

He atom, ground state

$$\hat{H} = -\frac{1}{2} \Delta_1 - \frac{Z}{r_1} - \frac{1}{2} \Delta_2 - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (Z=2)$$

Method B: variation

Motivation → we have seen: $E = \int d\tau_1 d\tau_2 r_1^2 r_2^2 e^{-2Zr_1} \frac{1}{r_1} \left\{ 1 - e^{-2Zr_2} [1 + 2Zr_2 + 2Z^2 r_2^2] \right\}$

Trick (after $r_1 \rightarrow r$)

$$E = 2 \cdot \frac{Z^3}{\pi} \int_0^\infty dr r^2 \cdot e^{-2Zr} \cdot \frac{1}{r} \left\{ 1 - e^{-2Zr} [1 + 2Zr + 2Z^2 r^2] \right\}$$

! $U_{\text{eff}}(r)$

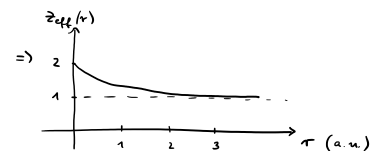
and remember: $1s_Z(r) = \sqrt{\frac{Z^3}{\pi}} \cdot e^{-Zr}$

$$\Rightarrow E = 2 \cdot \langle 1s_Z(r) | U_{\text{eff}}(r) | 1s_Z(r) \rangle$$

↑
2 electrons

⇒ The U -interaction between the 2 electrons is replaced by a modified electron-nucleus potential!

Each electron feels a screened attractive potential: $-\frac{Z}{r} + U_{\text{eff}}(r) = -\frac{Z_{\text{eff}}(r)}{r}$, where $Z_{\text{eff}}(r) = Z - 1 + e^{-2Zr} [1 + 2Zr + 2Z^2 r^2]$



⇒ Idea:

instead of $Z_{\text{eff}}(r) \rightarrow$ a single variational parameter ξ (zeta)

Obviously $1 < \xi < 2$ for He

$$1s_\xi(r) = \sqrt{\frac{\xi^3}{\pi}} e^{-\xi r} \quad (\text{normalized to 1})$$

Variational Ansatz: $\psi(r_1, r_2) = 1s_\xi(r_1) \cdot 1s_\xi(r_2) = \frac{\xi^3}{\pi} e^{-\xi(r_1+r_2)}$

$$\Rightarrow E(\xi) = \langle \psi(r_1, r_2) | H | \psi(r_1, r_2) \rangle = 2 \cdot \left(-Z \cdot \xi + \xi^2 \right) + \frac{5}{8} \xi = \xi^2 - 4\xi + \frac{5}{8} \xi$$

↑ true nuclear charge
↑ pot
↑ kin

$$E(\xi) = \text{minimum} \Rightarrow 0 = 2\xi^* - 4 + \frac{5}{8} \Rightarrow \xi^* = 2 - \frac{5}{16} = \frac{27}{16} = 1.6875 \quad \leftarrow \text{average screening effect}$$

$$E_{\text{min}} = \xi^{*2} \left(\xi^* - 4 + \frac{5}{8} \right) = -\left(\frac{27}{16}\right)^2 \approx -2.848 \text{ a.u.} \approx -77.488 \text{ eV}$$

Remember

$$E_{\text{pot}} = -2.75 \text{ a.u.} \approx -74.831 \text{ eV}$$

$$E_{\text{exp}} = -2.903 \text{ a.u.} \approx -79.005 \text{ eV}$$

Conclusion: the screening effect alone (only 1 variational parameter!) results in significant improvement!