West CHEM

UNIVERSITY of GLASGOW

Getting More from NMR

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SOLID-STATE NMR RESEARCH

Purpose:

- To provide a guide to the background knowledge necessary for recording good quality NMR spectra

- To introduce some of the many modern NMR techniques available to laboratory chemists for both assignment and structure determination

- To give a brief introduction to what is possible (and not possible!) with solid-state NMR

Overview:

1. NMR basics: recording and processing good spectra (SCW)

2. NMR experiments for assignment (MJT)

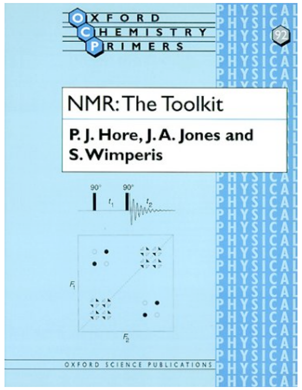
3. NMR experiments for structure determination (MJT)

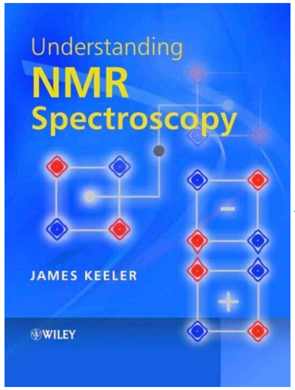
4. Introduction to NMR of solids (SCW)

NMR basics: recording and processing good spectra

Suggested reading:

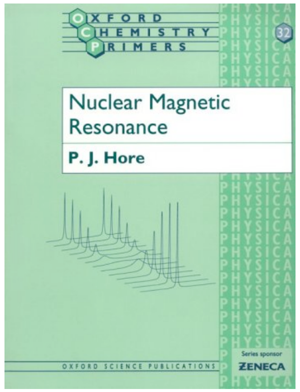
more for the real enthusiast

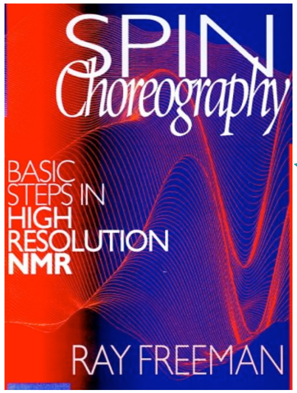




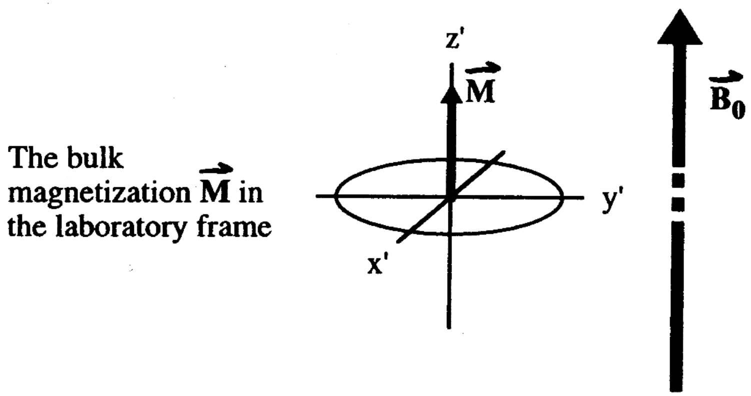
highly recommended at this level

good under-graduate text

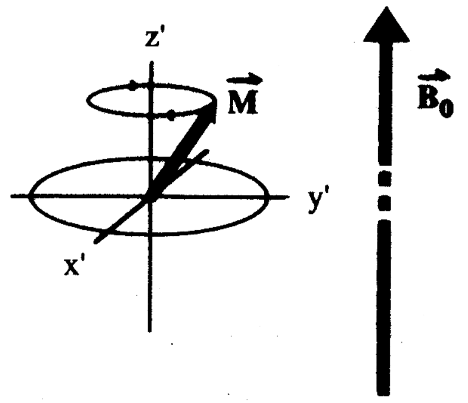




more for the real enthusiast

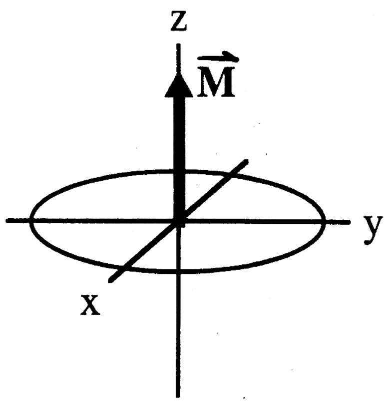


Bulk magnetization

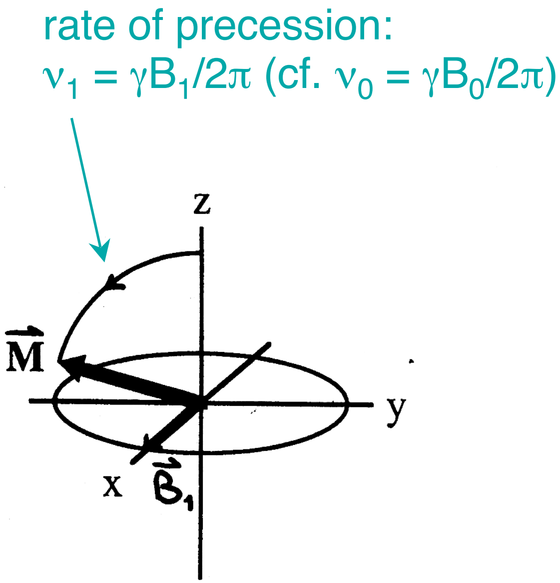


Larmor precession: $d\vec{M}/dt = -\gamma \vec{B}_0 \times \vec{M}$

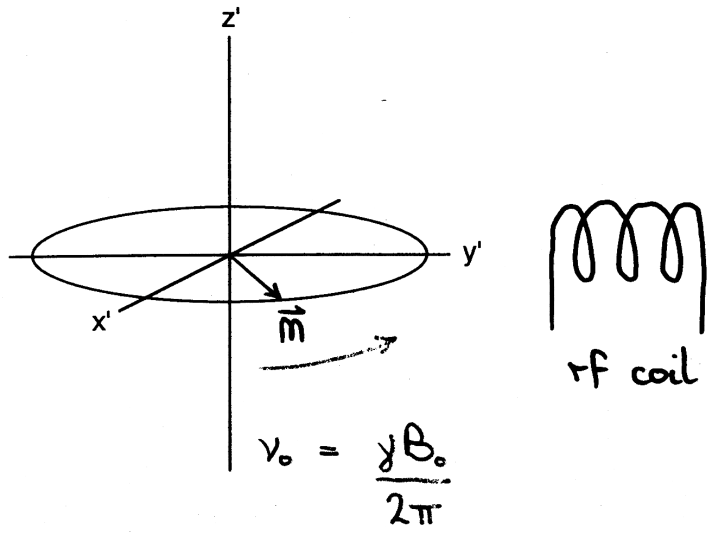
Motion is complex ⇒ view problem in “rotating frame”
where Larmor precession is removed (or nearly removed)

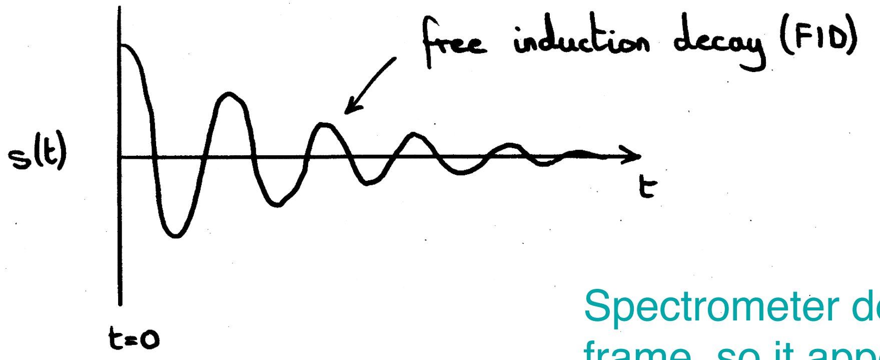


Before pulse: $\vec{\mathbf{M}}$ aligned along z axis of rotating frame



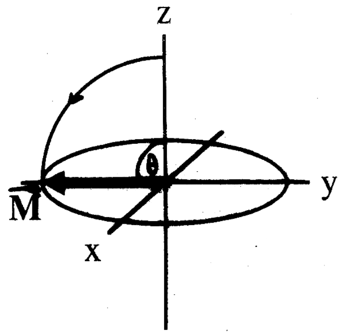
During pulse: $\vec{\mathbf{M}}$ precessing about field along x axis



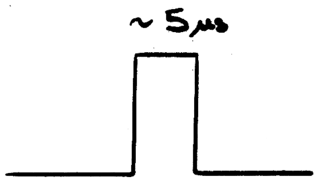


Spectrometer detects FID in rotating frame, so it appears to oscillate at audio- and not radio-frequencies

$$\theta = 2\pi \gamma_1 \tau = \frac{\pi}{2} \; (90°)$$

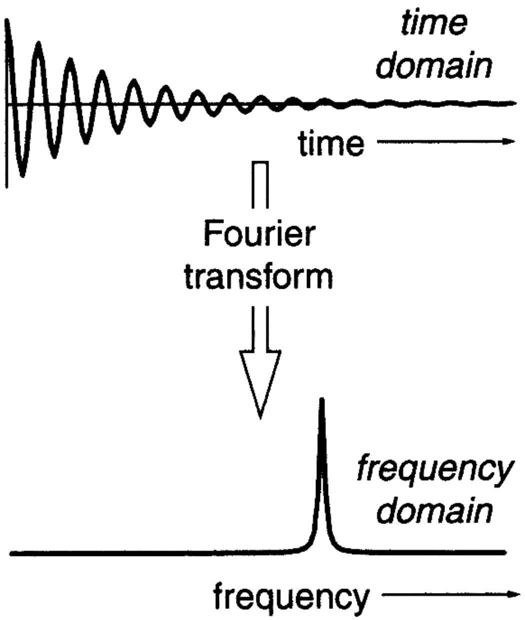


Effect of a 90° pulse about
the rotating frame x axis



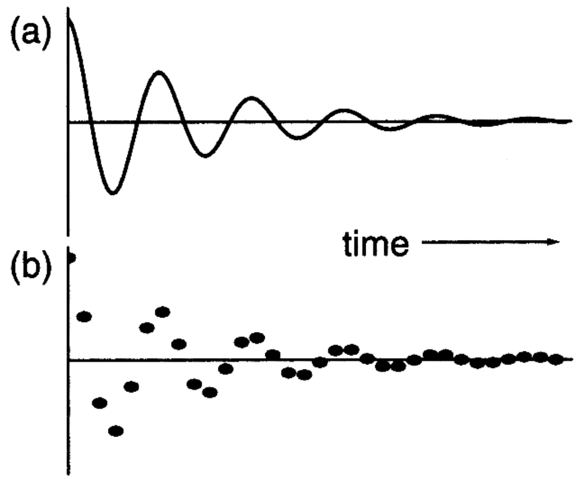
maximum signal obtained with "90°" or "π/2" pulse

Fourier transformation



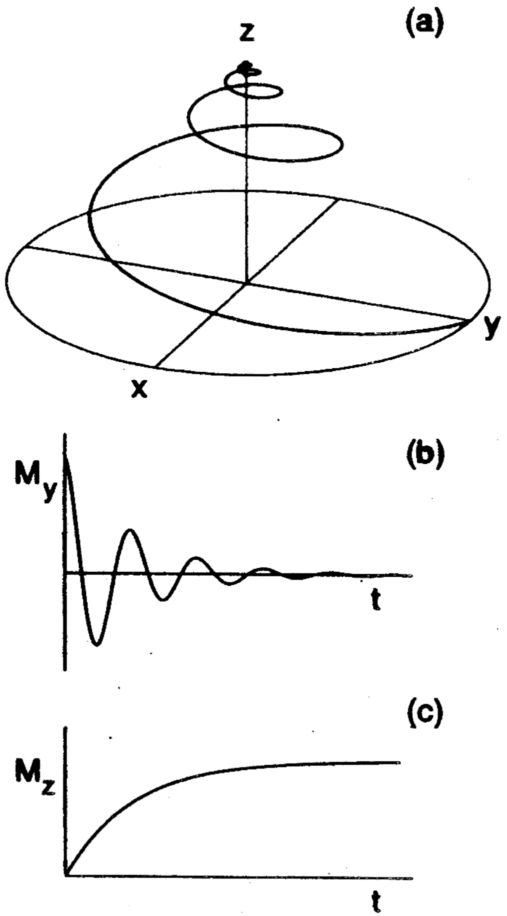
Stolen from: “Understanding NMR Spectroscopy” by J. Keeler

Signal is digitized



Stolen from: “Understanding NMR Spectroscopy” by J. Keeler

Relaxation

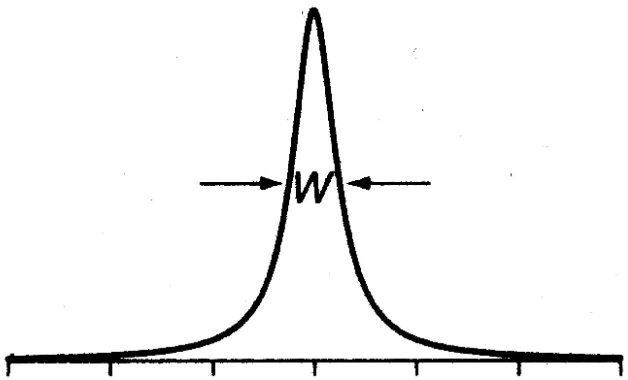


transverse (T_2) relaxation

longitudinal (T_1) relaxation

Stolen from: "Nuclear Magnetic Resonance" by P. J. Hore

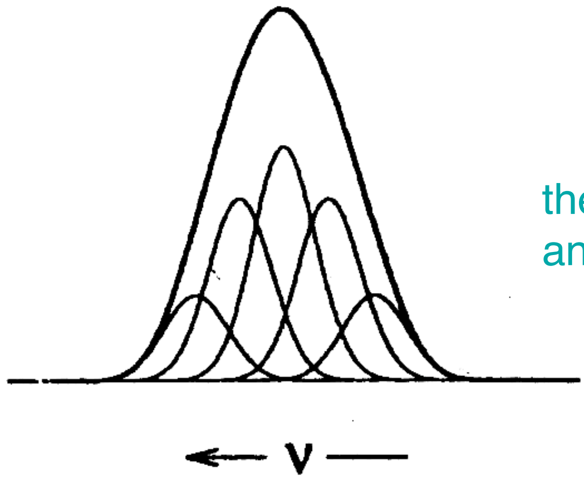
In ideal world…



$$W = 1/(\pi T_2)$$

Stolen from: "Understanding NMR Spectroscopy" by J. Keeler

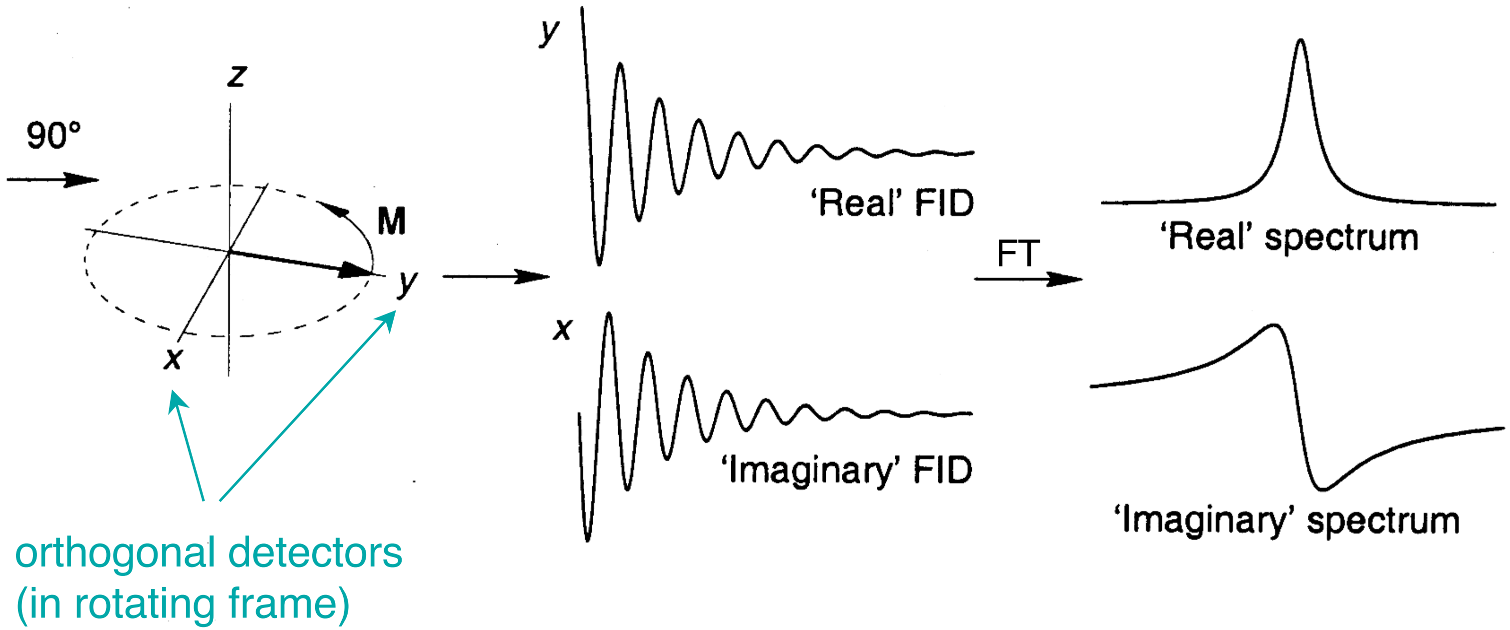
But spatial B_0 inhomogeneity broadens lines and hides natural linewidth



therefore, we **shim** the magnet and **spin** the sample

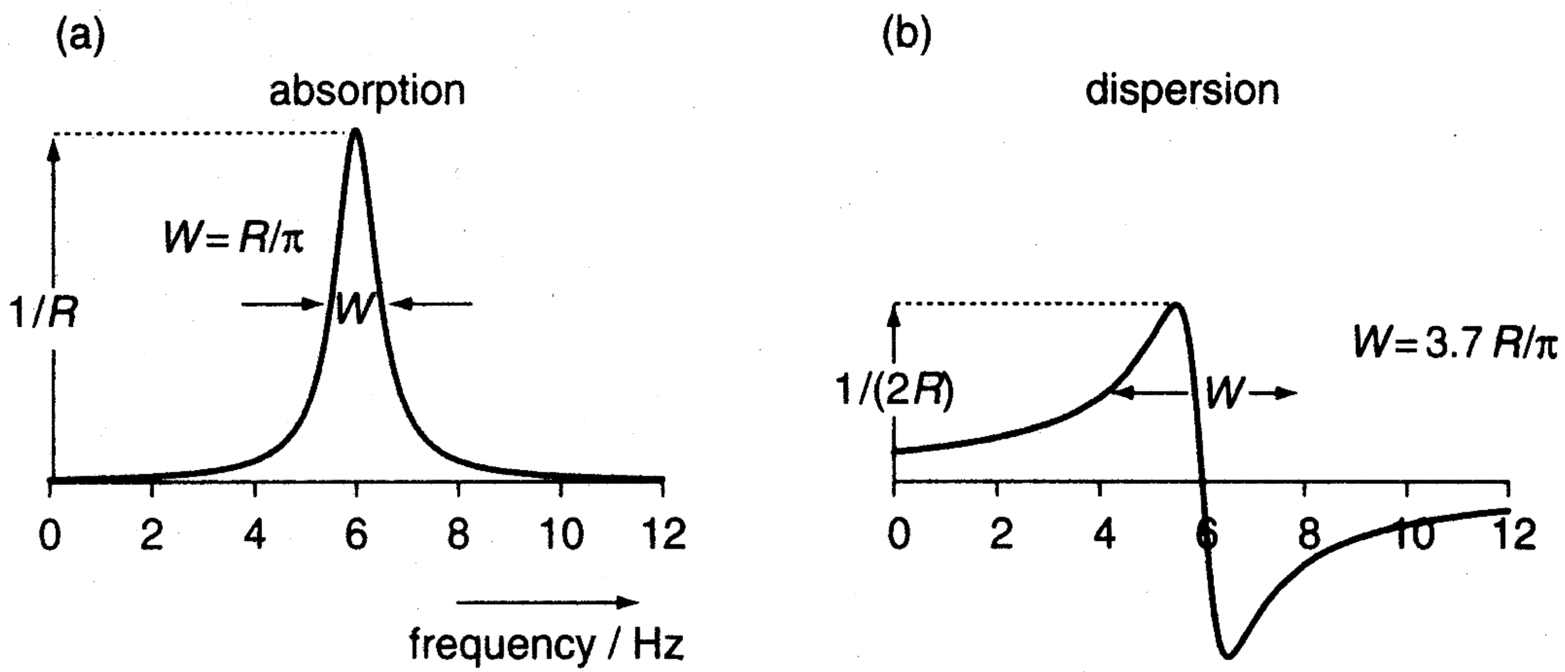
Stolen from: "Nuclear Magnetic Resonance" by P. J. Hore

Quadrature detection



Stolen from: "NMR: The Toolkit" by P. J. Hore et al.

Absorption and dispersion Lorentzian lineshapes



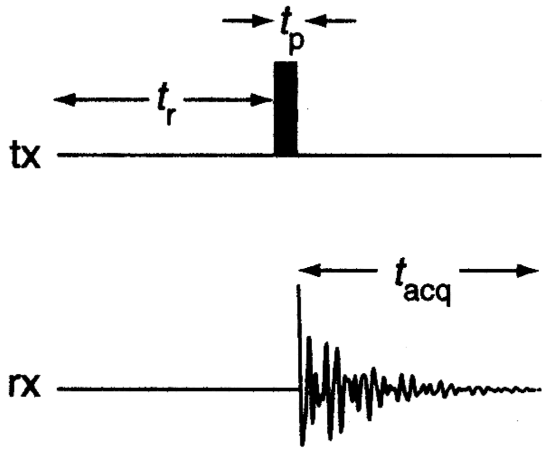
$R = 1/(\pi T_2)$

Stolen from: "Understanding NMR Spectroscopy" by J. Keeler

NMR basics: recording and processing good spectra

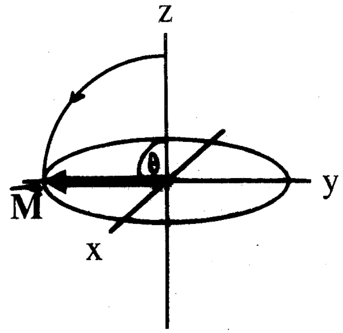
Acquiring spectra

The “pulse-acquire” experiment



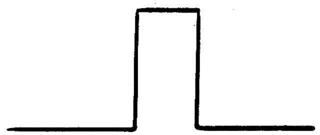
Stolen from: “Understanding NMR Spectroscopy” by J. Keeler

$\theta = 2\pi \nu_1 \tau = \frac{\pi}{2}$ (90°)

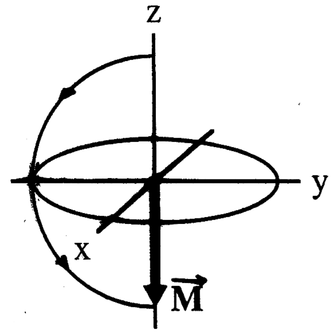


Effect of a 90° pulse about the rotating frame x axis

~ 5μs

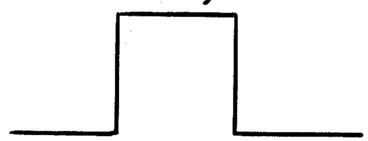


$\theta = \pi$ (180°)

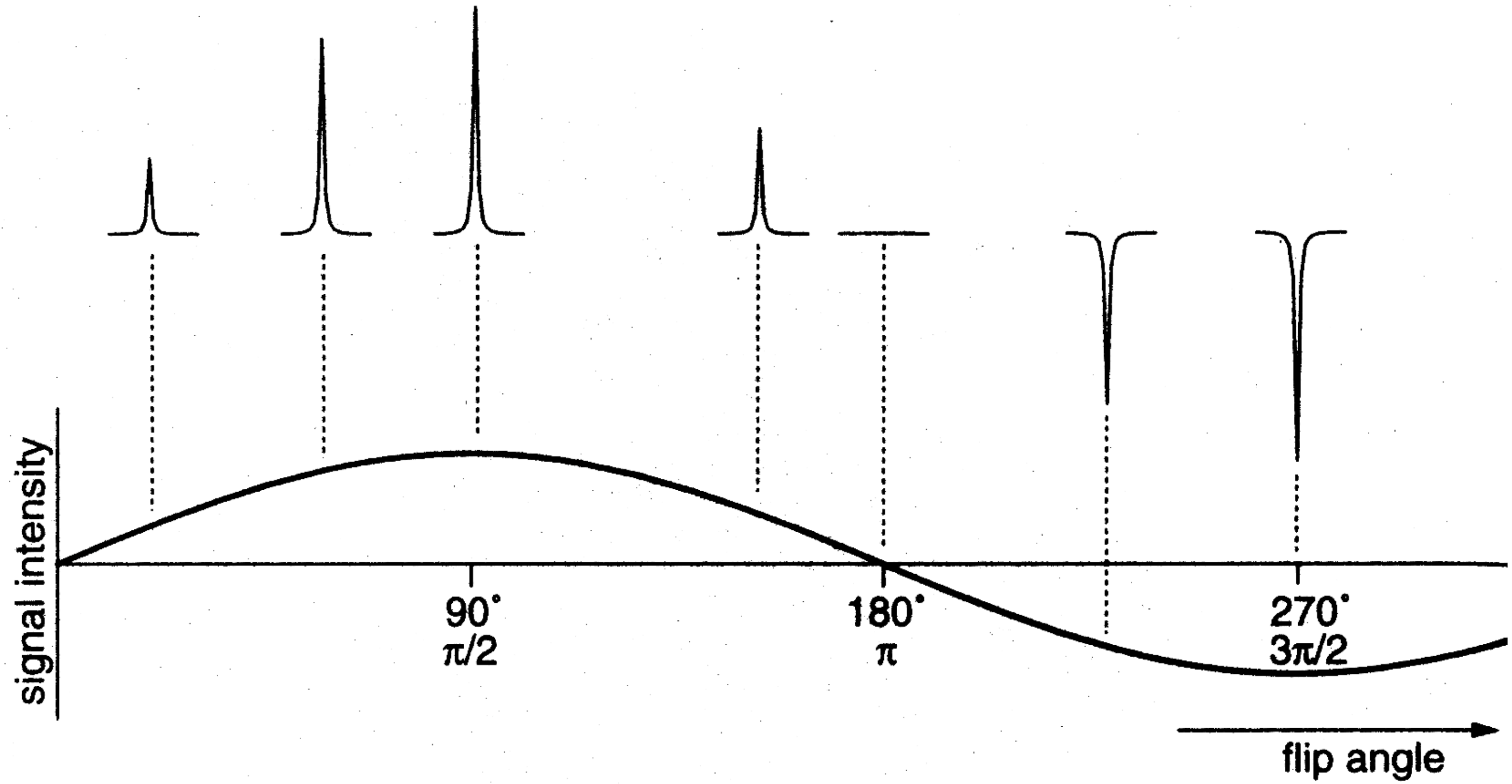


Effect of a 180° pulse about the rotating frame x axis

~ 10μs

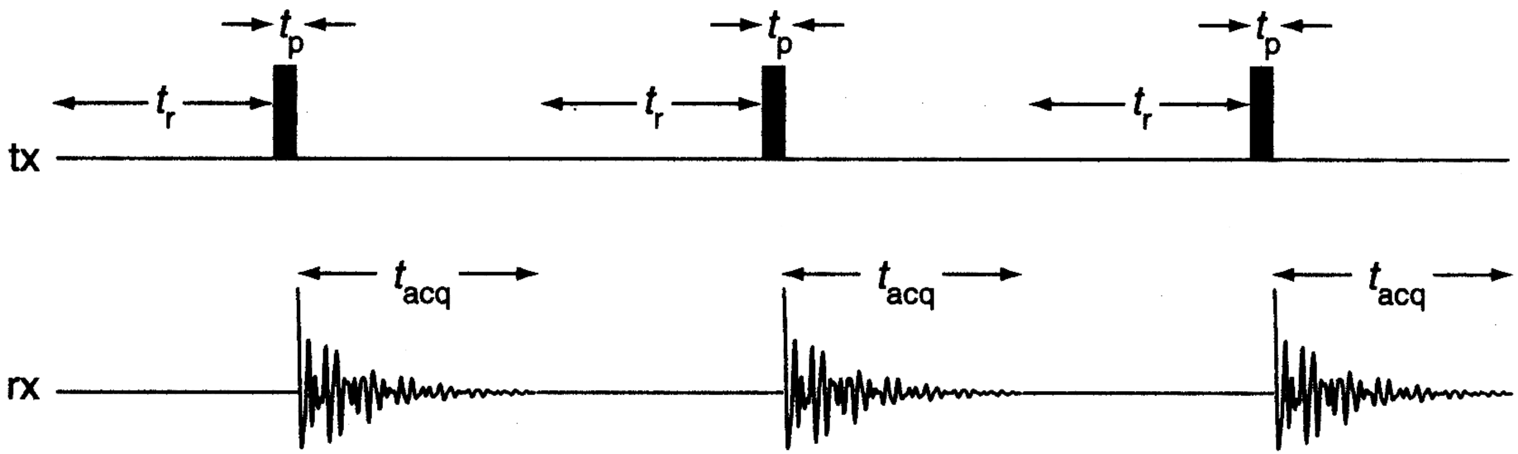


Pulse length calibration



Stolen from: “Understanding NMR Spectroscopy” by J. Keeler

Signal averaging



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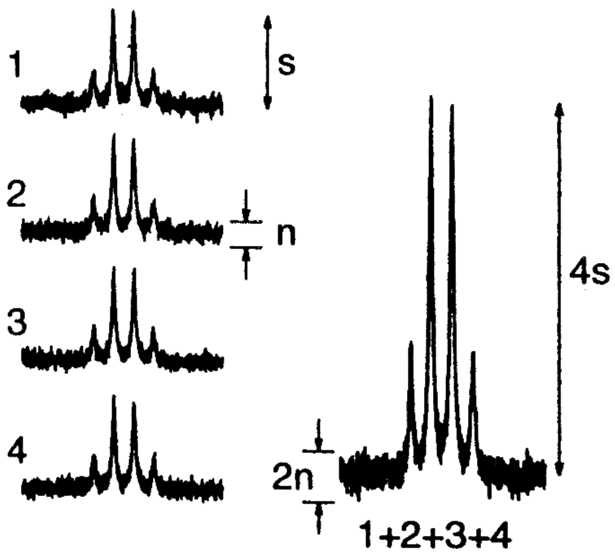
Signal averaging

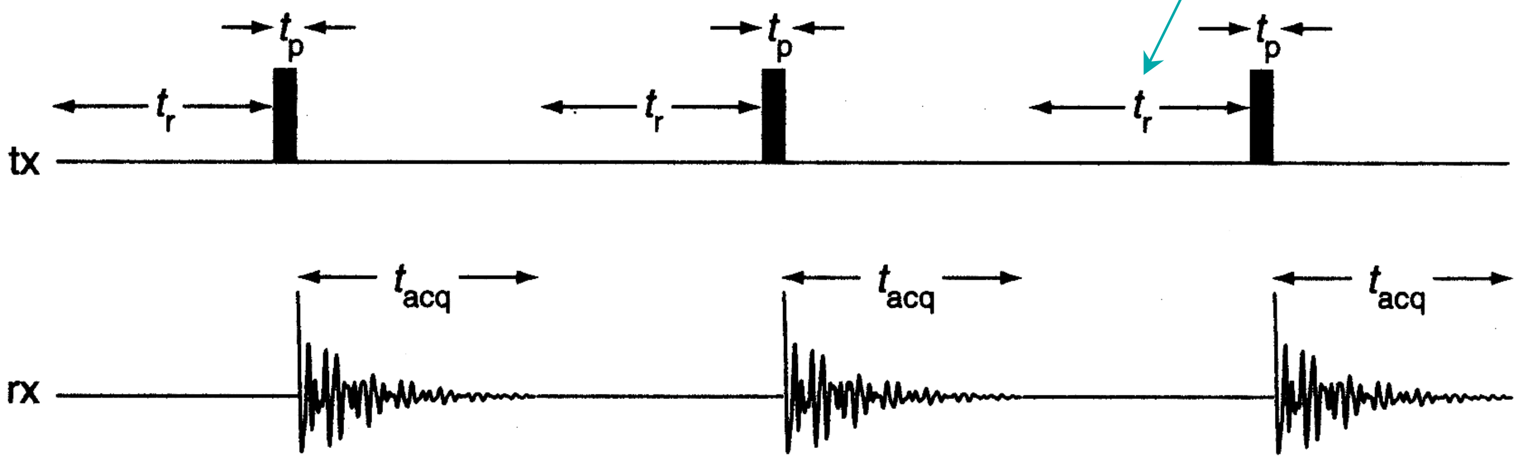


if we acquire N transients (or “scans”) then s/n increases by $\sqrt{N}$

Stolen from: “Nuclear Magnetic Resonance” by P. J. Hore

Signal averaging

how long should we wait between scans?



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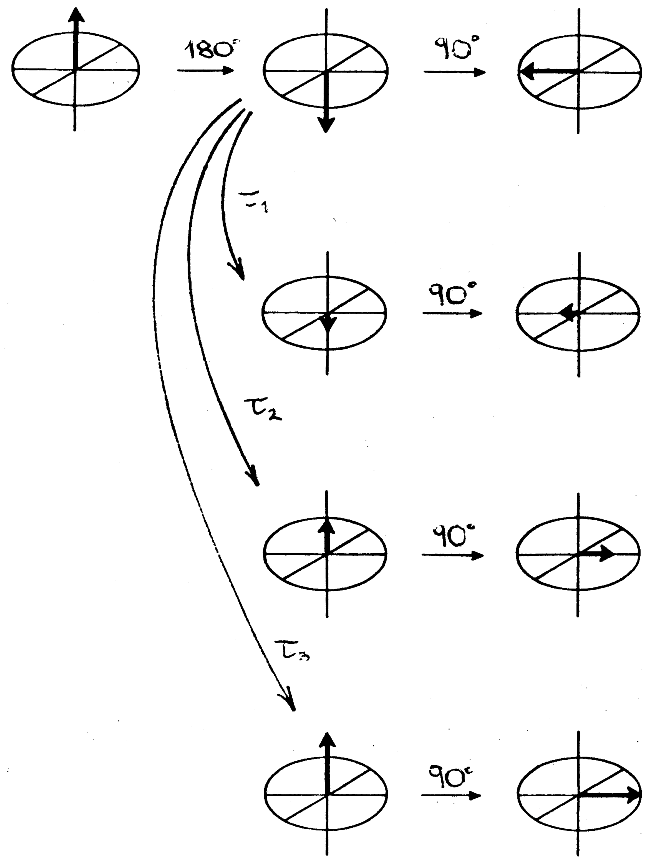
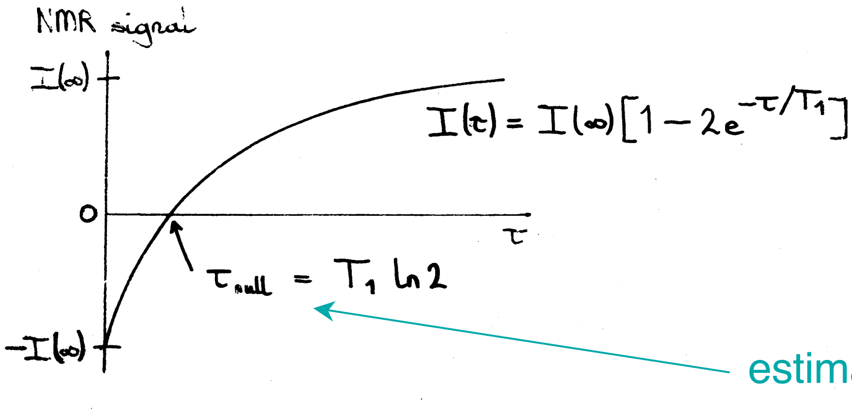
T_1 measurement



inversion-recovery experiment:
180° – τ – 90° acquire

T_1 measurement



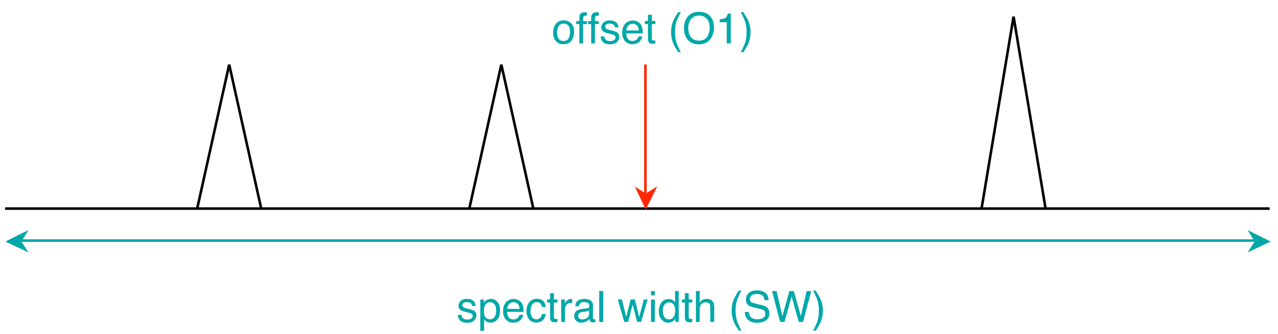
estimate T_1 from null point

How long between scans?

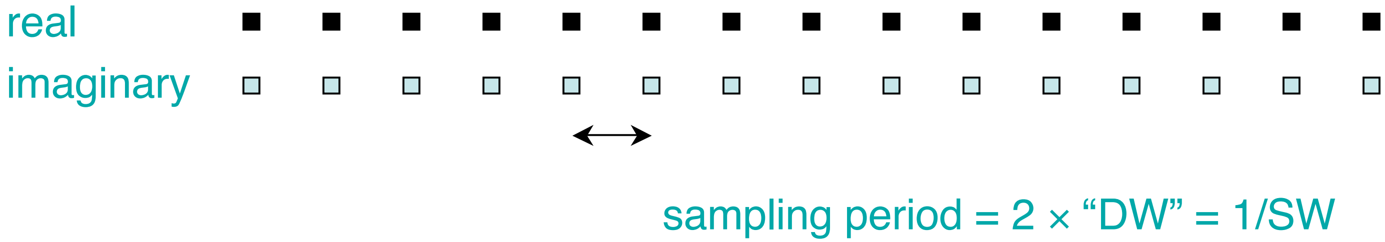
Allow ~5 T_1 for a careful relaxation time (T_1) measurement (!);

~1.5 T_1 for a typical pulse-acquire experiment

Spectrum parameters

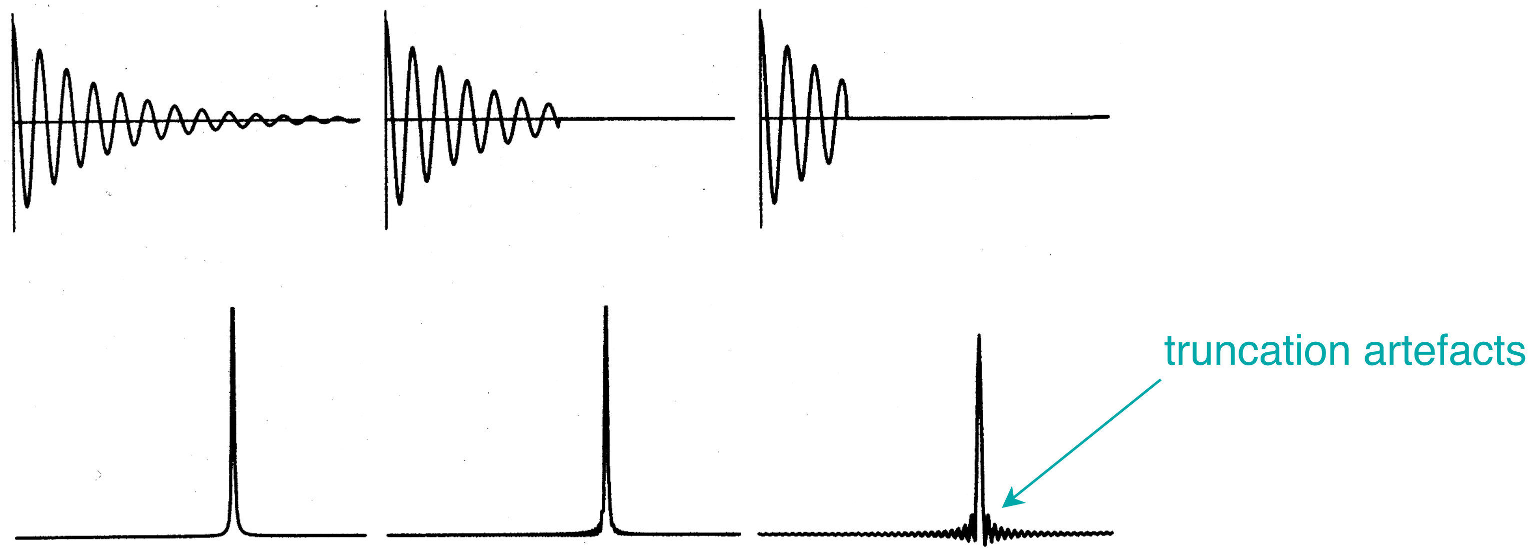


In time domain



Acquire "TD" points in FID (TD/2 real and TD/2 imaginary), so total duration of FID is TD.DW = TD/(2.SW)

Importance of acquisition time



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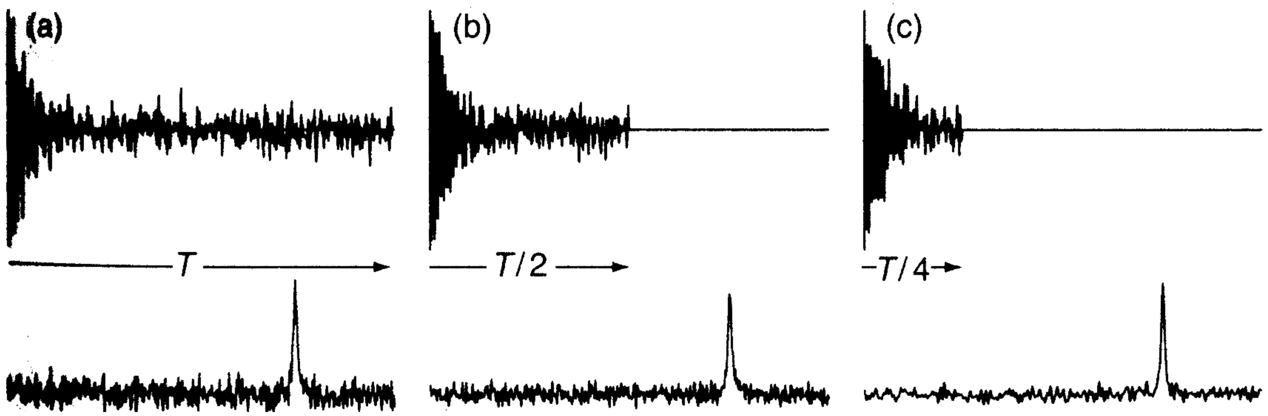
Importance of acquisition time



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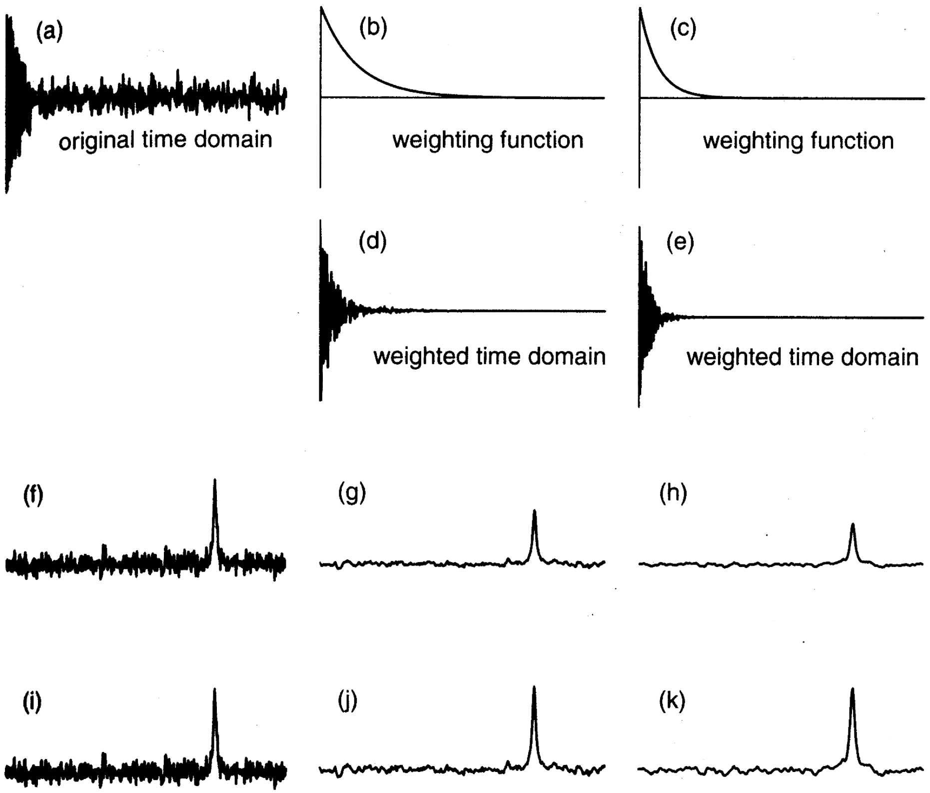
NMR basics: recording and processing good spectra

Processing

Weighting functions



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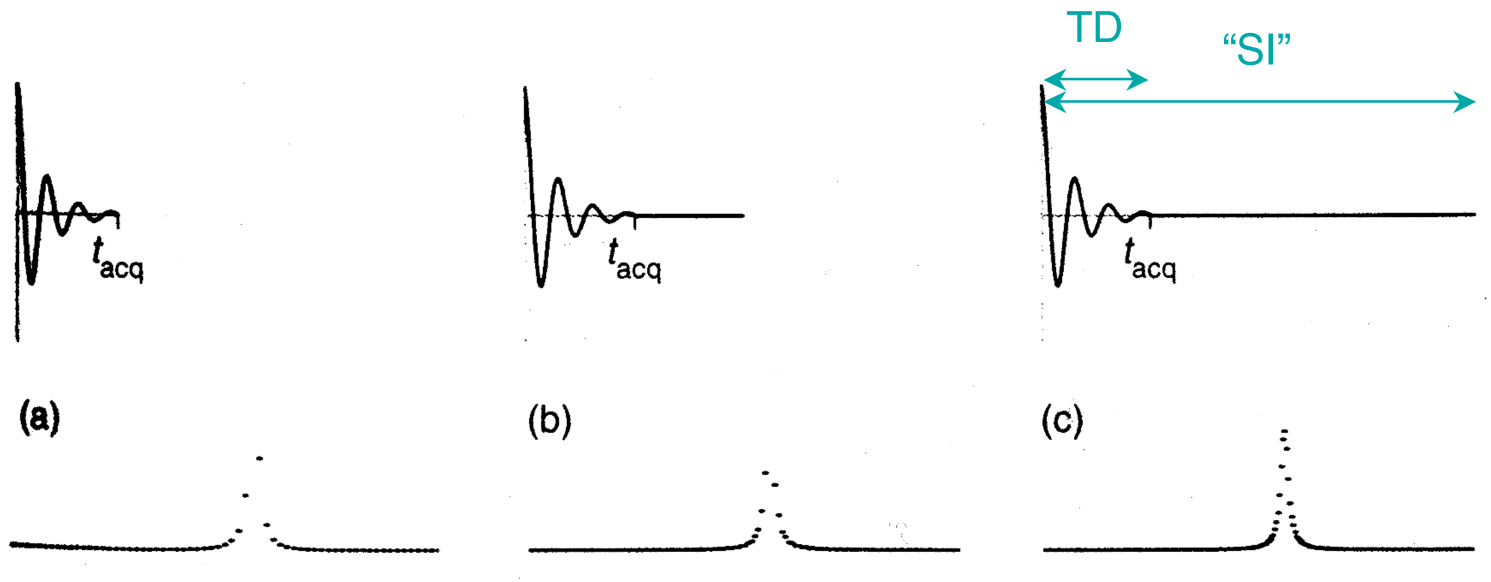
Zero filling



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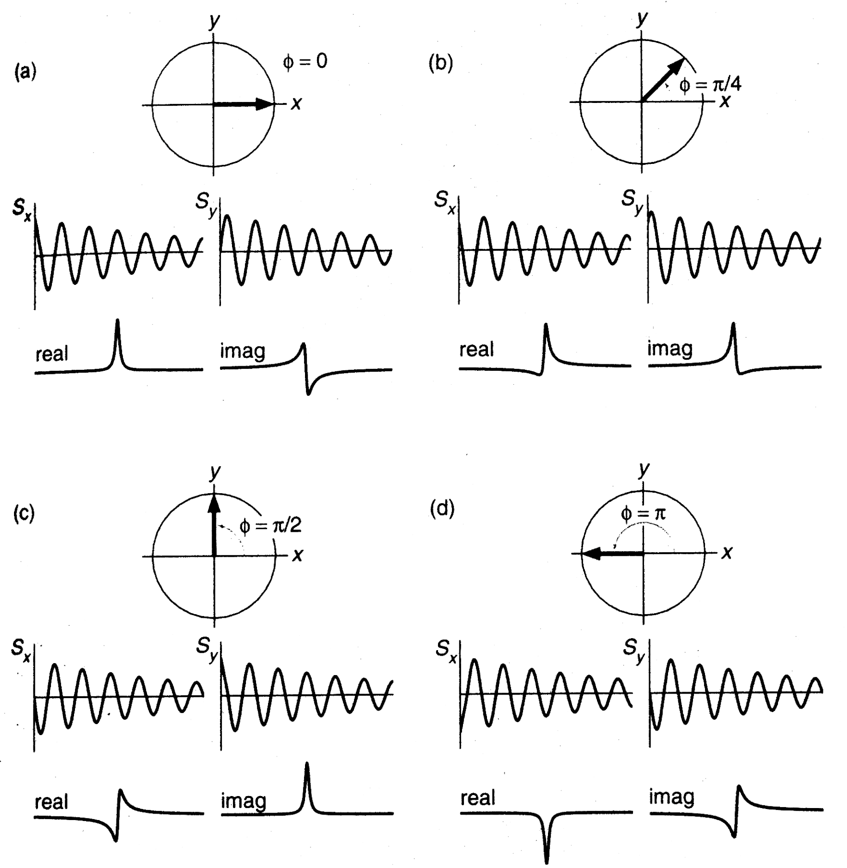
Signal phase



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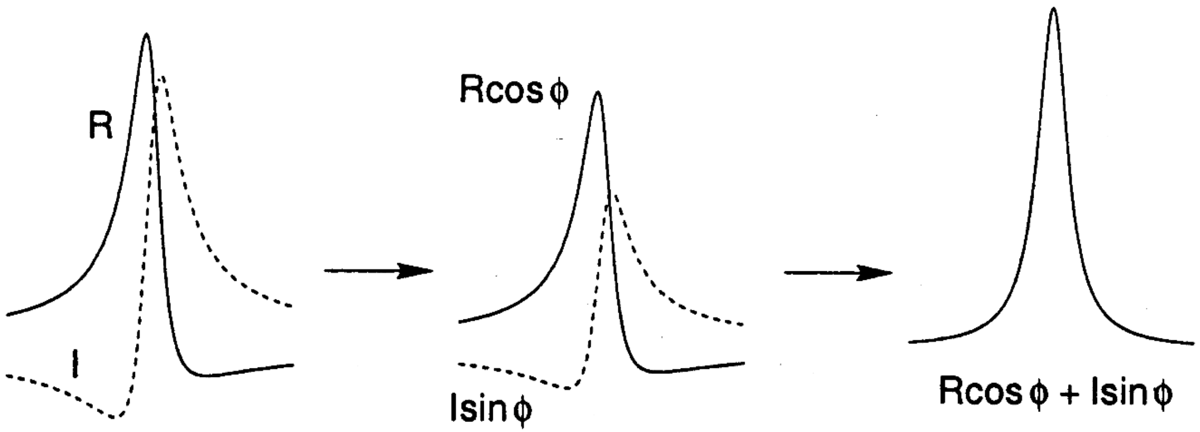
“Phasing” the spectrum



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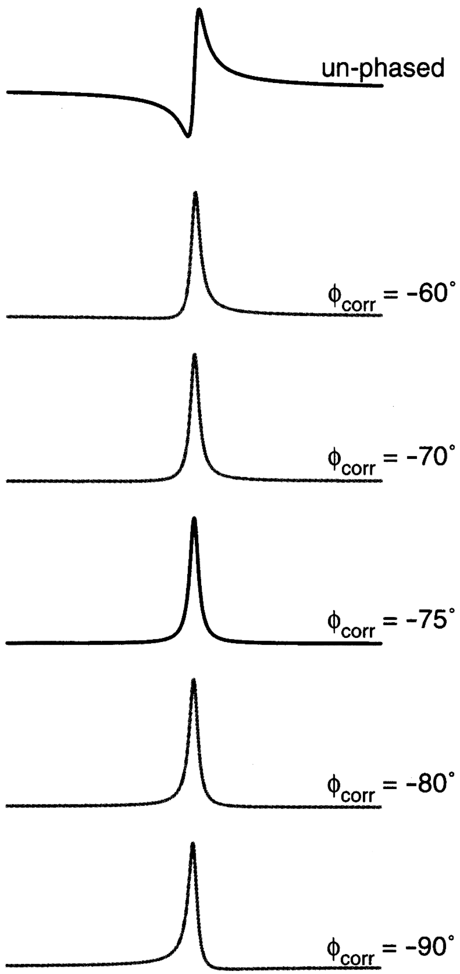
“Phasing” the spectrum



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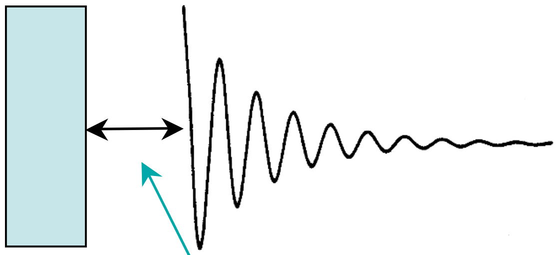
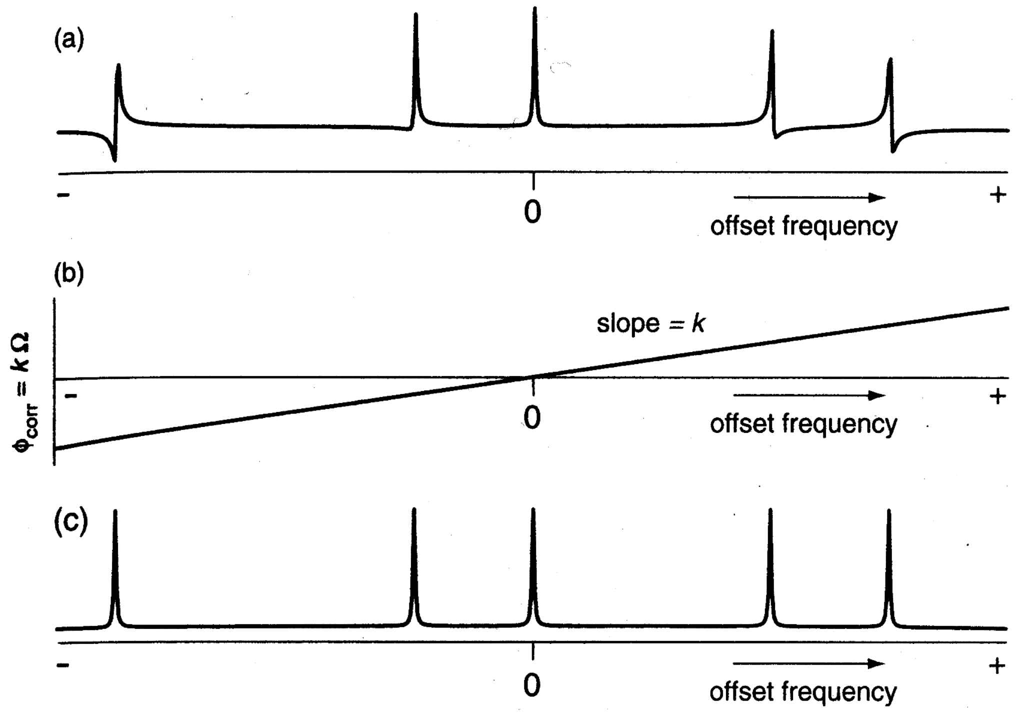


there is a deadtime ("DE") between
pulse and start of acquisition

⇒ need to do **two** phase corrections: a **frequency-independent** ("zeroth-order") correction and a **frequency-dependent** ("first-order") one

Frequency-dependent phase correction

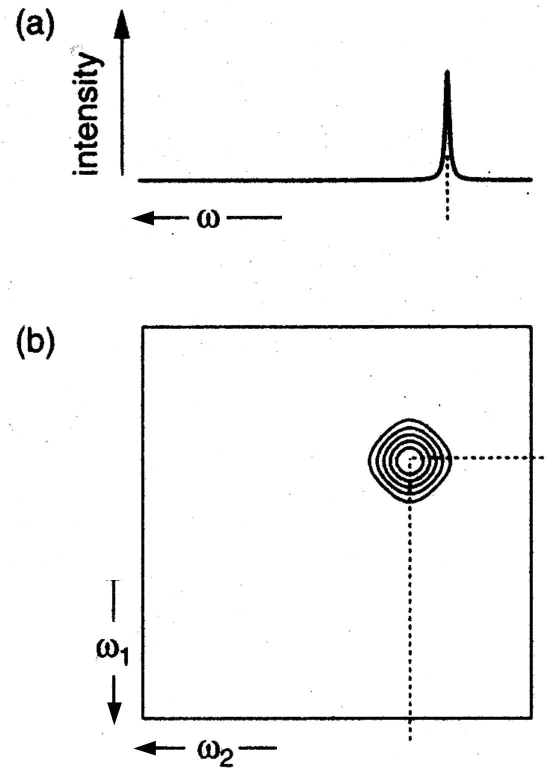


note that this correction varies the phase across the linewidth, which is wrong!

Stolen from: "Understanding NMR Spectroscopy" by J. Keeler

NMR basics: recording and processing good spectra

Two-dimensional NMR

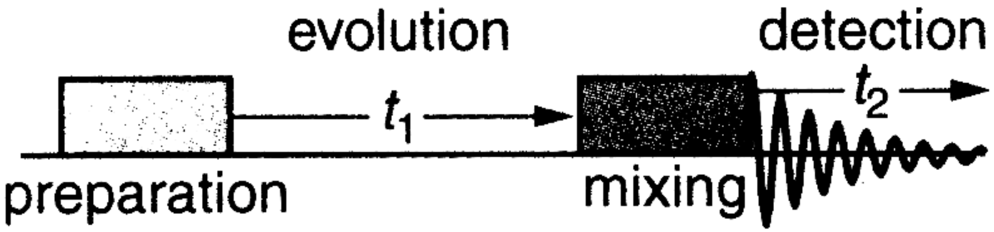


1D

2D

Stolen from: “Understanding NMR Spectroscopy” by J. Keeler

Basic experiment



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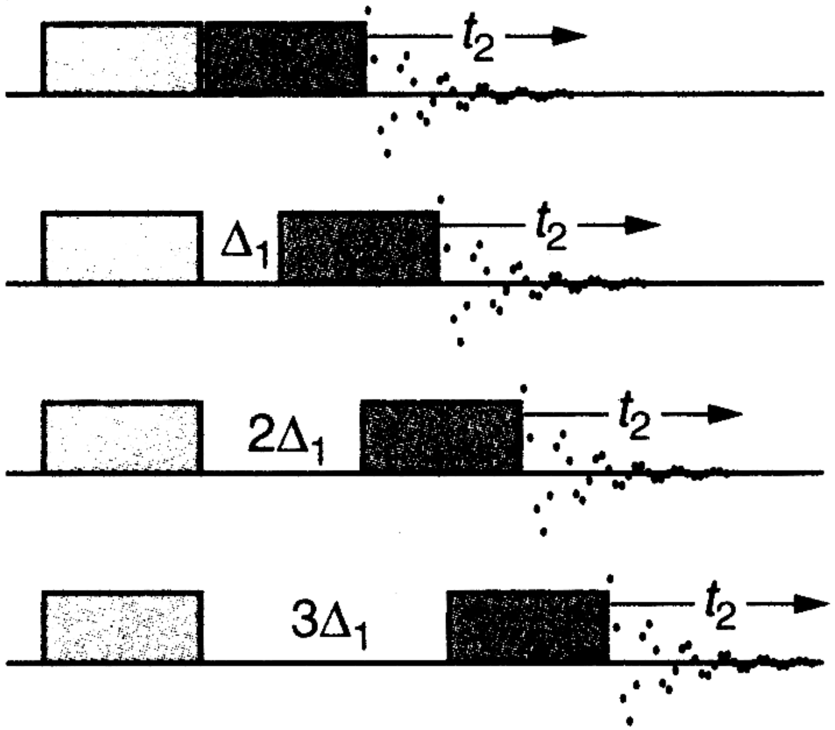
Basic experiment



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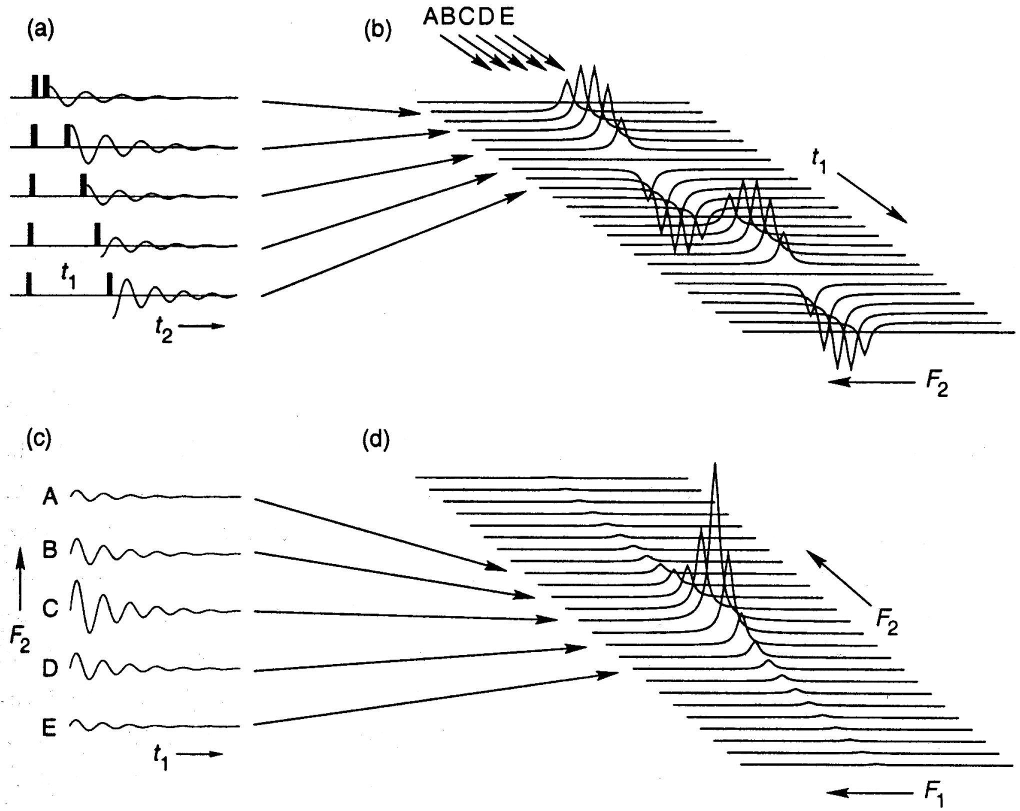
Two-dimensional Fourier transform



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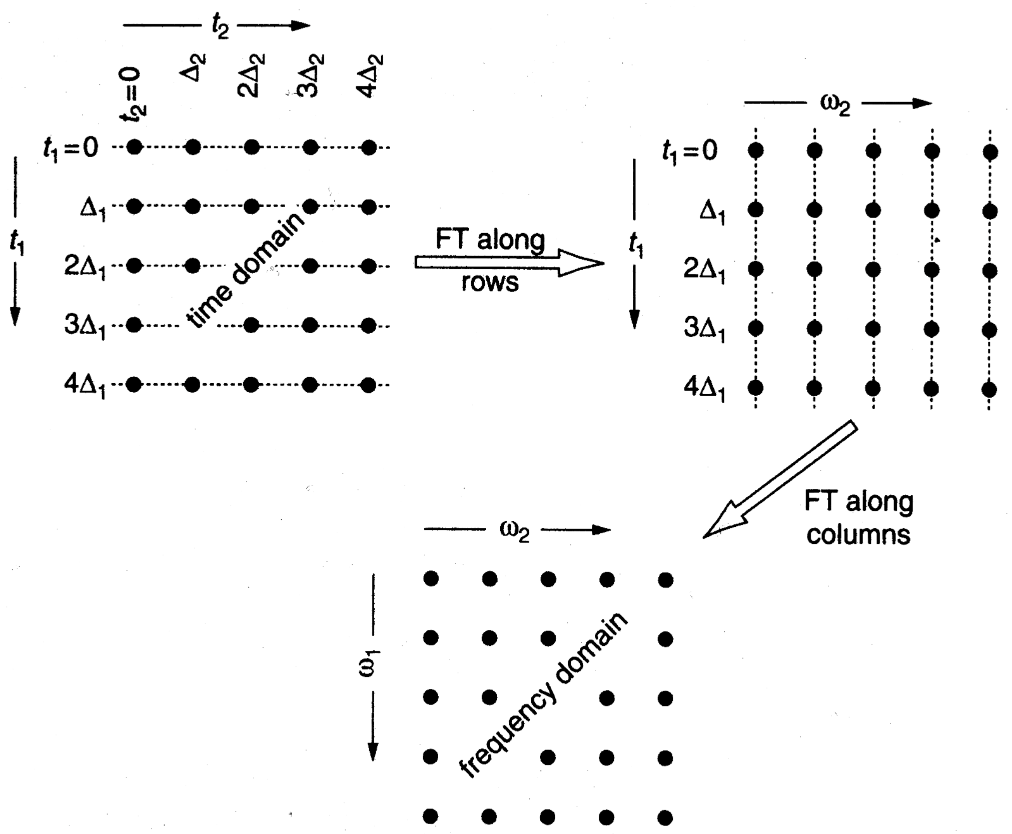
Two-dimensional Fourier transform



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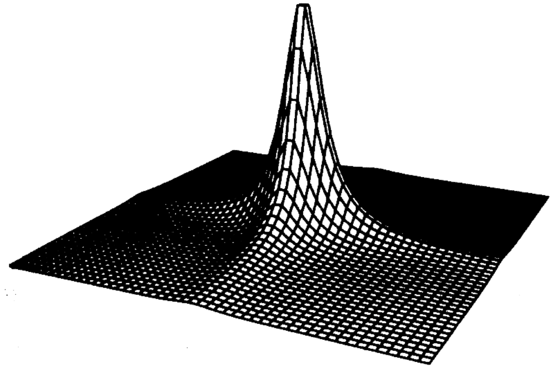
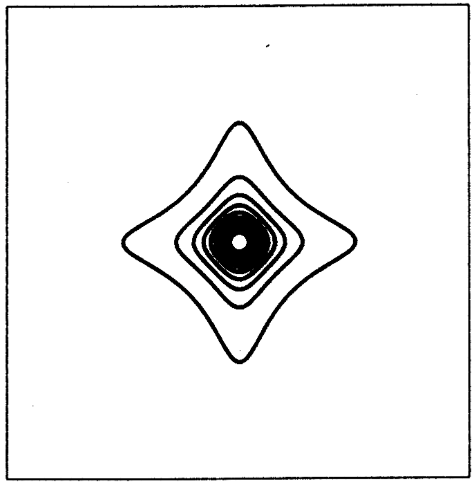
Double-absorption Lorentzian lineshape





Stolen from: “Understanding NMR Spectroscopy” by J. Keeler

To end…

- Have discussed some of the basic features of practical NMR spectroscopy
- In next two lectures (5 pm tomorrow and Tuesday) MJT will discuss some of the advanced NMR methods available for spectral assignment and structure determination

Thank you for your attention!