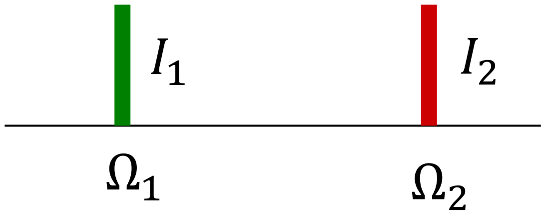
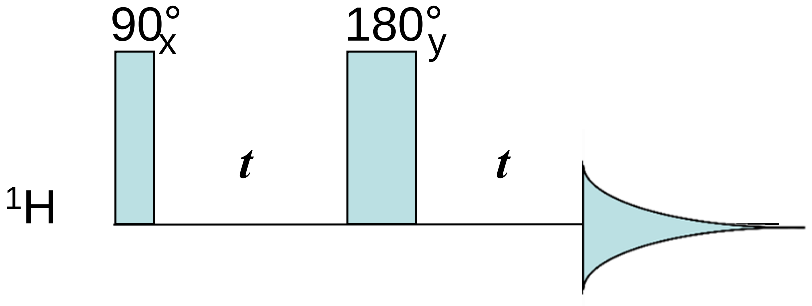
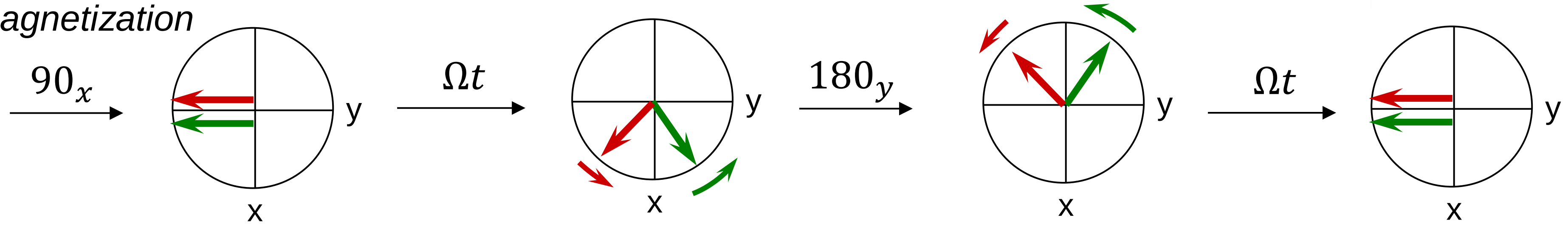
Spin echo

Two hydrogens WITHOUT J interaction





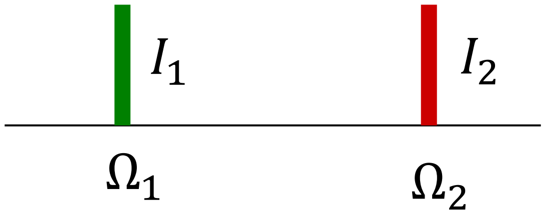
Magnetization

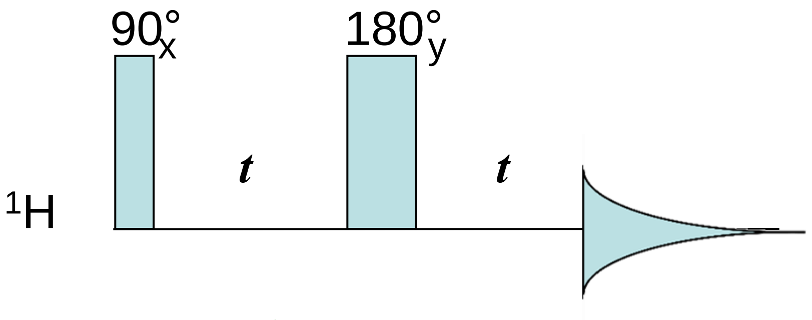


Product operators

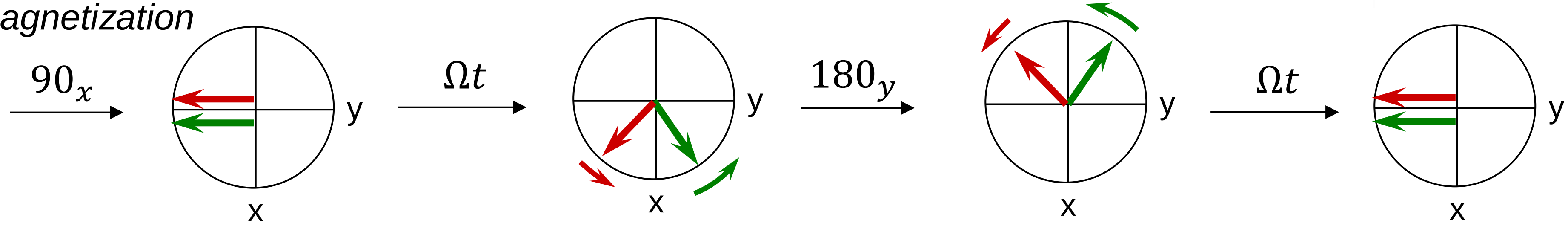
Spin echo

Two hydrogens WITHOUT J interaction





Magnetization



Product operators

$$I_{1z}\xrightarrow{90_x}-I_{1y}\xrightarrow{\Omega_1 t}-I_{1y}\cos\Omega_1 t+I_{1x}\sin\Omega_1 t\xrightarrow{180_y}-I_{1y}\cos\Omega_1 t-I_{1x}\sin\Omega_1 t$$

$$\xrightarrow{\Omega_1 t}-\left(I_{1y}\cos\Omega_1 t-I_{1x}\sin\Omega_1 t\right)\cos\Omega t-\left(I_{1x}\cos\Omega_1 t+I_{1y}\sin\Omega_1 t\right)\sin\Omega_1 t\ =$$

$$=-I_{1y}\left(\cos^2\Omega_1 t+\sin^2\Omega_1 t\right)+$$

$$+I_{1x}(\sin\Omega_1 t\cos\Omega_1 t-\cos\Omega_1 t\sin\Omega_1 t)=$$

$$=-I_{1y}$$

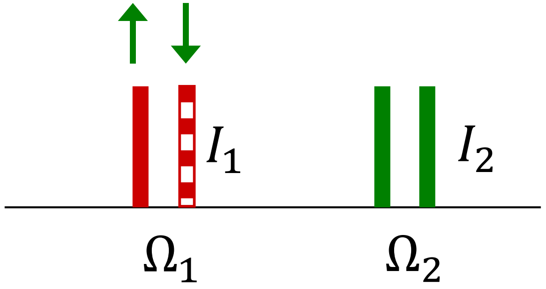
+ same calculation for I_{2z}

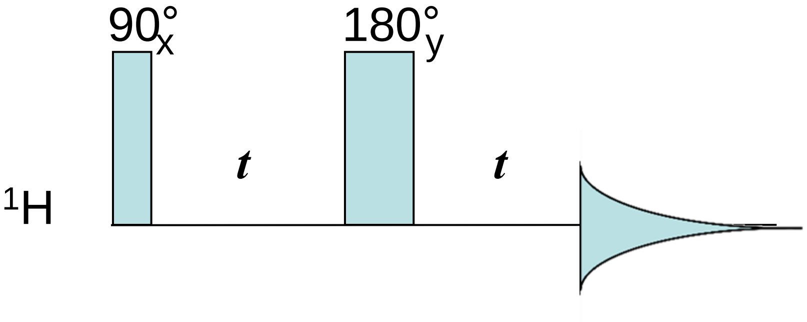
chemical shift is refocused

as well as inhomogeneities of B_0

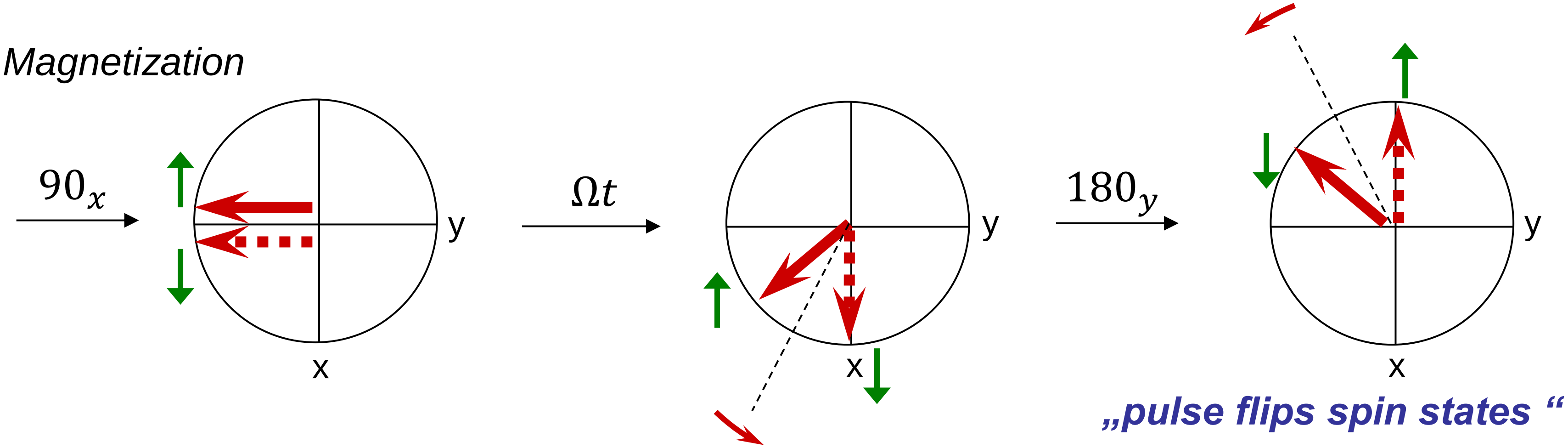
Spin echo

Two hydrogens WITH J interaction

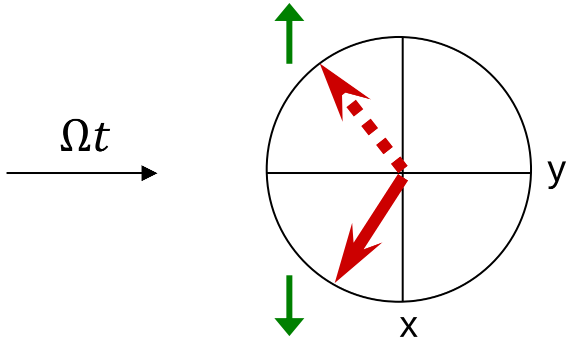




Magnetization



„pulse flips spin states “

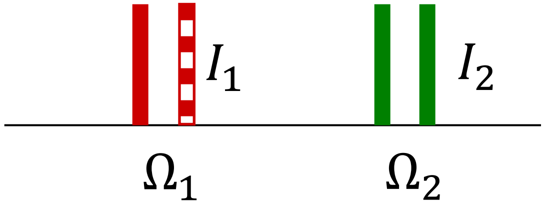


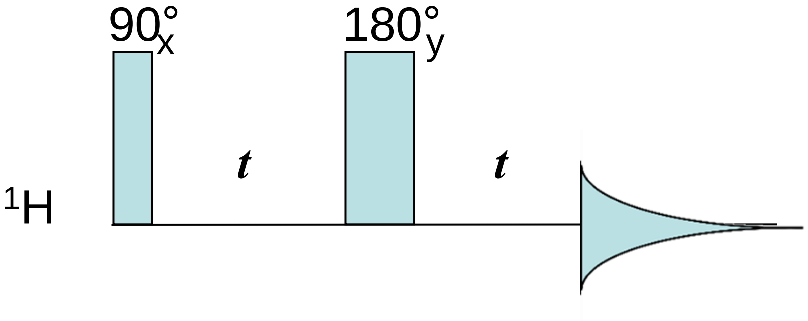
chemical shift is refocused

J coupling remains active

Spin echo

Two hydrogens WITH J interaction

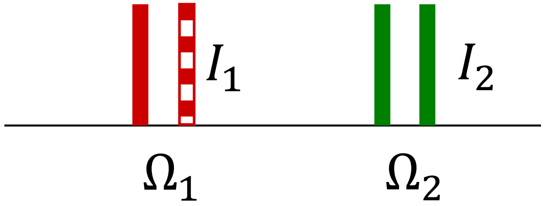


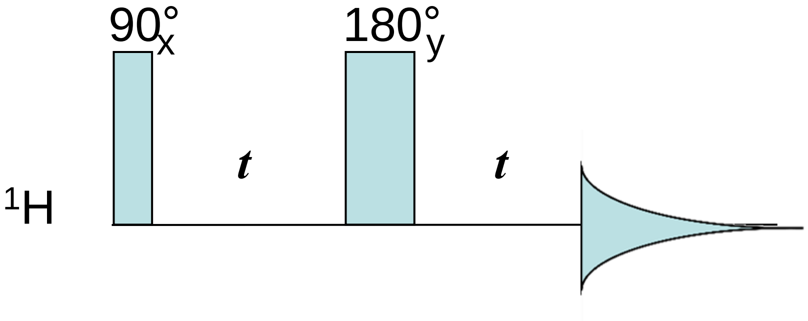


Product operators

Spin echo

Two hydrogens WITH J interaction





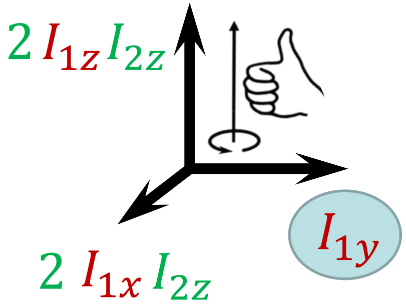
Product operators

$$I_{1z} \xrightarrow{90_x} -I_{1y} \xrightarrow{\Omega_1 t} -I_{1y}\cos\Omega_1 t + I_{1x}\sin\Omega_1 t \xrightarrow{\pi J t}$$

J-interaction Hamiltonian

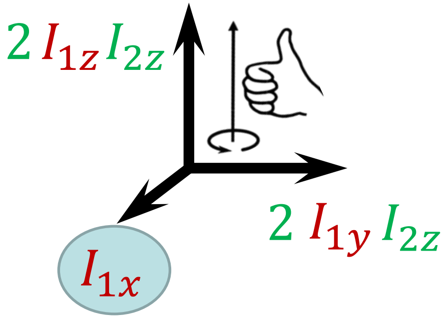
$$H_J = \pi J\, 2I_{1z}I_{2z}$$

$$-I_{1y}\cos\Omega_1 t$$



$$\left(-I_{1y}\cos\pi J t + 2I_{1x}I_{2z}\sin\pi J t\right)\cos\Omega_1 t$$

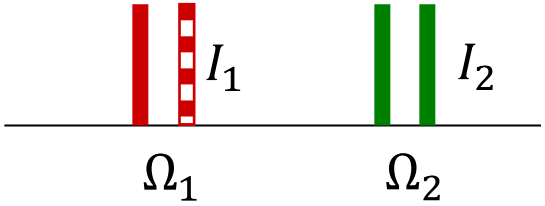
$$I_{1x}\sin\Omega_1 t$$

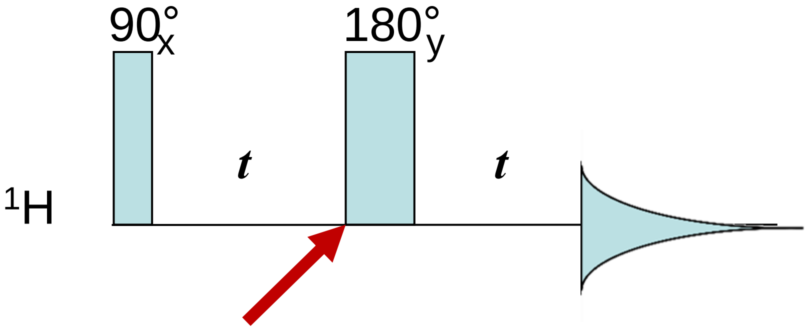


$$\left(I_{1x}\cos\pi J t + 2I_{1y}I_{2z}\sin\pi J t\right)\sin\Omega_1 t$$

Spin echo

Two hydrogens WITH J interaction





$$-I_{1y}\cos\pi Jt\cos\Omega_1 t + 2I_{1x}I_{2z}\sin\pi Jt\cos\Omega_1 t + I_{1x}\cos\pi Jt\sin\Omega_1 t + 2I_{1y}I_{2z}\sin\pi Jt\sin\Omega_1 t$$

$$\xrightarrow{180_y} \quad -I_{1y}\cos\pi Jt\cos\Omega_1 t + 2(-I_{1x})(-I_{2z})\sin\pi Jt\cos\Omega_1 t -$$

$$-I_{1x}\cos\pi Jt\sin\Omega_1 t + 2I_{1y}(-I_{2z})\sin\pi Jt\sin\Omega_1 t$$

$$\xrightarrow{\Omega_1 t} \quad \left(-I_{1y}\cos\Omega_1 t + I_{1x}\sin\Omega_1 t\right)\cos\pi Jt\cos\Omega_1 t \; -\left(I_{1x}\cos\Omega_1 t + I_{1y}\sin\Omega_1 t\right)\cos\pi Jt\sin\Omega_1 t$$

$$+2\left(I_{1x}\cos\Omega_1 t + I_{1y}\sin\Omega_1 t\right)I_{2z}\sin\pi Jt\cos\Omega_1 t \; -2\left(I_{1y}\cos\Omega_1 t - I_{1x}\sin\Omega_1 t\right)I_{2z}\sin\pi Jt\sin\Omega_1 t$$

$$= -I_{1y}\cos\pi Jt\cos^2\Omega_1 t - I_{1y}\cos\pi Jt\sin^2\Omega_1 t \; +2I_{1x}I_{2z}\sin\pi Jt\cos^2\Omega_1 t + 2I_{1x}I_{2z}\sin\pi Jt\sin^2\Omega_1 t$$

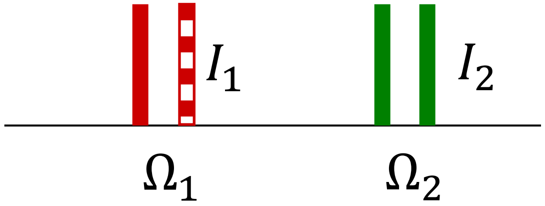
$$= -I_{1y}\cos\pi Jt + 2I_{1x}I_{2z}\sin\pi Jt$$

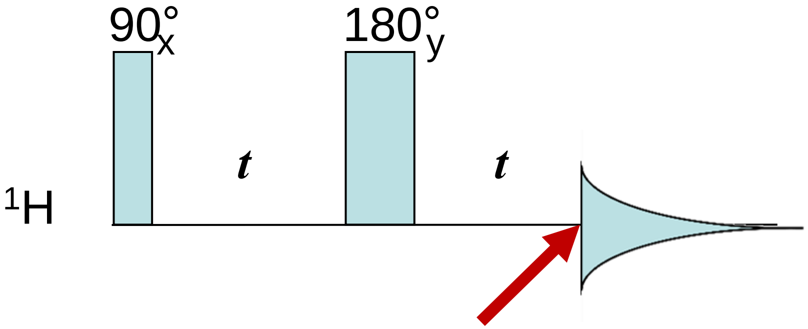
chemical shift is refocused

$$\xrightarrow{\pi Jt}$$

Spin echo

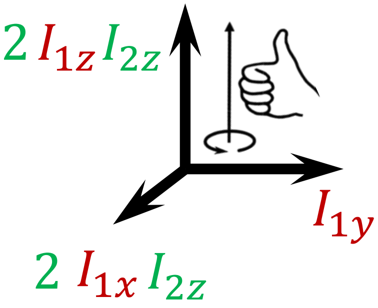
Two hydrogens WITH J interaction





$$-I_{1y}\cos\pi Jt + 2I_{1x}I_{2z}\sin\pi Jt \xrightarrow{\pi Jt} -\left(I_{1y}\cos\pi Jt - 2I_{1x}I_{2z}\sin\pi Jt\right)\cos\pi Jt$$

$$+\left(2I_{1x}I_{2z}\cos\pi Jt + I_{1y}\sin\pi Jt\right)\sin\pi Jt$$



$$= -I_{1y}\left(\cos^2\pi Jt - \sin^2\pi Jt\right) + 2I_{1x}I_{2z}2\cos\pi Jt\sin\pi Jt$$

$$= -I_{1y}\cos 2\pi Jt + 2I_{1x}I_{2z}\sin 2\pi Jt$$

$$= -I_{1y}\cos\pi J2t + 2I_{1x}I_{2z}\sin\pi J2t$$

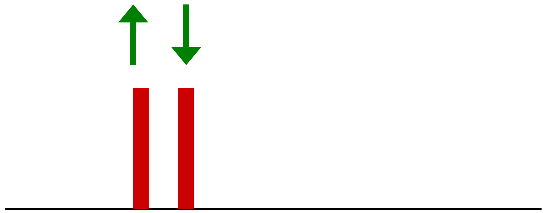
evolution due to J-coupling over time 2t

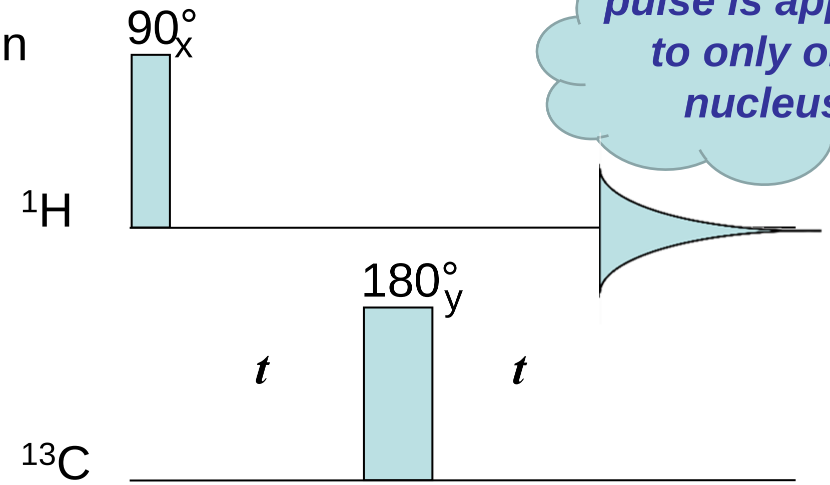
chemical shift is refocused

J coupling remains active

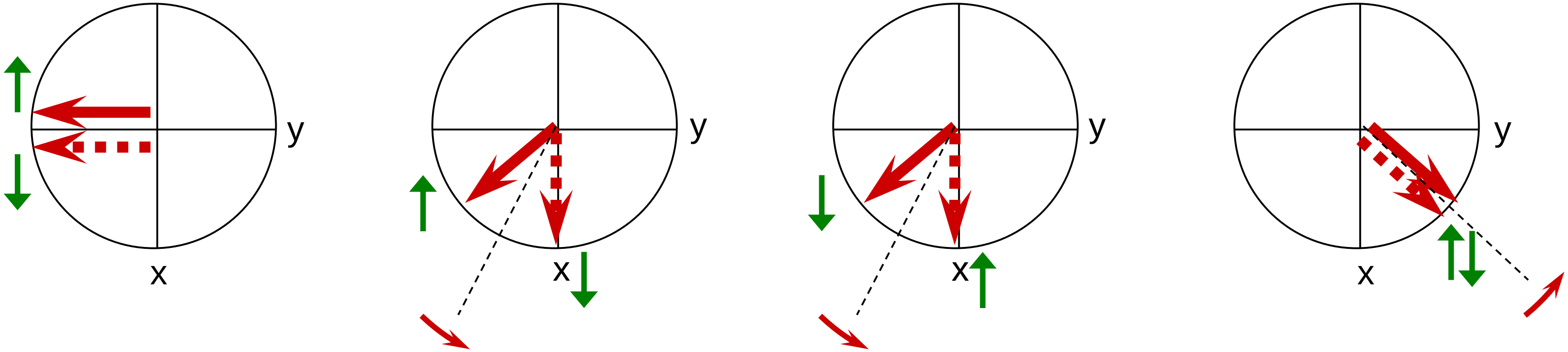
Spin echo

Hydrogen and carbon with J interaction





pulse is applied to only one nucleus



"Pulse flips the spin states of carbon"

Chemical shift remains active

J coupling evolution is refocused

Homework: analysis with Product Operators

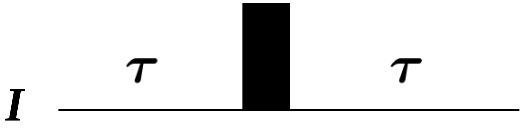
Spin echo

Homonuclear system

I_1, I_2

chemical shift for 2τ

J interaction for 2τ



chemical shift refocused

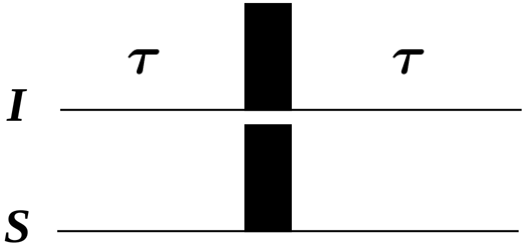
J interaction for 2τ

Heteronuclear system

I, S

chemical shift of S for 2τ, for I it is refocused

J interaction refocused

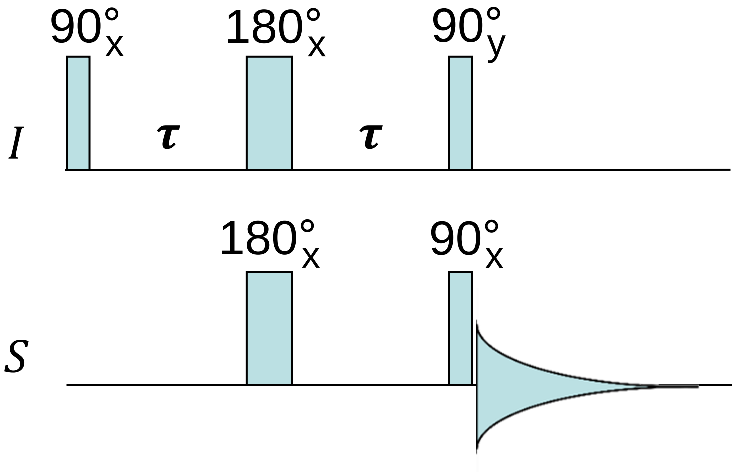


chemical shift refocused

J interaction for 2τ

INEPT

Insensitive Nuclei Enhanced by Polarization Transfer



$$\tau = \frac{1}{4J}$$

Two spins with J-coupling

$$\rho_{eq} = \beta_I I_z + \beta_S S_z$$

$$\beta_I = \frac{\gamma_I B_0}{k_B T} \qquad \beta_S = \frac{\gamma_S B_0}{k_B T}$$

^1H $\beta_I \approx 4$

^{13}C $\beta_S \approx 1$

Spin echo

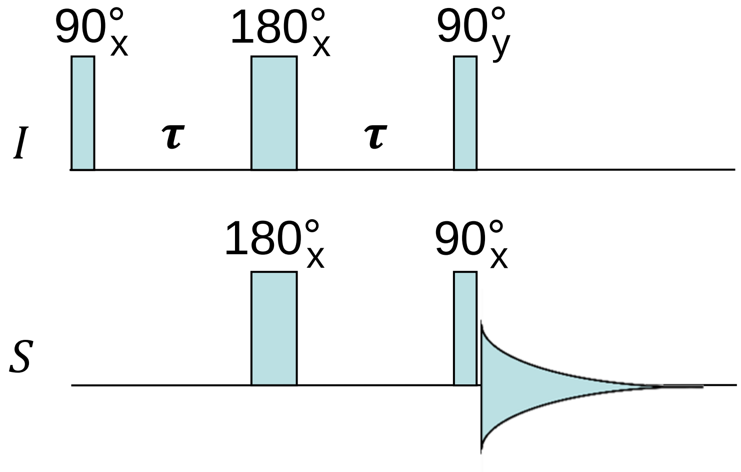
$$\xrightarrow{\Omega_I\tau} \quad \xrightarrow{\Omega_S\tau} \quad \xrightarrow{\pi J\tau} \quad \xrightarrow{180_x} \quad \xrightarrow{\Omega_I\tau} \quad \xrightarrow{\Omega_S\tau} \quad \xrightarrow{\pi J\tau}$$

Simplification for analysis $\xrightarrow{180_x} \quad \xrightarrow{\pi J 2\tau}$

$$\pi J 2\tau = \pi J 2\frac{1}{4J} = \frac{\pi}{2}$$

INEPT

Insensitive Nuclei Enhanced by Polarization Transfer



$$\tau = \frac{1}{4J}$$

Two spins with J-coupling

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$$\beta_I = \frac{\gamma_I B_0}{k_B T} \qquad \beta_S = \frac{\gamma_S B_0}{k_B T}$$

^{1}H $\beta_I \approx 4$ $\qquad$ ^{13}C $\beta_S \approx 1$

Spin echo

$$\xrightarrow{\Omega_I\tau}\quad\xrightarrow{\Omega_S\tau}\quad\xrightarrow{\pi J\tau}\quad\xrightarrow{180_x}\quad\xrightarrow{\Omega_I\tau}\quad\xrightarrow{\Omega_S\tau}\quad\xrightarrow{\pi J\tau}$$

Simplification for analysis $\xrightarrow{180_x}\quad\xrightarrow{\pi J 2\tau}$

$$\pi J 2\tau = \pi J 2\frac{1}{4J} = \frac{\pi}{2}$$

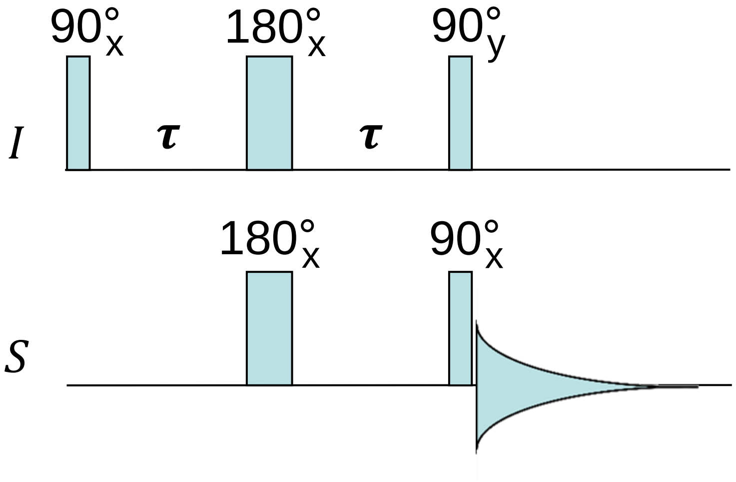
$$I_z \xrightarrow{I:90_x} -I_y \xrightarrow{I:180_x} I_y \xrightarrow{\pi J 2\tau} I_y \cos\pi J 2\tau - 2I_xS_z \sin\pi J 2\tau = -2I_xS_z$$

$$\xrightarrow{I:90_y} 2I_zS_z \xrightarrow{S:90_x} -2I_zS_y$$

1H polarization transferred to coherence of 13C

INEPT

Insensitive Nuclei Enhanced by Polarization Transfer



$$\tau = \frac{1}{4J}$$

Two spins with J-coupling

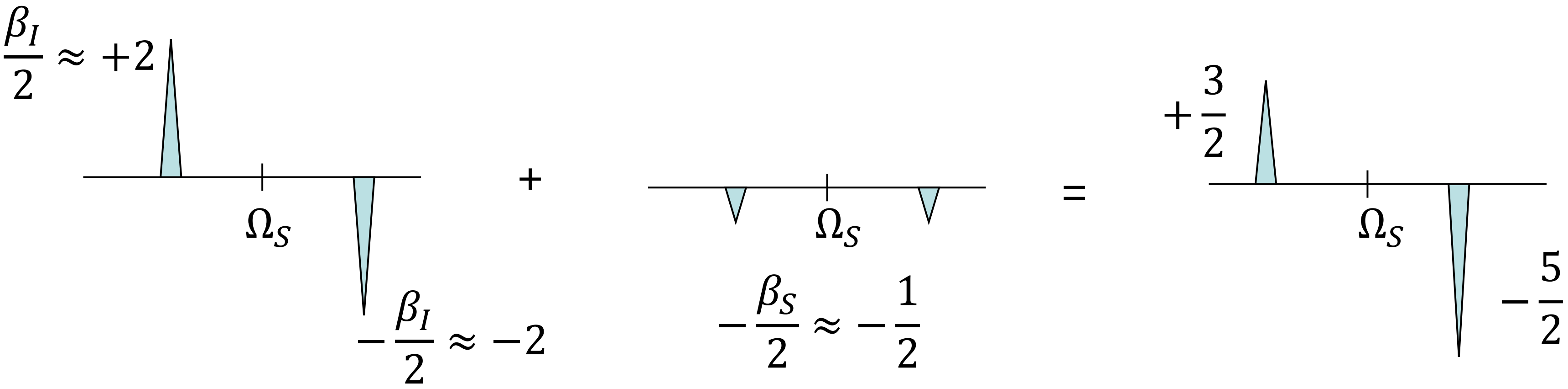
$$\boldsymbol{\rho_{eq} = \beta_I I_z + \beta_S S_z}$$

$$\beta_I = \frac{\gamma_I B_0}{k_B T} \qquad \beta_S = \frac{\gamma_S B_0}{k_B T}$$

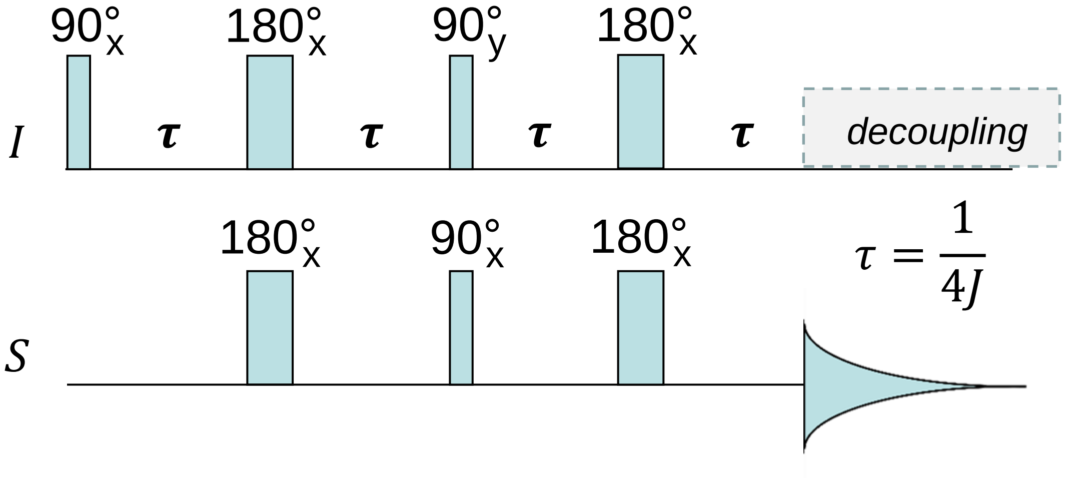
^{1}H $\quad \beta_I \approx 4$ $\qquad$ ^{13}C $\quad \beta_S \approx 1$

$$I_z \longrightarrow -2I_zS_y$$

$$S_z \xrightarrow{S:180_x} -S_z \xrightarrow{\pi J 2\tau} -S_z \xrightarrow{S:90_x} S_y$$



Refocused INEPT



$$\tau = \frac{1}{4J}$$

Two spins with J-coupling

$$\boldsymbol{\rho_{eq} = \beta_I I_z + \beta_S S_z}$$

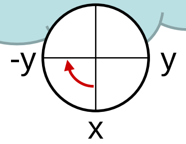
$$\boldsymbol{\beta_I = \frac{\gamma_I B_0}{k_B T}} \qquad \boldsymbol{\beta_S = \frac{\gamma_S B_0}{k_B T}}$$

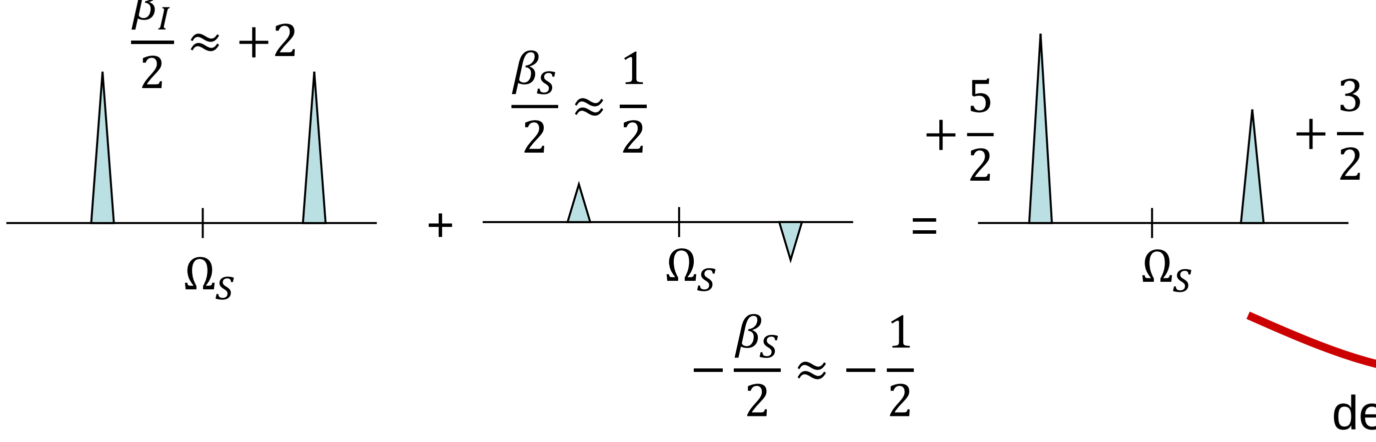
^{1}H $\boldsymbol{\beta_I \approx 4}$

^{13}C $\boldsymbol{\beta_S \approx 1}$

$$\begin{array}{ccccccccc} I_z & \longrightarrow & -2I_zS_y & \xrightarrow[S:180_x]{I:180_x} & -2I_zS_y & \xrightarrow{\pi J 2\tau} & S_x & \longrightarrow & -S_y \\ S_z & \longrightarrow & S_y & & -S_y & & 2I_zS_x & & -2I_zS_y \end{array}$$

phase correction
-90°



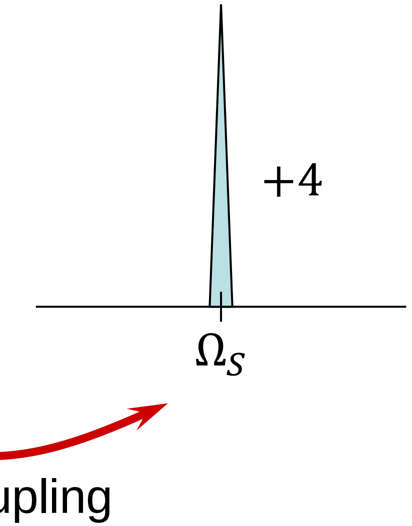


$\frac{\beta_I}{2} \approx +2$

$\frac{\beta_S}{2} \approx \frac{1}{2}$

$-\frac{\beta_S}{2} \approx -\frac{1}{2}$

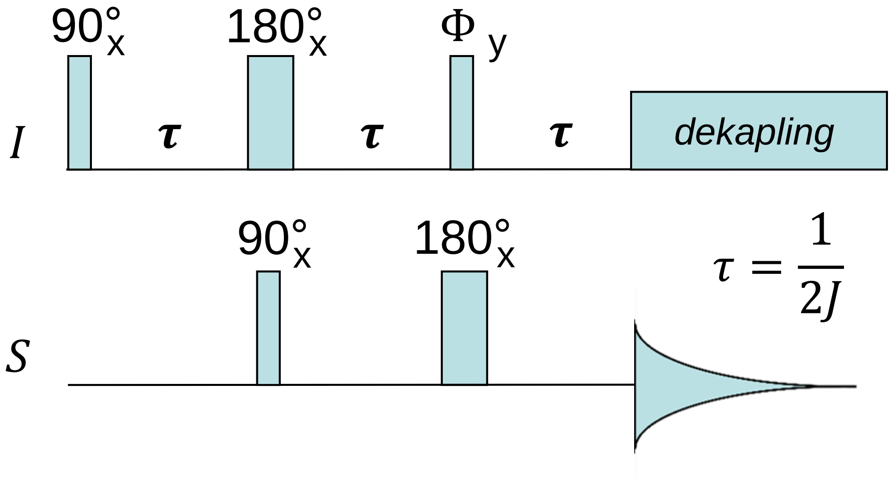
$+\frac{5}{2}$ $+\frac{3}{2}$



$+4$

DEPT

Distorsionless Enhancement by Polarization Transfer



$$\tau = \frac{1}{2J}$$

$\mathbf{\Phi}$	CH	CH_2	CH_3
45°	positive	positive	positive
90°	positive	none	none
135°	positive	negative	positive

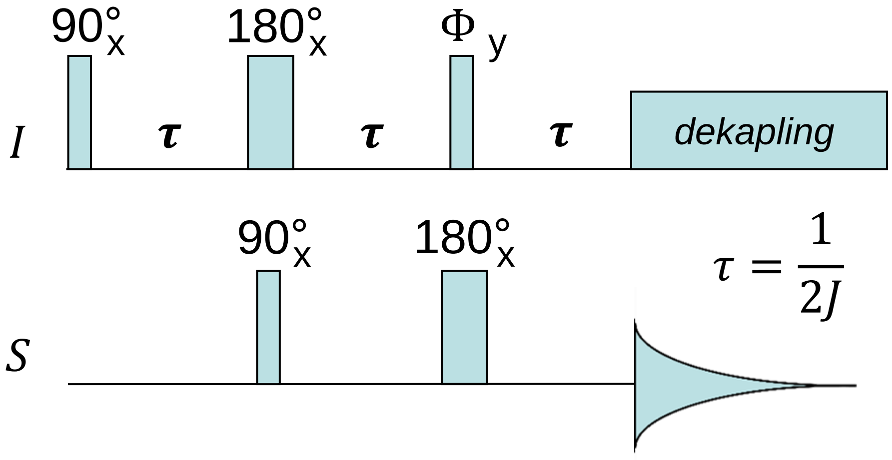
<u>Two spins with J-coupling, $\Phi = 90^\circ$</u>

$$\boldsymbol{\rho_{eq}} = \boldsymbol{\beta_I I_z} + \boldsymbol{\beta_S S_z}$$

$$\pi J \tau = \pi J \frac{1}{2J} = \frac{\pi}{2}$$

DEPT

Distorsionless Enhancement by Polarization Transfer



$$\tau = \frac{1}{2J}$$

Φ	CH	CH_2	CH_3
45°	positive	positive	positive
90°	positive	none	none
135°	positive	negative	positive

Two spins with J-coupling, $\Phi = 90^\circ$

$$\boldsymbol{\rho_{eq} = \beta_I I_z + \beta_S S_z}$$

$$\pi J\tau = \pi J\frac{1}{2J} = \frac{\pi}{2}$$

$$I_z \xrightarrow{I:90_x} -I_y \xrightarrow{\pi J\tau} 2I_xS_z \xrightarrow[S:90_x]{I:180_x} -2I_xS_y \xrightarrow{\pi J\tau} -2I_xS_y \xrightarrow[S:180_x]{} 2I_xS_y$$

$$\xrightarrow{I:90_y} -2I_zS_y \xrightarrow{\pi J\tau} S_x$$

Polarization transfer from 1H to 13C

in-phase doublet $\xrightarrow{\text{decoupling}}$ ***singlet***

$$S_z \xrightarrow[S:90_x]{} -S_y \xrightarrow{\pi J\tau} 2I_zS_x \xrightarrow[S:180_x]{I:90_y} 2I_xS_x \xrightarrow{\pi J\tau} 2I_xS_x$$ ***no signalu***

Polarization transfer and inverse detection

Signal intensity proportional to the difference of populations of energy levels $\beta_I = \frac{\gamma_I B_0}{k_B T}$

How to increase the signal:noise ratio?

$$\mathrm{S/N} \propto n\ \gamma_{exc} \sqrt{\gamma_{det}^3 B_0^3}\ \sqrt{\mathrm{NS}}\ \left(1 - e^{t/T_1}\right)$$

More sample

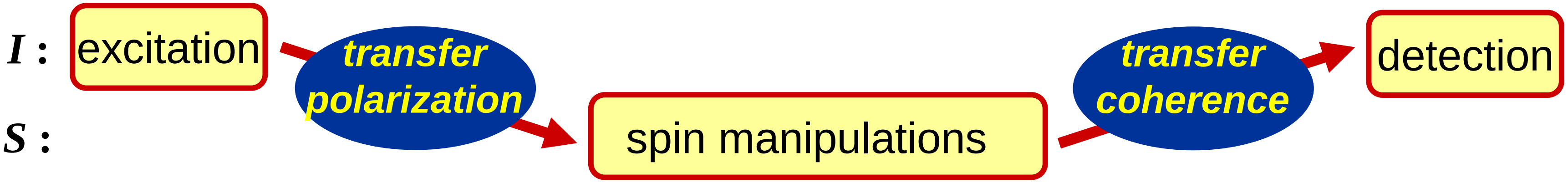
Higher magnetic field

coherent averaging (repeated measurements)

Direct detection

S **:** excitation → spin manipulations → detection

Inverse detection



I **:** excitation → ***transfer polarization*** → spin manipulations → ***transfer coherence*** → detection

S **:**

	Relative sensitivity	***Reduction of experiment time to achieve the same S/N***
^{1}H / ^{13}C	32×	1 024×
^{1}H / ^{15}N	292×	85 264×

+ Relaxation advantage