Métodos de RMN

no estado sólido

Jair C. C. Freitas

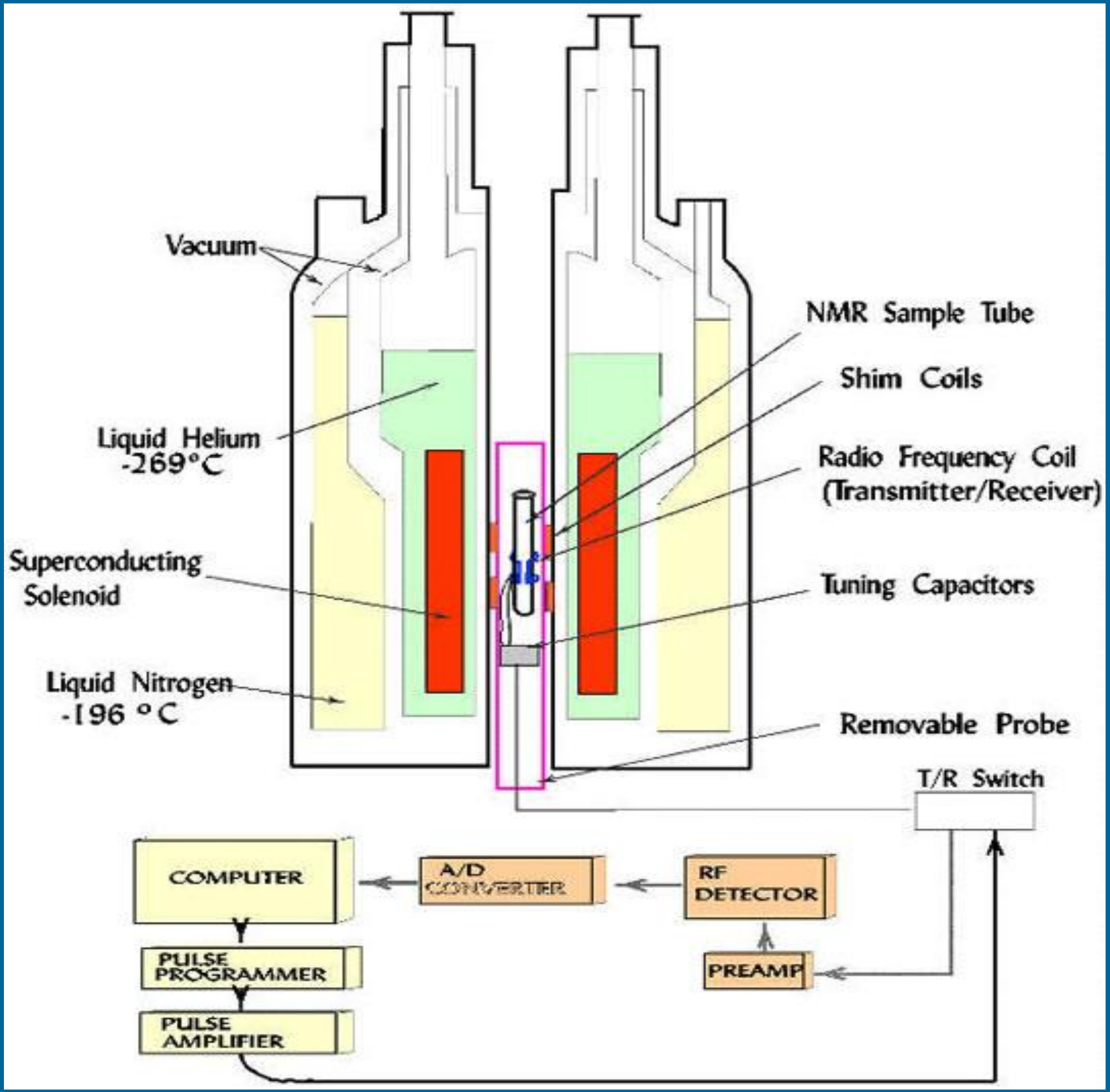
Programa de Pós-graduação em Física – UFES

Programa de Pós-graduação em Química - UFES

Sumário

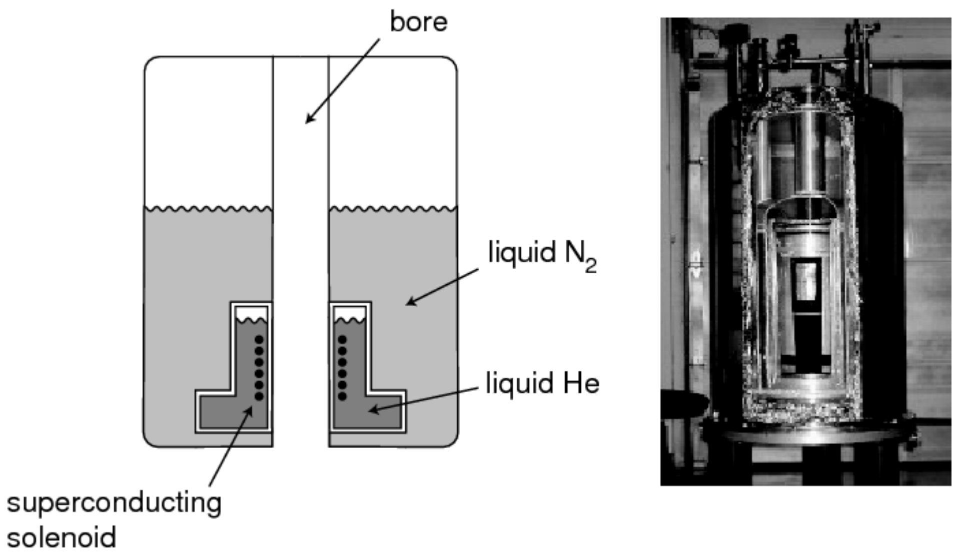
- Instrumentação para RMN:
  - Espectrômetro de RMN.
  - Magnetos supercondutores.
  - Componentes principais do espectrômetro:
    - Transmissor de RF.
      - Banda de excitação.
      - Pulsos seletivos e não-seletivos.

Espectrômetro de RMN



Espectrômetro de RMN

Magneto supercondutor



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

Magneto supercondutor

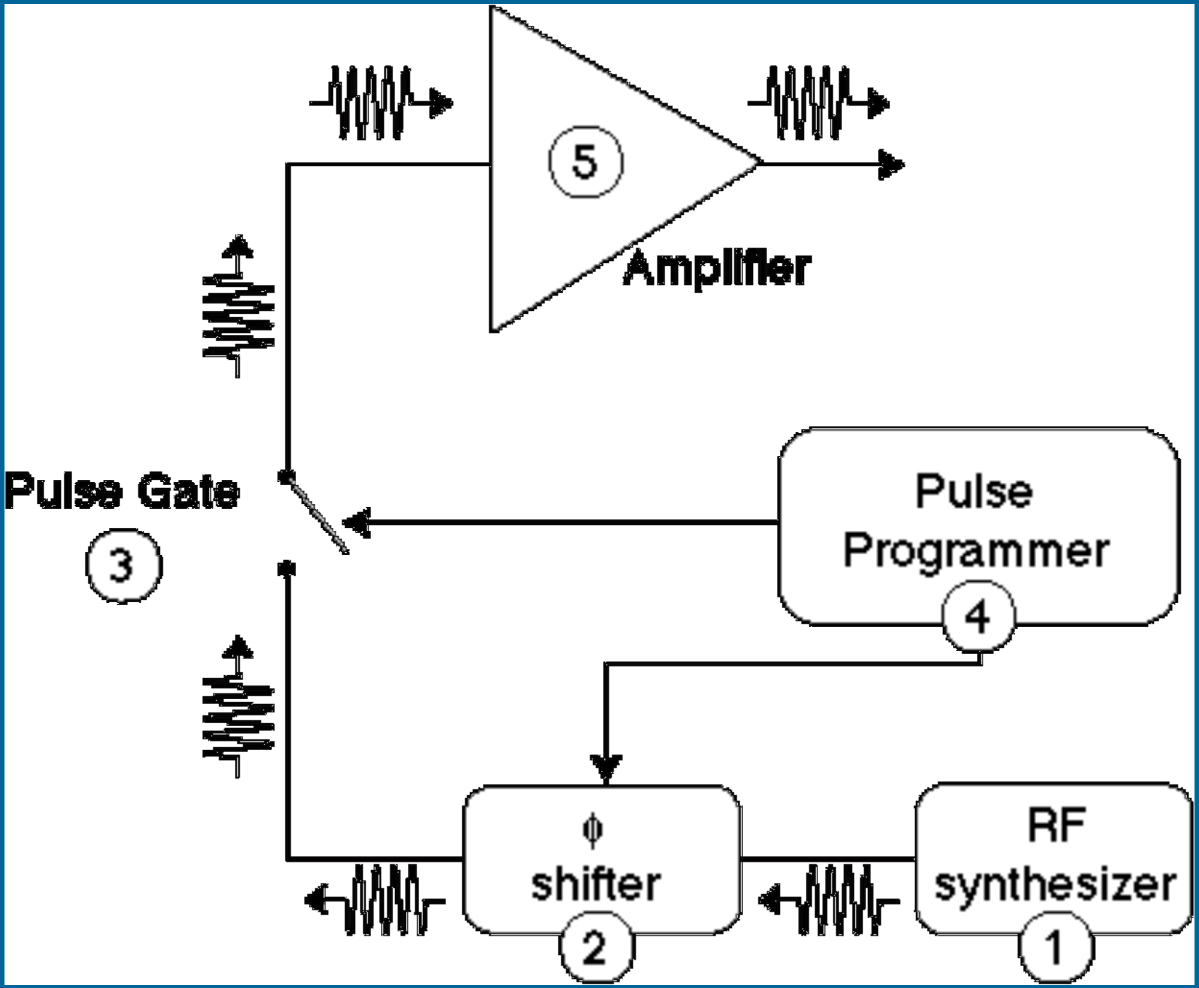
http://www.lut.ac.uk/departments/cm/research/NMR/cut_magnet.html

Magnetos supercondutores

Espectrômetros: frequências e campos magnéticos

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

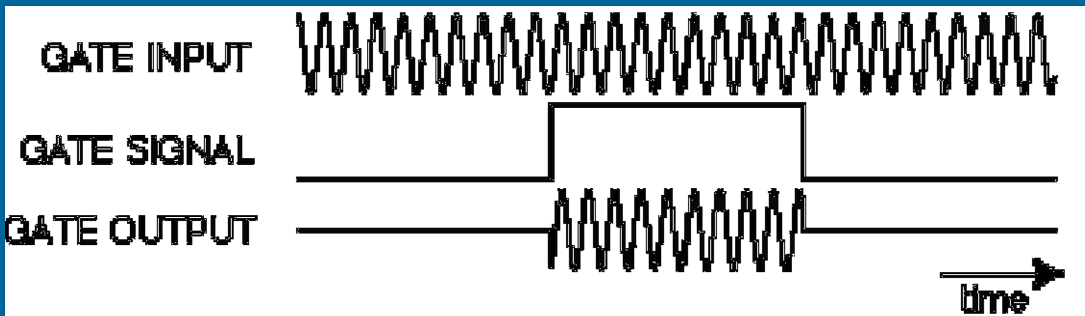
Transmissor de RF

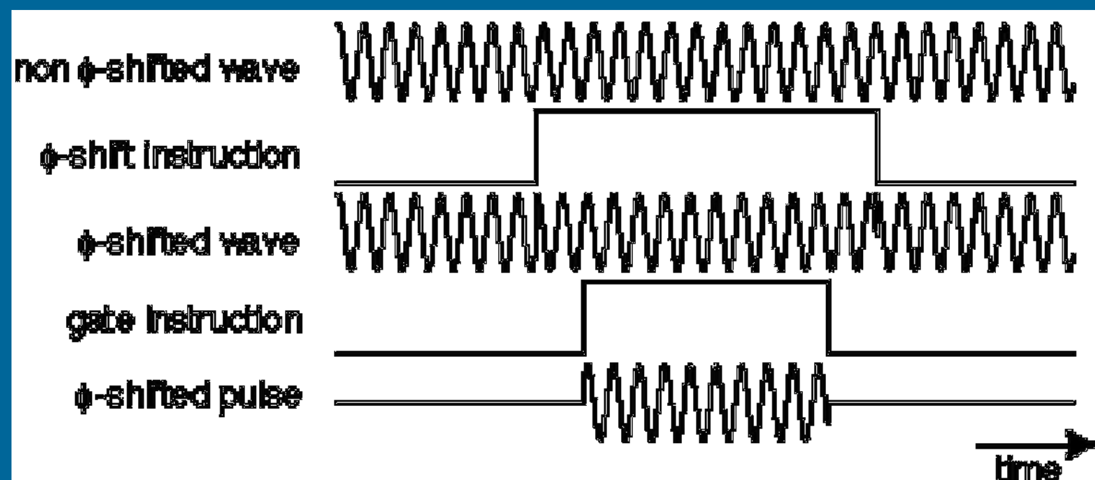


"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Transmissor de RF

Geração de pulsos de RF:





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

Transmissor de RF

Amplificação de pulsos de RF:

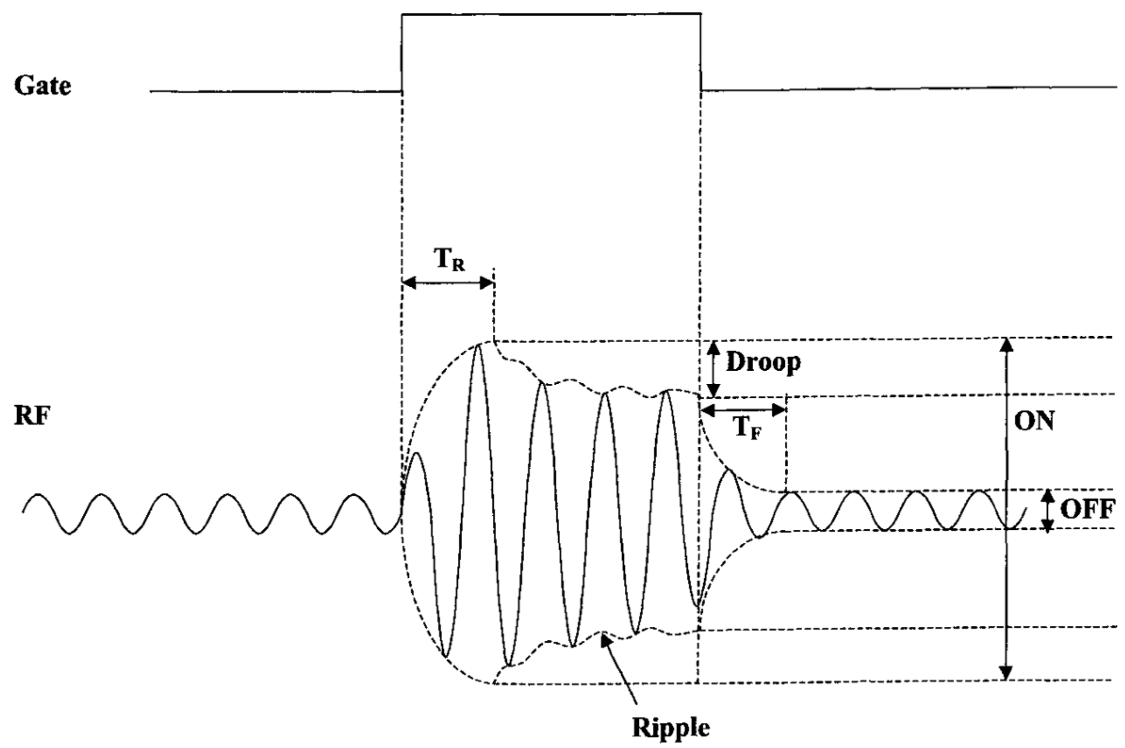


Figure 3.5. Schematic representation of pulse imperfections with T_R the rise time and T_F the fall time.

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

Pulsos de RF – banda de excitação

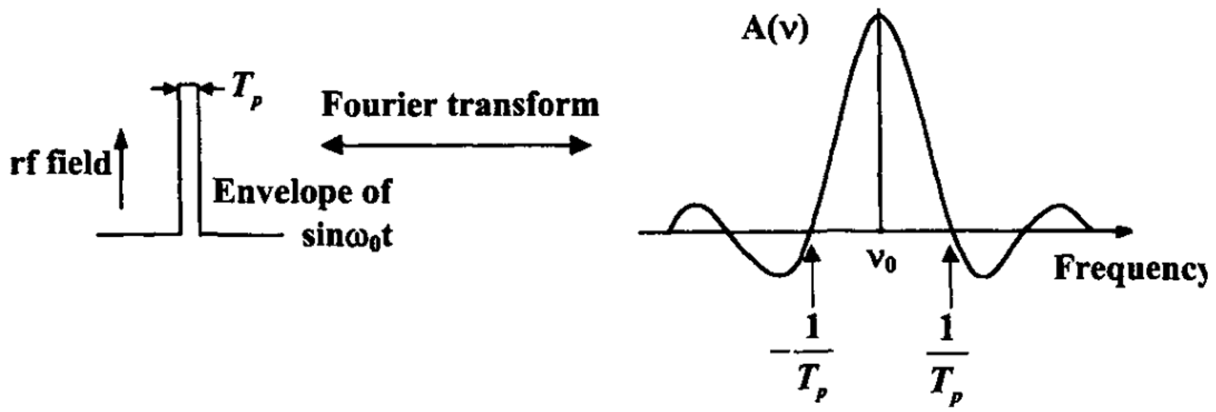
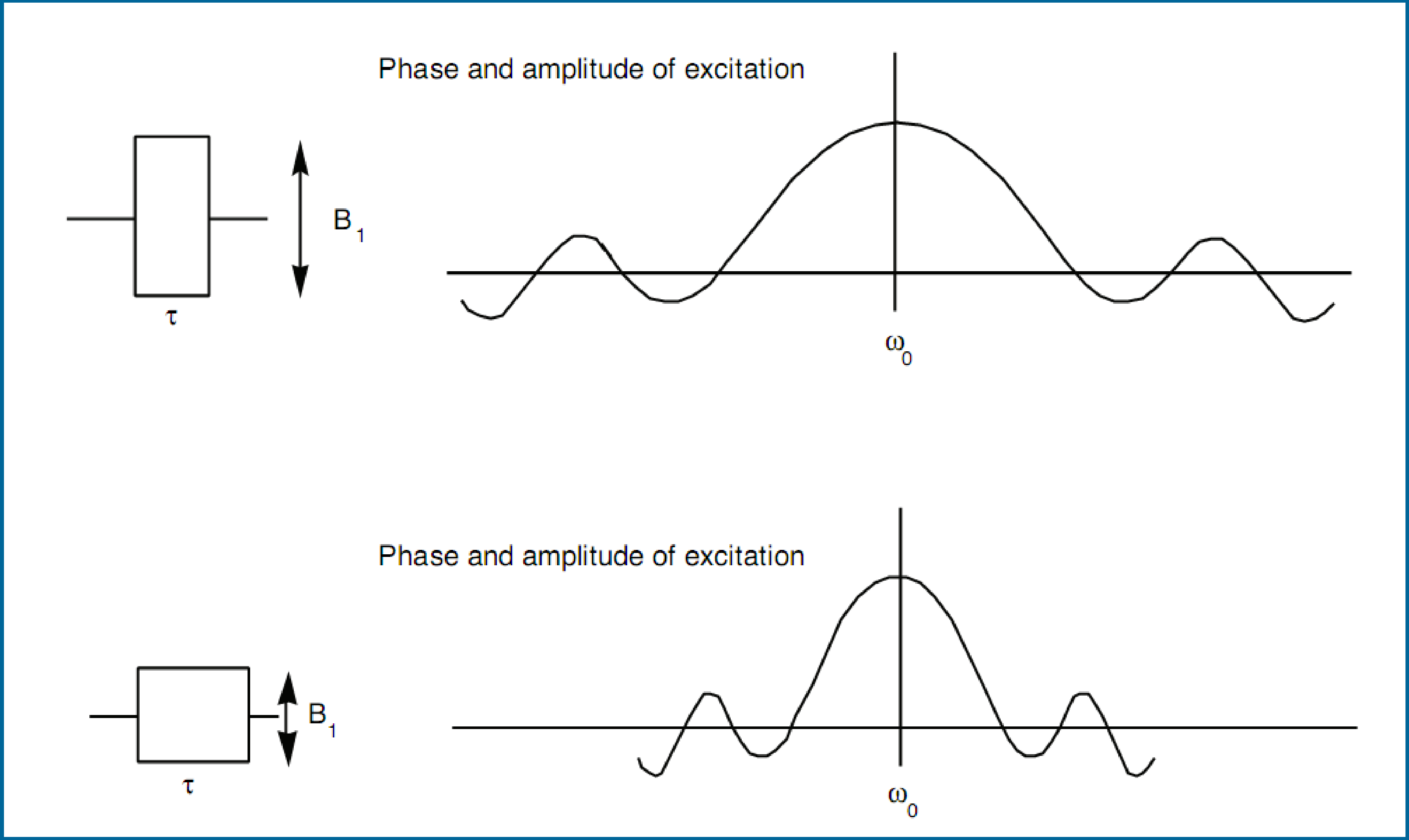


Figure 3.1. Fourier relationship between an rf pulse of duration T_p and the amplitude distribution $A(\nu)$ of the frequency components present.

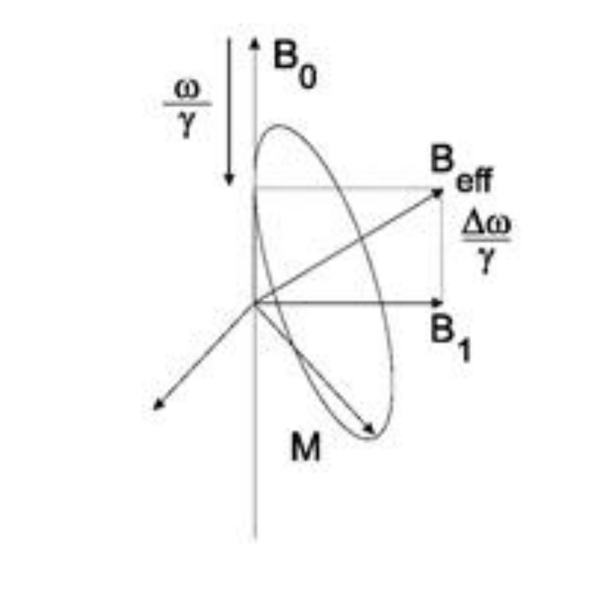
"Multinuclear solid-state NMR of inorganic materials", Mackenzie & Smith. Pergamon, 2002.

Pulsos de RF – banda de excitação



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

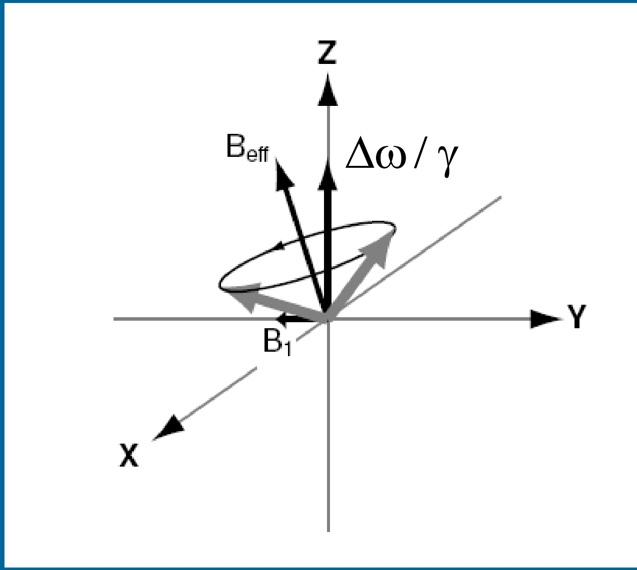
Pulsos fora da ressonância



http://www.bruker-biospin.com/pulsetheory.html

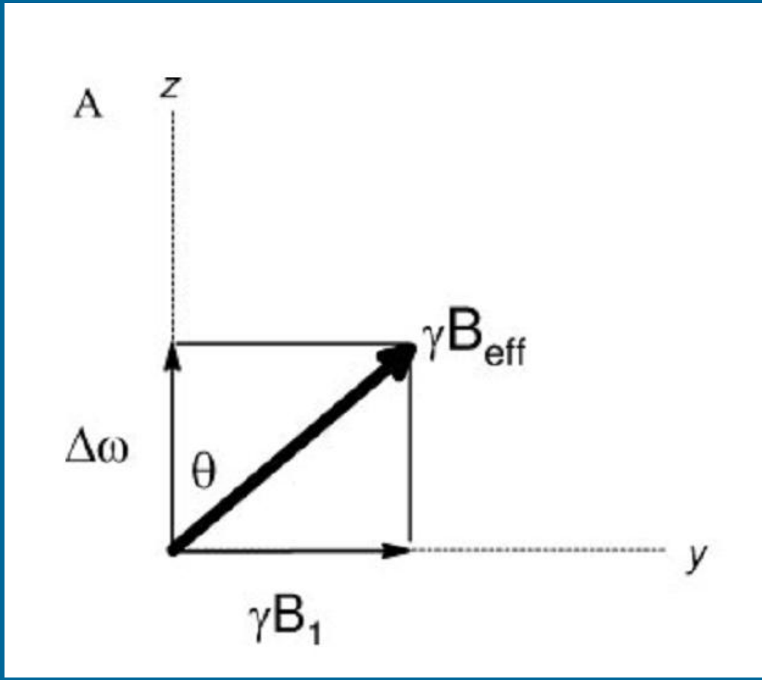
$$\vec{\omega} = -\omega\,\hat{z}$$

$$\vec{B}_{ef} = \gamma^{-1}(\omega_L - \omega)\hat{z} + B_1\hat{x}$$



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

Pulsos fora da ressonância



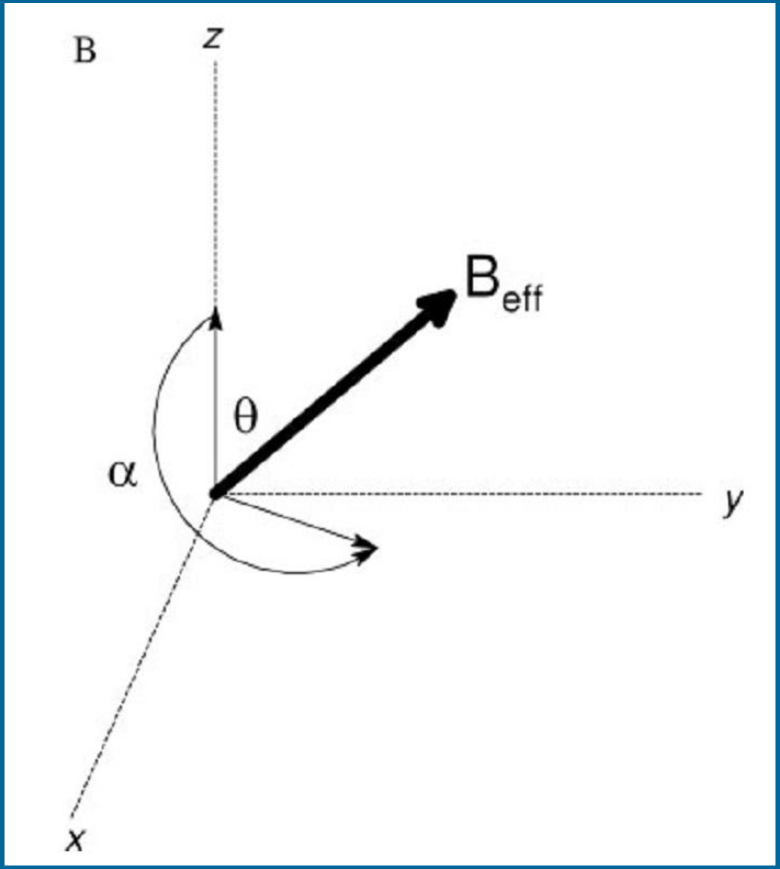
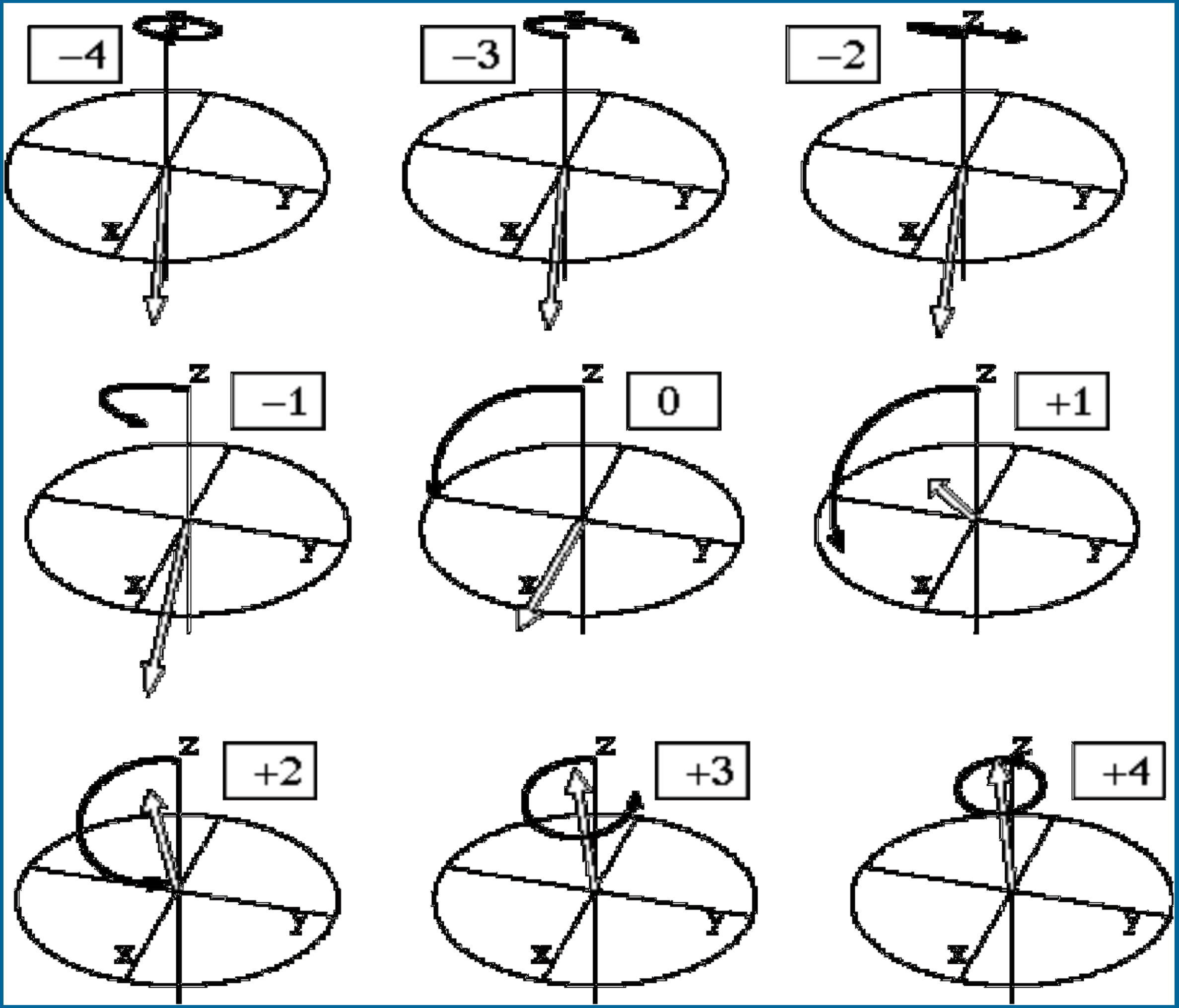


Figure 1 (A) Effective field for off-resonance pulses, γB_{eff}. It is the vector sum of the offset from resonance, $\Delta\omega$, and the RF magnetic field in frequency units, γB_1. It forms an angle θ with the z axis. (B) During the pulse, the magnetization precesses around the effective field through an angle α.

Gregory & Bain. *Concepts Magn. Reson.* 2009;34A:305-314.

Pulsos fora da ressonância



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

Pulsos de RF – banda de excitação

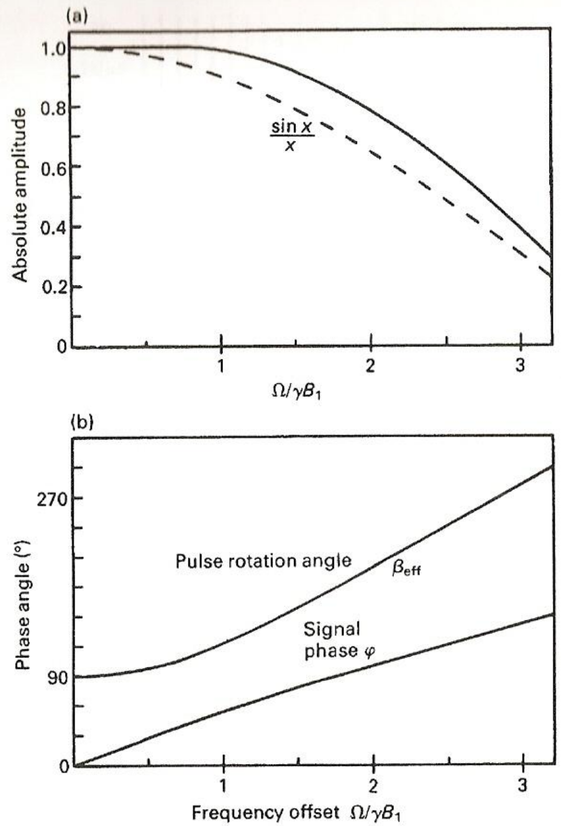


FIG. 4.2.3. Dependence of signal amplitude and signal phase on the frequency offset Ω for a single-pulse Fourier experiment. An on-resonance pulse rotation angle $\beta = 90°$ has been assumed. (a) Absolute value of signal amplitude as a function of $\Omega/\gamma B_1$. For comparison the corresponding $\sin x/x$ dependence of eqn (4.2.31) is included. (b) Signal phase φ and effective pulse rotation angle β_{eff} as functions of $\Omega/\gamma B_1$.

"Principles of NMR...", Ernst, Bodenhausen, Wokaun. Oxford, 1987.

Pulsos fora da ressonância

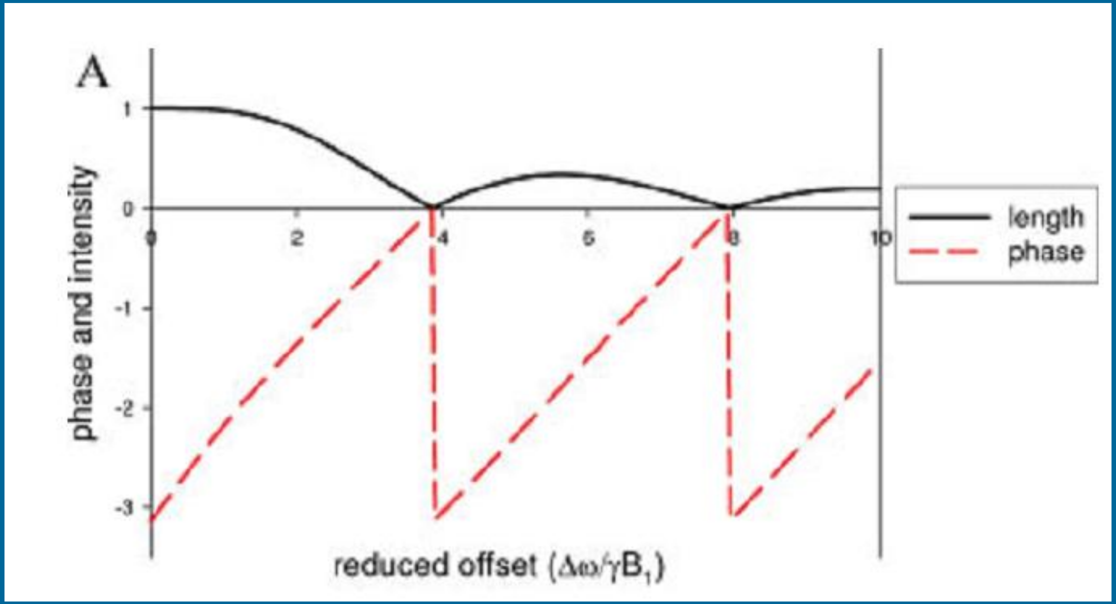
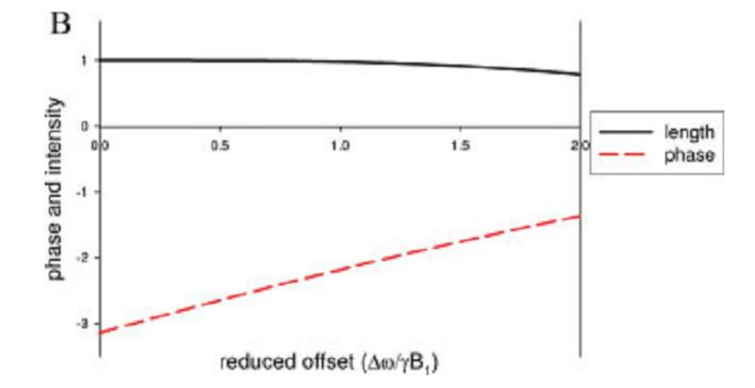


Figure 3 (A) Absolute value of intensity (black solid line, relative to on-resonance value) and phase (red dashed line, in radians) for a single line excited by a finite pulse, as a function of offset. The reduced offset is the actual offset divided by γB_1. (B) As in (A), but plotted only to a reduced offset of 2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Gregory & Bain. *Concepts Magn. Reson.* 2009;34A:305-314.

Pulsos fora da ressonância

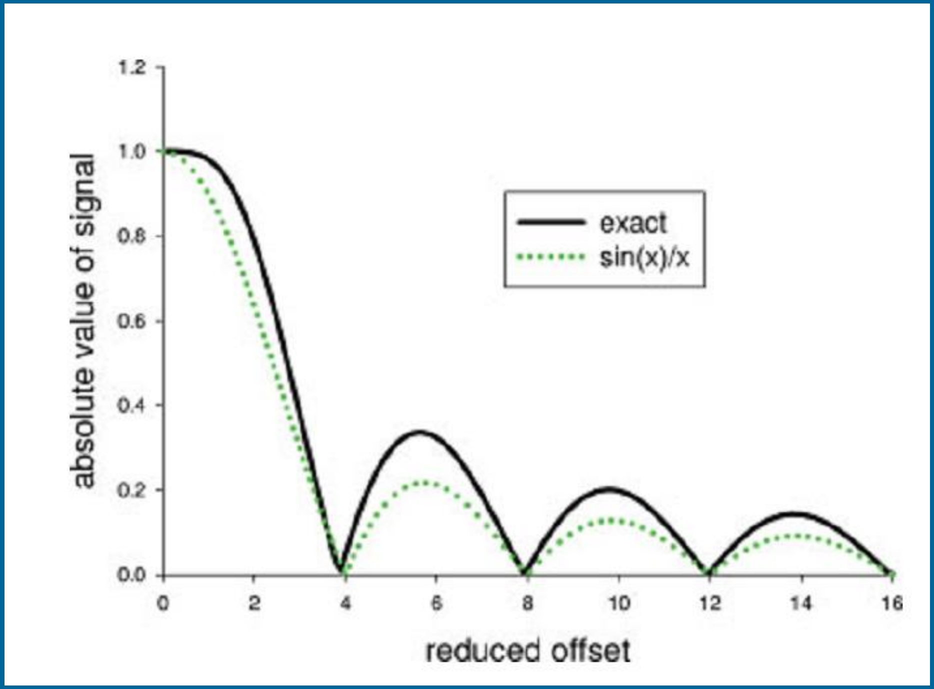


Figure 6 Comparison of the exact absolute value of the signal (black solid line) and the Fourier transform of the rectangular pulse (dotted green line), which has the form sin(x)/x. As the phase relation for the FT of the pulse is exactly linear with slope of $\pi/4$, the corresponding phase comparison is identical to Fig. 4(A). [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

Gregory & Bain. *Concepts Magn. Reson.* 2009;34A:305-314.

Pulsos fora da ressonância

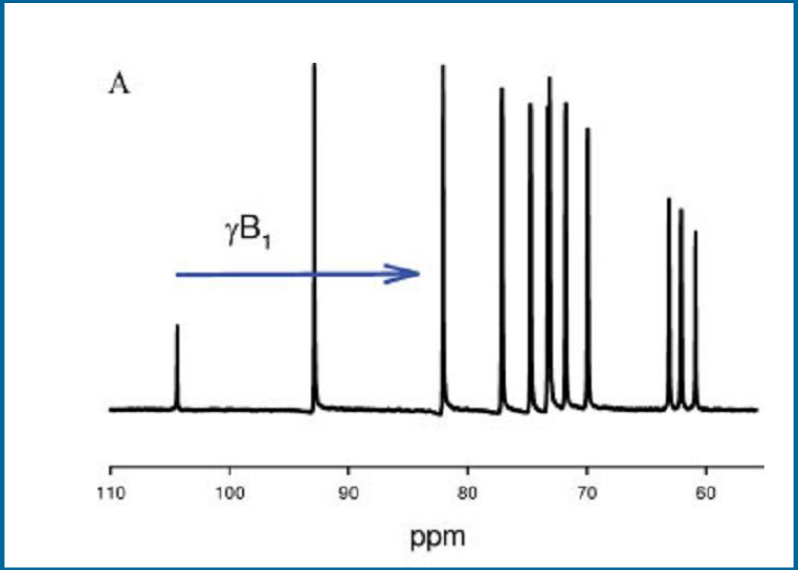
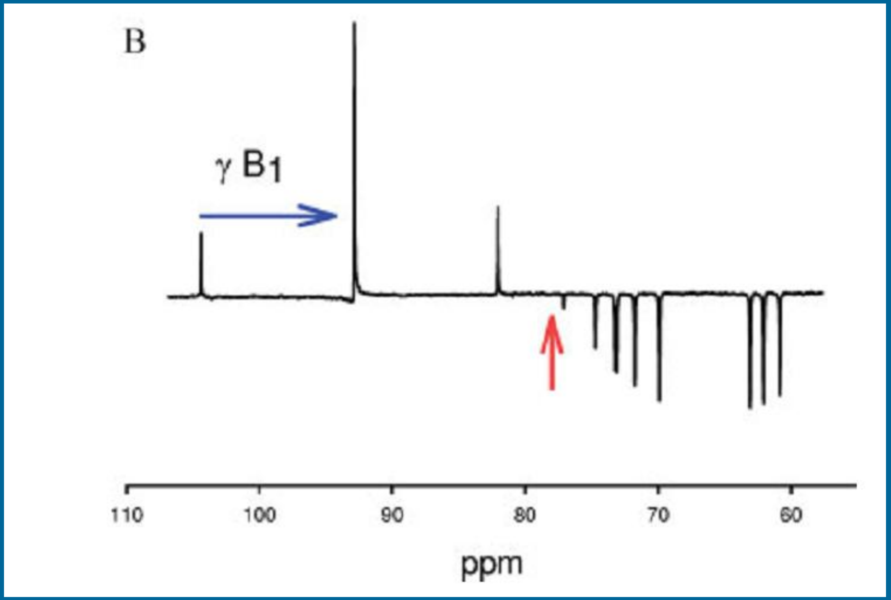


Figure 2 (A) ^{13}C spectrum of sucrose in D_2O, excited with an RF field of 2,630 Hz (corresponding to 21 ppm for carbon) and a $2\pi/3$ pulse. The blue horizontal arrow represents the size of γB_1. The high frequency peak was put on resonance and used to set the zero-order phase correction. The first-order phase correction was set to make the lowest frequency peak pure absorption. Note the small errors in phase of the intermediate peaks. (B) ^{13}C spectrum as in (A), but with a $2\pi/3$ pulse and a weaker RF field. The blue horizontal arrow represents the size of γB_1, and the red vertical arrow indicates the position of the null, corresponding to a 2π precession. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Gregory & Bain. *Concepts Magn. Reson.* 2009;34A:305-314.

Pulsos de RF – banda de excitação

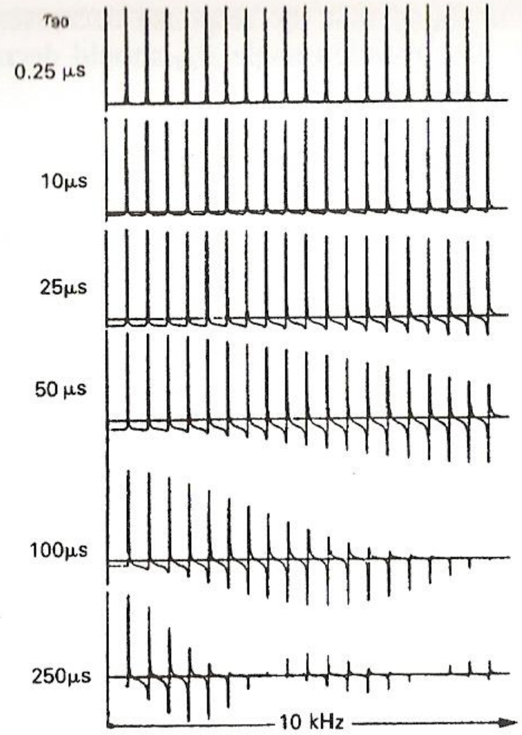
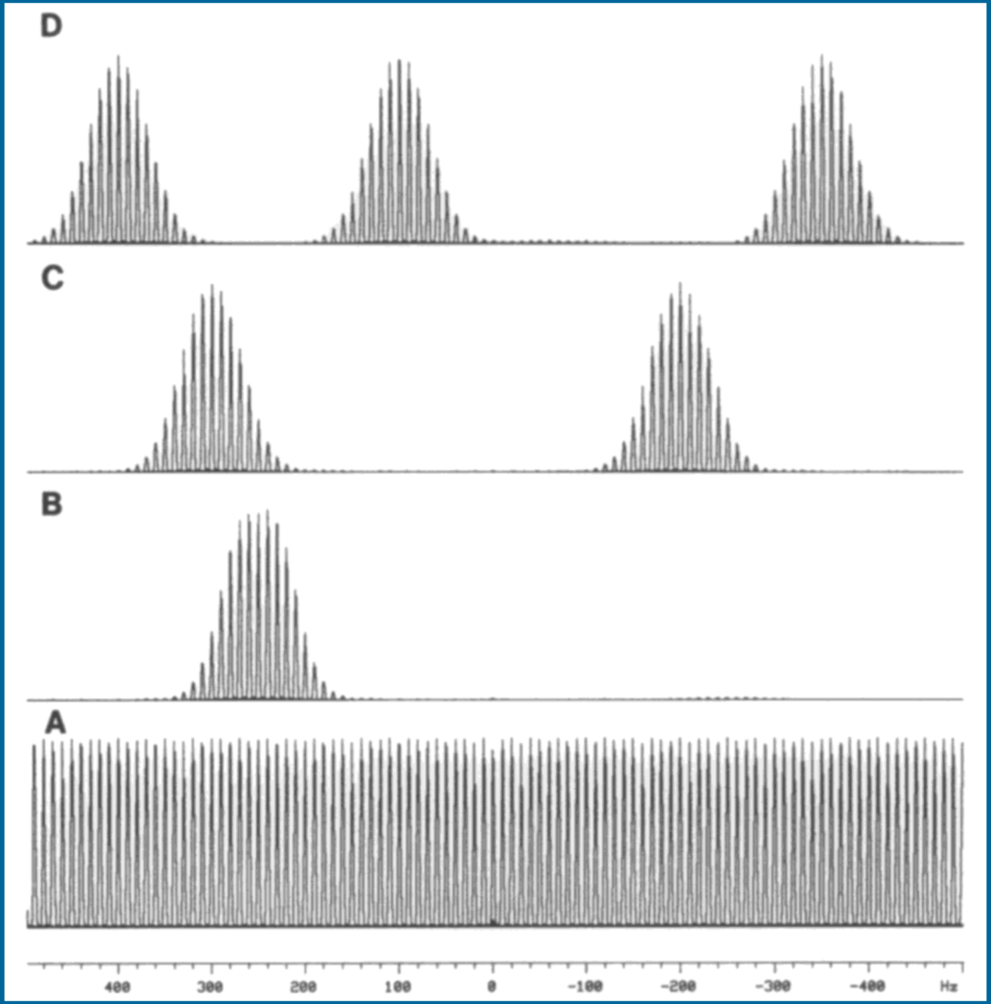


FIG. 4.2.4. Experimental offset dependence of the lineshapes for pulses with six different pulse lengths of 0.25, 10, 25, 50, 100, and 250 μs with on-resonance r.f. rotation angles $\beta = \pi/2$. (Reproduced from Ref. 4.84.)

"Principles of NMR...", Ernst, Bodenhausen, Wokaun. Oxford, 1987.

Pulsos de RF – banda de excitação



Patt, J. Magn. Reson.1992;96:94-102.

Pulsos seletivos
(“soft”)
t_p = 31 ms

Pulso não-seletivo
(“hard”)
t_p = 10 μs

Bibliografia recomendada

- "Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.
- "Ressonância magnética nuclear: fundamentos, métodos e aplicações", V. M. S. Gil, C. F. G. C. Geraldes. Fundação Calouste Gulbekian, 1987.
- "Nuclear magnetic resonance for the people", P. J. Grandinetti (notas de aula), disponível em http://grandinetti.org/Teaching/Chem824/Notes.
- "Structural determination by NMR", B. Jaun (e-book), disponível em http://www.analytik.ethz.ch/praktika/phys_anal/nmr/ft-nmr.pdf.
- "Principles of nuclear magnetic resonance in one and two dimensions", R. R. Ernst, G. Bodenhausen, A. Wokaun. Oxford, 1987.
- "Understanding NMR spectroscopy", J. Keeler. Wiley, 2005.
- "Multinuclear solid-state NMR of inorganic materials", K. J. D. Mackenzie, M. E. Smith. Pergamon, 2002.
- "The effects of finite rectangular pulses in NMR: phase and intensity distortions for a spin-1/2", R. M. Gregory, A. D. Bain. *Concepts Magn. Reson.* 2009;34A:305-314.