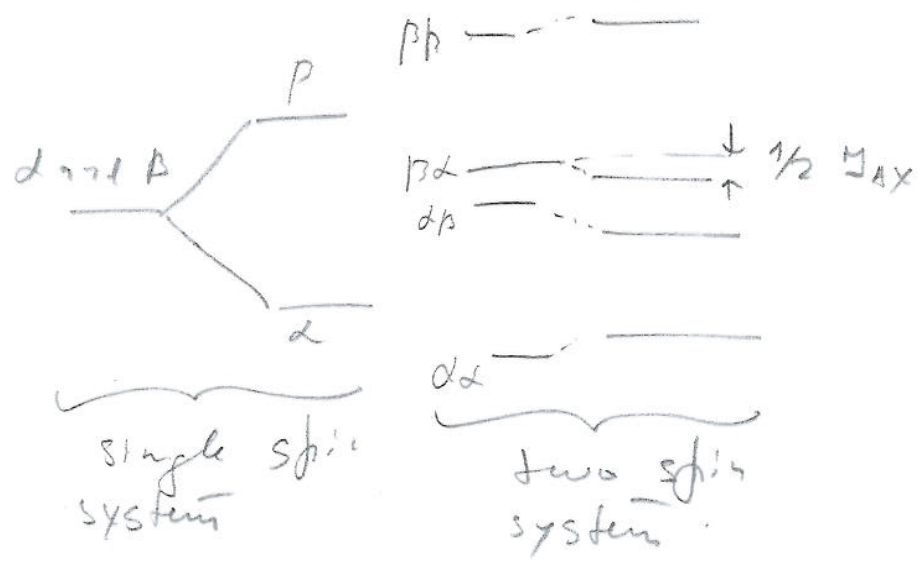Example: two spin system

$\alpha\alpha , \alpha\beta, \beta\alpha , \beta\beta$.

Yabelling nuclei A and X

$$\hbar^{-1} U = -\nu_A m_A - \nu_X m_X + J_{AX} m_a m_X$$

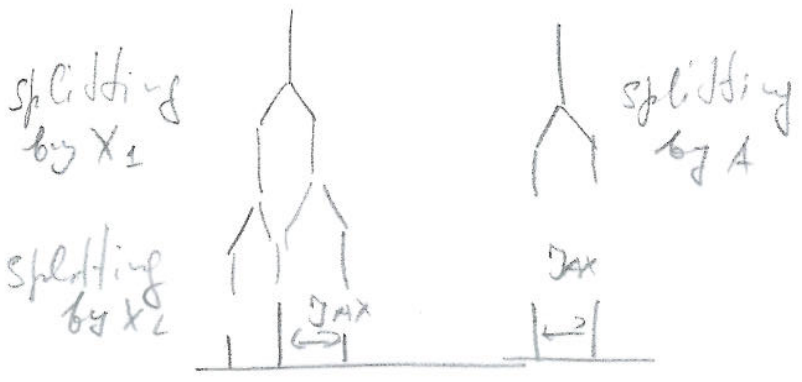single spin system

two spin system

Allowed transitions

A - transitions $\Delta m_A = \pm 1$ $\Delta m_X = 0$

X - transitions $\Delta m_A = 0$ $\Delta m_X = \pm 1$.
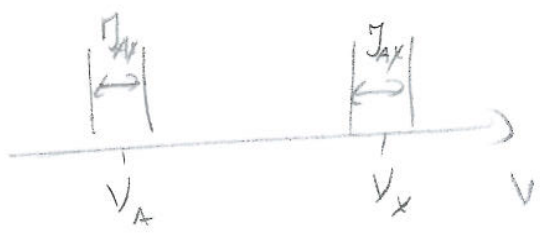
Spectra involving magnetic equivalence
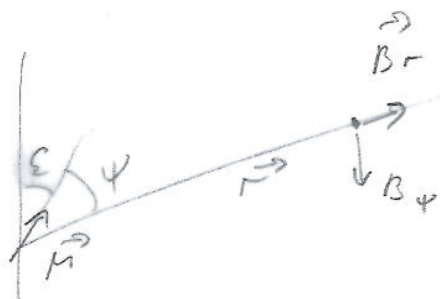
AX_2 spin system

splitting by X_1

splitting by A

splitting by X_2

J_{AX}

relative intensities AX_p	
P	
1	1/1
2	1/2/1
3	1/3/3/1
4	1/4/6/4/1

2.1 Dipolar interactions

nuclei → small magnets
dipolar interactions.

For nuclear magnetic moment M at angle ε to the z direction the field at a distance r

$$B_r = \frac{\mu_0}{4\pi} \frac{2M}{r^3} \cos\psi$$

$$B_\psi = \frac{\mu_0}{4\pi} \frac{M}{r^3} \sin\psi$$

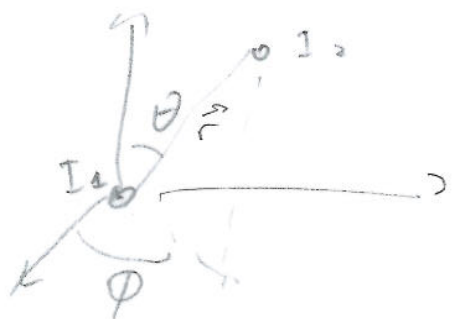Typical distances ≈ 2 Å   B ≈ 0,2 mT (10 kHz)

Compare with chemical shift

10 ppm @ 2 T → 20 µT

Acting via free space (contrary to J coupling)

Interaction between 2 nuclei ∽ two point dipoles

$$U = \frac{\vec{M_1}\vec{M_2}}{r^3} - 3\frac{(\vec{M_1}\cdot\vec{r})(\vec{M_2}\cdot\vec{r})}{r^5} \cdot \frac{\mu_0}{4\pi}$$
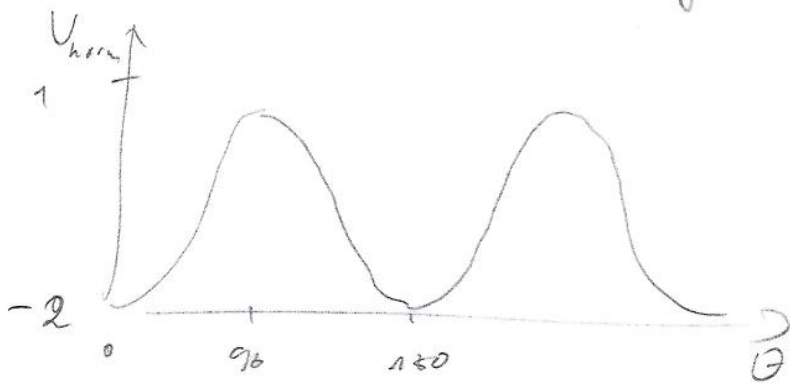
Case when $\gamma B_0 \gg E_{coupling}$.

$$(\vec{M_1} \cdot \vec{r}) \cdot (\vec{M_2} \cdot \vec{r}) = (\vec{M_1} \cdot \vec{M_2}) r^2 \cos^2\theta$$

$$U = \frac{\mu_0}{4\pi} (\vec{M_1} \cdot \vec{M_2}) r^{-3} (1 - 3\cos^2\theta)$$

Interaction energy has angular dependance

The first null at $\cos\theta = \frac{1}{\sqrt{3}} \Rightarrow \theta = 54,7°$

Interaction hamiltonian (general case)

QM description $\vec{\mu} = \gamma \hbar I$

$$H_{dd} = \gamma_1 \gamma_2 \hbar^2 \left(\frac{\vec{I_1} \cdot \vec{I_2}}{r^3} - 3 \frac{(\vec{I_1} \cdot \vec{r})(\vec{I_2} \cdot \vec{r})}{r^5} \right) \cdot \frac{\mu_0}{4\pi}$$

We can write $\vec{r}$ in polar coordinates.

$$\vec{r}(r_x, r_y, r_z) = (r\sin\theta\cos\varphi, r\sin\theta\sin\varphi, r\cos\theta)$$

and

$$\vec{H_b} = \frac{\mu_0}{4\pi} \frac{\gamma_1 \gamma_2 \hbar^2}{r^3} (A + B + C + D + E + F)$$

where

$$A = I_{1z} I_{2z} (3\cos^2\theta - 1)$$

$$B = \frac{1}{4} [\vec{I}_{1+} \vec{I}_{2-} + \vec{I}_{1-} \vec{I}_{2+}] (3\cos^2\theta - 1)$$

$$C = [I_{1z} I_{2+} + I_{1+} I_{2z}] \times \ldots$$

$$D = [I_{1z} I_{2-} + I_{1-} I_{2z}] \times \ldots$$

$$E = \vec{I}_{1+} \cdot \vec{I}_{2+} \times \ldots$$

$$F = \vec{I}_{1-} \vec{I}_{2-} \times \ldots$$

In secular approx

$$|\omega_1 - \omega_2| >> \frac{\mu_0}{4\pi} \cdot \frac{\gamma_1 \gamma_2 \hbar^2}{r^3}$$

A — zz coupling (must be kept).

B $I_{1+} I_{2-}$, $I_{1-} I_{2+}$ flip flops

   forbidden for $\omega_1 - \omega_2 >> $ coupling
   (heteronuclear coupling)

   Allowed for $\omega_1 = \omega_2$ (homonuclear
              coupling).

C,D $I_{1z} I_{2+}$ connect levels separated
              by γB_0, can be neglected

E,F   connect levels separated by $2\gamma B_0$
              (double quantum)
              can be neglected

Homonuclear coupling

$$H_D = \frac{\mu_0}{4\pi} \frac{\gamma_1 \gamma_2 \hbar^2}{r^3} (3\cos^2\theta - 1) \left(\bar{I}_{1z}\bar{I}_{2z} - \frac{1}{2}\bar{I}_1 \cdot \bar{I}_2 \right)$$
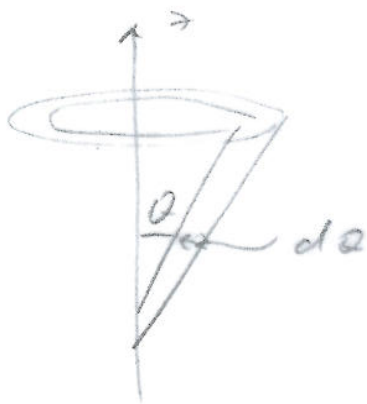
Heteronuclear coupling

$$H_D = \frac{\mu_0}{4\pi} \frac{\gamma_1 \gamma_2 \hbar^2}{r^3} (3\cos^2\theta - 1) \bar{I}_{1z} \bar{I}_{2z}$$

Solid state ⟶ all angles
dipolar broadening

picture

3.3 Averaging by molecular motion

solid angle to $d\theta$
$2\pi \cdot \sin\theta \cdot d\theta$

fraction of spins in $d\theta$

$$\frac{d\mu}{\mu} = \frac{2\pi \sin\theta \, d\theta}{4\pi} = \frac{1}{2}\sin\theta \, d\theta$$

Theorem, for any function of θ, $f(\theta)$

$$\langle f(\theta) \rangle = \int_0^\pi F(\theta) f(\theta) \, d\theta$$
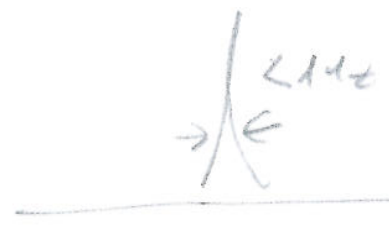
where $F(\theta)$ — distribution function

$$F(\theta) = \frac{1}{\mu}\left(\frac{d\mu}{d\theta}\right)$$

$$\langle 3\cos^2\theta - 1 \rangle = \int_0^\pi \frac{1}{2}\sin\theta (3\cos^2\theta - 1) \, d\theta =$$

$$\frac{1}{2} \left[\cos^3 \theta \right]_0^\pi + \frac{1}{2} \left[\cos \theta \right]_0^\pi = 0$$

For fast rotation dipolar coupling
is averaged to zero!

Small molecules
solution

Solids

$< 1 Hz$

Broad (kHz).
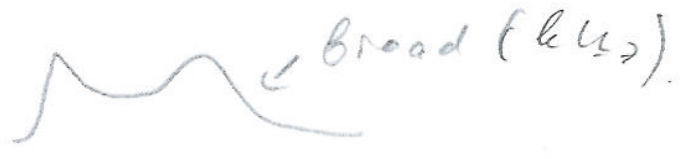
Magic angle spinning.

$\vec{B_0}, z$

$54,2°$

z
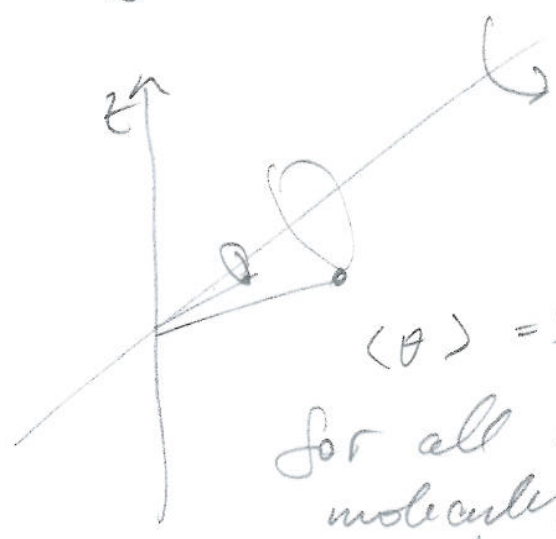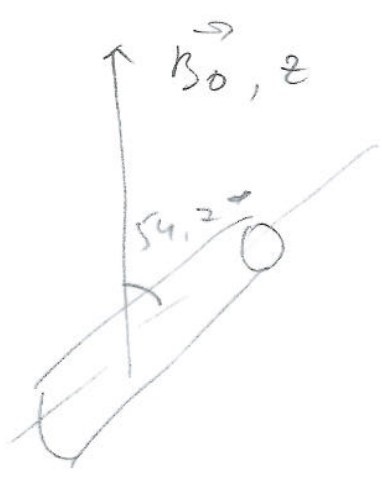
$\langle \theta \rangle = 54,7°$
for all sample
molecules.

Requirement → rotation faster
than dipolar coupling.

2.4. Coupled systems (AX, AMX)
polarisation transfer and sensitivity

$I_1 \circ \overline{}\!\!\!\!\!\!\!\!\overset{r}{} \circ I_2$
$\qquad H_{DD} = \dfrac{\gamma_1 \gamma_2 \hbar^2}{r^3}\dfrac{\mu_0}{4\pi}\left(A+B+C+D+E+F\right)$
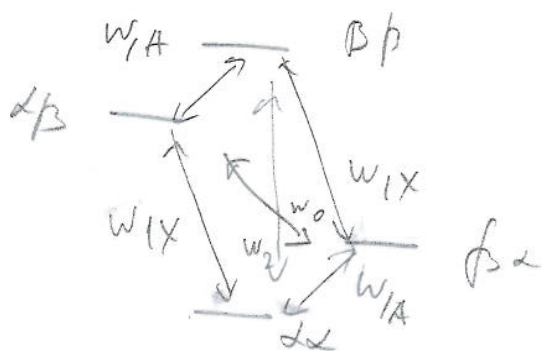
$$A \Rightarrow I_{1z}I_{2z}$$

$$B \Rightarrow I_{1+}I_{2-} + I_{1-}I_{2+}$$

$$C \Rightarrow I_{1z}I_{2+} + I_{1+}I_{2z}$$

$$D \Rightarrow I_{1z}I_{2-} + I_{1-}I_{2z}$$

$$E \Rightarrow I_{1+}I_{2+} \quad , \quad F \Rightarrow I_{2-}I_{1-}$$

spin state	$\beta\beta$	$\alpha\beta$	$\beta\alpha$	$\alpha\alpha$
$\beta\beta$	A	D	D	F
$\alpha\beta$	C	A	B	D
$\beta\alpha$	C	B	A	D
$\alpha\alpha$	E	C	C	A

Interactions with RF
field $\Rightarrow \Delta m = \pm 1$

Relaxation $\Rightarrow$ all possible transitions
(if there is fluctuating B field)
     Molecular tumbling $\Rightarrow$ terms B to F
     are important.

Transition rates

   W_{1X} — single photon transition, spin X
   W_{1A} — single photon transition, spin A

W_2, W_0 — zero, two quantum transitions

kinetics analysis of relaxation

(*) $$\frac{dn_{\alpha\alpha}}{dt} = -(W_{1A} + W_{1X} + W_2)(n_{\alpha\alpha} - n_{\alpha\alpha}^0) + W_2(n_{\beta\beta} - n_{\beta\beta}^0)$$

$$+ W_{1A}(n_{\beta\alpha} - n_{\beta\alpha}^0) + W_{1X}(n_{\alpha\beta} - n_{\alpha\beta}^0)$$

n_{XX}^0 — populations at Boltzmann equilibrium, absence of any RF field

Signals in NMR $\hookrightarrow$ ~ population difference

Total number of polarized spins (A and X)

$$N_A = (n_{\alpha\alpha} - n_{\beta\alpha}) + (n_{\alpha\beta} - n_{\beta\beta})$$

$$N_X = (n_{\alpha\alpha} - n_{\alpha\beta}) + (n_{\beta\alpha} - n_{\beta\beta})$$

from (*) $\Rightarrow$

and similar eq. for other states

$$\frac{dN_A}{dt} = -(W_0 + 2W_{1A} + W_2)(N_A - N_A^0) -$$

$$-(W_2 - W_0)(N_X - N_X^0)$$

$$\frac{dN_X}{dt} = -(W_2 - W_0)(N_A - N_A^0) +$$

$$+ (W_0 + 2W_{1X} + W_2)(N_X - N_X^0)$$

Experiment to observe coupling

irradiate (saturate) spin $X \hookrightarrow N_X = 0$

$(n_{\alpha\alpha} = n_{\alpha\beta} ; n_{\beta\alpha} = n_{\beta\beta}$

In addition for steady state

$$\frac{dN_A}{dt} = 0 \implies 0 = (W_2 - W_0)N_x^0 - (W_0 + 2W_{1A} + W_2) \times$$
$$\times (N_A^* - N_x^0)$$

N_A^* - population corresponding to
particular cond. of experiment

Rearrangement $\quad \dfrac{N_A^*}{N_A^0} = 1 + \dfrac{N_x^0}{N_A^0}\left(\dfrac{W_2 - W_0}{W_2 + 2W_{1A} + W_0}\right.$

$$\frac{N_x^0}{N_A^0} \sim \frac{\gamma_x}{\gamma_A} \implies \text{signals } (S_A, S_x)$$

$$\frac{S_A^*}{S_A^0} = 1 + \frac{\gamma_x}{\gamma_A}\left(\frac{W_2 - W_0}{W_2 + 2W_{1A} + W_0}\right)$$

Intensity change $\iff$ nuclear overhauser effect
$$(\text{NOE})$$

If π - pulse is applied to A (inversion)
and recovery is monitored (X spins
are irrad.)

$$\frac{dN_A}{dt} = (W_2 - W_0)N_x^0 - (W_0 + 2W_{1A} + W_2)(N_A - N_A^*)$$

relaxation towards steady state N_A^*

$$N_x = 0$$

$$\implies \frac{dN_A}{dt} = -(W_0 + 2W_{1A} + W_2)(N_A - N_A^*)$$

Single exponential, rate constant

$$T^{-1} = W_0 + 2W_{1A} + W_2$$

In order to calculate dipolar contributions to T^{-1} $\Rightarrow$ need to obtain W_0, W_{1A} and W_2

result (extreme narrowing limits)

$$W_0 / W_1 / W_2 = 1/6 / 1/4 / 1$$

3. Coupling of nuclear spins to electrons, Dynamic nuclear polarisation.

$$H = g \mu_B \vec{B} \cdot \vec{S} - g_N \mu_N \vec{B} \cdot \vec{I} + A \vec{S} \cdot \vec{I}$$

$\underbrace{\phantom{A \vec{S} \cdot \vec{I}}}_{\text{Hyperfine coupling.}}$

$$A \vec{S} \cdot \vec{I} = \frac{A}{2}(S^+ I^- + S^- I^+) + A S_z I_z$$
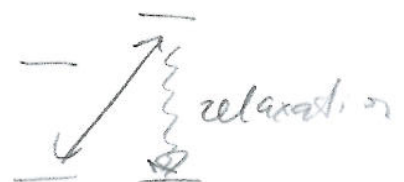
$$S^{\pm} = S_x \pm i S_y \quad (\text{spin operators})$$

Zero field $H = A \vec{S} \cdot \vec{I}$ but

at $B = 0$ $\rightarrow$ no E spin polaris.

3.(1 a). Hartmann - Hahn resonance

$$\Omega_{Rabi \, el} = V_{Larmor} \; \frac{-}{+} \; \overline{I \, \Omega_n} = \frac{u}{T}$$

b) Solid effect.

$$-\overline{\int \begin{smallmatrix} z \\ z \\ z \end{smallmatrix}} \text{relaxation}$$

^3He, ^{129}Xe → optical pumping.

σ^+ quenching σ^+ (circularly
by N_2 polarized light)
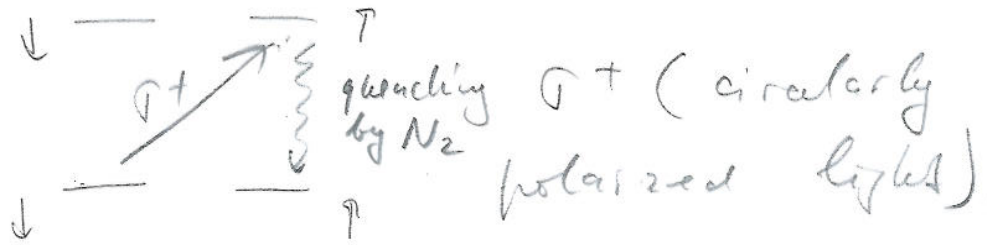
Advantage → very efficient process.
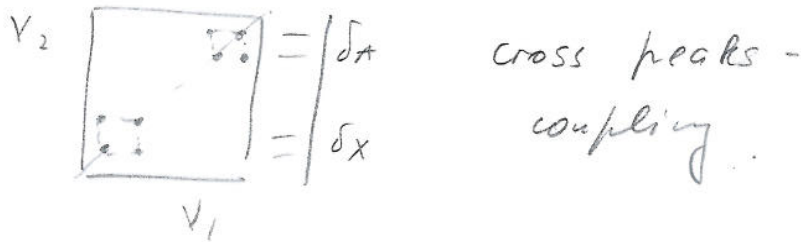Disadvantage → limited only to
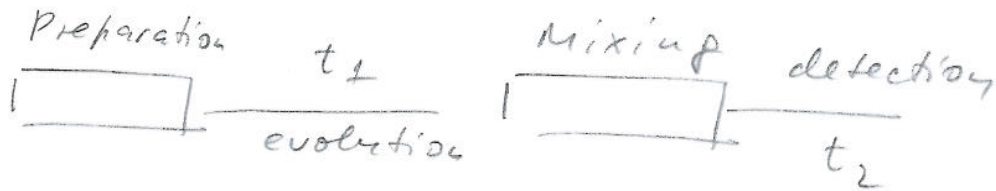a few gas molecules

4. Two dimensional NMR

Conventional NMR

(1D)   signal $= f(\nu)$

2D NMR → signal $= f(\nu_1, \nu_2)$

Example   AX system (2 spins)
δ_X δ_A coupled by J coupling

ν_2 [ ] $= \delta_A$ cross peaks -
    $= \delta_X$ coupling.

ν_1

General scheme

Preparation   Mixing   detection
|_____|____t_1____ |____|____
        evolution t_2

4.1. Two dimensional experiment
      using coherence transfer via
      scalar (J) coupling

   COSY experiment (coherent spectroscopy)

① start with equilibrium magnetisation

   I_{1z}

② apply $\pi/2$ pulse

   $I_{1z} \xrightarrow[\left(\frac{\pi}{2} I_{1x}\right)\left(\pi/2\ I_{2x}\right)]{} -I_{1y}$

③ State evolves for t_1 under the influence
      of offset of spin 1

$$-I_{1y} \xrightarrow{\Omega_1 t_1 I_{1z}} \cos \Omega_1 t_1 \, I_{1y} + \sin \Omega_1 t_1 \, I_{1x}$$

(precession in xy plane)

Both terms on the right evolve
under the coupling

$$-\cos \Omega_i t_1 \, I_{1y} \xrightarrow{2\pi J_{12} I_{1z} I_{2z}}$$

$$\cos \pi J_{12} t_1 \cos \Omega_1 t_1 \, I_{1y} + \sin(\pi J_{12} t_1) \cos(\Omega_1 t_1) 2 I_{1x} I_{2z}$$

$$\sin \Omega_1 t_1 I_{1x} \xrightarrow{2\pi J_{12} t_1 I_{1z} I_{2z}} \cos(\pi J_{12} t_1) \sin(\Omega_1 t_1) I_{1x} +$$

$$+ \sin \pi J_{12} t_1 \sin \Omega_1 t_1 \, 2 I_{1y} I_{2z}$$

---

end of "evolution" period.

now 2nd pulse

$$-\cos(\pi J_{12} t_1) \cos(\Omega_1 t_1) I_{1y} \xrightarrow{\frac{\pi}{2} I_{1x}} \xrightarrow{\frac{\pi}{2} I_{2x}}$$

$$-\cos \pi J_{12} t_1 \cos \Omega_1 t_1 \, I_{1z} \qquad (1)$$

$$\sin(\pi J_{12} t_1) \cos \Omega_1 t_1 \, 2 I_{1x} I_{2z} \xrightarrow{\frac{\pi}{2} I_{1x}} \xrightarrow{\frac{\pi}{2} I_{2x}}$$

$$-\sin \pi J_{12} t_1 \cos \Omega_1 t_1 \cdot 2 I_{1x} I_{2y} \qquad (2$$

$$\cos \pi J_{12} t_1 \sin \Omega_1 t_1 \, I_{1x} \xrightarrow{\pi/2 \, I_{1x}} \xrightarrow{\frac{\pi}{2} I_{2x}}$$

$$\cos \pi J_{12} t_1 \, I_{1x} \qquad (3)$$

$$\sin(\pi J_{12} t_1) \sin(\Omega_1 t_1) 2 I_{1y} I_{2x} \xrightarrow{\frac{\pi}{2} I_{1x}} \xrightarrow{\frac{\pi}{2} I_{2x}}$$

$$-\sin \pi J_{12} t_1 \sin \Omega_1 t_1 \, 2 I_{1z} I_{2y} \qquad (4)$$

Terms (1) and (2) are unobservable

(3) → in phase magnet of spin 1 (along x)

t_1 evolution at t_2 goes with Ω_1

→ diagonal peak at (Ω_1, Ω_1) is predicted

(4) → anti-phase magnet of spin 1 is transferred to spin 2

$$I_{1y} I_{2z} \rightarrow I_{1z} I_{2y}$$

evolves during t_1 with Ω_1

t_2 with Ω_2

cross peak (Ω_1, Ω_2).

other sequence based on nuclear Overhauser effect

NOESY ⟷ detect dipolarly coupled spins.