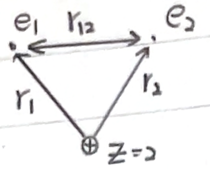
Helium



$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2+\nabla_2^2) - \frac{1}{4\pi\epsilon_0}\left(\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} - \frac{e^2}{r_{12}}\right) = \underbrace{-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_1}}_{H_1} \underbrace{- \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_2}}_{H_2} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{H_{12}}$$

H_1 H-like Hamiltonian

we know $\hat{H}_1\psi_1 = E_1\psi_1$ $\quad H_1\psi_{1s}(1) = E_{1s}\psi_{1s}(1)$

$\hat{H}_2\psi_2 = E_2\psi_2$, $\quad H_2\psi_{1s}(2) = E_{1s}\psi_{1s}(2)$

consider ground state, neglect $\hat{H}_{12}$ and spins

$\psi(1,2) = \psi_{1s}(1)\psi_{1s}(2) \equiv 1s(1)\,1s(2)$ electronic configuration

$= R_{10}(r_1)Y_0^0(\theta_1,\phi_1)R_{10}(r_2)Y_0^0(\theta_2,\phi_2)$

$= \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr_1}{a_0}} \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr_2}{a_0}}$

$E = \langle\psi|\hat{H}_1+\hat{H}_2|\psi\rangle = 2E_{1s}(Z=2) = 2\times(-13.6)\times 2^2 = -108.8$ eV

$E = \langle\psi|\hat{H}_1+\hat{H}_2+\hat{H}_{12}|\psi\rangle = \underbrace{108.8\text{ eV}}_{\text{zero order}} + \underbrace{\langle\psi|\frac{e^2}{4\pi\epsilon_0 r_{12}}|\psi\rangle}_{\text{first order}}$ with electron replusion (perturbation)

$= -74.8$ eV $\quad$ 5.3% $\quad = \frac{5Ze^2}{4\pi\epsilon_0 8a_0}$ Exc.

Experminent: -78.975 eV

Variational wavefunction

$\psi(\alpha) = \frac{1}{\pi}\left(\frac{\alpha}{a_0}\right)^3 e^{-\frac{\alpha r_1}{a_0}} e^{-\frac{\alpha r_2}{a_0}}$ $\quad \alpha$: effective charge

① $\langle\psi|\hat{H}|\psi\rangle = \langle\psi|\hat{H}_1|\psi\rangle + \langle\psi|\hat{H}_2|\psi\rangle + \langle\psi|\hat{H}_{12}|\psi\rangle = 2\langle\psi|\hat{H}_1|\psi\rangle + \langle\psi|\hat{H}_{12}|\psi\rangle \rightarrow \frac{5\alpha}{8}\frac{e^2}{4\pi\epsilon_0 a_0} = -\frac{5}{4}ZE_1$ Exc.

$= \frac{e^2}{4\pi\epsilon_0 a}\left[-\alpha^2 - 2\alpha(Z-\alpha) + \frac{5\alpha}{8}\right]$

$$\boxed{\begin{gathered}\hat{H}_1 = \underbrace{-\frac{\hbar^2}{2m_e}\nabla_1 - \frac{\alpha e^2}{4\pi\epsilon_0 r_1}}_{\hat{H}_1'} - \frac{(Z-\alpha)e^2}{4\pi\epsilon_0 r_1} \\ \hat{H}_1'|\psi(\alpha)\rangle = -\frac{\alpha^2 e^2}{4\pi\epsilon_0 a_0}\frac{1}{2} \\ \langle\psi(\alpha)|\frac{(Z-\alpha)e^2}{4\pi\epsilon_0 r_1}|\psi(\alpha)\rangle = -\frac{\alpha(Z-\alpha)e^2}{4\pi\epsilon_0 a_0}\end{gathered}}$$

$\frac{dE_{trial}}{d\alpha} = -2\alpha - 2(Z-\alpha) + 2\alpha + \frac{5}{8} = 0$

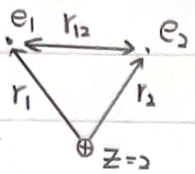
if $Z=2$, $\alpha_{min} = \frac{27}{16}$

$\Rightarrow E_{min} = -77.5$ (1.9%) $= \frac{1}{2}\left(\frac{3}{2}\right)^6 E_1$

① $= 2Z^2E_1 + 2(Z-2)\frac{e^2}{4\pi\epsilon_0}\langle\frac{1}{r}\rangle + \langle V_{ee}\rangle$

$\frac{Z}{a}$

Helium

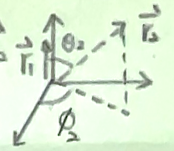


$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2+\nabla_2^2) - \frac{1}{4\pi\epsilon_0}($$

we know $\hat{H}_1\psi_1 = E_1\psi_1$

$\hat{H}_2\psi_2 = E_2\psi_2$,

$$\langle V_{ee}\rangle = \frac{e^2}{4\pi\epsilon_0}\left(\frac{8}{\pi a^3}\right)^2 \int \frac{e^{-4\frac{r_1+r_2}{a}}}{|\vec{r}_1-\vec{r}_2|} d^3\vec{r}_1\, d^3\vec{r}_2$$



$$|\vec{r}_1-\vec{r}_2| = \sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}$$

$$I_2 \equiv \int \frac{e^{-\frac{4r_2}{a}}}{|\vec{r}_1-\vec{r}_2|} = \int \frac{e^{-\frac{4r_2}{a}}}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}} r_2^2 \sin\theta_2\, dr_2\, d\theta_2\, d\phi_2$$

$$\int_0^\pi \frac{\sin\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}} d\theta_2 = \frac{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}{r_1r_2}\Big|_0^\pi$$

$$= \frac{1}{r_1r_2}\left[(r_1+r_2)-|r_1-r_2|\right] = \frac{2}{r_1} \text{ if } r_2<r_1, \ \frac{2}{r_2} \text{ if } r_2>r_1$$

$$\Rightarrow I_2 = 4\pi\left(\frac{1}{r_1}\int_0^{r_1} e^{-\frac{4r_2}{a}} r_2^2\, dr_2 + \int_{r_1}^{\infty} e^{-\frac{4r_2}{a}} r_2\, dr_2\right)$$

[illegible]

$$= \frac{\pi a^3}{8r_1}\left[1-\left(1+\frac{2r_1}{a}\right)e^{-\frac{4r_1}{a}}\right]$$

$$\langle V_{ee}\rangle = \frac{e^2}{4\pi\epsilon_0}\frac{8}{\pi a^3}\int \left[1-\left(1+\frac{2r_1}{a}\right)e^{-\frac{4r_1}{a}}\right] e^{-\frac{4r_1}{a}} r_1 \sin\theta_1\, dr_1\, d\theta_1\, d\phi_1$$

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$\frac{Z}{a}$ α