

H atom

$$\psi_1 = \sqrt{\frac{1}{\pi a^3}} e^{-\frac{r}{a_0}} \quad \psi_2 = \sqrt{\frac{1}{32\pi a_0^3}} (2 - \frac{r}{a_0}) e^{-\frac{r}{2a_0}}$$

$$\Psi_{\text{trial}} = C_1 \psi_1 + C_2 \psi_2, \quad S_{11} = S_{22} = 0 \quad S_{12} = S_{21} = 0$$

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

$$H_{11} = (r-1)bcR \quad H_{22} = \frac{1}{4}(r-1)$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} =$$

$$E = \frac{1}{8}(r-1)(5 + 3\sqrt{1+2r^2})bcR$$

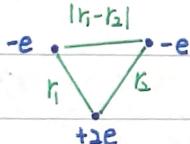
$$= -0.99946bcR$$

$$\Rightarrow C_1(H_{11} - E) + C_2(H_{21} - E) = 0$$

$$C_1(H_{12} + C_2(H_{22} - E)) = 0$$

$$\begin{aligned} \langle \frac{1}{|r_1 - r_2|} \rangle &= \left(\frac{8}{\pi a^3}\right)^2 \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \int_0^\infty \sin^2 \theta_1 d\theta_1 \int_0^\pi \sin^2 \theta_2 d\theta_2 \\ &\quad e^{-\frac{4(r_1+r_2)}{a}} \frac{1}{r_1 r_2} r_1^2 r_2^2 dr_1 dr_2 \\ &= \left(\frac{8}{\pi a^3}\right)^2 (4\pi)^2 \int_0^\infty \left( \int_{r_2}^{r_1} \frac{r_1^2 e^{-\frac{4r_1}{a}}}{r_2} dr_1 + \int_{r_1}^\infty \frac{r_2^2 e^{-\frac{4r_2}{a}}}{r_1} dr_2 \right) b e^{-\frac{4r_1+r_2}{a}} \\ &= \left(\frac{8}{\pi a^3}\right)^2 (4\pi)^2 \frac{5}{27} \left(\frac{a_0}{2}\right)^5 = \frac{5}{8} \frac{2}{a_0} \end{aligned}$$

The Ground State of Helium



$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|r_1 - r_2|} \right)$$

if we ignore e-e repulsion

$$\Rightarrow \Psi(r_1, r_2) = \psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-\frac{2(r_1+r_2)}{a}}$$

$$E = \langle \Psi | \hat{H} | \Psi \rangle = 2E_{1s}(Z=2) = 2(-13.6) \times 2^3 = -108.8 \text{ eV} \quad (\text{Experiment: } -78.915 \text{ eV})$$

to improve accuracy

$$\langle \frac{1}{|r_1 - r_2|} \rangle = \left(\frac{8}{\pi a^3}\right)^2 \iiint \frac{e^{-\frac{4(r_1+r_2)}{a}}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}} d^3 k_1 d^3 k_2$$

$$\bullet = 2\pi \int_0^\infty -\frac{4(r_1+r_2)}{a} \left[ \int_0^\pi \frac{\sin\theta_2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}} d\theta_2 \right] r_1^2 dr_1 = 2\pi \int_0^\infty e^{-\frac{4r_1}{a}} \frac{1}{r_1 r_2} [(r_1+r_2) - |r_1 - r_2|] r_1^2 dr_1$$

$$\bullet = \frac{1}{r_1 r_2} \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2} \Big|_0^\pi = \frac{1}{r_1 r_2} (\sqrt{r_1^2 + r_2^2 + 2r_1 r_2} - \sqrt{r_1^2 + r_2^2 - 2r_1 r_2}) = \frac{4\pi}{r_1 r_2} \left( \int_{r_2}^{r_1} \frac{1}{r_1} e^{0} r_1^2 dr_1 + \int_{r_1}^{r_2} \frac{1}{r_2} e^{0} r_2^2 dr_2 \right)$$

$$= \frac{1}{r_1 r_2} [(r_1+r_2) - |r_1 - r_2|] = \frac{2}{a}, \quad r_2 < r_1$$

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

$$= \frac{1}{r_1} \left[ -\frac{a}{4} r_2^2 e^{-\frac{4r_2}{a}} + \frac{a}{2} \left( \frac{a}{4} \right)^2 e^{-\frac{4r_2}{a}} \left( -\frac{4r_2}{a} - 1 \right) \right] \Big|_0^{r_1}$$

$$= -\frac{a}{4r_1} (r_1^2 e^{-\frac{4r_1}{a}} + \frac{ar_1}{2} e^{-\frac{4r_1}{a}} + \frac{a^2}{8} e^{-\frac{4r_1}{a}} - \frac{a^2}{8})$$