Ch 11.5

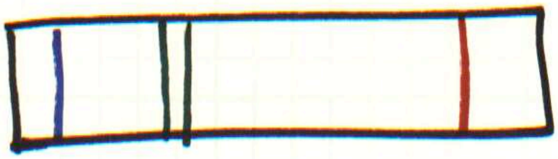
Spectroscopy:

Continuous spectrum: The sun, ligh bulb, ...

Descrete spectrum: gas discharge tubes...

Cont.

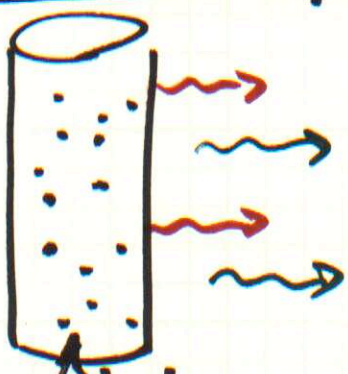
400nm 700c



Desc.

Each element has its own descrete spectrum.

Emission Spectra:



H, He, ...

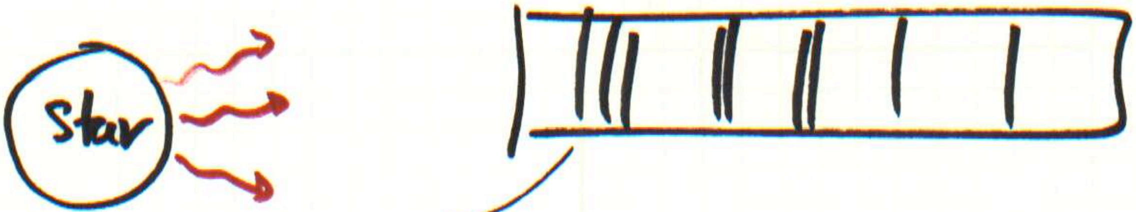
produce their own descrete spectrum

~~based on~~

Hot Gas

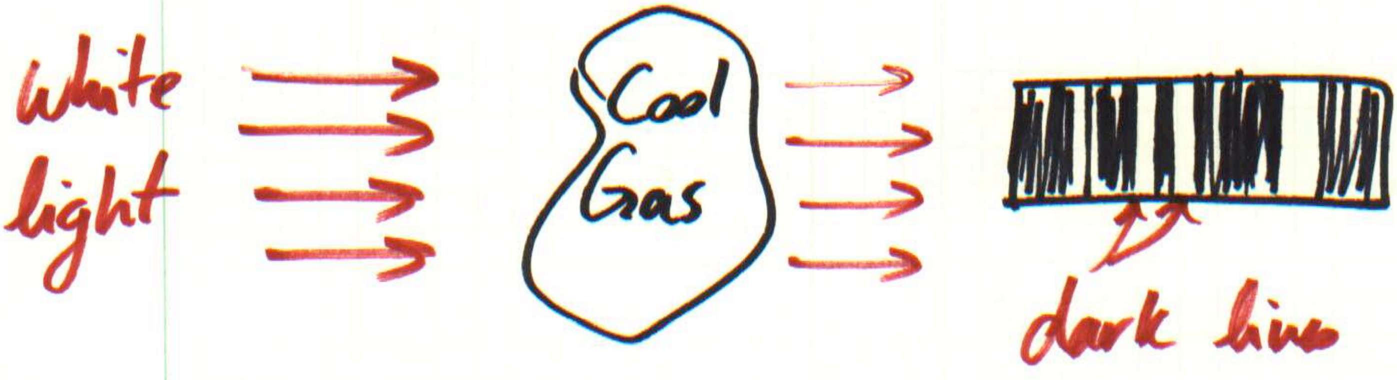
⇒ No two atoms have the same spectra

⇒ Emission spectra is used for atom identification



by studying the emission spectra of a star one can find the elements that are present in that star

Absorption Spectra



Balmer Series

1885 → four visible emission lines of t

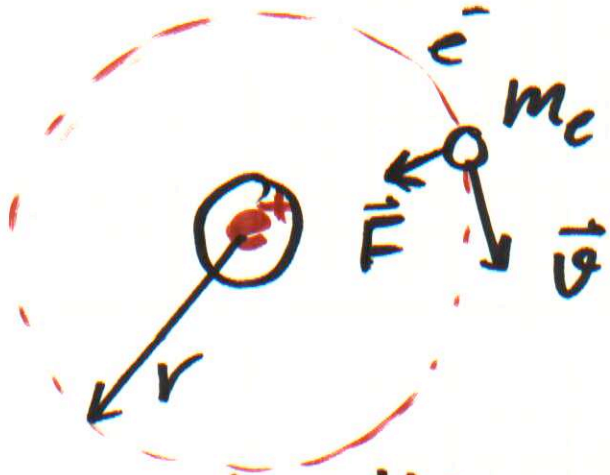
$$\boxed{\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2}\right)} \qquad n = 3, 4, \ldots$$

$R_H = 1.097 \times 10^7 \ m^{-1}$
Rydberg const.

Bohr's theory of H:

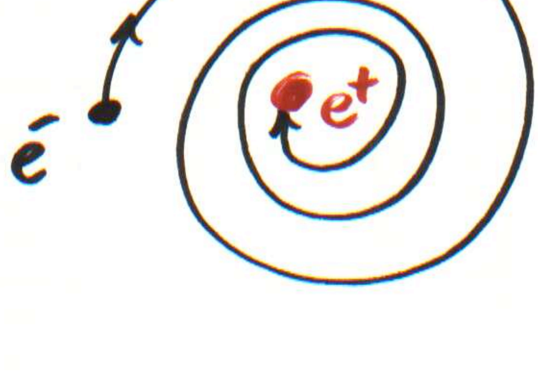
1913 → explanation of atomic spectra

* This model included both classical & non-classical ideas
* He applied Planck's idea of quantization



e^- goes around the ~~nucle~~ proton in a circular orbit.

- e^- is only found in specific orbits:
  * No energy emission in these orbits
  * E of atom remains const.
  * Centripetal acceleration of e^- does not emit E & eventually spiral in



* Emission only happens when e^- goes from a higher energy level to a lower one

$$\boxed{E_i - E_f = hf}$$

Size of allowed orbits is determined for those w/ e^- ang. mom. about the nucleus is an int. multiple of $\hbar = \frac{h}{2\pi}$:

$$\boxed{m_e v r = n\hbar \quad ; \quad n = 1, 2, 3, \dots}$$

Total E of the atom

$$E = K + U = \frac{1}{2} m_e v^2 - k_e \frac{e^2}{r}$$

or $$E = -\frac{k_e e^2}{2r}$$

bound e^--proton system

Radii of Bohr's orbits:

$$\boxed{r_n = \frac{n^2 \hbar^2}{m_e k_e e^2} \quad n = 1, 2, 3, \cdots}$$

* Radii are also quantized
* $n=1 \longrightarrow$ Bohr's radius $\equiv a_0 = \dfrac{\hbar^2}{m_e k_e e^2}$

$= 0.0529$ nm

$$\Longrightarrow \boxed{r_n = n^2 a_0}$$

Energy of any orbit:

$$\boxed{E_n = -\frac{ke^2}{2a_0}\left(\frac{1}{n^2}\right)} \qquad n = 1, 2, 3, \ldots$$

or

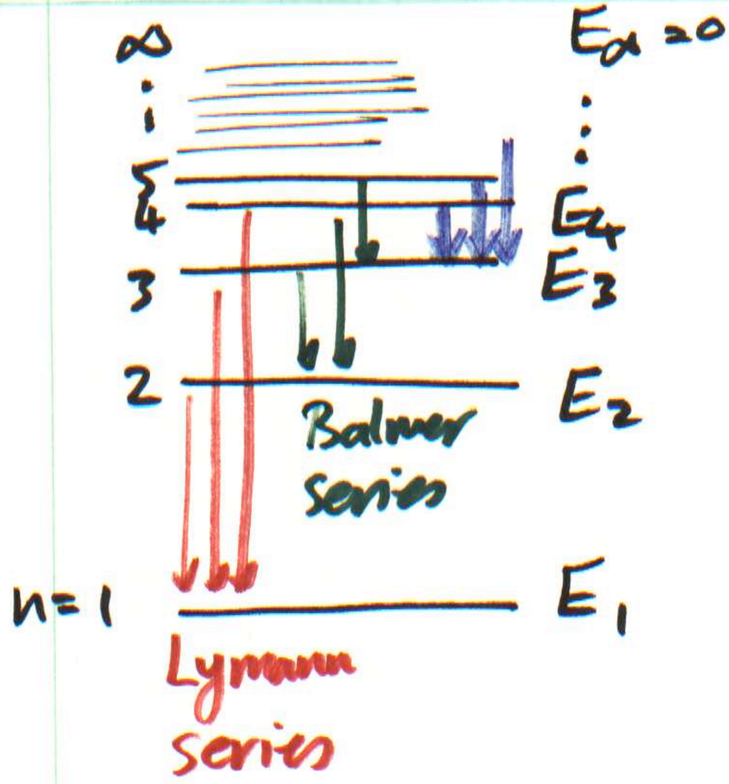
$$\boxed{E_n = \frac{-13.606 \text{ eV}}{n^2}}$$

Only specific energy values are allowed.

$n = 1 \Longrightarrow$ ground state $\quad E_1 = -13.606$ eV

Ionization Energy:
E need to completely remove an e^- from the atom

I.E. for H atom: $+13.606$ eV



Frequency of emitted photons:

$$\boxed{f = \frac{E_i - E_f}{h} = \left(\frac{k_e e^2}{2a_0 h}\right)\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)}$$

or

$$\frac{1}{\lambda} = \frac{f}{c} = \left(\frac{k_e e^2}{2a_0 hc}\right)\left(\frac{1}{n_f^2} - \frac{1}{n_f^2}\right) = R_H\left(\frac{1}{R_f^2} - \frac{1}{R_i^2}\right)$$

Chapter 29 Atomic Physics

H-atom → only atom that can be solved exactly

H-atom's model can be used to study He^{+}, and Li^{2+}

Hydrogen Model:

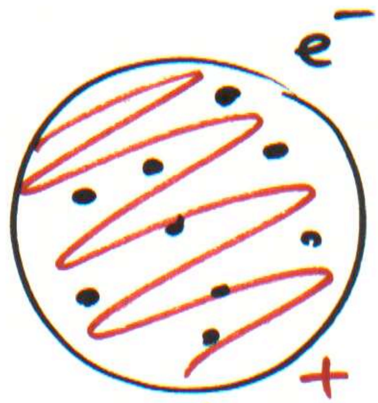
- ideal sys. to match theory & experiment
- quantum # used to investigate more complex atoms
- Simplest atom to be understood before more complex ones

Early Atom Models

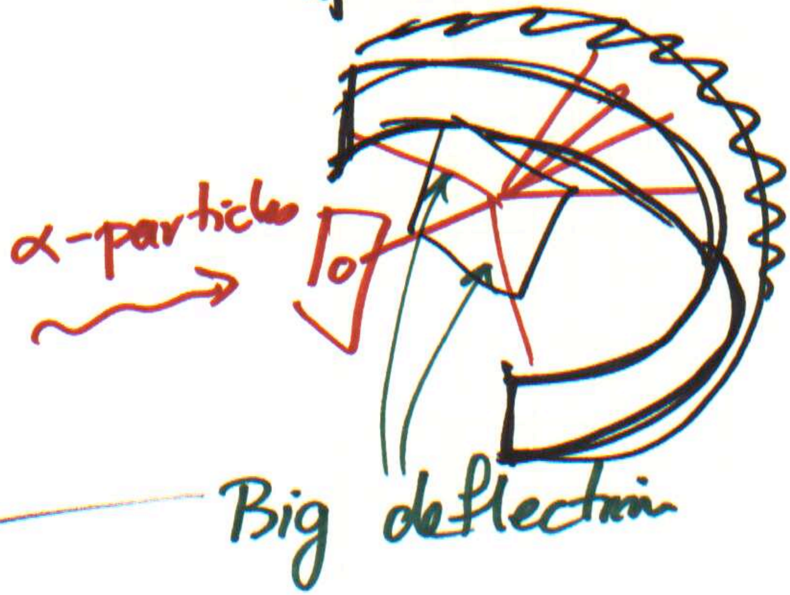
Tiny, structureless sphere

⇒ used in theory of gases

J. J. Thompson:

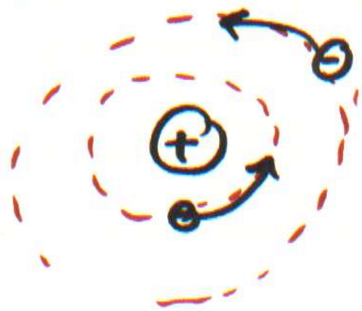


Rutherford's thin foil experiment:



Could not be explained using Thompson's model

Rutherford $\longrightarrow$ planetary model



* This was based on the results of thin foil scattering.

This model could not explain:

- Discrete ~~em~~ emitted frequencies
- e^- emission and decrease of it's orbits radius

Bohr's model:

* Classical or non-classical ideas
* ~~Energy~~ Quantized energy levels
* Stable non-radiating orbits
* Explanation for discrete spectra

Problems:

* Some spectra lines could be split into more
* In presence of B field also splitting happens

Mathematical Desc. of H.

Shrödinger's eqn → desc. of H-atom

→ determine the allowed func. & E of atom

Hyd. atom → 3D system

→ 3 quatum #s

→ +1 for ang. mom.

$$U(r) = -k_e \frac{e^2}{r}$$

$$\xrightarrow{\text{Allowed } E} \quad E_n = -\left(\frac{k_e e^2}{2a_0}\right)\frac{1}{n^2}$$

$$= \frac{-13.606\ eV}{n^2} \qquad n = 1, 2 \cdots$$

Boundry Cond.

→ Orbital quatum # l

→ Orbital magnetic quatum # m_l

1st q. #

~~ξ~~ → radial func.

a.k.a. principle q. #

n

* $U(r)$ only depends on n ~~...~~ E_n

* Allowed $E \to E_n$

l → Orbital q. #

~~...~~ Ass. w/ orbital ang. mom.

an integer

m_l → * Orbital mag. ~~q~~. #

* ass. w/ ang. orbital mom. of e^-

* integer

$n = 1, 2, \ldots, \infty$

$l = 0, 1, 2, \ldots, n-1$

$m_l = -l, -l+1, \ldots, l-1, l$

e.g. for $n=2$:

$$\rightarrow l = 0, 1$$

$$m_l = -1, 0, 1$$

States w/ same n → form a <u>shell</u>

Shells are identified by

K, L, M, …

States w/ same l → subshells

s, p, d, f, g, h, …

for $l = 0, 1, 2, \ldots$

Wave Function of Hyd.

Simplest $\rightarrow$ 1st state

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

As $r \rightarrow \infty$ $\quad \psi_{1s}(r) \rightarrow 0$

ψ_{1s} is sph. sym.

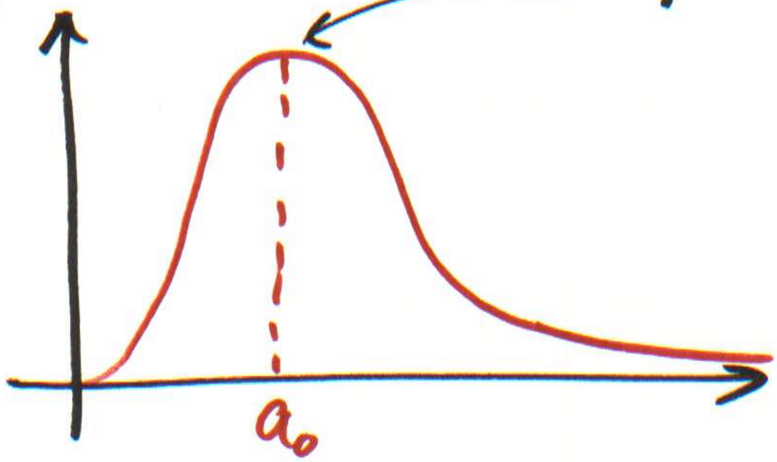
$\Rightarrow$ Prob. density $|\psi_{1s}|^2 = \left(\frac{1}{\pi a_0^3}\right) e^{-2r/a_0}$

$\xrightarrow{P(r)}$ the prob. of finding the e^- in a spherical shell of radius $\underline{r}$ & thickness $\underline{dr}$

$$P(r) = 4\pi r^2 |\psi^2|$$

$$P_{1s}(r) = \left(\frac{4r^2}{a_0^3}\right) e^{-2r/a_0}$$

most prob.



Ave for ground state $= \frac{3}{2} a_0$

$\Rightarrow$ Atom has no sharp edges (unlike Bohr's model)

$\psi_{1s} \longrightarrow$ describes an e^- cloud

charge of $\bar{e}$ is not localized

* e^- cloud diff from Bohr's model
* e^- cloud structure doesn't change over time
* radiation happens when atom goes from a higher state to a lower state

---

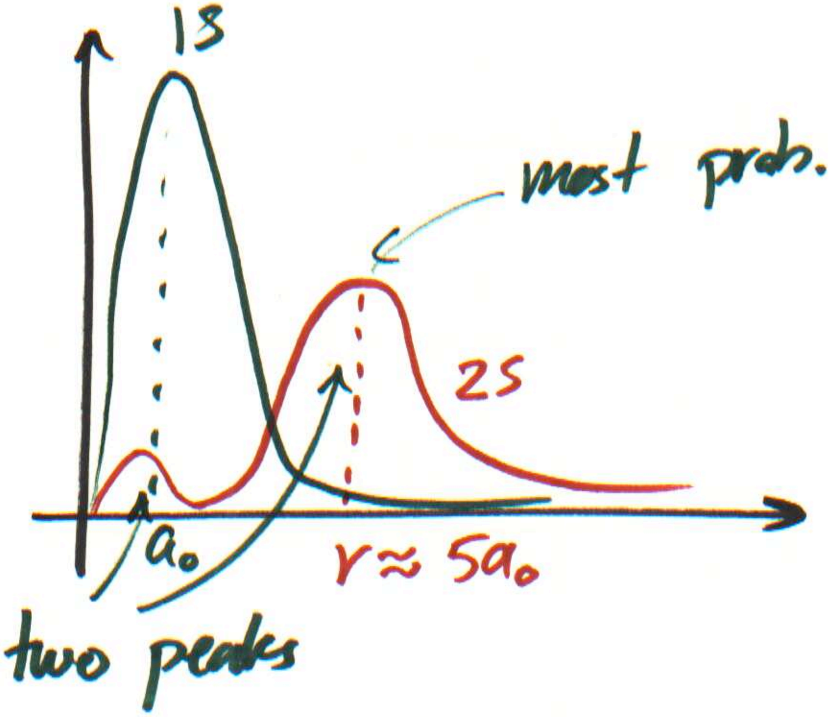
Next simplest model:

$n=2$; $l=0$

$$\psi_{2s}(r) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$$

$\psi_{2s}(r)$ only dep. on r

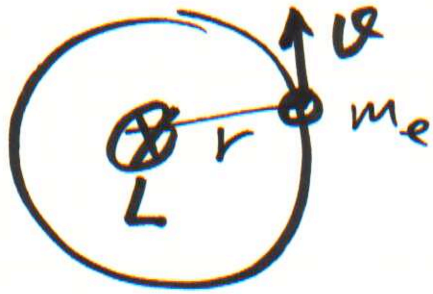
& sph. symm.



Physical Interpretation of l:

Ang. mom. of e^- in circular motion:

$$L = m_e v r$$



$\vec{L} \perp$ plane of circle

Ang. mom. $\longrightarrow$ int. multiples of $\hbar$

in quantum mech.

$$\longrightarrow |\vec{L}| = L = \sqrt{\ell(\ell+1)}\,\hbar$$

$$\ell = 0, 1, 2, \dots, n-1$$

$L = 0 \xrightarrow{\text{means}}$ sph. symm. state w/ no axis of rotation

Physical Interpretation of m_ℓ:

* Orbital ang. mom. of atom
* Ang. mom $\longrightarrow$ vector
  $\Longrightarrow$ has a specific direction
* Orbiting e^- $\longrightarrow$ effective current loop w/ mag. moment.

* direction of ang. mom. relative to an axis is quantized

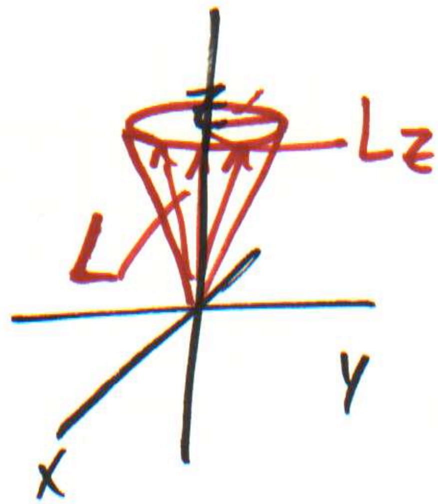
$\Rightarrow L_z$ can only have discrete values

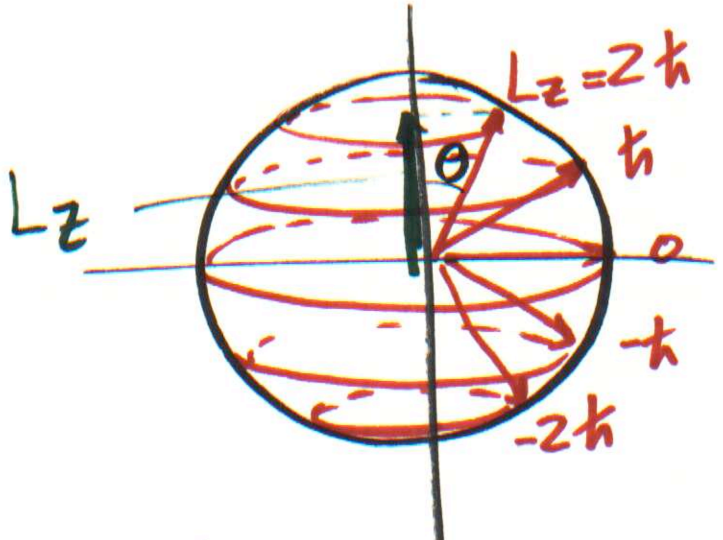
$\Rightarrow m_l$ specifies the allowed values of L_z

* $L_z = m_l \hbar$

* $\vec{L}$ does not point is specific direction

Although L_z is fixed





$$\cos\theta = \frac{L_z}{|\vec{L}|} = \frac{m_\ell}{\sqrt{\ell(\ell+1)}}$$

$m_\ell < \ell$

L is never parallel to z-axis

Spin Quantum Number m_s:

* Not from Schrödinger equ.
* Additional states by having a 4th q. #

$m_s \longrightarrow$ spin magnetic q. #

Spin only has two directions

up (↑) & down (↓)

* In presence of mag. field the E of e^- is diff for ~~[illegible]~~ spin ↑ & ↓

$\Rightarrow$ doublets in spectra of some gases

no $B=0$ $B \neq 0$

* e^- is not physically spinning
* Spin is an intrinsic characteristic of e^-
* $S = -\frac{1}{2}, \frac{1}{2}$
* spin ang. mom. of the e^- never changes

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

$\Rightarrow$ Spin ang. mom. has two orientation

$m_s = \pm 1/2$ $\oplus \rightarrow \uparrow$

$\ominus \rightarrow \downarrow$

Allowed val. of z-comp. of spin

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

$\Rightarrow$ Spin ang. mom. $\rightarrow$ quantized

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

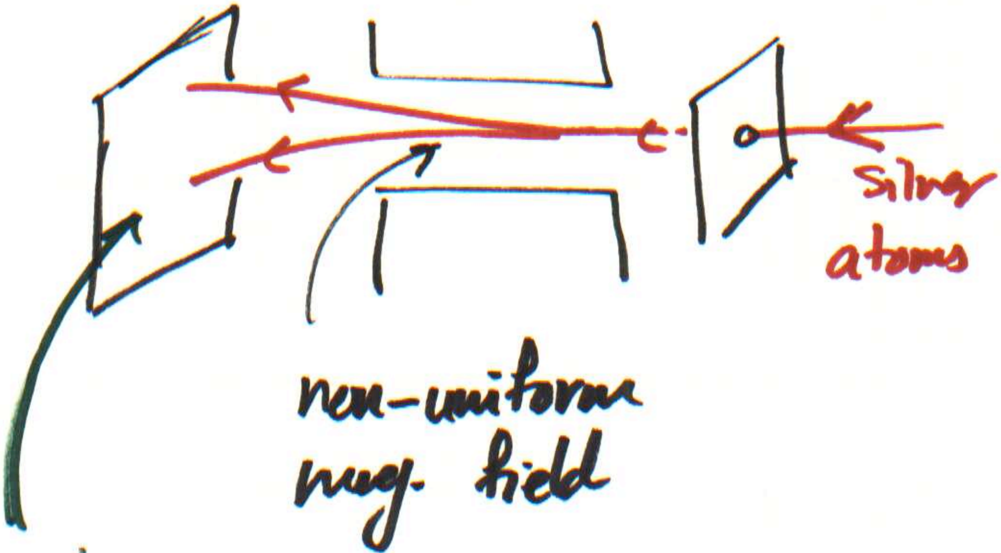
spin magnetic mom.

$$\mu_{s,z} = \pm \frac{e\hbar}{2m_e}$$

$\rightarrow$ Bohr's magneton

z-comp.

Stern-Gerlach Exp.



two comp. $\longrightarrow$ in contradiction w/ prediction

$\Longrightarrow$ this exp.

- verified the concept of space quantization
- Existance of spin

Pauli's Exclusion Principle

We used 4 q.# to describe $\bar{e}$ states of an atom.

E.P. → No two ~~e~~ $\bar{e}$ of an atom can be in the same state

⟹ (no two $\bar{e}$ have the same set of 4 q#s)

· Filling Subshells:

As a subshell is filled the next $\bar{e}$ goes into the next lowest-energy vacant state

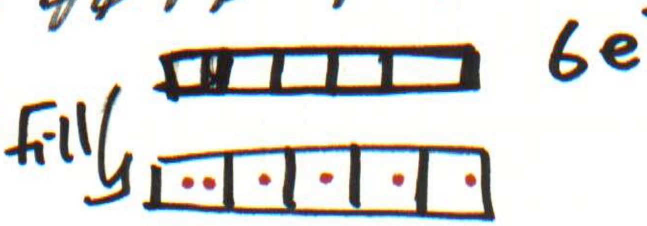
Orbital: Characterized by n, l, m_l

from E.P. $\longrightarrow$ two e^- per orbital
↑ & ↓

n	1	2				3	
l	0	0		1		0	1 ...
m_l	0	0	+1	0	-1	0	
m_s	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	

In general $\longrightarrow$ $2n^2$ states in each state

Hunds Rule:



some exceptions:

subshells being close to being filled or ½ filled.

Periodic Table:

Dimitrgi Meneleten

→ arranged atoms according to their atomic mass.

× Blank spaces.

→ Undiscovered elements

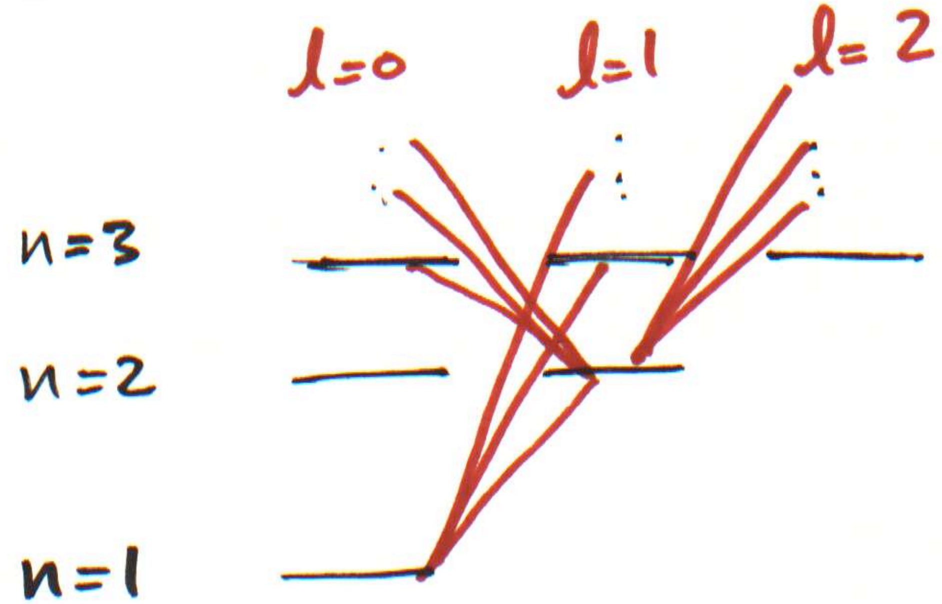
* prediction about chemicals of undiscovered elements.
* In 20 years most missing elements were discovered
* Elements in the same col. have similar chemical prop.

↳ dep. on their outmost shell

e.g. nobel gases

→ Filled outmost shell

H. E. levels:



- Allowed val. of l. are separated.
- Transitions in which l does not change are very unlikely

Selection Rule:

$\Delta l = \pm 1$

$\Delta m_l = 0$ or ± 1

b/c $\rightarrow$ Ang. mom. of atom-photon is conserved

$\Longrightarrow$ therefore, γ has ang. mom.

$\rightarrow$ ang. mom equi. to that of a particle w/ spin 1

$\uparrow \quad \rightarrow \quad \downarrow$

$+1 \quad 0 \quad -1$

$\Longrightarrow$ γ has E, lin. mom, & ang. mom.

Multi-e^- atoms:

- Positive nuclear charge Ze is shielded by negative charge of e^- of inner shells

  $\Rightarrow$ Outer e^- deal w/ a smaller charge

- Allowed E: $E_n \approx \frac{-13.6\, Z_{eff}^2}{n^2}$ eV

  Z_{eff} dep. on $\underline{n}$, $\underline{l}$

X-Ray Spectra

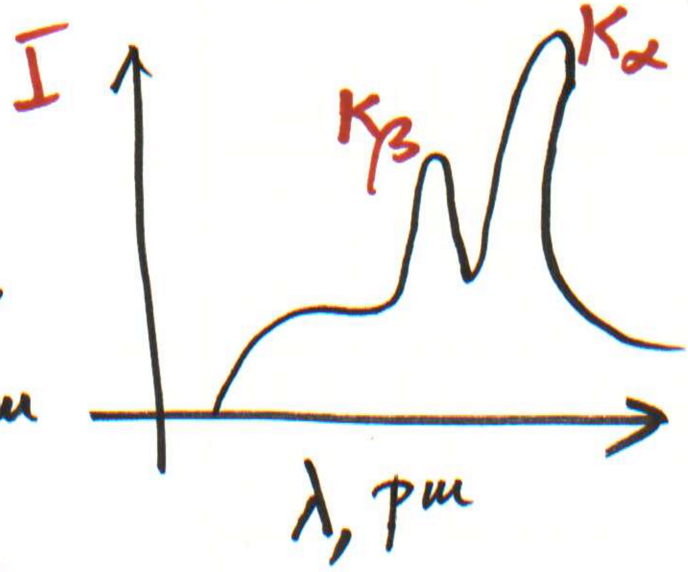
* A result of high E e^-, slowing down as they strike a metal surface.

* K.E lost o→ KE.

* Cont. Spectrum → Bremsstrahlung

  Desc. lines → characteristic x-rays

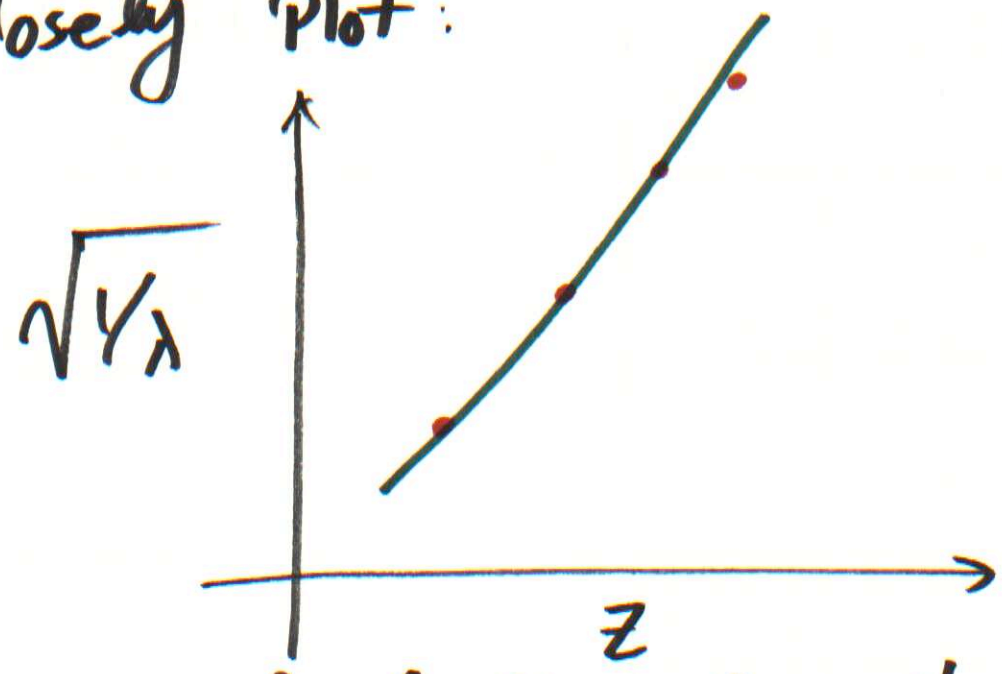
→ created when:



- e^- collides w/ a target atom
- e^- removes an inner-shell e^-
- e^- of higher orbits fills the vacancy

* γ has E equal to this
E. diff. (typically $\gtrsim$ 1,000 eV)
($0.01 \text{ nm} < \lambda < 1$ nm)

Mosely Plot:



* λ is w.l. of K_α of each element

  ▲ $K_\alpha \longrightarrow$ (L $\rightarrow$ K shell)