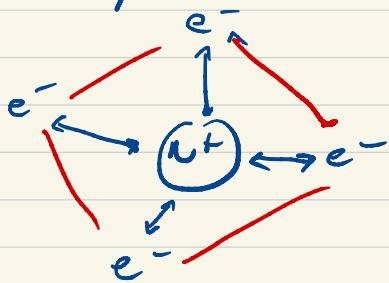
Many-electron atoms



competition between attraction of e^- for nuclei & repulsion between e^-

Schrödinger eq for an e^-

$$\left\{ -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{r} + v_{ee} \right\} \psi_i = \varepsilon_i \psi_i$$

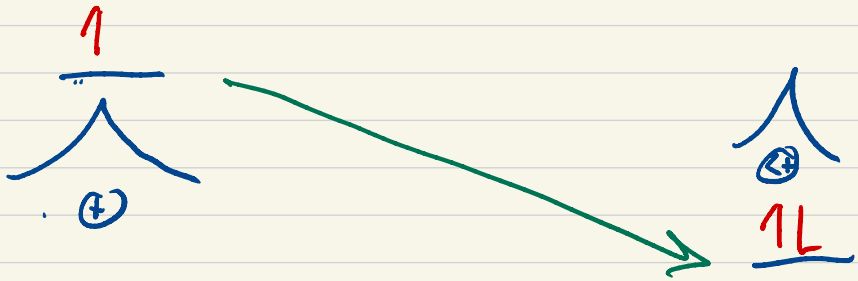
effective repulsion w/ all other e^-

Exact solutions must be constructed on computer.

Qualitative results

1) For given atom, will get ψ_i & ε_i that are qualitatively similar to H atom.

H ⟶ He



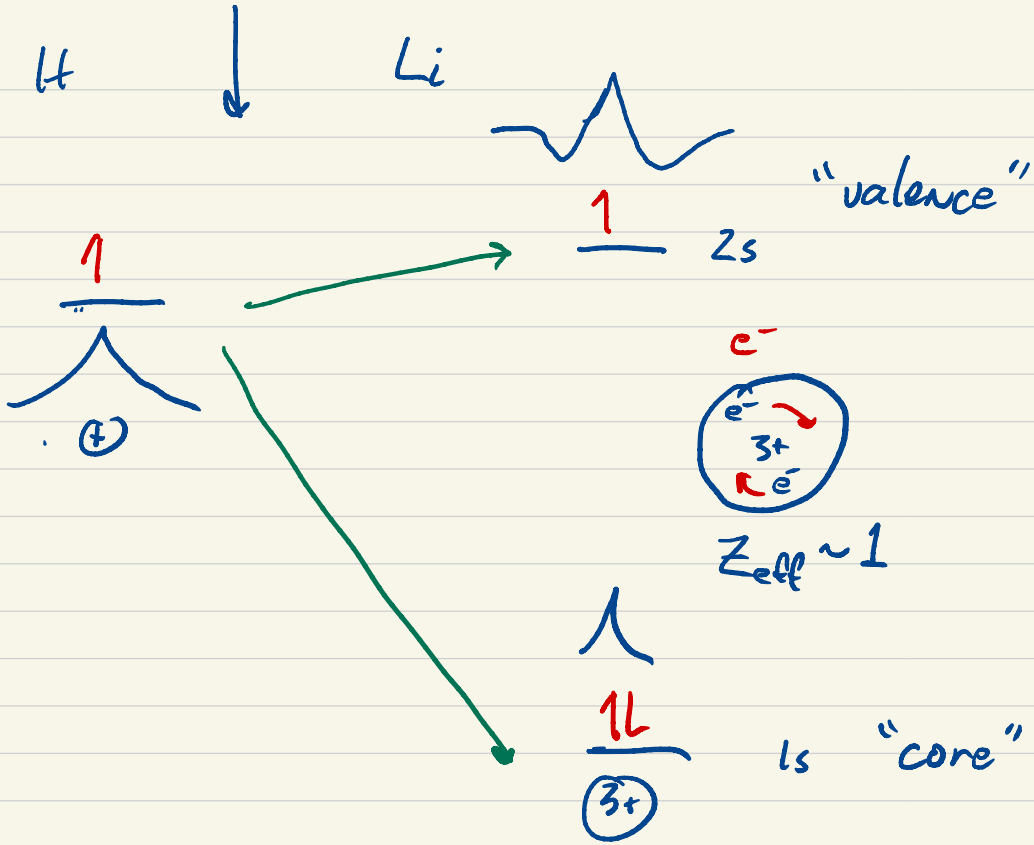
Electrons in 1s "feel" the nucleus the same.
As $Z\uparrow$, more nucleus to feel

$\langle r \rangle_{H\,1s} = 1.5\ au \qquad \langle r \rangle_{He\,1s} \approx 0.9\ au$

$\langle 1/r \rangle = 1.0\ au^{-1} \qquad \langle 1/r \rangle \approx 1.7\ au^{-1}$

(Show from FDA)

<u>Pauli principle</u> - wavefunction/orbital can contain up to 2 e^- of opposite spin.



Aufbau principle – "add" electrons from bottom-up

Core & valence electrons experience different "effective charge"

$$-\frac{Ze^2}{r} + v_{ee} \approx -\frac{(Z-\sigma)e^2}{r}$$

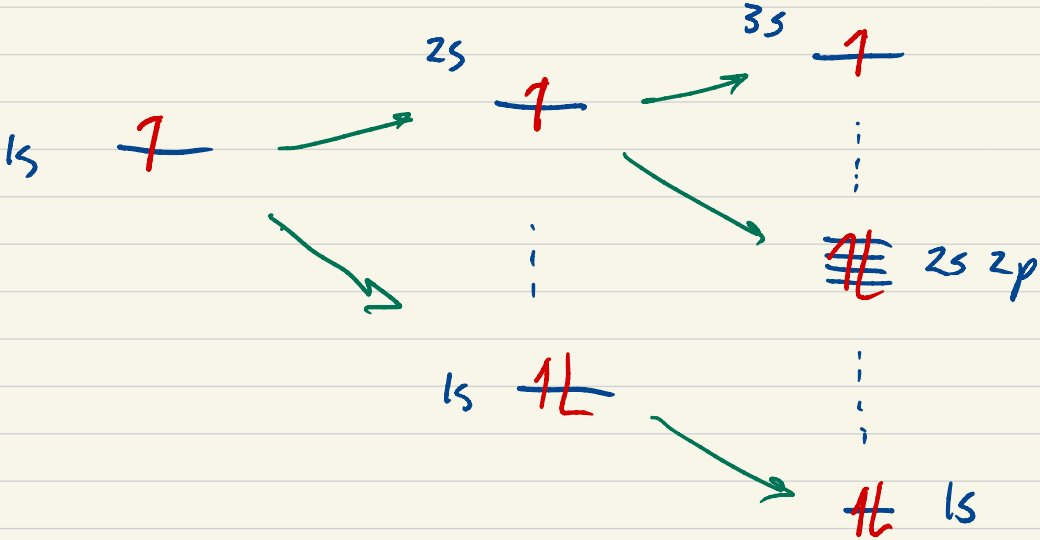
$Z-\sigma \rightarrow$ effective charge "Z_{eff}"

"Core" levels drop in energy as Z gets bigger.
"Unscreened" from nucleus.

"Valence" levels "screened" from core, higher in energy

Down a family

H ⟶ Li ⟶ Na



Core levels "fingerprint" an atom.

Basis of X-ray spectroscopy

Valence levels

$Z_{eff} \uparrow$

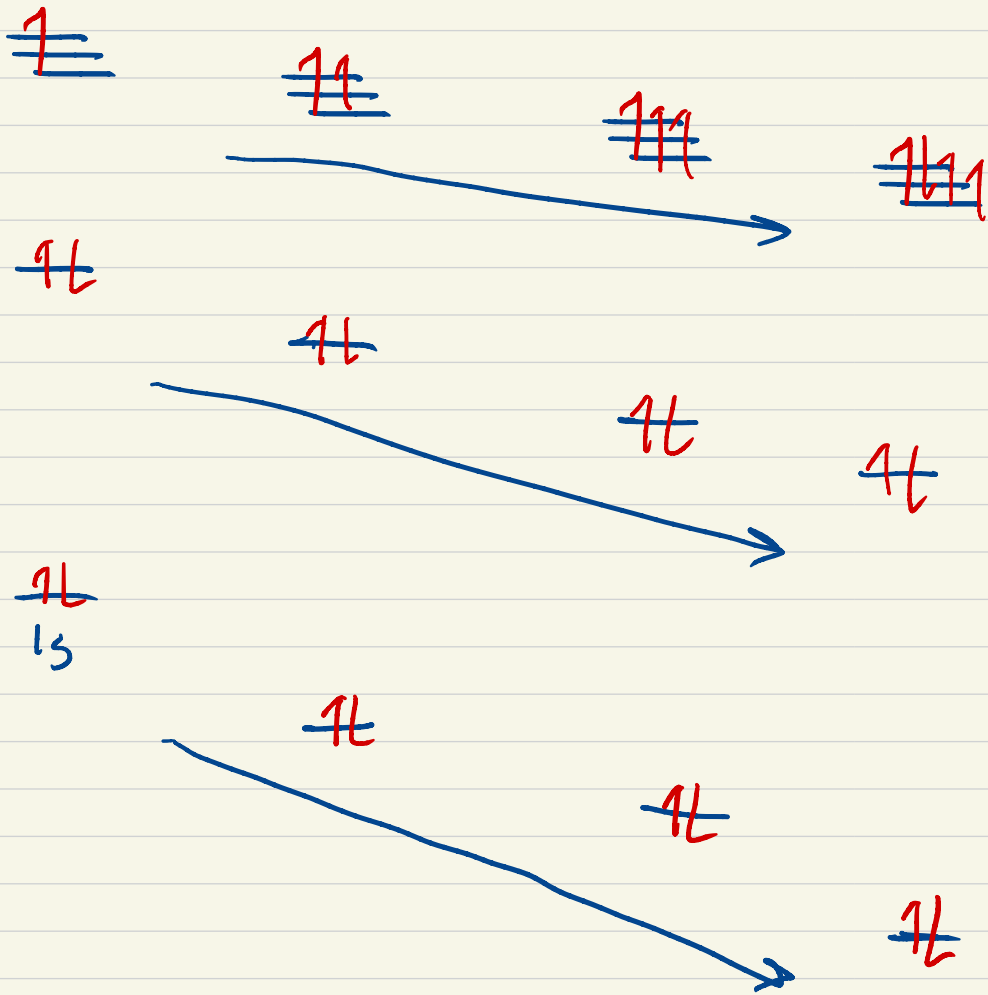
$n \uparrow$ further from nucleus

$\langle 1/r \rangle \downarrow$

$E \uparrow$ down family

Across a row

B → C → N → O



Z ↑ core ↓

Zeff ↑ valence ↓

Illustrates Hund's rule

Given a choice, electrons will choose to spin align rather than spin-pair

(Why? minimize $e^- - e^-$ repulsion)

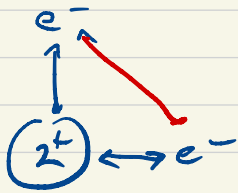
Illustrates spin multiplicity

	S	$2S+1$	
↑	$1/2$	2	"doublet"
↑↓	0	1	"singlet"
↑ ↑	1	3	"triplet"
↑ ↑ ↑	$3/2$	4	"quartet"

Degeneracy of configuration

All of this gives us periodic nature of properties of the elements

Quantitative solutions



nucleus @ c.o.m

$$\psi(\vec{r}_1, \vec{r}_2)$$

$$\left\{ -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{|\vec{r}_1|} + \frac{1}{|\vec{r}_2|}\right) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r}_1 - \vec{r}_2|} \right\}$$

$KE_1 + KE_2$ $\quad V_{Ne_1} \quad V_{Ne_2}$ $\quad V_{ee}$

$$\Psi(\vec{r}_1, \vec{r}_2) = E\,\Psi(\vec{r}_1, \vec{r}_2)$$

unsolvable in closed form! Shit

Must approximate, but how?

variational principle

We know Ψ must obey appropriate boundary conditions

We can guess an acceptable Ψ^g

$$\langle \Psi^g | \hat{H} | \Psi^g \rangle = E^{guess} \geq E^{truth}$$

"Truth" is a lower bound on the possible energies.

If Ψ^g has a parameter in it, for instance, can solve

$$\frac{\partial \langle \Psi^g(\lambda) | \hat{H} | \Psi^g(\lambda) \rangle}{\partial \lambda} = 0$$

and find "best" λ, closest to truth.

Will do on HW for H atom

Can apply this principle to the many-electron Schrödinger eq

$$\Rightarrow \quad \Psi = |\psi_1 \cdot \psi_2 \cdots \psi_n|$$

$$\Rightarrow$$

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0} \cdot \frac{1}{|\vec{r}|} + v_{ee}[\psi_i] \right\} \psi_i = \epsilon_i \psi_i$$

<u>Coupled</u> set of differential eqs

$\mathcal{V}_{ee}[\phi_i]$: effective e^--e^- repulsion

Three pieces.

Coulomb: e^--e^- repulsion averaged over all locations

exaggerates repulsion
but can be calculated exactly

Exchange: accounts for QM indistinguishability of e^- (and self-interaction)

reduces repulsion
can be calculated exactly
expensive

Correlation: accounts for errors in Coulomb, for fact that e^- will avoid one another

Numerous approximations/implementations

Given name "density functional theory" (DFT)

Comes from fact that v_{ee} potentials can be written in terms of the "density"

$$\rho = |\underline{\Psi}|^2 = \sum_i |\psi_i|^2$$

$v_{coul} \rightarrow v_{coul}[\rho]$ exact

$v_{ex} \rightarrow v_{ex}[\rho]$ ~ exact

$v_{corr} \rightarrow v_{corr}[\rho]$ approx

But wait... a priori we don't know ψ_i or ρ... that's what we are trying to solve for!!

self-consistent field

guess ψ_i, ρ

$\downarrow$

compute $v_{coul}, v_{ex}, v_{corr}$

$\downarrow$

set up Schrödinger eq

$\downarrow$

solve for new $\psi_i, \rho, \varepsilon_i, E$

$\downarrow$

$\psi_i^{in} = \psi_i^{out}$?

NO $\rightarrow$ update ψ_i $\rightarrow$ compute $v_{coul}, v_{ex}, v_{corr}$

$\downarrow$ Yes

All done!!

First solved for all atoms, by hand, by numerical integration on radial grid

by Hartree & Hartree

Basis of fda results in outline

More commonly solved today in general purpose codes.