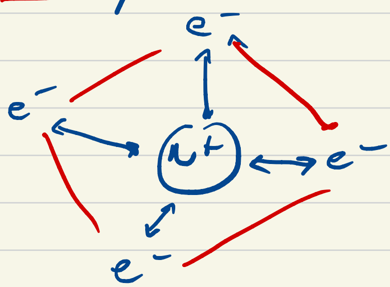
Many-electron atoms



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

Schrödinger eq for an e^-

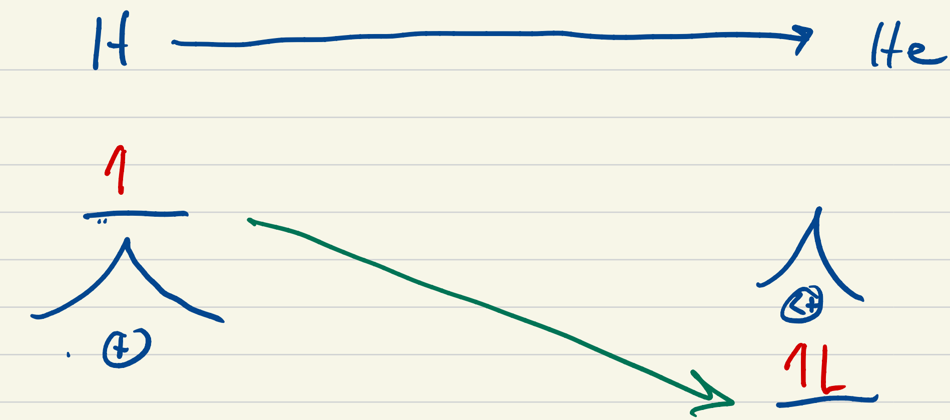
$$\left\{-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{r} + v_{ee}\right\}\psi_i = \varepsilon_i \psi_i$$

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.



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

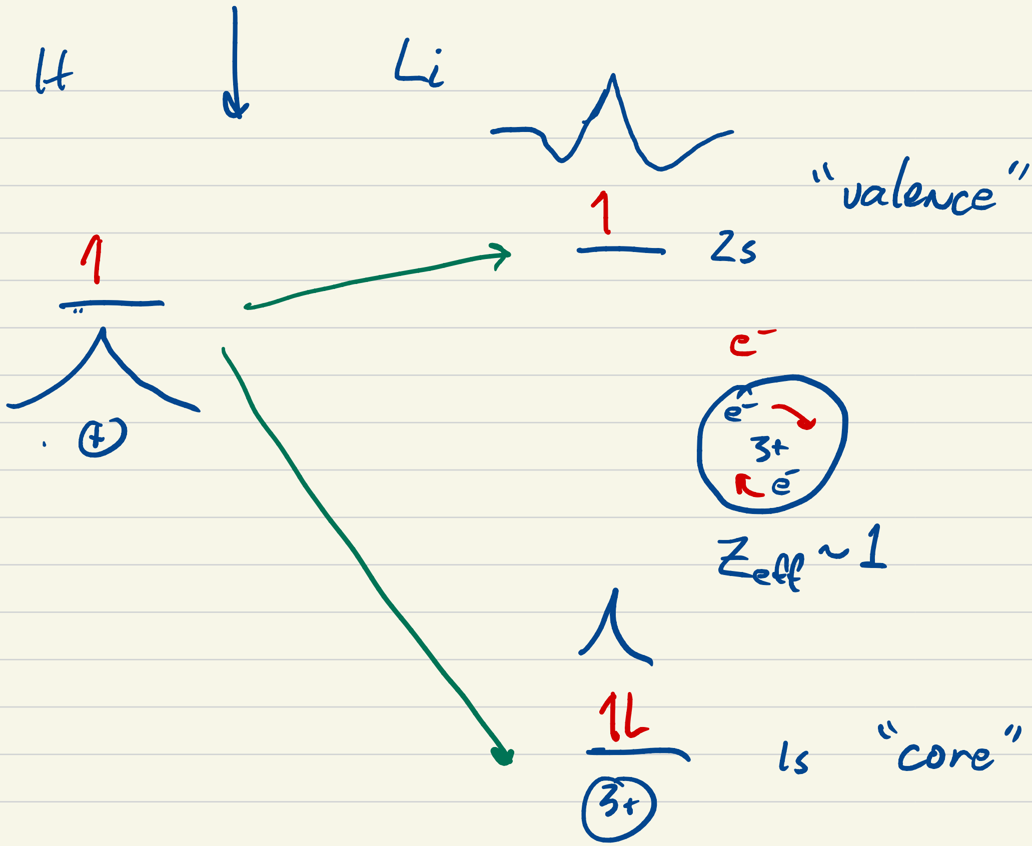
$\langle r \rangle_{H\,1s} = 1.5$ au $\langle r \rangle_{He\,1s} \approx 0.9$ au

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

dominates PE
larger → lower energy
driven by Z

(Show from FDA)

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



3) Aufbau principle – "add" electrons from bottom-up

Core & valence electrons experience different "effective charge"

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

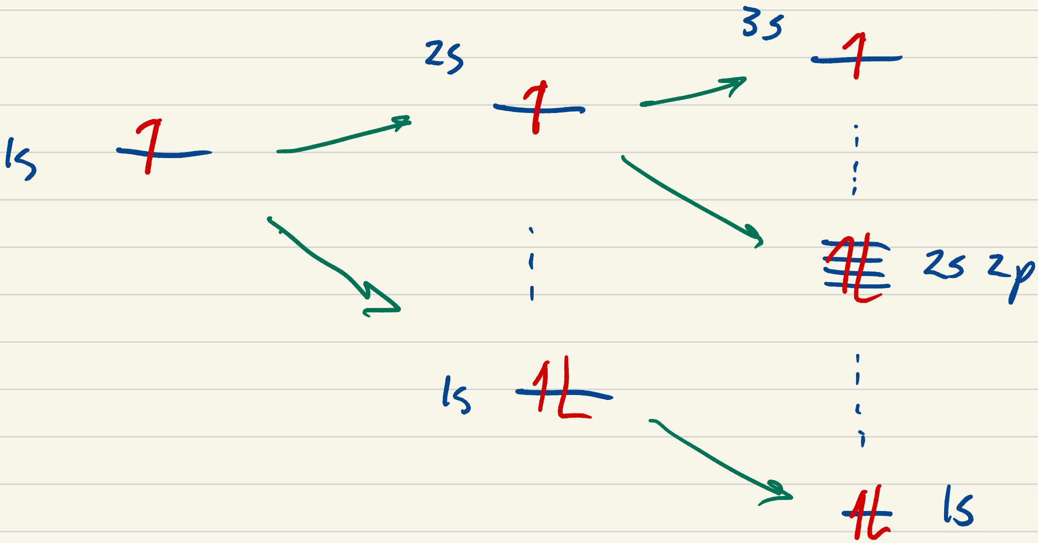
$Z-\sigma \rightarrow$ effective charge
"Z_{eff}"

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

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

Down a family

H $\longrightarrow$ Li $\longrightarrow$ Na



Core levels "fingerprint" an atom.

Basis of X-ray spectroscopy

Valence levels

$Z_{eff} \uparrow$

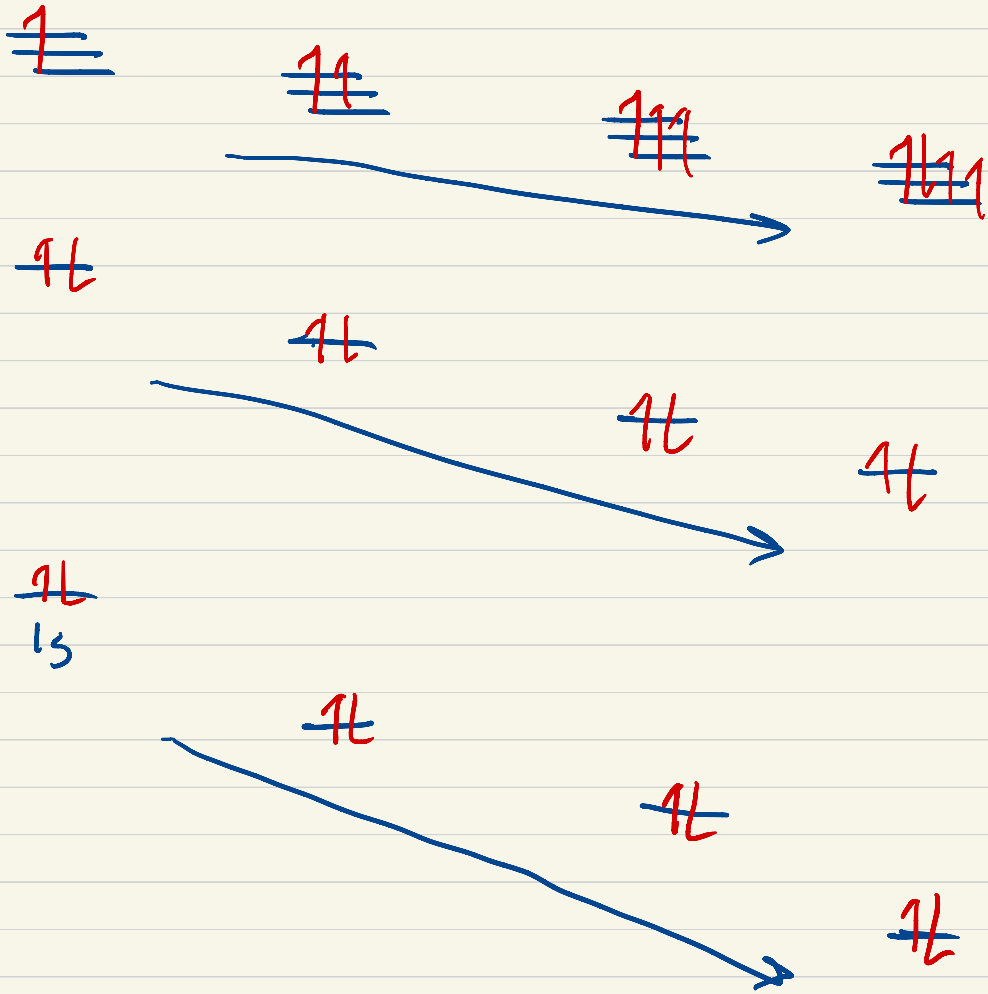
$n \uparrow$ further from nucleus

$\langle 1/r \rangle \downarrow$

$E \uparrow$ down family

Across a row

B $\longrightarrow$ C $\longrightarrow$ N $\longrightarrow$ O



$Z \uparrow$ core $\downarrow$

$Z_{eff} \uparrow$ valence $\downarrow$

4) Illustrates Hund's rule

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

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

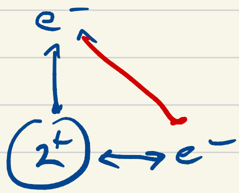
Illustrates spin multiplicity

	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

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

$$\left\{ -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{|\vec{r}_1|} + \frac{1}{|\vec{r}_2|}\right) + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1 - \vec{r}_2|} \right\}$$

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

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

unsolvable in closed form! Shit

Lots of strategies, active research

Most successful based on electron density:

$$\rho(\vec{r}) = \sum_i n_i |\psi_i(\vec{r})|^2$$

n_i : occupancy $(0 < n_i < 2)$

ψ_i : orbital wavefunctions

ρ : density, probability per volume to find an electron

If electrons were really "clouds" of charge, could write exactly

$$\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1-\vec{r}_2|} = \frac{e^2}{4\pi\varepsilon_0}\int \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,'$$

"Coulomb" potential

Basis of Hartree model, 1930's

Still must be solved numerically

Son hit on this idea, father solved by hand for all atoms!

Basis of fda results in outline

Kohn (Noble prize in Chemistry, 1998)

showed that many electron problem can be recast in terms of electron density

Basis of density functional theory (DFT) equation for ψ_i:

$$\left\{ \underbrace{-\frac{\hbar^2}{2m_e}\nabla^2}_{\text{KE}} \underbrace{- \frac{Ze^2}{4\pi\varepsilon_0}\cdot\frac{1}{|\vec{r}|}}_{\text{nuclear attraction}} + \underbrace{v_{ee}[\rho]}_{e^- - e^- \text{ repulsion}} \right\} \psi_i = \varepsilon_i \psi_i$$

ε_i : orbital energies

total $E = \sum n_i \varepsilon_i$ − correction for double counting $e^- - e^-$ repulsions

What is v_{ee}? Three parts:

$$v_{ee}[\rho] = v_{coul}[\rho] + v_{ex}[\rho] + v_{corr}[\rho]$$

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

exaggerates repulsion
but can be calculated exactly

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

reduces repulsion
can be calculated exactly
expensive

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

MUST BE APPROXIMATED

All are functionals of ρ

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

Guess & check

Benefit from <u>variational principle</u>

"correct" ρ / ψ_i must minimize energy

$\Rightarrow$ optimization in $E[\rho]$

self-consistent field

guess ψ_i, ρ

$\downarrow$

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

$\downarrow$

set up Schrödinger eq$^{\underline{n}}$

$\downarrow$

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

$\downarrow$

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

NO → update ψ_i → 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 lda results in outline

More commonly solved today in general purpose codes.

SKIP

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.

Can apply this principle to the many-electron Schrödinger eq

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

$\Rightarrow$

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

Coupled set of differential eqs

$v_{ee}[\psi_i]$: effective e^--e^- repulsion

Hartree

Hartree-Fock

perturbation theory

coupled cluster

CI