

1. Introduction to NMR

1.1. Nuclear magnetization.

Atomic nuclei \rightarrow inherently quantum mechanical

Conventional NMR $\leftrightarrow > 10^{10}$ spins

ensemble \leftrightarrow vector quantity,
"magnetisation"

1.2 QM description of spins.

quantum state

example \leftrightarrow angular momentum, \vec{m}
measured along \vec{z} axis \leftrightarrow discrete states
"eigenstates" $-I, -I+1, \dots I-1, I$
 I - momentum quantum number.

Arbitrary state $|\psi\rangle$ can be written as
linear comb. of basis states.

$$|\psi\rangle = \sum_m a_m |m\rangle$$

Eigenvalue equation

$$I_z |m\rangle = m |m\rangle$$

Eigenvalue m is a result of observation

I_z - operator for angular momentum
along \vec{z} axis

discrete set of $|m\rangle$, can be represented as
vectors

$$\text{for } I = \frac{1}{2} \quad |+\frac{1}{2}\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad |- \frac{1}{2}\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

\Rightarrow operator I_z is a matrix

$$I_z = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Result of measurement \rightarrow calculating

$\langle m' | I_z | m \rangle$, where $|m\rangle \rightarrow$ row vector
conjugate to $|m\rangle$
bra

Observable of I_z

spin-up $\langle \frac{1}{2} | I_z | \frac{1}{2} \rangle = [1, 0] \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} [1, 0]$
 $= \frac{1}{2}$.

Suppose that nucleus is not in eigenstate

$$|\Psi\rangle = \sum_m a_m |m\rangle$$

result of measurement \rightarrow expectation value

$$\langle \Psi | I_z | \Psi \rangle = \sum_{m, m'} a_m a_m^* \langle m' | I_z | m \rangle =$$
$$= \sum_{m, m'} a_m a_m^* m \langle m' | m \rangle$$

Since basis vectors are orthogonal

$$\langle \Psi | I_z | \Psi \rangle = \sum_m |a_m|^2 m$$

Ensemble of nuclei \rightarrow a mean of
eigenvalues

Single nuclear spin or probability
 $|a_m|^2$ of returning
result m

3 directions \leftrightarrow 3 operators

$$I_x, I_y, I_z. \quad I_x = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad I_y = \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

Commutation relations w.f.

$$[I_x I_y] = I_x I_y - I_y I_x = i I_z$$

Operator of rotation (about z axis)

$$R_z(\phi) = \exp(-i\phi I_z)$$

$$\text{with } (e^F = 1 + F + \frac{F^2}{2!} + \dots)$$

Rising and lowering operators

$$I_+ = I_x + i I_y ; I_- = I_x - i I_y$$

conversion $|-\frac{1}{2}\rangle \leftrightarrow |+\frac{1}{2}\rangle$

$$I_+ |-\frac{1}{2}\rangle = |+\frac{1}{2}\rangle ; I_- |+\frac{1}{2}\rangle = |-\frac{1}{2}\rangle$$

Spin evolution is described by Schrödinger equation.

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle$$

Hamiltonian

if H is constant

$$|\psi(t)\rangle = U(t) |\psi(0)\rangle$$

Where $U(t) = \exp(-iHt/\hbar)$ - evolution operator

Atomic nuclei \rightarrow dipole moment proportion to angular momentum

Interaction energy $\vec{\mu} \cdot \vec{B}_0$

$$H = -\gamma \hbar B_0 I_z$$

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$I = 2$

m_J
-2
-1
0
+1
+2

Usually we drop to add
Show Hamiltonian with units
of angular frequency

$$\omega_0 = \gamma B_0$$

Example	Protons	40	MHz/T
	C^{13}	10	MHz/T

Large ensembles \rightarrow different nuclei, diff. states $|\psi\rangle$

Average by a sum over subensembles,
each with probability p_ψ

$$\overline{\langle \psi | I_z | \psi \rangle} = \sum_{\psi} p_{\psi} \langle \psi | I_z | \psi \rangle$$

Example, spin $1/2$ system.

$$\psi = a_{1/2} \begin{bmatrix} 1 \\ 0 \end{bmatrix} + a_{-1/2} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \text{ using } I_z$$

$$\langle \psi | I_z | \psi \rangle = \frac{1}{2} (|a_{1/2}|^2 - |a_{-1/2}|^2)$$

Interpretation \rightarrow difference in
population between levels.

Thermal equilibrium

$$\frac{1}{|a_{\pm 1/2}|^2} = \frac{\exp(\pm \gamma \beta B_0 / 2 k_B T)}{\exp(-\gamma \beta B_0 / 2 k_B T) + \exp(\gamma \beta B_0 / 2 k_B T)}$$

$\gamma \hbar B_0 \ll k_B T$ (300K)

$$|a_{\pm 1/2}|^2 = \frac{1}{2} [1 \pm \hbar \gamma B_0 / 2 k_B T]$$

In general, for any I

$$|\overline{a_m|^2} = \frac{1}{(2I+1)} [1 + m \hbar \gamma B / k_B T]$$

NMR experiment \rightarrow measurement of X component

$$I_x = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$\langle \Psi | I_x | \Psi \rangle = \frac{1}{2} [a_{1/2}^* a_{-1/2} + a_{1/2} a_{-1/2}^*]$$

different from I_z

Transverse magnetization vs longitudinal magnetization

$a_{1/2}^* a_{-1/2}$ terms are connected

w/ the "density function"

"generalises method of ensemble av."

Definition

$$\text{operator } \rho = \sum_{\Psi} P_{\Psi} |\Psi\rangle \langle \Psi|$$

ρ - matrix, elements are

$$\rho_{mn} = \langle m | \rho | n \rangle = \sum_k p_k \langle m | \psi \rangle \langle \psi | n \rangle = \overline{a_m^* a_n} = a_m^* a_n$$
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Expectation value of any operator O can be written as,

$$\langle \psi | O | \psi \rangle = \text{Tr}(O\rho)$$

Schrödinger eq. for density matrix -

Liouville eq.

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

$$\text{solution } \rho(t) = \exp(-iHt)\rho(0)\exp(iHt)$$

For $S = 1/2$ system,

$$\rho = \begin{bmatrix} 1/2 + \langle \bar{I}_z \rangle & \langle \bar{I}_x - i\bar{I}_y \rangle \\ \langle \bar{I}_x + i\bar{I}_y \rangle & 1/2 - \langle \bar{I}_z \rangle \end{bmatrix}$$

in macroscopic terms \Rightarrow

magnetisation vector

$$\vec{M} = N\gamma h [\langle \bar{I}_x \rangle \hat{i} + \langle \bar{I}_y \rangle \hat{j} + \langle \bar{I}_z \rangle \hat{k}]$$

ρ can be expressed as product of I_1, I_2, I_x, I_y higher dimensions (coupled spins).

Example : 2 spin system.

$$\underline{(1/2; 1/2)}$$

$$(1/2; -1/2) - \underline{-1-1/2; 1/2}$$

$$\underline{-1-1/2; -1/2}$$

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

16 terms.

Basis operators

I_{1z}, I_{2z} - polarisation, spin 1, 2

I_{1x}, I_{2x} \rightarrow "in phase" x coherence

I_{1y}, I_{2y} \rightarrow in phase y coherence.

other operators.

$$I_{1x} I_{2z}, I_{1z} I_{2x}$$

$$I_{1y} I_{2z}, I_{1z} I_{2y}$$

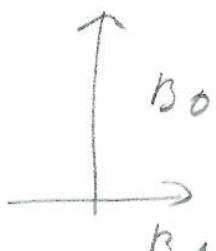
$$I_{1x} I_{2x}, I_{1y} I_{2y}$$

$$I_{1x} I_{2y}, I_{1y} I_{2x}$$

$$I_{1z} I_{2z}$$

+ unity operator (16 in total).

Resonant excitation and rotating frame



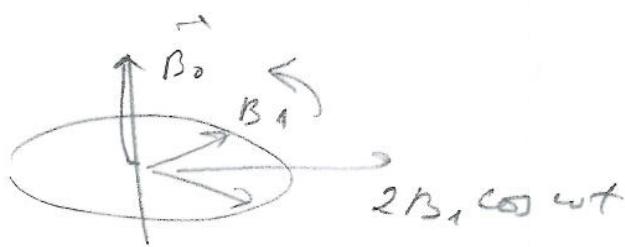
Example oscillating b-field

$$\vec{B}_\perp$$

longitudinal static field \vec{B}_0

Hamiltonian (Lab. frame) ⑧

$$H_{\text{lab}} = -\gamma B_0 I_z - 2\gamma B_1 \cos \omega t I_x$$



B_1 = \sum two circularly polarised components

Case $B_1 \ll B_0$, counter-rotating term can be ignored.

coordinate transformation.

rotation field is stationary.

$$H_{\text{rot}} = -\gamma (B_0 - \omega/\gamma) - \gamma B_1 I_x$$

1.2 Semi-classical description of NMR

ensemble of spins as magnetization vector

$$\vec{M}$$

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B} \quad (\text{L})$$

precession at rate $\omega = \gamma B$

static field B_0 , rotating field B_1 .

$$\vec{B}_1(t) = B_1 \cos \omega_0 t \cdot \vec{i} - B_1 \sin \omega_0 t \cdot \vec{j}$$

$\vec{i}, \vec{j}, \vec{k}$ - unit vectors along x, y, z

& equation (L) transforms into

$$\frac{dM_x}{dt} = \gamma [M_y B_0 + M_z B_1 \sin \omega_0 t]$$

$$\frac{dM_y}{dt} = \gamma [M_z B_1 \cos \omega_0 t - M_x B_0]$$

$$\frac{dM_z}{dt} = \gamma [-M_x B_1 \sin \omega_0 t - M_y B_1 \cos \omega_0 t]$$

initial condition $\vec{M} = M_0 \hat{k}$; $\omega_1 = \gamma B_1$

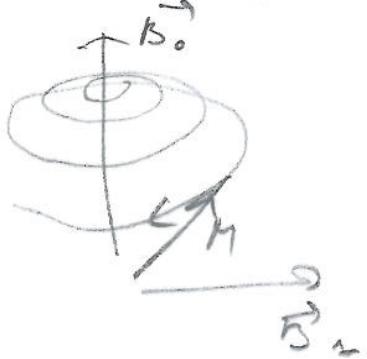
$$M_x = M_0 \sin \omega_1 t \sin \omega_0 t$$

$$M_y = M_0 \sin \omega_1 t \cos \omega_0 t$$

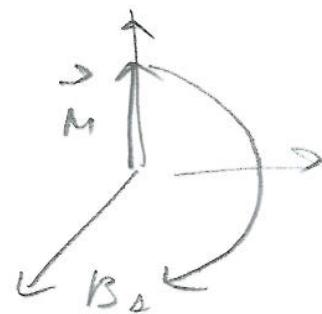
$$M_z = M_0 \cos \omega_1 t$$

Simultaneous precession about \vec{B}_0, \vec{B}_1

Laboratory frame



Rotating frame



Relaxation

Spin system interacts with both
"spin lattice relaxation"

Phenomenological description.

$$\frac{dM_2}{dt} = -(M_2 - M_0)/T_1$$

with solution.

$$M_2(t) = M_2(0) \exp(-t/T_1) + M_0 (1 - \exp(-t/T_1))$$

T_1 - spin lattice, "longitudinal" relaxation time.

Protons in dielectric materials
 $0, 1 - 10$ seconds.

Decoherence, dephasing, T_2 time

$$\frac{dM_{x,y}}{dt} = -\frac{M_{x,y}}{T_2}$$

$$M_{x,y}(t) = M_{x,y}(0) \exp(-t/T_2)$$

Block equations.

$$\frac{dM_x}{dt} = \gamma(M_y B_0 + M_2 B_1 \sin \omega t) - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = \gamma(M_2 B_1 \cos \omega t - M_x B_0) - \frac{M_y}{T_2}$$

$$\frac{dM_2}{dt} = \gamma(-M_x B_1 \sin \omega t - M_y B_1 \cos \omega t) - \frac{M_2 - M_0}{T_1}$$

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Solutions, case of weak RF field
 $(\delta B_1)^2 T_1 T_2 \ll 1$ steady state.

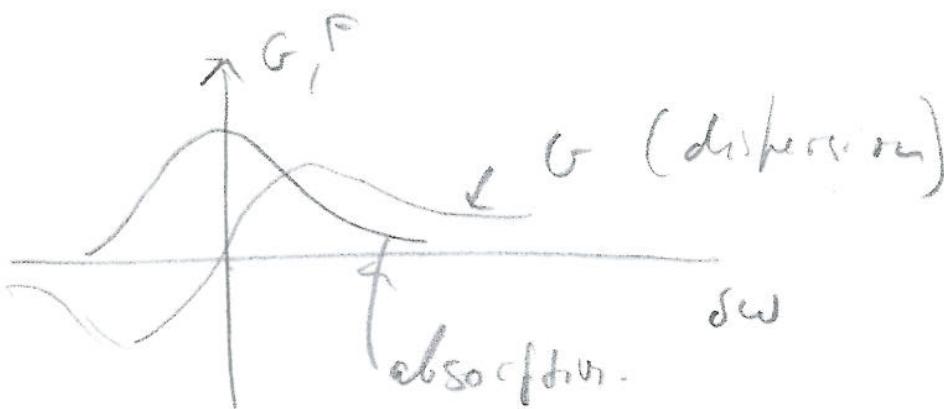
$$M_x = (\omega_1 M_0) \frac{T_2^2 \delta \omega}{1 + (T_2 \delta \omega)^2} = \omega_1 M_0 G(\delta \omega)$$

$$M_y = (\omega_1 M_0) \frac{T_2}{1 + (T_2 \delta \omega)^2} = \omega_1 M_0 F(\delta \omega)$$

where F and G are absorption and dispersion lineshapers

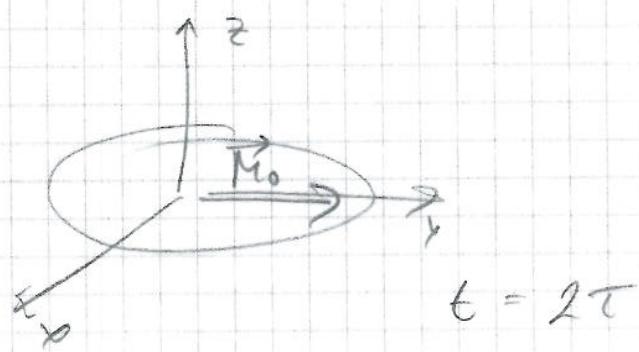
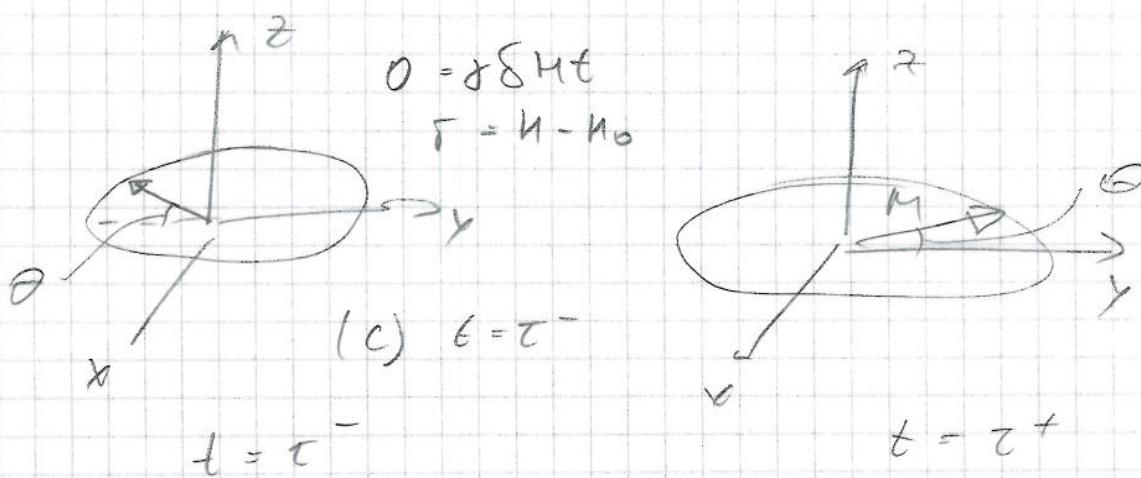
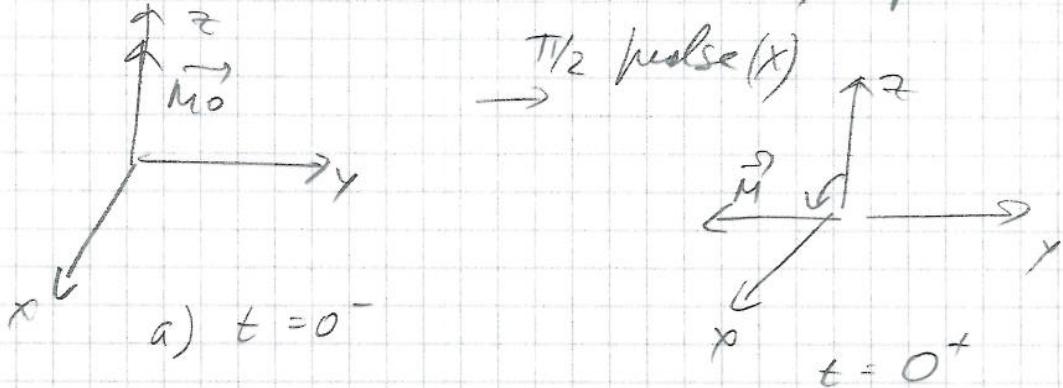
$$G(\delta \omega) = \frac{T_2^2 \delta \omega}{1 + (T_2 \delta \omega)^2}$$

$$F(\delta \omega) = \frac{T_2}{1 + (T_2 \delta \omega)^2}$$

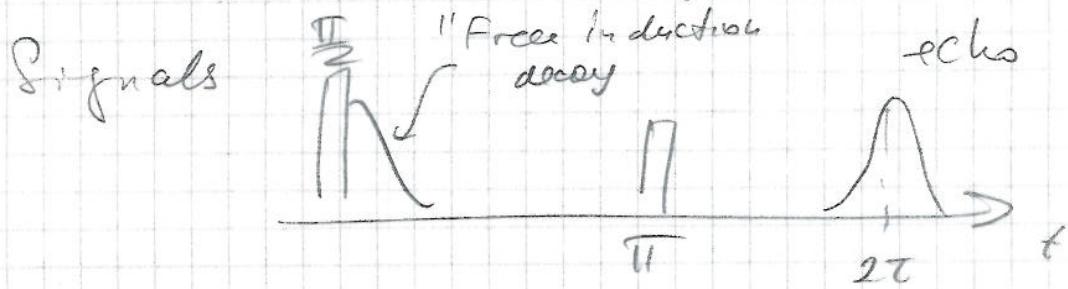


Spin Echoes

Erwin Hahn, key for development of pulsed methods. $\Rightarrow \omega = \gamma H_0$, pulses ($\pi/2$)

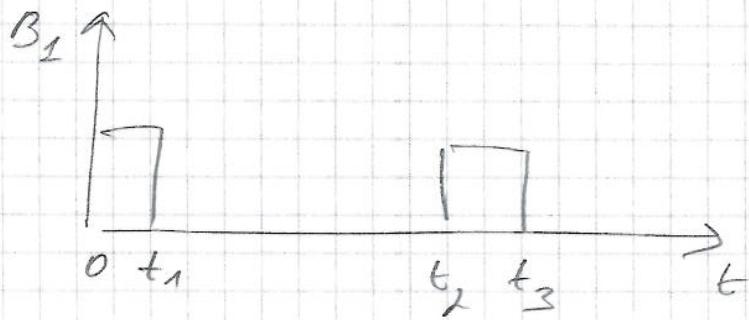


All spins are in phase at $t = 2\tau$
after \rightarrow out of phase again owing
to field inhomogeneity



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QM treatment of spin echo experiment



Ψ obeys Schrödinger equations.

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = H\Psi$$

$$H = -\gamma \hbar \left(\underbrace{(B_0 - \frac{\omega}{\tau}) I_z + B_z I_x}_{B_0 - \text{field inhom.}} \right)$$

Inhomogeneous field $B_0 \rightarrow$ distribution function

$p(B_0) \rightarrow$ number of spins between B_0 and $B_0 + \delta B_0$

$$dN = N p(B_0) dB_0$$

N - total number of spins.

MW pulses $B_z < B_0$, but $B_z > B_0$
in this case MW pulse non-Hamiltonian.

$$H = -\gamma \hbar B_z I_x$$

Between pulses. $B_z = 0$

$$H = -\gamma \hbar B_0 I_z$$

H is time dependent but its time variation occurs only at $t = 0, t_1, t_2, t_3$

$$\psi(t_2) = e^{i\gamma B_1 t_2} I_x \psi(0) ; \quad \gamma B_1 t_2 = \frac{\pi}{2} \quad (14)$$

$$\psi(t_2) = e^{i\gamma B_0 (t_2 - t_1)} I_z \psi(t_1)$$

etc.

Convenient to define quantities.

$$T(t, \theta_0) \text{ and } X(\theta) \text{ by}$$

$$T(t, \theta_0) = e^{i\gamma B_0 t} I_z$$

T generates development of wave function during time when $B_1 = 0$ for spins which are off resonance by θ_0 .

$$X(\theta) = e^{i\theta I_x} \leftarrow \text{rotation about } x\text{-axis}$$

For $\theta = \frac{\pi}{2}$ spin components I_y, I_z, I_x transforms $(\frac{\pi}{2} - \text{pulse})$	$X^{-1}(\frac{\pi}{2}) I_y X(\frac{\pi}{2}) = I_z$ $X^{-1}(\frac{\pi}{2}) I_z X(\frac{\pi}{2}) = -I_y$ $X^{-1}(\frac{\pi}{2}) I_x X(\frac{\pi}{2}) = I_x$
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$$\text{For } \theta = \pi \quad (\text{Pi-pulse})$$

$$X^{-1}(\pi) I_y X(\pi) = -I_x$$

$$X^{-1}(\pi) I_z X(\pi) = -I_z$$

$$X^{-1}(\pi) I_x X(\pi) = I_x$$

We consider $B_1 > \theta_0 \Rightarrow$ neglect time evol between t_1 and $t_2 + \frac{\pi}{2}$

$$\Rightarrow \psi(t_1) = X(\frac{\pi}{2}) \psi(0)$$

$$\psi(t_2) = T(t, \theta_0) X(\frac{\pi}{2}) \psi(0).$$

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we get $\psi(t)$ for time t (after the second pulse)

$$\psi(t) = T(t-\tau, B_0) \chi(\tau) T(\tau, B_0) X\left(\frac{\pi}{2}\right) \psi(0)$$

for a single value of B_0

Observable signal. I_y

for a single set of spins

$$\langle I_y(t) \rangle = \int \psi^*(t) I_y \psi(t) dT_I$$

dT_I - volume element in spin space

we must sum over all spins

with different orientations B_0

$$\langle I_y, \text{total } (t) \rangle = N \int p(h_0) dh_0 \langle \psi^*(B_0, t) I_y \psi(B_0, t) \rangle$$

it can be shown using properties of
exp. operators

$$\int \psi^*(B_0, t) I_y \psi(B_0, t) dT_I =$$

$$= \int \psi^*(t) X^{-1} \left(\frac{\pi}{2}\right) T^{-1}(\tau, B_0) \chi^{-1}(\tau) T^{-1}(t-\tau, h_0) \cdot$$

$$\cdot I_y T(t-\tau, B_0) \chi(\tau) T(\tau, B_0) X\left(\frac{\pi}{2}\right) \psi(0) dT_I$$

$$\text{use } X^{-1} X = X X^{-1} = 1$$

we do following transformation.

$$X^{-1}(\tau) T^{-1}(t-\tau) I_y T(t-\tau) \chi(\tau) =$$

$$= \underbrace{X^{-1}(\tau) T^{-1} X(\tau)}_1 \cdot \underbrace{X(\tau) I_y X(\tau)}_2 \cdot$$

$$\cdot \underbrace{X^{-1}(\tau) T(t-\tau) \chi(\tau)}_3$$

first deal w. th term 2

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$$x^{-1}(\pi) I_y x(\pi) = -I_y$$

term 3:

$$x^{-1}(\pi) T(+\tau) x(\pi) = x^{-1}(\pi) e^{i b_0 (+\tau) I_2} x(\pi)$$

This term has I_2 exponent.

$$\text{use theorem } R^{-1}(e^{i G})R = e^{i(R^{-1}GR)}$$

Therefore

$$\begin{aligned} x^{-1}(\pi) \exp(i b_0 (+\tau) I_2) x(\pi) &= \\ = \exp(i x^{-1}(\pi) I_2 x(\pi) b_0 (+\tau)) &= \\ = \exp(-i \gamma b_0 (\tau - \tau) I_2) &= T^{-1}(\tau - \tau, b_0) \end{aligned}$$

we therefore get

$$\langle I_y \text{ total } (+) \rangle = N \int p(b_0) db_0 \int \psi(0) x\left(\frac{\pi}{2}\right) T^{-1}(\tau, b_0) T(\tau - \tau, b_0).$$

$$\cdot I_y T^{-1}(\tau - \tau, b_0) T(\tau, b_0) x\left(\frac{\pi}{2}\right) \psi(0) d\tau$$

special case, $\tau - \tau = \tau$, i.e. $\tau = 2\tau$

(time of echo)

At this time

$$T^{-1}(\tau - \tau, b_0) T(\tau, b_0) = 1$$

$$\begin{aligned} \langle I_y \text{ total } (\tau = 2\tau) \rangle &= -N \int p(b_0) db_0 \times \\ \times \int \psi(0) x^{-1}\left(\frac{\pi}{2}\right) I_y x\left(\frac{\pi}{2}\right) \psi(0) d\tau \end{aligned}$$

b_0 disappears from integral over $d\tau$

\Rightarrow integrate over db_0

$$\langle I_y \text{ total } (t = 2T) \rangle = -N(\psi/\phi_0) \chi^{-1}\left(\frac{\pi}{2}\right) I_y \chi\left(\frac{\pi}{2}\right) \psi/\phi_0 dt_y$$

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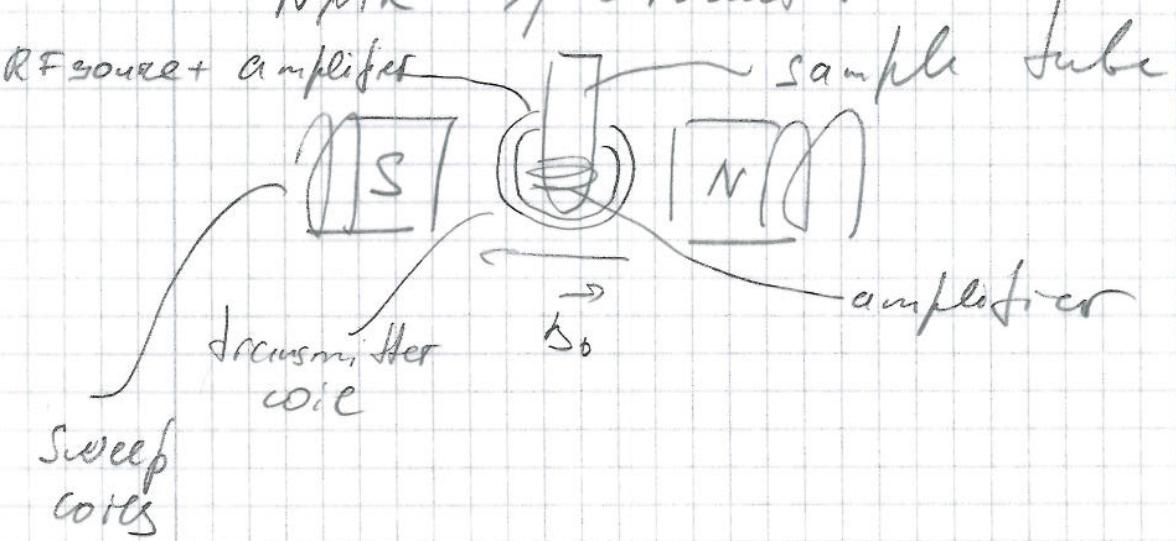
Identical to the state after $\frac{T}{2}$ pulse

$$\langle I_y \text{ total } (t = 2T) \rangle = -N \langle I_z (0^-) \rangle$$

0^- - time before $t=0$

Hahn echo \leftrightarrow important advantage
refocusing field inhomogeneities
and noise (but only static)

NMR spectrometer



The theory of relaxation

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Simple example - system of spins in fluctuating field

$$B_{xL}(t) = B_{xL}^0 f(t)$$

$$\langle f \rangle = 0 \quad \langle (f(t))^2 \rangle = 1$$

$B_{xL}^0 \leftarrow$ RMS amplitude of field.

$$\text{Hamiltonian} \quad H(t) = -\gamma t I_x B_{xL}^0 f(t)$$

Perturbation theory shows that it induces transitions at rate

$$W_1 = \hbar^{-2} \langle \dot{x} | -\gamma t I_x B_{xL}^0 | \beta \rangle^2 Y(\omega_0)$$

$$= \gamma^2 [B_{xL}^0]^2 \langle x | I_x | \beta \rangle^2 Y(\omega_0) =$$

$$= \frac{1}{4} \langle B_{xL}^0 \rangle^2 Y(\omega_0)$$

$Y(\omega_0)$ - power available from fluctuations
at the relevant transition frequency

→ "spectral density" (related to $f(t)$)

B_y will contribute equal terms

B_z will not cause transitions.

$$\Rightarrow W_1 = \frac{1}{2} \gamma^2 [B_{xL}^0]^2 Y(\omega_0)$$

However each transition alters the population difference by 2

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$$T_1^{-1} = 2\omega_1 = \delta^2 [B_{XL}]^2 Y(\omega_0)$$

$f(t)$ can be expressed in terms of correlation function

$$G(t) = \langle f(t) f(t+\tau) \rangle$$

$$\text{usually } G(\tau) = \exp(-\tau/\tau_c) \quad (*)$$

τ_c - correlation time

$G(\tau)$ corresponds to $Y(\omega)$

(time domain vs. frequency domain).
two functions are related by Fourier transformation.

$$Y(\omega) = \int_{-\infty}^{\infty} G(t) \exp(-i\omega t) dt$$

$$G(t) = \frac{1}{(2\pi)} \int_{-\infty}^{\infty} Y(\omega) \exp(i\omega t) d\omega$$

$$\rightarrow \text{substitution } (*) \quad Y = \frac{2\tau_c}{1 + \omega^2 \tau_c^2}$$

for T_1 time we will obtain

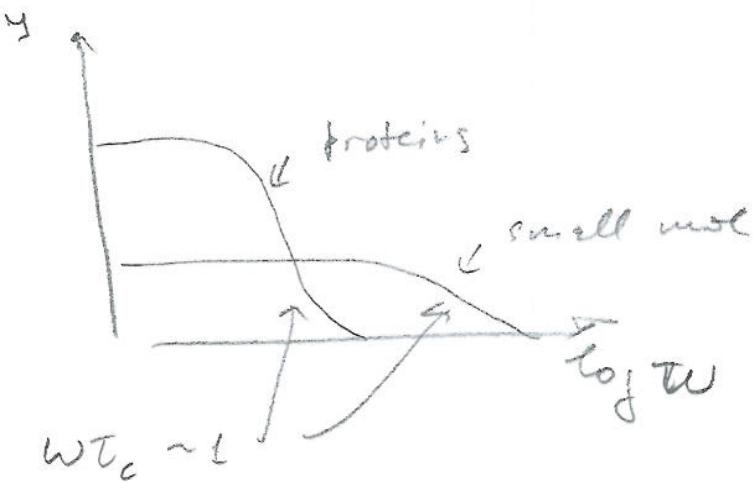
$$T_1 = \delta^2 [B_{XL}]^2 \frac{2\tau_c}{1 + \omega_0^2 \tau_c^2}$$

τ_c is often related to random rotation

$\approx 10 \text{ ps}$ for small molecules

$\approx 10 \text{ ns}$ for proteins.

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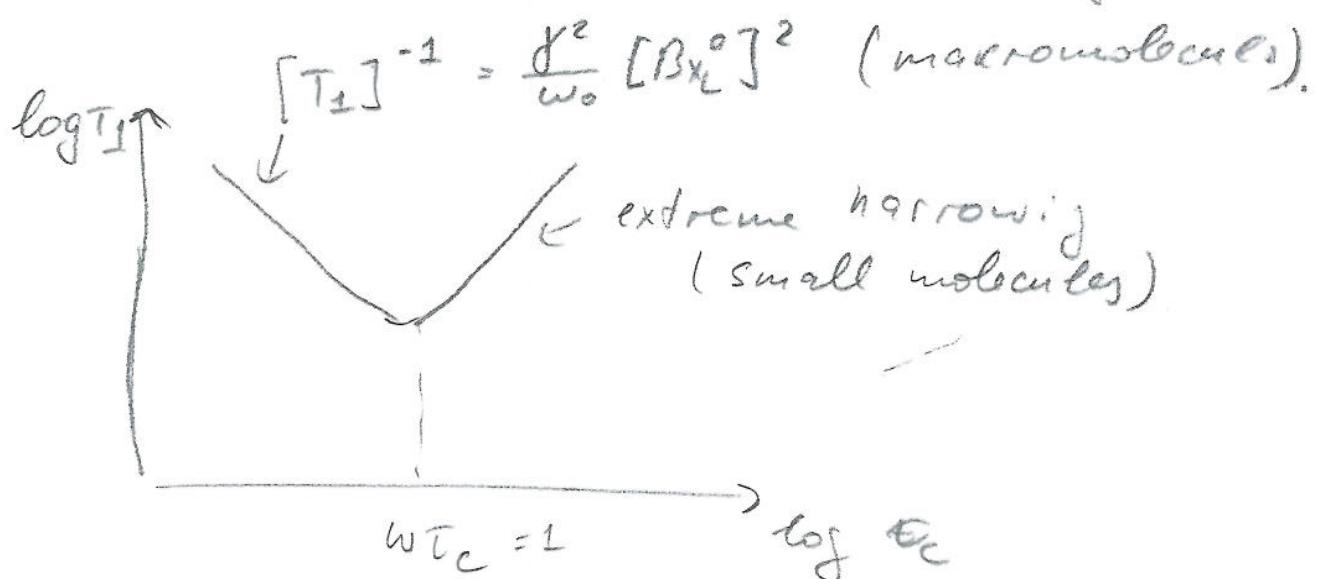
$(wT_c)^2 \ll 1$ - "extreme narrowing conditions"

$$T_1^{-1} \approx 2\gamma^2 [B_{x_L}^0]^2 \tau_c$$

for small molecules ($10 \text{ ps} = \tau_c$) this holds
($\omega_0 \approx 100 \text{ MHz}$).

T_1 time increases as T_c increases, i.e.
mobility decreases (for example by
lowering T)

when $wT_c \approx 1$ reached, new regime



$T_1 = f(\omega_0) \rightarrow$ higher B_0 field leads to increase
of T_1

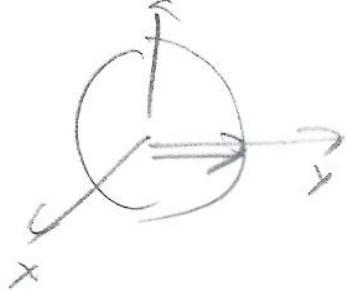
Relaxation mechanisms for spin $\frac{1}{2}$ nuclei (21)

- dipole-dipole interaction with other nuclei
- interactions with electrons (radicals)

Studies of relaxation

Spin locking.

$(\frac{1}{2})_x - \text{(long pulse)}_y$



if $B_L > B_{L_x}^0$ - no relaxation

T_{1_p} - relaxation measured by spin locking.

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Higher order echoes

$$\frac{\pi}{2} - \pi_x - \pi_y - \pi_x - \pi_y - \pi_y - \pi_x - \pi_y - \pi_x$$

filter out noise at all frequencies

$$\text{except } \gamma_0 = \frac{1}{2\tau}$$

$$\Delta v (\text{width}) = \frac{2\gamma_0}{N}$$

Robust for pulse errors.

variation of rotations (x,y) -

Phase cycling

(relaxation)

The intensity of NMR signal.

$$n_\uparrow - n_\downarrow = \Delta n_0 = N \frac{\Delta E}{2\pi\tau}$$

Magnetisation

$$M_0 = \frac{1}{4} N g \hbar \frac{\Delta E}{kT} = \frac{1}{4} N (g \hbar)^2 B_0 / kT$$

(Curie equation)

Stady state NMR experiment

Spin system absorbs energy from RF source at rate R , which depends on factors.

1) Probability P (per unit time and spin) of a transition being induced

2) Population difference between states

Detailed treatment shows that

$$P \sim (g B_1)^2 g(\nu)$$

$g(v)$ - signal shape factor

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rate of absorption of RF radiation

$$R = P \cdot \Delta U \cdot \Delta n_0 = \gamma^4 B_0^2 N B_{\perp}^2 g(v)/T$$

However NMR spectrometers do not detect R directly, but rather the rate of induced magnetisation change in the direction of receiver

$$S \sim \frac{dM_y}{dt} \text{ This turns to be } R/B_{\perp}$$

$$\Rightarrow S = \gamma^4 B_0^2 N B_{\perp} g(v)/T$$

a) $S \sim N$, large samples

b) $S \sim \gamma^4$: high sensitivity for ^{14}N , low for ^{15}N ($0.3 \text{ e}^{14}, 1/6$)

c) $S \sim B_0^2 \Rightarrow$ work at high fields is desirable

Electronic shielding

Diamagnetism: motion of electrons induced by B_0 .

$$\omega_1 = \left(\frac{e}{2me} \right) B_0$$

associated magnetic moment
(note that e circulation is right handed and negative charge)



$$M_i = -\left(\frac{e^2}{4m_e}\right) r^2 B_0 \sin^2 \theta$$

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\vec{r} - vector connecting e and nucleus

θ - angle between \vec{r} and B_0

Effective field $\rightarrow B = B_0 (1-\sigma)$

small fraction,

\approx parts per million (ppm)

Nuclear frequency $\nu_i = \frac{1}{2\pi} B_0 (1-\sigma_i)$

Reference sample \rightarrow TMS (tetramethylsilane
 $\text{C}_3(\text{CH}_3)_4$)

$$\delta = 10^6 (\nu_{\text{sample}} - \nu_{\text{TMS}}) \quad \text{at constant } B_0$$

Examples

$$\text{Benzene } \delta_{\text{H}} = 7.37$$

$$\delta_{\text{C}} = 128.5$$

$$\text{water } \delta_{\text{H}} = 4.76$$

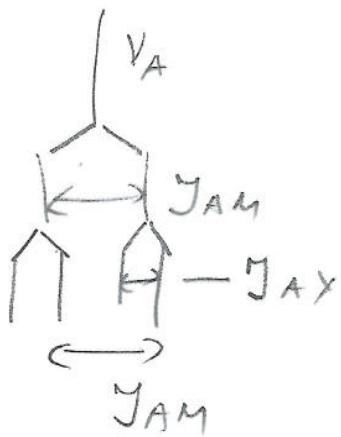
Spin-spin coupling.

more than 1 nucleus \rightarrow complex, multiple structure

$I_1, I_2 \rightarrow$ resonance of spin I_1 , splits into $2I_1 + 1$ lines, equal intensity

I_2 splits into $2I_2 + 1$ lines,
 3 nuclei (A, M, X)

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Description of spectra

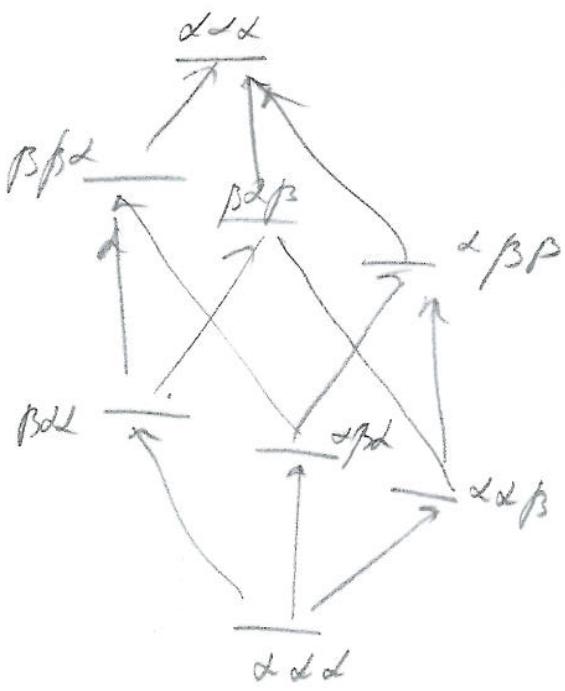
wavefunctions

 α for $m_I = +\frac{1}{2}$, β for $m_I = -\frac{1}{2}$

Basic product functions

according to total component
of angular momentum

$$m_T = \sum m_I$$

 m_T $-\frac{3}{2} \quad \beta\beta\beta$ $-\frac{1}{2} \quad \beta\beta\alpha, \beta\alpha\beta, \alpha\beta\beta$ $+\frac{1}{2} \quad \beta\alpha\alpha, \alpha\beta\alpha, \alpha\alpha\beta$ $+\frac{3}{2} \quad |\alpha\alpha\alpha\rangle$ selection rule for
NMR transitions

$$\Delta m_I = \pm 1, \Delta m_k (k \neq j) = 0$$

Energy spectrum

$$h^{-1} U = - \sum_j Y_j m_j + \sum_{j < k} Y_{jk} m^m$$

where

$$Y_i = \left(\frac{\delta i}{2\pi} \right) B_0 (1 - \sigma_i)$$

Second term \rightarrow coupling
summation $j < k$ - to avoid double counting

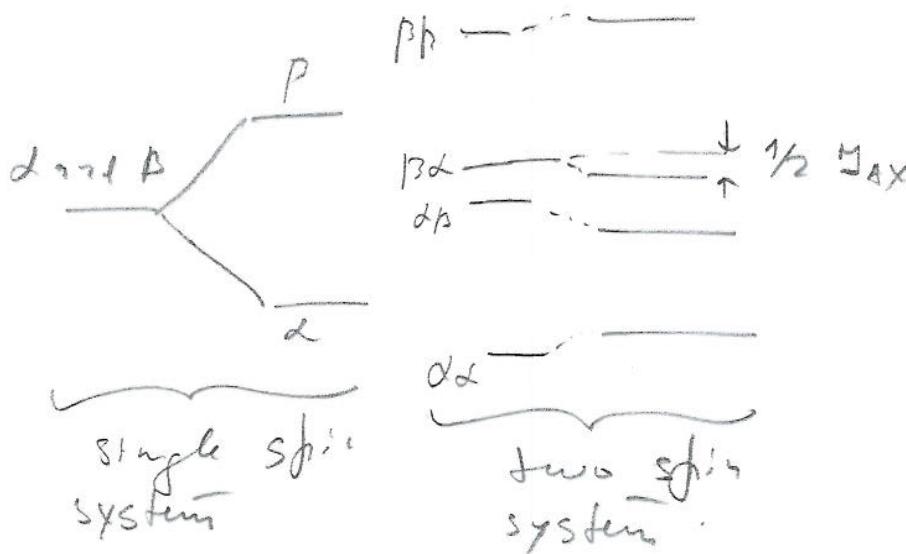
Example: two spin system

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$d\alpha, d\beta, f\alpha, f\beta p$

Labelling nuclei A and X

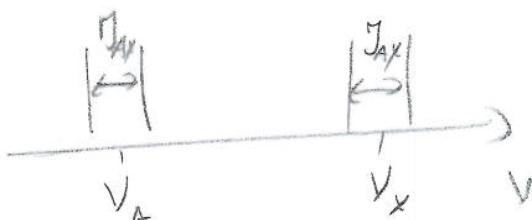
$$\hbar^{-1} v = -V_A m_A - V_X m_X + J_{AX} m_A m_X$$



Allowed transitions

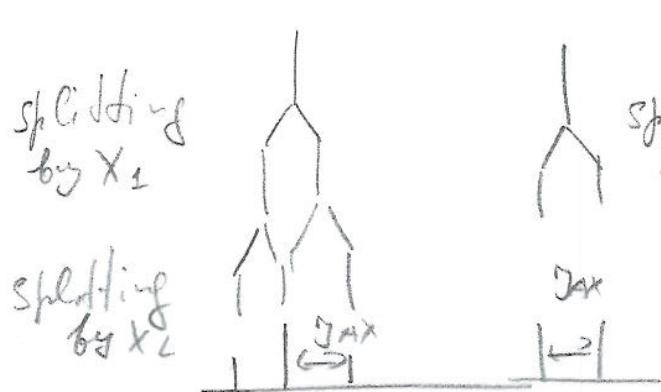
A - transitions $\Delta m_A = \pm 1$ $\Delta m_X = 0$

X - transitions $\Delta m_A = 0$ $\Delta m_X = \pm 1$.



Spectra involving magnetic equivalence

AX_2 spin system



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