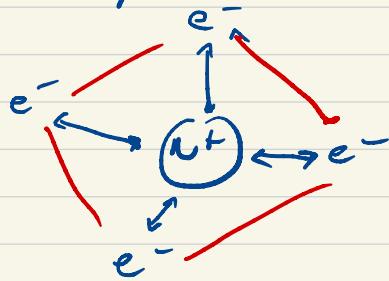


Many-electron atoms



competition between
attraction of e⁻
for nuclei &
repulsion between e⁻

Schrödinger eq for an e⁻

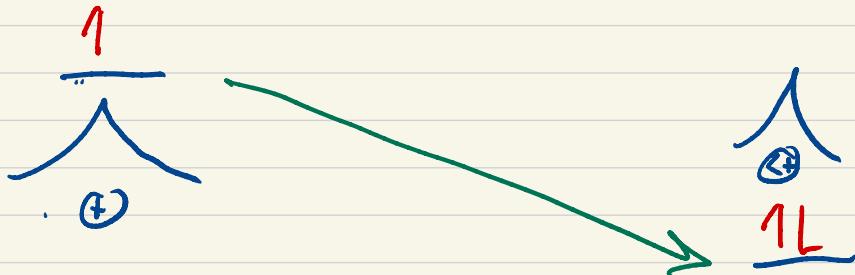
$$\left\{ -\frac{\hbar^2}{2me} \nabla^2 - \frac{Ze^2}{r} + \underline{U_{ee}} \right\} \psi_i = E_i \psi_i$$

effective repulsion
w/ all other e⁻

Exact solutions must be constructed
on computer.

Qualitative results

- For given atom, will get ψ_i & E_i that are qualitatively similar to H atom.



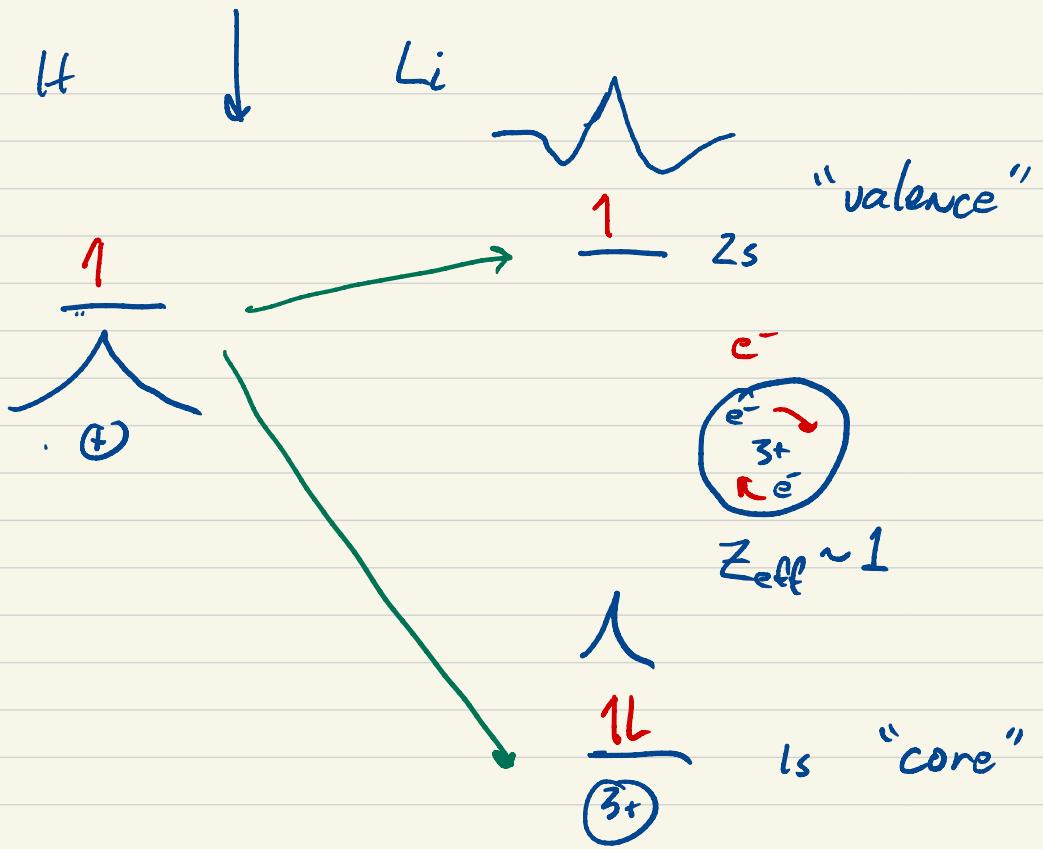
Electrons in 1s "feel" the nucleus the same.
As $Z \uparrow$, more nucleus to feel

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

$$\langle 'r \rangle = 1.0 \text{ au}^{-1} \quad \langle 'r \rangle \approx 1.7 \text{ au}^{-1}$$

(Show from EDA)

Pauli principle - 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"

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

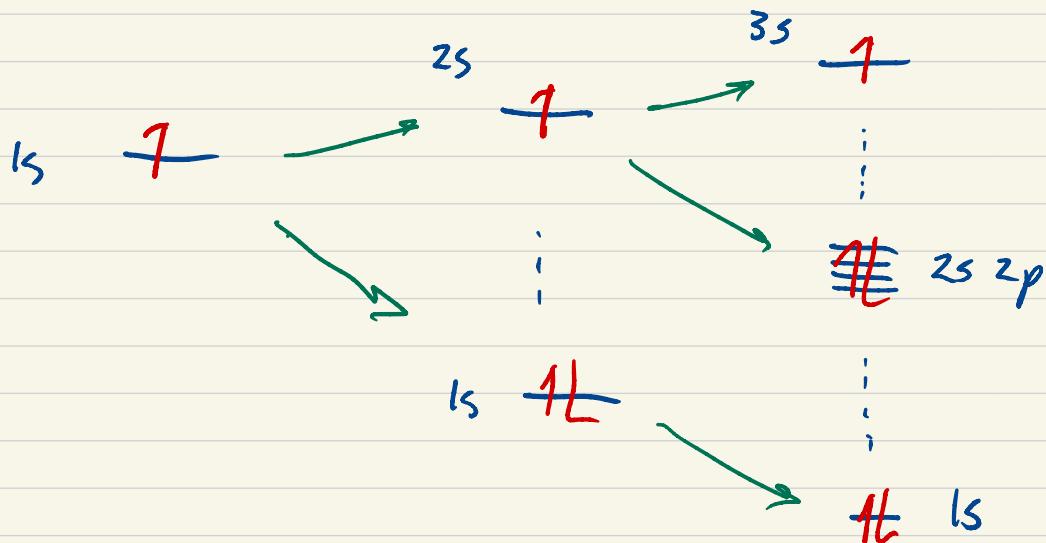
$Z-\sigma \rightarrow$ effective charge
"Z_{eff}"

"Core" levels drop in energy as Z gets bigger.

"Unscreened" from nucleus.

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

Down a family



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



~~1~~

~~11~~

~~111~~

~~1111~~

~~1L~~

~~1L~~

~~1L~~

~~1L~~

~~1L
1S~~

~~1L~~

~~1L~~

~~1L~~

$Z \uparrow$ core \downarrow

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

Illustrates Hund's rule

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

(why? maximize $e^- \cdot e^-$ repulsion)

Illustrates spin multiplicity

$$1 \quad \frac{S}{1/2} \quad \frac{2S+1}{2} \quad \text{"doublet"}$$

$$1L \quad 0 \quad 1 \quad \text{"singlet"}$$

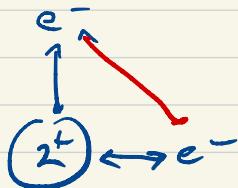
$$11 \quad 1 \quad 3 \quad \text{"triplet"}$$

$$111 \quad \frac{3}{2} \quad 4 \quad \text{"quartet"}$$

Degeneracy of configuration

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

Quantitative solutions



nucleus @ c.o.m

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

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

$$KE_1 + KE_2$$

$$V_{ne_1} \quad V_{ne_2}$$

$$V_{ee}$$

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

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

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

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

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

$$\underbrace{2\langle \Psi^g(\lambda) | \hat{H} | \Psi^g(\lambda) \rangle}_{\partial \lambda} = 0$$

and find "best" λ , closest to truth.

Will do on HU for H atom

Can apply this principle to the many-electron Schrödinger eq

$$\rightarrow \Psi = |\psi_1 \cdot \psi_2 \dots \psi_n|$$

2

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

Coupled set of differential eqs

Week [4i] : 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 we
potentials can be written in
terms of the "density"

$$N = |\Psi|^2 = \sum_i |\psi_i|^2$$

$$V_{\text{coul}} \rightarrow V_{\text{coul}}[\rho] \quad \text{exact}$$

$$V_{\text{ex}} \rightarrow V_{\text{ex}}[\rho] \quad \sim \text{exact}$$

$$V_{\text{corr}} \rightarrow V_{\text{corr}}[\rho] \quad \text{approx}$$

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



compute $V_{\text{coul}}, V_{\text{ext}}, V_{\text{com}}$



update Ψ_i

set up Schrödinger eq



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



NO

$\Psi_i^{\text{in}} = \Psi_i^{\text{out}} ?$



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.