

$$\begin{aligned}
 &= 4\pi \left\{ \frac{a^3}{32r_1} e^{-\frac{4r_1}{a}} + \left[-\frac{ar_1}{4} - \frac{a^2}{8} - \frac{a^3}{32r_1} + \frac{ar_1}{4} - \frac{a^2}{16} \right] e^{-\frac{8r_1}{a}} \right\} \\
 &= \frac{\pi a^3}{8} \left[\frac{a}{r_1} e^{-\frac{4r_1}{a}} - (2 + \frac{a}{r_1}) e^{-\frac{8r_1}{a}} \right] \\
 \Rightarrow \langle \frac{1}{|r_1 - r_2|} \rangle &= \frac{8}{\pi a^4} 4\pi \int_0^\infty \left[\frac{a}{r_1} e^{-\frac{4r_1}{a}} - (2 + \frac{a}{r_1}) e^{-\frac{8r_1}{a}} \right] r_1^2 dr_1 = \frac{e^2}{4\pi\epsilon_0} \frac{8}{\pi a^3} \int_{r_1}^{(1+\frac{2r_1}{a})} \frac{1-(1+\frac{2r_1}{a}) e^{-\frac{4r_1}{a}}}{r_1 \sin \theta dr_1 d\theta d\phi} e^{-\frac{8r_1}{a}} dr_1 \\
 &= \frac{32}{a^4} a \int_0^\infty r_1 e^{-\frac{4r_1}{a}} dr_1 - 2 \int_0^\infty r_1^2 e^{-\frac{8r_1}{a}} dr_1 - a \int_0^\infty r_1 e^{-\frac{8r_1}{a}} dr_1 \\
 &= \frac{32}{a^4} \left[a \left(\frac{a}{4} \right)^2 - 2 \cdot 2 \left(\frac{a}{8} \right)^3 - a \cdot \left(\frac{a}{8} \right)^2 \right] = \frac{32}{a} \left(\frac{1}{16} - \frac{1}{128} - \frac{1}{64} \right) = \frac{5}{4a} \\
 V_{ee} \approx \frac{e^2}{4\pi\epsilon_0} \langle \frac{1}{|r_1 - r_2|} \rangle &= \frac{5}{4} \frac{e^2}{4\pi\epsilon_0} \frac{1}{a} = \frac{5}{4} \frac{m}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \\
 &= \frac{5}{2} (-E_1) = 34 \text{ eV} \\
 \Rightarrow E &= -108.8 + 34 = -74.8 \text{ eV (error 5.3%)}
 \end{aligned}$$

effective nuclear charge

use a trial function $\psi_r(\vec{r}_1, \vec{r}_2) = \left(\frac{z}{a_0} \right)^3 \frac{1}{\pi} e^{-\frac{zr_1}{a_0}} e^{-\frac{zr_2}{a_0}}$

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

$$\begin{aligned}
 \langle H \rangle &= \langle \psi | \hat{H}_1 | \psi \rangle + \langle \psi | \hat{H}_2 | \psi \rangle + \langle \psi | \hat{H}_{12} | \psi \rangle = 2 \langle \psi | \hat{H}_1 | \psi \rangle + \langle \psi | \hat{H}_{12} | \psi \rangle \\
 &= 2z^2 E_1 + 2(z-2) \frac{e^2}{4\pi\epsilon_0} \langle \frac{1}{r} \rangle + \langle V_{ee} \rangle = -\frac{5z}{8} \frac{e^2}{4\pi\epsilon_0} = -\frac{5z}{4} E_1 \\
 &= (-2z^2 + \frac{27}{4} z) E_1
 \end{aligned}$$

$$\frac{d\langle H \rangle}{dz} = (-4z + \frac{27}{4}) E_1 = 0, \quad z = \frac{27}{16}, \quad \langle H \rangle = -77.5 \text{ eV (error 1.9%)}$$

In general

$$\psi_r = \frac{1}{\pi} \left(\frac{z_0}{a_0} \right)^3 e^{-\frac{z_0 r_1}{a_0}} e^{-\frac{z_0 r_2}{a_0}}$$

$$\langle H \rangle = 2z_0^2 E_1 - \frac{5}{4} z_0 E_1 - 4z(z-z_0) E_1 = (-2z^2 + 4zz_0 - \frac{5}{4} z) E_1$$

$$\frac{d\langle H \rangle}{dz} = (-4z + 4z_0 - \frac{5}{4}) E_1 = 0, \quad z = z_0 - \frac{5}{16}$$

$$\langle H_{\min} \rangle = \frac{(16z_0 - 5)^2}{128} E_1$$

$$z_0 = 1 \text{ (H^-)} \quad E_{\min} = -12.9 \text{ eV}$$

$$z_0 = 2 \text{ (He)} \quad E_{\min} = -77.5 \text{ eV}$$

$$z_0 = 3 \text{ (Li^+)} \quad E_{\min} = -196 \text{ eV}$$