

Double Resonance NMR Spectroscopy in Solids

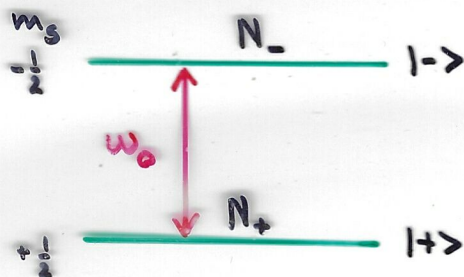
High Resolution NMR
Spectroscopy in Solids.
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by M. Mehring

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1. Density Matrix

a. Coherence

Spin $S = \frac{1}{2}$



$$\mathcal{H}_{\text{Lab}} = -\gamma_s H_0 S_z = -\omega_0 S_z$$

$$\mathcal{H}_{\text{rf}} = -2\omega_1 S_x \cos \omega t$$

Spin System : $\psi = \alpha_+ |+\rangle + \alpha_- |-\rangle$ spin state

$$\rho_{ij} = \{\alpha_i \alpha_j^*\}$$

spin density matrix

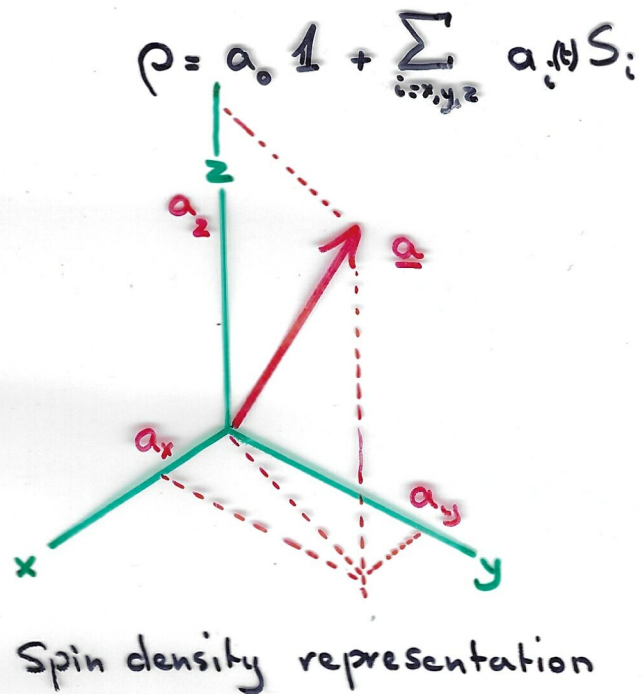
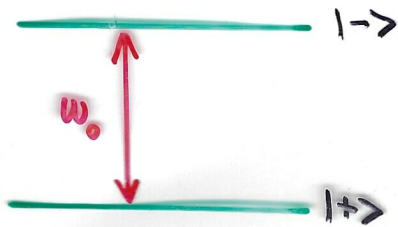
$$\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 2a_0 + a_z & a_x - ia_y \\ a_x + ia_y & 2a_0 - a_z \end{pmatrix}$$

$$= a_0 \mathbf{1} + a_x S_x + a_y S_y + a_z S_z$$

Off diagonal - Coherence

Diagonal - "Spin equilibrium"

$$a_z \propto N_+ - N_-$$



Liouville - von Neumann equation

$$i \frac{\partial \rho(t)}{\partial t} = [\mathcal{H}, \rho(t)]$$

Time independent $\mathcal{H}$: $\rho(t) = e^{-i\mathcal{H}t} \rho(0) e^{i\mathcal{H}t}$

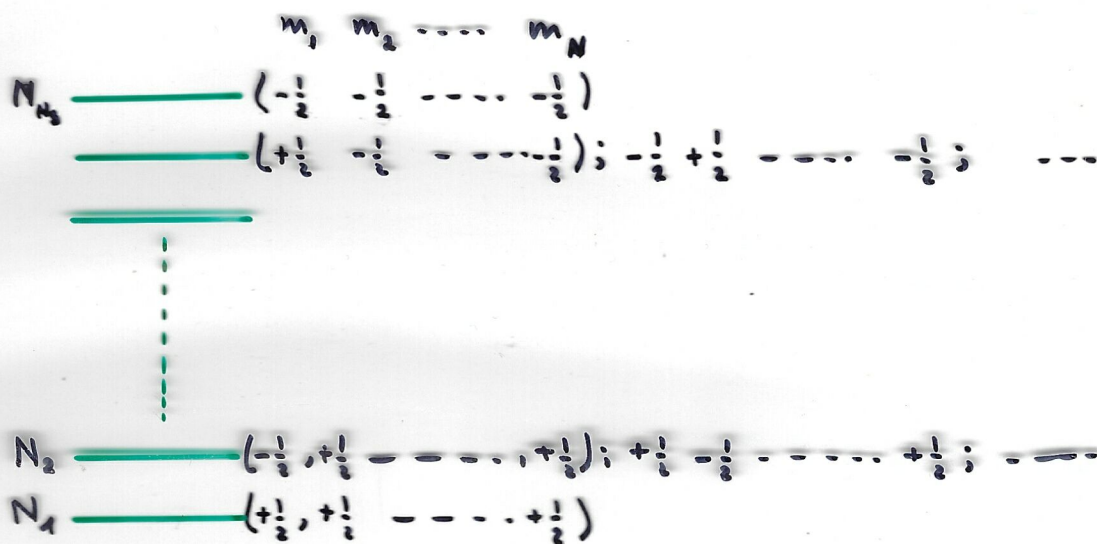
If

$$\mathcal{H} = -\omega S_z : \rho(t) = a_0 \mathbb{1}$$

$$+ a_x (S_x \cos \omega t + S_y \sin \omega t)$$

$$+ a_y (S_y \cos \omega t - S_x \sin \omega t)$$

Ensemble of Spins $S = \frac{1}{2}$



$(2S+1)^{N_s}$ states

$\rho : (2S+1)^N \times (2S+1)^N$ matrix

$$\rho = a_0 \mathbb{1} + a_x S_x + a_y S_y + a_z S_z + \dots$$

multiple quantum terms

$$S_x = \sum_{i=1}^{N_s} S_{xi}$$

$$S_y = \sum_{i=1}^{N_s} S_{yi}$$

i. Spin Equilibrium :

$$\rho = a_0 + a_z S_z$$

ii.

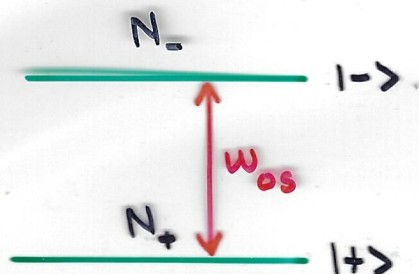
In a system with no interaction between spins,

$$\rho = a_0 \mathbb{1} + \sum_{xyz} a_p S_p \text{ and two levels describe the system}$$

b. Temperature

For a single spin

$$\frac{N_-}{N_+} = e^{-\beta_L \omega_0 S_z}$$



$$\beta_L = \frac{1}{kT_L}$$

$$\mathcal{H}_z = -\omega_0 S_z$$

For an ensemble in thermal equilibrium with lattice

$$p_i = \frac{e^{\beta_L \omega_0 S_z}}{\text{Tr}\{e^{\beta_L \omega_0 S_z}\}} = \frac{e^{-\beta_L \mathcal{H}_z}}{\text{Tr}\{e^{-\beta_L \mathcal{H}_z}\}}$$

High temperature

$$\begin{aligned} p_i &= \frac{1 - \beta_L \mathcal{H}_z}{\text{Tr}\{1\}} = (2S+1)^{-N_s} \{1 - \beta_L \mathcal{H}_z\} \\ &= (2S+1)^{-N_s} \{1 + \beta_L \omega_0 S_z\} \end{aligned}$$

In "spin equilibrium" state

$$\begin{aligned} \rho &= (2S+1)^{-N_s} \{1 + a_z S_z\} \\ &= (2S+1)^{-N_s} \{1 + \beta \omega_0 S_z\} \end{aligned}$$

Spin Temperature coefficient (Internal Boltzmann dis)

c. Signal intensities.

In rotating frame

$$\mathcal{H}_s = -\Delta\omega S_z - \omega_1 S_x$$

$$\rho = a_0 \mathbb{1} + \sum_p a_p S_p$$

$$\rho_{eq} = (2S+1)^{-N_s} \{ 1 + \beta_L \omega_{os} S_z \}$$

For $\Delta\omega = 0$ $\omega_1 t = \frac{\pi}{2}$: 90° pulse

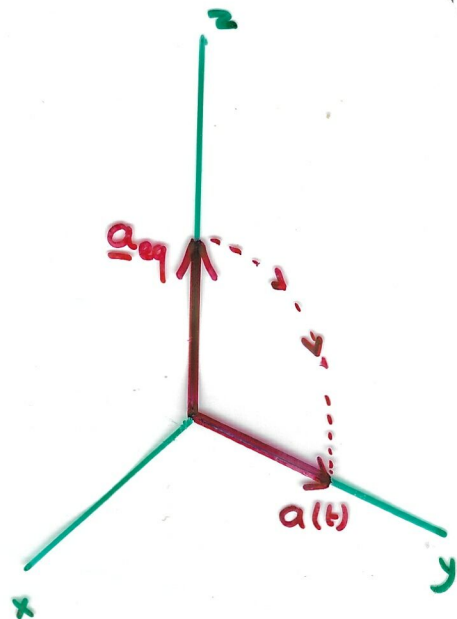
$$\begin{aligned} \rho(t) &= e^{-i\mathcal{H}_s t} \rho_{eq} e^{i\mathcal{H}_s t} = e^{-i\frac{\pi}{2} S_x} \rho_{eq} e^{i\frac{\pi}{2} S_x} \\ &= (2S+1)^{-N_s} \{ 1 + \beta_L \omega_{os} S_y \} \end{aligned}$$

Signal intensity $\propto M_y \propto S_y$

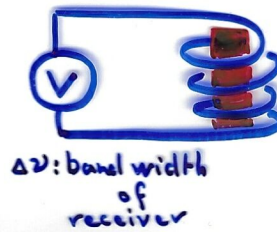
$$M_y \equiv \langle S_y \rangle = \text{Tr}(\rho(t) S_y) = \frac{2\beta_L \omega_{os}}{(2S+1)^{N_s}} \text{Tr}\{S_y^2\}_{N_s}$$

$$= \frac{\beta_L \omega_{os}}{(2S+1)^{N_s}} N_s (2S+1)^{N_s-1} \text{Tr}\{S_y^2\}_1$$

$$M_y = \frac{\beta_L \omega_{os} N_s}{(2S+1)} = \frac{1}{4} \beta_L \omega_{os} N_s$$



d. Single to Noise



$$S = \gamma_s \hbar \text{Tr}(\rho(H) S_y)$$

$$= \frac{\hbar}{4} \beta_L \gamma_s \omega_{os} N_s$$

L : inductance

Q : quality factor

$R = Q \omega_0 L$ resistance

A : area of coil

γ : filling factor

$$V_s = 4\pi \omega_0 A Q S$$

signal voltage

$$V_N = [4kTR \Delta\nu]^{1/2}$$

noise voltage

$$S/N = \frac{4\pi A Q}{(4kTR \Delta\nu)^{1/2}} \omega_0^{1/2} S \propto N_s \gamma_s^{5/2} H_0^{3/2}$$

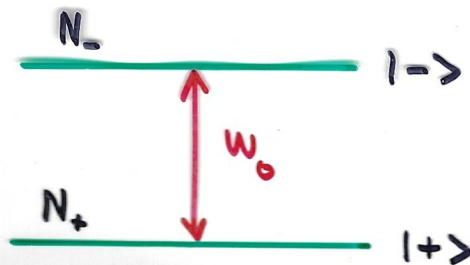


see Mehring's notes

2. Spin Temperature

a. Laboratory Frame

Laboratory Frame:



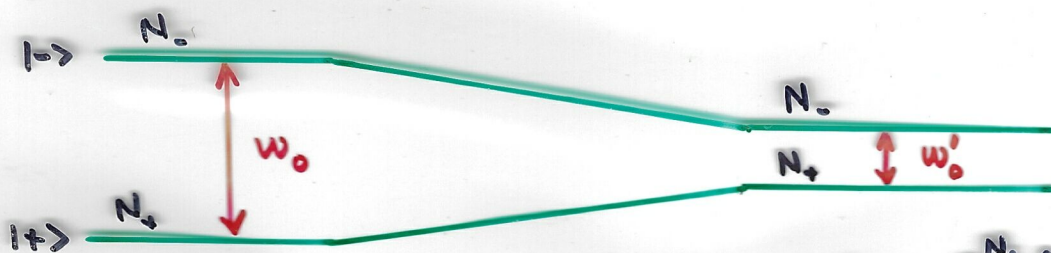
$$\mathcal{H} = -w_0 S_z$$

$$\rho = (2S+1)^{-N_s} \{ 1 - \beta \mathcal{H} \}$$

$$= (2S+1)^{-N_s} \{ 1 + \beta w_0 S_z \}$$

Example 1.

$$\rho_{\text{initial}} = (2S+1)^{-N_s} \{ 1 + \beta_L w_0 S_z \}$$

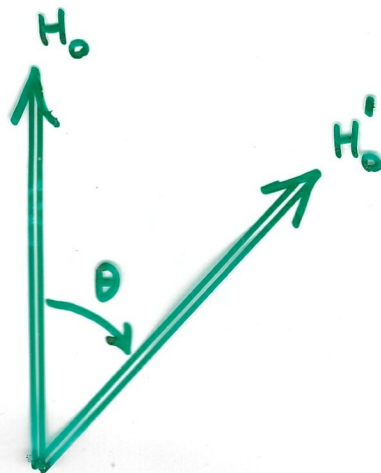


$$\rho_{\text{final}} = (2S+1)^{-N_s} \{ 1 + \beta_L w_0 S_z \}$$

$$= (2S+1)^{-N_s} \left\{ 1 + \beta_L \underbrace{\frac{w_0}{w'_0}}_{\text{Spin Temperature coefficient}} w'_0 S_z \right\}$$

Spin Temperature coefficient

Example 2.



$$\rho_{\text{initial}} = (2S+1)^{-N_s} \{1 + \beta_L \omega_0 S_z\}$$

$$\begin{aligned} \rho_{\text{final}} &= (2S+1)^{-N_s} \{1 + \beta_L \omega_0 S_z\} \\ &= (2S+1)^{-N_s} \{1 + \cos\theta \beta_L \omega_0 S'_z \\ &\quad + \sin\theta \beta_L \omega_0 S'_x\} \end{aligned}$$

$$\rho_{\text{final}} = (2S+1)^{-N_s} \{1 + \cos\theta \beta_L \omega_0 S'_z\}$$

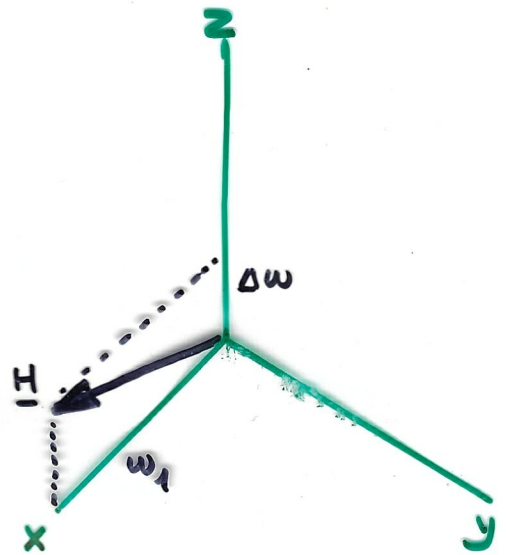
Spin temperature coefficient

b. Rotating frame

$$\mathcal{H} = -\Delta\omega S_z - \omega_1 S_x$$

$$\rho = (2S+1)^{-N_s} [1 - \beta \mathcal{H}]$$

Spin temperature coefficient
in the rotating frame



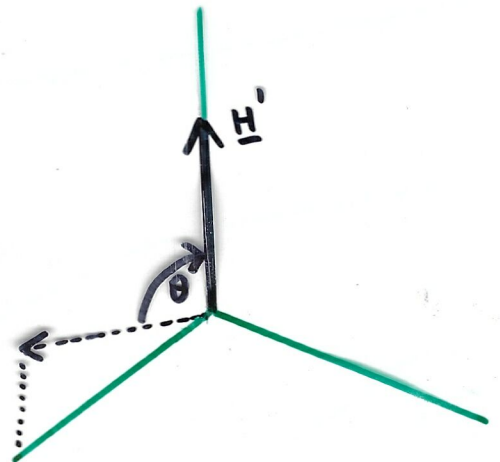
In order to obtain $\mathcal{H}$ in general form $-\omega S_z$:

Transform space according to
unitary transformation

$$U_y = e^{-i\theta I_y}$$

$$\theta = \tan^{-1} \frac{\omega_1}{\Delta\omega}$$

$$\begin{aligned} \mathcal{H}^T &= U_y^\dagger \mathcal{H} U_y \\ &= -(\Delta\omega^2 + \omega_1^2)^{1/2} S_z \\ &= -\omega_e S_z \end{aligned}$$



$$\rho^T = (2S+1)^{-N_s} [1 - \beta \mathcal{H}^T] = (2S+1)^{-N_s} [1 + \beta_s \omega_e S_z]$$

Example 1.

$$\rho_{\text{initial}} = (2S+1)^{-N_s} [1 + \beta_L w_{0s} S_z]$$

$$\rho_{\text{initial}}^T = (2S+1)^{-N_s} [1 - \beta_L w_{0s} S_x]$$

In rotating frame



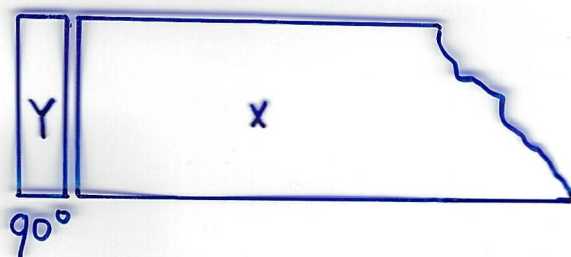
$$\mathcal{H}^T = -w_{1s} S_z$$

$$\rho_{\text{final}}^T = (2S+1)^{-N_s} [1 - \beta_L w_{0s} S_x]$$

$$= (2S+1)^{-N_s} [1 + \underset{\beta_s = 0}{0} w_1 S_z - \cancel{\beta_L w_{0s} S_x}]$$

$$\beta_s = 0$$

Example 2.



$$\rho_{\text{initial}} = (2S+1)^{-N_s} [1 + \beta_L w_{0s} S_x]$$

$$\rho_{\text{initial}}^T = (2S+1)^{-N_s} [1 + \beta_L w_{0s} S_z]$$

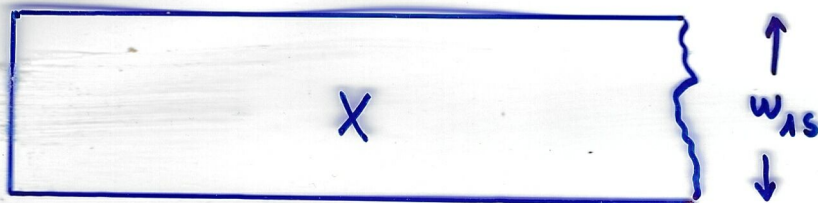
$$\rho_{\text{final}}^T = (2S+1)^{-N_s} [1 + \beta_L w_{0s} S_z]$$

$$= (2S+1)^{-N_s} [1 + \underbrace{\beta_L \frac{w_{0s}}{w_{1s}}}_{\beta_s} w_{1s} S_z]$$

$$\beta_s = \beta_L \frac{w_{0s}}{w_{1s}}$$

Spin Temperature in Rotating Frame

$$\rho = Z^{-1} \{ 1 - \beta \mathcal{H} \}$$

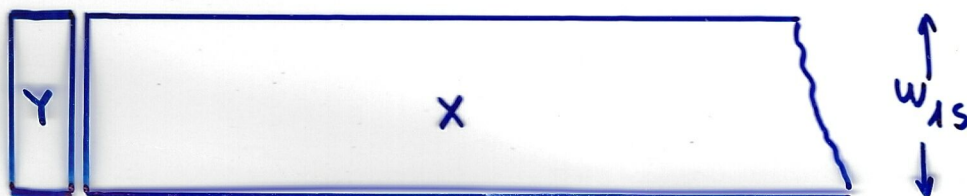


$$\mathcal{H} = -w_{1s} S_x$$

$$\mathcal{H}^T = -w_{1s} S_z$$

$$\rho_{\text{initial}} = Z^{-1} \{ 1 + \beta_L w_{0s} S_z \}$$

$$\rho_{\text{initial}}^T = Z^{-1} \{ 1 - \beta_L w_{0s} S_x \} \Rightarrow Z^{-1} \{ 1 - \beta \mathcal{H}^T \} \quad \beta_s = 0$$



$$\mathcal{H} = -w_{1I} I_x$$

$$\mathcal{H}^T = -w_{1I} I_z$$

$$\rho_{\text{initial}} = Z^{-1} \{ 1 + \beta_L w_{0I} I_x \}$$

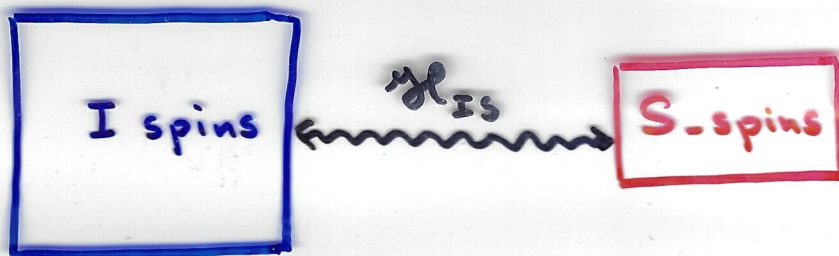
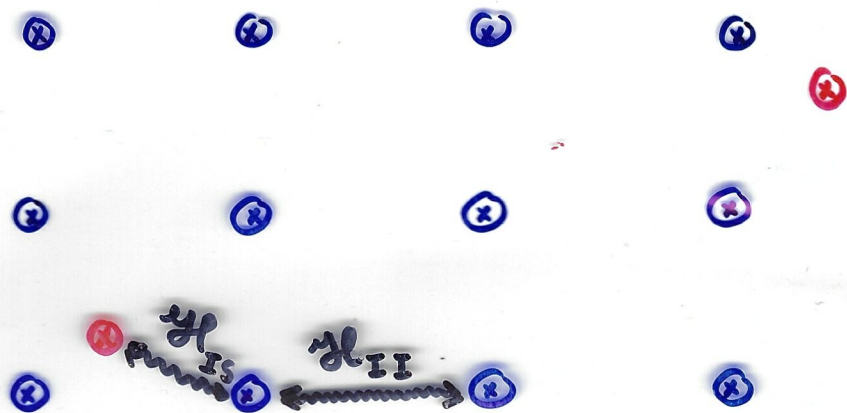
$$\rho_{\text{initial}}^T = Z^{-1} \{ 1 + \beta_L w_{0I} I_z \} = Z^{-1} \left\{ 1 - \beta_L \frac{w_{0I}}{w_{1I}} \mathcal{H}^T \right\}$$

$$\beta_I = \beta_L \frac{w_{0I}}{w_{1I}}$$

Remember

$$M_y^0 = \frac{1}{4} \beta_L w_{0s} N_s \quad \text{after } 90^\circ \text{ pulse.}$$

3. Dipolar Interactions



$$\beta_I = \beta_L \frac{\omega_{0I}}{\omega_{1I}}$$

$$\beta_S = 0$$

$$\beta_{\text{final}} = \beta_L \frac{\omega_{0I}}{\omega_{1I}}$$

$$\rho_S^T = Z^{-1} \{ 1 - \beta_f \mathcal{H}^T \} = Z^{-1} \{ 1 + \beta_f \omega_{1S} S_z \}$$

$$\rho_S = Z^{-1} \{ 1 + \beta_f \omega_{1S} S_x \}$$

$$M_x^S = \langle S_x \rangle = \text{Tr}(\rho_S S_x) = \frac{1}{4} \beta_f \omega_{1S} N_S$$

$$\frac{M_x}{M_y^0} = \frac{\frac{1}{4} \beta_f \omega_{1S} N_S}{\frac{1}{4} \beta_L \omega_{0S} N_S} = \frac{\omega_{0I}}{\omega_{0S}} \frac{\omega_{1S}}{\omega_{1I}} \approx \frac{\gamma_I}{\gamma_S}$$

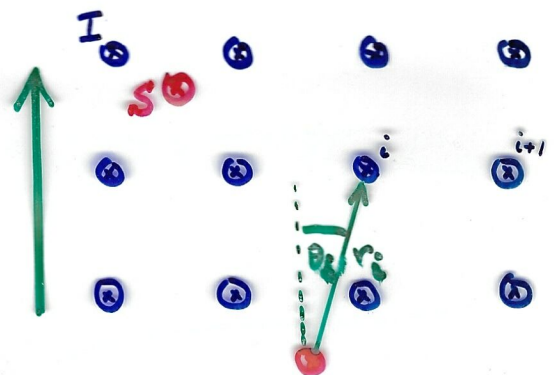
Enhancement!

a. Heteronuclear interaction

Two spin systems $\begin{cases} I = \frac{1}{2} & \text{abundance high} \\ S = \frac{1}{2} & \text{—||— low} \end{cases}$

$$\mathcal{H}_{IS} = 2 \sum_i b_i I_{zi} S_z$$

$$b_i = -2\gamma_I \gamma_S r_i^{-3} \left(\frac{1-3\cos^2\theta_i}{2} \right)$$



If we tilt the Hamiltonian

from $\mathcal{H} = -\omega_{IS} S_x - \omega_{II} I_x$ to $\mathcal{H}^T = -\omega_{IS} S_z - \omega_{II} I_z$

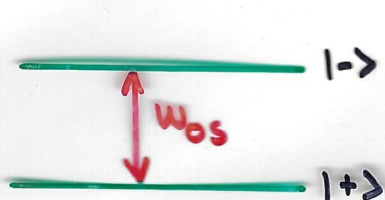
then

$$\mathcal{H}_{IS} = 2 \sum_i b_i I_{zi} S_z \implies \mathcal{H}_{IS}^T = 2 \sum_i b_i I_{xi} S_x$$

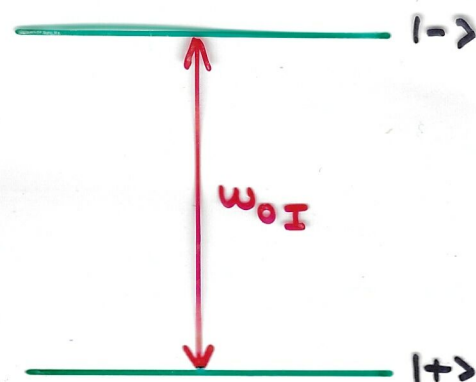
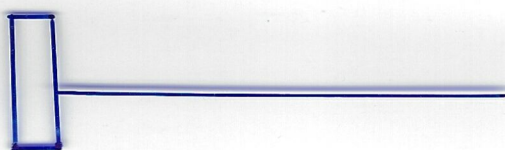
$\mathcal{H}_{IS}^T$ is not diagonal and it will "rotate" S_z and I_z

Example 1. Evolution of ρ^T

i. $\rho_{eq} = (2S+1)^{-N_S} (2I+1)^{-N_I} \{ 1 + \beta_L \omega_{0S} S_z + \beta_L \omega_{0I} I_z \}$



S-spins



I-spins

ii. 90° pulse on S-spins

$$\rho_{initial} = (2S+1)^{-N_S} (2I+1)^{-N_I} \{ 1 + \beta_L \omega_{0S} S_x + \beta_L \omega_{0I} I_z \}$$

$$\rho_{initial}^T = (2S+1)^{-N_S} (2I+1)^{-N_I} \{ 1 + \beta_L \omega_{0S} S_z + \beta_L \omega_{0I} I_x \}$$

iii.

Evolution of ρ^T :

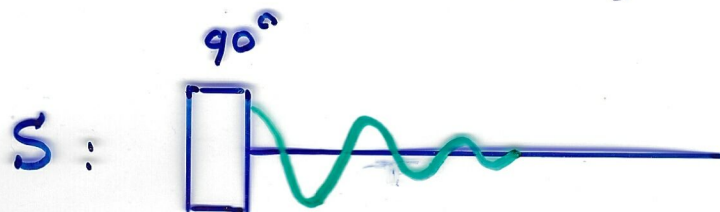
$$\rho^T(t) = e^{-i\mathcal{H}_{IS}^T} \rho_{in}^T e^{i\mathcal{H}_{IS}^T} = e^{-i\sum b_i I_x S_x t} \rho_{in}^T e^{i\sum b_i I_x S_x t}$$

For only two spins:

$$\rho^T(t) = (2S+1)^{-N_S} (2I+1)^{-N_I} \left\{ 1 + \beta_L \omega_{0S} (\cos 2bt S_z + \sin 2bt S_y I_x) - \beta_L \omega_{0I} I_x \right\}$$

DQ term

Example 2. Decoupling of $\mathcal{H}_{IS}$:



$$\mathcal{H} = 2 \sum_i b_i S_z I_{zi} - \omega_{1I} I_x$$

What do the S-spins "feel"?

$$\mathcal{H}_S = 2 \sum_i b_i S_z (I_{zi} \cos \omega_{1I} t + I_{yi} \sin \omega_{1I} t)$$

$\mathcal{H}_S$: periodic-time dependent

Use average Hamiltonian theory:

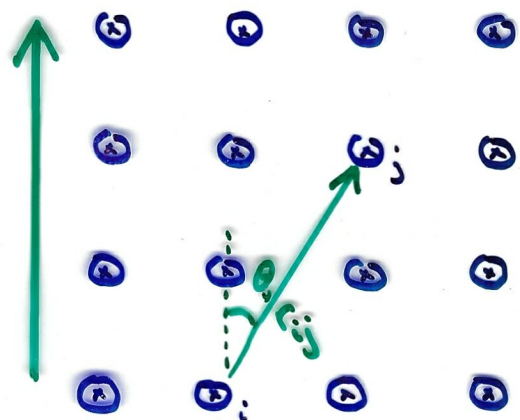
$$\bar{\mathcal{H}}_S = \mathcal{H}_S^{(0)} + \mathcal{H}_S^{(1)} + \mathcal{H}_S^{(2)} + \dots$$

$$\mathcal{H}_S^{(0)} = 0$$

$$\mathcal{H}_S^{(1)} = -\frac{1}{i} \sum \frac{b_i^2}{\omega_{1I}} I_{zi} S_z^2$$

$$\mathcal{H}_S^{(2)} = \frac{1}{2} \sum \frac{b_i^2}{\omega_{1I}^2} I_{zi} S_z^3 = \boxed{\sum \frac{b_i^3}{\omega_{1I}^2} I_{zi} S_z}$$

b. Homonuclear dipolar interaction



$$\mathcal{H}_{II} = \sum_{ij} a_{ij} (3 I_{zi} I_{zj} - \underline{I}_i \cdot \underline{I}_j)$$

$$a_{ij} = \gamma_I^2 r_{ij}^{-3} \frac{(4 - 3 \cos^2 \theta_{ij})}{2}$$

In tilted frame:

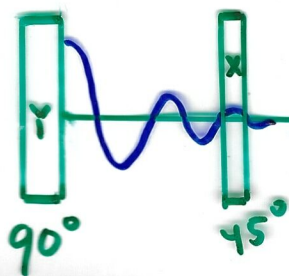
$$\mathcal{H}_{II}^T = \sum_{ij} a_{ij} (3 I_{xi} I_{xj} - \underline{I}_i \cdot \underline{I}_j)$$

$$= -\frac{1}{2} \sum_{ij} a_{ij} (3 I_{zi} I_{zj} - \underline{I}_i \cdot \underline{I}_j)$$

$$+ \frac{3}{2} \sum_{ij} a_{ij} (I_{xi} I_{xj} - I_{yi} I_{yj})$$

If $\mathcal{H}_I^T = -\omega_{HI} I_z$ is also present, then take only first term

Example: Two spins $I = \frac{1}{2}$



$$\mathcal{H} = a_{12} (3I_{z1}I_{z2} - I_1 \cdot I_2)$$

First pulse: $\rho_I^{90^\circ} = (2I+1)^{-N_I} \left\{ 1 - \beta_L \omega_{0I} (I_{x1} + I_{x2}) \right\}$

$$\rho(t) = e^{-i a_{12} (3I_{z1}I_{z2} - I_1 \cdot I_2) t} \rho_I^{90^\circ} e^{i a_{12} (3I_{z1}I_{z2} - I_1 \cdot I_2) t}$$

$$= (2I+1)^{-N_I} \left\{ 1 - \beta_L \omega_{0I} (I_{x1} \cos a_{12} t + I_{y1} I_{z2} \sin a_{12} t) \right. \\ \left. - \beta_L \omega_{0I} (I_{x2} \cos a_{12} t + I_{y2} I_{z1} \sin a_{12} t) \right\}$$

For $a_{12} t = \frac{\pi}{2}$

$$\rho\left(\frac{\pi}{2}\right) = (2I+1)^{-N_I} \left\{ 1 - \beta_L \omega_{0I} (I_{y1} I_{z2} + I_{y2} I_{z1}) \right\}$$

Second pulse:

$$\rho\left(\frac{\pi}{2}\right) = (2I+1)^{-N_I} \left\{ 1 - \frac{1}{2} \beta_L \omega_0 [(I_{y1} - I_{z1})(I_{z2} + I_{y2}) \right. \\ \left. + (I_{y2} - I_{z2})(I_{z1} + I_{y1})] \right\}$$

$$= (2I+1)^{-N_I} \left\{ 1 + \beta_L \omega_0 (I_{z1} I_{z2} - I_{y1} I_{y2}) \right\}$$

$$\beta_I = \frac{\frac{1}{2} \beta_L \omega_{0I}}{a_{12}}$$

spin temperature

$$= (2I+1)^{-N_I} \left\{ 1 + \frac{1}{2} \beta_L \omega_0 (3I_{z1} I_{z2} - I_1 \cdot I_2) + \frac{1}{2} \beta_L \omega_0 (I_{x1} I_{x2} - I_{y1} I_{y2}) \right\}$$

4. Cross Polarization

$$\rho_{eq} = Z^{-1} \{ 1 + \beta_I w_{0I} I_z + \beta_S w_{0S} S_z \}$$



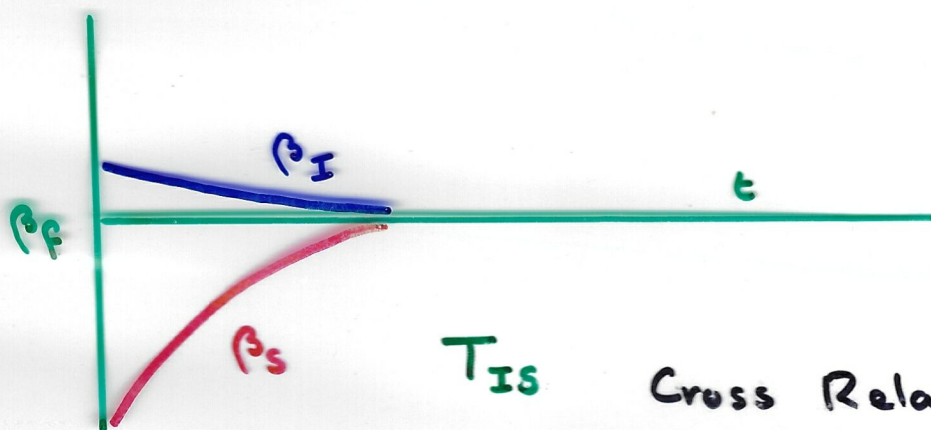
$$\mathcal{H}_I^T = -w_{1I} I_z + \mathcal{H}_{II}^0$$



$$\mathcal{H}_S^T = -w_{1S} S_z$$



$$\rho_{initial}^T = Z^{-1} \{ 1 - \underline{\beta_I} \mathcal{H}_I - \underline{\beta_S} \mathcal{H}_S \}$$



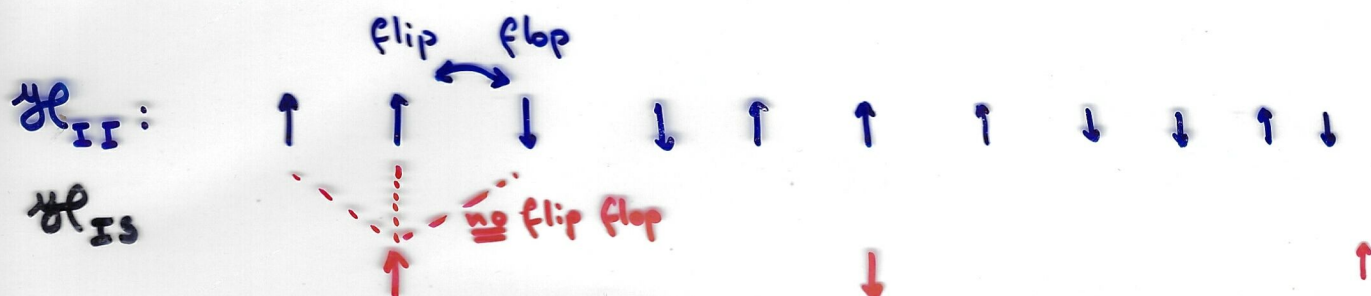
Cross Relaxation time

$$\frac{d}{dt} \beta_S = -\frac{1}{T_{IS}} (\beta_S - \beta_I)$$

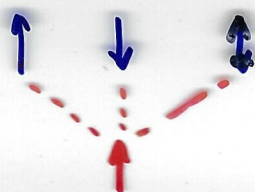
$$\frac{d}{dt} \beta_I = -\frac{\epsilon}{T_{IS}} (\beta_I - \beta_S)$$

(assume $T_{1\rho} = \infty$!)

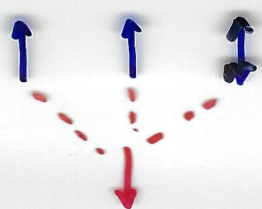
? model for T_{IS} ?



The $\mathcal{H}_{IS}$ Hamiltonian is fluctuated by $\mathcal{H}_{II}$



If $\uparrow\downarrow$ has same energy as $\downarrow\uparrow$



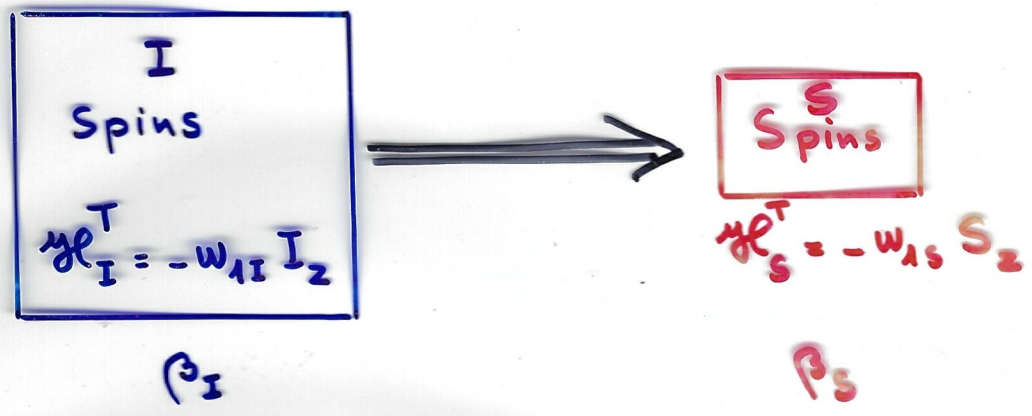
and



$$w_{1I} = w_{1S}$$

$$T_{IS}^{-1} = \frac{1}{\text{Tr}\{\mathcal{H}_S^T\}} \int_0^\infty dt [\mathcal{H}_{IS}, \mathcal{H}_S] e^{-i(\mathcal{H}_I^T + \mathcal{H}_S^T + \mathcal{H}_{IS}^{OT})t} [\mathcal{H}_{IS}^T, \mathcal{H}_S^T] \\ \times e^{i(\mathcal{H}_I^T + \mathcal{H}_S^T + \mathcal{H}_{IS}^{OT})t}$$

a. Thermodynamics ($\Delta W=0$)



$$\rho_{\text{initial}}^T = Z^{-1} \{ 1 - \beta_I \mathcal{H}_I^T - \beta_S \mathcal{H}_S^T \}$$

$$\begin{aligned} \text{Energy: } E_{\text{initial}} &= \text{Tr} \{ \rho_{\text{initial}}^T (\mathcal{H}_I^T + \mathcal{H}_S^T) \} \\ &= Z^{-1} \beta_I w_{1I}^2 \text{Tr}(I_z^2) + \beta_S w_{1S}^2 \text{Tr}(S_z^2) \\ &= \underline{\beta_I C_I + \beta_S C_S} \end{aligned}$$

with heat capacities

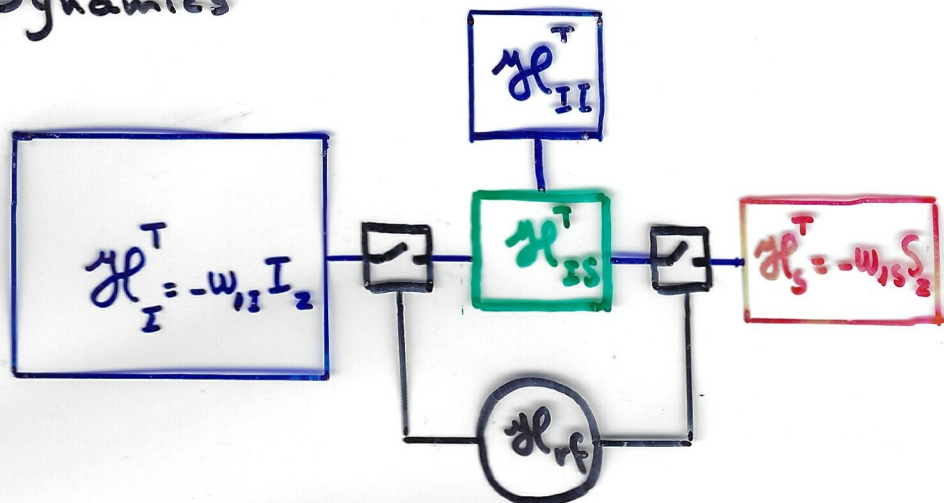
$$\begin{aligned} C_I &= \frac{\partial}{\partial \beta_I} E = \frac{1}{4} N_I w_{1I}^2 \\ C_S &= \frac{\partial}{\partial \beta_S} E = \frac{1}{4} N_S w_{1S}^2 \end{aligned}$$

$$E_{\text{final}} = \underline{\beta_f (C_I + C_S)}$$

Energy conservation :

$$\beta_f = \frac{\beta_I C_I + \beta_S C_S}{C_I + C_S}$$

b. Dynamics



The part of $\mathcal{H}_{IS}^T$ which is not commutative with $\mathcal{H}_S^T$
 $[\mathcal{H}_{IS}^T, \mathcal{H}_S^T] \rightarrow 2 \sum_i b_i I_{xi} S_x$

The fluctuations of $[\mathcal{H}_{IS}, \mathcal{H}_S]$ due to $\mathcal{H}_{II}$
 and the rotations of $[\mathcal{H}_{IS}, \mathcal{H}_S]$ due to $\mathcal{H}_S, \mathcal{H}_I$

fluctuated by $\mathcal{H}_{II}$

$$\therefore 2 \sum b_i (I_{xi} \cos \omega_{AI} t + I_{yi} \sin \omega_{AI} t) (S_z \cos \omega_{AS} t + S_y \sin \omega_{AS} t)$$

fluctuated by $\mathcal{H}_{II}$

$$= \frac{1}{2} 2 \sum b_i I_{xi} S_z \cos(\omega_{AI} - \omega_{AS}) t + \text{high rotating terms}$$

$$T_{IS}^{-1} = \frac{1}{2} \frac{\text{Tr}[\mathcal{H}_{IS}^T S_z]^2}{\text{Tr}(S_z)^2} \int_0^\infty d\tau \cos(\omega_{AI} - \omega_{AS}) t \frac{\text{Tr}\{(\sum b_i I_{xi})(\sum b_i I_{xi})(\tau)\}}{\text{Tr}(\sum b_i I_{xi})^2}$$

Dynamics ($\Delta\omega \neq 0$)

$$T_{IS}^{-1} = \frac{1}{2} M_2^S J_2(\omega_{1I} - \omega_{1S})$$

$$M_2^S = \frac{\text{Tr}[\mathcal{H}_{IS}^T S_z]^2}{\text{Tr}[S_z]^2}$$

Second moment

$J_2(\omega)$

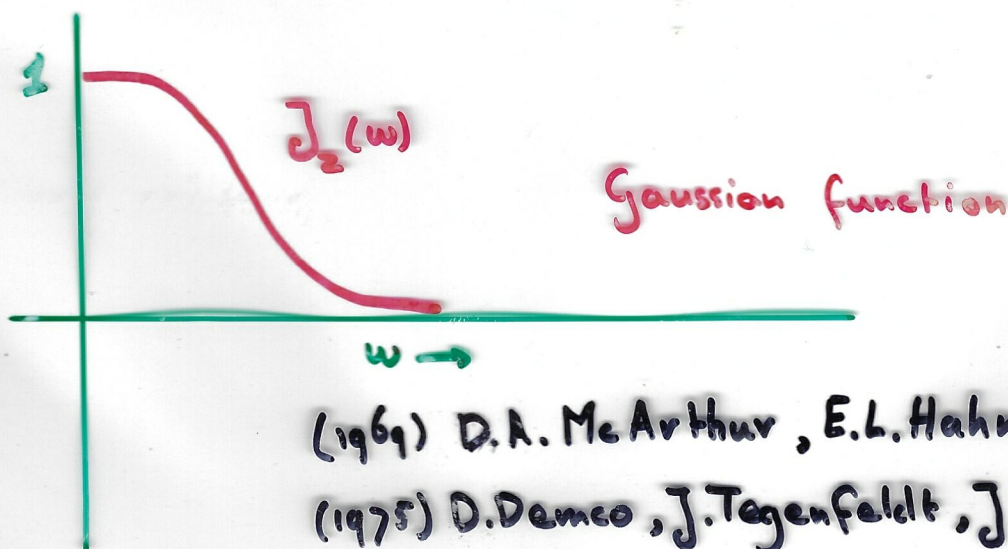
spectral density

$C_2(\tau)$

correlation function

$$J_2(\omega) = \int_0^\infty d\tau \cos \omega \tau C_2(\tau)$$

$$C_2(t) = \frac{1}{\text{Tr}\{\sum_i b_i I_{zi}\}^2} \text{Tr} \left\{ \left(\sum_i b_i I_{zi} \right) e^{-i\mathcal{H}_{IS}^0 t} \left(\sum_i b_i I_{zi} \right) e^{i\mathcal{H}_{IS}^0 t} \right\}$$



(1969) D.A. McArthur, E.L. Hahn, R.E. Walster

(1975) D. Demco, J. Tegenfeldt, J.S. Waugh

c. Hartmann Hahn condition ($\Delta\omega=0$)

$$\omega_{1I} = \omega_{1S}$$

maximum in $J_2(\omega)$
maximum in T_{IS}^{-1} .

d. Results for "spin lock" case

$$\Delta\omega=0 \quad \begin{matrix} \beta_I \\ \beta_S \end{matrix} \rightarrow \beta_f = \frac{\beta_I C_I + \beta_S C_S}{C_I + C_S} = \beta_I \frac{1}{1+\epsilon} + \beta_S \frac{\epsilon}{1+\epsilon}$$

$$\epsilon = \frac{C_S}{C_I} = \frac{N_S}{N_I} \frac{\omega_{IS}^2}{\omega_{II}^2}$$

$$T_{IS}^{-1} = \frac{1}{2} M_2^S J_2(\omega_{1S} - \omega_{1I})$$

H.H. condition

$$\Delta\omega_S \neq 0 \quad \begin{matrix} \beta_I \\ \beta_S \end{matrix} \rightarrow \beta_f = \beta_I \frac{1}{1+\epsilon} + \beta_S \frac{\epsilon}{1+\epsilon}$$

$$\epsilon = \frac{N_S}{N_I} \frac{\omega_{IS}^2 + \Delta\omega_S^2}{\omega_{II}^2}$$

$$T_{IS}^{-1} = \frac{1}{2} \frac{\omega_{1I}}{(\omega_{II}^2 + \Delta\omega_S^2)^{1/2}} J_2(\underbrace{(\omega_{II}^2 + \Delta\omega_S^2)^{1/2} - \omega_{1I}}_{\text{H.H. condition}})$$

5 Enhancement Experiments

1. Preparation : cooling of I spins $\beta_I \approx \infty$

2. Thermal mixing : T_{IS} seconds

3a. Measuring S-signal

direct detection

3b Measuring I-signal

indirect detection

(1972) A Pines, M.G. Gibby, J.S. Waugh

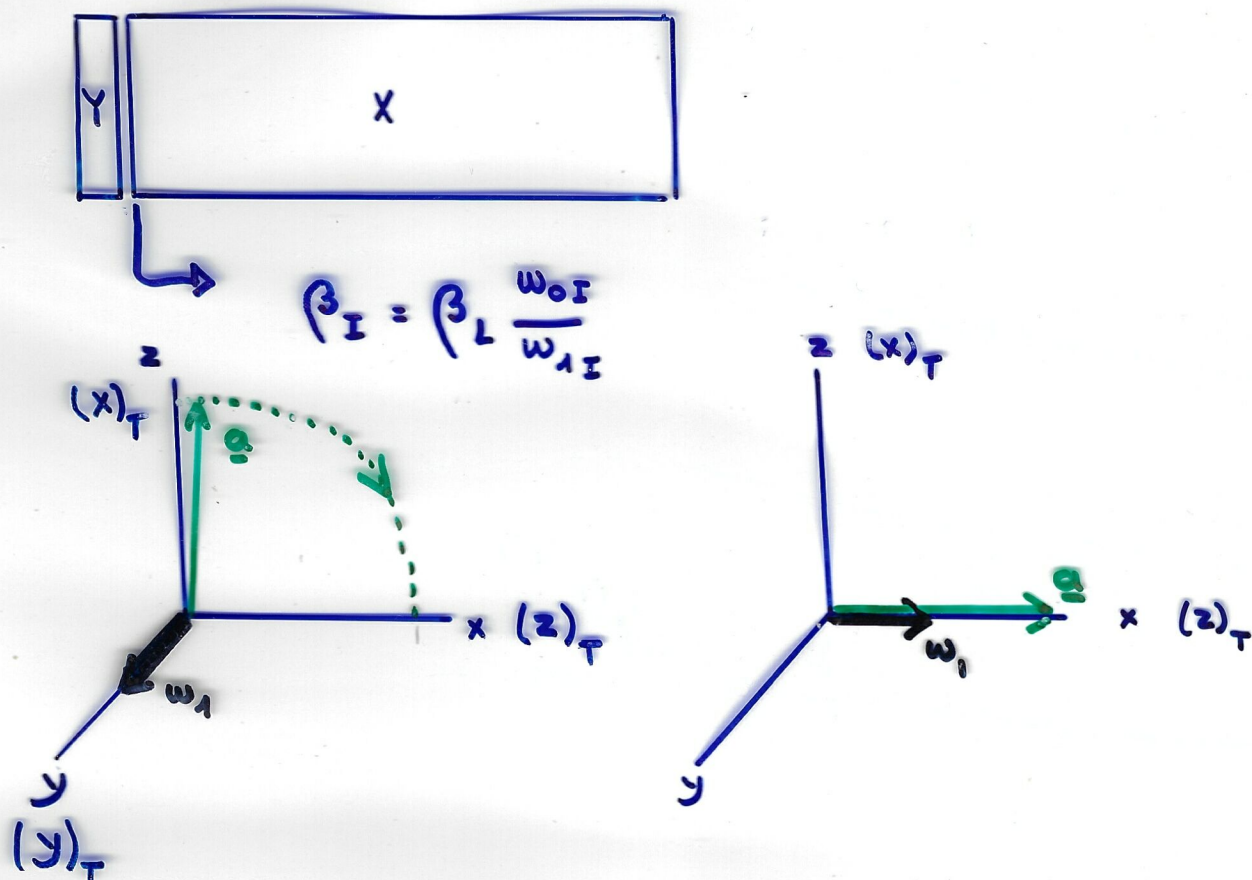
(1962) S.R. Hartmann, E.L. Hahn

(1964) F.M. Lurie, C.P. Slichter

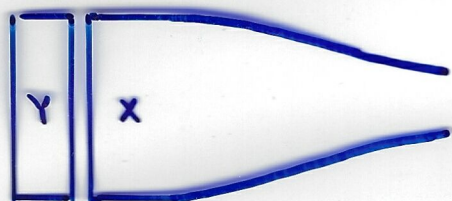
↓
→ P.E.N.I.S method

a. Preparation - Cooling of I spins

i. Spin Lock



∴ **ADRF** adiabatic demagnetization
in the rotating frame.

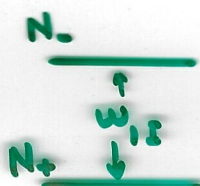


$$\mathcal{H}_I^T = -\omega_{1I} I_z$$

$$\beta_I = \beta_L \frac{\omega_{0I}}{\omega_{1I}}$$

$$\rho = Z^{-1} \{ 1 - \beta_I \mathcal{H}_I \}$$

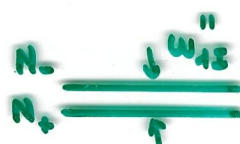
adiabatic:



$$\beta_I = \beta_L \frac{\omega_{0I}}{\omega_{1I}}$$



$$\beta_L \frac{\omega_{0I}}{\omega_{1I}}$$

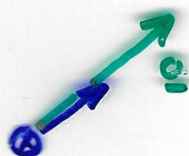
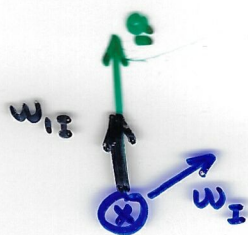


$$\beta_L \frac{\omega_{0I}}{\omega_{1I}}$$

→ ?

→ ?

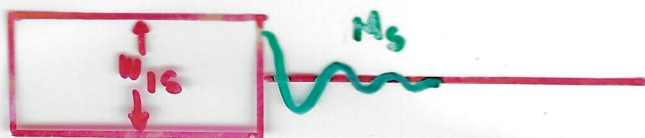
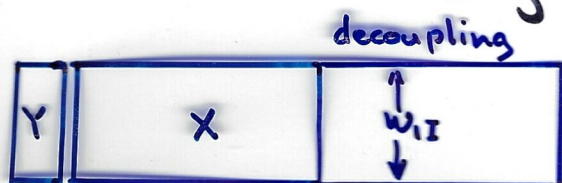
$$\omega_I^2 = \frac{\text{Tr}[\mathcal{H}_{II}^2]}{\text{Tr}(I_z^2)}$$



$$\rho = Z^{-1} \{ 1 - \beta_I \mathcal{H}_{II} \}$$

$$\beta_I = \beta_L \frac{\omega_{0I}}{\omega_I}$$

Thermal Mixing and Signal Intensities



$$\beta_I = \beta_L \frac{w_{0I}}{w_{1I}} \quad \beta_S = 0$$

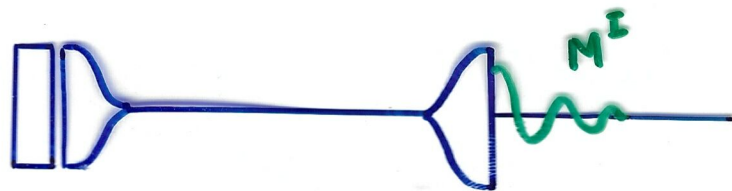
$$\beta_f = \beta_I \frac{1}{1+\epsilon} \approx (1-\epsilon) \beta_I$$

$$\begin{aligned} \rho_{\text{final}}^T &= Z^{-1} (1 - \beta_f \mathcal{H}_I^T - \beta_f \mathcal{H}_S^T) \\ &= Z^{-1} (1 + \beta_f w_{1I} I_z + \beta_f w_{1S} S_z) \end{aligned}$$

$$M^S = \langle S_z \rangle = \frac{1}{4} \beta_f w_{1S} N_S \xrightarrow{\text{direct}} \frac{M^S}{M_0^S} = \frac{\frac{1}{4} \beta_f w_{1S} N_S}{\frac{1}{4} \beta_L w_{0S} N_S} = (1-\epsilon) \frac{\gamma_I}{\gamma_S}$$

$$M^I = \langle I_z \rangle = \frac{1}{4} \beta_f w_{1I} N_I \xrightarrow{\text{indirect}} \frac{M_0^I - M^I}{M_0^I} = \frac{\frac{1}{4} N_I (\beta_L w_{0I} - \beta_f w_{1I})}{\frac{1}{4} N_I \beta_L w_{0I}}$$

$$\frac{M_0^I - M^I}{M_0^I} = \epsilon$$



$$\beta_I = \beta_L \frac{\omega_{OI}}{\omega_I} \quad \beta_S = 0$$

Notice

$$\begin{aligned} \frac{c_S}{c_I} &= \frac{\omega_{IS}^2 \text{Tr}(S_2^*)}{\text{Tr}(\mathcal{H}_{II}^2)} \\ &= \frac{\frac{1}{4} N_S \omega_{IS}^2}{\frac{1}{4} N_I \omega_I^2} \end{aligned}$$

$$\omega_I^2 = \frac{\text{Tr}(\mathcal{H}_{II}^2)}{\text{Tr}(S_2^*)}$$

Some comments.

SL

$$C_I = \frac{1}{4} N_I \omega_{1I}^2$$

$$T_{IS}^{-1} = \frac{1}{2} M_2^S J_2 (\omega_{1I} - \omega_{1S})$$

$$\omega_{1I} = \omega_{1S}$$

ADRF

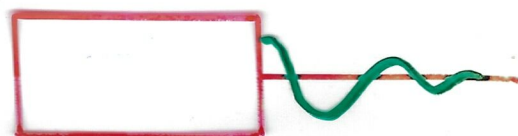
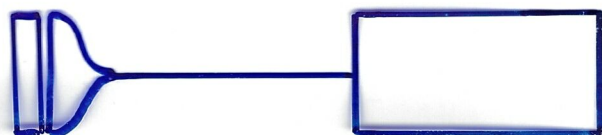
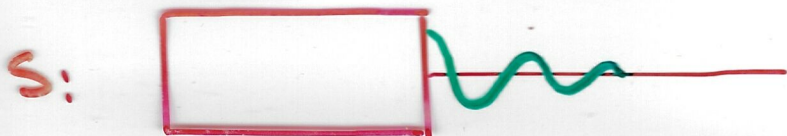
$$C_I = \frac{1}{4} N_I \omega_I^2$$

$$T_{IS}^{-1} = M_2^S J_x (\omega_{1S})$$

$$? \omega_{1S} = \omega_I ?$$

In actual experiments:

Decouple I spins



$$T_{IS} : 100 \mu\text{sec} - 10 \text{ msec}$$

$$\tau_{\text{mixing}} : 1 - 20 \text{ msec}$$

$$\omega_1 : 20 \text{ KHz}$$

$$\omega_{1I} \rightarrow 6 \text{ Gauss}$$

$$\omega_{1S} \rightarrow 20 \text{ Gauss}$$

6. Other Methods

If we start $\begin{cases} \beta_I^i = \beta_L \frac{w_{0I}}{w_{1I}} \\ \beta_S^i = 0 \end{cases}$

Ideal

and we end up in $\begin{cases} \beta_I^f = 0 \\ \beta_S^f \neq 0 \end{cases}$

Entropy Conservation

Entropy $S = -k \text{Tr}(\rho \log \rho)$

$$= -\frac{k}{c} \text{Tr} \{ (1 - \beta_I \mathcal{H}_I - \beta_S \mathcal{H}_S) (-\beta_I \mathcal{H}_I - \beta_S \mathcal{H}_S) \}$$

$$= \text{Constant} - k \beta_I^2 \text{Tr}(\mathcal{H}_I^2) - \beta_S^2 \text{Tr}(\mathcal{H}_S^2)$$

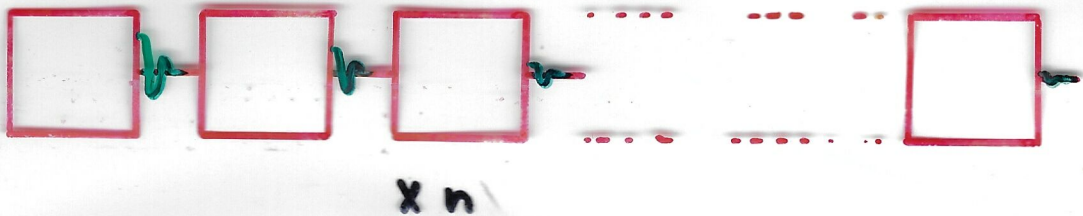
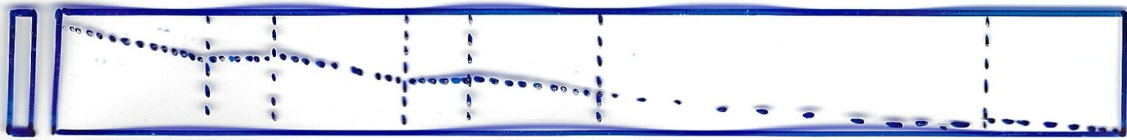
$$= \text{Constant} - \frac{k}{4} N_I \beta_I^2 w_{1I}^2 - \frac{k}{4} N_S \beta_S^2 w_{1S}^2$$

$$\Rightarrow -\frac{k}{4} N_I \beta_I^2 w_{1I}^2 = -\frac{k}{4} N_S \beta_S^2 w_{1S}^2$$

With H.H condition

$$\beta_S^f = \beta_I^i \sqrt{\frac{N_I}{N_S}}$$

a. Multiple Contact



$$M_I^{(1)} = M_0(1-\epsilon)$$

$$M_I^{(2)} = M_0(1-\epsilon)^2$$

⋮

$$M_I^{(n)} = M_0(1-\epsilon)^n$$

$$\downarrow$$

$$M_I^{(n)} \approx 0 \text{ for } n \gg \frac{1}{\epsilon}$$

$$M_S^{(1)} = M_S^0 \frac{\sigma_I}{\sigma_S} \frac{1}{1+\epsilon} \approx M_S^0 (1-\epsilon) \frac{\sigma_I}{\sigma_S}$$

$$M_S^{(2)} = M_S^0 (1-\epsilon)^2 \frac{\sigma_I}{\sigma_S}$$

⋮

$$M_S^{(n)} = M_S^0 (1-\epsilon)^n \frac{\sigma_I}{\sigma_S}$$

+

$$M_S^{\text{Total}} = M_S^0 \frac{\sigma_I}{\sigma_S} \sum_n (1-\epsilon)^n$$

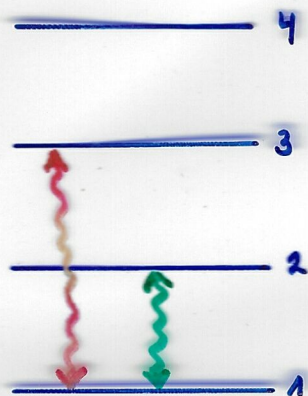
$$\approx M_S^0 \frac{\sigma_I}{\sigma_S} n$$

$$\left(\frac{S}{N}\right)_n = \frac{\sigma_I}{\sigma_S} \frac{\sqrt{n}}{n} \left(\frac{S}{N}\right)_0 n$$

$$= \frac{\sigma_I}{\sigma_S} \sqrt{n} \left(\frac{S}{N}\right)_0$$

$$\approx \frac{\sigma_I}{\sigma_S} \sqrt{\frac{N_I}{N_S}} \left(\frac{S}{N}\right)_0$$

Fictitious Spin- $\frac{1}{2}$ Operators



$$\rho = \begin{pmatrix} \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \odot & \odot \\ \cdot & \cdot & \odot & \odot \end{pmatrix}$$

$$I_x^{1-2} ; I_y^{1-2} ; I_z^{1-2}$$

$$\rho = \begin{pmatrix} \odot & \cdot & \odot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \odot & \cdot & \odot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

$$I_x^{1-3} ; I_y^{1-3} ; I_z^{1-3}$$

$$[I_x^{i-j}, I_y^{i-j}] = i I_z^{i-j}$$

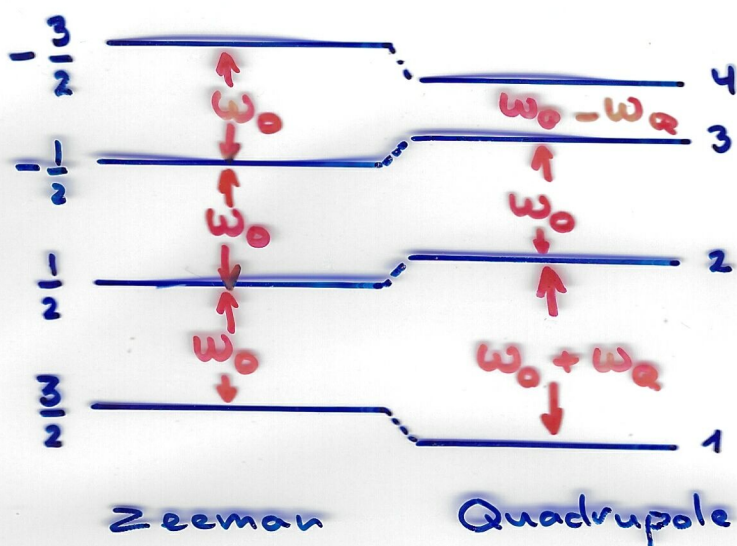
cyclic permutations

rotating vector $\underline{a}^{i-j}$

Example :

$$\frac{1}{2} \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix} = \sqrt{3} (I_x^{1-2} + I_x^{3-4}) + 2 I_x^{2-3}$$

b. $S = \frac{3}{2}$ Spins in Solids



$$\mathcal{H} = \frac{1}{2} \begin{pmatrix} 3\omega_0 & 0 & 0 & 0 \\ 0 & \omega_0 & 0 & 0 \\ 0 & 0 & -\omega_0 & 0 \\ 0 & 0 & 0 & -3\omega_0 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} -\omega_Q & 0 & 0 & 0 \\ 0 & \omega_Q & 0 & 0 \\ 0 & 0 & \omega_Q & 0 \\ 0 & 0 & 0 & -\omega_Q \end{pmatrix}$$

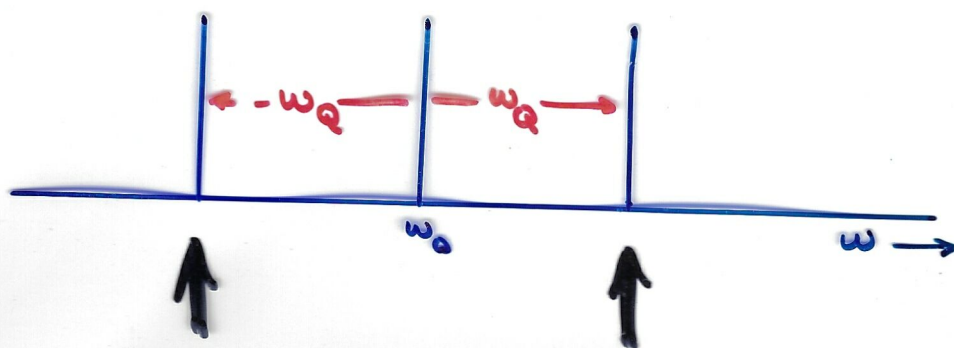
$$\mathcal{H} = \omega_0 (3I_z^{1-4} + I_z^{2-3}) + \omega_Q (I_z^{3-4} - I_z^{1-2})$$

In rotating frame

$$\mathcal{H} = \omega_Q (I_z^{3-4} - I_z^{1-2}) - \omega_A (\sqrt{3} I_x^{1-2} + \sqrt{3} I_x^{3-4} + 2 I_x^{2-3})$$

Spin Temperature:

$$\rho = z^{-1} \{ 1 - \beta \mathcal{H} \}$$



Modulated rf Irradiation: $2\omega_1 (\cos \omega_0 t \cos \omega_Q t) I_x$

$$\omega_1 \ll \omega_Q$$

In rotating frame

$$\mathcal{H} = \omega_Q (I_z^{3-4} - I_z^{1-2}) - \omega_1 (\cos \omega_Q t (I_x^{1-2} + I_x^{3-4}) \sqrt{3})$$

In rotating rotating frame

$$\mathcal{H} = -\frac{\sqrt{3}}{2} \omega_1 I_x^{1-2} - \frac{\sqrt{3}}{2} \omega_1 I_x^{3-4}$$

Spin Temperature $\rho = 2^{-1} \left\{ 1 - \underbrace{\beta_1 \mathcal{H}^{1-2}} - \underbrace{\beta_2 \mathcal{H}^{3-4}} \right\}$

1-2 system

3-4 system

β_1

and

β_2

Cross Polarization
with

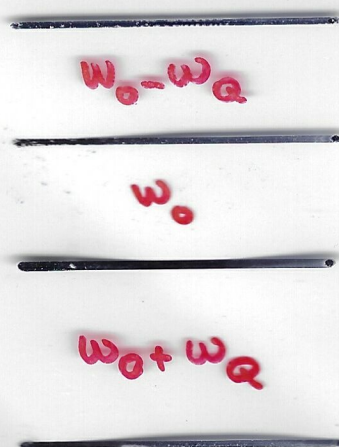
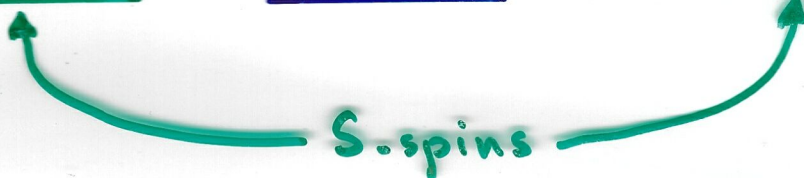
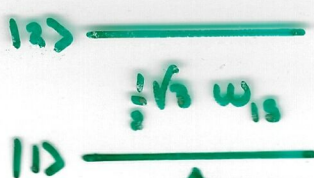
β_I

β_{F1}

β_{F2}

$$\omega_{1I} = \frac{1}{2} \sqrt{3} \omega_{1S}$$

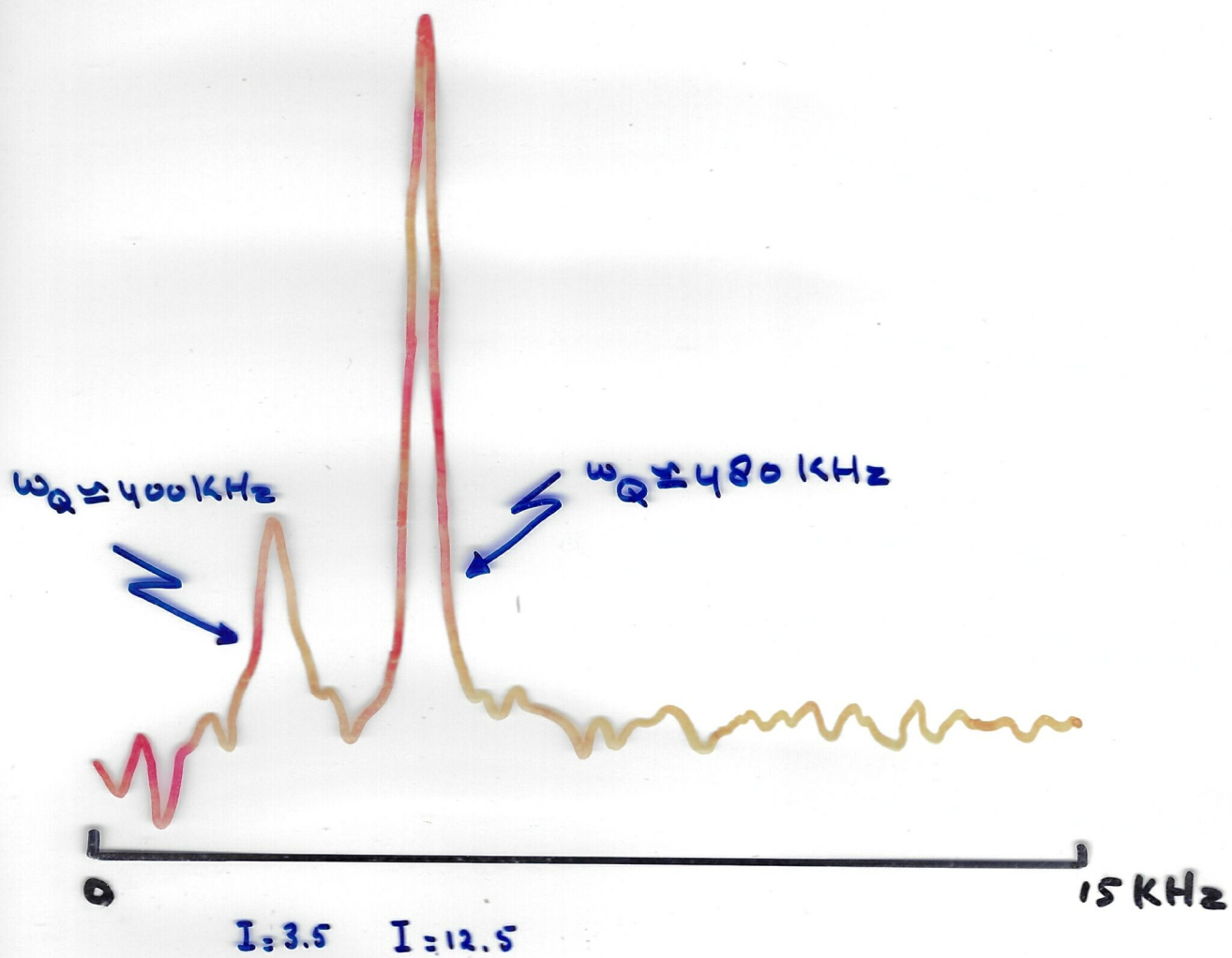
I spins



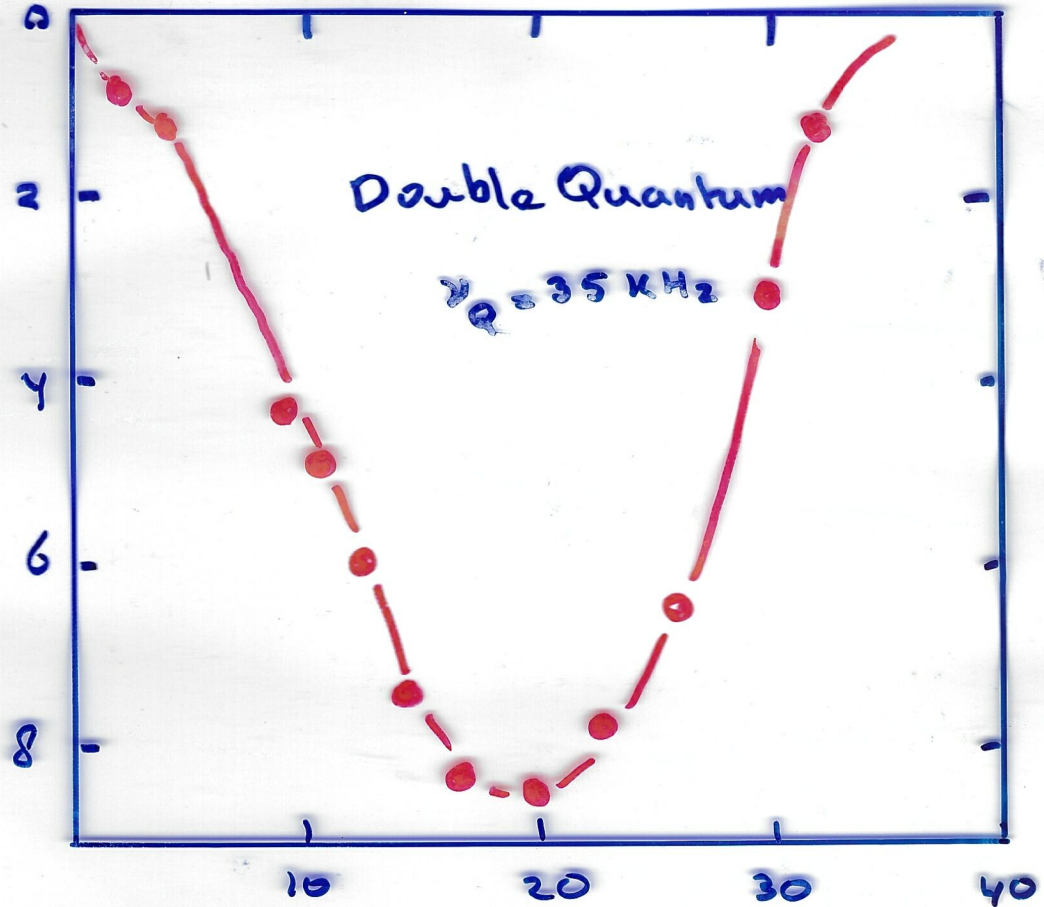
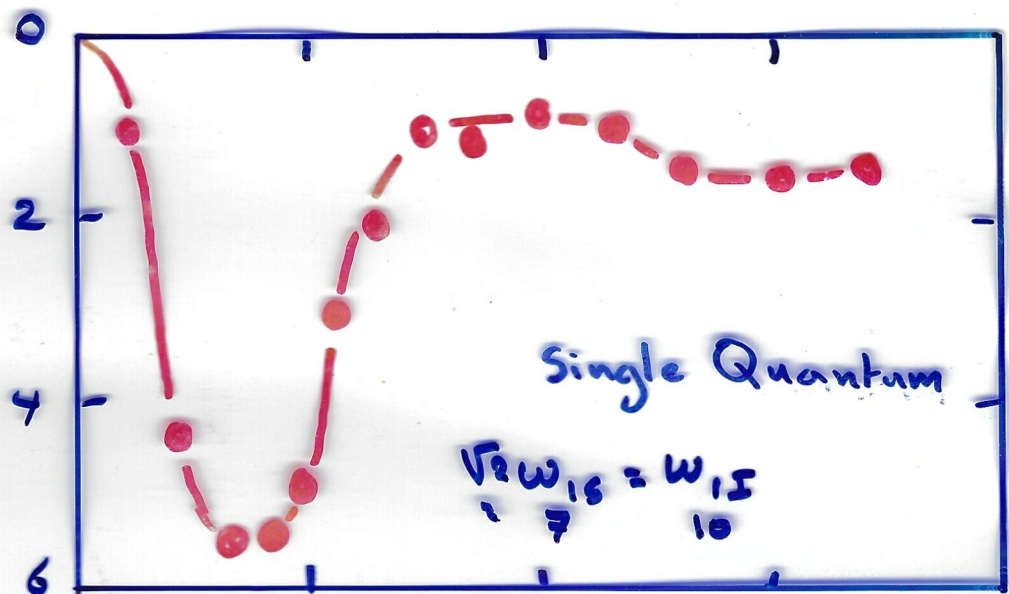
$$\langle S_x^{3-4} \rangle = \frac{\delta_I}{\delta_S}$$

"with pulse" $\langle S_x^{2-3} \rangle = (2 + \frac{\delta_I}{\delta_S})$

$$\langle S_x^{1-2} \rangle = \frac{\delta_I}{\delta_S}$$



% Destruction



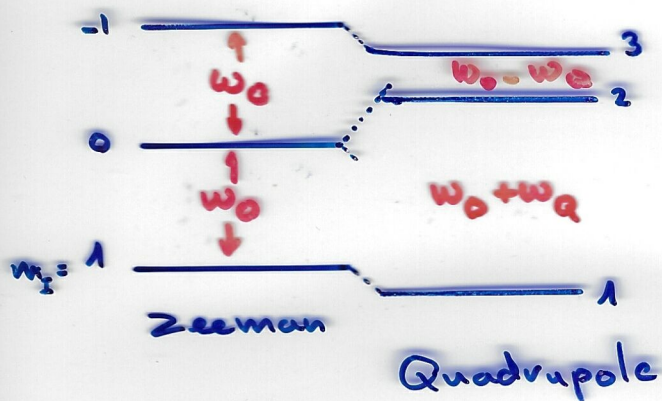
$\nu_{1I} = 10 \text{ KHz}$

$\nu_{1I} = \sqrt{2} \nu_{1S} \rightarrow \nu_{1S} = 7$

$\nu_{1I} = \frac{\nu_{1S}^2}{\nu_Q} \rightarrow \nu_{1S} = 19$

c. Spin $I=1$

Double quantum cross polarization



$$\mathcal{H} = \frac{1}{2} \begin{pmatrix} 2\omega_0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -2\omega_0 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} -\frac{2}{3}\omega_Q & 0 & 0 \\ 0 & \frac{4}{3}\omega_Q & 0 \\ 0 & 0 & -\frac{2}{3}\omega_Q \end{pmatrix}$$

$$= 2\omega_0 I_z^{1-3} + \frac{2}{3}\omega_Q (I_z^{2-3} - I_z^{1-2})$$

In Rotating Frame

$$\mathcal{H} = \frac{2}{3}\omega_Q (I_z^{2-3} - I_z^{1-2}) - \sqrt{2}\omega_1 (I_x^{1-2} + I_x^{2-3})$$

for $\omega_1 \ll \omega_Q$

$$\mathcal{H} = \underbrace{\frac{2}{3}\omega_Q (I_z^{2-3} - I_z^{1-2})}_{\mathcal{H}_1} - \underbrace{\frac{\omega_1^2}{\omega_Q} I_x^{1-3}}_{\mathcal{H}_2} = \mathcal{H}_1 + \mathcal{H}_2$$

commutative

$$[\mathcal{H}_1, \mathcal{H}_2] = 0$$

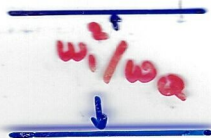
Spin Temperature

$$\rho = Z^{-1} \{ 1 - \beta_1 \mathcal{H}_1 - \beta_2 \mathcal{H}_2 \}$$

$$\mathcal{H}_1 = \frac{2}{3} \omega_Q (I_z^{2-3} - I_z^{1-2})$$

$$\mathcal{H}_2 = -\frac{\omega_1^2}{\omega_Q} I_x^{1-3}$$

$\mathcal{H}_2$:



Hartmann-Hahn condition

$$\frac{\omega_1^2}{\omega_Q} = \omega_1 I$$