ESEEM spectroscopy

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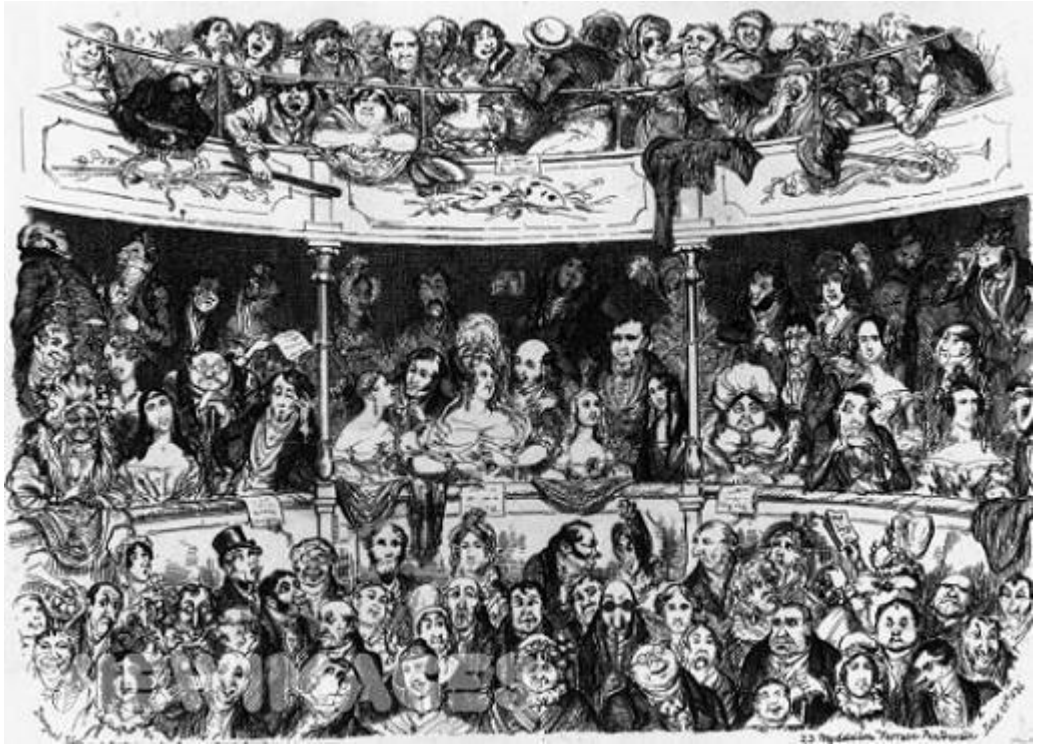
1. General concepts needed to understand ESEEM
2. Two-pulse ESEEM
3. Three-pulse ESEEM
4. Possible solutions to reduce overlap of signals
5. Four-pulse ESEEM
   - 5.1. HYSCORE
   - 5.2. DEFENCE
   - 5.3. Combination-peak experiment
6. Matched pulses
7. DONUT HYSCORE
8. Hyperfine-decoupling
9. Solving the cross-suppression effect
10. Future - ESEEM in the age of AWG

Full text: S. Van Doorslaer, Hyperfine spectroscopy: ESEEM, *eMagRes*, 2017, 6: 51–70.
DOI 10.1002/9780470034590.emrstm1517


THE EPR SCHOOL STUDENT &
HIS DAY'S WORK...
MYCARTOONS.ORG
TODAY'S
TO-DO LIST
1) MAKE
COFFEE
2) LEARN IN ONE
DAY WHAT TOOK MY
SUPERVISOR YEARS
& PRETEND I
UNDERSTAND
#1

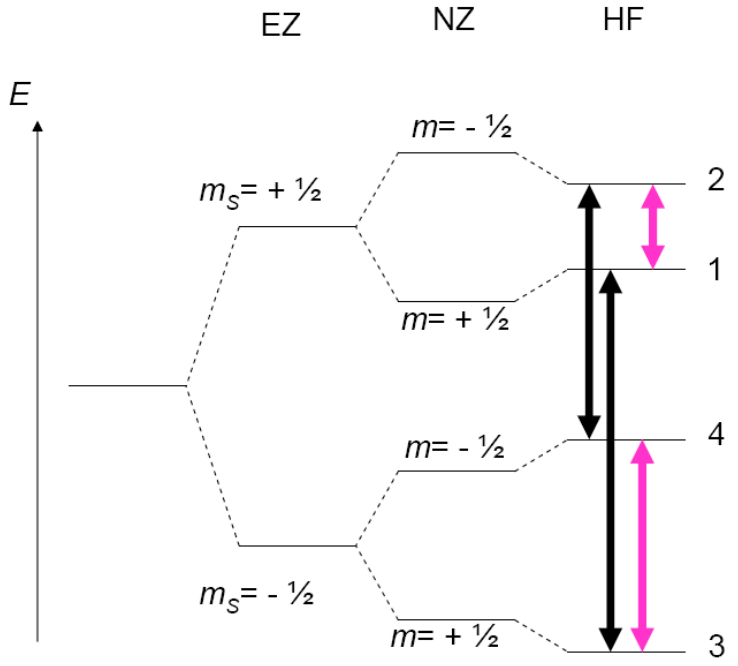

KEEP
CALM
AND
REPEAT
KeepCalmAndPosters.com

IF YOU HAVE QUESTION, PLEASE SHOUT

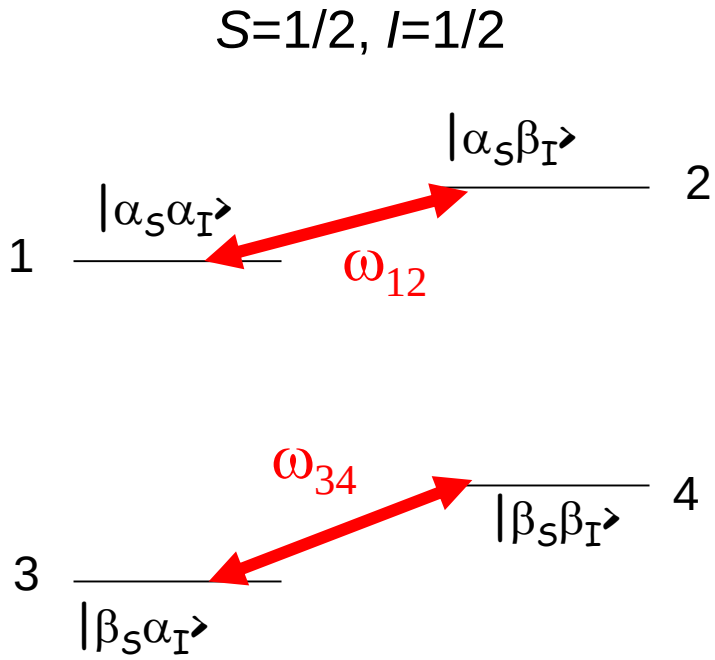


ESEEM = electron spin echo envelope modulation

Aim of ESEEM experiments =
measuring the nuclear frequencies
⇒ “hyperfine spectroscopy”
(remark: also ENDOR and ELDOR-detected NMR are hyperfine spectroscopies)



$$\hat{\mathcal{H}}_0 = \omega_S \hat{S}_z + \omega_I \hat{I}_z + \tilde{\boldsymbol{S}}\boldsymbol{A}\boldsymbol{I}$$



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Aim of ESEEM experiments =
measuring the nuclear frequencies
⇒ "hyperfine spectroscopy"
(remark: also ENDOR and ELDOR-detected NMR are hyperfine spectroscopies)

$$\hat{\mathcal{H}}_0 = \omega_S \hat{S}_z + \omega_I \hat{I}_z + A\hat{S}_z\hat{I}_z + B\hat{S}_z\hat{I}_x$$

$$\downarrow \quad \hat{U} = \exp(-i(\xi \hat{I}_y + \eta 2\hat{S}_z\hat{I}_y))$$

$$\hat{\mathcal{H}}_0^d = \omega_S \hat{S}_z + \omega_{12}\hat{S}^\alpha \hat{I}_z + \omega_{34}\hat{S}^\beta \hat{I}_z$$

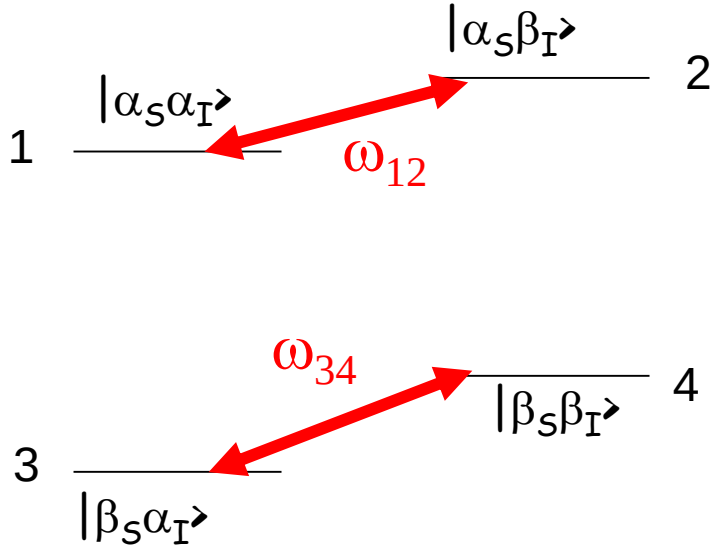
$$\omega_{12} = \left(\omega_I + \frac{A}{2}\right)\cos\eta_\alpha - \frac{B}{2}\sin\eta_\beta$$

$$\omega_{34} = \left(\omega_I - \frac{A}{2}\right)\cos\eta_\alpha + \frac{B}{2}\sin\eta_\beta$$

$$\eta_{\alpha,\beta} = \tan^{-1}\left(-\frac{\pm B/2}{\pm A/2 + \omega_I}\right) = \tan^{-1}\left(-\frac{m_S B}{m_S A + \omega_I}\right),$$

$$\xi = \frac{\eta_\alpha + \eta_\beta}{2}, \eta = \frac{\eta_\alpha - \eta_\beta}{2}$$

S=1/2, I=1/2

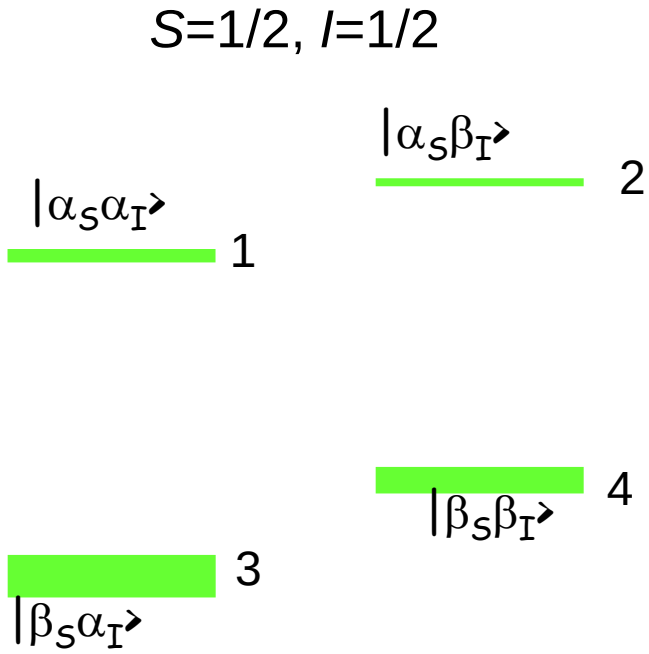


Schematic cartoon of the density matrix

This is the bookkeeper for the experiment

Populations / polarization

	$\lvert\alpha_S\alpha_I\rangle$	$\lvert\alpha_S\beta_I\rangle$	$\lvert\beta_S\alpha_I\rangle$	$\lvert\beta_S\beta_I\rangle$
$\langle\alpha_S\alpha_I\rvert$	P	NC	EC_a	EC_f
$\langle\alpha_S\beta_I\rvert$	NC	P	EC_f	EC_a
$\langle\beta_S\alpha_I\rvert$	EC_a	EC_f	P	NC
$\langle\beta_S\beta_I\rvert$	EC_f	EC_a	NC	P

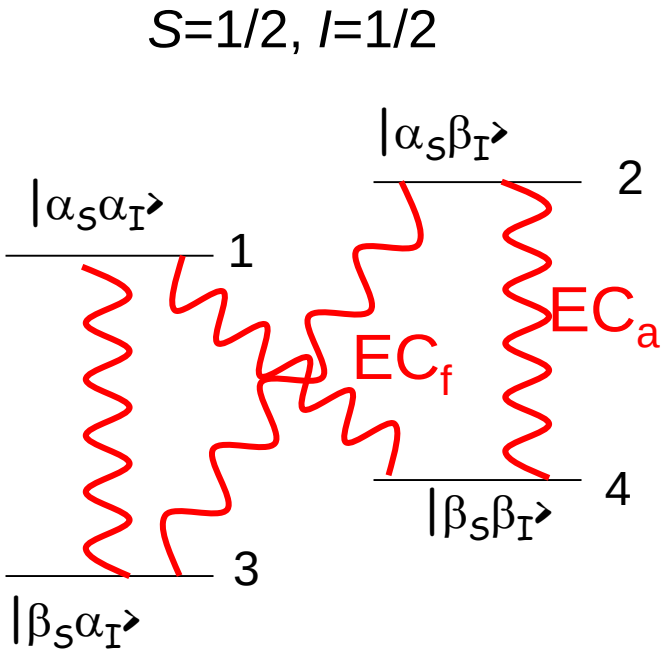


Schematic cartoon of the density matrix

This is the bookkeeper for the experiment

Electron coherences

	$\|\alpha_S\alpha_I\rangle$	$\|\alpha_S\beta_I\rangle$	$\|\beta_S\alpha_I\rangle$	$\|\beta_S\beta_I\rangle$
$\langle\alpha_S\alpha_I\|$	P	NC	EC_a	EC_f
$\langle\alpha_S\beta_I\|$	NC	P	EC_f	EC_a
$\langle\beta_S\alpha_I\|$	EC_a	EC_f	P	NC
$\langle\beta_S\beta_I\|$	EC_f	EC_a	NC	P

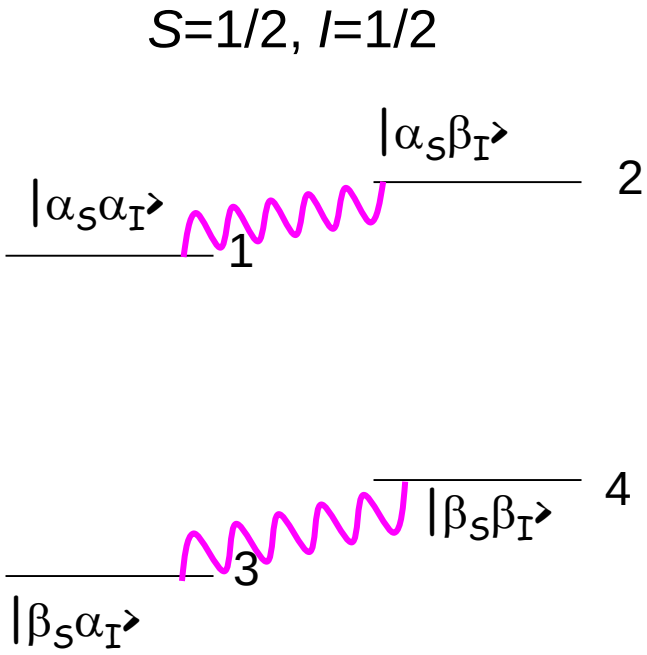


Schematic cartoon of the density matrix

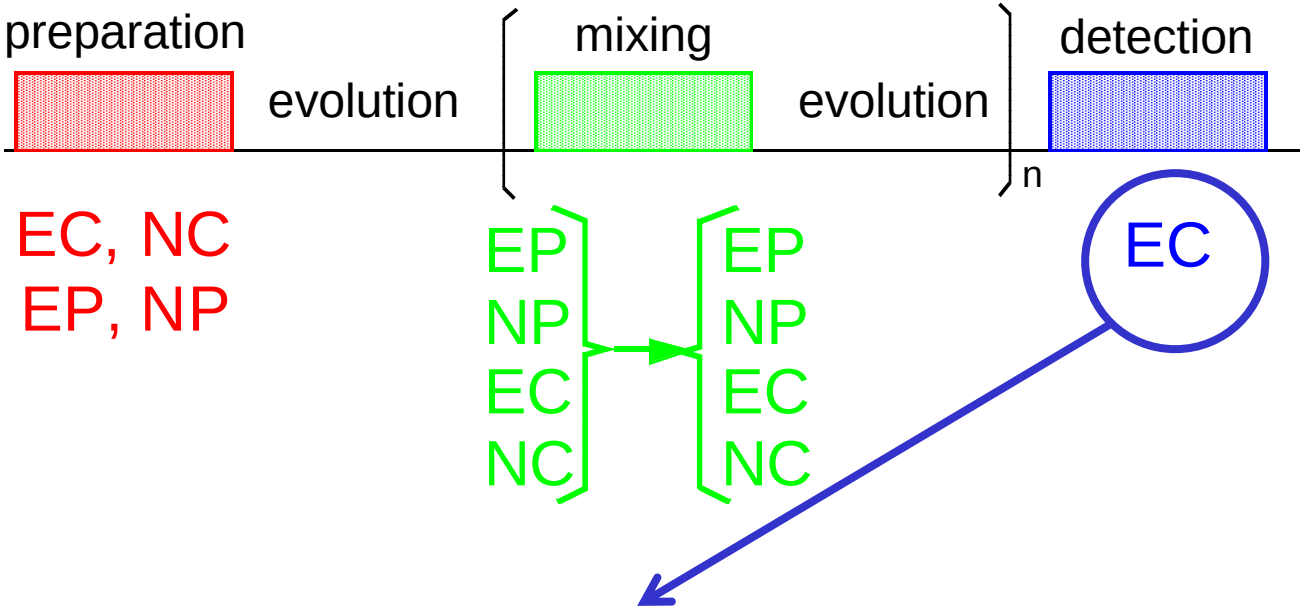
This is the bookkeeper for the experiment

Nuclear coherences

	$\lvert\alpha_S\alpha_I\rangle$	$\lvert\alpha_S\beta_I\rangle$	$\lvert\beta_S\alpha_I\rangle$	$\lvert\beta_S\beta_I\rangle$
$\langle\alpha_S\alpha_I\rvert$	P	NC	EC_a	EC_f
$\langle\alpha_S\beta_I\rvert$	NC	P	EC_f	EC_a
$\langle\beta_S\alpha_I\rvert$	EC_a	EC_f	P	NC
$\langle\beta_S\beta_I\rvert$	EC_f	EC_a	NC	P



General outline of an ESEEM experiment



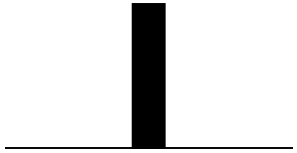
detection of electron spin echo vs. the inter-pulse distance

Fourier transform

Time-domain signal ⟶ frequency-domain signal

Creating electron and nuclear coherence

$(\pi/2)_x$



$\pi/2$ pulse creates EC

S_y

S=1/2, I=1/2

$$\sigma_{eq} \xrightarrow{(\pi/2)S_x} S_y$$

$$\xi I_y + \eta\, 2S_z I_y \xrightarrow{\text{change to eigenbase of } H} \cos(\eta)\, S_y - \sin(\eta)\, 2S_x I_y$$

$\eta = (\eta_\alpha - \eta_\beta)/2$

$\eta_\alpha = \text{atan}(-B/(A+2\omega_I))$

$\eta_\beta = \text{atan}(-B/(A-2\omega_I))$

	$\lvert\alpha_S\alpha_I\rangle$	$\lvert\alpha_S\beta_I\rangle$	$\lvert\beta_S\alpha_I\rangle$	$\lvert\beta_S\beta_I\rangle$
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Creating electron and nuclear coherence

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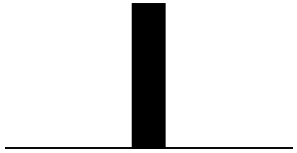

$\pi/2$ pulse creates EC

$2S_xI_y$

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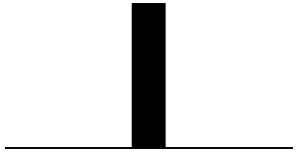
$\langle\beta_S\alpha_I\rvert$	EC_a	EC_f	P	NC
$\langle\beta_S\beta_I\rvert$	EC_f	EC_a	NC	P

Creating electron and nuclear coherence

$(\pi/2)_x$



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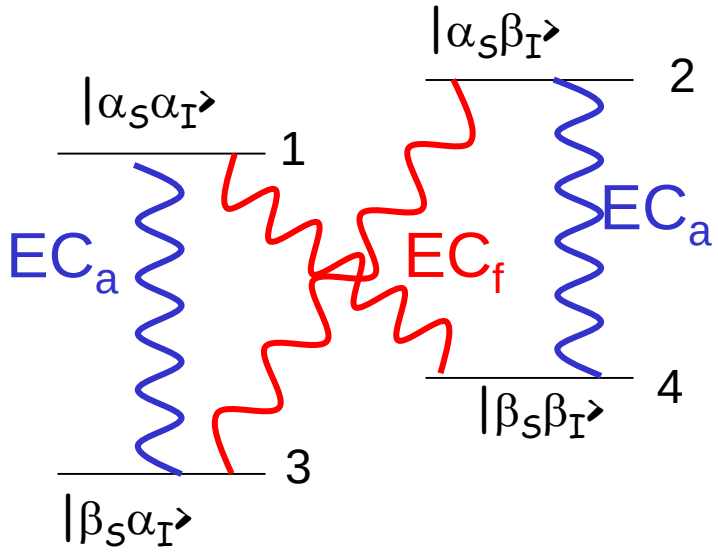
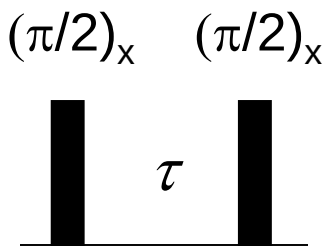
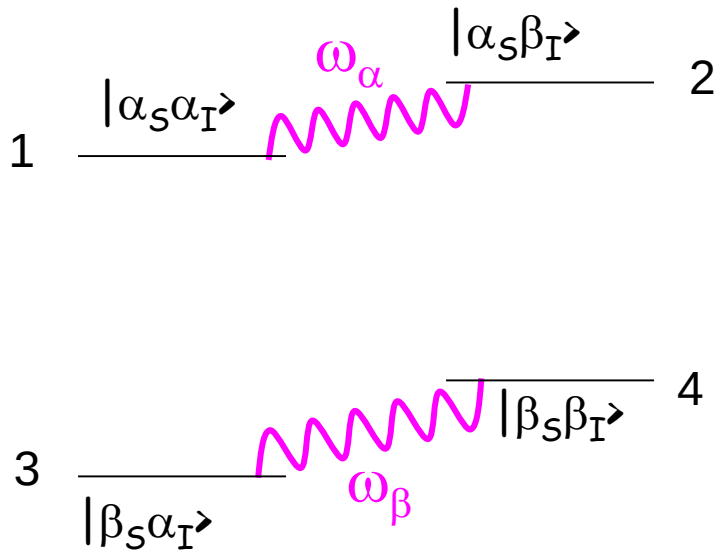


Creating electron and nuclear coherence



π/2-τ-π/2 pulse sequence creates NC and polarization

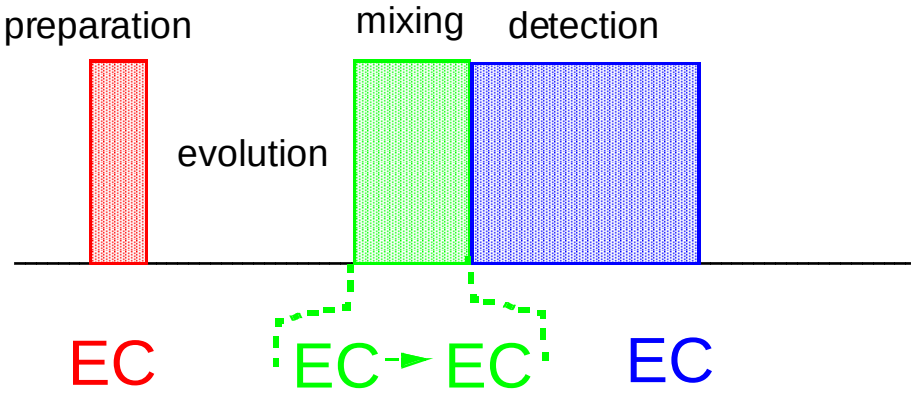
S=1/2, I=1/2

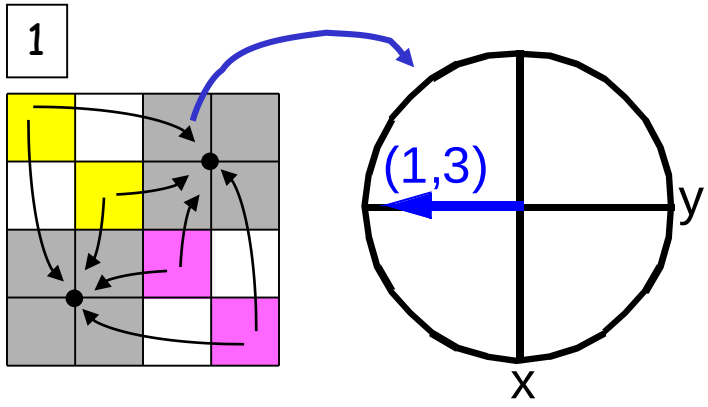


	$\lvert\alpha_S\alpha_I\rangle$	$\lvert\alpha_S\beta_I\rangle$	$\lvert\beta_S\alpha_I\rangle$	$\lvert\beta_S\beta_I\rangle$
$\langle\alpha_S\alpha_I\rvert$	P	NC	EC_a	EC_f
$\langle\alpha_S\beta_I\rvert$	NC	P	EC_f	EC_a
$\langle\beta_S\alpha_I\rvert$	EC_a	EC_f	P	NC
$\langle\beta_S\beta_I\rvert$	EC_f	EC_a	NC	P

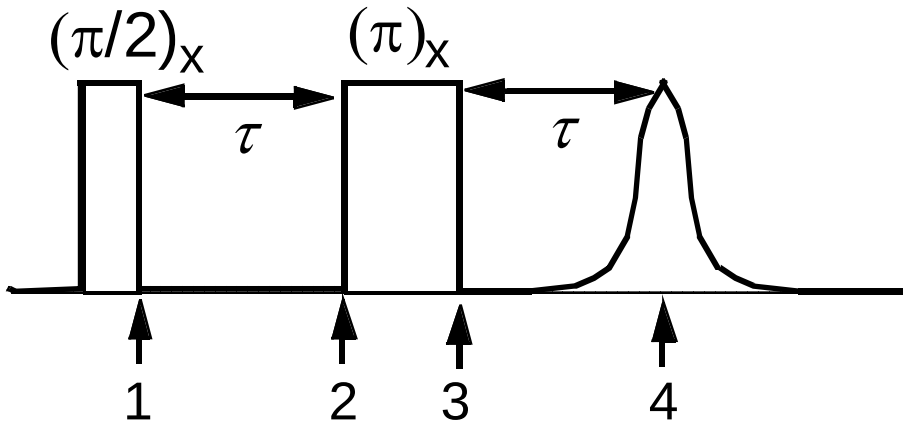
Let's apply this to the simplest ESEEM sequence

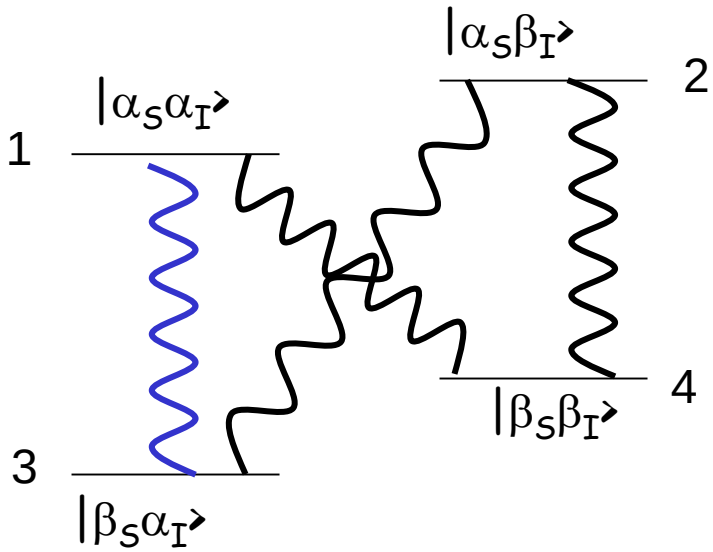
$S=1/2$, $I=1/2$





(rotating frame)





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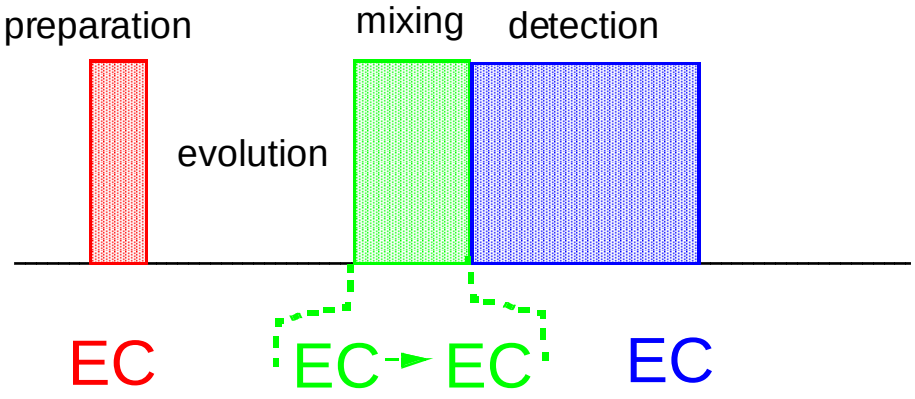
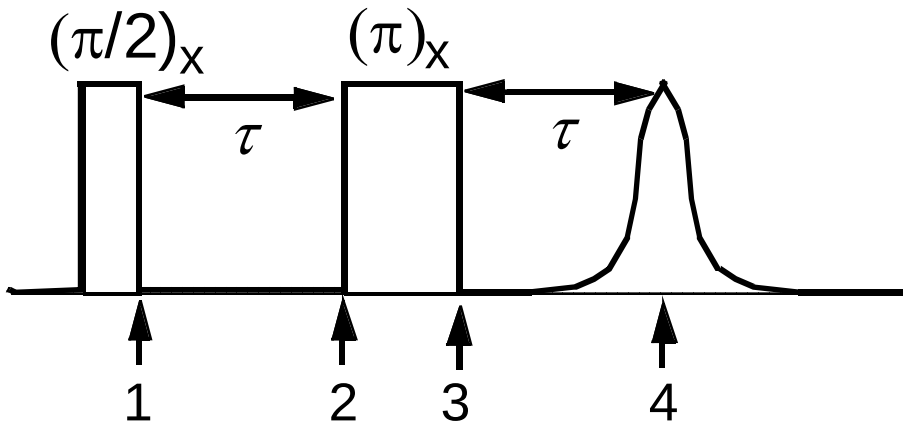
$S=1/2$, $I=1/2$





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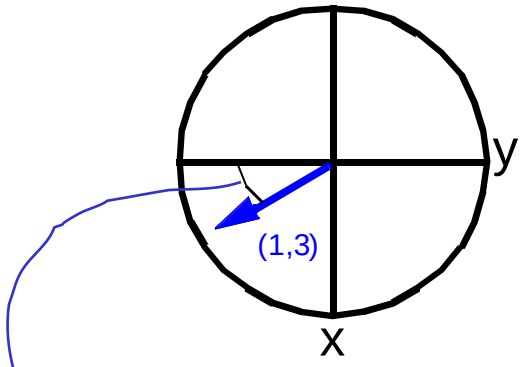
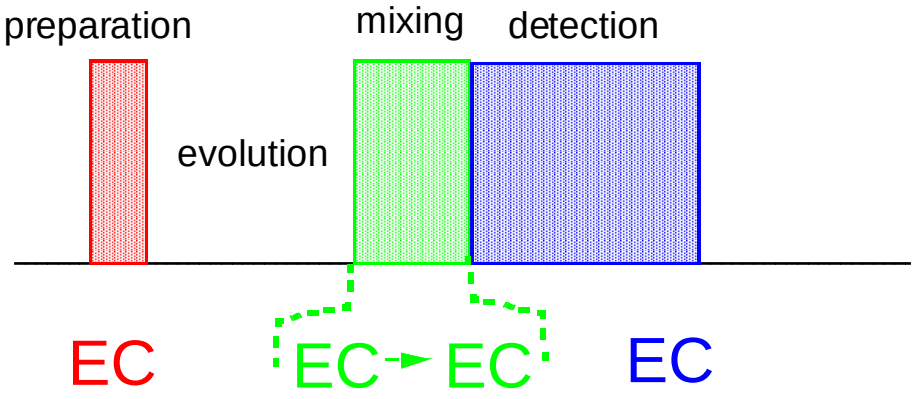


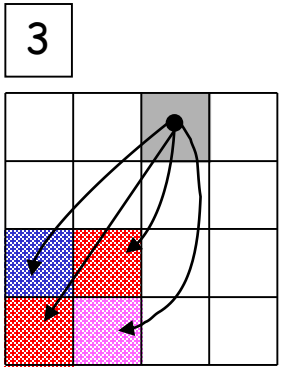
After time τ
magnetization has gained phase

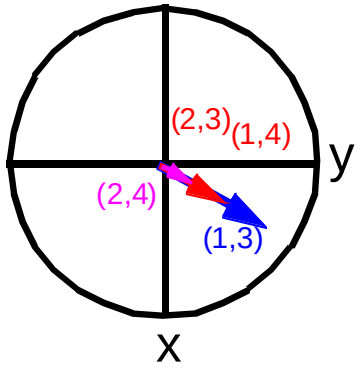
$$\Omega_S^{(1,3)}\tau=(\omega_{13}-\omega_{mw})$$

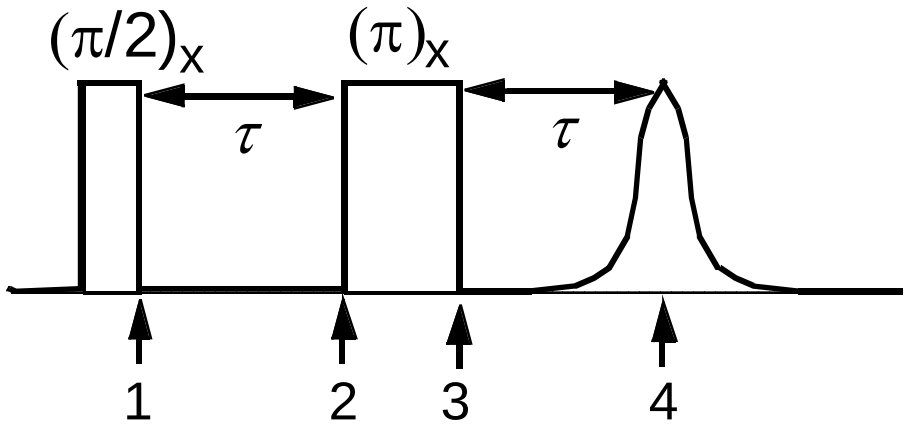
Let's apply this to the simplest ESEEM sequence

$S=1/2$, $I=1/2$







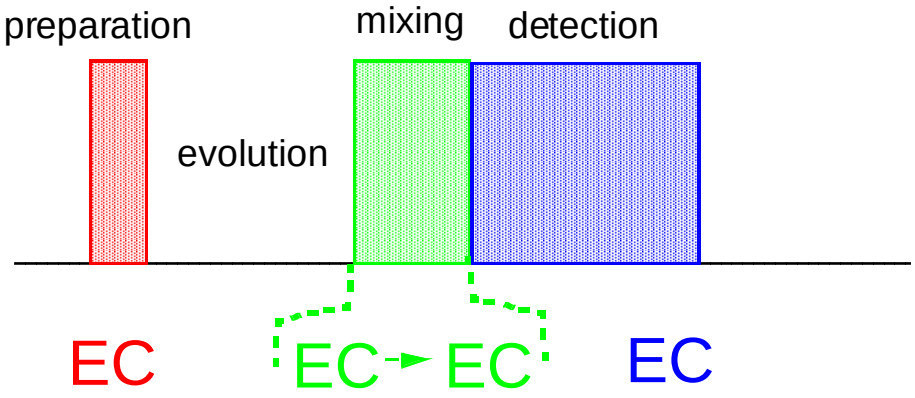


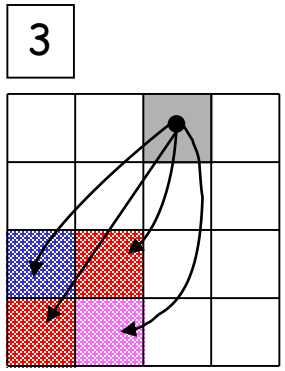
π pulse induces
flip of magnetization but also
redistribution of EC

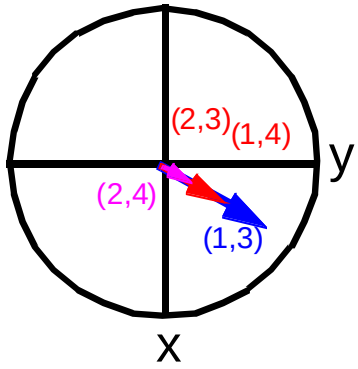
Weights: $\cos^2\eta$, $\sin\eta\cos\eta$, $\sin^2\eta$

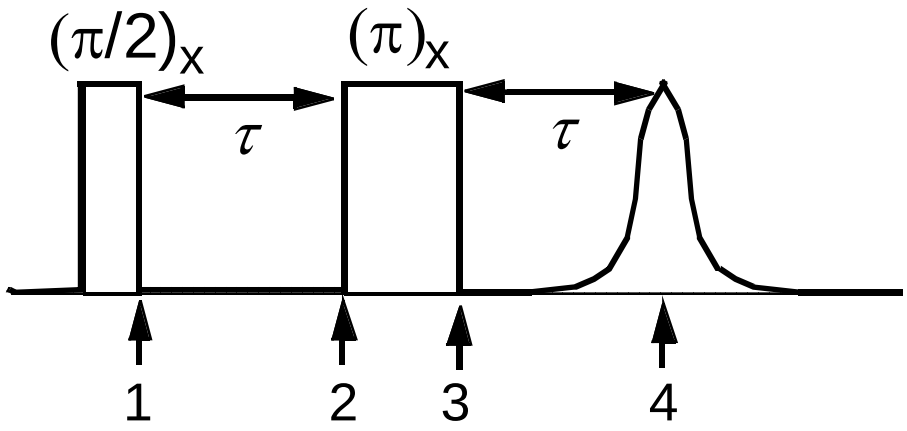
Let's apply this to the simplest ESEEM sequence

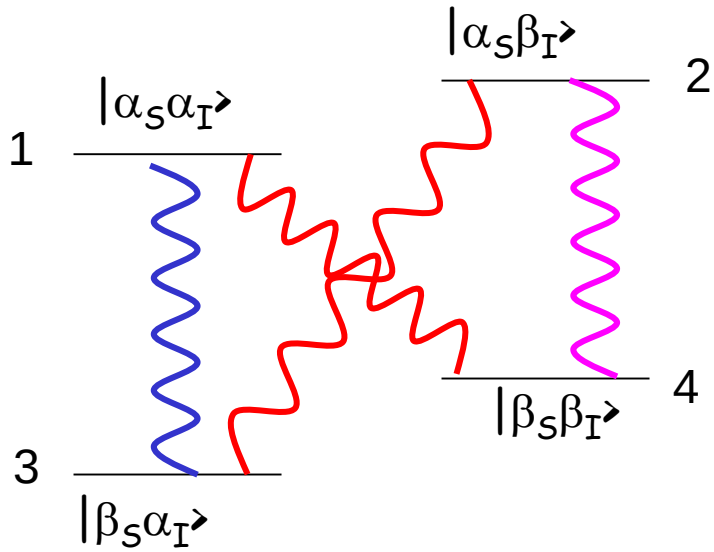
$S=1/2$, $I=1/2$





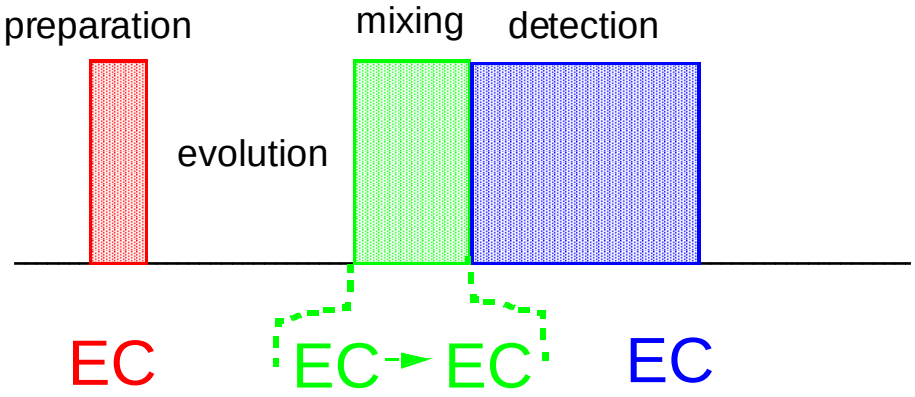


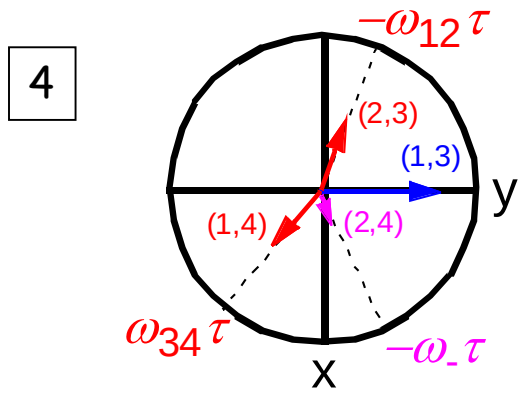


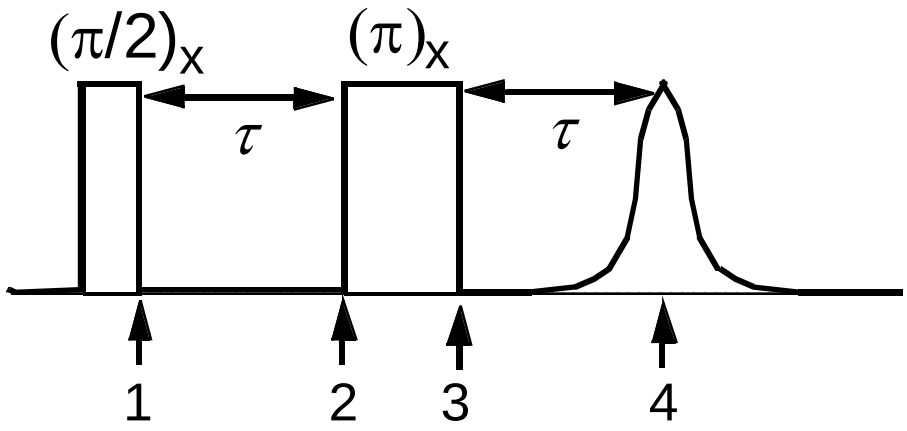


Let's apply this to the simplest ESEEM sequence

$S=1/2$, $I=1/2$



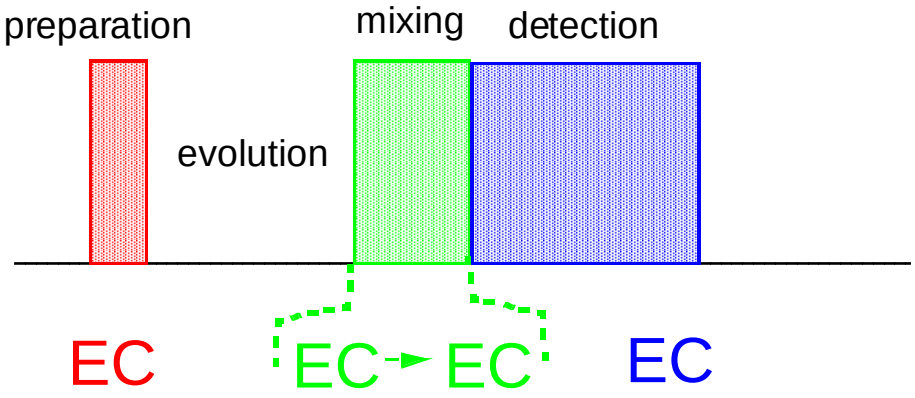


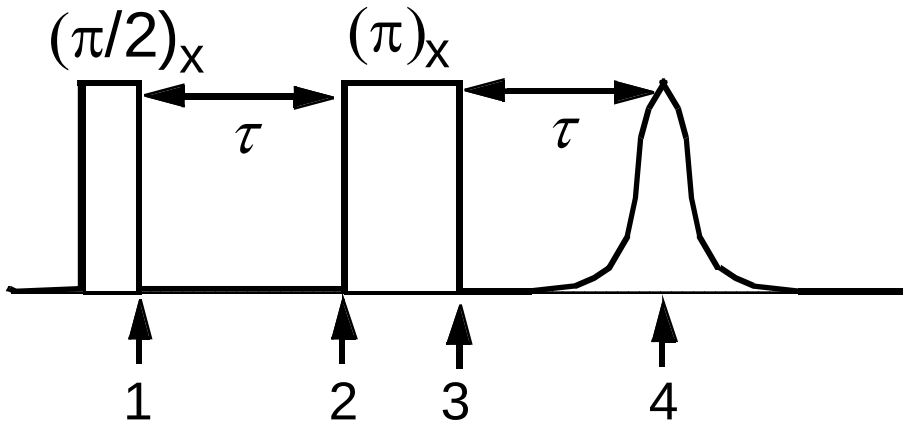


After time τ
the magnetization M(i,j) have gained a phase

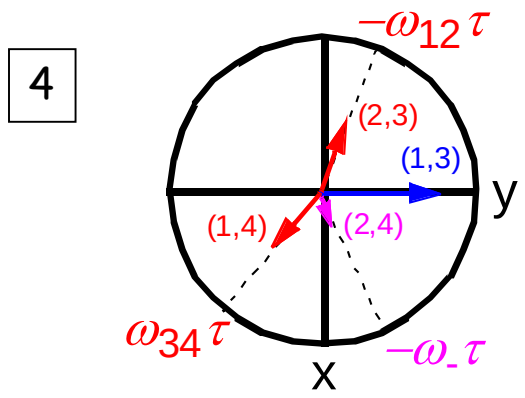
$$(\Omega_S^{(i,j)} - \Omega_S^{(1,3)})\tau = (\omega_{ij} - \omega_{13})\tau$$

Let's apply this to the simplest ESEEM sequence





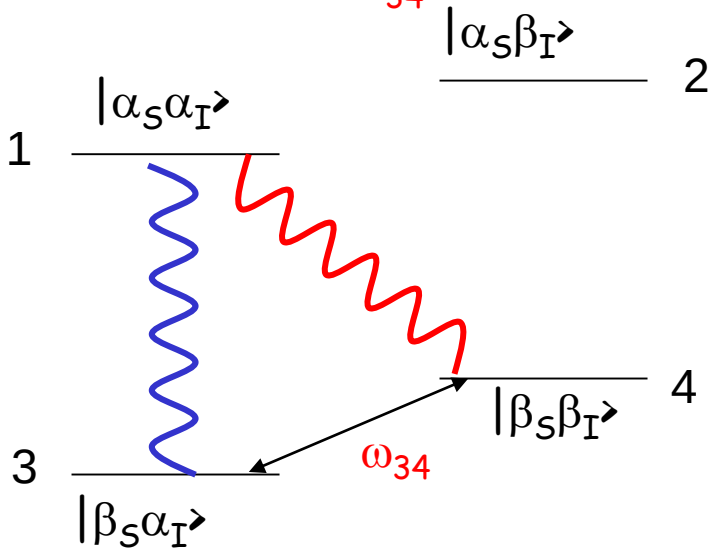
$S=1/2$, $I=1/2$



Example:

$(\Omega_S^{(1,4)} - \Omega_S^{(1,3)})\tau = (\omega_{14} - \omega_{13})\tau$

$= \omega_{34}\tau$



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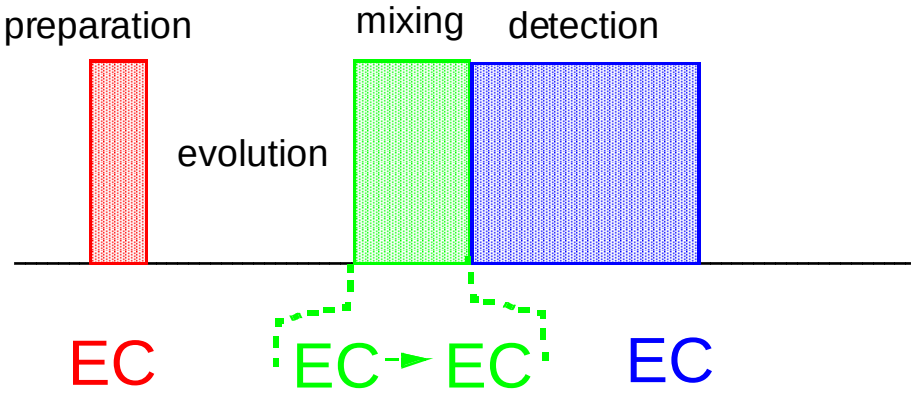
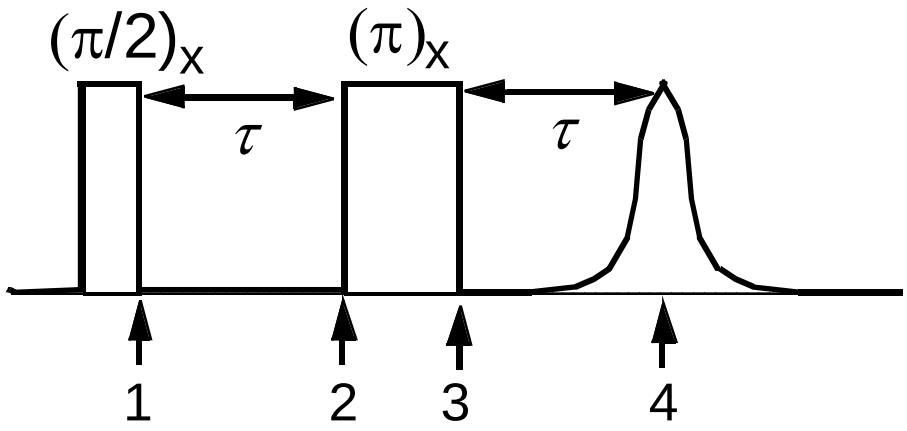
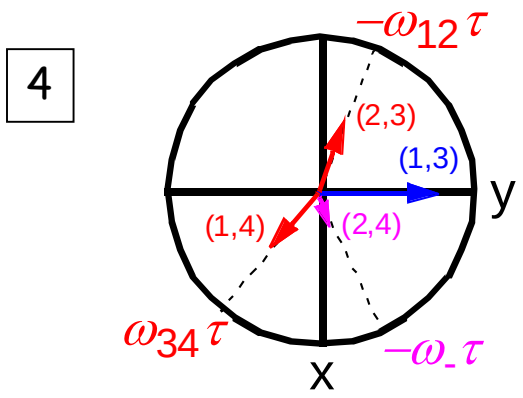




S=1/2, I=1/2



Example:

$(\Omega_S^{(1,4)} - \Omega_S^{(1,3)})\tau = (\omega_{14} - \omega_{13})\tau$

$= \omega_{34}\tau$

Changing pulse interval τ

Echo modulates with nuclear frequencies !

Modulation formula for an S=1/2, I=1/2 system

$$V_{2p}(\tau) = 1 - (k/4)[2-2\cos(\omega_\alpha\tau)-2\cos(\omega_\beta\tau)+\cos(\omega_-\tau)+\cos(\omega_+\tau)]$$

$(|\omega_{12}|=\omega_\alpha,\ |\omega_{34}|=\omega_\beta,\ \omega_+=\omega_{12}+\omega_{34},\ \omega_-=\omega_{12}-\omega_{34})$

With the modulation depth k depending on the weighting factors in each step of the EC transfer pathway

$$\cos^2\eta\sin^2\eta=\sin^2(2\eta)/4=k/4$$

$$\eta = (\eta_\alpha-\eta_\beta)/2$$
$$\eta_\alpha = \mathrm{atan}(-B/(A+2\omega_I))$$
$$\eta_\beta = \mathrm{atan}(-B/(A-2\omega_I))$$

No ESEEM for isotropic hyperfine or hyperfine principal directions !

(B=0 -> η=0 -> k=0)

Modulation formula for an S=1/2, I=1/2 system

$$V_{2p}(\tau) = 1 - (k/4)[2-2\cos(\omega_\alpha\tau)-2\cos(\omega_\beta\tau)+\cos(\omega_-\tau)+\cos(\omega_+\tau)]$$

$(|\omega_{12}|=\omega_\alpha,\ |\omega_{34}|=\omega_\beta,\ \omega_+=\omega_{12}+\omega_{34},\ \omega_-=\omega_{12}-\omega_{34})$

- modulation formula is derived assuming ideal pulses
- Holds for hard pulses $\omega_1 \gg |\omega_I|, |A|, |B|$
- No modulation if $\omega_1 < \min(|\omega_{12}|, |\omega_{34}|)$
- Only smaller of nuclear frequencies is observed if $\min(|\omega_{12}|, |\omega_{34}|) < \omega_1 < \max(|\omega_{12}|, |\omega_{34}|)$

Can be exploited to unravel ESEEM spectrum

Modulation formula for an S=1/2, I=1/2 system

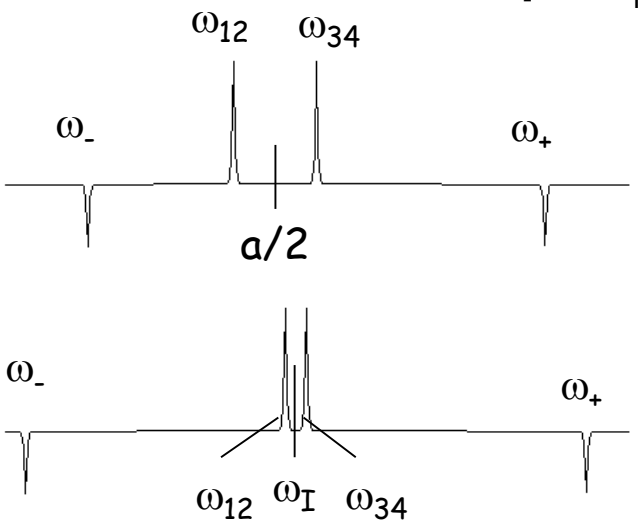
$$V_{2p}(\tau) = 1 - (k/4)[2-2\cos(\omega_\alpha\tau)-2\cos(\omega_\beta\tau)+\cos(\omega_-\tau)+\cos(\omega_+\tau)]$$

Strong coupling ($|a/2| > \omega_I$)

$\omega_+ \approx a$

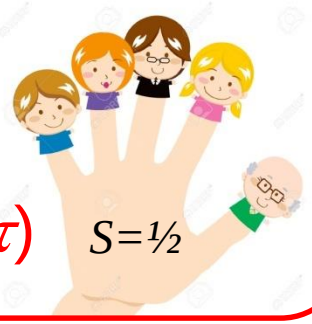
$\omega_- \approx 2\omega_I$

Schematic representation of 2-pulse ESEEM in frequency domain (after cosine FT)



If S is interacting with several nuclei product rule

$$V_{tot}(\tau) = \prod_i V_i(\tau)$$



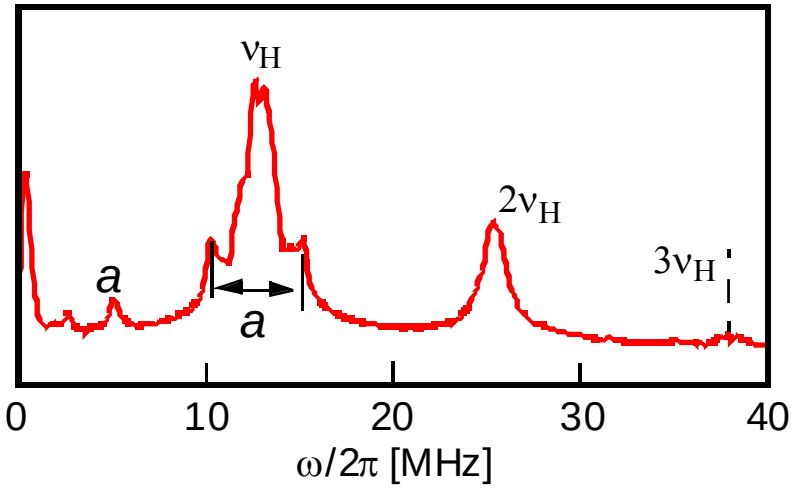
Weak coupling ($|a/2| < \omega_I$)

$\omega_- \approx a$

$\omega_+ \approx 2\omega_I$

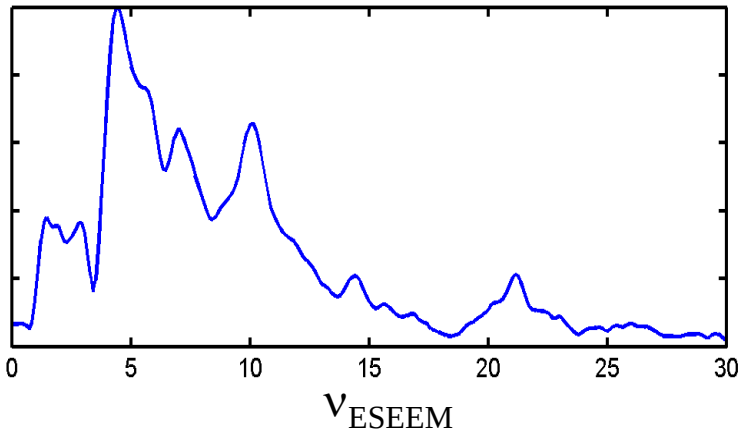
Very fast method

-> spectrum in a few seconds to a few minutes



Cu(II) a-picolinate in a single crystal of Zn α-picolinate

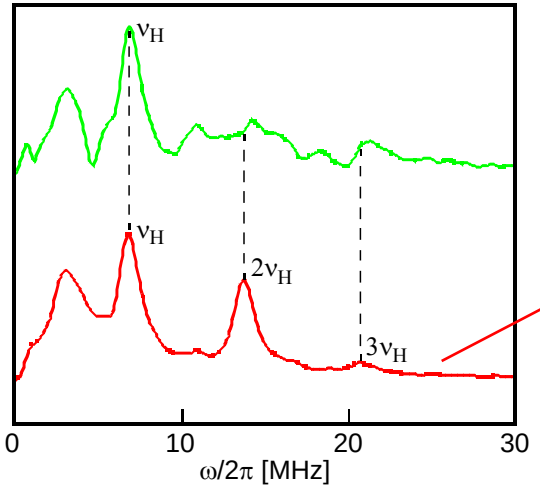
1. One-dimensional technique : possible overlap of signals



Example of ferric cytoglobin (low-spin Fe(III)), excitation at $g=g_z$

Overlap of lines ascribed to different ^{14}N and ^{1}H nuclei

2. Depends on electron phase-memory time (T_m) which is often very short, so that one has broad signals
3. Suffers from severe deadtime-dependent distortions

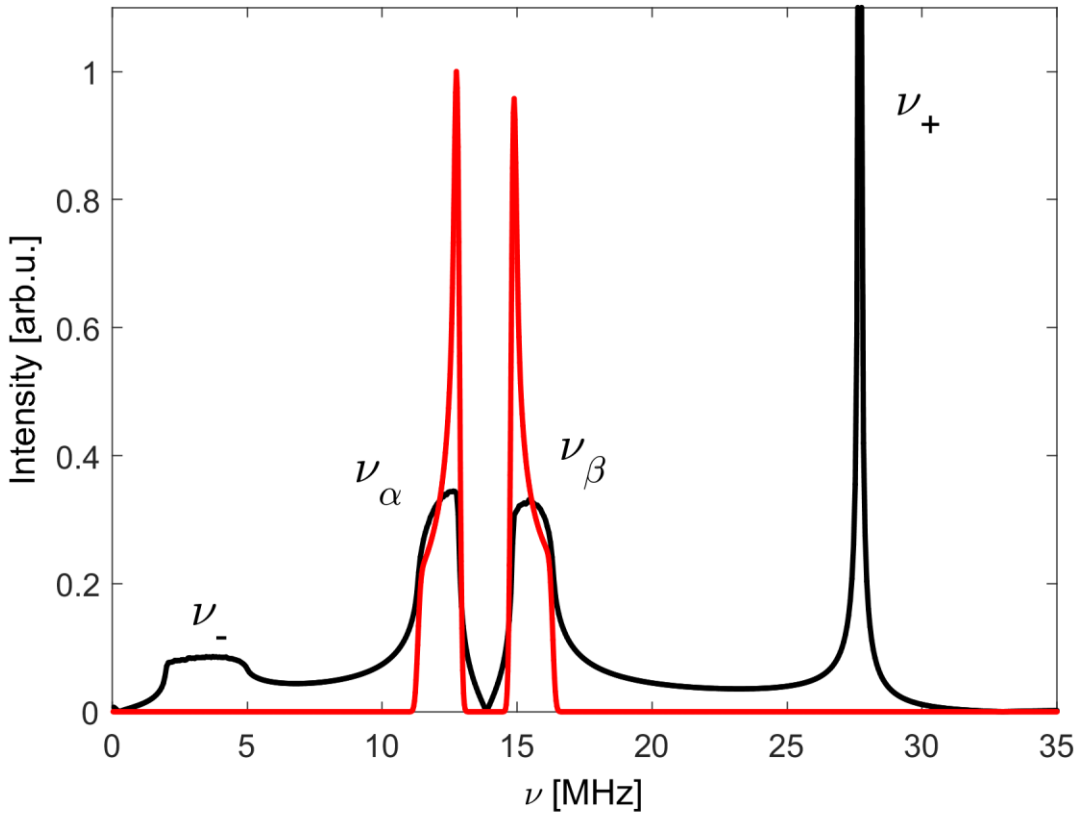


Example of Co(II)TPP in Zn(II)TPP

Corrected for deadtime

S. Van Doorslaer, G. A. Sierra, A. Schweiger, *J. Magn. Reson*, **136**, 152 (1999)

4. Comparison of ESEEM with ENDOR



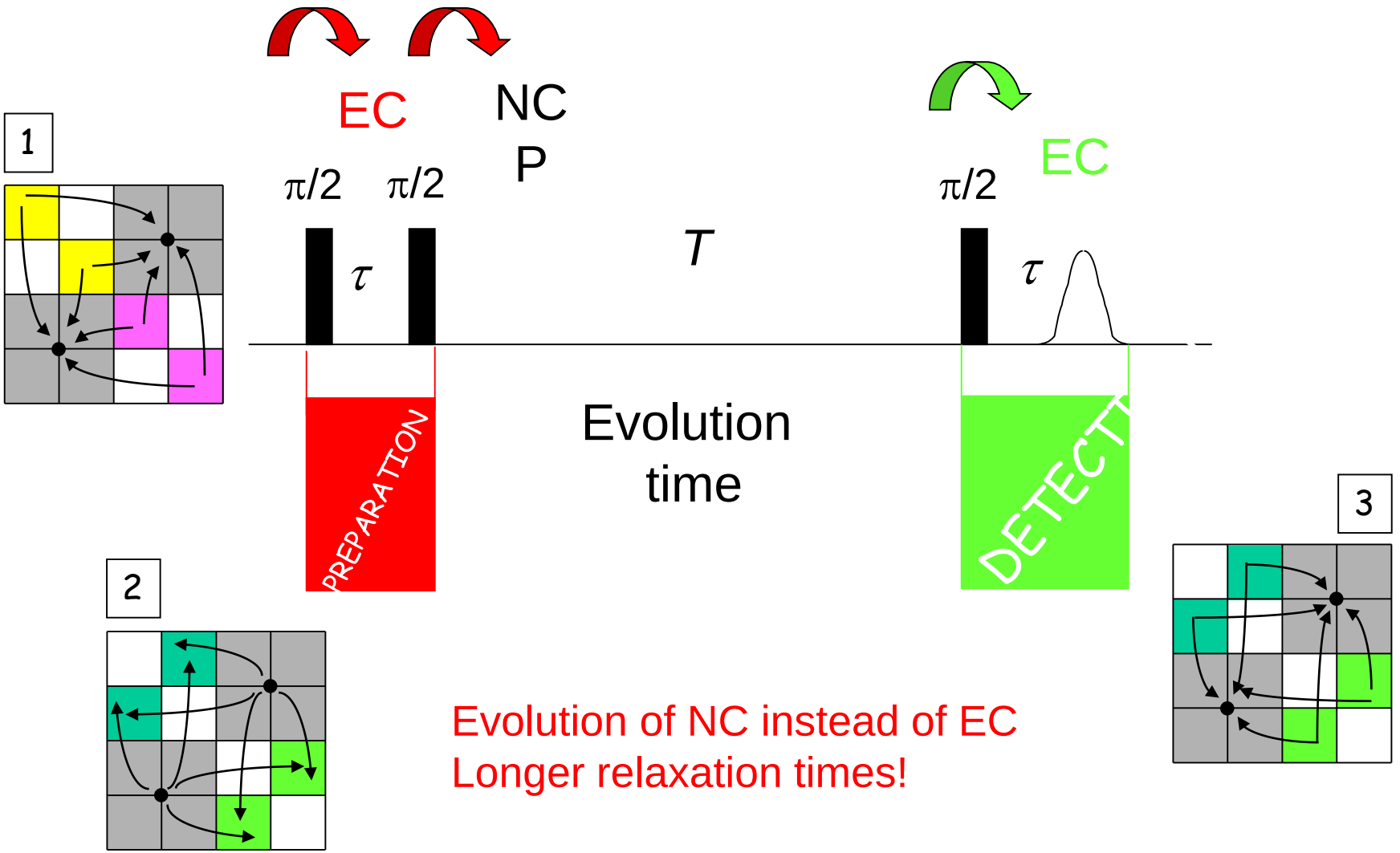
Example:
g=2, *S*=1/2,
I=1/2 (^{1}H),
A=[2 2 5]
MHz

No ESEEM effect for hyperfine principal directions !
(*B*=0 -> η=0 -> *k*=0)

2-pulse ESEEM

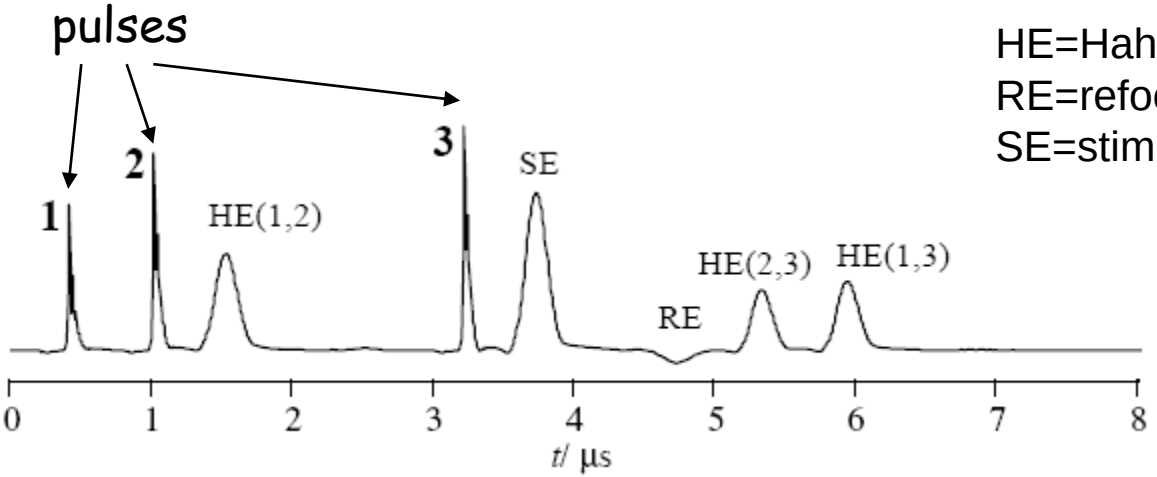
Simple and cheap tool, but limited use

This is what we want



Evolution of NC instead of EC
Longer relaxation times!

Phase cycling is needed to remove unwanted echoes



HE=Hahn echo or primary echo
RE=refocused echo
SE=stimulated echo

(Measurement on γ-irradiated quartz (G. Jeschke))

1	2	3	detection
x	x	x	-y
-x	x	x	y
x	-x	x	-y
-x	-x	x	y

Modulation formula for an S=1/2, I=1/2 system

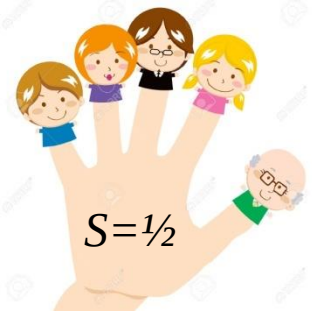
$$V_{3p}(T;\tau) = [v^{\alpha}(T;\tau) + v^{\beta}(T;\tau)]/2$$

$$v^{\alpha}(T;\tau) = 1 - (k/2)\{[1-\cos(\omega_{\beta}\tau)][1-\cos(\omega_{\alpha}(\tau+T))]\}$$

$$v^{\beta}(T;\tau) = 1 - (k/2)\{[1-\cos(\omega_{\alpha}\tau)][1-\cos(\omega_{\beta}(\tau+T))]\}$$

If S is interacting with several nuclei
product rule
is no longer the same as in 2-pulse ESEEM !

$$V_{tot}(\tau,T)=[\prod_i V_{\alpha}^{i}(\tau,T) + \prod_i V_{\beta}^{i}(\tau,T)]/2$$



$$V_{3p}(T;\tau) = [v^{\alpha}(T;\tau) + v^{\beta}(T;\tau)]/2$$

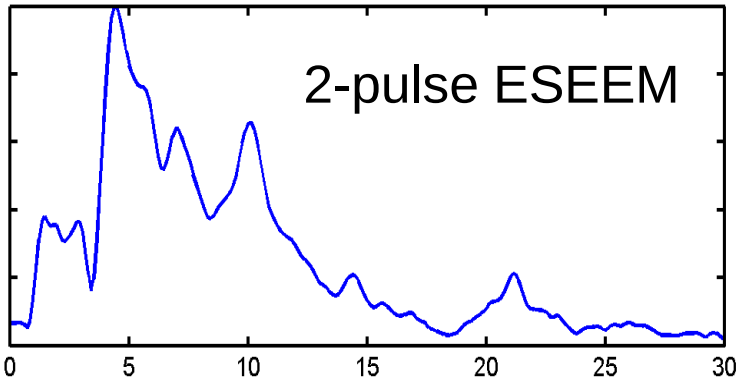
$$v^{\alpha}(T;\tau) = 1 - (k/2)\{[1-\cos(\omega_{\beta}\tau)][1-\cos(\omega_{\alpha}(\tau+T))]\}$$

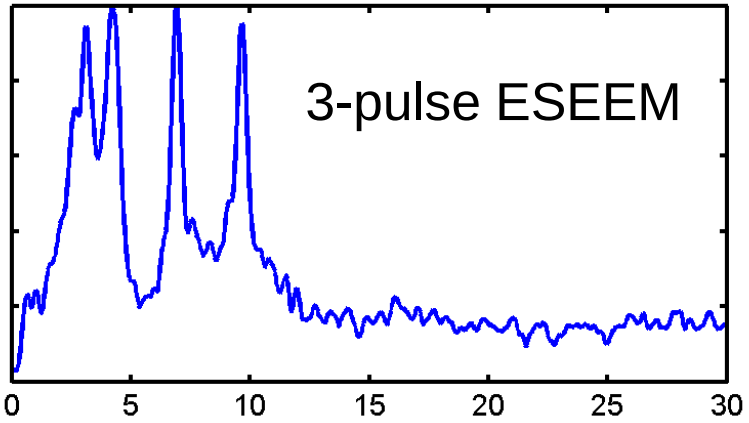
$$v^{\beta}(T;\tau) = 1 - (k/2)\{[1-\cos(\omega_{\alpha}\tau)][1-\cos(\omega_{\beta}(\tau+T))]\}$$

In three-pulse ESEEM no ω_- and ω_+ frequencies are found
→ Simpler spectrum than for 2-pulse ESEEM

dependence of signal on
nuclear phase memory time

→ narrower lines





$$V_{3p}(T;\tau) = [v^{\alpha}(T;\tau) + v^{\beta}(T;\tau)]/2$$

$$v^{\alpha}(T;\tau) = 1 - (k/2)\{[1-\cos(\omega_{\beta}\tau)][1-\cos(\omega_{\alpha}(\tau+T))]\}$$

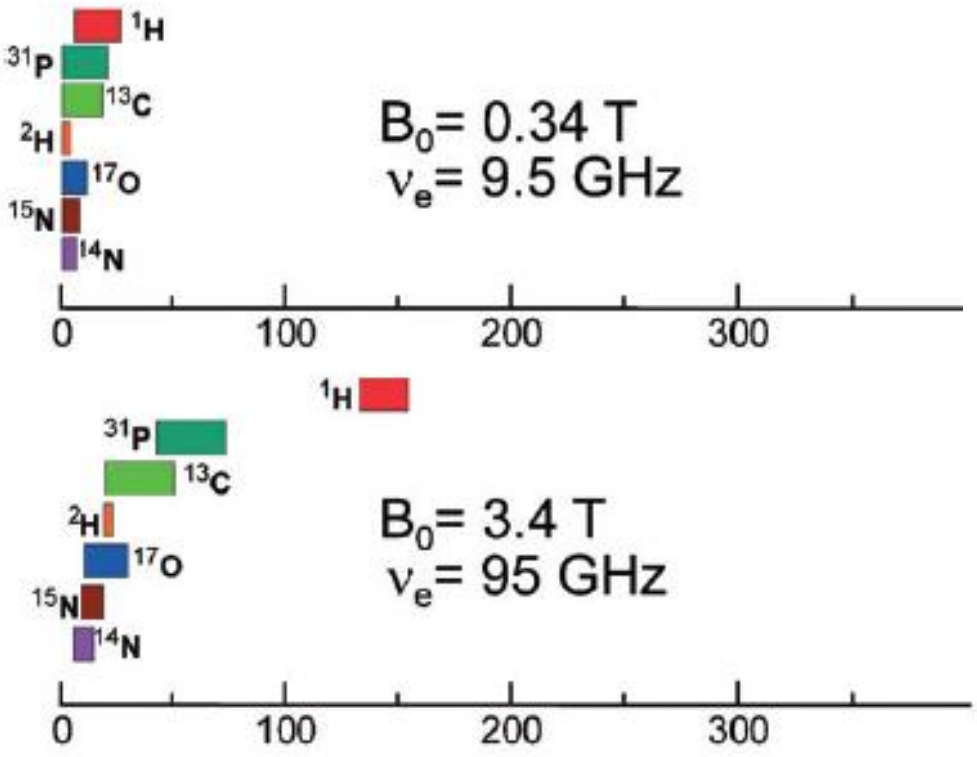
$$v^{\beta}(T;\tau) = 1 - (k/2)\{[1-\cos(\omega_{\alpha}\tau)][1-\cos(\omega_{\beta}(\tau+T))]\}$$

1. For $\omega_{\alpha,\beta}=2\pi n/\tau$ (n=0,1,2,…) -> BLIND SPOTS
   Consequence : experiment needs to be taken for different τ-values and added together

→ time consuming in comparison to 2-pulse ESEEM

2. 3-pulse ESEEM still gives a 1-dimensional experiment

OVERLAP of contributions !



(Figure from K. Möbius & A. Savitsky)

$$\omega_\alpha = \sqrt{(\omega_I + A/2)^2 + B^2/4}$$

$$\omega_\beta = \sqrt{(\omega_I - A/2)^2 + B^2/4}$$

Unraveling through use of different microwave frequencies

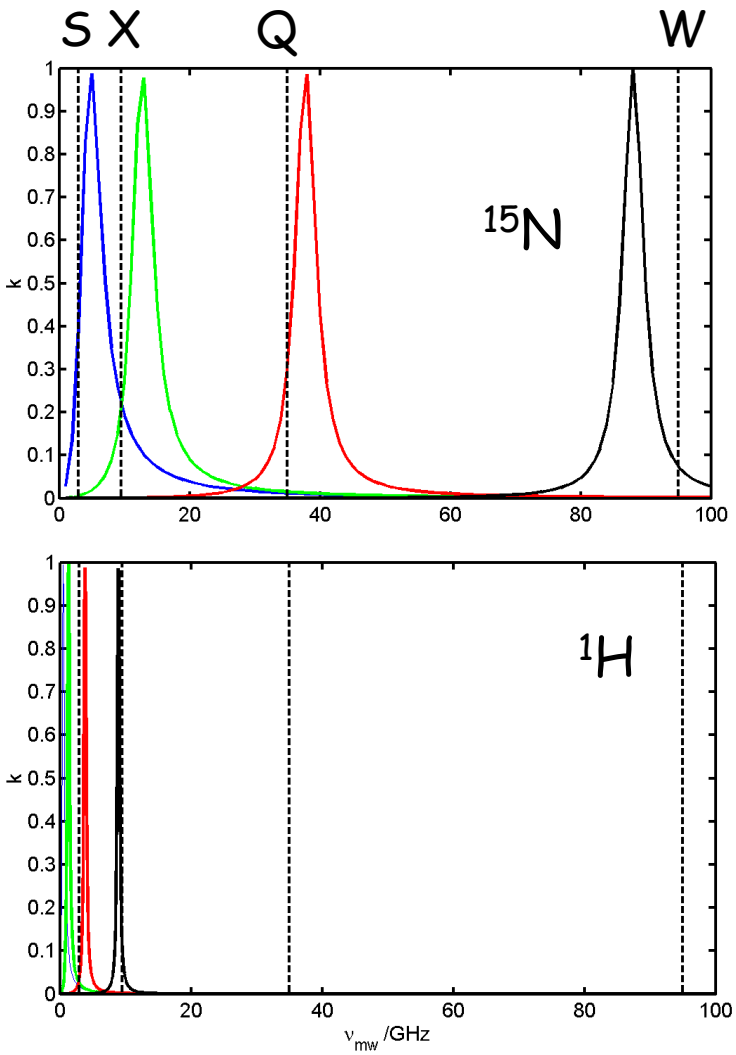
But, is not always straightforward for ESEEM !

Modulation depth for S=1/2, I=1/2

$$k = \sin^2(2\eta) = (B\omega_I/(\omega_\alpha\omega_\beta))^2$$

B = 0.6 MHz

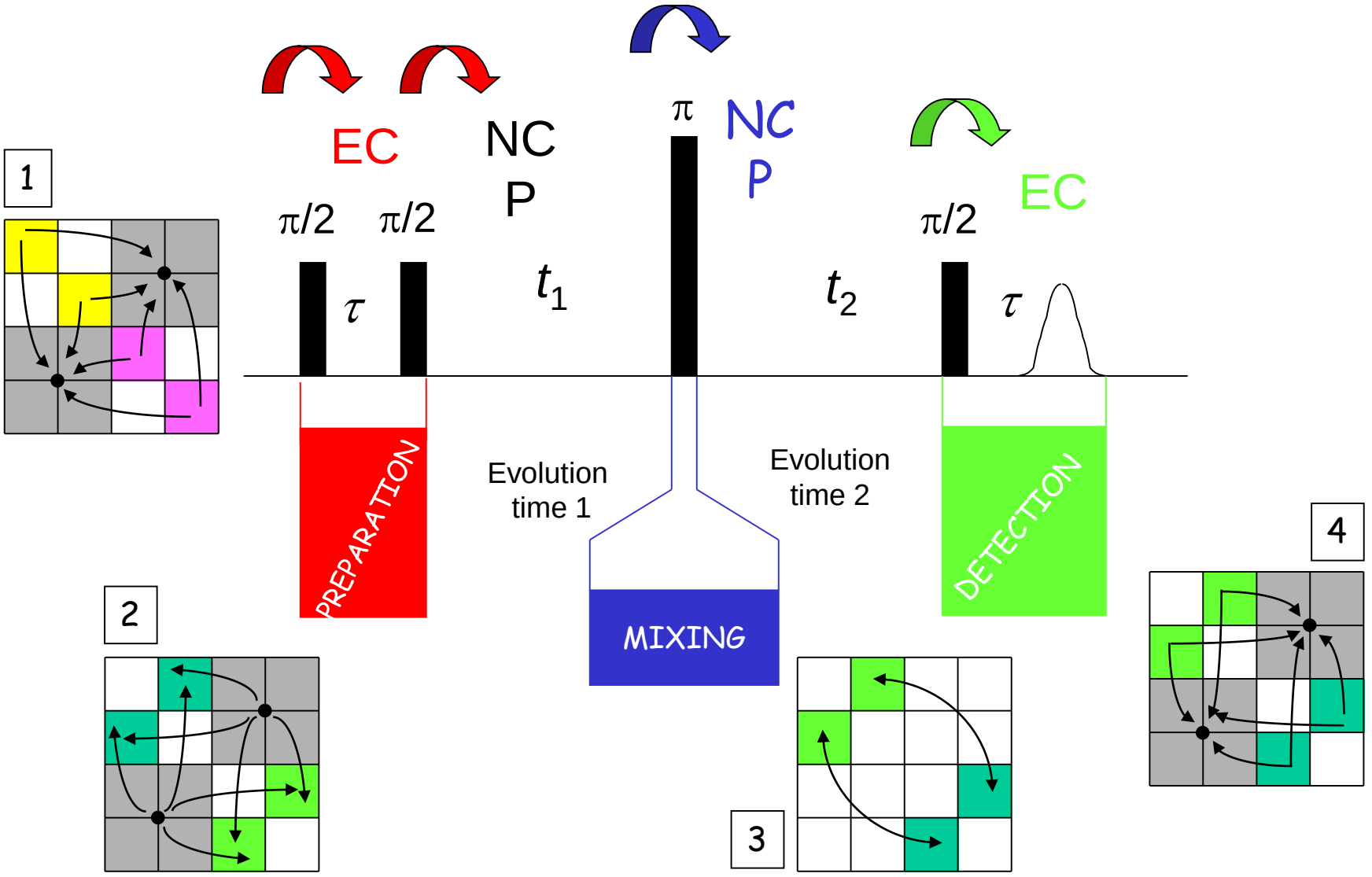
- A = 1.5 MHz
- A = 4 MHz
- A = 12 MHz
- A = 28 MHz



Unravel spectrum in a second dimension !

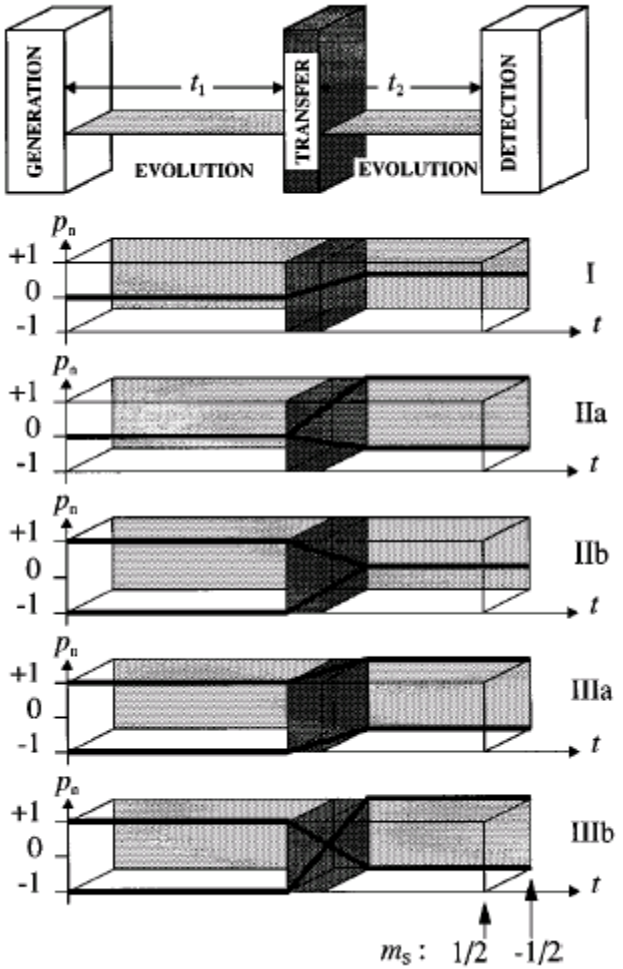
Need of sequence in which you vary two time intervals

after 2D FT $\rightarrow$ correlation peaks

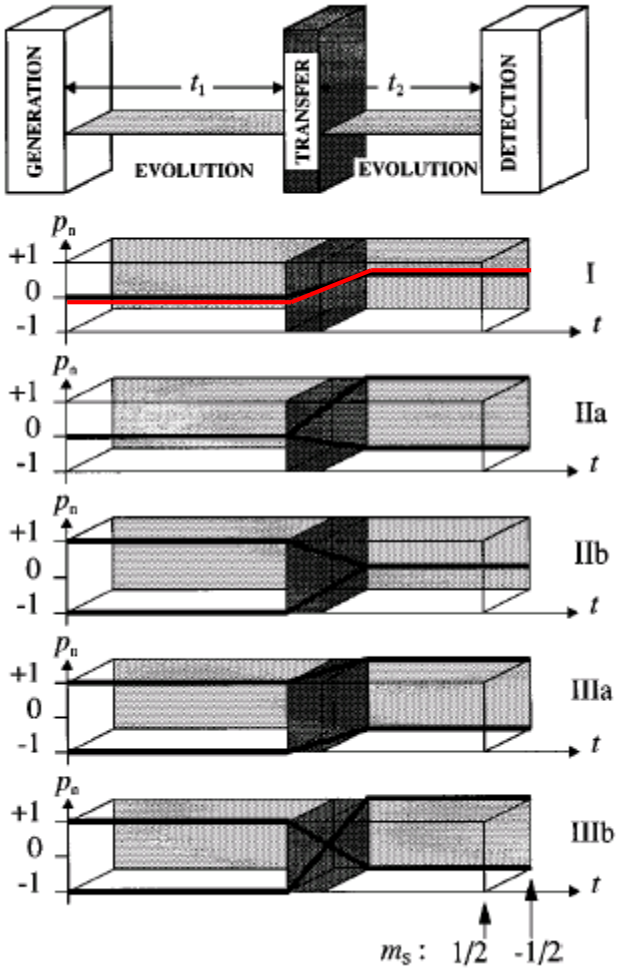

EC
NC
P
π
NC
P
EC
π/2
π/2
π/2
τ
τ
t1
t2
1
2
3
4
PREPARATION
Evolution
time 1
MIXING
Evolution
time 2
DETECTION

Modulation formula for an S=1/2, I=1/2 system

$$V_{4p}(\tau,t_1,t_2) = 1 - (k/2)[V_I + V_{IIa} + V_{IIb} + V_{IIIa} + V_{IIIb}]$$



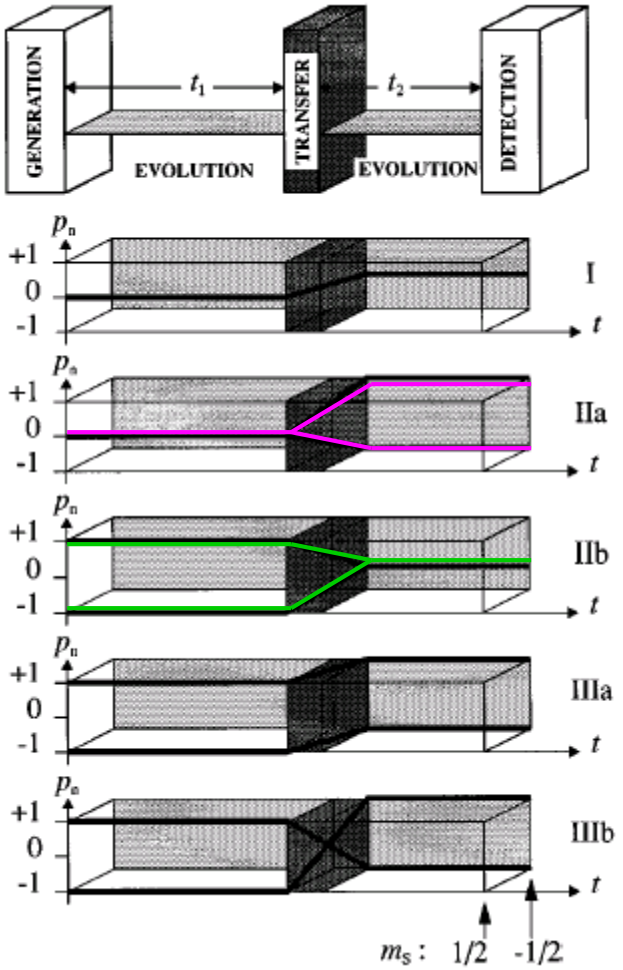
$$V_{4p}(\tau,t_1,t_2) = 1 - (k/2)[V_I + V_{IIa} + V_{IIb} + V_{IIIa} + V_{IIIb}]$$



P -> P

$$V_I = 3 - \cos(\omega_\beta \tau) - \cos(\omega_\alpha \tau) - \sin^2\eta \cos(\omega_+ \tau) - \cos^2\eta \cos(\omega_- \tau)$$

$$V_{4p}(\tau,t_1,t_2) = 1 - (k/2)[V_I + V_{IIa} + V_{IIb} + V_{IIIa} + V_{IIIb}]$$



P -> NC

$$V_{IIa} = C_\alpha(\tau)\cos(\omega_\alpha(t_2+\tau/2)) + C_\beta(\tau)\cos(\omega_\beta(t_2+\tau/2))$$

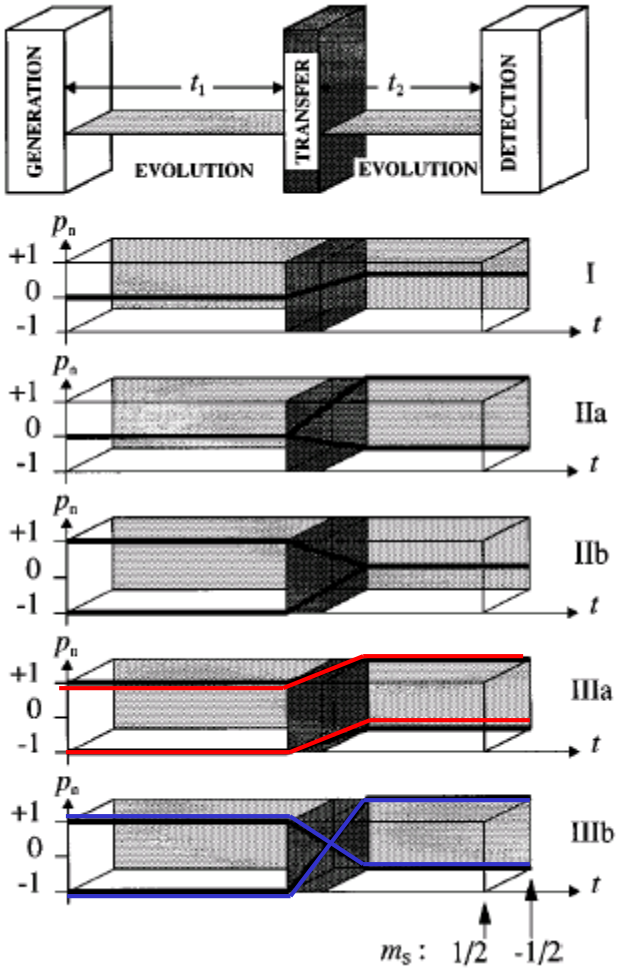
NC -> P

$$V_{IIb} = C_\alpha(\tau)\cos(\omega_\alpha(t_1+\tau/2)) + C_\beta(\tau)\cos(\omega_\beta(t_1+\tau/2))$$

$$C_\alpha(\tau) = \cos^2\eta\cos(\omega_\beta\tau-\omega_\alpha\tau/2) + \sin^2\eta\cos(\omega_\beta\tau+\omega_\alpha\tau/2) - \cos(\omega_\alpha\tau/2)$$

$$C_\beta(\tau) = \cos^2\eta\cos(\omega_\alpha\tau-\omega_\beta\tau/2) + \sin^2\eta\cos(\omega_\alpha\tau+\omega_\beta\tau/2) - \cos(\omega_\beta\tau/2)$$

$$V_{4p}(\tau,t_1,t_2) = 1 - (k/2)[V_I + V_{IIa} + V_{IIb} + V_{IIIa} + V_{IIIb}]$$



NC -> NC

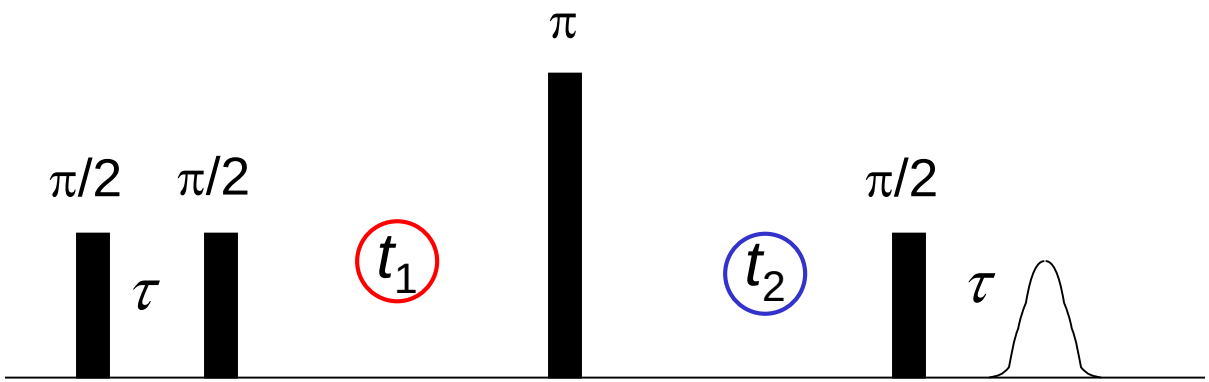
$$V_{IIIa} = C_c(\tau)\cos^2\eta \times [\cos(\omega_\alpha t_1 + \omega_\beta t_2 + \omega_+ \tau/2) + \cos(\omega_\beta t_1 + \omega_\alpha t_2 + \omega_+ \tau/2)]$$

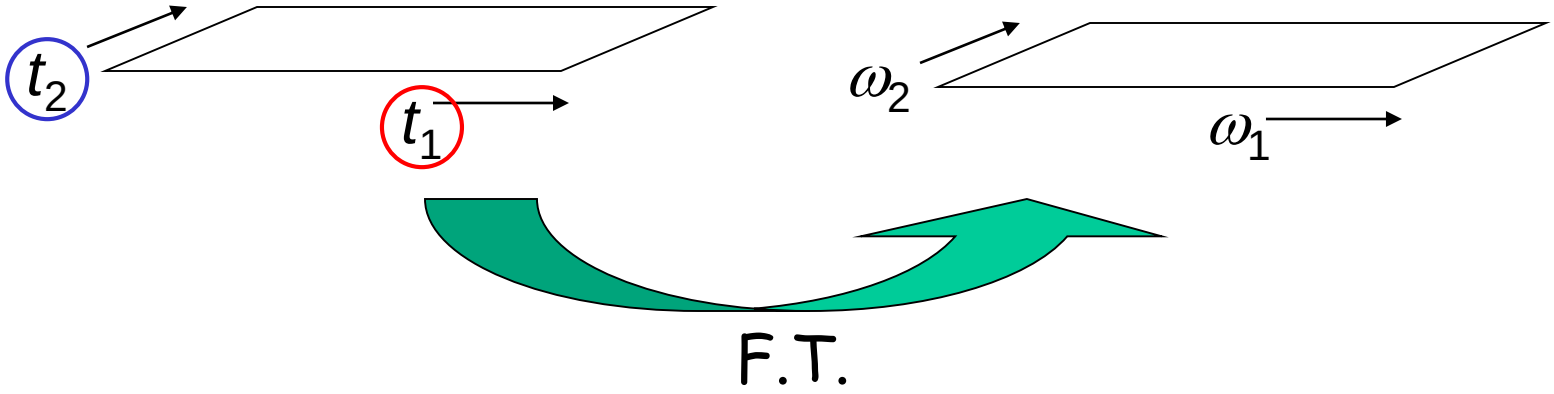
NC -> NC

$$V_{IIIb} = -C_c(\tau)\sin^2\eta \times [\cos(\omega_\alpha t_1 - \omega_\beta t_2 + \omega_- \tau/2) + \cos(\omega_\beta t_1 - \omega_\alpha t_2 - \omega_- \tau/2)]$$

$$C_c(\tau) = -2\sin(\omega_\alpha \tau/2)\sin(\omega_\beta \tau/2)$$

HYSCORE =
Hyperfine sublevel correlation spectroscopy

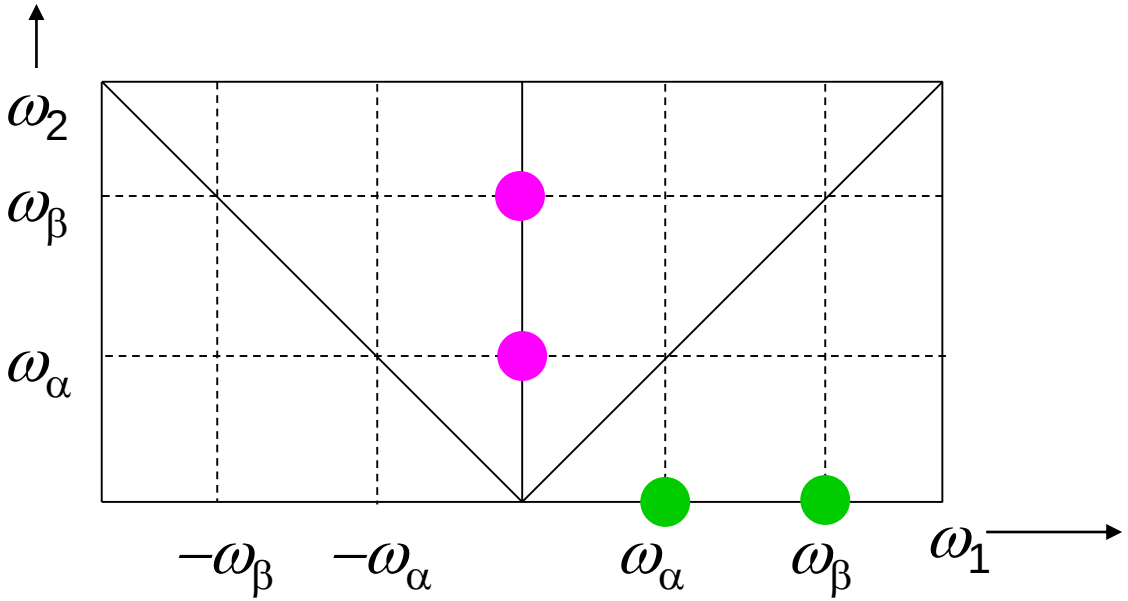




(Positive hyperfine)

P -> NC

$$V_{IIa} = C_\alpha(\tau)\cos(\omega_\alpha(t_2+\tau/2)) + C_\beta(\tau)\cos(\omega_\beta(t_2+\tau/2))$$



NC -> P

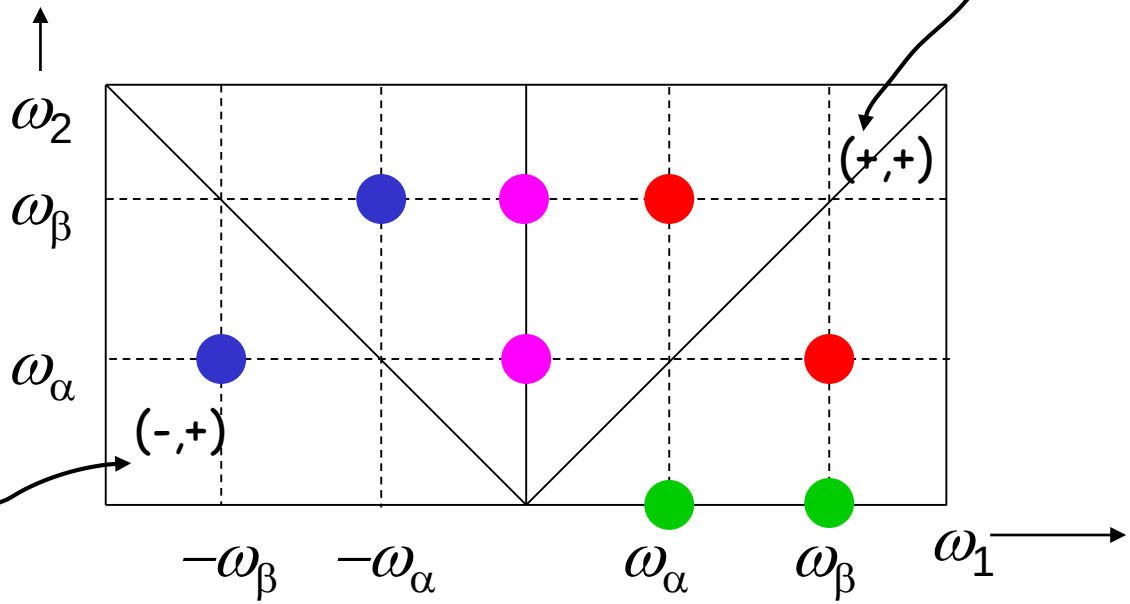
$$V_{IIb} = C_\alpha(\tau)\cos(\omega_\alpha(t_1+\tau/2)) + C_\beta(\tau)\cos(\omega_\beta(t_1+\tau/2))$$

$$V_{IIIa} = C_c(\tau)\cos^2\eta \times [\cos(\omega_\alpha t_1+\omega_\beta t_2+\omega_+\tau/2) + \cos(\omega_\beta t_1+\omega_\alpha t_2+\omega_+\tau/2)]$$

NC -> NC

(Positive hyperfine)

weak coupling



strong coupling

$$V_{IIIb} = -C_c(\tau)\sin^2\eta \times [\cos(\omega_\alpha t_1-\omega_\beta t_2+\omega_-\tau/2) + \cos(\omega_\beta t_1-\omega_\alpha t_2-\omega_-\tau/2)]$$

NC -> NC

Correlation peaks

In order to eliminate all unwanted pathways:
16-step phase cycle needed

Luckily, usually the anti-echoes are negligible

Minimum 4-step phase cycle needed

π/2	π/2	π	π/2	detection
x	x	x	x	y
x	x	x	-x	-y
x	x	-x	x	y
x	x	-x	-x	-y

PRO's and CON's of HYSCORE

PRO

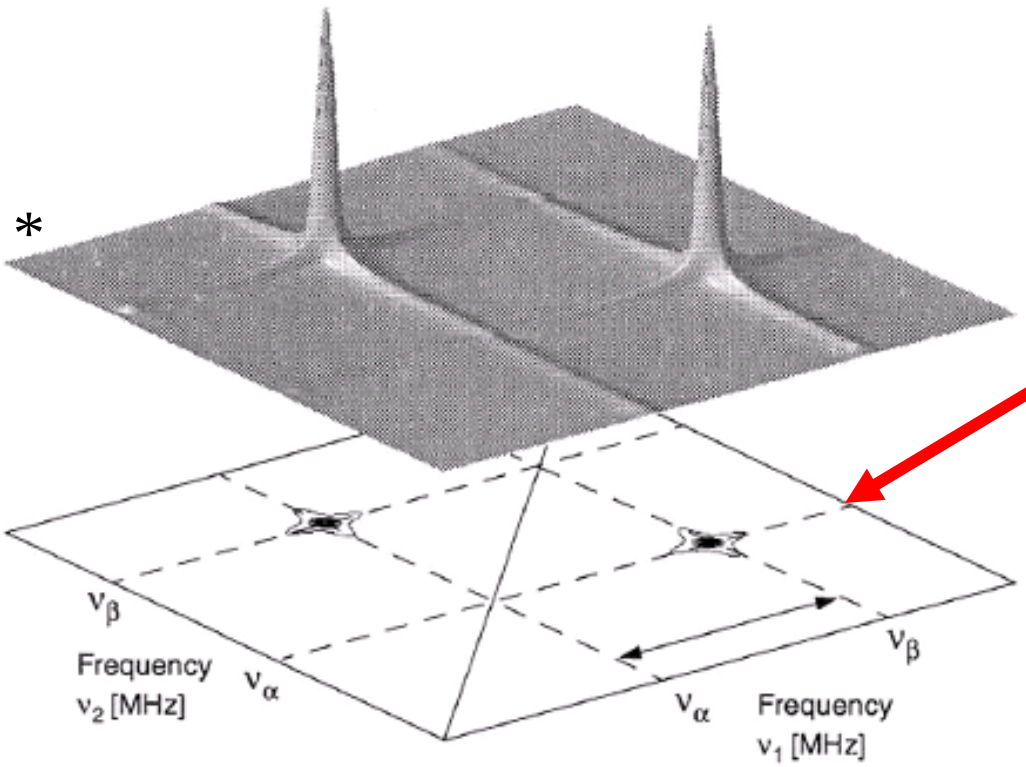
Correlation between frequencies (2D experiment)
$T^{(n)}_m$ ($\approx T_1$) dependence: narrow lines

CONTRA

Blind spots
Time consuming

Interaction with single nucleus

Single crystal – *S*=1/2, *I*=1/2



Simple system:
Nuclear frequencies for observer position can be directly read from axis

*Figure adapted from P. Schosseler

Interaction with single nucleus

Powder – S=1/2, I=1/2

Different molecular orientations are excited at observer position

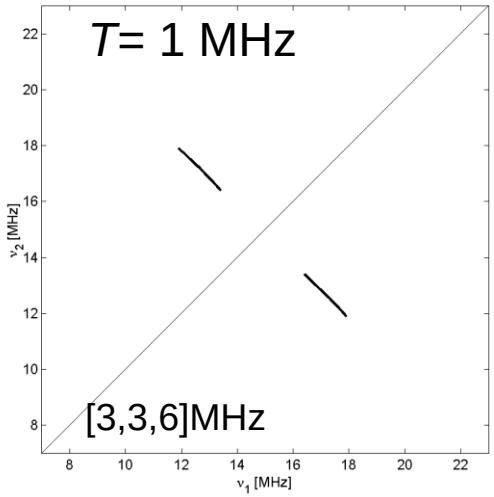
Powder HYSCORE spectrum =
Sum of all single-crystal HYSCORE spectra corresponding to the different excited orientations

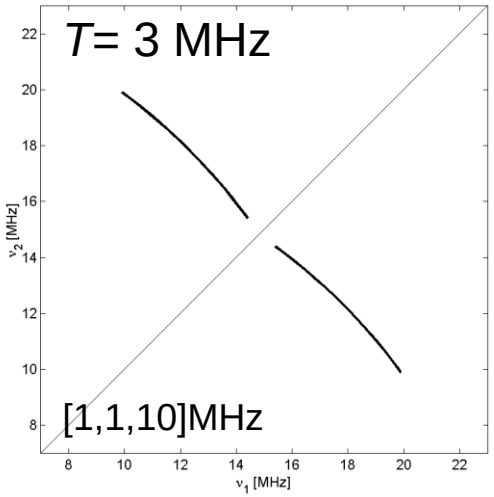
Powder pattern – $S = ½$, $I = ½$

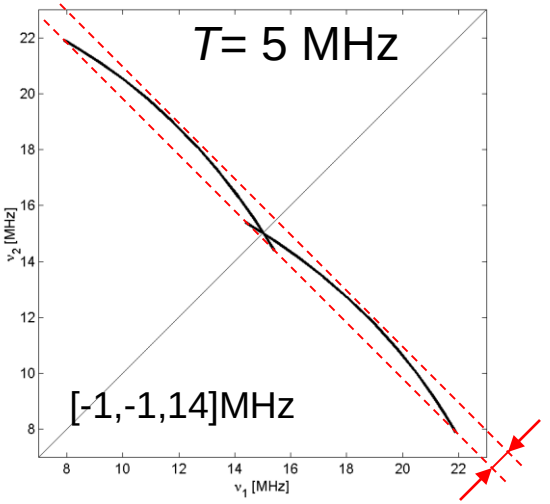
"Weak coupling"

$$\mathbf{A} = a_{iso} + [-T, -T, 2T]$$

a_{iso} = 4 MHz, ν_I = 14.9 MHz (^{1}H at 350 mT)







T influences the width of the ridge

$$(\Delta\nu_S)_{max} = 9T^2/(32|\nu_I|)$$

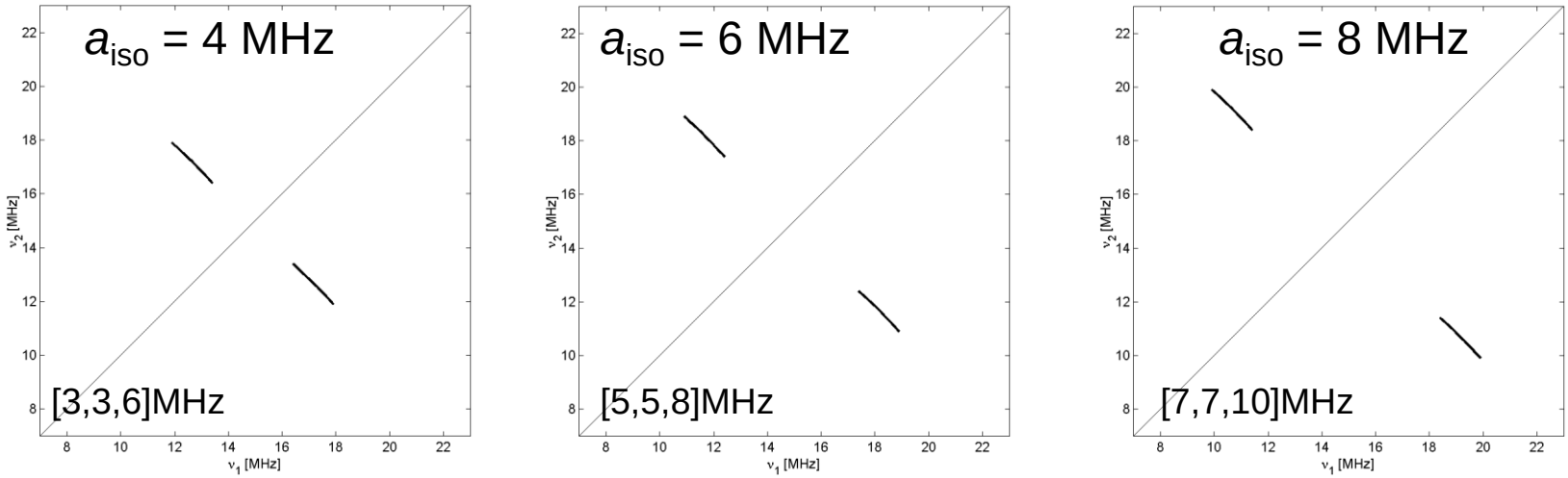
T determines max. shift

Powder pattern – $S = ½$, $I = ½$

"Weak coupling"

$$\mathbf{A} = a_{iso} + [-T, -T, 2T]$$

T = 1 MHz, ν_I = 14.9 MHz (^{1}H at 350 mT)



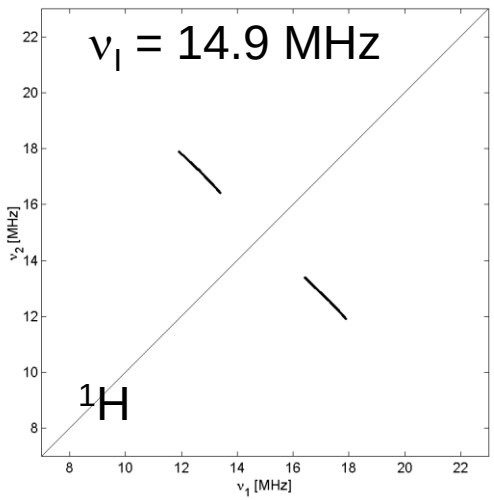
a_{iso} influences the anti-diagonal distance between the ridges

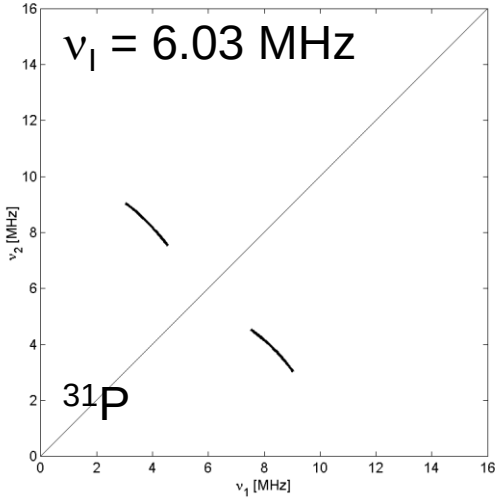
Powder pattern – $S = ½$, $I = ½$

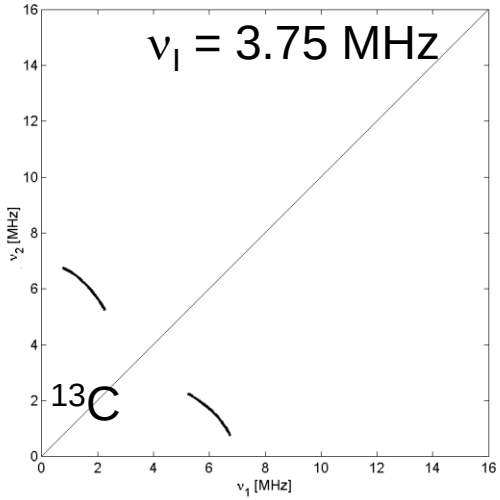
"Weak coupling"

$$\mathbf{A} = a_{iso} + [-T, -T, 2T]$$

T = 1 MHz, a_{iso} = 4 MHz







ν_I influences position around which peaks are centered.

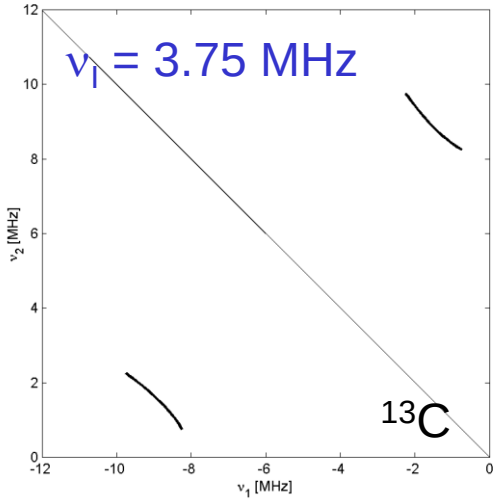
$$(\Delta\nu_S)_{max} = 9T^2/(32|\nu_I|)$$

ν_I determines max. shift

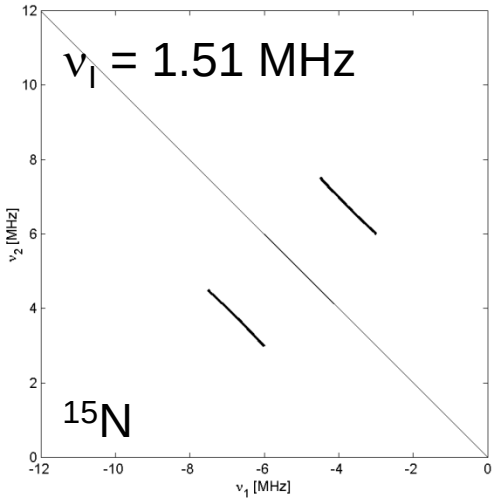
Powder pattern – $S = ½$, $I = ½$

"Strong coupling"

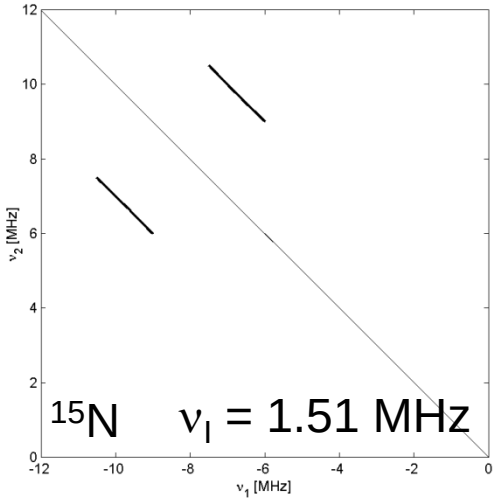
A = a_{iso} + [$-T$,$-T$,$2T$]



T = 1 MHz
a_{iso} = 10 MHz

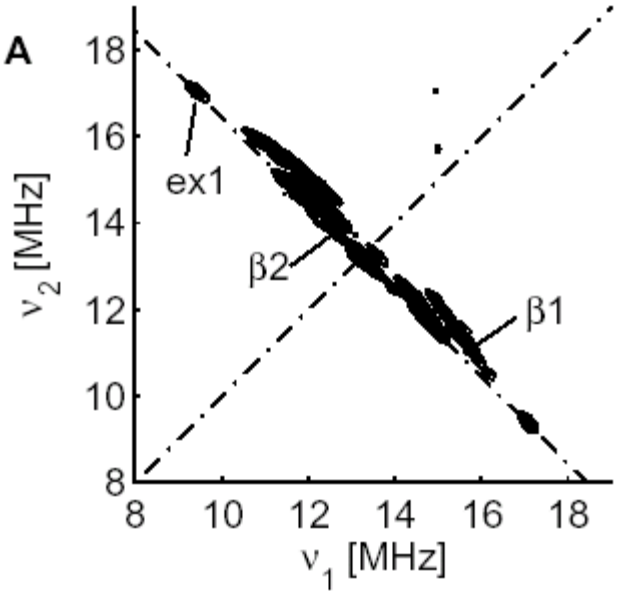


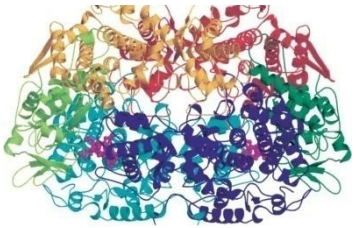
T = 1 MHz
a_{iso} = 10 MHz



T = 1 MHz
a_{iso} = 16 MHz

Powder pattern – $S = ½$, $I = ½$





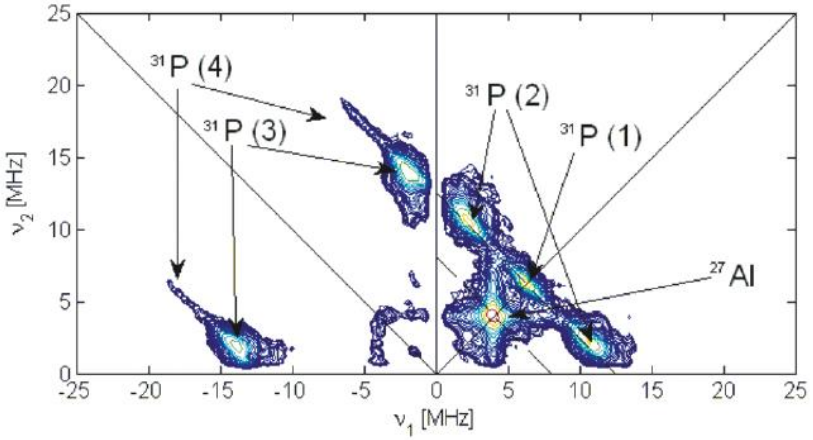
Proton HYSCORE
at X-band of
MCRox1

Weak coupling

J. Harmer et al., JACS, 2005, 127, 17744

^{31}P HYSCORE
at X-band of

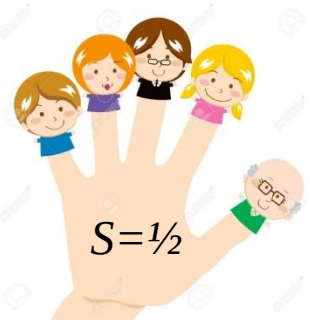
TiAlPO-5



Strong coupling
P(3) and P(4)

S. Maurelli et al., JACS, 2011, 33, 7340

Interaction with several nuclei



Product rule

$$V_{4p}(\tau,t_1,t_2) = \tfrac{1}{2}\left[\prod_i^N V_i{}^{\alpha}(\tau,t_1,t_2) + \prod_i^N V_i{}^{\beta}(\tau,t_1,t_2)\right]$$

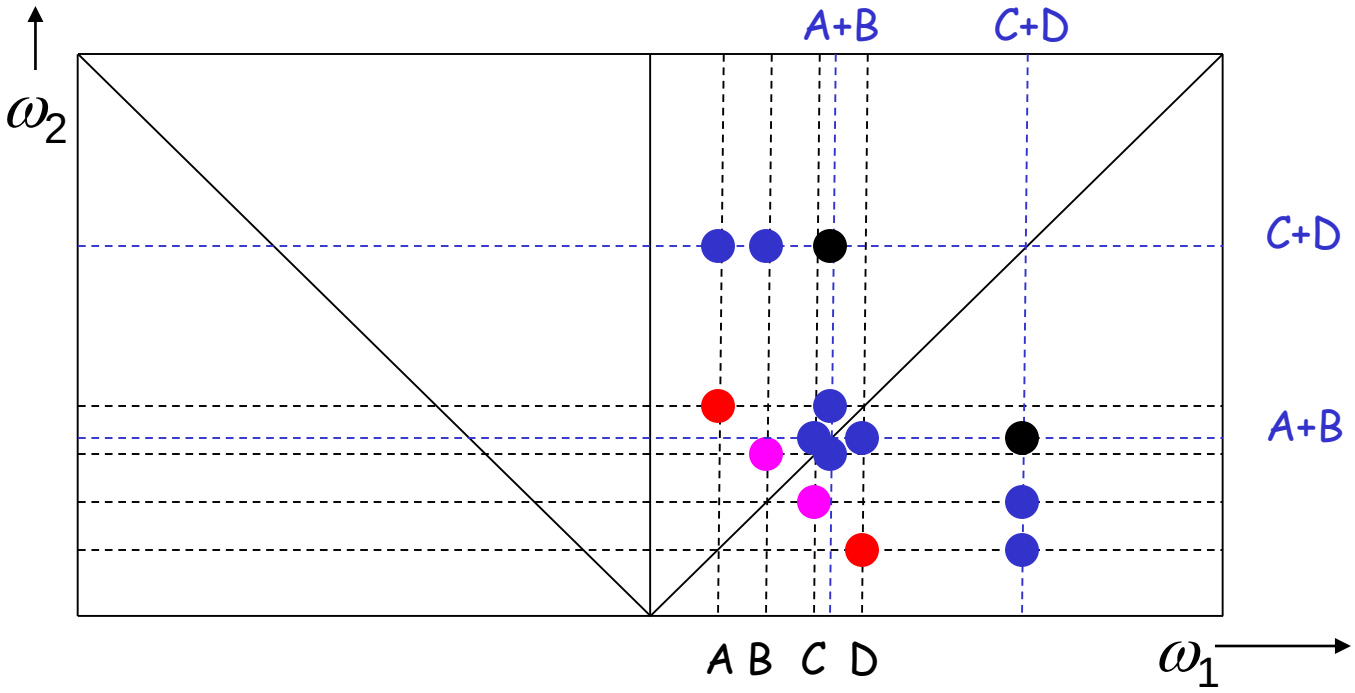
Product of cosines = cosines of summed angles

Leads to combination frequencies (sums)

Allows to determine relative sign of hyperfine

Interaction with several nuclei

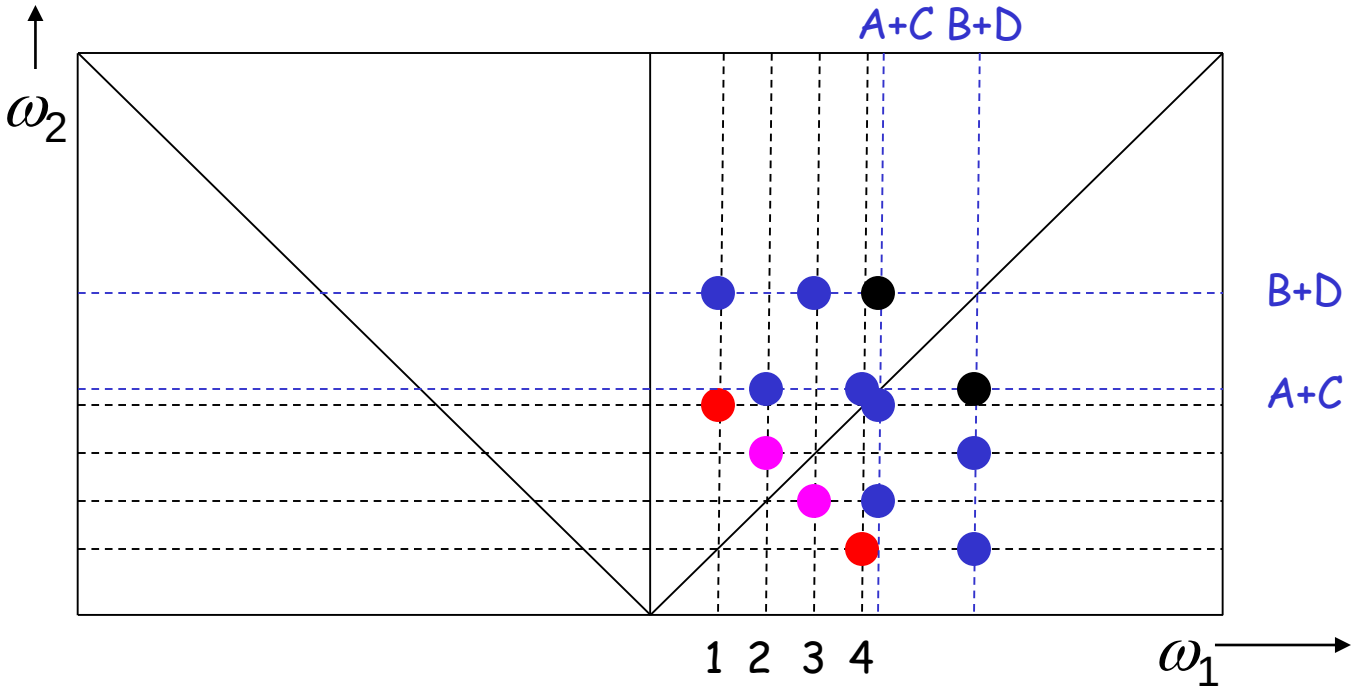
A,B : both nuclear frequencies within M_S= +½ branch
C,D : both nuclear frequencies within M_S= -½ branch



Hyperfine same sign (e.g. both positive)

Interaction with several nuclei

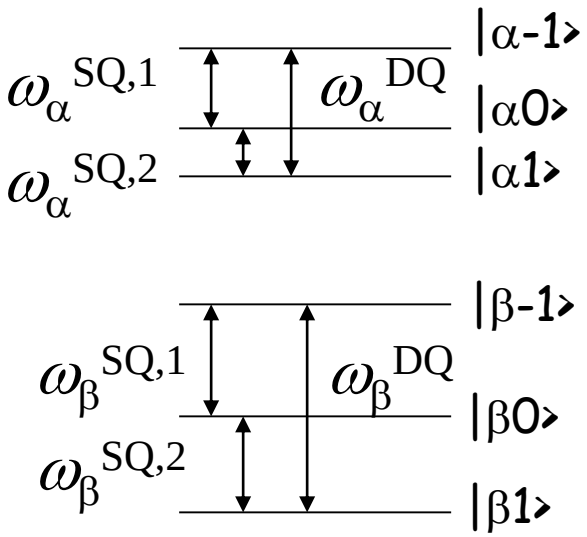
A,C : both nuclear frequencies within M_S= +½ branch
B,D : both nuclear frequencies within M_S= -½ branch



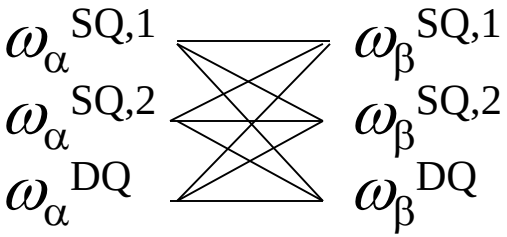
Hyperfine opposite sign

Increasing complexity $S = ½$, $I > ½$ systems

Case example, $S = ½$, $I = 1$ systems



Possible cross-peaks



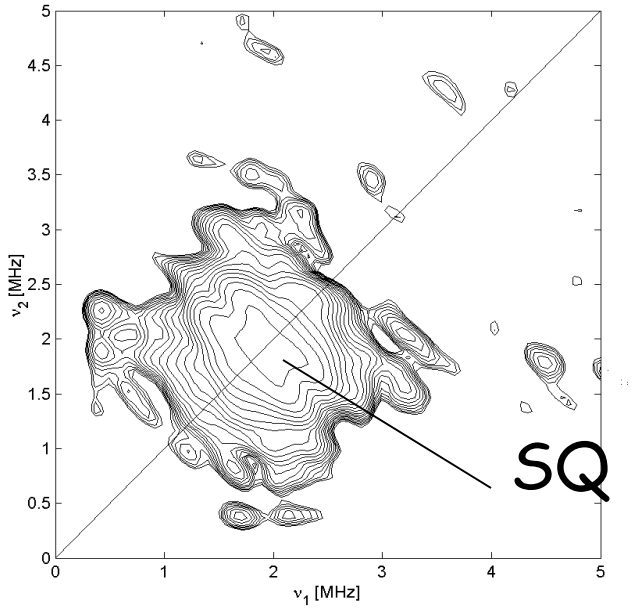
DQ cross-peaks are dominant
in case of large nuclear-quadrupole interaction

$$\nu_{\alpha\beta}^{DQ} = 2\sqrt{(a/2 \pm \nu_I)^2 + K^2(3+\eta^2)}$$

$K = e^2qQ/(4h)$

$\eta = |Q_x - Q_y|/|Q_z|$ $(|Q_z| > |Q_y| > |Q_x|)$

$S = ½$, $I = 1$ systems



^{2}H HYSCORE

Relatively small Q

Single-quantum cross-peaks dominate

Sample:

(R,R) Copper Jacobsen in
deuterated (S) methylbenzyl amine/Toluene

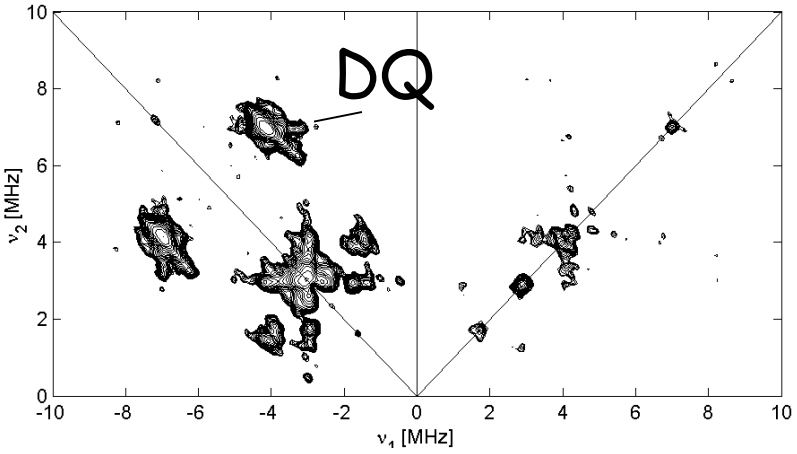
^{14}N HYSCORE

Relatively large Q

Double-quantum cross-peaks dominate

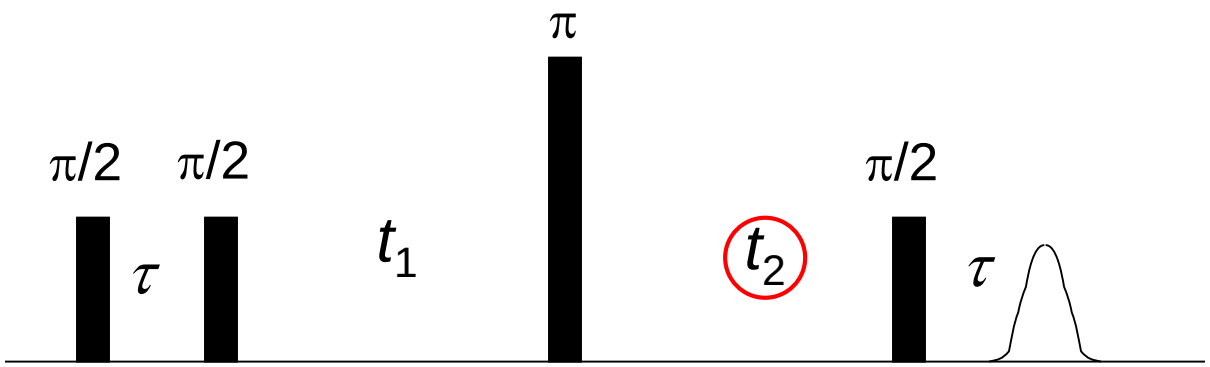
Sample:

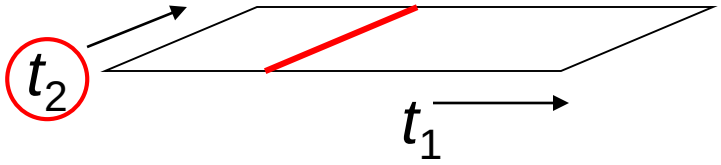
Ferric mouse neuroglobin



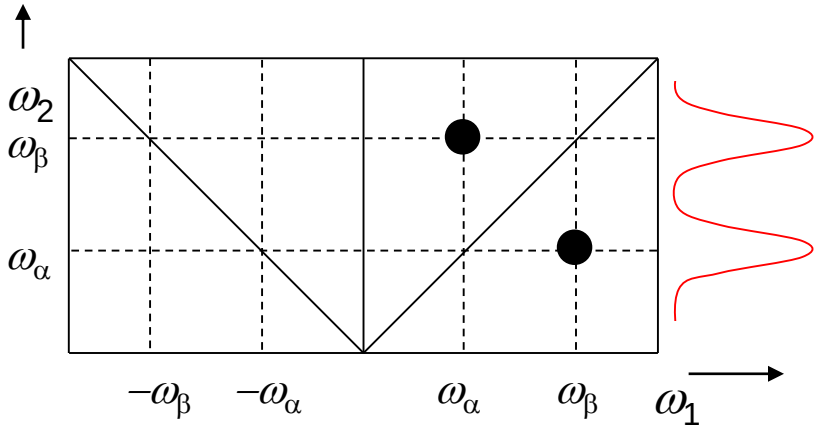
P. Höfer *et al*., Chem. Phys. Lett, 132, 279 (1986)
P. Höfer, J. Magn. Reson., A111, 77 (1994)
E. J. Reijerse and S. A. Dikanov, Pure & Appl. Chem., 64, 789 (1992)
A. Pöppl and L. Kevin, J. Phys. Chem., 100, 3387 (1996)
A. Pöppl and R. Böttcher, Chem. Phys., 221, 53 (1997)
S. A. Dikanov *et al*., J. Am. Chem. Soc., 118, 8408 (1996)
M. Gutjahr, et al., Appl. Magn. Reson., 22, 401 (2002)
N. Ploutarch Benetis, et al, J. Magn. Reson., 158, 126 (2002)
A. G. Maryasov and M. K. Bowman, J. Phys. Chem. B, 108, 9412 (2004)

DEFENCE =
deadtime free ESEEM by nuclear coherence-transfer echoes

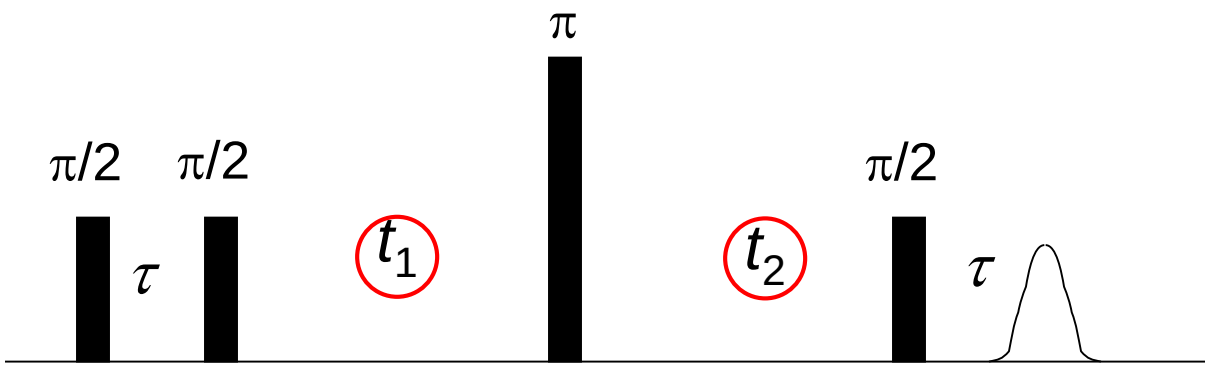




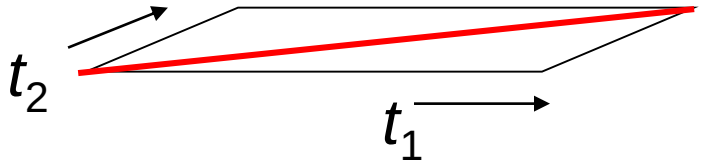
slice of a
HYSCORE experiment



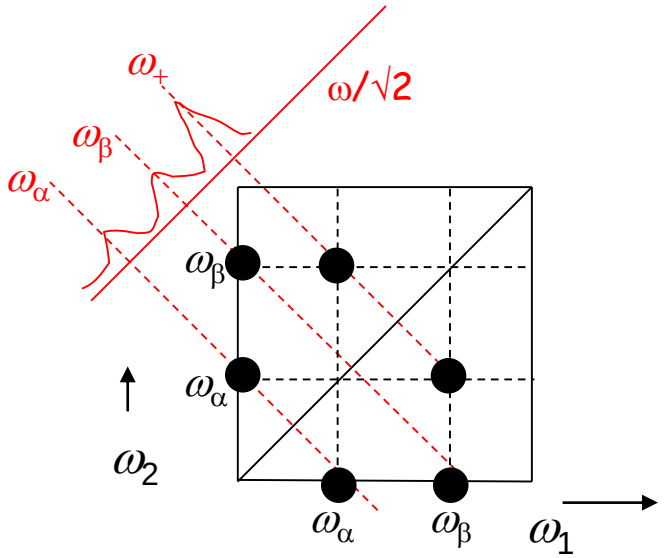
A. Ponti and A. Schweiger, J. Chem. Phys., 102, 5207 (1995)



$t_1 = t_2$



diagonal of a
HYSCORE experiment



Rewriting modulation formula for $t_1=t_2=T$

$$V_I = 3-\cos(\omega_\beta \tau) - \cos(\omega_\alpha \tau) - \sin^2\eta\cos(\omega_+ \tau) - \cos^2\eta\cos(\omega_- \tau)$$

$$\begin{aligned} V_{IIa} + V_{IIb} = & -\cos(\omega_\beta T) -\cos(\omega_\alpha T) -\cos(\omega_\beta T+ \omega_\beta \tau) -\cos(\omega_\alpha T+ \omega_\alpha \tau) \\ & + \cos^2\eta\,[\cos(\omega_\alpha T+ \omega_\beta \tau) +\cos(\omega_\beta T+ \omega_\alpha \tau) +\cos(-\omega_\beta T+ \omega_- \tau) +\cos(\omega_\alpha T+ \omega_- \tau)] \\ & + \sin^2\eta\,[\cos(-\omega_\beta T+ \omega_\alpha \tau) +\cos(-\omega_\alpha T+ \omega_\beta \tau) +\cos(\omega_\beta T+ \omega_+ \tau) +\cos(\omega_\alpha T+ \omega_+ \tau)] \end{aligned}$$

$$V_{IIIa} = \cos^2\eta\,[\cos(\omega_+ T) +\cos(\omega_+ T+ \omega_+ \tau) -\cos(\omega_+ T+ \omega_\beta \tau) -\cos(\omega_+ T+ \omega_\alpha \tau)]$$

$$V_{IIIb} = \sin^2\eta\,[\cos(\omega_- T) +\cos(\omega_- T+ \omega_- \tau) -\cos(-\omega_- T+ \omega_\beta \tau) -\cos(\omega_- T+ \omega_\alpha \tau)]$$

Combination-peak experiment can be done 2D
Variation of *t* and *T*
Blind-spot free !

A. M. Tyryshkin et al., J. Magn. Reson., A105, 271 (1993)
K. Matar and D. Goldfarb, J. Magn. Reson., A 111, 50 (1994)
S. Van Doorslaer and A. Schweiger, Chem. Phys. Lett., 281, 297 (1997)

Starting point:

To generate NC from EP we need a semi-selective mw pulse
Non-selective and ideally selective pulses cannot create NC from EP
(follows from density operator formalism)

Idea:

There must be an optimum mw field strength
for creation of NC

In a matching experiment:

Look for the optimal mw strength (i.e. ω_1) and pulse length
to optimize creation of specific NC

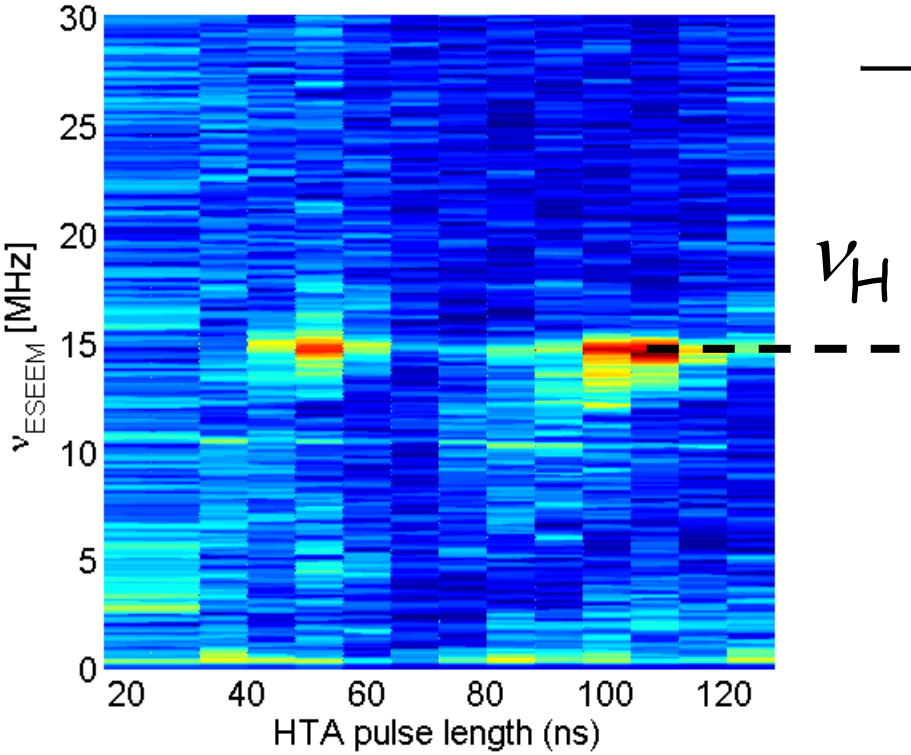
G. Jeschke *et al*., J. Magn. Reson., 131, 261 (1998)

Conditions for mw field strength depend on specific interaction you want to enhance

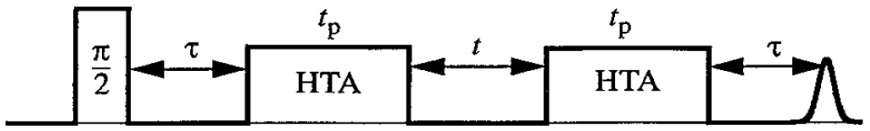
$A << |\omega_I| \quad \omega_1^m \approx |\omega_I|$

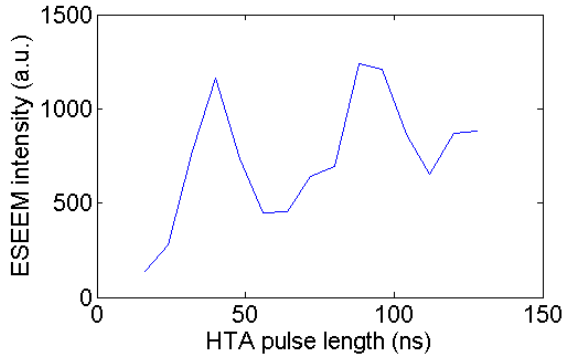
$A >> |2\omega_I| \quad \omega_1$ as large as possible

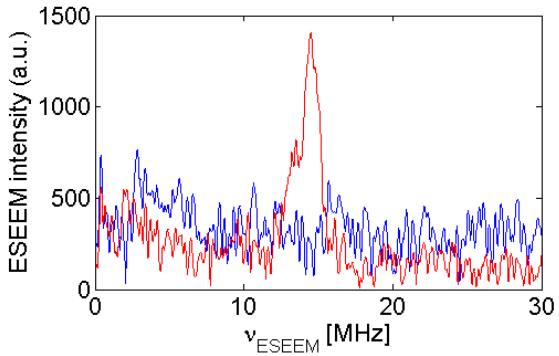
Pulse length optimization can be done in a three-pulse ESEEM experiment

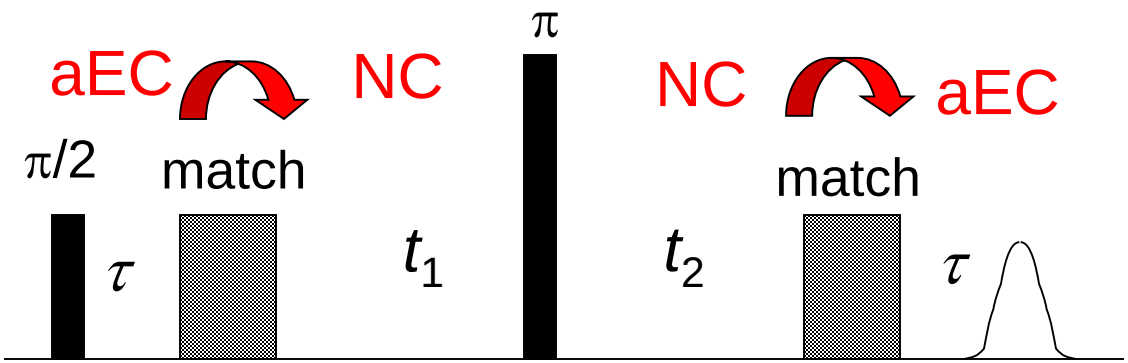


ν_H





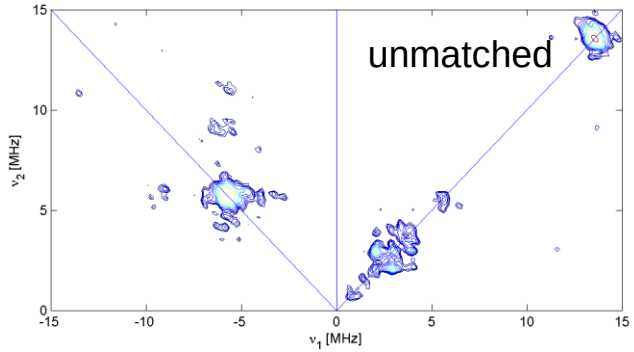


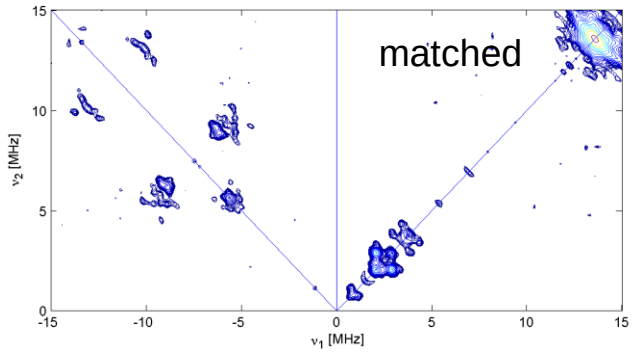


Enhancement of forbidden transfers

G. Jeschke *et al*., J. Magn. Reson., 131, 261 (1998)

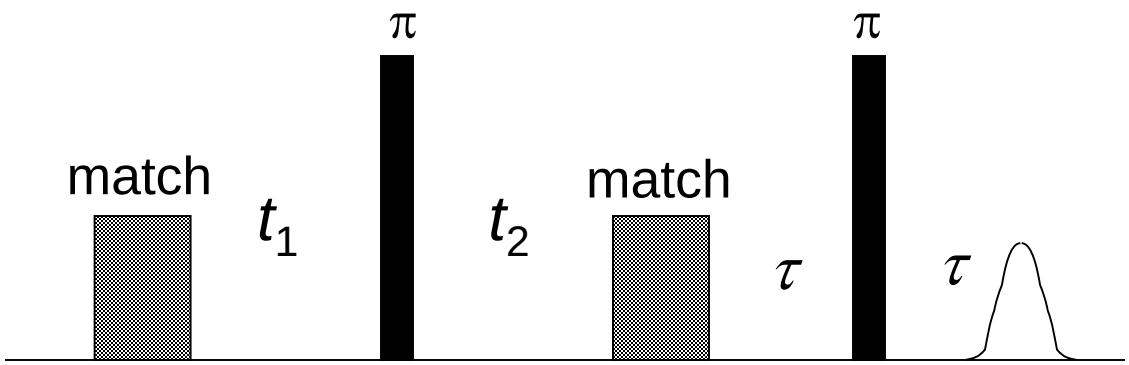
Length of pulse, determined via matched 3-pulse ESEEM





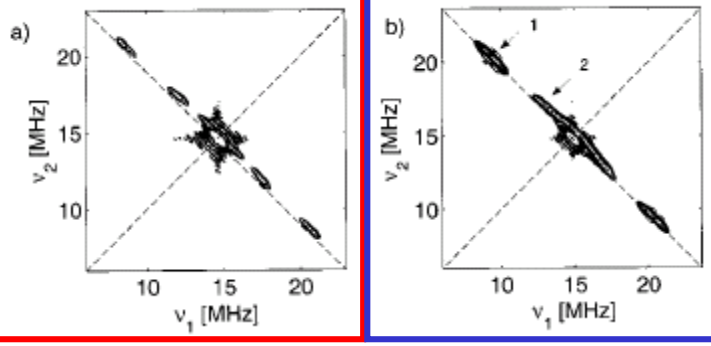
MetMb (high-spin Fe(III)), matching on nitrogen interaction

M. Fittipaldi *et al*.,*J. Phys. Chem. B*., 112, 3859 (2008)



Blindspot-free experiment

Conventional HYSCORE

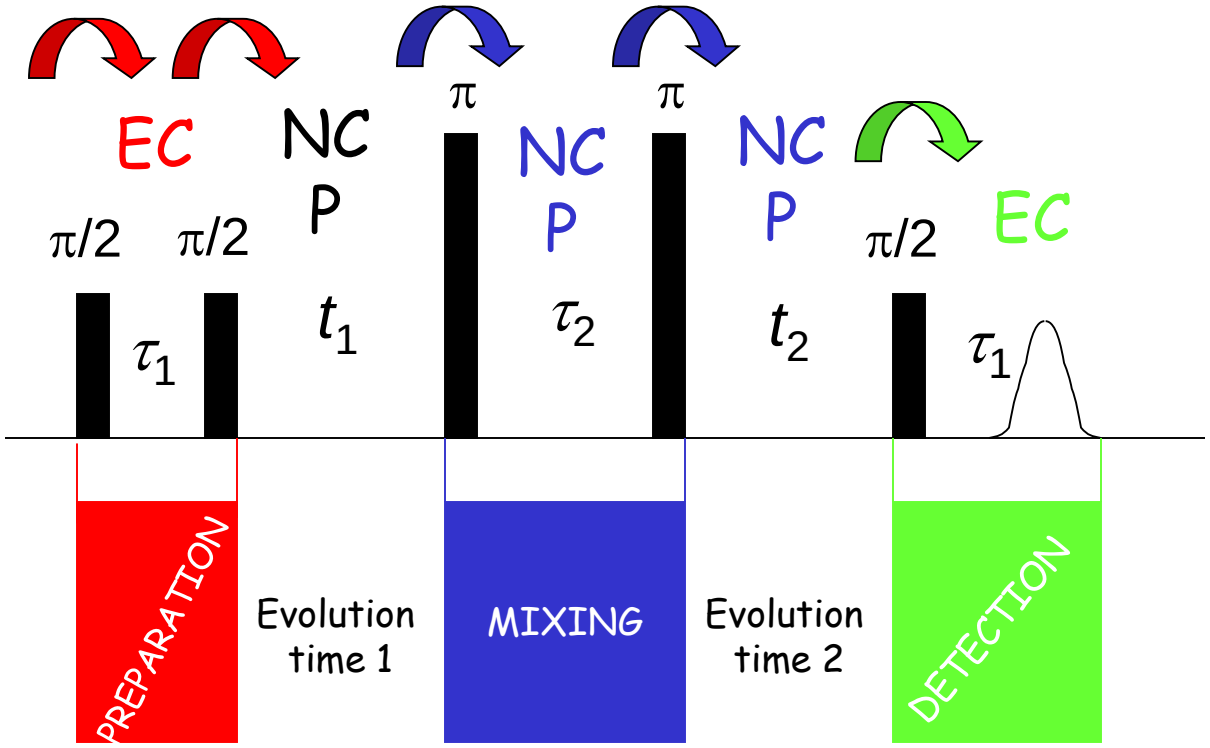


SMART HYSCORE

$Cu(sal)_2$ in $Ni(sal)_2$

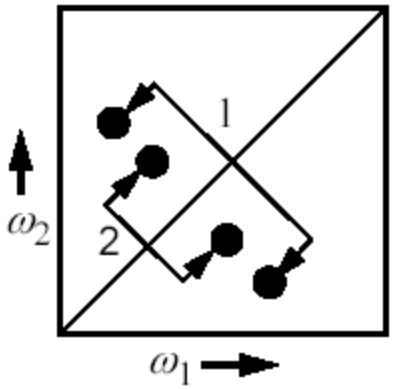
L. Liesum et al., J. Chem. Phys., 114, 9478 (2001)

DONUT = double nuclear coherence transfer

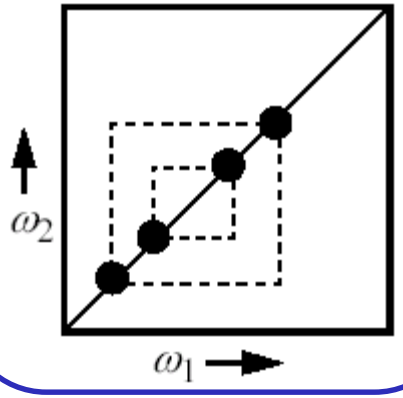


In case of overlapping EPR signals:
do signals belong to the same electron spin system or not?

HYSCORE

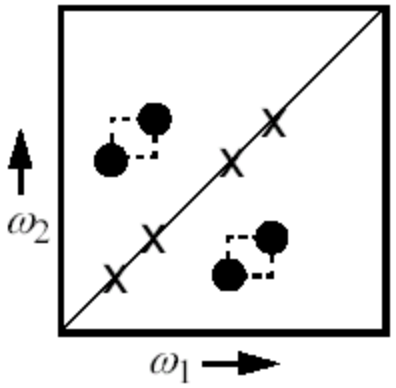


DONUT S_1=1/2, I_1=1/2
S_2=1/2, I_2=1/2

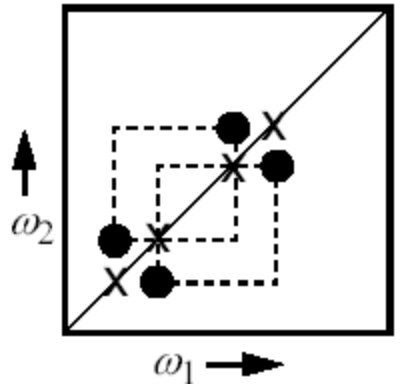


DONUT S_1=1/2, I_1=1/2, I_2=1/2

Hyperfine
same sign

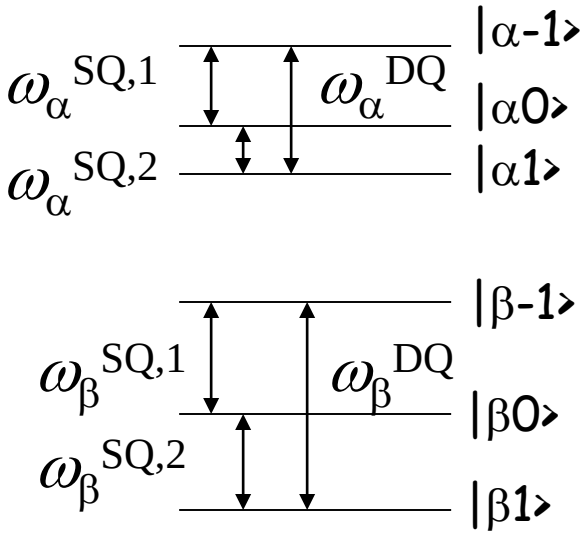


Hyperfine
different sign



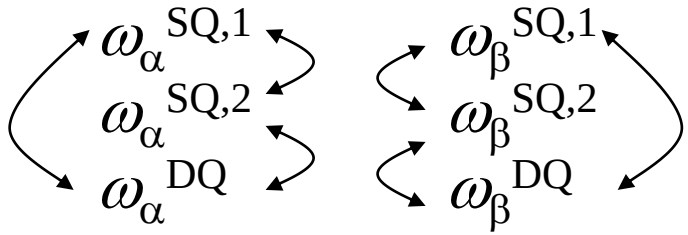
In case of complex HYSCORE
Helping to assign different nuclear frequencies

DONUT S_1=1/2, I_1=1



Possible cross-peaks

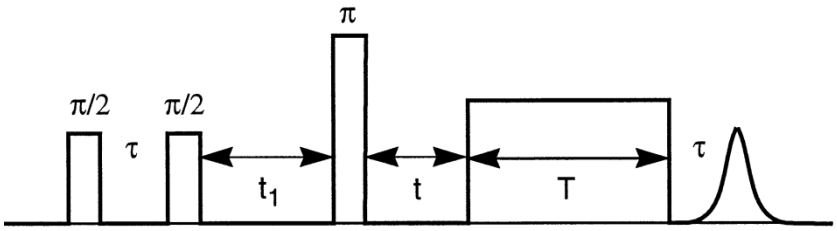
Again only within one M_S manifold



For detailed information:

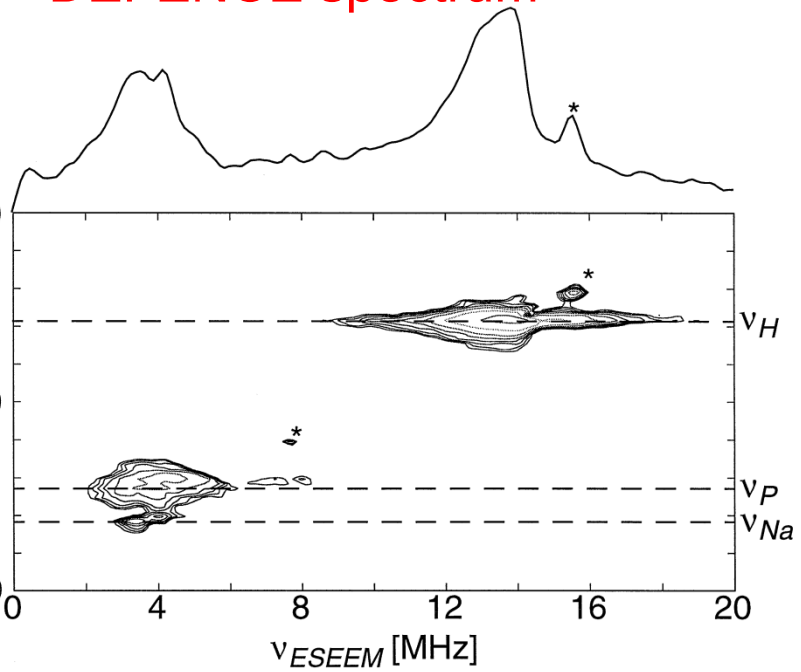
D. Goldfarb et al., JACS, 120, 7020 (1998)

If you have difficulty assigning nuclear frequencies to a type of nucleus
→Think of a hyperfine-decoupling experiment
→ gets rid of (majority of) hyperfine coupling



Hyperfine decoupled DEFENCE

DEFENCE spectrum



Direct assignment of contributions →

Read more and discover different pulse sequences:

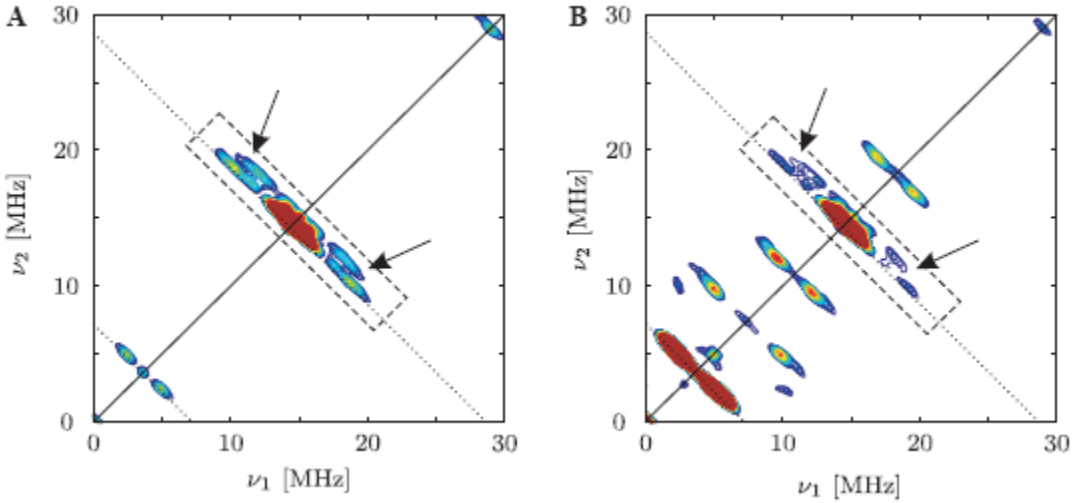
G. Jeschke, A. Schweiger, J. Chem. Phys. 106, 9979 (1997)
S. Van Doorslaer, A. Schweiger, Chem. Phys. Lett, 308, 187 (1999)
G. Mitrikas, A. Schweiger, J. Magn. Reson., 168, 88 (2004)

All the standard ESEEM experiments suffer from the cross-suppression effect*

= peaks of nuclei with shallow modulations are totally suppressed by contributions of nuclei with deep modulations

$Cu(gly)_2$ (^{13}C in natural abundance)

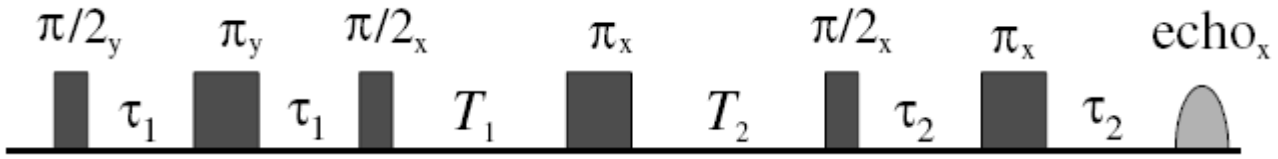
$Cu(gly)_2$ (^{13}C labelled)

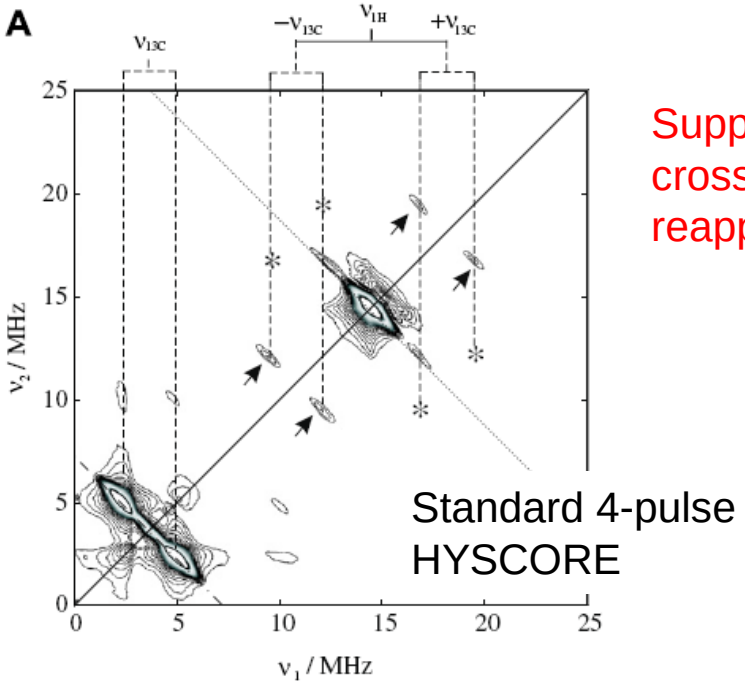


Strong ^{13}C modulation suppress ^{1}H HYSCORE cross peaks (arrows)

Example taken from: *S. Stoll *et al*., J. Magn. Reson., 177, 93 (2005))

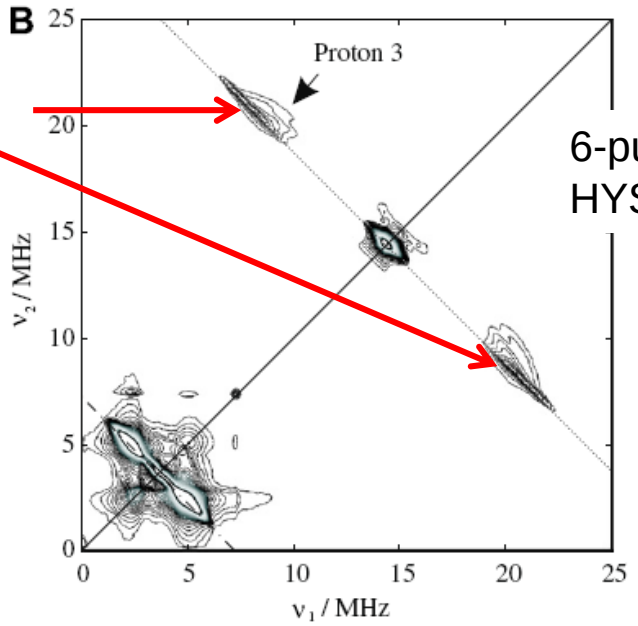
Cross-suppression problem may be circumvented by alternative pulse sequences
e.g. 6-pulse HYSCORE





Standard 4-pulse HYSCORE

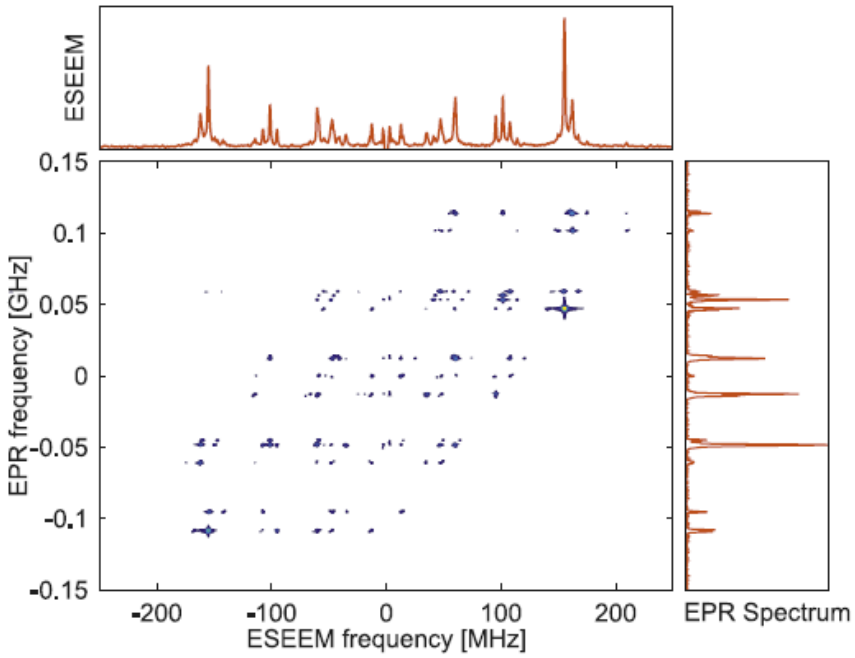
Suppressed cross-peaks reappear !



6-pulse HYSCORE

Example of $Cu(gly)_2$ (^{13}C labelled) taken from:
B. Kasumaj and S. Stoll, J. Magn. Reson., 190, 233 (2008))

Ultra-wide band pulses -> allows for detection of frequencies that go far beyond range that can be addressed with standard ESEEM (even with the rectangular matched pulses)



Example of Cu^{2+} in rutile crystal
T. Segawa, A. Doll, S. Pribitzer, G. Jeschke, J. Chem. Phys., 143, 044201 (2015)