

# Lecture #12

## POF practice: Polarization Transfer

- Topics
  - POF practice
  - INEPT, INEPT-R,
  - pulsed field gradients
- References
  - van de Ven, sections 3.6, 4.8, pages 119-127, 211-223

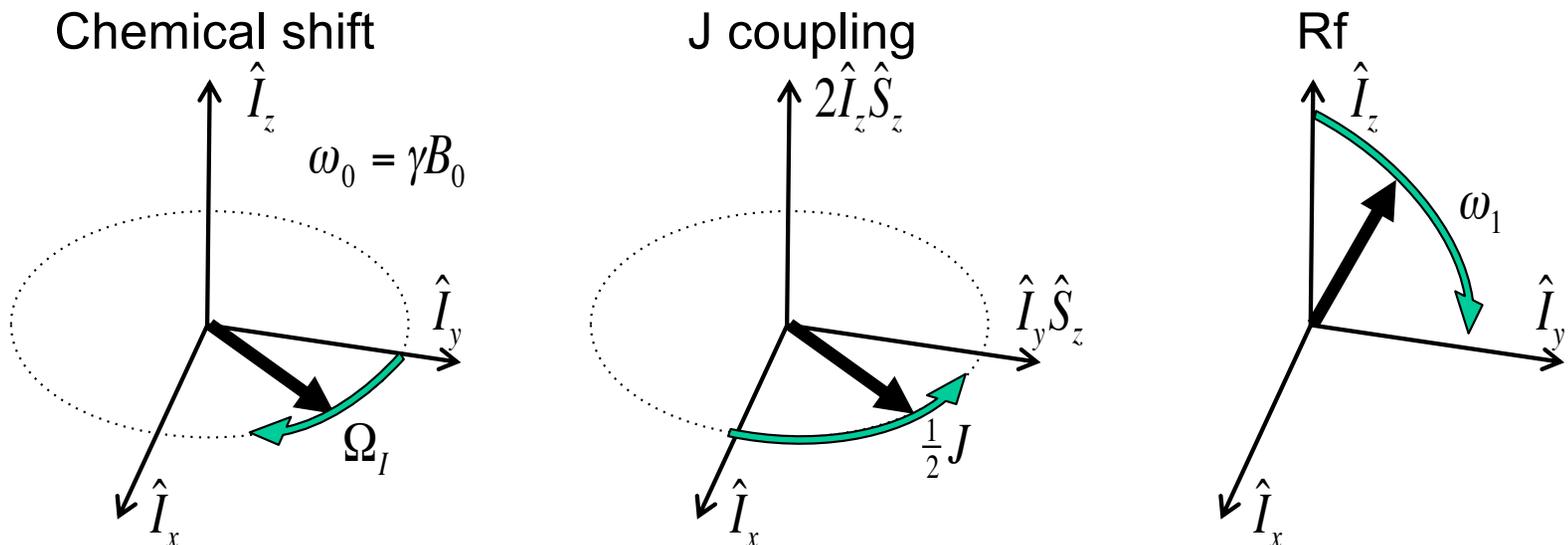
# Branch Diagrams

- The branch diagram equation for product operators is

$$\hat{C}_p \xrightarrow{\hat{C}_q(\theta)} \begin{cases} \hat{C}_p & \leftarrow \text{“cosine” branch} \\ -i[\hat{C}_q, \hat{C}_p] & \leftarrow \text{“sine” branch} \end{cases}$$

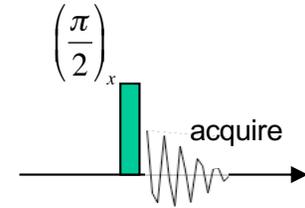
where  $\hat{C}_p$  and  $\hat{C}_q$  are any pair of product operator coherences.

- Use commutator tables or just remember these sign conventions:



# Polarization Transfer

- The SNR for a simple pulse and acquire sequence:



$${}^1\text{H}: \text{SNR}_H = N \underbrace{\frac{\hbar\gamma_H}{2}}_{\substack{\text{Magnetic} \\ \text{moment}}} \underbrace{\left(\frac{\hbar\gamma_H B_0}{2kT}\right)}_{\text{Polarization}}$$

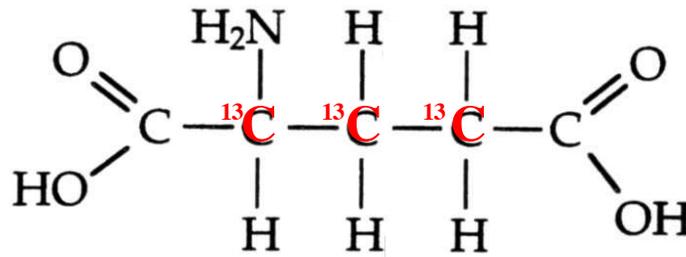
# of spins

$${}^{13}\text{C}: \text{SNR}_C = N \frac{\hbar\gamma_C}{2} \left(\frac{\hbar\gamma_C B_0}{2kT}\right)$$

Given  $\gamma_H \approx 4\gamma_C \longrightarrow \text{SNR}_H \approx 16 \text{SNR}_C$

- Often desirable to enhance the SNR of the  ${}^{13}\text{C}$  signal by exploiting the higher  ${}^1\text{H}$  polarization.

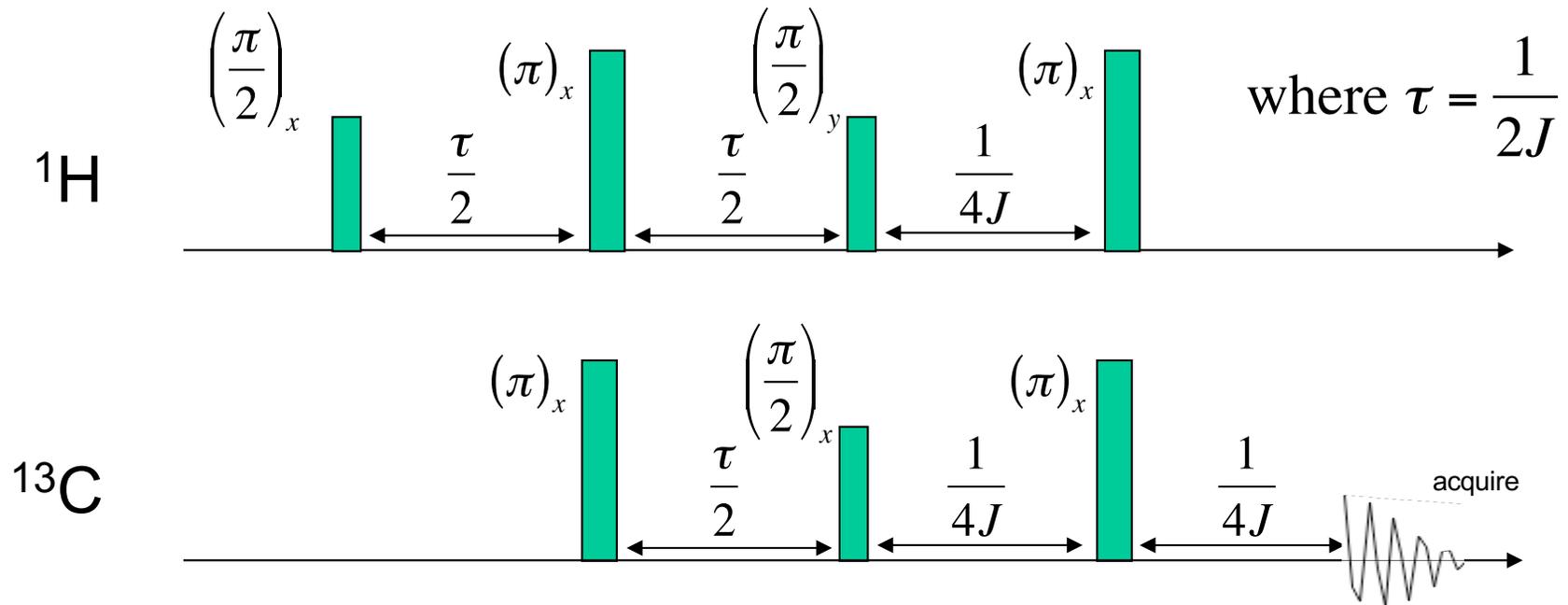
Example:  ${}^{13}\text{C}$ -glutamate



Note: Glutamate is the brain's primary excitatory neurotransmitter.

# INEPT

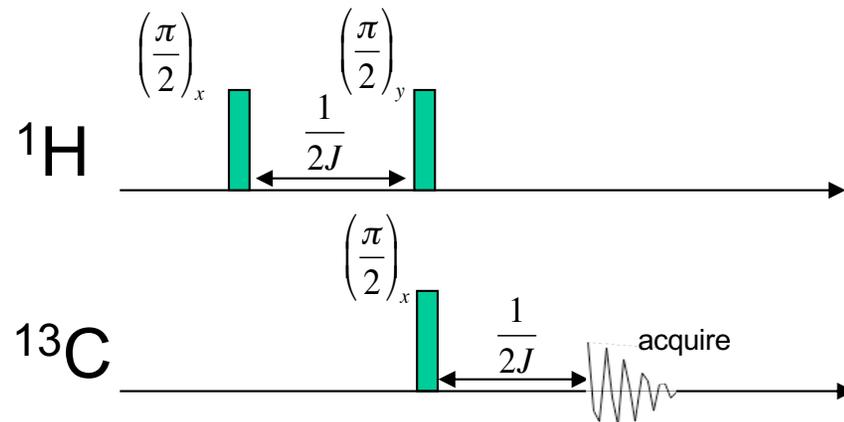
- Insensitive Nuclei Enhanced by Polarization Transfer



- Gradient-enhanced INEPT



# Consider a simple sequence...



- For now, let's assume that the chemical shift evolution during  $1/2J$  is negligible, and the  $^1\text{H}$  and  $^{13}\text{C}$  spins are weakly J-coupled.
- Letting  $I = ^1\text{H}$  and  $S = ^{13}\text{C}$ , then the initial density operator is:

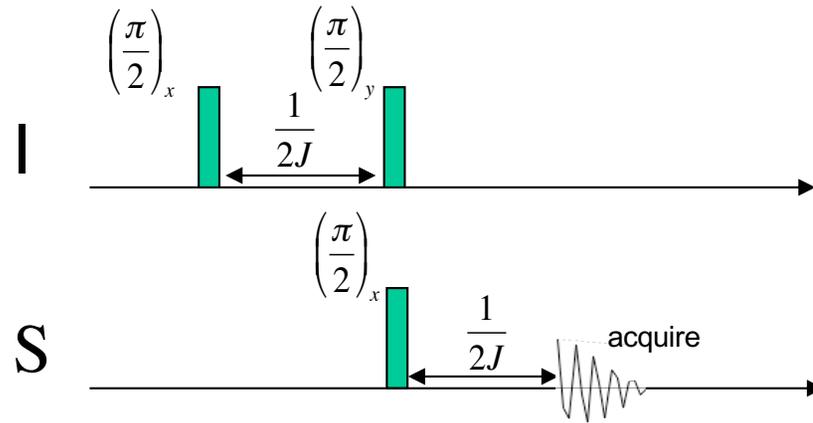
$$\hat{\sigma}(0) = \frac{\hbar B_0}{4kT} (\gamma_I \hat{I}_z + \gamma_S \hat{S}_z)$$

- The Hamiltonian during free precession is:

During  $1/2J$  intervals:  $\hat{H}_{\text{free}} \approx 2\pi J \hat{I}_z \hat{S}_z$       During acquisition:  $\hat{H}_{\text{free}} = -\Omega_I \hat{I}_z - \Omega_S \hat{S}_z + 2\pi J \hat{I}_z \hat{S}_z$

- We now wish to compute the branch diagram.

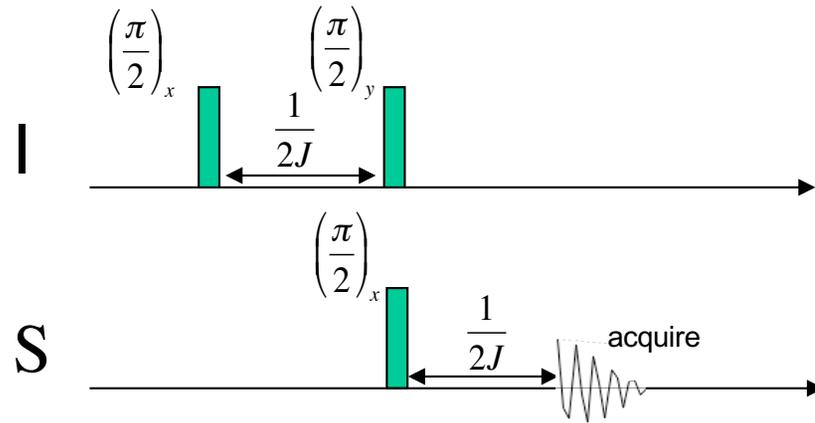
# Branch Diagram



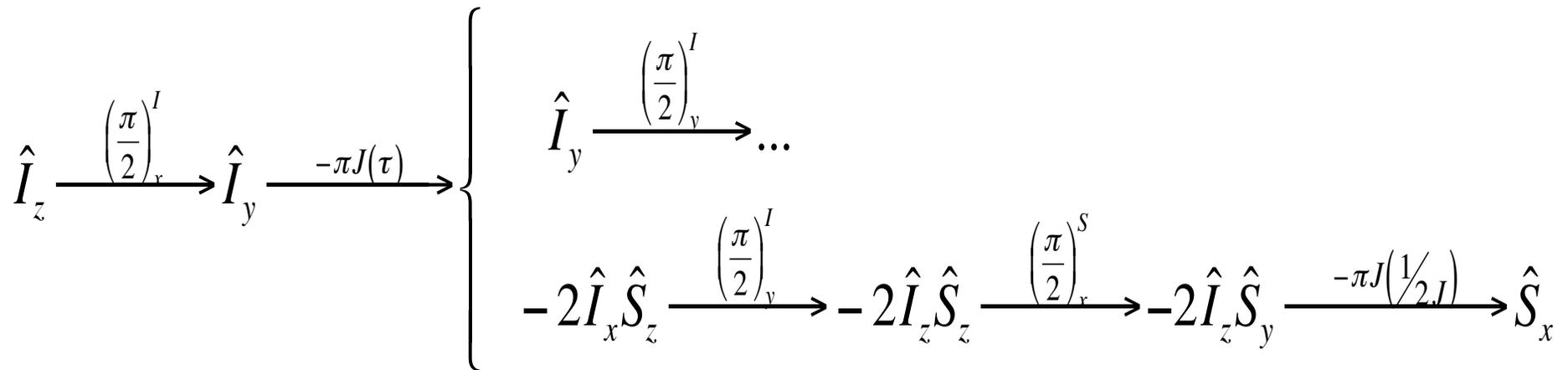
- Starting with the I spin...

Fill in branch diagram

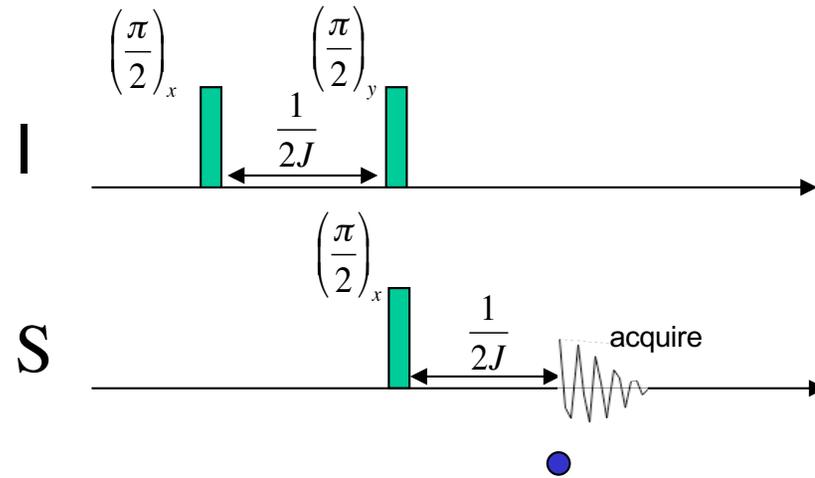
# Branch Diagram



- Starting with the I spin...



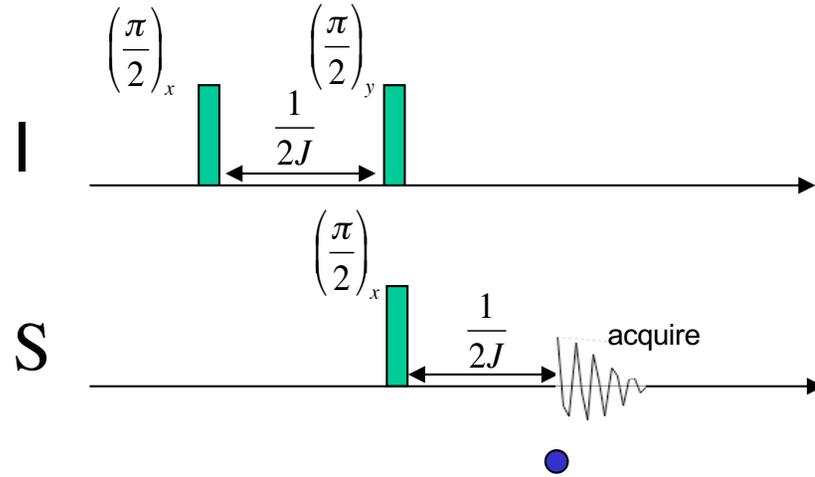
# Branch Diagram



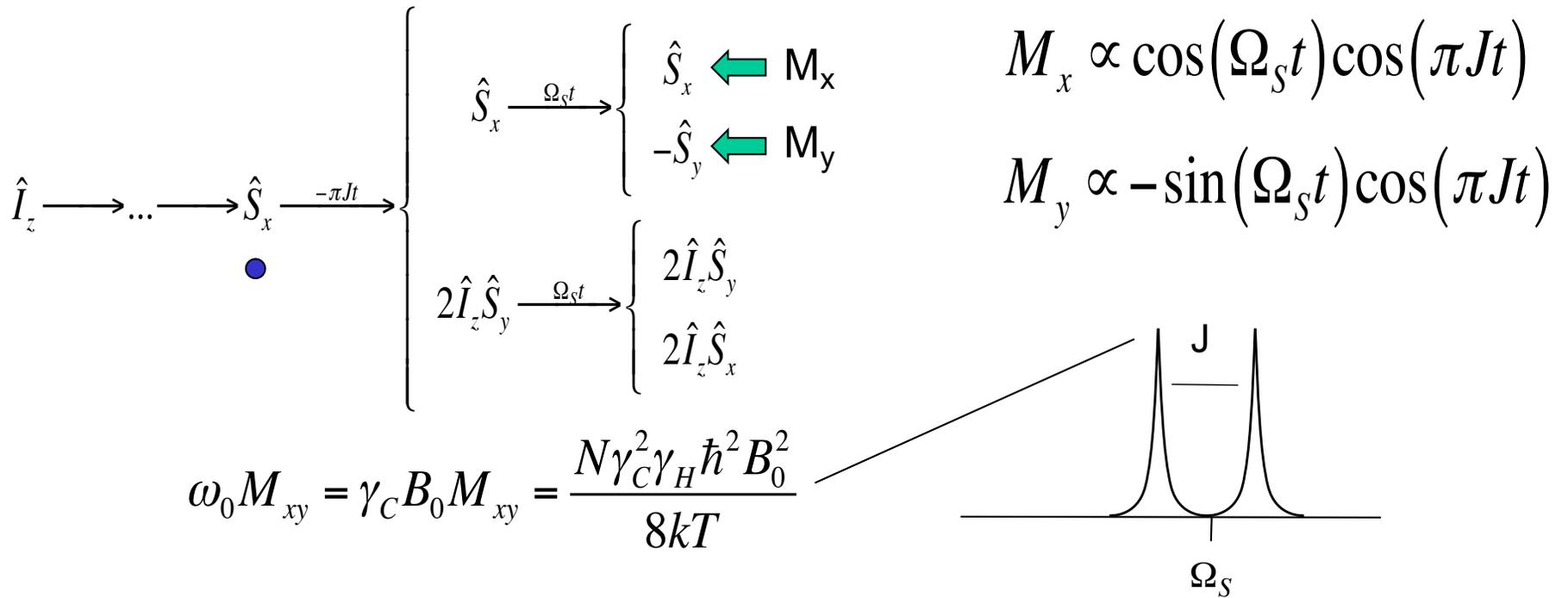
- During acquisition...

Fill in branch  
diagram

# Branch Diagram

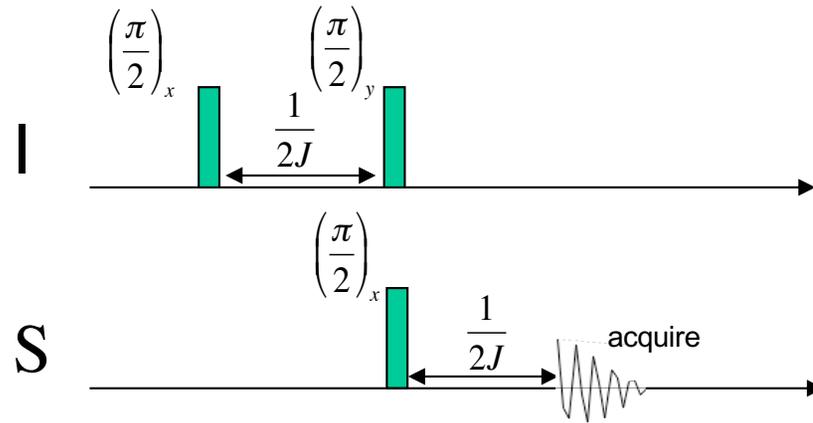


- During acquisition...



This yields a factor of  $\gamma_H/\gamma_C \approx 4$  SNR gain over direct  $^{13}\text{C}$  detection.

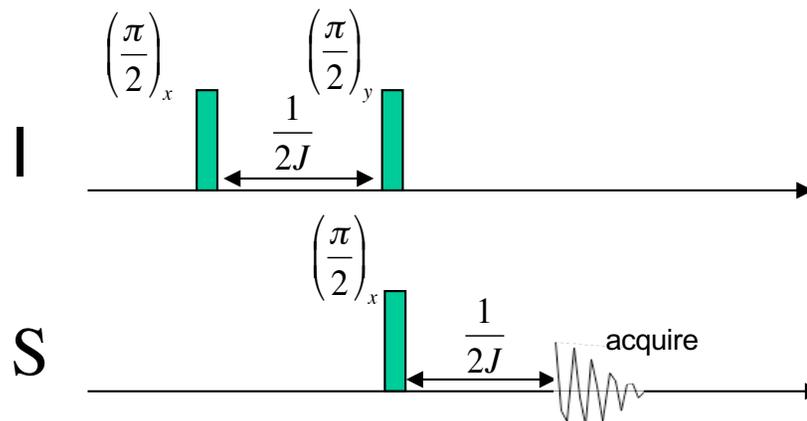
# Branch Diagram



- What about the S spin?

Fill in branch  
diagram

# Branch Diagram



- What about the S spin?

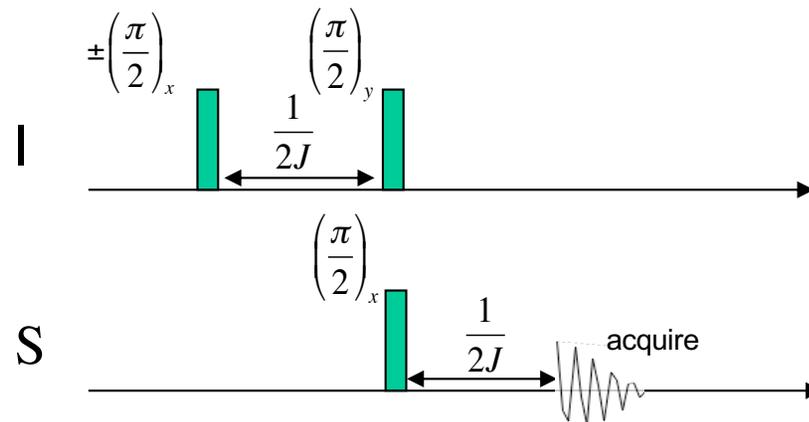
$$\hat{S}_z \xrightarrow{\left(\frac{\pi}{2}\right)_x} \hat{S}_y \xrightarrow{-\pi J t} -2\hat{I}_z \hat{S}_x \xrightarrow{-\pi J t} \left\{ \begin{array}{l} -2\hat{I}_z \hat{S}_x \xrightarrow{\Omega_S t} \left\{ \begin{array}{l} -2\hat{I}_z \hat{S}_x \\ 2\hat{I}_z \hat{S}_y \end{array} \right. \begin{array}{l} M_y \propto -\cos(\Omega_S t) \sin(\pi J t) \\ M_x \propto \sin(\Omega_S t) \sin(\pi J t) \end{array} \\ -\hat{S}_y \xrightarrow{\Omega_S t} \left\{ \begin{array}{l} -\hat{S}_y \\ \hat{S}_x \end{array} \right. \begin{array}{l} \leftarrow M_y \\ \leftarrow M_x \end{array} \end{array} \right.$$

$$\omega_0 M_{xy} = \gamma_C B_0 M_{xy} = \frac{N \gamma_C^2 \gamma_C \hbar^2 B_0^2}{8kT}$$

- We usually want to get rid of this “antiphase” doublet as well as any uncoupled  $^{13}\text{C}$  spins.

# Phase cycling

- Unwanted coherences can be eliminated by making multiple acquisitions while cycling the phase of the Rf pulses.
- For example,  $Rf1 = \pm 90_x$

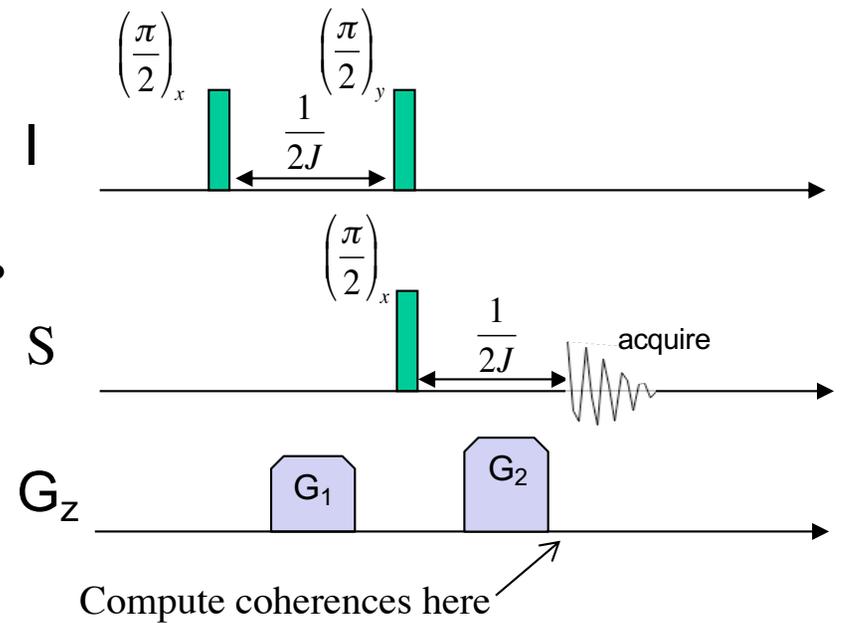


# Alternatively, let's add gradients...

- Free precession Hamiltonian

$$\hat{H}_{\text{free}} = -\Omega_I \hat{I}_z - \Omega_S \hat{S}_z + 2\pi J \hat{I}_z \hat{S}_z - \gamma_I G_z z \hat{I}_z - \gamma_S G_z z \hat{S}_z$$

- Find areas  $G_1$  and  $G_2$



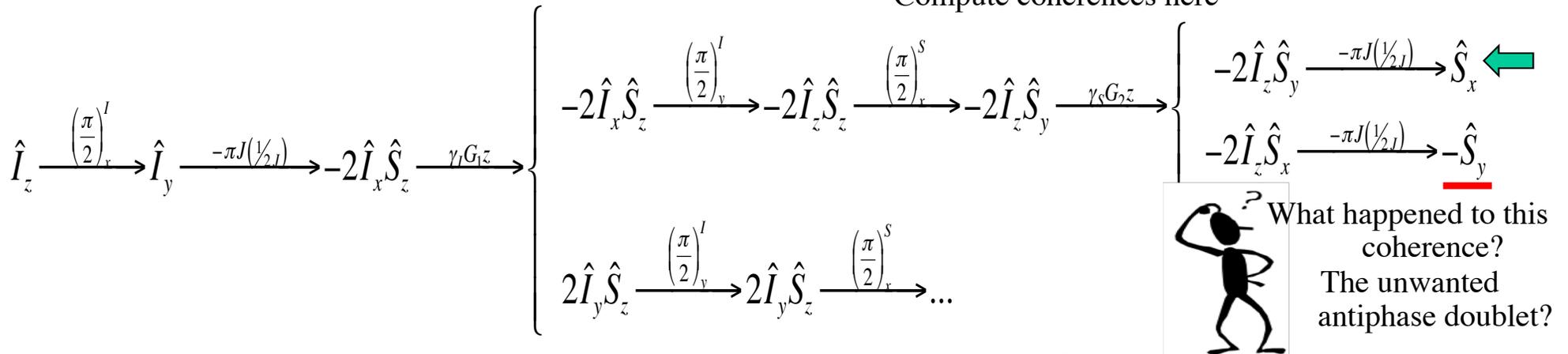
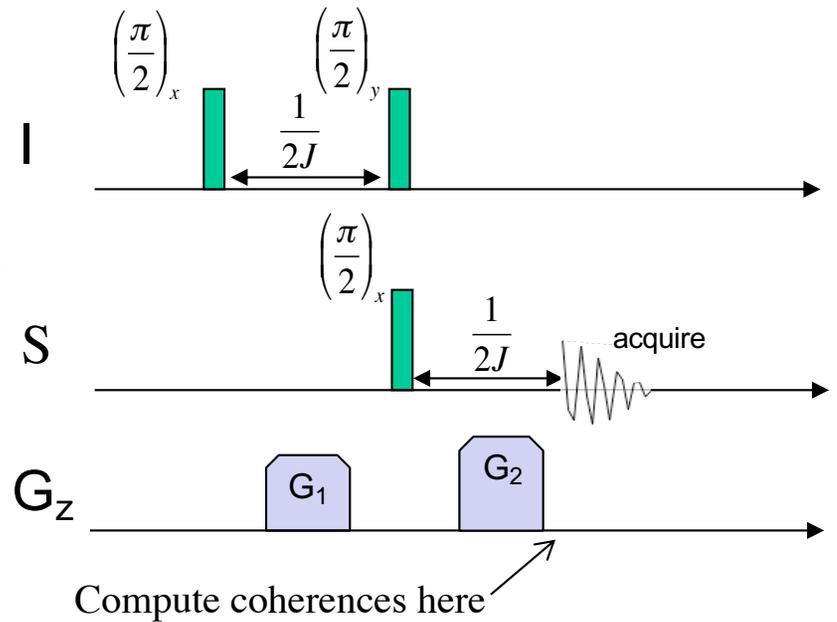
Fill in branch diagram

# Alternatively, let's add gradients...

- Free precession Hamiltonian

$$\hat{H}_{\text{free}} = -\Omega_I \hat{I}_z - \Omega_S \hat{S}_z + 2\pi J \hat{I}_z \hat{S}_z - \gamma_I G_z z \hat{I}_z - \gamma_S G_z z \hat{S}_z$$

- Find areas  $G_1$  and  $G_2$



$$\rightarrow M_x \propto \cos(\gamma_C G_2 z) \cos(\gamma_H G_1 z) \implies M_{xy}(t) \propto e^{-i\Omega_S t} \cos(\pi J t) \int_z \cos(\gamma_C G_2 z) \cos(\gamma_H G_1 z) dz$$

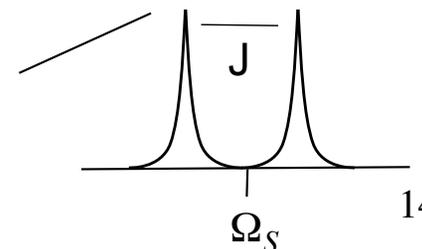
acquired signal Integration due to RF coil

- Letting  $G_2 = \frac{\gamma_H}{\gamma_C} G_1 \approx 4G_1$ , yields a received signal during acquisition of:

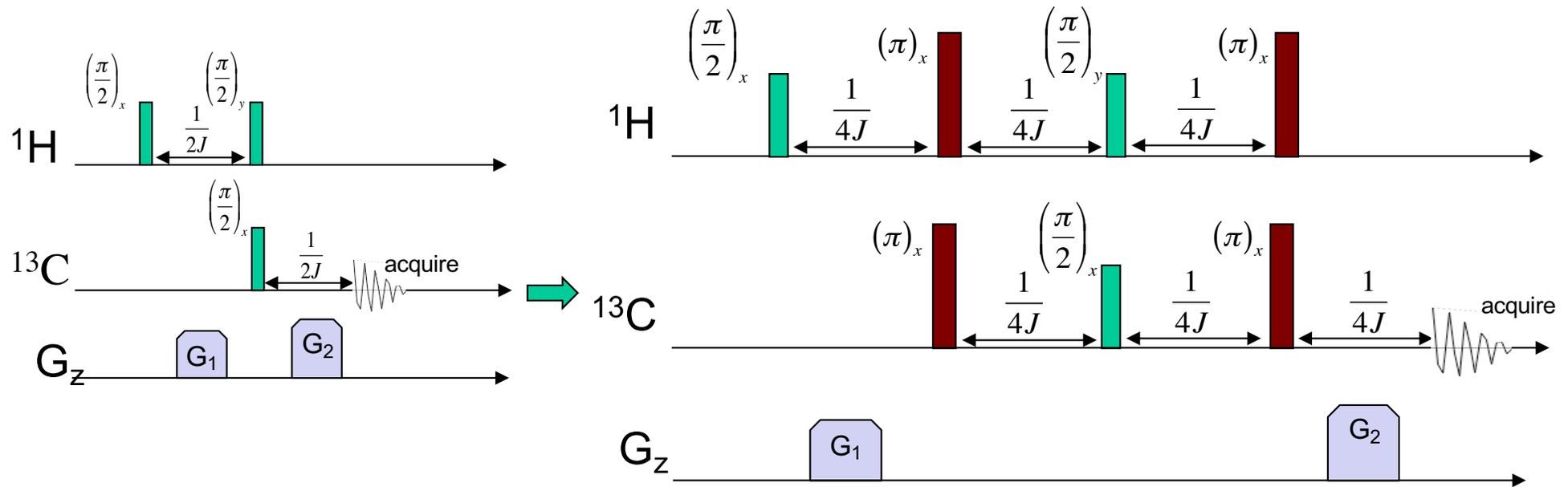
$$M_{xy}(t) \propto e^{-i\Omega_S t} \cos(\pi J t) \int_z \cos^2(\gamma_H G_1 z) dz$$



$$\frac{N\gamma_C^2 \gamma_H \hbar^2 B_0^2}{16kT}$$



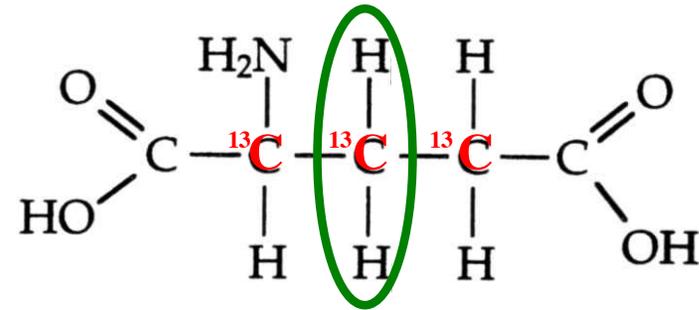
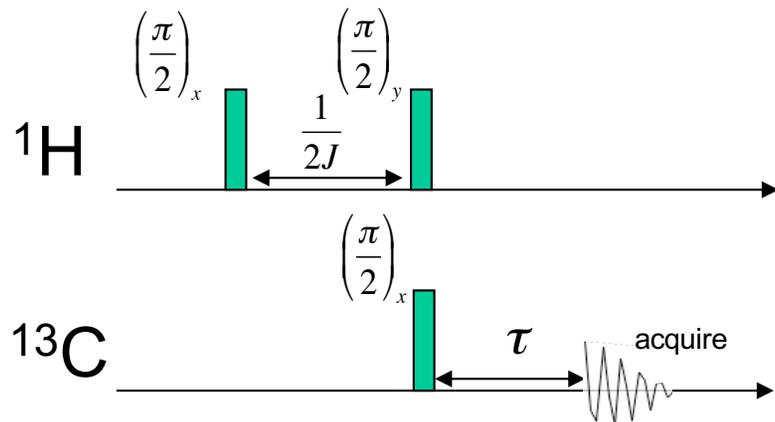
# Refocusing chemical shift...



## Gradient-enhanced INEPT-R

- $180^\circ$  Rf pulses refocus chemical shift for both I and S spins.
- J-coupling unaffected.

# What about an I<sub>2</sub>S spin system...



Example: <sup>13</sup>C-glutamate

- Letting I<sub>1</sub> = <sup>1</sup>H, I<sub>2</sub> = <sup>1</sup>H, and S = <sup>13</sup>C, then the initial density operator is:

$$\hat{\sigma}(0) = \frac{\hbar B_0}{4kT} (\gamma_I \hat{I}_{1z} + \gamma_I \hat{I}_{2z} + \gamma_S \hat{S}_z)$$

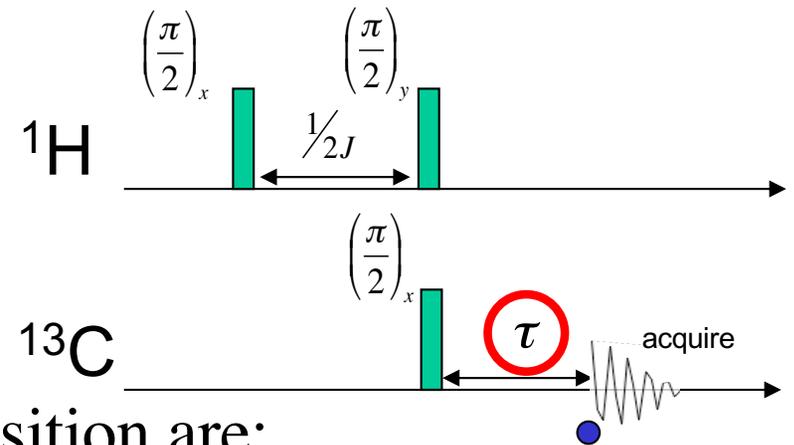
- The Hamiltonian during free precession is:

$$\hat{H}_{\text{free}} = -\Omega_I \hat{I}_{1z} - \Omega_I \hat{I}_{2z} - \Omega_S \hat{S}_z + 2\pi J \hat{I}_{1z} \hat{S}_z + 2\pi J \hat{I}_{2z} \hat{S}_z + 2\pi J_{HH} \hat{I}_{1z} \hat{I}_{2z} ?$$



# I<sub>2</sub>S spin system...

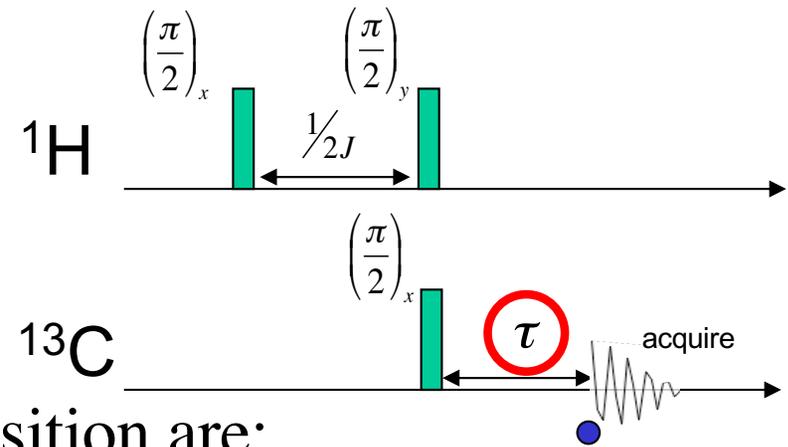
- As before, we are going to ignore chemical shift evolution during the  $1/2J$  and  $\tau$  time intervals (can always add  $180^\circ$ s later)
- The coherences just before data acquisition are:



Fill in branch diagram

# I<sub>2</sub>S spin system...

- As before, we are going to ignore chemical shift evolution during the 1/2J and τ time intervals (can always add 180°s later)
- The coherences just before data acquisition are:



$$\hat{I}_{1z} \xrightarrow{(\pi/2)_x^I, -\pi J_{IS}(1/2J)} -2\hat{I}_{1x}\hat{S}_z \xrightarrow{(\pi/2)_y^I, (\pi/2)_x^S} -2\hat{I}_{1z}\hat{S}_y \xrightarrow{-\pi J_{IS}\tau} \left\{ \begin{array}{l} -2\hat{I}_{1z}\hat{S}_y \xrightarrow{-\pi J_{IS}\tau} \left\{ \begin{array}{l} -2\hat{I}_{1z}\hat{S}_y \\ 4\hat{I}_{1z}\hat{I}_{2z}\hat{S}_x \end{array} \right. \\ \hat{S}_x \xrightarrow{-\pi J_{IS}\tau} \left\{ \begin{array}{l} \hat{S}_x \\ 2\hat{I}_{2z}\hat{S}_y \end{array} \right. \end{array} \right.$$

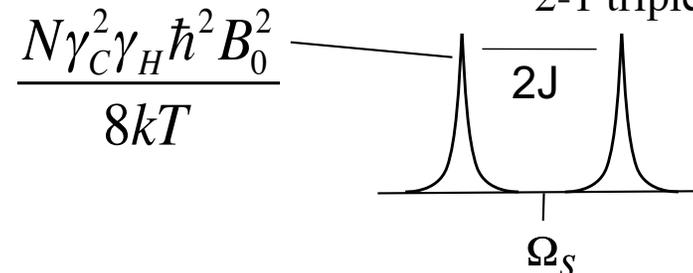
Normalization factor for 3-spin operators.

Why is this not a 1-2-1 triplet?

→  $M_x \propto \sin(\pi J\tau)\cos(\pi J\tau)$

Similarly  $\hat{I}_{2z} \longrightarrow \dots \longrightarrow \hat{S}_x \sin(\pi J\tau)\cos(\pi J\tau)$

Total:  $M_x \propto 2\sin(\pi J\tau)\cos(\pi J\tau)$



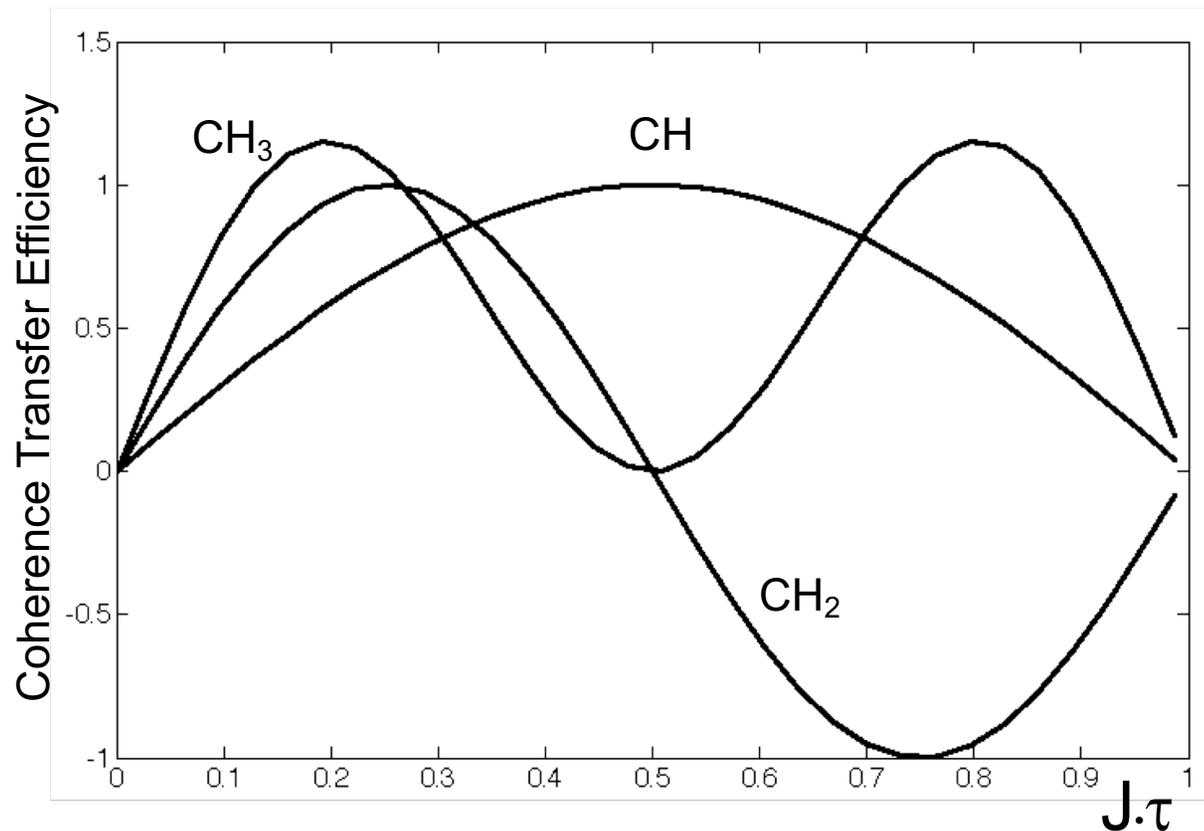
# INEPT-R

- In general, the value of  $\tau$  in an INEPT-R sequence needs to be optimized for different spin systems.

$$\text{CH} : \sin(\pi J\tau)$$

$$\text{CH}_2 : 2\sin(\pi J\tau)\cos(\pi J\tau)$$

$$\text{CH}_3 : 3\sin(\pi J\tau)\cos^2(\pi J\tau)$$



# Summary

- Rotations in 16-dimensional space are really not that hard.
- In fact, for the CH<sub>2</sub> spin system, we were actually computing rotations in a 64-dimensional vector space. Try a CH<sub>3</sub> system for a 256-dimensional adventure!
- POF is a very convenient way of tracking spin coherences. It is particularly useful for weakly coupled spin systems.
- Next lecture: Spectral Editing