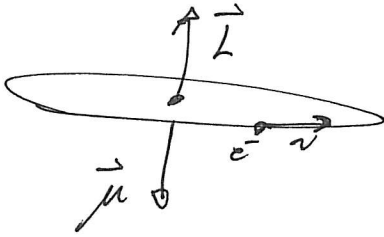


e^- orbital motion, $\vec{L} \hat{=} \vec{\mu}$, Zeeman

Classical orbit



$$\vec{\mu} = I A \hat{u} = \left(\frac{-e}{T}\right) \pi r^2 v = \frac{-e v}{2\pi r} (\pi r^2) = -\frac{e v r}{2}$$

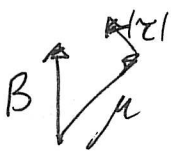
$$|\vec{L}| = |m v r| \quad \text{or} \quad \frac{|\vec{L}|}{m} = v r$$

$$\Rightarrow |\vec{L}| = \frac{2m}{e} |\vec{\mu}| \quad \text{or} \quad \boxed{\vec{\mu} = -\frac{e}{2m} \vec{L}}$$

Common: $\mu_B = \frac{e}{2m} \hbar \Rightarrow \underline{\underline{\vec{\mu} = -\mu_B \vec{L}}}$ fund unit μ_B

$$\mu_B = 57.9 \mu\text{eV/T}$$

further: $\vec{\mu}$ in field \vec{B}



feels torque $\vec{\tau} = \vec{\mu} \times \vec{B}$

\Rightarrow precession of $\vec{\mu}$ about \vec{B}

there is then energy associated w/ orientation of $\vec{\mu} \hat{=} \vec{B}$!

$$U = \int \tau d\theta \quad \Rightarrow \quad \boxed{E_B = -\vec{\mu} \cdot \vec{B}} \quad \text{or} \quad E_B = \underbrace{\frac{e}{2m} \vec{L} \cdot \vec{B}}_{\text{Along } \hat{z}} = \frac{e}{2m} L_z B$$

$\vec{\mu}$ wants to align with \vec{B}

$\vec{\mu}$ is antipar \vec{L} , so \vec{L} aligns against \vec{B}

Consequence: Zeeman effect! • E depends on μ , $\mu \propto L \dots$

• L depends on $l \dots |\vec{L}| = \sqrt{l(l+1)} \hbar$ quantized
 $l = 0, 1, \dots, (n-1)$

for a given n , in B field states split! states w/ diff l have diff E

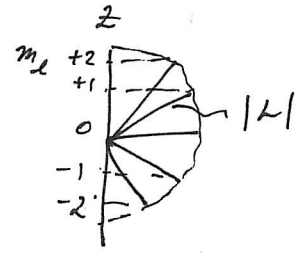
take atom in B along \hat{z}

- L cannot be arbitrary - uncertainty
- z component quantized

$$L_z = m_l \hbar \quad m_l = l, (l-1), (l-2) \dots 0 \dots -(l-1), -l$$

i.e. l to -l

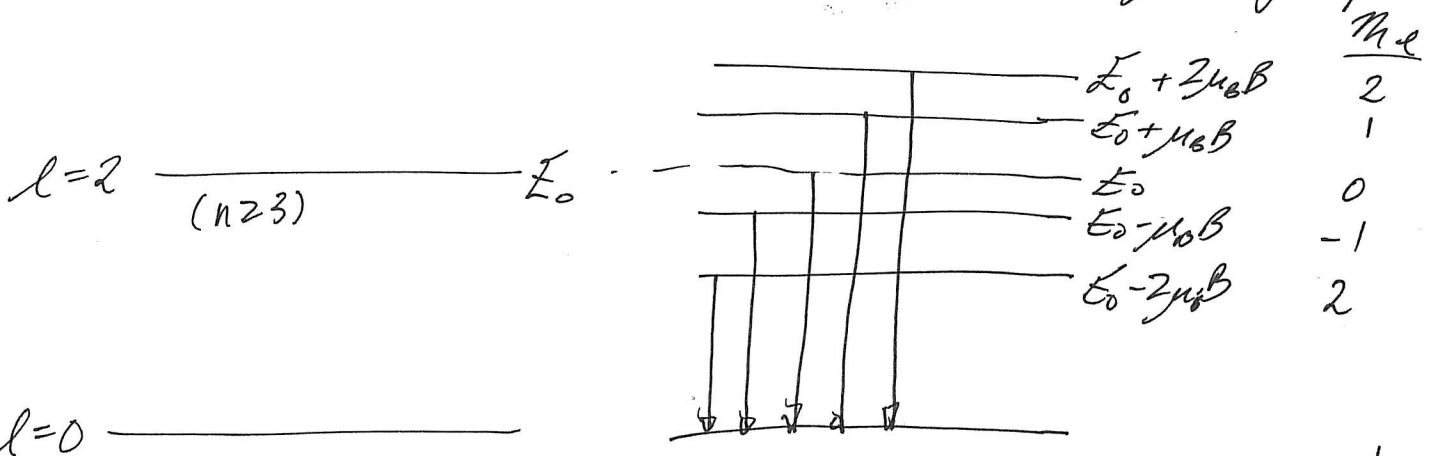
- max $L_z = l \hbar$
- max $|L| = \sqrt{l(l+1)} \hbar$



• if B is along z, energy of states w/ diff L_z are changed!

$$E = E_0 + E_B = E_0 + m_l \left(\frac{e\hbar}{2m} \right) B = E_0 + m_l \mu_B B$$

• in B, each level E_0 split into $2l+1$ equally-spaced levels



$l=0$
 $B=0$

no splitting
since $l=0$
 $m_l=0$

1 transition

5 transitions!

e.g. Hg or Na
Spectral PHS5

Conservation of L requires

$$\Delta l = \pm 1 \quad \left(\Delta m_l = \pm 1 \text{ or } 0 \right) \quad \text{"Selection rules"}$$

Why? photon carries angular momentum (circ pol)
 $\pm \hbar \dots$ so $L_{atom} + L_{ph} = 0$ overall

\Rightarrow no $\Delta l = 0$ (no photon)

\Rightarrow no $\Delta l = \pm 2$ etc (2 photons very improb.)

"Electric dipole transitions"

can have other processes (eg w/ spin flip, 2 photons, ...)
but strongly suppressed, i.e., very weak

• simplifies $\Delta E = \Delta E_0 \pm \mu_B B$

or 2 new lines for every l , shifted by abs amount

$$\Delta E_{\text{zeeman}} = \frac{e\hbar}{2m} B = \mu_B B$$

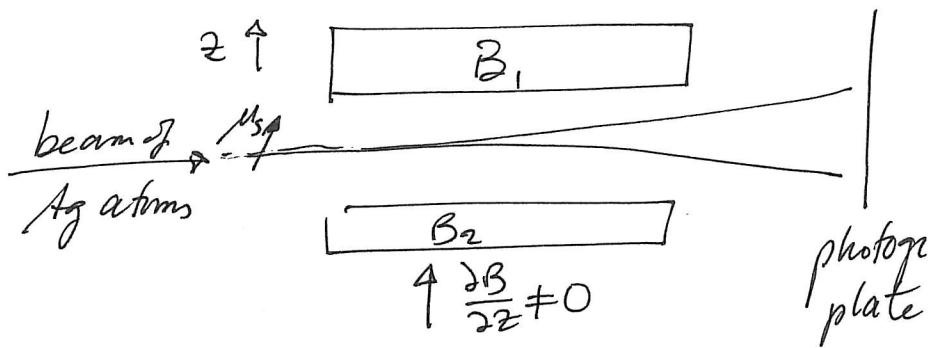
• "normal" Zeeman effect ... neglects spin

Stern - Gerlach : Spin

1921: Send a beam of Ag atoms through a B gradient

ensure $L_{tot} = 0$ for atoms (e.g., S state)
orbital

expect if orbital ang. mom zero, nothing happens!



• if $\mu \neq 0$, deflection of beam expected

• if B is homogenous ($\frac{\partial B}{\partial z} = 0$)
 no torque / force on moments

• if $\frac{\partial B}{\partial z} \neq 0$ and moment μ_s ? net force on atom if $L_{net} \neq 0$

$$F_z = \mu_s \cos \theta \frac{\partial B}{\partial z} \quad \theta = \text{angle of } \vec{\mu}_s, \vec{B}$$

• found: even if orbital $\vec{L} = 0$, deflection of beam!
 - split into 2 parts! some atoms \uparrow , some \downarrow

• Suggestion: electrons have their own intrinsic ang. momentum & moment! Spin

• moment $\vec{\mu}_s$, ang mom. \vec{S}

• in addition to moment / L from orbital motion

Spin has only 2 values, unlike angular (orbital) momentum

new quantum # m_s

~~$m_s = \pm 1$~~

$m_s = \pm \frac{1}{2}$

like ang. orb momentum, can specify $|\vec{S}|$ and $|S_z|$

$$|\vec{S}| = \sqrt{s(s+1)} \hbar$$

$$S = \text{spin ang mom} = \frac{1}{2} \text{ always}$$

$$S_z = m_s \hbar$$

$$m_s = \text{spin quant \#} = \pm \frac{1}{2}$$

(like $l, m_l \dots$ but less mult.)

so

$|\vec{S}| = \frac{\sqrt{3}}{2} \hbar$
 $S_z = \pm \frac{1}{2} \hbar$

total spin ang mom

z component ... e.g. projection onto B

$\pm \frac{1}{2} \rightarrow$ "up", "down"

moment? proportional to ang mom, like orbital

$$\vec{\mu}_s = -g_s \left(\frac{e}{2m} \right) \vec{S} = -g_s \mu_B \vec{S}$$

we observe \vec{z}

$\mu_z = -g \mu_B m_s = \pm \mu_B$

$$g_s = \text{"gyromagnetic ratio"} \approx 2.0 = \frac{|\vec{\mu}_s| / |\vec{S}|}{|\vec{\mu}_l| / |\vec{L}|}$$

i.e. magnetic moment to angular momentum ratio
is twice as big as orbital case (if $s=0$ is energy diff)

e.g. e^- alone in B_z : $\mathcal{L}_B = -\vec{\mu}_s \cdot \vec{B} = -(g \mu_B) \vec{S} \cdot \vec{B} = -g \mu_B S_z B$

$$= -2 \mu_B$$

Spin-Orbit

• So now we have 2 kinds of angular momentum!

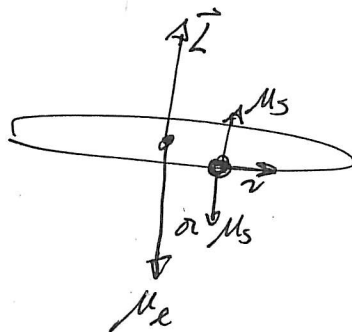
Spin \vec{S} orbital \vec{L}

• Strictly: combine as vectors - they couple to each other!

e.g. bar magnets or current loops - moments



$$E_{NN} > E_{NS}$$



(L can't be purely along z ; just pic)

• $\vec{L} + \vec{S}$ should be conserved

total angular momentum

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



previous rules imply

$$J = \sqrt{j(j+1)} \hbar$$

$$J_z = m_j \hbar$$

$$j = l \pm \frac{1}{2}$$

$$m_j = -j, -j+1, \dots, j$$

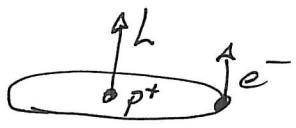
(always fraction eg $\frac{5}{2}, -\frac{1}{2}$)

- as before w/ \vec{L} , $(2j+1)$ states of total L

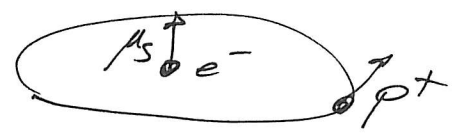
- better way to char multi- e^- atoms... or if L, S coupled

$\vec{L} \parallel \vec{S} \rightarrow \vec{\mu}_e, \vec{\mu}_p, \dots$ should couple like bar magnets!

classical model of groundstate



p^+ rest frame
 e^- orbits = current loop!



e^- rest frame:
atom/ p^+ orbits it

- e^- feels a current due to proton orbiting it!

as before, $B_e = \frac{\mu_0 I}{2r} = \frac{\mu_0 e v}{4\pi r^2}$ since $I = \frac{e}{T} = \frac{e v}{2\pi r}$

but $v = \frac{\hbar}{mr}$ (since $L = mvr = \hbar$ in lowest state)

$\Rightarrow B_e = \frac{\mu_0 e \hbar}{4\pi m r^2} = \frac{\mu_0 \mu_B}{2\pi r^3}$ } e^- feels an effective B field due to rel motion of atom!

e.g. $r \sim 0.1 \text{ nm}, \mu_B = 58 \mu\text{eV/T} \Rightarrow B \sim 2 \text{ T!}$ Sign!

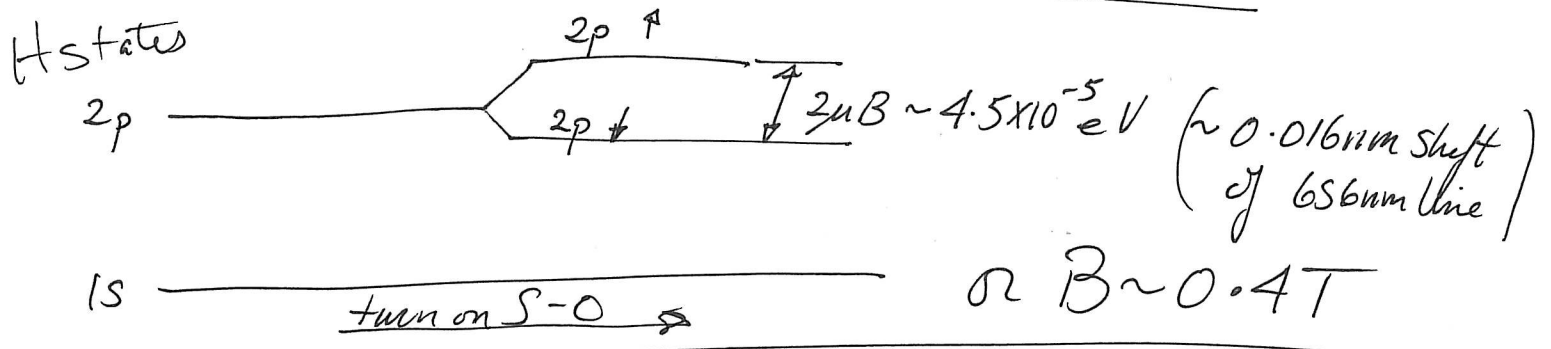
So? Since $\mathcal{E} = -\vec{\mu} \cdot \vec{B}$, e^- energy depends on orientation relative to L !

$\Delta E \sim 2\mu_B B \sim 0.25 \text{ meV}$ shift of M_s levels!

- ΔE much smaller than E of levels or other spacings \Rightarrow "fine structure"

- for lowest l level, really no splitting - $l=0$ (all s states no $s-0$)

- 1st excited state ($n=2$) $\Delta E \sim 0.9 \times 10^{-4} eV$

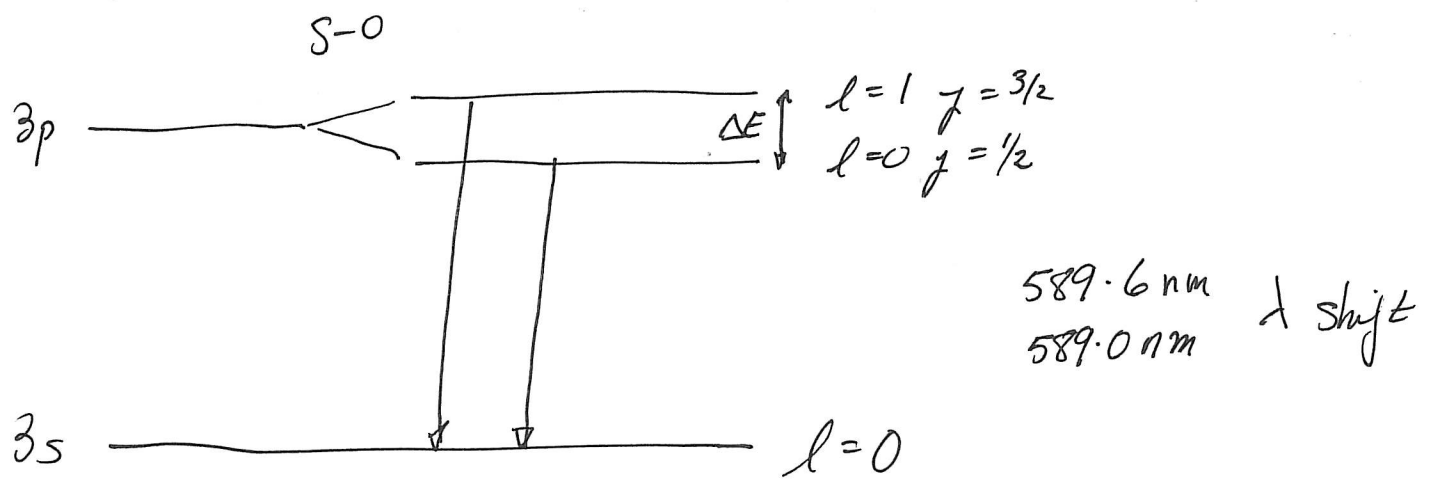


another example: Sodium transitions "D lines"

lowest state $l=0$; 1st excited $l=1$

$\Delta E_{l=1} \approx 2.14 meV$ (10x hydrogen)

observable in optical spectra (PH2SS)



generally splits p, d, f states

This is where HW6-7 #1 came from!

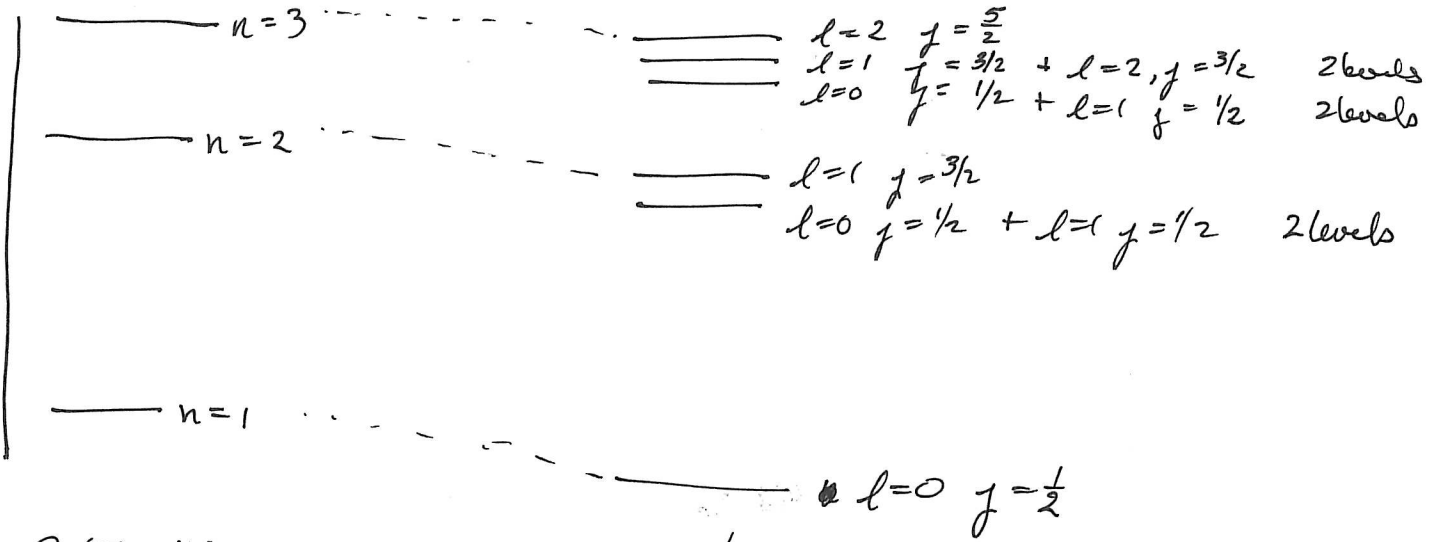
$$E_{n,l} = E_n \left[1 + \frac{\alpha^2}{n} \left(\frac{1}{l + \frac{1}{2}} - \frac{3}{4n} \right) \right] \quad \text{from Dirac eqn}$$

fine structure due to spin-orbit!

$$j = l \pm \frac{1}{2} \begin{cases} +\frac{1}{2} & \text{parallel L, S} \\ -\frac{1}{2} & \text{antipar L, S} \end{cases}$$

Bohr

w/ S-O (Dirac)

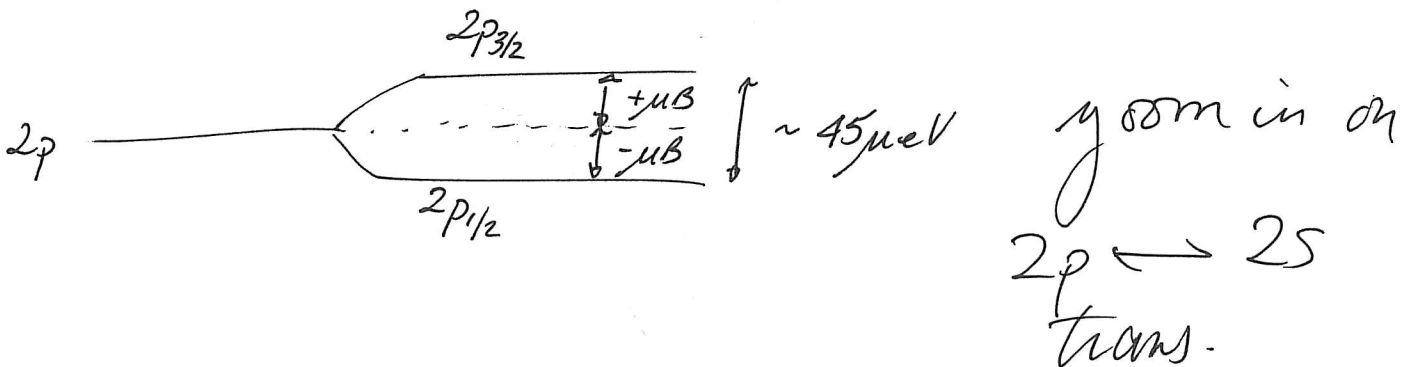


3 transitions \rightarrow many transitions

e.g. $n=2 \rightarrow n=1$
Single line

e.g. $n=2 \rightarrow n=1$ 2 lines

$n=3 \rightarrow n=1$ 3 lines



Spectroscopic notation

a necessary evil to read literature

$l: \quad 0 \quad 1 \quad 2 \quad 3 \quad 4$
 $\quad \quad s \quad p \quad d \quad f \quad g$

} conversion from l
to orbital letters

earlier times: letters come from spectra, not l !

$s =$ sharp

$p =$ principal

$d =$ diffuse

$f =$ fundamental

• add to this state of an indiv. e^- (except L_z)

write value of n
 follow by letter for l

} $3p \quad 3d \quad 4f$ etc

• add subscript for j value

$3p_{3/2} \rightarrow n=3, l=1, j=3/2$ (so $s = +\frac{1}{2} = \uparrow$ $L \parallel S$)

$3p_{1/2} \rightarrow n=3, l=1, j=1/2$ ($s = -\frac{1}{2} = \downarrow$)

finally, fine structure ($S-O$) turns each level of $l \neq 0$ into a doublet (pair, split)

\Rightarrow Superscript in front of l symbol/letter \rightarrow denote multiplicity or # of states

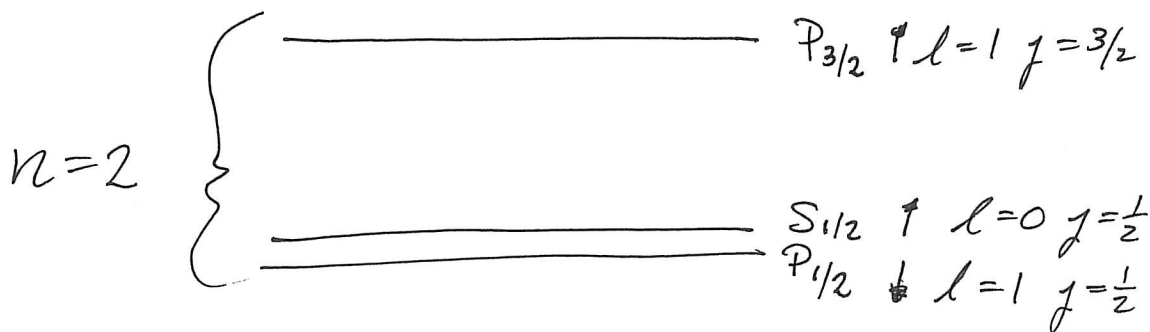
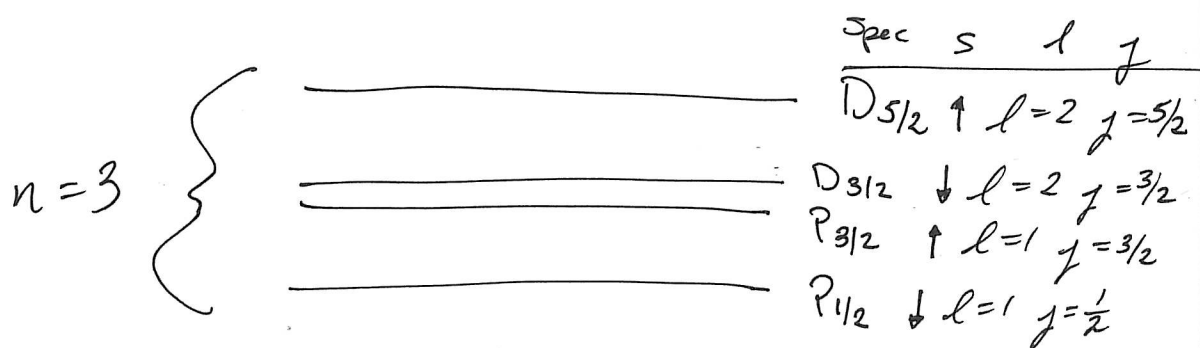
e.g. $n=3, l=1, j=\frac{3}{2} \rightarrow 3^2 P_{3/2}$ or $3^2 P_{3/2}$

(makes more sense w/ many electrons)

if letter is LOWER case ... single e^- state

if letter is UPPER CASE ... state of whole atom

e.g. H fine structure



Selection rules for level transitions

fine str examples

①

- when an e^- changes levels, must still conserve \vec{L}, E
 - E consv easy if photon is involved

- angular momentum is less clear...

- general rules for probability of transitions
 - "Selection rules"

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

- if obeyed - strong!

- if violated - just unprobable (weaker), not impossible

- have to consider interaction w/ EM wave...

- wave resembles an electric dipole, implies consrv.
implies \vec{L} change

- always need net change of 1

in orbital angular momentum

$$\Delta l = \pm 1 \text{ (NOT zero)}$$

- magnetic quantum # can change by 1 unit

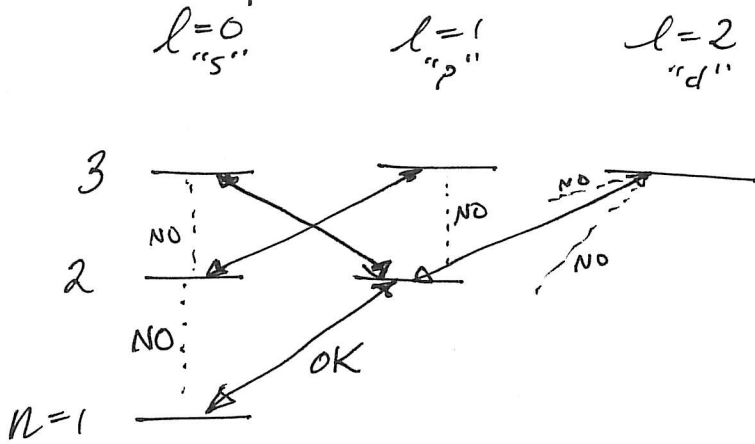
$$\Delta m_l = 0, \pm 1$$

- another "why" - photon has spin 1, electron $\frac{1}{2}$
photon implies must take away / add L !

- for these strong "dipole" transitions, electron spin does not change
 $\Delta m_s = 0$ no spin flips

- if \vec{L} and \vec{S} are coupled, photon interaction requires at least total angular momentum rule (Spin-orbit coupling...)

Example: H levels



(assume no spin)

(assume all m_l have same E for given n, l)

$\Delta l = \pm 1 \Rightarrow$ cannot stay in same orbital
 no $3s \leftrightarrow 2s$

- photon gives/takes $\pm \hbar$ of L from atom, so final state must change by $\Delta l = \pm 1$
- magnetic dipole ($\sim 10^5$ weaker) - can have $\Delta l = 0, \Delta m = 0, \pm 1$ $\Delta m_s = 0, \pm 1$ (spin flip)

Pauli - no 2 e^- can have same quantum #'s
 $|n, l, m_l, m_s\rangle$ one unique e^- state!

example: 2 e^- with same (n, l, m) must have opposite spins

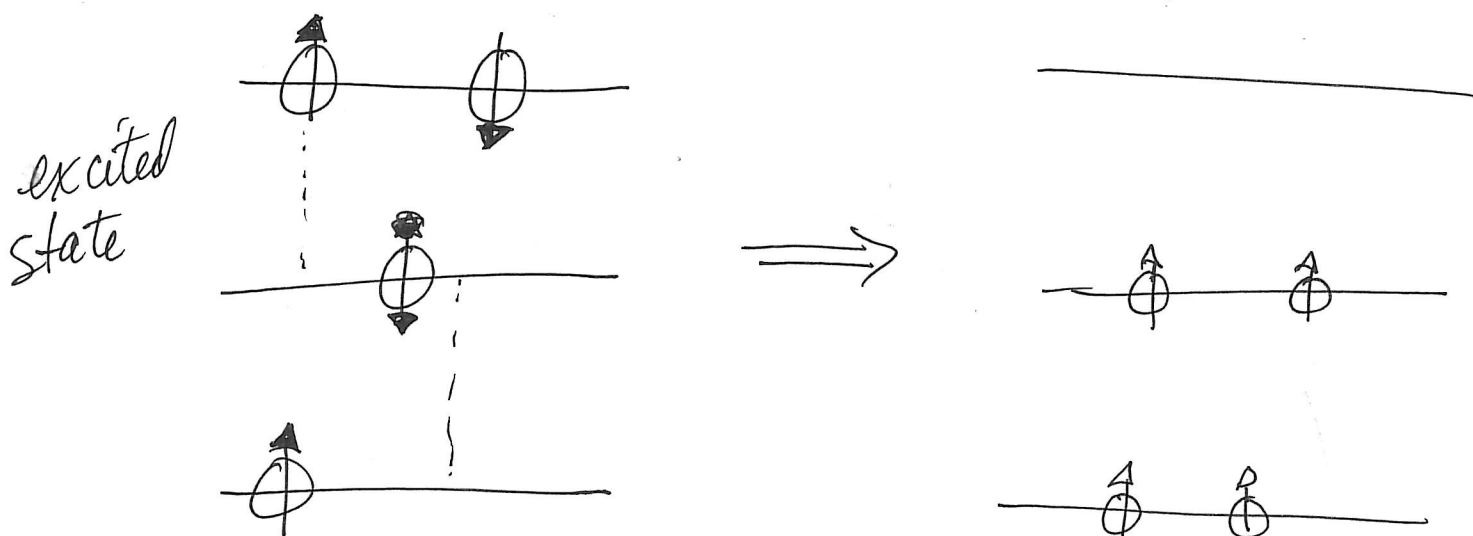
3s \equiv 3p : ~~$\uparrow\downarrow$~~ ~~$\uparrow\downarrow$~~ ~~$\uparrow\downarrow$~~ 3p holds $6e^-$; 3 $\uparrow\downarrow$ pairs

$\uparrow\downarrow$ 3s holds $2e^-$ $\uparrow\downarrow$

• in a given level with 2 states (holds $2e^-$) they must be of opposite spin

• more on this next week ($\hat{=}$ its origin); for now, just a rule for building larger atoms

• example: HW #7



- (2)
- Consequences of Pauli:
- filling of energy levels with e^-
 - "exchange" energy of multi- e^- atoms
i.e. energy depends on spins' orient
 - magnetism

Comes from? only that e^- are indistinguishable!

- if we try to fill levels of H atom w/ many electrons (while adding protons)

given $n \rightarrow l$ substates $\rightarrow m_l$ substates \rightarrow spin

n in number $2l+1$ in # $\times 2$

so at a given n , $2(2l+1)$ electrons can be accommodated
"shell"
with different $m_l \equiv m_s$

- This leads to periodic table, filling of levels, etc
 - if not for Pauli, all e^- in lowest level perhaps
 - that's why we say each $|n, l, m_l\rangle$ level holds 2

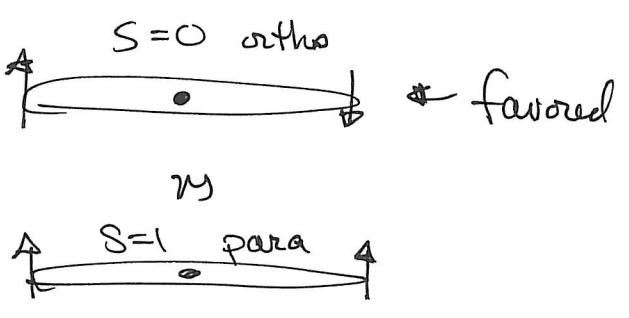
Let's look at He and work our way up!

- spectral lines classified by 2 seemingly separate energy level diagrams (HW #5)
- thought for a while to be 2 elements! (para, or the He)
- now known to just be 2 different spin arrangements!

2 e⁻ in He

◦ both spins ↑↑, S_{tot} = 1
"triplet" or "ortho"

◦ both spins ↑↓, S_{tot} = 0
"singlet" or "para"



◦ why "singlet" vs "triplet"? think about \vec{J}

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

- if S=0 ∴ spins cancel, J=L only one energy state for L

- if S=1 ∴ spins align, J = {L-1, L, L+1} three energy states for L

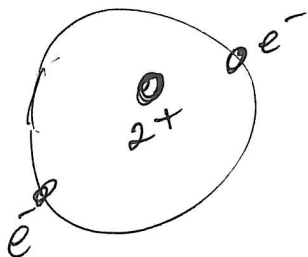
so for S=0, ~~3 states~~ 3 levels of same energy (degenerate)
S=1, 3 slightly different energy levels

- ! can measure this - see triplet lines for ortho-He
- So He can exist in these 2 forms. but the 2 cannot easily mix! would not conserve \vec{I} or \vec{L} !
 - would require an e^- to flip its spin, forbidden by transition rules \Rightarrow very hard, takes along time
 - So, prepare ortho-He, it is higher E, but longer-lived!
See HW

Ground state of He - lowest energy

- both e^- have $n=1, l=0, m_l=0$ ($2s^2$)
- requires by Pauli that they have spins $\uparrow \downarrow$ for lowest E ("exchange energy" is the difference)

- Pretend the 2 e^- don't interact. Then it's just H w/ extra p^+



$$E_n = -\frac{Z^2 m e^4}{2 \hbar^2} \cdot \frac{1}{n^2} = -13.6 \frac{Z^2}{n^2} \text{ eV}$$

HW

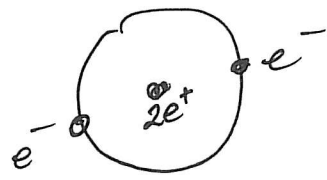
$$E_1 = -54.4 \text{ eV for either electron}$$

- ionization energy

problem: expt measures

$$-24.5 \text{ eV! d'oh!}$$

- Clearly, $e^- - e^-$ interaction is key, as it halves lowest energy!
- interaction is Coulomb repulsion!



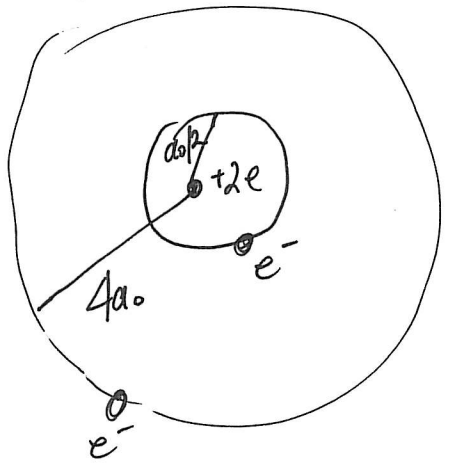
- e^- will try to be far apart
- treat like hydrogen, $r = \frac{a_0}{2}$ ($\because Z=2$)
- electric PE: $\frac{ke^2}{r} = \frac{2ke^2}{a_0} \sim 27eV$

! nearly makes up the difference!
(about 3eV off yet)

message: electron interactions are crucial!

How about excited states? one e^- in $n=1, l=0$
second in $n=2$

- likely to work better, since for $n \geq 2$ observed levels match H pretty well (see HW) either para- or ortho-



- ignoring e^- interaction again (and spin)
 $r_1 = a_0/2$ $r_2 = 4a_0$
- e^- ~~at least~~ ~ 4 times farther apart
 \Rightarrow interaction energy reduced
 \Rightarrow more "H-like"? sort of...

Difference

- inner e^- feels full $+2e$ from nucleus
- before, other e^- partly "screened" the nucleus
now not so much - too far (8x further!)

- from inner e^- POV, stronger nucleus PE (lower E)
- from outer e^- POV, weaker and more concentrated spatially (higher E)

Consequence: l -dependence of $n \geq 2$ levels, slightly



or: orbits that bring 2nd e^- farther from nucleus have E diff than those bringing it closer

e.g. $l=0$ $|\psi|^2$ spherical, has nonzero value near nucleus
 \Rightarrow stronger attraction \Rightarrow lower E

$l=1$ $|\psi|^2 = 0$ at nucleus, "farther"
 \Rightarrow less attraction \Rightarrow higher E

Quantum Model

we can just write down Schrödinger

$$\left[\underbrace{\left(-\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{2ke^2}{r_1} \right)}_{\text{K+PE for } e^- 1} + \underbrace{\left(-\frac{\hbar^2}{2m} \nabla_2^2 - \frac{2ke^2}{r_2} \right)}_{e^- \# 2} + \frac{ke^2}{r_{12}} \right] \psi = E \psi$$

feeling nucleus

feels nucleus

interaction of 2 e⁻

- ! 1/r₁₂ term is the problem ⇒ not separable
- ⇒ 3 body problem
- ⇒ no analytic soln

(can do numerically w/ arbitrary accuracy)

- even for He, problem must be done numerically
- next week, discuss approx schemes
- simplest: Self-consistent!

~~basic idea: write interaction as V(r₁₂)~~

~~guess its form & value~~

~~Calculate ψ~~

Basic method

- guess ψ ←
- solve for E
- plug E back in to get new ψ } repeat

(More on this next week)

Classification of He levels

- 2 e⁻ now, so 2 sets of quantum #'s (n₁, l₁, ...) (n₂, l₂, ...)
- spins ↑↑ or ↑↓

net orbital: $\vec{L}_1 + \vec{L}_2 \Rightarrow |l_1 - l_2| \leq |\vec{L}| \leq l_1 + l_2$

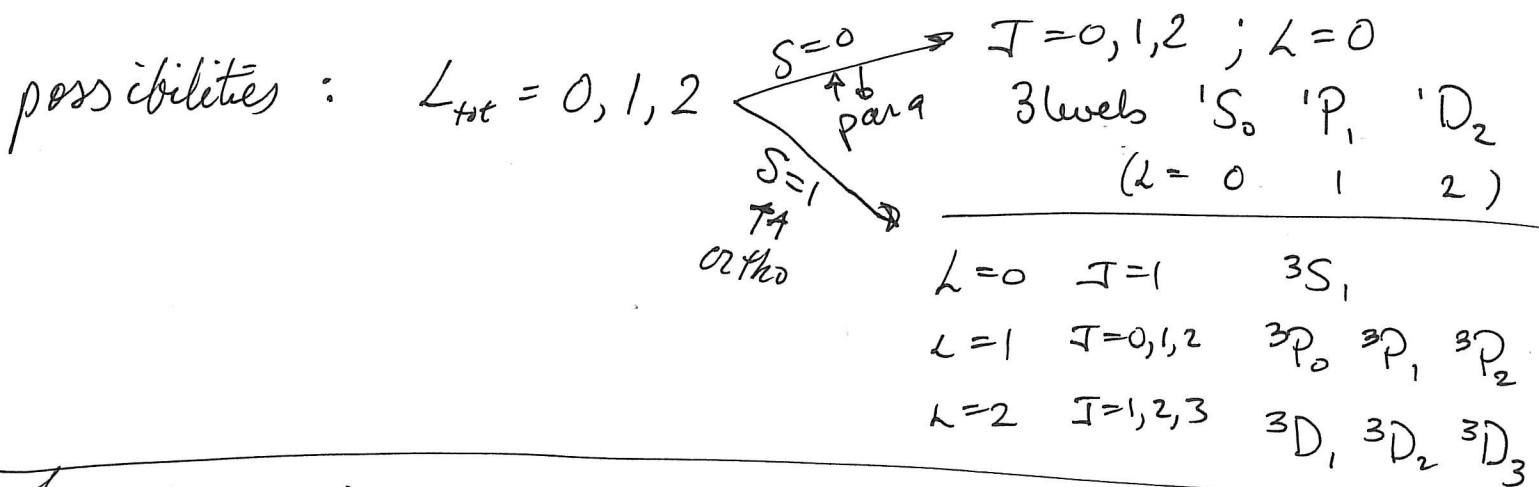
- o still quantized, but many more values
- ⇒ more lines in Zeeman
- more lines from spin-orbit

Total \vec{J}

if spins ↑↓ in ground state? $\vec{J} = \vec{L}$ ∵ spins cancel
S = 0

↑↑ case? $|\vec{J}| = L-1, L, L+1$
S = 1 } ~~all~~ 3 diff levels

Specific case: n₁ = n₂ = 2
l₁ = l₂ = 1



Based on L & S: 2 types of ground states
different multiplicities & energies

• last point: how can we say "2p" or "3s" or 500n when the 2e⁻ might have different n's?

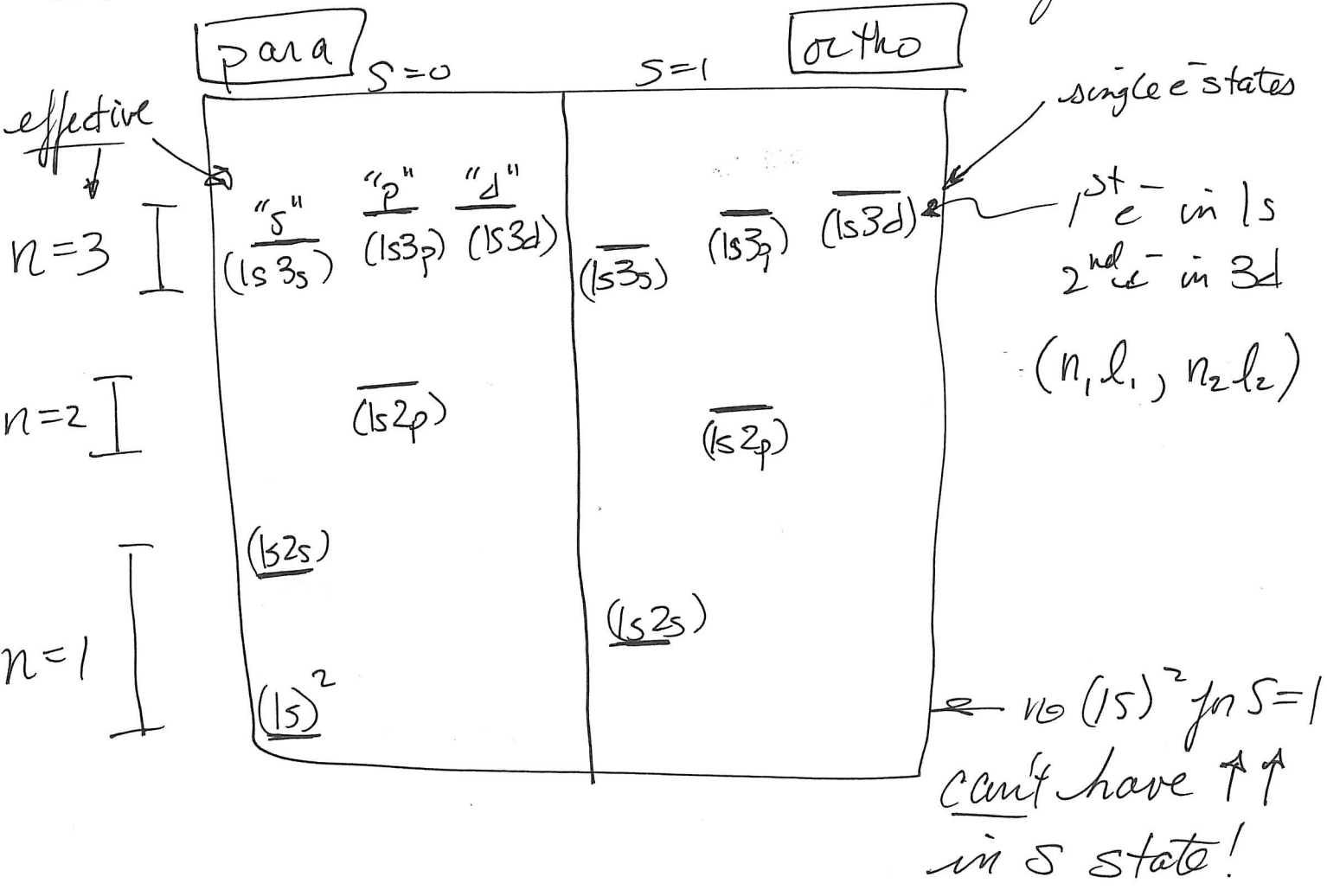
"effective quantum #"
 $n = n_1 + n_2 - 1$

(So previous case : $n = 2 + 2 - 1 = 3$)

• "1s" etc no longer VACED for whole atom --- just analogy

• making this effective n lets us re-use our H terminology
 same for L values - use L_{tot} and S_{tot}

• label states also like (2s, 2p) to denote both n e⁻ quantum #'s



Rest of the table?

- Hopeless like this. how about Pb? Z=82 forget it
- approx (numerical) methods + intuition/terminology from H & He!

K Shell

n=1 or "1s"

- holds 2e⁻, antiparallel spins
- a 3rd e⁻ must then enter n=2 state! (l=0,1)

- first 2 e⁻ "screen" nucleus

- 3rd is loosely bound (farther + screening)

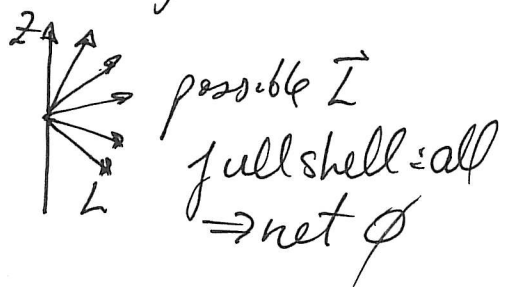
↳ reactive ... will give up easily finding E lower

What happens when a shell fills up? in General?

- in this case, next e⁻ is a loner ... weakly bound

- net \bar{L} is ZERO for a filled shell!

⇒ sum of lobes ≈ sph. symm again like "s" state



⇒ no dipole (quad-etc) ⇒ no elect. attraction!



L Shell $n=2$ (2s, 2p)

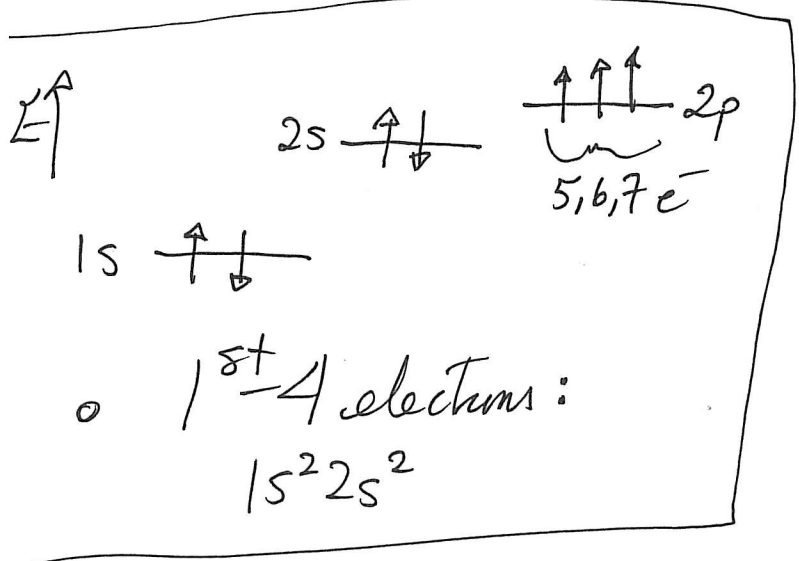
- 3rd e^- "sees" a central charge $\sim (Z-2)$ "screened"

UNLESS it is in an orbit/subshell that brings it close to nucleus (within cloud of 1st 2 electrons)

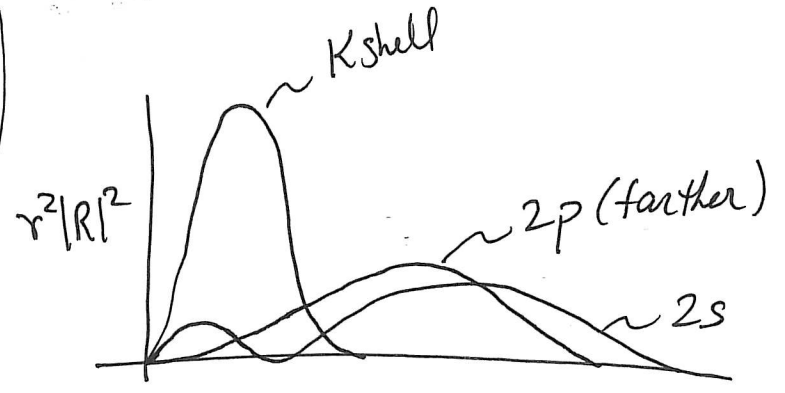
- more it penetrates, more of (+) chg it sees
 \Rightarrow more attr \Rightarrow lower ϵ

\Rightarrow 2s ($l=0$) lower than 2p ($l=1$)
fills just!

- 4th electron also in 2s, w/ spin antipar 3rd



o 1st 4 electrons:
 $1s^2 2s^2$



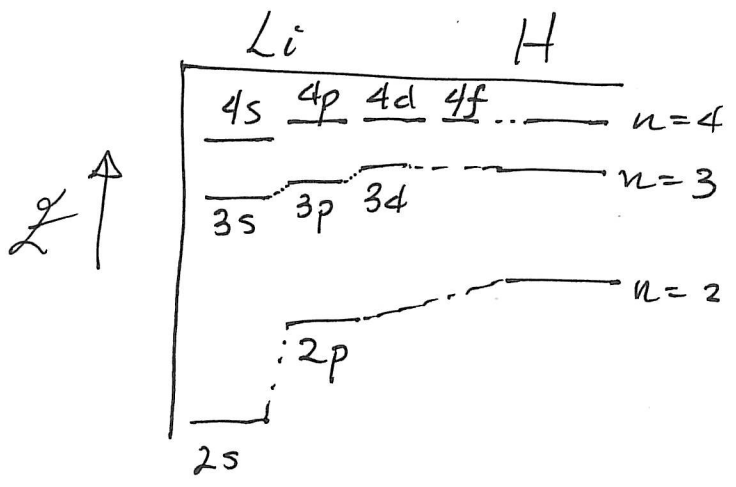
2s closer to nucleus
 \Rightarrow more electr PE
 \Rightarrow lower ϵ state

o 5th has to go to 2p }
Because of Pauli }
• 2p holds 6 electrons
• if there is no spin-orbit, ~~they~~ spins go in \uparrow same direction

3 e⁻: Lithium can descr. by 1s²2s¹ or just 1s²2s

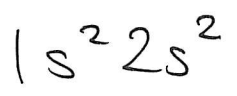
lone 2s electron much like n=2 of Hydrogen

inner 2 e⁻ screen nucleus to look like Z=1

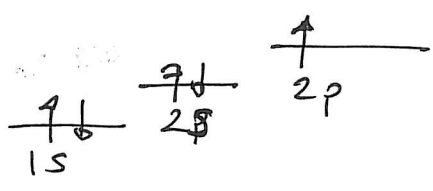
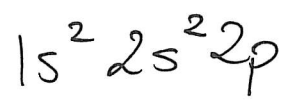


higher levels (farther from)
look more like H

4 e⁻: Be

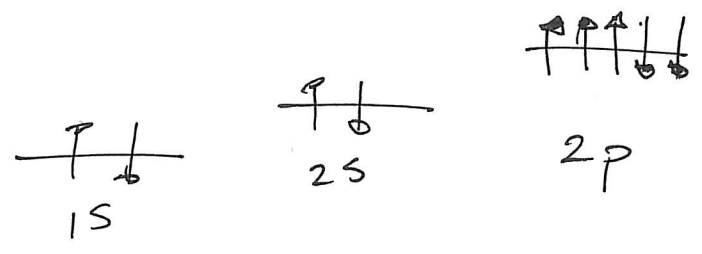


5 e⁻: B



∴ C
∴ N
∴ O

9 e⁻: F



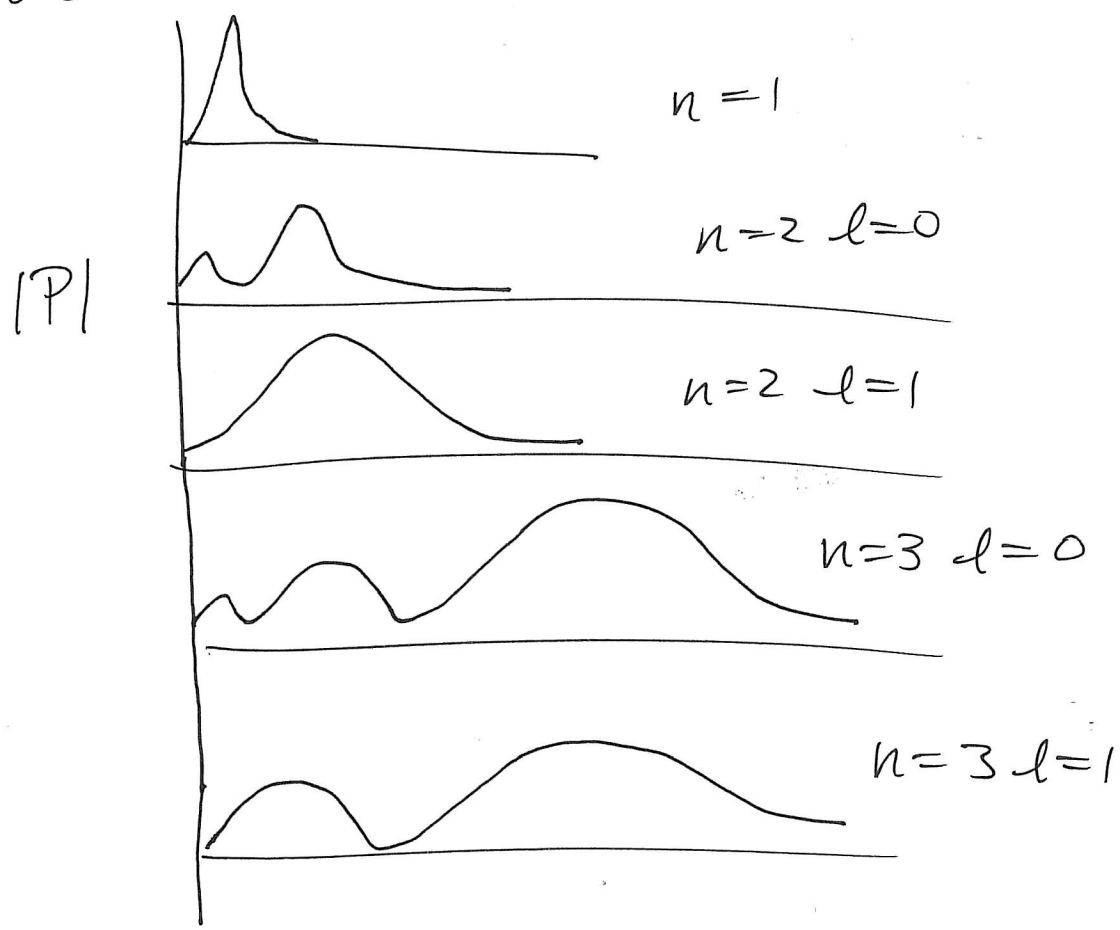
• Subshells like "p" "d" "f" fill to MAX spin S
e.g. p level ↑ → ↑↑ → ↑↑↑ → ↑↑↑↓ etc

When we get to Ne, "L" shell fills! $Z=10$

- like He case
- zero angular momentum
- all e^- fairly tightly bound
- very unreactive - + or - one e^- less stable

M Shell
 $n=3$

Starts with Na, $Z=11$



after 2p, fill 3s - still closer to nucleus \Rightarrow lower E

1s, 2s, 2p, 3s, 3p fill "in order" i.e. order Energy

by $Z=11$ (Na) screening gets more & more important

K shell filled = net $-2e$ chg

L shell filled = net $-8e$ chg
 $10e^-$

• So 11^{th} e^- to make Na feels a H-like potential again!
(whole 1^{st} row!)

e^- very loosely bound - H-like, but MUCH farther away

⇒ easily ionized

easily "trades" its last electron

VERY reactive

1^{st} row: reactivity ↑ as you go to table

Last row: perfectly filled shell, does not want to give up!

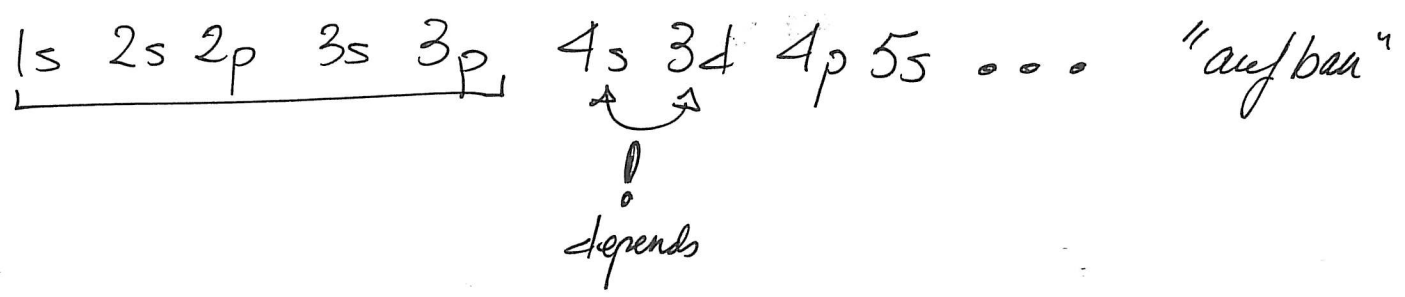
Screening @ max efficiency

add one: weak binding

loose one: less screening

Shell Structure for higher filling

	(n, l)	Shell Capacity	Cumulative total		
1s	(1, 0)	2	2	He	H
2s 2p	(2, 0) (2, 1)	8	10	Ne	Li
3s 3p	(3, 0) (3, 1)	8	18	Ar	Na
3d 4s 4p	(3, 2) (4, 0) (4, 1)	18	36	Kr	K
4d 5s 5p	(4, 2) (5, 0) (5, 1)	18	54	Xe	Rb
4f 5d 6s 6p	(4, 3) (5, 2) (6, 0) (6, 1)	32	86	Rn	Cs
				↑	↑
				full	one



Next time : more on multi-electron atoms
 more on identical particles $\hat{=}$ spin
 close to applications...