Multielectron atoms

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Helium atom

$$\text{He} \rightarrow \text{He}^{+} + e \qquad I_1 = 24.59 \text{ eV}$$

$$\text{He}^{+} \rightarrow \text{He}^{2+} + e \qquad I_2 = \frac{Z^2}{n^2} \text{ hartree} = 54.42 \text{ eV}$$

Ground state energy of helium is $-(I_1 + I_2) = -79.02$ eV.

Helium atom Schrödinger equation

Hamiltonian in atomic units: set $\hbar = m_e = e = 4\pi\epsilon_0 = 1$

$$\hat{\mathcal{H}} = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + \frac{1}{r_{12}}$$

Kinetic energies of two electrons (nuclei fixed), e_1-nuclear attraction, e_2-nuclear attraction, interelectronic repulsion

$$\hat{\mathcal{H}}\psi(\mathbf{r_1}, \mathbf{r_2}) = E\psi(\mathbf{r_1}, \mathbf{r_2})$$

Wavefunction function of six coordinates

Ignore interelectronic repulsion as a zeroth order approximation

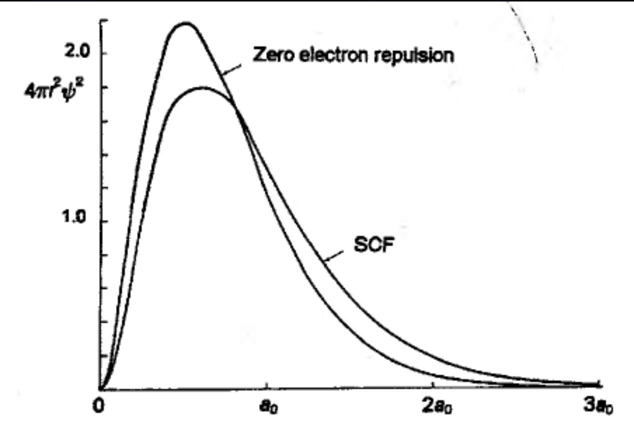
$$\left(-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{2}{r_2}\right)\psi(\mathbf{r_1}, \mathbf{r_2}) = E\psi(\mathbf{r_1}, \mathbf{r_2})$$

Compare with H-atom $-\frac{1}{2}\nabla^2 - \frac{1}{r}$; only difference is nuclear charge of 2.

$$\psi(\mathbf{r_1}, \mathbf{r_2}) = \psi_{1s}(r_1)\psi_{1s}(r_2) = \mathrm{e}^{-Z(r_1+r_2)}$$

$E = -2\frac{Z^2}{2} = -4$ hartree. Experimental value is -2.90 hartree.

Repulsions affect wavefunctions



Average interelectronic repulsion contribution to the energy

$$\left\langle \frac{1}{r_{12}} \right\rangle = \int \psi_{1s}(r_1)\psi_{1s}(r_2)\frac{1}{r_{12}}\psi_{1s}(r_1)\psi_{1s}(r_2)d\tau_1 d\tau_2$$

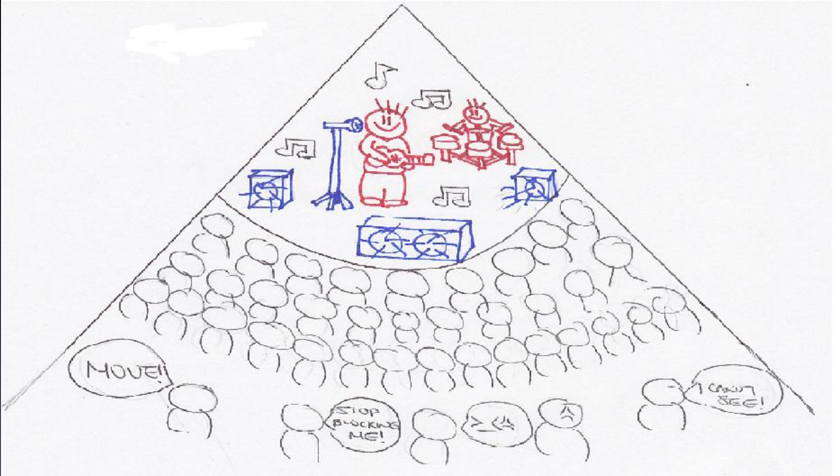
This is a six-dimensional integral

$$\left\langle \frac{1}{r_{12}} \right\rangle = \frac{10}{8}$$

$$E = -4 + \frac{10}{8}\ \text{hartree} = -2.75\text{hartree}$$

Experimental value is -2.90 hartree.

Nuclear charge is shielded by the presence of other electrons



Variational method for $e - e$ repulsion

$$\psi(r_1, r_2) = \psi_{1s}(r_1)\psi_{1s}(r_2) = \mathrm{e}^{-Z_e(r_1+r_2)}$$

$$E = \int \psi(r_1, r_2)\hat{\mathcal{H}}\psi(r_1, r_2)d\tau_1 d\tau_2$$

$$\left\langle -\frac{1}{2}\nabla_1^2 \right\rangle = \left\langle -\frac{1}{2}\nabla_2^2 \right\rangle = \frac{Z_e^2}{2}$$

$$\left\langle -\frac{2}{r_1} \right\rangle = \left\langle -\frac{2}{r_2} \right\rangle = -2Z_e$$

$$\left\langle \frac{1}{r_{12}} \right\rangle = \frac{5}{8}Z_e$$

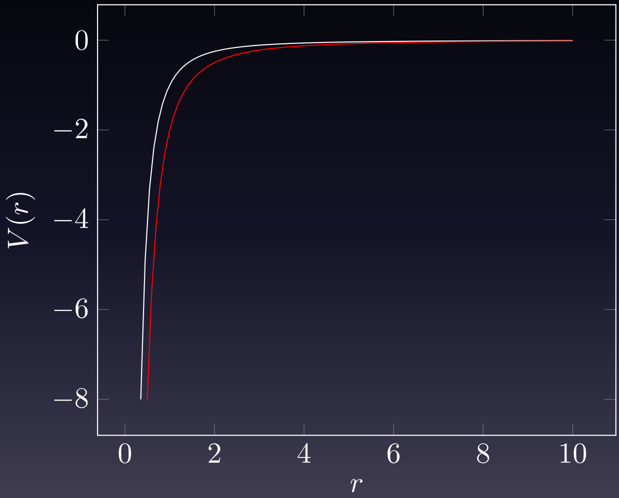
$$\tilde{E}(Z_e) = Z_e^2 - 4Z_e + \frac{5}{8}Z_e$$

$$Z_e = Z - \frac{5}{16} = 1.69$$

Effective nuclear charge for helium is 1.7

Nuclear charge is shielded

- Nuclear charge unshielded when electron is close to the nucleus
- Nuclear charge shielded when electron is far from the nucleus



Treating electrons as independent provides many advantages

$$\hat{H} = \sum_i -\frac{1}{2}\nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j>i} \frac{1}{r_{ij}}$$

If $\sum_i \sum_{j>i} \frac{1}{r_{ij}}$ is not present,

$$\hat{\mathcal{H}} = \sum_i \hat{\mathcal{H}}_i$$

$$\psi = \phi_1 \phi_2 \cdots$$

where ϕ_i are solutions of one-particle Schrödinger equations

$$\hat{\mathcal{H}}_i \phi_i = \epsilon_i \phi_i$$

Find the average field due to inter-electronic repulsion

$$\hat{\mathcal{H}} = \sum_i \hat{\mathcal{H}}_i^{eff}$$

Orbital approximation

$$V_i^{eff} = \sum_j \left[\int \phi_j^* \phi_j \frac{1}{r_{ij}} d\tau_j \right]$$

Solve

$$\left(-\frac{1}{2} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{Z}{r_i} + V_i^{eff} \right) g(r) = \epsilon g(r)$$

Wavefunctions have the form

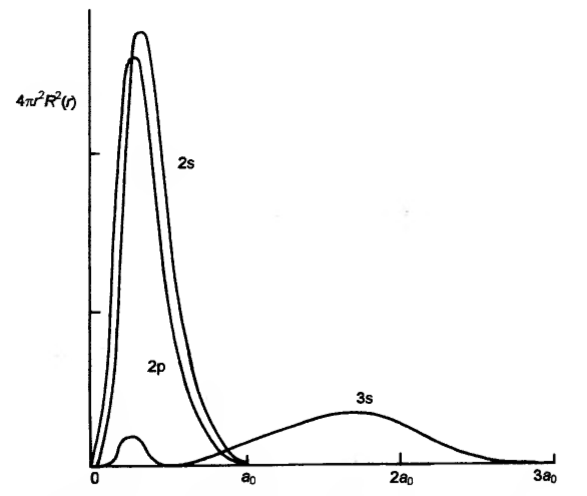
$$\phi = g(r) Y_{lm}(\theta, \phi)$$

Compare with H-atom

$$\psi = R(r) Y_{lm}(\theta, \phi)$$

Angular part same: shapes of atomic orbitals unchanged

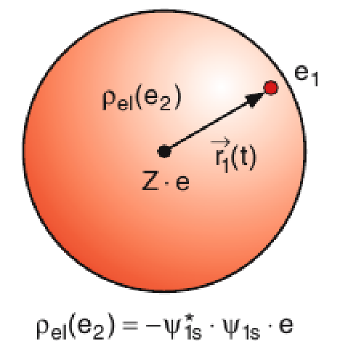
Radial wavefunctions are different from H-atom



Self consistent field method

Suppose there are N electrons in the atom

1. Guess plausible wavefunctions for all electrons
2. Choose an electron and find the averaged repulsion energy by the distribution $\phi_j^*\phi_j$ of each of the others $\int \phi_j^*\phi_j \frac{1}{r_{ij}} d\tau_j$
3. Obtain a value for the potential energy of electron i:
   $V_i = \sum_j \left[\int \phi_j^*\phi_j \frac{1}{r_{ij}} d\tau_j\right]$



Self consistent field method for N-electrons (contd.)

4. Solve the one-electron Schrödinger equation for i to get a new wavefunction

$$\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + V_i\right)\phi_i = \epsilon_i\phi_i$$

5. Obtain first improved wavefunction
6. Repeat the procedure for all electrons
7. Repeat all steps one more time

SCF results match with experiment