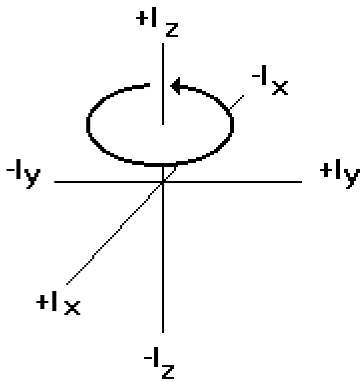
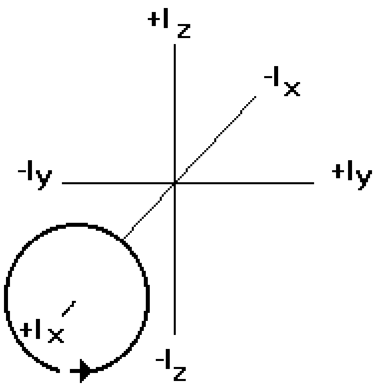

$+I_z$
$-I_x$
$-I_y$
$+I_y$
$+I_x$
$-I_z$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$+I_x$
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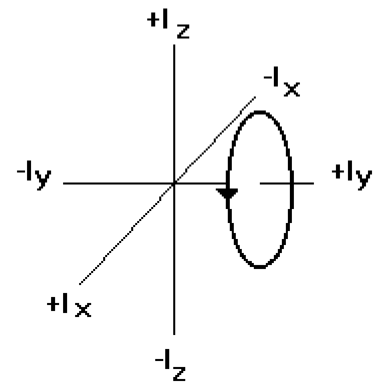
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$+I_y$
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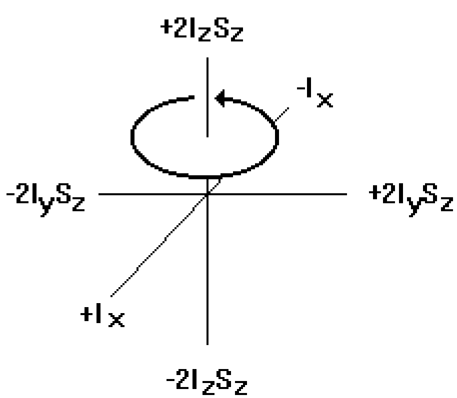
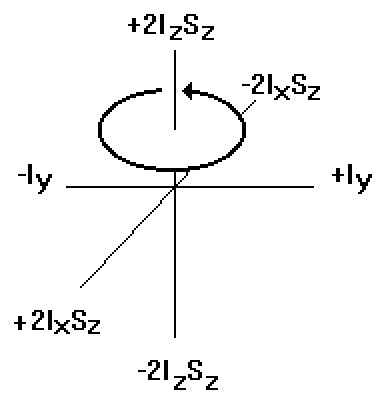
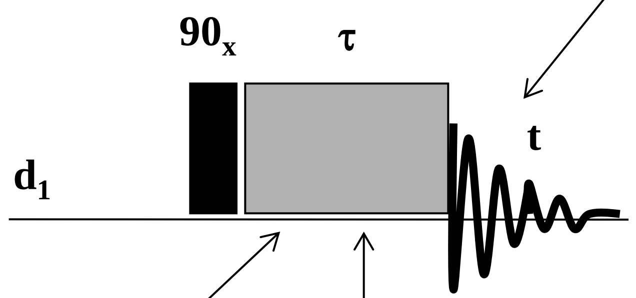

$+2I_zS_z$
$-I_x$
$-2I_yS_z$
$+2I_yS_z$
$+I_x$
$-2I_zS_z$


$+2I_zS_z$
$-2I_xS_z$
$-I_y$
$+I_y$
$+2I_xS_z$
$-2I_zS_z$

σ[eq.] ----> σ[0]
preparation: generating transverse magnet.

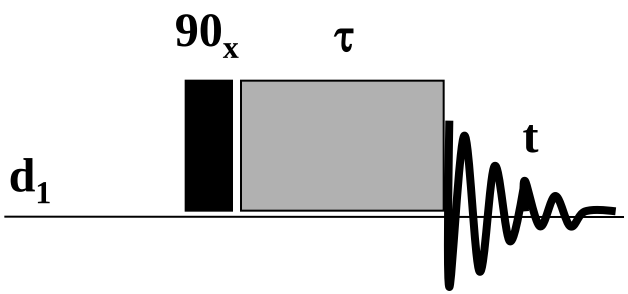
$\sigma[t_1,0]$ ----> $\sigma[t_1,t_2]$
detection (or acquisition): The product (FID) is recorded



σ[0] ----> $\sigma[t_1]$
evolution: „things" evolving under the Hamiltonian(s)

$\sigma[t_1]$ ----> $\sigma[t_1,0]$
mixing: coherence/magnetiza tion transferred from one spine to another.

Ekhó a visszhang nimfája (görög mitológia)



Preparation: Ekhó elvonja Héra figyelmét **csacsogás**ával, ezzel segített Zeusznak szerelmi dolgai bonyolításában.

***Evolution**:* Héra rájön a cselre, s büntetésből Ekhót azzal bünteti hogy örökké **mások mondatait ismételgesse** (azt se tudja egészen kimondani, csak mindig a végét ismételgeti.)

Mixing: Az elátkozott nimfa beleszeretett ezután a hiú Narkisszoszba. Nárcisz saját magába van belehabarodva, s így nem vesz tudomást Ekhóról.

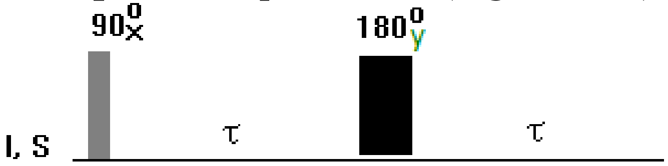
Detection (or acquisition): Nárcisz addig nézte a saját tükörképét amíg meg nem halt, Ekhó pedig addig bámulhatta a hiú istent, míg fájdalmában elemésztődik, s így csak a **hangja maradt** meg.

„Az emberi képesség, hogy gondolkodunk, és érzéseinket gondolatokká tudjuk váltani, ez vezet ki a nárcizmusból."

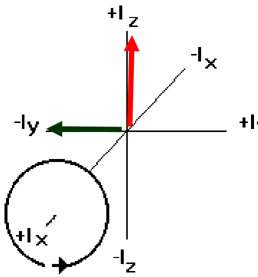
A.S. Byatt

Spin Echo: one-spin system

The pulse sequence is (*e.g.* I= ^{1}H):



Consider **spin I** only of Ω_I (thus, no S and no J_{IS})



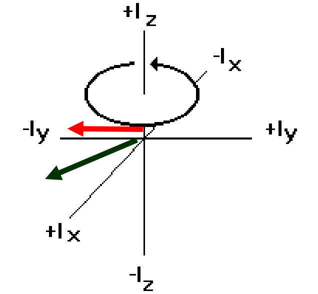
For spin I:

σ[eq.] $\quad\quad\quad\quad$ $\mathbf{I_z}$

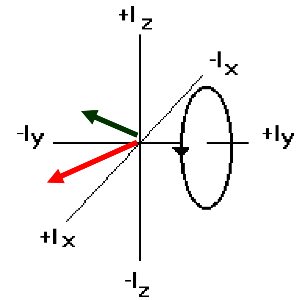
$\hat{H} = \pi/2\ (\hat{I}_x)$ $\quad\quad$ $\downarrow 90°_x$

σ[0] $\quad$ "echo module starts here" $\quad$ $\mathbf{-I_y}$

$\hat{H} = \hat{I}_z(\Omega_I\tau)$ $\quad\quad$ $\downarrow$

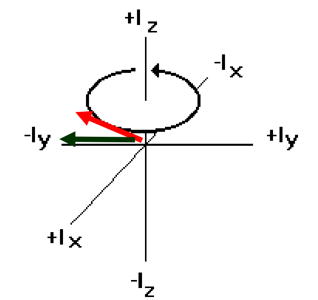


$\mathbf{-I_y}\cos(\Omega_I\tau)$ and $\mathbf{+I_x}\sin(\Omega_I\tau)$



$\hat{H} = \pi\hat{I}_y$ $\quad\quad$ $\downarrow \mathbf{180°_y}$

$\mathbf{-I_y}\cos(\Omega_I\tau)$ and $\mathbf{-I_x}\sin(\Omega_I\tau)$



$\hat{H} = \hat{I}_z(\Omega_I\tau)$ $\quad\quad$ $\downarrow$

$\mathbf{-I_y}\cos(\Omega_I\tau)\cos(\Omega_I\tau)$, $\mathbf{+I_x}\cos(\Omega_I\tau)\sin(\Omega_I\tau)$,
$\mathbf{-I_x}\sin(\Omega_I\tau)\cos(\Omega_I\tau)$, $\mathbf{-I_y}\sin(\Omega_I\tau)\sin(\Omega_I\tau)$

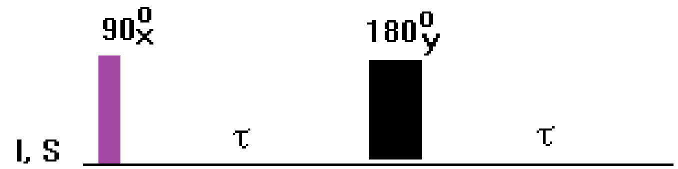
memo 1. $+\mathbf{I_x}\cos(\Omega_I\tau)\sin(\Omega_I\tau)\ \mathbf{-I_x}\sin(\Omega_I\tau)\cos(\Omega_I\tau) = 0$

memo 2. $\mathbf{-I_y}[\cos^2(\Omega_I\tau) + \sin^2(\Omega_I\tau)] = \mathbf{-I_y}$

For spin I the effect of echo is: $\mathbf{-I_y} \Rightarrow$ echo $\Rightarrow \mathbf{-I_y}$

Spin Echo: two spins; homonuclear I and S

The pulse sequence (*e.g.* I=S=^{1}H)



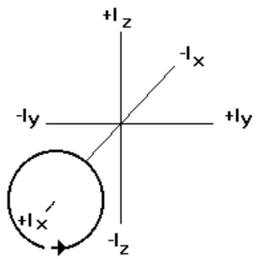
Consider: Ω_I, Ω_S and J_{IS} (I and S are homonuclear)

For spin I:

σ[eq.]

$\hat{H} = \pi/2 \ (\hat{I}_x)$

σ[0] "echo starts"



$\mathbf{I}_z$

$\downarrow$

$-\mathbf{I}_y$

$\hat{H} = \hat{I}_z(\Omega_I\tau)$

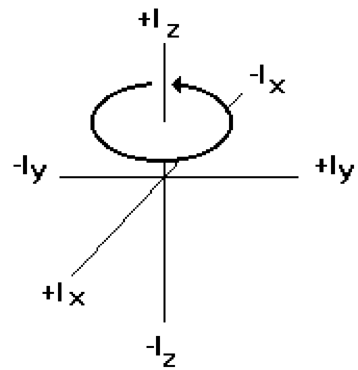
$\downarrow$

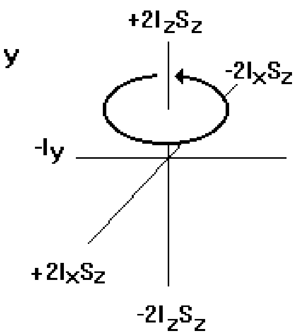
$-\mathbf{I}_y \cos(\Omega_I\tau) + \mathbf{I}_x \sin(\Omega_I\tau)$

$\hat{H} = 2\hat{I}_z\hat{S}_z(J_{IS}\pi\tau)$

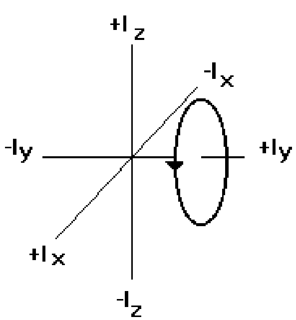
$\downarrow$

$$-\mathbf{I}_y \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$$
$$+2\mathbf{I}_x\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$$
$$+\mathbf{I}_x \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$$
$$+2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$$



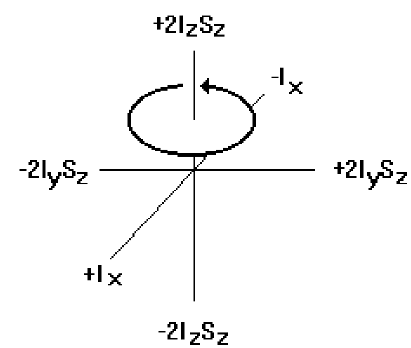


$\hat{H} = \pi\hat{\mathbf{I}}_y$



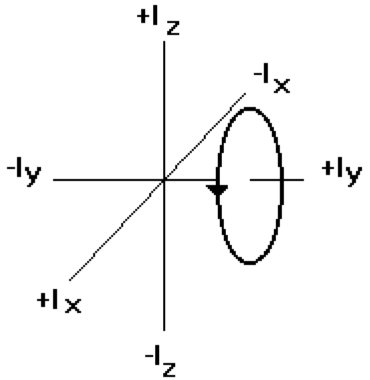
$\downarrow$

$$-\mathbf{I}_y \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$$
$$-2\mathbf{I}_x\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$$
$$-\mathbf{I}_x \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$$
$$+2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$$



$-\mathbf{I}_y \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$
$\quad -2\mathbf{I}_x\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$
$-\mathbf{I}_x \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$
$\quad +2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

all S!



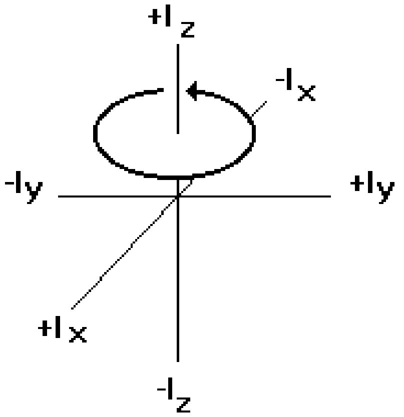
$\hat{H} = \pi\mathbf{S_y}$

↓

$-\mathbf{I}_y \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$
$\quad +2\mathbf{I}_x\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$
$-\mathbf{I}_x \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$
$\quad -2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$\hat{H} = \hat{I}_z(\Omega_I\tau)$

↓



$-\mathbf{I}_y \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau)$
$\quad +\mathbf{I}_x \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau)$
$+2\mathbf{I}_x\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau)$
$\quad +2\mathbf{I}_y\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau)$
$-\mathbf{I}_x \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau)$
$\quad -\mathbf{I}_y \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau)$
$-2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau)$
$\quad +2\mathbf{I}_x\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau)$

memo 1. $+\mathbf{I}_x \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau) - \mathbf{I}_x \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau) = \mathbf{0}$

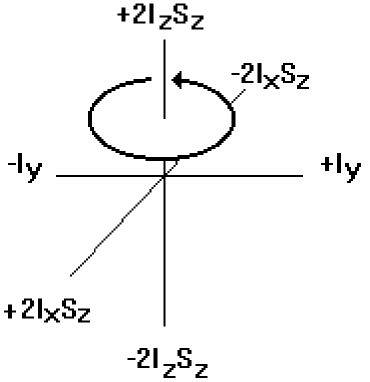
memo 2. $+2\mathbf{I}_y\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau) - 2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau) = \mathbf{0}$

memo 3. $-\mathbf{I}_y \cos(\pi J_{IS}\tau)[\cos^2(\Omega_I\tau) + \sin^2(\Omega_I\tau)] = \mathbf{-I_y \cos(\pi J_{IS}\tau)}$

memo 4. $+2\mathbf{I}_x\mathbf{S}_z \sin(\pi J_{IS}\tau)[\cos^2(\Omega_I\tau) + \sin^2(\Omega_I\tau)] = \mathbf{+2I_xS_z \sin(\pi J_{IS}\tau)}$

Therefore, the following 2 terms remain: $-\mathbf{I}_y \cos(\pi J_{IS}\tau)$ and $+2\mathbf{I}_x\mathbf{S}_z \sin(\pi J_{IS}\tau)$.

$\hat{H} = 2\hat{I}_z\hat{S}_z(J_{IS}\pi\tau)$ ↓



$-\mathbf{I}_y \cos(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)$ and $+2\mathbf{I}_x\mathbf{S}_z \cos(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)$

$+2\mathbf{I}_x\mathbf{S}_z \sin(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)$ and $+\mathbf{I}_y \sin(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)$

memo 5: /$\cos^2 A - \sin^2 A = \cos 2A$/

$$-\mathbf{I}_y \{\cos^2(\pi J_{IS}\tau) - \sin^2(\pi J_{IS}\tau)\} = -\mathbf{I}_y \cos(2\pi J_{IS}\tau)$$

memo 6: /$2\cos A \sin A = \sin 2A$/

$$2\{+2\mathbf{I}_x\mathbf{S}_z \sin(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)\} = +2\mathbf{I}_x\mathbf{S}_z \sin(2\pi J_{IS}\tau)$$

Thus, for spin I the result is: $-\mathbf{I}_y \Rightarrow \text{echo} \Rightarrow -\mathbf{I}_y \cos(2\pi J_{IS}\tau) + 2\mathbf{I}_x\mathbf{S}_z \sin(2\pi J_{IS}\tau)$

For spin S similarly the result is : $-\mathbf{S}_y \Rightarrow \text{echo} \Rightarrow -\mathbf{S}_y \cos(2\pi J_{IS}\tau) + 2\mathbf{S}_x\mathbf{I}_z \sin(2\pi J_{IS}\tau)$

For both spins the result is :

$$-(\mathbf{S}_y+\mathbf{I}_y) \Rightarrow \text{echo} \Rightarrow -(\mathbf{I}_y+\mathbf{S}_y)\cos(\pi J_{IS}2\tau) + (2\mathbf{I}_x\mathbf{S}_z + 2\mathbf{S}_x\mathbf{I}_z)\sin(\pi J_{IS}2\tau)$$

CONCLUSION:

The homonuclear coupling (J_{IS}) has evolved. (Evolution rate: πJ_{IS}, evolution time: 2τ.)

The offset or chemical shift (Ω_I, Ω_S) is refocused, thus hasn't evolved .

memo: the **$180°_y$** pulse at the middle **effects both** I and S spins, as they are **homonuclear**.

Example of J-modulation:

as J_{IS} evolves at an evolution rate of πJ_{IS}, during the evolution time of 2τ.

$-\mathbf{I}_y \Rightarrow$ echo $\Rightarrow$ two terms, namely:

1) one in-phase (two lines of the same sign and amplitude): $-\mathbf{I}_y \cos(2\pi J_{IS}\tau)$

2) one anti-phase (two lines of the same amplitude but opposite sign): $+2\mathbf{I}_x\mathbf{S}_z \sin(2\pi J_{IS}\tau)$

conclusions:

1) A superimposition of two doubles at Ω_I is detected, namely
   - an **in-phase** absortpive doublet of an **intesnity** modulated by $\mathbf{\cos(2\pi J_{IS}\tau)}$**,** and
   - an **anti-phase** dispersive doublet of an **intesnity** modulated by $\mathbf{\sin(2\pi J_{IS}\tau)}$**.**

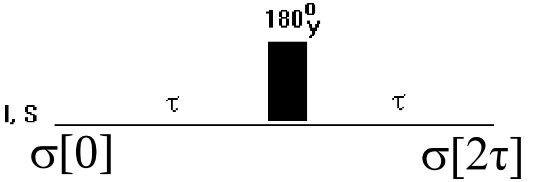
1) As τ changes the ratio between them changes:

τ	$\alpha=2\pi J_{IS}\tau$	**cos(α)**	**in-ph term**	**sin(α)**	**anti-ph term**	**overall look**
0	0°	1	100%	0	0%	pure abs. positive, in-ph.
$1/(8J_{IS})$	45°	0,707	50%	0,707	50%	mixed
$2/(8J_{IS})$	90°	0	0%	1	100%	pure abs. positive, anti-ph.
$3/(8J_{IS})$	135°	-0,707	50%	0,707	50%	mixed
$4/(8J_{IS})$	180°	-1	100%	0	0%	pure abs. negative, in-ph.
$6/(8J_{IS})$	270°	0	0%	-1	100%	pure abs. negative, anti-ph.

(Keeler 7.8.3 / 163 o.)

3) Oscillatory inter change between in-phase and anti-phased terms,
4) Complete conversion of one form to the other requires a $\tau = k/(8J_{IS})$, k=2, 4, 6, 8, …

Shortcut for homonuclear spin echo: Ω_I, Ω_S and J_{IS} (I and S)



Considering the above set of Hamiltonians the following holds:

$\hat{H}_2 = \hat{I}_z(\Omega_I\tau)$

$\hat{H}_3 = 2\hat{I}_z\hat{S}_z(J_{IS}\pi\tau)$

$\hat{H}_4 = \pi\hat{\mathbf{I}}_{\mathbf{y}}$

$\hat{H}_5 = \pi\mathbf{S}_{\mathbf{y}}$

$\hat{H}_6 = \hat{I}_z(\Omega_I\tau)$

$\hat{H}_7 = 2\hat{I}_z\hat{S}_z(J_{IS}\pi\tau)$

Chemical shift is refocused, thus the effect of $\hat{H}_2$ is cancelled by $\hat{H}_6$

$\hat{H}_3 = 2\hat{I}_z\hat{S}_z(J_{IS}\pi\tau)$

$\hat{H}_4 = \pi\hat{\mathbf{I}}_{\mathbf{y}}$

$\hat{H}_5 = \pi\mathbf{S}_{\mathbf{y}}$

$\hat{H}_7 = 2\hat{I}_z\hat{S}_z(J_{IS}\pi\tau)$

J coupling evolves during $\tau+\tau = 2\tau$, thus $\hat{H}_3 + \hat{H}_7 = \hat{H}_8 = 2\hat{I}_z\hat{S}_z(J_{IS}\pi\mathbf{2\tau})$

$\hat{H}_4 = \pi\hat{\mathbf{I}}_{\mathbf{y}}$

$\hat{H}_5 = \pi\mathbf{S}_{\mathbf{y}}$

$\hat{H}_8 = 2\hat{I}_z\hat{S}_z(J_{IS}\pi2\tau)$

The effect of both $\hat{H}_4$ and $\hat{H}_5$ were considered thus, can be ignored:

Therefore, the only relevant Hamiltonian is $\hat{H}_8$:

σ[0] "echo starts" $-\mathbf{I}_y$

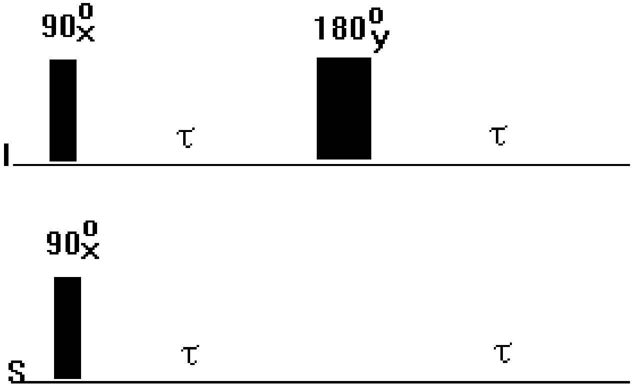
$\hat{H}_8 = 2\hat{I}_z\hat{S}_z(J_{IS}\pi2\tau)$ ↓

σ[2τ] "echo ends" $-\mathbf{I}_y\cos(2\pi J_{IS}\tau) + 2\mathbf{I}_x\mathbf{S}_z\sin(2\pi J_{IS}\tau)$

CONCLUSION:

Indeed this is the same as calculated on the long way, however here one has to be **smart**!

Spin Echo: two spins; hetereonuclear I and S



The pulse sequence:

(e.g.^{1}H) I: $90°_x$ -----τ----- $180°_y$ ------τ-----

(e.g.^{15}N, ^{13}C) S: $90°_x$ -----τ-------------------τ-----

------------e c h o ------------

Consider: Ω_I, Ω_S and J_{IS} (I and S are heteronuclear)

For spin I:

σ[eq.]

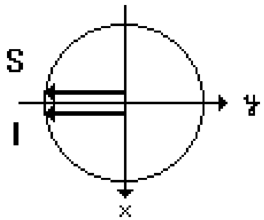
$\mathbf{I}_z$

$\hat{H} = \pi/2 \ (\hat{I}_x)$

$\downarrow 90°_x$

σ[0] "echo starts"

$-\mathbf{I}_y$



$\hat{H} = \hat{I}_z(\Omega_I\tau)$

$\downarrow$

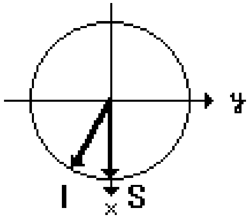
$-\mathbf{I}_y \cos(\Omega_I\tau) + \mathbf{I}_x \sin(\Omega_I\tau)$

$$-\mathbf{I}_y \cos(\Omega_I\tau) + \mathbf{I}_x \sin(\Omega_I\tau)$$

$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$

$$\downarrow$$

$$-\mathbf{I}_y \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$$
$$+2\mathbf{I}_x\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$$
$$+\mathbf{I}_x \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$$
$$+2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$$

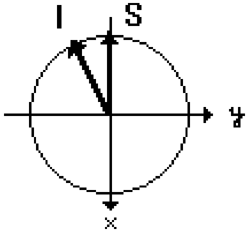


$\hat{H} = \pi\hat{I}_y$

memo : $\pi\hat{I}_y$ is selective

$$\downarrow$$

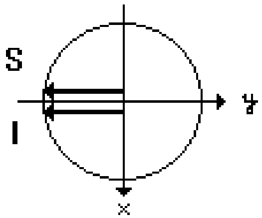
$$-\mathbf{I}_y \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$$
$$-2\mathbf{I}_x\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$$
$$-\mathbf{I}_x \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$$
$$+2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$$



$\hat{H} = \hat{I}_z(\Omega_I\tau)$

$$\downarrow$$

$$-\mathbf{I}_y \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau)$$
$$+\mathbf{I}_x \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau)$$
$$-2\mathbf{I}_x\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau)$$
$$-2\mathbf{I}_y\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau)$$
$$-\mathbf{I}_x \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau)$$
$$-\mathbf{I}_y \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau)$$
$$+2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau)$$
$$-2\mathbf{I}_x\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau)$$



memo 7. $+\mathbf{I}_x \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau) - \mathbf{I}_x \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau) = 0$

memo 8. $+2\mathbf{I}_y\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau) - 2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau) = 0$

memo 9. $-\mathbf{I}_y \cos(\pi J_{IS}\tau)[\cos^2(\Omega_I\tau) + \sin^2(\Omega_I\tau)] = -\mathbf{I}_y \cos(\pi J_{IS}\tau)$

memo 10. $-2\mathbf{I}_x\mathbf{S}_z \sin(\pi J_{IS}\tau)[\cos^2(\Omega_I\tau) + \sin^2(\Omega_I\tau)] = -2\mathbf{I}_x\mathbf{S}_z \sin(\pi J_{IS}\tau)$

Therefore

$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$

$-\mathbf{I}_y \cos(\pi J_{IS}\tau)$
$-2\mathbf{I}_x\mathbf{S}_z \sin(\pi J_{IS}\tau)$ remains.

$\downarrow$

$-\mathbf{I}_y \cos(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)$
$+2\mathbf{I}_x\mathbf{S}_z \cos(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)$
$-2\mathbf{I}_x\mathbf{S}_z \sin(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)$
$-\mathbf{I}_y \sin(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)$

memo 11: /$\cos^2 A + \sin^2 A = 1$/

$-\mathbf{I}_y \{\cos(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau) + \sin(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)\} = -\mathbf{I}_y$

thus: $-\mathbf{I}_y \Rightarrow$ echo $\Rightarrow -\mathbf{I}_y$

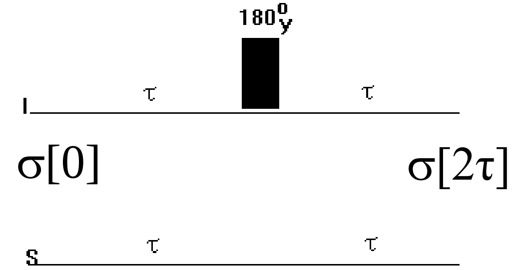
CONCLUSION:

The heteronuclear coupling (J_{IS}) hasn't evolved . The chemical shift (Ω_I) hasn't evolved (offste is refocused).

memo : the $180°_y$ pulse (in the middle) effects only spin I or S (but never both), since they are heteronuclear.

memo: due to relaxtion intensity will decrease, but this is out of the scope during the POF

Shortcut for heteronuclear spin echo: Ω_I, Ω_S and J_{IS} (I and S)



Considering the above set of Hamiltonians the following holds:

$\hat{H}_2 = \hat{I}_z(\Omega_I\tau)$
$\hat{H}_3 = 2\hat{I}_z\hat{S}_z(J_{IS}\pi\tau)$
$\hat{H}_4 = \pi\hat{\mathbf{I}}_{\mathbf{y}}$
$\hat{H}_5 = \pi\mathbf{S}_{\mathbf{y}}$
$\hat{H}_6 = \hat{I}_z(\Omega_I\tau)$
$\hat{H}_7 = 2\hat{I}_z\hat{S}_z(J_{IS}\pi\tau)$

Chemical shift is refocused, thus the effect of $\hat{H}_2$ is cancelled by $\hat{H}_6$ →

$\hat{H}_3 = 2\hat{I}_z\hat{S}_z(J_{IS}\pi\tau)$
$\hat{H}_4 = \pi\hat{\mathbf{I}}_{\mathbf{y}}$
$\hat{H}_5 = \pi\mathbf{S}_{\mathbf{y}}$
$\hat{H}_7 = 2\hat{I}_z\hat{S}_z(J_{IS}\pi\tau)$

J coupling is also refocudsed ,thus the effect of $\hat{H}_3$ is cancelled by $\hat{H}_7$ →

$\hat{H}_4 = \pi\hat{\mathbf{I}}_{\mathbf{y}}$
$\hat{H}_5 = \pi\mathbf{S}_{\mathbf{y}}$

The effect of both $\hat{H}_4$ and $\hat{H}_5$ were considered thus, can be ignored: →

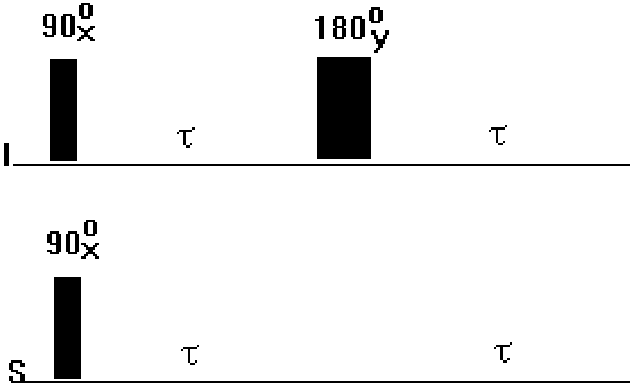
Therefore, no Hamiltonian remains:

σ[0]	"echo starts"	$-\mathbf{I}_y$
	„no influence"	↓
σ[2τ]	"echo ends"	$-\mathbf{I}_y$

CONCLUSION:

Indeed this is the same as calculated on the long way, however here one has to be **very smart**!

What is happening with spin S?



For spin S:

σ[eq.] $\quad S_z$

$\hat{H} = \pi/2 \ (\hat{S}_x)$

σ[0] "echo starts" $\quad -S_y$

$\hat{H} = \hat{S}_z(\Omega_S\tau)$

$-S_y \cos(\Omega_S\tau) + S_x \sin(\Omega_S\tau)$

$\hat{H} = \hat{S}_z(\Omega_S\tau)$

$-S_y \cos^2(\Omega_S\tau) + S_x \cos(\Omega_S\tau) \sin(\Omega_S\tau)$

$+S_x \sin(\Omega_S\tau) \cos(\Omega_S\tau) + S_y \sin^2(\Omega_S\tau)$

memo: as coupling is refocused, thus the effect of both $\hat{H}_3$ and $\hat{H}_7$ ($2I_zS_z$) is ignored!

$+S_x 2\cos(\Omega_S\tau)\sin(\Omega_S\tau) = +S_x \sin(\Omega_S 2\tau)$

$-S_y [\cos^2(\Omega_S\tau) - \sin^2(\Omega_S\tau)] = -S_Y \cos(\Omega_S 2\tau)$

Conclusion: off-set (chemical shift) of spin S evolves during the heteronuclear spin-echo:

$+S_x \sin(\Omega_S 2\tau)$ and $-S_Y \cos(\Omega_S 2\tau)$

Generalisation of Spin Echoes

A. Heteronuclear I, S

Consider: Ω_I, Ω_S and J_{IS}

The pulse sequence:

(e.g.^{1}H)	I	-----τ----- $180°_y$ ------τ-----
(e.g.^{15}N)	S	-----τ------------------τ-----
	input⇒	-----------e c h o ------------ ⇒**output**

input : I_x (in-phase transverse magnetization)

σ[0] "echo starts" $+\mathbf{I}_x$

$\hat{H} = \hat{I}_z(\Omega_I\tau)$ ↓

$+\mathbf{I}_x$ $+\mathbf{I}_y$

$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$ ↓ ↓

$+\mathbf{I}_x$ $+2\mathbf{I}_y\mathbf{S}_z$ $+\mathbf{I}_y$ $-2\mathbf{I}_x\mathbf{S}_z$

$\hat{H} = \pi\hat{I}_y$ ↓

$-\mathbf{I}_x$ $+2\mathbf{I}_y\mathbf{S}_z$ $+\mathbf{I}_y$ $+2\mathbf{I}_x\mathbf{S}_z$

$\hat{H} = \hat{I}_z(\Omega_I\tau)$ ↓ ↓ ↓ ↓

$-\mathbf{I}_x$ $-\mathbf{I}_y$ $+2\mathbf{I}_y\mathbf{S}_z$ $-2\mathbf{I}_x\mathbf{S}_z$ $+\mathbf{I}_y$ $-\mathbf{I}_x$ $+2\mathbf{I}_x\mathbf{S}_z$ $+2\mathbf{I}_y\mathbf{S}_z$

memo 12. $-\mathbf{I}_y \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau) + \mathbf{I}_y \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau) = 0$

memo 13. $-2\mathbf{I}_x\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau) + 2\mathbf{I}_x\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau) = 0$

memo 14. $-\mathbf{I}_x \cos(\pi J_{IS}\tau)[\cos^2(\Omega_I\tau) + \sin^2(\Omega_I\tau)] = -\mathbf{I}_x \cos(\pi J_{IS}\tau)$

memo 15. $+2\mathbf{I}_y\mathbf{S}_z \sin(\pi J_{IS}\tau)[\cos^2(\Omega_I\tau) + \sin^2(\Omega_I\tau)] = +2\mathbf{I}_y\mathbf{S}_z \sin(\pi J_{IS}\tau)$

$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$

$$
\begin{array}{ccccc}
 & -\mathbf{I}_x & & +2\mathbf{I}_y\mathbf{S}_z & \\
\downarrow & & \downarrow & & \\
-\mathbf{I}_x & -2\mathbf{I}_y\mathbf{S}_z & +2\mathbf{I}_y\mathbf{S}_z & & -\mathbf{I}_x
\end{array}
$$

memo 16: /$\cos^2 A - \sin^2 A = \cos 2A$/ $-\mathbf{I}_x \cos(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau) - \mathbf{I}_x \sin(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau) = -\mathbf{I}_x$

memo 17: /$2\cos A \sin A = \sin 2A$/ $-2\mathbf{I}_y\mathbf{S}_z \cos(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau) + 2\mathbf{I}_y\mathbf{S}_z \sin(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau) = 0$

the final result is: $+\mathbf{I}_x \Rightarrow$ echo $\Rightarrow -\mathbf{I}_x$

(The heteronuclear coupling (J_{IS}) as well as the chemical shift (Ω_I) has not evolved.)

input : S_x (in-phase transverse magnetization) **see also page 10**

$\sigma[0]$ "echo starts" $+\mathbf{S}_x$

$\hat{H} = S_z(\Omega_S \tau)$ $\downarrow$

$+\mathbf{S}_x$ $+\mathbf{S}_y$

$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$ $\downarrow$ $\downarrow$

$+\mathbf{S}_x$ $+2\mathbf{I}_z\mathbf{S}_y$ $+\mathbf{S}_y$ $-2\mathbf{I}_z\mathbf{S}_x$

$\hat{H} = \pi\hat{I}_y$ $\downarrow$

$+\mathbf{S}_x$ $-2\mathbf{I}_z\mathbf{S}_y$ $+\mathbf{S}_y$ $+2\mathbf{I}_z\mathbf{S}_x$

$\hat{H} = S_z(\Omega_S \tau)$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$

$+\mathbf{S}_x$ $+\mathbf{S}_y$ $-2\mathbf{I}_z\mathbf{S}_y$ $+2\mathbf{I}_z\mathbf{S}_x$ $+\mathbf{S}_y$ $-\mathbf{S}_x$ $+2\mathbf{I}_z\mathbf{S}_x$ $+2\mathbf{I}_z\mathbf{S}_y$

$\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$

$[+\mathbf{S}_x, +2\mathbf{I}_z\mathbf{S}_y]$ $[-2\mathbf{I}_z\mathbf{S}_y, +\mathbf{S}_x]$ $[+\mathbf{S}_y, -2\mathbf{I}_z\mathbf{S}_x]$ $[+2\mathbf{I}_z\mathbf{S}_x, +\mathbf{S}_y]$

$[+\mathbf{S}_y, -2\mathbf{I}_z\mathbf{S}_x]$ $[+2\mathbf{I}_z\mathbf{S}_x, +\mathbf{S}_y]$ $[-\mathbf{S}_x, -2\mathbf{I}_z\mathbf{S}_y]$ $[+2\mathbf{I}_z\mathbf{S}_y, -\mathbf{S}_x]$

$+\mathbf{S}_x$ $\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$+2\mathbf{I}_z\mathbf{S}_y$ $\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$+\mathbf{S}_y$ $\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$-2\mathbf{I}_z\mathbf{S}_x$ $\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$-2\mathbf{I}_z\mathbf{S}_y$ $\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$+\mathbf{S}_x$ $\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$+2\mathbf{I}_z\mathbf{S}_x$ $\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$+\mathbf{S}_y$ $\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$+\mathbf{S}_y$ $\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$-2\mathbf{I}_z\mathbf{S}_x$ $\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$-\mathbf{S}_x$ $\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$-2\mathbf{I}_z\mathbf{S}_y$ $\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$+2\mathbf{I}_z\mathbf{S}_x$ $\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$+\mathbf{S}_y$ $\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$+2\mathbf{I}_z\mathbf{S}_y$ $\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$-\mathbf{S}_x$ $\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

memo 18: The anti phase terms ($+2\mathbf{I}_z\mathbf{S}_x$ and $+2\mathbf{I}_z\mathbf{S}_y$) add up to zero.

$$+\mathbf{S}_x\cos^2(\Omega_S\tau)[\cos^2(\pi J_{IS}\tau) + \sin^2(\pi J_{IS}\tau)] -\mathbf{S}_x\sin^2(\Omega_S\tau)[\cos^2(\pi J_{IS}\tau) + \sin^2(\pi J_{IS}\tau)] =$$
$$= +\mathbf{S}_x\cos^2(\Omega_S\tau) - \mathbf{S}_x\sin^2(\Omega_S\tau) = \mathbf{S}_x \cos(\Omega_S 2\tau)$$

$$+\mathbf{S}_y\cos(\Omega_S\tau)\sin(\Omega_S\tau)[\cos^2(\pi J_{IS}\tau) + \sin^2(\pi J_{IS}\tau)] +\mathbf{S}_y\sin(\Omega_S\tau)\cos(\Omega_S\tau)[\cos^2(\pi J_{IS}\tau) + \sin^2(\pi J_{IS}\tau)] =$$
$$=2\,\mathbf{S}_y\sin(\Omega_S\tau)\cos(\Omega_S\tau) = \mathbf{S}_y \sin(\Omega_S 2\tau)$$

the final result is: $+\mathbf{S}_x \Rightarrow \text{echo} \Rightarrow +\mathbf{S}_x\cos(\Omega_S 2\tau) + \mathbf{S}_y \sin(\Omega_S 2\tau)$

The heteronuclear coupling (J_{IS}) is decoupled but the chemical shift (Ω_s) has evolved.

input : $2I_zS_x$ (anti-phase magnetization on spin S)

$\sigma[0]$ "echo starts" $+\mathbf{2I_zS}_x$

$\hat{H} = S_z(\Omega_S\tau)$ ↓

$+\mathbf{2I_zS}_x$ $+\mathbf{2I_zS}_y$

$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$ ↓ ↓

$+\mathbf{2I_zS}_x$ $+\mathbf{S}_y$ $+\mathbf{2I_zS}_y$ $-\mathbf{S}_x$

$\hat{H} = \pi\hat{I}_y$ ↓

$-\mathbf{2I_zS}_x$ $+\mathbf{S}_y$ $-\mathbf{2I_zS}_y$ $-\mathbf{S}_x$

$\hat{H} = S_z(\Omega_S\tau)$ ↓ ↓ ↓ ↓

$-\mathbf{2I_zS_x}$ $-\mathbf{2I_zS}_y$ $+\mathbf{S}_y$ $-\mathbf{S}_x$ $-\mathbf{2I_zS}_y$ $+\mathbf{2I_zS}_x$ $-\mathbf{S}_x$ $-\mathbf{S}_y$

↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓

[$-2\mathbf{I}_z\mathbf{S}_x$, $-\mathbf{S}_y$] [$-2\mathbf{I}_z\mathbf{S}_y$,$+\mathbf{S}_x$] [$+\mathbf{S}_y$, $-2\mathbf{I}_z\mathbf{S}_x$] [$-\mathbf{S}_x$,$-2\mathbf{I}_z\mathbf{S}_y$] [$-2\mathbf{I}_z\mathbf{S}_y$, $+\mathbf{S}_x$] [$+2\mathbf{I}_z\mathbf{S}_x$, $+\mathbf{S}_y$] [$-\mathbf{S}_x$,$-2\mathbf{I}_z\mathbf{S}_y$] [$-\mathbf{S}_y$,$+2\mathbf{I}_z\mathbf{S}_x$]

$-2I_zS_x$ $\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$-S_y$ $\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$-2I_zS_y$ $\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$+S_x$ $\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$+S_y$ $\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$-2I_zS_x$ $\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$-S_x$ $\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$-2I_zS_y$ $\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$-2I_zS_y$ $\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$+S_x$ $\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$+2I_zS_x$ $\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$+S_y$ $\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$-S_x$ $\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$-2I_zS_y$ $\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

$-S_y$ $\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_S\tau)\cos(\pi J_{IS}\tau)$

$+2I_zS_x$ $\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_S\tau)\sin(\pi J_{IS}\tau)$

memo 19: The in-phase terms ($\mathbf{S}_x$ and $\mathbf{S}_y$) add up to zero.

$-2\mathbf{I}_z\mathbf{S}_x\cos^2(\Omega_S\tau)[\cos^2(\pi J_{IS}\tau) + \sin^2(\pi J_{IS}\tau)]$ $+2\mathbf{I}_z\mathbf{S}_x\sin^2(\Omega_S\tau)[\cos^2(\pi J_{IS}\tau) + \sin^2(\pi J_{IS}\tau)] =$

$= -2\mathbf{I}_z\mathbf{S}_x\cos^2(\Omega_S\tau)$ $+2\mathbf{I}_z\mathbf{S}_x\sin^2(\Omega_S\tau) = -2\mathbf{I}_z\mathbf{S}_x \cos(\Omega_S 2\tau)$

$-2\mathbf{I}_z\mathbf{S}_y\cos(\Omega_S\tau)\sin(\Omega_S\tau)[\cos^2(\pi J_{IS}\tau) + \sin^2(\pi J_{IS}\tau)]$ $-2\mathbf{I}_z\mathbf{S}_y\sin(\Omega_S\tau)\cos(\Omega_S\tau)[\cos^2(\pi J_{IS}\tau) + \sin^2(\pi J_{IS}\tau)] =$

$= -2\mathbf{I}_z\mathbf{S}_y\, 2\sin(\Omega_S\tau)\cos(\Omega_S\tau) = -2\mathbf{I}_z\mathbf{S}_y \sin(\Omega_S 2\tau)$

the final result is: $+2\mathbf{I}_z\mathbf{S}_x \Rightarrow \text{echo} \Rightarrow -2\mathbf{I}_z\mathbf{S}_x\cos(\Omega_S 2\tau)\ -2\mathbf{I}_z\mathbf{S}_y \sin(\Omega_S 2\tau)$

The heteronuclear coupling (J_{IS}) is decoupled but the chemical shift (Ω_s) has evolved.

input : $2I_xS_z$ (anti-phase magnetization on spin I)

σ[0] "echo starts" $+2I_xS_z$

$\hat{H} = I_z(\Omega_I\tau)$ ↓

$+2I_xS_z$ $+2I_yS_z$

$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$ ↓ ↓

$+2I_xS_z$ $+I_y$ $+2I_yS_z$ $-I_x$

$\hat{H} = \pi\hat{I}_y$ ↓

$-2I_xS_z$ $+I_y$ $+2I_yS_z$ $+I_x$

$\hat{H} = I_z(\Omega_S\tau)$ ↓ ↓ ↓ ↓

$-2I_xS_z$ $-2I_yS_z$ $+I_y$ $-I_x$ $+2I_yS_z$ $-2I_xS_z$ $+I_x$ $+I_y$

↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓

$[-2I_xS_z, -I_y]$ $[+I_y, -2I_xS_z]$ $[+2I_yS_z, -I_x]$ $[+I_x, +2I_yS_z]$

$[-2I_yS_z, +I_x]$ $[-I_x, -2I_yS_z]$ $[-2I_xS_z, -I_y]$ $[+I_y, -2I_xS_z]$

$-2I_xS_z$ $\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$-I_y$ $\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$-2I_yS_z$ $\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$+I_x$ $\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$+I_y$ $\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$-2I_xS_z$ $\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$-I_x$ $\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$-2I_yS_z$ $\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$+2I_yS_z$ $\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$-I_x$ $\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$-2I_xS_z$ $\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$-I_y$ $\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$+I_x$ $\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$+2I_yS_z$ $\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$+I_y$ $\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$-2I_xS_z$ $\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

memo 20: The in-phase terms ($\mathbf{I}_x$ and $\mathbf{I}_y$) add up to zero.

$$-2\mathbf{I}_x\mathbf{S}_z\cos^2(\Omega_I\tau)[\cos^2(\pi J_{IS}\tau) + \sin^2(\pi J_{IS}\tau)] -2\mathbf{I}_\mathbf{x}\mathbf{S}_z\sin^2(\Omega_I\tau)[\cos^2(\pi J_{IS}\tau) + \sin^2(\pi J_{IS}\tau)] =$$
$$= -2\mathbf{I}_x\mathbf{S}_z\cos^2(\Omega_I\tau) -2\mathbf{I}_\mathbf{x}\mathbf{S}_z\sin^2(\Omega_I\tau) = -2\mathbf{I}_\mathbf{x}\mathbf{S}_z$$

$$-2\mathbf{I}_y\mathbf{S}_z\cos(\Omega_I\tau)\sin(\Omega_I\tau)[\cos^2(\pi J_{IS}\tau) + \sin^2(\pi J_{IS}\tau)]+2\mathbf{I}_\mathbf{y}\mathbf{S}_\mathbf{z}\sin(\Omega_S\tau)\cos(\Omega_S\tau)[\cos^2(\pi J_{IS}\tau)+\sin^2(\pi J_{IS}\tau)]=$$
$$=-2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I\tau)\cos(\Omega_I\tau) +2\mathbf{I}_\mathbf{y}\mathbf{S}_\mathbf{z}\sin(\Omega_S\tau)\cos(\Omega_S\tau) = 0$$

the final result is: $+2\mathbf{I}_\mathbf{x}\mathbf{S}_z \Rightarrow$ echo $\Rightarrow -2\mathbf{I}_x\mathbf{S}_z$

input : $2I_xS_y$ (multiple-quantum coherence)

$\sigma[0]$ "echo starts"				$+2\mathbf{I}_x\mathbf{S}_y$	
$\hat{H} = S_z(\Omega_S\tau)$				↓	
		$+2\mathbf{I}_x\mathbf{S}_y$			$-2\mathbf{I}_x\mathbf{S}_x$
$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$	↓			↓	
		$+2\mathbf{I}_x\mathbf{S}_y$			$-2\mathbf{I}_x\mathbf{S}_x$
$\hat{H} = \pi\hat{I}_y$	↓			↓	
		$-2\mathbf{I}_x\mathbf{S}_y$			$+2\mathbf{I}_x\mathbf{S}_x$
$\hat{H} = S_z(\Omega_S\tau)$		↓			↓
	$-2\mathbf{I}_x\mathbf{S}_y$	$+2\mathbf{I}_x\mathbf{S}_x$		$+2\mathbf{I}_x\mathbf{S}_x$	$+2\mathbf{I}_x\mathbf{S}_y$
$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$			↓		
	$-2\mathbf{I}_x\mathbf{S}_y$	$+2\mathbf{I}_x\mathbf{S}_x$		$+2\mathbf{I}_x\mathbf{S}_x$	$+2\mathbf{I}_x\mathbf{S}_y$

memo 21:

$+2\mathbf{I}_x\mathbf{S}_x\cos(\Omega_S\tau)\sin(\Omega_S\tau) + 2\mathbf{I}_x\mathbf{S}_x\sin(\Omega_S\tau)\cos(\Omega_S\tau) = +2\mathbf{I}_x\mathbf{S}_x\, 2\sin(\Omega_S\tau)\cos(\Omega_S\tau) = +2\mathbf{I}_x\mathbf{S}_x \sin(\Omega_S 2\tau)$

$-2\mathbf{I}_x\mathbf{S}_y\cos(\Omega_S\tau)\cos(\Omega_S\tau) + 2\mathbf{I}_x\mathbf{S}_y\sin(\Omega_S\tau)\sin(\Omega_S\tau) = -2\mathbf{I}_x\mathbf{S}_y\cos(\Omega_S 2\tau)$

the final result is: $+2\mathbf{I}_x\mathbf{S}_y \Rightarrow$ echo $\Rightarrow -2\mathbf{I}_x\mathbf{S}_y\cos(\Omega_S 2\tau) + 2\mathbf{I}_x\mathbf{S}_x\sin(\Omega_S 2\tau)$

The heteronuclear coupling (J_{IS}) is decoupled but the chemical shift (Ω_s) has evolved. Ω_I doesn't evolve since it is refocused.

B. Homonuclear I, S

Consider: Ω_I, Ω_S and J_{IS}

The pulse sequence:

(e.g. ^{1}H, or ^{13}C) I and S -----τ----- $180°_y$ ------τ-----

input ⇒----------e c h o -------------⇒**output**

input : $\mathbf{I}_x$ [or $\mathbf{S}_x$] (in-phase transverse magnetization)

σ[0]	"echo starts"				$+\mathbf{I}_x$			
$\hat{H} = \hat{I}_z(\Omega_I\tau)$					↓			
			$+\mathbf{I}_x$				$+\mathbf{I}_y$	
$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$		↓				↓		
		$+\mathbf{I}_x$	$+2\mathbf{I}_y\mathbf{S}_z$			$+\mathbf{I}_y$	$-2\mathbf{I}_x\mathbf{S}_z$	
$\hat{H} = \pi\hat{I}_y$				↓				
		$-\mathbf{I}_x$	$+2\mathbf{I}_y\mathbf{S}_z$			$+\mathbf{I}_y$	$+2\mathbf{I}_x\mathbf{S}_z$	
$\hat{H} = \pi S_y$				↓				
		$-\mathbf{I}_x$	$-2\mathbf{I}_y\mathbf{S}_z$			$+\mathbf{I}_y$	$-2\mathbf{I}_x\mathbf{S}_z$	
$\hat{H} = \hat{I}_z(\Omega_I\tau)$		↓	↓			↓	↓	
	$-\mathbf{I}_x$	$-\mathbf{I}_y$	$-2\mathbf{I}_y\mathbf{S}_z$	$+2\mathbf{I}_x\mathbf{S}_z$	$+\mathbf{I}_y$	$-\mathbf{I}_x$	$-2\mathbf{I}_x\mathbf{S}_z$	$-2\mathbf{I}_y\mathbf{S}_z$

memo 22. $-\mathbf{I}_y \cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau) + \mathbf{I}_y \sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau) = 0$

memo 23. $+2\mathbf{I}_x\mathbf{S}_z \cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau) - 2\mathbf{I}_x\mathbf{S}_z \sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau) = 0$

memo 24. $-\mathbf{I}_x \cos(\pi J_{IS}\tau)[\cos^2(\Omega_I\tau) + \sin^2(\Omega_I\tau)] = -\mathbf{I}_x \cos(\pi J_{IS}\tau)$

memo 25. $-2\mathbf{I}_y\mathbf{S}_z \sin(\pi J_{IS}\tau)[\cos^2(\Omega_I\tau) + \sin^2(\Omega_I\tau)] = -2\mathbf{I}_y\mathbf{S}_z \sin(\pi J_{IS}\tau)$

$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$

$-\mathbf{I}_x \downarrow$ $\quad$ $-2\mathbf{I}_y\mathbf{S}_z \downarrow$

$-\mathbf{I}_x \quad -2\mathbf{I}_y\mathbf{S}_z \quad -2\mathbf{I}_y\mathbf{S}_z \quad +\mathbf{I}_x$

memo 26: / $\cos^2 A - \sin^2 A = \cos 2A$ */*

$-\mathbf{I}_x \cos(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau) + \mathbf{I}_x \sin(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)\} = -\mathbf{I}_x \cos(\pi J_{IS} 2\tau)$

memo 27: / $2\cos A \sin A = \sin 2A$ */*

$-2\mathbf{I}_y\mathbf{S}_z \cos(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau) - 2\mathbf{I}_y\mathbf{S}_z \sin(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau) = -2\mathbf{I}_y\mathbf{S}_z \sin(\pi J_{IS}2\tau)$

final result: $+\mathbf{I}_x \Rightarrow \text{echo} \Rightarrow -\mathbf{I}_x \cos(\pi J_{IS}2\tau) - 2\mathbf{I}_y\mathbf{S}_z \sin(\pi J_{IS}2\tau)$

due to symmetry: $+\mathbf{S}_x \Rightarrow \text{echo} \Rightarrow -\mathbf{S}_x \cos(\pi J_{IS}2\tau) - 2\mathbf{I}_z\mathbf{S}_y \sin(\pi J_{IS}2\tau)$

(The homonuclear coupling (J_{IS}) has evolved but the chemical shift (neither Ω_I nor Ω_S) hasn't evolved.)

input : $2I_xS_z$ (anti-phase magnetization on spin I)

$\sigma[0]$ "echo starts" $+2I_xS_z$ $\downarrow$

$\hat{H} = I_z(\Omega_I\tau)$

$+2I_xS_z$ $+2I_yS_z$

$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$ $\downarrow$ $\downarrow$

$+2I_xS_z$ $+I_y$ $+2I_yS_z$ $-I_x$

$\hat{H} = \pi\hat{I}_y$ $\downarrow$

$-2I_xS_z$ $+I_y$ $+2I_yS_z$ $+I_x$

$\hat{H} = \pi S_y$ $\downarrow$

$+2I_xS_z$ $+I_y$ $-2I_yS_z$ $+I_x$

$\hat{H} = I_z(\Omega_I\tau)$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$

$+2I_xS_z$ $+2I_yS_z$ $+I_y$ $-I_x$ $-2I_yS_z$ $+2I_xS_z$ $+I_x$ $+I_y$

$\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$

$[+2I_xS_z, +I_y]$ $[+I_y, -2I_xS_z]$ $[-2I_yS_z, +I_x]$ $[+I_x, +2I_yS_z]$

$[+2I_yS_z, -I_x]$ $[-I_x, -2I_yS_z]$ $[+2I_xS_z, +I_y]$ $[+I_y, -2I_xS_z]$

$+2I_xS_z$ $\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$+I_y$ $\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$+2I_yS_z$ $\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$-I_x$ $\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$+I_y$ $\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$-2I_xS_z$ $\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$-I_x$ $\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$-2I_yS_z$ $\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$-2I_yS_z$ $\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$+I_x$ $\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$+2I_xS_z$ $\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$+I_y$ $\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$+I_x$ $\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$+2I_yS_z$ $\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

$+I_y$ $\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau)\cos(\pi J_{IS}\tau)$

$-2I_xS_z$ $\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I\tau)\sin(\pi J_{IS}\tau)$

The in-phase term $\mathbf{I}_x$ and the anti-phase $\mathbf{-2I}_y\mathbf{S}_z$ add up to zero.

the final result is: $+2\mathbf{I}_x\mathbf{S}_z \Rightarrow \text{echo} \Rightarrow +2\mathbf{I}_x\mathbf{S}_z\cos(\pi J_{IS}2\tau) \;\; +\mathbf{I}_y \sin(\pi J_{IS}2\tau)$

due to symmetry: $+2\mathbf{I}_z\mathbf{S}_x \Rightarrow \text{echo} \Rightarrow +2\mathbf{I}_z\mathbf{S}_x\cos(\pi J_{IS}2\tau) \;\; +\mathbf{S}_y \sin(\pi J_{IS}2\tau)$

(The homonuclear coupling (J_{IS}) has evolved but the chemical shift (neither Ω_I nor Ω_S) hasn't evolved.)

input : $2I_xS_y$ (multiple-quantum coherence)

$\sigma[0]$ "echo starts" $+2I_xS_y$

$\hat{H} = S_z(\Omega_S\tau)$ ↓

$+2I_xS_y$ $-2I_xS_x$

$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$ ↓ ↓

$+2I_xS_y$ $-2I_xS_x$

$\hat{H} = \pi\hat{I}_y$ ↓ ↓

$-2I_xS_y$ $+2I_xS_x$

$\hat{H} = \pi S_y$ ↓ ↓

$-2I_xS_y$ $-2I_xS_x$

$\hat{H} = S_z(\Omega_S\tau)$ ↓ ↓

$-2I_xS_y$ $+2I_xS_x$ $-2I_xS_x$ $-2I_xS_y$

$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi\tau)$ ↓

$-2I_xS_y$ $+2I_xS_x$ $-2I_xS_x$ $-2I_xS_y$

memo 28: The two multiple-quantum terms $+2I_xS_x$ and $-2I_xS_x$ add up to zero, as follows: $+2I_xS_x\cos(\Omega_S\tau)\sin(\Omega_S\tau)$ $-2I_xS_x\sin(\Omega_S\tau)\cos(\Omega_S\tau) = 0$

The remaining term is the $-2I_xS_y$

the final result is: $+2I_xS_y \Rightarrow$ echo $\Rightarrow -2I_xS_y$

Nor the homonuclear coupling (J_{IS}) neither the chemical shift (Ω_I or Ω_S) evolve.

Summary

A. Heteronuclear I, S

The pulse sequence:

(e.g. ^1H)	I	-----τ----- 180°y ------τ-----
(e.g. ^{15}N)	S	-----τ-------------------τ-----
	input => ----------e c h o ------------- => **output**	

coherence type	input	output	comment
			J_{IS} doesn't evolve at all
in-phase on I	$+I_x$	$-I_x$	chemical shift doesn't evolve!
in-phase on S	$+S_x$	$+S_x\cos(\Omega_S 2\tau) + S_y\sin(\Omega_S 2\tau)$	chemical shift evolves
anti-phase on S	$+2I_zS_x$	$-2I_zS_x\cos(\Omega_S 2\tau) -2I_zS_y\sin(\Omega_S 2\tau)$	chemical shift evolves
anti-phase on I	$+2I_xS_z$	$-2I_xS_z$	chemical shift doesn't evolve !
multiple quantum	$+2I_xS_y$	$-2I_xS_y\cos(\Omega_S 2\tau) +2I_xS_x\sin(\Omega_S 2\tau)$	chemical shift evolves

Summary

B. Homonuclear I, S

The pulse sequence:

(e.g. ^{1}H) I,S -----τ----- 180°y ------τ-----

input => ----------e c h o -------------- => **output**

coherence type	input	output	comment
			chemical shift doesn't evolve at all
in-phase on I	$+I_x$	$-I_x\cos(\pi J_{IS}2\tau) - 2I_yS_z\sin(\pi J_{IS}2\tau)$	J_{IS} evolves
in-phase on S	$+S_x$	$-S_x\cos(\pi J_{IS}2\tau) - 2I_zS_y\sin(\pi J_{IS}2\tau)$	J_{IS} evolves
anti-phase on S	$+2I_zS_x$	$+2I_zS_x\cos(\pi J_{IS}2\tau) + S_y\sin(\pi J_{IS}2\tau)$	J_{IS} evolves
anti-phase on I	$+2I_xS_z$	$+2I_xS_z\cos(\pi J_{IS}2\tau) + I_y\sin(\pi J_{IS}2\tau)$	J_{IS} evolves
multiple quantum	$+2I_xS_y$	$-2I_xS_y$	J_{IS} doesn't evolve

Application of homonuclear spin-echo for coherence transfer:

As shown above:

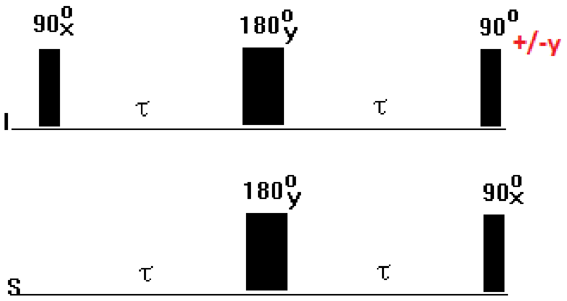
coherence type	input	output
in-phase on I	$+I_x$	$-I_x\cos(\pi J_{IS}2\tau) - 2I_yS_z\sin(\pi J_{IS}2\tau)$

If τ is set smartly with respect to J_{IS} ($\tau = 1/(4J)$), then the cos term gets 0 and the sin equals to 1:

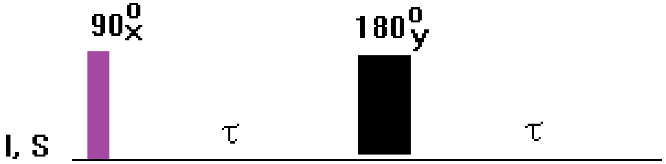
coherence type	input	output
in-phase on I	$+I_x$	$- 2I_yS_z$

Thus from in-phased I-type coherence (*e.g.* +Ix) a homonulcelar echo can generate an anti-phased I-type coherence (*e.g.* $-2\mathbf{I}_y\mathbf{S}_z$) coherence.

Indeed an INEPT type pulse (homo echo + two 90º(s)) transfers coherence form I to S.

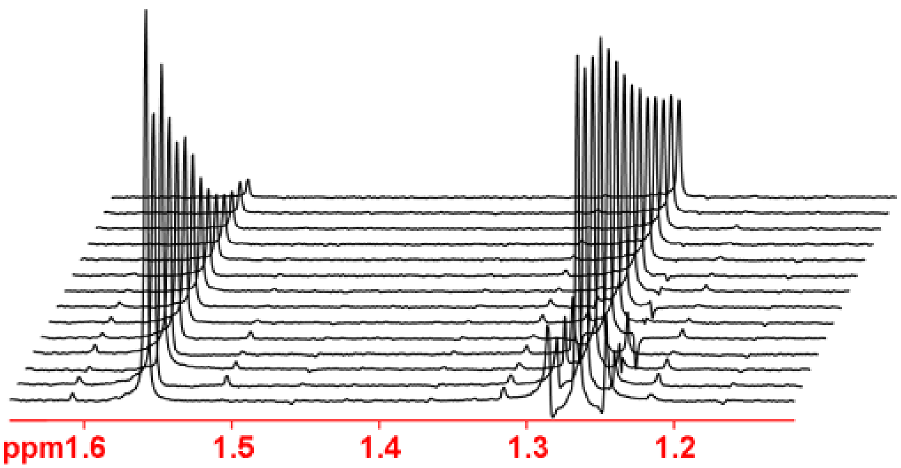


Application of spin-echo: measuring T_2



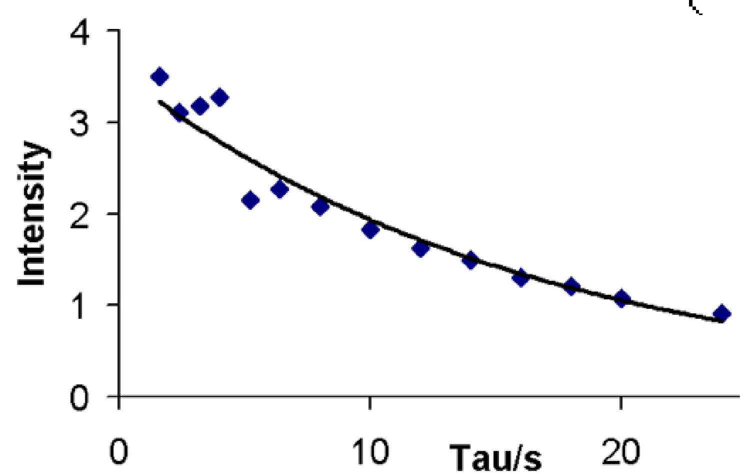
R_2 **or** $(T_2)^{-1}$ is the transverse (or spin-spin) relaxation rate constant associated with the relaxation of the *x,y* components of the excited magnetization vector. The CPMG (Carr-Purcell-Meiboom-Gill) (T_2) experiment is to determine T2 values, based on a spin-echo experiment best for singlets.

$$\mathbf{M} = \mathbf{M}_0 \exp\left(\frac{-\tau}{T_2}\right)$$



1H spin-echo experiments of ethylbenzene (0.1%) in CDCl3 at 400 MHz. The residual water peak (left) relaxes faster than that of the methyl (right).

$$I_0 \exp\left(\frac{-\tau}{T_2}\right)$$

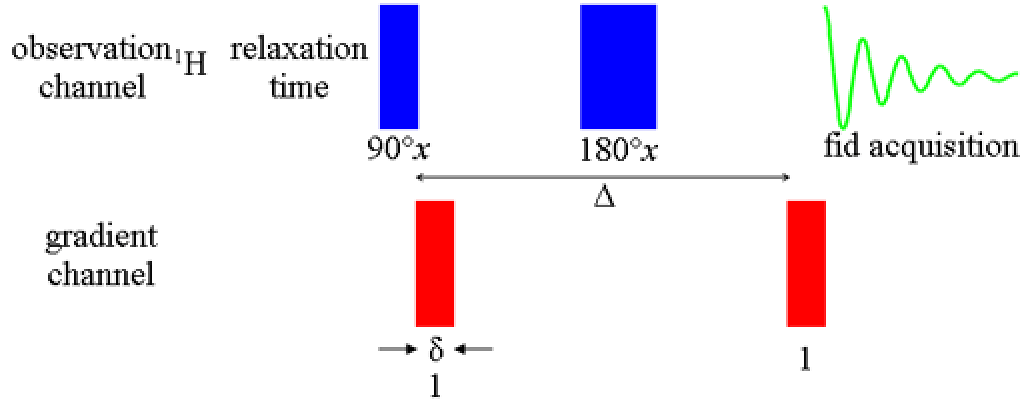


Exponential decay curve for the methyl protons of ethylbenzene.

http://chem.ch.huji.ac.il/nmr/index.html

Application of spin-echo: DOSY

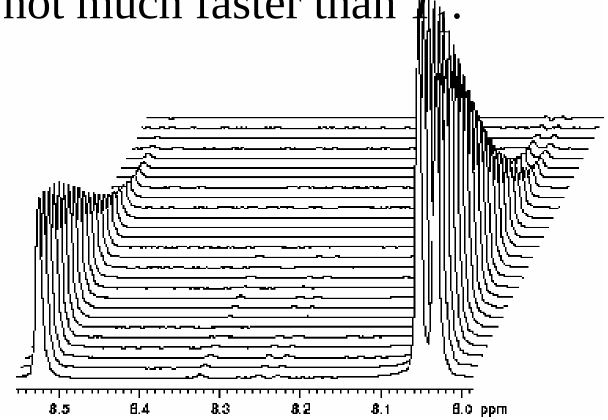
Using spin-echo and gradient pulses one can measuring self-diffusion constant of molecules (aggregates up to micelles). Pulsed Gradient Spin Echo (PGSE) is the simplest approach best for singlets especially if T_2 is not much faster than T_1.



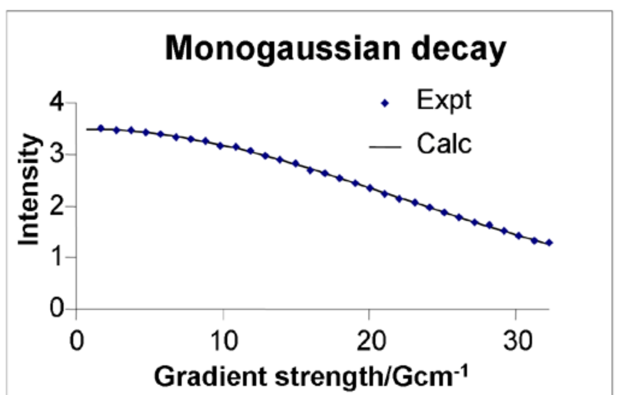
During such an experiment, delays are kept constant and the experiment is repeated several times (e.g. 32) while incrementing the gradient strength (5%<<95%).
The diffusion constant, D, **is extracted from the** plot made from the intensity against gradient strength.
The intensity, *I*, is proportional to

$$\exp\left[-(\gamma g\delta)^2 D\left(\Delta-\frac{\delta}{3}\right)\right]$$

γ (gyromagnetic ratio), g (gradient strength), δ and Δ are delays



A „diffusion spectrum”, where the left peak decays faster (higher diffusion constant) than that on the right.



Gaussian fit to diffusion peak intensity

http://chem.ch.huji.ac.il/nmr/index.html