Atomic energy levels (cont)

Each stationary state in H-atom is characterized by 3 quantum numbers

Principle quantum number n : $E_n = -\frac{E_R}{n^2}$

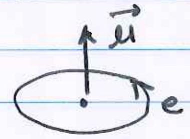
Total angular momentum quantum number $\ell = 0, \ldots n-1$

$\langle L^2 \rangle = \hbar^2 \ell(\ell+1)$

Azimuthal (or magnetic) quantum number $m = 0, \pm 1 \ldots \pm m$

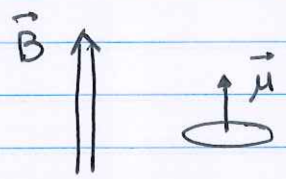
$\langle L_z \rangle = \hbar m$

Classical magnetic moment



$\vec{\mu} = -\frac{e}{2m_e} \vec{L}$

Potential energy $U_m = -\vec{\mu} \cdot \vec{B} = +\frac{e}{2m} \vec{L} \cdot \vec{B}$



if $\vec{B} \uparrow\uparrow$ z-axis

$U_m = -\frac{e}{2m} L_z \cdot B$

In a classical situation $\vec{\mu} \uparrow\uparrow \vec{B}$ to minimize potential energy

Quantum case — angular momentum length and z-component are quantized.
How to figure out what applied magnetic field does to energy levels.

Classical energy expression for electron inside the atom

$$E = \frac{p^2}{2m} - \frac{ke^2}{r} + \frac{e}{2m_e} L_z \cdot B$$

kinetic — Coulomb — magnetic

Quantum Hamiltonian

$$\hat{H}\psi = \underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{ke^2}{r}\psi}_{\text{H-atom at zero magnetic field. original Hamiltonian } \hat{H}_0\psi} + \frac{e}{2m_e}B\hat{L}_z\psi = \hat{H}_0\psi + \frac{e}{2m_e}B\hat{L}_z$$

H-atom at zero magnetic field.
original Hamiltonian $\hat{H}_0\psi$

We can use the same eigenstates! ψ_{nlm}

$$\hat{H}_0\psi_{nlm} = E_n^{(0)}\psi_{nlm} \qquad E_n^{(0)} = -\frac{E_R}{n^2}$$

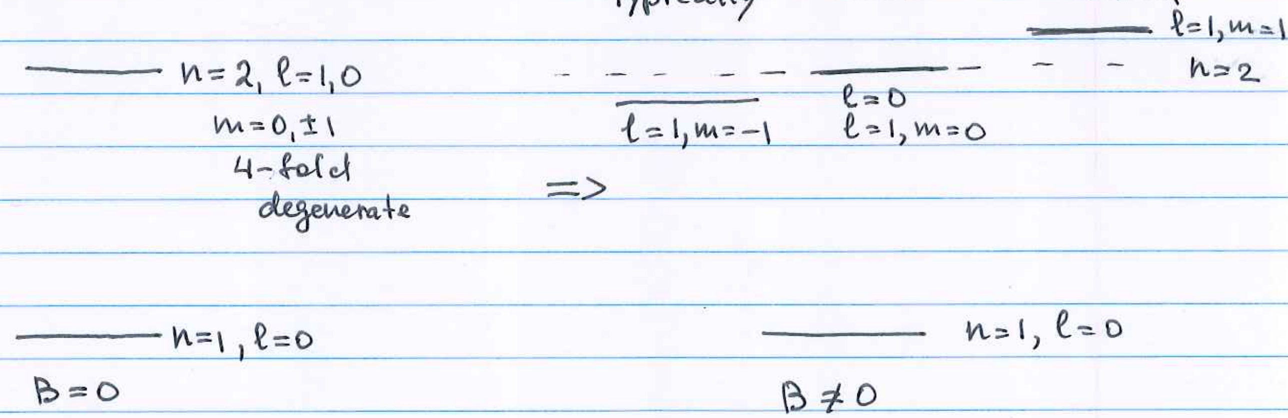
$$E^{(new)}\psi_{nlm} = \left(\hat{H}_0 - \frac{e}{2m}B\hat{L}_z\right)\psi_{nlm} = \hat{H}_0\psi_{nlm} + \frac{e}{2m_e}B\hat{L}_z\psi_{nlm}$$

$L_z\psi_{nlm} = \hbar m\psi_{nlm}$

$$E_{n,m}^{(new)}\psi_{nlm} = -\frac{E_R}{n^2}\psi_{nlm} + \frac{\hbar e}{2m_e}Bm\psi_{nlm}$$

$$E_{n,m}^{(new)} = -\frac{E_R}{n^2} + \underbrace{\frac{\hbar e}{2m_e}Bm}_{\text{typically small correction}}$$

typically small correction



Optical transitions : $\hbar\omega = E_i - E_f$; $\hbar\omega_{2\to1} = E_2^{(new)} - E_1$

B = 0: only one frequency $\hbar\omega_{21} = -\frac{E_R}{4} - (-E_R) = \frac{3E_R}{4}$

B ≠ 0: three possible transitions, depending on m ~~of~~ value of the excited state

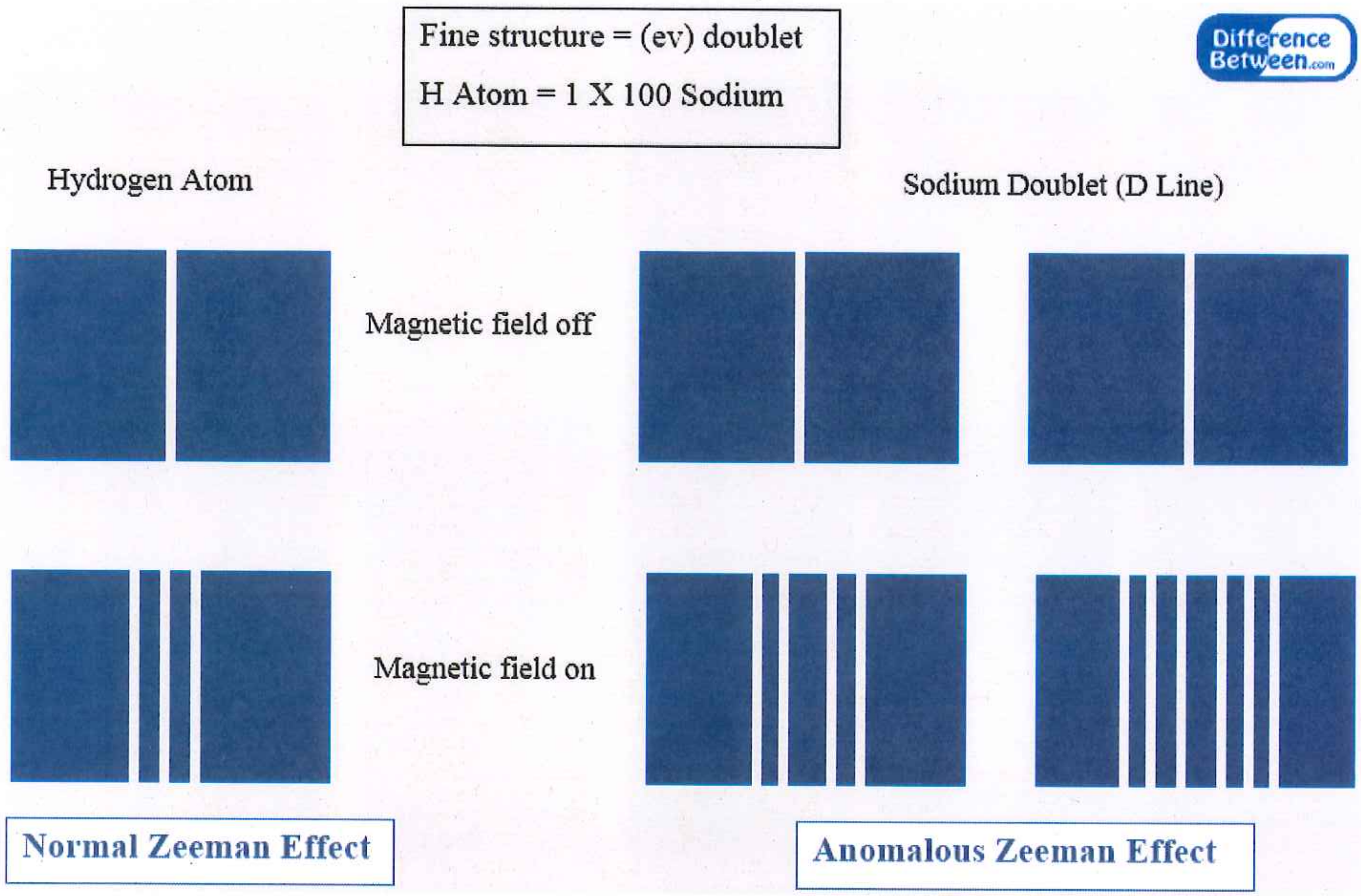
$$\hbar\omega = \frac{3E_R}{4} \text{ (if } m_i = 0) ; \quad \frac{3E_R}{4} + \frac{\hbar e}{2m_e}B \quad (m_i = 1)$$

$$\frac{3E_R}{4} - \frac{\hbar e}{2m_e}B \quad (m_i = -1)$$

There are certain selection rules, that only allow photon emission b/w states with $\Delta l = \pm 1$ ~~&~~ and $\Delta m = 0, \pm 1$ (these are consequences of the angular momentum conservation, photon angular momentum ~~is~~ can only be $\hbar \cdot 1$)

Thus, we would expect to see only three spectral lines when magnetic field is applied.

Normal Zeeman effect.


Fine structure = (ev) doublet
H Atom = 1 X 100 Sodium
Hydrogen Atom
Sodium Doublet (D Line)
Magnetic field off
Magnetic field on
Normal Zeeman Effect
Anomalous Zeeman Effect

Internal electron magnetic momentum – electron spin

It turned out, however, that situation is more complex, and the magnetic moment depends not only on the orbital angular momentum, but on something else → spin angular momentum

$$\vec{\mu}_{total} = \vec{\mu}_L + \vec{\mu}_s$$

orbital   spin, intrinsic to an electron

$$\vec{\mu}_{total} = -\frac{e}{2m_e}\vec{L} - \frac{e}{m}\vec{S}$$

Electron (proton, neutron) – spin 1/2 particles

$$\langle \vec{S}^2 \rangle = \hbar^2 s(s+1) = \frac{3}{4}\hbar^2 \quad \text{since } s = \frac{1}{2}$$

$$S_z = \hbar m_s \qquad m_s = \pm 1/2$$

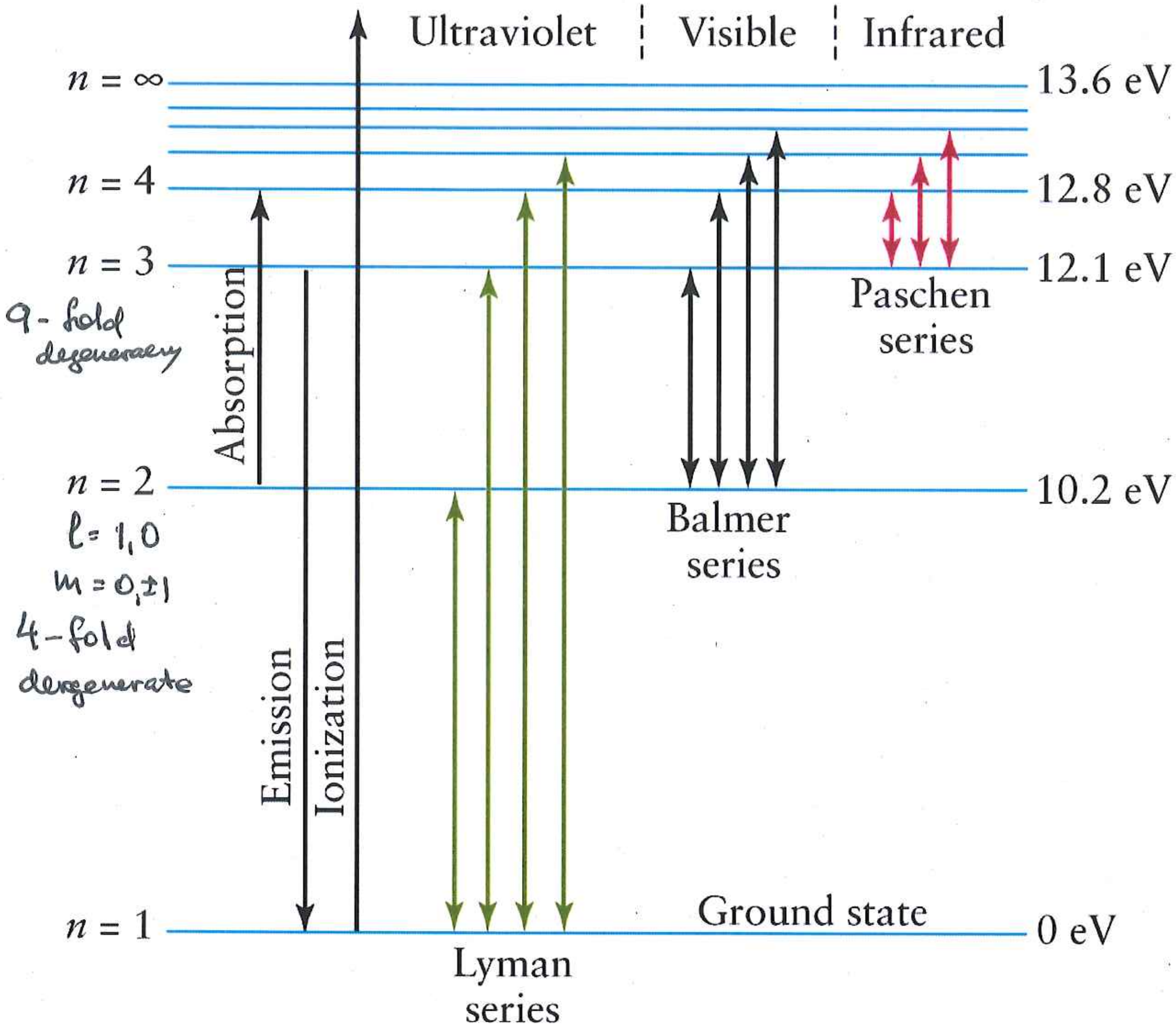
~~Energy shift~~ Energy shift $\Delta E_{m_\ell, m_s} = \left(\frac{e\hbar}{2m_e}\right)(m_\ell + 2m_s)B$

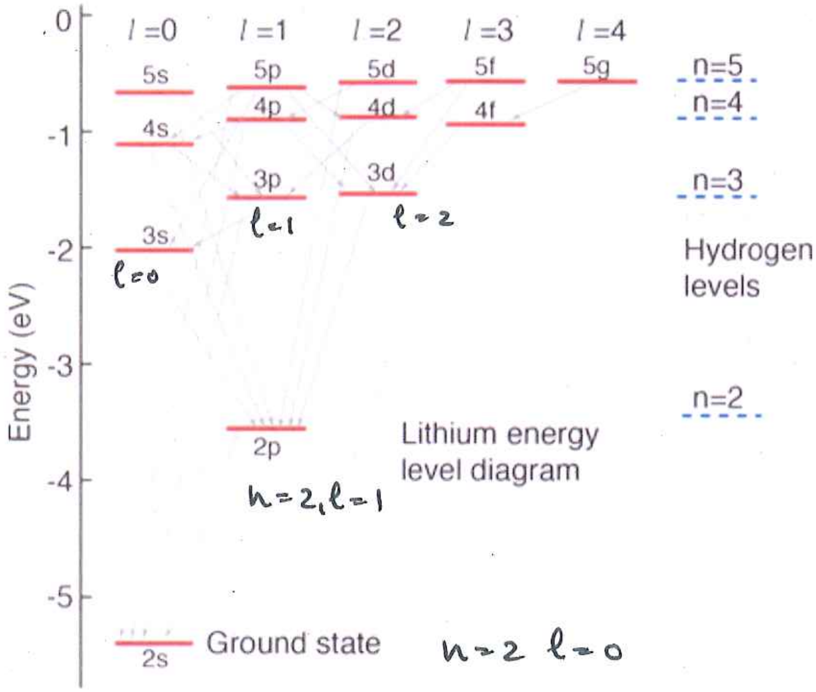
μ_B, Bohr's magneton

We also now need to characterize the ~~wav~~ quantum state with the spin quantum numbers!

$\Psi_{n,\ell,m_\ell,s,m_s}$

↑ always 1/2 for an electron


Ultraviolet
Visible
Infrared
$n = \infty$
13.6 eV
$n = 4$
12.8 eV
$n = 3$
12.1 eV
9-fold degeneracy
Absorption
Paschen series
$n = 2$
10.2 eV
$l = 1, 0$
$m = 0, \pm 1$
4-fold degenerate
Balmer series
Emission
Ionization
$n = 1$
Ground state
0 eV
Lyman series



l=0 – S(harp)
l=1 – P(rinciple)
l=2 – D(iffuse)
l=3 – F(undamental)
l=4 – G
⋮

Selection rules

$\Delta l = 1$ or -1

$\Delta m = 0, \pm 1$