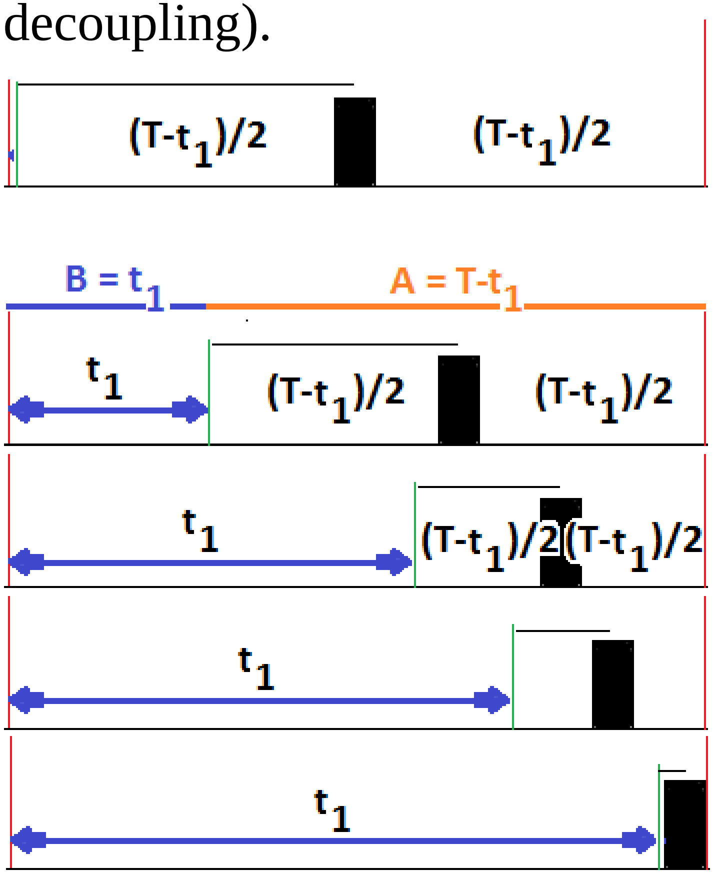
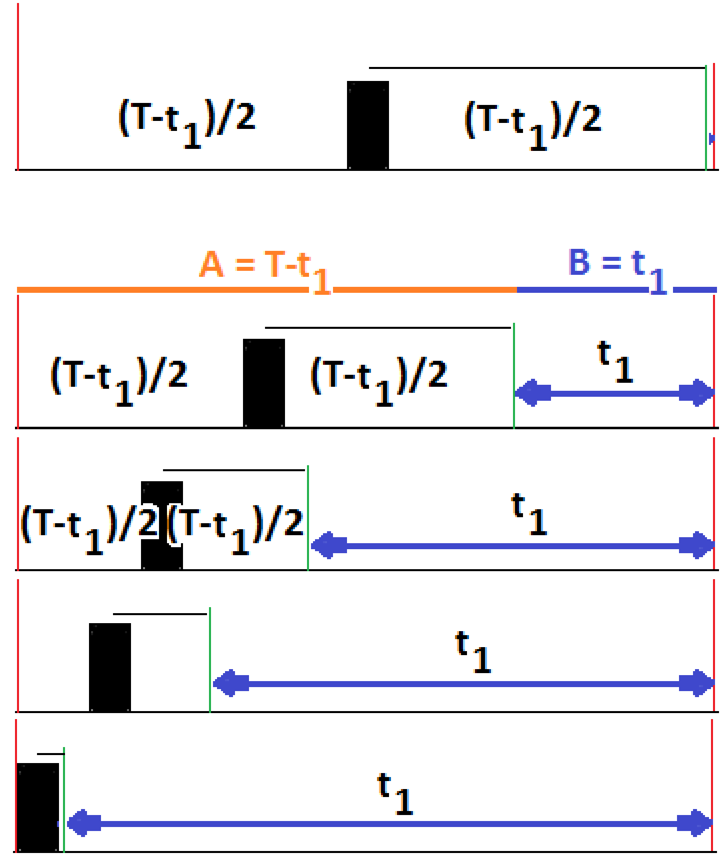
The Constant-Time module

The **ultimate goal** of the CT module is to **eliminate homonuclear coupling**, a more difficult task than to remove heteronulear coupling (*e.g. via* broadband decoupling).



180° pulse moved
from the center to the right

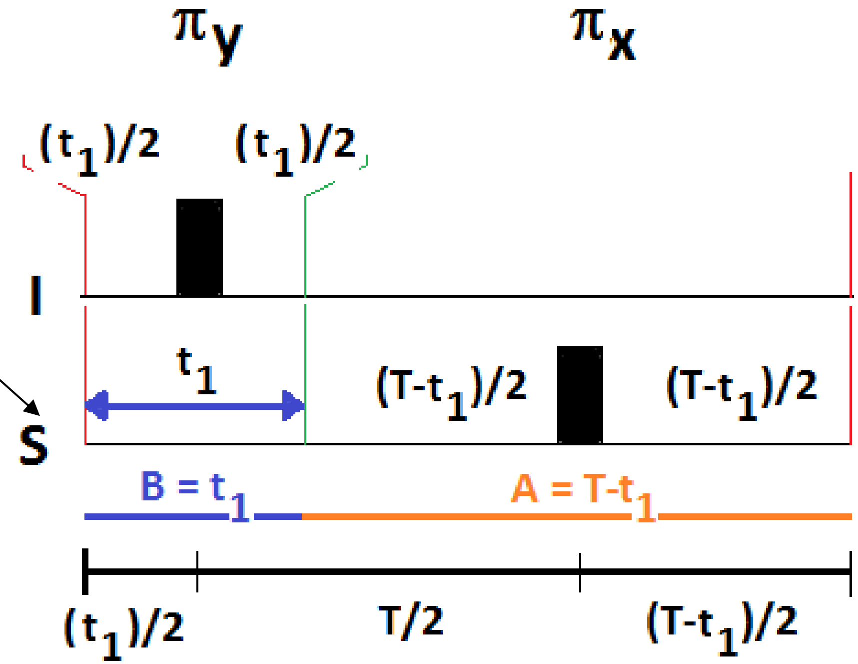


180° pulse moved from the center to the left

Both approaches are equivalent solutions of the same problem

input : $-2I_zS_y$

(anti-phase magnetization on spin S) *e.g.* this is the case in HNCA: before t_1 σ is $\mathbf{-2H_zN_y}$



A) chemical shift only

$\sigma[0]$ "CT-increment starts,, $\mathbf{-2I_zS_y}$

Hem. = $S_z(\Omega_S[t_1/2])$ ↓

$\mathbf{-2I_zS_y}$ | $\mathbf{+2I_zS_x}$

Hem. = $\pi\hat{I}_y$ ↓ | ↓

$\mathbf{+2I_zS_y}$ | $\mathbf{-2I_zS_x}$

Hem. = $S_z(\Omega_S[T/2])$ ↓ | ↓

$\mathbf{+2I_zS_y}$ | $\mathbf{-2I_zS_x}$ | $\mathbf{-2I_zS_x}$ | $\mathbf{-2I_zS_y}$

Hem. = πS_x ↓ ↓ ↓ ↓

$\mathbf{-2I_zS_y}$ | $\mathbf{-2I_zS_x}$ | $\mathbf{-2I_zS_x}$ | $\mathbf{+2I_zS_y}$

Hem. = $S_z(\Omega_S[(T-t_1)/2])$ ↓ ↓ ↓ ↓

$\sigma[t]$ "CT-increment ends"

$\mathbf{-2I_zS_y}$ $\mathbf{+2I_zS_x}$ | $\mathbf{-2I_zS_x}$ $\mathbf{-2I_zS_y}$ | $\mathbf{-2I_zS_x}$ $\mathbf{-2I_zS_y}$ | $\mathbf{+2I_zS_y}$ $\mathbf{-2I_zS_x}$

$\sigma[t]$ "CT-increment ends"

$\mathbf{-2I_zS_y}$ $\mathbf{+2I_zS_x}$ $\mathbf{-2I_zS_x}$ $\mathbf{-2I_zS_y}$ $\mathbf{-2I_zS_x}$ $\mathbf{-2I_zS_y}$ $\mathbf{+2I_zS_y}$ $\mathbf{-2I_zS_x}$

If $\Omega_S[t_1/2] = A$, $\Omega_S[T/2] = B$ and $\Omega_S[T/2-t_1/2] = B-A$.

memo: $\cos(B-A) = \cos(B)\cos(A) + \sin(B)\sin A)$

$\sin(B-A) = \sin(B)\cos(A) - \cos(B)\sin(A)$

i) The four $2I_zS_y$ terms add up as follows:

$\mathbf{-2I_zS_y}\cos(A)*\cos(B)*\cos(B-A)=$	$-\cos^2(A)*\cos^2(B)$	$-\cos(A)*\cos(B)*\sin(A)*\sin(B)$
$\mathbf{-2I_zS_y}\cos(A)*\sin(B)*\sin(B-A) =$	$-\cos^2(A)*\sin^2(B)$	$+\cos(A)*\cos(B)*\sin(A)*\sin(B)$
$\mathbf{-2I_zS_y}\sin(A)*\cos(B)*\sin(B-A) =$	$-\cos(A)*\cos(B)*\sin(A)*\sin(B)$	$+\sin^2(A)*\cos^2(B)$
$\mathbf{+2I_zS_y}\sin(A)*\sin(B)*\cos(B-A)=$	$+\cos(A)*\cos(B)*\sin(A)*\sin(B)$	$+\sin^2(A)*\sin^2(B)$

The squared terms remain, the other 4 cancels out.

$-\cos^2(A)*\cos^2(B)+\sin^2(A)*\cos^2(B)-\cos^2(A)*\sin^2(B)+\sin^2(A)*\sin^2(B) =$

$= -\cos^2(B)\{\cos^2(A)-\sin^2(A)\}-\sin^2(B)\{\cos^2(A)-\sin^2(A)\} =$

$= -\cos^2(B)*\cos(2A)-\sin^2(B)*\cos(2A) =$

$= -\cos(2A)\{\cos^2(B)+\sin^2(B)\} =$

$= -\cos(2A)$ $\rightarrow +2I_zS_y*(-\cos(2\Omega_S[t_1/2])$

In summary : $\mathbf{-2I_zS_y\cos(\Omega_S t_1)}$

σ[t] "CT-increment ends"

$-2I_zS_y$ $+2I_zS_x$ $-2I_zS_x$ $-2I_zS_y$ $-2I_zS_x$ $-2I_zS_y$ $+2I_zS_y$ $-2I_zS_x$

If $\Omega_S[t_1/2] = A$, $\Omega_S[T/2] = B$ and $\Omega_S[T/2-t_1/2]= B-A$.

memo: cos(B-A) = cos(B)cos(A) + sin(B)sinA)

sin(B-A) = sin(B)cos(A) - cos(B)sin(A)

ii) The four $2I_zS_x$ terms add up as follows:

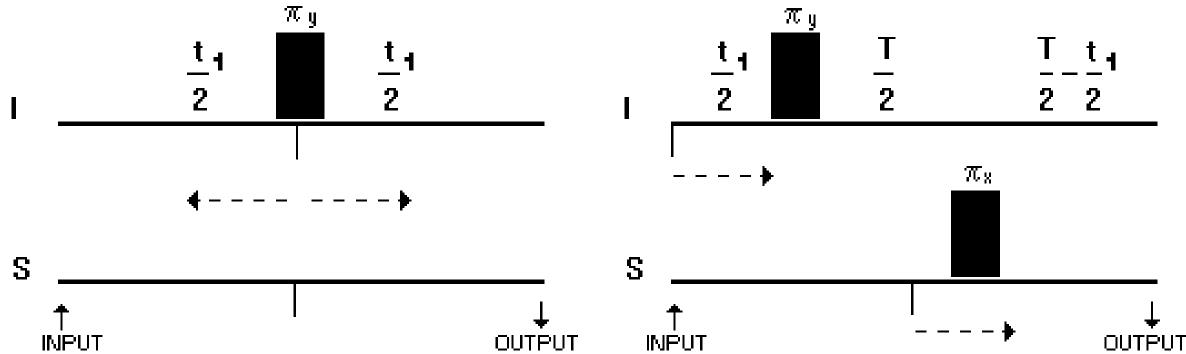
$+2I_zS_x$ cos(A)*cos (B)*sin(B-A) = +cos^2(A)*cos(B)*sin(B) -cos(A)*cos^2(B)*sin(A)
$-2I_zS_x$ cos(A)*sin (B)*cos(B-A) = -cos^2(A)*sin(B)*cos(B) -cos(A)*sin(A)*sin^2(B)
$-2I_zS_x$ sin(A)*cos (B)*cos(B-A) = -cos(A)*cos^2(B)*sin(A) -sin^2(A)*cos(B)*sin(B)
$-2I_zS_x$ sin(A)*sin (B)*sin (B-A) = -cos(A)*sin(A)*sin^2(B) +sin^2(A)*sin(B)*cos(B)

since +cos^2(A)*cos(B)*sin(B)-cos^2(A)*sin(B)*cos(B) = 0
-sin^2(A)*cos(B)*sin(B)+sin^2(A)*sin(B)*cos(B) = 0
and -2*cos(A)*cos^2(B)*sin(A)-2*cos(A)*sin(A)*sin^2(B) =
= -2cos(A)*sin(A){cos^2(B)+sin^2(B)} =
= -2*cos(A)*sin(A) =

-sin(2A) → $+2I_zS_x*(-\sin(2\Omega_S[t_1/2])$

In summary: $+2I_zS_x \sin(\Omega_S t_1)$

Thus, chemical shift (offset) evolves : $-2I_zS_y \cos(\Omega_S t_1) + 2I_zS_x \sin(\Omega_S t_1)$



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

B) J_{IS} coupling only

$\sigma[0]$ "CT-increment starts" $\quad$ $\mathbf{-2I_zS_y}$

Hem. = $2I_zS_z(J_{IS}\,\pi\,[t_1/2])$ $\downarrow$

$\mathbf{-2I_zS_y}$ $\quad$ $+\,\mathbf{S_x}$

Hem. = $\pi\hat{I}_y$ $\quad\downarrow\quad\downarrow$

$\mathbf{+2I_zS_y}$ $\quad$ $+\,\mathbf{S_x}$

Hem. = $2I_zS_z(J_{IS}\,\pi[T/2])$ $\quad\downarrow\quad\downarrow$

$\mathbf{+2I_zS_y}$ $\quad$ $\mathbf{-S_x}$ $\quad$ $\mathbf{+S_x}$ $\quad$ $\mathbf{+2I_zS_y}$

Hem. = πS_x $\quad\downarrow\quad\downarrow\quad\downarrow\quad\downarrow$

$\mathbf{-2I_zS_y}$ $\quad$ $\mathbf{-S_x}$ $\quad$ $\mathbf{+S_x}$ $\quad$ $\mathbf{-2I_zS_y}$

Hem. = $2I_zS_z(J_{IS}\,\pi\,[T/2-t_1/2])$ $\quad\downarrow\quad\downarrow\quad\downarrow\quad\downarrow$

$\sigma[t]$ "CT-increment ends"

$\mathbf{-2I_zS_y}$ $\quad$ $\mathbf{+S_x}$ $\quad$ $\mathbf{-S_x}$ $\quad$ $\mathbf{-2I_zS_y}$ $\quad$ $\mathbf{+S_x}$ $\quad$ $\mathbf{+2I_zS_y}$ $\quad$ $\mathbf{-2I_zS_y}$ $\quad$ $\mathbf{+S_x}$

σ[t] "CT-increment ends"

$-2I_zS_y$ $+S_x$ $-S_x$ $-2I_zS_y$ $+S_x$ $+2I_zS_y$ $-2I_zS_y$ $+S_x$

If $J_{IS}\pi[t_1/2] = A$, $J_{IS}\pi[T/2] = B$ and $J_{IS}\pi[T/2 - t_1/2] = B - A$.

memo: $\cos(B-A) = \cos(B)\cos(A)+\sin(B)\sin(A)$

$\sin(B-A) = \sin(B)\cos(A)-\cos(B)\sin(A)$

i) The four $2I_zS_y$ terms add up as follows:

$-2I_zS_y \cos(A)*\cos(B)*\cos(B-A) = -\cos^2(A)*\cos^2(B) -\cos(A)*\cos(B)*\sin(A)*\sin(B)$

$-2I_zS_y \cos(A)*\sin(B)*\sin(B-A) = -\cos^2(A)*\sin^2(B) +\cos(A)*\cos(B)*\sin(A)*\sin(B)$

$+2I_zS_y \sin(A)*\cos(B)*\sin(B-A) = +\cos(A)*\cos(B)*\sin(A)*\sin(B) -\sin^2(A)*\cos^2(B)$

$-2I_zS_y \sin(A)*\sin(B)*\cos(B-A) = -\cos(A)*\cos(B)*\sin(A)*\sin(B) -\sin^2(A)*\sin^2(B)$

The square terms remain the other cancels out.

$-\cos^2(A)*\{\cos^2(B)+\sin^2(B)\} -\sin^2(A)\{\cos^2(B)+\sin^2(A)\} =$

$= -1*[\cos^2(A)+\sin^2(A)] = -1 \rightarrow +2I_zS_y(-1)$

In summary: $-2I_zS_y$

The same as the input was, thus coupling has no effect

σ[t] "CT-increment ends"

$-2I_zS_y$ $+S_x$ $-S_x$ $-2I_zS_y$ $+S_x$ $+2I_zS_y$ $-2I_zS_y$ $+S_x$

If $J_{IS}\pi[t_1/2]$= A, $J_{IS}\pi[T/2]$= B and $J_{IS}\pi[T/2-t_1/2]$= B-A.

memo: cos(B-A) = cos(B)cos(A)+sin(B)sin(A)
sin(B-A) = sin(B)cos(A)-cos(B)sin(A)

ii) The four S_x terms add up as follows:

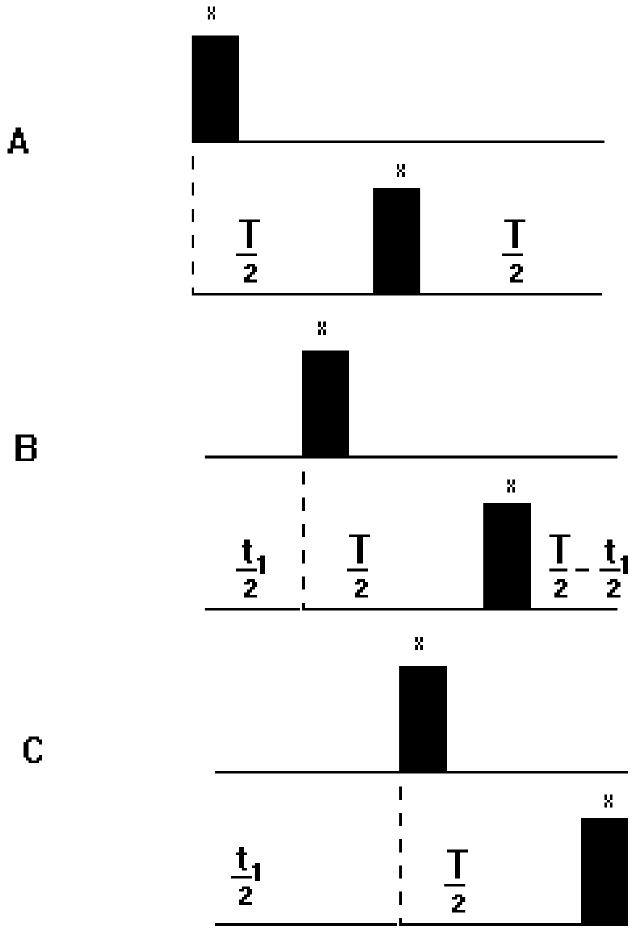
$+S_x$ cos(A)*cos(B)*sin(B-A) = $+\cos^2$(A)*cos(B)*sin(B) -cos(A)*$\cos^2$(B)*sin(A)
$-S_x$ cos(A)*sin(B)*cos(B-A) = $-\cos^2$(A)*sin(B)*cos(B) -cos(A)*sin(A)*$\sin^2$(B)
$+S_x$ sin(A)*cos(B)*cos(B-A) = +cos(A)*$\cos^2$(B)*sin(A)+$\sin^2$(A)*cos(B)*sin(B)
$+S_x$ sin(A)*sin(B)*sin(B-A) = +cos(A)*sin(A)*$\sin^2$(B)-$\sin^2$(A)*sin(B)*cos(B)

since $+\cos^2$(A)*cos(B)*sin(B)-$\cos^2$(A)*sin(B)*cos(B) =0
$-\sin^2$(A)*cos(B)*sin(B)+$\sin^2$(A)*sin(B)*cos(B) =0
and +cos(A)*sin(A)-cos(A)*sin(A) =**0**

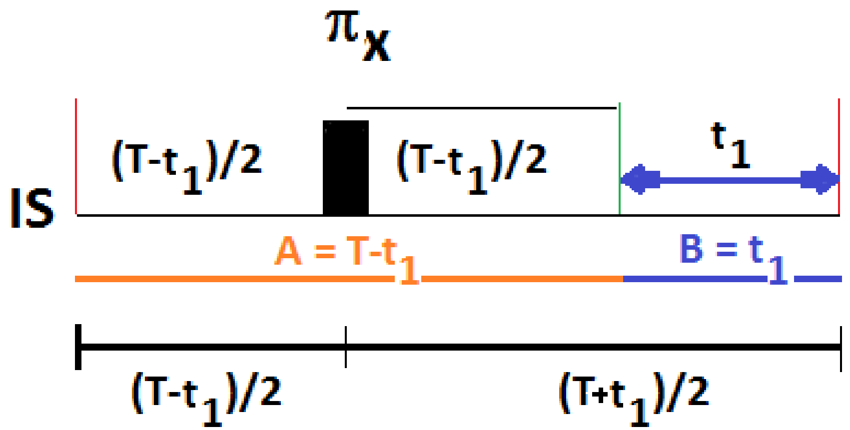
therefore: S_x term doesn't appear.

In conclusion:
no modulation by J_{IS} but chemical shift evolves: $-2I_zS_y$ --- > $-2I_zS_y \cos(\Omega_S t_1)$ $+2I_zS_x \sin(\Omega_S t_1)$

memo: the result is the same as obtained from a **hetero nuclear echo** experiment (the sign difference of the ***$2I_zS_y$* term {minus in the CT exp. and plus in the echo} is to be neglected, since the sign is unimportant here. [Just a phasing question.])**



ntifazisu S (pl. IzSx) allapotra kifejteni
CT, ez van most és ha CT-vel keszitjuk a
C, HNCA) , de lehet hogy az echo
sszevetni viszont akkor konyebb ha egy
is megnezzuk?
meg kellene csinalni valamikor



I) chemical shift only $\alpha = [\Omega_I(T-t_1)/2]$, $\beta = [\Omega_I(T+t_1)/2]$

σ[0] "CT-increment starts,, $-\mathbf{I}_y$

Hem. = $I_z(\alpha)$ ↓

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

Hem. = $\pi\hat{I}_x$ ↓ ↓

$+\mathbf{I}_y\cos(\alpha)$ $+\mathbf{I}_x\sin(\alpha)$

Hem. = $I_z(\beta)$ ↓ ↓

$+\mathbf{I}_y\cos(\alpha)\cos(\beta)$ $-\mathbf{I}_x\cos(\alpha)\sin(\beta)$ $+\mathbf{I}_x\sin(\alpha)\cos(\beta)$ $+\mathbf{I}_y\sin(\alpha)\sin(\beta)$

σ[t] "CT-increment ends"

$+\mathbf{I}_x\sin(\alpha-\beta) + \mathbf{I}_y\cos(\alpha-\beta)$

1) Homonuclear J_{IS} evolves under T time
2) Offset is refocused in $2\tau=T$ but evolves only during t_1 (which is incremented) => chem. shift

Start with Z magnetization	I_z	
Hamiltonian: $I_x(\pi/2)$	$-I_y$	
Hamiltonian: $2I_zS_z(\pi J_{IS}\tau)$	$-I_y\cos(\pi J_{IS}\tau)$	$+2I_xS_z\sin(\pi J_{IS}\tau)$
Hamiltonian: $I_x(\pi)$	$+I_y\cos(\pi J_{IS}\tau)$	$+2I_xS_z\sin(\pi J_{IS}\tau)$
Hamiltonian: $S_x(\pi)$	$+I_y\cos(\pi J_{IS}\tau)$	$-2I_xS_z\sin(\pi J_{IS}\tau)$
Hamiltonian: $2I_zS_z(\pi J_{IS}\tau)$	$+I_y\cos(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)$ $-2I_xS_z\cos(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)$	$-2I_xS_z\sin(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)$ $-I_y\sin(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)$
Hamiltonian: $I_z(\Omega_I t_1)$	$+I_y\cos(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I t_1)$ $-I_x\cos(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I t_1)$ $-2I_xS_z\cos(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I t_1)$ $-2I_yS_z\cos(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I t_1)$	$-2I_xS_z\sin(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)\cos(\Omega_I t_1)$ $-2I_yS_z\sin(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)\sin(\Omega_I t_1)$ $-I_y\sin(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)\cos(\Omega_I t_1)$ $+I_x\sin(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)\sin(\Omega_I t_1)$

$2[-2I_xS_z\cos(\Omega_I t_1)\cos(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)]$ $\quad +I_y\cos(\Omega_I t_1)[\cos(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)-\sin(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)]$

$2[-2I_yS_z\sin(\Omega_I t_1)\cos(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)]$ $\quad +I_x\sin(\Omega_I t_1)[\sin(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)-\cos(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)]$

$+I_y\cos(\Omega_I t_1)[\cos(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)-\sin(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)]$ $\quad -2I_xS_z\cos(\Omega_I t_1)2[\cos(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)]$

$+I_x\sin(\Omega_I t_1)[\sin(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)-\cos(\pi J_{IS}\tau)\cos(\pi J_{IS}\tau)]$ $\quad -2I_yS_z\sin(\Omega_I t_1)2[\cos(\pi J_{IS}\tau)\sin(\pi J_{IS}\tau)]$

$+I_y\cos(\Omega_I t_1)\cos(2\pi J_{IS}\tau)$ $\quad -2I_xS_z\cos(\Omega_I t_1)\sin(2\pi J_{IS}\tau)$

$-I_x\sin(\Omega_I t_1)\cos(2\pi J_{IS}\tau)$ $\quad -2I_yS_z\sin(\Omega_I t_1)\sin(2\pi J_{IS}\tau)$

Hamiltonian: $I_x(\pi/2)$ $\quad +I_z\cos(\pi J_{IS}T)\cos(\Omega_I t_1)$ $\quad -2I_xS_z\sin(\pi J_{IS}T)\cos(\Omega_I t_1)$

$-I_x\cos(\pi J_{IS}T)\sin(\Omega_I t_1)$ $\quad -2I_zS_z\sin(\pi J_{IS}T)\sin(\Omega_I t_1)$

Hamiltonian: $S_x(\pi/2)$ $\quad$ ~~$+I_z\cos(\pi J_{IS}T)\cos(\Omega_I t_1)$~~ $\quad$ ~~$+2I_xS_y\sin(\pi J_{IS}T)\cos(\Omega_I t_1)$~~

$-I_x\cos(\pi J_{IS}T)\sin(\Omega_I t_1)$ $\quad +2I_zS_y\sin(\pi J_{IS}T)\sin(\Omega_I t_1)$

$-I_x\cos(\pi J_{IS}T)\sin(\Omega_I t_1)$ $\quad +2I_zS_y\sin(\pi J_{IS}T)\sin(\Omega_I t_1)$

Hamiltonian: $I_z(\Omega_I t_2)$

$-I_x\cos(\pi J_{IS}T)\sin(\Omega_I t_1)\cos(\Omega_I t_2)$ $\quad +2I_zS_y\sin(\pi J_{IS}T)\sin(\Omega_I t_1)$

$-I_y\cos(\pi J_{IS}T)\sin(\Omega_I t_1)\sin(\Omega_I t_2)$

Hamiltonian: $S_z(\Omega_S t_2)$

$-I_x\cos(\pi J_{IS}T)\sin(\Omega_I t_1)\cos(\Omega_I t_2)$ $\quad +2I_zS_y\sin(\pi J_{IS}T)\sin(\Omega_I t_1)\cos(\Omega_S t_2)$

$-I_y\cos(\pi J_{IS}T)\sin(\Omega_I t_1)\sin(\Omega_I t_2)$ $\quad -2I_zS_x\sin(\pi J_{IS}T)\sin(\Omega_I t_1)\sin(\Omega_S t_2)$

Hamiltonian: $2I_zS_z(\pi J_{IS} t_2)$

$-I_x\cos(\pi J_{IS}T)\sin(\Omega_I t_1)\cos(\Omega_I t_2)\cos(\pi J_{IS} t_2)$ $\quad +2I_zS_y\sin(\pi J_{IS}T)\sin(\Omega_I t_1)\cos(\Omega_S t_2)\cos(\pi J_{IS} t_2)$

$-2I_xS_z\cos(\pi J_{IS}T)\sin(\Omega_I t_1)\cos(\Omega_I t_2)\sin(\pi J_{IS} t_2)$ $\quad -S_x\sin(\pi J_{IS}T)\sin(\Omega_I t_1)\cos(\Omega_S t_2)\sin(\pi J_{IS} t_2)$

$-I_y\cos(\pi J_{IS}T)\sin(\Omega_I t_1)\sin(\Omega_I t_2)\cos(\pi J_{IS} t_2)$ $\quad -2I_zS_x\sin(\pi J_{IS}T)\sin(\Omega_I t_1)\sin(\Omega_S t_2)\cos(\pi J_{IS} t_2)$

$+2I_xS_z\cos(\pi J_{IS}T)\sin(\Omega_I t_1)\sin(\Omega_I t_2)\sin(\pi J_{IS} t_2)$ $\quad -S_y\sin(\pi J_{IS}T)\sin(\Omega_I t_1)\sin(\Omega_S t_2)\sin(\pi J_{IS} t_2)$

Put on x axis

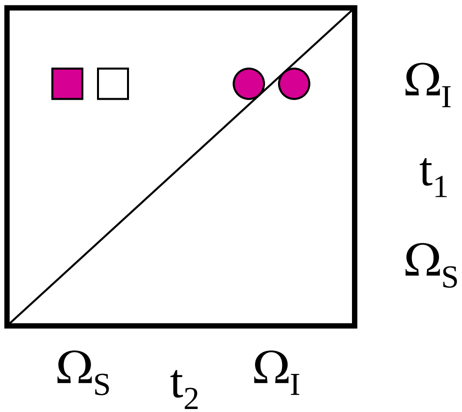
$-I_x\cos(\pi J_{IS}T)\sin(\Omega_I t_1)\cos(\Omega_I t_2)\cos(\pi J_{IS} t_2)$ $\quad -S_x\sin(\pi J_{IS}T)\sin(\Omega_I t_1)\cos(\Omega_S t_2)\sin(\pi J_{IS} t_2)$

$$-I_x[\cos(\pi J_{IS}T)\sin(\Omega_I t_1)+1/2[\cos\{(\Omega_I+\pi J_{IS})t_2\}+\cos\{(\Omega_I-\pi J_{IS})t_2\}]]$$

$$-S_x[\cos(\pi J_{IS}T)\sin(\Omega_I t_1)+1/2[\sin\{(\Omega_S+\pi J_{IS})t_2\}-\sin\{(\Omega_S-\pi J_{IS})t_2\}]]$$

$$-I_x[\cos(\pi J_{IS}T)\sin(\Omega_I t_1)+1/2[\cos\{(\Omega_I+\pi J_{IS})t_2\}+\cos\{(\Omega_I-\pi J_{IS})t_2\}]]$$
$$-S_x[\cos(\pi J_{IS}T)\sin(\Omega_I t_1)+1/2[\sin\{(\Omega_S+\pi J_{IS})t_2\}-\sin\{(\Omega_S-\pi J_{IS})t_2\}]]$$

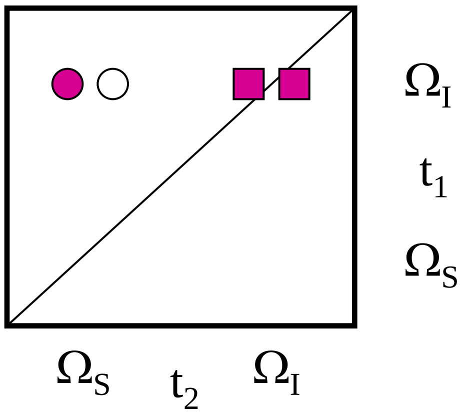
sin is absorptive in t_1 and cos is absorptive in t_2



$-I_x[\alpha+a+1/2(+a+a)]$ at Ω_I, Ω_I
$-S_x[\alpha+a+1/2(+d-d)]$ at Ω_I, Ω_S

so diagonal peaks are absorptive
and off-diagonals are dispersive in t_2
and no fine structure is seen in t_1

sin is absorptive in t_1 as well as in t_2



$-I_x[\alpha+a+1/2(+d+d)]$ at Ω_I, Ω_I
$-S_x[\alpha+a+1/2(+a-a)]$ at Ω_I, Ω_S

so diagonal peaks are dispersive
and off-diagonals are absorptive in t_2
and no fine structure is seen in t_1