



# BASICS OF MR SPECTROSCOPY

Lijing Xin

*CIBM EPFL MRI*

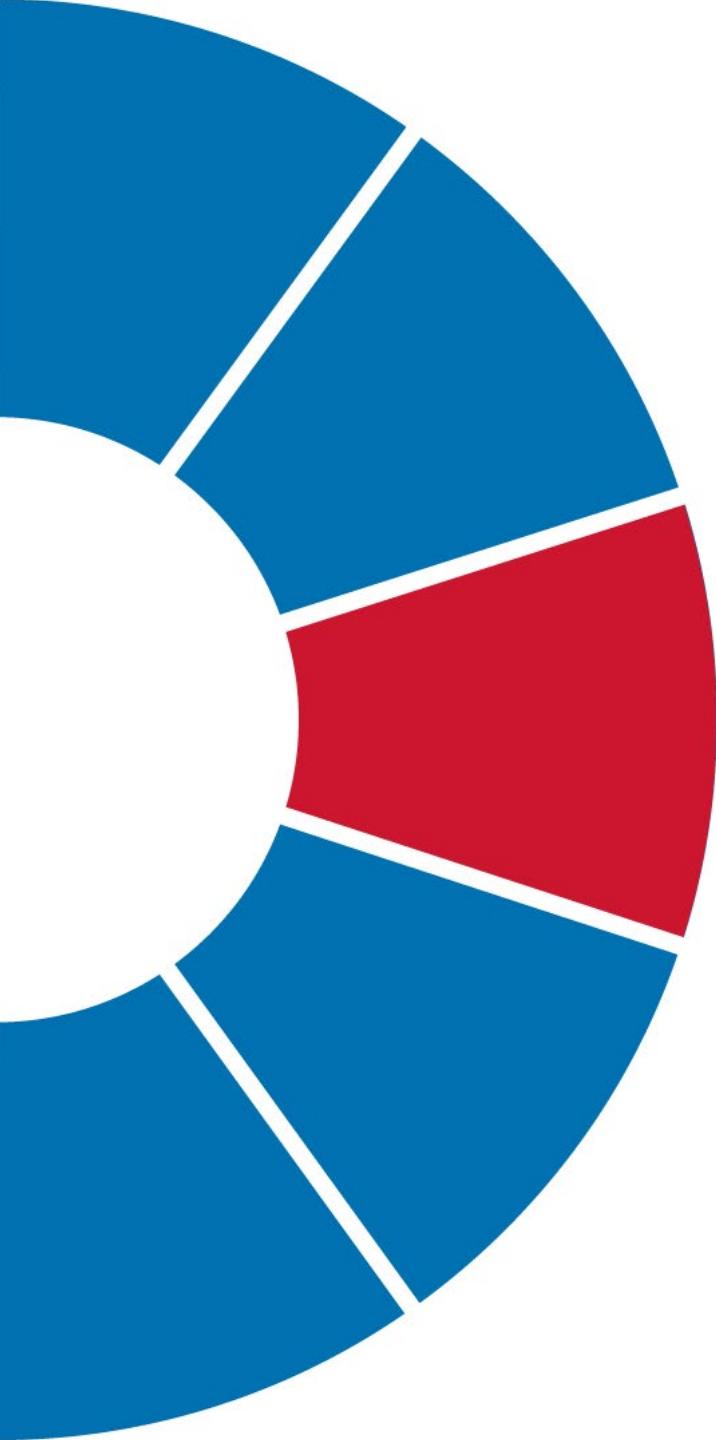
27.03.2025



[Lijing.xin@epfl.ch](mailto:Lijing.xin@epfl.ch)

# OUTLINE

- Introduction of MRS (chemical shift and J-coupling)
- Localization techniques
- $B_0$  Shimming
- $B_1^+$  calibration
- Water suppression
- Outer volume suppression

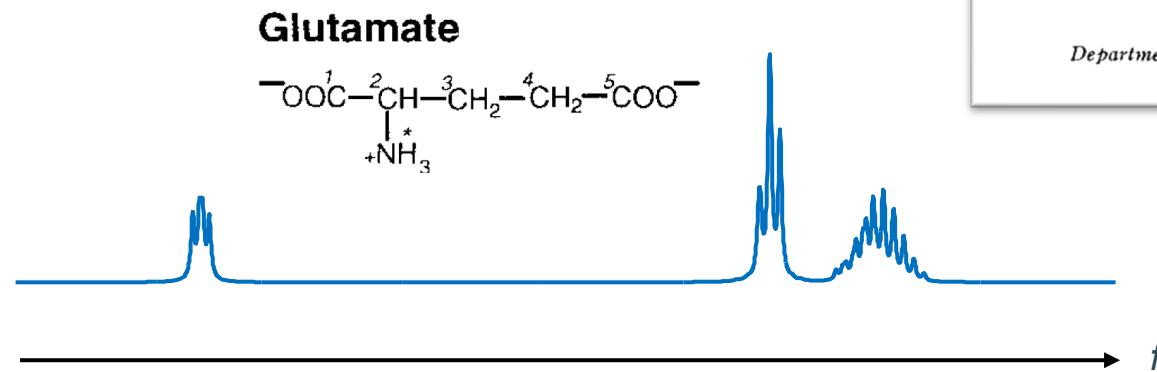
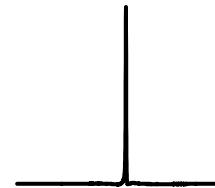


## CHEMICAL SHIFT AND J-COUPLING

# RESONANCE FREQUENCY

Resonance frequency of a nucleus  $\omega_0 = \gamma B_0$

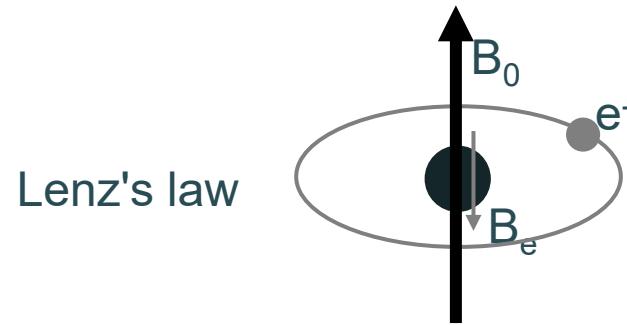
7T  
300MHz



nuclei in a molecule resonant at different frequencies

**The Dependence of a Nuclear Magnetic Resonance Frequency upon Chemical Compound\***  
W. G. PROCTOR AND F. C. YU  
*Department of Physics, Stanford University, Stanford, California*  
January 18, 1950

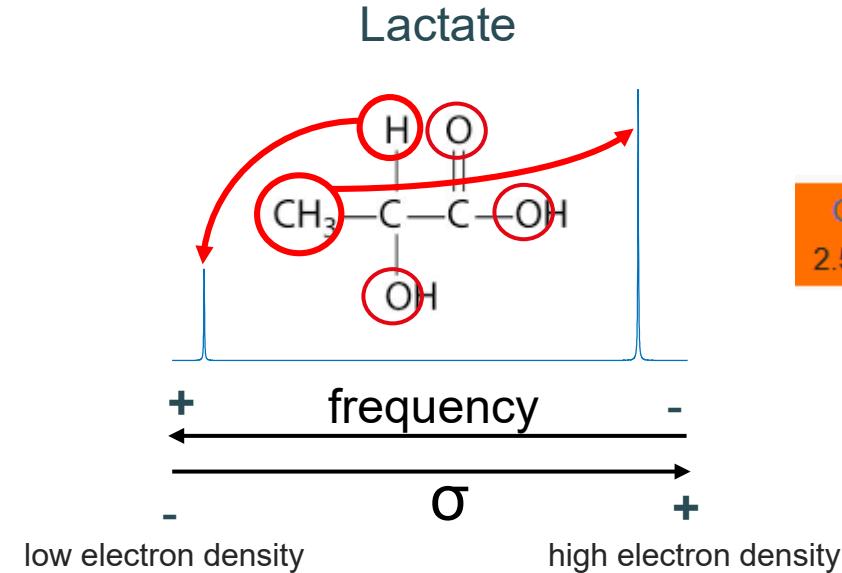
# SHIELDING AND RESONANCE FREQUENCY



$$B_{eff} = B_0 - B_e = B_0(1 - \sigma)$$

$\sigma$  , the shielding constant

Electrons around the nucleus shield it from the applied field



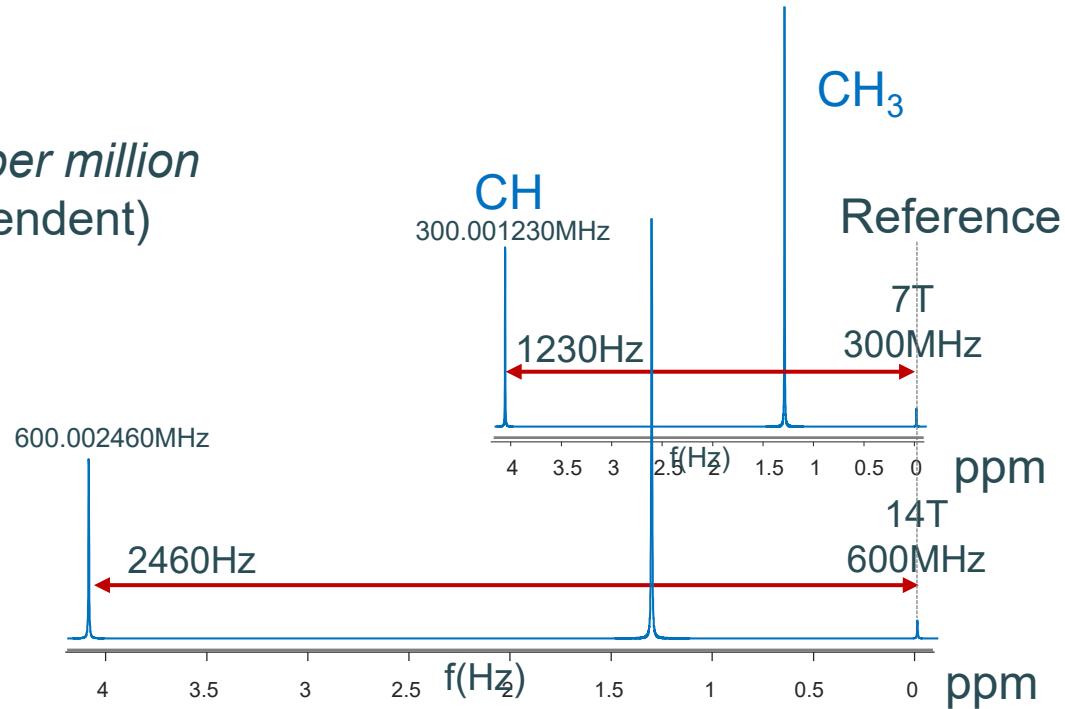
$$\omega_0 = \gamma B_0(1 - \sigma)$$

Resonance frequency depends on the chemical environment of the nucleus

# CHEMICAL SHIFT

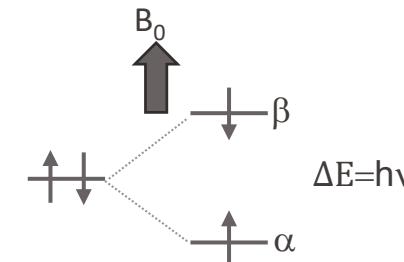
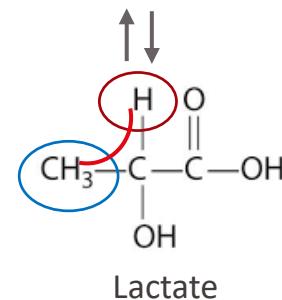
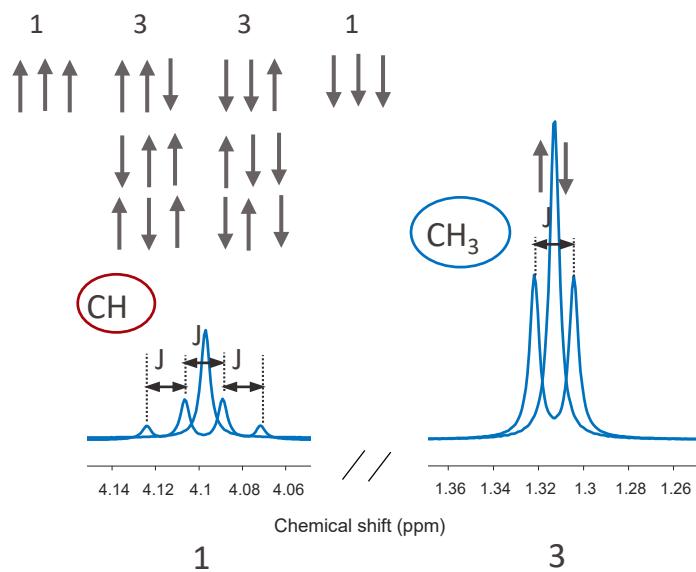
Chemical shift in *parts per million*  
(magnetic field independent)

$$\delta = \frac{\omega - \omega_{ref}}{\omega_{ref}} \times 10^6$$



# J-COUPLING

## J-coupling (spin-spin coupling, scalar coupling) Interactions between neighboring nuclear spins

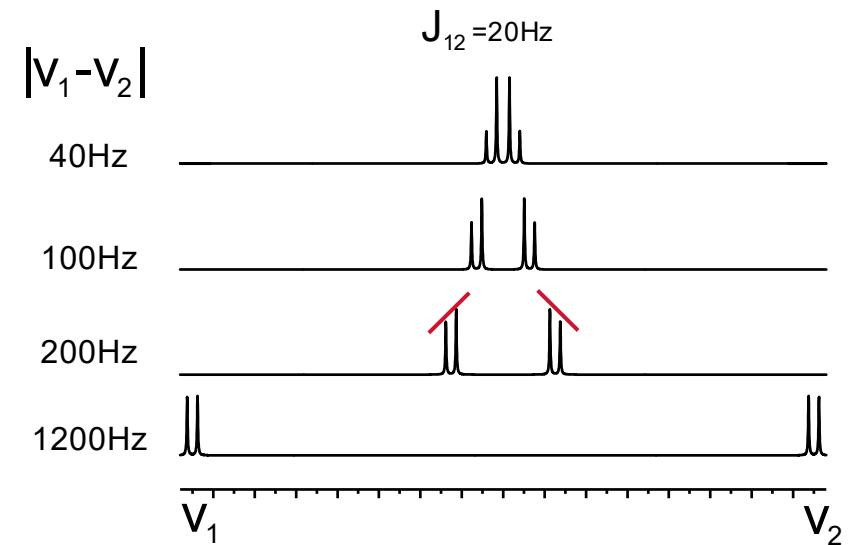


Number of splitting peaks:  $n+1$   
 $n$ : the number of neighboring identical nuclei  
 $J$ : coupling constant in Hz

n	Pascal's triangle							
0								1
1							1	1
2					1	2	1	
3				1	3	3	1	
4			1	4	6	4	1	
5		1	5	10	10	5	1	
6	1	6	15	20	15	6	1	
7	1	7	21	35	35	21	7	1
8	1	8	28	56	70	56	28	8

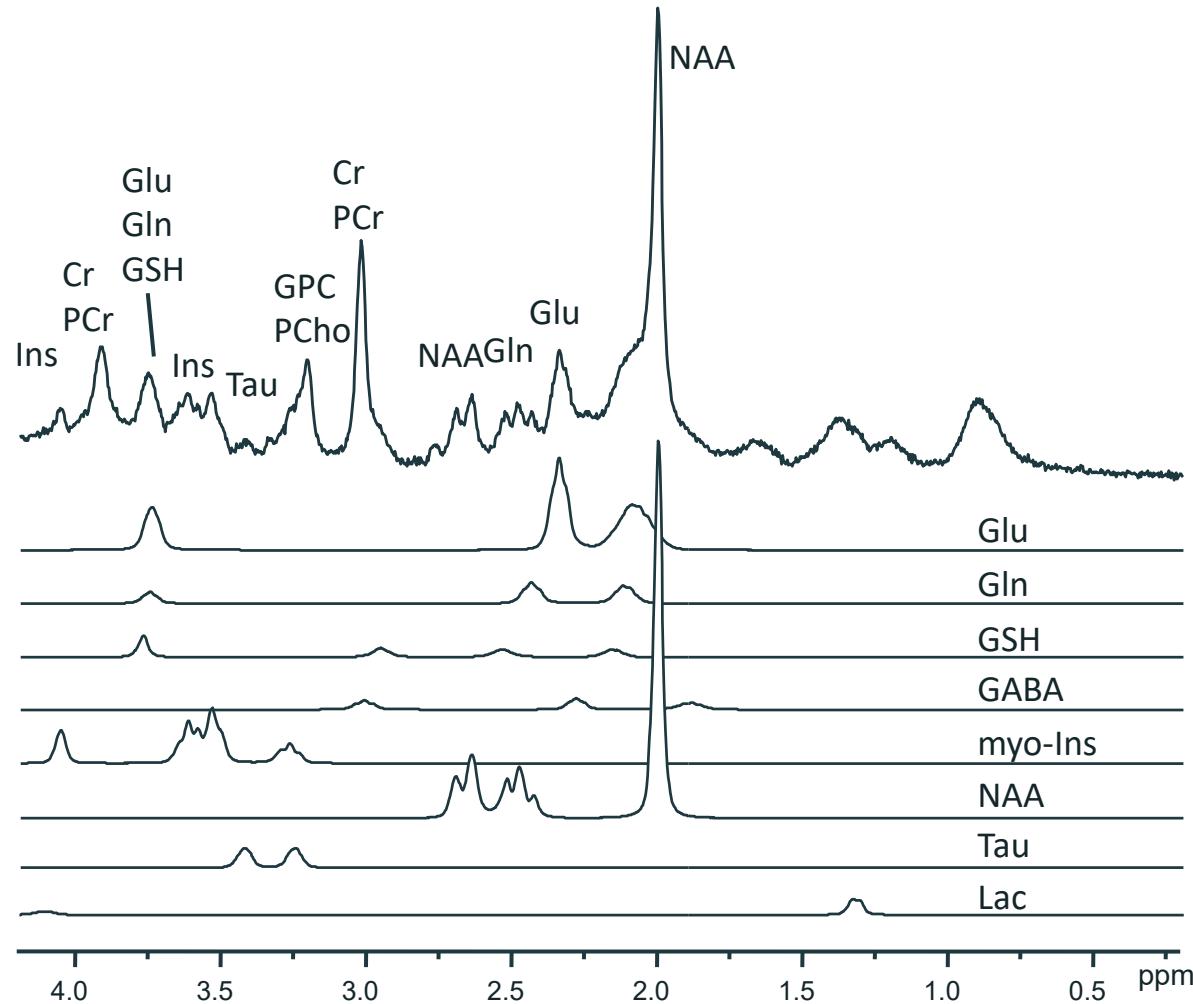
# MORE ABOUT J-COUPLING

- $J$  is independent of the magnetic field
- Peak splitting
  - Weakly coupled ( $|\nu_1 - \nu_2| \gg J_{12}$ ), e.g.  $^1\text{H}$ - $^{13}\text{C}$ , product operator formalism
  - Strongly coupled (roof effect): e.g.  $^1\text{H}$ - $^1\text{H}$ , density matrix formalism

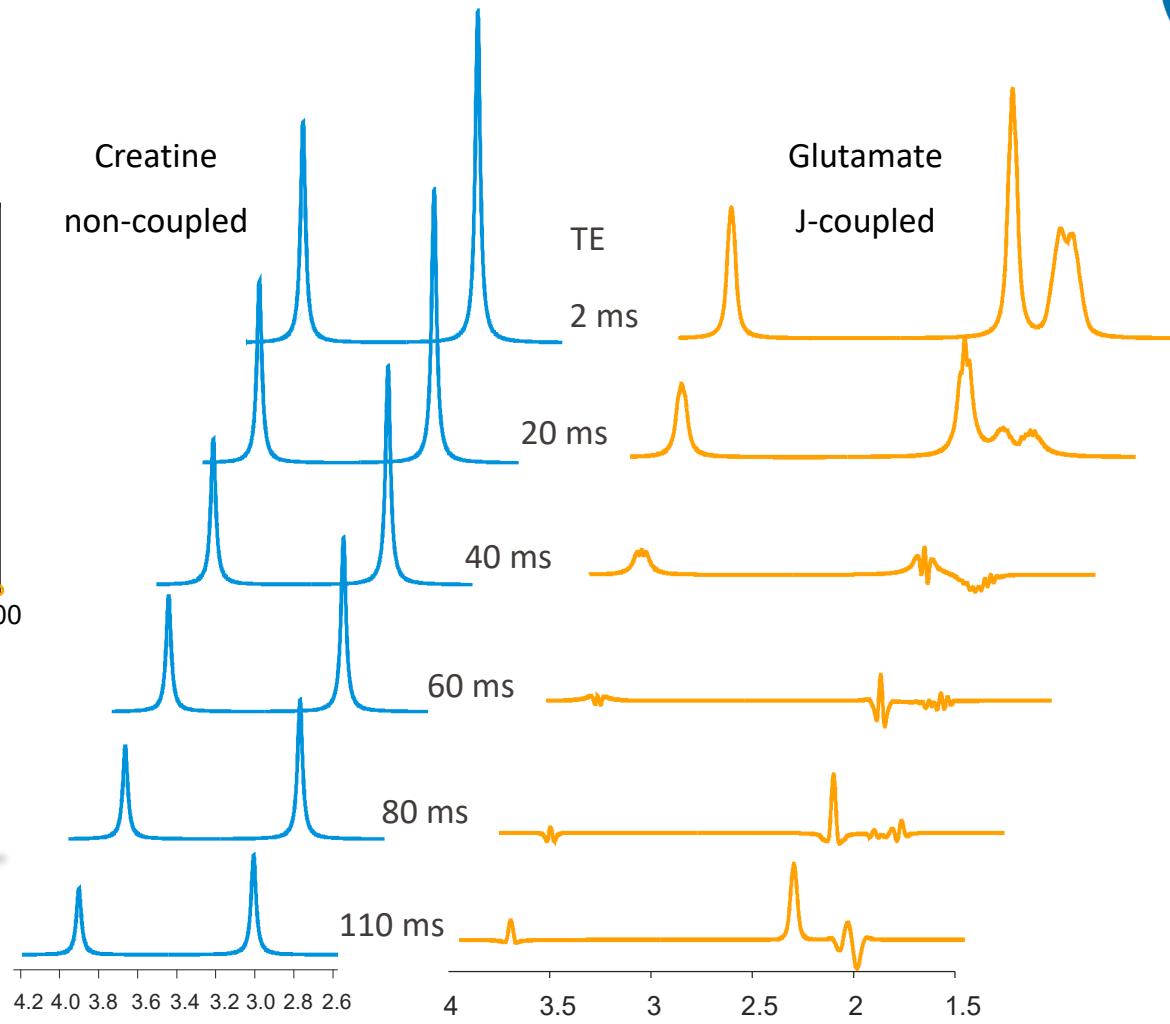
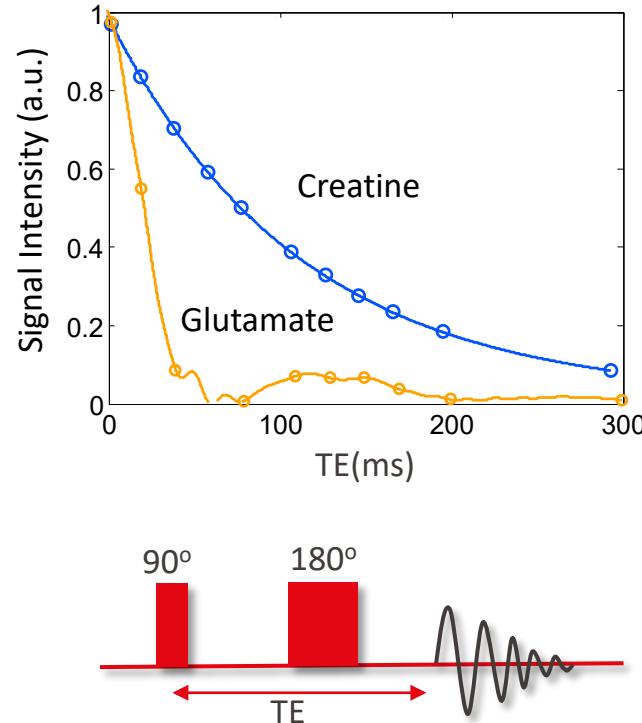


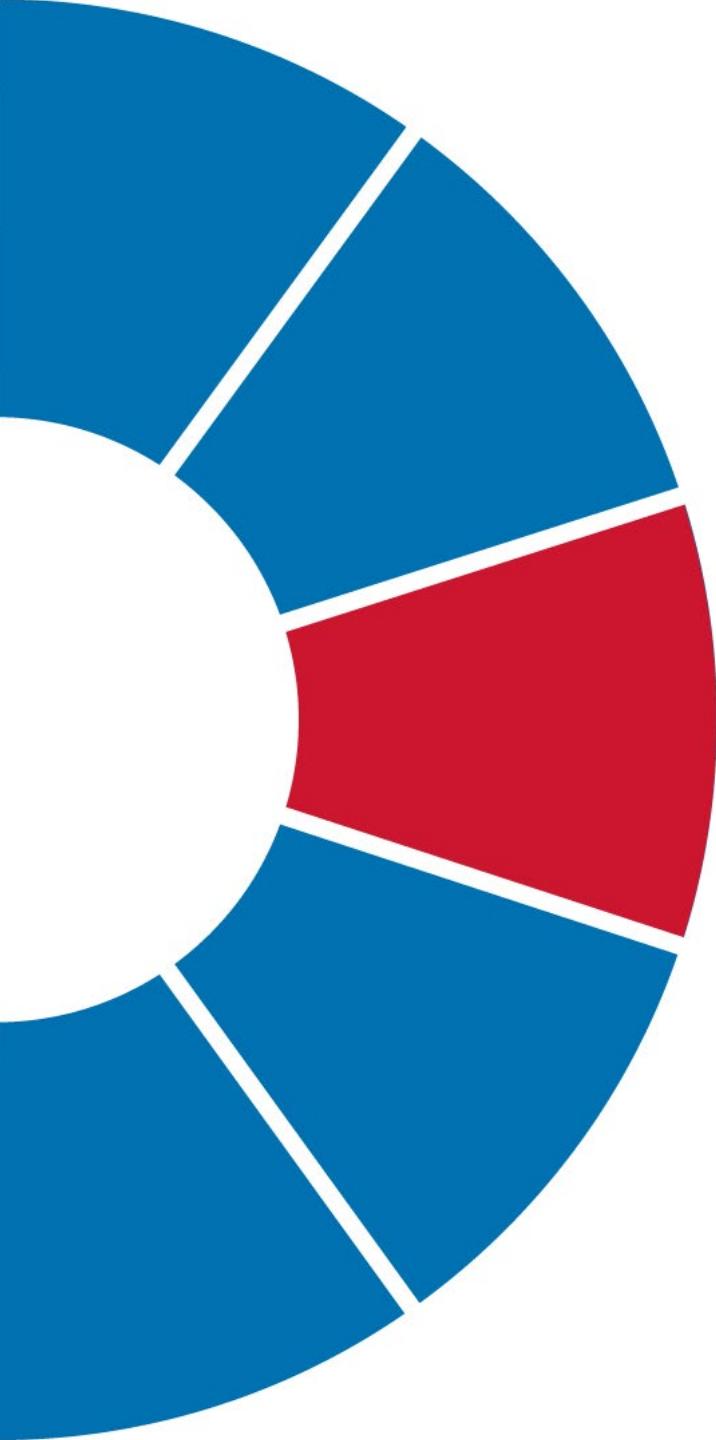
# FINGERPRINTS OF MOLECULES

Chemical shift  
J-coupling



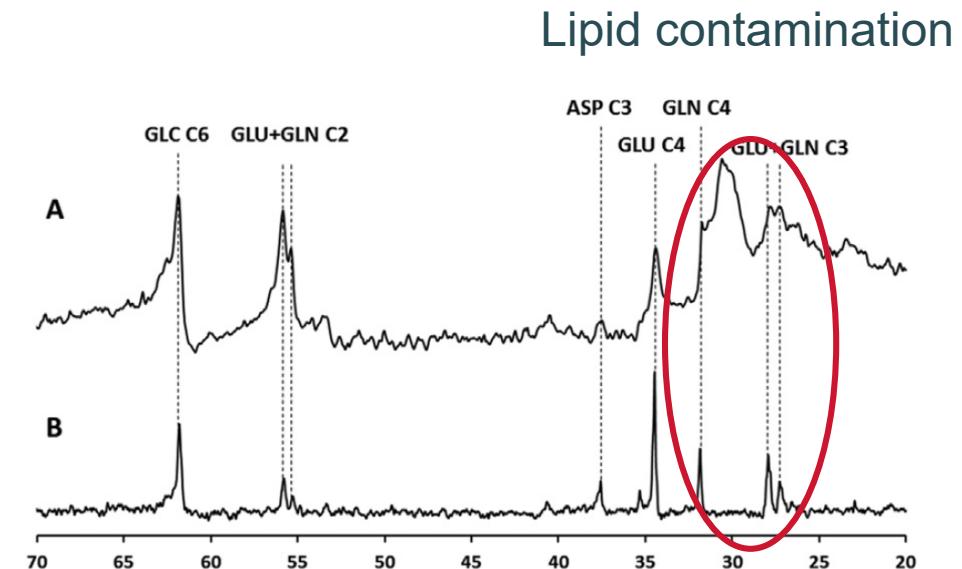
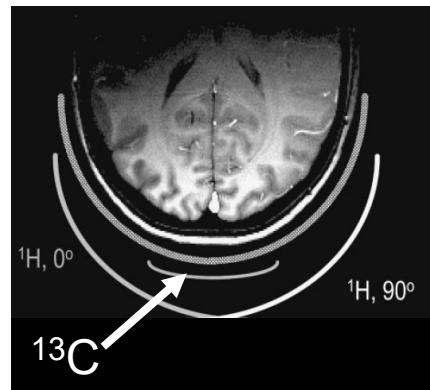
# J-EVOLUTION WITH TE





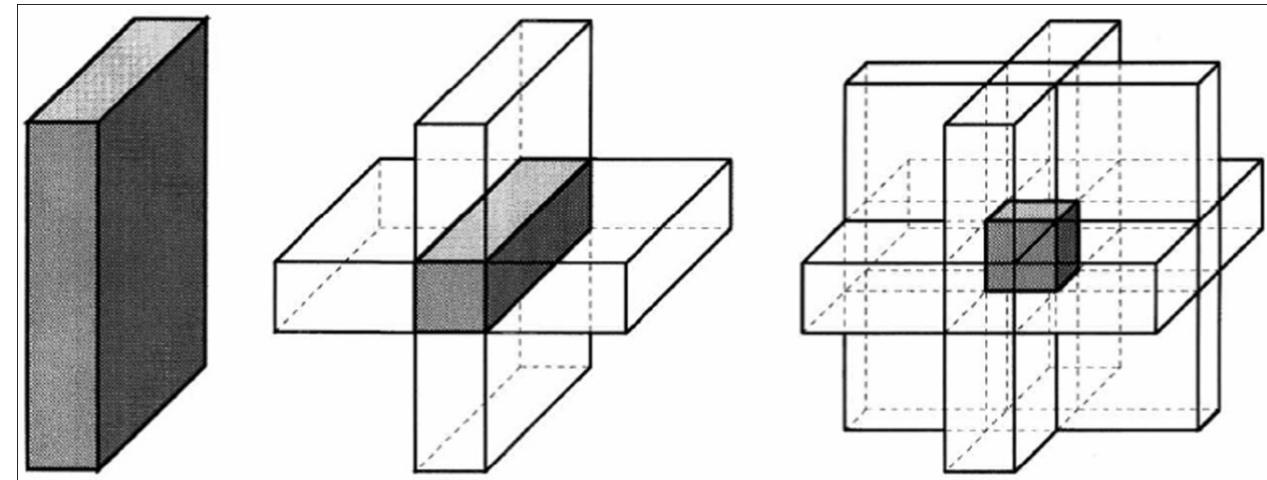
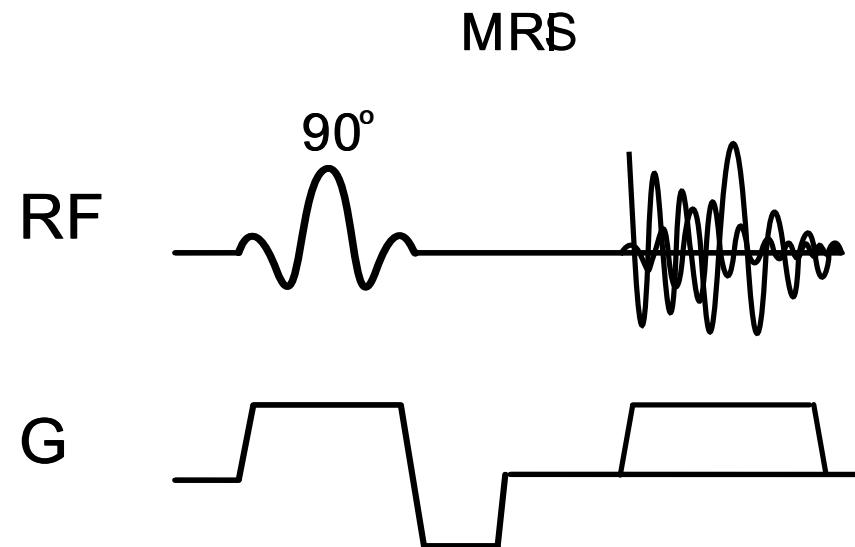
## LOCALIZATION METHODS

# LOCALIZATION WITH SURFACE COIL

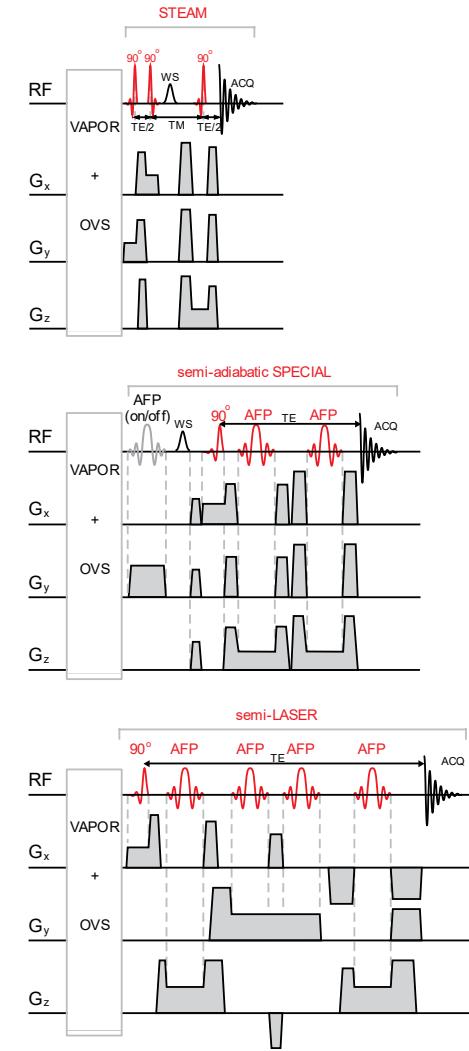
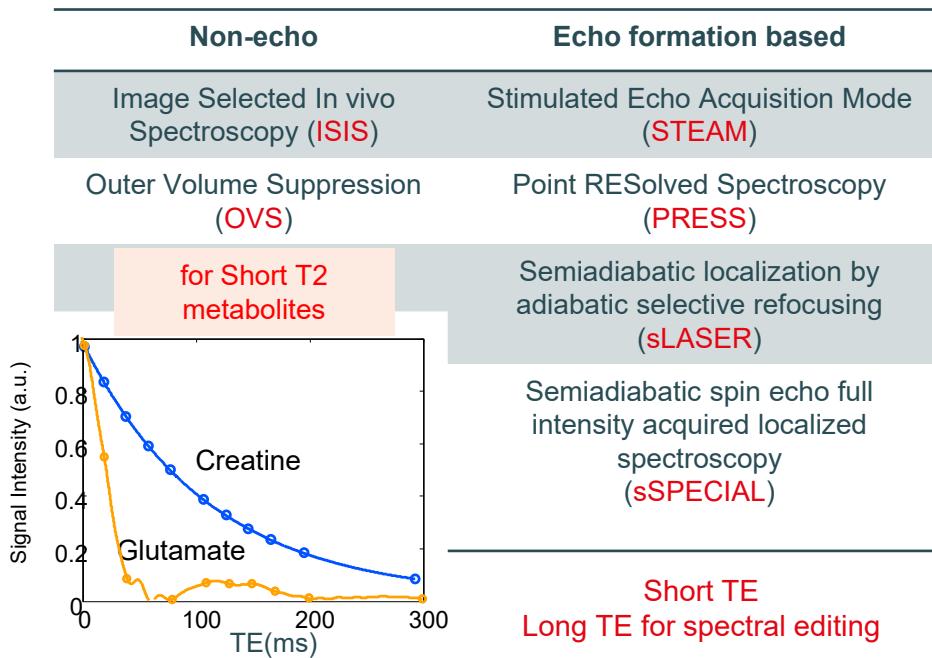


Valette et al., *Anal. Biochem.*, 529,.216-228, 2017

# PRINCIPLE OF LOCALIZATION



# LOCALIZATION SEQUENCES



# CHEMICAL SHIFT DISPLACEMENT (CSD) ERROR

Different resonances may experience different slice selection in the localization sequence due to limited excitation bandwidth of the RF pulses

$$\text{CSDE (\%)}: \frac{\Delta x}{x} = \frac{\Delta f}{BW}$$

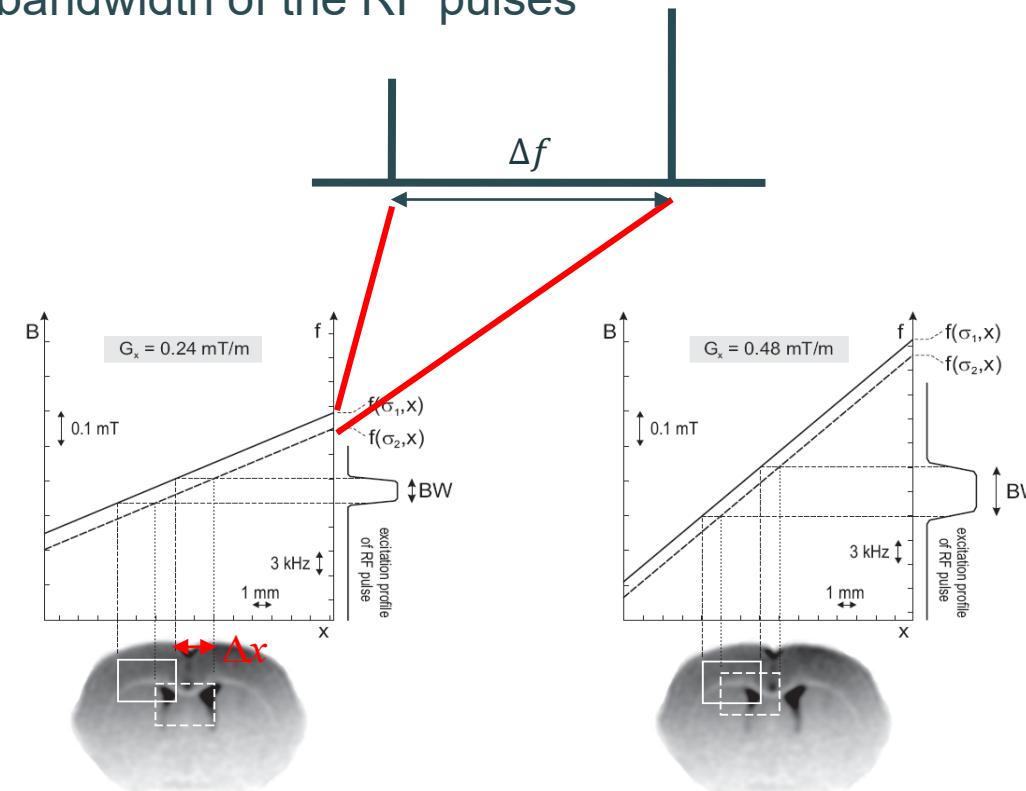
e.g. 10% error along one axis

Origin VOI:

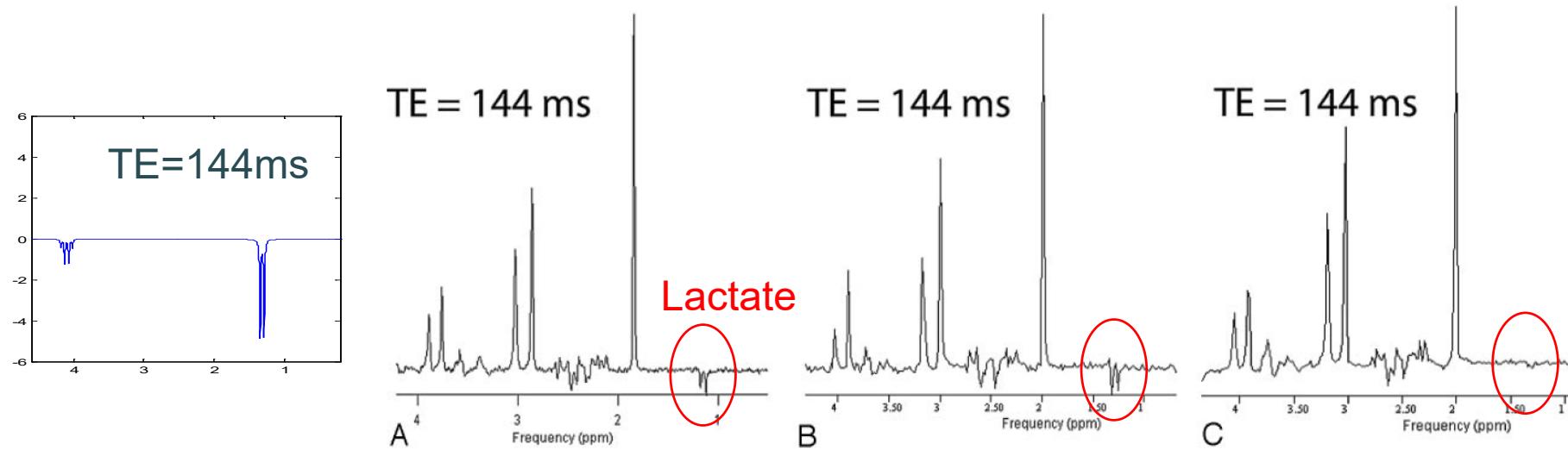
$$1*1*1\text{cm}^3=1\text{cm}^3$$

$$0.9*0.9*0.9\text{cm}^3=0.73\text{cm}^3$$

- Broadband RF pulse
- Strong gradient



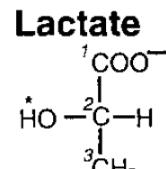
# CSDE FOR J-COUPLED METABOLITES



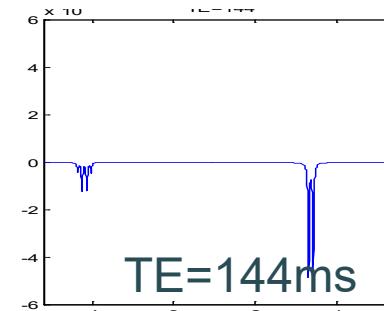
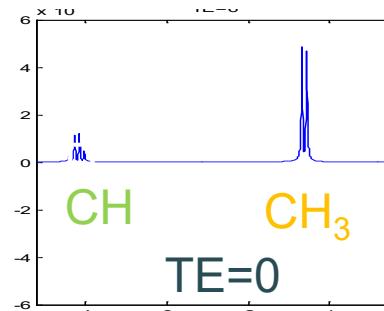
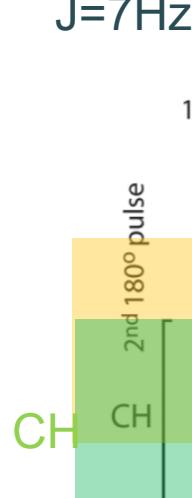
Radio-frequency pulse bandwidths for the selective refocusing pulses vary between vendors in the range of 874–2300 Hz.

*Lange et al, Am J Neuroradiol 27,2006.*

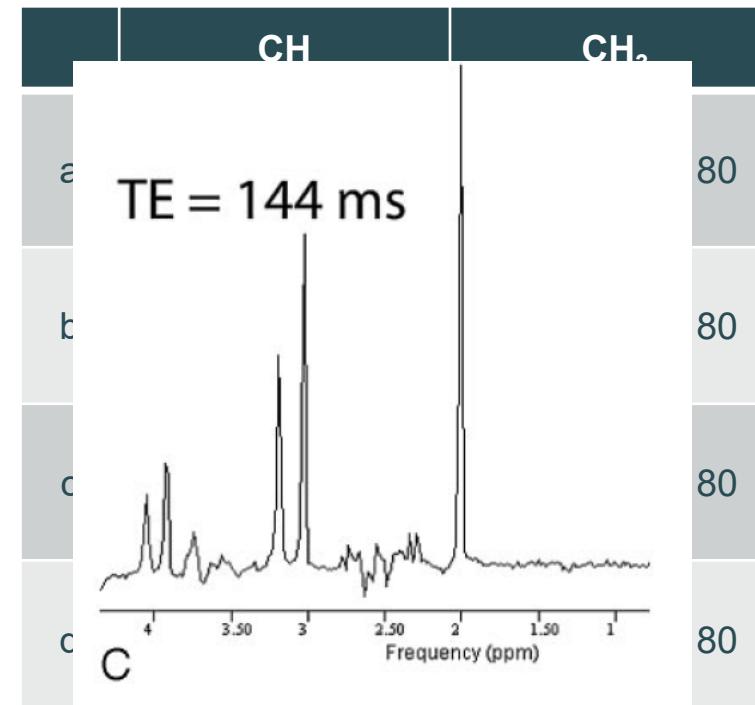
# CSDE FOR J-COUPLED METABOLITES



J=7Hz

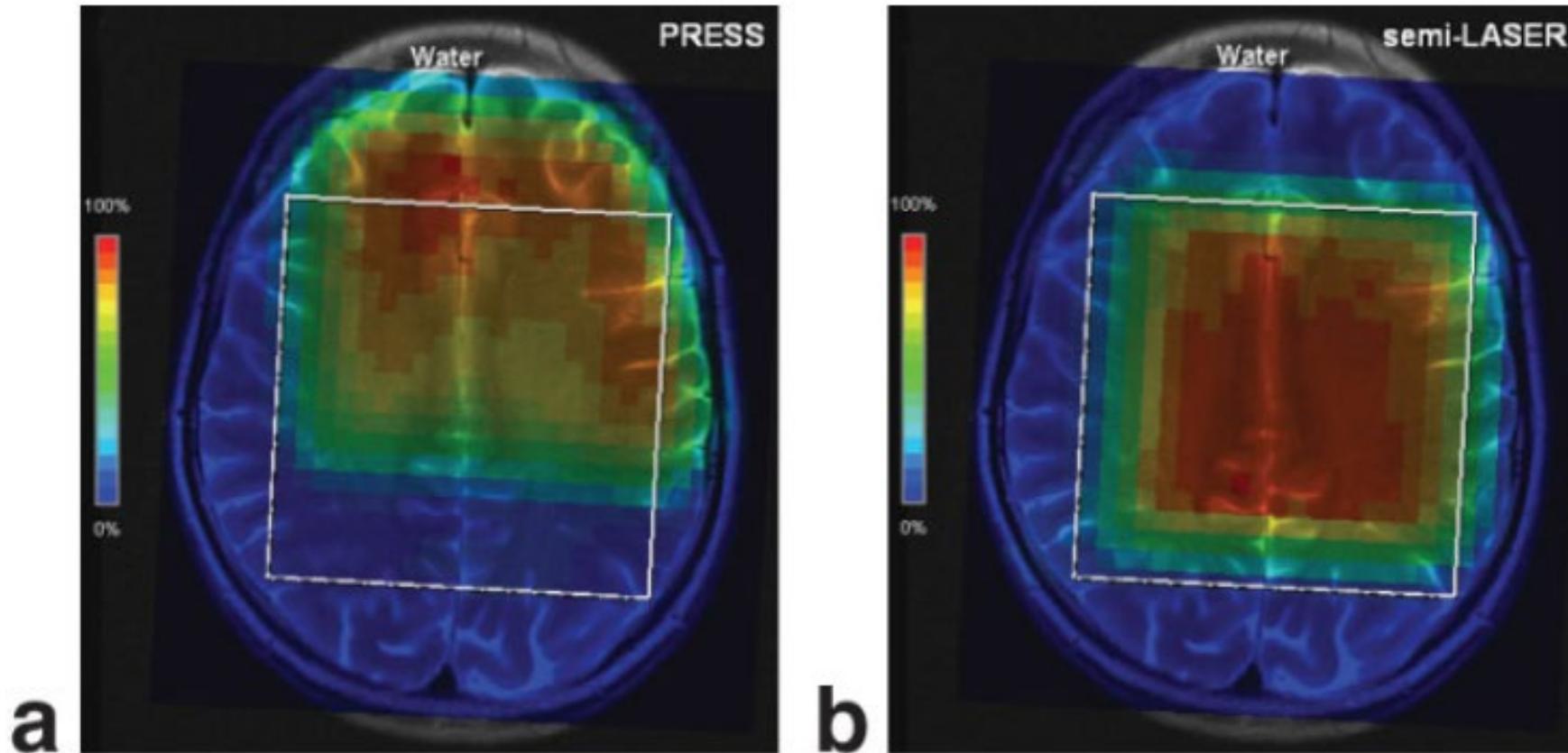


Edden et al, Magn Reson Med, 56, 2006



CIBM.CH

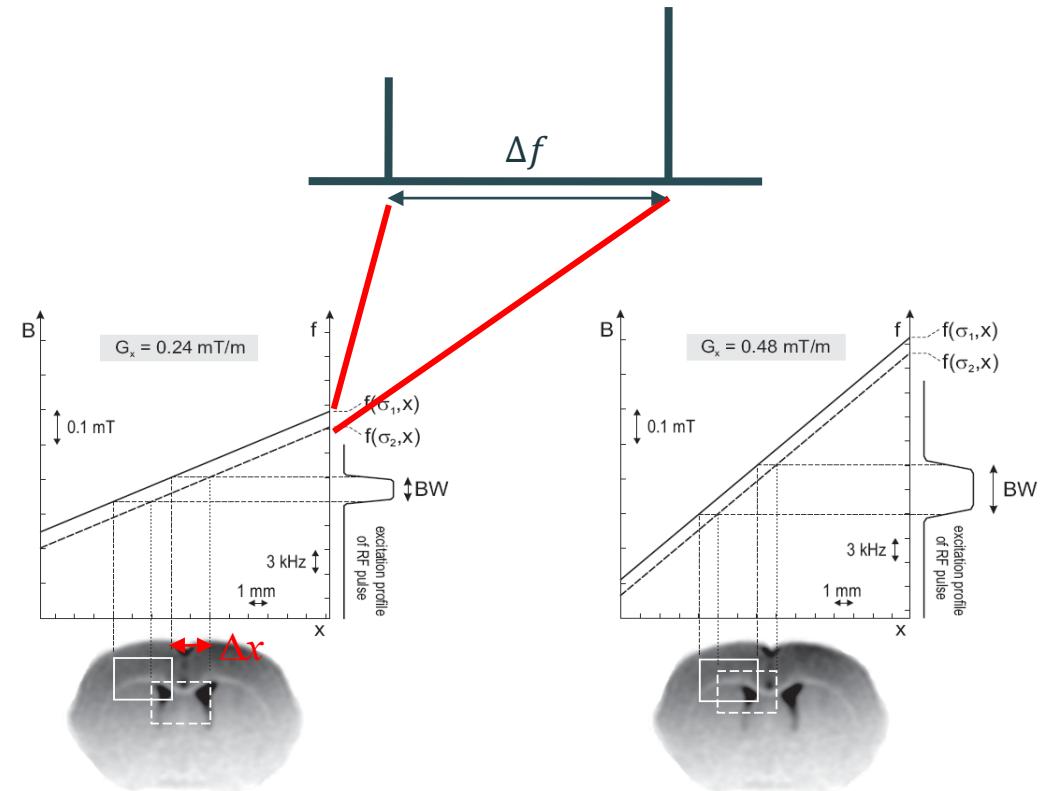
# EXAMPLE OF CSDE IN MRSI



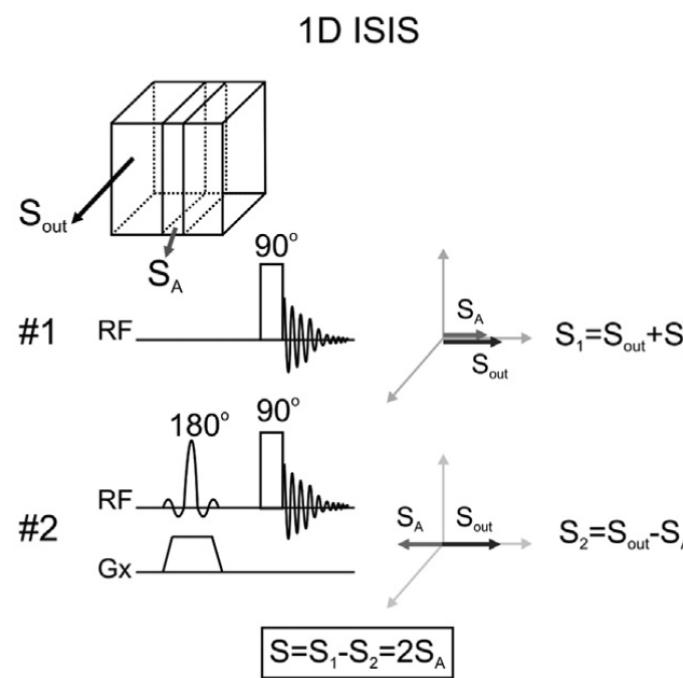
# SUMMARY FOR REDUCING CSDE

$$\text{CSDE (\%)}: \frac{\Delta x}{x} = \frac{\Delta f}{BW}$$

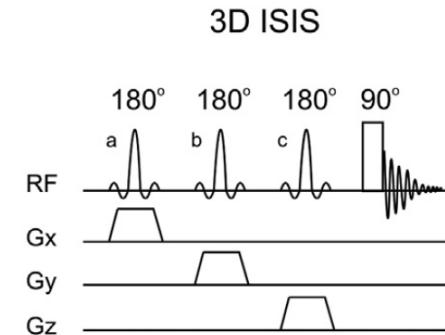
- Broadband RF pulse
- Strong gradient



# IMAGE SELECTED IN VIVO SPECTROSCOPY (ISIS)



Multiple scans with add/subtract scheme



#	a	b	c	
1	OFF	OFF	OFF	+
2	ON	OFF	OFF	-
3	OFF	ON	OFF	-
4	OFF	OFF	ON	-
5	ON	ON	OFF	+
6	ON	OFF	ON	+
7	OFF	ON	ON	+
8	ON	ON	ON	-

■ Pros

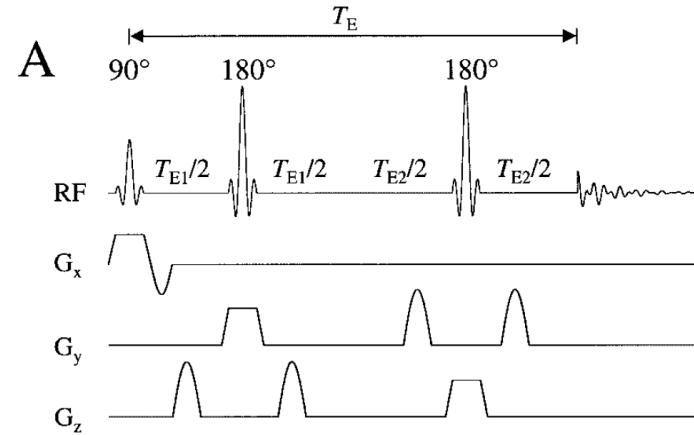
- No signal loss due to  $T_2$  and J-evolution

■ Cons

- Sensitive to motion during addition and subtraction
- Signal loss due to  $T_1$  relaxation

# POINT-RESOLVED SPECTROSCOPY (PRESS)

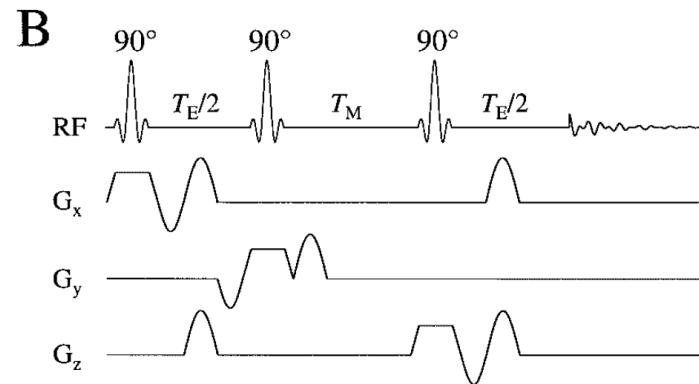
Three slice-selective pulses form a double spin echo – one-shot technique



- Pros: - full signal intensity detected
  - insensitive to motion
- Cons: - rather long echo times
  - sufficient  $B_1$  peak power necessary for  $180^\circ$  pulses

# STIMULATED ECHO ACQUISITION MODE (STEAM)

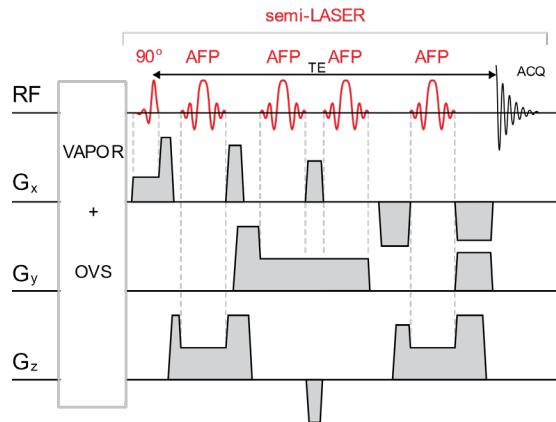
Three slice-selective pulses form a stimulated echo – one-shot technique



- Pros: - short echo time (relative to PRESS)
  - insensitive to motion
  - less sensitive to  $B_1$  inhomogeneity than PRESS
- Cons: - only one half of the magnetization available

# SLICE-SELECTIVE LOCALIZATION BY ADIABATIC SELECTIVE REFOCUSING (semi-LASER)

Slice-selective excitation + 2 pairs of slice-selective adiabatic refocusing pulses

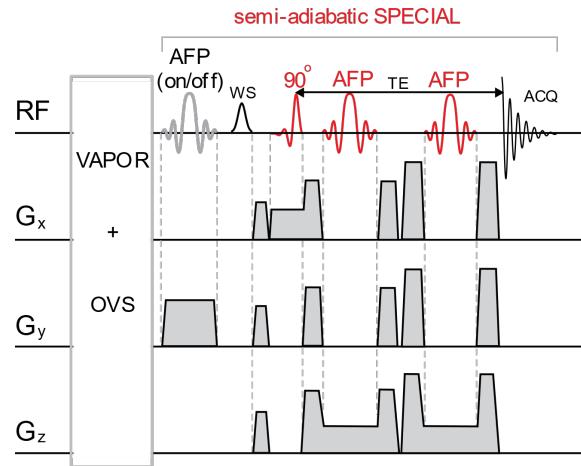


Adiabatic pulses generate a nonlinear phase variation across the slice and must be applied in pairs to obtain a slice-selective spin echo

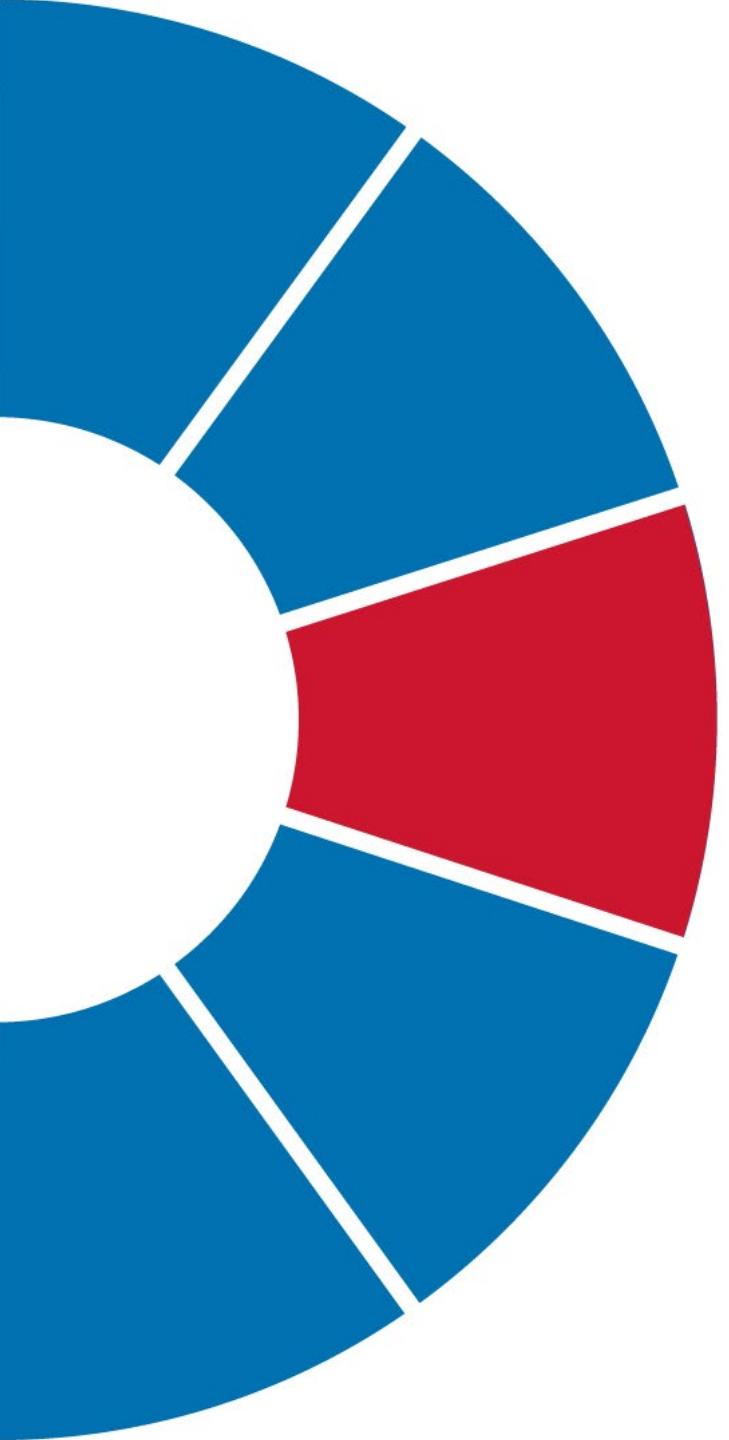
- Pros:
  - full signal intensity available
  - longer minimum echo time but suppressed J-evolution
  - insensitive to  $B_1$  inhomogeneity in two dimensions
- Cons:
  - Longer echo time leads to  $T_2$  weighting of signal
  - high  $B_1$  peak power necessary for 180° pulses

# SEMI-ADIABATIC SPIN ECHO, FULL INTENSITY ACQUIRED LOCALIZED SPECTROSCOPY (sSPECIAL )

Spin-echo based add/subtract scheme - two shots technique

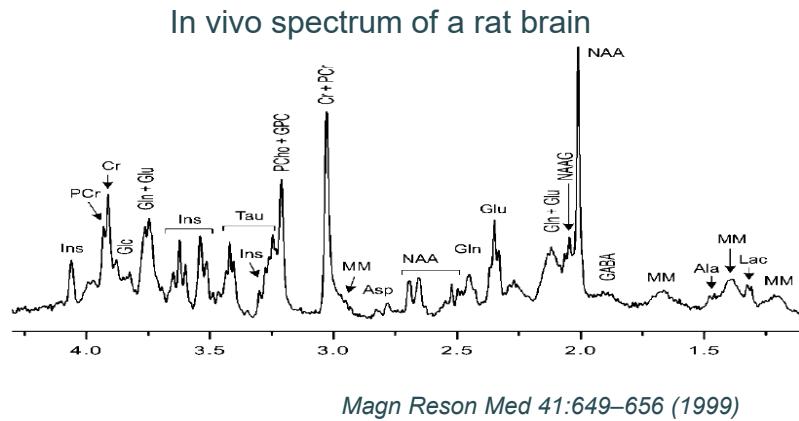
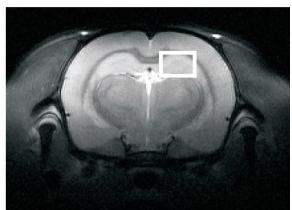
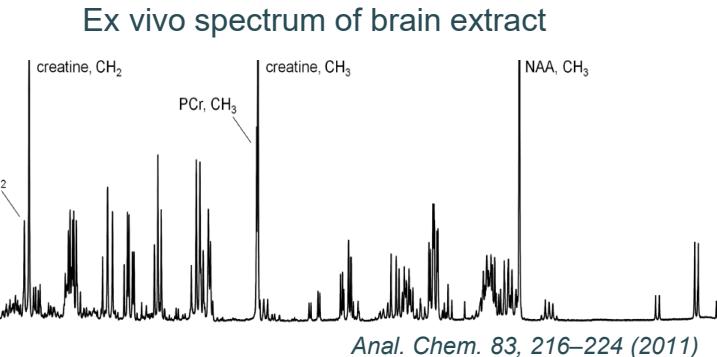


- Pros:
  - full signal intensity available
  - short TE (minimal signal loss due to  $T_2$  and J-evolution)
  - insensitive to  $B_1$  inhomogeneity in two dimensions
- Cons:
  - two scans necessary for localization
  - more sensitive to motion than single-shot methods
  - high  $B_1$  peak power necessary for  $180^\circ$  pulses



$B_0$  SHIMMING

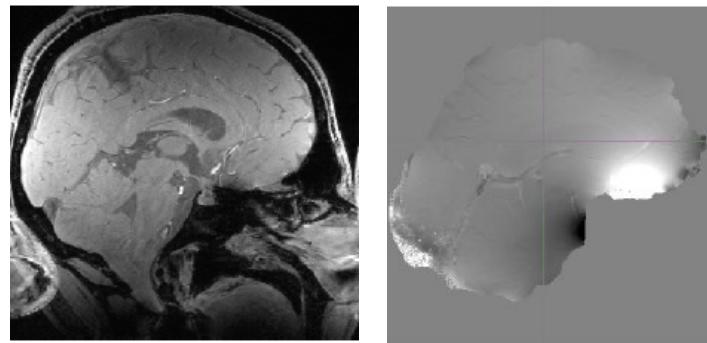
# MAGNETIC FIELD INHOMOGENEITY



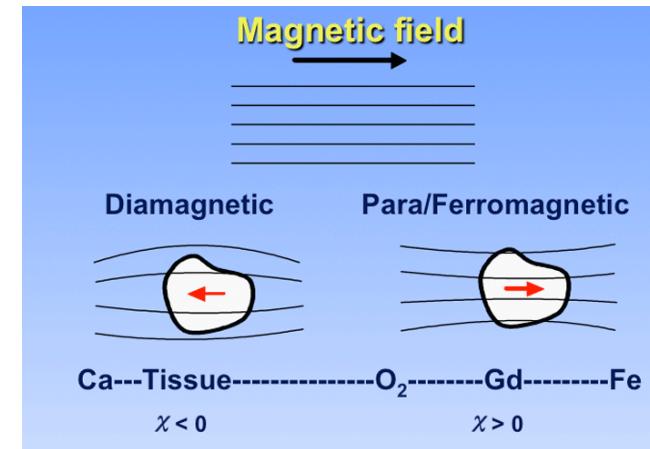
# ORIGIN OF MAGNETIC FIELD INHOMOGENEITY

- magnetic susceptibility difference between air and tissue
  - Brain tissue(70-80% of water): diamagnetic
  - Oxygen: paramagnetic

e.g. prefrontal cortex (close to nasal sinus cavity, air-tissue surface)



<http://mriquestions.com>



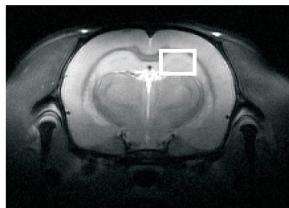
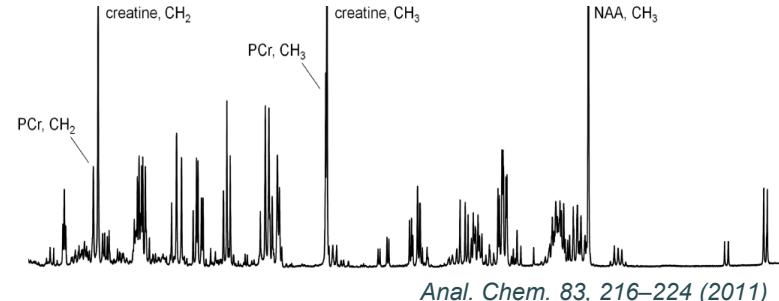
Water  
Fat  
tissues

$O_2$

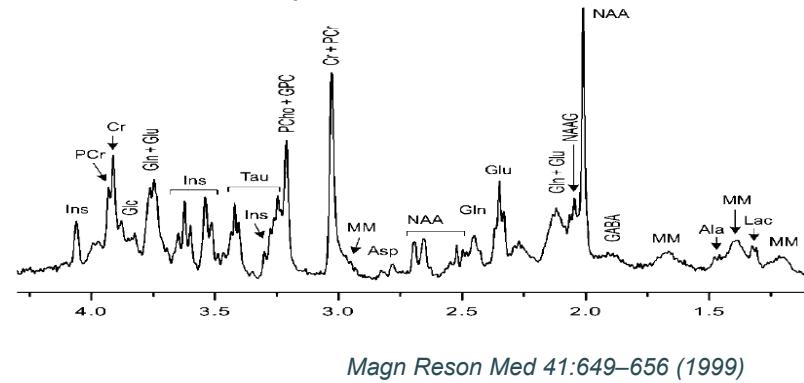
# MAGNETIC FIELD INHOMOGENEITY



Ex vivo spectrum of brain extract

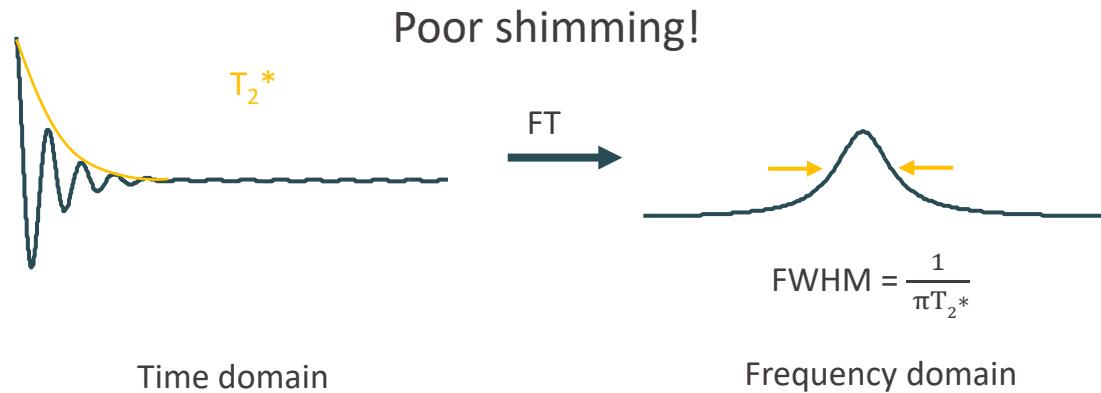


In vivo spectrum of a rat brain



Higher magnetic susceptibility  
gradient in living tissue

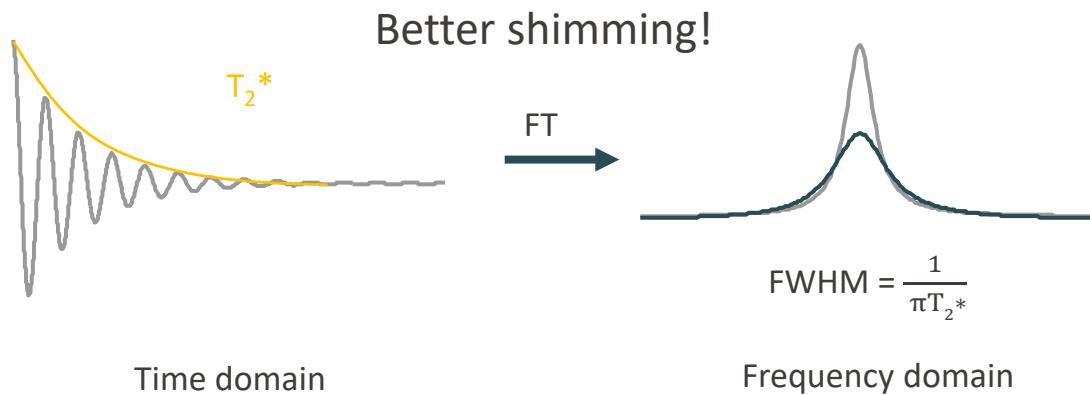
# $B_0$ SHIMMING: OPTIMIZE FIELD INHOMOGENEITY



$$FWHM \sim \frac{1}{\pi T_2^*} = \frac{1}{\pi T_2} + \frac{\gamma}{2\pi} \Delta B_0$$

Compensated by shimming

# $B_0$ SHIMMING: OPTIMIZE FIELD INHOMOGENEITY



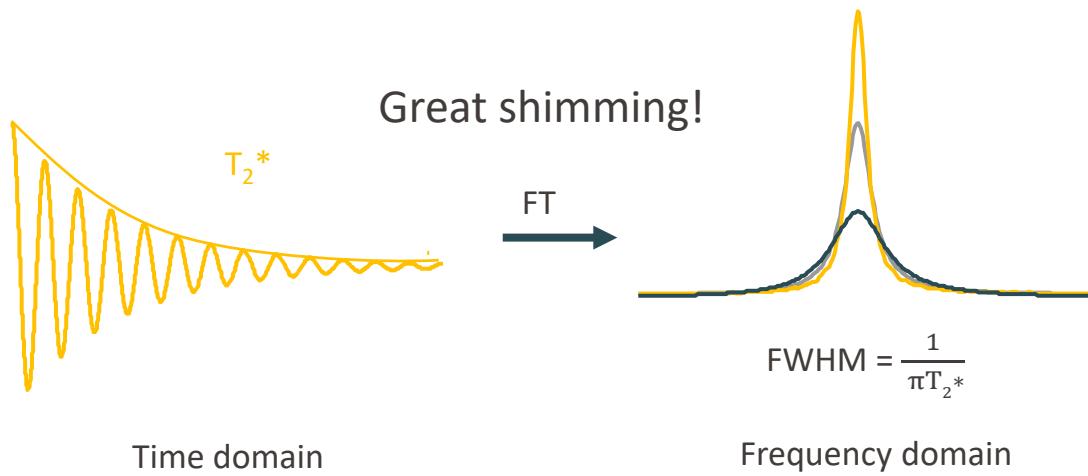
Time domain

Frequency domain

$$FWHM \sim \frac{1}{\pi T_2^*} = \frac{1}{\pi T_2} + \frac{\gamma}{2\pi} \Delta B_0$$

Compensated by shimming

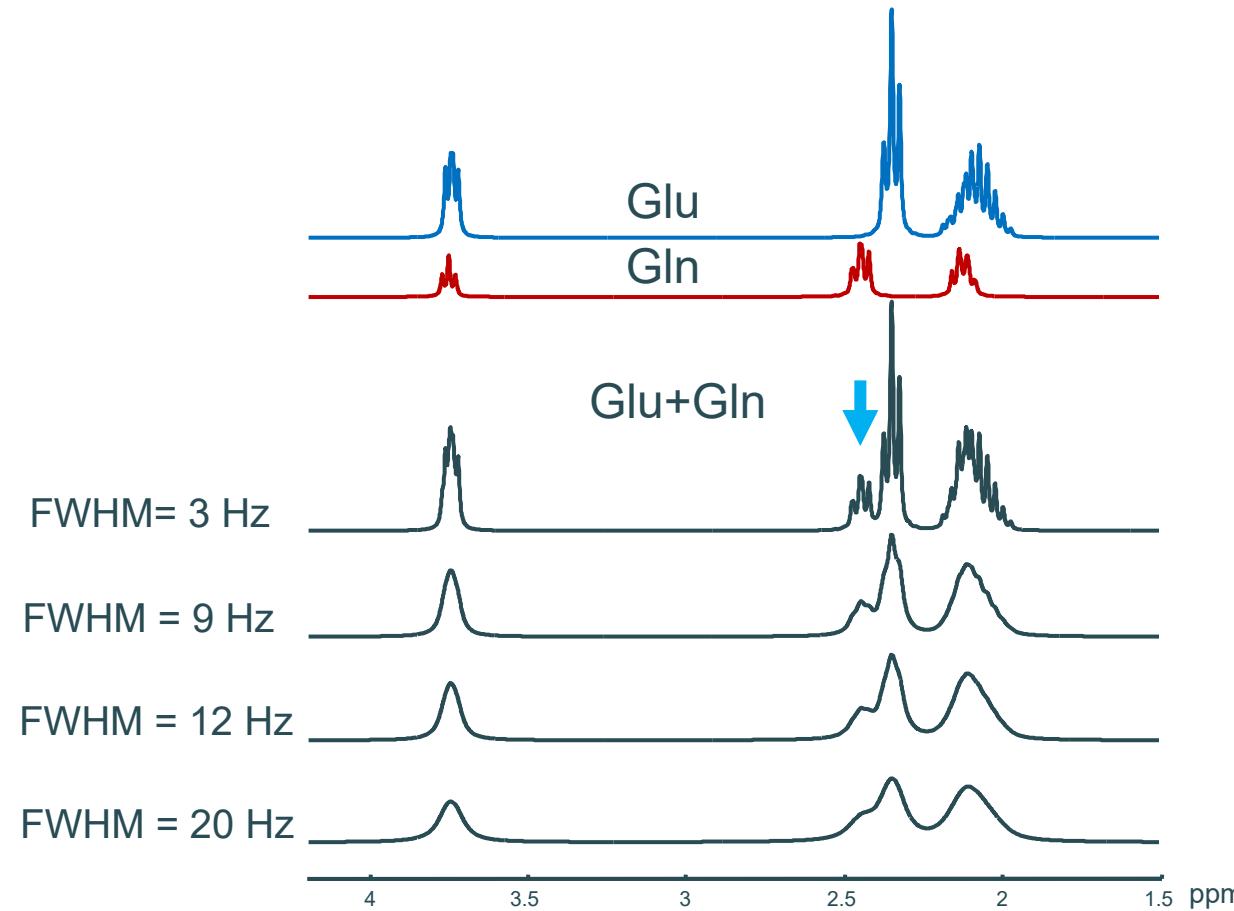
# $B_0$ SHIMMING: OPTIMIZE FIELD INHOMOGENEITY



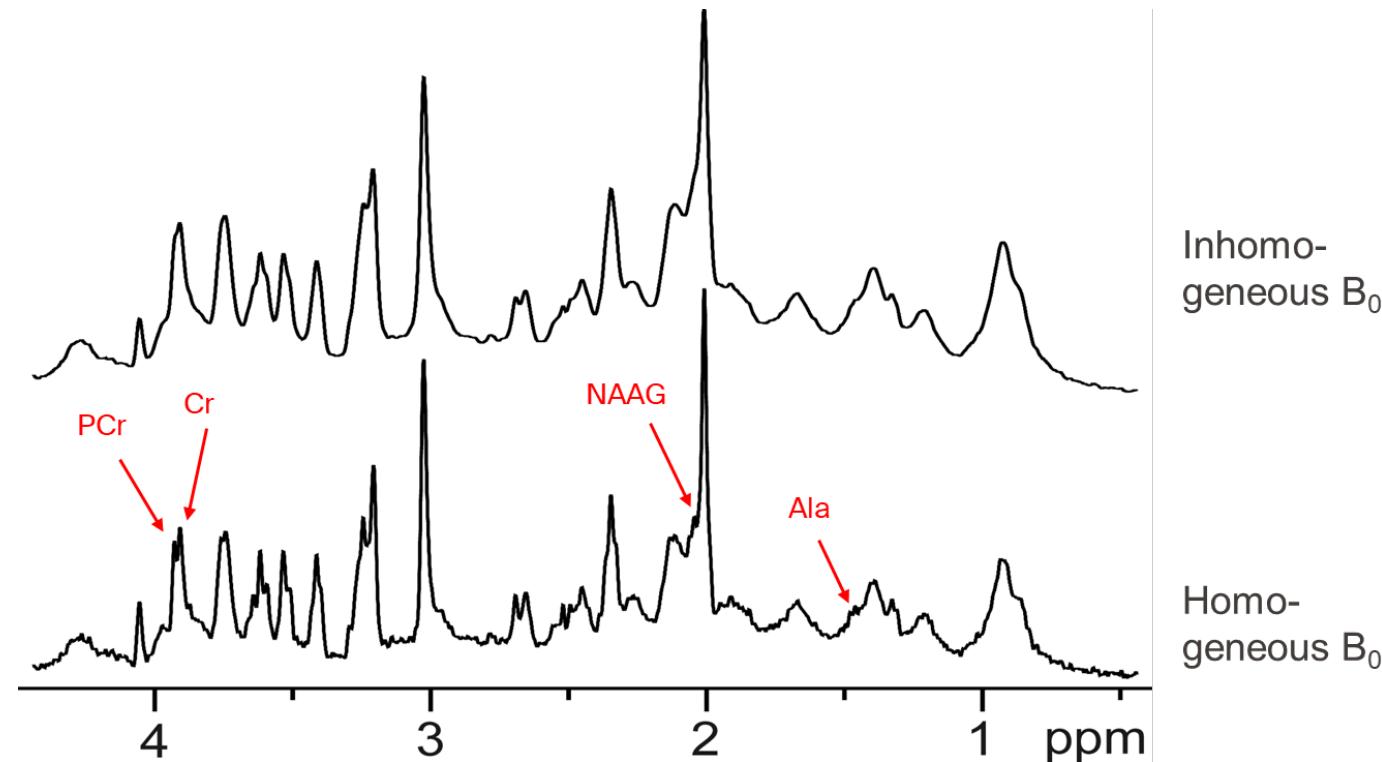
$$FWHM \sim \frac{1}{\pi T_2^*} = \frac{1}{\pi T_2} + \frac{\gamma}{2\pi} \Delta B_0$$

Compensated by shimming

# EFFECT OF $B_0$ INHOMOGENEITY ON SPECTRAL RESOLUTION



# EFFECT OF $B_0$ INHOMOGENEITY ON SPECTRAL RESOLUTION

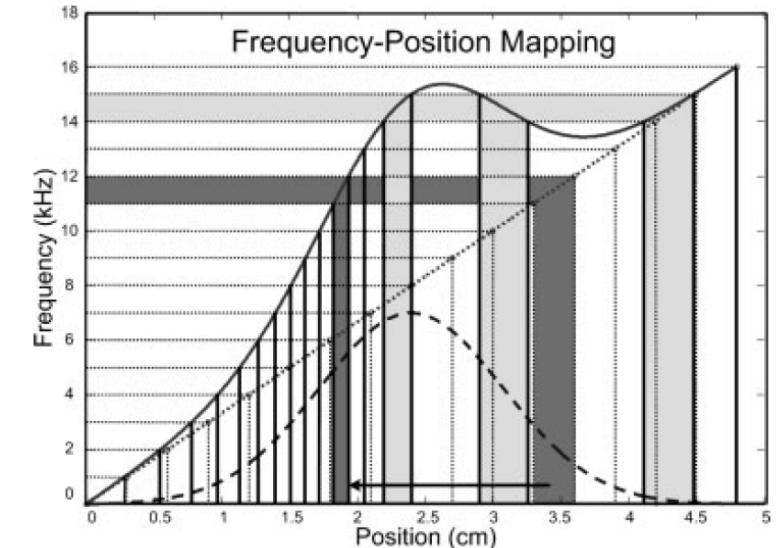


# WHY: $B_0$ SHIMMING

- Improved SNR
- Improved spectral resolution
- Efficient water suppression, outer volume suppression and editing performance (especially for MRSI)
- Avoiding mislocalization and distortion of localization profile

Dotted line: frequency-position mapping without  $B_0$  inhomogeneities

Solid line: frequency-position mapping with superposition of metal induced field inhomogeneities



W. Lu et al. Magn Reson Med 62, 2009.

# SPHERICAL HARMONICS FOR $B_0$ FIELD

- Magnetic field can be described as a linear combination of spherical harmonics

$$B_0(r, \theta, \phi) = \sum_n \left( r^n * \sum_i (k_{nm} * W_{nm}(\phi, \theta)) \right)$$

$r$  : Vector to spatial location (x,y,z) in the magnet

$W_{nm}(\phi, \theta)$  : Angular functions based on spherical harmonics

$K_{nm}$  : Coefficients of expansion

$\phi, \theta$  : fixed for a given projection

Field Generated by Low-Order Shims and Associated Spherical Harmonic Functions  
in Spherical and Cartesian Coordinates<sup>a</sup>

$n$	$m$	Shorthand notation	Coefficients <sup>b</sup> ( $k_{nm}$ )	Spatial dependence $r^n W_{nm}(\theta, \phi)$	
				Spherical	Cartesian
1 <sup>c</sup>	0	$Z^c$	$C_1$	$r \cos \theta$	$z$
	1	$X^c$	$A_{11}$	$r \sin \theta \cos \phi$	$x$
	1	$Y^c$	$B_{11}$	$r \sin \theta \sin \phi$	$y$
2 <sup>c</sup>	0	$Z^{2c}$	$C_2$	$r^2(3 \cos^2 \theta - 1)/2$	$z^2 - (x^2 + y^2)/2$
	1	$XZ$	$3A_{21}$	$r^2 \sin \theta \cos \theta \cos \phi$	$xz$
	1	$YZ$	$3B_{21}$	$r^2 \sin \theta \cos \theta \sin \phi$	$yz$
	2	$X^2 - Y^2$	$3A_{22}$	$r^2 \sin^2 \theta \cos 2\phi$	$x^2 - y^2$
	2	$2XY$	$3B_{22}$	$r^2 \sin^2 \theta \sin 2\phi$	$2xy$
3 <sup>c</sup>	0	$Z^3$	$C_3$	$r^3(5 \cos^3 \theta - 3 \cos \theta)/2$	$z[z^2 - 3(x^2 + y^2)/2]$
	1	$XZ^2$	$\frac{3}{2}A_{31}$	$r^3 \sin \theta (5 \cos^2 \theta - 1) \cos \phi$	$x(4z^2 - x^2 - y^2)$
	1	$YZ^2$	$\frac{3}{2}B_{31}$	$r^3 \sin \theta (5 \cos^2 \theta - 1) \sin \phi$	$y(4z^2 - x^2 - y^2)$
	2	$Z(X^2 - Y^2)$	$15A_{32}$	$r^3 \sin^2 \theta \cos \theta \cos 2\phi$	$z(x^2 - y^2)$
	2	$XYZ$	$15B_{32}$	$r^3 \sin^2 \theta \cos \theta \sin 2\phi$	$2xyz$
	3	$X^3$	$15A_{33}$	$r^3 \sin^3 \theta \cos 3\phi$	$x^3 - 3xy^2$
	3	$Y^3$	$15B_{33}$	$r^3 \sin^3 \theta \sin 3\phi$	$3x^2y - y^3$

1<sup>st</sup> order

2<sup>nd</sup> order

3<sup>rd</sup> order

Gradient coils

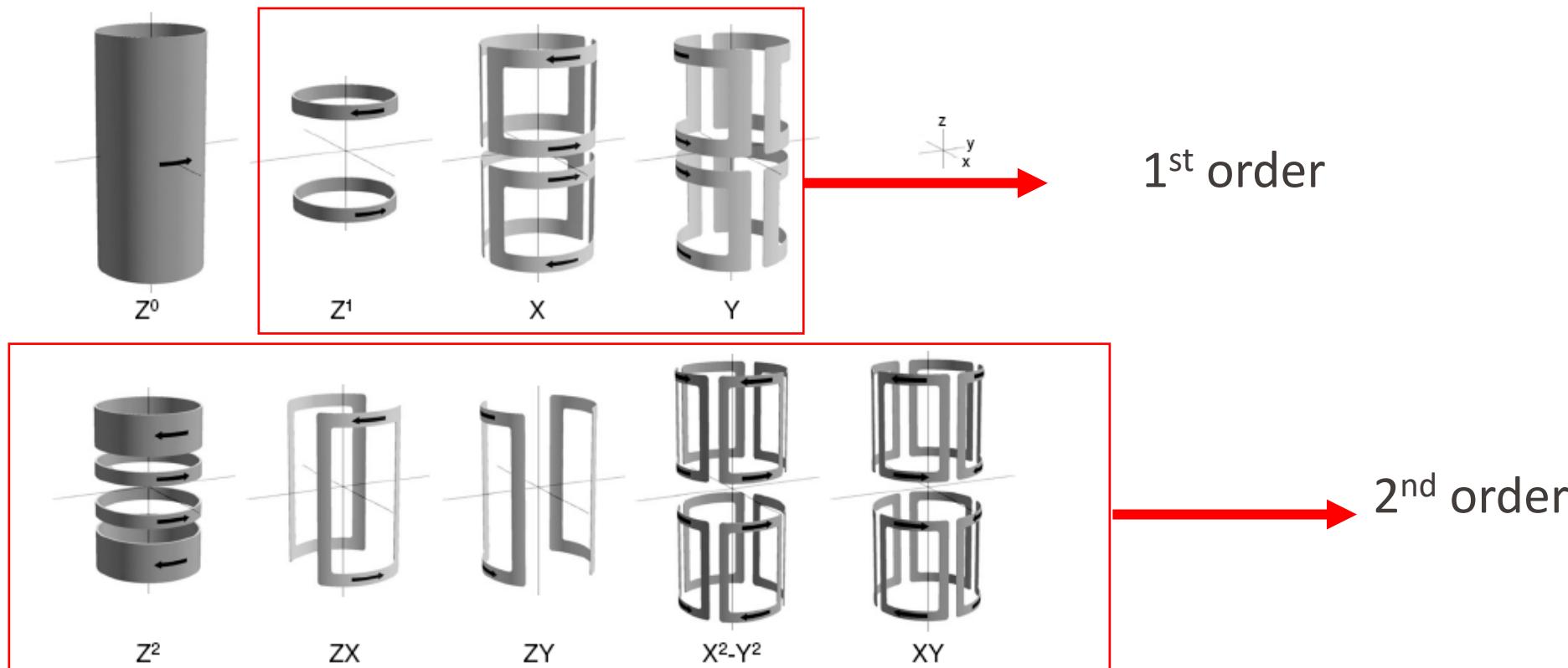
Shim coils

C I B M . C H

Gruetter et al, JMR, 96 (1992)

# SHIM COILS

Each shim coil produces magnetic field corresponding to one spherical harmonic field.



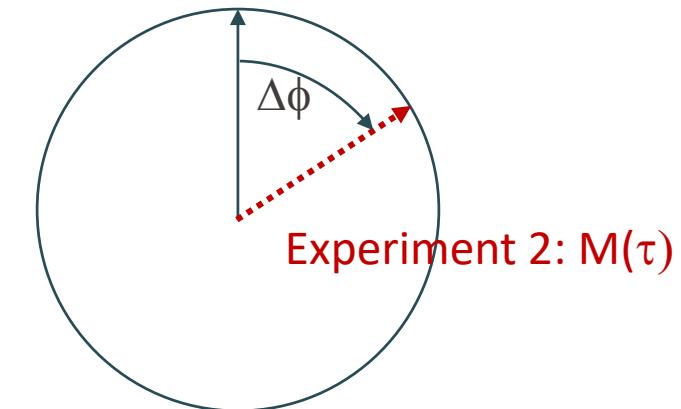
# $B_0$ SHIMMING METHODS

- $B_0$  can be measured from the **phase differences** of magnetization during a given period of free precession

- Manual shimming
  - Time-consuming

- Automated shimming methods (quantitative, accurate and fast)
  - 3D field mapping
  - projection based mapping: e.g. FASTMAP (high spatial sampling, preferred for small volume optimization)

Experiment 1:  $M(0)$



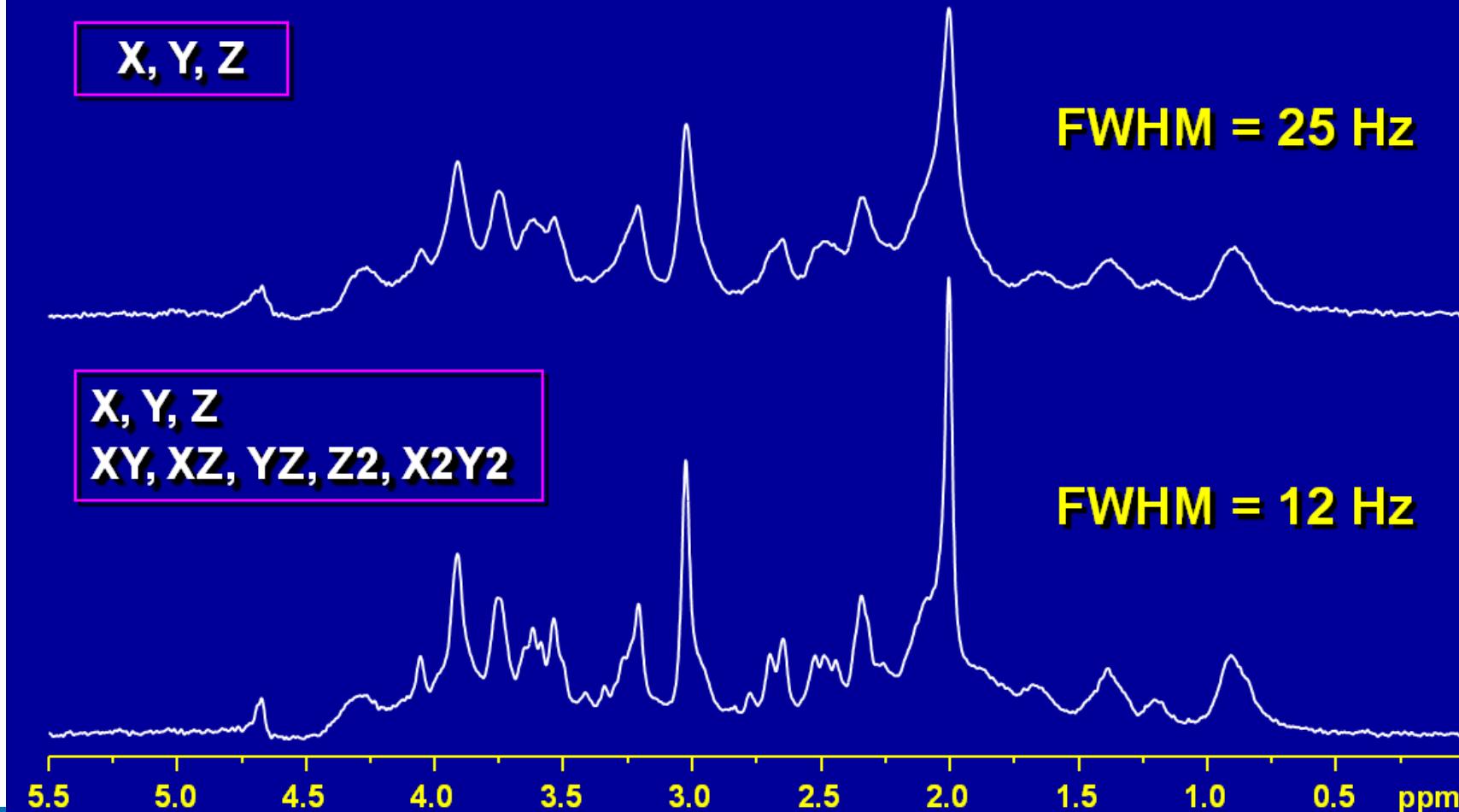
$$\Delta\phi^{(j)}(r, \tau) = \gamma B_0(r, \theta^{(j)}, \phi^{(j)})\tau$$

# EXAMPLE OF IN VITRO WATER SHIMMING RESULTS



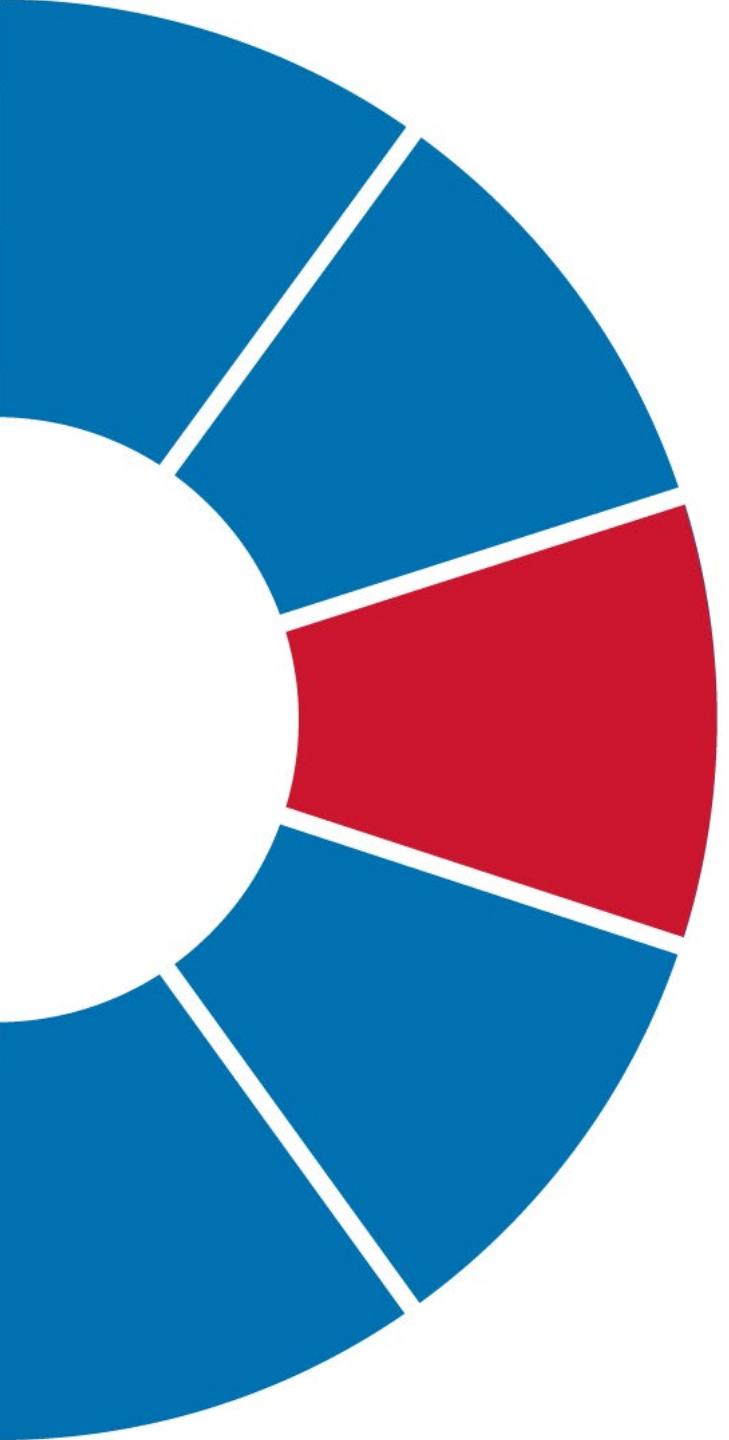
# Effect of 2<sup>nd</sup>-order shimming at 7 T

STEAM TE = 6 ms, VOI = 2 x 2 x 2 cm<sup>3</sup>, occipital lobe, FASTMAP shimming



Tkac, University of Minnesota

I B M . C H



$B_1$  CALIBRATION

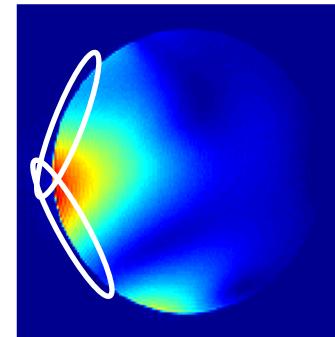
# B<sub>1</sub><sup>+</sup> CALIBRATION

## ■ Why?

- Achieve the required flip angle  $\alpha = \gamma B_1 T$
- Maximal signal intensity
- Optimal slice profile to reach the best localization performance

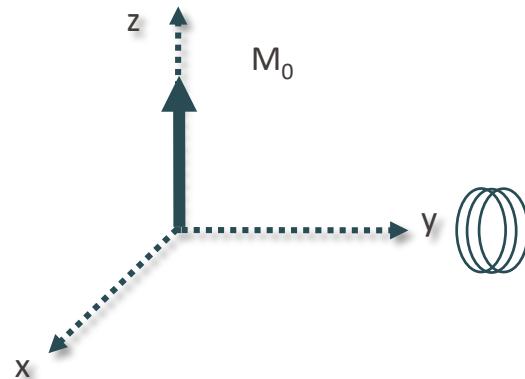
## ■ B<sub>1</sub><sup>+</sup> Calibration is critical before each scan

- Different B<sub>1</sub> distribution for different subjects and coils



# $B_1^+$ CALIBRATION

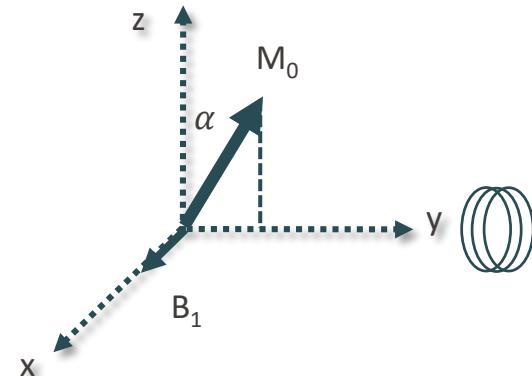
- Flip angle calibration  $\alpha = \gamma B_1 T$



# $B_1^+$ CALIBRATION

- Flip angle calibration  $\alpha = \gamma B_1 T$

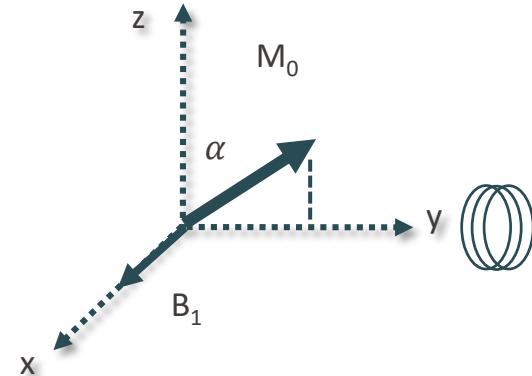
$$SI = \sin(\alpha)$$



# $B_1^+$ CALIBRATION

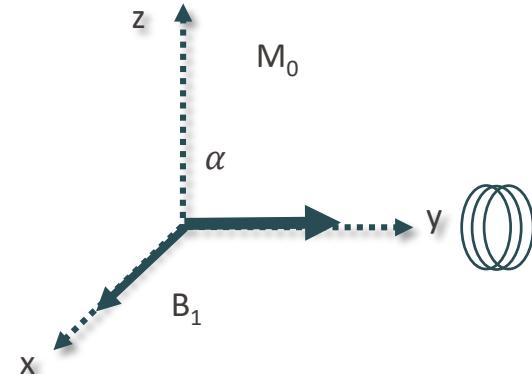
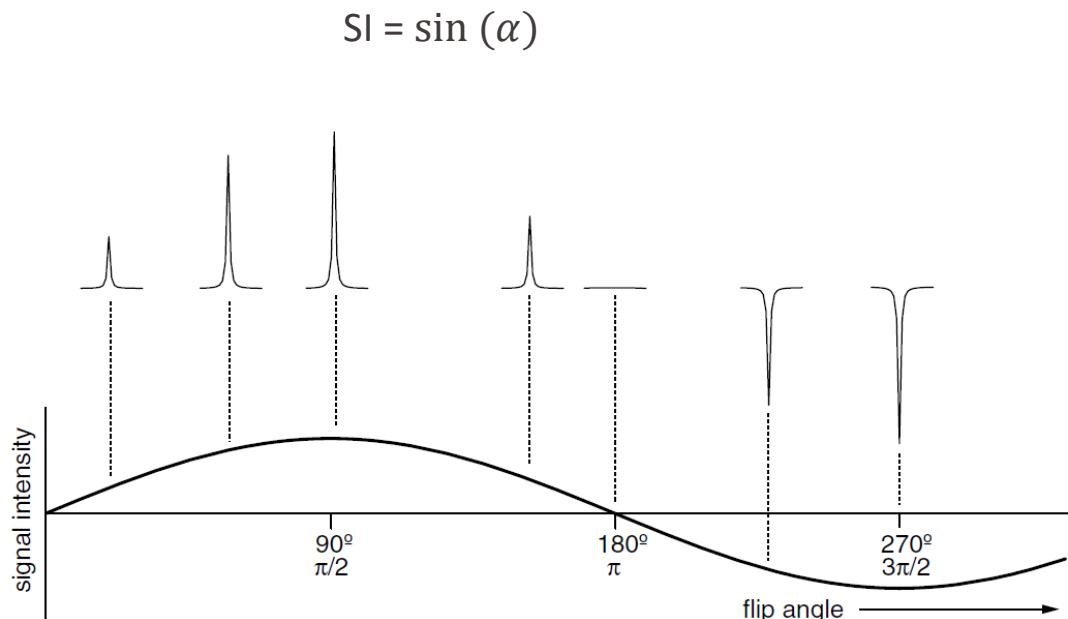
- Flip angle calibration  $\alpha = \gamma B_1 T$

$$SI = \sin(\alpha)$$



# B<sub>1</sub><sup>+</sup> CALIBRATION

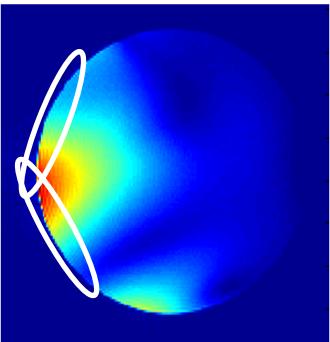
## ■ Flip angle calibration $\alpha = \gamma B_1 T$



# $B_1^+$ CALIBRATION

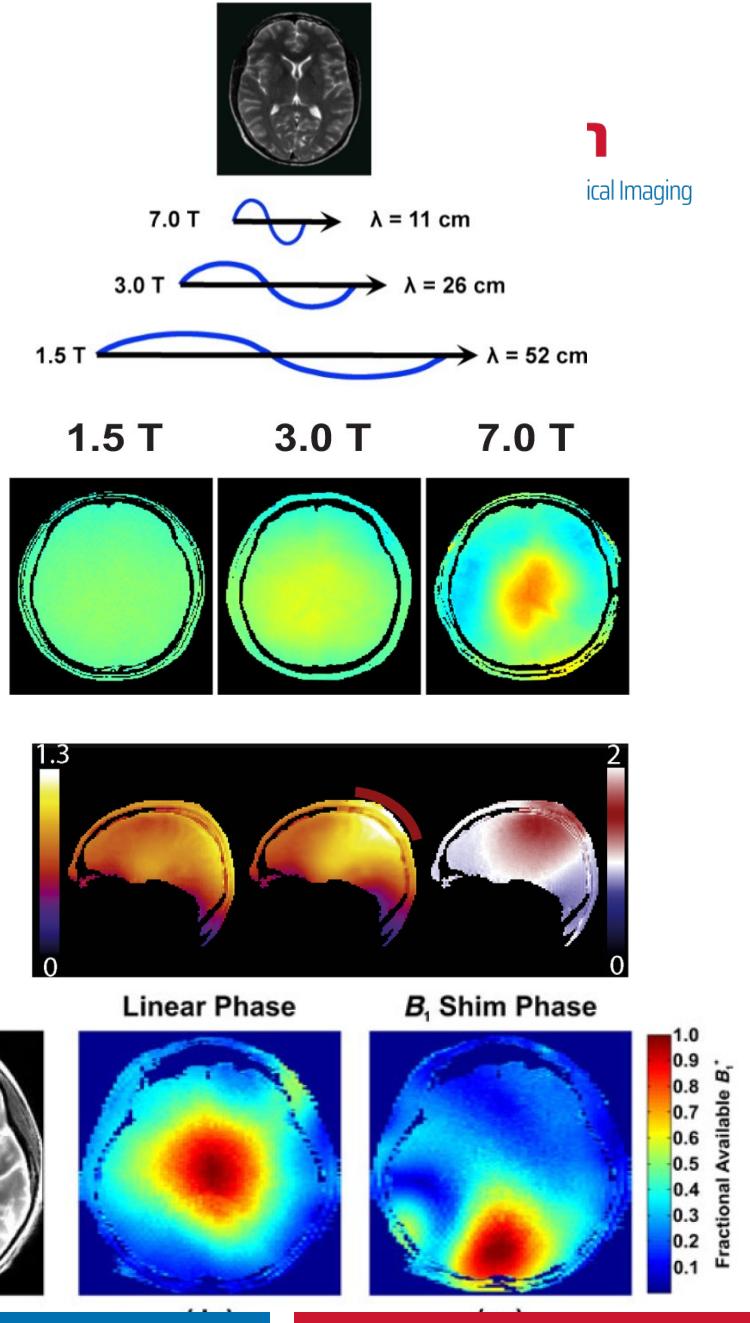
## ■ Surface coil

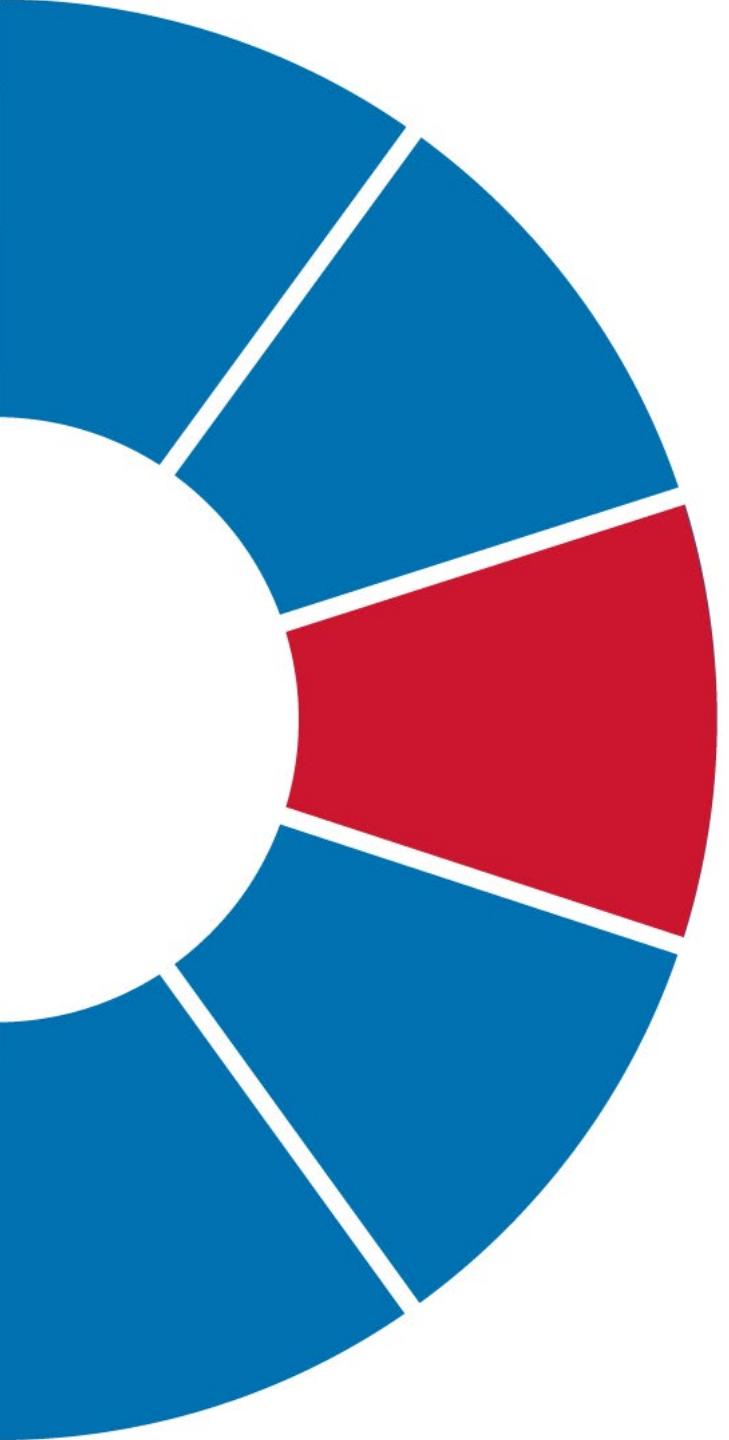
- Calibrate local RF power for  $B_1^+$



## ■ Volume coil

- Destructive and constructive interferences from standing waves at high magnetic fields (RF wavelength  $\leq$  sample size) lead to inhomogeneous  $B_1$  distribution
- High permittivity dielectric pad
- $B_1^+$  shimming using transmit arrays is desirable to achieve maximal local  $B_1^+$

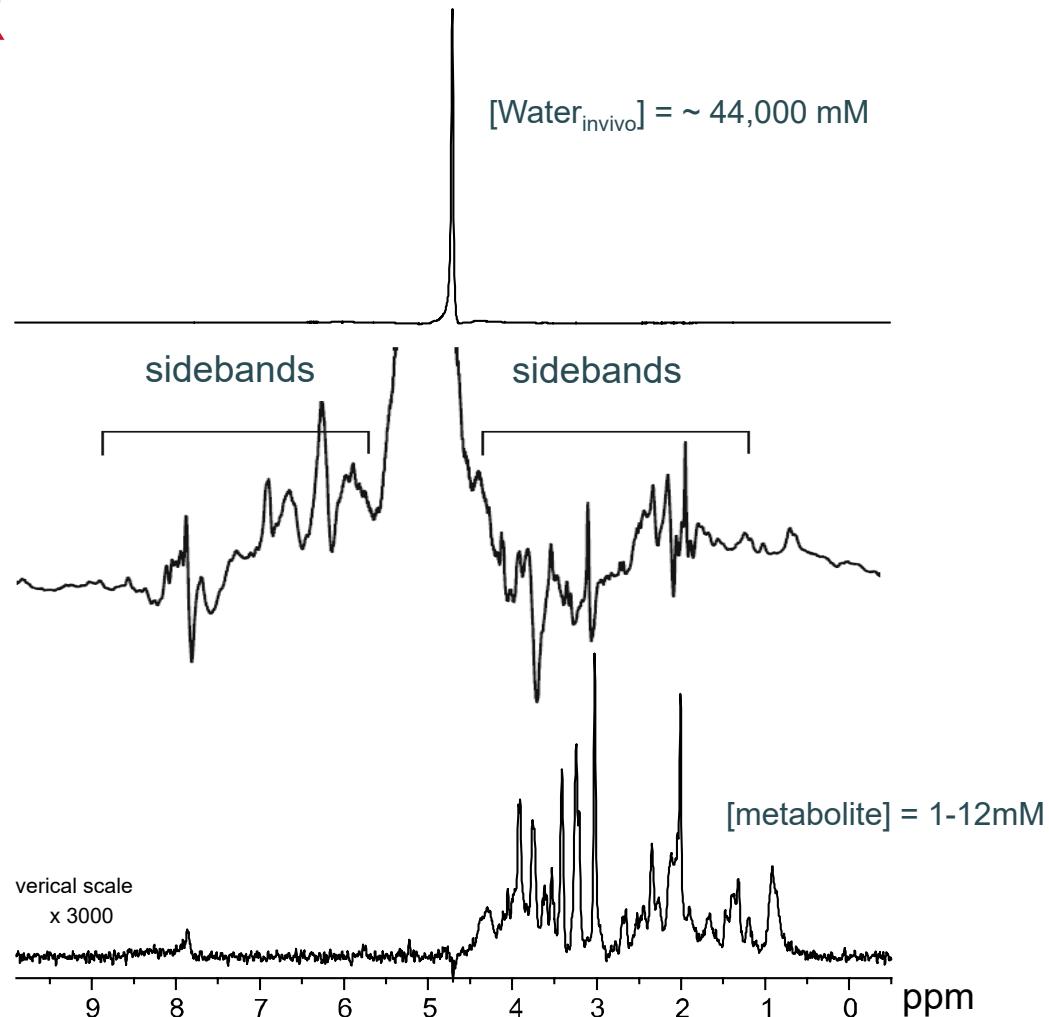




WATER SUPPRESSION

# WHY SUPPRESS WATER

- Water is about 10000 times bigger than metabolites
- Vibration induced water sidebands
- Baseline distortion

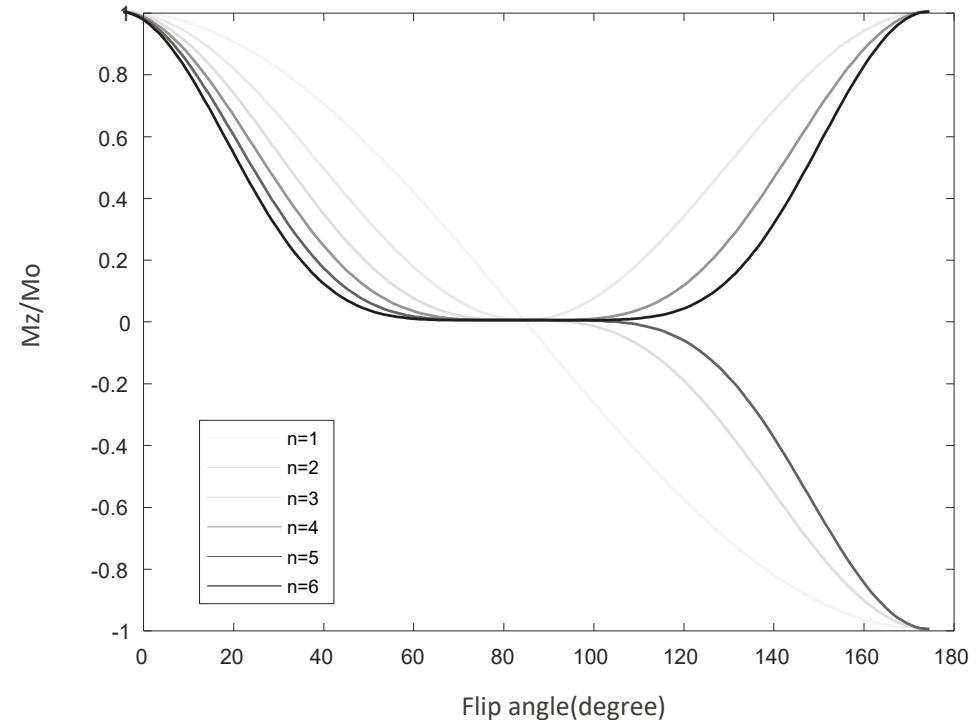
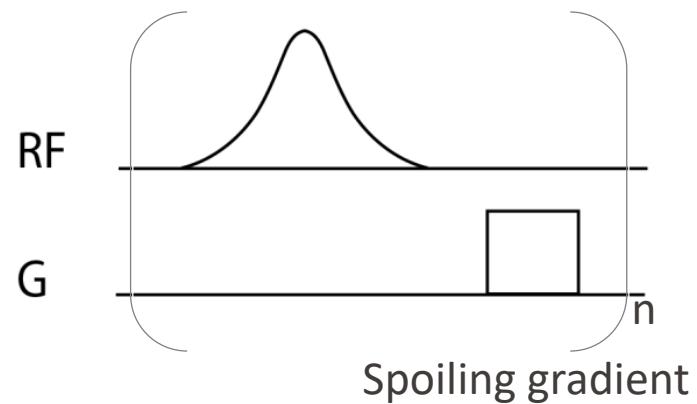


de Graaf R.A. (2012) Principles of  $^1\text{H}$  NMR Spectroscopy In Vivo. In: Choi IY., Gruetter R. (eds) Neural Metabolism In Vivo.

# WATER SUPPRESSION MODULE

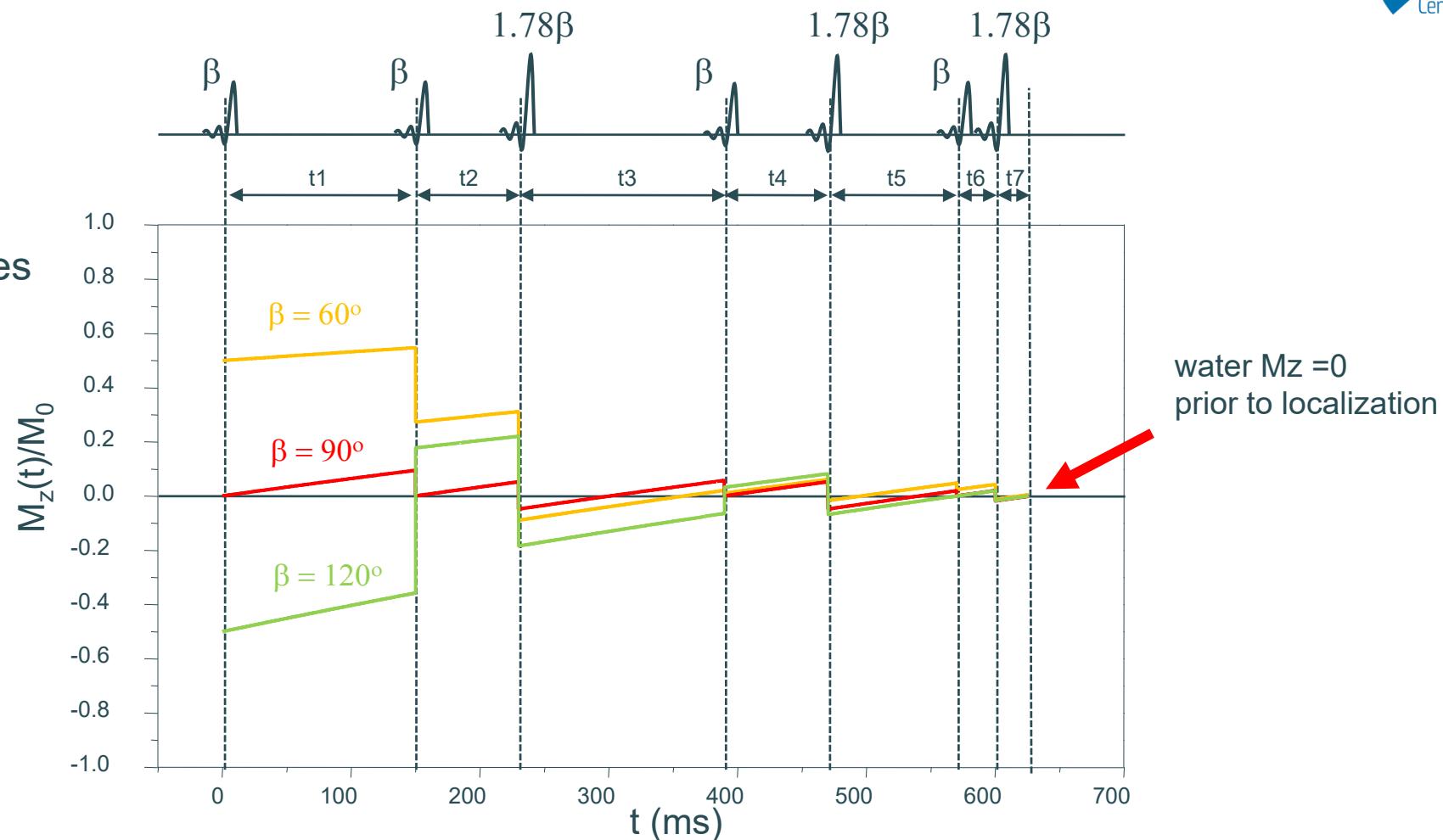
## CHEmical Shift-Selective (CHESS)

Frequency selective pulse for water resonance

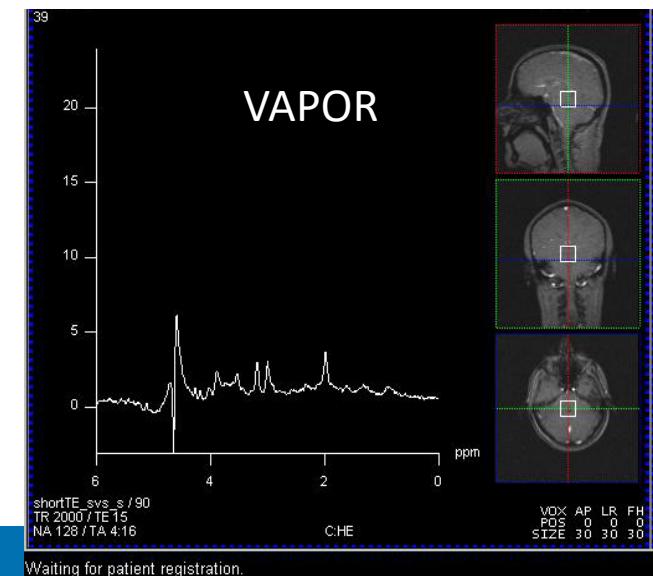
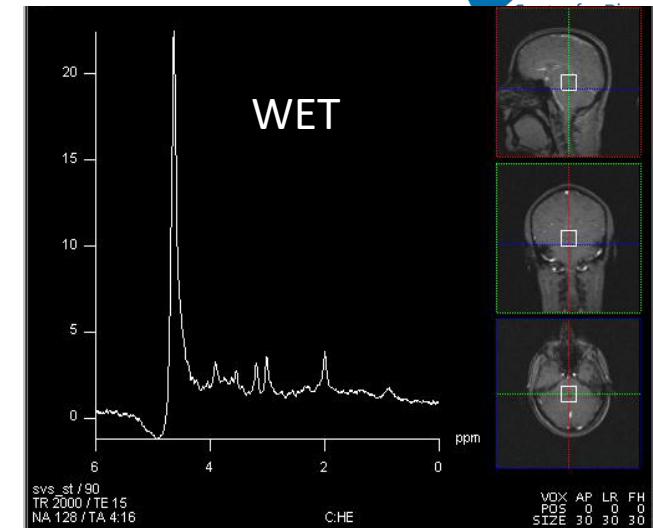
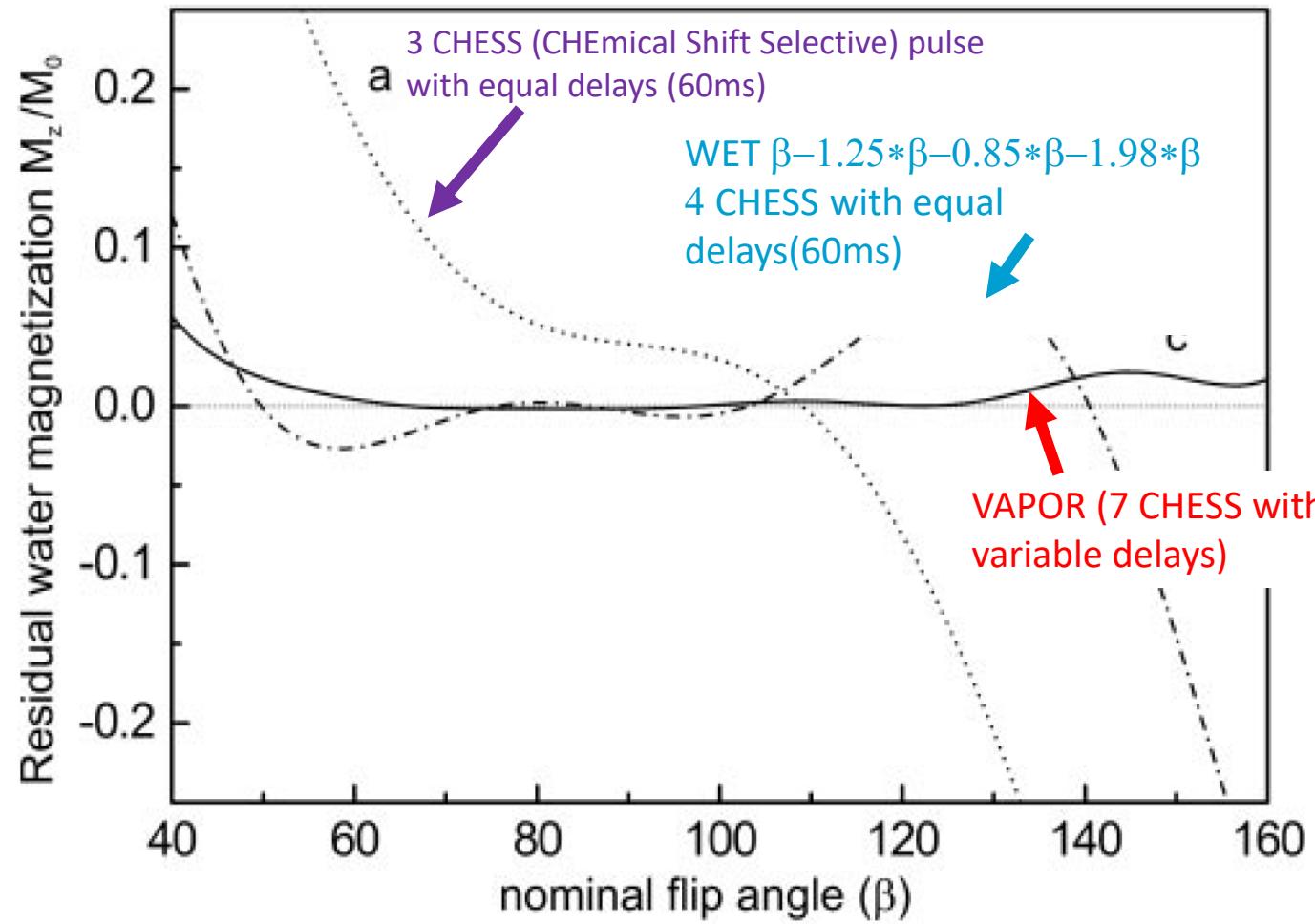


# VAriable pulse Power and Optimized Relaxation delays (VAPOR)

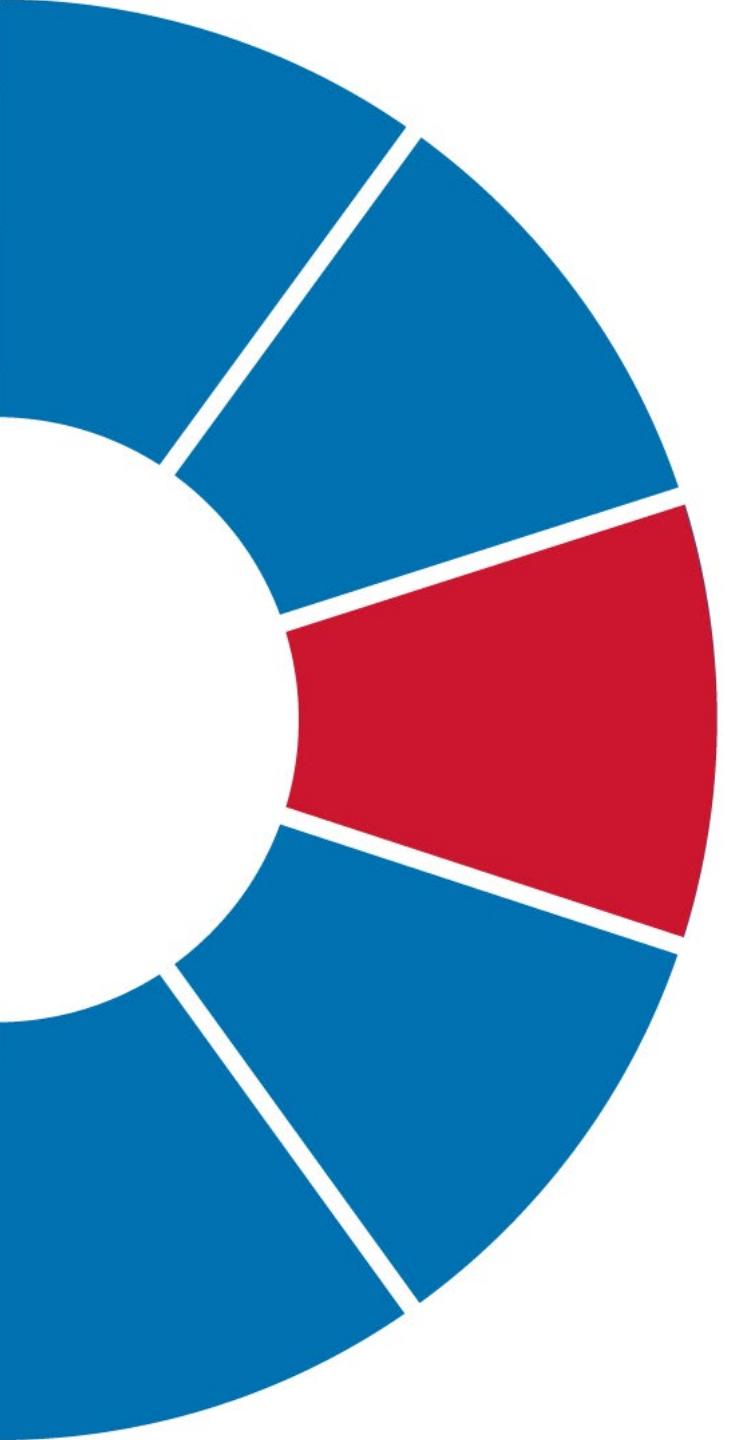
- Multiple CHESS
- Variable delays
- Variable flip angles



# COMPARISON WITH OTHER WATER SUPPRESSION METHODS

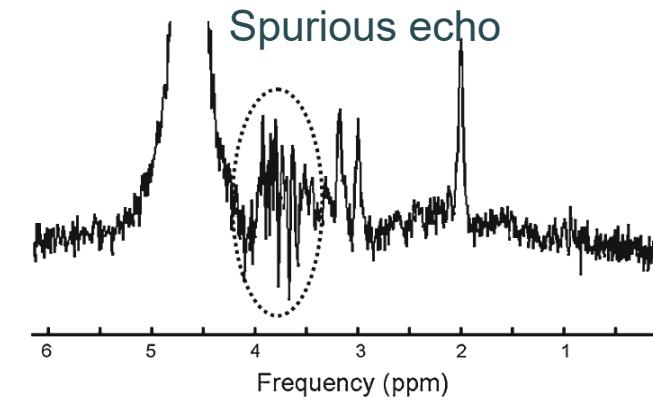
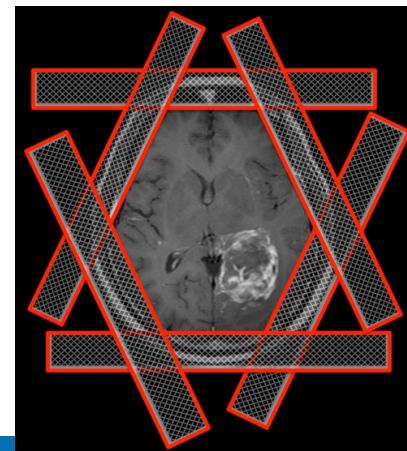
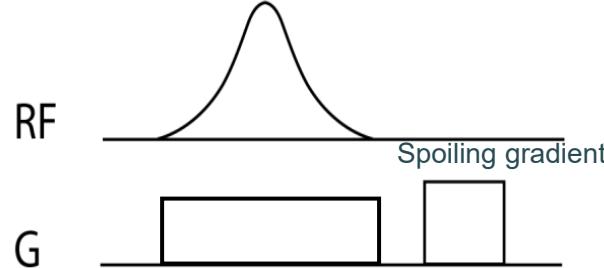
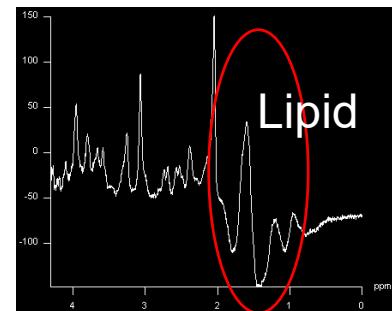
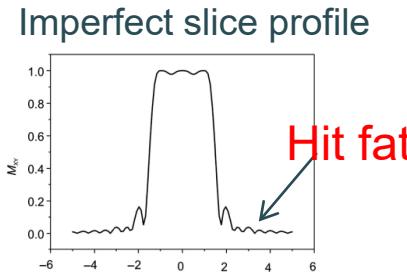
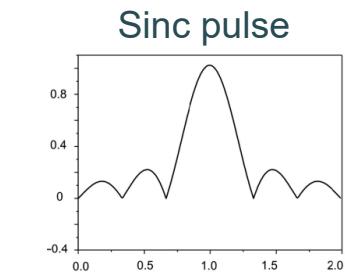


C H

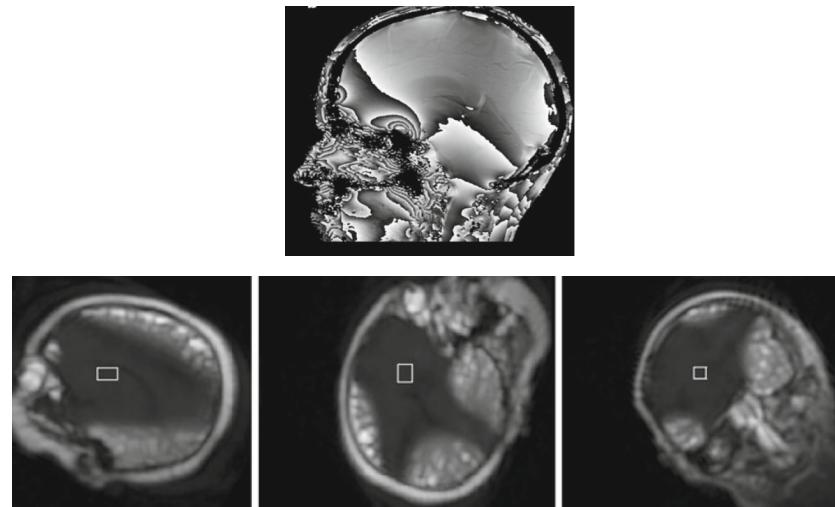


OUTER VOLUME SUPPRESSION

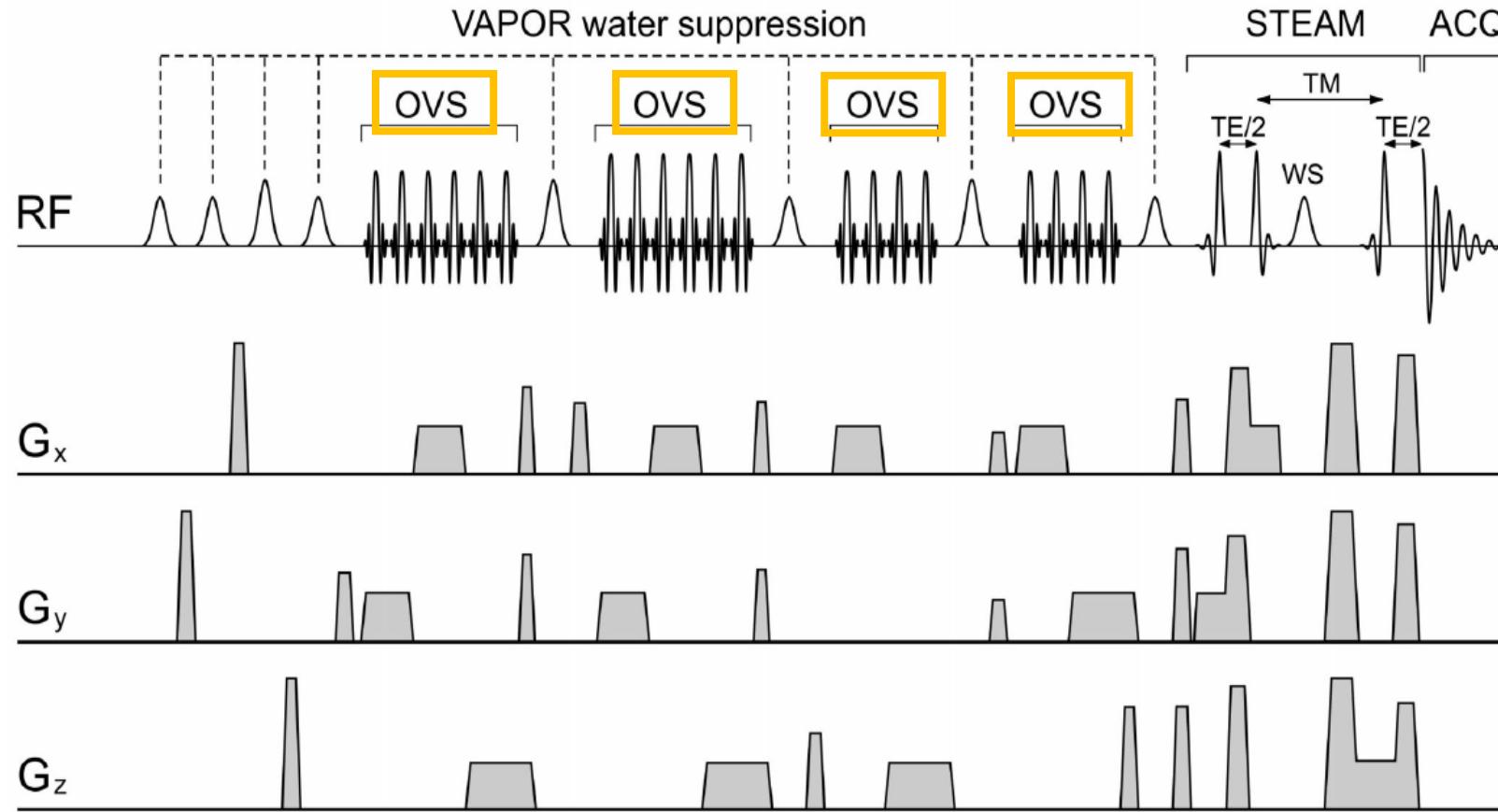
# OUTER VOLUME SUPPRESSION (OVS)



Water from elsewhere

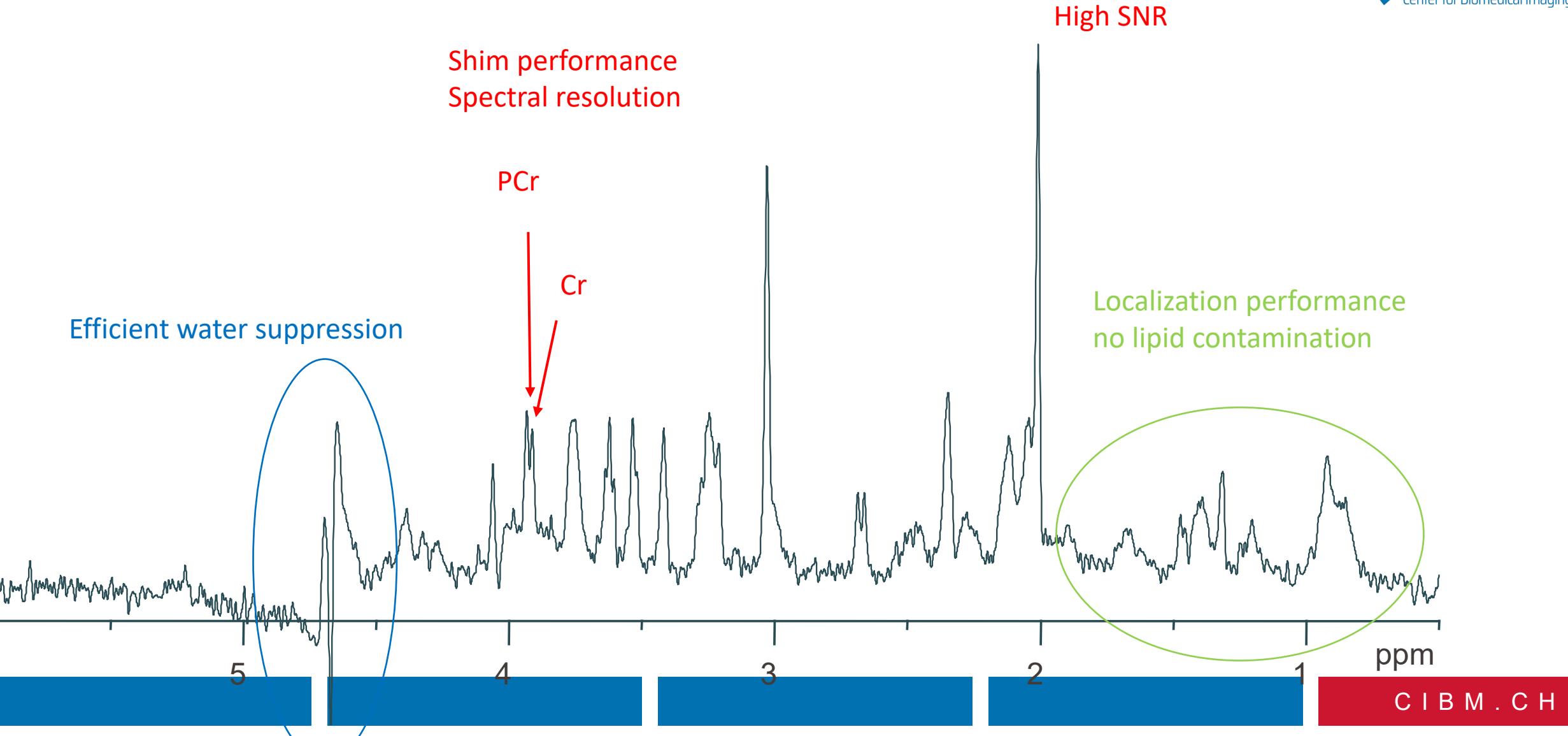


[mriquestions.com](http://mriquestions.com); Carlsson et al., Magn Reson Mater Phys 24, 2011.



Application of several blocks of slice selective pulses saturating regions adjacent to the VOI. For a surface RF coil, variable amplitudes of the saturation pulses are useful.

# FINALLY, MR SPECTRUM QUALITY CONTROL





# THANK YOU FOR YOUR ATTENTION

