Métodos de RMN no estado sólido

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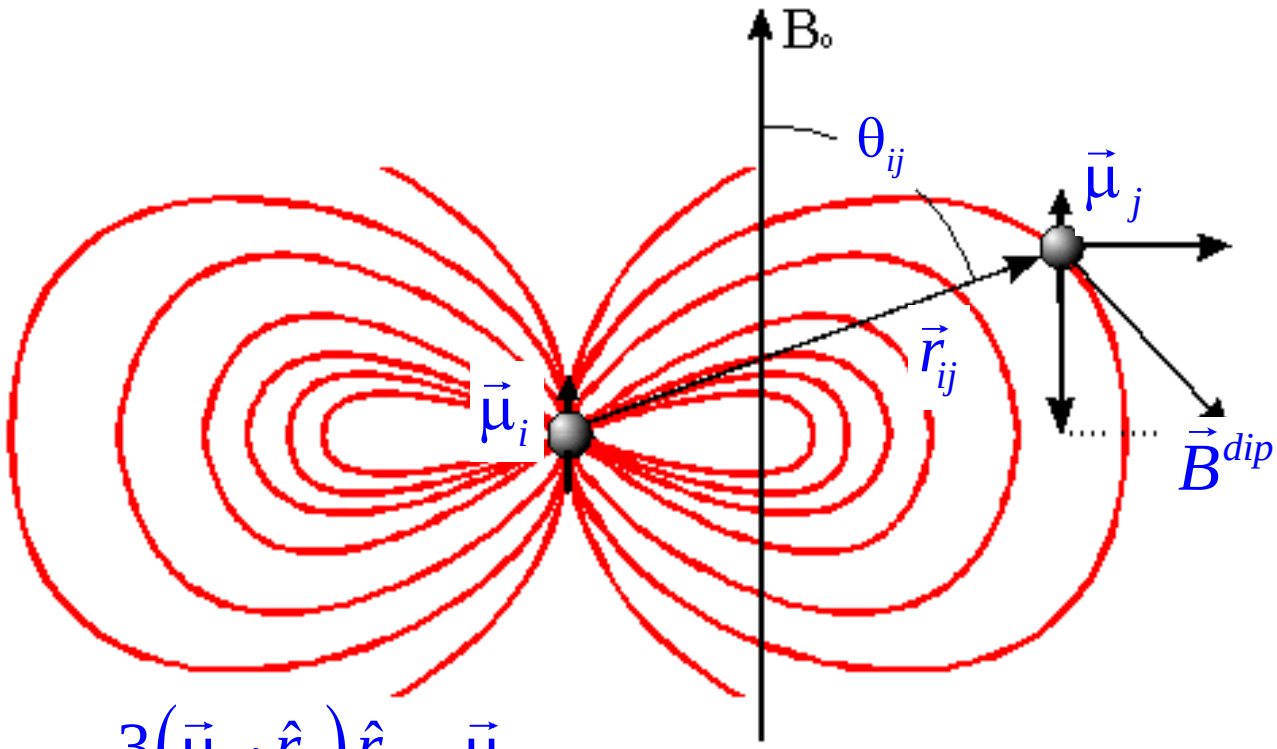
Sumário

- Interações de spin nuclear:
  - Interação dipolar direta.
    - Interação homonuclear e heteronuclear.
    - Espectros de pó.
  - Acoplamento escalar (J)

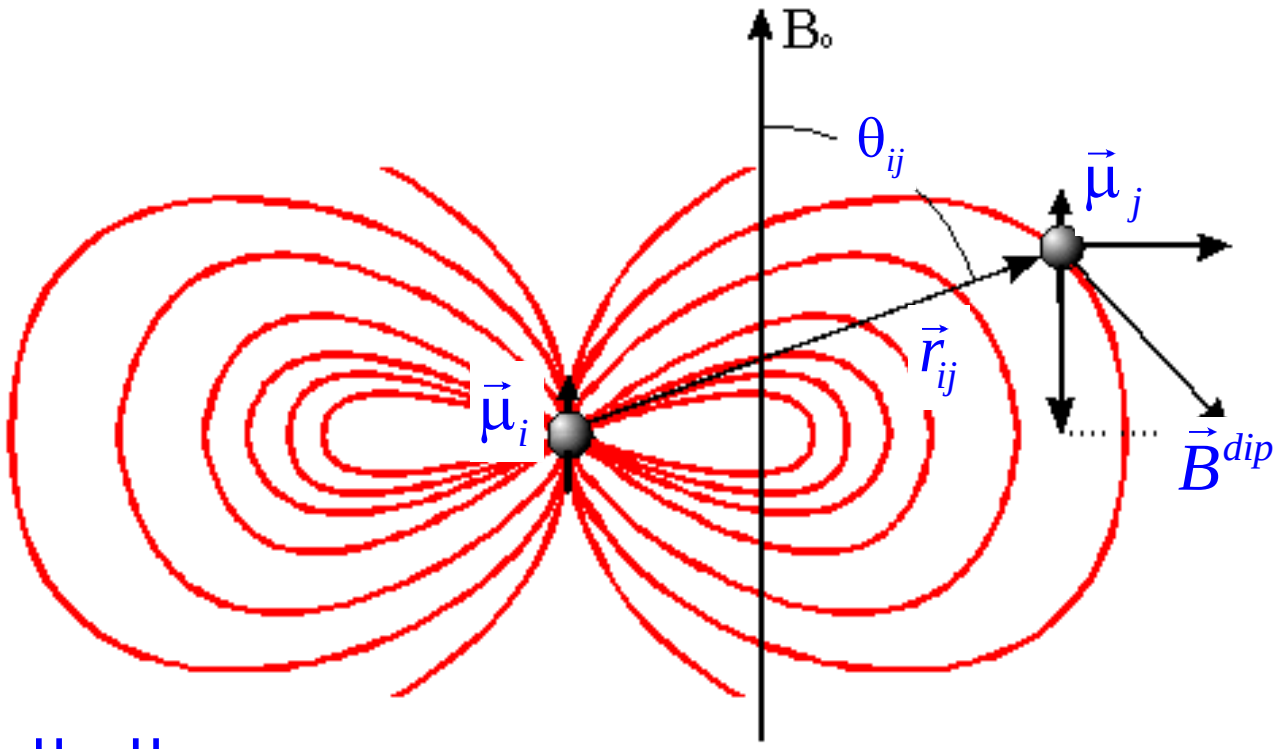
Interação dipolar internuclear



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

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 internuclear

$$\vec{B}^{dip} = \frac{\mu_0}{4\pi}\frac{3(\vec{\mu}_S \cdot \hat{r})\hat{r} - \vec{\mu}_S}{r^3}$$

$$E_{dip} = -\vec{\mu}_I \cdot \vec{B}^{dip} = -\frac{\mu_0}{4\pi}\frac{3(\vec{\mu}_I \cdot \hat{r})(\vec{\mu}_S \cdot \hat{r}) - \vec{\mu}_I \cdot \vec{\mu}_S}{r^3}$$

$$H_{dip} = -\vec{\mu} \cdot \vec{B}^{dip} = \frac{\mu_0}{4\pi}\gamma_I \gamma_S \hbar^2 \vec{I} \cdot \tilde{D} \cdot \vec{S}$$

$$\tilde{D}^{SLAB} = \begin{pmatrix} (r^2 - 3x^2)/r^5 & -3xy/r^5 & -3xz/r^5 \\ -3xy/r^5 & (r^2 - 3y^2)/r^5 & -3yz/r^5 \\ -3xz/r^5 & -3yz/r^5 & (r^2 - 3z^2)/r^5 \end{pmatrix}$$

$$\tilde{D}^{SEP} = \begin{pmatrix} 1/r^3 & 0 & 0 \\ 0 & 1/r^3 & 0 \\ 0 & 0 & -2/r^3 \end{pmatrix}$$

$\vec{r}_{ij} \parallel \hat{Z}$

- Traço nulo.
- Simetria axial.

Interação dipolar internuclear

"Alfabeto" dipolar:

$$H_{dip} = -\vec{\mu} \cdot \vec{B}^{dip} = \frac{\mu_0}{4\pi} \gamma_I \gamma_S \hbar^2 \vec{I} \cdot \tilde{D} \cdot \vec{S}$$

$$H_{dip} = \frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S \hbar^2}{r^3} \left(A + B + C + D + E + F \right)$$

$$A = -I_z S_z (3\cos^2\theta - 1)$$

$$B = \tfrac{1}{4}(I_+ S_- + I_- S_+)(3\cos^2\theta - 1)$$

$$C = \tfrac{3}{2}(I_z S_+ + I_+ S_z)\,\mathrm{sen}\,\theta\cos\theta e^{-i\phi}$$

$$D = -\tfrac{3}{2}(I_z S_- + I_- S_z)\,\mathrm{sen}\,\theta\cos\theta e^{i\phi}$$

$$E = -\tfrac{3}{4} I_+ S_+ \mathrm{sen}^2\theta e^{-2i\phi}$$

$$E = -\tfrac{3}{4} I_- S_- \mathrm{sen}^2\theta e^{2i\phi}$$

Hamiltoniano secular – caso heteronuclear:

$$H_{dip}^{(sec)} = -\frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S \hbar^2}{r^3} I_z S_z (3\cos^2\theta - 1)$$

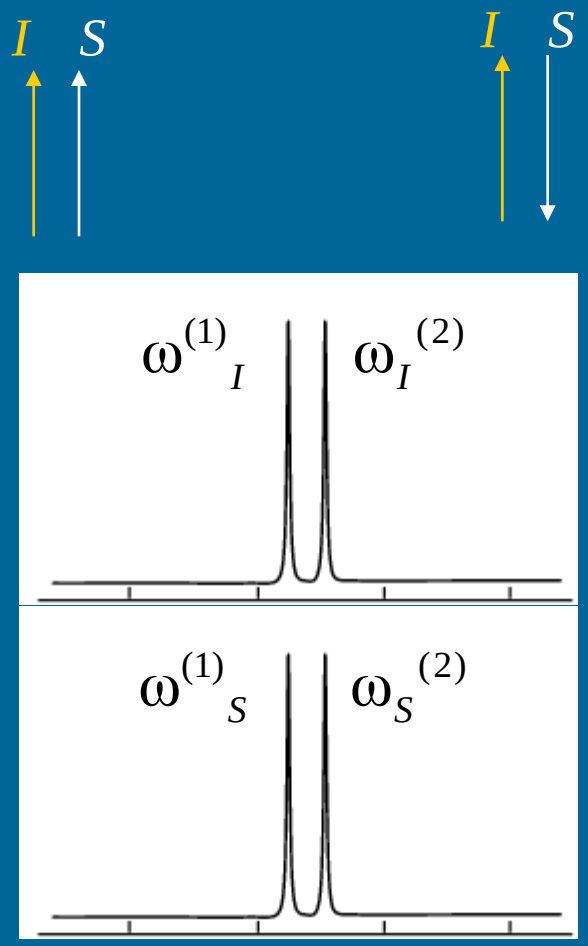
$$B_z^{dip} = \frac{\mu_0}{4\pi} \frac{\mu}{r_{ij}^3} (3\cos^2\theta - 1)$$

Constante de acoplamento dipolar:

$$d = \frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S \hbar}{r^3}$$

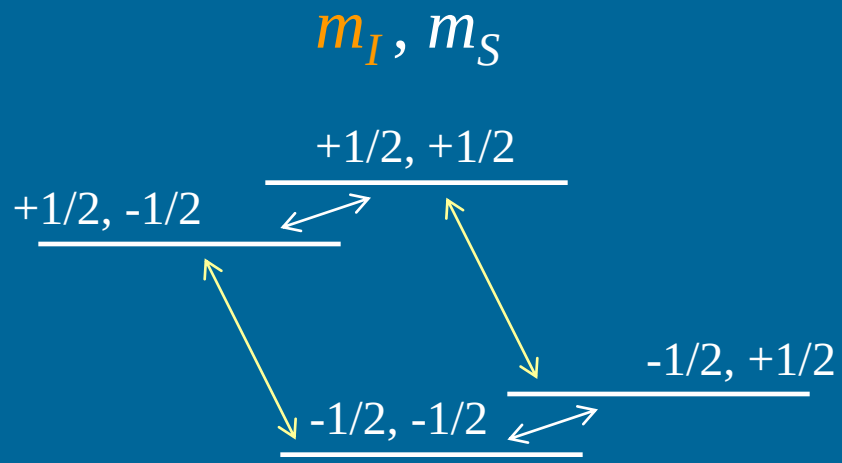
Interação dipolar internuclear

Par isolado de spins em um monocristal (caso heteronuclear):



$$H_{dip}^{(sec)} = -dI_z S_z (3\cos^2\theta - 1)$$

$$H_0 = -\hbar\omega_I I_z - \hbar\omega_S S_z$$



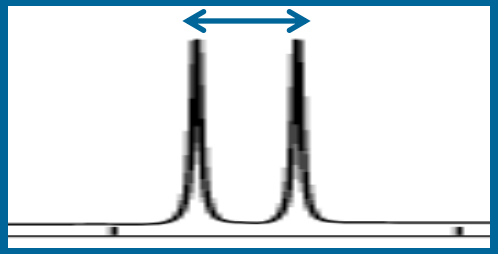
Interação dipolar internuclear - monocristal

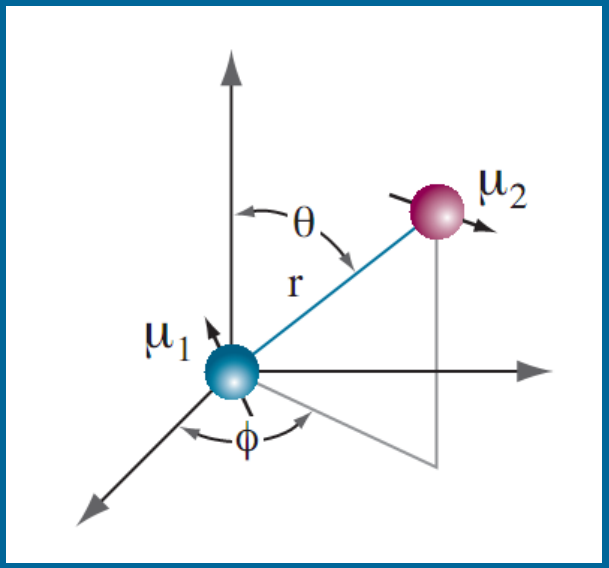
Frequência dependente da orientação molecular (caso heteronuclear):

$$\omega(\theta) = \omega_I \pm d\,\frac{3\cos^2\theta - 1}{2}$$

$$d = \frac{\mu_0}{4\pi}\,\frac{\gamma_I \gamma_S \hbar}{r^3}$$

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





- Medida de distâncias internucleares.

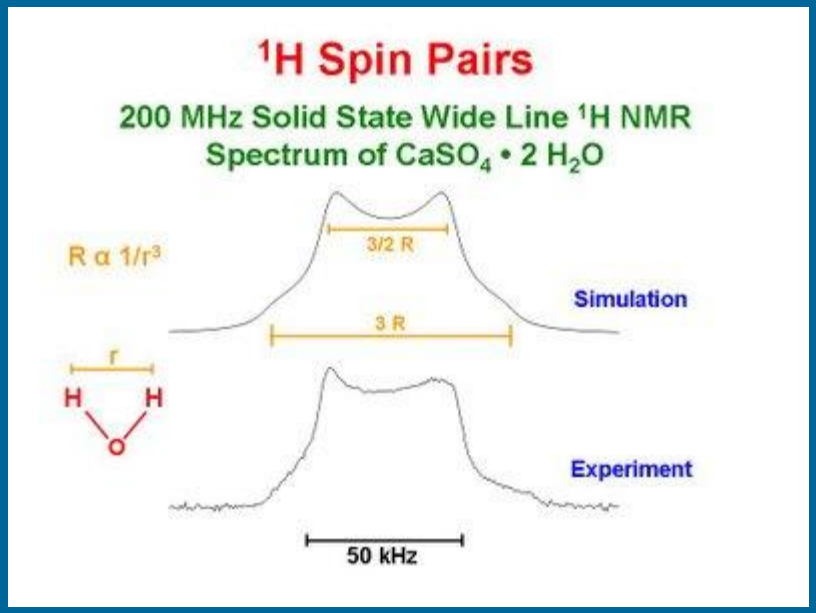
Interação dipolar em sólidos

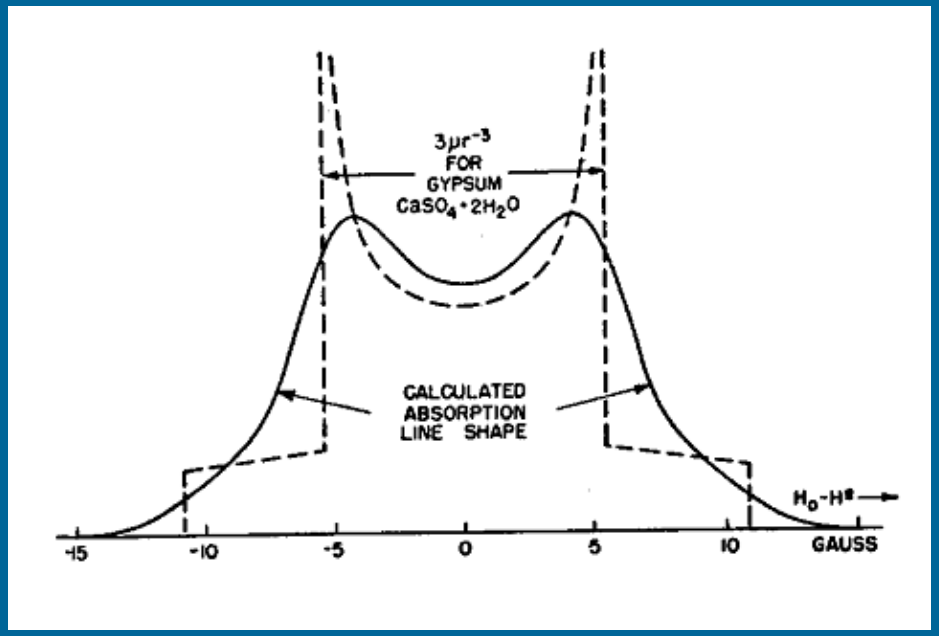
Frequência dependente da orientação molecular (caso homonuclear):

$$\omega(\theta) = \omega_L \pm 3d\,\frac{3\cos^2\theta - 1}{4}$$

$$d = \frac{\mu_0}{4\pi}\,\frac{\gamma^2\hbar}{r^3}$$

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 dipolar em sólidos

Espectros de pó para interação dipolar:

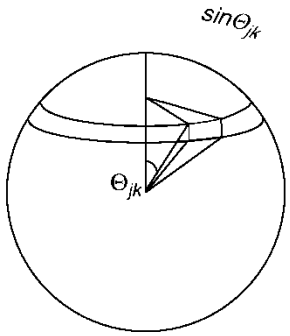


Figure 9.21
Area elements on the surface of a sphere.

$$\omega(\theta) = \omega_L \pm 3d\,\frac{3\cos^2\theta - 1}{4}$$

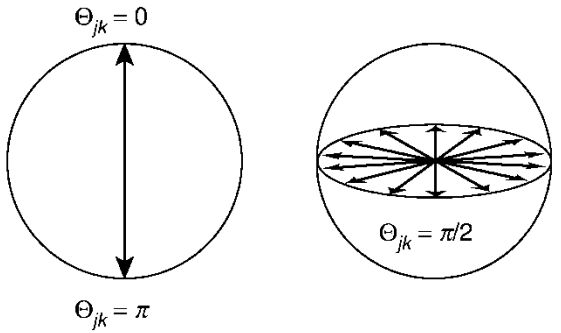


Figure 9.22
Relative probabilities for parallel and perpendicular orientations.

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

Interação dipolar em sólidos

Interação entre vários pares de spins:

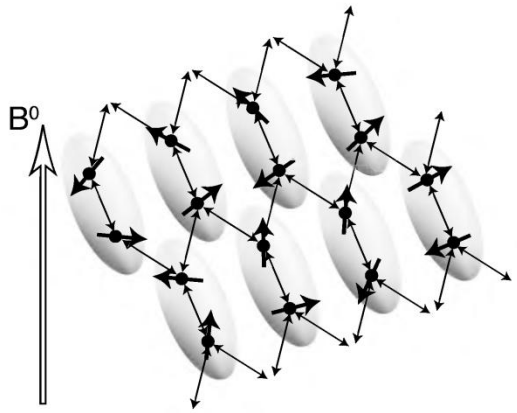


Figure 9.24
Dipole–dipole couplings in a normal molecular solid. For simplicity, only short range couplings are shown.

$$d_{ij} = \frac{\mu_0}{4\pi} \frac{\gamma_i \gamma_j \hbar}{r_{ij}^{\ 3}}$$

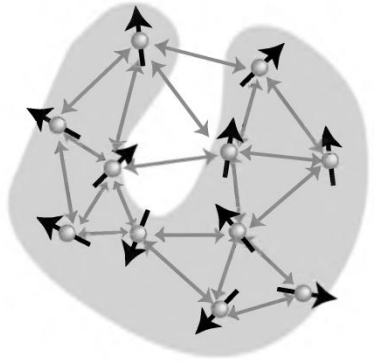
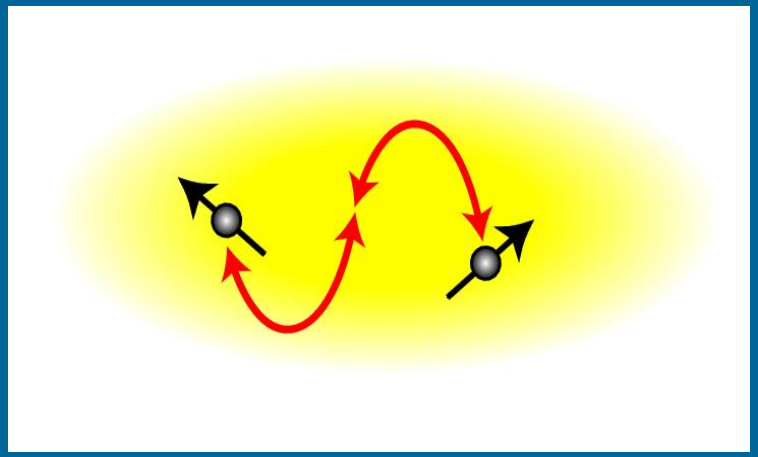
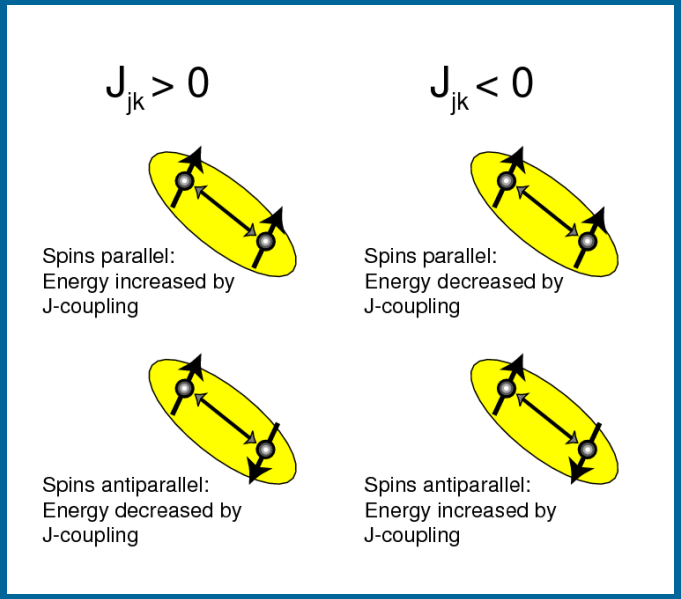


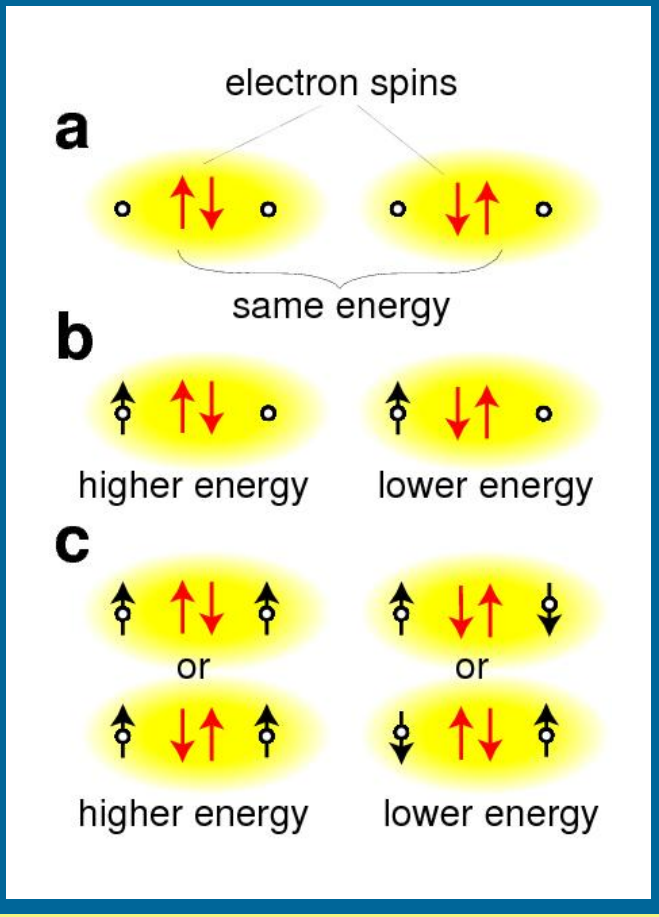
Figure 9.19
The magnitudes of many dipole-dipole couplings may be used to determine the molecular structure.

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

Acoplamento escalar ou indireto (*J*)



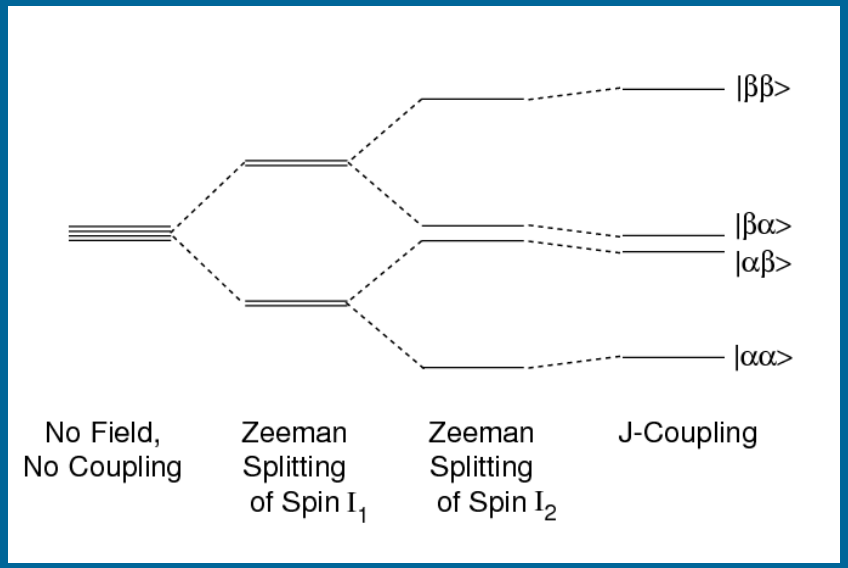


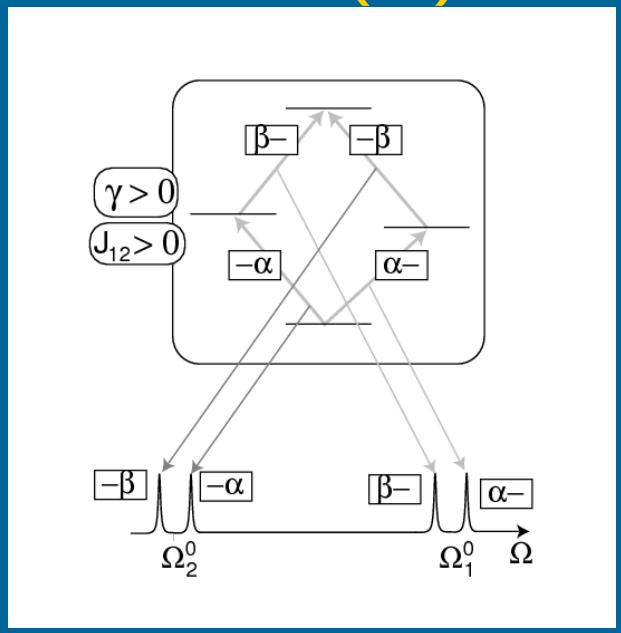


Interação através de ligações químicas

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

Acoplamento escalar ou indireto (*J*)

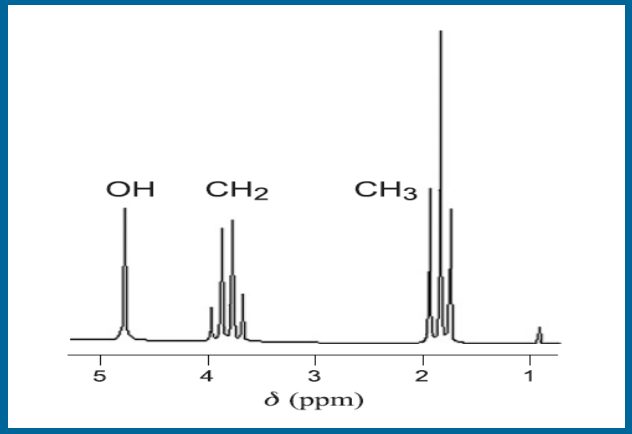




$$H_J = 2\pi\hbar\vec{I}\cdot\tilde{J}\cdot\vec{S}$$

$$H_{tot} \cong -\hbar\omega_I I_z - \hbar\omega_S S_z + 2\pi\hbar J I_z S_z$$

- Termo isotrópico.
- Importante principalmente em líquidos.



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

Acoplamento escalar ou indireto (*J*)

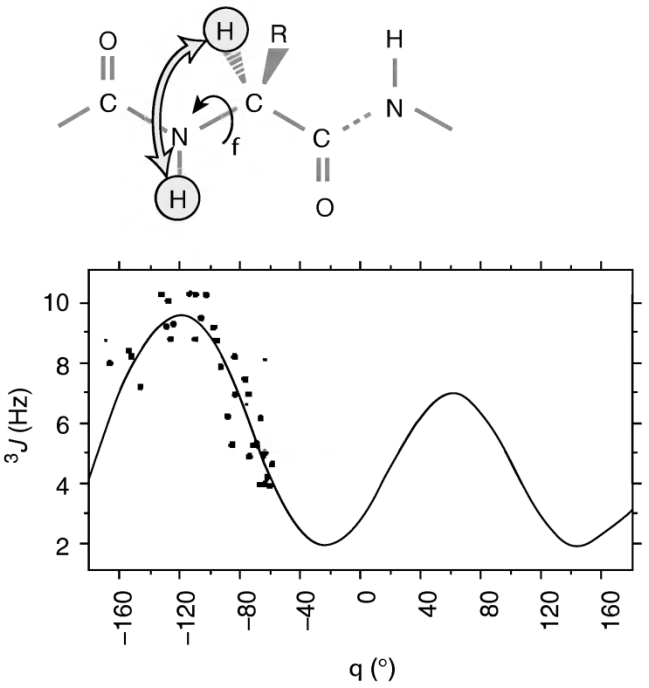


Figure 9.28 The three-bond *J*-couplings between H^N protons and H^α protons in a protein have a well-defined dependence on the molecular torsional angle ϕ. Each filled circle represents a single amino acid residue in a protein. The *x*-coordinate is the torsional angle as determined by X-ray crystallography; the *y*-coordinate is the *J*-coupling as measured by solution NMR. The solid line is a semi-empirical curve called the Karplus equation, which has the form $^3J = (6.4\cos^2\theta - 1.4\cos\theta + 1.9)$ Hz, where θ is the H–N–C–H torsional angle, given in terms of the backbone torsional angle ϕ by $\theta = \phi - \pi/3$. Adapted from A. Pardi, M. Billeter and K. Wüthrich, *J. Mol. Biol.*, **180**, 741–751 (1984). (Copyright Academic Press).

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

Acoplamento escalar ou indireto (*J*)

Exemplos - acoplamento *J* em RMN de sólidos:

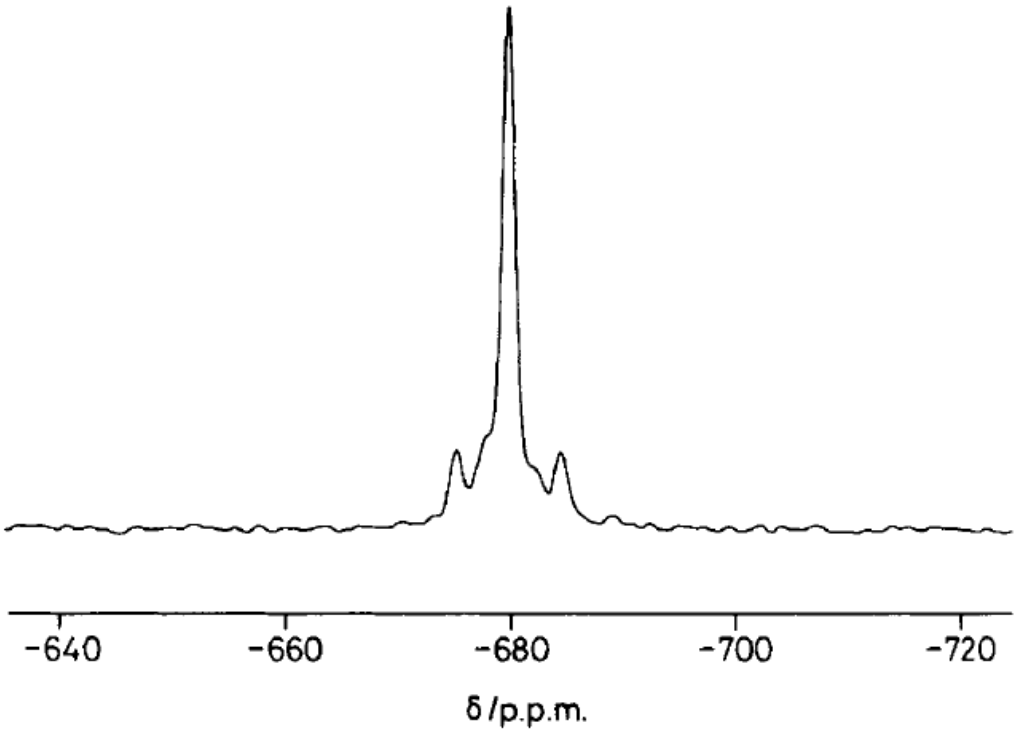


Figure 5. The 74.54-MHz ^{119}Sn m.a.s. n.m.r. spectrum of $BaSnO_3$

Clayden et al., *J. Chem. Soc. Dalton Trans*. 1989;843-847.

Acoplamento escalar ou indireto (*J*)

Exemplos - acoplamento *J* em RMN de sólidos:

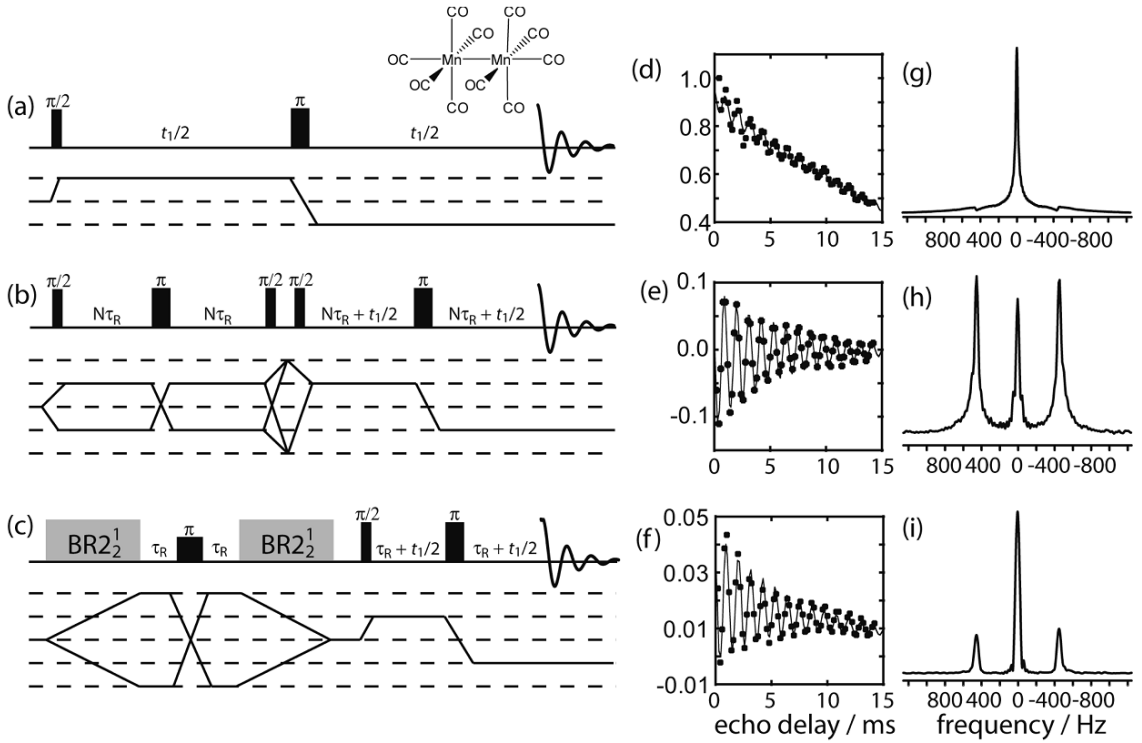


Figure 1. *J*-resolved solid-state NMR experiments for half-integer spin quadrupolar nuclei. Pulse sequences for the regular, *J*-DQF, and dipolar-DQF *J*-resolved experiments are shown in (a), (b), and (c), respectively; coherence transfer pathways are shown below the pulse schemes. The modulations of the echo intensities as a function of the echo delay for ^{55}Mn in dimanganese decacarbonyl subjected to each of the three experiments are shown in (d), (e), and (f), and the Fourier transforms of these signals are shown in (g), (h), and (i). The vertical scales in (d), (e), and (f) show the relative intensities for an equivalent number of scans; however, the data shown here were acquired with differing numbers of scans to ensure good signal-to-noise (see SI).

Perras & Bryce, *J. Amer. Chem. Soc.* 2013;135:12596.

Bibliografia recomendada

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