



EPR “no paradójico” y Ecos de Espín

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~~➤ Paradoja de Einstein-Podolsky-Rosen~~

~~➤ Epitelio Pigmentario Retiniano (oftalmología)~~

~~➤ Exposición y Prevención de Respuesta (psiquiatría)~~

~~➤ Evaluación Postural Rápida (ergonomía)~~

~~➤ Electronic Patient Record~~

~~➤ Cable de Alta Tensión EPR (electrotecnia)~~

~~➤ Ejército Popular Revolucionario (Mejora)~~

~~➤ EPR Architects (Elsom, Pack & Roberts.)~~

~~➤ Education Policy and Reform Unit (EPR) UNESCO Bangkok.~~

~~➤~~

Electron Paramagnetic Resonance



ECOS de Espín Electrónico ESE

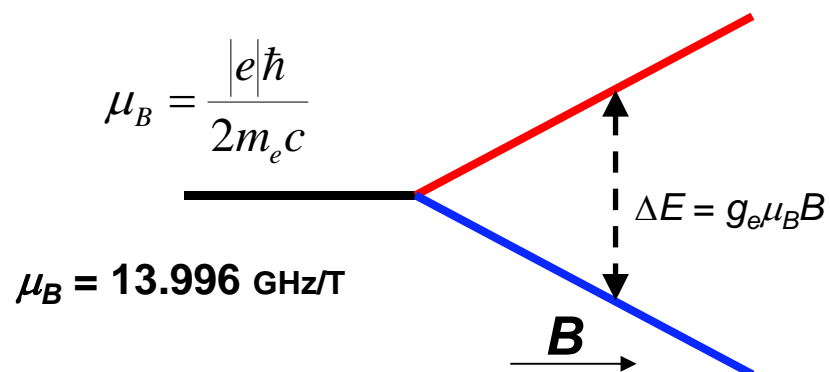
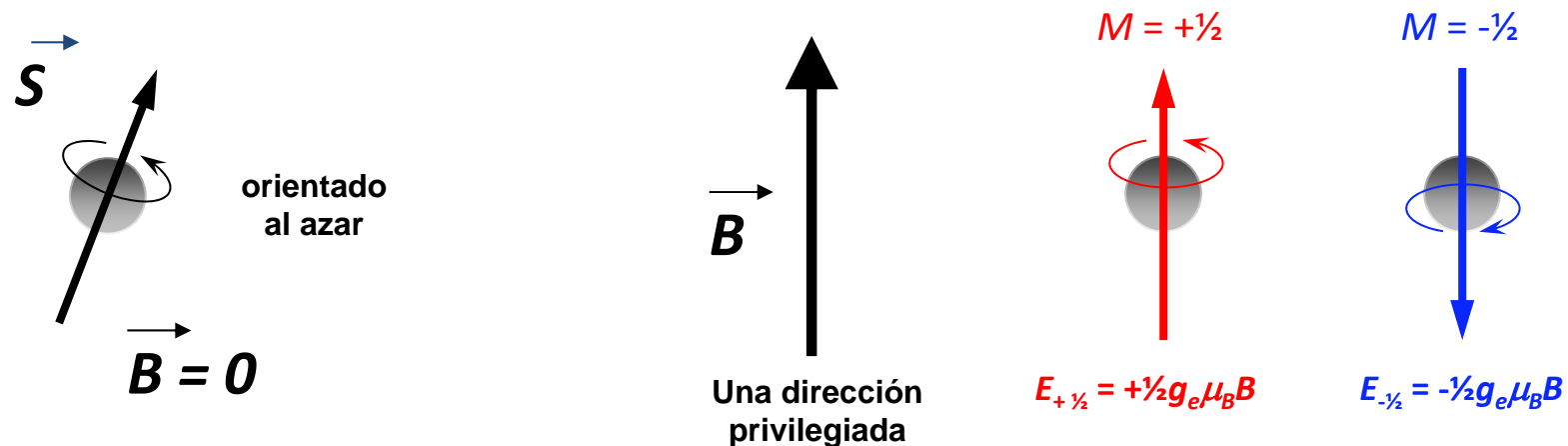
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- Espectroscopia cw-EPR.
- Espectroscopia TD-EPR.
- Formulación básica.
- Señal FID (TD-EPR .vs. cw-EPR).
- Ensanchamiento inhomogéneo.
- Experimento de Hahn (2p-ESE): medida de T_2 .
- Experimento de Carr-Purcell (CP) y variante de Meiboom-Gill (CPMG)
- Secuencia 3p (medidas de T_1).
- Apertura a nuevas espectroscopias

Espectroscopia EPR de onda continua

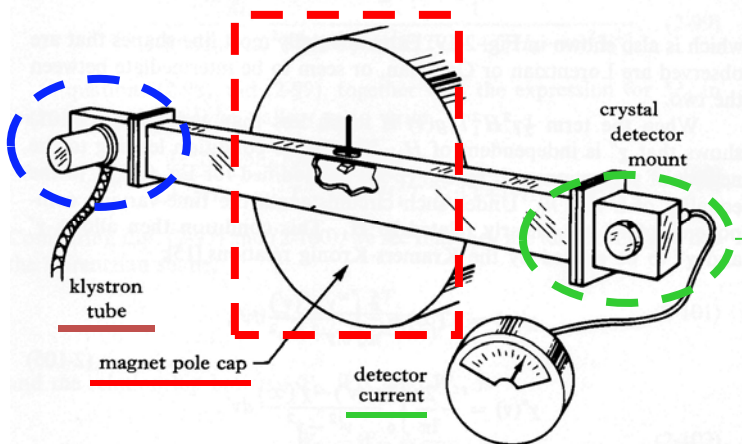
Observación de transiciones (M1) inducidas por un campo magnético oscilante entre estados de un sistema paramagnético desdoblados por la aplicación de un campo magnético d.c. (en situaciones estacionarias).



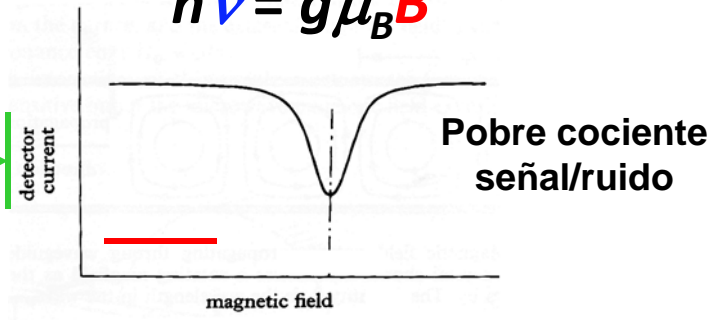
RESONANCIA $h\nu = g_e \mu_B B$

Se alcanza variando la **frecuencia** o el **campo**.

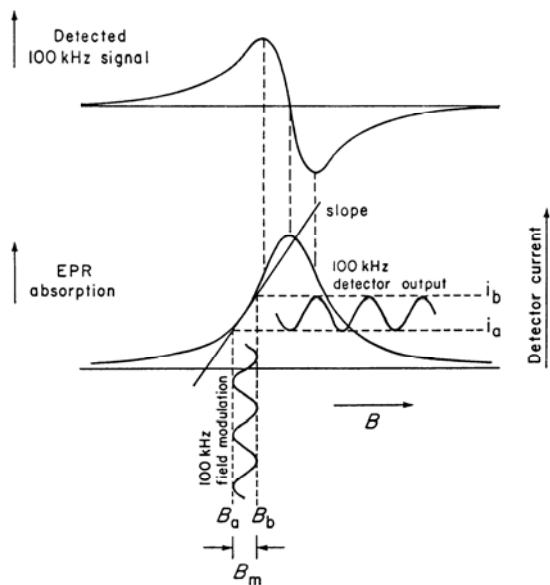
$$g_e = 2.0023 (\approx 2)$$



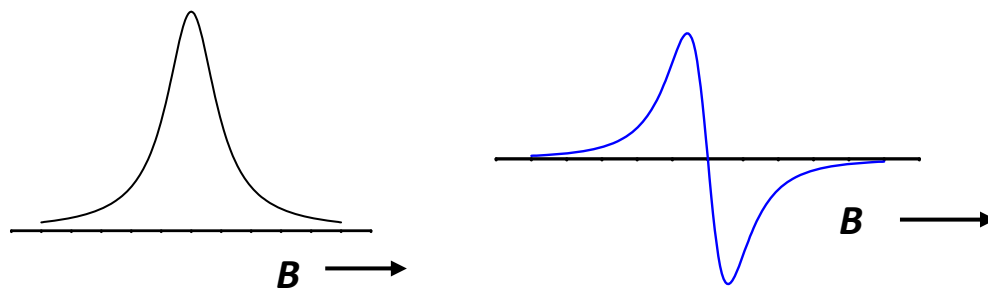
$$h\nu = g\mu_B B$$



Modulación de campo magnético y técnicas de detección "lock-in"

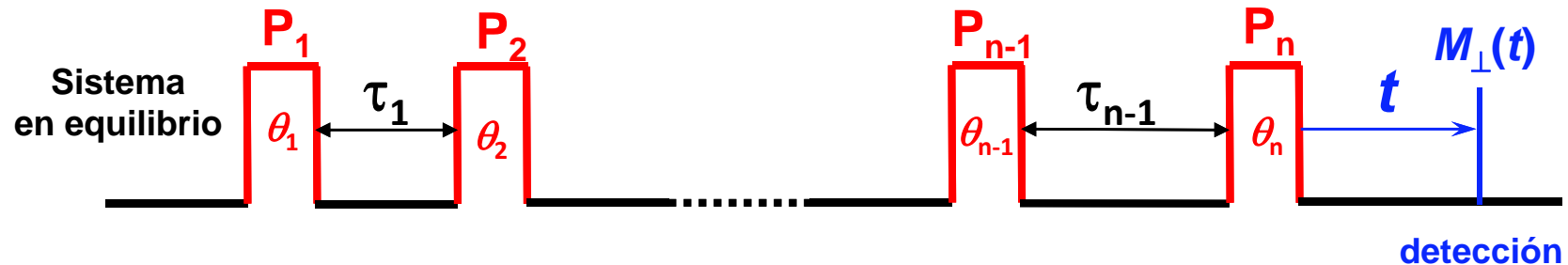


Presentación en 1ª derivada



Espectroscopia EPR en el dominio temporal (TD-EPR)

Medida de la evolución temporal de la magnetización transversal, $M_{\perp}(t)$, tras aplicar a un sistema paramagnético (en equilibrio) en presencia de un campo magnético estático, \vec{B}_0 , una sucesión de pulsos de radiación (resonantes) que lo apartan del equilibrio.



Obviamente, τ_k suficientemente cortos para que el sistema no relaje al equilibrio

$$M(t) = U(\theta_k, \tau_k; t) \cdot M(0)$$

$$U(\theta_k, \tau_k; t) = T(t) \cdot P(\theta_n) \cdot T(\tau_{n-1}) \cdot P(\theta_{n-1}) \cdot \dots \cdot P(\theta_2) \cdot T(\tau_1) \cdot P(\theta_1)$$

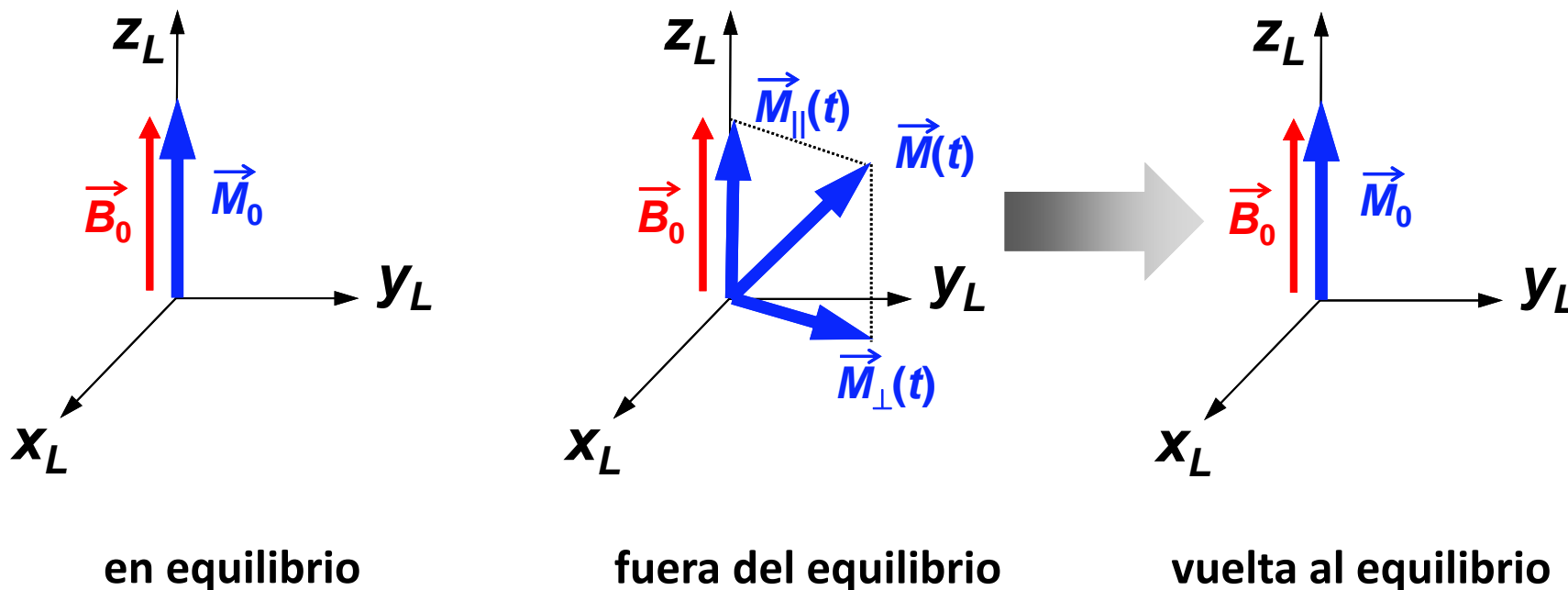
T evolución libre (relajación)

P evolución bajo un pulso



TD-EPR

¿Qué se mide y como se mide?



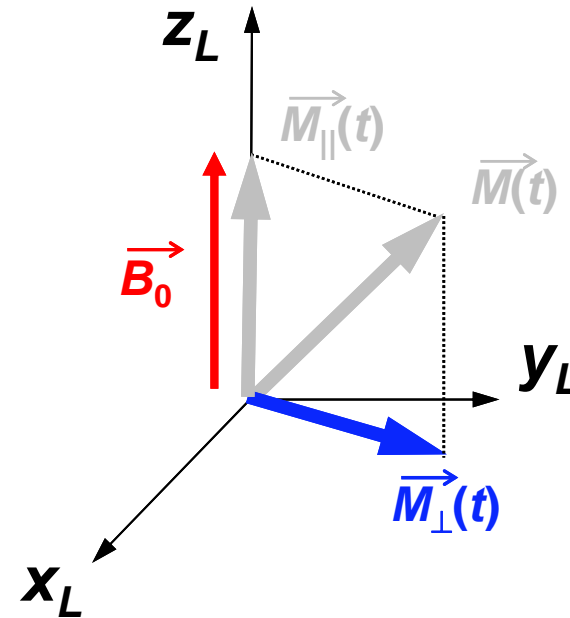
$$\vec{M}(t) = \vec{M}_{\parallel}(t) + \vec{M}_{\perp}(t)$$

$\vec{M}_{\parallel}(t)$ y $\vec{M}_{\perp}(t)$ diferente escala temporal

Muestra en cavidad resonante
(filtro pasa-banda 100 MHz)

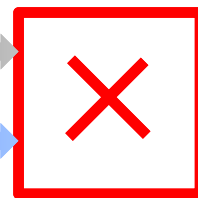
$$\vec{M}_{\perp}(t) = M_{x_L}(t)\hat{i}_L + M_{y_L}(t)\hat{j}_L$$

detección HETERODINA fase sensible
señal de referencia, $V_r(t)$, (excitación)



$$V_r(t) = V_{r0}\cos(\omega_r t - \phi_r)$$

$$V(t) = V_0\cos(\omega t - \phi)$$



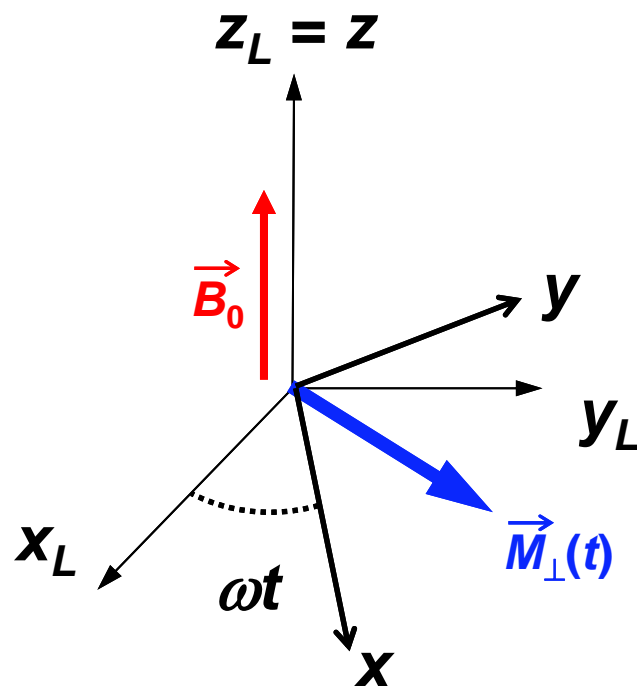
$$V_{out}(t) = V_{r0}V_0\cos\{(\omega - \omega_r)t - (\phi - \phi_r)\}$$

$$V_{out}(t) = V_{r0}V_0\cos\{(\omega - \omega_r)t\}\delta(\phi - \phi_r)$$

señal de referencia

sistema laboratorio: $B_1(t) = B_1 \cos(\omega t) \hat{i}_L + B_1 \sin(\omega t) \hat{j}_L$

sistema giratorio: $B_1(t) = B_1 \hat{i}$



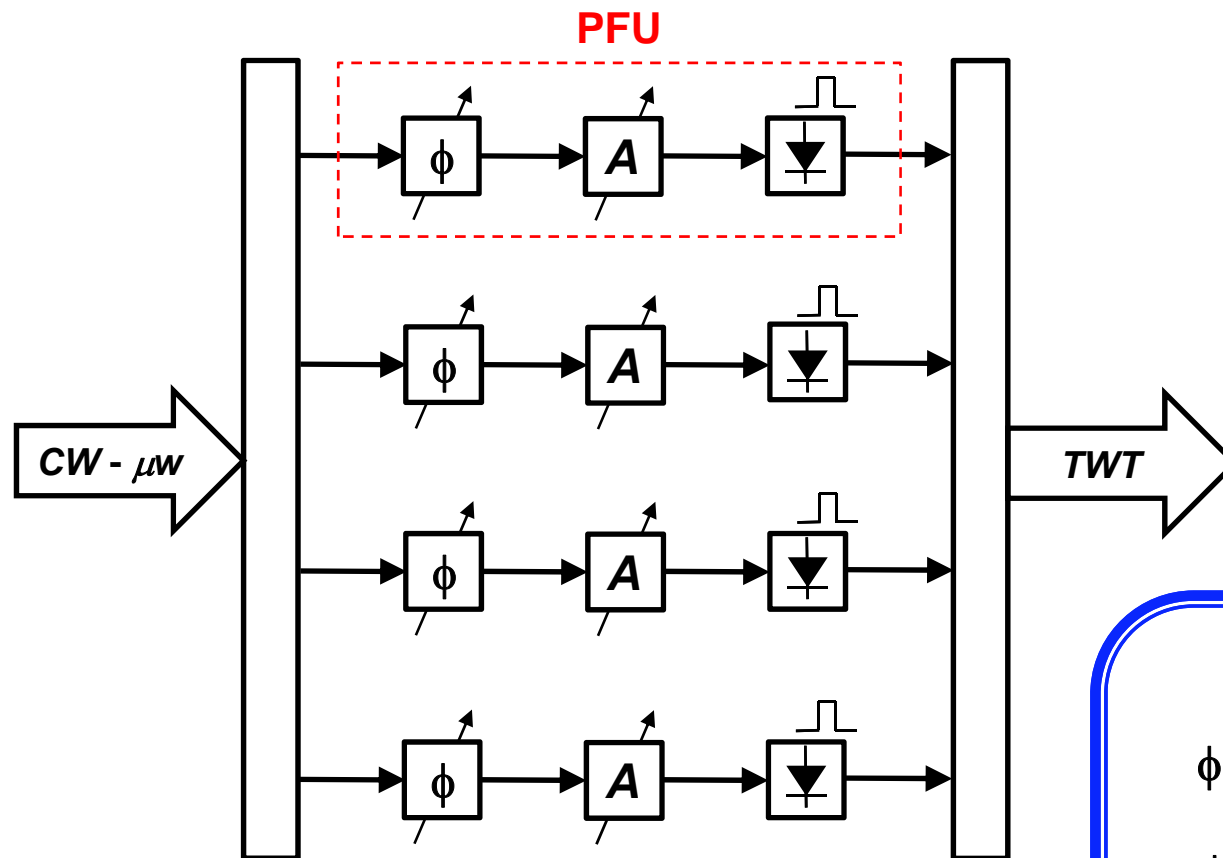
detección HETERODINA fase sensible

detección MONOCANAL

$M_x(t) \text{ o } M_y(t)$

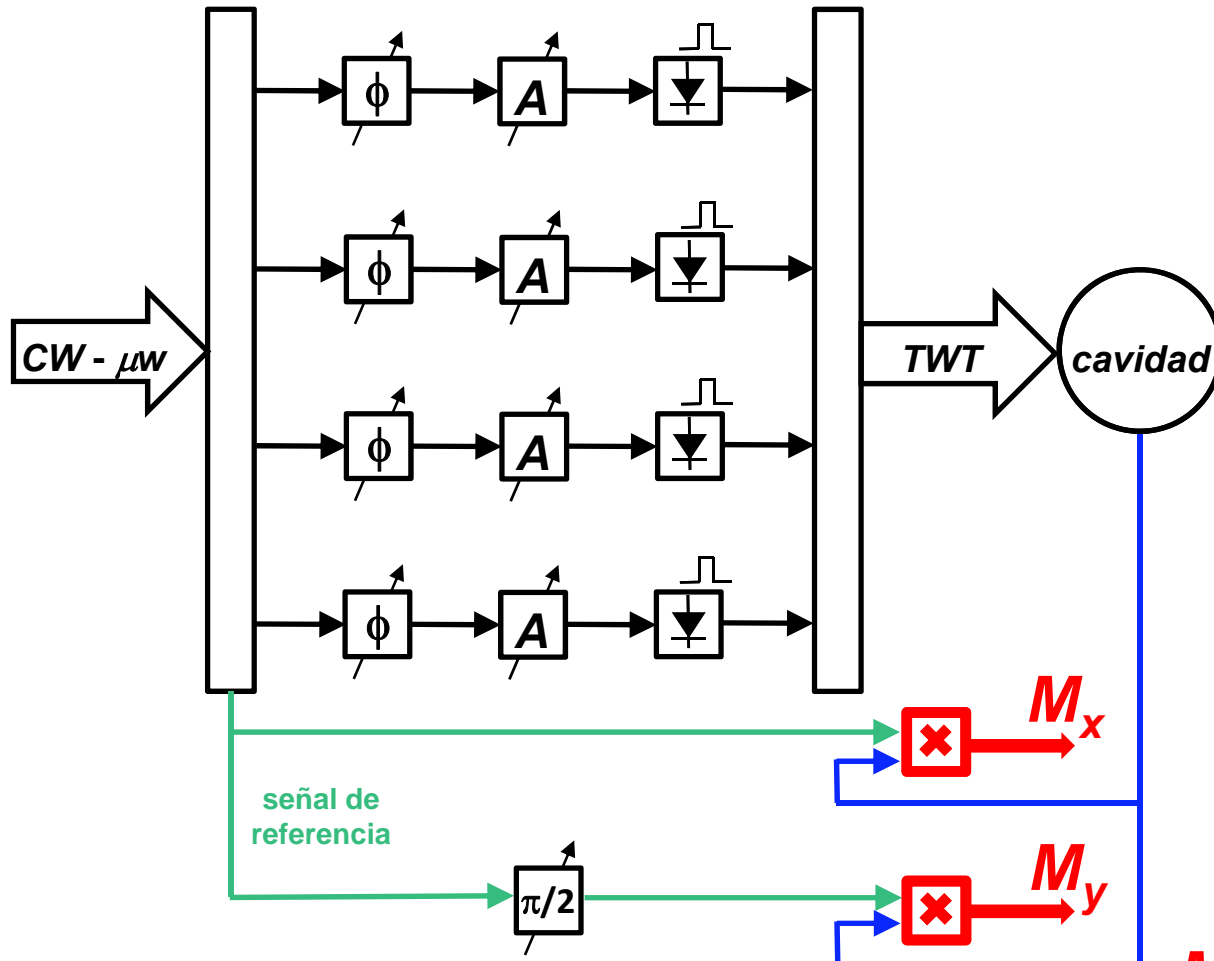
detección EN CUADRATURA

$M_x(t) \text{ y } M_y(t)$



señal de referencia
 $\vec{B}_1(t) = B_1 \hat{i}$
 (sistema rotatorio)

jerga		
$\phi = 0$	$\vec{B}_{\mu W} = AB_1 \hat{i}$	+X
$\phi = \pi$	$\vec{B}_{\mu W} = -AB_1 \hat{i}$	-X
$\phi = \pi/2$	$\vec{B}_{\mu W} = AB_1 \hat{j}$	+y
$\phi = 3\pi/2$	$\vec{B}_{\mu W} = -AB_1 \hat{j}$	-y



$$M_{x,y}(t) \propto \text{tr}\{\rho(t)S_{x,y}(t)\}$$

$$M_{\pm}(t) = M_x(t) \pm iM_y(t)$$

$$M_{x,y}(t) \propto \text{tr}\{\rho(t)S_{x,y}(t)\}$$

Sistema laboratorio y aproximación a un espín “promedio”

$$\frac{\partial \rho(t)}{\partial t} = -i[H(t), \rho(t)] - \underbrace{R\{\rho(t) - \rho_{eq}\}}_{\text{relajación}}$$

$$\begin{aligned} H(t) &= g\mu_B \vec{B}(t) \cdot \vec{S} = g\mu_B B_0 S_Z + g\mu_B B_1 \{ \cos(\omega t) S_X + \sin(\omega t) S_Y \} = \\ &= \omega_L S_Z + \omega_1 e^{-i\omega t S_Z} S_X e^{i\omega t S_Z} \end{aligned}$$

$$\omega_L = g\mu_B B_0$$

frecuencia LARMOR

$$\omega_1 = g\mu_B B_1$$

frecuencia NUTACIÓN

$$M_{x,y}(t) \propto \text{tr}\{\rho(t)S_{x,y}(t)\}$$

Sistema laboratorio y aproximación a un espín “promedio”

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$$\omega_L = g\mu_B B_0$$

frecuencia LARMOR

$$\omega_1 = g\mu_B B_1$$

frecuencia NUTACIÓN

Sistema laboratorio y sistema giratorio

$$M_{x,y}(t) \propto \text{tr}\{\rho(t)S_{x,y}(t)\} = \text{tr}\{\rho_R(t)S_{x,y}\}$$

$$\rho_R(t) = e^{i\omega t S_Z} \rho(t) e^{-i\omega t S_Z}$$

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

$$\frac{\partial \rho_R(t)}{\partial t} = -i[H_R, \rho_R(t)]$$

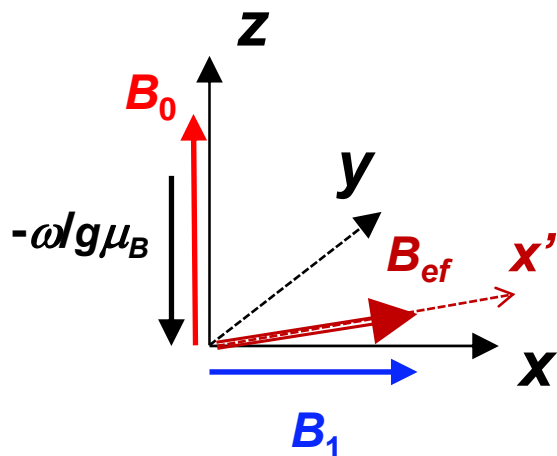
$$H(t) = \omega_L S_Z + \omega_1 e^{-i\omega t S_Z} S_X e^{i\omega t S_Z}$$

$$H_R = (\omega_L - \omega) S_Z + \omega_1 S_X = \omega'_L S_Z + \omega_1 S_X$$

$$H_R = \omega_{ef} S_{X'} \quad \omega_{ef} = \sqrt{(\omega_L - \omega)^2 + \omega_1^2}$$

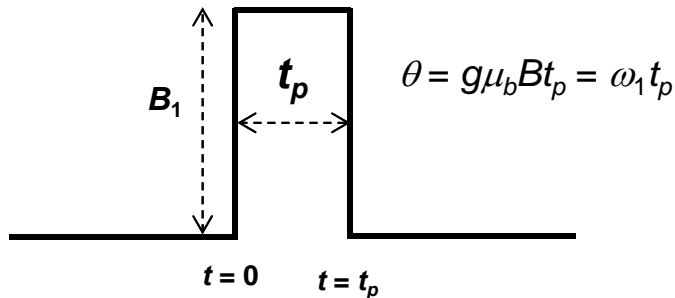
$$\rho_R(t) = P_x(t)^{-1} \cdot \rho_R(0) \cdot P_x(t)$$

$$P_x(t) = e^{i\omega_{eff} t S_{X'}} \approx e^{i\omega_1 t S_x}$$



En resonancia ($\omega'_L = 0$) o pulso duro ($\omega_1 \gg \omega'_L$)

Respuesta a un pulso “duro” (+x)



$$M_k(t_p) = A \cdot \text{tr}\{\rho_R(t_p) \cdot S_k\} \quad (k = x, y, z)$$

$$\rho_R(t_p) = e^{-i\omega_1 t_p S_x} \cdot \rho_R(0) \cdot e^{i\omega_1 t_p S_x} = e^{-i\theta S_x} \cdot \rho_R(0) \cdot e^{i\theta S_x}$$

$$M_k(t_p) = A \cdot \text{tr}\{e^{-i\theta S_x} \cdot \rho_R(0) \cdot e^{i\theta S_x} \cdot S_k\} = A \cdot \text{tr}\{\rho_R(0) \cdot (e^{i\theta S_x} \cdot S_k \cdot e^{-i\theta S_x})\}$$

$$\begin{aligned} e^{i\theta S_x} \cdot S_x \cdot e^{-i\theta S_x} &= S_x \\ e^{i\theta S_x} \cdot S_y \cdot e^{-i\theta S_x} &= S_y \cos \theta - S_z \sin \theta \\ e^{i\theta S_x} \cdot S_z \cdot e^{-i\theta S_x} &= S_y \sin \theta + S_z \cos \theta \end{aligned}$$

$$\begin{pmatrix} M_x(t_p) \\ M_y(t_p) \\ M_z(t_p) \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta \\ 0 & \sin \theta & \cos \theta \end{pmatrix} \cdot \begin{pmatrix} M_x(0) \\ M_y(0) \\ M_z(0) \end{pmatrix}$$

rotación de la magnetización (en el sistema giratorio) un ángulo $\theta = \omega_1 t_p$ en torno al eje x

evolución libre (relajación)

$$\frac{\partial \rho_R(t)}{\partial t} = -i[\omega'_L S_Z, \rho_R(t)] - \underbrace{R\{\rho_R(t) - \rho_{eq}\}}_{\text{relajación}}$$

Teoría BWR (modos normales de relajación)

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

$$\rho = \begin{pmatrix} \rho_{++} & \rho_{+-} \\ \rho_{-+} & \rho_{--} \end{pmatrix} \quad -R\{\rho_R(t) - \rho_{eq}\} = - \begin{pmatrix} \frac{\rho_{++} - (\rho_{++})_{eq}}{T_1} & \frac{\rho_{+-}}{T_2} \\ \frac{\rho_{-+}}{T_2} & \frac{\rho_{--} - (\rho_{--})_{eq}}{T_1} \end{pmatrix}$$



Ecuaciones de Bloch para la magnetización

S = 1/2 (evolución libre y teoría BWR de relajación)

$$H_R = \omega'_L S_z = (\omega_L - \omega) S_z$$

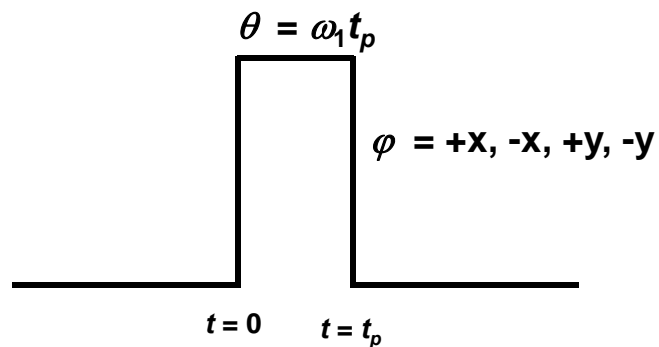
$$\begin{pmatrix} M_x(t) \\ M_y(t) \\ M_z(t) \\ M_0 \end{pmatrix} = \underbrace{\begin{pmatrix} e^{-t/T_2} \cos(\omega'_L t) & -e^{-t/T_2} \sin(\omega'_L t) & 0 & 0 \\ e^{-t/T_2} \sin(\omega'_L t) & e^{-t/T_2} \cos(\omega'_L t) & 0 & 0 \\ 0 & 0 & e^{-t/T_1} & 1 - e^{-t/T_1} \\ 0 & 0 & 0 & 1 \end{pmatrix}}_{\mathbf{T}(t, \omega'_L)} \cdot \begin{pmatrix} M_x(0) \\ M_y(0) \\ M_z(0) \\ M_0 \end{pmatrix}$$

$$\mathbf{M} = \begin{pmatrix} M_x \\ M_y \\ M_z \\ M_0 \end{pmatrix}$$

$$M_0 = \chi_0 B_0$$

$$\mathbf{M}(t) = \mathbf{T}(t, \omega'_L) \cdot \mathbf{M}(0)$$

y (recordemos) pulso duro



$$\mathbf{M} = \begin{pmatrix} M_x \\ M_y \\ M_z \\ M_0 \end{pmatrix}$$

$$\mathbf{M}(t) = \mathbf{P}_\varphi(\theta) \cdot \mathbf{M}(0)$$

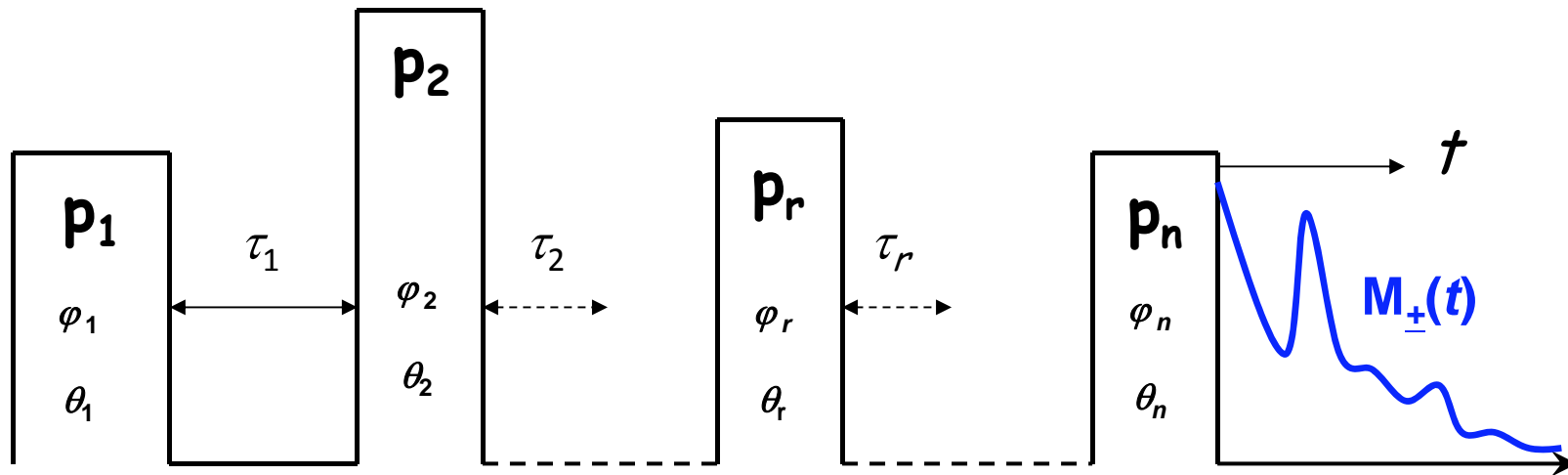
pulsos
+x y -x

$$\mathbf{P}_{\pm x}(\theta) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos \theta & \mp \sin \theta & 0 \\ 0 & \pm \sin \theta & \cos \theta & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

pulsos
+y e -y

$$\mathbf{P}_{\pm y}(\theta) = \begin{pmatrix} \cos \theta & 0 & \pm \sin \theta & 0 \\ 0 & 1 & 0 & 0 \\ \mp \sin \theta & 0 & \cos \theta & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Espectroscopia EPR en el dominio temporal (TD-EPR)



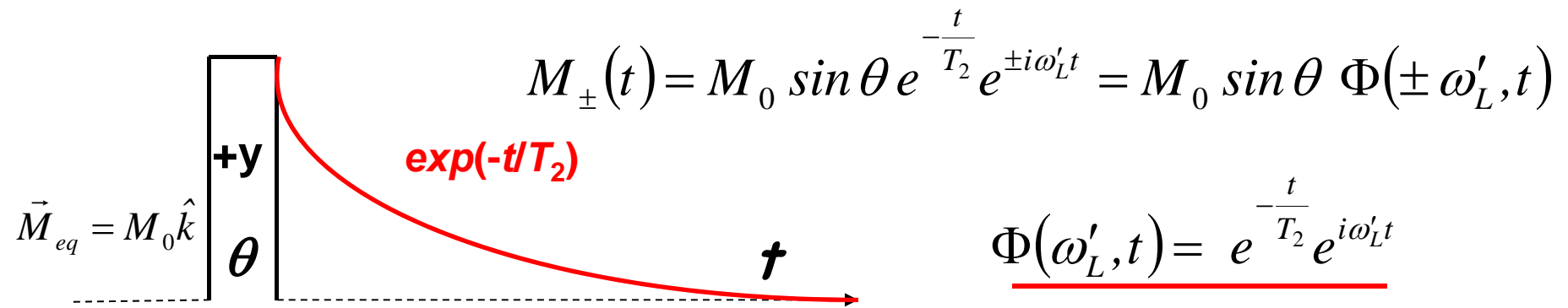
$$\mathbf{M}(t) = \mathbf{U}(\theta_k, \tau_k; t, \omega'_L) \cdot \mathbf{M}(0)$$

$$\mathbf{U}(\theta_k, \tau_k; t, \omega'_L) = \mathbf{T}(t, \omega'_L) \cdot \mathbf{P}_{\varphi_n}(\theta_n) \cdot \dots \cdot \mathbf{T}(\tau_r, \omega'_L) \cdot \mathbf{P}_{\varphi_r}(\theta_{n-1}) \cdot \dots \cdot \mathbf{T}(\tau_1, \omega'_L) \cdot \mathbf{P}_{\varphi_1}(\theta_1)$$

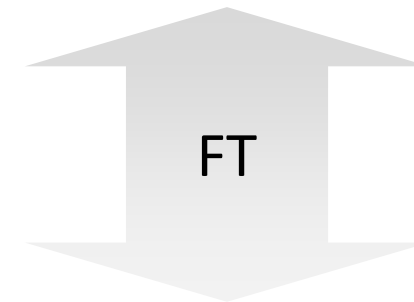
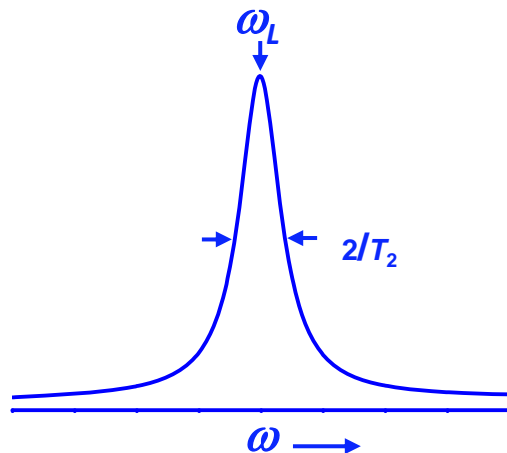
$$\mathbf{M}(0) = \begin{pmatrix} 0 \\ 0 \\ M_0 \\ M_0 \end{pmatrix} \quad \longrightarrow \quad \mathbf{M}(t) = \begin{pmatrix} M_x(t) \\ M_y(t) \\ M_z(t) \\ M_0 \end{pmatrix}$$

$$\mathbf{M}_{\pm}(t) = M_x(t) \pm iM_y(t)$$

Respuesta a un pulso: señal FID

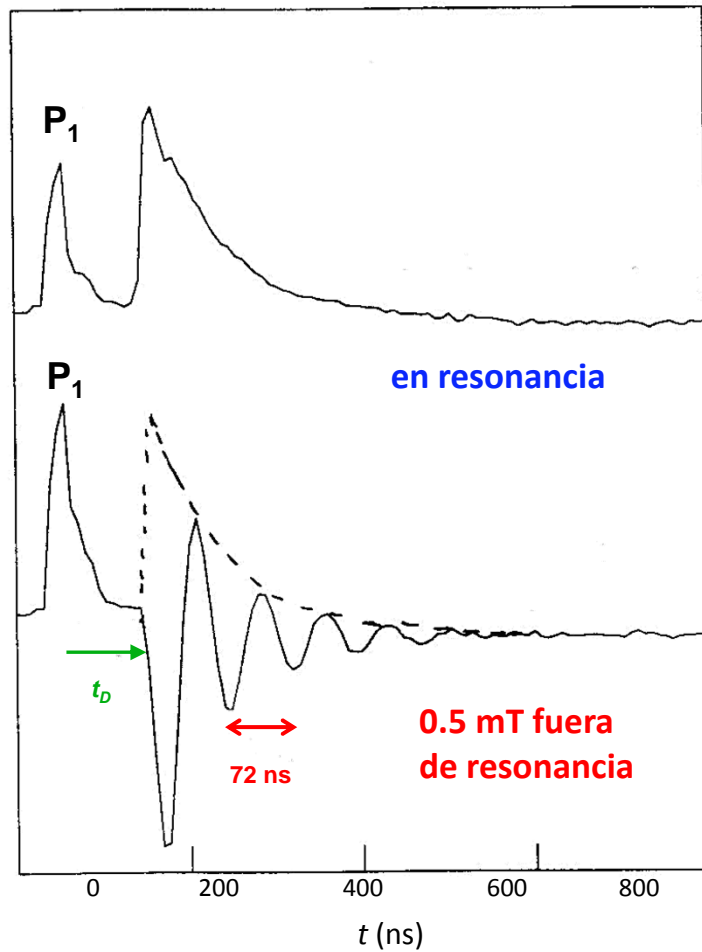


señal cw-EPR



$$\chi''(\omega_L, \omega) = \frac{1}{T_2^2 (\omega_L - \omega)^2 + 1}$$

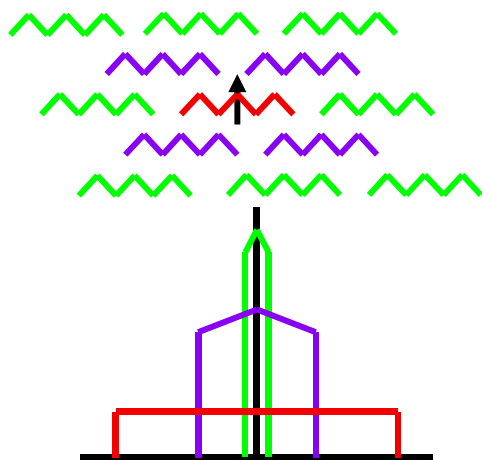
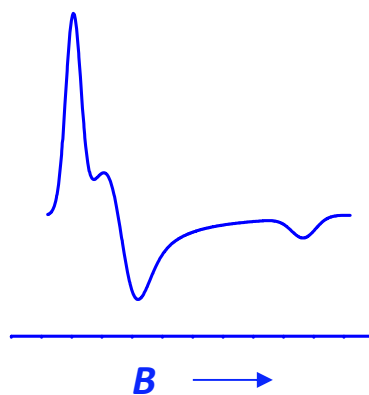
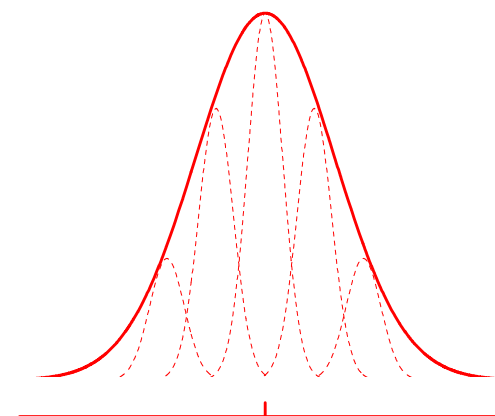
DPPH (señal FID excitada por un pulso)

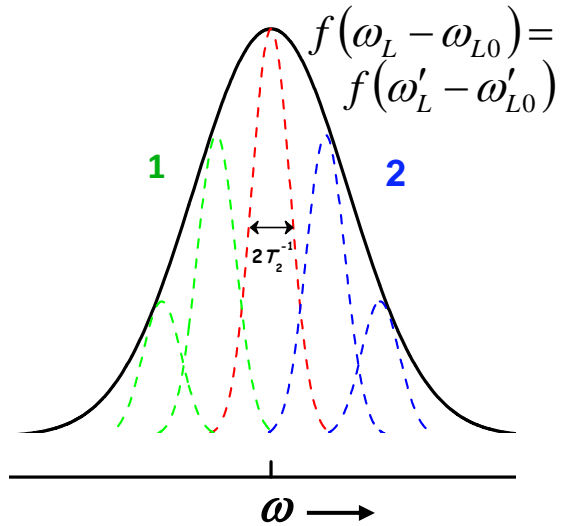


$$\Phi(\omega'_L, t) = e^{-\frac{t}{T_2}} e^{i\omega'_L t}$$

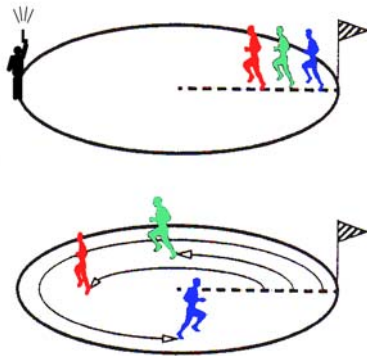
$$\omega'_L = \omega_L - \omega$$

tiempo muerto del detector, t_D ($t_D = 150 - 250$ ns)

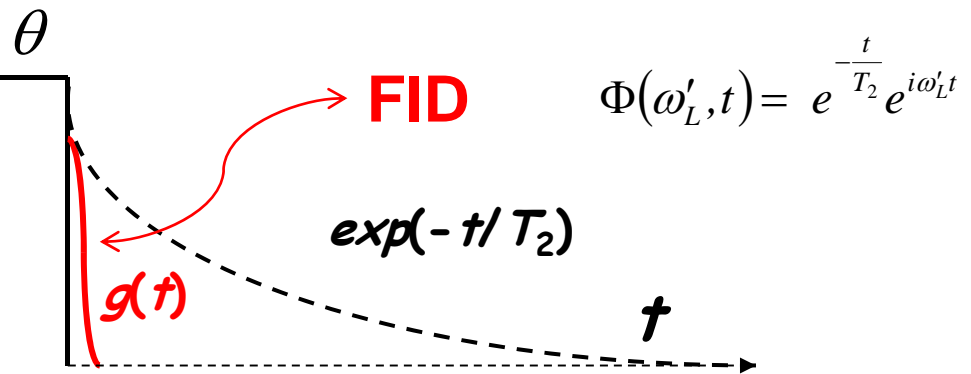
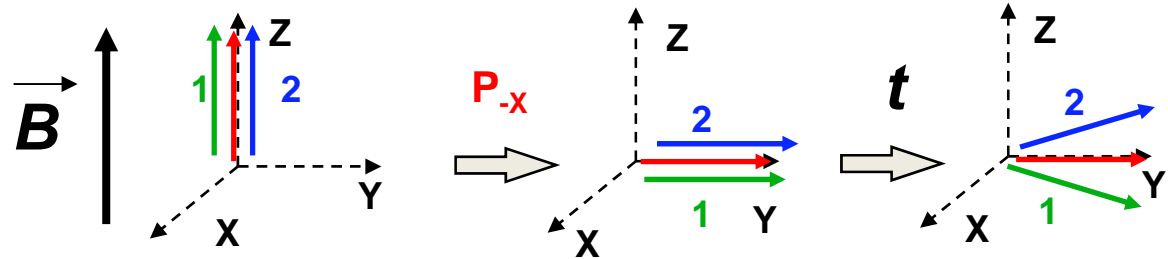
Ensanchamiento inhomogéneo**Estructura hf compleja**
(^1H and ^{14}N)**Desorden espacial**
(anisotropía)**Entornos diferentes**
(g-strain)



1 espines "lentos"
 2 espines "rápidos"



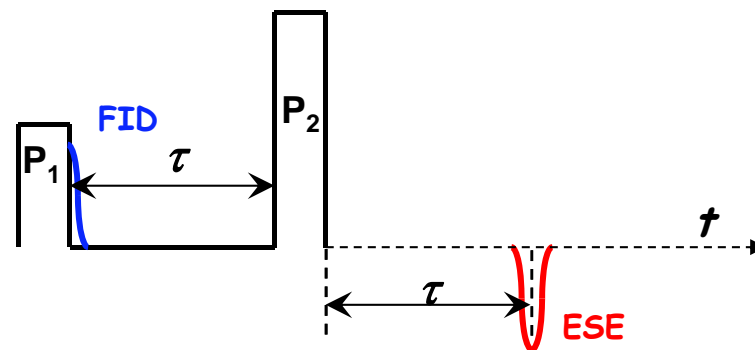
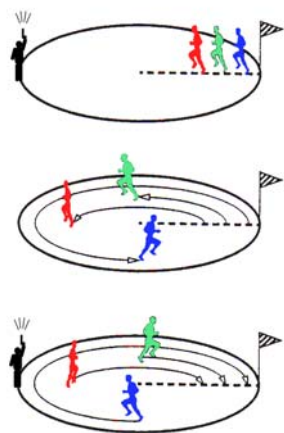
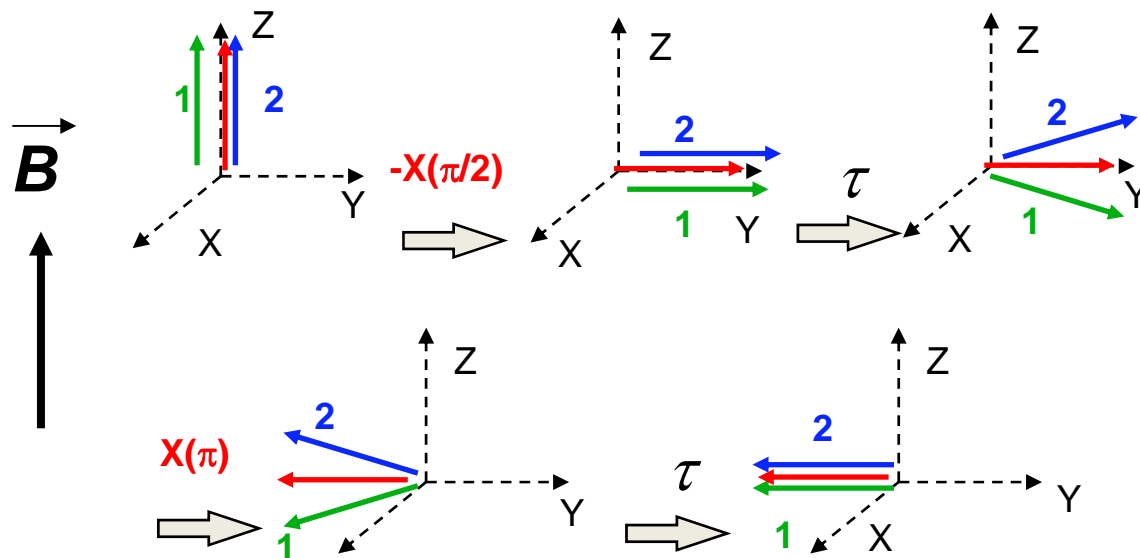
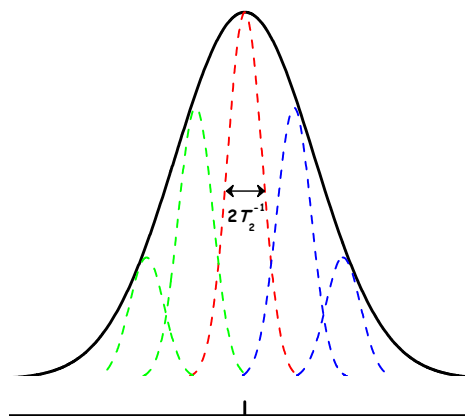
Corredores lentos
 Corredores rápidos



$$g(t) = \int_{-\infty}^{\infty} f(\omega) e^{i\omega t} d\omega \quad M_{\pm}(t) = M_0 \sin \theta g(t) \Phi(\pm \omega'_{L0}, t)$$

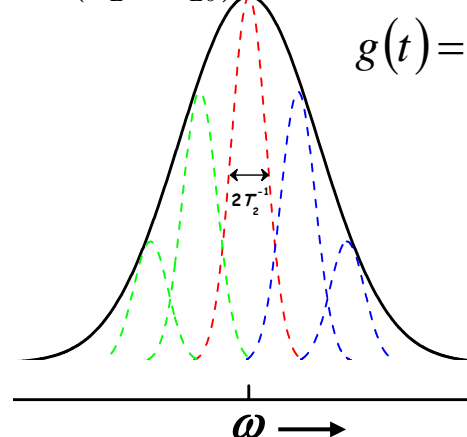
tiempo muerto del detector, t_D ($t_D = 150 - 250$ ns)

$g = 2$ distribución gussiana ($\Delta B_{pp} = 1$ mT $\Rightarrow \sigma_t = 100$ ns)

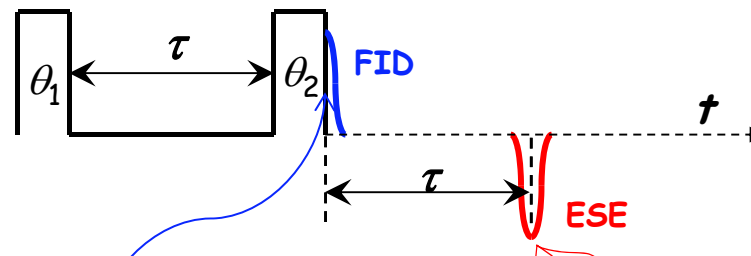


$$E(\tau) \propto e^{-2\tau/T_2}$$

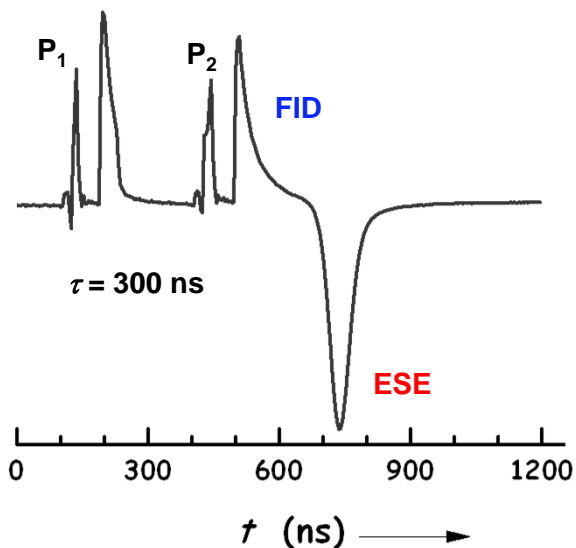
$$f(\omega_L - \omega_{L0}) = f(\omega'_L - \omega'_{L0})$$



$$g(t) = \int_{-\infty}^{\infty} f(\omega) e^{i\omega t} d\omega$$



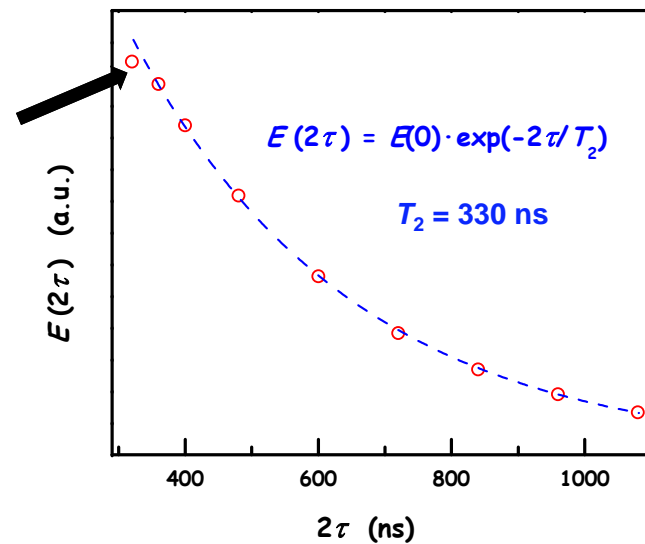
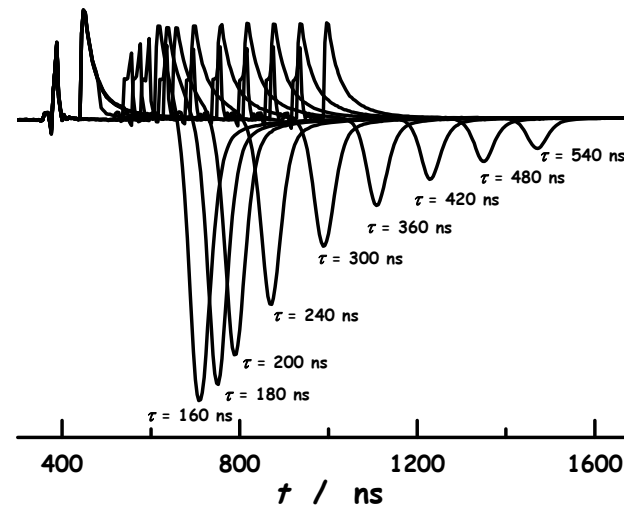
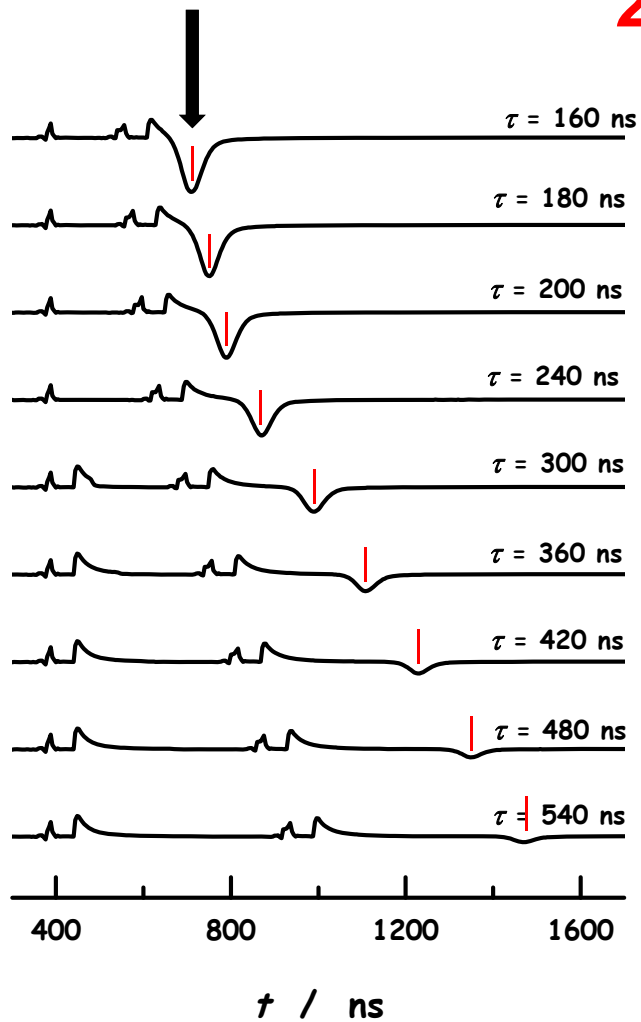
$$M_+(t) = M_0 \cos \theta_1 \sin \theta_2 g(t) - M_0 \sin \theta_1 \sin^2 \frac{\theta_2}{2} e^{-(t+\tau)/T_2} g(t-\tau)$$



$$E_{2p}(\tau) = -M_0 \sin \theta_1 \sin^2 \frac{\theta_2}{2} e^{-2\tau/T_2} g(0) = E_{2p}(0) e^{-2\tau/T_2}$$

$$E_{2p}(\tau) \propto e^{-2\tau/T_2}$$

2p-ESE .vs. τ



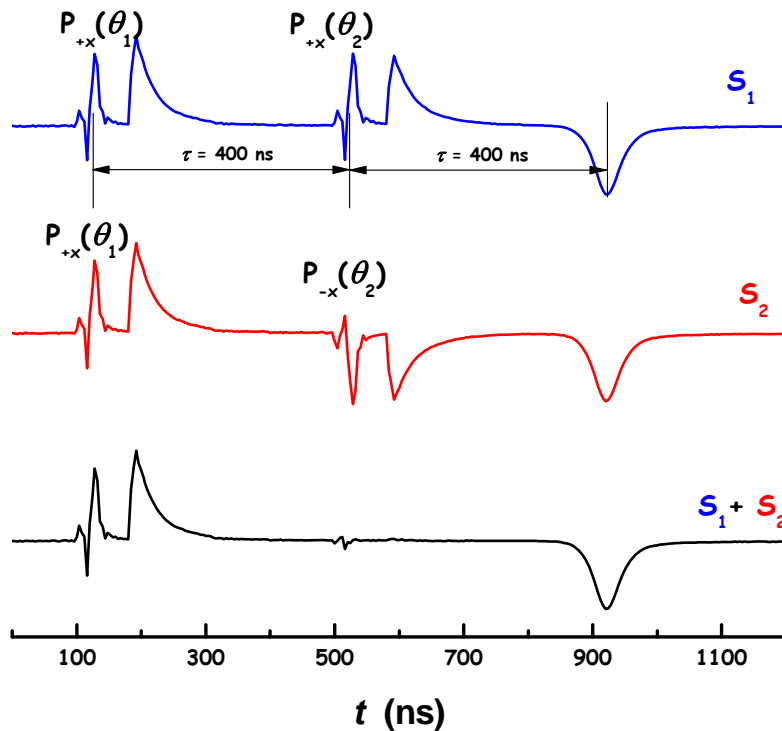
CYCLOPS (cyclically ordered phase sequence)

$P_{+x}(\theta_1) \rightarrow \tau \rightarrow P_{+x}(\theta_2) \rightarrow t$

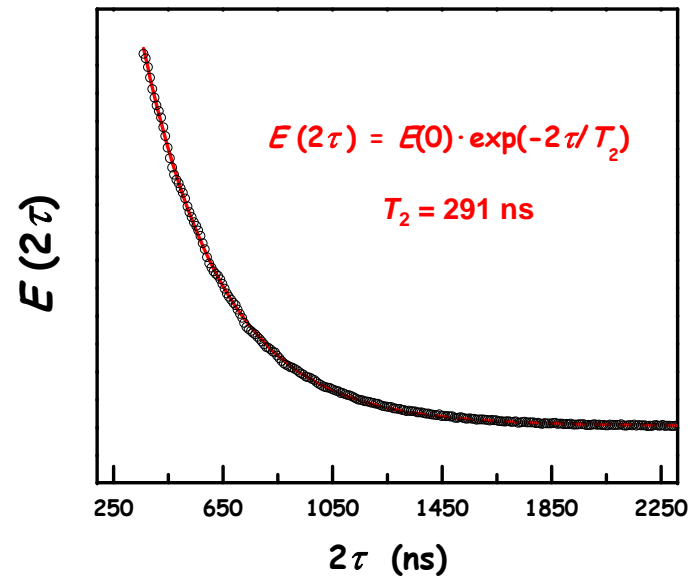
$$M_+^{(1)}(t) = M_0 \cos \theta_1 \sin \theta_2 g(t) - M_0 \sin \theta_1 \sin^2 \frac{\theta_2}{2} e^{-(t+\tau)/T_2} g(t-\tau)$$

$P_{+x}(\theta_1) \rightarrow \tau \rightarrow P_{-x}(\theta_2) \rightarrow t$

$$M_+^{(2)}(t) = -M_0 \cos \theta_1 \sin \theta_2 g(t) - M_0 \sin \theta_1 \sin^2 \frac{\theta_2}{2} e^{-(t+\tau)/T_2} g(t-\tau)$$



$$M_+^{(1)}(t) + M_+^{(2)}(t) = -2M_0 \sin \theta_1 \sin^2 \frac{\theta_2}{2} e^{-(t+\tau)/T_2} g(t-\tau)$$

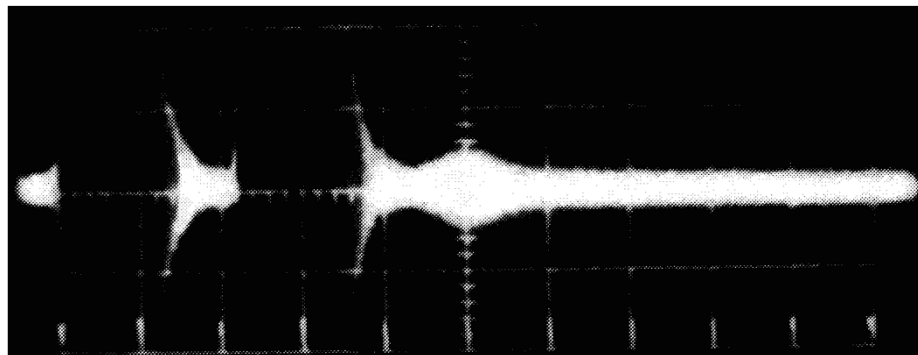


Origen (ECO de espín nuclear)

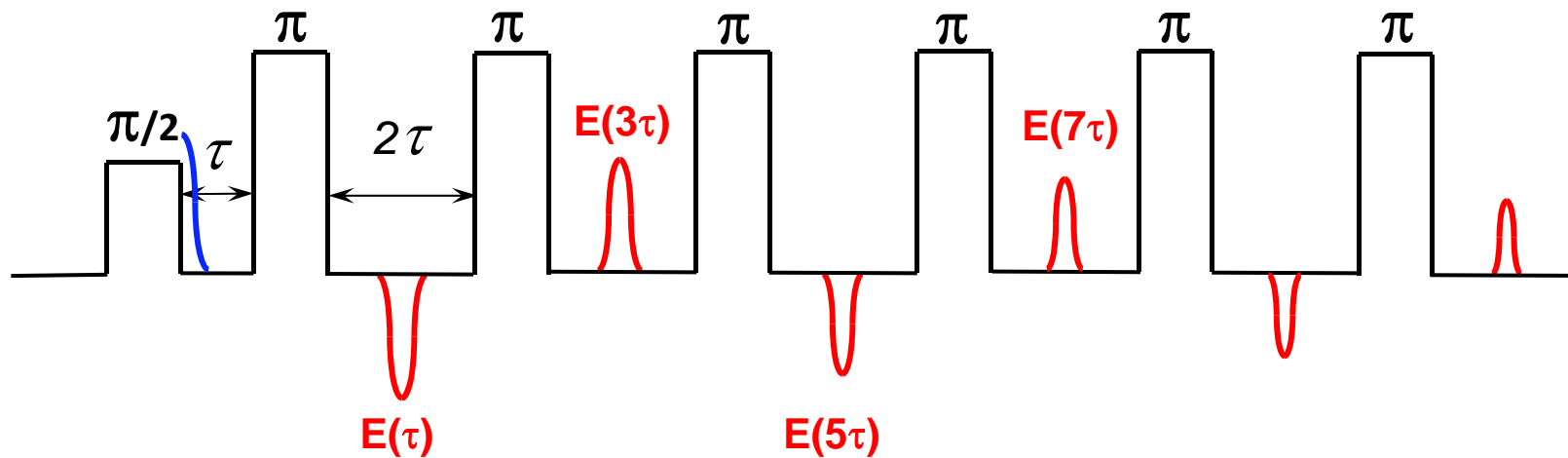
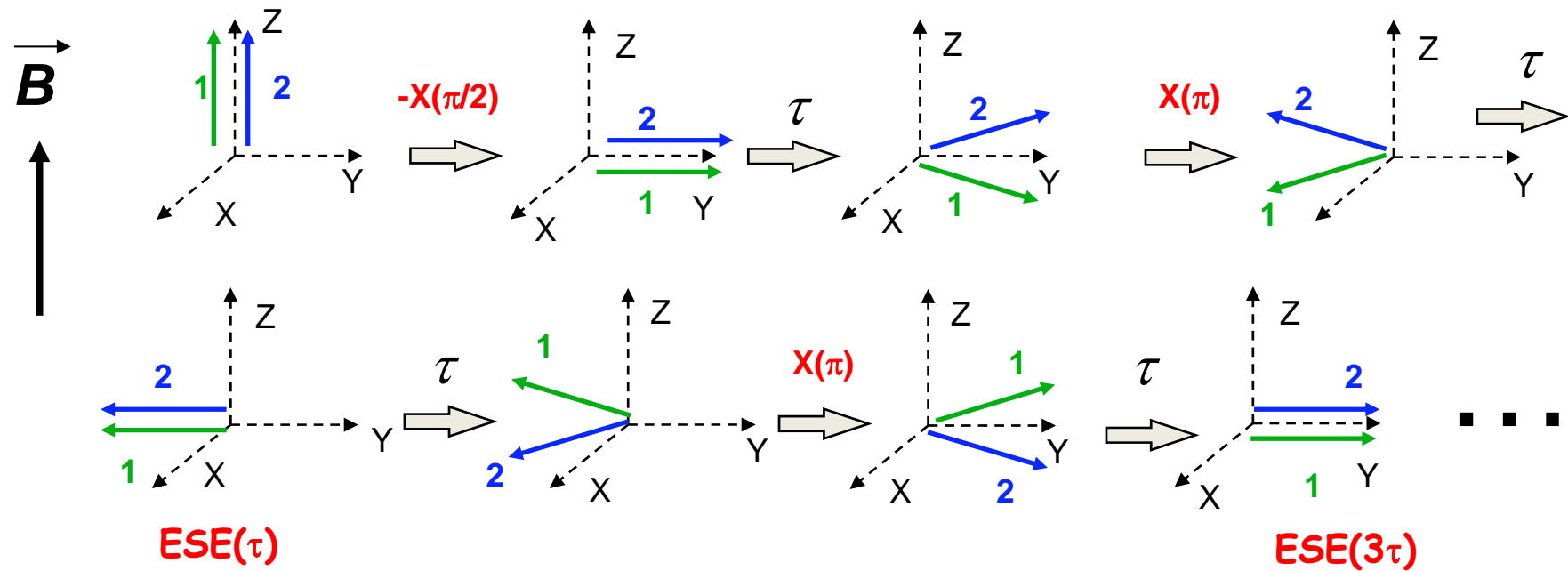
- E.L. Hahn. “**Spin Echoes**” *Phys. Rev.* **80**, 580 (1950).
Resonancia NMR de protones en H₂O.

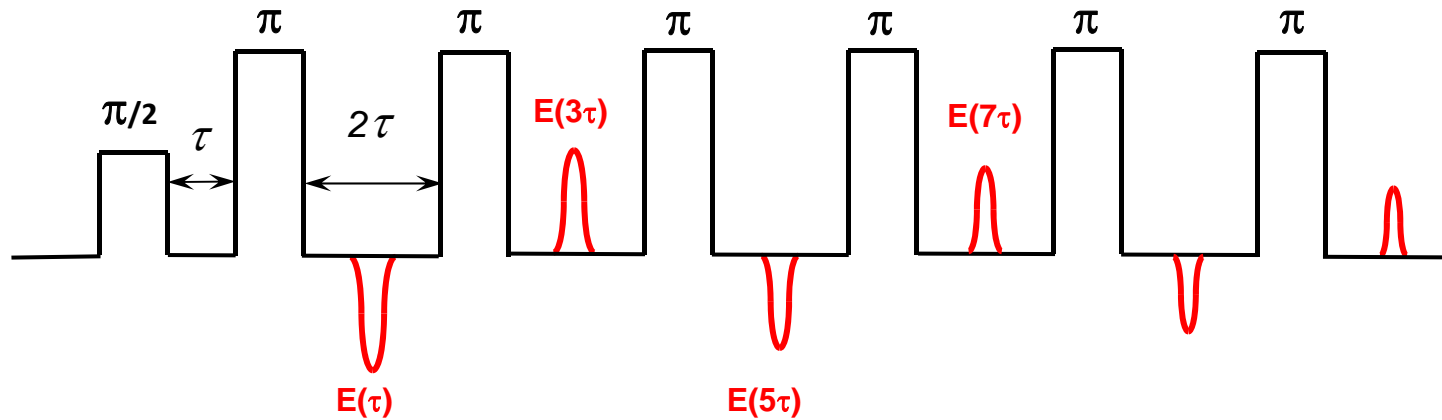
Primera observación de 2p-ESE

- R.J. Blume. *Phys. Rev.* **109**, 1867 (1958).
Solución de sodio en amoniaco (TA, 17.4 MHz, anchura de pulsos 300 ns y 600 ns)



- J.P. Gordon y K.D. Browsers. *Phys. Rev. Lett.* **1**, 368 (1958).
Impureza profunda en Si (23 GHz, banda K)





Experimento de Carr-Purcell (CP)

H.Y. Carr, E.M. Purcell *Phys. Rev.* **94**, 630 (1954).

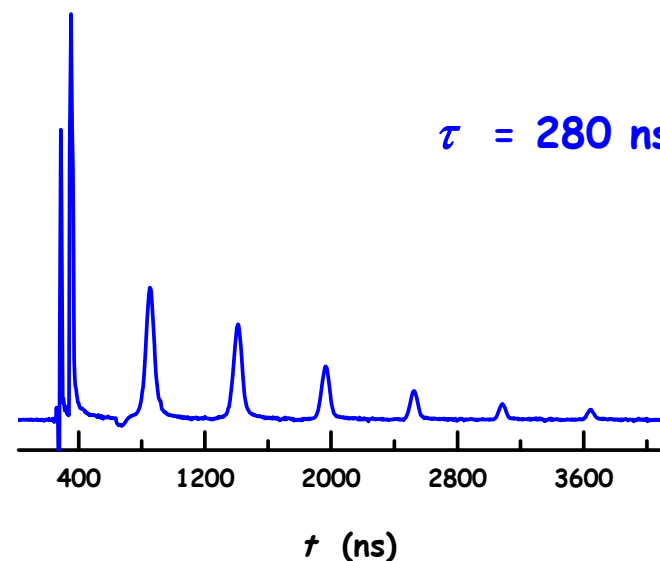
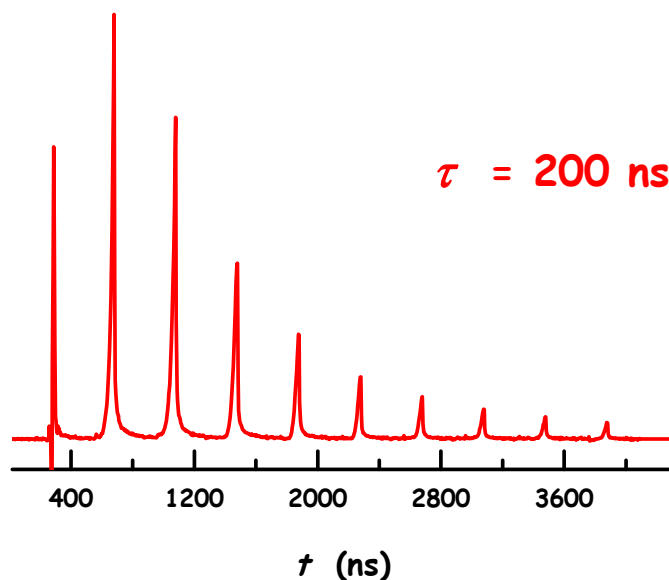
$$(\pi/2)_x \rightarrow [\tau \rightarrow (\pi)_x \rightarrow \tau \rightarrow \text{ESE} \rightarrow]_n$$

Errores en los pulsos π son acumulativos

Variante de Meiboom-Gill (CPMG)

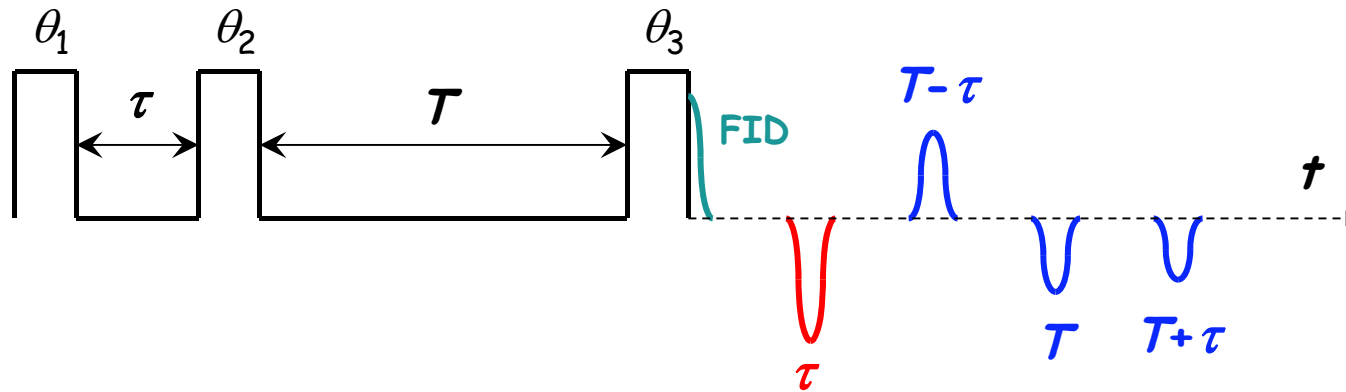
S. Meiboom, D. Gill *Rev. Sci. Instrum.* **29**, 6881 (1958).

$$\begin{aligned}
 &+ (\pi/2)_x \rightarrow [\tau \rightarrow (\pi)_y \rightarrow \tau \rightarrow \text{ESE} \rightarrow]_n \\
 &+ (\pi/2)_{-x} \rightarrow [\tau \rightarrow (\pi)_y \rightarrow \tau \rightarrow \text{ESE} \rightarrow]_n
 \end{aligned}$$



3p-ESE

W.B. Mims. *Phys. Rev.* **B5**, 2409 (1972); *Phys. Rev.* **B5**, 3543 (1972).



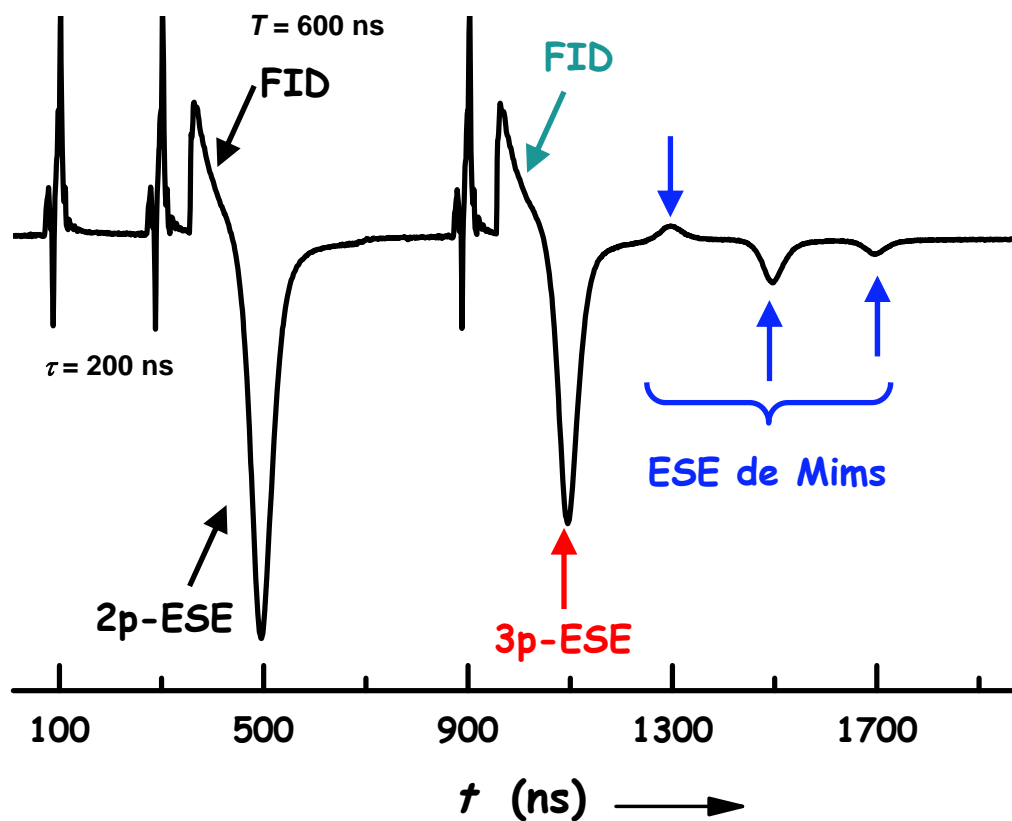
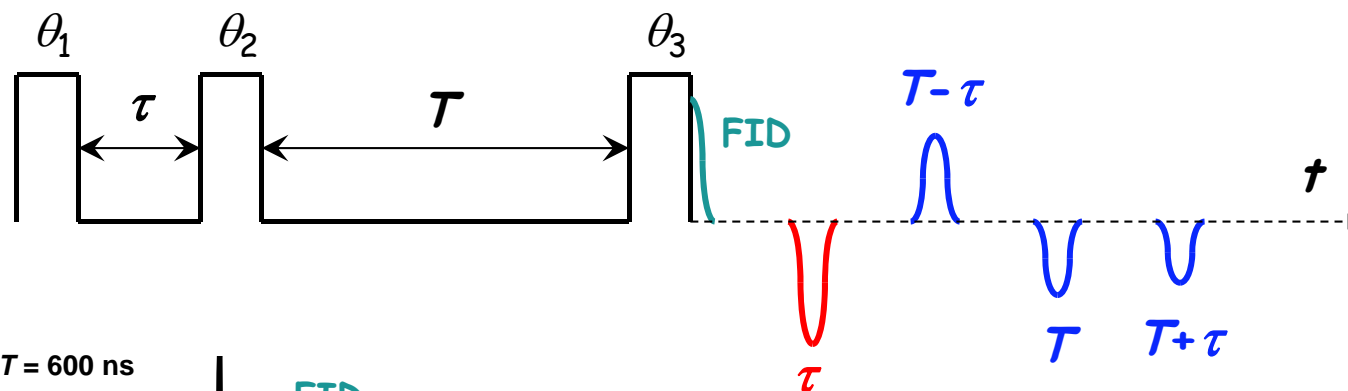
$$M_+(t) = M_0 \left\{ 1 - 2e^{-T/T_1} \cos^2 \frac{\theta_2}{2} - 2e^{-(\tau+T)/T_1} \sin^2 \frac{\theta_1}{2} \cos \theta_2 \right\} \sin \theta_3 e^{-t/T_2} g(t) - \text{FID}$$

$$\text{ESE estimulado} \left\{ -\frac{M_0}{2} \sin \theta_1 \sin \theta_2 \sin \theta_3 e^{-T/T_1} e^{-(t+\tau)/T_2} g(t-\tau) + \right.$$

optimizado
 $\theta_1 = \theta_2 = \theta_3 = \pi/2$

$$S(T) \propto e^{-T/T_1}$$

$$\text{ESE de Mims} \left\{ \begin{aligned} &+ M_0 \sin \theta_1 \sin^2 \frac{\theta_2}{2} \sin^2 \frac{\theta_3}{2} e^{-(t+T+\tau)/T_2} g[t-(T-\tau)] - \\ &- M_0 \left(1 - 2e^{-\tau/T_1} \sin^2 \frac{\theta_1}{2} \right) \sin \theta_2 \sin^2 \frac{\theta_3}{2} e^{-(t+T)/T_2} g(t-T) - \\ &- M_0 \sin \theta_1 \cos^2 \frac{\theta_2}{2} \sin^2 \frac{\theta_3}{2} e^{-(t+T+\tau)/T_2} g[t-(T+\tau)] \end{aligned} \right.$$

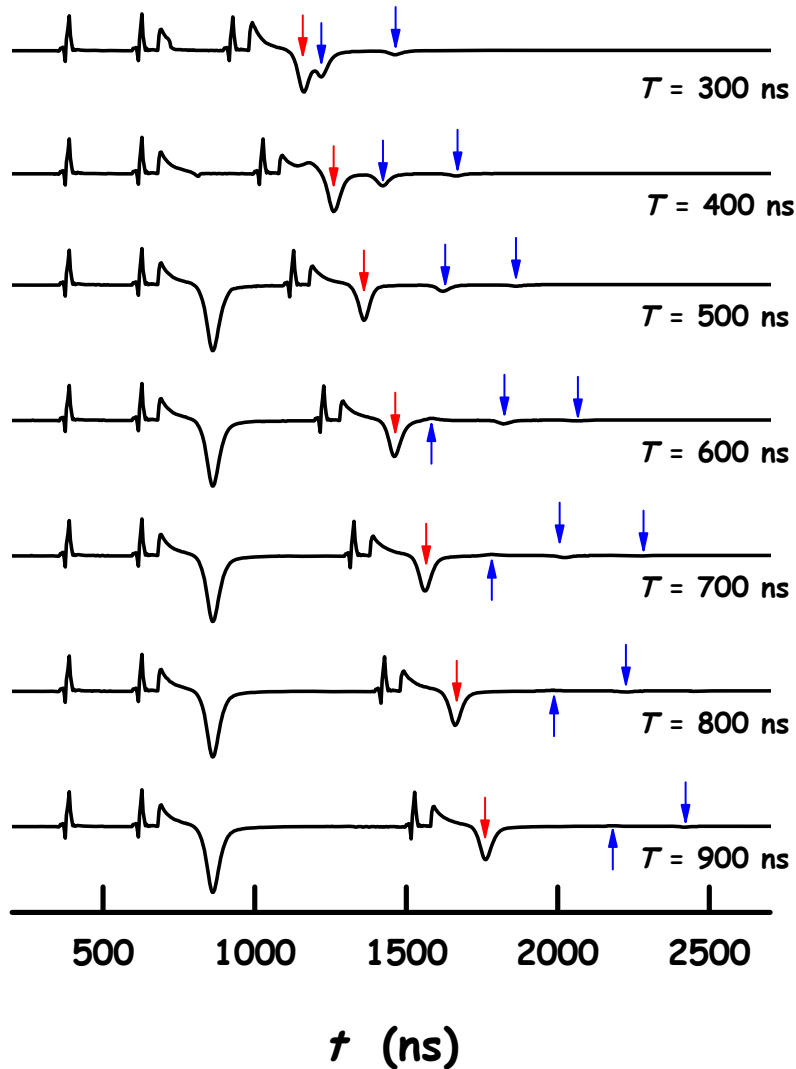


$$\left\{ 1 - 2e^{-T/T_1} \cos^2 \frac{\theta_2}{2} - 2e^{-(\tau+T)/T_1} \sin^2 \frac{\theta_1}{2} \cos \theta_2 \right\} \sin \theta_3$$

$$\begin{aligned} & \sin \theta_1 \sin^2 \frac{\theta_2}{2} \sin^2 \frac{\theta_3}{2} e^{-2T/T_2} \\ & - \left(1 - 2e^{-\tau/T_1} \sin^2 \frac{\theta_1}{2} \right) \sin \theta_2 \sin^2 \frac{\theta_3}{2} e^{-2T/T_2} \\ & - \sin \theta_1 \cos^2 \frac{\theta_2}{2} \sin^2 \frac{\theta_3}{2} e^{-2(T+\tau)/T_2} \end{aligned}$$

$$-\frac{1}{2} \sin \theta_1 \sin \theta_2 \sin \theta_3 e^{-T/T_1} e^{-2\tau/T_2}$$

$\tau = 240 \text{ ns}$



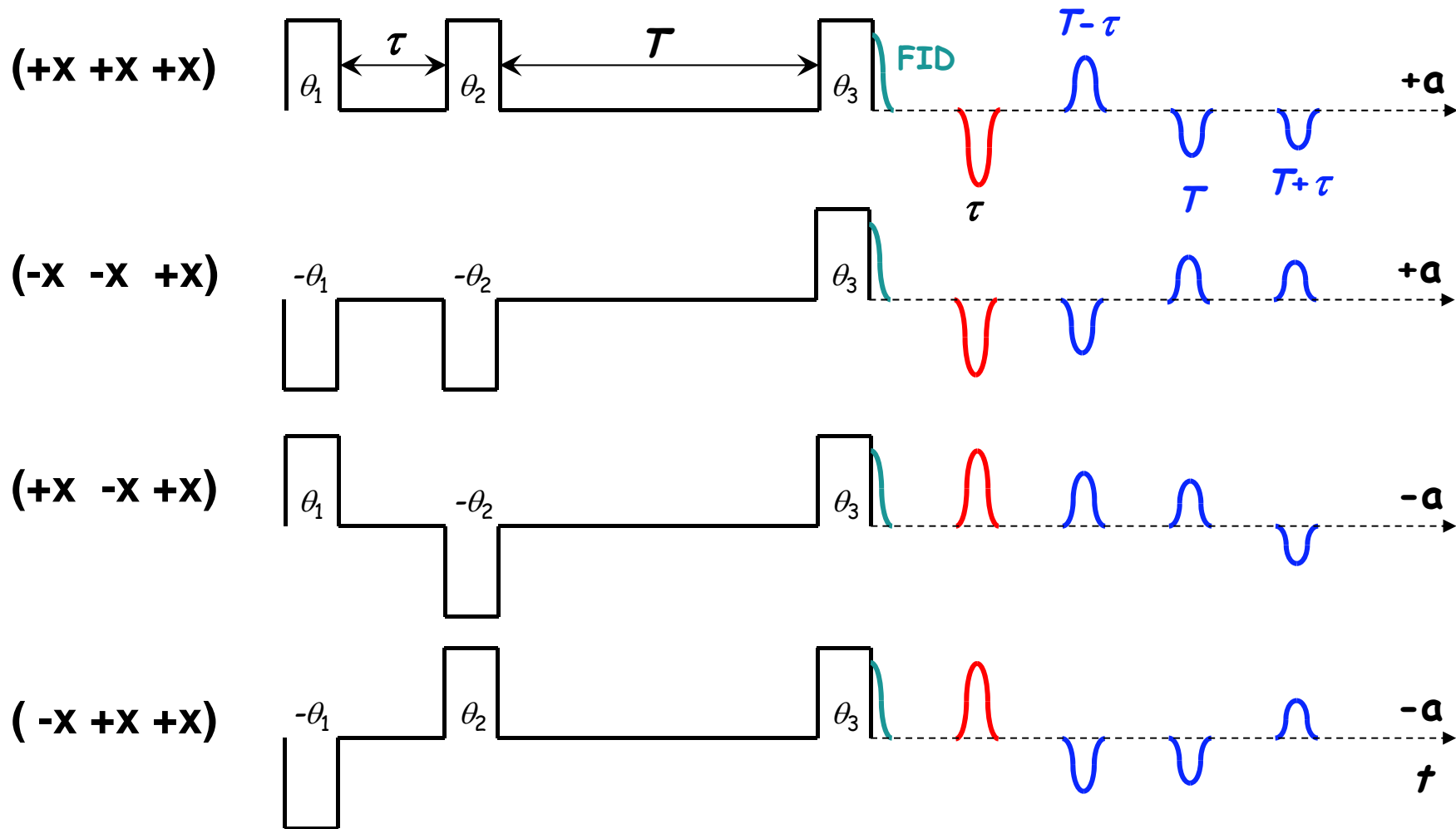
$$-\frac{1}{2} \sin \theta_1 \sin \theta_2 \sin \theta_3 e^{-T/T_1} e^{-2\tau/T_2}$$

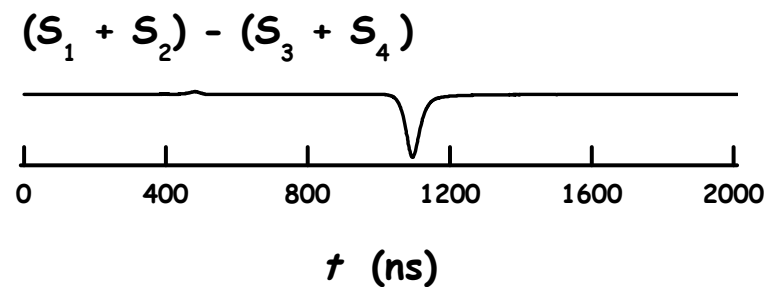
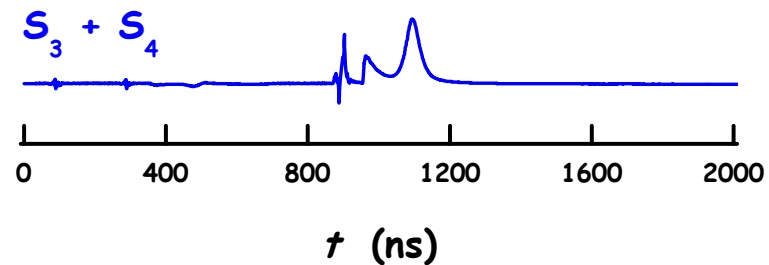
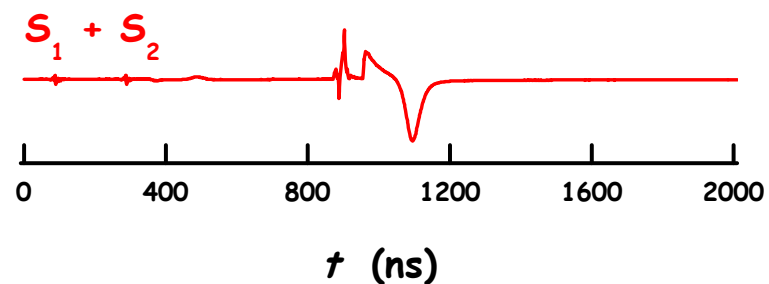
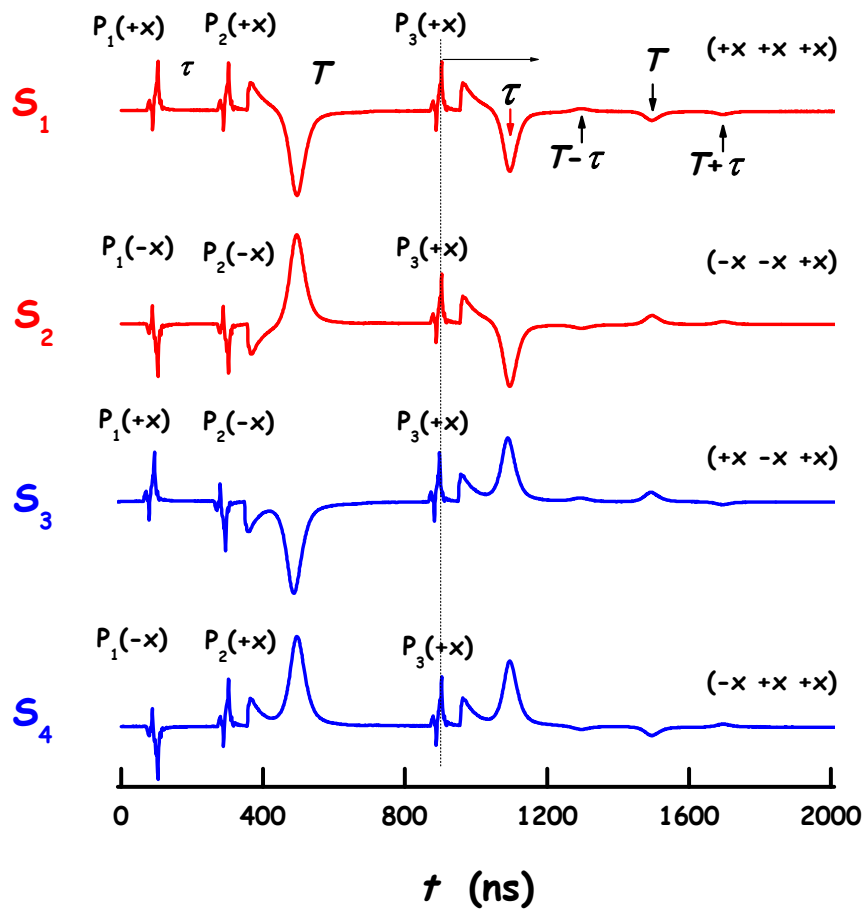
$$S(T) \propto e^{-T/T_1}$$

¿Cómo eliminar la influencia de los ECOS de Mims y de la señal FID?

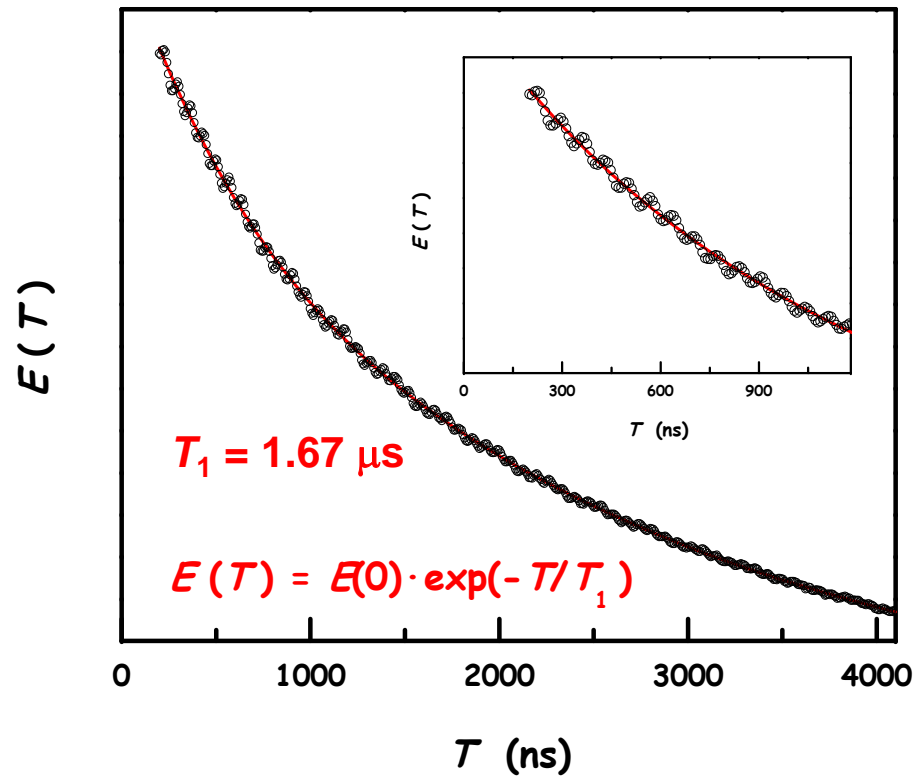
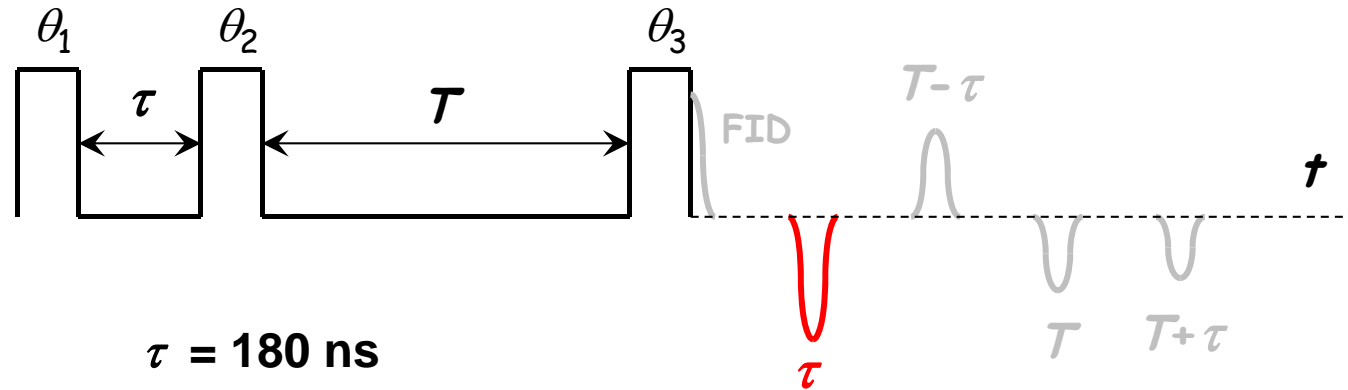
CYCLOPS

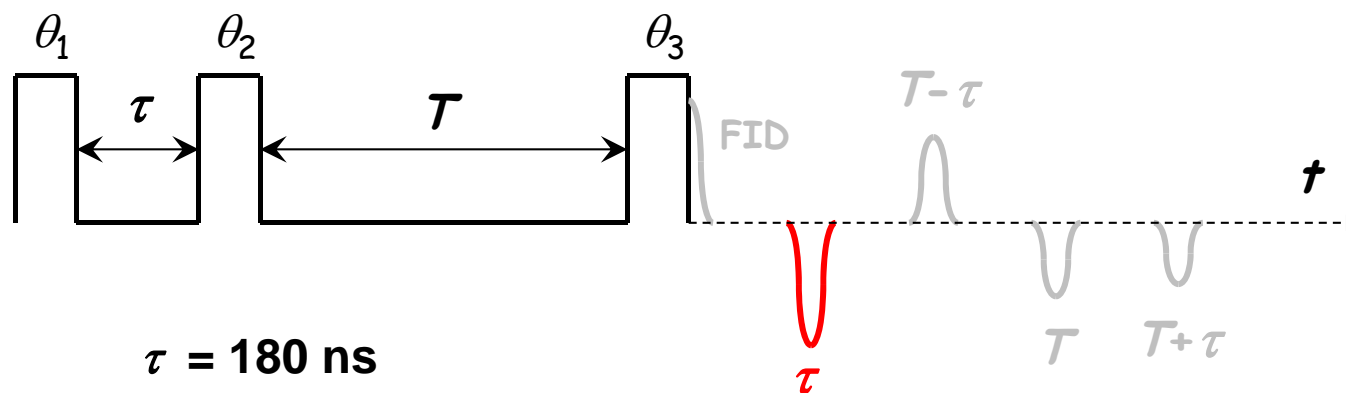
CYCLOPS (3p-ESE)



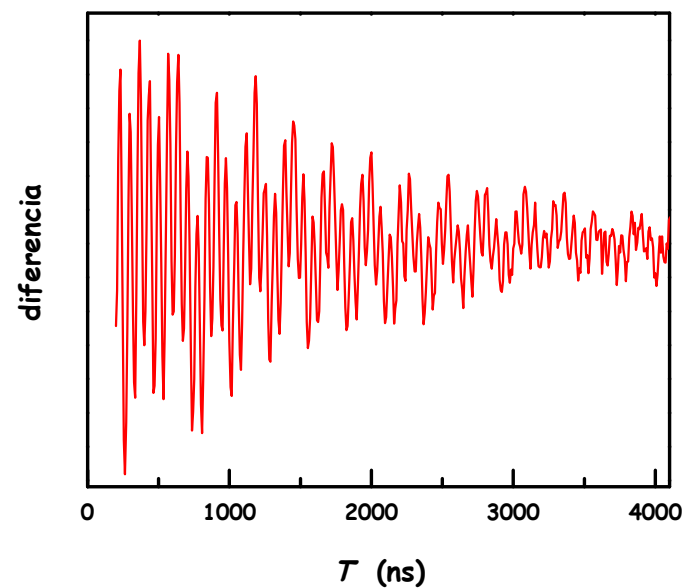
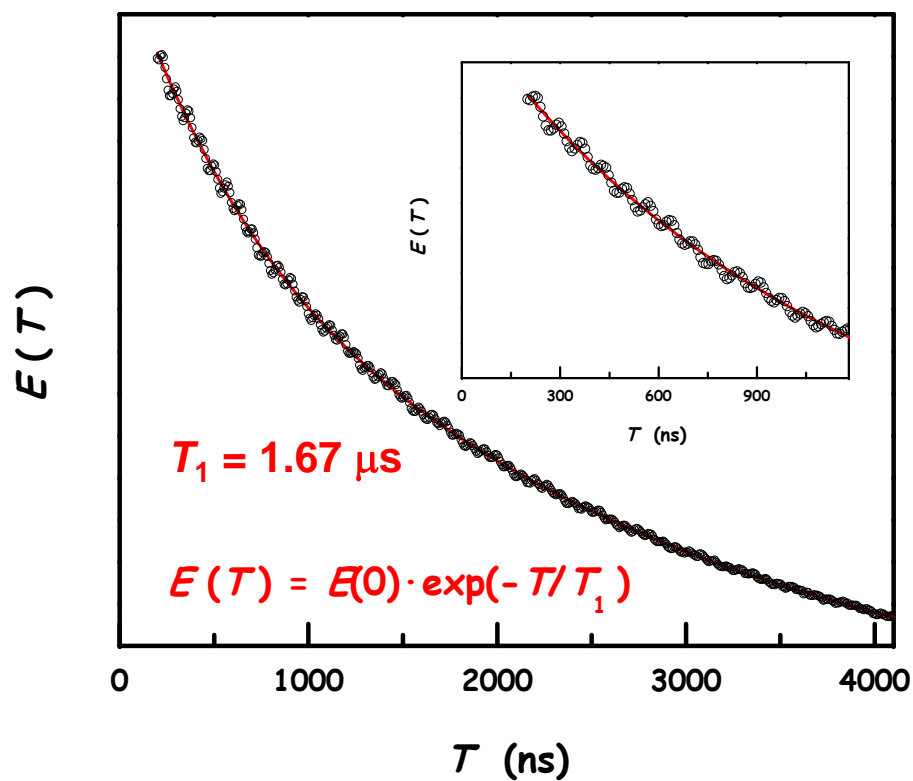


CYCLOPS (3p-ESE)





$\tau = 180 \text{ ns}$

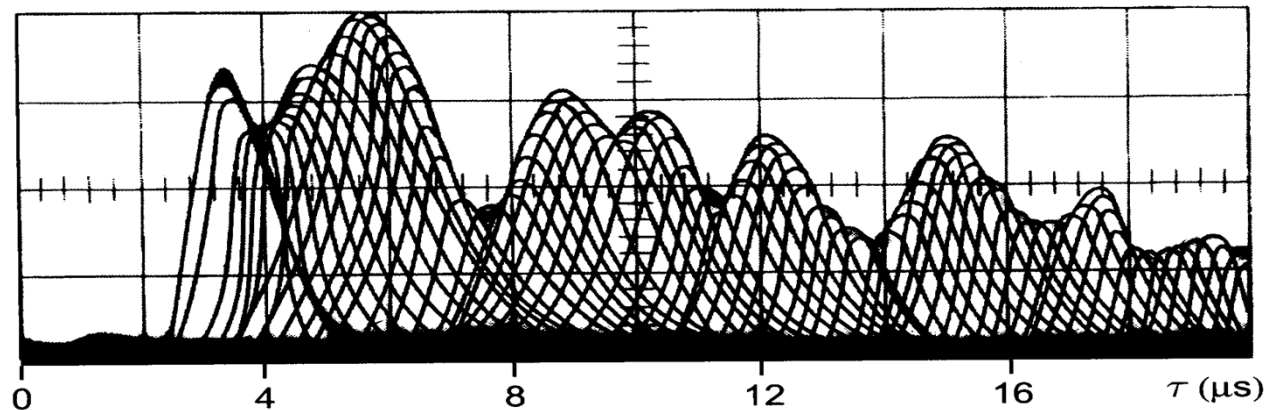


ESEEM

Electron Spin Echo Envelope Modulation

Modulaciones en el decaimiento del 2p-ESE al variar el intervalo entre pulsos (ESEEM)

W.B. Mims K. Nassau y J.D. McGee. *Phys. Rev.* 123, 2059 (1961). $\text{CaWO}_4:\text{Ce}^{3+}$ (4.2 K, 6.7 GHz).



- J.A. Cowen y D.E. Kaplan. *Phys. Rev.* 124, 1098 (1961). Ce^{3+} doped magnesium and lanthanum nitrate

Observación de 3p-ESEEM y una explicación de la señal de ESEEM asociándola a modulaciones de frecuencia asociada con las transiciones entre subniveles nucleares (transiciones NMR)

- W.B. Mims. *Phys. Rev.* **B5**, 2409 (1972).
- W.B. Mims. *Phys. Rev.* **B5**, 3543 (1972).