$$\left.\begin{aligned} a_0 &= \frac{4\pi\epsilon_0\hbar^2}{m e^2} \\ E_1 &= \frac{m e^4}{32\pi^2\epsilon_0^2\hbar^2} \end{aligned}\right\} \quad E_1 = \frac{h}{2M a_0}$$

where S.I. system is used $\frac{1}{4\pi\epsilon_0}$

Helium Atom – Ground State energy

Variational Calculation / Theory

$\psi(\alpha)$ - Variational wave function

$$\frac{\langle\psi(\alpha)|H|\psi(\alpha)\rangle}{\langle\psi(\alpha)|\psi(\alpha)\rangle} = E(\alpha)$$

|| chosen
Boundary condition
Normalizable

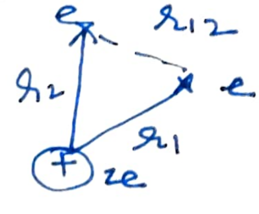
$$\frac{dE(\alpha)}{d\alpha} = 0 \Rightarrow \alpha \text{ is determined}$$

Putting it back to $\psi \Rightarrow$ Variational state

$E =$ upper bound.

Use Variational Method to find the energy of Ground State of He-atom.

Helium atom has nucleus with $2e$ charge and 2 electrons



$$P.E \Rightarrow V = -\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$

Laplace operator of electrons

$$H = KE + PE$$

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$

$$\Rightarrow H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - 2e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{r_{12}}$$

Interaction Energy
$\Downarrow$
Neglect.

2

$$\psi(r_1, r_2) = u_{100}(r_1)\, u_{100}(r_2)$$

$$\psi_1^0 = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{Z r_1}{a_0}}$$

$$\psi_2^0 = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{Z r_2}{a_0}}$$

$$\psi(r_1, r_2) = \frac{Z^3}{\cancel{4}\pi a_0^3}\, e^{-\frac{Z}{a_0}(r_1 + r_2)}.$$

$$Z = 2, \quad a_0 = \frac{\hbar^2}{me^2}$$

$$E = \frac{Z^2 m_0 e^4}{2n^2\hbar^2} = \frac{-Z^2 W_H}{n^2}$$

where $W_H = \frac{m_0 e^4}{2\hbar^2} = \frac{e^2}{2a_0}$ where $\boxed{a_0 = \frac{\hbar^2}{Z me^2}}$

$$\langle H \rangle = \langle KE \rangle + \langle PE \rangle$$

$$= T + V + \text{Interaction Energy}$$

$$\boxed{\langle H \rangle = \langle T \rangle + \langle V \rangle} + \left\langle \frac{e^2}{r_{12}} \right\rangle$$

For 2 Hydrogen

For Hydrogen atom

$$\langle T \rangle = \frac{Z^2 e^2}{2a_0} \quad \text{and} \quad \langle V \rangle = \frac{-2Ze^2}{a_0}$$

$$\langle T \rangle = \int \psi^* \left[-\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) \right] \psi \, d\tau$$

For Helium atom $\langle T \rangle = 2 \times \frac{Z^2 e^2}{2a_0} = \frac{Z^2 e^2}{a_0}$

$$\langle V \rangle = 2 \times \frac{-2Ze^2}{a_0} = \frac{-4Ze^2}{a_0}$$

$$\langle H \rangle = \frac{Z^2 e^2}{a_0} - \frac{4Ze^2}{a_0} + \left\langle \frac{e^2}{r_{12}} \right\rangle$$

Now we need to find $\left\langle \frac{e^2}{r_{12}} \right\rangle$

3

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \iint \psi^*(r_1, r_2) \frac{e^2}{r_{12}} \psi(r_1, r_2)\, dr_1\, dr_2$$

$$= \left(\frac{Z^3}{\pi a_0^3}\right)^2 e^2 \iint \frac{1}{r_{12}} e^{-\frac{2Z}{a_0}(r_1+r_2)} \cdot dr_1 dr_2$$

Now $\frac{2Z}{a_0} r_1 = \rho_1$ and $\frac{2Z}{a_0} r_2 = \rho_2$

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \frac{Ze^2}{32\pi^2 a_0} \underbrace{\iint \frac{e^{-(\rho_1+\rho_2)}}{\rho_{12}} d\rho_1 d\rho_2}_{20\pi^2}$$

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \frac{Ze^2}{32\pi^2 a_0} \times 20\pi^2 = \frac{5Ze^2}{8a_0} = \text{Interaction Energy}$$

$$\langle H \rangle = \frac{Z^2 e^2}{a_0} - \frac{4Ze^2}{a_0} + \frac{5Ze^2}{8a_0}$$

$$= \frac{e^2}{a_0}\left(Z^2 - 4Z + \frac{5}{8}Z\right)$$

$$\langle H \rangle = \frac{e^2}{a_0}\left(Z^2 - \frac{27}{8}Z\right)$$

$$\frac{\partial \langle H \rangle}{\partial Z} = \frac{e^2}{a_0} \cdot \left(2Z - \frac{27}{8}\right) = 0$$

For minimum

$$\Rightarrow Z = \frac{27}{16} = 1.69$$

$$\langle H \rangle = -2.85 \frac{e^2}{a_0}$$