Many-electron atoms

$$\hat{H} = \sum_{i=1}^{Z} \left(\frac{p_i^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right) + \sum_{i>j} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}$$

Z electrons in the field of the nucleus with charge $|Ze|$

electrostatic interaction between all e^- (pairwise)

if we ignore e–e interaction → H-like Coulomb field

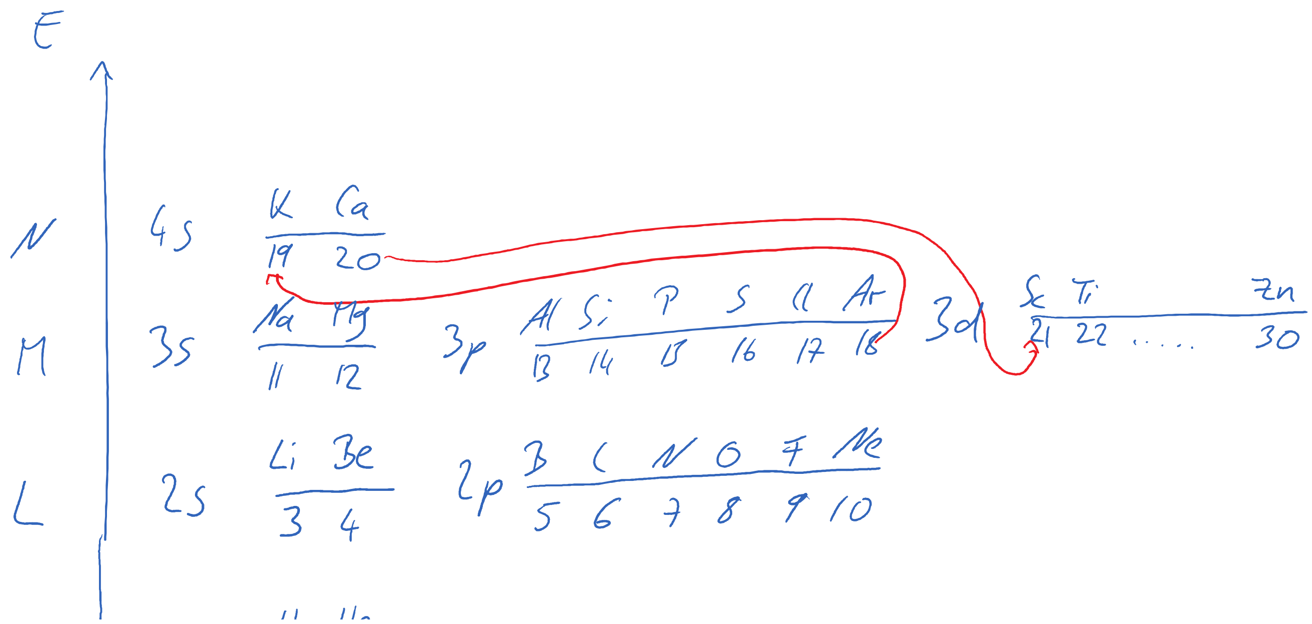
Pauli exclusion principle
→ only $2e^-$ in each atomic state

n: each n state has n values of ℓ
$\ell = 0, 1, \dots n-1$

ℓ: each ℓ state has $(2\ell+1)$ values of m_ℓ
$m_\ell = -\ell, -\ell+1, \dots 0, 1, \dots \ell-1, \ell$

each of these states can have $2e^-$ with different m_s

⇒ each (n, ℓ) can support $2(2\ell+1)$ electrons
each n holds $2n^2$ electrons $\quad \sum_{\ell=0}^{n-1} 2(2\ell+1) = 2n^2$



$$K \quad 1s \quad \frac{H \quad He}{1 \quad 2}$$

$2(2l+1)$ $\quad 2e^-$ $\quad 6e^-$ $\quad 10e^-$

Why is the 4s state filled before the 3d state?

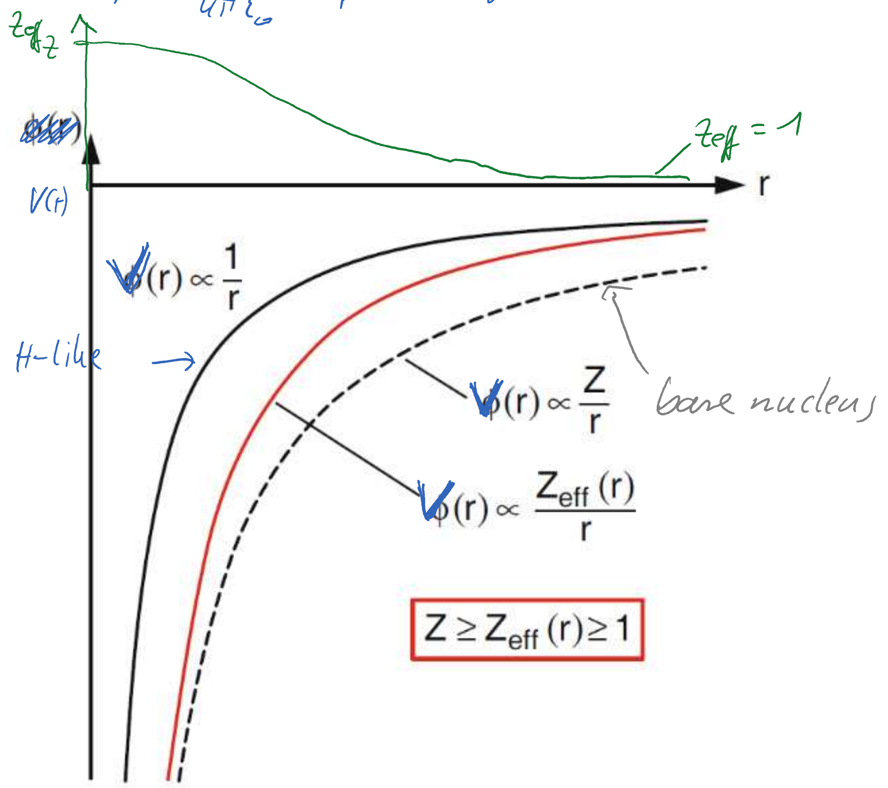
$\Rightarrow$ look @ single e^- in field of nucleus + all other e^-

- at $r=0$ the e^- sees charge Ze
  (all other e^- are "outside")

$$V(r) = \frac{Ze^2}{4\pi\varepsilon_0} \cdot \frac{1}{r} \quad \text{for small } r$$

- at large distances: $(Z-1)\,e^-$ shield $(Z-1)$ protons

$$V(r) = \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{r} \quad \text{large } r$$



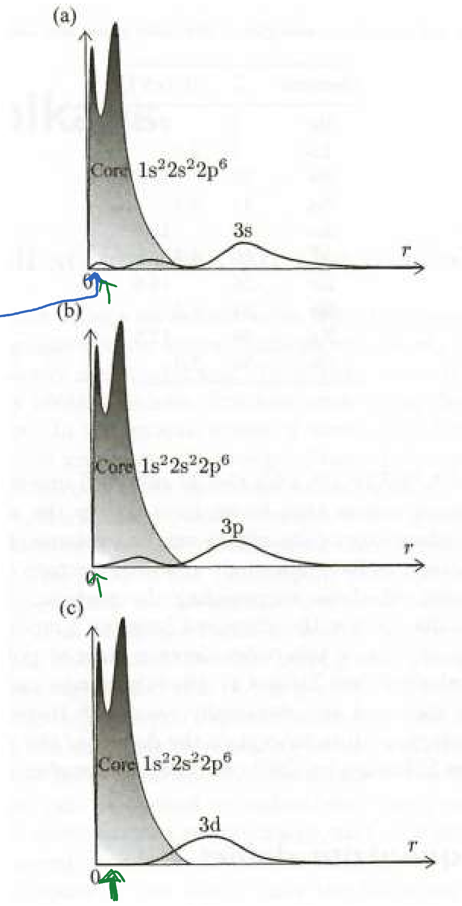
Look @ wave functions

Na

s states have a higher probability to be at small r

→ they see "more of the bare $|Ze|$ nucleus"

→ stronger binding



Foot, Atomic Physics

$$E(ns) < E(np) < E(nd)$$

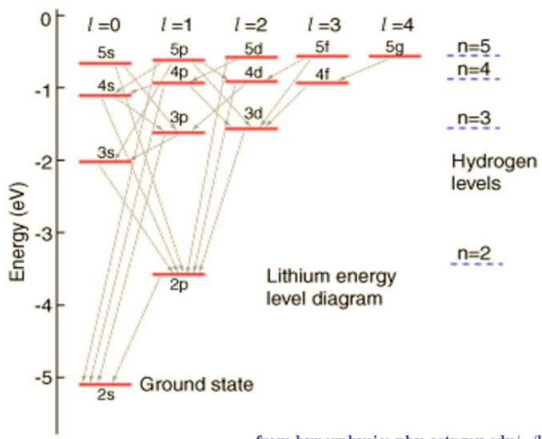
$$\underset{l=0}{\uparrow} \qquad \underset{l=1}{\uparrow} \qquad \underset{l=2}{\uparrow}$$

in contrast to H, states with different l are not degenerate any more

Screening can be significant: several eV

for example: Li $Z=3$

Lithium Energy Levels



from hyperphysics.phy-astr.gsu.edu/.../lithium.html

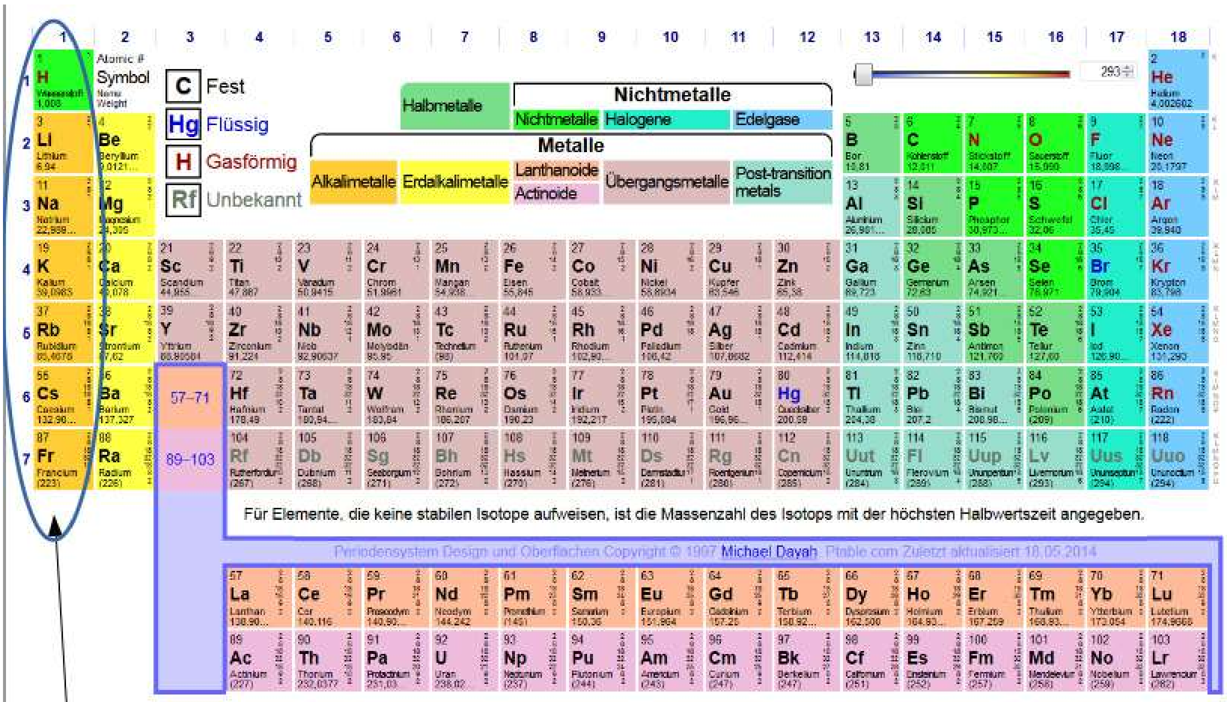
screening effect in Li

$2s \to 2p$ "D lines"

671 nm (red light)

few 100 THz

H: $2s - 2p$: 1 GHz



Alkalis

http://www.ptable.com/

The Alkalis : filled shells + $1e^-$

empiric formula for the energy levels:

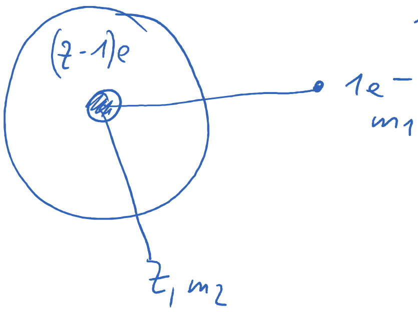
$$E_{n,l} = -\frac{1}{2}\mu c^2 \frac{\alpha^2}{(n - \Delta(n,l))^2}$$

↳ $\Delta(n,l)$: quantum defect

$\hookrightarrow \Delta(n,l)$: quantum defect

$\rightarrow \mu = \frac{m_1 m_2}{m_1 + m_2}$ reduced mass

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$



quantum defect e.g. Na (3s)

$l \backslash n$	$n=3$	4	5	6
0	1.37 eV	1.36	1.35	1.34
1	0.88	0.87	0.86	0.86
2	0.10	0.11	0.13	0.11
3		0.00		

$\Delta(n,l)$ is approx. constant in n
larger for smaller l
small for "circular orbits" $l = n-1$

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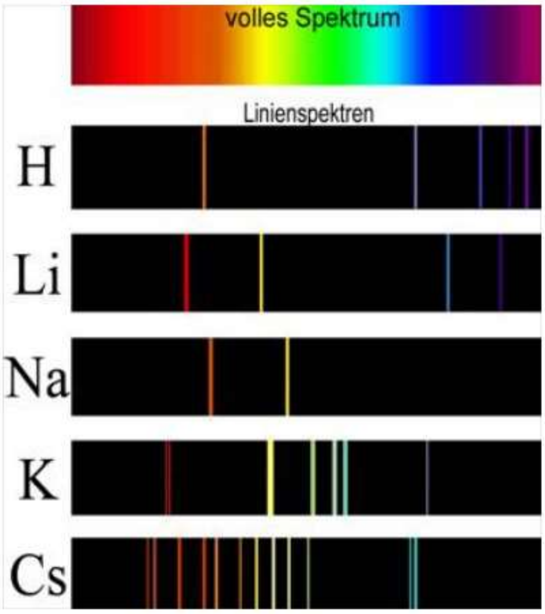
side remark: equivalent description

$$Z_{eff} = Z - \sigma(n,l)$$

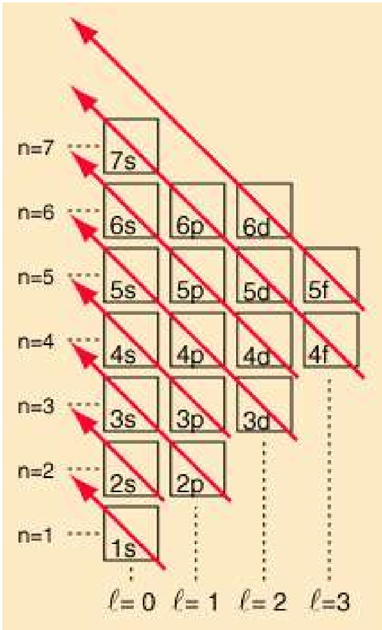
$$E_{nl} = -\frac{1}{2}\mu c^2 \alpha^2 \frac{(Z - \sigma(n,l))^2}{n^2}$$

$\sigma(n,l)$: screening parameter



Many-electron atoms and Hund's rules

5S 5P 5D 5F 5G
4S 4P 4D 4F
3S 3P 3D
2S 2P
1S



Z electrons, all spin $\vec{s}_i$, angular momentum $\vec{l}_i$

all coupled to all others

$\Rightarrow$ very complicated

Easier: How to find the ground state of atom?

$\hookrightarrow$ $\boxed{\text{Hund's rules}}$

Z		e^- configuration	1s	2s	2p	total spin
1	H	$1s^1$	↑			$1/2$
2	He	$1s^2$	↑↓			0
3	Li	$1s^2\, 2s^1$	↑↓	↑		$1/2$
4	Be	$1s^2\, 2s^2$	↑↓	↑↓		0
5	B	$1s^2\, 2s^2\, 2p^1$	↑↓	↑↓	↑	$1/2$
6	C	$1s^2\, 2s^2\, 2p^2$	↑↓	↑↓	↑ ↑	1 ← 2nd Hund
7	N	$1s^2\, 2s^2\, 2p^3$	↑↓	↑↓	↑ ↑ ↑	$3/2$
8	O	– " – $2p^4$			↑↓ ↑ ↑	1
9	F	$2p^5$			↑↓ ↑↓ ↑	$1/2$
10	Ne	$2p^6$			↑↓ ↑↓ ↑↓	0

(1) Full subshells $s^2, p^6, d^{10}, f^{14}, \dots$

have $\vec{S} = \sum_i \vec{s}_i = 0$

and $\vec{L} = \sum_i \vec{l}_i = 0$ $\quad \hat{=} \quad J = 0$

Nomenclature

$$n\;{}^{2S+1}L_J$$

"spectroscopic symbol"

total angular momentum (of atom)

total orbital angular momentum

multiplicity

principal quantum number of last

(un)filled shell

$\Rightarrow$ noble gases He, Ne, ...

filled shells s^2, p^6, d^{10}, f^{14} $\hat{=}$ $^1S_0$

You have to look only at <u>not full</u> shells

How to couple all spins & angular momenta?

2 ways: • L-S-coupling (Russell-Saunders coupling)
→ the "usual" way, in particular for light atoms

• j-j-coupling: heavy atoms (Pb)

A LS coupling

all spins couple to total spin

$$\vec{S} = \sum_{i=1}^{Z} \vec{s_i}$$

2nd Hund

lowest energy ($\hat{=}$ ground state) is achieved with <u>maximal</u> multiplicity $2S+1$ ($S = \max$)

e.g. ^6C $2p^2 = \uparrow\uparrow$ not $\uparrow\downarrow$ _ _

also all orbital ang. momenta couple

$$\vec{L} = \sum_{i}^{Z} \vec{l_i}$$

3rd Hund

$$\vec{L} = \sum_{i=1}^{Z} \vec{l_i}$$

3rd Hund

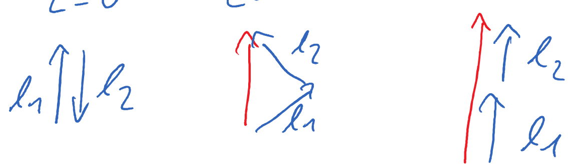
lowest energy with <u>maximal L</u>

total angular momentum

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

e.g. 2 electrons $l_1 = 1$, $l_2 = 1$

$L=0$ $\quad$ $L=1$ $\quad$ $L=2$



S Term $\quad$ P Term $\quad$ D term

for light atoms: spin-orbit interaction for each e^- is weaker than spin-spin interaction