

1. PRODUCING POLARIZATION ECHOES.

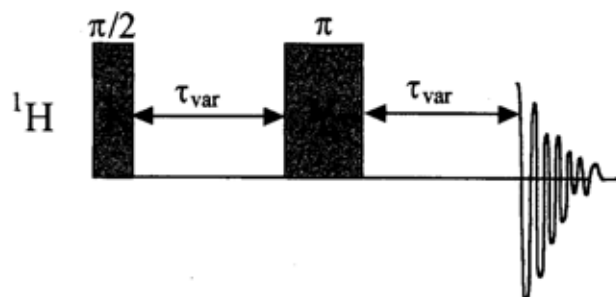
In a spin-containing crystalline sample, by means of the NMR, we can create a measurable polarization. However, the polarization, evolving, loses coherence. This is traduced by a decay of the NMR signal with time.

However, using adequate NMR pulse sequences, we can make the signal(=the polarization) to reborn, even after it has lost coherence.

1.1. The Hahn echo [Hah50]

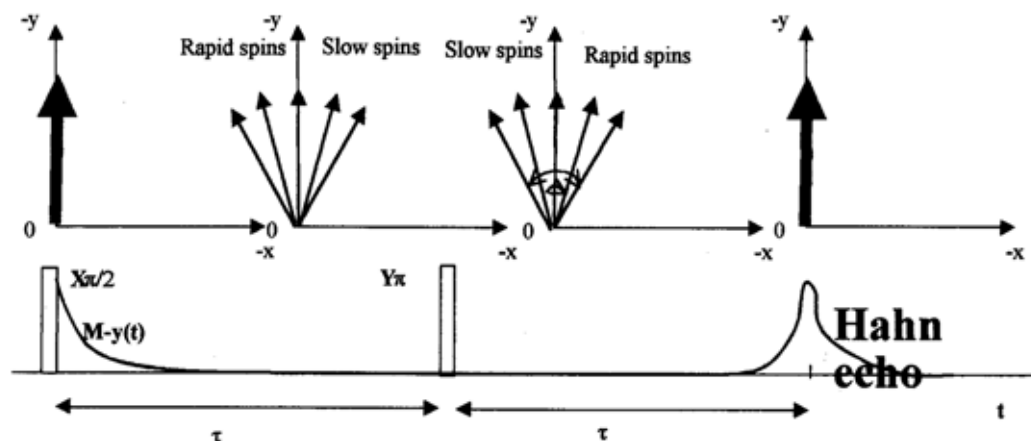
1.1.1. Intuitive interpretation

Let's consider an ensemble of 1H spins, in a bath of inhomogeneous B_0 field. We can invert the decoherence of the magnetization due to the field inhomogeneities, with the following pulse sequence:



- a) The Hahn echo pulse sequence, for the measure of T_2 . We measure the amplitude of the echo as a function of the variable time τ_{var} .
- b) A typical T_2 curve as obtained with the SCB.

The effect of the Y_π pulse, at the time τ , is to invert the evolution of the "local magnetizations", so that at $t = \tau + \tau$ all join back in their departure point.



The effect of the Hahn echo pulse sequence on the spin decoherence, seen in the rotating frame :

- 1) a $\pi/2$ pulse puts the magnetization in the xy plane
- 2) it evolves, losing coherence because of the B_0
- 3) a π pulse makes the magnetizations all rotate of a π angle round the y axis. The magnetizations begin their way back.
- 4) Magnetization is refocalized : it is the Hahn echo.

1.1.2. Interpretation in terms of the density matrix

The hamiltonian of N non-interacting spins in an inhomogeneous field is, in the rotating frame:

$$\mathcal{H}_{inh} = -\gamma_I \hbar \sum_{i=1}^N B_{i_{local}} I_i^z$$

The effect of the Y_π pulse, at the time τ , is to invert this hamiltonian. As we have:

$$Y_\pi I_i^z Y_{-\pi} = -I_i^z$$

Then

$$Y_\pi \mathcal{H}_{inh} Y_{-\pi} = -\mathcal{H}_{inh}$$

The density matrix at a time $t > \tau$ is:

$$\begin{aligned} \rho(t) &= U(t-\tau) Y_\pi U(\tau) X_{\frac{\pi}{2}} \rho(0) X_{-\frac{\pi}{2}} U(-\tau) Y_{-\pi} U(-(t-\tau)), \quad \text{with} \\ \rho(0) &= \frac{1}{2^N} \left(1 + \frac{\hbar \omega_0 I}{kT} I^z \right), \quad \text{and} \\ U(t) &= \exp \left(-it \frac{\mathcal{H}_{inh}}{\hbar} \right) \end{aligned}$$

Then

$$\begin{aligned} M_y(t > \tau) &= \text{Tr}(\rho(t) M_y) = \frac{4}{2^N} M_0 \text{Tr} (U(t-\tau) Y_\pi U(\tau) X_{\frac{\pi}{2}} I^z X_{-\frac{\pi}{2}} U(-\tau) Y_{-\pi} U(-(t-\tau)) I_y) \\ &= -\frac{4}{2^N} M_0 \text{Tr} (Y_{-\pi} U(t-\tau) Y_\pi U(\tau) I^y U(-\tau) Y_{-\pi} U(-(t-\tau)) Y_\pi I_y) \quad ([Y_\pi, I_y] = 0) \end{aligned}$$

Remembering that $Y_\pi \mathcal{H}_{inh} Y_{-\pi} = -\mathcal{H}_{inh}$, then $Y_\pi U(t) Y_{-\pi} = U(-t)$, and

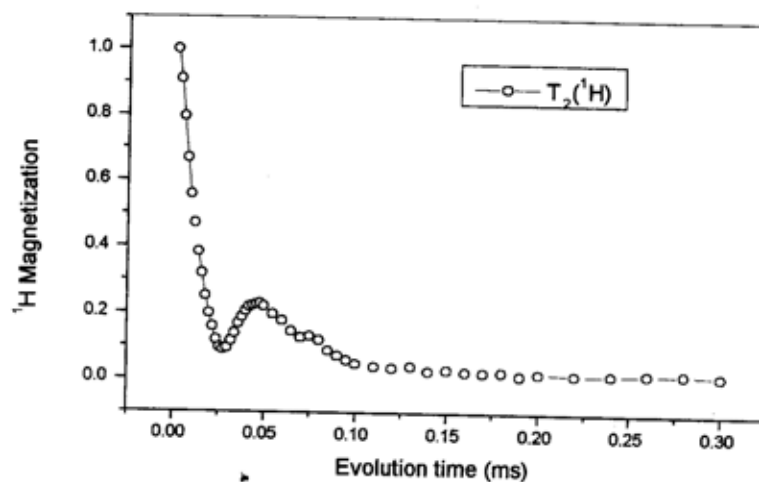
$$M_y(t) = -\frac{4}{2^N} M_0 \text{Tr} (U(2\tau - t) I^y U(-\tau) U(-(2\tau - t)) I_y)$$

and, for $t = 2\tau$,

$$M_y(2\tau) = -\frac{4}{2^N} M_0 \text{Tr} (I^{y2}) = -M_0$$

That is the same magnetization that just following a single $X_{\frac{\pi}{2}}$ pulse!!!

(NB: Experimentally, we don't recover 100% of the magnetization: this pulse sequence does not invert the dipolar hamiltonian. This pulse sequence is used to measure the spin-spin relaxation time T_2 , without the artefacts due to the field inhomogeneities, that has no physical interest.



A characteristic measure of T_2 in a liquid crystal (5CB). It is obtained using the Hahn sequence, and represents the amplitude of the Hahn echo in function of the evolution time τ . The dipolar dynamics are the only cause of attenuation of the echo.

1.1.3. Conclusions:

-To invert the hamiltonian of a system is equivalent, for the dynamics studies, to invert the time!:

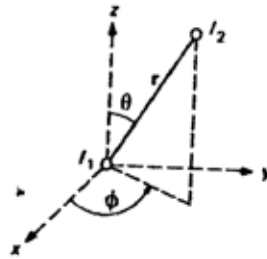
$$U(-\mathcal{H}, t) = \exp\left(-it\left(\frac{-\mathcal{H}}{\hbar}\right)\right) = \exp\left(-i(-t)\left(\frac{\mathcal{H}}{\hbar}\right)\right) = U(\mathcal{H}, -t)$$

- In particular cases, in NMR, it is possible to experimentally realize this sign change in the hamiltonian. (Here simply with the Y_π pulse).

1.2. The Magic Echo [RPW71]:

The Hahn echo refocalises the loss of coherence due to the field inhomogeneities, but not the dipolar evolution. How could we invert the dipolar hamiltonian ?

1.2.1. The dipolar hamiltonian:



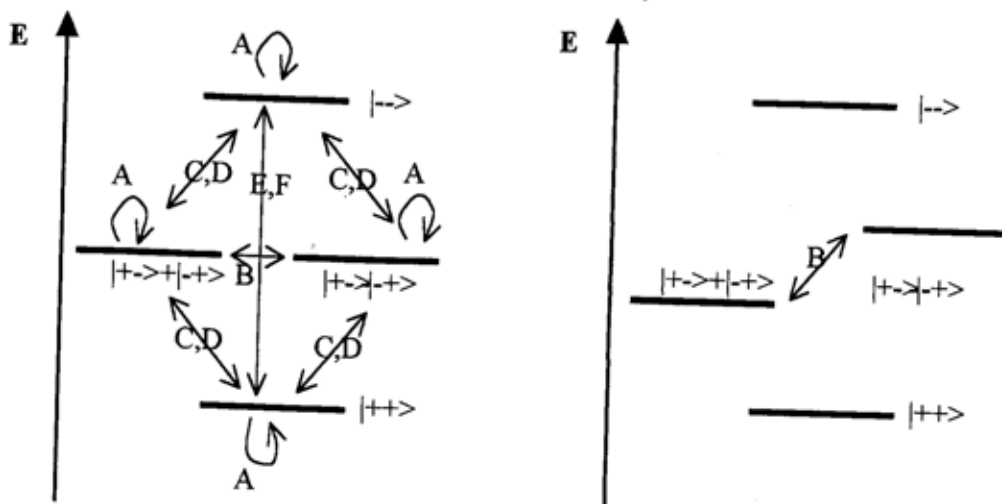
Definitions of geometry for the dipole-dipole interaction of nuclei.

Let's consider two spins, I_1 and I_2 interacting between them via the dipolar interaction, and with $B_0 e_z$ via the Zeeman interaction.

The dipolar interaction hamiltonian is:

$$\begin{aligned}\mathcal{H}_d^{II} &= \frac{\mu_0 (\gamma_1 \hbar)(\gamma_2 \hbar)}{4\pi r_{12}^3} (A + B + C + D + \mathcal{E} + \mathcal{F}) \\ A &= -[I_1^z I_2^z] (3 \cos(\theta_{12})^2 - 1) \\ B &= \frac{1}{4} [I_1^+ I_2^- + I_1^- I_2^+] (3 \cos(\theta_{12})^2 - 1) \text{ (flip-flop)} \\ C &= -\frac{3}{2} [I_1^z I_2^+ + I_1^+ I_2^z] \sin(\theta) \cos(\theta) e^{-i\varphi}, \quad D = C^* \\ \mathcal{E} &= -\frac{3}{4} [I_1^+ I_2^+] \sin(\theta)^2 e^{-2i\varphi}, \quad \mathcal{F} = \mathcal{E}^*\end{aligned}$$

for $\frac{H_d}{H_z} = \frac{B_{local}}{B_0} \ll 1$, which is usual, we can treat \mathcal{H}_d as a perturbation that produces coupling between the Zeeman levels of the system:



The energy levels and their corresponding spin functions for a two-spins dipolar interaction Hamiltonian.

The double arrows represents the couplings between the energy levels by each term in the Hamiltonian.

-the first diagram represents an heteronuclear system (ex : two H)

-the second diagram represents an heteronuclear system (ex : one H and one C)

The secular approximation consists in neglecting the terms coupling levels of different energies :

- in homonuclear systems we only conserve terms A and B ;
- in heteronuclear systems we only conserve term A.

In all the work we'll do the secular approximation: in the dipolar hamiltonian we neglect the terms that couple levels of different energies $E_{Z_i} \neq E_{Z_j}$: their correction to the proper states and energies are of the order of $\frac{H_d}{E_{Z_i} - E_{Z_j}}$, and we can neglect them for $B_0 \gg B_{local}$.

We considerate then:

- $^1H - ^1H$ interactions (specie I)

$$\mathcal{H}_d^{II} = -\frac{\mu_0}{4\pi} \frac{(\gamma_I \hbar)^2}{2r_{12}^3} (3 \cos(\theta_{12})^2 - 1) \left[I_1^z I_2^z - \frac{1}{2} (I_1^+ I_2^- + I_1^- I_2^+) \right]$$

- $^1H - ^{13}C$ interactions (abundant I and rare specie S):

$$\mathcal{H}_d^{IS} = -\frac{\mu_0}{4\pi} \frac{(\gamma_I \hbar)(\gamma_S \hbar)}{2r_{12}^3} (3 \cos(\theta_{12})^2 - 1) [I_1^z I_2^z]$$

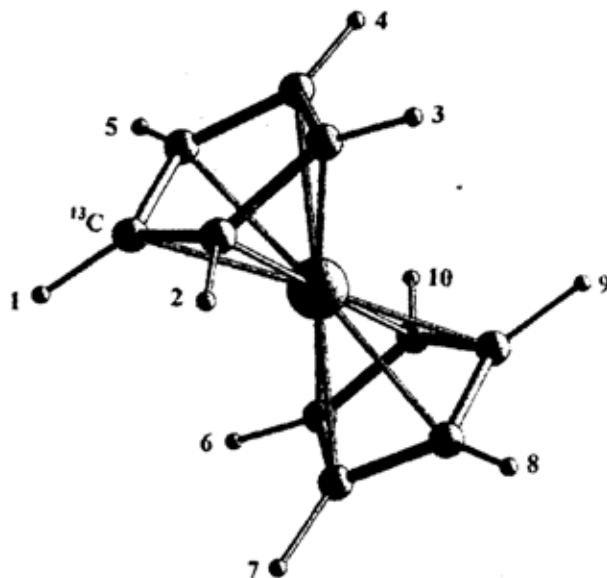
(we neglect the flip-flop term, that couples energy levels of different energies)

Both Hamiltonians commute with the Zeeman hamiltonian ($[\mathcal{H}_{d_{sec}}, \mathcal{H}_z] = 0$)

We won't take into account the $^{13}C - ^{13}C$ interactions, this specie being too dilute (the natural abundance of the ^{13}C is of around 1%, and the interatomic distances between ^{13}C are in general sufficiently son large to despreciate the interactions

1.2.2. Inverting the dipolar hamiltonian: the Magic Echo [RPW71]

Let's consider an ensamble of N 1H spins, of equal resonance frequency ω_0 and interacting via the dipolar interaction. (As it can be found in the ferrocene molecule)



The ferrocene molecule : two carbonyl pentagons, with a Fe nucleo in the middle.
All the H in this molecule are equivalent.

The hamiltonian of the system, in the ω_0 -rotating frame, is

$$\mathcal{H} = \mathcal{H}_{d_{zz}} = \sum_{j>k} d_{jk} \left[I_j^z I_k^z - \frac{1}{2} (I_j^+ I_k^- + I_j^- I_k^+) \right], \quad d_{jk} = -\frac{\mu_0 (\gamma_I \hbar)^2}{4\pi} \frac{3 \cos(\theta_{jk})^2 - 1}{2r_{jk}^3}$$

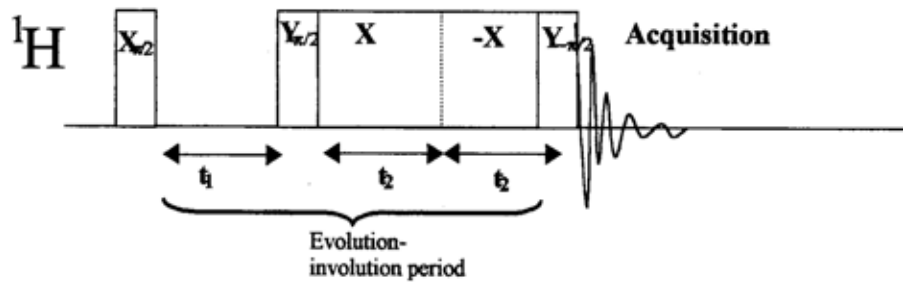
When we applicate to the probe a resonant field $\mathbf{B}_1(t) = 2B_1 \cos(\omega t) \mathbf{e}_x$, it turns to be

$$\mathcal{H}_{irr} = \mathcal{H}_{zz} + \mathcal{H}_{d_{zz}} = -\gamma_I \hbar B_1 \sum_{j=1}^N I_j^x - \frac{1}{2} \sum_{j>k} d_{jk} \left[I_j^x I_k^x - \frac{1}{2} (I_j^+ I_k^- + I_j^- I_k^+) \right]$$

the spin operators I_j^+ , I_j^- being relative to \mathbf{e}_x , that is the axis of the efective field and thus the new quantization axis.

We can see that formally, irradiate the 1H changes \mathcal{H}_d to $-\frac{1}{2}\mathcal{H}_d$, the what corresponds, for the spin dynamics, to a temporal inversion: $t \rightarrow -\frac{1}{2}t$.

Now, let 's consider the following pulse sequence, applicated to the 1H . Let 's prove that it produces a rebirth in the macroscopic magnetization, even after the dipolar-induced loss of coherence.



The spin-echo sequence :

The polarization evolves in H_d in a time t and then involutes in $-H_d/2$ in a time $2t$.

The refocalized polarization is measured in function of the evolution-involution time.

- The $X_{\frac{\pi}{2}}$ y $X_{-\frac{\pi}{2}}$ pulses surrounding the evolution period are a "frame change" to change $\mathcal{H}_{d_{zz}}$ to $\mathcal{H}_{d_{xx}}$, and really invert the dipolar hamiltonian.

- The phase change in the middle of the irradiation period is in order to cancel the phase that gets added to the density matrix during the evolution of the system in the hamiltonian $\mathcal{H}_{zz} = -\gamma \hbar B_1 I^z$.

The density matrix, following the pulse sequence, is (in the rotating frame)

$$\begin{aligned} \rho(\text{acquisition}) = & Y_{-\frac{\pi}{2}} \exp(-i\omega_1 t_2 (-I^x)) \exp(-i\omega_1 t_2 (I^x)) \\ & \exp\left(-i2t_2 \left(-\frac{1}{2} \frac{\mathcal{H}_{d_{zz}}}{\hbar}\right)\right) Y_{\frac{\pi}{2}} \exp\left(-it_1 \frac{\mathcal{H}_{d_{zz}}}{\hbar}\right) X_{\frac{\pi}{2}} \rho(0) \{\text{conj}\} \end{aligned}$$

($\{\text{conj}\}$) means that at the right of $\rho(0)$ comes the conjugate of what is on the left)

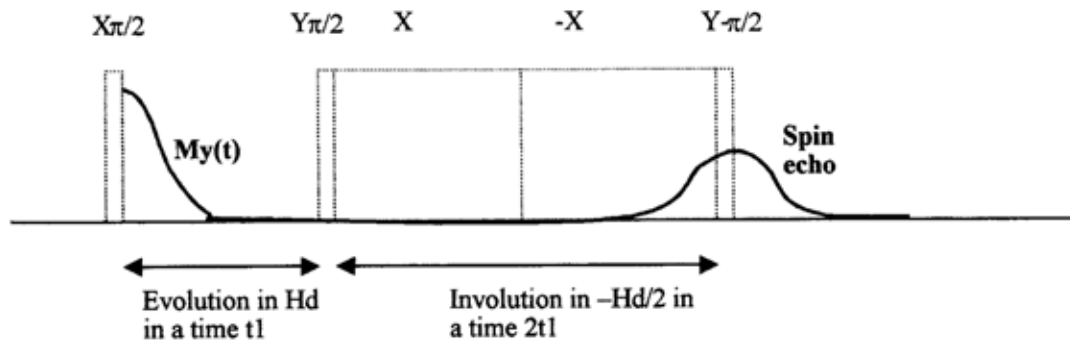
then the magnetization is:

$$\begin{aligned}
 M_y(acq) &= \text{Tr}(\rho(acq)M_y) \\
 &= -\frac{4}{2^N} M_0 \text{Tr} \left(Y_{-\frac{\pi}{2}} \exp\left(+it_2 \frac{\mathcal{H}_{dzz}}{\hbar}\right) Y_{\frac{\pi}{2}} \exp\left(-it_1 \frac{\mathcal{H}_{dzz}}{\hbar}\right) I^y \right) \\
 &= -\frac{4}{2^N} M_0 \text{Tr} \left(\exp\left(+it_1 \frac{\mathcal{H}_{dzz}}{\hbar}\right) Y_{-\frac{\pi}{2}} \exp\left(-it_2 \frac{\mathcal{H}_{dzz}}{\hbar}\right) Y_{\frac{\pi}{2}} I^y \right) \\
 &= -\frac{4}{2^N} M_0 \text{Tr} \left(\exp\left(+i(t_2 - t_1) \frac{\mathcal{H}_{dzz}}{\hbar}\right) I^y \exp\left(-i(t_2 - t_1) \frac{\mathcal{H}_{dzz}}{\hbar}\right) I^y \right)
 \end{aligned}$$

and, if $t_2 = t_1$,

$$M_y(acq) = -\frac{4}{2^N} M_0 \text{Tr}(I^y^2) = M_0$$

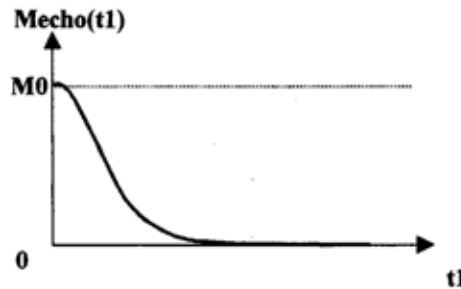
What is the same of simply following a $X_{\frac{\pi}{2}}$ pulse! The magnetization has been refocalized:



The spin echo sequence and its effect to the transverse M_y magnetization. When the evolution and involution are equivalent, an echo may be observed.

Experimentally, we don't recover all the magnetization. The rate of recovered magnetization decays in function of the evolution time t_1 .

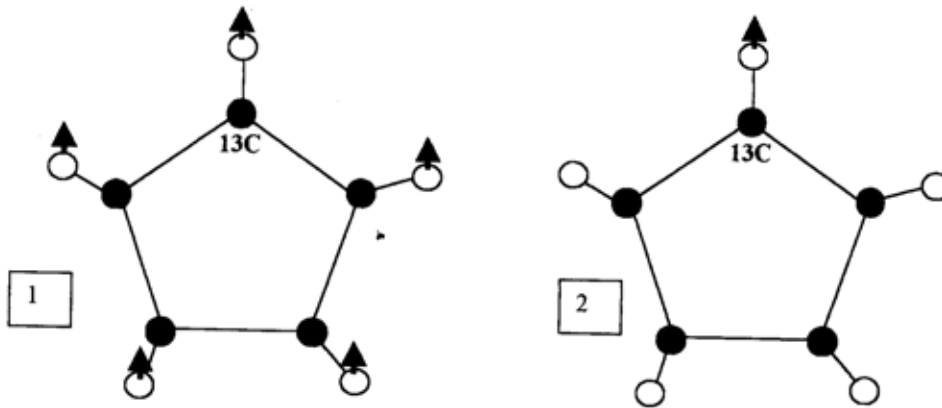
This is caused by the spin diffusion: interaction of the spins with local gradients of B_0 , and presents a characteristic attenuation form in $\exp(-t^3)$.



The decay of the refocalized magnetization as a function of t_1 . This has a particular form in $\exp(-t_1^3)$

1.3. The polarization echo [EMTP98]

Resembles the spin echo (the dipolar hamiltonian gets reversed) , but in the beginning we create a local, (not global) polarization, in the 1H , polarizing only the direct neighbours of a ^{13}C



A $\pi/2$ pulse polarizes all the 1H in the sample. (1)

We will see how we can create a local polarization, polarizing only the 1H directly bonded to a ^{13}C . (2)

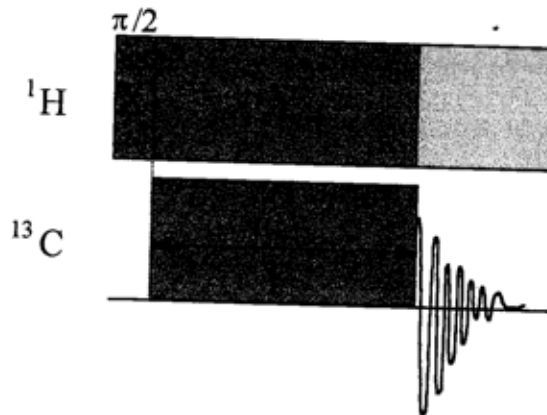
1.3.1. The cross polarization [HH62],[MKBE74].

Let 's consider 1H and a ^{13}C , interacting via the dipolar interaction \mathcal{H}_d^{IS} .

We can transfer polarization from the 1H to the ^{13}C , and vice-versa, irradiating both with two resonant fields at the same time [HH62]:

$$B_1(t) = (B_{1I} \cos(\omega_{0I}t) + B_{1S} \cos(\omega_{0S}t)) e_x$$

The pulse sequence is as follows:



The cross-polarization pulse sequence. We measure the signal amplitude of the ^{13}C as a function of the cross-polarisation « contact » time τ_{var}

The hamiltonian of the system, during the double irradiation, is , in the rotating frame: ($|\psi'\rangle = \exp(-i\omega_{0I}tI^z - i\omega_{0S}tS^z)|\psi\rangle$):

$$\mathcal{H}_{cp} = -\hbar\omega_{1I}I^x - \hbar\omega_{1S}S^x + \mathcal{H}_d^{IS}$$

The flip-flop term of \mathcal{H}_d^{IS} can induce transitions between the Zeeman levels $|+I -s\rangle$ and $|-I +s\rangle$, realizing a spin-transfer, that at the macroscopic scale is traduced by a polarization transfer, if and only if it doesn't induce modifications in the energy of the system, that is:

$$E_z(|+I -s\rangle) = E_z(|-I +s\rangle)$$

$$\begin{aligned} \text{that is } \hbar(-\omega_{1I} + \omega_{1S}) &= \hbar(\omega_{1I} - \omega_{1S}) \\ \text{that is } \omega_{1I} &= \omega_{1S}, \quad \Leftrightarrow \gamma_I B_{1I} = \gamma_S B_{1S} \end{aligned}$$

Condition known as the Hartman-Hahn condition [HH62]. It can be thought as a resonance condition, setting the proper frequencies of 1H and ^{13}C at the same value.

1.3.2. Interpretation of the pulse sequence in terms of density matrix

Let's consider a resonant- Hartman-Hahn double irradiation, in the double rotating frame:

$$\begin{aligned} \rho(0) &= \frac{1}{2^N} \left(1 + \frac{\hbar\omega_{0I}}{kT} I^z + \frac{\hbar\omega_{0S}}{kT} S^z \right) \\ \mathcal{H}_{cp} &= -\hbar\omega_{1cp}(I^x + S^x) - \frac{1}{2}d_{IS} \left[I^x S^x - \frac{1}{2}(I^+ S^- + I^- S^+) \right], \end{aligned}$$

$$\text{with } \omega_{1cp} = \gamma_I B_{1I} = \gamma_S B_{1S}, \quad d_{IS} = -\frac{\mu_0}{4\pi} \frac{(\gamma_I \hbar)(\gamma_S \hbar)}{2r_{IS}^3} (3 \cos(\theta_{IS})^2 - 1)$$

at acquisition time,

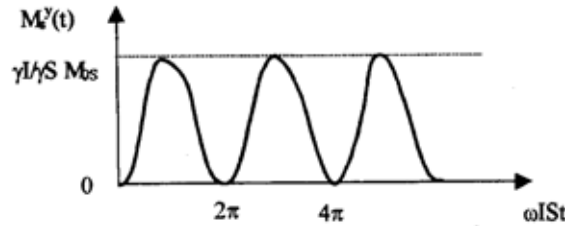
$$\rho(acq) = \exp\left(-it_{cp} \frac{\mathcal{H}_{cp}}{\hbar}\right) Y_{\frac{I}{2}}^I \rho(0) Y_{-\frac{I}{2}}^I \exp\left(it_{cp} \frac{\mathcal{H}_{cp}}{\hbar}\right)$$

The magnetization in e_x of the ^{13}C is:

$$\begin{aligned} M_y^S(t_{cp}) &= \frac{\gamma_I}{\gamma_S} \frac{4}{2^N} M_{0S} \text{Tr} \left(\exp\left(-it_{cp} \frac{\mathcal{H}_{cp}}{\hbar}\right) Y_{\frac{I}{2}}^I (I^x + S^x) Y_{-\frac{I}{2}}^I \exp\left(it_{cp} \frac{\mathcal{H}_{cp}}{\hbar}\right) S^x \right) \\ &= \frac{\gamma_I}{\gamma_S} \frac{4}{2^N} M_{0S} \text{Tr} \left(\exp\left(-it_{cp} \frac{\mathcal{H}_{cp}}{\hbar}\right) (I^x + S^x) \exp\left(it_{cp} \frac{\mathcal{H}_{cp}}{\hbar}\right) S^x \right) \\ &= \frac{\gamma_I}{\gamma_S} \frac{4}{2^N} M_{0S} \text{Tr} \left(\exp\left(-it_{cp} \frac{\mathcal{H}_{cp}}{\hbar}\right) I^x \exp\left(it_{cp} \frac{\mathcal{H}_{cp}}{\hbar}\right) S^x \right) \end{aligned}$$

All calculs made, we have:

$$M_y^S(t) = \frac{\gamma_I}{\gamma_S} M_{0S} \left(1 - \cos\left(\frac{d_{IS}}{\hbar} t_{cp}\right) \right)$$

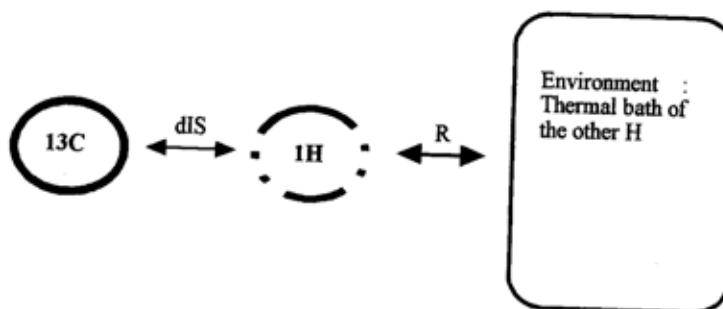


The transverse magnetization in the rare (Carbon) spin system, as a function of the cross-polarization time.
Perfect resonant conditions and no relaxation are assumed.

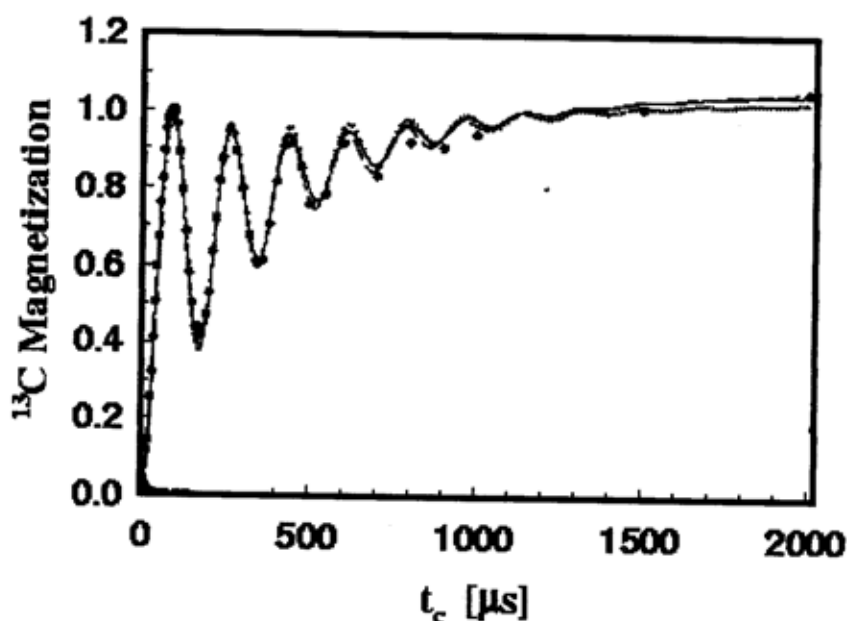
The cross polarization allows us to observe a signal $\frac{\gamma_I}{\gamma_S}$ bigger than the one we could observe following a simple $\frac{\pi}{2}$ pulse! (in the case of carbon and hydrogen, we gain a factor 4).

taking into account the dipolar coupling between the 1H coupled to the ^{13}C , to the others 1H that surround him, considered as forming part of a reserve of polarization, one can obtain the more realistic formula for the ^{13}C magnetization [MKBE74]:

$$M_y^S(t_{cp}) = M_0 \left(1 - \frac{1}{2} e^{-Rt_{cp}} - \frac{1}{2} e^{-\frac{3}{2}Rt_{cp}} \cos\left(\frac{d_{IS}}{\hbar} t_{cp}\right) \right)$$



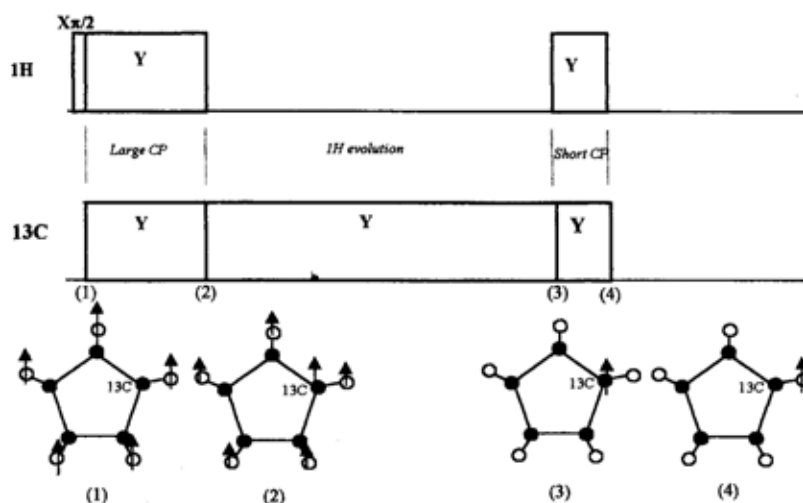
Schematization of the considered interactions in our model for the cross-polarization.



The typical result of a cross-polarization experiment in the ferrocene molecule, and its fitting with the obtained formula.

1.3.3. Create a local polarization in ^1H

Let's polarize, in a probe, selectionnally the ^1H directly linked to a ^{13}C . For this, let's consider the following pulse sequence:



The schematic evolution of the magnetization, following the pulse sequence.

- (1) The $X_{\pi/2}$ pulse polarizes the ^1H spin system
- (2) A large cross polarization polarizes the ^{13}C spin system. The polarization in ^1H remains nearly equal as the initial one.
- (3) We let the ^1H evolve and lose their polarization, while the polarization in ^{13}C is spin-locked.
- (4) A short time cross-polarization transfer the ^{13}C polarization to its nearest ^1H neighbour only. Local polarization is achieved.

1) we polarize, with a large cross-polarization, all the ^{13}C .

2) we let the magnetization of the ^1H lose coherence in a time order of T_{2H} , while we maintain the magnetization transferred to the ^{13}C via a resonant "spin-lock" field.

3) we transfer, with a cross-polarization, the ^{13}C magnetization selectively to his nearest neighbours.

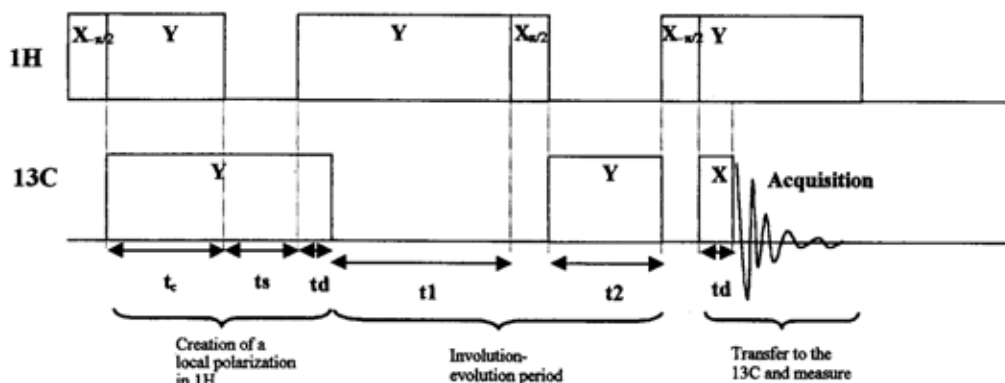
Like that, just the ^1H directly bonded to a ^{13}C , will be polarized.

1.3.4. The local polarization echo [ZME92],[EMTP98]

Let's;

- 1) create a local polarization in ^1H
- 2) let it evolutionize in the dipolar hamiltonian H_d and then involute in $-\frac{1}{2}H_d$,
- 3) locally measure the refocalized polarization, via the ^{13}C

Let's consider for this the following pulse sequence:



The ZME sequence for the polarization echo

- 1) a local polarization is created in the ^1H
- 2) this polarization involutes in $-1/2 H_d$ in a time t_1 , then evolves in H_d in a time $t_2 = t_1/2$
- 3) the refocalized polarization is locally measured, by means of the ^{13}C

Soon we will study the decay of the echo: the magnetization measured in the site 1H , selectively polarized (via the ^{13}C more linked), as a function of the evolution time.

1.4. Conclusions

It is possible to invert the quantic dynamics of many interacting bodies:

- the many bodies being the spins of a NMR probe,
- the inversion being realized by appropriated pulse-sequences to invert the interaction hamiltonian between them ($H_d \rightarrow -\frac{1}{2}H_d$), that is, in the dynamics studies, equivalent to invert the time.

This quantic inversion, (even if it's not perfect as we will see), doesn't have a classic equivalent.