

SQ 11

We only consider normal Zeeman effect.

$$\vec{S} = 0 \Rightarrow \vec{\mu} = \vec{\mu}_L = -\frac{e}{2m_e} \vec{L}$$

$$\hat{H}_{\text{Zeeman}} = (-\vec{\mu}_L \cdot \vec{B}_{\text{ext}})$$

$$= \frac{e}{2m_e} \vec{L} \cdot \vec{B}_{\text{ext}}$$

$$E_{\text{Zeeman}}^{(1)} = \frac{e\hbar}{2m_e} B_{\text{ext}} m_l$$

$$= E' m_l$$

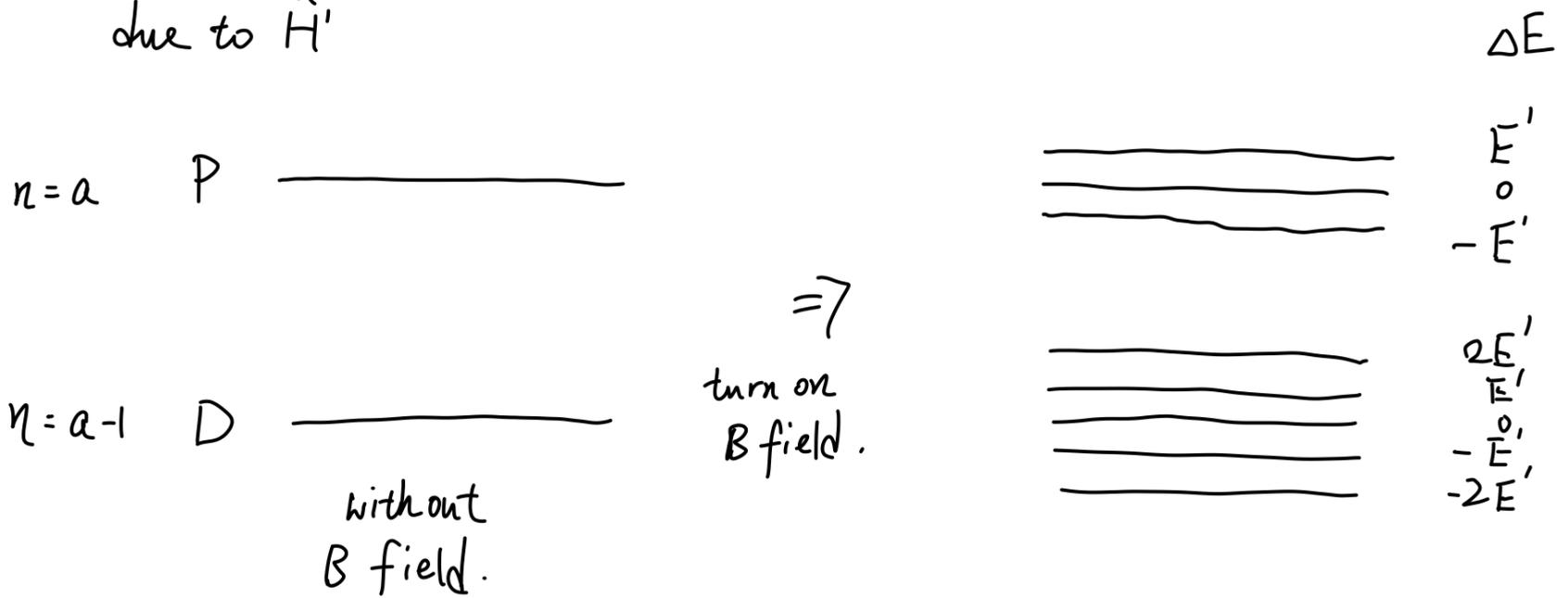
$$= \frac{e}{2m_e} \hat{L}_z B_{\text{ext}} \quad (\text{without loss of generality, we assume B field is in z direction})$$

Now consider an upper P level and lower D level.

P level:  $l=1 \Rightarrow m_l = 1, 0, -1$

D level:  $l=2 \Rightarrow m_l = 2, 1, 0, -1, -2$

Under an external B field, The two levels is split into multiple levels due to  $\hat{H}'$



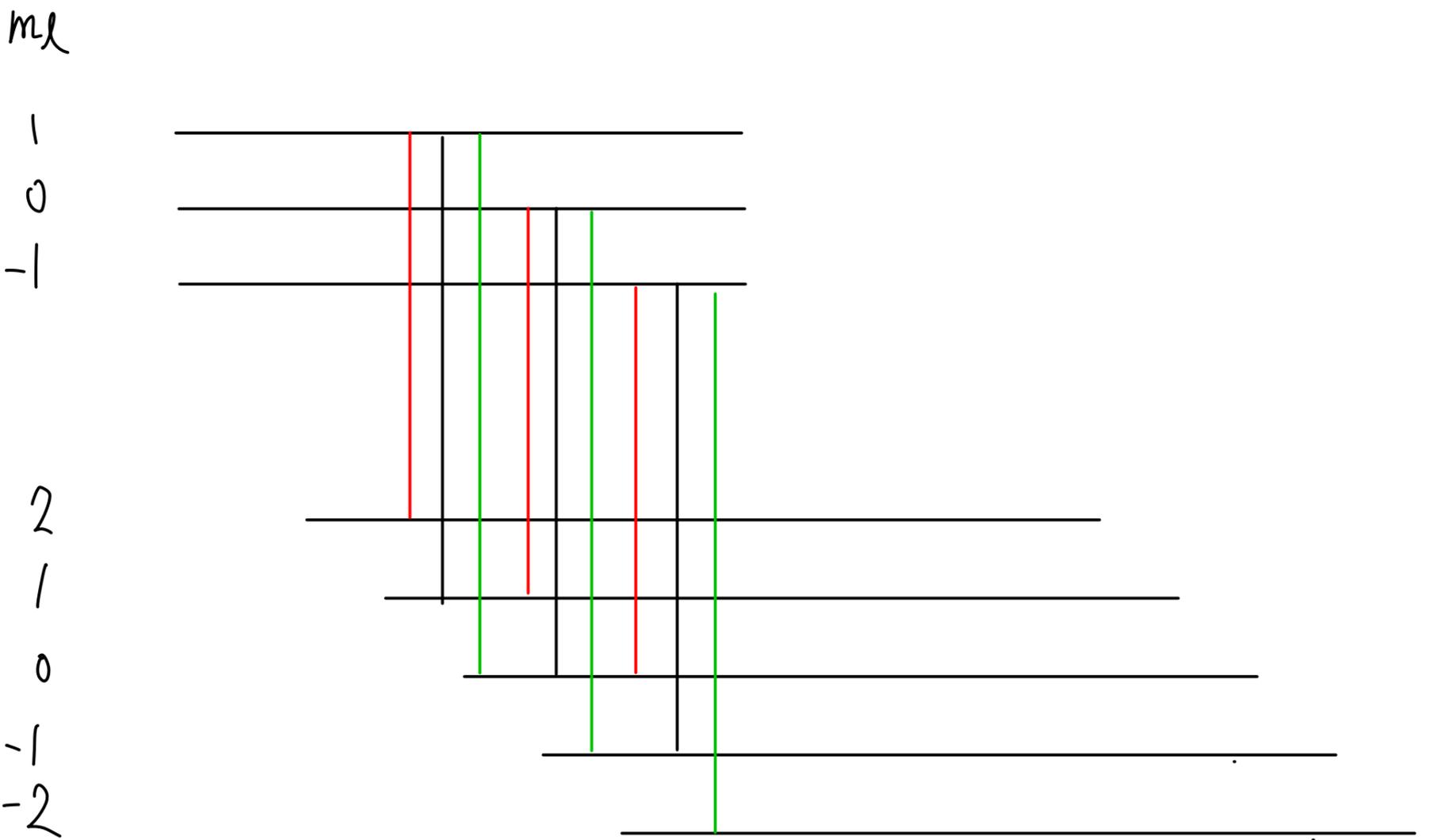
The energy difference of two levels:

$$E_P - E_D = E_a - E_{a-1} + E'(m_P - m_D) \quad \text{where } m_P \text{ and } m_D \text{ are the } m_l \text{ of P level and D level}$$

$$= \Delta E + E' \Delta m_l$$

Here  $\Delta E$  is the 'normal' transition energy, depend only on quantum number  $n$ . Substitute  $\Delta m_l = 0, \pm 1$ , we immediately see that there are two spectral line besides the normal line which corresponds to  $\Delta E$ .

# Supplementary graph



$$E_p - E_D = \Delta E + \begin{cases} +E' \\ 0 \\ -E' \end{cases}$$

In fact it also works for jumping up  
from D to P

SQ12

Consider Na atom as an effective H atom.

We know the  $B_{int}$  would cause a splitting:  $E_3 \longrightarrow \begin{array}{c} \text{---} \\ \text{---} \end{array} \updownarrow 2\mu_B B_{int}$ .

From lab, we know the energy difference from the two spectral lines.

$$\Delta E = hc \left( \frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right) = 2\mu_B B_{int}$$

$$\frac{hc}{2\mu_B} \left( \frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right) = B_{int}$$

$$\frac{1239.841 \text{ nm}}{2 \cdot 5.78838 \cdot 10^{-5} \text{ eV T}^{-1}} \left( \frac{1}{588.995 \text{ nm}} - \frac{1}{589.592 \text{ nm}} \right) = B_{int}$$

$$B_{int} = 18.1034 \text{ Tesla}$$

# SQ13

a)  $a_0 = 5.29 \times 10^{-11} \text{ m}$

$m_e = 9.109 \times 10^{-31} \text{ kg}$

$e = 1.602 \times 10^{-19} \text{ C}$

$E_h = 4.360 \times 10^{-18} \text{ J}$

$1 \text{ h of } L = 1.055 \times 10^{-34} \text{ J s}$

$= 1.055 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$

$4\pi\epsilon_0 = 1.113 \times 10^{-10} \text{ F}\cdot\text{m}$

b)  $E_h = 27.2 \text{ eV}$

$= 2 \times 13.6 \text{ eV}$  related to ground state energy of hydrogen

c) i)  $E_h$  (eV per atom)

$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

$= 1.602 \times 10^{-22} \text{ kJ}$

$1 \text{ mol} = N_A \text{ atoms}$

$1 \text{ atom} = \frac{1}{N_A} \text{ mol} =$

$\therefore E_h$  (eV per atom)

$= 27.2 \cdot 1.602 \times 10^{-22} \cdot \frac{1}{6.022 \times 10^{23}} \text{ (kJ mol}^{-1}\text{)}$

$= 27.2 \times 1.602 \cdot 60.22 \text{ (kJ mol}^{-1}\text{)}$

$= 2624 \text{ (kJ mol}^{-1}\text{)}$

ii) From i),  $1 \text{ eV} = 1.602 \cdot 60.22 = 96.5 \text{ kJ/mol} \approx 100 \text{ kJ/mol}$  worth remembering

$5.1 \text{ eV} = 5.1 \cdot 96.5 = 492 \text{ (kJ mol}^{-1}\text{)}$

$$d) \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

$$\text{Since } \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

$$\text{make } x, y, z \text{ dimensionless } \Rightarrow \begin{aligned} x' &= \frac{x}{a_0} \\ y' &= \frac{y}{a_0} \\ z' &= \frac{z}{a_0} \end{aligned}$$

$$\begin{aligned} r' &= \sqrt{x'^2 + y'^2 + z'^2} \\ &= \frac{r}{a_0} \end{aligned}$$

$$\begin{aligned} \text{New } \nabla'^2 &= \frac{\partial^2}{\partial x'^2} + \frac{\partial^2}{\partial y'^2} + \frac{\partial^2}{\partial z'^2} \\ &= a_0^2 \nabla^2 \end{aligned}$$

$$-\frac{\hbar^2}{2ma_0^2} \nabla'^2$$

$$\text{Recall bohr radius } a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$$

$$\begin{aligned} \frac{\hbar^2}{ma_0^2} &= \frac{\hbar^2}{m_e a_0} \frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} \\ &= \frac{e^2}{4\pi\epsilon_0 a_0} = E_h \end{aligned}$$

$$\begin{aligned} \therefore \hat{H} &= -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \\ &= -\frac{E_h}{2} \nabla'^2 - \frac{E_h}{r'} \end{aligned}$$

$$\frac{\hat{H}}{E_h} = \hat{H} \text{ (atomic units)} = -\frac{1}{2} \nabla'^2 - \frac{1}{r'} \quad \text{which is now dimensionless}$$