Electron Spin

Electrons have an intrinsic angular momentum m_s, with spin quantum number $s = +1/2$ ("α" electrons) or $s = -1/2$ ("β" electrons)

Pauli Exclusion Principle

Electrons are Fermions (like protons & neutrons) and can only occupy the same orbital if their spins are opposite. Thus, each orbital (1s, P_x, ...) can accomodate up to two electrons (a pair).

[By contrast, photons (s=0) or deuterons are Bosons and can occupy the same state, leading to Bose-Einstein condensation (Nobel phys. 2001)]

Spin Multiplicity

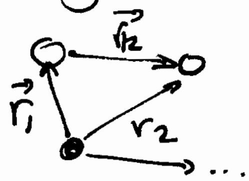
When there are unpaired electrons (e.g. in free radicals such as $\dot{O}\cdot$), the quantity $2 \cdot S + 1$ (S is the total angular spin momentum) determines filling of multiple orbitals of the same energy -

E.g. If $S = 0$ (no unpaired electrons) $2S+1 = 1$ (Singlet)

$S = 1/2$ (1 unpaired) $2S+1 = 2$ (doublet)

$S = 1$ (2 unpaired) $2S+1 = 3$ (triplet)

Many-electron atoms



nucleus
Charge Ze

n electrons
mass m_e

assume stationary nucleus (mass $\gg m_e$)

Hamiltonian for Schrödinger's equation:

$$\mathcal{H} = \sum_{i=1}^{n} \left(-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right) + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

one-electron operator $\hat{h}^{(i)}(\vec{r}_i) = -\frac{\hbar^2}{2m_e} \nabla_i - \frac{Ze^2}{4\pi\varepsilon_0 r_i}$

two-electron operator $\hat{g}(\vec{r}_i, \vec{r}_j) = \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$

Total operator $\hat{H} = \sum_{i=1}^{n} \hat{h}^{(i)}(\vec{r}_i) + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \hat{g}(\vec{r}_i, \vec{r}_j)$

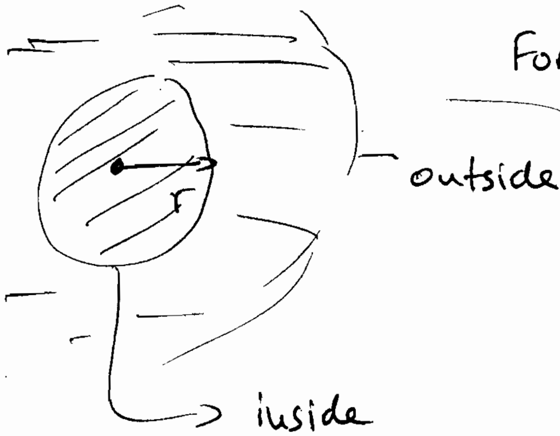
To solve: $\hat{H}\psi = \varepsilon\psi$

Need to make approximations because of the $\hat{g}(\vec{r}_1, \vec{r}_2)$ terms. In the "orbital" approximation each electron occupies its "own" orbital

$$\psi(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_n) \simeq \psi(\vec{r}_1) \cdot \psi(\vec{r}_2) \ldots \psi(\vec{r}_n)$$

where the orbitals are similar to those of the H atom, <u>modified</u> by the presence of all other electrons

Effective charge of nucleus: $Z_{eff} \cdot e < Z \cdot e$



For electron at mean distance r, the effect of electrons at distances less than r is to reduce the effective charge of the nucleus.

This approach is very approximate and only works for atoms.

<u>Aufbau Principle</u> (building-up)

Orbitals fill up in succession:

	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p	6s
# of orbitals	1	1	3	1	3	1	5	3	1	5	3	1

Each orbital can be occupied by up to 2 electrons (of opposite spin $\downarrow\uparrow$)

<u>Hund's rule</u>: An atom in its ground state adopts a configuration with the greatest number of unpaired electrons

<u>Example</u> - Na atom UHF calculation

Na^+ emission

energy $\leftrightarrow$ wavelength $E = \frac{hc}{\lambda}$