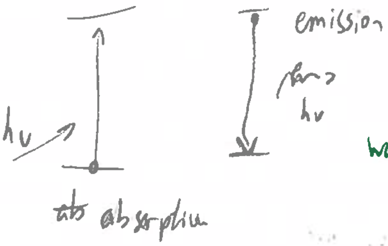
Phys chem Y2 T2.

Atomic spectra

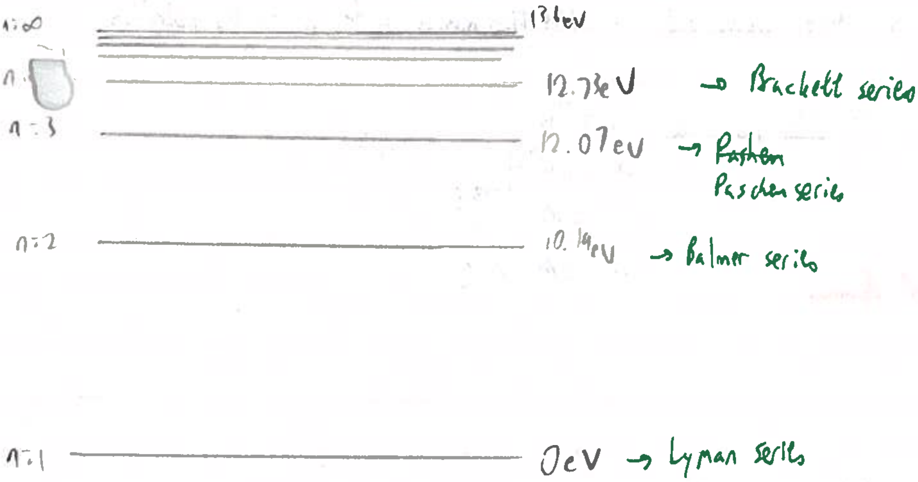


$E = hf$

$= \frac{hc}{\lambda} = hc\tilde{\nu}$

wavenumber $= \frac{1}{\lambda} = \tilde{\nu}$ (cm^{-1})

For hydrogen atom



emission spectrum of hydrogen:

wavenumbers of all observed lines can be fit into one equation

$$\tilde{\nu} = -R_H\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \quad [\text{cm}^{-1}]$$

quantum number of transition (en), that of low levels

$n: 1, 2, 3, 4$

Rydberg constant of H atom

Experimentally:

$R_H = 109677.8\text{cm}^{-1}$

R_X: different value for different atoms.

Energy of photon emitted:

$E_1 \to E_2$

$E = hc\tilde{\nu} = \left(-\frac{hcR}{n_2^2}\right) - \left(-\frac{hcR}{n_1^2}\right)$

$= E_2 - E_1$

Bohr's 3 postulate (proposals)

- e/s move in circular orbit around +ve charged nucleus

~~only certain orbits~~

- only certain orbits are allowed w/ integer values of n
  ↳ e/s do not emit energy while they are in orbit
- single photon is emitted/absorbed when an e/ moves from one orbit to another

angular momentum → always conserved → direction always ⊥ to plane of rotation

$L = I\omega$ (rad s^{-1})

$I = \sum m_i r_i^2$

[angular equivalent of mass

For one particle: $L = I\omega$

$\rightarrow = mr^2\omega$ $\quad \omega = v/r$

$= mr^2 \frac{v}{r}$

$\rightarrow = mrv$

For hydrogen atom, $F = \frac{-e^2}{4\pi\varepsilon_0 r^2}$

Bohr postulated angular momentum ($m_e v r$) to have multiples of $h/2\pi = \hbar$

$L = m_e v r = \frac{nh}{2\pi}$

$= n\hbar$

$mvr = n\hbar$

$v = \frac{n\hbar}{mr}$

↳

$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}$

$m\left(\frac{n\hbar}{mr}\right)^2 = \frac{e^2}{4\pi\varepsilon_0 r}$

$m \times \frac{n^2\hbar^2}{m^2 r^2} = \frac{e^2}{4\pi\varepsilon_0 r}$

$\frac{n^2 h^2}{4\pi^2 mr} = \frac{e^2}{4\pi\varepsilon_0}$

$\frac{n^2 h^2 \varepsilon_0}{me^2} = r$

$r = \frac{n^2 h^2 \varepsilon_0}{\pi m e^2}$] radius of an e/ should be diff for diff n.

$E = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_0 r}$

$E = \frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0 r}\right) - \frac{e^2}{4\pi\varepsilon_0 r}$

$= \frac{e^2}{8\pi\varepsilon_0 r} - \frac{2e^2}{8\pi\varepsilon_0 r}$

$= -\frac{e^2}{8\pi\varepsilon_0 r}$

$\hbar = \frac{h}{2\pi}$

$2\pi\hbar = h$

Subbing r:

$E = -\frac{e^2}{8\pi\varepsilon_0} \times \frac{\pi m e^2}{n^2 h^2 \varepsilon_0} = -\frac{me^4}{8\varepsilon_0^2 n^2 h^2}$

$= \underbrace{-\frac{e^4 m}{8\varepsilon_0^2 h^2}}_{-hcR}\left(\frac{1}{n^2}\right)$

$R = \frac{e^4 m_e}{8\varepsilon_0^2 h^3 c}$

Extentions to Bohr model

e^- and p^+ both rotate about common centre of mass

↳ $\mu = \frac{m_e m_n}{m_e + m_n}$

↳ $R_{calc} = \frac{e^4 \mu}{8 \varepsilon_0 h^3 c}$

if $m_n >> m_e$

$\mu = \frac{m_e m_n}{m_e + m_n} \simeq \frac{m_e m_n}{m_n} = m_e$

$R_\infty = R_{calc} = \frac{e^4 m_e}{8 \varepsilon_0^2 h^3 c} = 109737 \text{ cm}^{-1}$

[using 1800 $m_e = m_n$] → correct reduced mass for hydrogen atom

$\mu = \frac{1800 m_e^2}{1801 m_e} = 0.99944 m_e$

~~$R_{H(calc)} = 0.99944\, e^4 m_e$~~

$R_{H(calc)} = \frac{0.99944 m_e e^4}{8 \varepsilon_0 h^3 c} = 0.99944 R_\infty$

$= 109675.5 \text{ cm}^{-1}$

∴ If for polyelectronic atoms:

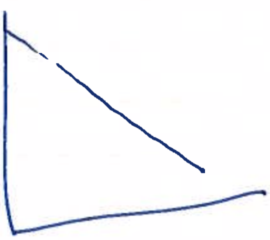
~~$E = hc^2$~~ $E = hc\underbrace{Z^2}_{\text{atomic number}} R_x \left[\frac{1}{\underbrace{n^2}_{\text{energy lvl}}}\right]$

Ionization energies → energy required to remove an e^- from the ground state of an atom to infinite distance

$IE = -R\left(\underbrace{\frac{1}{\infty^2}}_{\text{as } n_2 \to \infty} - \frac{1}{n_1^2}\right) = R/n_1^2$

when determining ionization energy w/ a graph [Lyman series]

$\tilde{\nu}$



$\tilde{\nu} = \underbrace{\frac{R}{n_1^2}}_{IE} - \frac{R}{n_2^2}$ [$n_1 = 1$ (constant)]

$\tilde{\nu} = -\frac{R}{n_2^2} + IE$

$y = mx + c$

gradient $= -R$

y-intercept: IE

eg. $1s^2 2s^2 2p^3$

$n = 1 \rightarrow (3)\ 2 \times 0.85 = 1.7$

$(2)\ 4 \times 0.3 = 1.2$

$Z_{eff} = 7 - 1.2 - 1.7$

$= 3.9$

* lower I.E. for B & O

- B : removal of 2p e⁻/s
  ∴ less energy

- B,C,N : removing 2p e⁻/ which sits on its own in its orbitals

- O,F,Ne : removing one pair of e⁻/s from 2p
  ↳ spin paired e⁻/s less stable than spin parallel in the same orbital

Breakdown of Bohr model:
∀ lines in atomic spectra of alkali metals contain similar series as H atom

↳ lines are all in pairs (doublets) → cannot be explained by Bohr theory

∴ using wave mechanics:

$E = -hcR/n^2$ ∀ energy level expression for H-atom.

Schrödinger ~~equati~~ equation for hydrogen atom → e⁻s occupy orbitals (spd) w/ quantized energies

using quantum numbers n, l, m, m_l

m_l → component of orbital angular momentum along the z-axis is quantized

$l_z = m_l \hbar$ $\quad$ $\vec{L}$ can have 3 orientation w/ z axis

$= \hbar\sqrt{l(l+1)}$ $\quad$ $L_z = \pm\hbar, 0$

Absorption Spectrum:
↳ transitions in absorption involve $1s \to np$ (∵ angular momentum & symmetry conservation)
↳ results in a selection rule for absorption/emission of photon: $\Delta l = \pm 1$

$\Delta m_l = 0, \pm 1$ $\quad$ ↳ upon absorbing/emitting a photon, l must change by 1.
∵ photon has one unit of $\vec{L}$ & has odd parity

Emission Spectrum: - more complicated ∵ H-atoms can be excited to many levels by excitation source → lots of transitions are then possible
- must conform to selection rules for all transition
↳ $\Delta l = \pm 1$ if a photon is emitted.
- calculate energy using Bohr formula:

$$\tilde{\nu} = R_H\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

Electron spin

proven by Stern - Gerlach experiment

↳ a beam of Ag atoms ($4d^{10}5s^1$) was sent into an inhomogeneous B-field.

↳ Beam observed to split into 2 parts

↳ Splitting was assigned to the outer e⁻ having a spin angular momentum $s = \frac{1}{2}$

$M_s = \pm\frac{1}{2}$ (spin up / down)

↳ in the homogeneous B-field these 2 spin orientations have diff energies & separate

spin → just a convenient name for the intrinsic momentum of the e⁻

[e⁻s possess a magnetic moment]

* interaction between the spin angular momentum (s) and orbital angular momentum (l) } spin-orbit coupling

Angular momenta in one-e⁻ atoms:

- spin-orbit interaction:

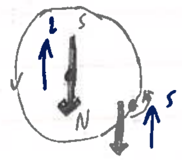
e⁻s have s & l

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

↳ presence of e⁻ spin splits all energy lvls of H atoms which have orbital angular momentum ($l > 0$) into 2. [apart from 1s lvls]

Splitting occurs ∵:

- ~~e/s have a~~
- e/ has a magnetic moment (just like a small bar magnet)
    - ↳ arose from charged e/ spinning on its axis
  - BUT when $l > 0$ → e/ has orbital angular momentum [picture as a charge orbiting the nucleus]
    - ↳ moving charges generate B-fields ∴ circulating e/ also generate a magnetic moment at the nucleus [like a bar magnet]
- two magnetic moments in our system
  - ↳ magnets can be alligned or opposed
    - ↳ interaction between e/ spin & its orbital motion via these magnetic effects ~~is ca~~
      - ↳ spin-orbital interaction



higher energy

~~↳ when $l > 0$ is a~~

↳ when a level w/ $l > 0$ is split into two magnetic moment alligned/opposed by spin-orbit interaction

lower energy

∴ reason why the lines in the sodium spectrum are ~~dd~~ doubled

- spin-orbit effects are not included in the Bohr equation : But in H atom, so small ∴ ignore

spin-orbit interactions ↑↑ with Z^+
- ↳ splittings are more obvious for heavier elements

Spin-orbit interaction :

orbital angular momentum $\rightarrow l$
spin " $\rightarrow s$
total " $\rightarrow j$

possible values of j given by

$j: l+s \ , \ l+s-1, ..., |l-s|$
[Clebsch-Gordon series]

j can take values from the sum of l & s, down in steps of one → value of l - s

- used in NMR (photon spins)
- rotational angular momentum in microwave spectra

eg. e^- in p-orbital
$s=\frac{1}{2}, \ l=1$

$j = \frac{3}{2} \qquad |l-s| = \frac{1}{2}$

$j = \frac{3}{2}$ to $\frac{1}{2}$

in a p-orbital
$(l>0)$ results in 2 states
↳ states w/ diff angular momentum

e^- in s orbital
$s=\frac{1}{2}, \ l=0$

$l+s = \frac{1}{2} \qquad |l-s| = \frac{1}{2}$

$j=\frac{1}{2}$ → only have one state

Term symbols: → summarizing l, s & j

multiplicity

$^{2s+1}l_j$

l: orbital angular momentum
s: spin angular momentum
j: total angular momentum

$2s+1$: multiplicity [one e^- atom : $2s+1 = 2(\frac{1}{2})+1 = 2$]
[for polyelectronic atom: need total s from combining spins of all e^-s eg. Na, He]

l: S, P, D etc for $l = 0, 1, 2$
[for multi e^- atom : combine the l values of all e^-s to get total orbital angular momentum]

j: $l+s$, $l+s-1$, ... $|l-s|$

eg. term symbol for 2 states arising from the $3d^1$ level of the H atom

eg. $s = \frac{1}{2}$
for d orbital $l = 2$

$^2D_{5/2, 3/2}$

Recap:

- energy levels of H atom varies : $E_H = -hc\frac{R_H}{n^2}$
- derivation of Rydberg constant by Bohr
- explaination of Radii & energies of orbits by Bohr
- Bohr's idea of orbits lead to idea of orbitals
- transitions observed in the H atom spectrum are governed by the selection rule $\Delta l = \pm 1$
- for H atoms good approximation of all orbitals w/ same n, have same energy
- e^- spin & spin orbit coupling → interaction between e^- spin & its orbital motion via magnet effect of the system
  ↳ means an e^- in p, d, f results in two energy states

Fine structure

when e/s are in p,d,f orbitals

↳ a pair of states w/ diff values of j

↳ evidence from doublet in Na spectrum

↳ when looking at very high resolutions at H atom transitions → modern spectroscopic techniques using lasers

using high resolution

↳ we might see more than one line

↳ multiple lines → termed as "<u>Fine structure</u>" of the transition

↳ fine structure is due to spin-orbit coupling

s from notes

n=3 to 2 has a fine structure ∵ splitting of levels by spin-orbit coupling

BUT ~~can~~ very small splitting

↳ not accounted for in Bohr formula

↳ 睇到七七條線

$n\,{}^{2s+1}l_j$ $\quad {}^{2s+1}l_j$

constructing a fine structure

(1)

✱ what levels we have?

- n=2 ⇒ l=0, 1
- n=3 ⇒ l=0, 1, 2
- each orbitals w/ l>0 will split into doublet

$2s$ $\quad l=0 \quad s=\frac{1}{2} \quad j=\frac{1}{2} \Rightarrow 2s\,{}^2S_{1/2}$

$2p$ $\quad l=1 \quad s=\frac{1}{2} \quad j=\frac{3}{2},\frac{1}{2} \Rightarrow 2p\,{}^2P_{1/2},\ 2p\,{}^2P_{3/2}$

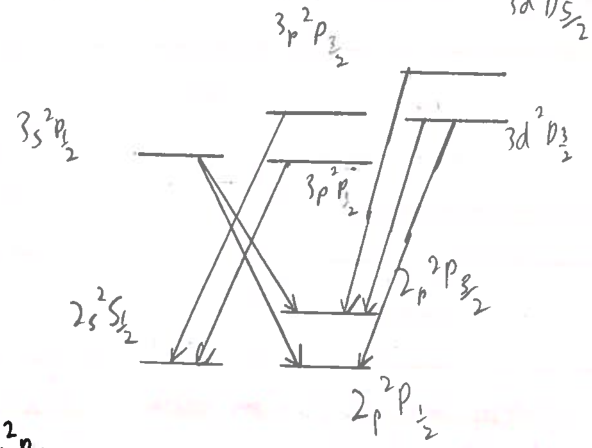
$3s$ $\quad l=0 \quad s=\frac{1}{2} \quad j=\frac{1}{2} \Rightarrow 3s\,{}^2S_{1/2}$

$3p$ $\quad l=1 \quad s=\frac{1}{2} \quad j=\frac{3}{2},\frac{1}{2} \Rightarrow 3p\,{}^2P_{3/2},\ 3p\,{}^2P_{1/2}$

$3d$ $\quad l=2 \quad s=\frac{1}{2} \quad j=\frac{5}{2},\frac{3}{2} \Rightarrow 3d\,{}^2D_{3/2},\ 3d\,{}^2D_{5/2}$

∴ We have 8 possible levels

✱ lowest j is lowest in energy



7 transitions as observed

↳ close to the single wavenumber of this transition predicted by the Bohr equation n=3→2

✱ selection rules:

$\Delta l = \pm 1$

$\Delta s = 0$ ⇒ spin does not change upon absorbing or emitting a photon

[not important for H atom ∵ have one electron, $s=\frac{1}{2}$ always]

$\Delta j = 0, \pm 1$ ⇒ total angular momentum can stay the same or change by one unit

(2) how many transitions are possible in the fine structure of the emission to the n=1-3 shell of an H atom with its e^- initially in a 4p orbital

✱ states & term symbols

always: $s = \frac{1}{2}$

4p : $l=0$ $j = \frac{1}{2}, \frac{3}{2}$ => $4p\,^2P_{3/2}$, $4p\,^2P_{1/2}$

remaining 1s, 2s, 2p, 3s, 3p, 3d

ns: $l=0$ $j=\frac{1}{2}$ => $^2S_{1/2}$

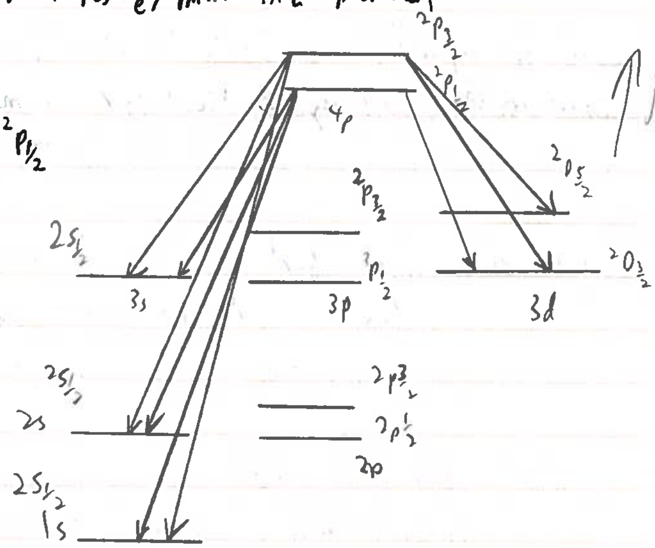
np: $l=1$ $j=\frac{3}{2}, \frac{1}{2}$ => $^2P_{3/2}$, $^2P_{1/2}$

nd: $l=2$ $j=\frac{5}{2}, \frac{3}{2}$ => $^2D_{5/2}$, $^2D_{3/2}$

✱ apply selection rules:

~~Δs=0, 0~~

$\Delta l = \pm 1$ $\Delta s = 0$ $\Delta j = 0, \pm 1$



9 transitions

Effect of applied fields:

~~tota~~ j has a quantized orientation → given by m_j

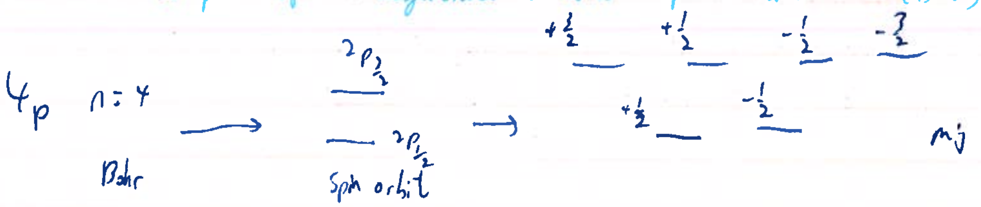
m_j: take values from j down ✱ in steps of ~~one~~ 1 → -j

↳ $m_j = j, j-1, \ldots, -j$

- in absence of an external field, all m_j sublevels of given j state

∴ 4p $^2P_{3/2}$ state w/ $j = \frac{3}{2}$ has $m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$

↳ composed of 4 degenerate sublevels if there is no field (B=0)



✱ in an external field (B or E), degeneracy of m_j levels is removed, atomic spectra exhibit many more lines

Removal of degeneracy of m_j levels in a B-field & consequent ↑ complexity of atomic spectra is called the Zeeman effect

↳ ~~AE~~ results in seeing more lines

Zeeman & Stark effect :

seperation of m_j levels by E-field => stark effect
seperation of m_j levels by B-field => Zeeman effect
[Zeeman effect for H atom is same for Na)

- Anomalous Zeeman effect :
  ↳ atom studied has non-zero spin angular momentum (S>0)
  eg. H atom , splitting in a B-field

magnetic ~~field~~ field energies of m_j sub-levels of given j state : $E_{zeeman} = k g_j m_j$

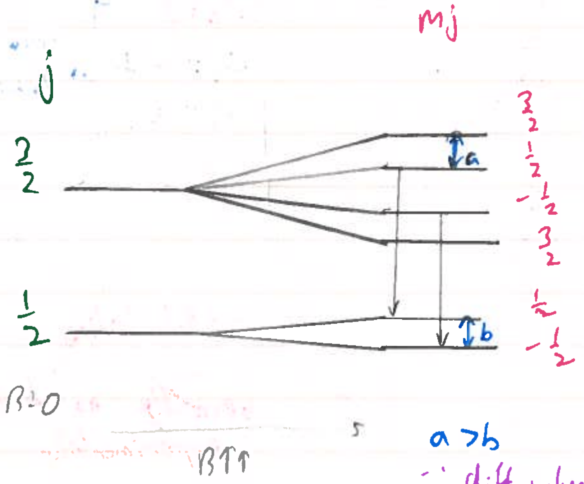
constant depending the size of the B-field & other fundamental constants

splittings between m_j levels from different j state aren't necessarily the same

- splitting ∝ m_j
  ↳ m_j sub levels w/ large +ve / -ve value of m_j shifted the most in energy
- -ve m_j values for m_j sublevels
  ↳ shifted to lower energy
- +ve m_j values for m_j sublevels
  ↳ shifted to higher energies
- splittings between m_j levels from the same j state are the same

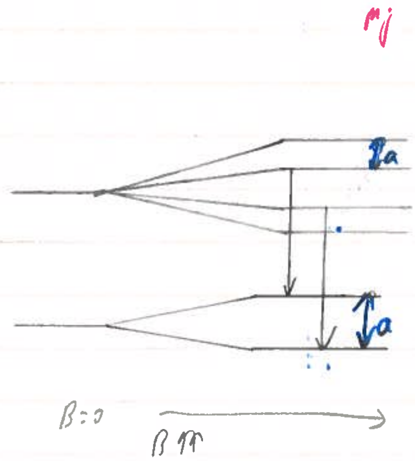
- splitting between different m_j levels of given j state is given by ~~g_j~~ g_j → "Lande g-factor"
- levels with diff combinations of l, s & j split to diff extents depending on g_j
- ∴ calculate g_j to know the relative splitting of the level
  ∴ working out what pattern lines will be observed

Why is value of g_j important?



$a > b$

∴ diff value of g_j



$a = a$

∴ same value of g_j

$$g_j = \frac{3j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}$$

for level you are considering

eg.: Zeeman effect for $3p \rightarrow 2s$

1. how individual j levels split when field is present
2. which transitions are possible between diff m_j levels

$3p\ ^2P_{\frac{3}{2}}$ $l = 1$, $s = \frac{1}{2}$, $j = \frac{3}{2}$, $m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ ⇒ $g_j = \frac{3 \times \frac{3}{2} \times \frac{5}{2} + \frac{1}{2} \times \frac{3}{2} - 1 \times 2}{2 \times \frac{3}{2} \times \frac{5}{2}}$

$= 1.33$

⇒ split into 4 components of m_j

$^2P_{\frac{1}{2}}$ $j = \frac{1}{2}$, $m_j = \frac{1}{2}, -\frac{1}{2}$ ⇒ $g_j = \frac{3 \times \frac{1}{2} \times \frac{3}{2} + \frac{1}{2} \times \frac{3}{2} - 1 \times 2}{2 \times \frac{1}{2} \times \frac{3}{2}}$

⇒ split into 2 components of m_j $= 0.67$

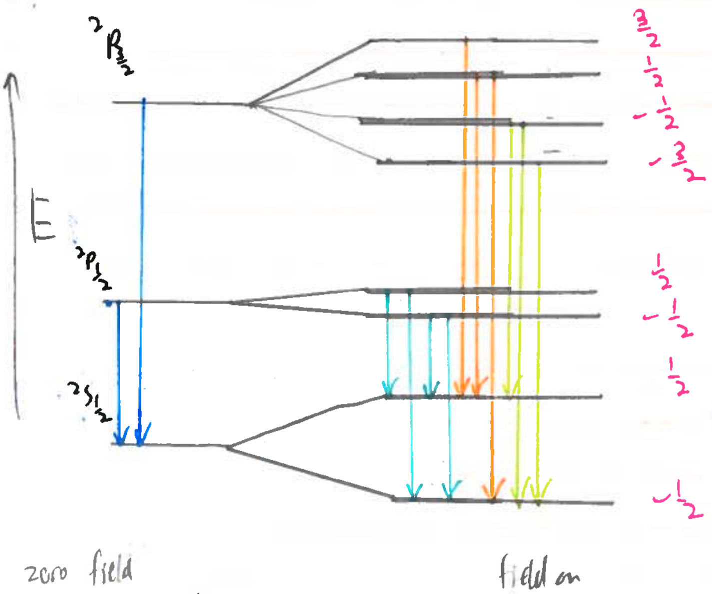
$2s\ ^2S_{\frac{1}{2}}$ $j = \frac{1}{2}$, $m_j = \frac{1}{2}, -\frac{1}{2}$

⇒ split into 2 components of m_j → ∴ g_j ⇒ $g_j = 2$

rk out how much the levels split ∴ we can tell if iff transitions will occur @ same energy & overlap in the spectrum

j same for 2 j levels → m_j components of the 2 levels will split the same amount

$3p \to 2s$



$g_j = \frac{4}{3}$

$g_j = \frac{2}{3}$

$g_j = 2$

selection rules

$\Delta s = 0$

$\Delta j = 0, \pm 1$ → show doublet

$\Delta l = \pm 1$

$m_j = 0, \pm 1$ → all possible transitions when B-field is present

⇒ total 10 lines

exactly as observed experimentally

eg. $3d \to 2s$; how many lines observed in transition between highest energy spin-orbit (fine structure) level of the 3d state of the hydrogen atom & the 2p orbital in a magnetic field

3d : $l = 2$, $s = \frac{1}{2}$, $j = \frac{5}{2}, \frac{3}{2}$ ⇒ $^2D_{3/2}$, $^2D_{5/2}$ ⇒ $g_j = \dfrac{3(\frac{5}{2})(\frac{7}{2}) + \frac{1}{2}(\frac{3}{2}) - 2\times 3}{2(\frac{5}{2})(\frac{7}{2})}$

2 spin orbit states

$m_j : \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$

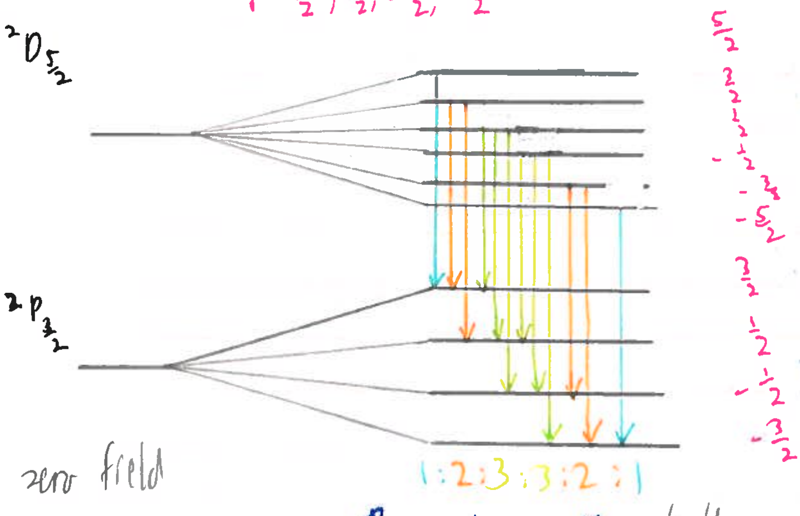
$\frac{6}{5} = 1.2$ ⇒ splits less

2p :

2 spin orbit state : $l = 1$, $s = \frac{1}{2}$, $j = \frac{3}{2}, \frac{1}{2}$ ⇒ $^2P_{3/2}$, $^2P_{1/2}$ ⇒ $g_j = \dfrac{3(\frac{3}{2})(\frac{5}{2}) + \frac{1}{2}(\frac{3}{2}) - 1\times 2}{2(\frac{3}{2})(\frac{5}{2})}$

$m_j : \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$

$= \frac{4}{3} = 1.33$ ⇒ splits more



selection rules

$\Delta m_j = \pm 1, 0$

total 12 lines w/ a field

symmetrical pattern

For sodium atoms → place to start considering multi-electron atoms
$1s^2 2s^2 2p^6 3p^1$ as they contain one e/ outside a closed-shell core

Term symbols for Sodium

l and spin of all e/s in any full set of orbitals cancel out
↳ ∴ only consider e/s in partially filled orbitals
for alkali metal atoms → only have single outer e/ to consider
↳ hard to excite any e/s from the core
↳ alkali metal atoms are termed pseudo-one-elec e/ atom
↳ expect their spectra to be similar to H-atom

introduce notation:

S → total spin angular momentum
s_i → spin angular momentum L → orbital angular momentum
l_i → orbital angular momentum
$i = 1, 2, 3, 4$ of the e/ of interest

$$\vec{J} = \vec{L} + \vec{S}$$
$$J = L+S,\ L+S-1 \ldots |L-S|$$

For alkali metals: one outer e/ → $i = 1$
$S = s_i$
$L = l_i$

term symbols are identical to the H atom

tate for alkali metals:

[core] ns^1	$S = s = \frac{1}{2}$	$L = l = 0$	$J = \frac{1}{2}$	$^2S_{\frac{1}{2}}$
[core] np^1	$S = \frac{1}{2}$	$L = l = 1$	$J = \frac{3}{2}, \frac{1}{2}$	$^2P_{\frac{1}{2}}, {}^2P_{\frac{3}{2}}$
[core] nd^1	$S = \frac{1}{2}$	$L = l = 2$	$J = \frac{5}{2}, \frac{3}{2}$	$^2D_{\frac{3}{2}}, {}^2D_{\frac{5}{2}}$
[core] nf^1	$S = \frac{1}{2}$	$L = l = 3$	$J = \frac{7}{2}, \frac{5}{2}$	$^2F_{\frac{7}{2}}, {}^2F_{\frac{5}{2}}$

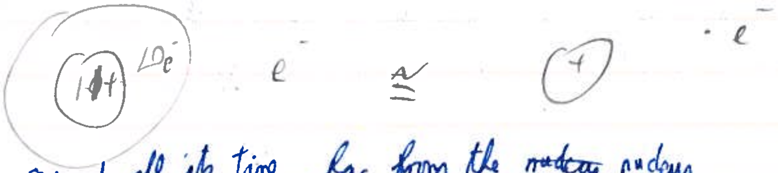
for alkali metals:
orbitals w/ same val of n does not have the same energy
$E(3s) \neq E(3p)$

diff energies for ab orbitals w/ same n but diff l in multi e/ atoms are due to ~~diff~~
↳ [diff orbitals experiencing effective nuclear charge ∵ of their shape]

Big difference in energy of states for Na
same value of n

$Na \rightarrow Z = 11$

↳ expect outer e⁻ in Na to 'see' only
one of the +ve charges
∴ rest of the +ve charges are 'screened'
by the 10 outer core e⁻s



∵ e⁻ doesn't spend all its time far from the ~~nuclear~~ nucleus
∴ for given value of n
↳ e⁻s w/ low values of l spend
more time near the nucleus → "inside" the core e⁻s
↳ l ↓ → ~~h+~~ ⇑ effective nuclear charge
the e⁻ experiences
↳ ∴ for given n, ~~s lowest~~ energies : s < p < d < f ...
↳ penetration of the orbitals ↑↑ as l ↓↓

$Na \rightarrow [core]\ 3s^1$, $^2S_{\frac{1}{2}}$

Absorption spectrum of Na

↳ all species start in their ground state

apply selection rules for possible transitions :

$\Delta S = 0$ → provide no restriction ∵ all available states have $S = \frac{1}{2}$

$\Delta l = \pm 1$ → restricts us to p-states ($l=0 \rightarrow l=1$)

$^2S_{\frac{1}{2}} \rightarrow {}^2P_{\frac{1}{2}}$

$^2S_{\frac{1}{2}} \rightarrow {}^2P_{\frac{3}{2}}$

predict series of doublets converging to a series limit [also is observed]

↳ Principal Series

↳ similar to H atom ∵ spin-orbit coupling

BUT spin-orbit splitting is much larger than in H-atom

∵ ~~Z~~ $Z_{Na} > Z_H$

4 vs 1

Emission spectrum

↳ observe several series of lines in emission

eg. $\underbrace{^2S_{\frac{1}{2}} \rightarrow 3p\ {}^2P_{\frac{3}{2},\frac{1}{2}}}_{\text{sharp series}}$

4 important series :

- Sharp series : $^2S_{\frac{1}{2}} \rightarrow {}^2P_{\frac{3}{2},\frac{1}{2}}$
- Principal series : $np\ ({}^2P_{\frac{3}{2}}, {}^2P_{\frac{1}{2}}) \rightarrow 3s\ ({}^2S_{\frac{1}{2}})$

see doublets [also seen in absorption]

- Diffuse series : $nd\ ({}^2D_{\frac{5}{2}}, {}^2D_{\frac{3}{2}}) \rightarrow 3p\ ({}^2P_{\frac{3}{2},\frac{1}{2}})$
- Fundamental series : $nf\ ({}^2F_{\frac{7}{2},\frac{5}{2}}) \rightarrow 3d\ ({}^2D_{\frac{5}{2},\frac{3}{2}})$

see triplets

only appear doublets @ $^2D_{\frac{5}{2}}, {}^2D_{\frac{3}{2}}$ level @ low res

Energy level expressions → predict energies of transitions

absorption & emission spectra of Na are made of series of lines : just like H atom

似 H atom

$$E_{nl} = \frac{-hc R_{Na}}{(n-\delta_{nl})^2}$$

~~δ_{nl} : a~~ → penetration ↑↑, δ_{nl} ↑↑

δ_{nl} : quantum defect

→ depends v. strongly on l

v. weakly on n

→ quantifies the degree of penetration of an e⁻ in a given orbital

For Na:

δ_{ns} : 1.3

δ_{np} : 0.8

$\delta_{nd} \approx 0$ (0.05)

if 計數 assumption: for d orbitals

↳ hardly penetrate the core

∴ $\delta_{nd} \approx 0$

Summary :

~~Na 似 H~~

- Na 極似 H
- spectrum diff → more series visible

↳ ∵ ∃ difference in energies of np, ns, nd for same n [penetration is the reason]

e.g. 3p to 3s transitions occurs in the visible spec for Na

BUT NOT POSSIBLE in the Bohr model of the H atom

∵ n = 3 level has the same energy

- Spin-orbit splittings are greater for Na.

Helium atom:

↳ consider 2 interacting e⁻'s $[1s^2]$

↳ excite an He atom → one of the 2 e⁻'s almost always remains in the 1s orbital.

↳ only consider $1s^1 n l^1$ as excited state

~~combining spin angular momentum~~

combining spin angular momentum:

$S = s_1 + s_2 \rightarrow s_1 + s_2 - 1, \ldots\ldots |s_1 - s_2|$ → He has only 2e⁻'s

$\therefore s_1 = s_2 = \frac{1}{2}$

↳ $S = \frac{1}{2} + \frac{1}{2} = 1$ Triplet state

$S = \frac{1}{2} - \frac{1}{2} = 0$ singlet state

by $2S+1$ = states

combining orbital angular momentum

$L = l_1 + l_2,\ l_1 + l_2 - 1 \ldots |l_1 - l_2|$

He configurations $1s^1 nl^1$

$1s^2$ closed shell → $^1S_0$

Selection rules: exactly analogous to the H-atom

$\Delta S = 0 \quad \Delta J = 0, \pm 1$

$\Delta L = 0, \pm 1$

$1s^1ns^1$ $l_1 = l_2 = 0 \Rightarrow L = 0$ $\quad s_1 = s_2 = \frac{1}{2} \Rightarrow S = 0, 1$ $\quad$ $^1S_0 \quad ^3S_1$

$J = 0, 1$ $[L+S = 0+0$ or $0+1]$

$1s^1np^1$ $l_1 = 0,\ l_2 = 1 \Rightarrow L = 1$ $\quad s_1 = s_2 = \frac{1}{2} \Rightarrow S = 0, 1$

$L = 1 \quad S = 0 \Rightarrow J = 1 \quad \rightarrow {}^1P_1$

$L = 1 \quad S = 1 \Rightarrow J = 2, 1, 0 \quad \rightarrow {}^3P_2,\ {}^3P_1,\ {}^3P_0 \quad ({}^3P_{2,1,0})$

$1s^1nd^1$ $l_1 = 0,\ l_2 = 2 \Rightarrow L = 2$ $\quad s_1 = s_2 = \frac{1}{2} \Rightarrow S = 0, 1$

$L = 2 \quad S = 0 \Rightarrow J = 2 \quad \rightarrow {}^1D_2$

$L = 2 \quad S = 1 \Rightarrow J = 3, 2, 1 \quad \rightarrow {}^3D_3,\ {}^3D_2,\ {}^3D_1 \quad ({}^3D_{3,2,1})$

Absorption spectrum

$\because \Delta S = 0$

↳ consider transitions to singlet states in absorption

$\because 1s^2$ ground state is a singlet $^1S_0$

↳ transitions are only single lines $\because {}^1P_1$ lvls only have $J=1$

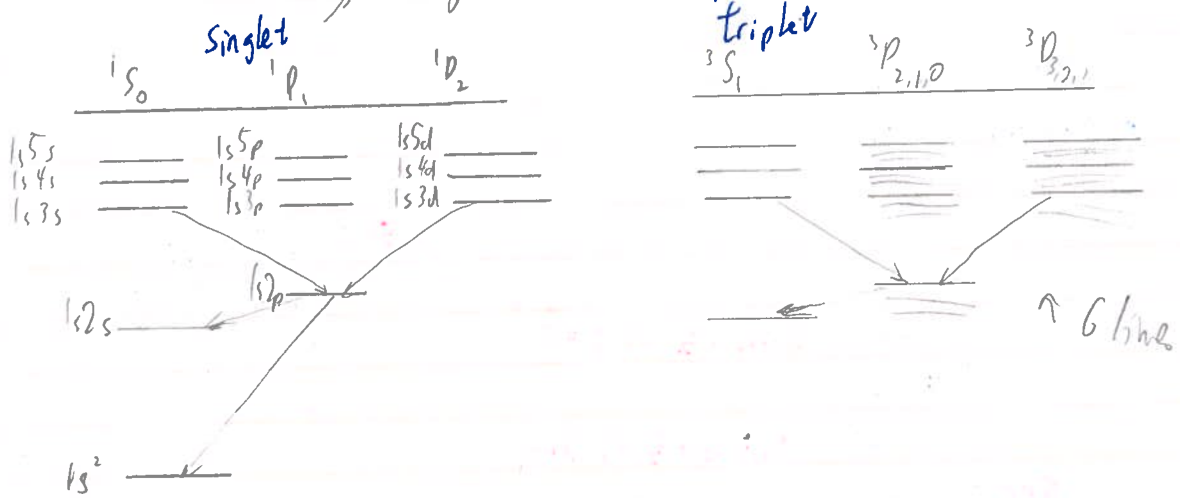
↳ no triplet states

↳ seeing a series of single lines:

$$1s^2\,(^1S_0) \rightarrow 1s^1 np^1\,(^1P_1)$$

Emission spectrum:

- more complex $\because$ atom can be excited to both singlet & triplet by excitation source [discharge, heat]
- two sets of emission lines: one set between singlet states $[^1S_0\ {}^1P_1\ {}^1D_2]$ ↗ all single lines
- triplet state $[^3S_1, {}^3P_{2,1,0}, {}^3D_{3,2,1}]$



For multi electron atoms

1. combine angular momenta of individual e^-'s → S & L
2. combine L & S → J
3. apply selection rules $\Delta S = 0$

$\Delta J = 0, \pm 1$

$\Delta L = 0, \pm 1$