Solid State Spectroscopy II

Particle Spectroscopy

types of probe particles:

- nuclei (internal) → NMR
- muons (extrinsic) → μSR
- electrons (internal) → ESR
- (external) → EELS
- neutrons (external) → neutron scattering

1 — Nuclear Magnetic Resonance (NMR)

- use the nuclei of the crystal lattice (with $I \neq 0$) as a local probe for the electronic environment.
- the nuclear spins interact with the surrounding electrons via "hyperfine coupling"

basic idea:

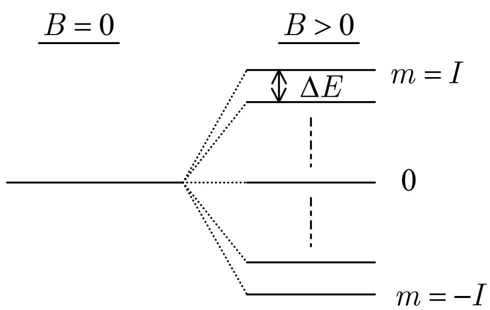
Apply magnetic field $\vec{B}_0 = B_0 \cdot \hat{z}$ to the sample. This lifts the degeneracy of the nuclear levels (for $I \neq 0$) with different magnetic quantum number, $m = -I, \ldots + I$.

Nuclear Zeeman effect: $H = -\vec{\mu}_N \cdot \vec{B}$

$2I+1$ levels

$m = -I, \ldots, +I$

$I = 2 \;\rightarrow\; m = 5$



$E_m = g \cdot \mu_N \cdot m \cdot B_0$

$$\boxed{\begin{aligned}\Delta E &= E_{m+1} - E_m \\ &= g \cdot \mu_N \cdot B_0\end{aligned}}$$

energy splitting

Nuclear Zeeman splitting

$$\mu_N = \frac{e \cdot \hbar}{m_P} = 5.05 \cdot 10^{-27} \left[A \cdot m^2 \right]$$ ‘nuclear magneton’

$$\approx \frac{1}{2000} \cdot \mu_B$$ since $m_p \approx 2000 \cdot m_e$

The g-factors depend on the particular nucleus in a more complicated way
→ look it up in tables

nuclei are made up of protons (p) and neutrons (n)
both are spin 1/2 particles

$$\begin{array}{lll} p = (uud) & g_s(p) = 5.59 & g_L(p) = 1 \\ n = (udd) & g_s(n) = -3.83 & g_L(n) = 0 \end{array}$$

Now one probes the level splitting with electromagnetic radiation, which induces transition between them.

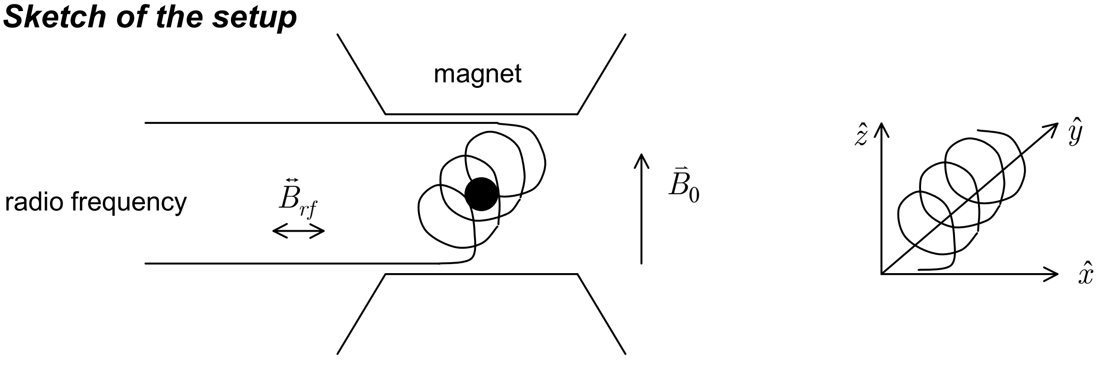
for $\hbar\omega = g \cdot \mu_N \cdot B$
with $B = 1\,T,\ I = 1,\ g = 2 \ \Rightarrow\ \Delta E \approx 0.1 \mu eV$
$\rightarrow$ need radio frequency waves

reminder: $k_B \cdot 300K \approx 25 meV$
$0.1 \mu eV \sim 1 mK$

measure:

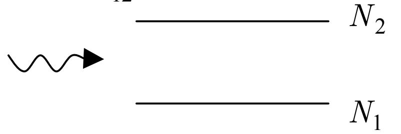
– frequency of absorption maximum $\Rightarrow$ local B-field at nuclear site
– line width $\Rightarrow$ relaxation rates either due to static distribution of B-fields or fluctuation as a function of time

Sketch of the setup



remember from optics:
time-dependent-perturbation-theory

$\hbar\omega = \Delta E_{12}$



transition rates for absorption and for stimulated emission are equal.

$\rightarrow$ if $N_1 = N_2 \Rightarrow$ no net absorption.

however: thermal population is somewhat lower for higher levels.

Average nuclear magnetization density:

$$\underset{\text{density of spins}}{M} = N \cdot g \cdot \mu_N \underbrace{\langle I_z \rangle}_{\text{thermal average}}$$

$$= N \cdot g \cdot \mu_N \frac{\sum_{m=-I}^{+I} \hbar \cdot m \; e^{-g\mu_N \frac{B_0 \cdot m}{k_B T}}}{\sum_{m=-I}^{I} e^{-g \cdot \mu_N \frac{B_0 \cdot m}{k_B T}}}$$

$\exp(1+x) \approx 1+x$ for $x \ll 1$

$$\approx N \cdot g \cdot \mu_N \frac{\sum_{m=-I}^{I} \hbar m \left(\cancel{1} + \frac{g\mu_N \cdot B_0 \cdot m}{k_B \cdot T} \right)}{\sum_{m=-I}^{I} 1 + \cancel{\frac{g\mu_N \cdot B_0 \cdot m}{k_B - T}}}$$

use: $\sum_{m=-I}^{I} m = 0 \qquad \sum_{m=-I}^{I} m^2 = \frac{(2I+1) \cdot I(I+1)}{3}$

$$\boxed{M = N \cdot g^2 \cdot \mu_N^2 \frac{B_0 I(I+1)}{3k_B T} \sim \frac{B_0}{T}}$$

= Curie law for paramagnetic moments

for $T = 300K,\ B = 1\,T,\ I = 1$

$\rightarrow \frac{\langle I_z \rangle}{\hbar} \sim 10^{-6}$

but there are typically 10^{20} nuclei

❍ Classical description of NMR

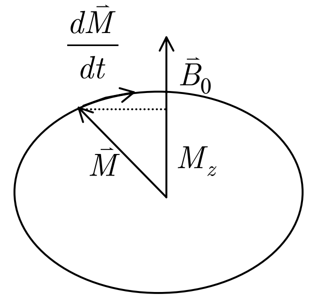
treat the net magnetization density $\vec{M}$ as a classical vector

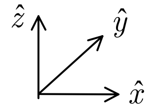
In a magnetic field $\vec{B}$ there is a torque $\vec{\tau}$.

$$\vec{\tau} = \vec{M} \times \vec{B}_0 = \frac{d\vec{I}}{dt} = \frac{\hbar}{g \cdot \mu_N} \frac{d\vec{M}}{dt}$$

= Bloch equation

change of angular momentum density





→ free precession of $\vec{M}$ around $\vec{B}_0$ where M_z is conserved.

→ precession frequency:

$\boxed{w_L = -\gamma \cdot B_0}$ **= *Larmor frequency***

Introduce relaxation mechanism:

longitudinal relaxation rate T_1 spin-lattice relaxation rate

transversal relaxation rate T_2 spin-spin relaxation rate

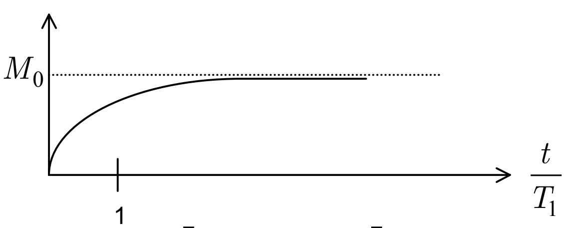
$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}$$

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

concerns the relaxation towards equilibrium $\langle \vec{M} \rangle = (0, 0, M_0)$

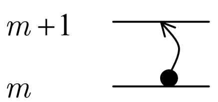
> *T_1 measurement*

Bring unmagnetized sample in a magnetic field $B_0 \cdot \hat{z}$



$$M_z(t) = M_0 \left[1 - \exp\left(-\frac{t}{T_1} \right) \right]$$

Here the population of levels needs to be changed → requires an energy transfer.



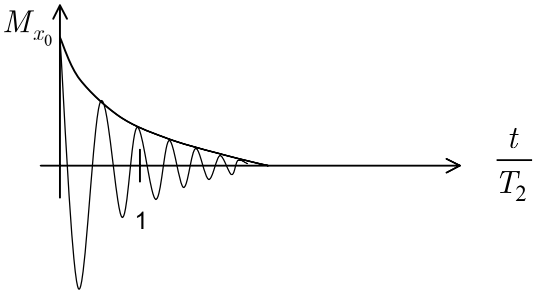
$$\Delta E = -g\mu_N \cdot B$$

The crystal lattice acts like a heat bath → spin-lattice relaxation rate T_1

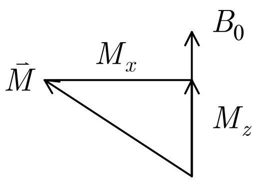
> T_2 *measurement*

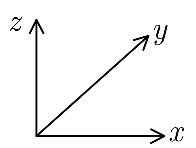
For example: partially magnetized sample along x so as to induce a component $\vec{M}(t=0)=(M_{x_0},0,0)$

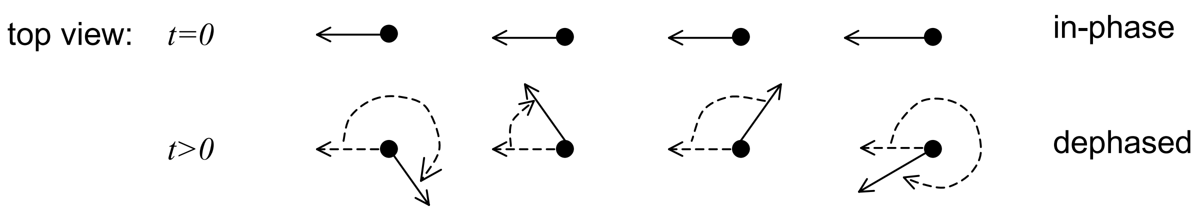
$$\frac{dM_x}{dt}=\frac{M_x}{t_2}\rightarrow M_x=M_{x_0}e^{-\frac{t}{T_2}}$$



static case: dephasing of spin ensemble due to inhomogeneous magnetic field B.







Dynamic processes also can contribute to T_2 since they also destroy the phase coherence.

> Combine both sets of equations (free percession and relaxation).

$$\frac{dM_z}{dt}=\gamma\cdot\left(M\times B\right)_z+\frac{M_0-M_z}{T_1}$$

$$\frac{dM_{x,y}}{dt}=\gamma\cdot\left(M\times B\right)_{x,y}+\frac{M_{x,y}}{T_2}$$

total field: $\underbrace{\vec{B}=B_0\,\hat{z}}_{\text{static field}}+B_1\underbrace{\left[\hat{x}\cos\left(\omega t\right)+\hat{y}\sin\left(\omega t\right)\right]}_{\text{rf-field}}$

Consider rotating coordinate system, with frequency ω

$$\begin{pmatrix} \hat{z} \rightarrow \hat{z}' = z \\ \hat{x} \rightarrow \hat{x}' = \hat{x} \wedge \cos\omega t \\ \hat{y} \rightarrow \hat{y}' = y \sin\omega t \end{pmatrix}$$

a vector $\vec{F}$ transforms according to

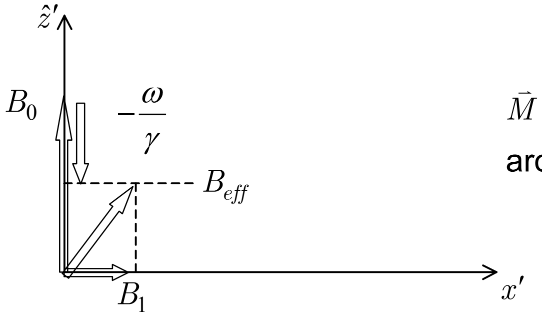
$$\underset{\text{fixed}}{\frac{d\vec{F}}{dt}} = \underset{\text{rotating}}{\frac{d\vec{F}'}{dt}} - \underbrace{\vec{\omega} \times \vec{F}'}_{\text{coriolis-force}}$$

$$\rightarrow \frac{d\vec{M}'}{dt} = \gamma\left(\vec{M}' \times \vec{B}'\right) + \vec{\omega} \times \vec{M}' + \text{ relaxation terms}$$

$$= \gamma\left\{M \times \underbrace{\left(\vec{B} - \frac{\vec{\omega}}{\gamma}\right)}\right\} + \text{ relaxation terms}$$

$$\vec{B}_{eff} = \vec{B} - \frac{\vec{\omega}}{\gamma} \qquad \vec{\omega} = \omega \cdot \hat{z}$$

$$\rightarrow \vec{B}_{eff} = \left(B_0 - \omega\right)\hat{z}' + B_1\,\hat{x}'$$



$\vec{M}$ now precesses around $\vec{B}_{eff}$

without relaxation and for $\omega_L = -\gamma B_0 \rightarrow \vec{B}_{eff} = \vec{B}_1$

with $$\gamma \cdot \begin{pmatrix} M_{x'} \\ M_{y'} \\ M_{z'} \end{pmatrix} \times \begin{pmatrix} B_1 \\ 0 \\ B_0 - \omega/\gamma \end{pmatrix} = \begin{pmatrix} M_{y'}\left(\gamma B_0 - \omega\right) \\ -M_x\left(\gamma B_0 - \omega\right) + B_1 M_{z'} \\ -\gamma M_{y'}\,B_1 \end{pmatrix}$$

$$\boxed{\begin{aligned} \frac{dM_{z'}}{dt} &= -\gamma \cdot B_1 \cdot M_{y'} - \frac{M_{z'} - M_0}{T_1} \\ \frac{dM_{x'}}{dt} &= \left(\gamma \cdot B_0 - \omega\right) M_{y'} - \frac{M_{x'}}{T_2} \\ \frac{dM_{y'}}{dt} &= -\left(\gamma \cdot B_0 - \omega\right) M_{x'} - \gamma B_1 \cdot M_{z'} - \frac{M_{y'}}{T_2} \end{aligned}}$$

Bloch equations in rotating coordinates

If equilibrium is maintained: "slow passage of ω or B_0 through the resonance condition"

$$\rightarrow \frac{d\langle M_x\rangle}{dt} = \frac{d\langle M_y\rangle}{dt} = \frac{d\langle M_z\rangle}{dt} = 0$$

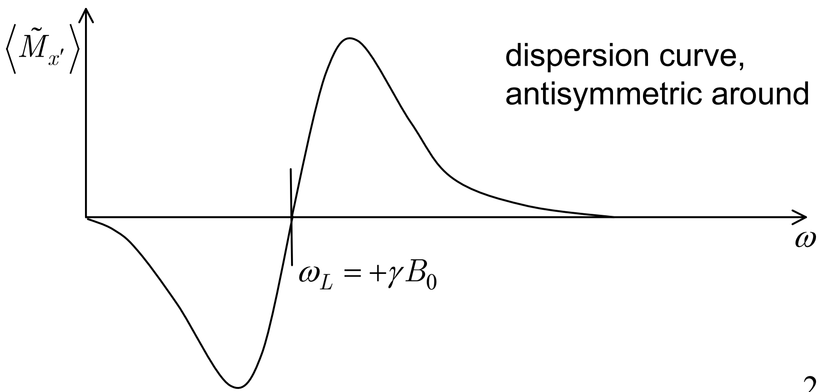
$\rightarrow 3$ linear equations

$$\langle M_{x'}\rangle = \gamma \cdot B_1 \cdot \langle M_0\rangle \cdot \frac{\omega - \gamma \cdot B_0}{(\omega - \gamma B_0)^2 + \frac{\pi^2}{4}}$$

$$\langle M_{y'}\rangle = \frac{\gamma \cdot B_1 \cdot \langle M_0\rangle}{T_2} \; \frac{1}{(\omega - \gamma \cdot B_0)^2 + \frac{\pi^2}{4}}$$

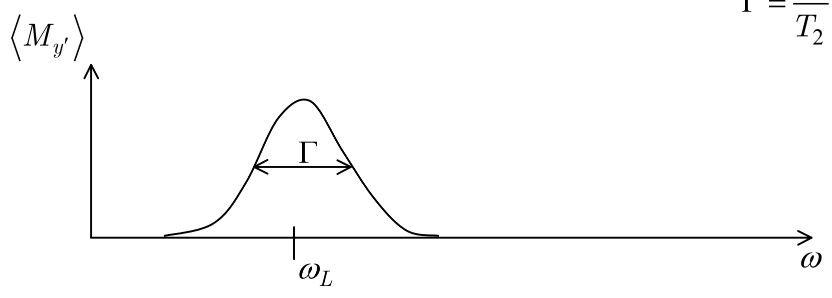
$$\langle M_{z'}\rangle = \frac{1 + (\omega - \gamma \cdot B_0)^2 \, T_2{}^2}{(\omega - \gamma B_0)^2 + \frac{\pi^2}{4}}$$

with $\Gamma = \frac{2}{T_2}\sqrt{1 + \gamma^2 B_1{}^2 T_1 T_2}$



dispersion curve, antisymmetric around ω_L

$$\Gamma = \frac{2}{T_2}\sqrt{1 + \gamma^2 B_1{}^2 T_1 T_2}$$



two cases:

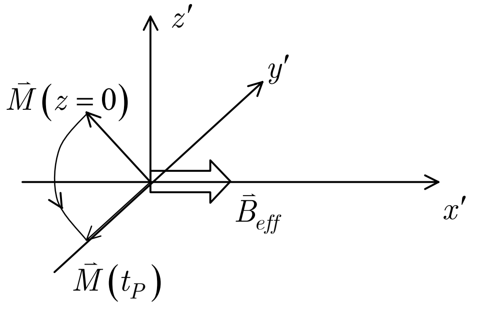
a) weak rf-field $B_1^2 << \frac{1}{\gamma^2 T_1 T_2}$

$\rightarrow \Gamma \approx \frac{2}{T_2}$ $\quad\quad\rightarrow T_2$ measurement

b) strong rf-field $B_1^2 >> \frac{1}{\gamma^2 T_1 T_2}$

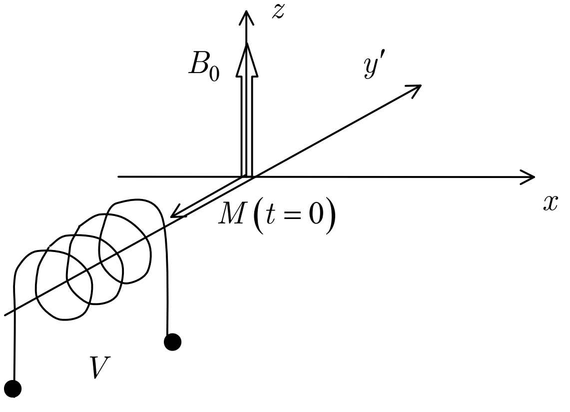
$\rightarrow \Gamma \approx 2\gamma B_1 \sqrt{\frac{T_1}{T_2}}$ $\quad\quad$ power broadening

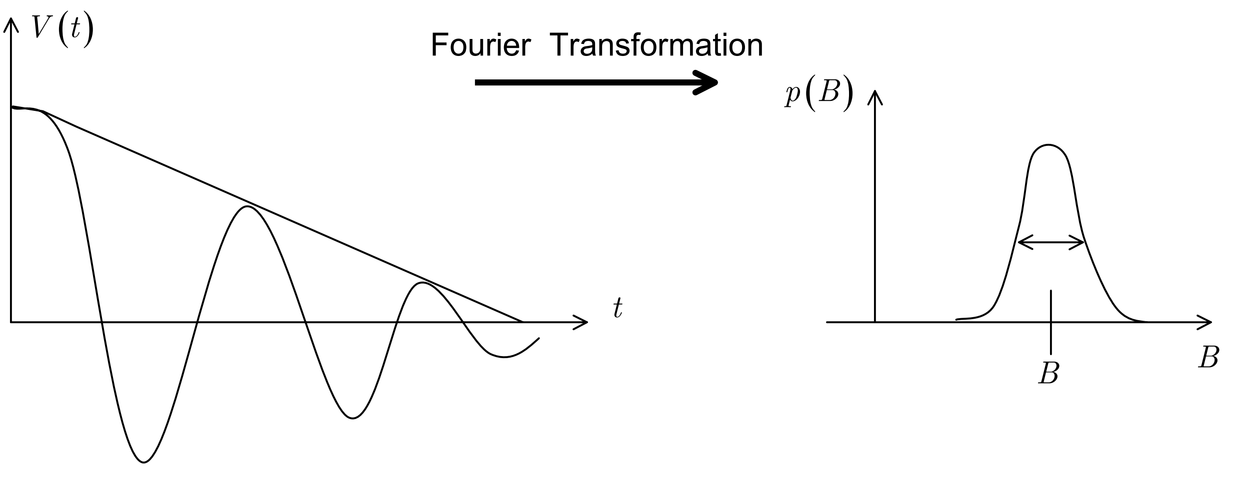
So far we considered the continuous wave techniques.
Alternative is the pulse method.
Apply a pulse of frequency ω_L for duration t_P
for $0 \rightarrow t_P \Rightarrow \vec{B}_{eff} = B_1 \hat{x}'$



Pulse of appropriate duration t_P rotates $\vec{M}$ into the y-plan, $t_P = \frac{\pi}{2}\frac{1}{\gamma \cdot B_1}$

After t_P the magnetic field B_1 is switched off.
$\rightarrow$ free precession around $\vec{B} = B_0 \hat{z}$
$\vec{M}(t=0) = (0, M_{y'_0}, 0)$



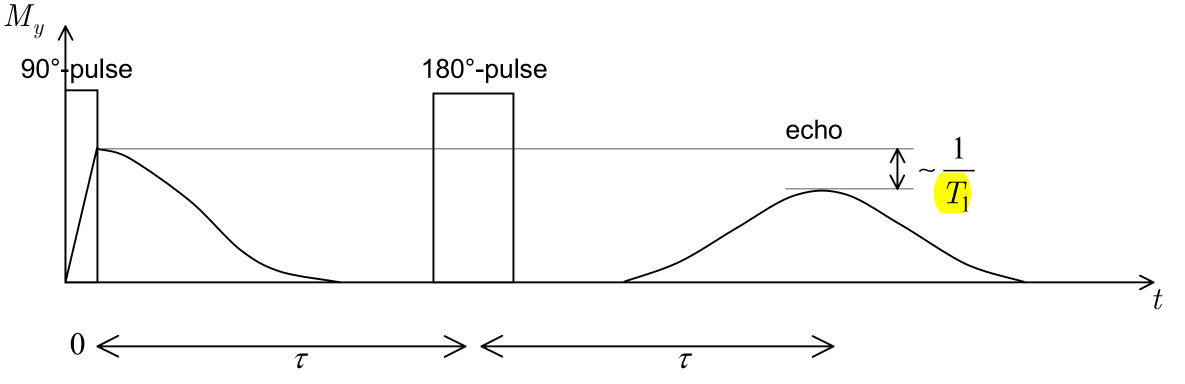


Two processes contribute to decay of $M_{y'}$, i.e. to Γ

– dynamic ones, $\frac{1}{T_1}$

– static field inhomogeneities

Spin-Echo-Technique



After some time τ apply a 180° pulse $(\pi - \text{pulse})$

$\rightarrow$ Dephasing process due to random but static local $B-$fields is reversed
$\Rightarrow$ echo signal appears because spin dephasing is reversed

$\rightarrow$ Dephasing due to dynamic $\frac{1}{T_1}$ processes is not reversed

$\rightarrow$ Amplitude of echo is smaller

Ratio of $\frac{I_{echo}}{I_{initial}} \rightarrow \frac{1}{T_1}$