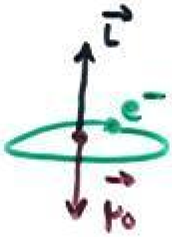
Chapter 9

Because of its orbital motion round the nucleus, the electron has an orbital magnetic moment $\vec{\mu}$ given by

$$\vec{\mu}_0 = -\frac{e}{2m_e}\vec{L}$$



Because $\vec{L}$ is quantized so is $\vec{\mu}_0$

$$\mu_z = -\frac{e\hbar}{2m_e} m_\ell = -\mu_B m_\ell$$

Bohr magneton

also $$|\vec{\mu}_0| = \mu_B\sqrt{\ell(\ell+1)}$$

If an external magnetic field is applied to the atom $\vec{\mu}_0$ will precess around the field direction.

The angular precession frequency is

$$\omega_L = \frac{eB}{2m_e} \Leftarrow \text{Larmor frequency}$$

$\frac{e}{2m_e}$ is called the gyromagnetic ratio.

The magnetic moment acquire an energy

$$U = -\vec{\mu}_0 \cdot \vec{B}$$

if $\vec{B}$ is along the z-axis: $U = \frac{eB}{2m_e} L_z$

$$\underbrace{U = \hbar\omega_L}_{\text{Zeeman energy}} m_\ell$$ ← it is quantized!

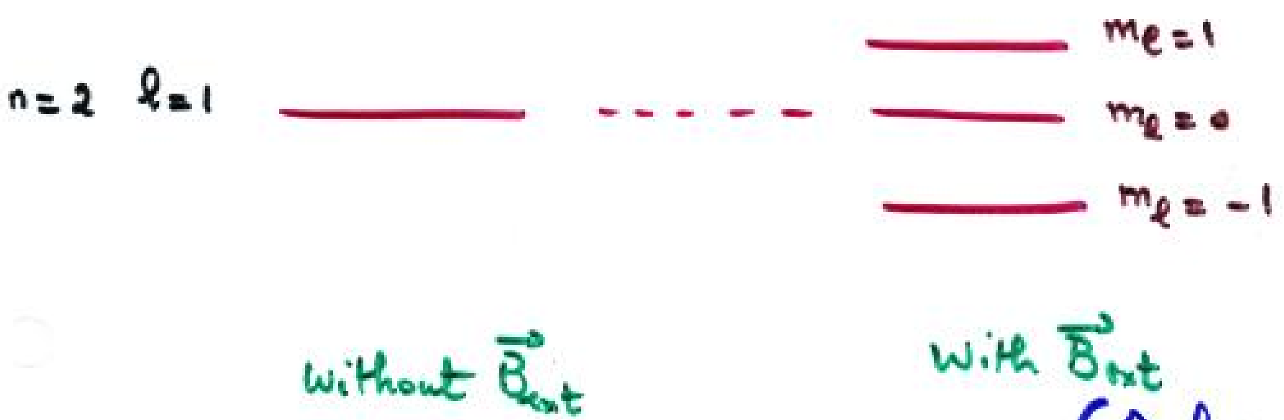
The total energy of the electron is

$$E = \underbrace{E_0}_{\text{without } \vec{B}_{ext}} + \underbrace{\hbar\omega_L m_\ell}_{\text{because of } \vec{B}_{ext}}$$

Example:

$n=2 \longrightarrow \ell=0 \quad m_\ell=0$ and $\ell=1 \quad m_\ell=0,\pm1$

$$E = E_2 + \hbar\omega_L m_\ell$$



$\Rightarrow$ Transitions occur only when $\begin{cases} \Delta\ell = \pm 1 \\ \Delta m_\ell = 0, \pm 1 \end{cases}$

Because of its spinning motion, the electron possesses a spin angular momentum $\vec{S}$ and a spin magnetic moment $\vec{\mu}_s$ related by

$$\vec{\mu}_s = -\frac{e}{2m_e} g \vec{S}$$

Lande factor

The existence of the spin moment was demonstrated by Stern and Gerlach in 1921.

It was found that the spin quantum number $s = \frac{1}{2}$

Both $\vec{S}$ and S_z are quantized.

spin up

$$|\vec{S}| = \sqrt{s(s+1)}\,\hbar = \frac{\sqrt{3}}{2}\hbar$$

spin down

$$S_z = m_s \hbar \qquad m_s = \pm \frac{1}{2}$$

$$\Rightarrow \quad S_z = \pm \frac{\hbar}{2}$$

The total magnetic moment is

$$\vec{\mu} = \vec{\mu}_o + \vec{\mu}_s = -\frac{e}{2m_e}\left(\vec{L} + g\vec{S}\right)$$

orbital

spin

The total angular momentum

$$\vec{J} = \vec{L} + \vec{S}$$

Note that $\vec{\mu}$ and $\vec{J}$ don't have the same direction! (because of g)

The component of $\vec{\mu}$ along $\vec{J}$ is reffered to as the effective magnetic moment (μ_{eff})

Now if $\vec{B}_{ext}$ exist, $\vec{\mu}$ will have a potential energy $U = -\vec{\mu} \cdot \vec{B}_{ext}$

total magnetic moment!

$\vec{B}$ along the z-axis:

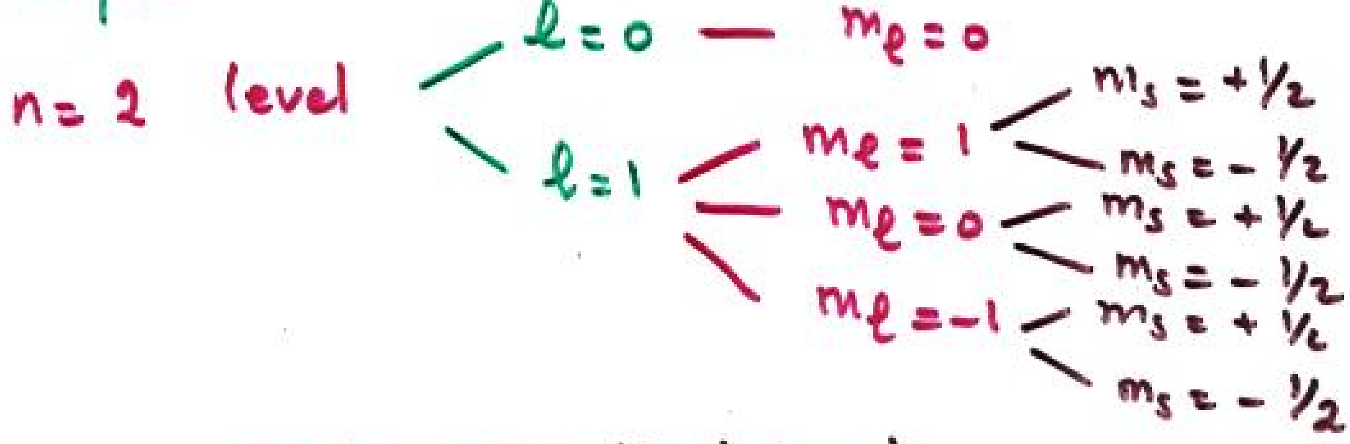
$$U = \omega_L \hbar m_\ell + \omega_L \hbar g m_s$$

$$-\ell \leq m_\ell \leq \ell \quad \text{and} \quad m_s = \pm \frac{1}{2}$$

The energy level will be split first because of $\underline{\underline{m_\ell}}$ and then because of $\underline{\underline{m_s}}$

For electron $g = 2$!

Example



Allowed transitions to n = 2 level must follow the selection rule $\Delta(m_\ell + m_s) = 0, \pm 1$!!!

Let us calculate U for $m_\ell = 1$ and $m_s = -1/2$

$$U = \omega_L \hbar \left(1 - 2 \times \frac{1}{2}\right) = 0$$

The energy of the electron will be E_2!

If $m_\ell = -1$ and $m_s = -1/2$

$$U = \hbar \omega_L \left(-1 - 2 \times \frac{1}{2}\right) = -2\hbar\omega_L$$

The energy of the electron will be

$E_2 - 2\hbar\omega_L$!

The interaction between $\vec{\mu}_s$ and $\vec{\mu}_o$ is called "spin-orbit interaction".

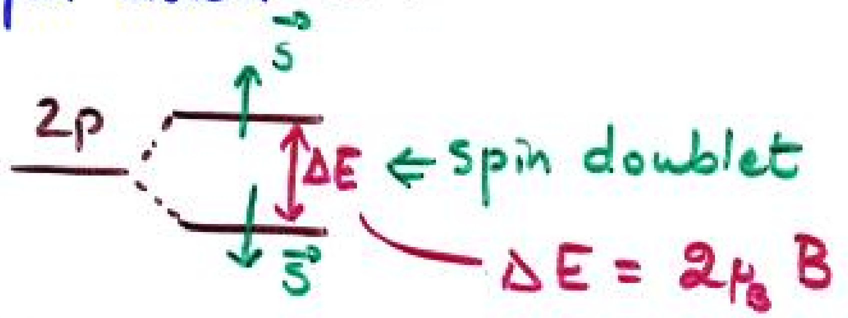
There is no spin-orbit interaction for $l=0$ states (s-states).

The spin moment acquire an energy

$$U = -\vec{\mu}_s \cdot \vec{B}_{int.}$$

$\vec{B}_{int.}$ due to the orbital motion of the electron.

The spin up electron will have higher energy than the spin down ($\vec{\mu}_s$ and $\vec{S}$ have opposite directio[ns])



The transition $2p \to 1s$ is plit into two lines.

The total-angular momentum $\vec{J} = \vec{L} + \vec{S}$ and its component along the z-axis J_z are both quantized

$$|\vec{J}| = \sqrt{j(j+1)}\,\hbar \qquad \begin{cases} j = \frac{1}{2} & (l=0) \\ j = l \pm \frac{1}{2} & (l>0) \end{cases}$$

$$J_z = m_j \hbar \qquad -j \le m_j \le j$$

It is important to understand that the existance of m_ℓ and m_s can be seen by the splitting of the energy levels when an external magnetic field is applied to the atom.

If there is <u>no</u> external magnetic field the level <u>does not</u> split !!!

However we will see that there is a splitting due to the coupling of $\vec{L}$ and $\vec{S}$. It is called "spin-orbit interaction" and results in splitting of energy levels into a doublet ! It exist in the abscence of an external magnetic field !

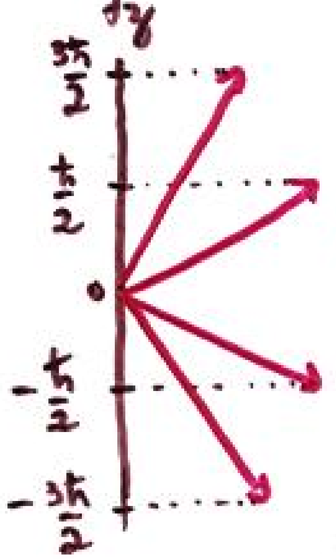
Example

$n = 2 \quad l = 1 \Rightarrow j = 1 + \frac{1}{2} = \frac{3}{2} \longrightarrow 2P_{3/2}$ ← $j = l + s$

and $j = 1 - \frac{1}{2} = \frac{1}{2} \longrightarrow 2P_{1/2}$ ← $j = l - s$

$n \quad l$

$j = 3/2$



$J = \frac{\sqrt{15}}{2}\hbar$

even number of orientations for $\vec{J}$!

Pauli exclusion principle states that no two electrons in an atom can have the same set of quantum number, that is same n, l, m_l and m_s.

Reason being electrons are identical particles!!!

All known particles are either fermions or bosons.

The wavefunctions for fermions are antisymmetric

$$\psi(r_1, r_2) = -\psi(r_2, r_1)$$

The wavefunctions for bosons are symmetric

$$\psi(r_1, r_2) = \psi(r_2, r_1)$$

Electrons, protons, and neutrons are fermions

Photons, pions, and gluons are bosons

Fermions are $\frac{1}{2}$ integral spin, only one per state.

Bosons are integral spin, many can occupy the same state.

For more than one electron atoms, the energy levels differ from those of the hydrogen atom because of the "screening effect".

$$E_n = \frac{-13.6\ (eV)}{(n - D(\ell))^2}$$

↑ quantum defect. It varies with ℓ (shell #)

From the exclusion principle, the maximum # of e^- in one subshell is $2(2\ell+1)$.

The order of filling the subshell levels with e^- follows the minimum energy principle.

Hund's rule states that e^- usually fill different orbitals with unpaired spins.

Example

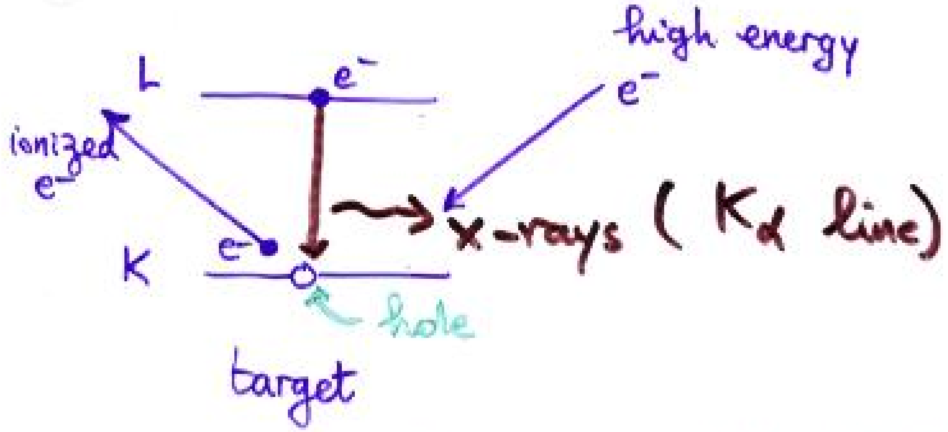
	1s	2s	2p			
B	↑↓	↑↓	↑			$1s^2\,2s^2\,2p^1$
			$2p_{1/2}$			
C	↑↓	↑↓	↑	↑		$1s^2\,2s^2\,2p^2$
			2p orbitals			
Ne	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2\,2s^2\,2p^6$
						Chemically inert atom!

The chemical properties of atoms are determined by the valence (outer) electrons.

The ionization energy is the energy necessary to remove one e^- from the outer filled subshell.

It is low when there is one e^- in the subshell and increases with increase in # of e^- in the subshell.

If a metal target is bombarded with high energy electrons then X-rays photons are emitted according to:



If a hole is formed in the K shell, electrons from outer shells fill this hole and we have the K-series of X-rays ; K_α, K_β, K_γ, ...

If a hole is formed in the L shell, electrons from outer shells fill the hole and we have the L-series of X-rays, L_α, L_β, L_γ, ...

K_α is from $L \to K$	L_α is from $M \to L$
K_β is from $M \to K$	L_β is from $N \to L$
K_γ is from $N \to K$	L_γ is from $O \to L$
$\vdots$ $\vdots$	$\vdots$ $\vdots$

The energy of the photon for a K_α transition is

$$E_{K_\alpha} = -13.6\,(Z-1)^2\left(\frac{1}{4}-\frac{1}{1}\right) = 10.2\,(Z-1)^2\,(eV)$$

The wavelength is

$$\lambda_{K_\alpha} = \frac{hc}{E_{K_\alpha}} = \frac{12400\ eV.\mathring{A}}{10.2\,(Z-1)^2\,eV}$$