

NMR Formalism and Techniques (I) [Mitrovic]

- NMR is both local and bulk probe, and requires only small sample ($\sim 1 \text{ mg}$), and is a low-energy ($\omega \approx 0 \text{ meV}$) probe. Applicable in extreme conditions (high pressure, high field, etc.)

- Principle: nuclear spin state split by Zeeman splitting. The splitting is proportional to local H-field (H_0 for a finite ant band)

Then we can couple the levels by RF-field $H_L \perp H_0$

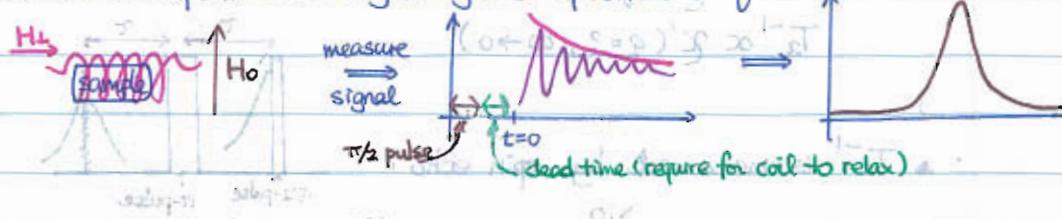
$$\Rightarrow H_L = \gamma_h H_J I_j e^{i\omega t}$$

$$\Rightarrow \frac{n_\downarrow}{n_\uparrow} = e^{\frac{i\omega_0}{kT}} \Rightarrow \Delta n \approx \frac{\omega_0}{kT}$$

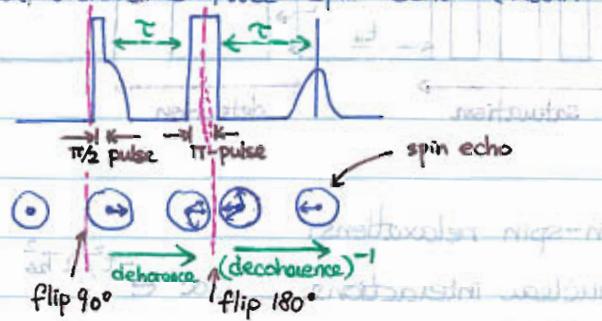
Apply a $\pi/2$ oscillating RF field; afterwards the nuclear spin relax.

As nuclear spin relax., it generates small current signal in external coil.

Fourier transform the signal gives spectral info.



- To avoid deadtime, use spin echo (Hahn 1950)



- Static NMR Measurements

For complex lattice, ion / atom at different site sees different local fields

$$\omega_n = \gamma_n H_{loc} = \gamma_n (H_0 + \langle H_{hf} \rangle)$$

$$\langle H_{hf} \rangle = - \sum_n A_{n,k} \langle S_k \rangle = - \sum_n A_{n,k} \frac{1}{g_k \mu_B} \chi_k(T) H_0 \quad [A_{n,k} = \text{hyperfine}]$$

$$\rightarrow \frac{\omega_n - \omega_0}{\omega_0} = K(T) \propto \chi(T) = \chi(q=0, \omega \rightarrow 0)$$

\sim Knight shift

[Lorentzian] (i) width of NMR spectrum \Rightarrow distribution of $\langle \vec{S}_z(r) \rangle$

- Thus, width of NMR spectrum \Rightarrow distribution of $\langle \vec{S}_z(r) \rangle$
- shift of NMR spectrum \Rightarrow magnetic susceptibility

- For $I > 1/2$ nuclei has quadrupole moments which interact with electric field gradient g_b surrounding e^- .

The quadrupole Hamiltonian gives additional splitting of nuclei levels.
(but the shift is not affected).

- Dynamic NMR measurements.

two rates : (1*) spin-spin relaxation

no spin-flip, energy conserved

$$T_2^{-1} \propto h_{\parallel}(t)$$

(2*) spin-lattice relaxation

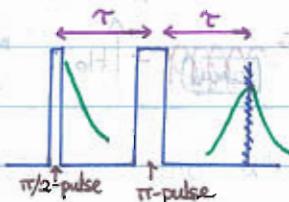
$$T_1^{-1} \propto h_{\parallel}(t)$$

population relaxation to equilibrium

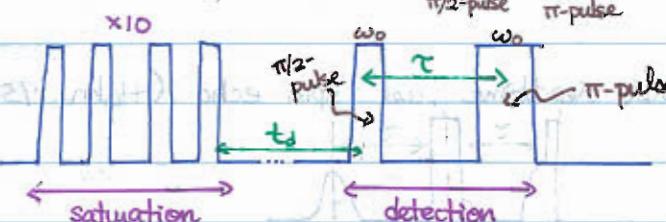
$$\Rightarrow T_1^{-1} \propto \chi''(q=?, \omega \rightarrow 0)$$

$$T_2^{-1} \propto \chi'(q=?, \omega \rightarrow 0)$$

- T_2^{-1} is measured by spin echo.



- For T_1^{-1} :



τ same as above. Negate effects of spin-spin relaxation

- Sources of spin-spin relaxations:

(1*) nuclear-nuclear interactions.

$$\propto e^{-t^2/2T_{20}^2}$$

(2*) "T₁" or Redfield processes : fluctuation of nearby e^- spin cause

T_1 relaxation and provide decay for M_z . $\propto e^{-t/T_{2R}}$

(3*) Indirect nuclear interaction:

$$(12) \text{ If } -\propto \sum_{i,j} \vec{I}(F_i) \cdot \vec{A}(F_i - F_j) \chi(F - F_i) \vec{A}(F' - F_j) \cdot \vec{I}(F_j) =$$

nearest neighbor
lowest neighbor = min A

$$-\langle \vec{I} \cdot \vec{A} \rangle \vec{S} = -\vec{S}(\vec{A} \cdot \vec{I}) = \langle gH \rangle$$

[zu H. 5.1] (I) $\omega_{\text{eff}} = \frac{1}{T} \int_0^T \omega(t) dt$

• Spin-Lattice Relaxation

$$W_{n \rightarrow m} = \frac{2\pi}{h} \sum_{e, e'} p(e) |\langle n' | e | H_{\text{hf}} | n, e \rangle|^2 \delta(E_e + E_n - E_{e'} - E_{n'})$$
$$\Rightarrow \frac{1}{T_{12} T} = C \sum_q \sum_{\beta=x,y,z} \left(A_{\beta\beta}^2(q) + A_{\beta\beta}^2(q) \right) \frac{\Im X_{\beta\beta}(q, \omega_{\text{eff}})}{\Im W_{nn}}$$

$$\frac{\Im X_{\beta\beta}(q, \omega)}{\Im W_{nn}} = \frac{\Im X_{\beta\beta}(q, \omega)}{\Im W_{nn}} \cdot \exp(-\omega T) =$$
$$\frac{\Im X_{\beta\beta}(q, \omega)}{\Im W_{nn}} = \frac{\Im X_{\beta\beta}(q, 0)}{\Im W_{nn}} = \frac{\omega}{T} = \omega$$

somit auch doppelt aufgetrennte und berührungslose Spinsysteme kündigt an ω_{eff} :

→ zu zweitem nachstehen

* $\omega_{\text{eff}} = \omega$ nicht zulässig: $\omega_{\text{eff}} = \omega$ nicht zulässig

(3) T_1 entsteht durch

$\omega \ll (3)T$ für Lissu

$$X_{\beta\beta}(q, \omega) = \Im \left[(q, \omega) \right] = \Im \left[(q, \omega) V \right] = \Im \left[\frac{1}{\omega - q} \right] = \frac{1}{\omega} \quad \text{für } \omega \gg q, \text{ d.h. } \omega \gg T$$

weiterhin: $\omega_{\text{eff}} = \omega$ möglich → $\omega_{\text{eff}} = \omega$ nicht zulässig.

mit nur 1 Spinsystem ist es so:

aber nur mit einem ω_{eff} .

$$(q, \omega)_1 + \frac{1}{T_1} + \frac{1}{T_2} - \omega = \omega_{\text{eff}} - \frac{1}{T_1} - \omega = (\omega, \omega)_2 \quad \text{kündigt an } \omega_{\text{eff}}.$$
$$[(\omega, \omega)_2] \propto \frac{1}{T_1}$$

$$(\omega, \omega)_1 / \omega_1^2 = (\omega - \omega_1)^2 / \omega_1^2 = \frac{1}{\omega_1^2} \cdot \frac{1}{1 - \frac{\omega_1^2}{\omega^2}} = \frac{1}{\omega_1^2} \cdot \frac{1}{1 - \frac{1}{\omega^2}} = \frac{1}{\omega_1^2} \cdot \frac{\omega^2}{\omega^2 - 1} = \frac{\omega^2}{\omega_1^2(\omega^2 - 1)}$$

und $\omega_1^2 \propto \omega_{\text{eff}}^2$, d.h. $\omega_1^2 \propto T_1^{-2}$, d.h. $\omega_1 \propto T_1^{-1}$

$1/T_1 \propto (3)T$, d.h.

also ω_{eff} mit ziemlich schneller Abnahme mit T_1