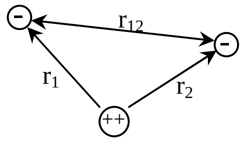
Many Electron Atoms-Independent Electron Approximation-Helium



$$V(r) = \frac{1}{4\pi\varepsilon_o}\left(-\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}\right)$$

$$\frac{-\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right)\Psi + \frac{1}{4\pi\varepsilon_o}\left(-\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}\right)\Psi = E\Psi$$

$$\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r_{12}} \to 0$$

---

(1) $\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_o r_1}\right)\Psi + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_o r_2}\right)\Psi = E\Psi$

---

(2) $\Psi(r_1,r_2) = \Psi_1(r_1)\ \Psi_2(r_2)$

---

where the one-electron wave functions are solutions to one-electron Schrödinger equations:

(3) $\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_o r_1}\right)\Psi_1(r_1) = E_1\Psi_1(r_1)$

(4) $\left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_o r_2}\right)\Psi_2(r_2) = E_2\Psi_2(r_2)$

Note that ∇_1^2 only operates on the coordinates of electron 1:

$\nabla_1^2\ \Psi_1(r_1)\ \Psi_2(r_2) = \Psi_2(r_2)\ \nabla_1^2\ \Psi_1(r_1)$

Substitute 2 into 1 and then 3 & 4:

$$\Psi_2(r_2)\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_o r_1}\right)\Psi_1(r_1) + \Psi_1(r_1)\left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_o r_2}\right)\Psi_2(r_2) = E\ \Psi_1(r_1)\Psi_2(r_2)$$

$\Psi_2(r_2)\ E_1\ \Psi_1(r_1) + \Psi_1(r_1)\ E_2\ \Psi_2(r_2) = E\ \Psi_1(r_1)\ \Psi_2(r_2)$

$E = E_1 + E_2$

$\Psi^2(r_1,r_2) = \Psi_1^2\ (r_1)\ \Psi_2^2\ (r_2)$

$\Psi_1(r_1) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr_1/a_o}$ $\qquad$ $\Psi_2(r_2) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr_2/a_o}$

$E = -13.6\text{ eV}\ \frac{Z^2}{n_1^2} - 13.6\text{ eV}\ \frac{Z^2}{n_2^2} = -13.6\text{ eV}\ \frac{2^2}{1^2} - 13.6\text{ eV}\ \frac{2^2}{1^2} = -108.8\text{ eV}$

experimental E = -79.0 eV

---

take e^--e^- repulsion into account for radial wave functions, but Y_{ℓ,m_ℓ} remain exact!