He-atom (2e): 3-particle system!
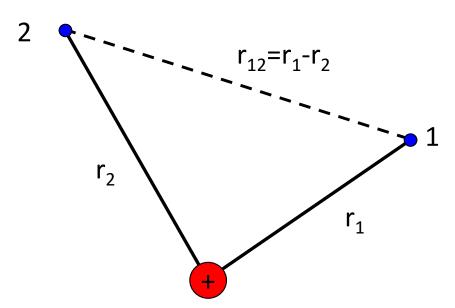

$$\widehat{H}_{He} = \widehat{H}_1^{1e}(r_1, \theta_1, \emptyset_1) + \widehat{H}_2^{1e}(r_2, \theta_2, \emptyset_2) + \frac{1}{r_{12}}$$

$$\Psi_{He}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$$

$$\widehat{H}_{He}\Psi_{He}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = E\,\Psi_{He}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$$

- Consequence: Binding energies is not in nice analytical forms- numerical solutions
- For atoms more than 3 electrons, SE can not be solved even numerically

Orbital Approximation for N electrons

One electron orbital approximation used

SE for He atom: 2 electron system

$$\Psi_{He}\left(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2\right) \approx \Psi_1\left(r_1,\theta_1,\phi_1\right)\Psi_2\left(r_2,\theta_2,\phi_2\right) \rightarrow \Psi_1\left(\vec{r_1}\right)\Psi_2\left(\vec{r_2}\right)$$

- ψ of He which is strictly a wave function with 6 variables
- Electron 1 have its own wave function and electron 2 have its own wave function
- Wave function for electron 1 have a hydrogen like wave function:$\psi100$ of the electron in He will be $\psi100$ of the H-atom.

Orbital Approximation

- We assume that each electron experiences the nuclear charge and an average repulsion from all the other electrons in the atoms

- This allows us to generate a set of a set of orbitals that closely relate to the AO's of hydrogen

$$\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_{lm}(\theta,\phi)$$

- The angular part remains the same but the radial parts differ- however the radial parts are quite similar in form

- The electronic structure of the multi electron atom can be described in terms of occupation of these orbitals

When we write Li $2s^1$ the orbitals are not the same as hydrogen- but it is sufficiently close in form to be used the same label

Electronic Configurations

- $\psi_{He} = \psi_{H1s} \times \psi_{H1s,}$ or generally, what we write as $1s^2$

- $\psi_{He}(r_1,\theta_1,\varphi_1,r_2,\theta_2,\varphi_2) = \psi_{100}(r_1,\theta_1,\varphi_1)\,\psi_{100}(r_2,\theta_2,\varphi_2)$

- $\psi_{Li}(r_1,\theta_1,\varphi_1,r_2,\theta_2,\varphi_2,r_3,\theta_3,\varphi_3) = \psi_{100}(r_1,\theta_1,\varphi_1)\,\psi_{100}(r_2,\theta_2,\varphi_2)\,\psi_{200}(r_3,\theta_3,\varphi_3)$, we write as $1s^2, 2s^1$

  Electronic configurations (ns^x, np^y,….) which you know are nothing but short hand notations for the electron wave functions within this one electron approximation.

Orbital Energy in multi-electron systems

- For multi-electron systems, the degeneracies between different "l" is broken: energy is f(n,l)
- Although an orbital in a multi-electron atom is the wave function of one electron, its energy is influenced by all the other electrons due to the electron-electron repulsion energy
- The 2s has lower energy than 2p and hence it is filled up first