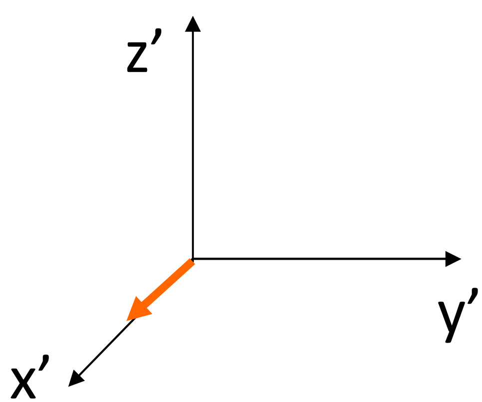
Magnetization Evolution after the r.f. Pulse (isofrequency)

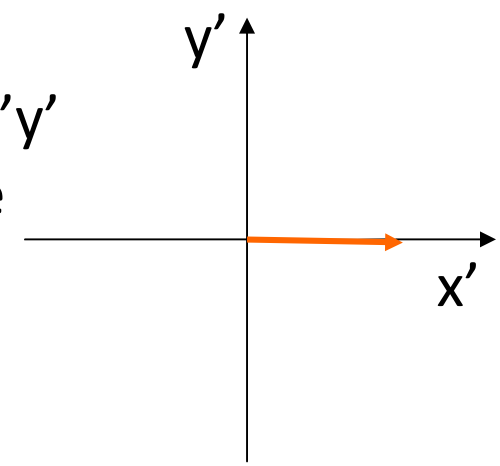
In this case $B^{r}_{eff} = \begin{vmatrix} 0 \\ 0 \\ 0 \end{vmatrix}$ therefore

$$\frac{dM^{r}_{x}(t)}{dt} = 0 \qquad \frac{dM^{r}_{y}(t)}{dt} = 0 \qquad \frac{dM^{r}_{z}(t)}{dt} = 0$$

In this case the magnetization is static in the rotating frame



in the x’y’ plane



Magnetization Evolution after the r.f. Pulse

For $\omega_0 \neq \omega_{rf}$

$$B_{eff}^{r} = \begin{vmatrix} 0 \\ 0 \\ \Delta B_0 \end{vmatrix}$$

$$\frac{dM_x^r(t)}{dt} = \gamma M_y^r(t)\Delta B_0$$

$$\frac{dM_y^r(t)}{dt} = -\gamma M_x^r(t)\Delta B_0$$

$$\frac{dM_z^r(t)}{dt} = 0$$

Time deriving the first equation and substituting the from the second equation the expression of the M_y^r derivative

$$\frac{d^2 M_x^r}{dt^2} = \gamma \Delta B_0 \frac{dM_y^r}{dt} = -\gamma^2 (\Delta B_0)^2 M_x^r$$

The general solution is: $$M_x^r = C_1 \cos(-\gamma \Delta B_0 t) + C_2 \sin(-\gamma \Delta B_0 t)$$

If at t=0 the magnetization was lying on x, the constant C_2= 0 and the solution is:

$$M_x^r = M_0 \cos(-\gamma \Delta B_0 t)$$

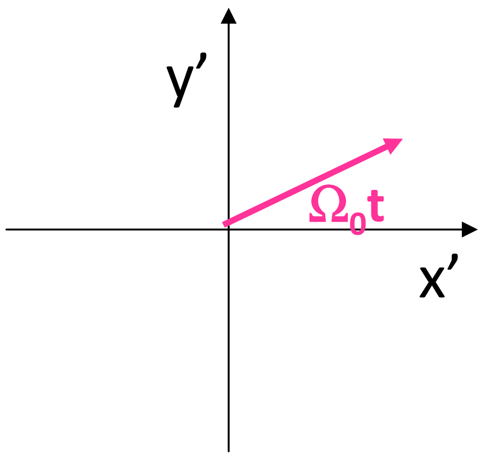
since $\Omega_0 = -\gamma \Delta B_0$

$$\boxed{M_x^r = M_0 \cos(\Omega_0 t)}$$

Substituting in:

$$\frac{dM_y^r(t)}{dt} = \Omega_0 M_x^r(t)$$

in the x'y' plane



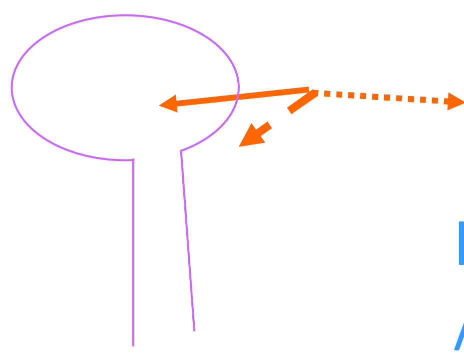
One obtains:

$$\boxed{M_y^r = M_0 \sin(\Omega_0 t)}$$

The magnetization is precessing in the rotating frame with angular frequency Ω_0

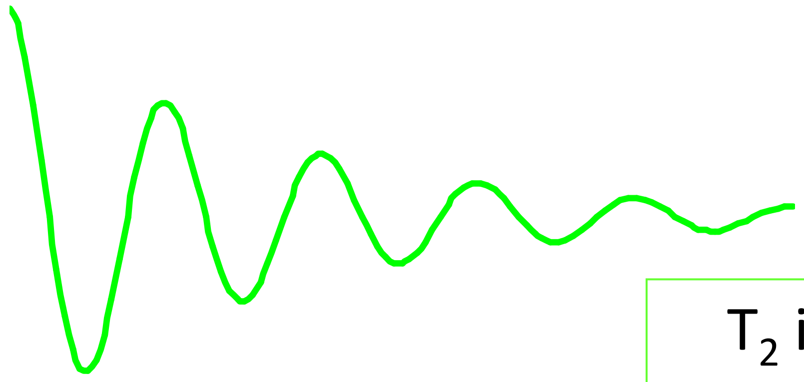
NMR Signal

- M, although static in the rotating fram((isofrequency case), is rotating with angular velocity $\omega_0 = \omega_{rf} + \Omega_0$ in the xy plane of the lab frame
- This causes an oscillating current in the receiver coil, which is parallel to the z axis



http://dotynmr.com/products /liquids-nmr-probes/

- The signal decays owing to the dephasing of the various isochromats components of the transverse magnetization (transverse relaxation).
- The term accounting for relaxaion must be added to the equations of motion
- According to experimetal observation the decay of the signal takes place with a kinetics of the first order



T_2 is the reciprocal of the rate constant

Equations of Motion for Transverse Magnetization in the Absence of B_1

$$\frac{dM_x^r(t)}{dt} = \gamma M_y^r(t)\Delta B_0 - \frac{M_x^r(t)}{T_2}$$

$$\frac{dM_y^r(t)}{dt} = -\gamma M_x^r(t)\Delta B_0 - \frac{M_y^r(t)}{T_2}$$

The solutions, starting with the transverse magnetization aligned with x' axis at t=0, are:

$$M_x^r(t)=M_0\cos(\Omega_0 t)\exp(-t/T_2)$$

$$M_y^r(t)=M_0\sin(\Omega_0 t)\exp(-t/T_2)$$

Longitudinal Relaxation
Spin-Lattice Relaxation

In the exclusive presence of the static magnetic field, B_0, the longitudinal component of magnetization reaches the equilibrium value, M_0, by exchanging energy with the surroundings, according to a first order kinetics

$$\frac{dM_z(t)}{dt} = -\frac{M_z(t) - M_0}{T_1}$$

$$\int_{Mz(t=0)}^{Mz(t=ta)} \frac{dM_z}{M_z - M_0} = -\frac{1}{T_1}\int_0^{ta} dt \qquad \int_{Mz(t=0)}^{Mz(t=ta)} \frac{d(M_z - M_0)}{M_z - M_0} = -\frac{1}{T_1}\int_0^{ta} dt$$

$$\ln \frac{M_z(t_a) - M_0}{M_z(t=0) - M_0} = -\frac{t_a}{T_1}$$

The value of $M_z(t=0)$ depends on the experimental conditions and on time considered as t= 0

Kinetics for M_0 Establishment

- If t= 0 when the sample was placed into the instrumental magnetic field In questo caso vale $M_z(t=0)=0$
- and the relevant solution is:

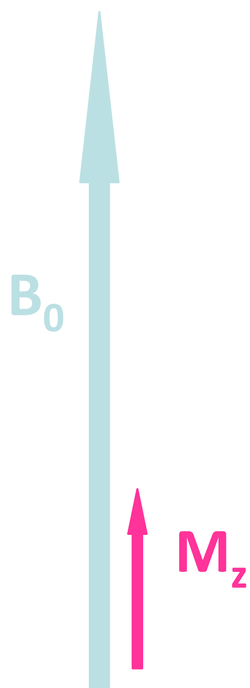
$$\ln \frac{M_z(t_a) - M_0}{-M_0} = -\frac{t_a}{T_1}$$

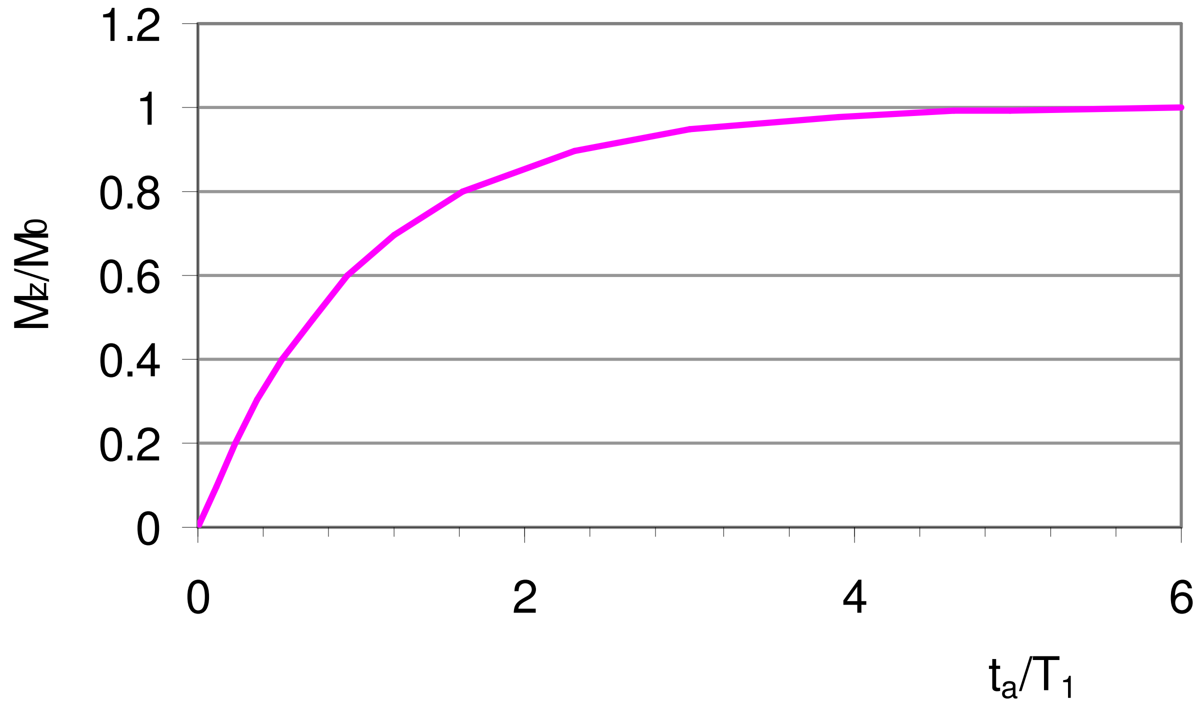
which, by exponentiation, corresponds to:

$$\frac{M_z(t_a) - M_0}{-M_0} = \exp\left(-\frac{t_a}{T_1}\right)$$

$$M_z(t_a) = M_0\left[1 - \exp\left(-\frac{t_a}{T_1}\right)\right]$$

$$M_z(t_a) = M_0\left[1 - \exp\left(-\frac{t_a}{T_1}\right)\right]$$





BLOCHPHENOMENOLOGICAL EQUATIONS

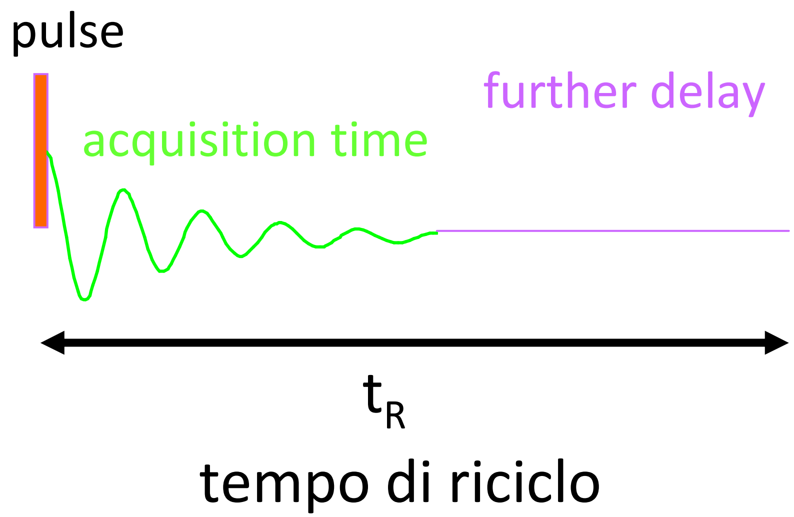
$$\frac{dM_x^r(t)}{dt} = \gamma\left[M_y^r(t)B_z^{eff} - M_z^r(t)B_y^{eff}\right] - \frac{M_x^r(t)}{T_2}$$

$$\frac{dM_y^r(t)}{dt} = \gamma\left[M_z^r(t)B_x^{eff} - M_x^r(t)B_z^{eff}\right] - \frac{M_y^r(t)}{T_2}$$

$$\frac{dM_z^r(t)}{dt} = \gamma\left[M_x^r(t)B_y^{eff} - M_y^r(t)B_x^{eff}\right] - \frac{M_z^r(t) - M_0}{T_1}$$

Ernst Angle

- Longitudinal interference for repetitive pulse experiments
- The need for signal averaging is typical of FT techniques
- Often it is not possible to neglect the interference of successive scans
- The highest repetition rate is advantageous in order to maximixe sensitivity



- The used t_R is such that magnetization does not fully reverts to equilibrium
- After few scans a dynamic steady state has established
- Calculation of the *steady state* signal

Defining:

$M_z(0+)$= const M_z after the pulse

β piulse length

$M_z(0+) = M_z(0-)\cos\beta = \text{const}$

$M_x(0+) = Mz(0-)\text{sen}\beta = \text{const}$ (<u>to be maximized)</u>

$Mz(0-) = Mz(t_R) = \text{cost}$

$Mz(t_R)=M_0-[M_z(0+)-M_0]\exp(-t_R/T_1)$

$M_z(t_R)=M_z(0_+)\exp(-t_R/T_1)+M_0\,[1-\exp(-t_R/T_1)]$

$M_z(t_R)=M_z(0_+)B+A$

$M_z(0_-)$ is obtained as

$M_z(0_-)=M_z(0_+)B+A$

$M_z(0_-)=M_z(0_-)\cos\beta B+A$

$$M_z(0_-)=\frac{A}{1-B\cos\beta}$$

We want maximize $M_x(0_+)= M_z(0_-)\mathrm{sen}\beta$

using

$$A = M_0\left[1 - \exp\left(-\frac{t_R}{T_1}\right)\right] \qquad B = \exp\left(-\frac{t_R}{T_1}\right)$$

$$M_x(0+) = \frac{A\sin\beta}{1 - B\cos\beta}$$

$$\frac{dM_x(0+)}{d\beta} = \frac{A\cos\beta(1 - B\cos\beta) - A\sin\beta B\sin\beta}{(1 - B\cos\beta)^2} = \frac{A(\cos\beta - B)}{(1 - B\cos\beta)^2}$$

is zero for:

$$\cos\beta_{Ernst} = \exp\left(-\frac{t_R}{T_1}\right)$$

optimum value

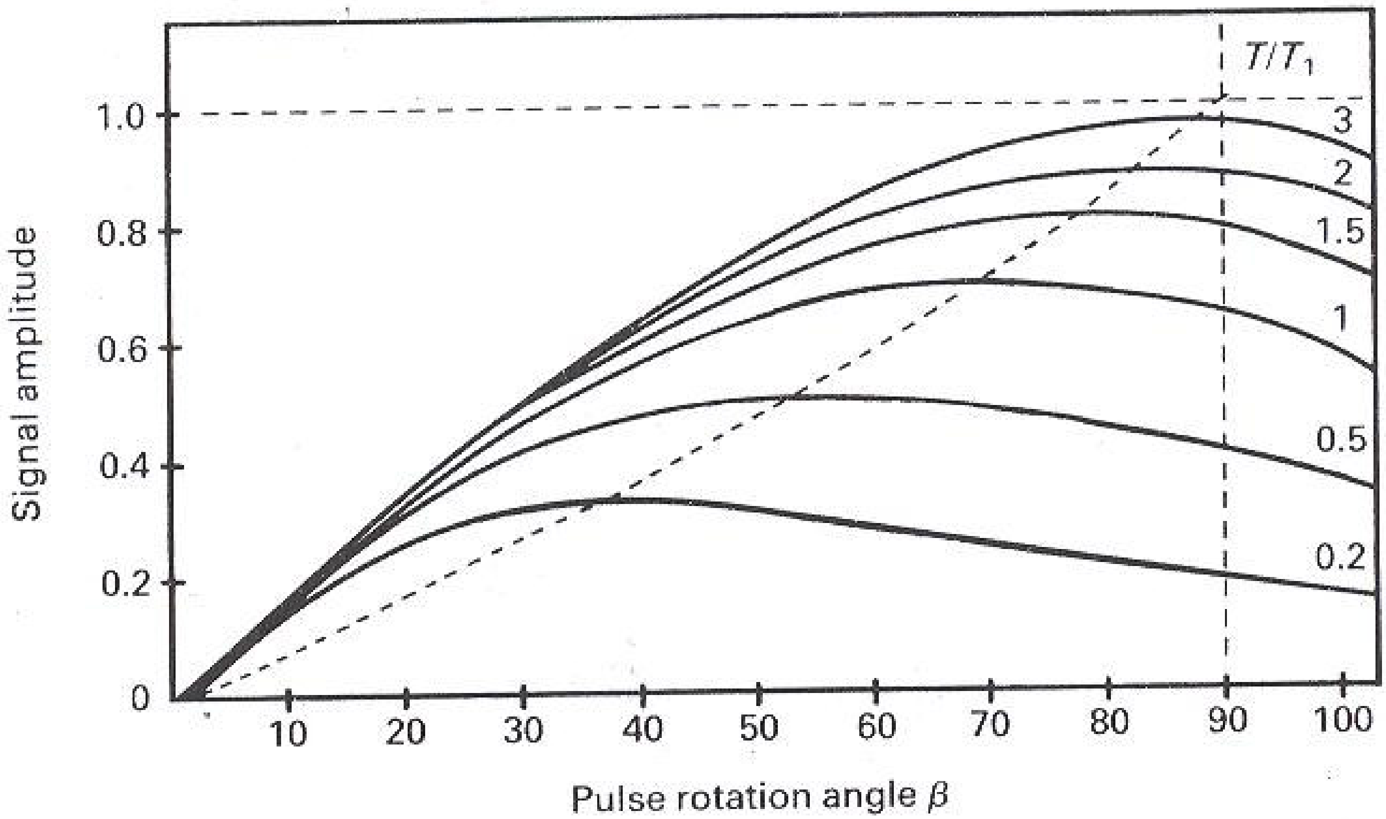


FIG. 4.2.5. Normalized peak amplitude of the absorption-mode signal v_{max}/M_0T_2 in a repetitive Fourier experiment with negligible transverse interference as a function of the pulse rotation angle β for various interpulse spacings T normalized by the longitudinal relaxation time T_1. The broken line connects the maximum amplitudes and indicates the optimum pulse rotation angle.

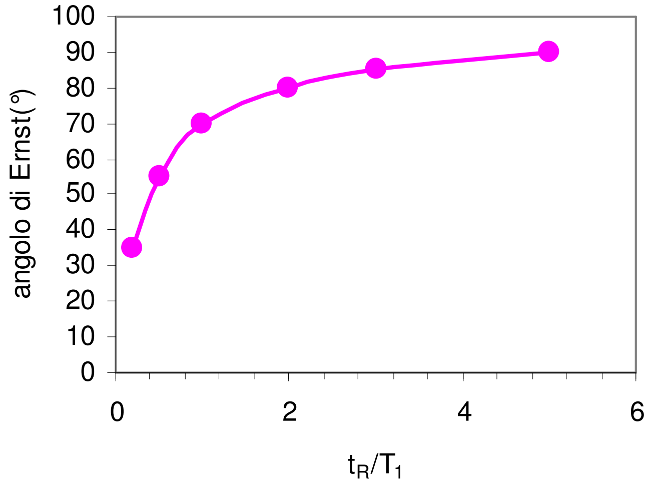
Ernst angle

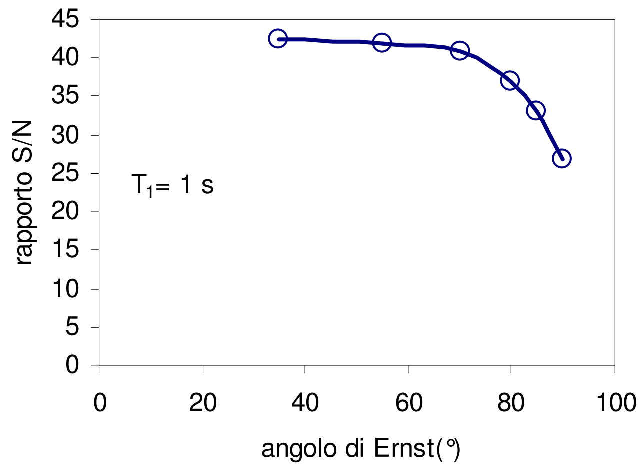
Angolo di Ernst e S/N

esempio

T_1= 1 s

tR/T1	angolo	Max	scans 1h	S	N	**S/N**
0.2	35	0.315702	18000	5683	134	**42**
0.5	55	0.49426	7200	3559	85	**42**
1	70	0.679495	3600	2446	60	**41**
2	80	0.872022	1800	1570	42	**37**
3	85	0.950722	1200	1141	35	**33**
5	90	1	720	720	27	**27**



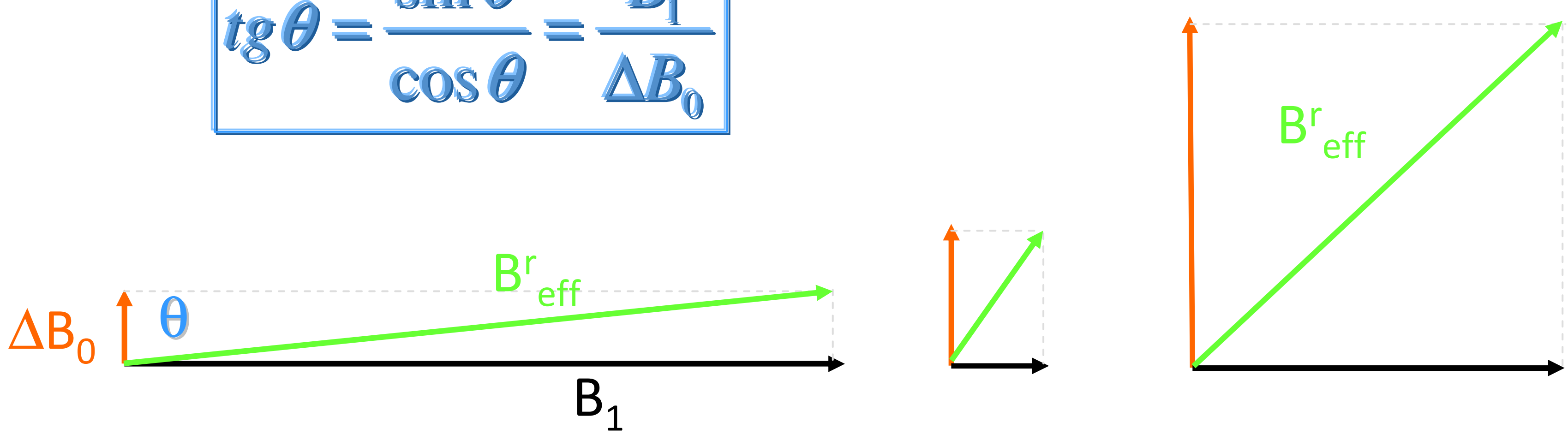


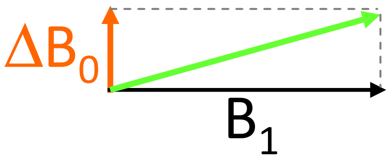
- S/N utilizzando l'angolo di Ernst diminuisce con l'aumentare di T_1. S/N va diviso per $\sqrt{T_1}$

Off-resonance Effects due to Pulse Finite Length

- Dependent on B_1 intensity
- For $\Omega_0 \neq 0$ M rotates about B^r_{eff}
- The weaker B_1 the more different B^r_{eff} and the higher Ω_0

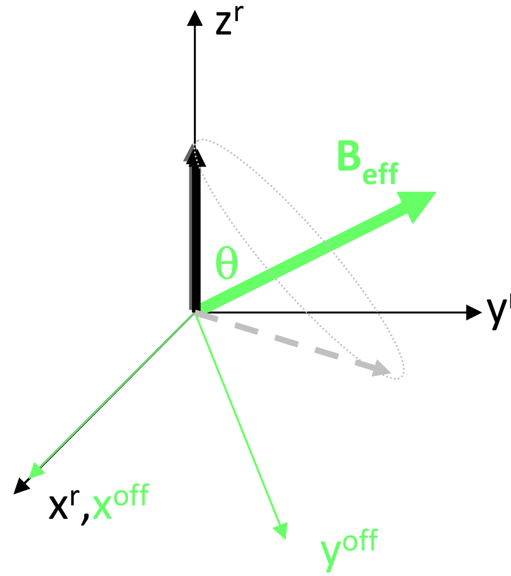
$$tg\theta = \frac{\sin\theta}{\cos\theta} = \frac{B_1}{\Delta B_0}$$





$$\vec{B}^{r}_{eff} = \begin{vmatrix} 0 \\ B^{r}_{eff}\, sen\theta \\ B^{r}_{eff} \cos\theta \end{vmatrix}$$

Transformation from the rotating frame to a systems with z axis along B_{eff} by rotating about x' by $-\theta$



$$\overline{\overline{T}}^{\,r-off} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -sen\theta \\ 0 & sen\theta & \cos\theta \end{vmatrix}$$

θ independentent of time!

$$\vec{B}^{off}_{eff} = \begin{vmatrix} 0 \\ 0 \\ B_{eff} \end{vmatrix}$$

Let's start (t= 0) from equilibrium

$$\vec{M}^{off}_{0}(t=0) = \begin{vmatrix} 0 \\ -M_0\, sen\theta \\ M_0 \cos\theta \end{vmatrix}$$

Evolution of magnetization in the frame with z axis along B_{eff}

$$\frac{d\vec{M}^{off}(t)}{dt} = \gamma \vec{M}^{off}(t) \wedge \vec{B}^{off}_{eff}$$

the transform matrix, $T^{r\text{-}off}$, is independent of time

Supplementary material

$$\frac{dM_x^{off}}{dt} = \gamma M_y^{off} B_{eff}$$

$$\frac{dM_y^{off}}{dt} = -\gamma M_x^{off} B_{eff}$$

$$\frac{dM_z^{off}}{dt} = 0$$

Making the time derivative of the first equation and substituting the second equation one obtains the second order differential equation:

$$\frac{d^2 M_x^{off}}{dt^2} = -\gamma^2 B_{eff}^2 M_x^{off}$$

Supplementary material

The general solution is: $M_x^{off} = C_1\cos(-\gamma B_{eff}t) + C_2 sen(-\gamma B_{eff}t)$

Considering the starting condition (t=0) $M_x^{off} = 0$, it ensues $C_1 = 0$

Substituting in the second equation $M_x^{off} = C_2 sen(-\gamma B_{eff}t)$

$$\frac{dM_y^{off}}{dt} = -\gamma B_{eff} C_2 sen(-\gamma B_{eff} t)$$

The solution is: $M_y^{off} = -C_2\cos(-\gamma B_{eff}t)$

Considering the starting condition (t=0) $M_y^{off}(t=0) = -M_0 sen\theta$

$C_2 = M_0 sen\theta$

M_z^{off} does not change because: $$\frac{dM_z^{off}}{dt} = 0$$

Solutions in the rotating frame

$M^r(t) = T^{r\text{-off-}\mathbf{1}} M^{off}(t)$

Supplementary material

$$\vec{M}^r(t) = \begin{vmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & sen\,\theta \\ 0 & -sen\,\theta & \cos\theta \end{vmatrix} \begin{vmatrix} M_0 sen\,\theta \cos\beta_{eff} \\ -M_0 sen\,\theta\cos\beta_{eff} \\ M_0\cos\theta \end{vmatrix} = M_0 \begin{vmatrix} sen\,\theta\cos\beta_{eff} \\ \cos\theta sen\,\theta(1-\cos\beta_{eff}) \\ \cos^2\theta + sen^2\theta sen\,\beta_{eff} \end{vmatrix}$$

$\beta_{eff} = -\gamma B_{eff} t$

$$M_x^r(t,\theta) = M_0 \sin\theta \sin\beta_{eff}$$

$$M_y^r(t,\theta) = M_0 \cos\theta \sin\theta(1-\cos\beta_{eff})$$

$$M_z^r(t,\theta) = M_0\left(\cos^2\theta + \sin^2\theta\cos\beta_{eff}\right)$$

The magnetization vector precesses about B_{eff} lying on a cone with vertex angle θ.

For small θ M does not even reach the equatorial plane.

For small ratios, but still $\mathbf{B_1/\Delta B_0 > 1}$

In order to obtain the maximum signal (magnetization in the transverse plane) $\beta_{eff} > 90°$ must be used

It can be calculated deriving $M_x^{r\,2}+M_y^{r\,2}$ with respect to $\cos\beta_{eff}$

Obtaining: $$\cos\beta_{eff} = -\frac{\cos^2\theta}{\sin^2\theta}$$

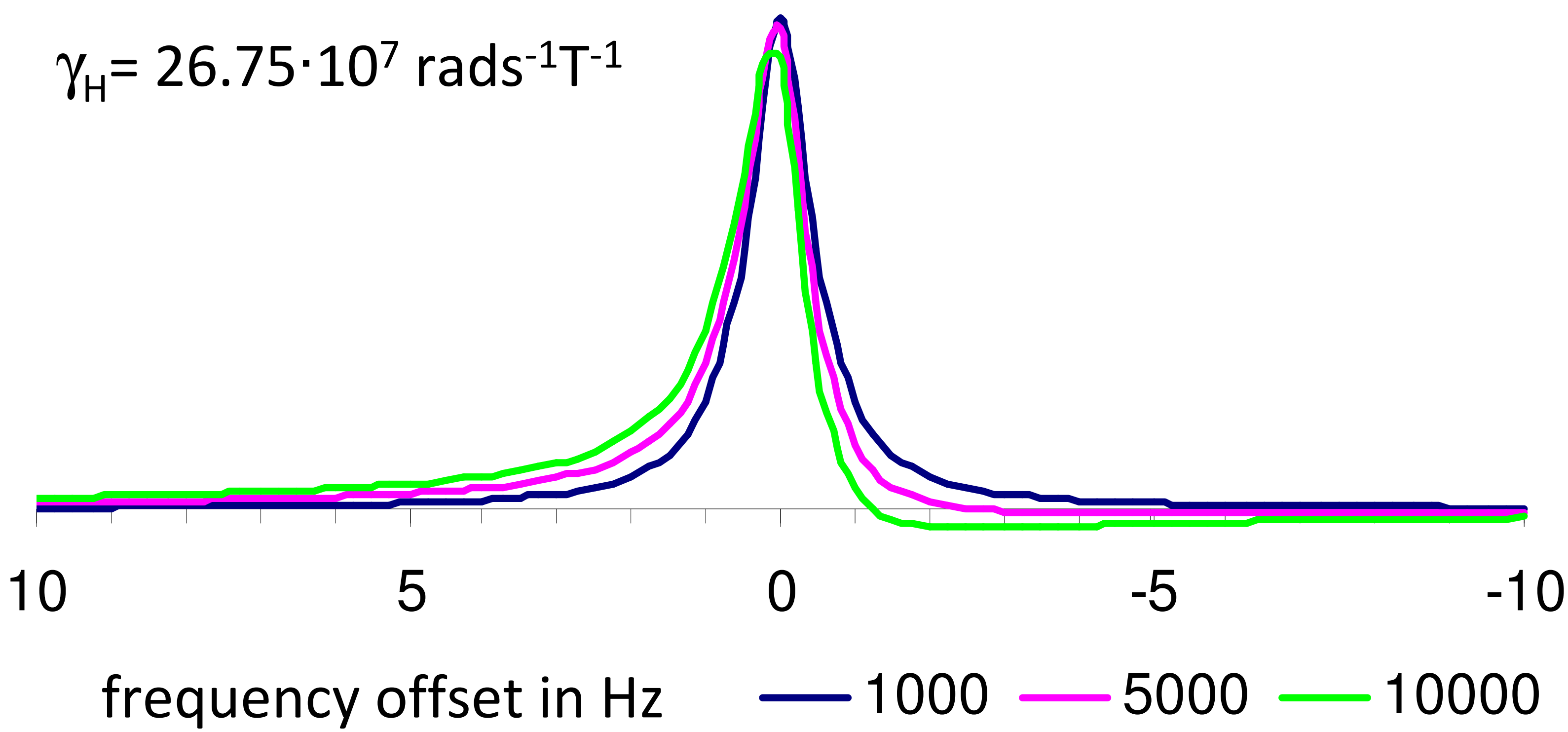
The maximum attainablevalue for transverse magnetization is M_0

On the contrary, for $\Delta \mathbf{B_0/B_1>}$ 1 the magnetization rotates about B_{eff} lying on the surface of a cone with vertex angle θ and it will never completely reach the transverse plane

$\tau_{\pi/2} = 10\ \mu s$

$B_1 = 5.87 \cdot 10^{-4}$ T

$\gamma_H = 26.75 \cdot 10^7$ rad $s^{-1} T^{-1}$



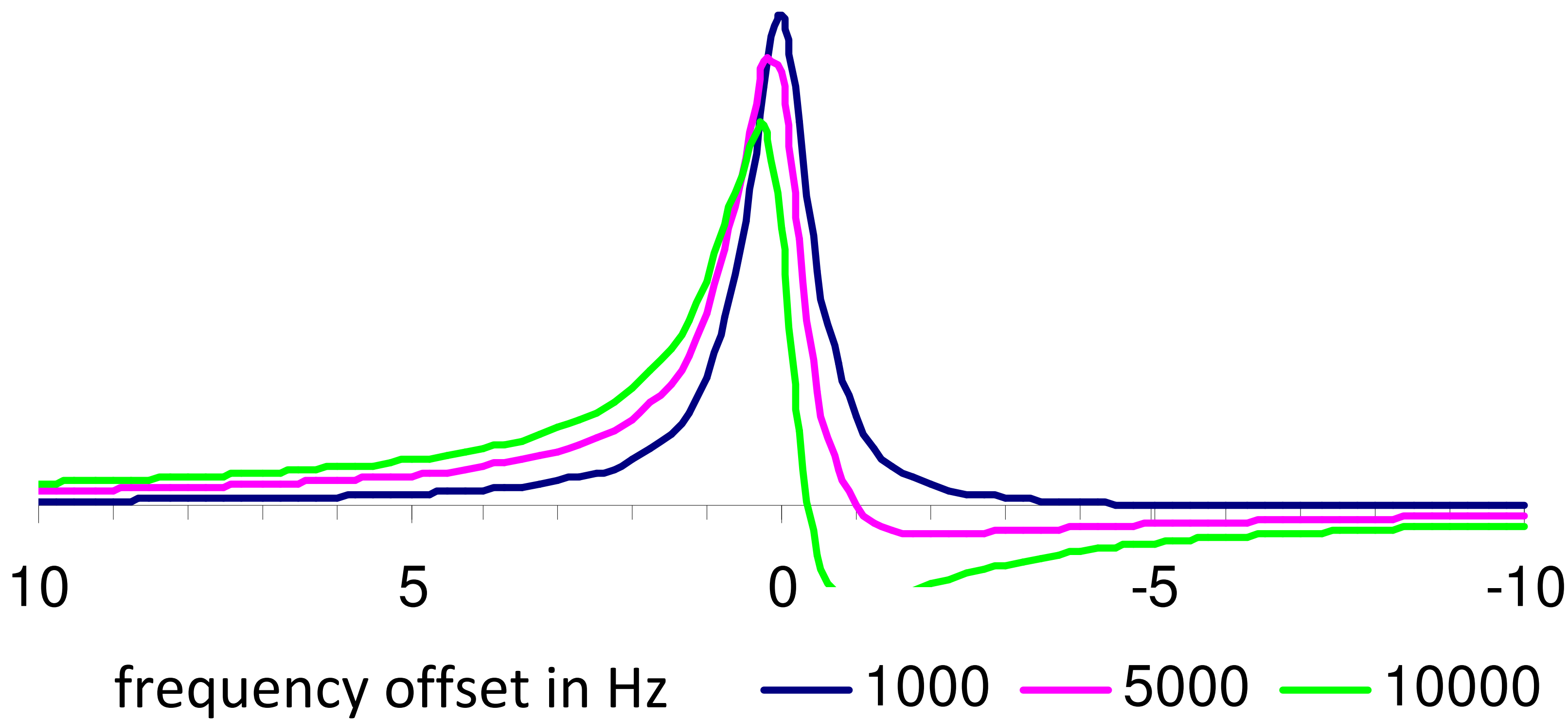
$\Delta B_0 = 3.74 \cdot 10^{-6}$ T

$\Delta B_0 = 1.87 \cdot 10^{-5}$ T

$\Delta B_0 = 3.74 \cdot 10^{-5}$ T

$\tau_{\pi/2}$= 25 µs

B_1= 2.35·10^-4 T



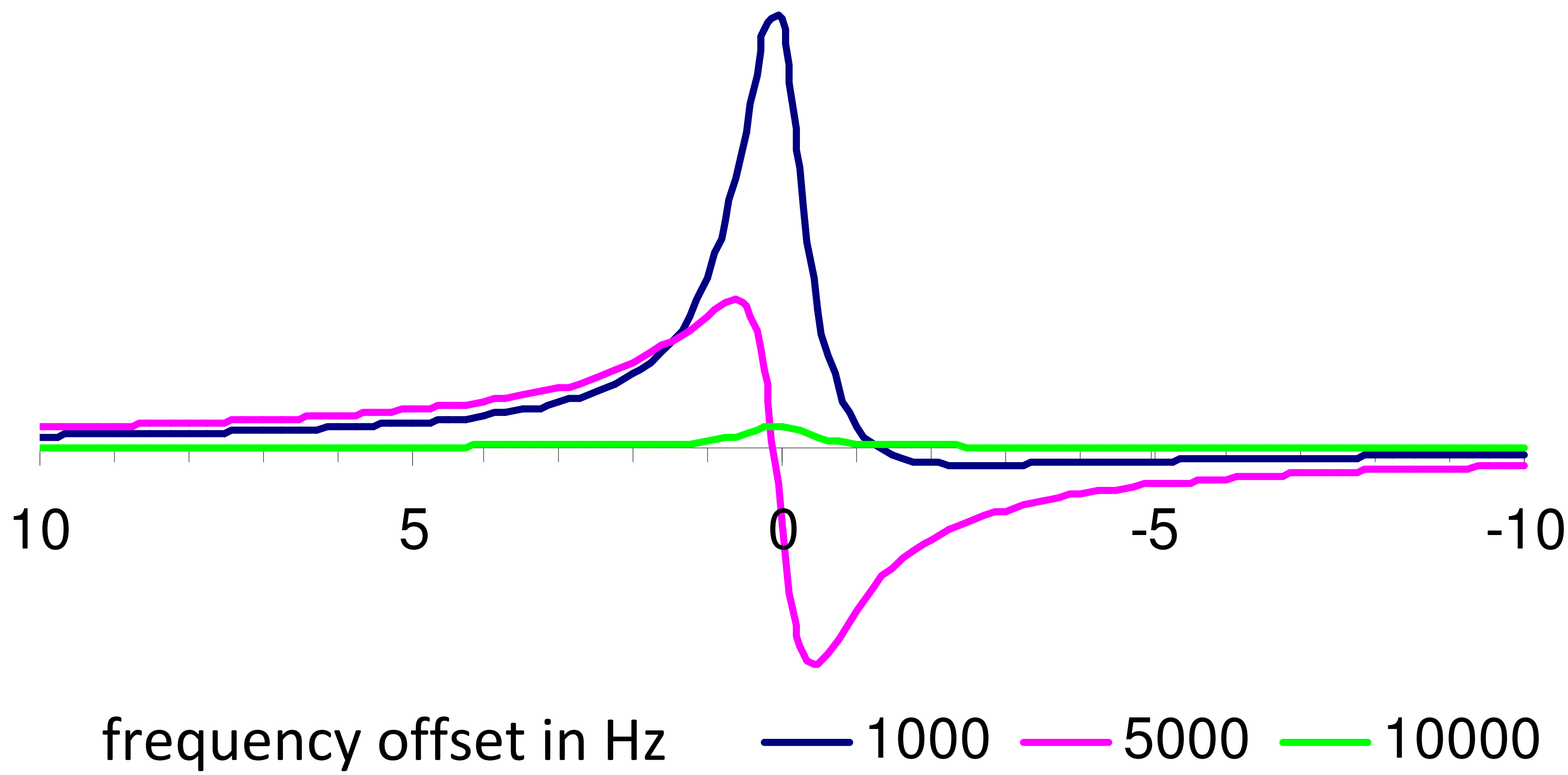
ΔB_0= 3.74·10^-6 T

ΔB_0= 1.87·10^-5 T

ΔB_0= 3.74·10^-5 T

$\tau_{\pi/2}$= 100 μs

B_1= 5.87·10^{-5} T



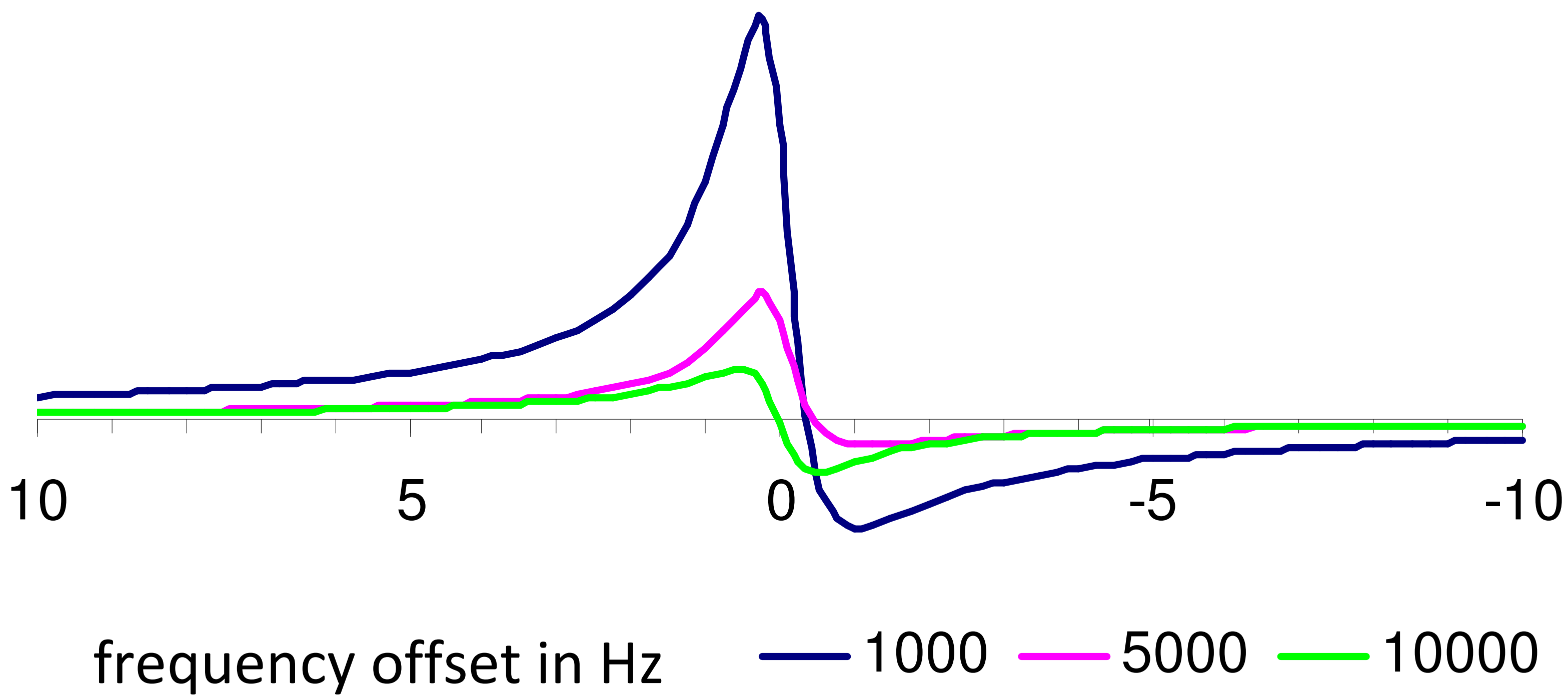
ΔB_0= 3.74·10^{-6} T

ΔB_0= 1.87·10^{-5} T

ΔB_0= 3.74·10^{-5} T

$\tau_{\pi/2}$= 250 μs

B_1= 2.35·10^{-5} T



ΔB_0= 3.74·10^{-6} T

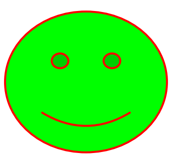
ΔB_0= 1.87·10^{-5} T

ΔB_0= 3.74·10^{-5} T

FT-NMR signal dependence on both B_1

and Ω_0

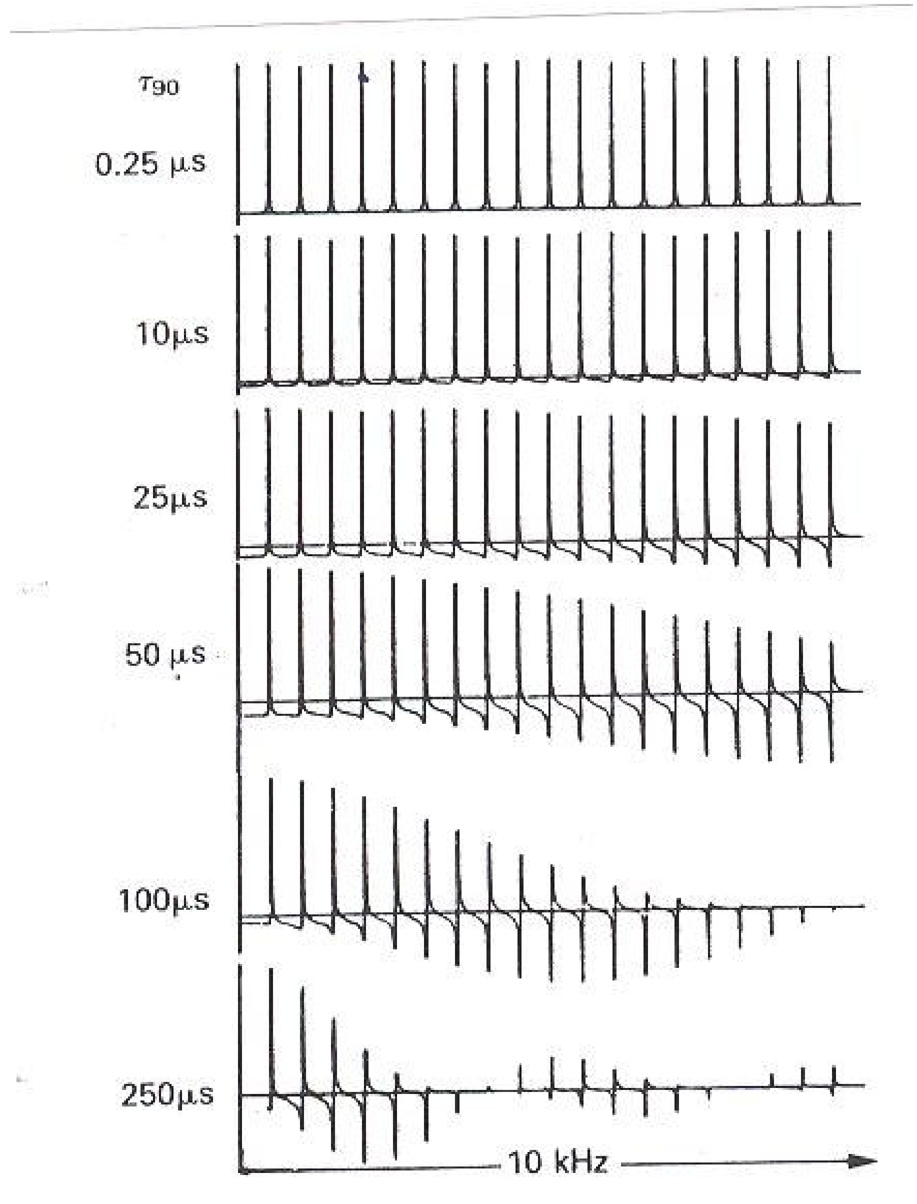
either exploited in



selective excitation

or

problem



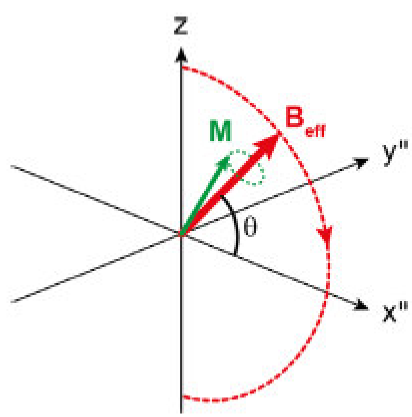
Adiabatic Passage for Broadband Inversion

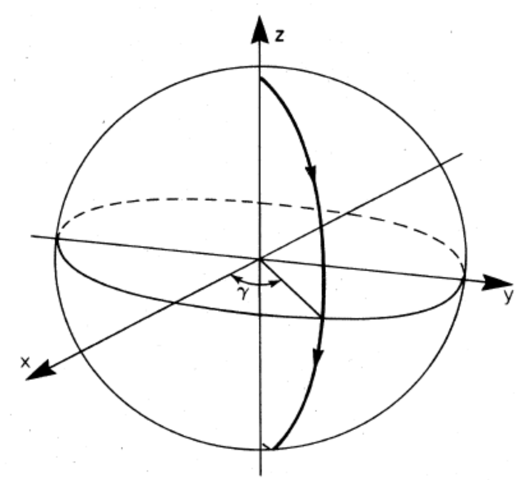
- The use of short pulses can overcome the off-resonance problems for excitation in 1D spectra
- An established technique for inverting spin populations over a large bandwidth is adiabatic rapid passage (old CW NMR spectroscopy with B_0 sweep):
- the frequency of B_0 (or the r.f. radiation) is swept through resonance at a constant rate that must be:
- small compared to the r.f. amplitude $|\gamma| B_{eff} >> d\theta/dt$ (**adiabatic condition**)
- large compared to the relaxation rates (actually R_2, because $R_2 > R_1$) and for this reason is known also **adiabatic fast passage** or simply **fast passage**
- If the adiabatic condition is satisfied and the sweep begins with B_{eff} aligned with M0, the magnetization will follow B_{eff}
- It succeeds in cases of inhomogeneity of both B_0 and B_1 (MRI applications)

Broadband and adiabatic inversion of a two-level system by phase-modulated pulses J. Baum, R. Tycko, A. Pines Phys. Rev. A 1985, 32, 3435

Phase Modulated Adiabatic Pulses

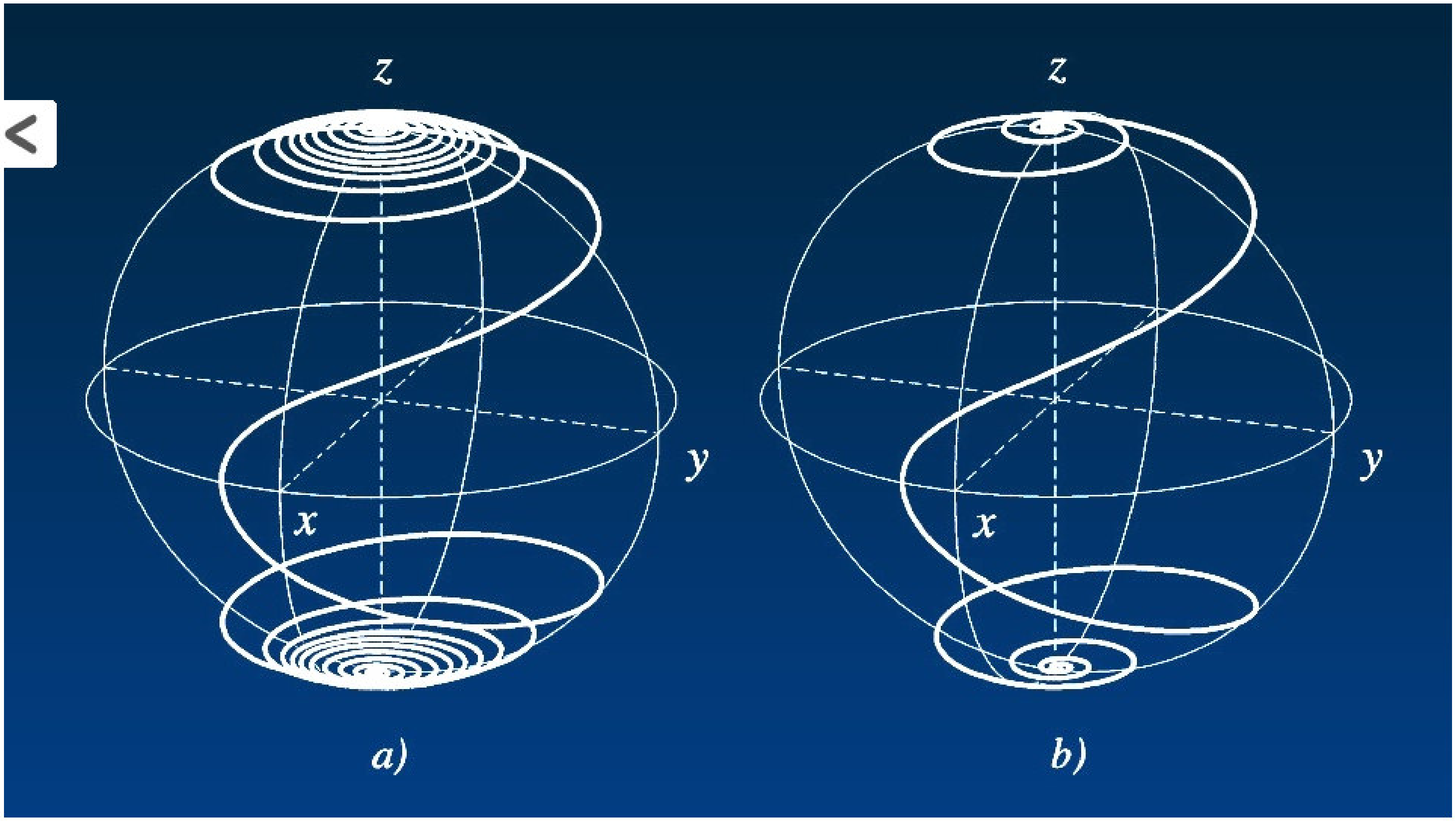
- Correspondence between phase and frequency modulation
- The magnetization describes a semicircular trajectory in a frequency modulated frame (frame rotating at the pulse instantaneous frequency)





Whereas it describes a more complex path in the usual rotating frame (rotating at the carrier frequency)

Magnetization trajectory in the rotating frame



WURST pulse Hyperbolic secant pulse

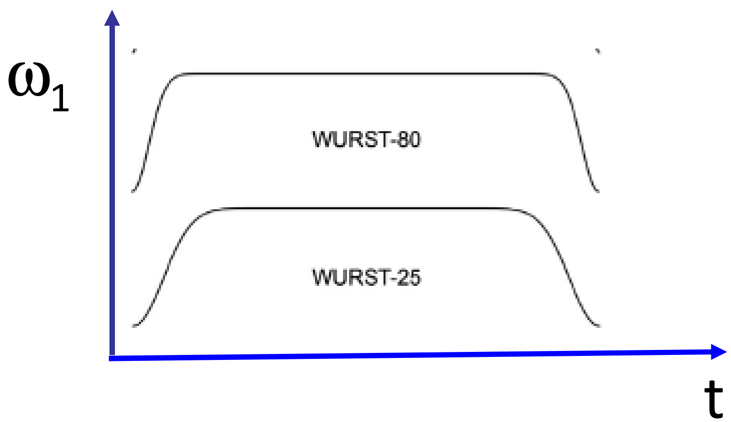
Nowadays: phase modulated pulses. In practice they are piece-wise approximations of continuously phase modulated pulses

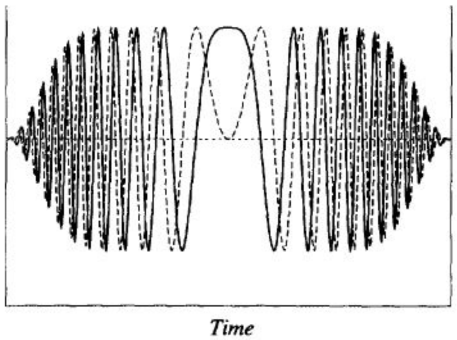
WURST pulses (wideband, uniform rate, smooth truncation)

Amplitude modulation:
smooth truncation

$$\omega_1(t) = \omega_{max}\left(1 - \left|\cos\left(\frac{\pi t}{\tau_w}\right)\right|^N\right)$$

N dictates the truncation steepness, best values 20< N< 80, t_w: overall pulse length on the order of several tens of ms, 100 ms





Real (full) and imaginary components (dashed) of WURST-20

Phase modulation

The phase $\phi(t)$ of a WURST pulse is modulated as a quadratic function of time, and can be described (in radians) as

$$\phi(t) = \pm 2\pi\left\{\left(\nu_{off} + \frac{\Delta}{2}\right)t - \left(\frac{\Delta}{2\tau_w}\right)t^2\right\}$$

The continuous phase modulation is implemented by **discrete steps**.

Wideband

Since the effective frequency of the pulse is proportional to $d\phi/dt$, assuming a symmetric sweep about the transmitter frequency (i.e. $\nu_{off}= 0$), the maximum sweep range Δ is limited by the duration of the individual element, τ^e, which is < 0.5 microseconds, so that $\Delta > 2$ MHz

$$\nu_{eff}(t) = \frac{d\phi}{dt}/2\pi = \pm\left(\nu_{off} + \frac{\Delta}{2} - \frac{\Delta}{\tau_w}t\right)$$

where Δ is the total sweep range (in Hz) and ν_{off} is the offset frequency for the centre of the sweep range

Uniform rate

This phase modulation results in the linear sweep of the pulse's effective frequency

There are many other possible forms for $\nu_{eff}(t)$ that result in adiabatic inversion

The WURST kind of pulses in solid-state NMR Luke A.O'Dell Solid State NMR 2013, 55-56, 28-41