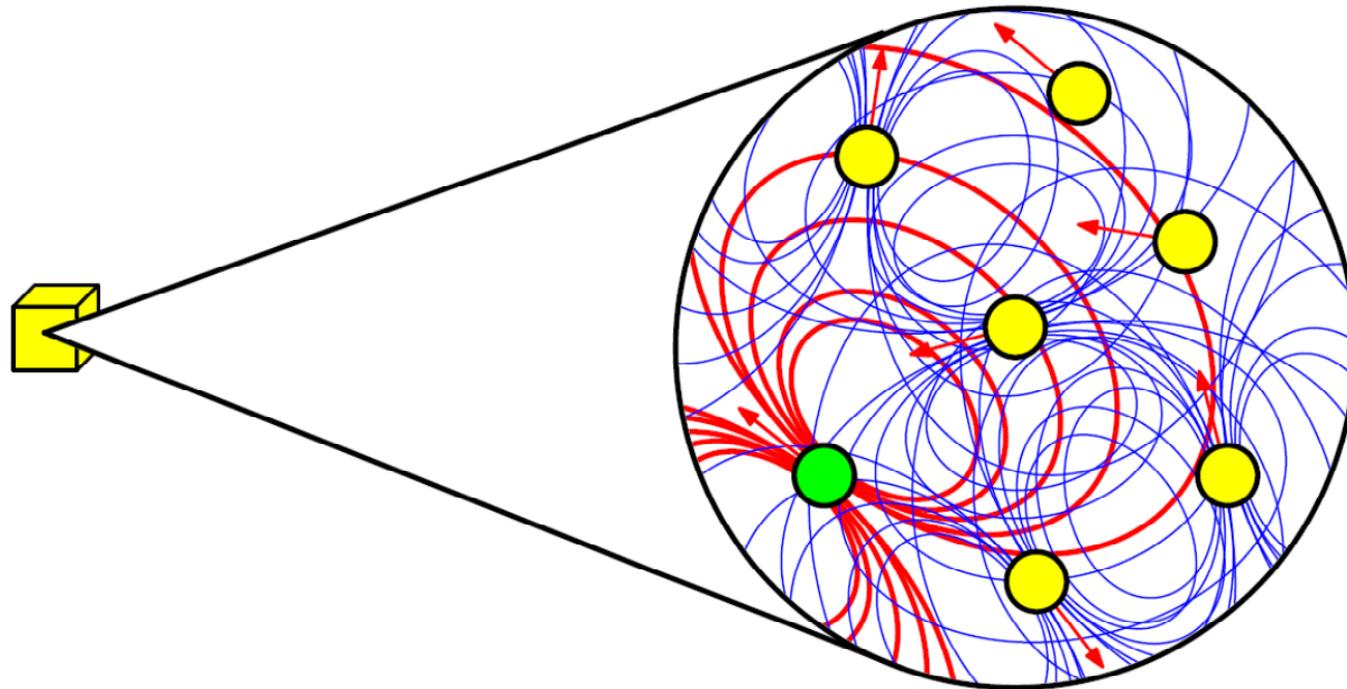
➤ Processamento

$$\nu_0 = \frac{\omega_0}{2\pi} = \frac{\gamma B_0}{2\pi}$$



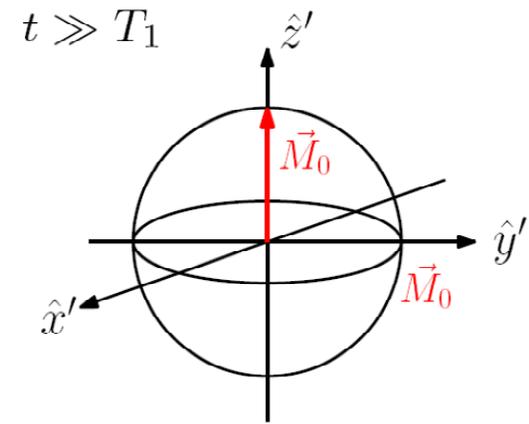
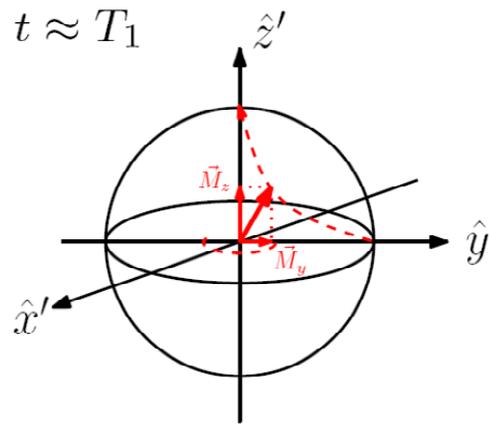
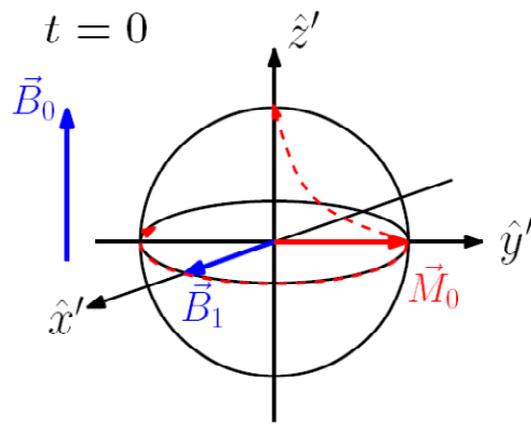
Amplitude ~ densidade de núcleos

Spins nucleares não estão isolados



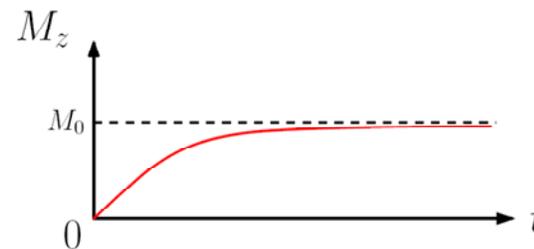
Interagem magnética e eletricamente com outros núcleos e o ambiente.

Se fora do equilíbrio a magnetização tende a retornar ao seu estado de equilíbrio



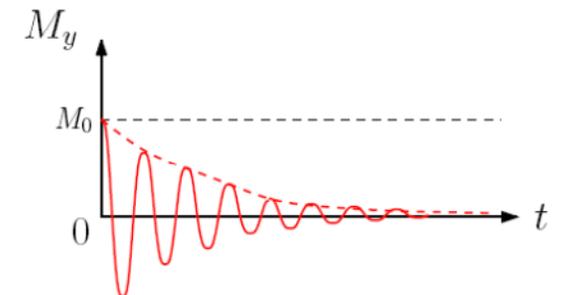
Relaxação Longitudinal

$$M_z(t) = M_0 \left(1 - e^{-\frac{t}{T_1}} \right)$$



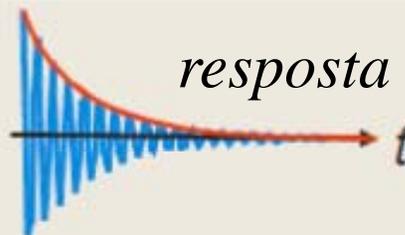
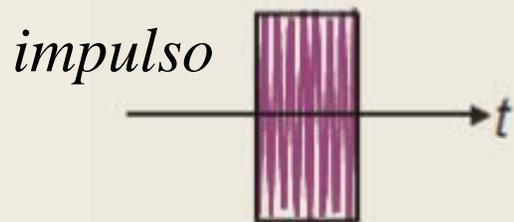
Relaxação Transversal

$$M_y(t) = M_0 e^{-\frac{t}{T_2}}$$



Tempos de relaxação dependem do ambiente magnético a que os spins nucleares estão submetidos. São particularmente sensíveis a flutuações dos campos magnéticos nos sítios nucleares.

Em Resumo: RMN é um forma de telecomunicação com os spins no campo magnético



- frequência de ressonância dos núcleos atômicos
- amplitudes (qtde de núcleos de um dado tipo).
- tempos de relaxação



$\omega_0 = \gamma |B_0|$
Freq. de ressonância
 $\omega_0 = 2\pi \nu_0$



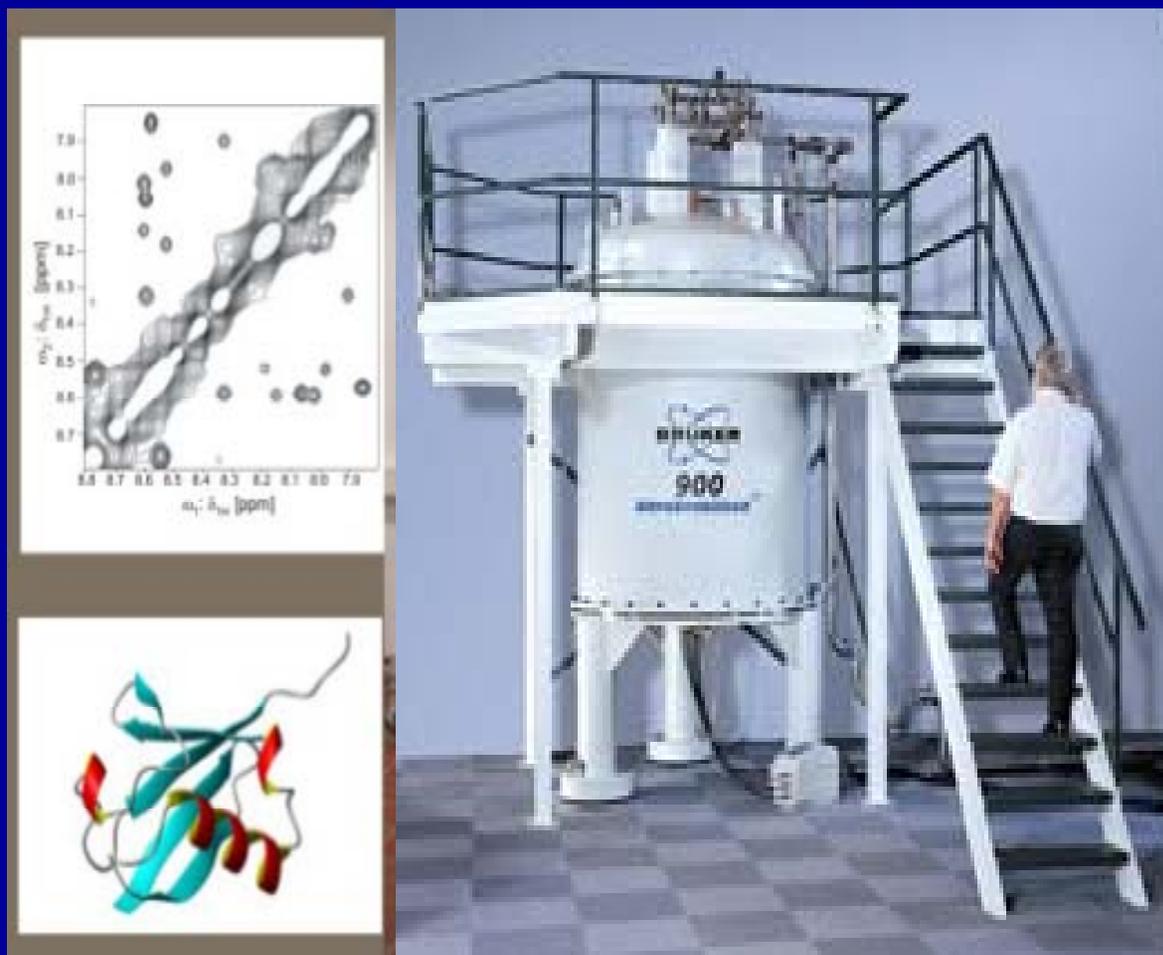
atomic nuclei
Núcleo atômico no campo B_0



10^{23} magnetos nucleares dão origem a magnetização total observada em RMN

Espectrômetro de RMN

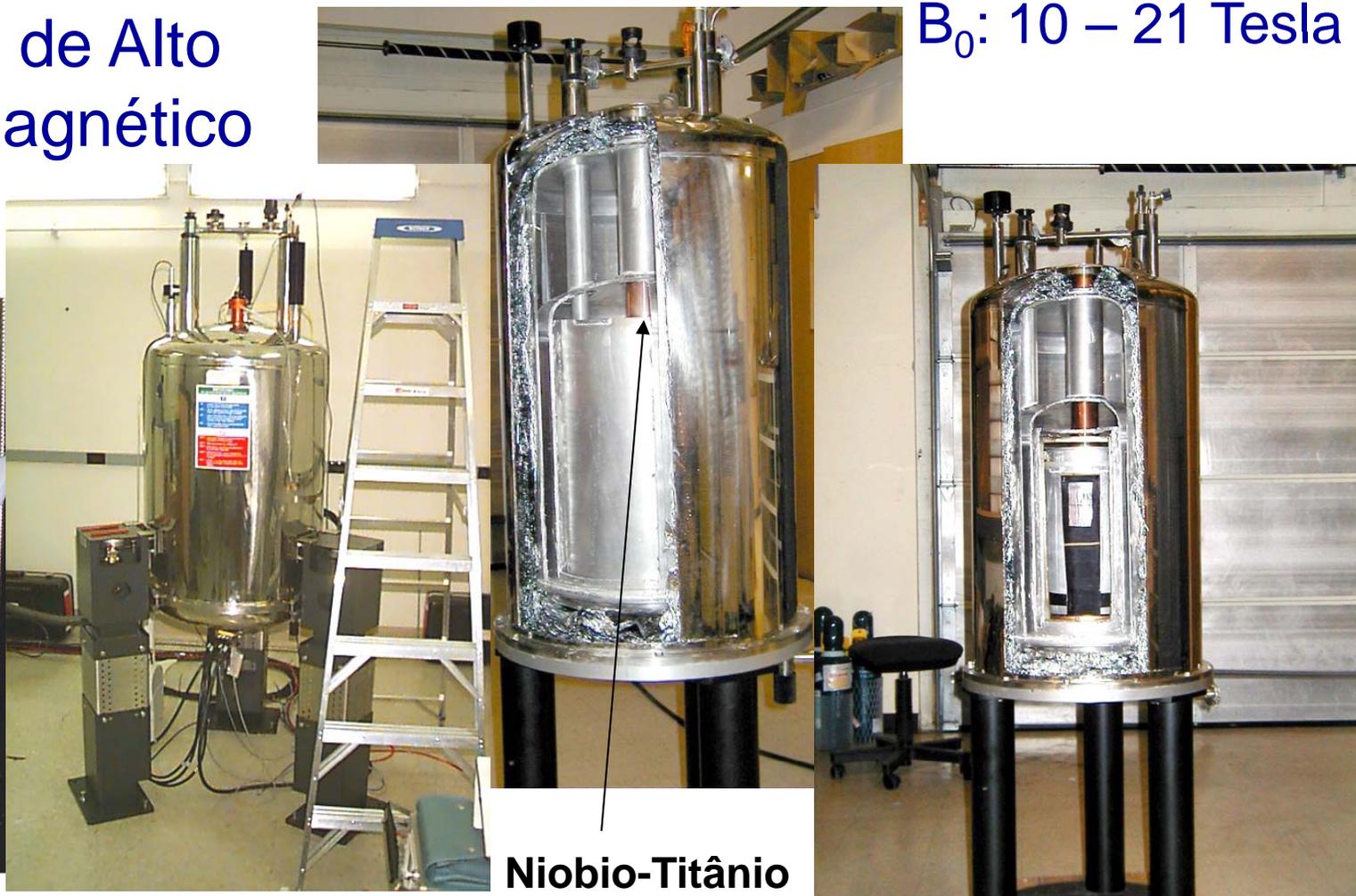
Espectroscopia por RMN



Alguns Tipos de Equipamentos de RMN

Sistemas de Alto
Campo Magnético

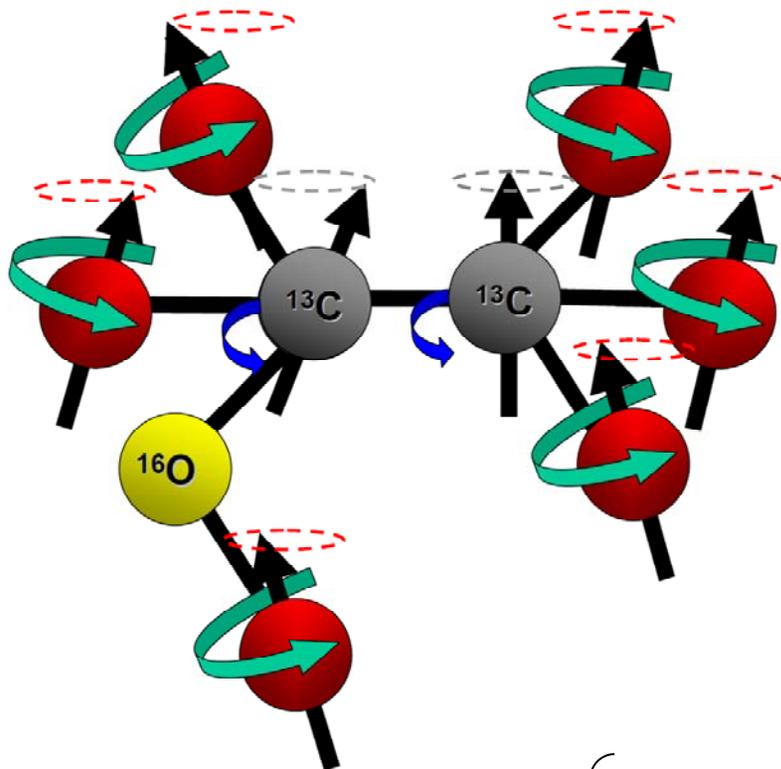
B_0 : 10 – 21 Tesla



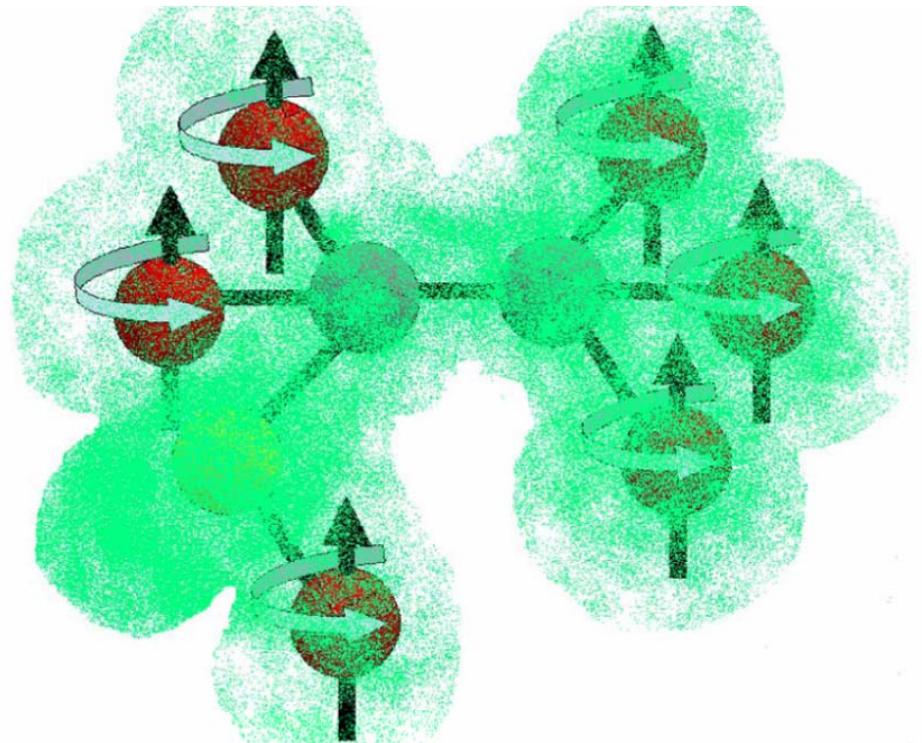
Niobio-Titânio



Até agora...



Mas de fato...

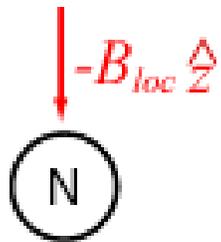
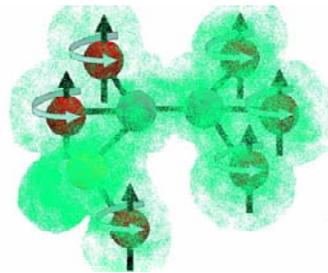


Freqüência de RMN
do núcleo

- Campos induzido por correntes eletrônicas
- Campos dipolares via nuvem eletrônicas
- Campos dipolares vi espaço
- Gradientes de campo elétrico locais ($I > \frac{1}{2}$)

Deslocamento Químico: Nada mais é que uma consequência da lei de Faraday-Lenz

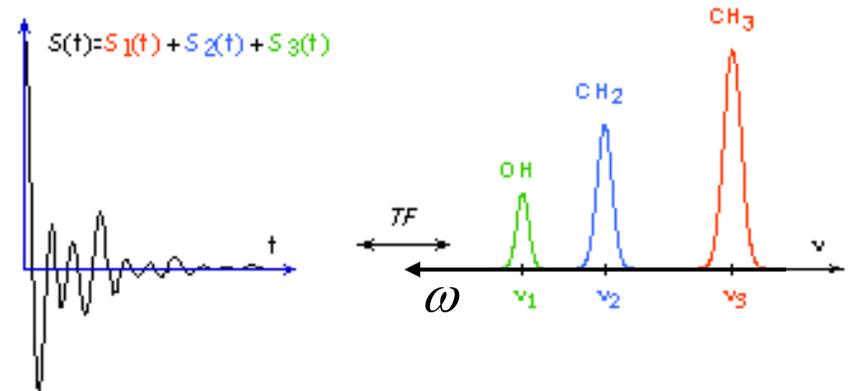
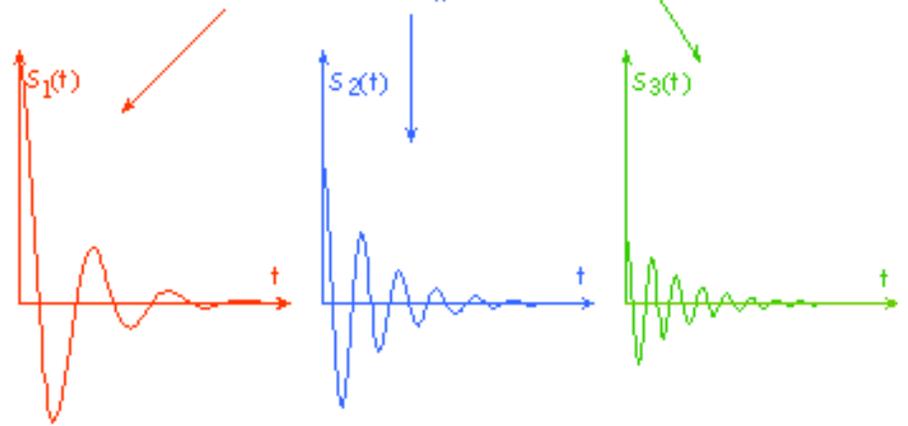
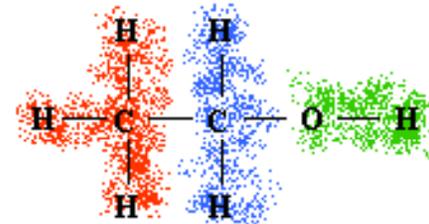
$$\vec{B}^i_{ind} = -\sigma_i \vec{B}$$



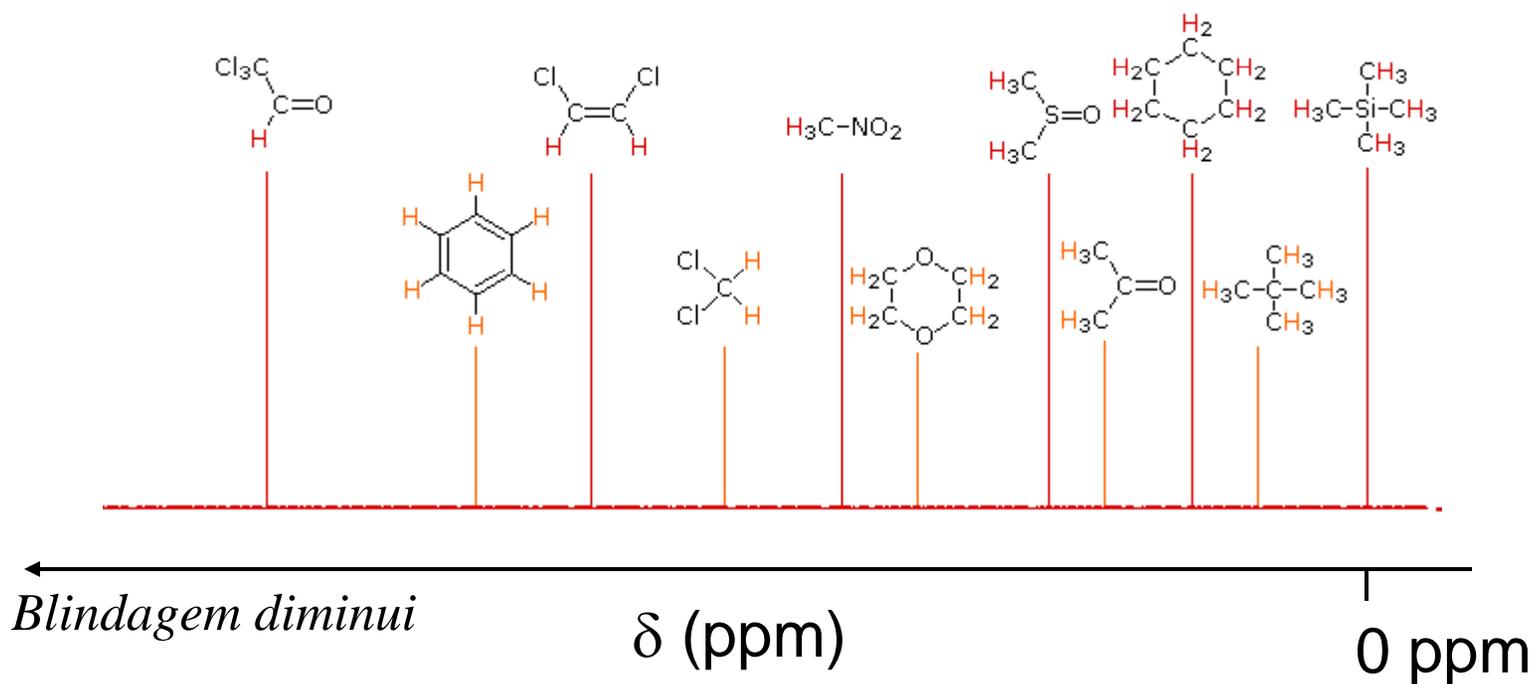
$$\vec{B}^i_{loc} = \vec{B}^i_{ind} + \vec{B}$$

$$\omega_i = \gamma (B_0 - \sigma_i B_0)$$

Impressão digital do grupo químico

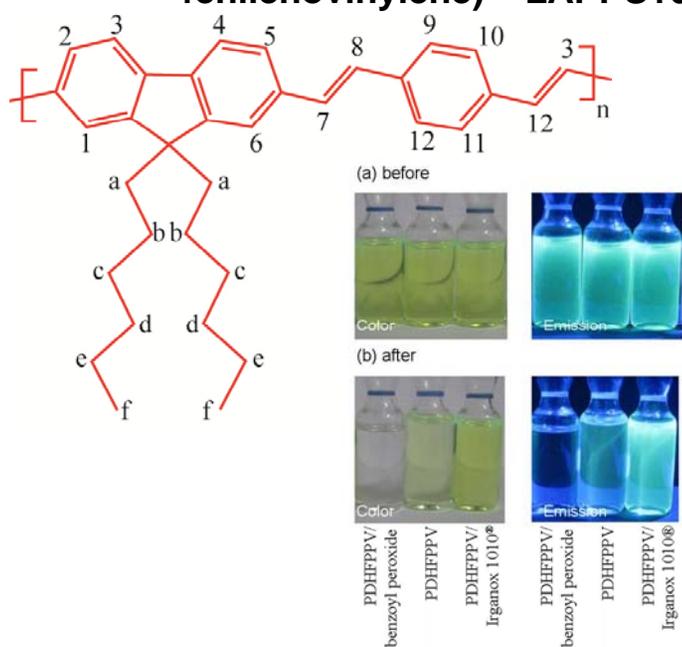


Deslocamento Químico



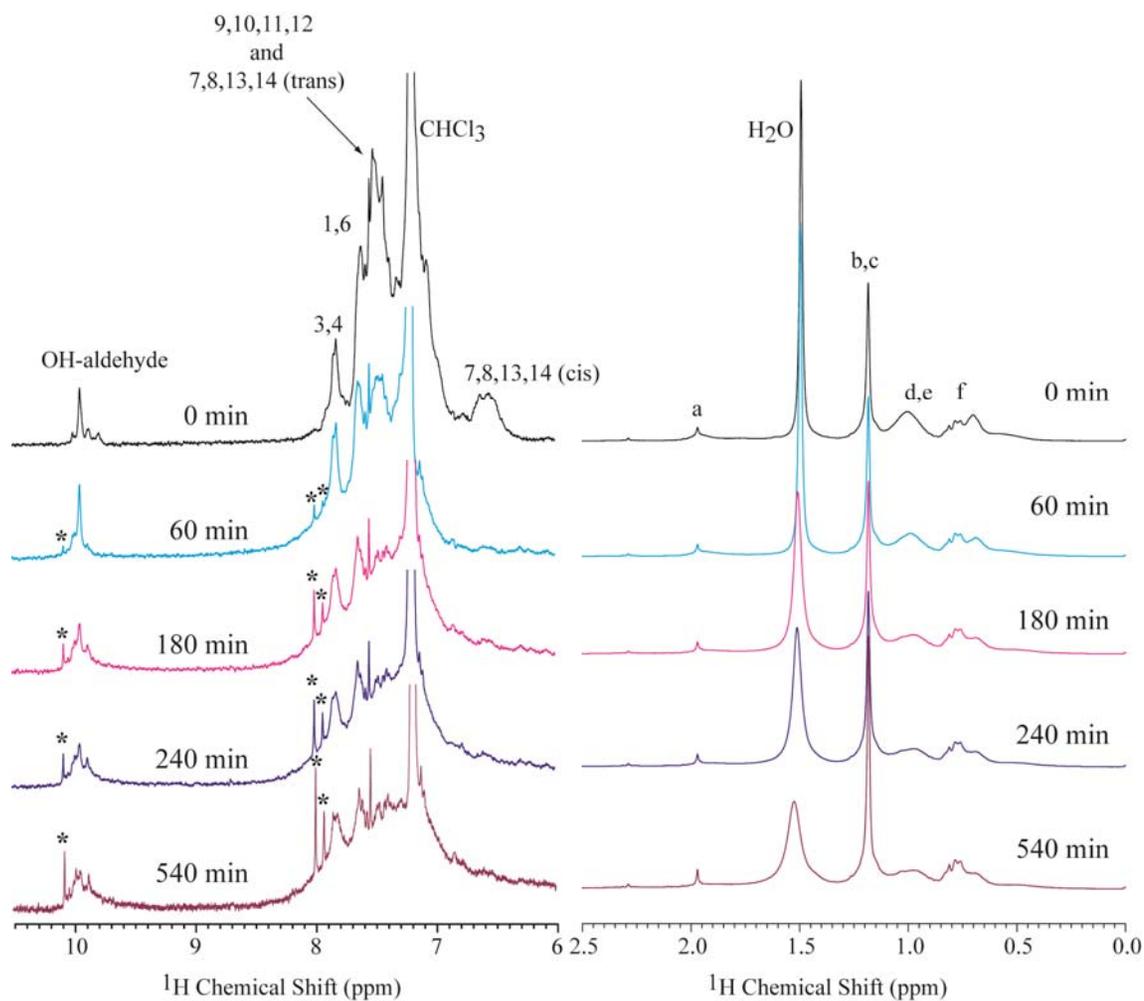
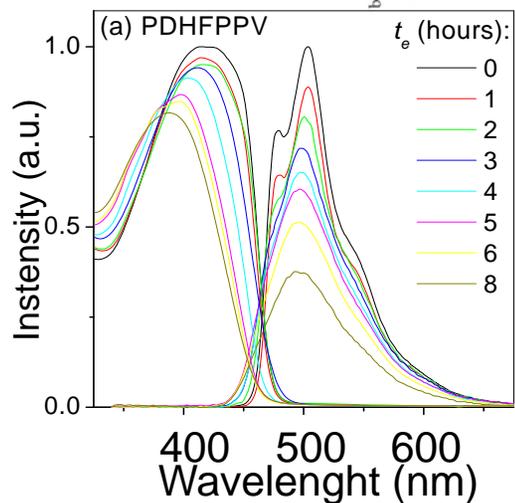
Modificações Químicas

poly(9,9-di-hexylfluorenydiilvinylene-alt-1,4-fenilenovinylene) – LAPPS16



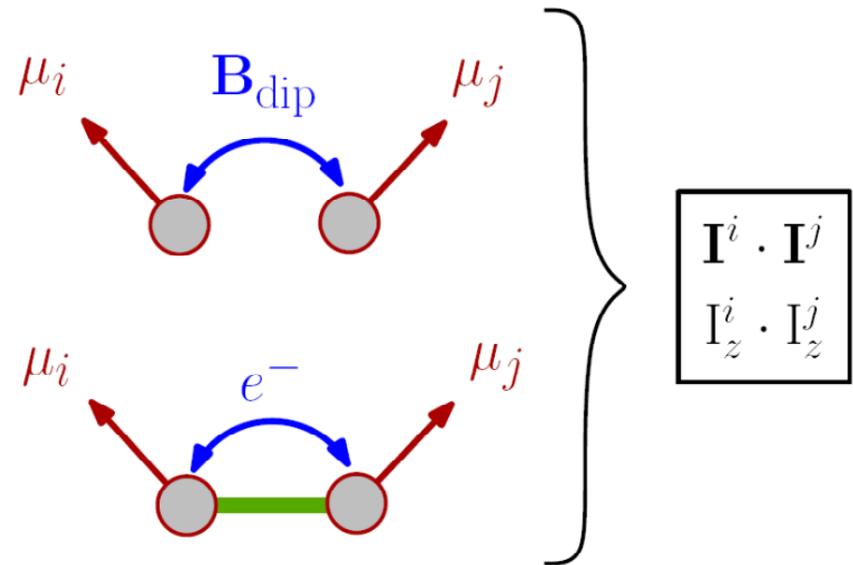
Degradação de Polímeros

G. R. Ferreira, B. Novack, E. R. deAzevedo, L. C. Akcelrud, R. F. Bianchi



Outras interações

Interação de dipolar
(Via espaço – proximidade espacial)



Interação de dipolar indireta
(Via ligação química – grupos ligados e orientação das ligações)

RMN Multidimensional: Informação além do espectro 1D



Excitação dos spins

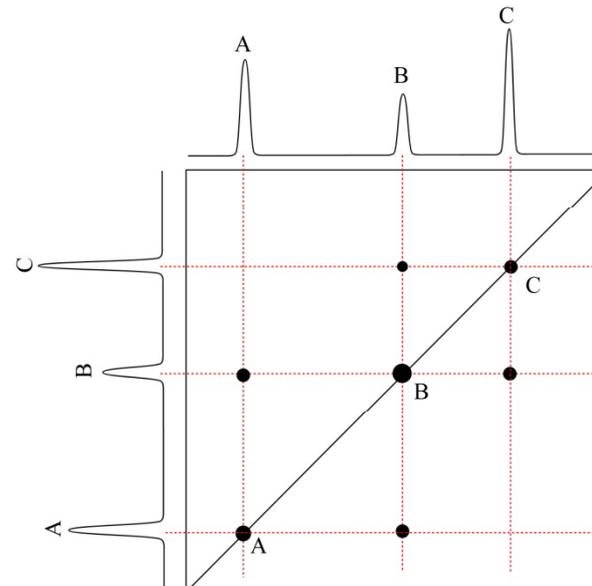
Evolução sob a ação de uma dada interação em t_1

Modulação da magnetização a ser detectada em t_2 pela evolução em t_1

Detecção da magnetização de um dado tipo de núcleo durante um tempo t_2

$$S(t_1, t_2) \xrightarrow{FT-2D} S(\omega_1, \omega_2)$$

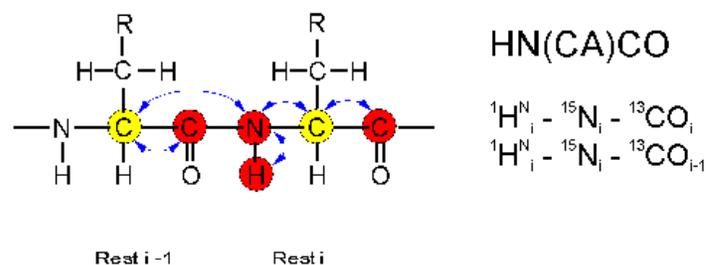
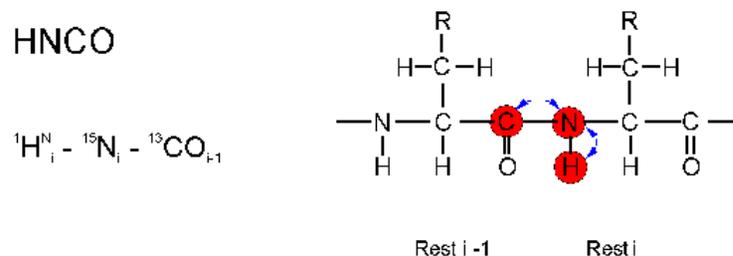
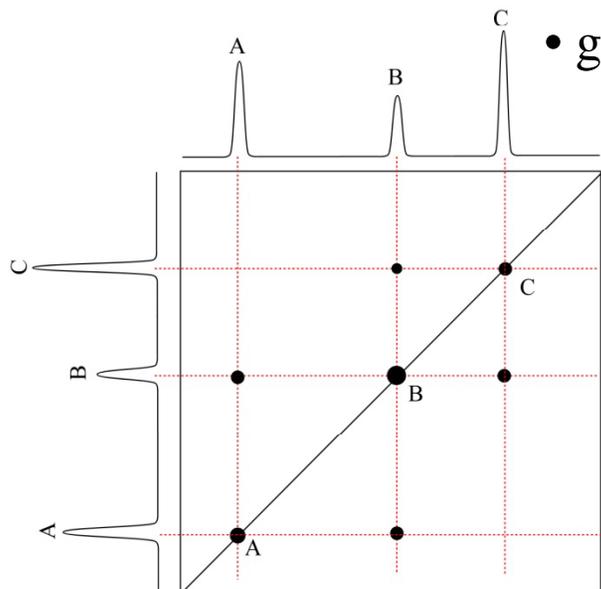
Correlações dependem do tipo de interação e codificação



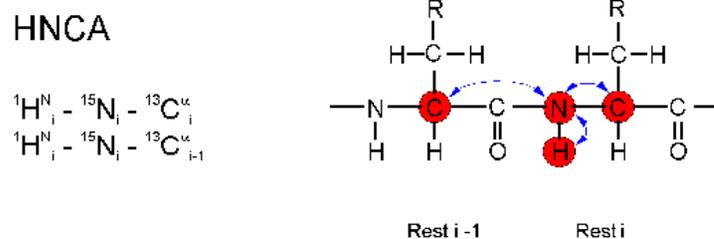
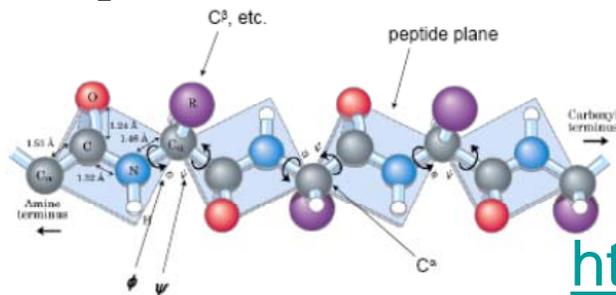
Ex: RMN de Solução

Correlação via interação dipolar indireta (acoplamento J) :

- grupos ligados quimicamente (até quatro ligações)

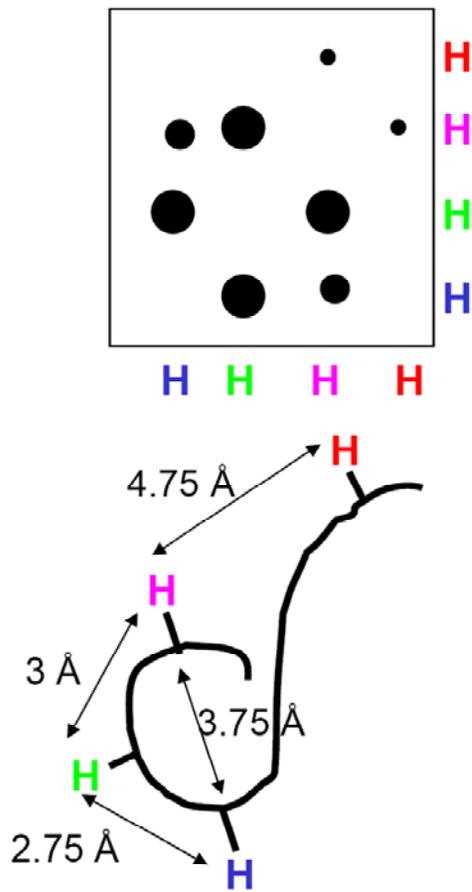


- determinação de constantes de acoplamento J

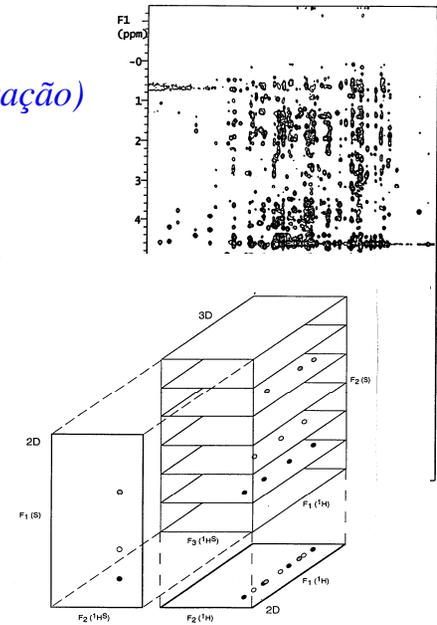
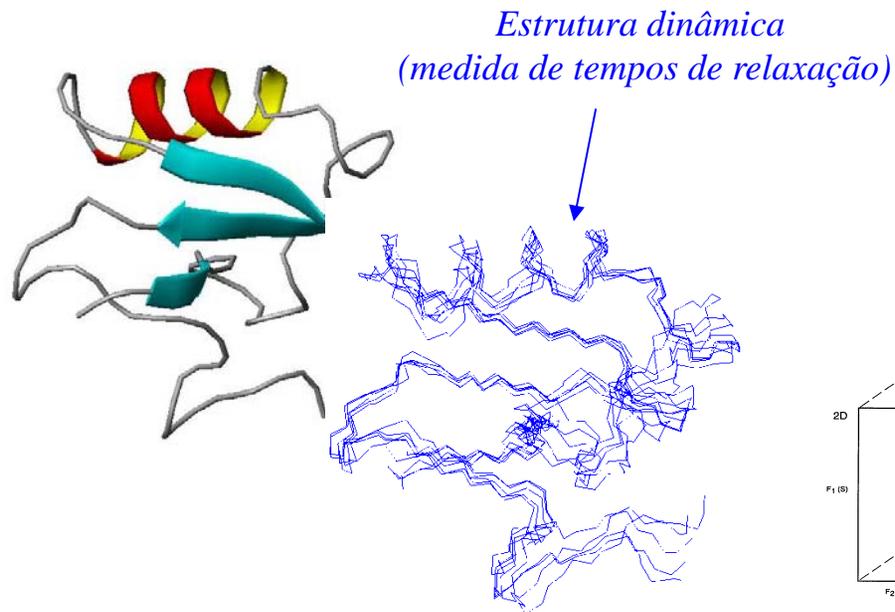


<http://www.protein-nmr.org.uk/spectra.html>

Correlação via interação dipolar (NOE - Nuclear Overhauser effect) :



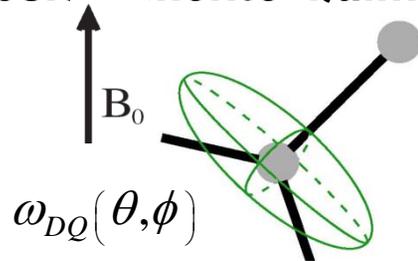
- grupos espacialmente próximos $d < 5 \text{ \AA}$.
- Isso, e muitos outros procedimentos e experimento podem levar a:



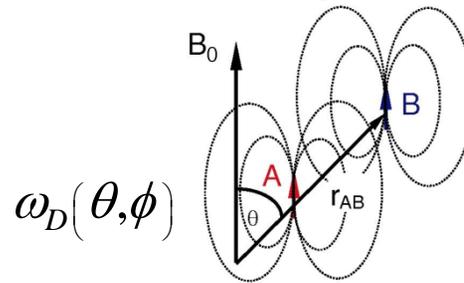
RMN de Sólidos

$$\omega(\theta, \phi) = \omega_{iso} + \omega_{aniso}(\theta, \phi) = \omega_{iso} + \frac{\delta}{2} (3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos(2\phi))$$

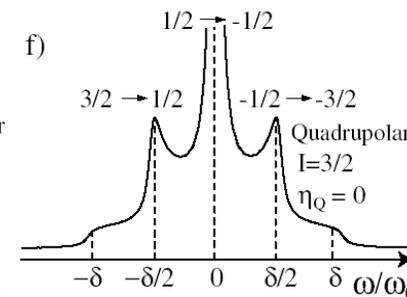
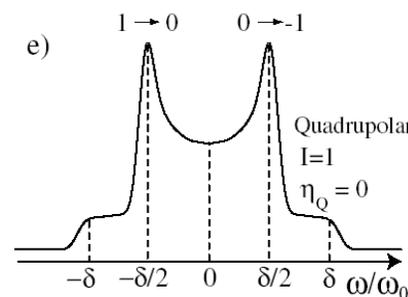
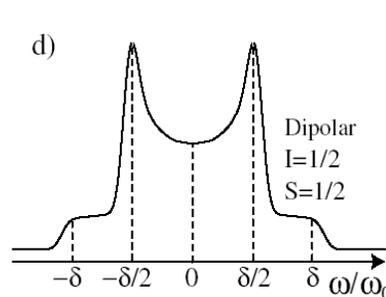
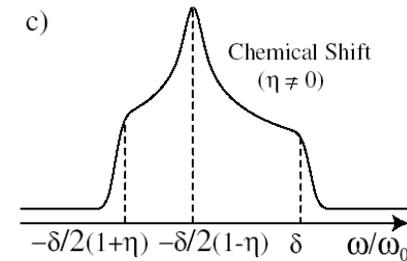
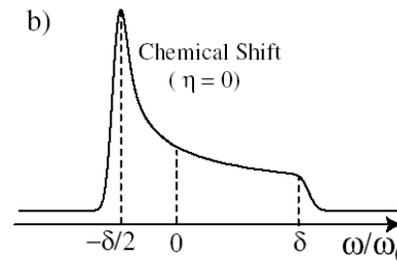
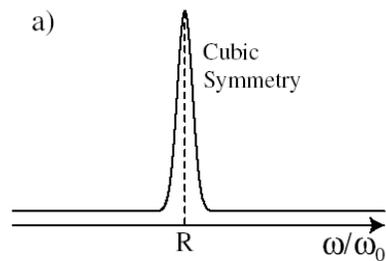
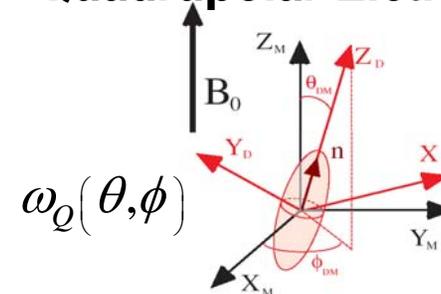
Deslocamento Químico



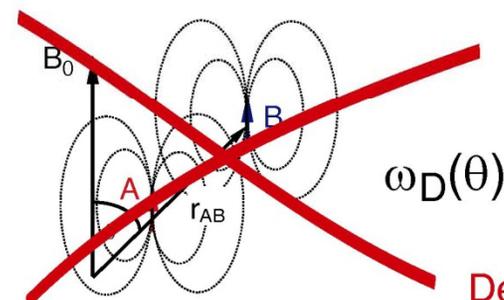
Dipolar Magnética



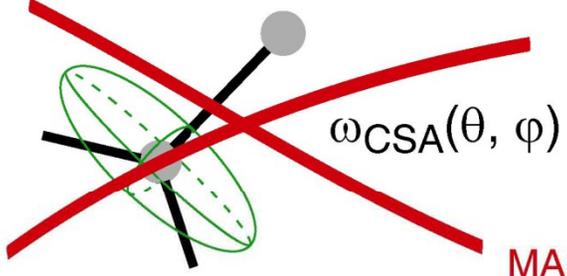
Quadrupolar Elétrica



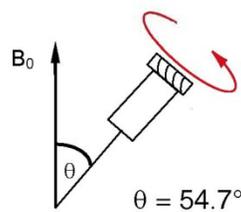
Espectroscopia de alta resolução em Sólidos



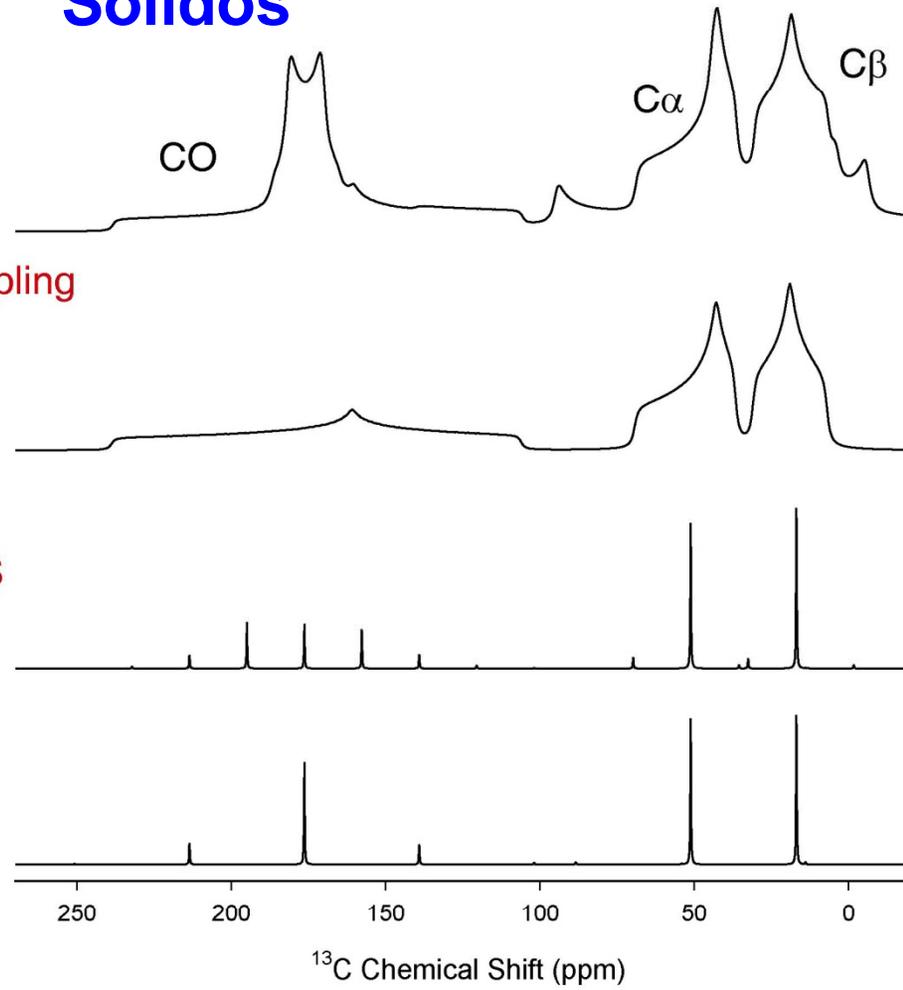
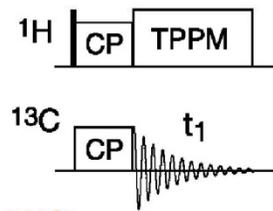
Decoupling



MAS

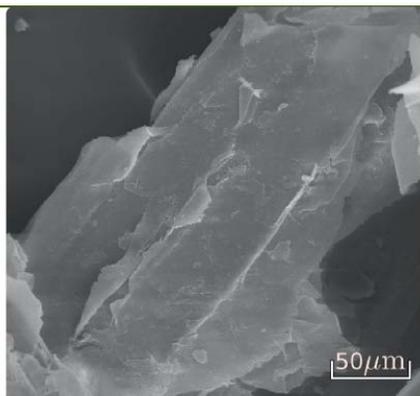


Magic Angle Spinning (MAS)

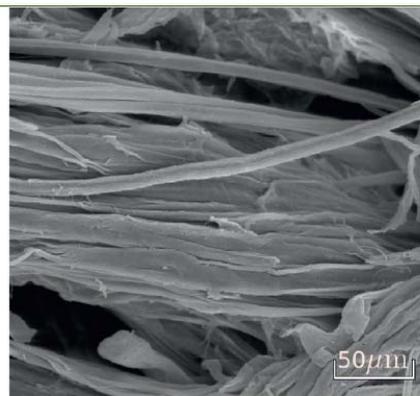




**Biotechnology
for Biofuels**



Untreated bagasse



Bagasse treated with
 H_2SO_4 1% + NaOH 2%

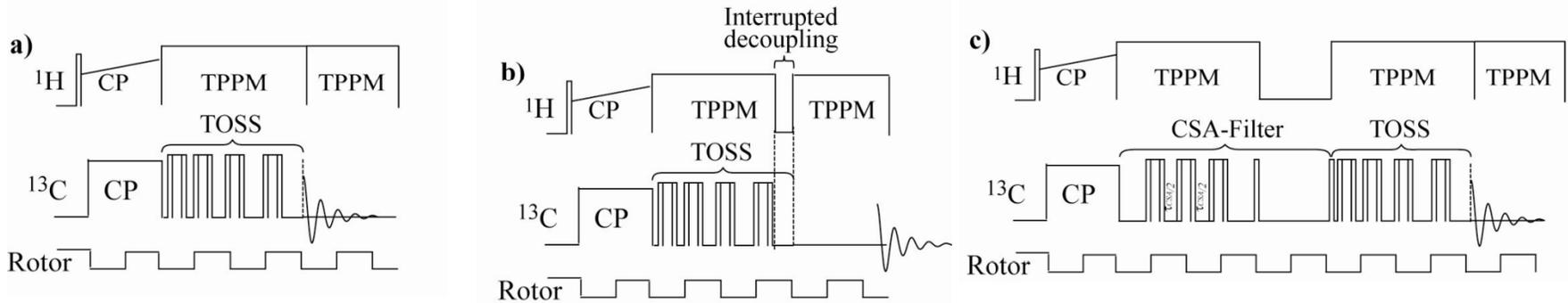
RESEARCH

Open Access

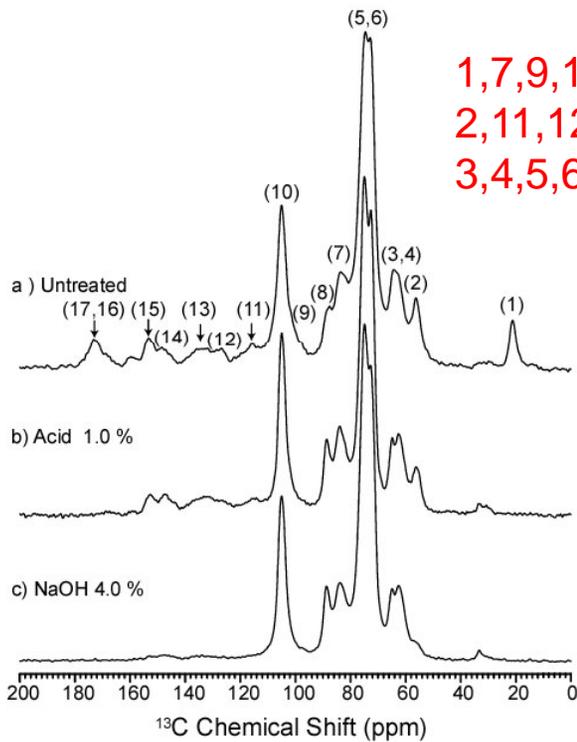
Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility

Camila Alves Rezende^{1†}, Marisa Aparecida de Lima^{1†}, Priscila Maziero², Eduardo Ribeiro deAzevedo¹, Wanius Garcia³ and Igor Polikarpov^{1*}

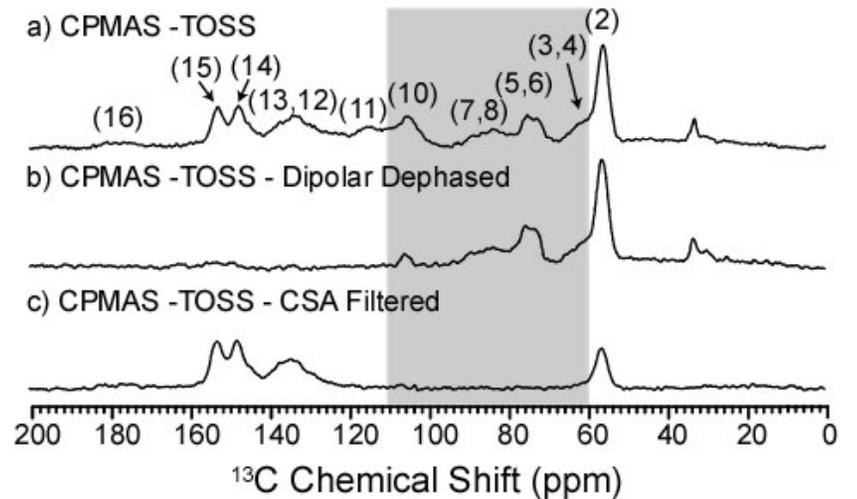
Modificações Químicas



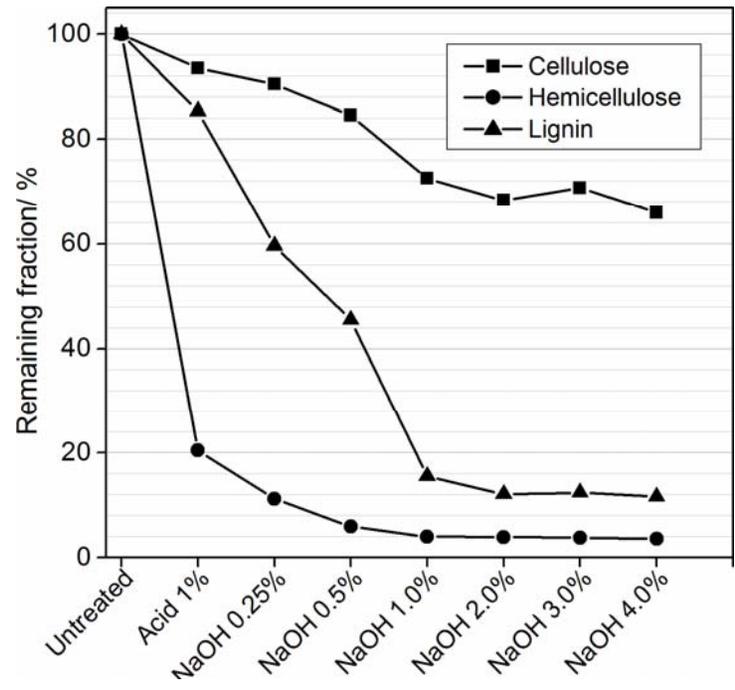
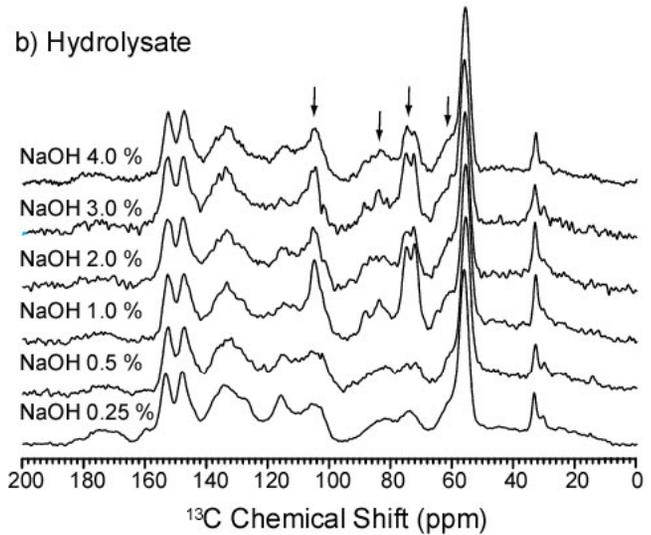
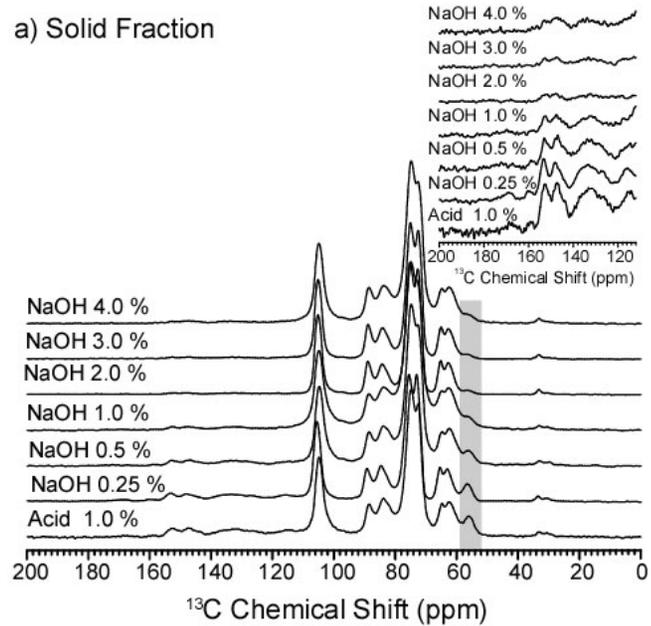
1,7,9,17 – hemicelulose
 2,11,12,13,14,15,16b – lignin
 3,4,5,6,7,8,10 - cellulose



Lyophilized hydrolysate from the NaOH 4.0 % pretreatment

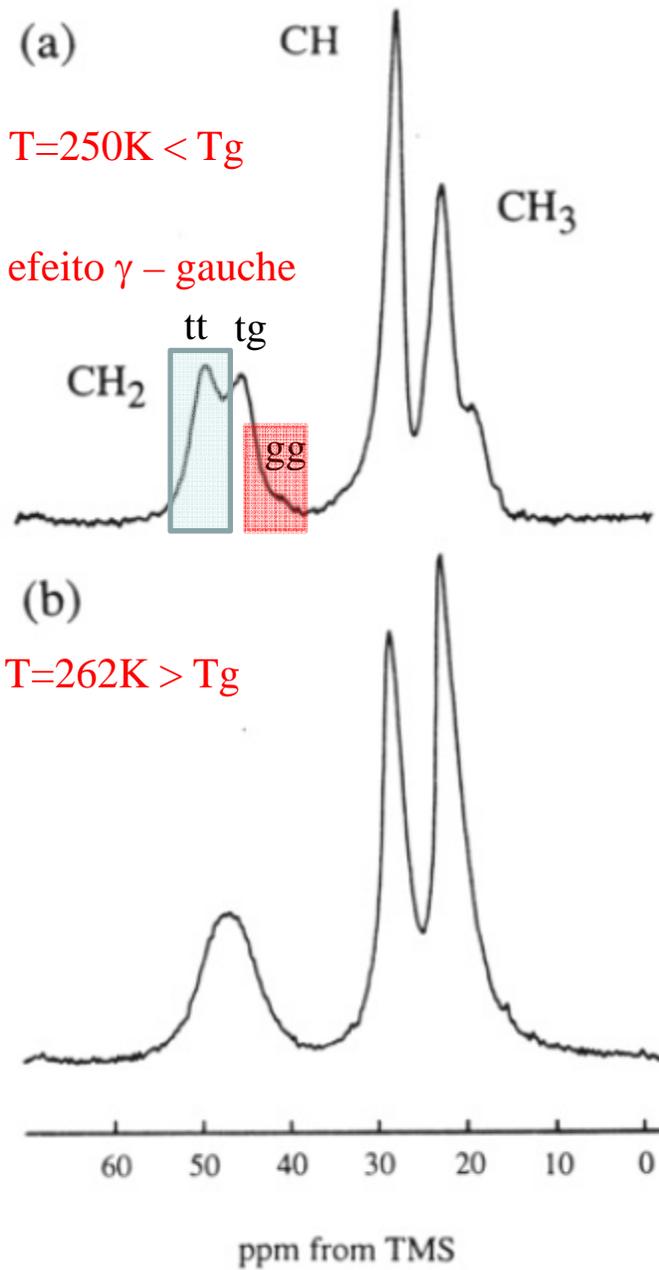


Modificações Químicas

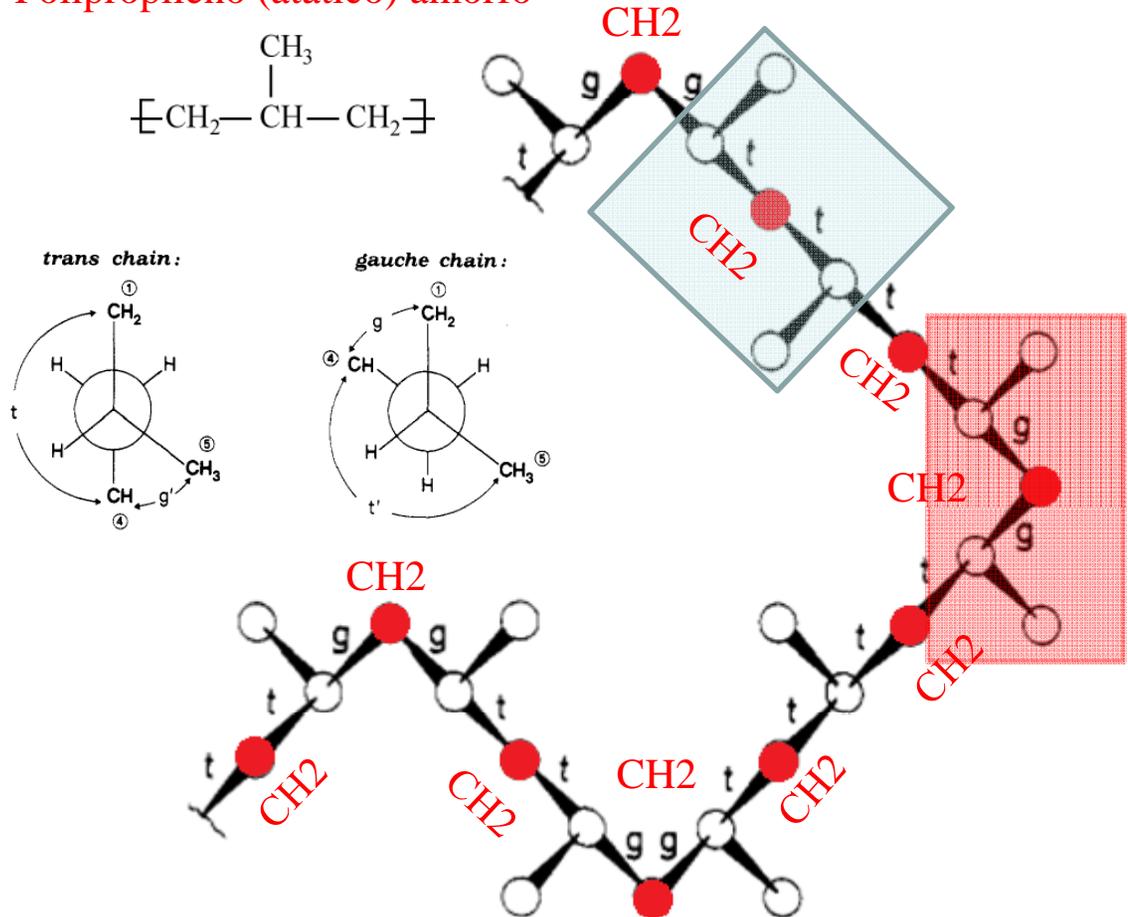


Only 1% of NaOH is needed
Cellulose is also extracted

Estrutura Local



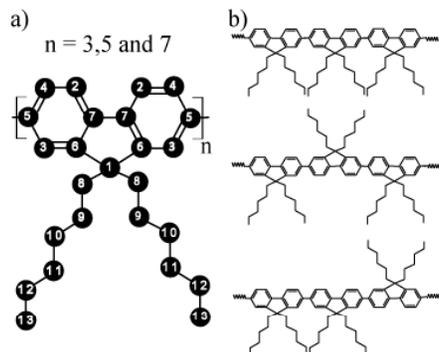
Polipropileno (atático) amorfo



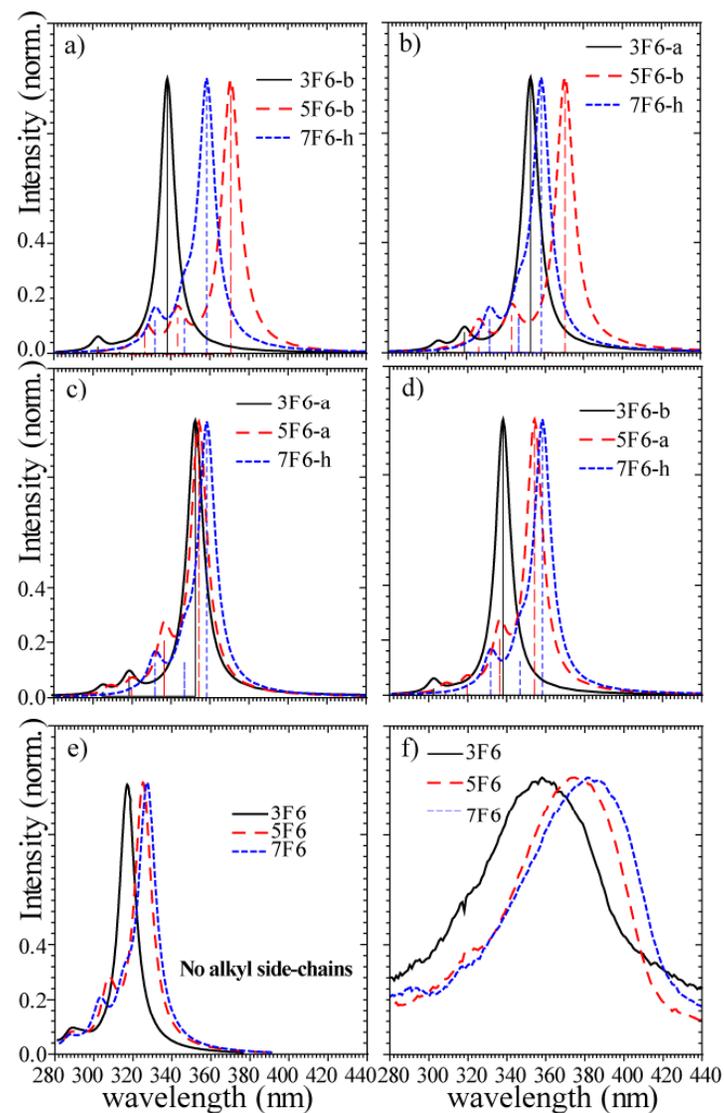
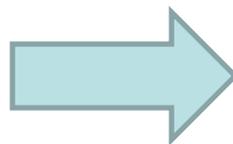
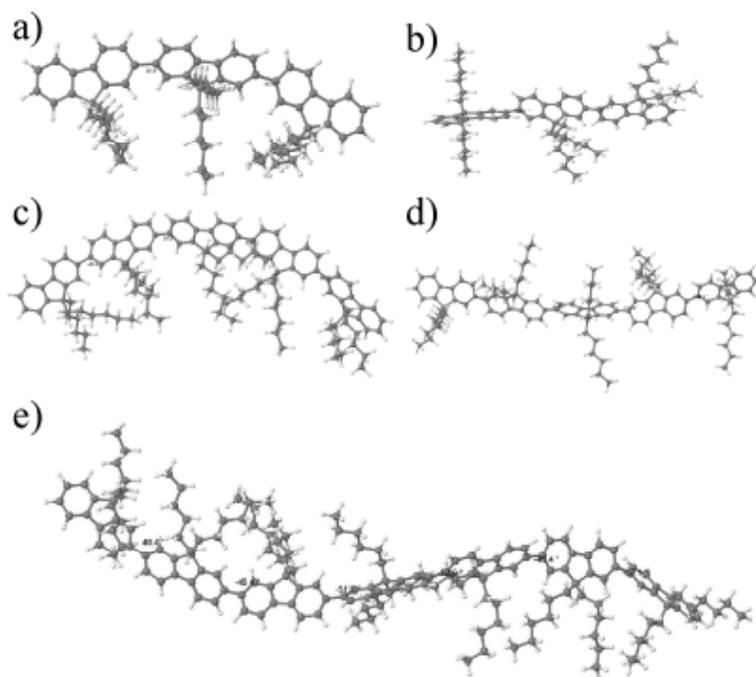
SCHMIDT-ROHR, K.; SPIESS, H. W.
Multidimensional solid-state NMR and polymers.
San Diego, CA: Academic Press, 1994.

Estrutura Local

Correlation between Molecular Conformation, Packing and Dynamics in Oligofluorenes

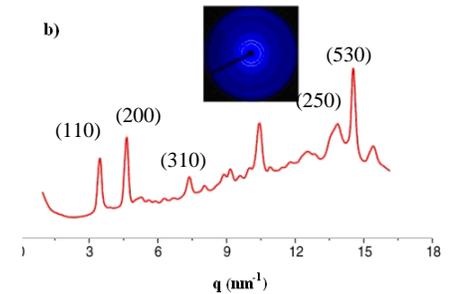
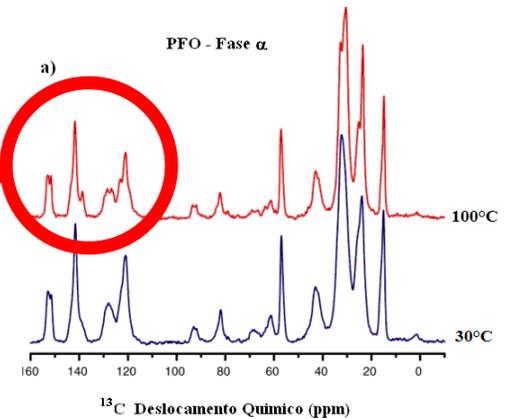
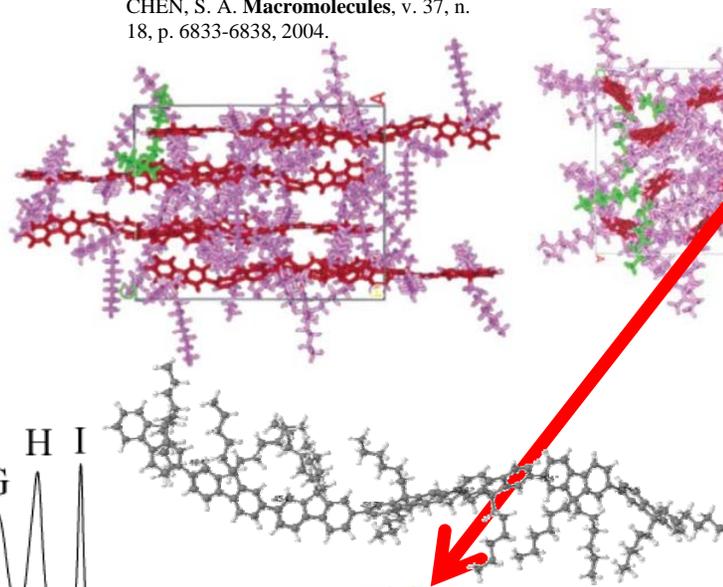
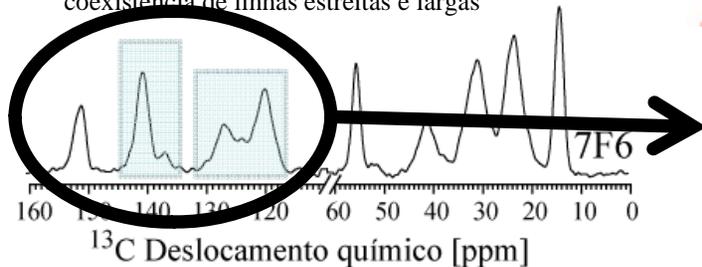
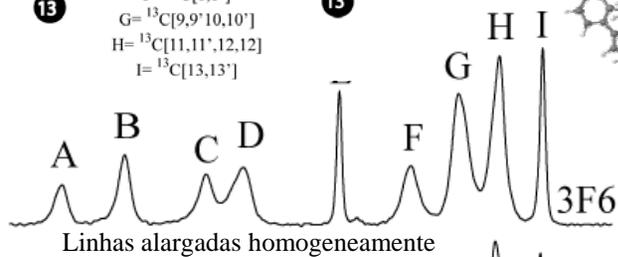
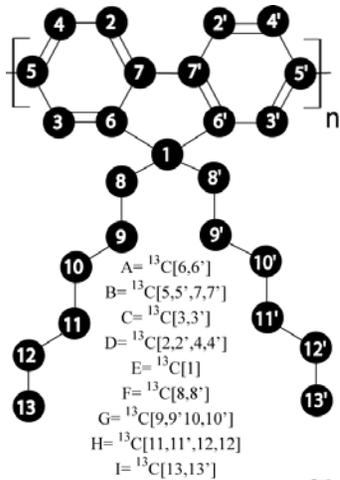


Oigres Daniel Bernardinelli¹,
 Gregório Couto Faria¹, Luiz
 Antonio de Oliveira Nunes¹,
 Roberto Mendonça Faria¹, Eduardo
 Ribeiro de Azevedo^{1*}, Melissa
 Fabíola Siqueira Pinto^{2*}



Estrutura Local

CHEN, S. H.; CHOU, H. L.; SU, A. C.;
CHEN, S. A. *Macromolecules*, v. 37, n.
18, p. 6833-6838, 2004.



Resumo

Diferentes conformações nas amostras

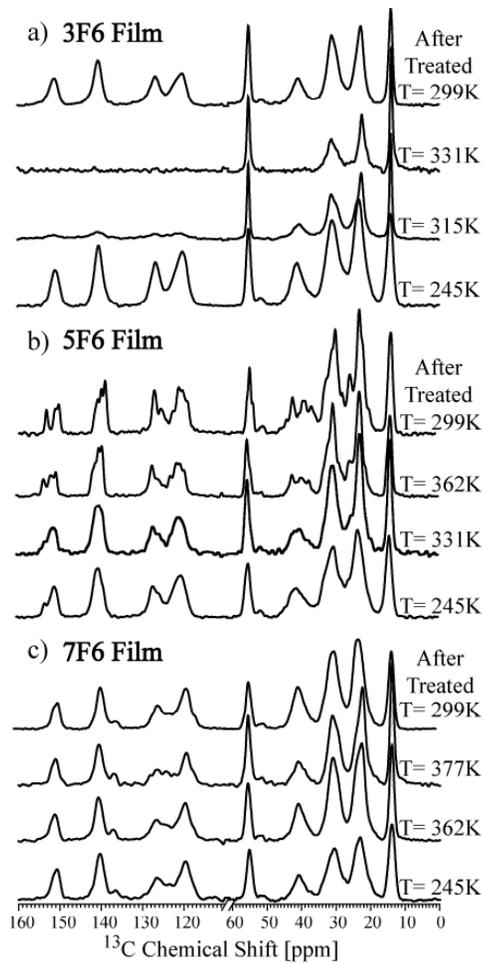
3F6 apresenta distribuição na conformação estrutural característico de material amorfo

5F6 & 7F6 fase organizada induzida pelo solvente com conformação preferencial distinta

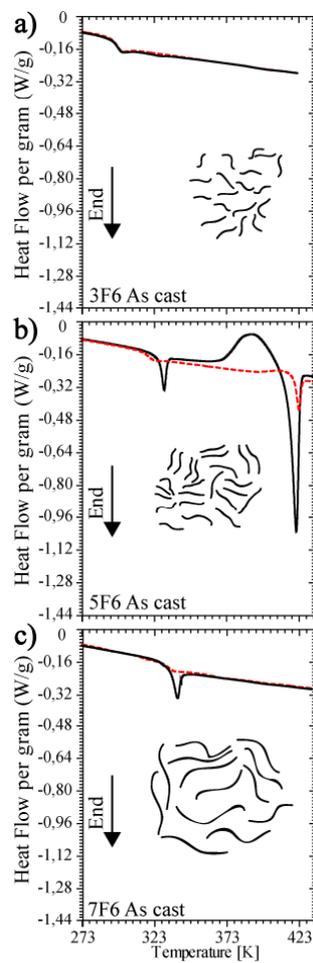
A fase organizada no 7F6 tende a conformação molecular helicoidal

Estrutura Local

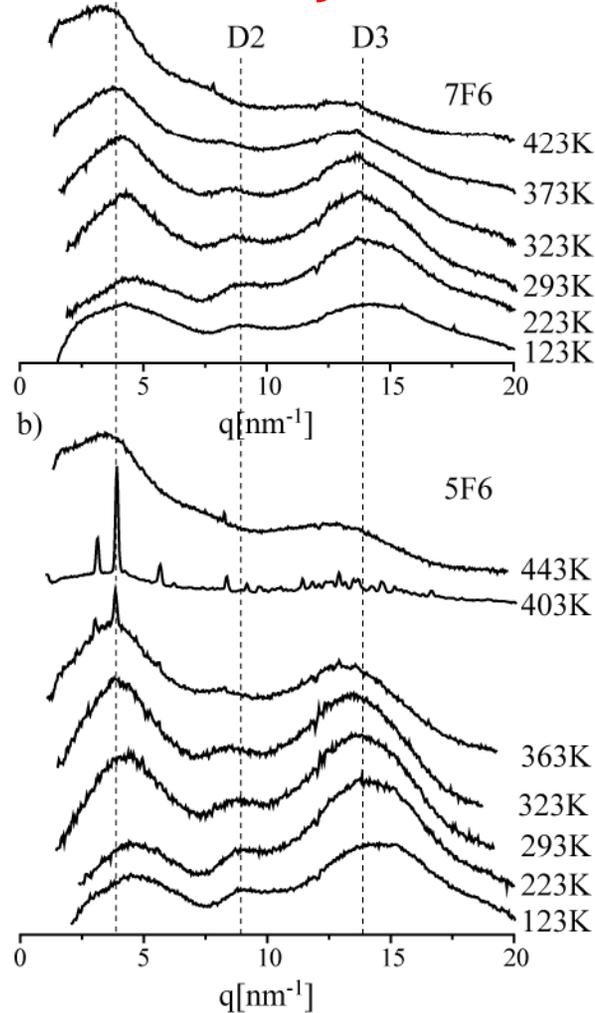
RMN



DSC

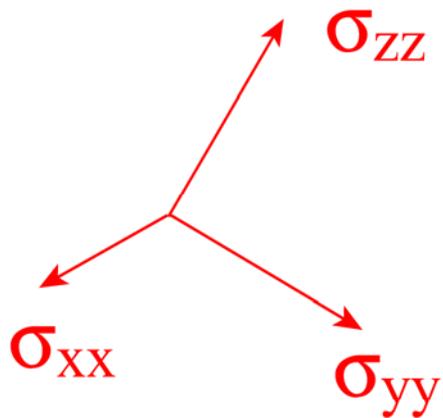


a) D1 Difração de R-X

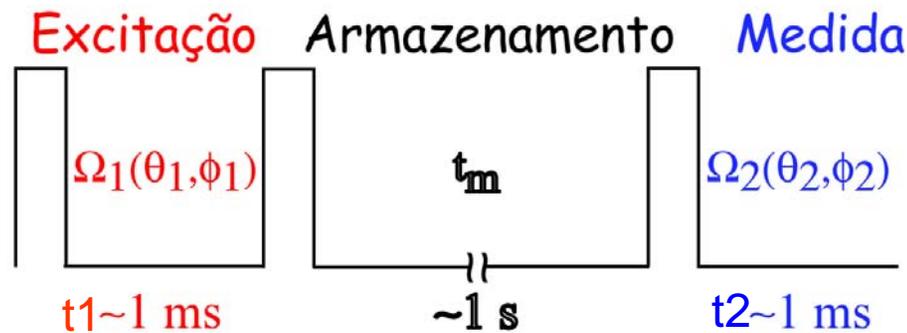


Dinâmica Molecular via RMN

Antes de t_m

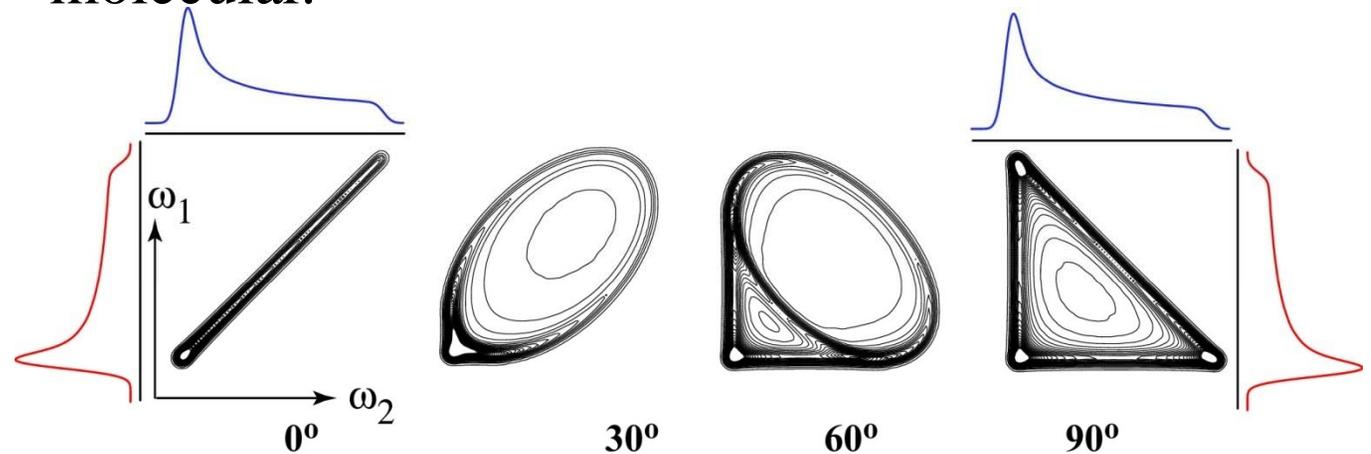
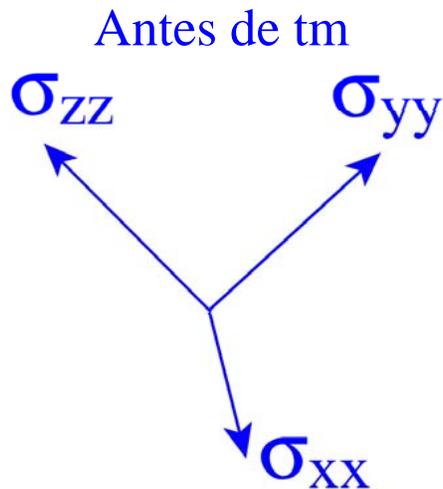


$$CSA: \omega(\theta, \phi) = \omega_{iso} + \frac{\delta}{2} [3\cos^2(\theta) - 1 - \eta\sin^2(\theta)\cos(2\phi)]$$

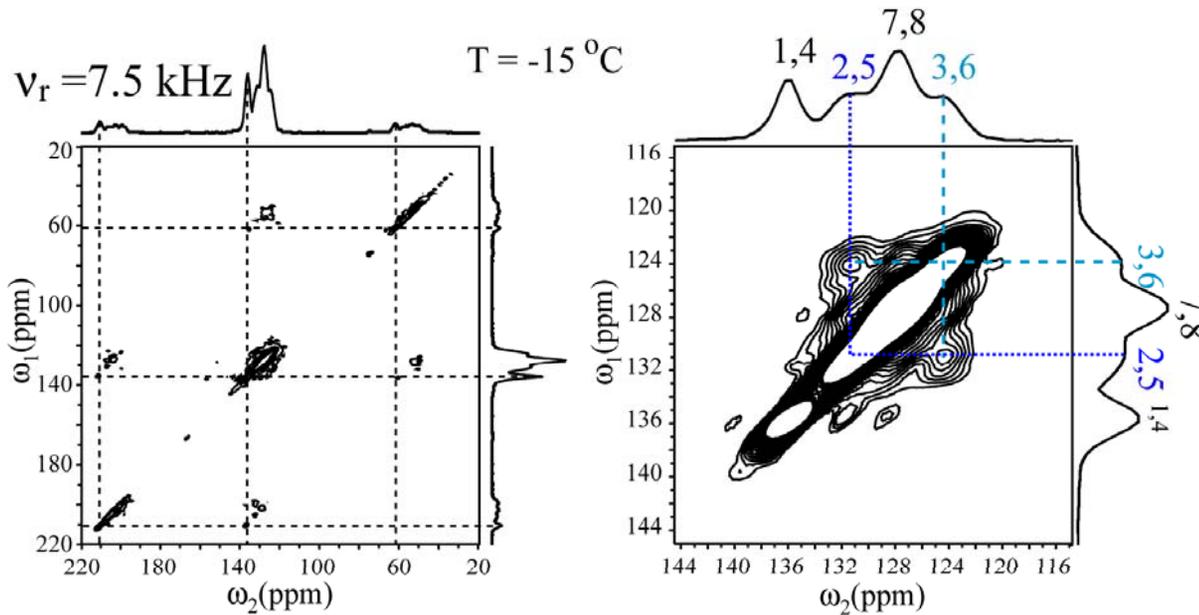
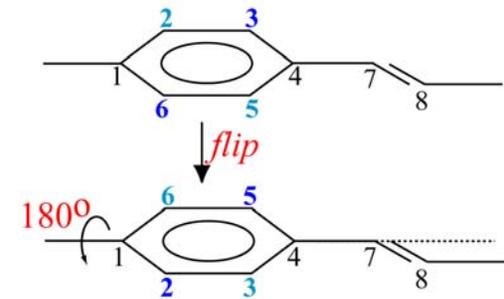
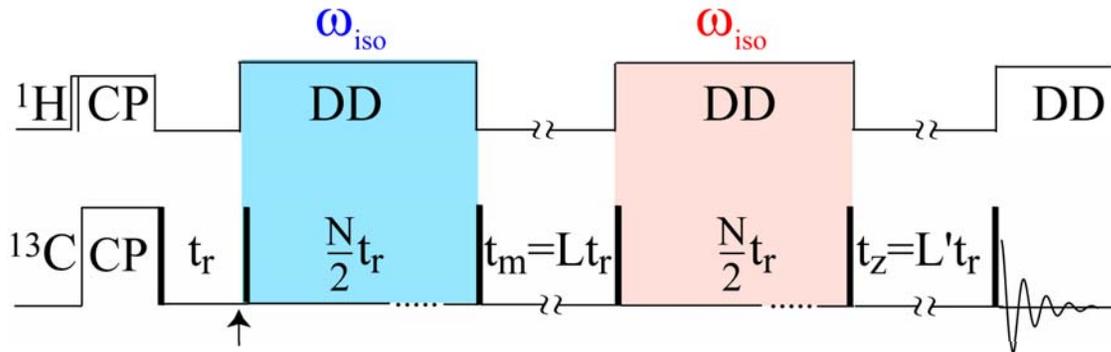


Reorientação Molecular:
mudança de θ, ϕ
↓
mudança de $\omega(\theta, \phi)$

Informação: amplitude e geometria do movimento molecular.



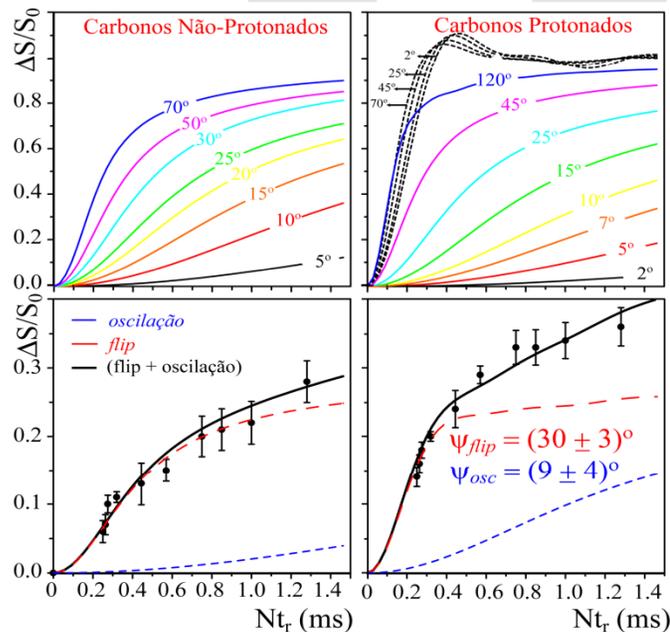
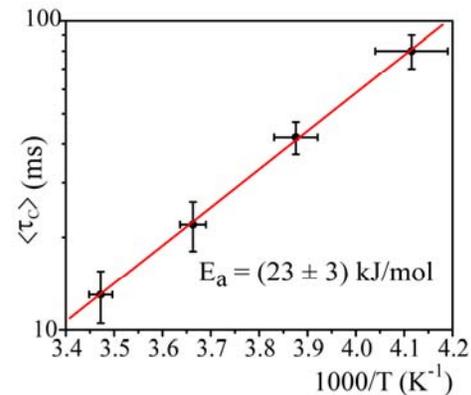
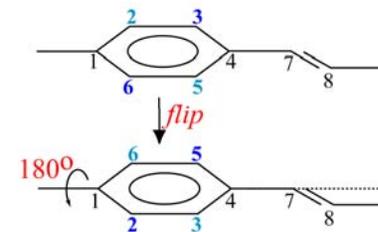
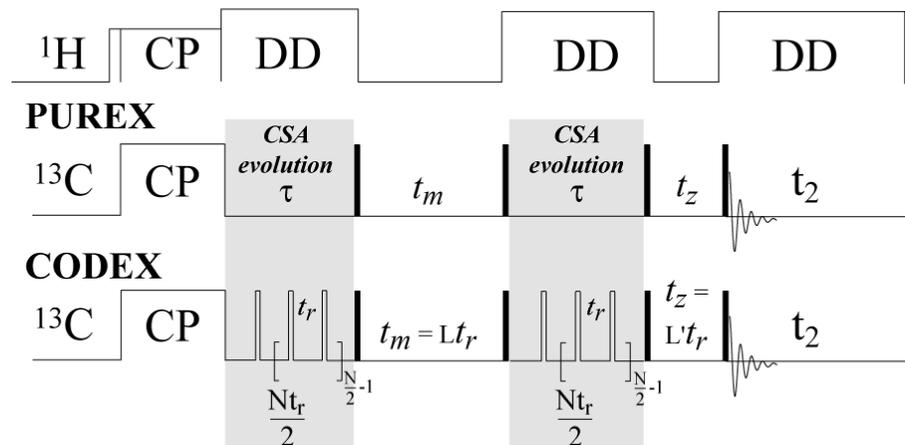
RMN de Exchange sob MAS 2D MAS Exchange\



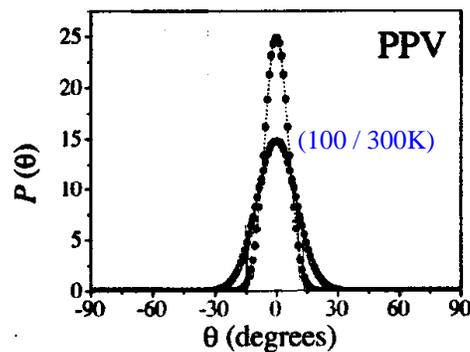
- Picos cruzados entre as bandas laterais 1,4: reorientações por pequenos ângulos
- Picos cruzados entre as linhas centrais 2,5 e 3,6: rotações de 180°

Centerband-Only Detection of Exchange (CODEX)

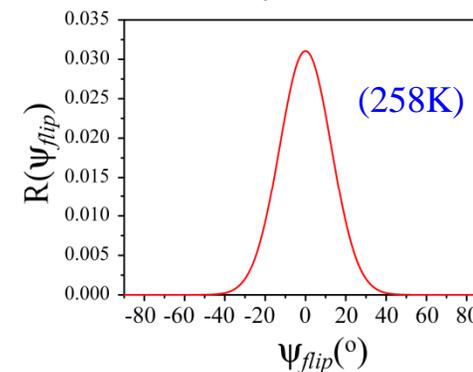
deAZEVEDO, E R ; HU, W ; BONAGAMBA, T J . SCHMIDT-ROHR K. Centerband-only detection of exchange: efficient analysis of dynamics in solids by NMR. J. Am. Chem. Soc., 121, 8411-8412, 1999.



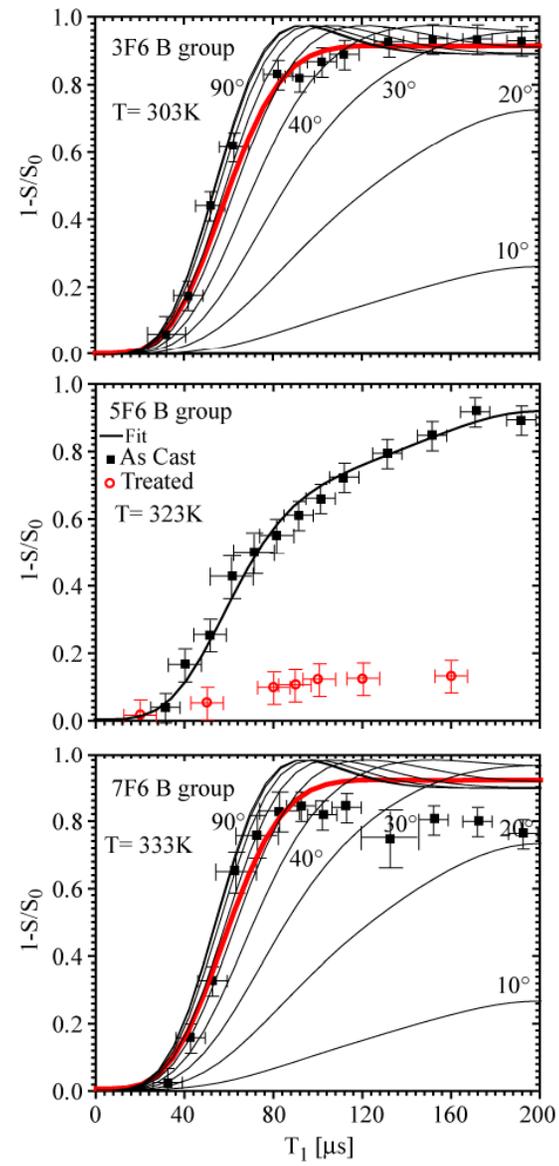
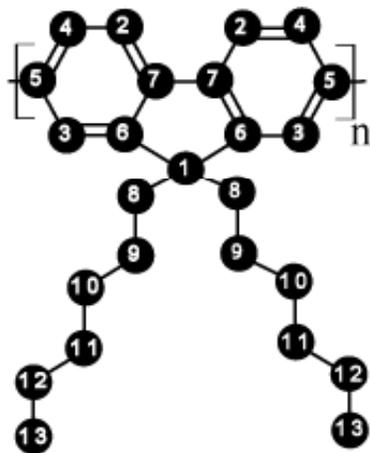
R.B. Capaz e M.Caldas, Phys. Rev. B., 67,2003



deAzevedo et. al. J. Chem. Phys., 119,2003



$n = 3, 5 \text{ and } 7$



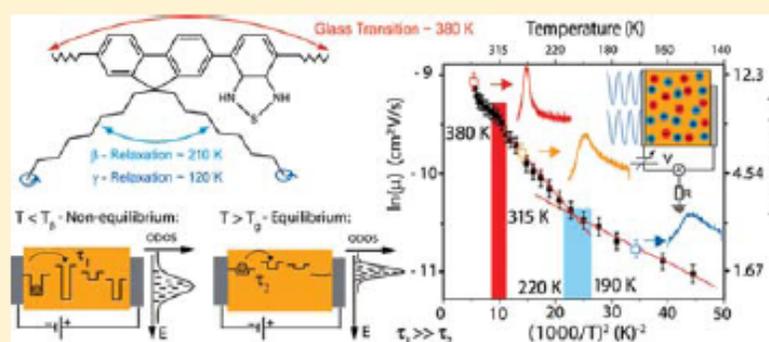
Temperature Dependence of the Drift Mobility of Poly(9,9'-dioctylfluorene-co-benzothiadiazole)-Based Thin-Film Devices

G. C. Faria,^{*,†,‡} R. M. Faria,[†] E. R. deAzevedo,[†] and H. von Seggern[‡]

[†]Instituto de Física de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560-970 São Carlos, SP, Brazil

[‡]Institute of Materials Science, Technische Universität Darmstadt, Petersenstrasse 23, 64287 Darmstadt, Germany

ABSTRACT: Charge transport in spin coated thin films of poly(9,9'-dioctylfluorene-co-benzothiadiazole) (F8BT) was studied using the Photo-Current Extraction by the Linear Increasing Voltage (Photo-CELIV) method in the temperature range of 120 to 420 K. A continuous change in the slope of a $\ln\mu$ versus T^{-2} plot was detected at 205 K with a very weak temperature dependence of the mobility at lower temperatures. According to the Gaussian Disorder Model (GDM), this behavior can be attributed to a progressive decrease in the dispersiveness of the charge transport. In this sense, the weak temperature dependence of the mobility at low temperatures arises from the nonequilibrium condition between thermal released and trapped charges, so the transport becomes trap controlled at low temperature. Furthermore, another change in the mobility behavior was observed at about 360 K, which was related to the glass transitions of the material. This indicates that even for thin films the drift mobility can be significantly affected by a variation in the dynamics and local packing of the polymer chains, which can be detected by Photo-CELIV experiments.



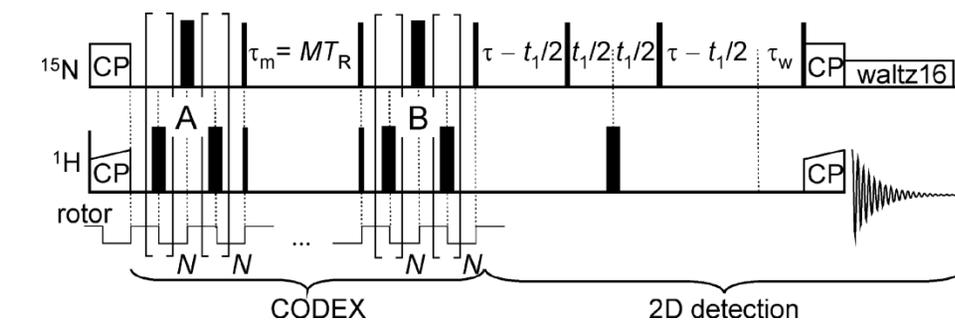
Física dos Spins: Desenvolvimento de Seqüências de pulsos

J|A|C|S
COMMUNICATIONS

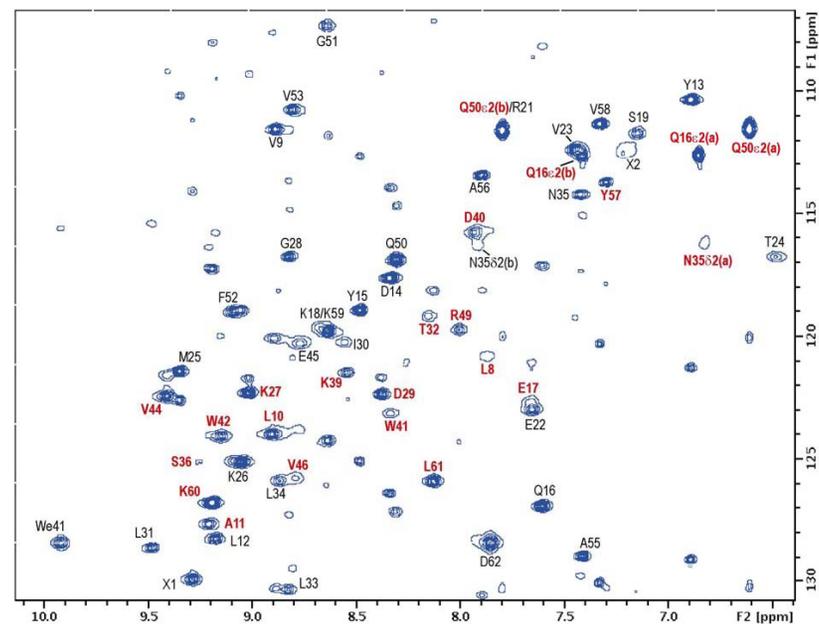
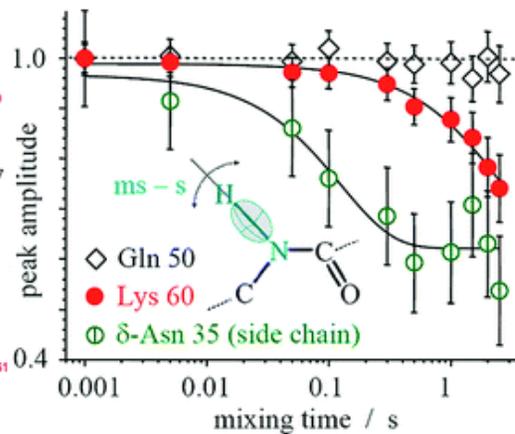
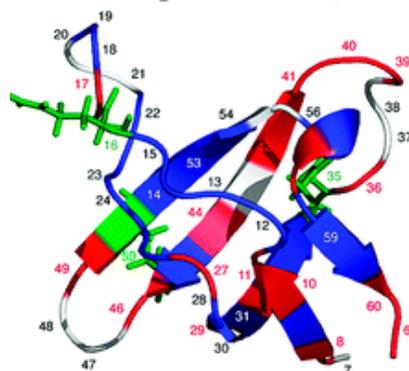
Published on Web 08/12/2009

Direct Observation of Millisecond to Second Motions in Proteins by Dipolar CODEX NMR Spectroscopy

Alexey Krushelnitsky,^{*,†} Eduardo deAzevedo,[‡] Rasmus Linser,[§] Bernd Reif,[§] Kay Saalwächter,^{*,||} and Detlef Reichert^{*,||}

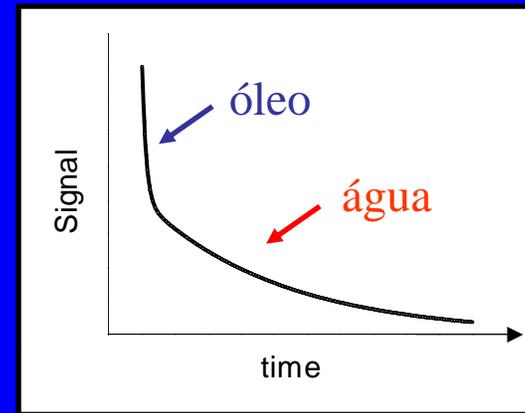


α -spectrin SH3



Relaxometria

Relaxometria: Determinação de características de materiais baseados em seus tempos de relaxação. Uma característica geral é o uso de campos magnéticos baixos



Controle de Qualidade de Alimentos



No IFSC:
Prof. Tito J. Bonagamba

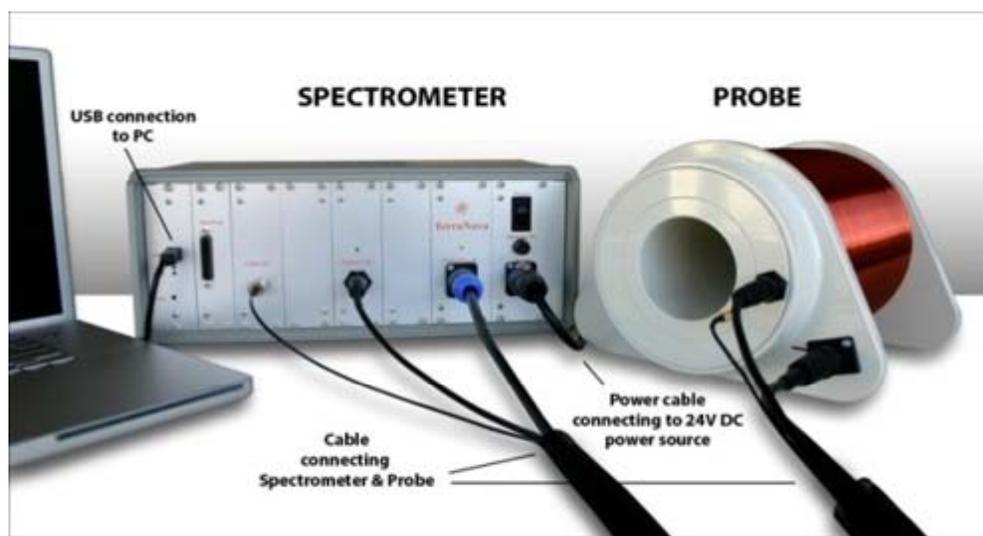


Análise de Materiais Moles, Porosos ou Líquidos viscosos (viscosimetria)



Alguns Tipos de Equipamentos de RMN

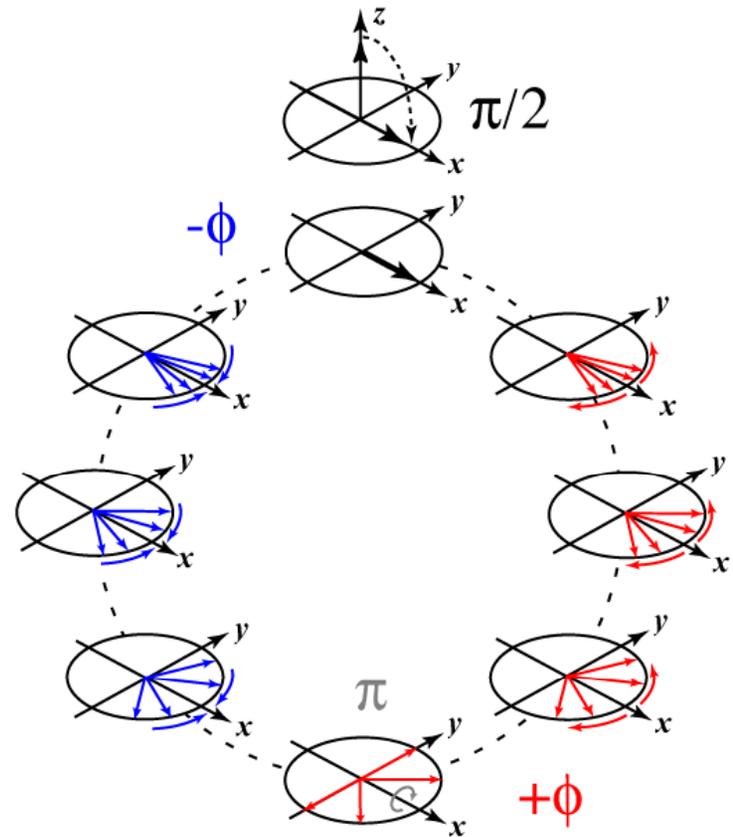
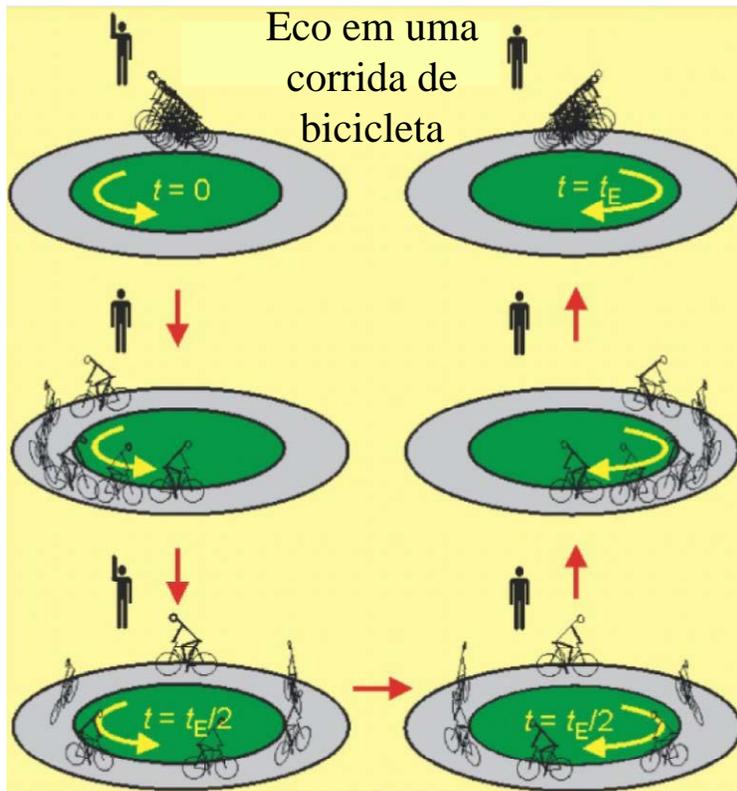
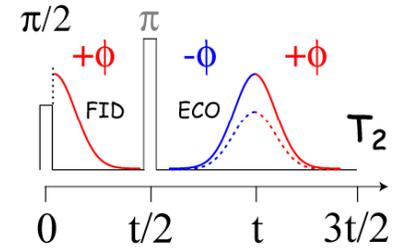
Sistemas de Baixo Campo (B_0 : 0.05×10^{-3} – 1 Tesla)

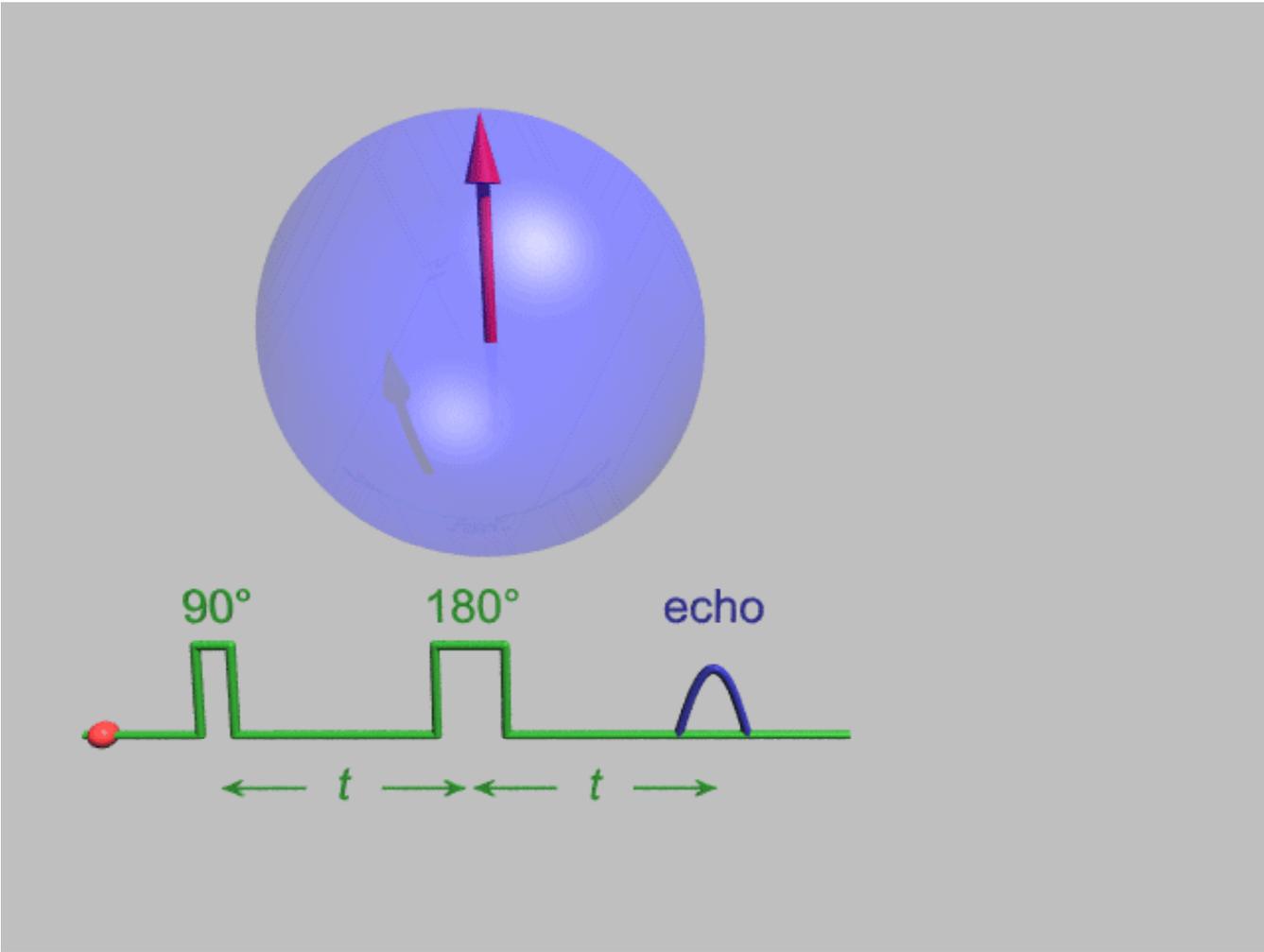


Ecos de Spin

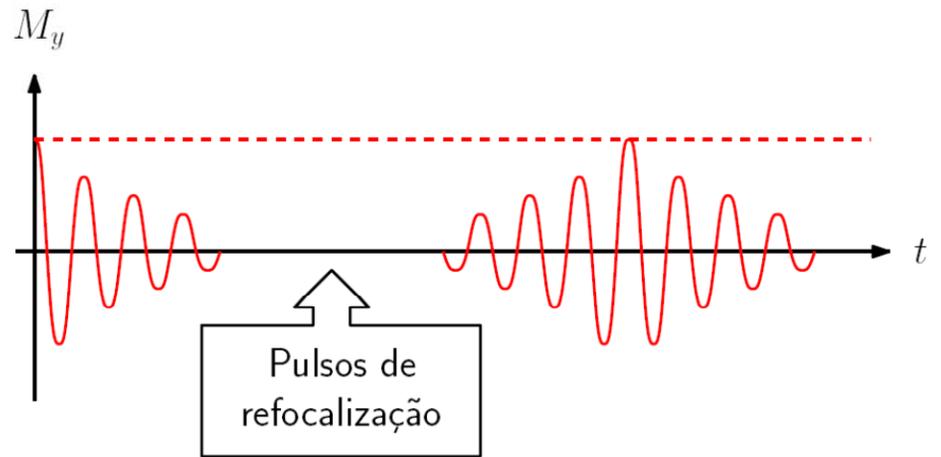
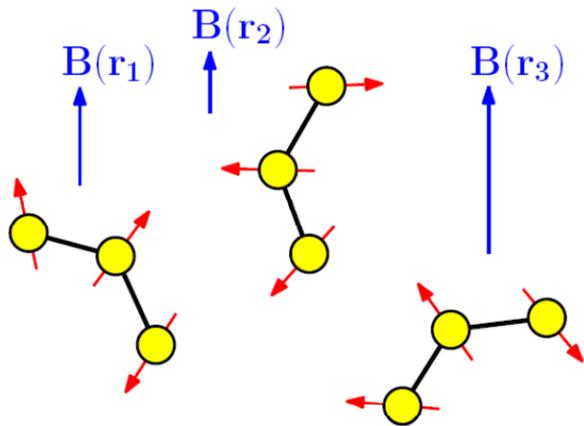
“ Spins can do everything for you as far as you treat them as human beings ” (Erwing Hahn)

Campos locais na direção

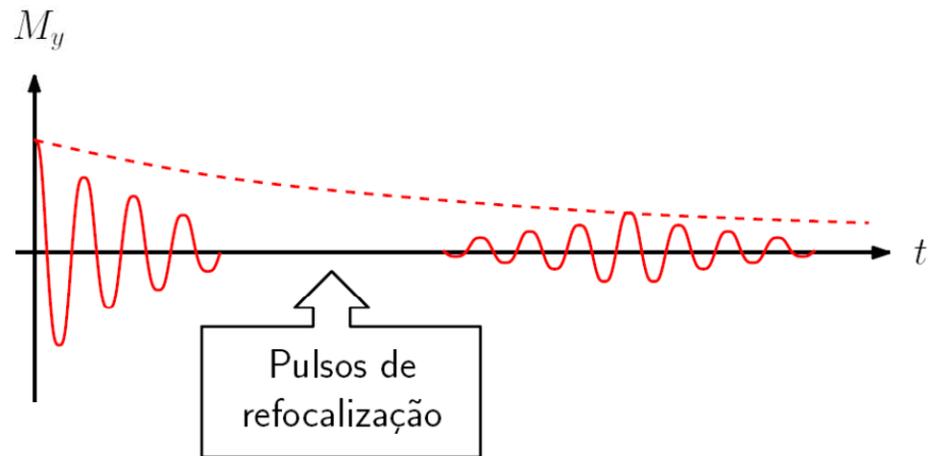
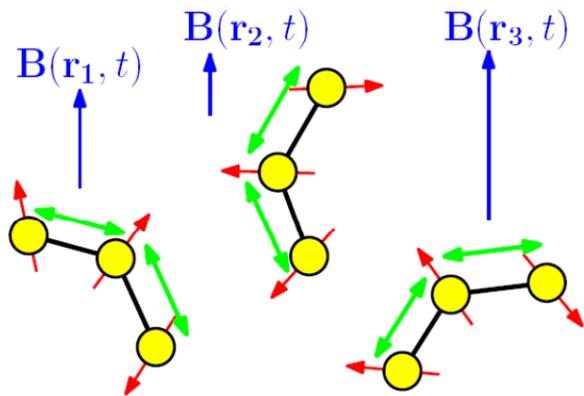




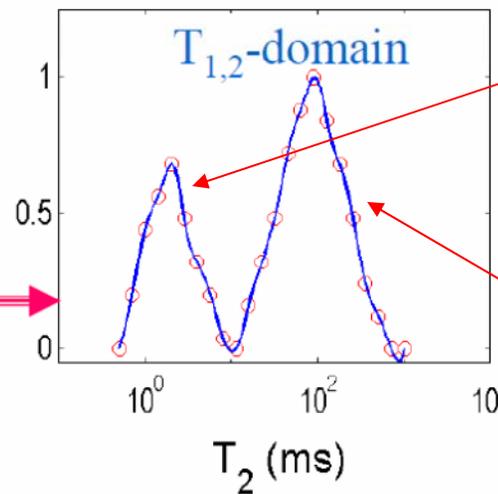
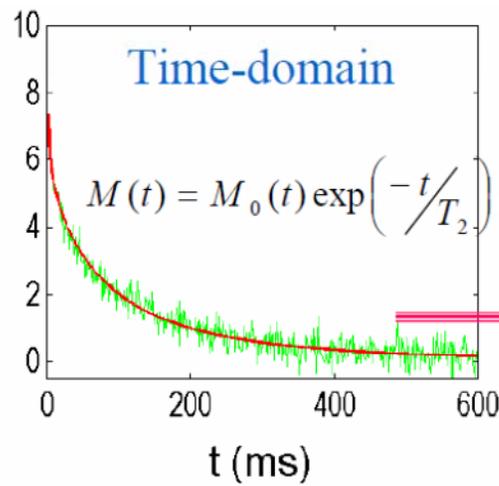
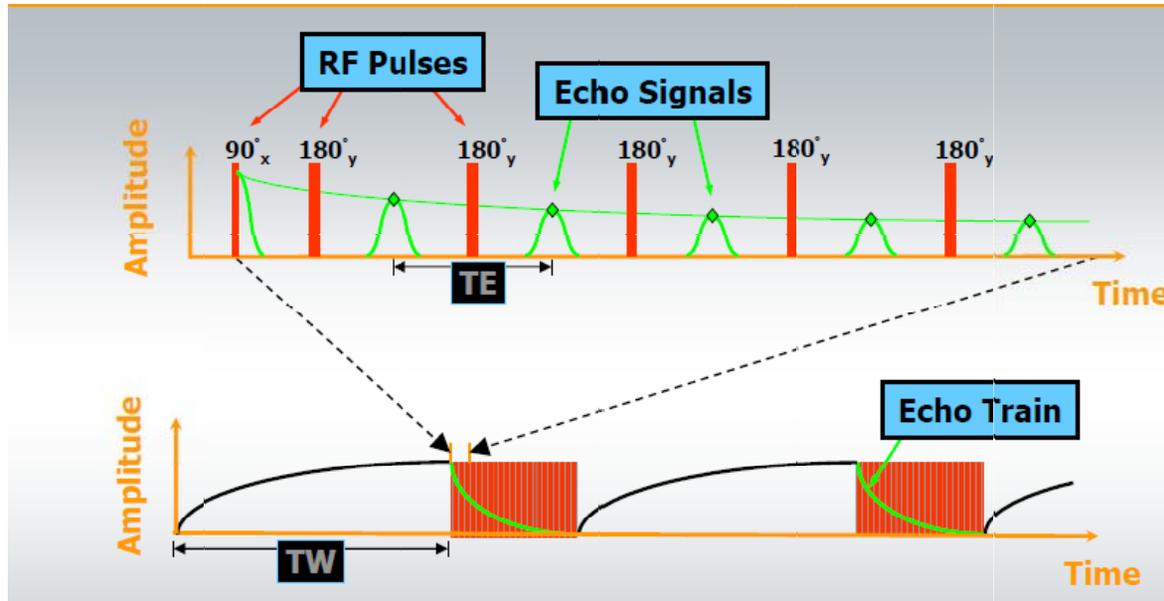
Efeitos estáticos



Efeitos dinâmicos



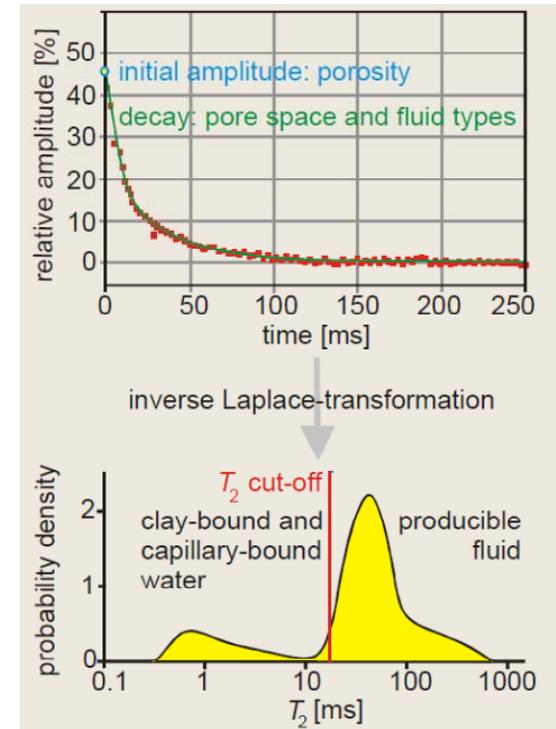
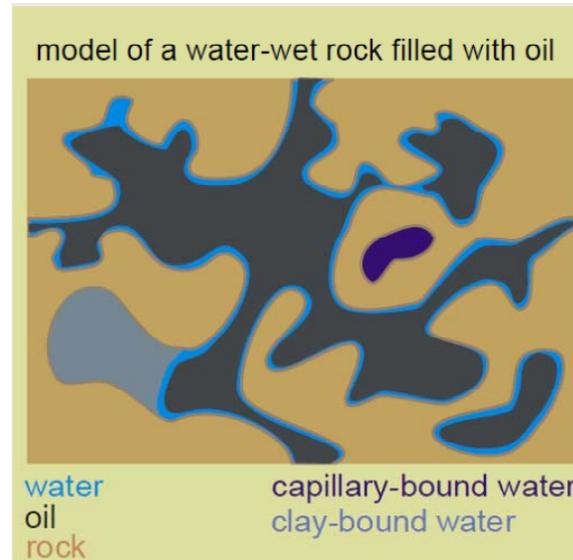
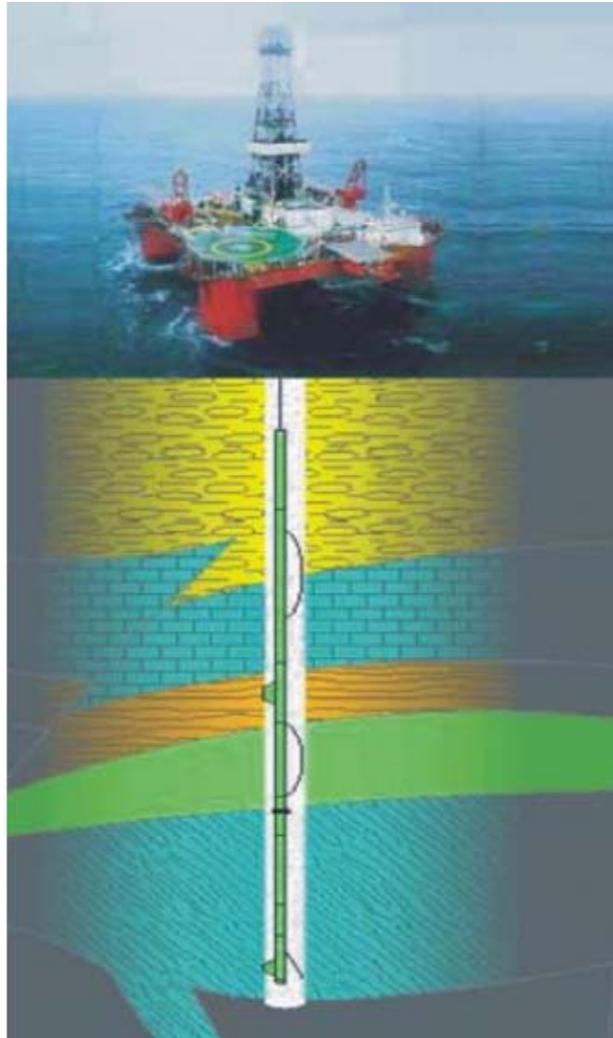
Medidas de T_2 e suas distribuições



*Moléculas
mais rígidas*

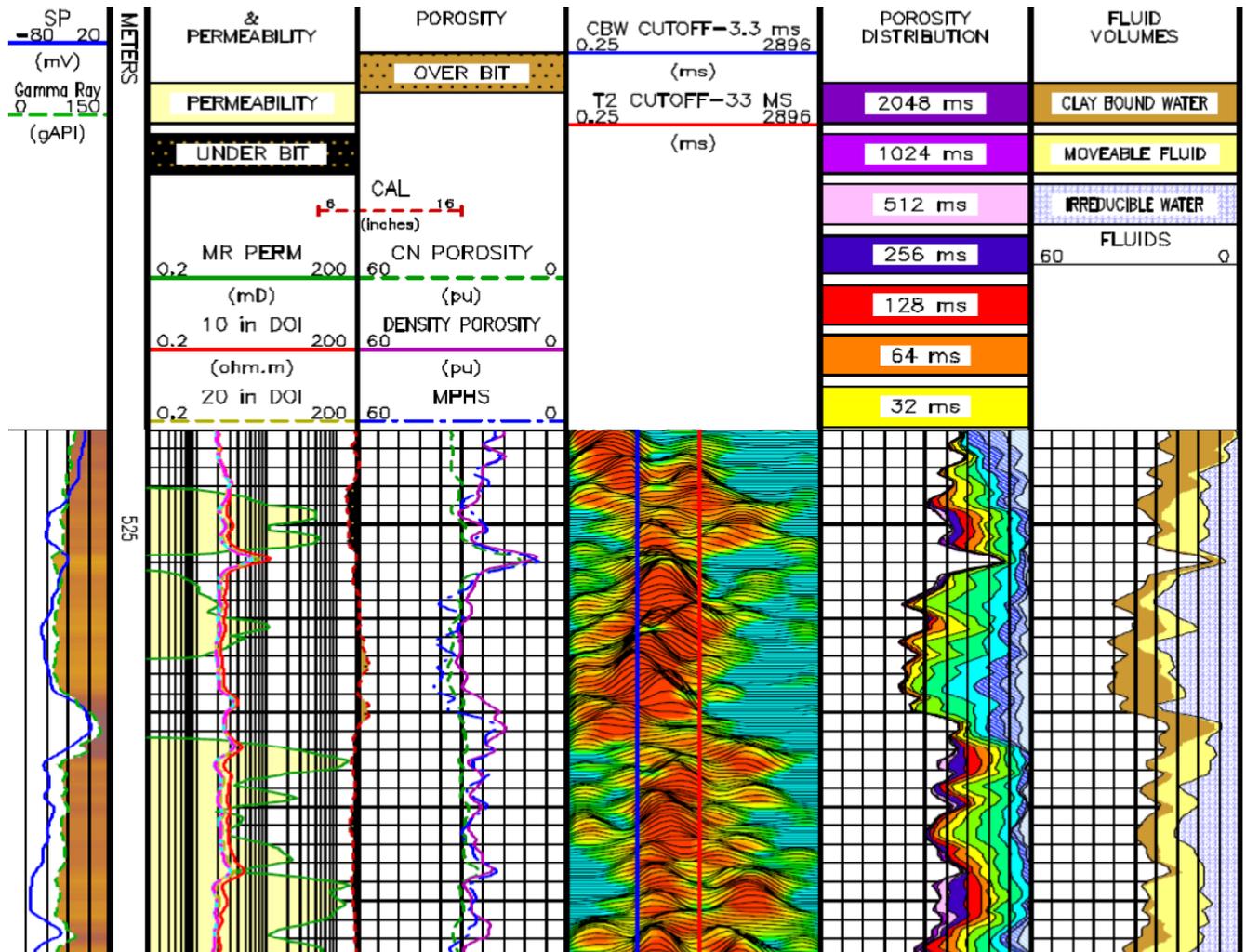
*Moléculas
mais flexíveis*

Uma Aplicação de Medidas de T_2 – *Well Logging NMR*

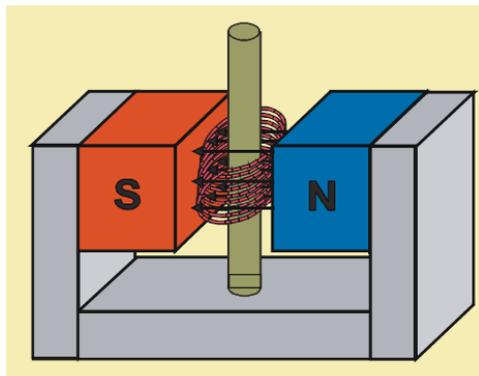


- Medida de distribuição de T_2 está entre as medidas padrões para determinação da capacidade produtiva de poços de petróleo.
- As distribuições de T_2 também são utilizadas para em outros vários estudos de meios porosos.

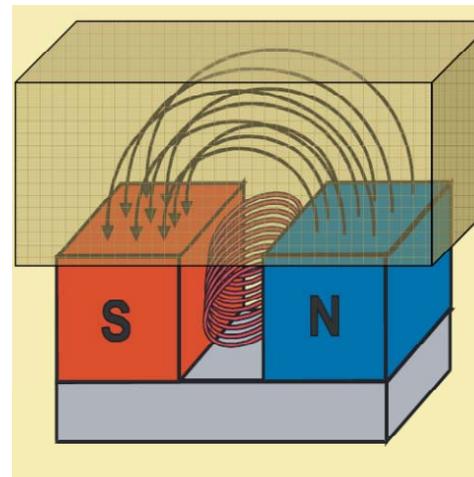
Uma Aplicação de Medidas de T_2 – *Well Logging NMR*



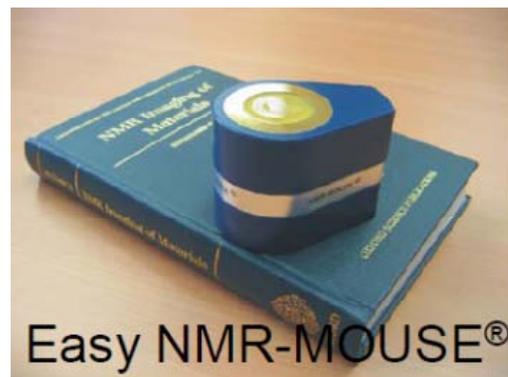
RMN de Superfície



RMN convencional:
*Amostra dentro
do magneto*

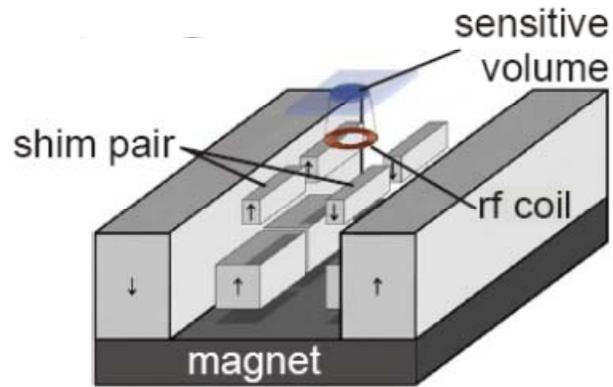


RMN de superfície:
*Amostra fora
do magneto*

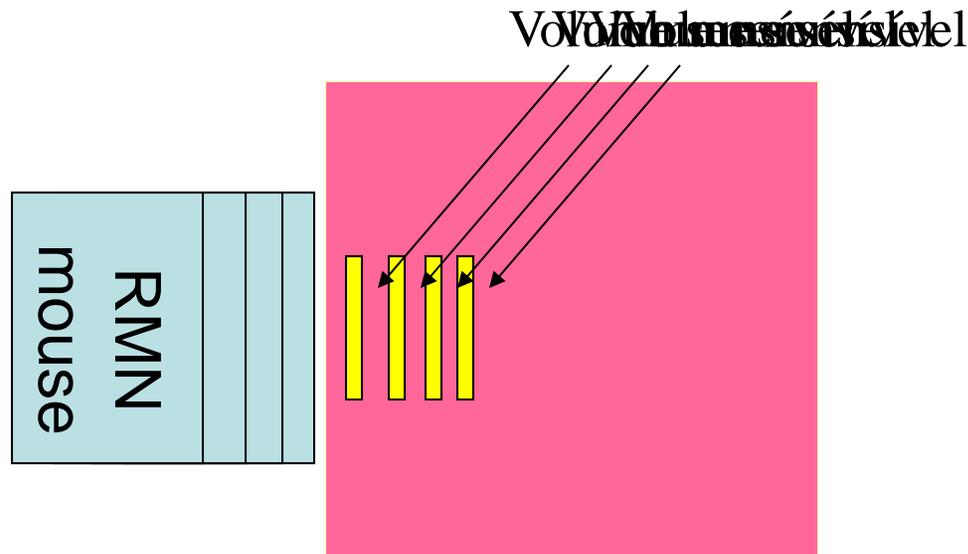


O RMN Mouse:
Relaxometria,
espectroscopia
ou imagens de
superfície

RMN de Superfície



the most sophisticated NMR-MOUSE
(2007): shimming the stray field



RMN E ARTE

APPLIED PHYSICS LETTERS 93, 033505 (2008)

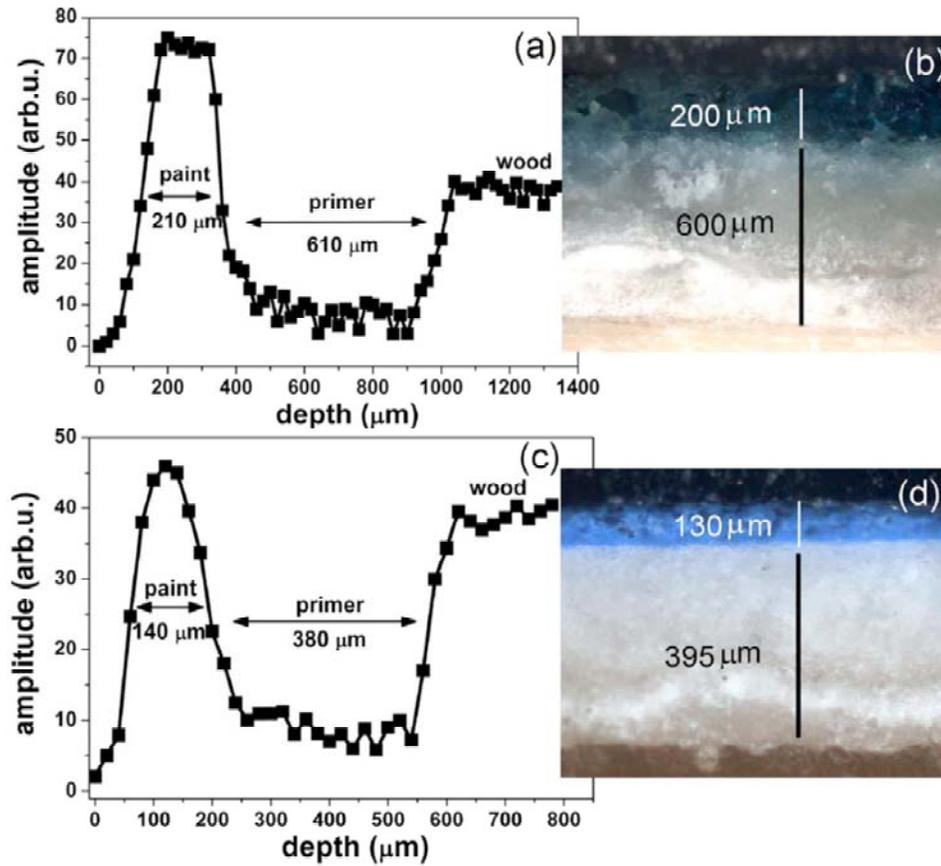
Noninvasive nuclear magnetic resonance profiling of painting layers

Federica Presciutti,^{1,a)} Juan Perlo,² Federico Casanova,² Stefan Glögger,²
Costanza Miliani,¹ Bernhard Blümich,² Brunetto Giovanni Brunetti,¹ and
Antonio Sgamellotti¹

¹*Centre of Excellence SMAArt and ISTM-CNR, c/o Chemistry Department, University of Perugia,
Via Elce di Sotto 8, Perugia 06123, Italy*

²*Institut für Technische Chemie und Makromolekulare Chemie, Rheinisch-Westfälische Technische
Hochschule, Aachen D-52056, Germany*

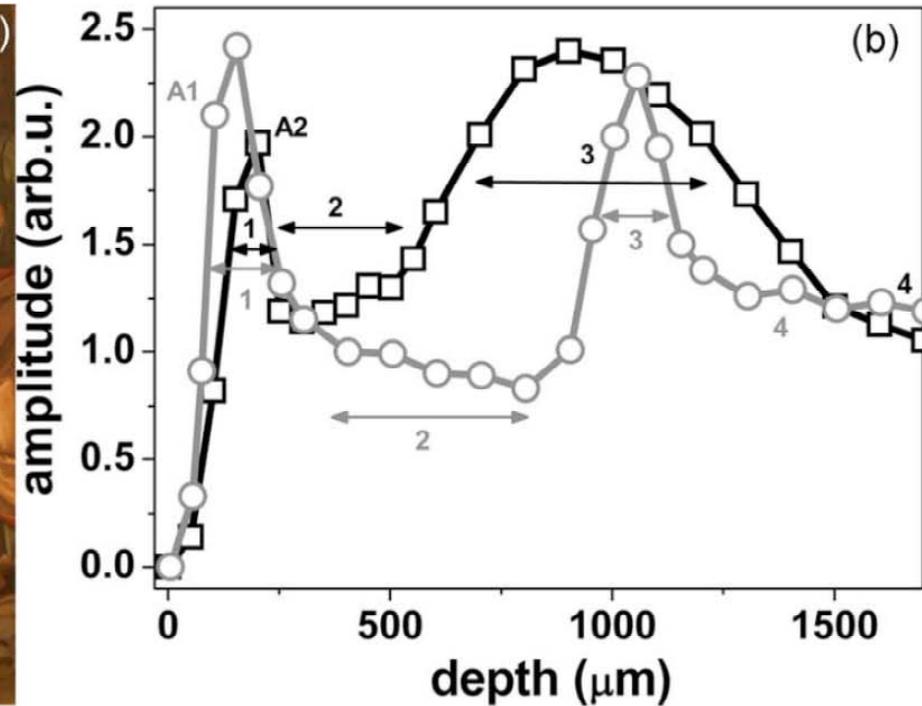
Identificação de diferentes camadas da pintura



NMR

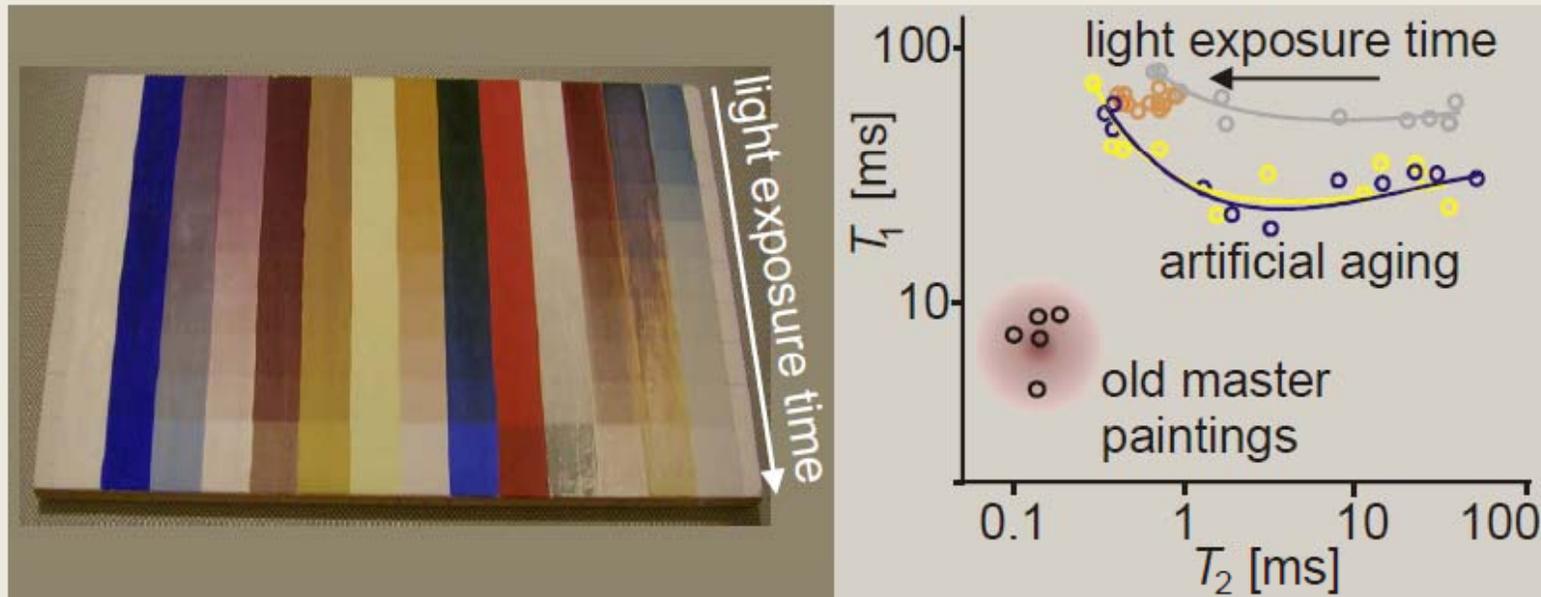
Microscopia
óptica

Mapeamento de técnicas de pintura



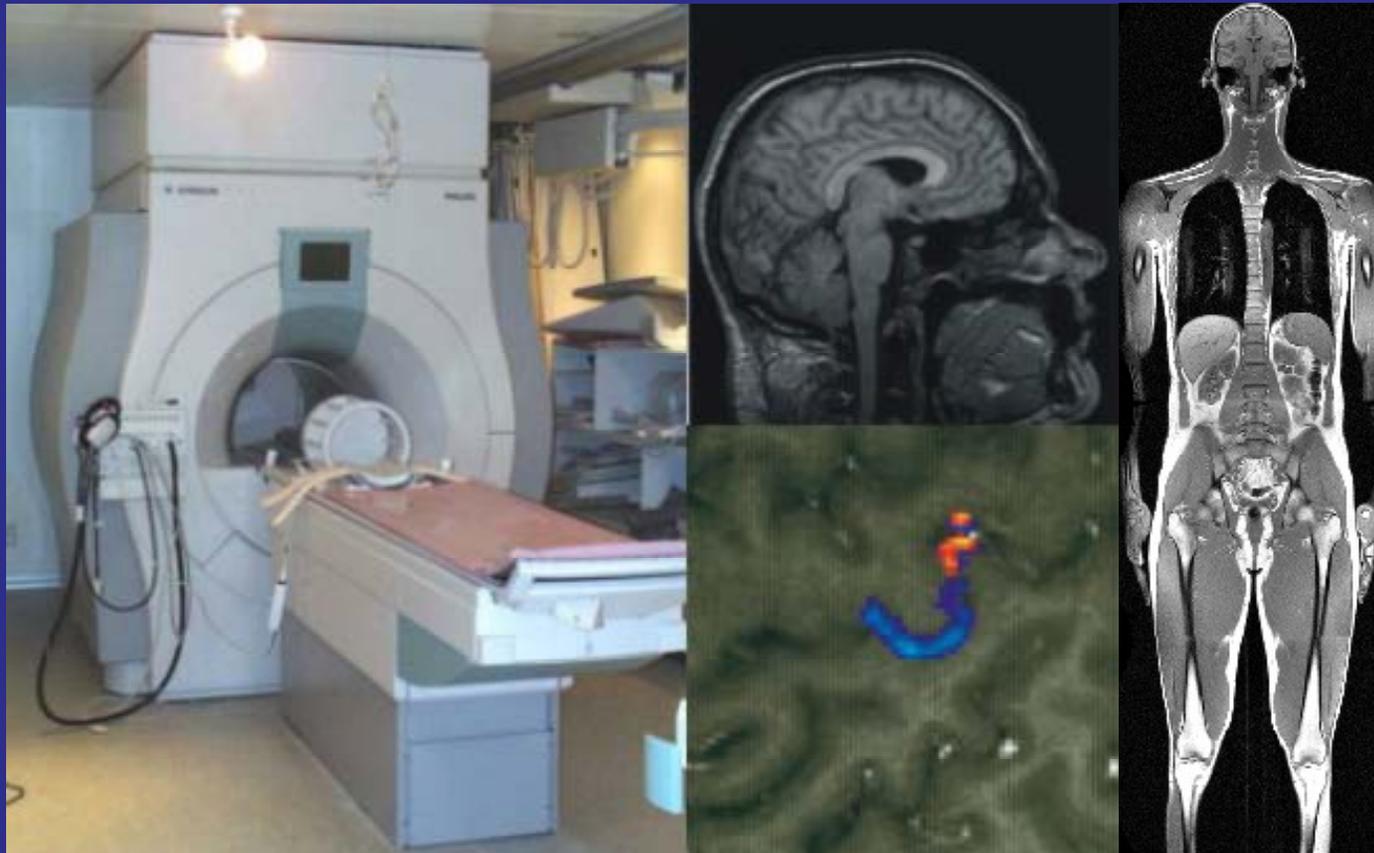
adoration of the Magi,
Perugino, 1470 AD

Identificação de falsificações obras de arte antigas



artificially aged samples: Marika Spring, The National Gallery, London

Imagens por RMN



Alguns Tipos de Equipamentos de RMN

Sistemas para Imagens Médicas

B_0 : 0.5 – 2 Tesla



Antes de mais nada, alguns pequenos esclarecimentos...

Imagens por Ressonância Magnética Nuclear = exame de Ressonância Magnética



Por que a mudança de nome ?

Essencialmente porque
Nuclear traz conotação ruim.

O que é uma imagem afinal ???

Representação fiel (ou o mais fiel possível) de um objeto, obtida pela reconstrução à partir de radiação emitida, refletida ou absorvida pelo mesmo.

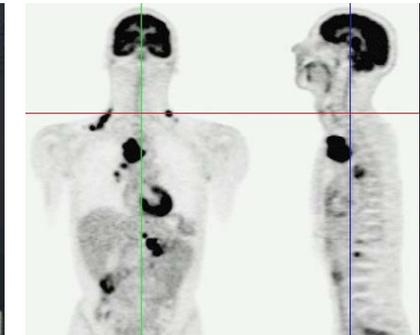
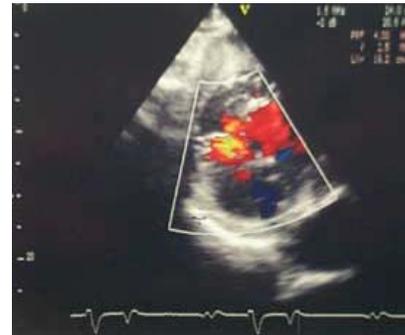
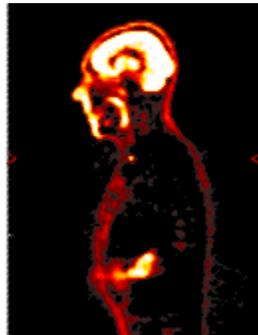
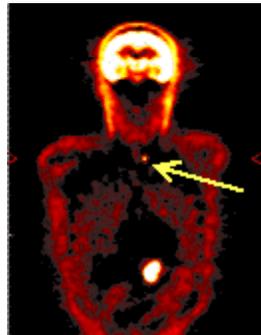
Tomografia
Computadorizada

Fotografia

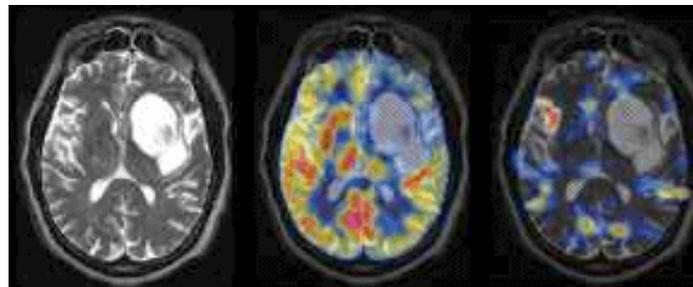
Termografia

Ultrasonografia

Raios-X



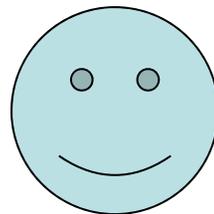
Ressonância Magnética



O que é uma imagem de Ressonância Magnética ?

A sensibilidade da RMN é maior quanto maior for a abundância dos núcleos medidos e quanto maior for a frequência de precessão.

- *O corpo humano é composto de cerca de 75% de H_2O*
- *O núcleo de hidrogênio é o que possui maior frequência de ressonância entre todos os demais.*
- *Um mapa das magnetizações de 1H do corpo é uma imagem da distribuição de água do corpo.*
- *Tempos de relaxação também influenciam na imagem.*



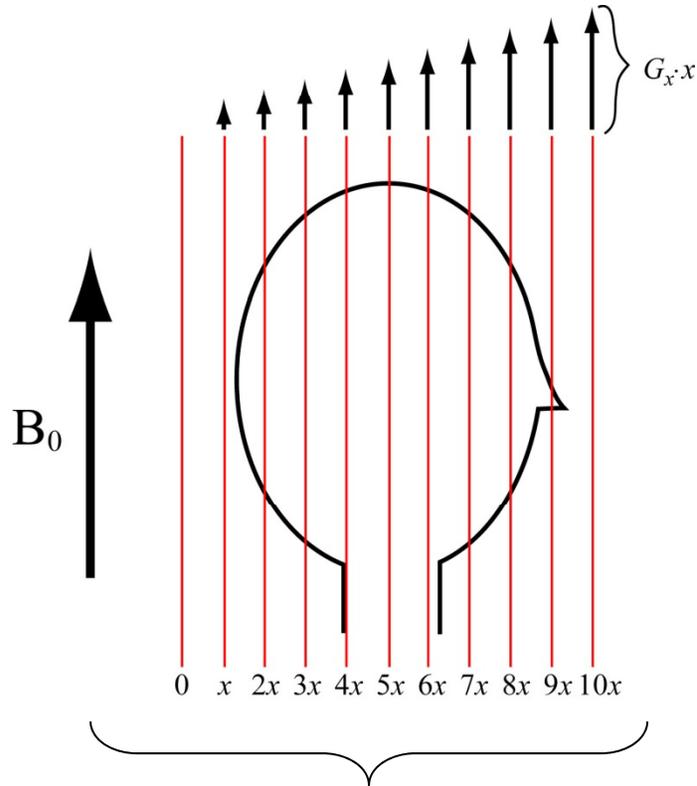
Como obter uma imagem de Ressonância Magnética ?

RMN mede magnetização e é capaz de discriminar as frequências de precessão dos spins nucleares se eles experimentarem campos magnéticos distintos.

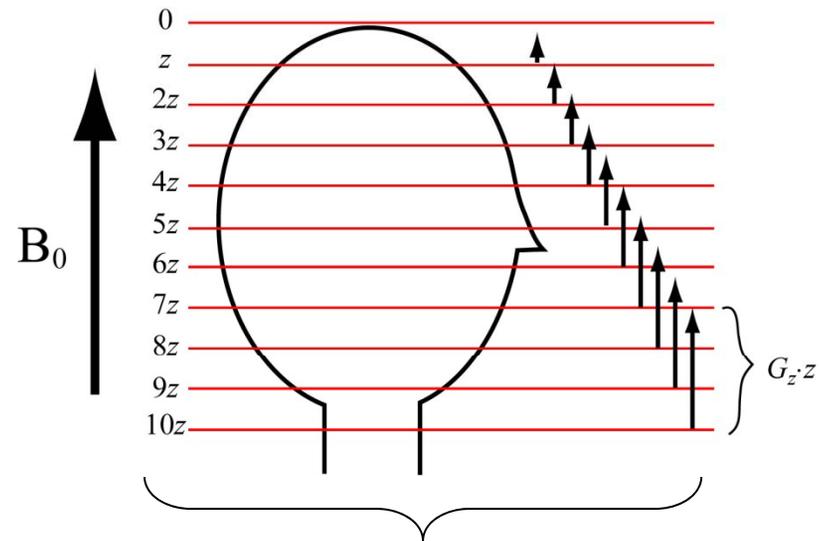
$$\omega = \gamma B$$

Temos que “arranjar um jeito” das frequências de precessão dependerem das posições onde os núcleos de ^1H se encontram, ou seja, fazer com que o campo magnético experimentados por cada núcleo varie com a sua posição.

Gradientes de Campo Magnético



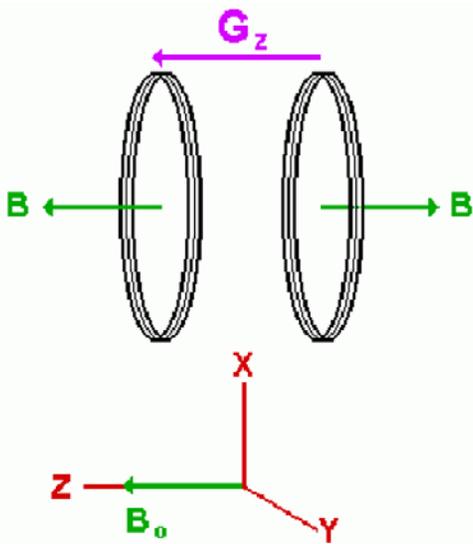
$$\omega(x) = \gamma(B_0 + G_x \cdot x)$$



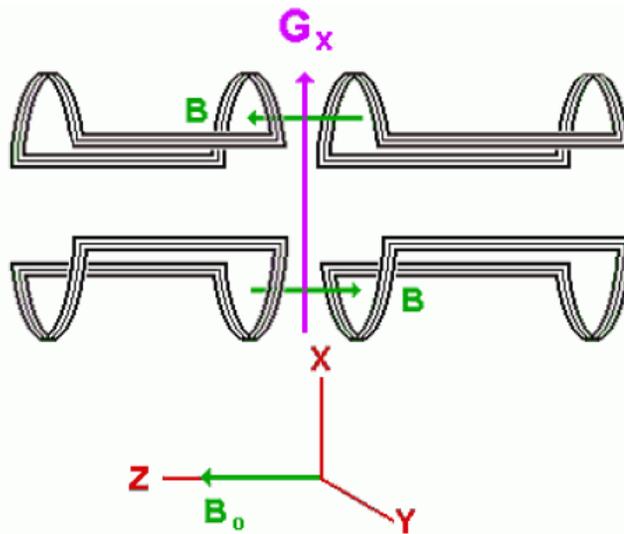
$$\omega(z) = \gamma(B_0 + G_z \cdot z)$$

Com a aplicação de gradientes de campo magnético é possível fazer a frequência de precessão depender da posição de forma conhecida.

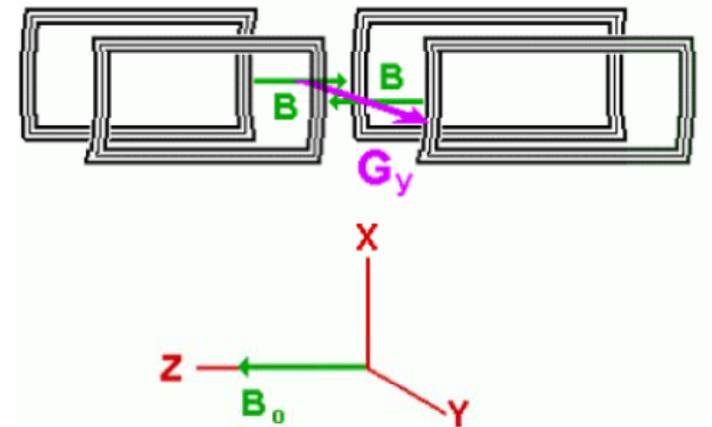
Bobinas para Geração de Gradientes de Campo Magnético



$$\omega(x) = \gamma(B_0 + G_x \cdot x)$$

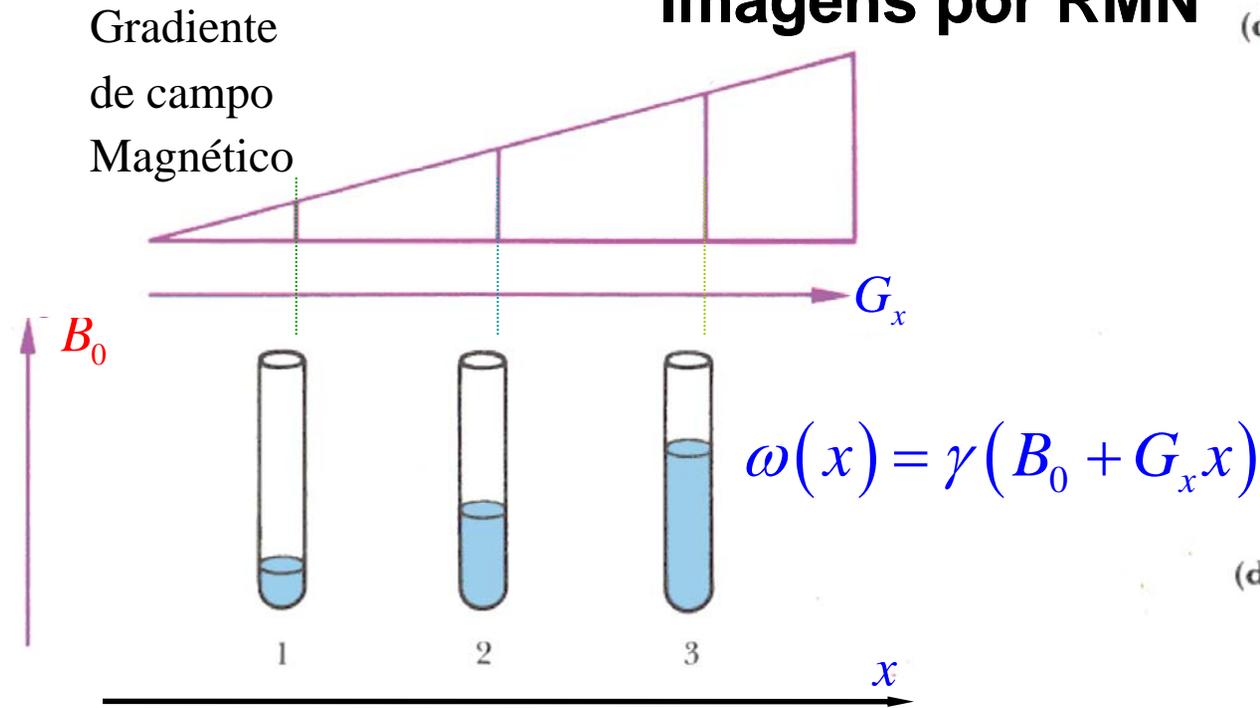


$$\omega(y) = \gamma(B_0 + G_y \cdot y)$$



$$\omega(z) = \gamma(B_0 + G_z \cdot z)$$

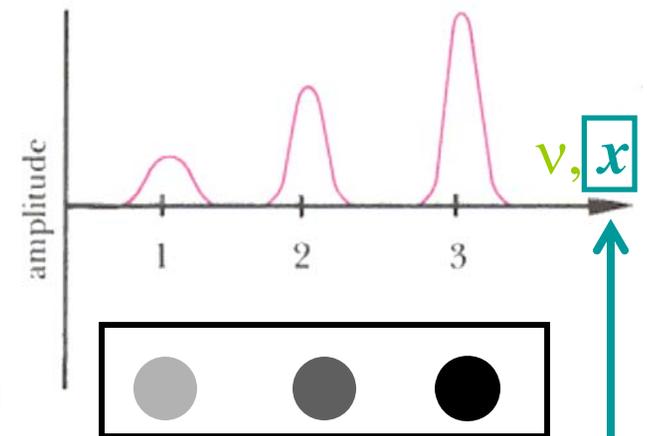
Imagens por RMN



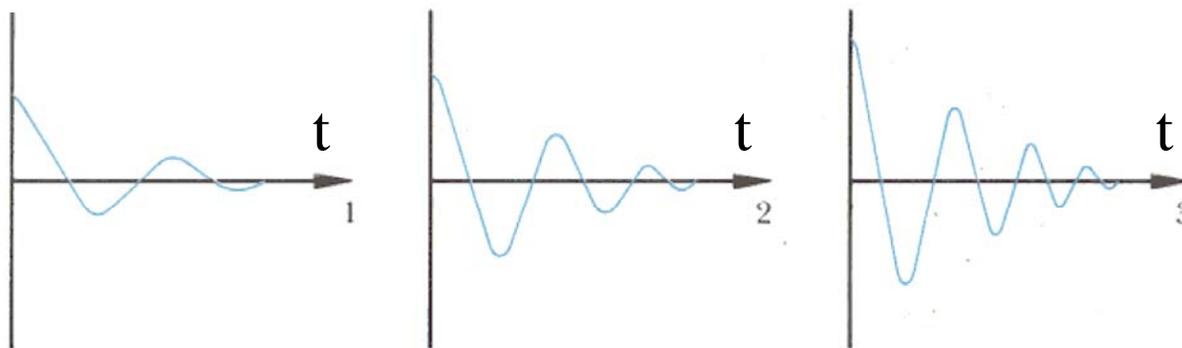
(c) fid composto



(d) espectro

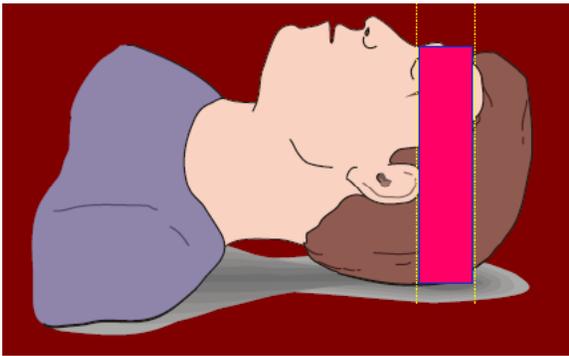


FID

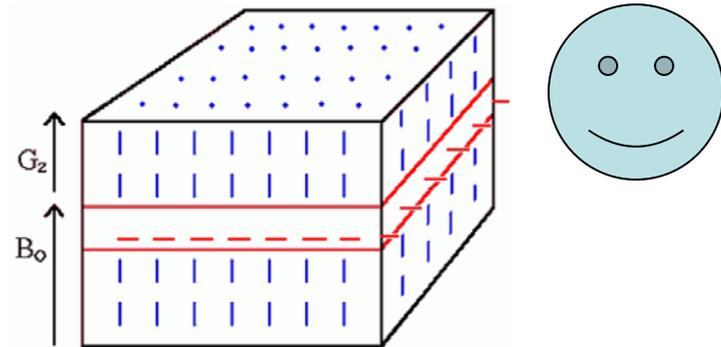


Seleção de Planos Tomográficos

O que queremos



Se conseguirmos

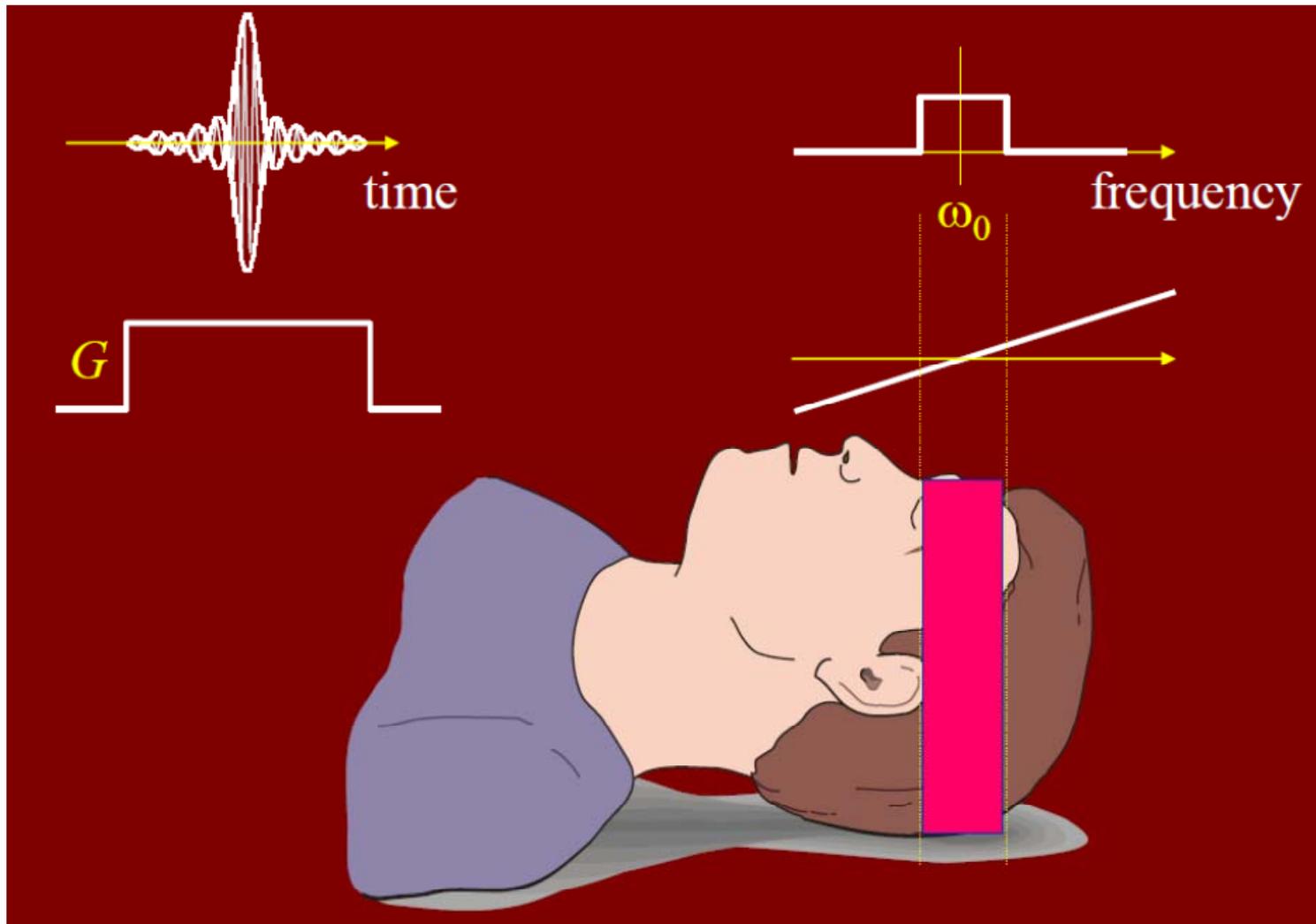


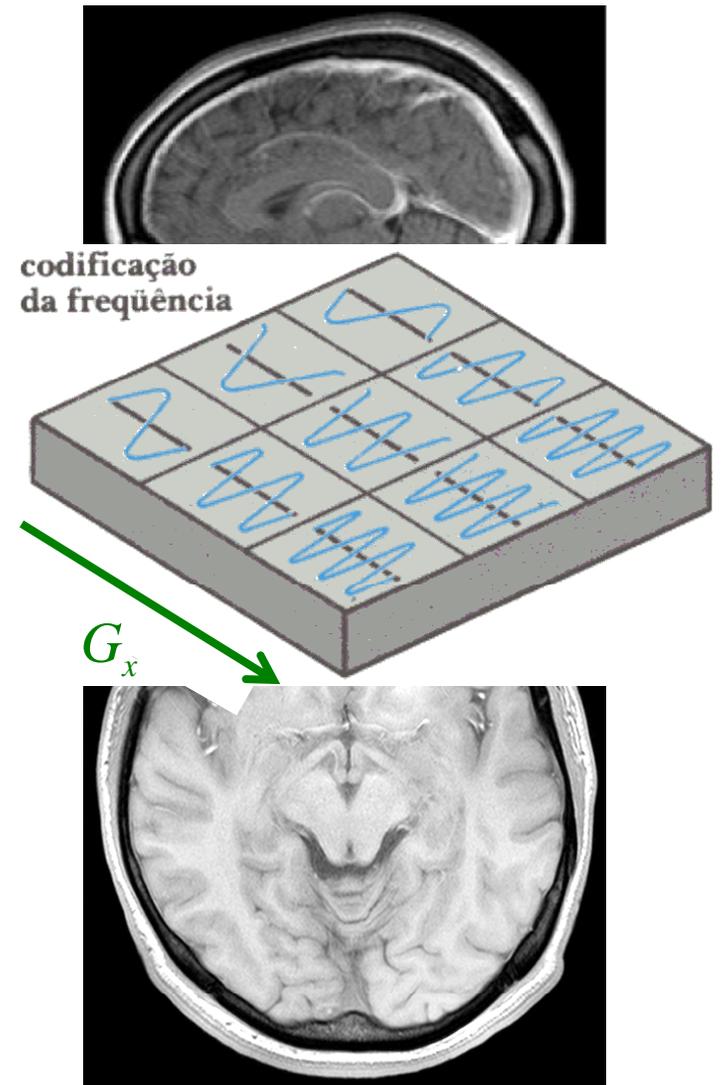
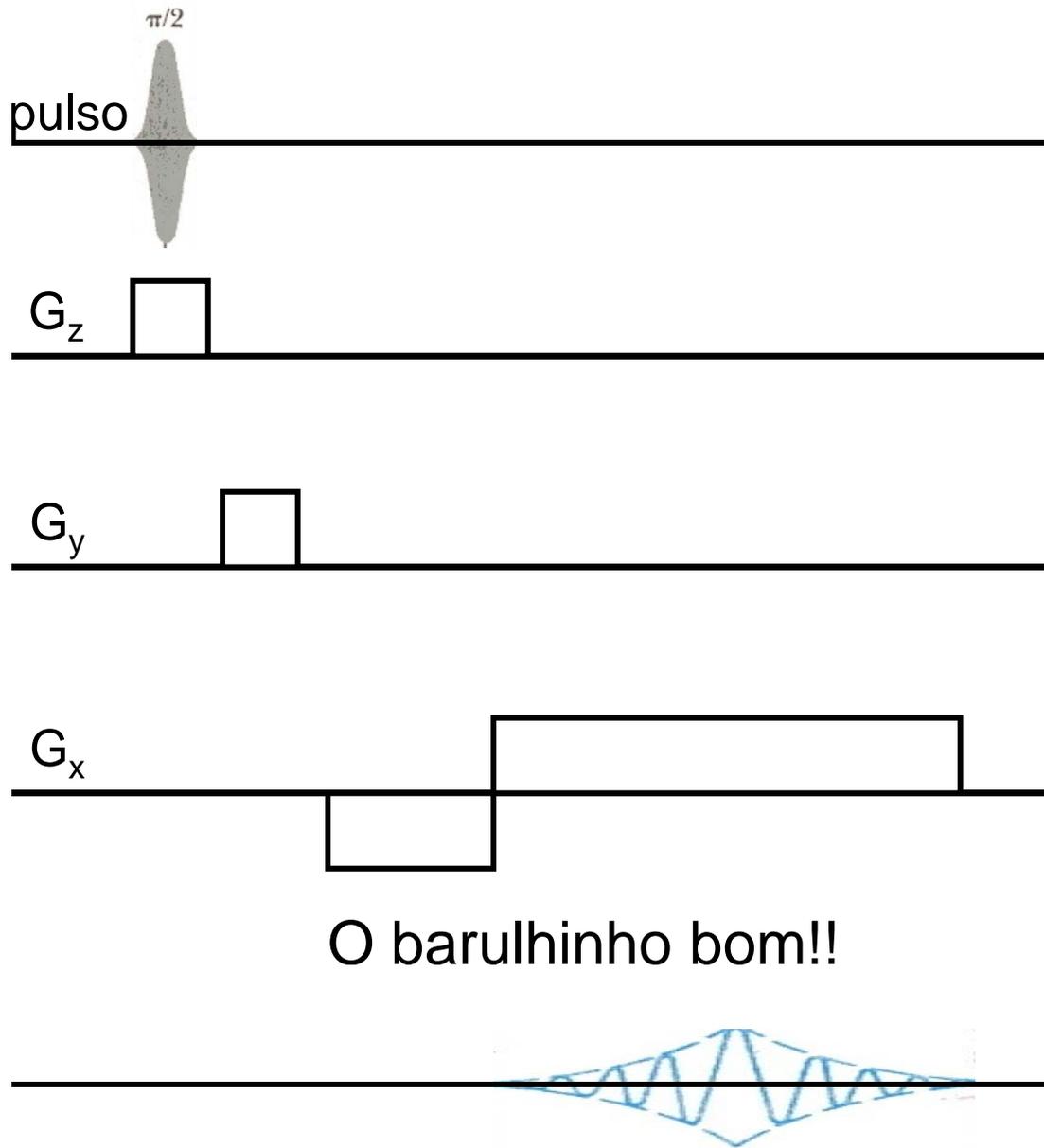
Mas como conseguir ?

Usamos uma propriedade básica da Transformada de Fourier



Seleção de Planos Tomográficos





Contraste por
Densidade de ^1H



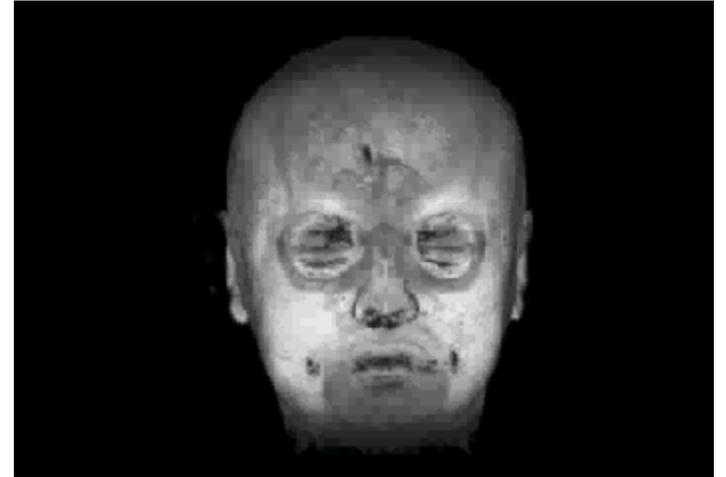
Neurinoma do nervo
acústico

Contraste por T_1



Joelho

Contraste por T_2

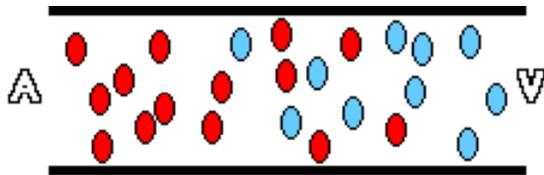


Angiografia

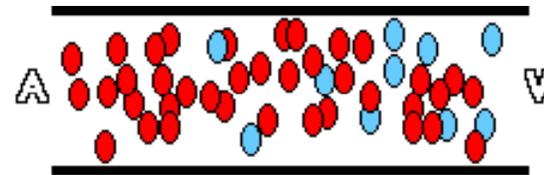


Princípio “muito básico” da imagem funcional

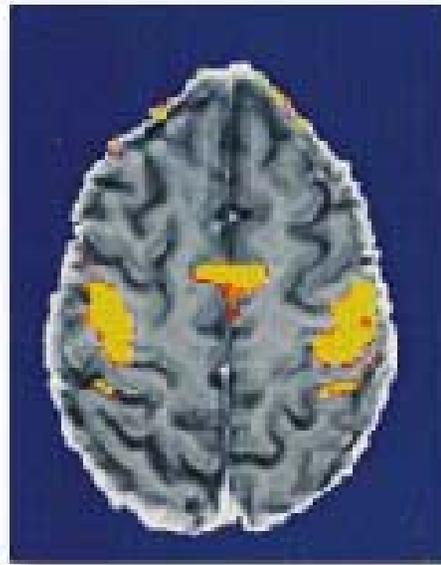
Fluxo de sangue normal



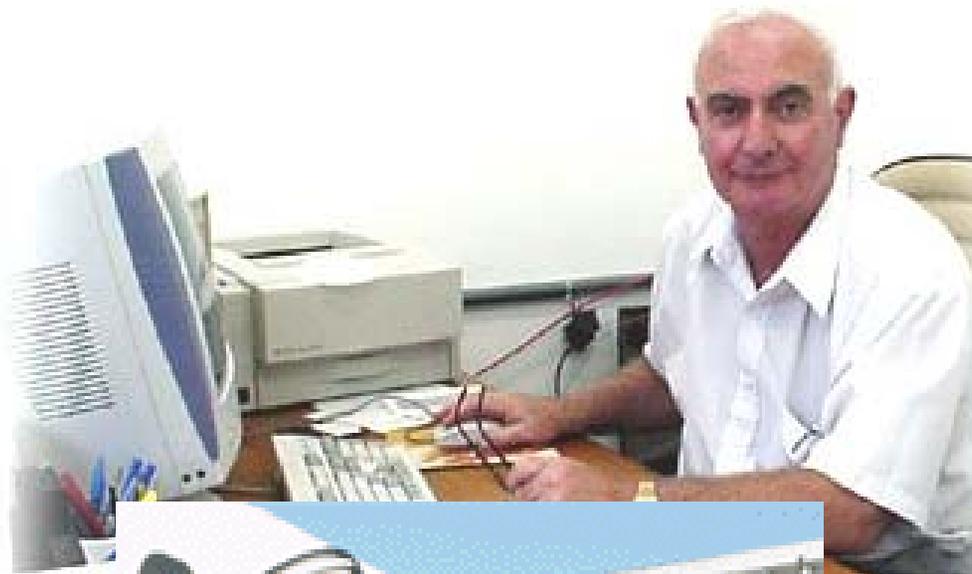
Fluxo de sangue alto



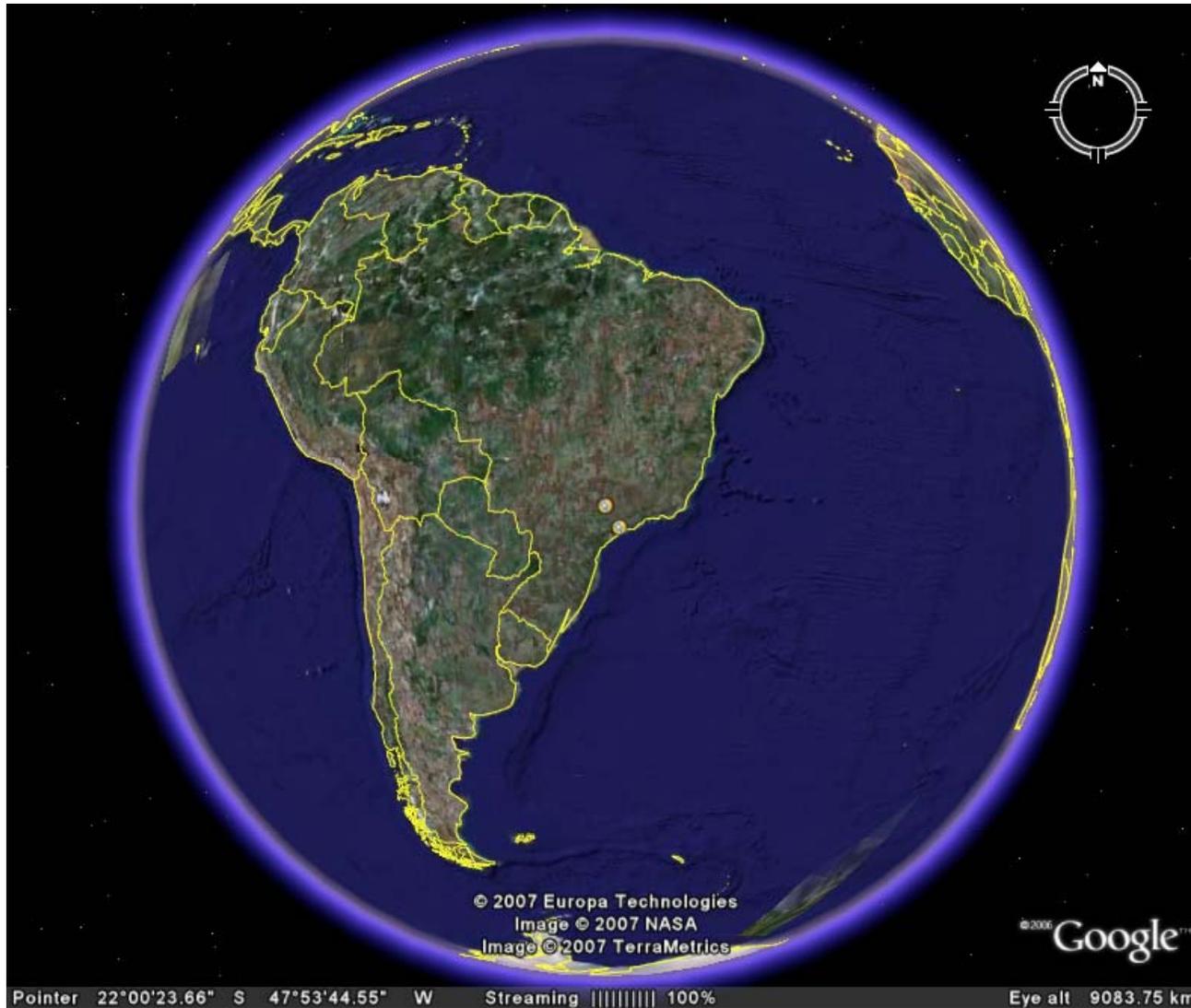
● oxihemoglobina
● desoxihemoglobina



Prof. Horácio C. Panepucci

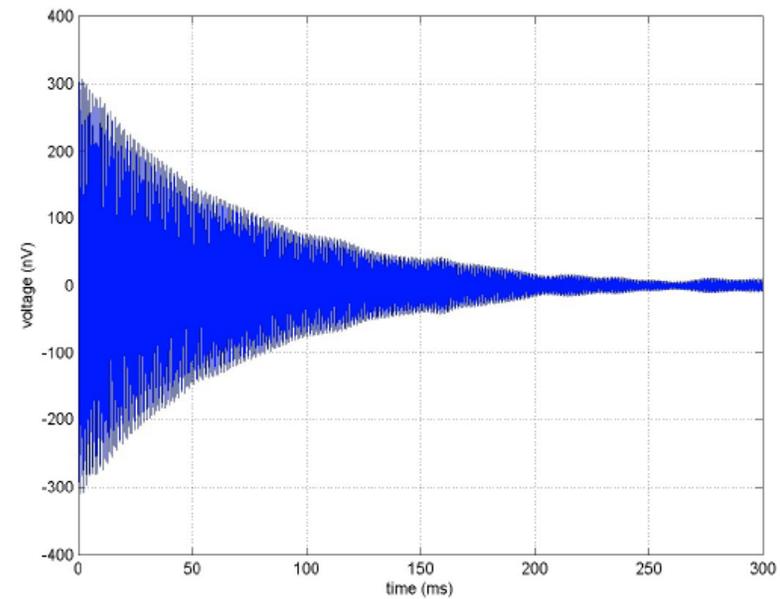
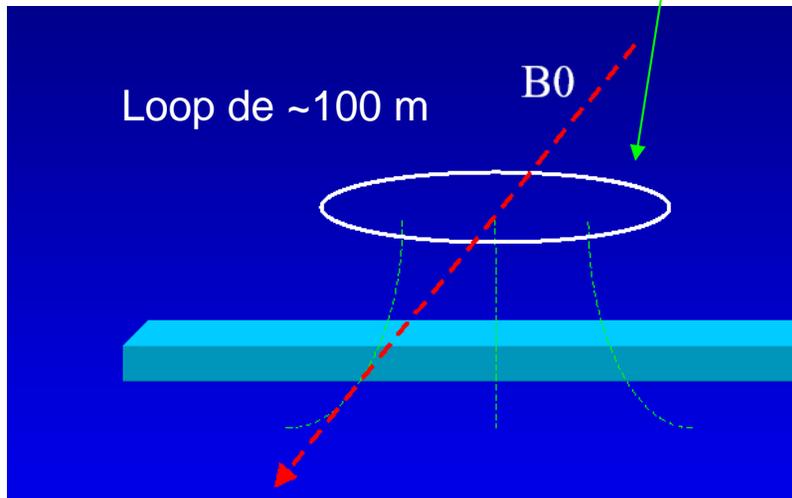


RMN com Magnetos Grandes



Perfilometria por RMN

RMN no Campo Terrestre



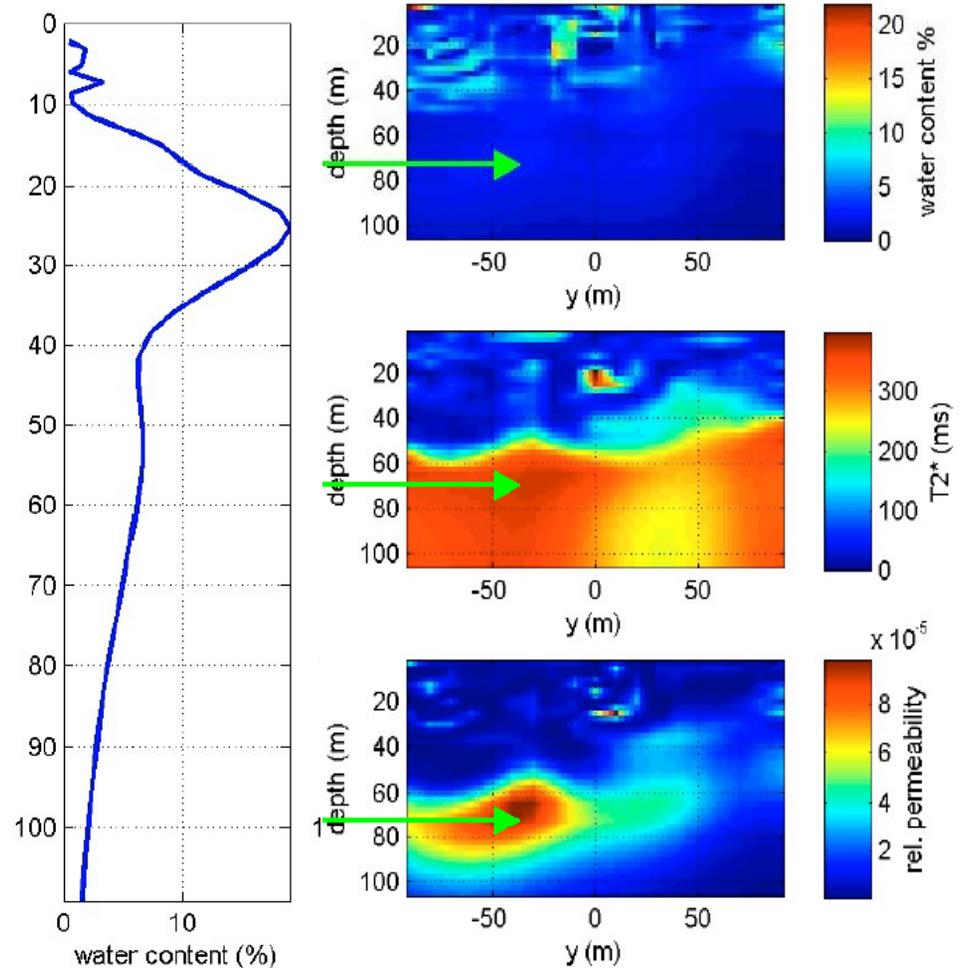
- Amplitude do sinal é proporcional a quantidade de água (porosidade efetiva)
- T_2 é proporcional ao diâmetro dos poros do aquífero
- Condutividade hidráulica depende de ambos T_2 e porosidade efetiva

Perfilometria por RMN

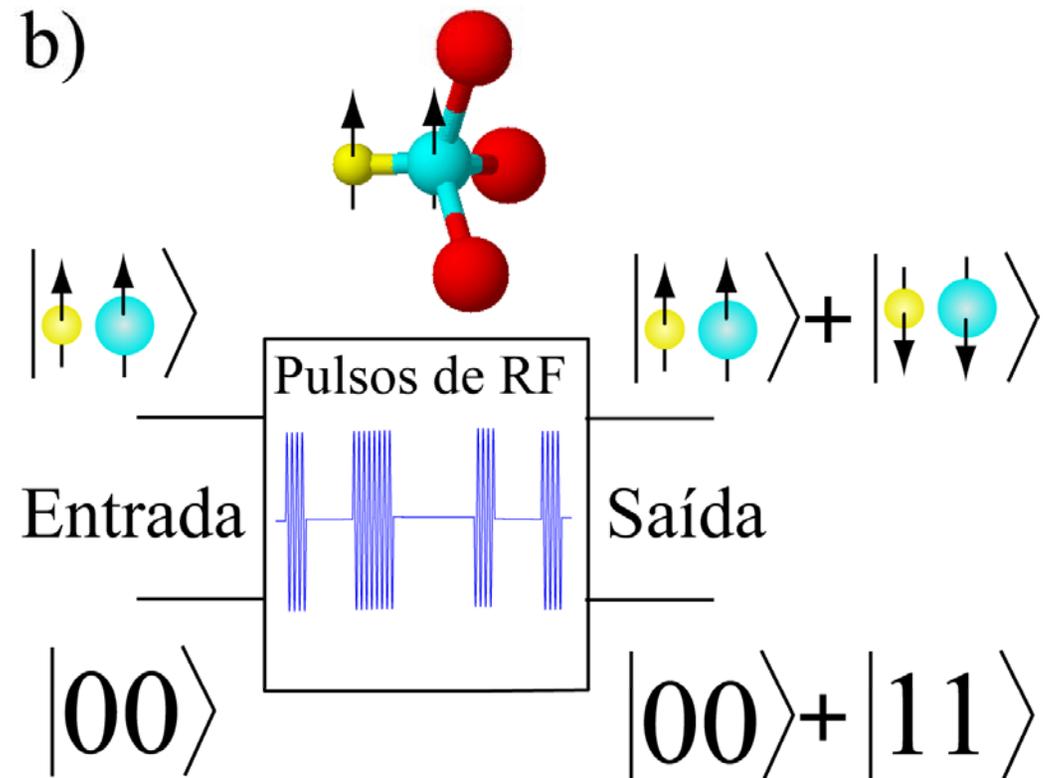
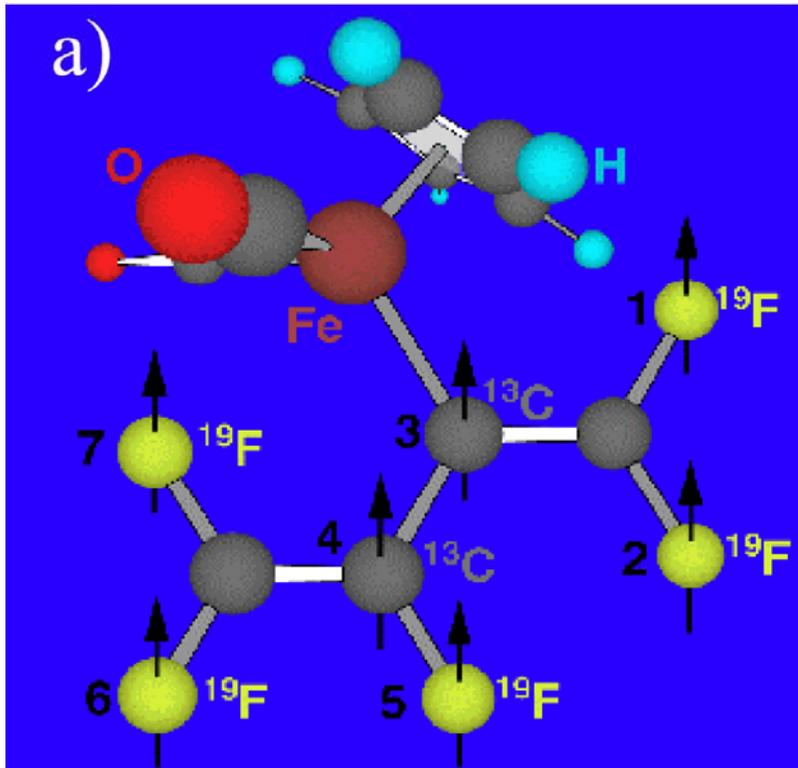
Baixo de conteúdo de água livre

Tamanhos de póros grandes (T_2 longo)

Região específica onde a condutividade hidráulica é máxima.



Informação Quântica via RMN



Informação Quântica

QIP Basis

1 Qubit Logical Operations

1 Qubit Quantum State $\Rightarrow |\Psi\rangle = \alpha|0\rangle + \beta|1\rangle \quad |\alpha|^2 + |\beta|^2 = 1$

Quantum Unitary Operations $\Rightarrow |\Psi\rangle \xrightarrow{U} |\Psi'\rangle \quad U \cdot U^\dagger = 1$

A quantum logical gate is a unitary quantum operation that transforms a quantum system in a controlled way

In NMR , quantum gates can be implemented by RF pulses or evolutions under nuclear spin interactions.

QIP Basis

Examples of 1 Qubit Logical Gates

- The NOT gate, X :

$$X \equiv \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$X \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \begin{bmatrix} \beta \\ \alpha \end{bmatrix}$$

Transform the state in its complementary

- The phase gate, S

$$S \equiv \begin{bmatrix} 1 & 0 \\ 0 & i \end{bmatrix}$$

$$S \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \begin{bmatrix} \alpha \\ i\beta \end{bmatrix}$$

Change the relative phase of the qubits by $\pi/2$.

QIP Basis

Examples of 1 Qubit Logical Gates

- The HADAMARD gate, H :

$$H \equiv \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$$

$$H|0\rangle = \frac{1}{\sqrt{2}} (|0\rangle + |1\rangle) \quad \text{e} \quad H|1\rangle = \frac{1}{\sqrt{2}} (|0\rangle - |1\rangle)$$

The Hadamard Gate executes a Walsh Hadamard transformation to create a superposition of states.

QIP Basis

Two Qubits Quantum states

$$|\Psi\rangle = \alpha|00\rangle + \beta|01\rangle + \gamma|10\rangle + \delta|11\rangle$$

$$|\Psi\rangle = \begin{bmatrix} \alpha \\ \beta \\ \gamma \\ \delta \end{bmatrix} \quad \langle\Psi| = [\alpha \quad \beta \quad \gamma \quad \delta]$$

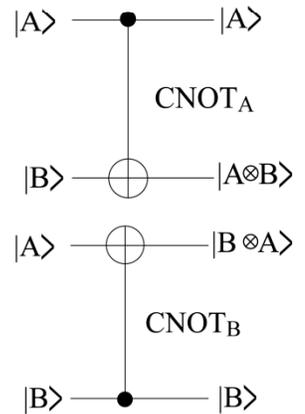
Logical Operations can act in a single or in both qubits.

QIP Basis

The CNOT Logical Gate

$$CNOT_a \begin{bmatrix} |00\rangle \\ |01\rangle \\ |10\rangle \\ |11\rangle \end{bmatrix} = \begin{bmatrix} |00\rangle \\ |01\rangle \\ |11\rangle \\ |10\rangle \end{bmatrix}$$

$$CNOT_b \begin{bmatrix} |00\rangle \\ |01\rangle \\ |10\rangle \\ |11\rangle \end{bmatrix} = \begin{bmatrix} |00\rangle \\ |11\rangle \\ |10\rangle \\ |01\rangle \end{bmatrix}$$



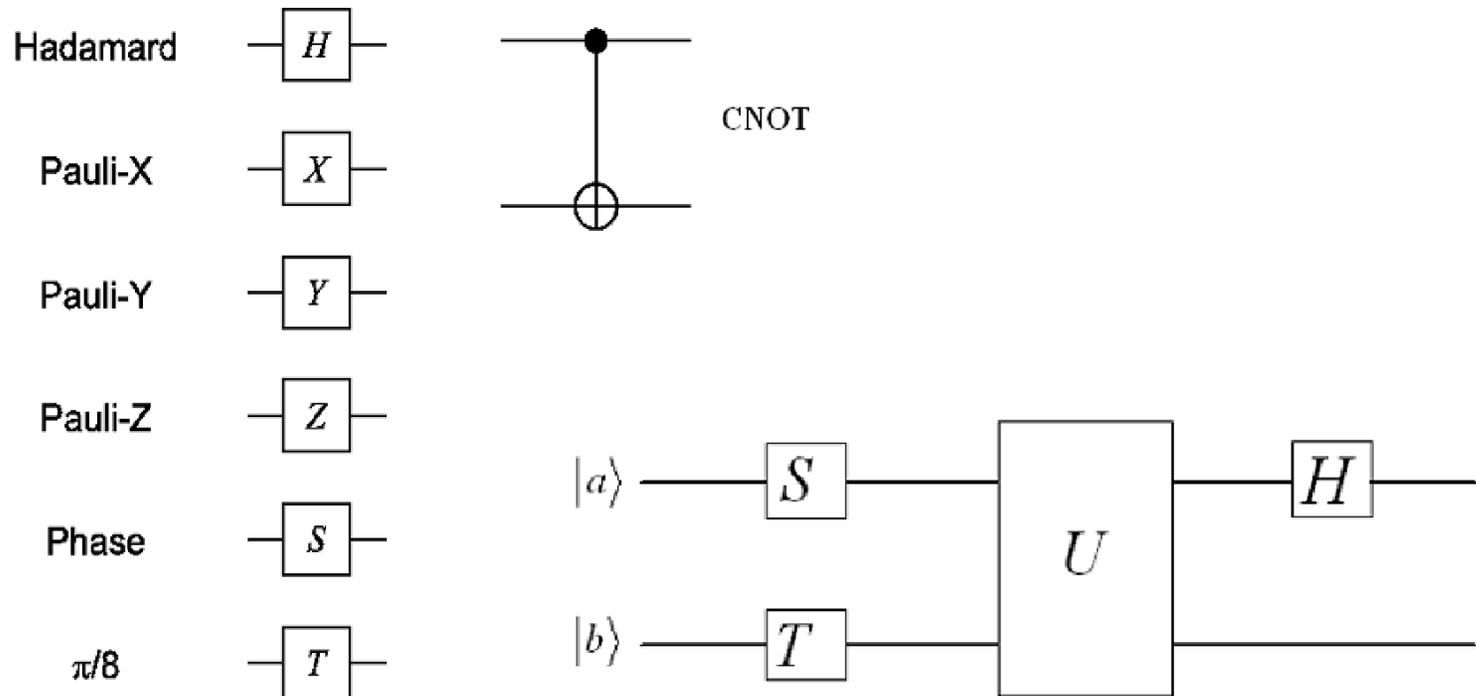
$|ab\rangle$

$$CNOT_a = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

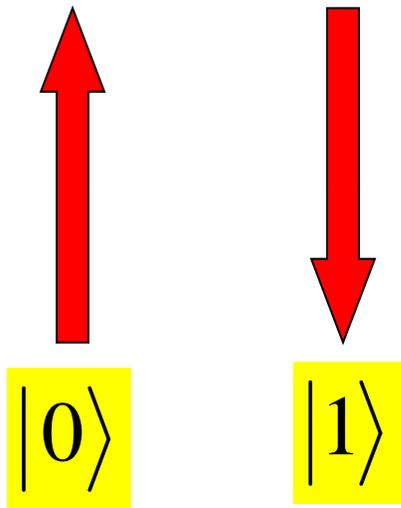
$$CNOT_b = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

QIP Basis

Representation of Logical Gate

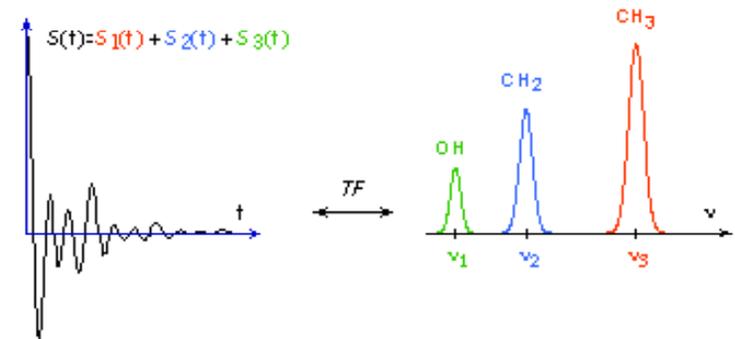
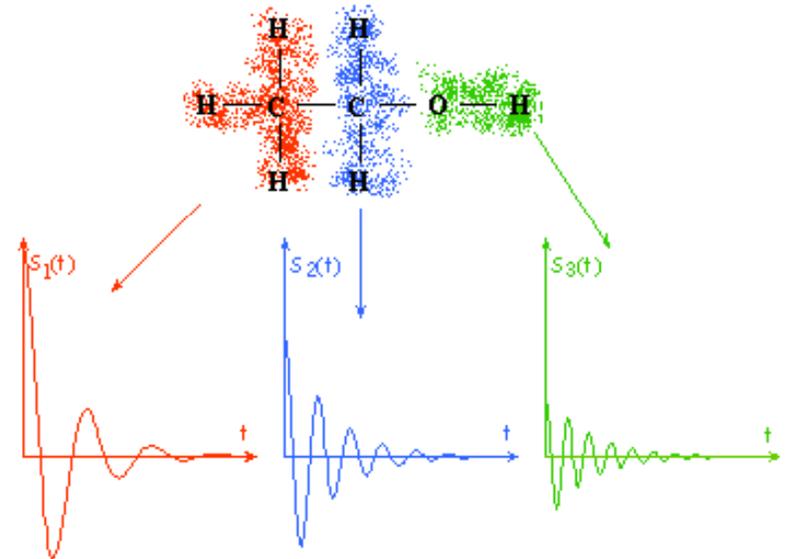


NMR Chemical Shift



$$\omega = -\gamma(B_{ind}^i + B)$$

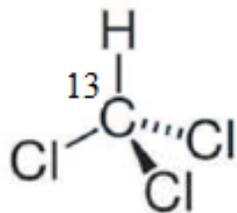
$$H = -\hbar\omega_L^A I_Z - \hbar\omega_L^B S_Z$$



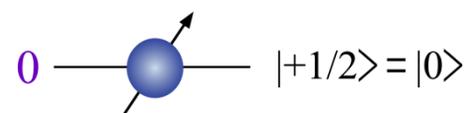
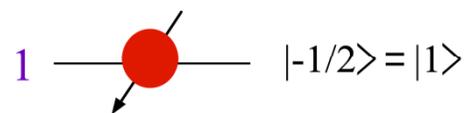
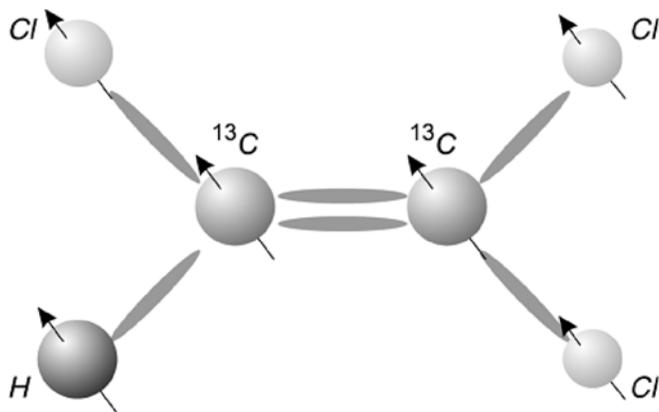
NMR QIP – The Qubit

Physical System: Coupled Spins 1/2 in solution or solid crystals

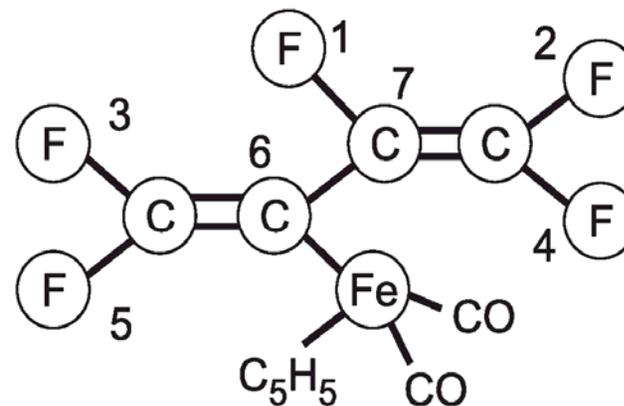
Two Qubit Molecule



Three Qubit Molecule

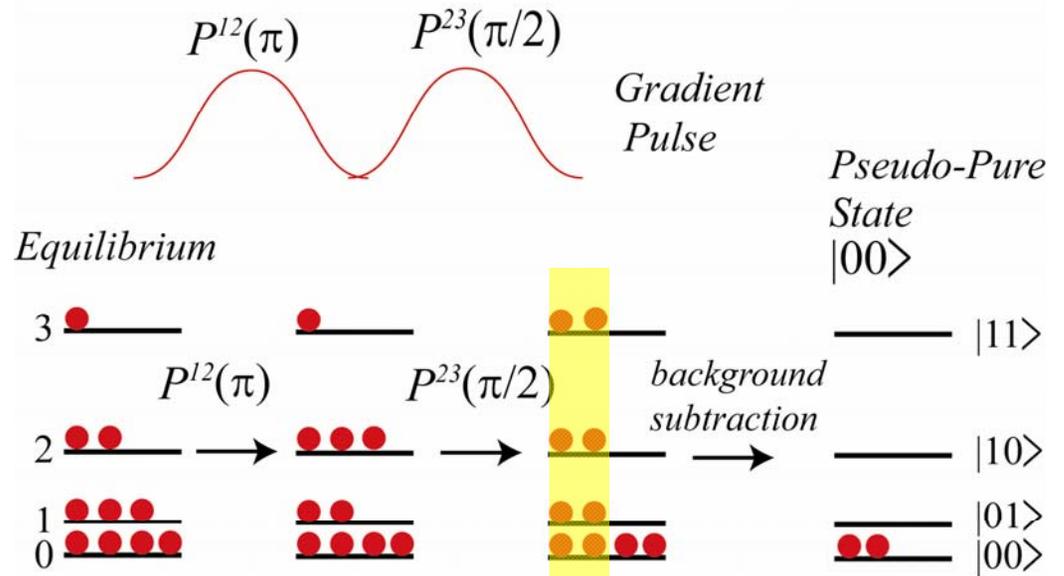


Seven Qubit Molecule



NMR QIP – State Preparation

Pictorial View:



Quantum view:

Pseudo-pure states

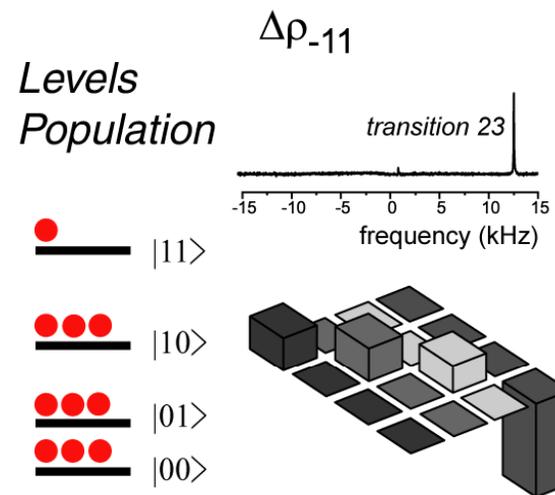
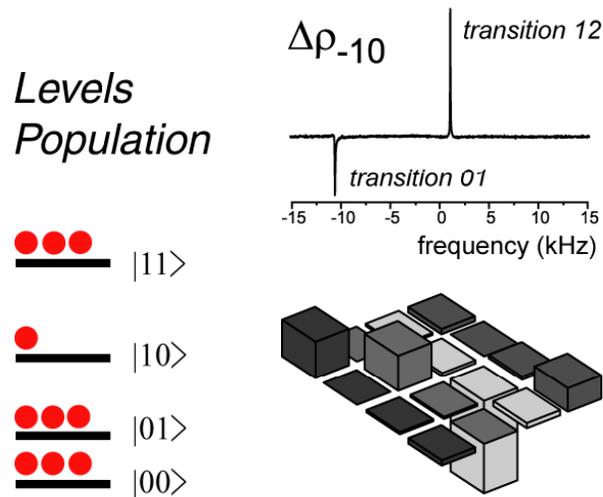
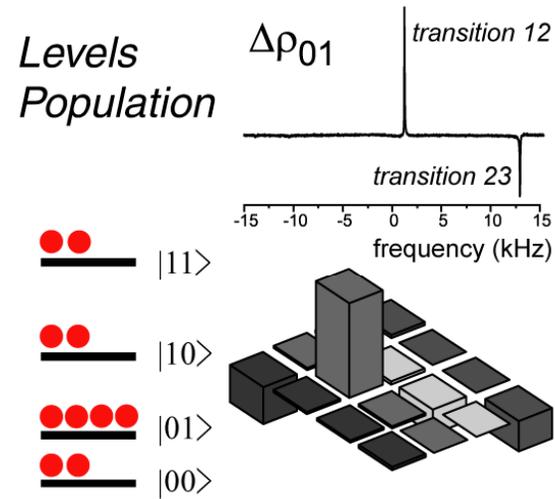
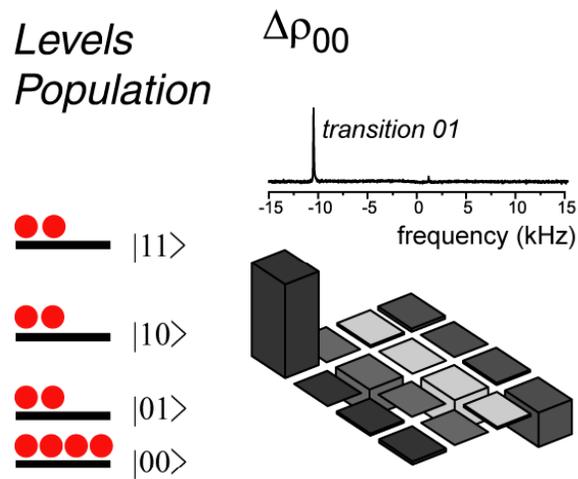
Not suitable for transformation/de

$$\bar{\rho} = \frac{1}{2^N} (1 - q) \mathbb{1}_{2^N} + q |\psi\rangle \langle \psi|$$

$$\bar{\rho} = \frac{1}{M} \sum_{\mu=1}^M U_{\mu} \rho_{eq} U_{\mu}^{\dagger}$$

RF and magnetic field
gradient pulses

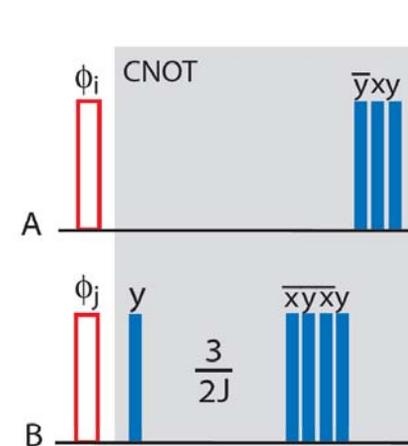
NMR QIP – Pseudo-Pure States



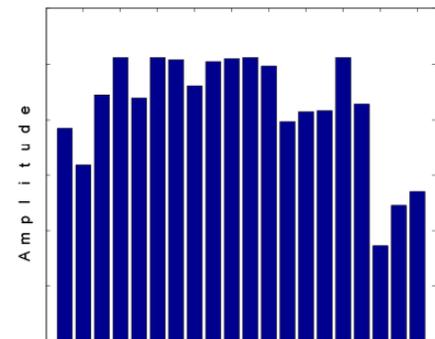
NMR QIP – Unitary transformations

$$U = \prod_{i=1}^n U_i$$

**Discrete
Pulse sequence**

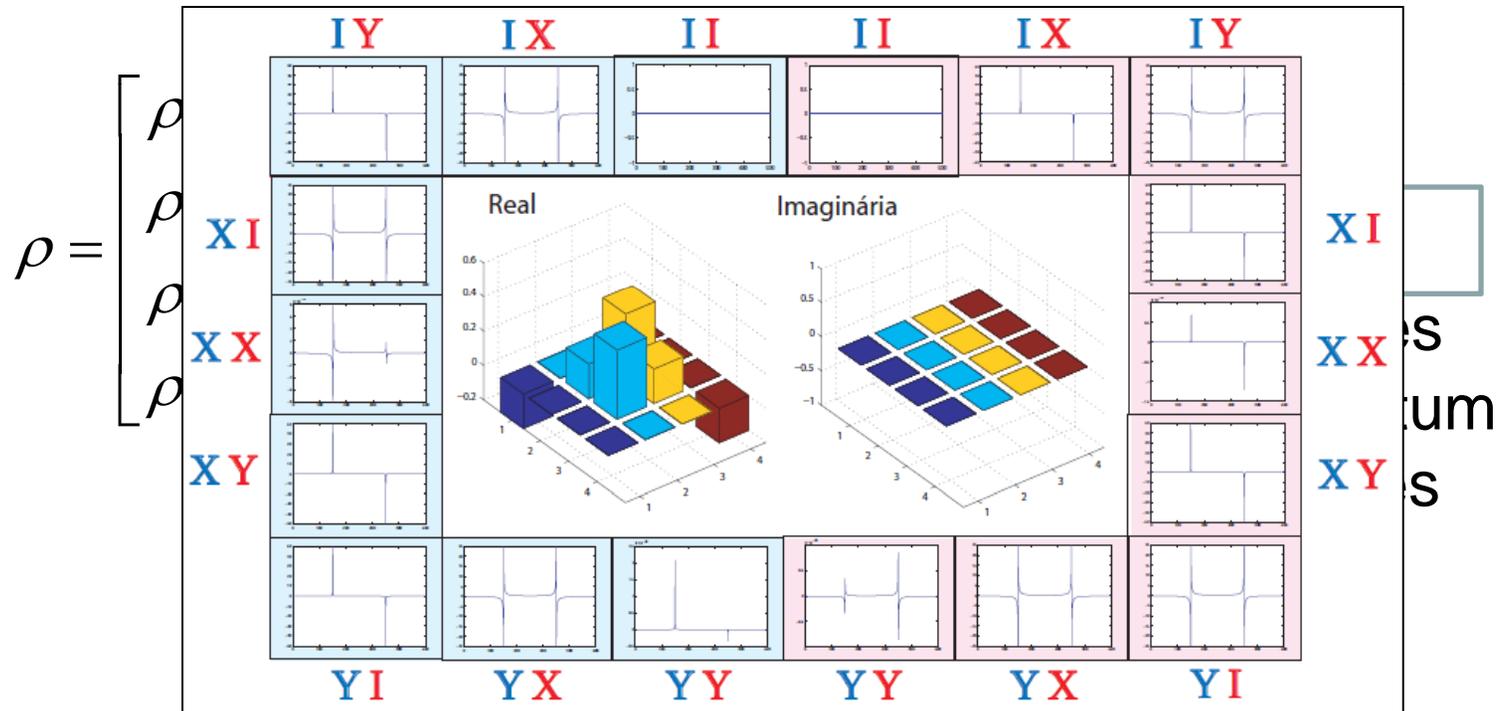


**Numerically
Optimized
Pulse sequence
(Optimal control:
Strongly
modulated pulse**



NMR QIP Read Out

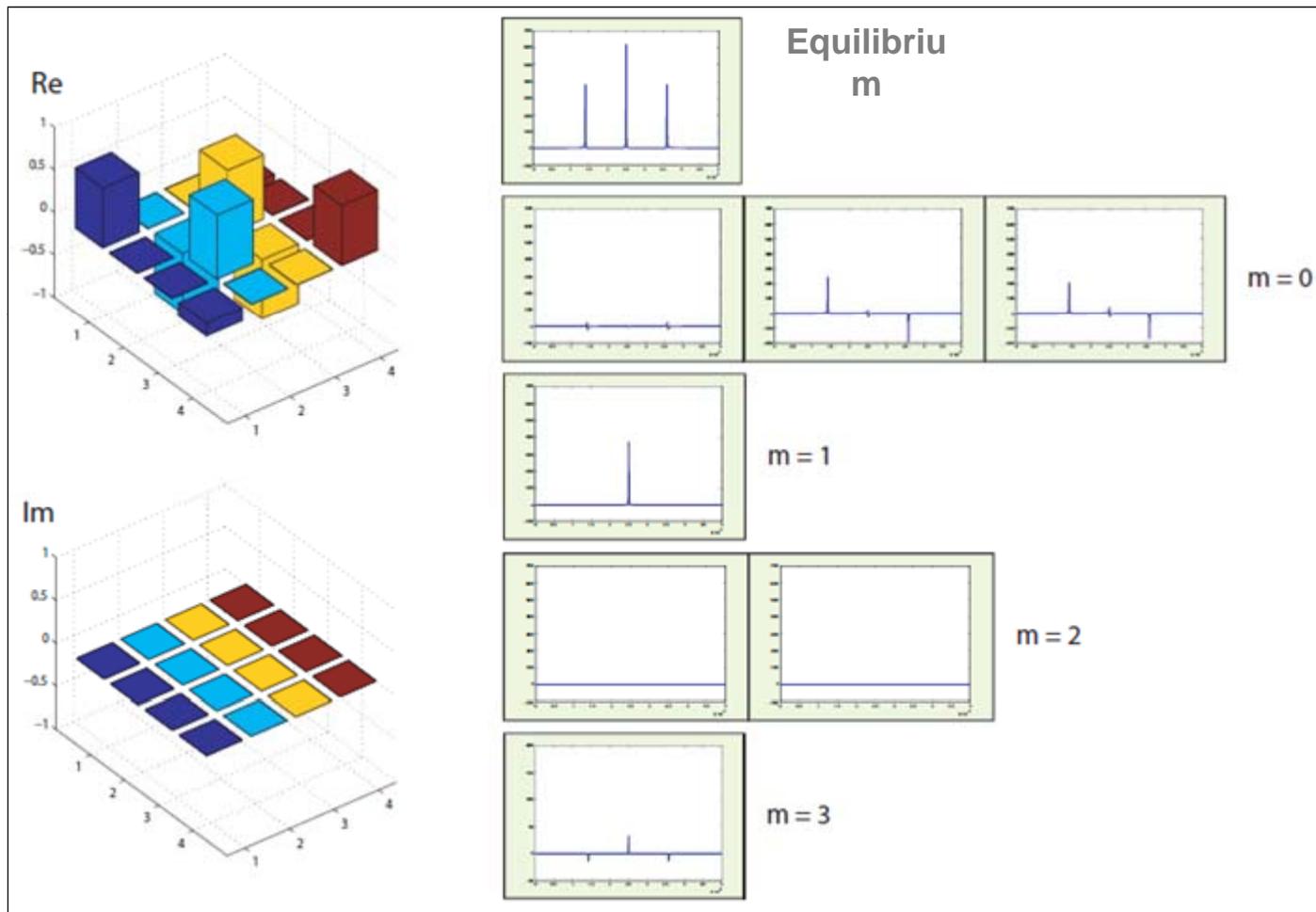
- Quantum State Tomography (QST)*:
 - 2 spins 1/2



*Nielsen, M. A.; Chuang, I.L. *Quantum computation and quantum information*. Cambridge: Cambridge University Press, 2000.

NMR QIP Read Out

- Spin 3/2



*Teles, J. and *et al.* Quantum state tomography for quadrupolar nuclei using global rotations of the spin system. *Journal of Chemical Physics*, v. 126, p. 154506, 2007.

NMR QIP Example

$$CNOT_A - \text{Pulse Seq: } (\pi)_x^{23}$$

$$U_{CNOT_A} |00\rangle = P_x^{23}(\pi) |00\rangle = |00\rangle$$

$$U_{CNOT_A} |01\rangle = P_x^{23}(\pi) |01\rangle = |01\rangle$$

$$U_{CNOT_A} |10\rangle = P_x^{23}(\pi) |10\rangle = i|11\rangle$$

$$U_{CNOT_A} |11\rangle = P_x^{23}(\pi) |11\rangle = i|10\rangle$$

$$CNOT_B - \text{Pulse Seq: } (\pi)_x^{12} - (\pi)_x^{23} - (\pi)_x^{12}$$

$$U_{CNOT_B} |00\rangle = P_x^{12}(\pi) P_x^{23}(\pi) P_x^{12}(\pi) |00\rangle = |00\rangle$$

$$U_{CNOT_B} |01\rangle = P_x^{12}(\pi) P_x^{23}(\pi) P_x^{12}(\pi) |01\rangle = -|11\rangle$$

$$U_{CNOT_B} |10\rangle = P_x^{12}(\pi) P_x^{23}(\pi) P_x^{12}(\pi) |10\rangle = -|10\rangle$$

$$U_{CNOT_B} |11\rangle = P_x^{12}(\pi) P_x^{23}(\pi) P_x^{12}(\pi) |11\rangle = -|01\rangle$$

PHYSICAL REVIEW A 69, 042322 (2004)

Quantum-state tomography for quadrupole nuclei and its application on a two-qubit system

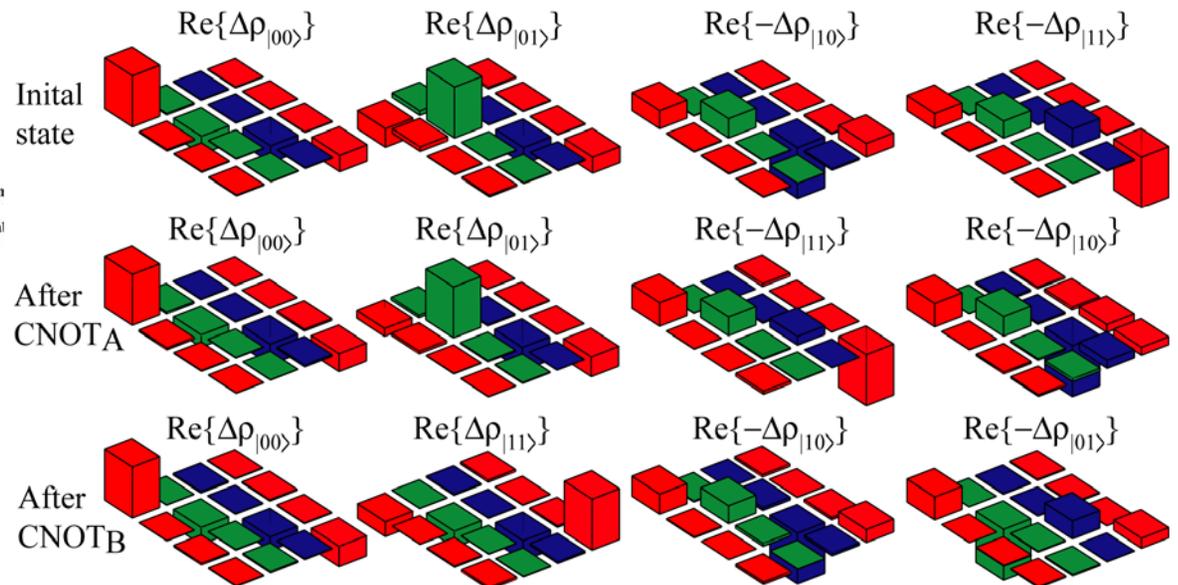
F. A. Bonk,¹ R. S. Sarthour,^{2*} E. R. deAzevedo,^{1,†} J. D. Bulnes,² G. L. Mantovani,¹ J. C. C. Freitas,³ T. J. Bonagami,
A. P. Guimarães,² and I. S. Oliveira²

¹Instituto de Física de São Carlos, Universidade de São Paulo, P.O. Box 369, São Carlos 13560-970, SP, Brazil

²Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud 150, Rio de Janeiro 22290-180, RJ, Brazil

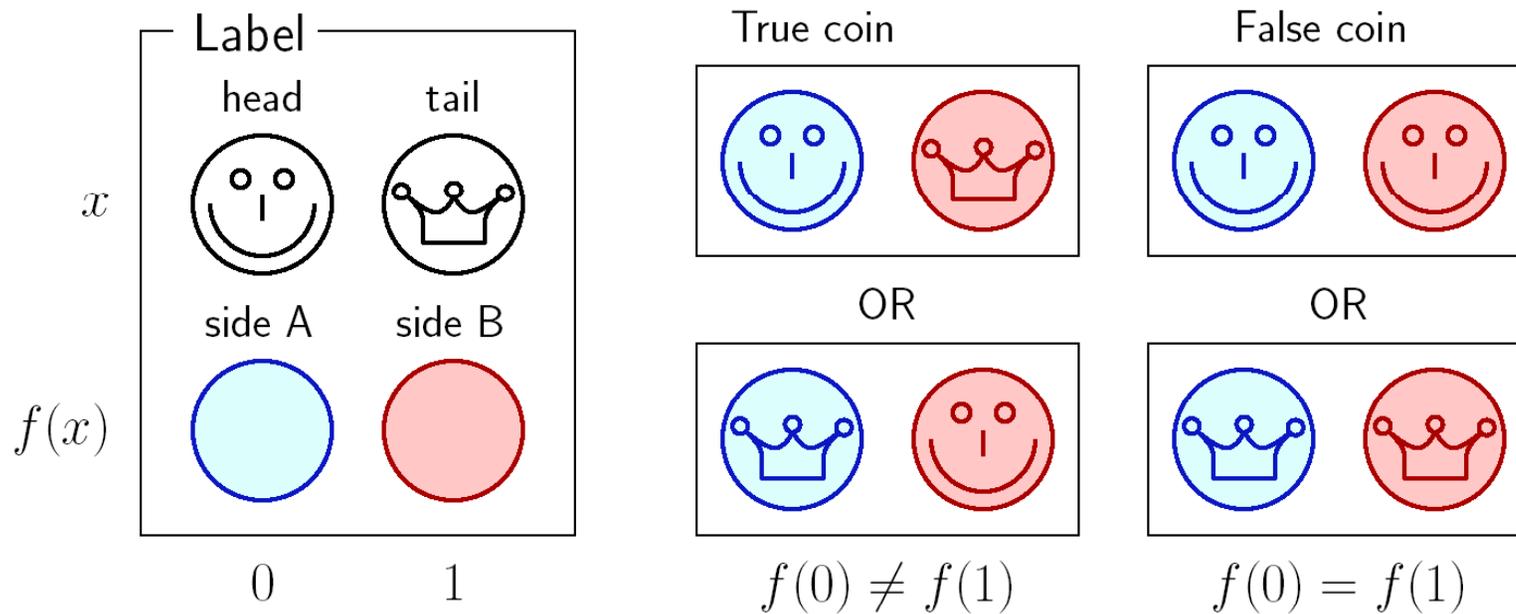
³Departamento de Física, Universidade Federal do Espírito Santo, Vitória 29060-900, ES, Brazil

(Received 13 October 2003; revised manuscript received 11 December 2003; published 29 April 2004)

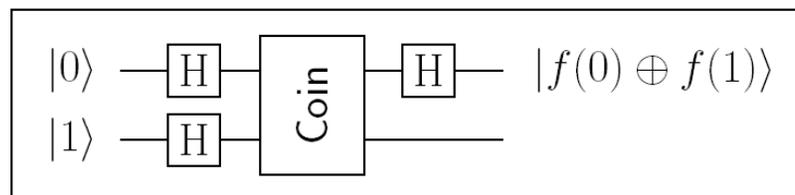


NMR QIP Example

Deutsch algorithm



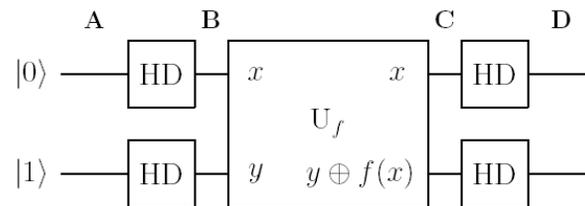
Quantum Algorithm



NMR QIP Example

Deutsch algorithm

Circuit:



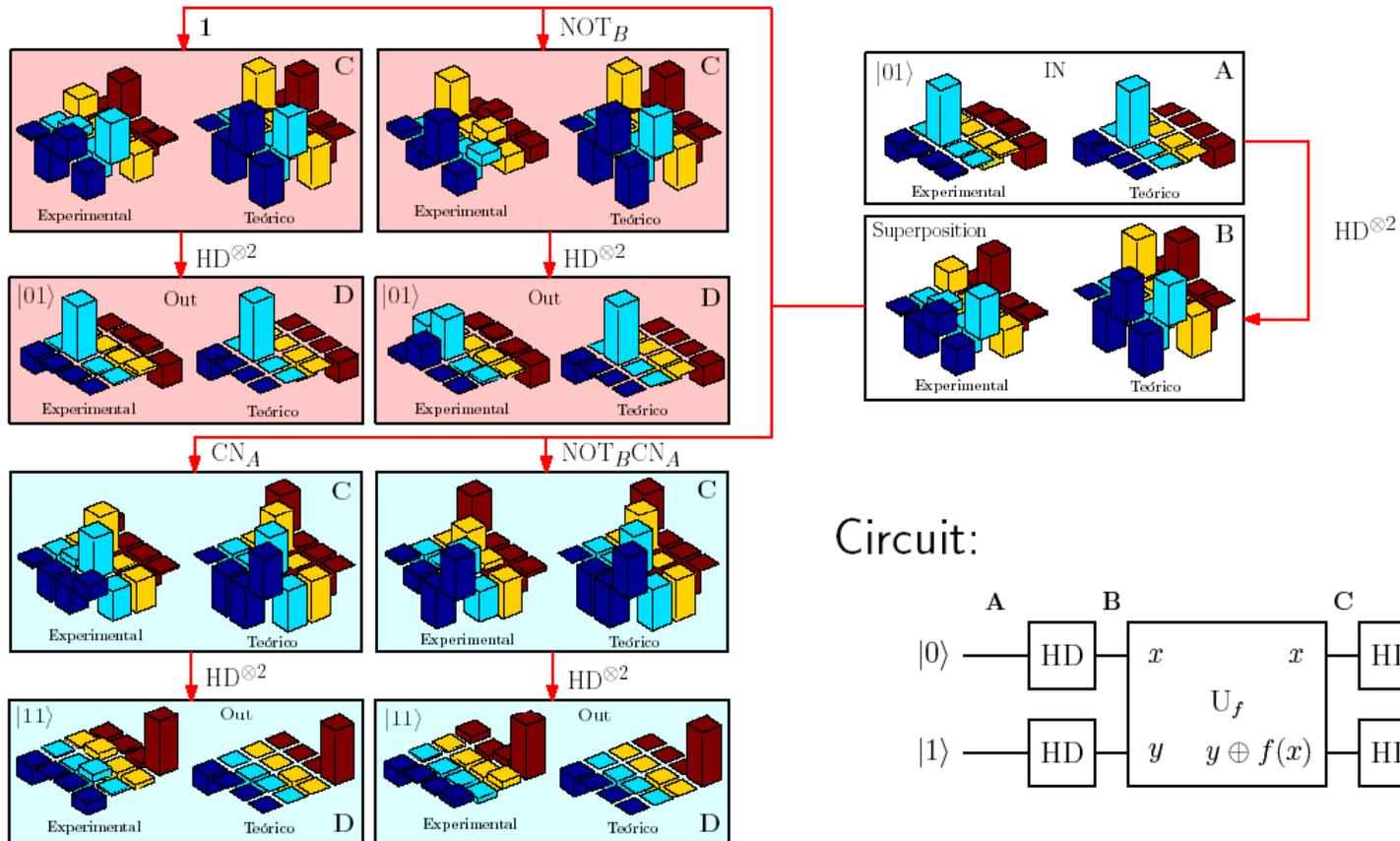
Numerical properties:

	Gate U_f	$\langle F \rangle$	σ_F	Duration (μs)	Segments
	$HD^{\otimes 2}$	0,990	0,004	152,51	5
constant \rightarrow	NOT_B	0,992	0,004	139,94	5
balanced $\left\{$	CN_A	0,993	0,003	162,35	5
	$NOT_B CN_A$	0,993	0,003	165,80	5

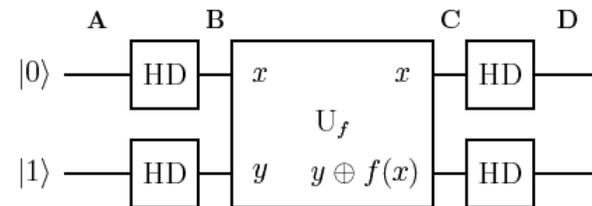
NMR QIP Example

Quantum computation experiments

Deutsch algorithm



Circuit:



Agradecimentos:

Estudantes e pós-docs do **L**aboratório de **R**MN para **M**ateriais **O**rgânicos - **LARMOR** (Oigres Bernardinelli, Marcio Cobo, Isabela Almeida, Gregório Faria, Fabiana Diulk)

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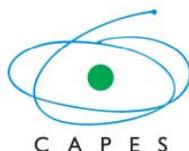
IFSC-USP

Bernhard Gross

Grupo de
Polímeros



TECHNISCHE
UNIVERSITÄT
DARMSTADT



DAAD INTERCÂMBIO ACADÊMICO
Brasil - Alemanha



Obrigada !!!

Why just NMR?

Because there is hardly another technique that is so informative for so many different types of applications, and because there is no other technique that provides so much fun.

Richard Ernst