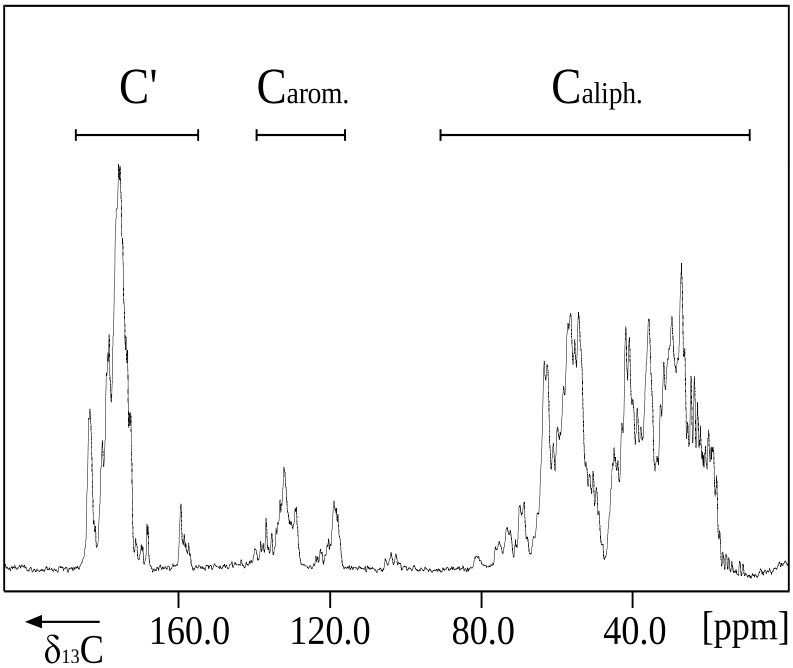
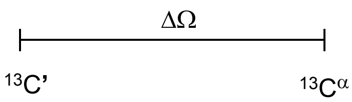
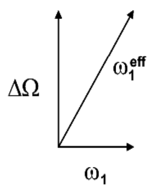
1D ^{13}C spectrum of a protein



Selective RF pulses: rectangular pulses





Flip angle of RF pulse:

$\beta = \omega_1 * \tau_p = -\gamma B_1 * \tau_p$

90° pulse:

$$\beta^{eff} = 4*\beta = 360° \Rightarrow (\omega_1^{eff})^2 = (4\omega_1)^2 = \omega_1^2 + (\Delta\Omega)^2 \Rightarrow \omega_1 = \Delta\Omega/\sqrt{15}$$

$$\boxed{\tau_{p(90°)} = \beta/\omega_1 = \pi/2 * \sqrt{15} / (2\pi*\Delta\Omega)}$$

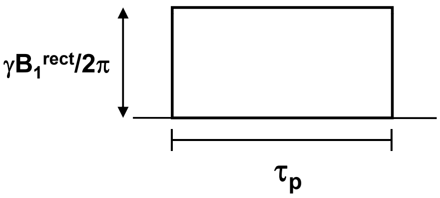
180° pulse:

$$\beta^{eff} = 2*\beta = 360° \Rightarrow (\omega_1^{eff})^2 = (2\omega_1)^2 = \omega_1^2 + (\Delta\Omega)^2 \Rightarrow \omega_1 = \Delta\Omega/\sqrt{3}$$

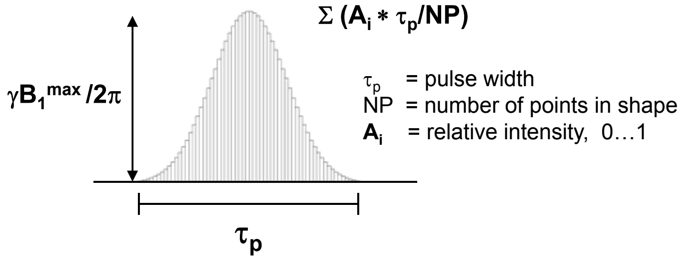
$$\boxed{\tau_{p(180°)} = \beta/\omega_1 = \pi * \sqrt{3} / (2\pi*\Delta\Omega)}$$

Band-selective RF pulses: shaped pulses

Rectangular pulse



Shaped pulse

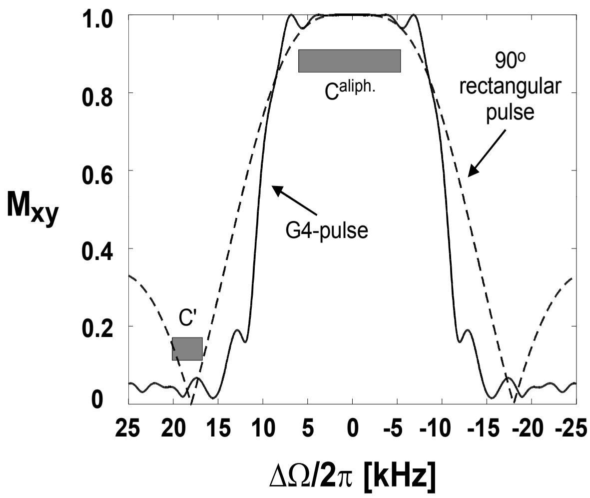


$$\beta = \gamma B_1^{rect} * \tau_p$$
$$= \gamma B_1^{rect}/2\pi * \tau_p * 360°$$

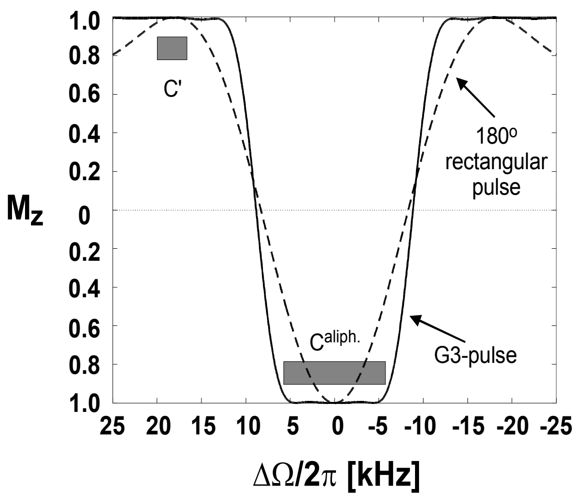
$$\beta = \gamma B_1^{max} * \Sigma A_i * \tau_p$$
$$= \gamma B_1^{rect} / \Sigma A_i * \tau_p$$

Band-selective RF pulses: rectangular vs. shaped pulses

Selective excitation



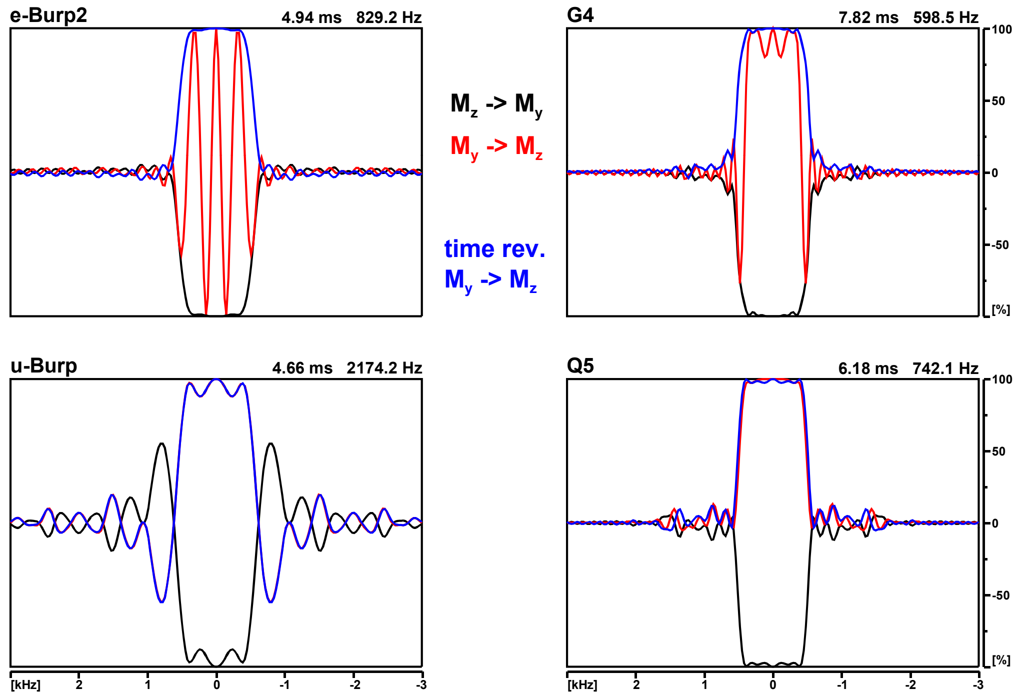
Selective inversion



Universal rotations – time-reversed pulses

Universal rotations: same behavior as hard pulse, independent of x,y,z direction

Point-to-point: optimized for a specific trajectory



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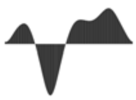
Band-selective RF pulses

Selective excitation (90°)	Selective inversion, refocusing (180°)	Adiabatic inversion
Gaussian (90° / 270°) 	I-BURP 	Hyperbolic secant 
E-BURP 	RE-BURP 	WURST 
G4 	G3 	CHIRP 
Q5 	Q3 	

References (shaped pulses and band-selective decoupling):

JMR (1991) 93, 93; Chem. Phys. Lett. (1990) 165, 469; JMR (1992) 97, 135;
JMR (1992) 100, 604; JMR (1993) A102, 364; JMR (1995) A115, 273; JMR (1996) A118, 299 .

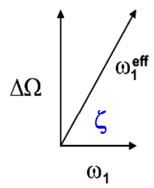
Band-selective RF pulses - adiabatic pulses

- **Adiabatic "fast" (relative to T1, T2) passage:**
  keep magnetization and rf field colinear: $|d\zeta/dt| \ll \omega^{eff}$
- **frequency sweep: $d\Delta\omega/dt$ (non-linear pulse phase modulation)**

☺ **broad-band inversion with low power**

☺ **insensitive to B1 inhomogeneity**

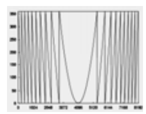
☹ **adiabaticity requires long τ_P**

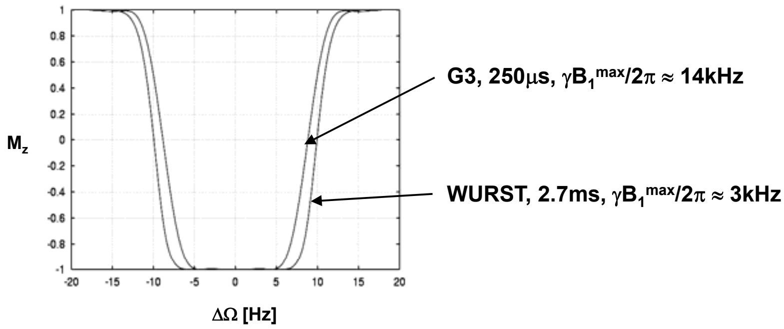


WURST

Amplitude

Phase





Adiabatic pulses

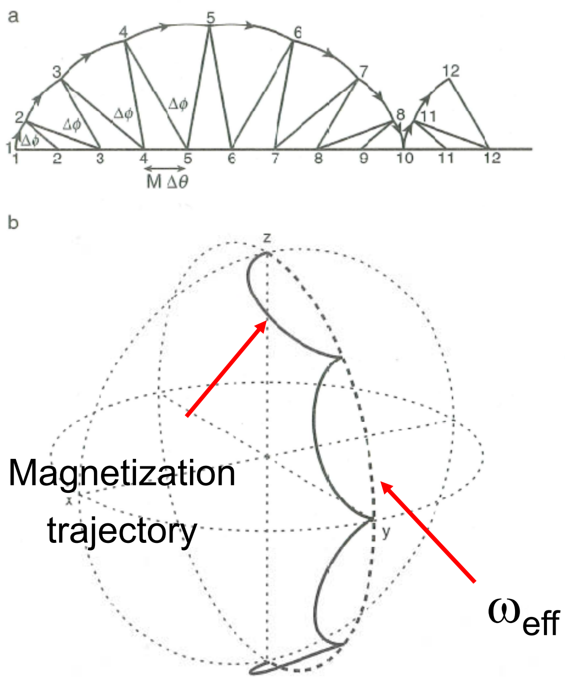


FIGURE 3.26 Magnetization trajectories during an adiabatic pulse. (a) Projection view of a simplified adiabatic sweep in which a constant amplitude effective field rotates in angular steps of $\Delta\theta$ and during the intervening intervals the magnetization vector precesses about the current effective field direction by a constant angle $\Delta\phi$. The horizontal line is a gnomonic projection of the path along a great circle followed by the tip of the effective field vector, while the arcs represent the path of the tip of the magnetization vector (adapted from Powles (55). (b) Perspective view of the trajectory (bold solid line) followed by the tip of the magnetization vector during an adiabatic sweep. The bold dashed line represents the path of the effective field. The numerical simulation was performed using an effective field with constant amplitude, the rate of change in the direction of the effective field was constant, and the precession frequency of the magnetization about the effective field was eight times faster compared to the rate of change of the direction of the effective field (i.e., the adiabaticity factor $Q = 8$).

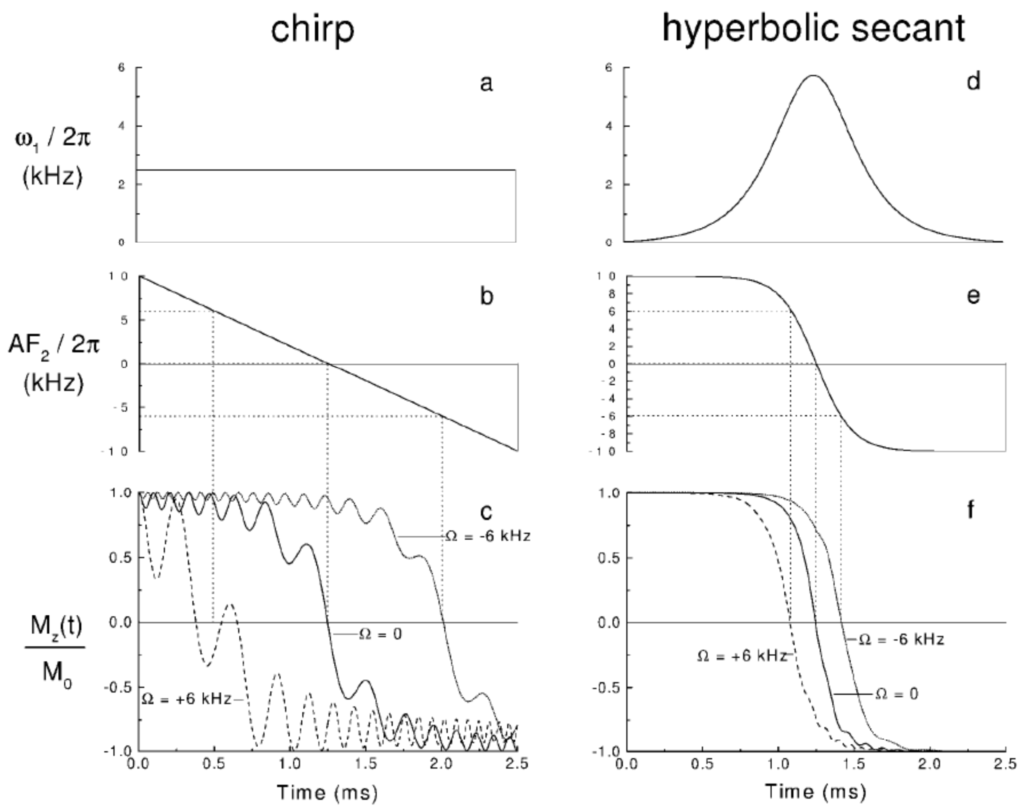
Cavanagh, … Palmer book

Adiabatic pulses

ω_1

frequency modulation

M_z/M_0



Garwood, DelaBarre JMR **153**, 155–177 (2001)

Off-resonance pulses: phase- and amplitude modulation

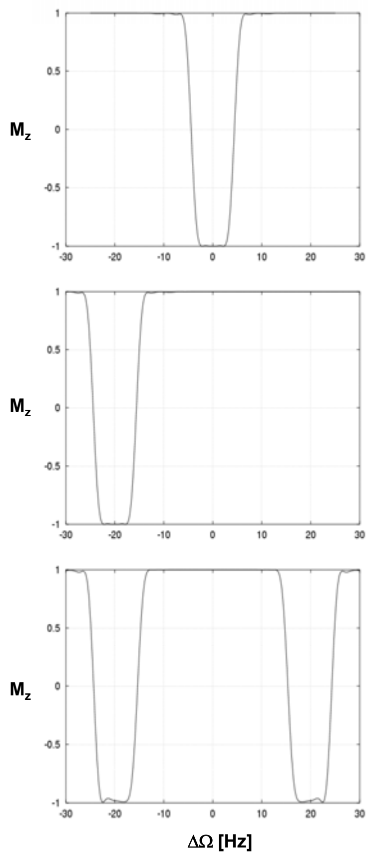
G3, 500μs
no modulation

Phase modulation:

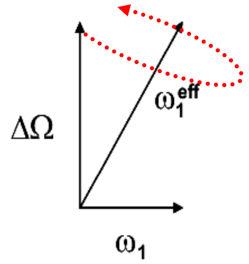
$\phi_i^{mod} = \phi_i - (2\pi * \Delta\Omega * \tau_p * i/NP)$

Amplitude modulation:

$A_i^{mod} = A_i * 2\cos(2\pi * \Delta\Omega * \tau_p * i/NP)$



Bloch-Siegert phase shifts (BSP)



Off-resonance: $\Delta\Omega \gg \omega_1$

Precession around ω_1^{eff} :

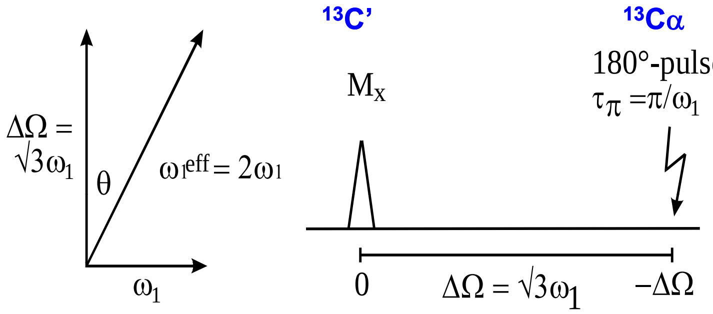
$\phi^{off\text{-}reson} \approx \langle\omega_1^{eff}\rangle * \tau_p = \beta^{eff}$

Instead of precession around *z-axis* with:

$\phi^{free} = \Delta\Omega * \tau_p$

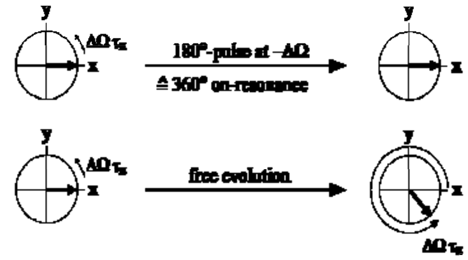
$\phi_{BSP} = (\Delta\Omega - \langle\omega_1^{eff}\rangle) * \tau_p$

Chem. Phys. Lett. (1990) 168, 297



$\phi_{BSP}(0) = -\Delta\Omega * \tau_\pi = -\sqrt{3}\,\omega_1 * \pi/\omega_1 = -\sqrt{3}\pi \approx 48.2°$

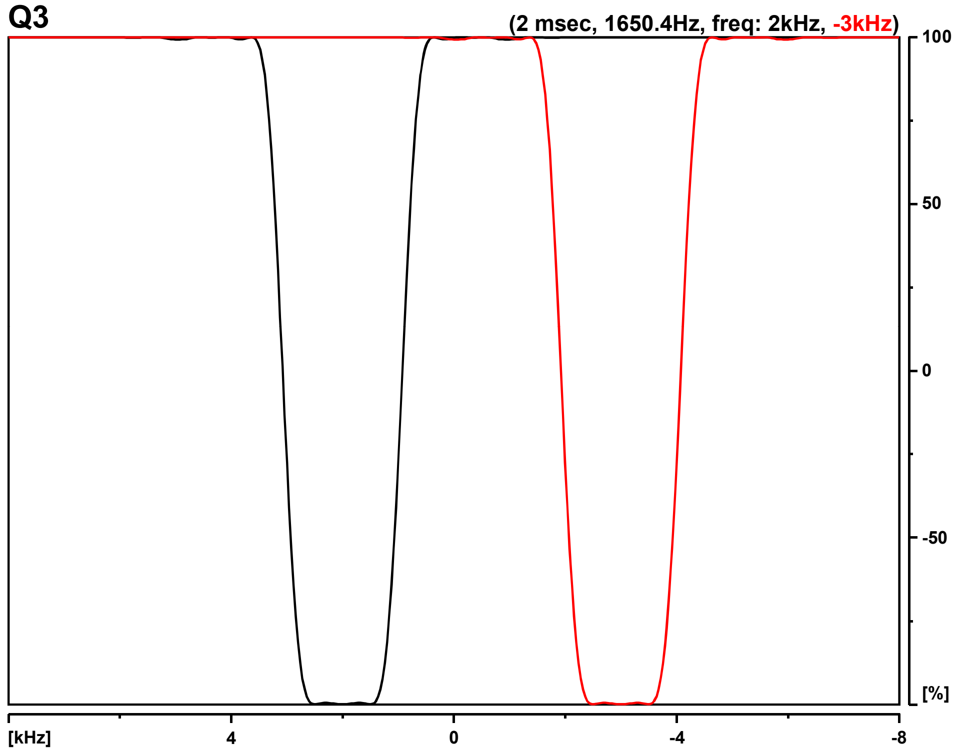
rotating coordinate system at $-\Delta\Omega$: (^{13}Cα)



BSP on ^{13}C' transverse magnetization

Bloch Siegert shift: inversion

simulation
M_z -> M_z



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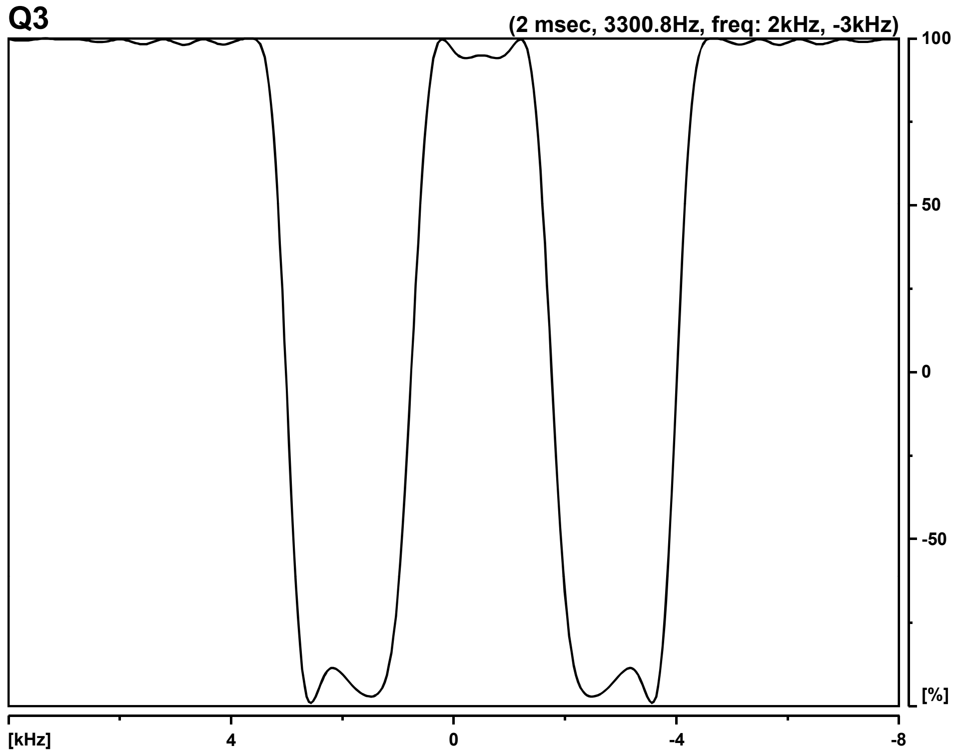
Bloch Siegert shift: inversion

simulation
M_z -> M_z



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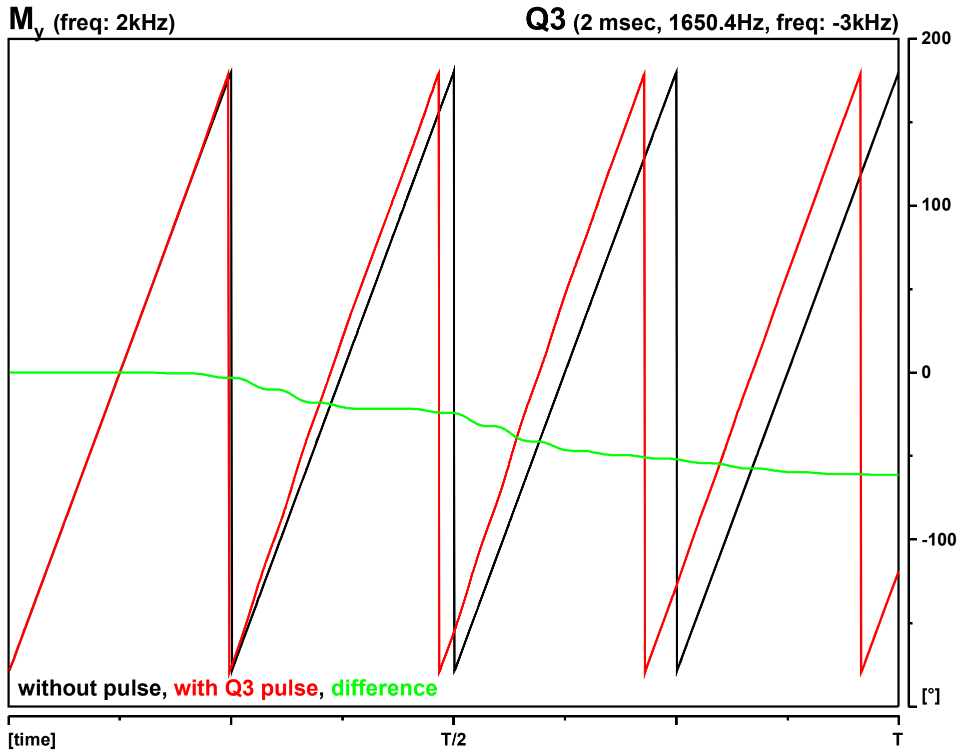
Bloch Siegert shift: inversion

simulation
phase



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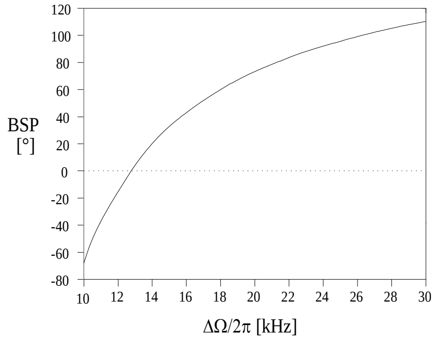
BSP compensation

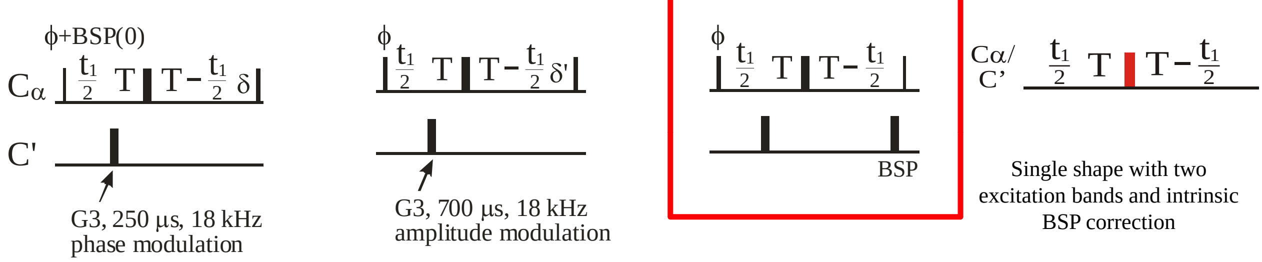
Bloch-Siegert phase for a band-selective (± 5kHz) G3 pulse



$\phi_{BSP} = \omega_1^2/(2\Delta\Omega)^*\tau_P$

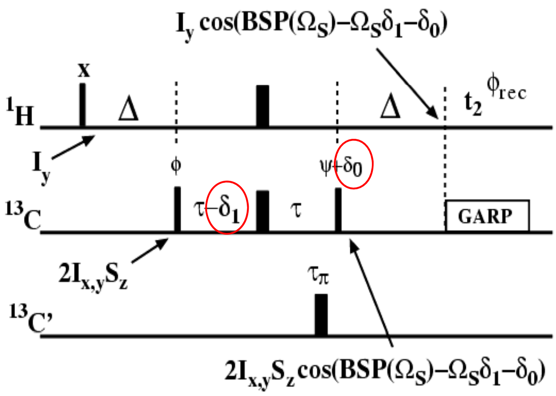
Calculate ϕ_{BSP} for each subpulse of a shaped pulse and add it to the phase to compensate for the BSP.

Determine phase *empirically* (0th and 1st order) | **Use *amplitude-modulated* inversion pulse (0th order)** | **Use *additional pulse* (all orders are corrected)** | ***Intrinsic correction* (all orders are corrected)**



JMR (1992) 100, 604; JMR (2000) 146, 369.

Experimental determination of Bloch Siegert Phase



ϕ = x −x

ψ = x x −x −x

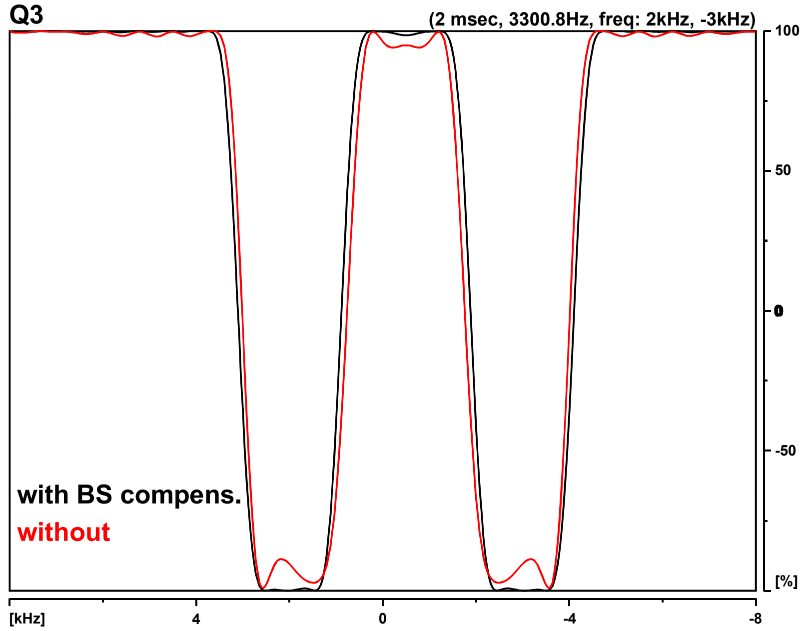
ϕ_{rec} = x −x −x x

- **Zero order phase correction δ_0 applied to the phase of a flanking 90° pulse**
- **First order phase correction by addition of a delay δ_1**

BSP compensation

Bloch Siegert shift: inversion

simulation
M_z -> M_z



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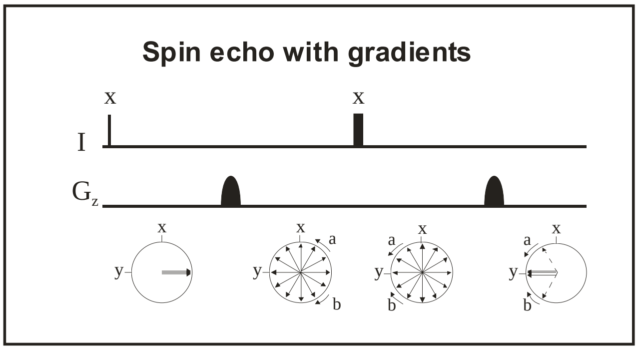
Gradients in heteronuclear NMR experiments

Coherence selection



Coherence rejection