Helium Atom

$$\widehat{H}_e = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{QZ_Ne^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{QZ_Ne^2}{r_2} + \frac{Qe^2}{r_{12}}$$

$$\widehat{H}_e = \widehat{H}_1 + \widehat{H}_2 + \frac{Qe^2}{r_{12}}$$

$$\widehat{H}_1 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{QZ_Ne^2}{r_1} \quad \text{and} \quad \widehat{H}_2 = -\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{QZ_Ne^2}{r_2}$$

The Hamiltonians $\hat{H}_1$ and $\hat{H}_1$ are one electron Hamiltonians similar to that of hydrogen atom

$$\widehat{H}_e\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = \widehat{H}_1\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) + \widehat{H}_2\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)$$

$$+ \frac{Qe^2}{r_{12}}\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)$$

Orbital Approximation

$$\psi_e(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = \psi_{1e}(r_1, \theta_1, \phi_1)\psi_{2e}(r_2, \theta_2, \phi_2)$$

$$\psi_e(1,2,3,...n) \approx \phi(1) \cdot \phi(2) \cdot \phi(3) \cdot \cdots \cdot \phi(n)$$

Orbital is a one electron wavefunction

The total electronic wavefunction of n number of electrons can be written as a product of n one electron wavefunctions

Helium Atom: Orbital Approximation

$$\widehat{H}_e \psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = \widehat{H}_1 \psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) + \widehat{H}_2 \psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)$$

$$+ \frac{Qe^2}{r_{12}} \psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)$$

$$\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = \psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$\widehat{H}_e \psi_e = \widehat{H}_1 \psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \widehat{H}_2 \psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$+ \frac{Qe^2}{r_{12}} \psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

Helium Atom: Orbital Approximation

$$\widehat{H}_e\psi_e = \widehat{H}_1\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \widehat{H}_2\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$+ \frac{Qe^2}{r_{12}}\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$\widehat{H}_e\psi_e = \varepsilon_1\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \varepsilon_2\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$+ \frac{Qe^2}{r_{12}}\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$\widehat{H}_e\psi_e = \left(\varepsilon_1 + \varepsilon_2 + \frac{Qe^2}{r_{12}}\right)\left[\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)\right]$$

$$\varepsilon_1 = \varepsilon_2 = -\frac{Z^2\mu e^4}{8\varepsilon_0^2 h^2 n^2} = \frac{-13.6Z^2}{n^2}eV$$

Helium Atom: Orbital Approximation

$$\widehat{H}_e \psi_e = \left(\varepsilon_1 + \varepsilon_2 + \frac{Qe^2}{r_{12}} \right) \left[\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) \right]$$

If we ignore the term $\dfrac{Qe^2}{r_{12}}$

$$\widehat{H}_e \psi_e = \left(\varepsilon_1 + \varepsilon_2 \right) \left[\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) \right]$$

$$E_{He} = \varepsilon_1 + \varepsilon_2 = -108.8 eV$$

$$\psi_e = \left(\frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_o} \right)^{3/2} e^{-Zr/a_o} \right) \cdot \left(\frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_o} \right)^{3/2} e^{-Zr/a_o} \right) = \psi_{1s}(1) \cdot \psi_{1s}(2)$$

Helium Atom: Orbital Approximation

$$E_{He} = \varepsilon_1 + \varepsilon_2 = -(54.4 + 54.4)eV = -108.8eV$$

$$E_{He} = -(24.59 + 54.4)eV = -78.99eV \text{ (Experimental)}$$

Ignoring $\dfrac{Qe^2}{r_{12}}$ is not justified! Need better approximation

Many Electron Atoms

$$\widehat{H} = -\frac{\hbar^2}{2m_\alpha}\nabla_N^2 - \frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - QZ_Ne^2\sum_{i=1}^{n}\frac{1}{r_i} + Qe^2\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

Nuclei are static

$$\widehat{H}_e = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - QZ_Ne^2\sum_{i=1}^{n}\frac{1}{r_i} + Qe^2\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

$$\widehat{H}_e = \sum_{i=1}^{n}H_i + Qe^2\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

Inter-electron repulsion term leads to deviation from the hydrogen atom. Unfortunately **CANNOT** be ignored

$$f\left(\frac{1}{r_{ij}}\right) \neq g\left(\frac{1}{r_i}\right) + h\left(\frac{1}{r_j}\right)$$

$\frac{1}{r_{ij}}$ term in the Hamiltonian is not separable

Many Electron Atoms

$$\widehat{H}_e = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - QZ_N e^2 \sum_{i=1}^{n}\frac{1}{r_i} + Qe^2 \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

$$\widehat{H}_e = \sum_{i=1}^{n}H_i + Qe^2 \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

Hamiltonian is no longer spherically symmetric and the Time-Independent Schrodinger Equation (**TISE**) cannot be solved using analytical techniques

Numerical methods must be used solve the **TISE**

Many Electron Atoms: Orbital Approximation

$$\psi_e(1,2,3,...n) \approx \phi(1) \cdot \phi(2) \cdot \phi(3) \cdot \cdots \cdot \phi(n)$$

He atom result indicate that neglecting the inter-electron interaction is not a good idea

Improvement

The term $\dfrac{1}{r_{ij}}$ in the Hamiltonian represents the interaction between the electrons. Which mean the electron move in the potential provided by the nucleus and rest of the electron.

Since the electron and nucleus have opposite charges, it can be thought that the rest of the electrons reduce the charge felt by a particular electron $\Rightarrow$ Shielding

Effective Nuclear Charge

Effective Nuclear Charge Z_{eff}

$$\widehat{H}_e = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - QZ_N e^2 \sum_{i=1}^{n}\frac{1}{r_i} + Qe^2 \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

$$\widehat{H}_e = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - QZ_N^{eff} e^2 \sum_{i=1}^{n}\frac{1}{r_i}$$

For Helium atom

$$\widehat{H}_e = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_N}\nabla_2^2 - \frac{QZ_N^{eff} e^2}{r_1} - \frac{QZ_N^{eff} e^2}{r_2}$$

$$\psi_e = \left(\frac{1}{\sqrt{\pi}}\left(\frac{Z_{eff}}{a_o}\right)^{3/2} e^{-Z_{eff}r/a_o}\right)\cdot\left(\frac{1}{\sqrt{\pi}}\left(\frac{Z_{eff}}{a_o}\right)^{3/2} e^{-Z_{eff}r/a_o}\right) = \psi_{1s}'(1)\cdot\psi_{1s}'(2)$$

Effective Nuclear Charge

Due to Shielding, the electrons do not see the full nuclear charge **Z**, but $\mathbf{Z_{eff}} = \mathbf{Z} - \sigma$ (σ = Shielding Constant)

$$Z_{eff} = Z - \sigma$$

$$E = E_{Hatom} \cdot \sum_{i=1}^{n} \left(\frac{Z - \sigma_i}{n_i} \right)^2$$

$$E_{He} = E_{Hatom} \cdot \left(Z_{eff}^2 + Z_{eff}^2 \right)$$

There are methods such as **Perturbation Theory** and **Variational Method** to estimate Z_{eff}

For Helium atom

$$Z_{eff} = Z - \sigma = 1.69$$

$$n = 1$$

$$E_{He} = E_{Hatom} \cdot \sum_{i=1}^{2} \left(\frac{Z_{eff}}{n_i} \right)^2$$
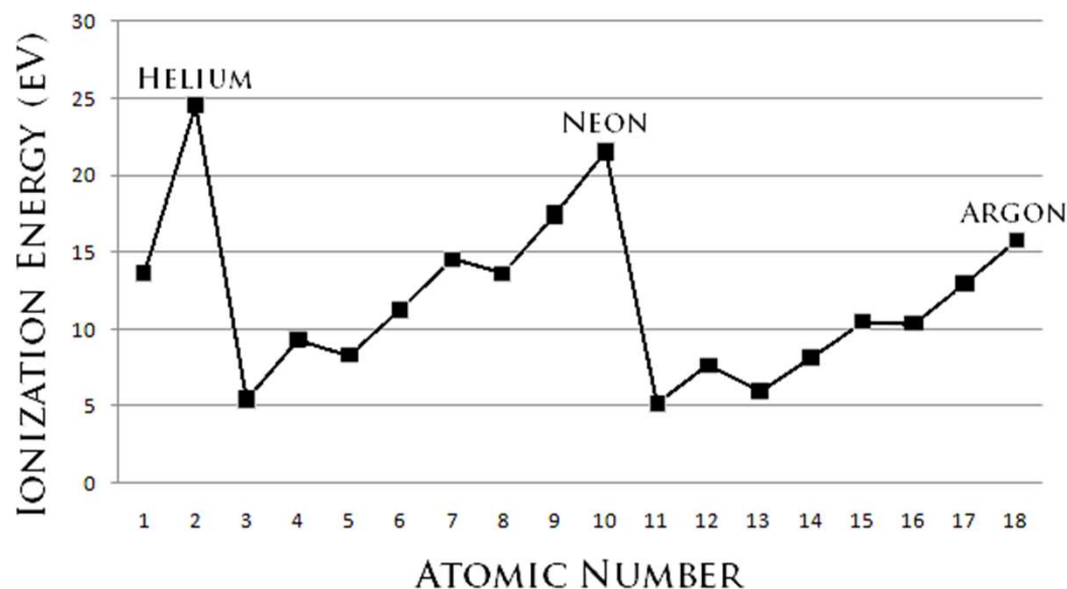
$$-13.6 X 5.712 = -77.68 eV$$

Compare with -78.99

Effective Nuclear Charge

Due to Shielding, the electrons do not see the full nuclear charge Z, but $Z_{eff} = Z - \sigma$ (σ = Shielding Constant)

$$Z_{eff} = Z - \sigma$$

$$E = E_{Hatom} \cdot \sum_{i=1}^{n} \left(\frac{Z - \sigma_i}{n_i} \right)^2$$

Effective nuclear charge is same for electrons in the same orbital, but varies greatly for electrons of different orbitals (s,p,d,f) and n.

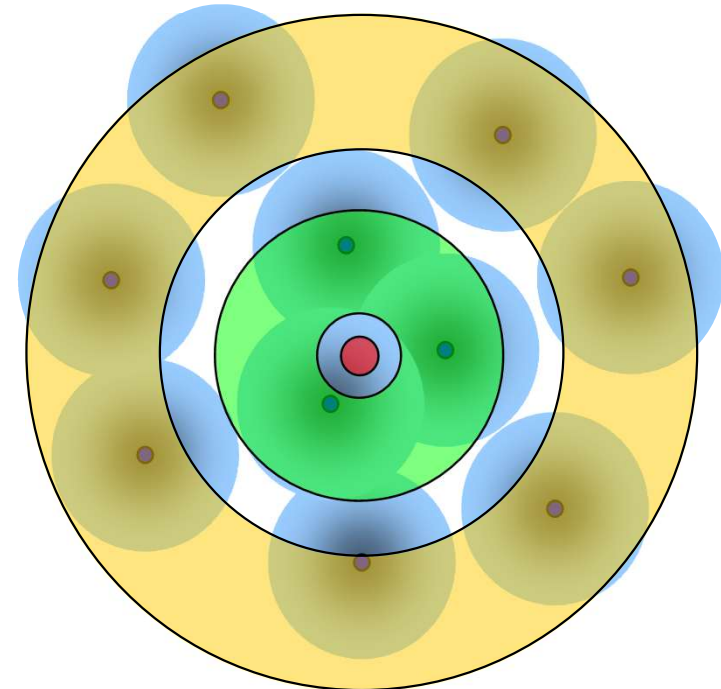Z_{eff} determines chemical properties of many electron atoms

Building-up (Aufbau) Principle

Effective nuclear charge varies for electrons of different orbitals. Different orbitals corresponding to same n. are no longer degenerate
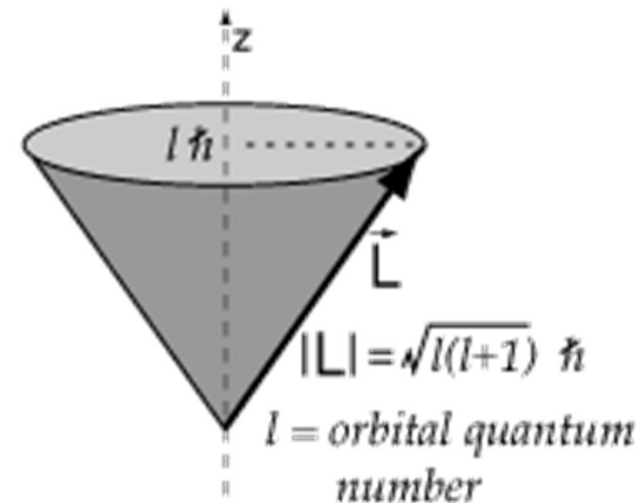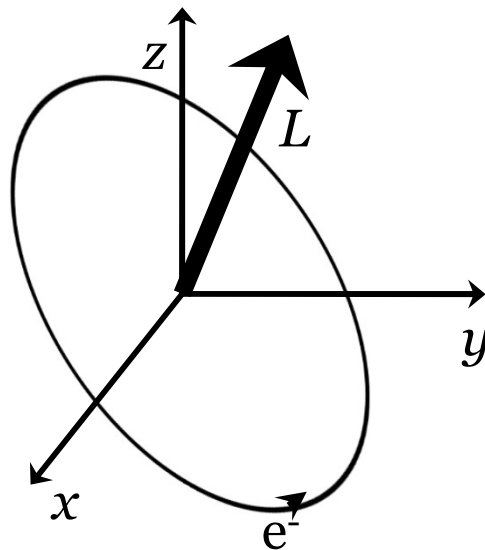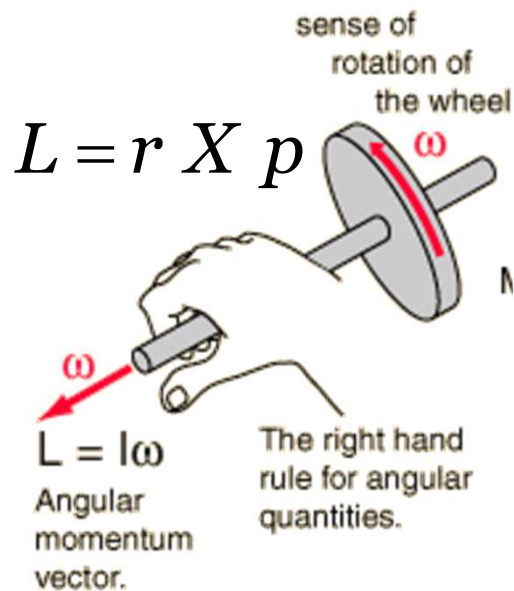
How do we get *2p* energy higher than *2s*?

How does Radial distributions change?

How does Z_{eff} affect atomic properties?

Orbital Angular Momentum

$$L = r \times p$$

sense of rotation of the wheel

ω

L = Iω

Angular momentum vector.

ω

The right hand rule for angular quantities.

z

L

x

y

e⁻

z

$l\hbar$

$\vec{L}$

$$|L| = \sqrt{l(l+1)}\ \hbar$$

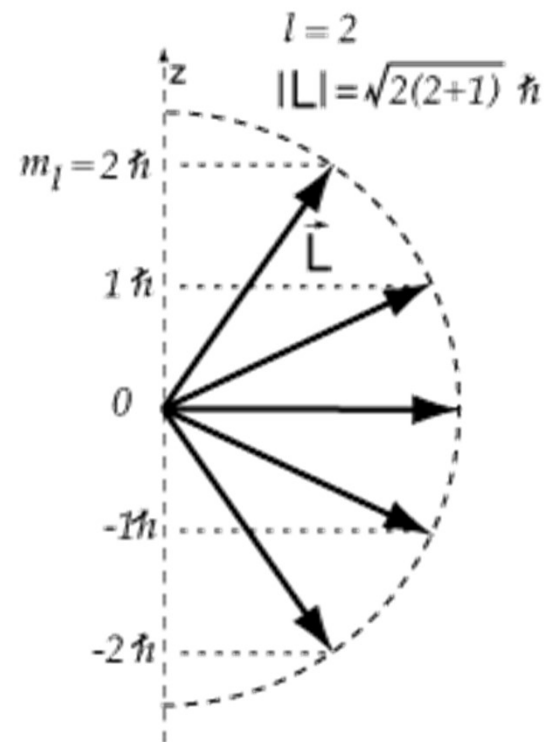l = orbital quantum number

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Orbital Angular Momentum 'L'

$$|L| = \hbar\sqrt{l(l+1)}$$

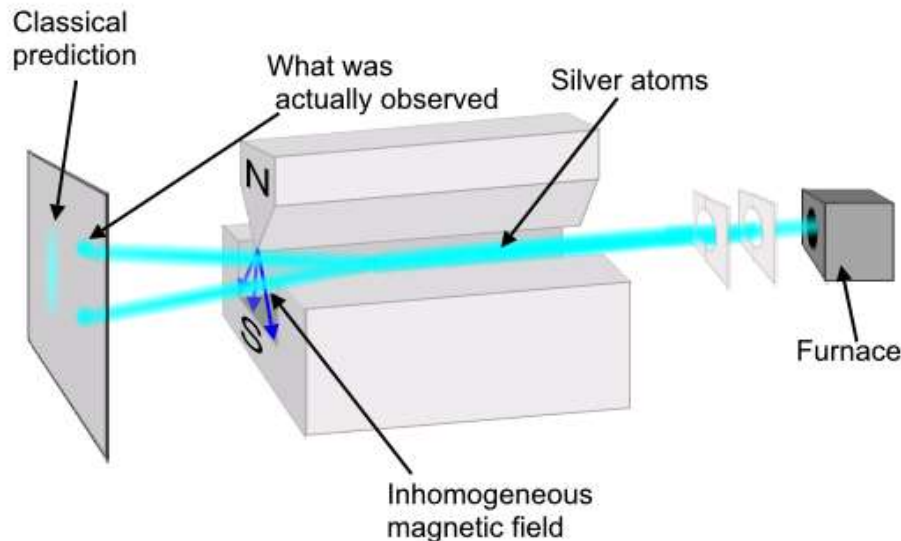l = orbital angular momentum quantum number

$$l \leq n-1$$

$$L_z = m\hbar$$

$$m = 0, \pm1, \pm2, \pm3, \dots, \pm l$$

$l = 2$

$$|L| = \sqrt{2(2+1)}\ \hbar$$

z

$m_l = 2\hbar$

$1\hbar$

$\vec{L}$

0

$-1\hbar$

$-2\hbar$

Spin Angular Momentum

Stern-Gerlach Experiment A beam of silver atoms ($4d^{10}5s^1$) thorough an inhomogeneous magnetic field and observer that the beam split into two of quantized components

Uhlenbeck-Goudsmit Suggested intrinsic spin angular momentum for electrons

Classical, "spinning" particles, would have truly random distribution of their spin angular momentum vectors. This would produce an even distribution on screen.

But electrons are deflected either up or down by a specific amount.