NMR Formalism and Techniques (I) [Mitrovic]

- NMR is both local and bulk probe, and requires only small sampl (~1 mg), and is a low-energy ($\omega \approx 0\ \mu eV$) probe. Appliable in extreme conditions (high pressure, high field, etc.)

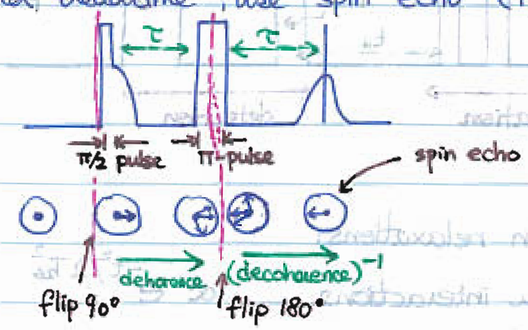
- Principle: nuclear spin state split by Zeeman spliting. The splitti is proportional to local H-field. H_0
  Then we can couple the levels by RF-field $H_1 \perp H_0$

  $$\Longrightarrow \mathcal{H}_1 = \gamma \hbar H_j I_j e^{i\omega_0 t}$$

  $$\Longrightarrow \frac{n_\downarrow}{n_\uparrow} = e^{\hbar\omega_0/k_BT} \Longrightarrow \Delta n \approx \frac{\hbar\omega_0}{k_BT}$$

  Apply a $\pi/2$ oscillating RF field, afterwards the nuclear spin relax. As nuclear spin relax, it generates small current singal in external coil.
  Fourier transform the singal gives spectral info.

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



- Static NMR Measurements
  For complicate lattice, ion/atom at different site sees different local fie

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

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

  $$\longrightarrow \frac{\omega_n - \omega_0}{\omega_0} = \underbrace{K(T)}_{\sim \text{Knight shift}} \propto \chi(T) = \chi(q=0, \omega \to 0)$$

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

- For $I > 1/2$ nuclei has quadruple moments which interact with electric field gradient of surrounding e^-.
  The quadruple Hamiltonian gives additional splitting of nuclei levels. (but the shift is not affected).

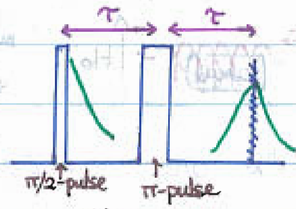
- Dynamic NMR measurements

  two rates: (1°) spin-spin relaxation $T_2^{-1} \propto h_{\parallel}(t)$ — no spin-flip, energy conserved

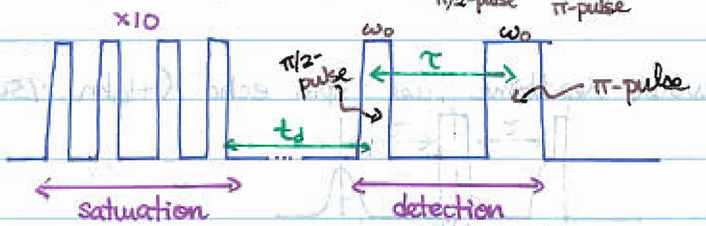
  (2°) spin-lattice relaxation $T_1^{-1} \propto h_{\perp}(t)$ — population relaxation to equilibrium

$$\Longrightarrow T_1^{-1} \propto \chi''(q=?, \omega \to 0)$$
$$T_2^{-1} \propto \chi'(q=?, \omega \to 0)$$

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

  (2°) "T_1" or Redfield processes: fluctuation of nearby e^- spin cause T_1 relaxation and provide decay for M_L. $\propto e^{-t/T_{2R}}$

  (3°) Indirect nuclear interaction:

$$\mathcal{H} \propto \sum_{r,r'} \underbrace{\vec{I}(\vec{r}_i) \cdot \vec{A}(\vec{r}_i - \vec{r})\, \chi(\vec{r}-\vec{r}')}_{\sim (\vec{I} \cdot \vec{A}) \vec{S}}\, \underbrace{\vec{A}(\vec{r}' - \vec{r}_j) \cdot \vec{I}(\vec{r}_j)}_{\sim \vec{S}(\vec{A} \cdot \vec{I})}$$

- Spin-Lattice Relaxation

$$W_{n\to m} = \frac{2\pi}{\hbar} \sum_{ee'} p(e) \left|\langle n', e' | \mathcal{H}_{hf} | n, e\rangle\right|^2 \delta(E_e + E_n - E_{e'} - E_{n'})$$

$$\Rightarrow \frac{1}{T_{1z}T} = C \sum_q \sum_{\beta = x,y,z} \left(A^2_{x\beta}(q) + A^2_{y\beta}(q)\right) \frac{\mathrm{Im}\, \chi_{\beta\beta}(q, \omega_{nn'})}{\hbar\, \omega_{nn'}}$$