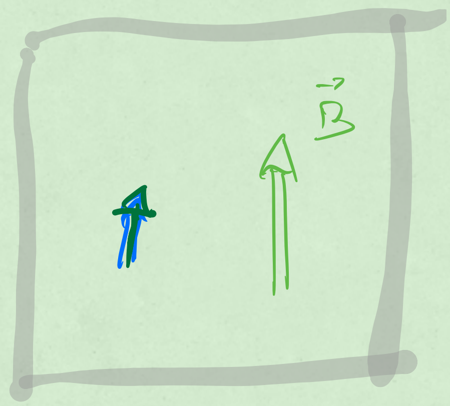
$S = \frac{1}{2}$

Lecture

19.12.2022

$$\langle \hat{O}(t) \rangle = \mathrm{Tr}\{\hat{\rho}(t)\, \hat{O}\}$$

$$\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|$$



$$|\psi(t)\rangle = a|\uparrow\rangle + b|\downarrow\rangle$$

$$\mathcal{H} = \underbrace{\Delta}_{\frac{1}{2} g \mu_B B} \hat{\sigma}^z + \Omega \hat{\sigma}^x$$

- Larmor precession – magn. resonance ESR/EPR NMR
- Quantum tunneling

time ev. density matrix

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

Larmor Precession

$$\mathcal{H} = g \mu_B B \hat{S}^z \underset{s=1/2}{=} \frac{1}{2} g \mu_B B \hat{\sigma}^z = \Delta \hat{\sigma}^z$$

Density matrix formalism I

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\mathcal{H}, \hat{\rho}] \,. \tag{1}$$

In the following we will focus on the Hamiltonian with $s = 1/2$

$$\mathcal{H} = \Delta \hat{\sigma}^z + \Omega \hat{\sigma}^x \,,$$

On the basis of eigenstates of $\hat{\sigma}^z$, $|\uparrow\rangle$ and $|\downarrow\rangle$, Eq. (1) takes the form

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \rho_{\uparrow\uparrow} & \rho_{\uparrow\downarrow} \\ \rho_{\downarrow\uparrow} & \rho_{\downarrow\downarrow} \end{pmatrix} = \overset{\mathcal{H}}{\boxed{\begin{pmatrix} \Delta & \Omega \\ \Omega & -\Delta \end{pmatrix}}} \begin{pmatrix} \rho_{\uparrow\uparrow} & \rho_{\uparrow\downarrow} \\ \underset{\downarrow\uparrow}{\rho_{\cancel{\uparrow\downarrow}}} & \rho_{\downarrow\downarrow} \end{pmatrix} - \begin{pmatrix} \rho_{\uparrow\uparrow} & \rho_{\uparrow\downarrow} \\ \underset{\downarrow\uparrow}{\rho_{\cancel{\uparrow\downarrow}}} & \rho_{\downarrow\downarrow} \end{pmatrix} \overset{\mathcal{H}}{\boxed{\begin{pmatrix} \Delta & \Omega \\ \Omega & -\Delta \end{pmatrix}}}$$

Typo!

Density matrix formalism II

$|\psi\rangle = a|\uparrow\rangle + b|\downarrow\rangle$

$\rho_{\uparrow\uparrow} = |a|^2 \quad \rho_{\downarrow\downarrow} = |b|^2$

Larmor precession $\Omega = 0$

Equations of motion ρ

Dynamics only here when $\Omega = 0$

$$i\hbar\frac{\partial}{\partial t}\rho_{\uparrow\uparrow} = -\Omega(\rho_{\uparrow\downarrow} - \rho_{\downarrow\uparrow})$$

1) $$i\hbar\frac{\partial}{\partial t}\rho_{\uparrow\downarrow} = 2\Delta\rho_{\uparrow\downarrow} - \Omega(\rho_{\uparrow\uparrow} - \rho_{\downarrow\downarrow})$$

2) $$i\hbar\frac{\partial}{\partial t}\rho_{\downarrow\uparrow} = -2\Delta\rho_{\downarrow\uparrow} + \Omega(\rho_{\uparrow\uparrow} - \rho_{\downarrow\downarrow})$$

$$i\hbar\frac{\partial}{\partial t}\rho_{\downarrow\downarrow} = \Omega(\rho_{\uparrow\downarrow} - \rho_{\downarrow\uparrow}) .$$

1) $i\hbar \frac{\partial}{\partial t}\rho_{\uparrow\downarrow} = 2 \, \frac{1}{2} \overbrace{g\mu_B B}^{\hbar\omega_L} = \rho_{\uparrow\downarrow}\hbar\omega_L$

2) $i\hbar \frac{\partial}{\partial t}\rho_{\downarrow\uparrow} = \ldots\ldots = -\rho_{\downarrow\uparrow}\hbar\omega_L$

Expectation values spin projections I

$$\langle S^\alpha(t) \rangle = \mathrm{Tr}\{\hat{\rho}(t)\,\hat{S}^\alpha\}$$

Density matrix Larmor precession

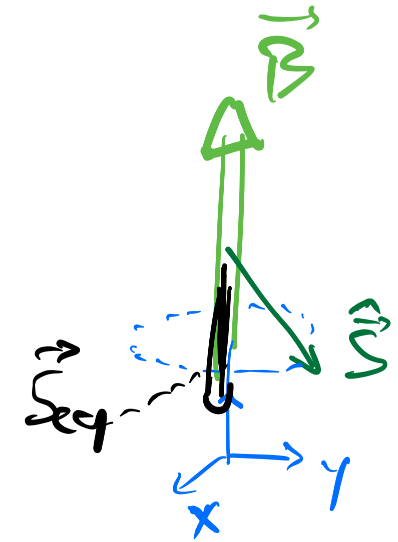
$$\hat{\rho}(t) = \begin{pmatrix} \rho_{\uparrow\uparrow,0} & \rho_{\uparrow\downarrow,0}\,\mathrm{e}^{-i\omega_{\mathrm{L}} t} \\ \rho_{\downarrow\uparrow,0}\,\mathrm{e}^{i\omega_{\mathrm{L}} t} & \rho_{\downarrow\downarrow,0} \end{pmatrix}$$

From which the average of each spin component can be computed:

$$\begin{aligned} \langle \hat{S}^x(t) \rangle &= \frac{1}{2}\,\mathrm{Tr}\left\{ \begin{pmatrix} \rho_{\uparrow\uparrow,0} & \rho_{\uparrow\downarrow,0}\,\mathrm{e}^{-i\omega_{\mathrm{L}} t} \\ \rho_{\downarrow\uparrow,0}\,\mathrm{e}^{i\omega_{\mathrm{L}} t} & \rho_{\downarrow\downarrow,0} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right\} \\ &= \frac{1}{2}\,\mathrm{Tr} \begin{pmatrix} \rho_{\uparrow\downarrow,0}\,\mathrm{e}^{-i\omega_{\mathrm{L}} t} & \rho_{\uparrow\uparrow,0} \\ \rho_{\downarrow\downarrow,0} & \rho_{\downarrow\uparrow,0}\,\mathrm{e}^{i\omega_{\mathrm{L}} t} \end{pmatrix} = \frac{1}{2}\,2\,\Re\mathrm{e}\left(\rho_{\uparrow\downarrow,0}\,\mathrm{e}^{-i\omega_{\mathrm{L}} t}\right) \end{aligned}$$

etc.

Expectation values spin projections II



generic initial state

$$|\psi(0)\rangle = a|\uparrow\rangle + b|\downarrow\rangle$$

choosing

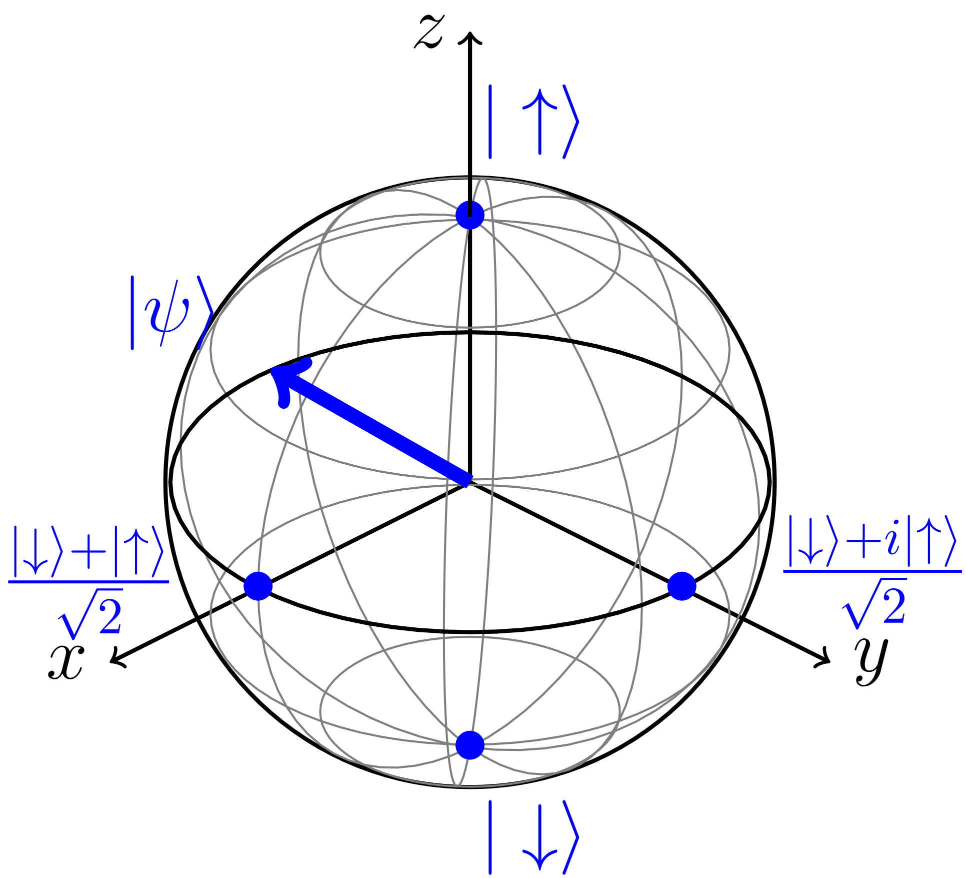
$$\begin{cases} a = \cos\left(\frac{\theta}{2}\right) \\ b = \sin\left(\frac{\theta}{2}\right) \end{cases}$$

the expectations values of the spin projections can be mapped into points on the unitary sphere

$$\begin{cases} \langle \hat{S}^x(t) \rangle = S \, \sin\theta \cos(\omega_{\rm L} t) \\ \langle \hat{S}^y(t) \rangle = S \, \sin\theta \sin(\omega_{\rm L} t) \\ \langle \hat{S}^z(t) \rangle = S \, \cos\theta \end{cases}$$

Probed in resonance experiment.
ESR or NMR

Bloch sphere

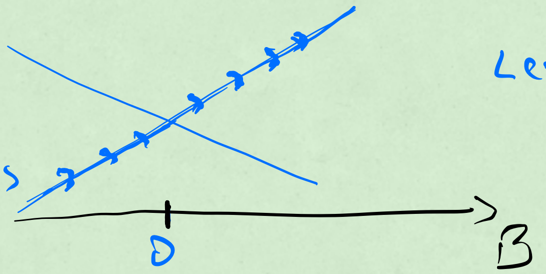


$$|\psi\rangle = \cos\left(\frac{\theta}{2}\right)|\uparrow\rangle + e^{i\phi}\sin\left(\frac{\theta}{2}\right)|\downarrow\rangle \tag{2}$$

Quantum tunneling (Landau Zener)

$$\mathcal{H} = \underbrace{\Delta(t)}_{\frac{1}{2} g \mu_B B(t)} \hat{\sigma}^z + \Omega \hat{\sigma}^x$$

$\Omega = 0$



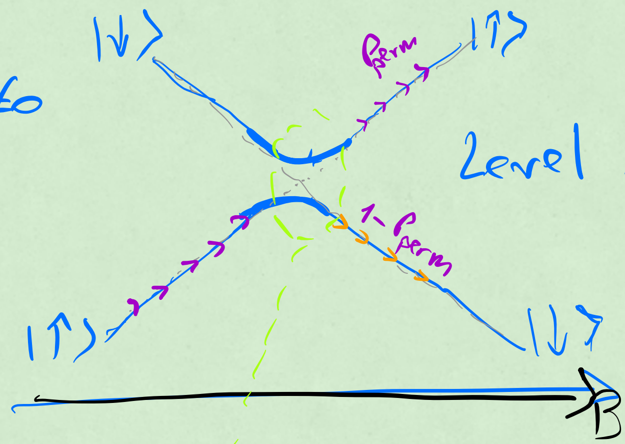
Level crossing

$|\psi(-\infty)\rangle = |\uparrow\rangle$

$t \to -\infty$ $|\psi\rangle = |\uparrow\rangle$ $\rho_{\uparrow\uparrow} = 1$

$\rho_{\alpha\beta} = 0$ otherwise

$\Omega \neq 0$



Level Anticrossing

$|\psi_\pm\rangle \sim |\uparrow\rangle \pm |\downarrow\rangle$ superposition

Eigenvalues

$$\begin{vmatrix} \Delta - \mu & \Omega \\ \Omega & -\Delta - \mu \end{vmatrix}$$

$$\mu^2 - \Delta^2 = \Omega^2$$

$$\mu = \pm \sqrt{\Delta^2 + \Omega^2} \xrightarrow[\Delta \to 0]{} \pm \Omega$$

$(B \to 0)$

$$\hat{\rho} = \begin{pmatrix} e^{-\pi\gamma_{LZ}} & \times \\ \times & 1-e^{-\pi\gamma_{LZ}} \end{pmatrix}$$

$$\gamma_{LZ} = \frac{\Omega^2}{\hbar \dot{\Delta}}$$ for our problem $\dot{\Delta} = \frac{1}{2} g \mu_B V_B$

Nor Larmor precession
nor Landau Zener (Q.T.) bring to
thermal equilibrium

$$\rho^{eq}_{th} = \begin{pmatrix} \rho^{eq}_{\uparrow\uparrow} & \emptyset \\ \emptyset & \rho^{eq}_{\downarrow\downarrow} \end{pmatrix}$$ with $$\rho^{eq}_{\downarrow\downarrow} = \frac{e^{-\beta E_{\downarrow\downarrow}}}{Z}$$

$$\rho^{eq}_{\uparrow\uparrow} = \frac{e^{-\beta E_{\uparrow\uparrow}}}{Z}$$

2 mechanism of Relaxation

$$\begin{pmatrix} \rho_{\uparrow\uparrow} & \rho_{\uparrow\downarrow} \\ \rho_{\downarrow\uparrow} & \rho_{\downarrow\downarrow} \end{pmatrix} \xrightarrow{1} \begin{pmatrix} \rho^{(t)}_{\uparrow\uparrow} & 0 \\ 0 & \rho^{(t)}_{\downarrow\downarrow} \end{pmatrix} \xrightarrow{2} \begin{pmatrix} \rho^{eq}_{\uparrow\uparrow} & 0 \\ 0 & \rho^{eq}_{\downarrow\downarrow} \end{pmatrix}$$

Thermal equilibrium

thermal averages of $\hat{S}^\alpha$ $(\alpha = x, y, z)$ for $S = 1/2$
with Hamiltonian $\mathcal{H} = g\mu_{\rm B}\vec{B}\cdot\hat{S}$

$$\langle\hat{S}^\alpha\rangle_{\rm th} = \frac{1}{\mathcal{Z}}\mathcal{T}_{\sigma}r\left\{\langle\sigma|\hat{S}^\alpha {\rm e}^{-\beta\mathcal{H}}|\sigma\rangle\right\} = \frac{1}{\mathcal{Z}}\sum_{\sigma=\pm 1}{\rm e}^{-\beta\hbar\omega_L\sigma/2}\langle\sigma|\hat{S}^\alpha|\sigma\rangle$$

$$\begin{cases} \langle\hat{S}^x\rangle_{\rm th} = 0 \\ \langle\hat{S}^y\rangle_{\rm th} = 0 \\ \langle\hat{S}^z\rangle_{\rm th} = -\frac{1}{2}\tanh\left(\frac{1}{2}\beta g\mu_{\rm B}B\right) = -\frac{1}{2}\tanh\left(\frac{1}{2}\beta\hbar\omega_L\right) \ . \end{cases}$$

Time evolution of “spin populations”

stochastic magnetization per spin as

$$M^z(t) = g\mu_{\mathrm{B}} S\,[P_\downarrow(t) - P_\uparrow(t)] = g\mu_{\mathrm{B}} S\, n(t)$$

$$\dot{n} = (\nu_\uparrow - \nu_\downarrow) - (\nu_\uparrow + \nu_\downarrow) n$$

$$\Rightarrow \text{ solution } n(t) = n^{\mathrm{eq}} + n_0\, \mathrm{e}^{-t/T_1}$$

relaxation time

$$\frac{1}{T_1} = \nu_\downarrow + \nu_\uparrow$$

and the difference between equilibrium populations

$$n^{\mathrm{eq}} = \frac{\nu_\uparrow - \nu_\downarrow}{\nu_\uparrow + \nu_\downarrow} = \frac{\mathrm{e}^{\beta\hbar\omega_L} - 1}{\mathrm{e}^{\beta\hbar\omega_L} + 1} = \tanh\left(\frac{1}{2}\beta\hbar\omega_L\right)$$

Spin-lattice T_1 and spin-spin relaxation T_2

Eq. motion of ρ with phenomenological relaxation terms for $\Omega = 0$

$$\begin{aligned}
\frac{\partial}{\partial t}\rho_{\uparrow\uparrow} &= -\nu_{\uparrow}\rho_{\uparrow\uparrow} + \nu_{\downarrow}\rho_{\downarrow\downarrow} \\
\frac{\partial}{\partial t}\rho_{\uparrow\downarrow} &= -i\omega_{\mathrm{L}}\rho_{\uparrow\downarrow} - T_2^{-1}\rho_{\uparrow\downarrow} \\
\frac{\partial}{\partial t}\rho_{\downarrow\uparrow} &= i\omega_{\mathrm{L}}\rho_{\downarrow\uparrow} - T_2^{-1}\rho_{\downarrow\uparrow} \\
\frac{\partial}{\partial t}\rho_{\downarrow\downarrow} &= -\nu_{\downarrow}\rho_{\downarrow\downarrow} + \nu_{\uparrow}\rho_{\uparrow\uparrow}\,.
\end{aligned}$$

The density matrix with $T1$ and T_2

$$\rho_{\sigma,\sigma'} = \begin{pmatrix} \cos^2\left(\frac{\theta}{2}\right) - \frac{1}{2}\left(n^0 - n^{\mathrm{eq}}\right)\mathrm{e}^{-t/T_1} & \sin\left(\frac{\theta}{2}\right)\cos\left(\frac{\theta}{2}\right)\mathrm{e}^{-i\omega_{\mathrm{L}}t}\mathrm{e}^{-t/T_2} \\ \sin\left(\frac{\theta}{2}\right)\cos\left(\frac{\theta}{2}\right)\mathrm{e}^{i\omega_{\mathrm{L}}t}\mathrm{e}^{-t/T_2} & \sin^2\left(\frac{\theta}{2}\right) + \frac{1}{2}\left(n^0 - n^{\mathrm{eq}}\right)\mathrm{e}^{-t/T_1} \end{pmatrix}$$

yields the averaged spin components

$$\begin{cases} \langle \hat{S}^x(t)\rangle = S\,\sin\theta\cos(\omega_{\mathrm{L}}t)\,\mathrm{e}^{-t/T_2} \\ \langle \hat{S}^y(t)\rangle = S\,\sin\theta\sin(\omega_{\mathrm{L}}t)\,\mathrm{e}^{-t/T_2} \\ \langle \hat{S}^z(t)\rangle = -S\,n(t) = -S\left[n_{eq}(T) + \left(n(0) - n_{eq}(T)\right)e^{-t/T_1}\right] \end{cases}$$

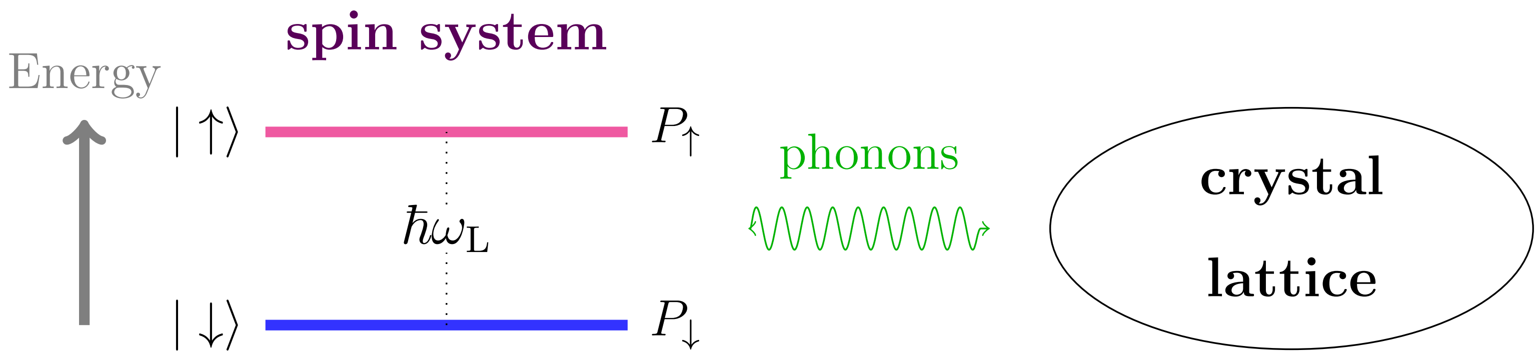
T_2 spin spin relax. time

with $S = 1/2$ in the present case.

T_1 spin-lattice relax. time.

Spin-lattice relaxation time T_1

$$\dot{M}^z = \frac{M^{z,\mathrm{eq}} - M^z}{T_1}$$



Spin-spin relaxation time T_2

$$\dot{M}^x = -\frac{1}{T_2} M^x$$

$$\dot{M}^y = -\frac{1}{T_2} M^y$$

$T_2 \sim 1/(\gamma B_\mathrm{loc})$ in the range of 100 μs for NMR experiments

Bloch equation

two relaxation terms plus spin precession:

$$\dot{M}^x = -\frac{1}{T_2} M^x - \gamma \left(\vec{M} \times \vec{B} \right)^x$$
$$\dot{M}^y = -\frac{1}{T_2} M^y - \gamma \left(\vec{M} \times \vec{B} \right)^y$$
$$\dot{M}^z = \frac{M^{z,\mathrm{eq}} - M^z}{T_1} - \gamma \left(\vec{M} \times \vec{B} \right)^z$$

VIDEO MRI: https://www.youtube.com/watch?v=1CGzk-nV06g

MAGNETIC RESONANCE TIME SCALES

$$\omega_L = g\frac{\mu_B B}{\hbar}$$

ESR $B \simeq 0.35\,T$

$$\mu_B = \frac{e\hbar}{2m_e} = 9.27 \cdot 10^{-24}\,\frac{J}{T}$$

$$\hbar \sim 10^{-34}\,J \cdot s$$

$$\omega_L^{ESR} \simeq 10\,GHz \Rightarrow T^{ESR} \simeq 10^{-10}\,s$$

NMR $\mu_B \longleftrightarrow \mu_N = \dfrac{e\hbar}{2m_p}$

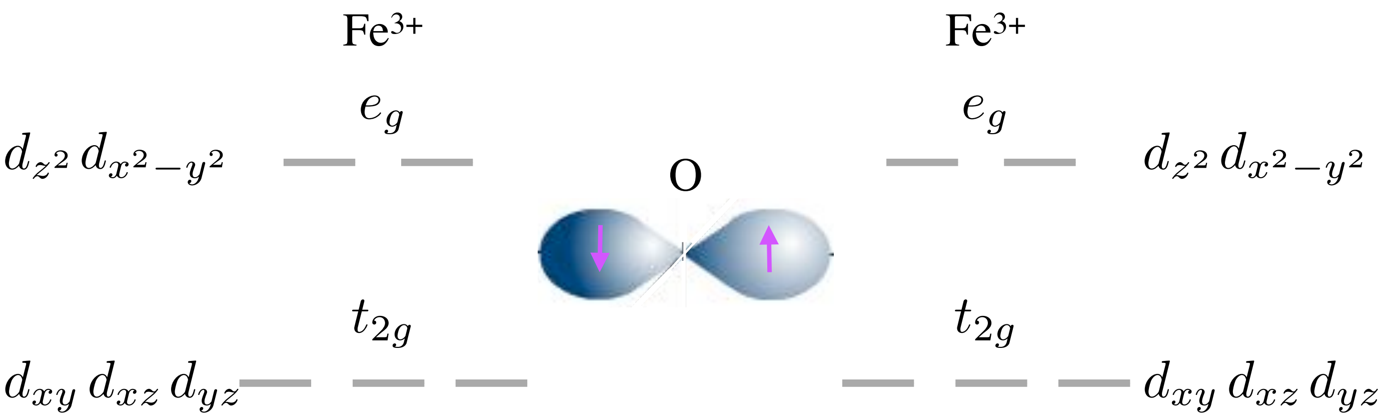
$$\frac{\omega_L^{NMR}}{\omega_L^{ESR}} \approx \frac{g_p}{g_e}\frac{\mu_N}{\mu_B} = \frac{g_p}{g_e}\frac{m_e}{m_p} \approx \frac{g_p}{g_e}\frac{1}{2000}$$

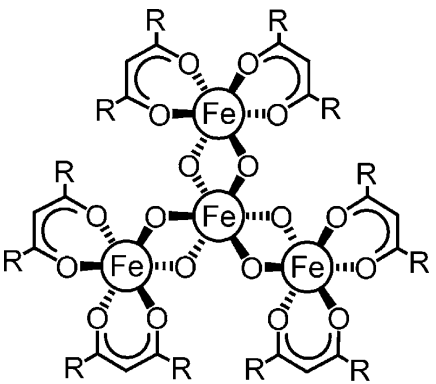
$$\omega_L^{NMR} = 100\,MHz \Rightarrow T^{NMR} \simeq 10^{-8}\,s$$

Spin Hamiltonian of the Fe4 cluster

Example Exam

- Assuming an O_h crystal field, determine the S of eachFe^{3+} ion





- Determine the sign (FM or AM) of the exchange interaction between two neighboring Fe^{3+} ions (see structure on the right)

- Referring to the Hamiltonian

$$\mathcal{H}_{\text{eff}} = -J\,\hat{\mathbf{S}}_1 \cdot \left(\hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_4\right)$$

determine the g.s. multiplet $\hat{\mathbf{S}}^{\mathrm{T}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_4$

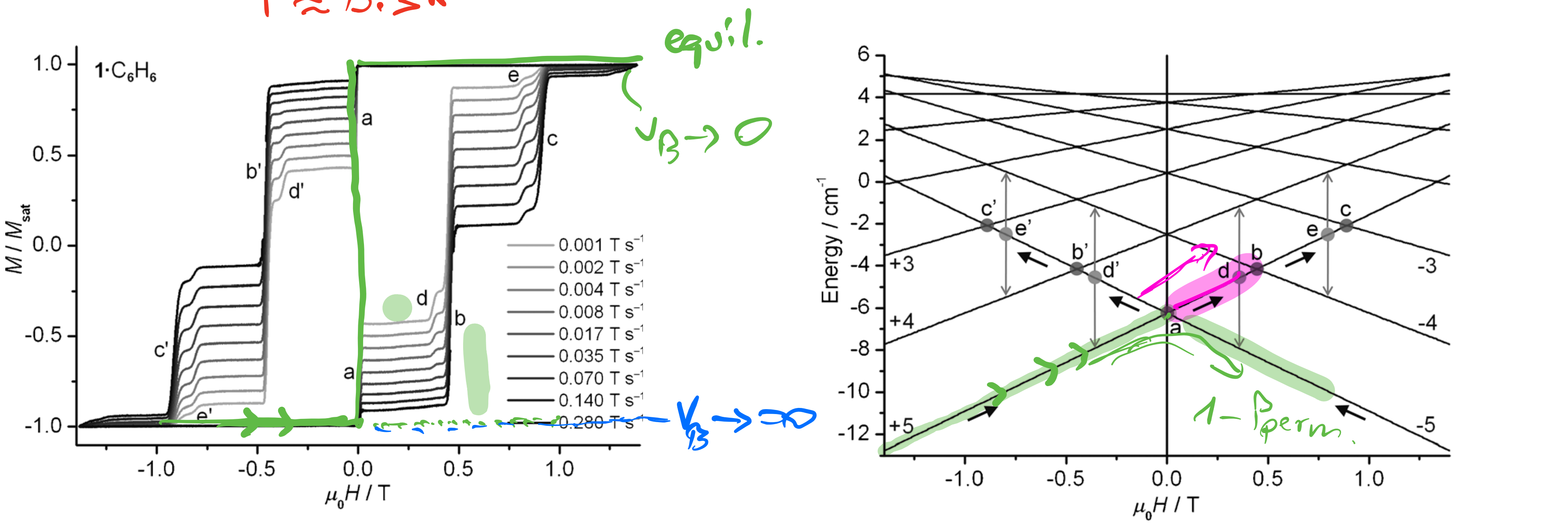
- Based on what you have determined above, explain with your own words why the Hamiltonian

Example Exam

$$\mathcal{H}_{\rm eff} = -D\left(\hat{\mathbf{S}}_z^{\rm T}\right)^2 + 2\mu_B\, B\, \hat{\mathbf{S}}_z^{\rm T}$$

produces the scheme of levels of the figure on the right panel

$T \approx 0.5\,K$



Taken from L. Vergnani *et al.* Chem. Eur. J. **18** 3390 (2012).

- Relate the level crossing to the steps observed in the magnetization curve of the Fe4 molecule.

Bloch vs stochastic LLG equation

Relaxation

th. noise

- **Stochastic LLG** $\dot{\vec{S}} = -\vec{S} \times \left\{ \gamma \left[\vec{B}^{\mathrm{eff}} + \vec{B}^{\mathrm{rnd}}(t) \right] + \alpha \, \dot{\vec{S}} \right\}$

  Gilbert damping

  stochastic magnetization $\vec{M}(t)$ obtained from many realizations of noise $\vec{B}^{\mathrm{rnd}}(t)$

$$\Uparrow$$

$$\boxed{\langle \dot{\hat{\mathbf{S}}} \rangle_{\mathrm{QM}} = -\gamma \, \langle \hat{\mathbf{S}} \rangle_{\mathrm{QM}} \times \vec{B}}$$

$$\Downarrow$$

- **Bloch equation** $\dot{\vec{M}} = -\gamma \vec{M} \times \vec{B} + T_{1,2}^{-1} \left(\vec{M}^{\mathrm{eq}} - \vec{M}(t) \right)$

  deterministic equation for the stochastic magnetization $\vec{M}(t)$