

Quantum Mechanics 2

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Helium
Optimization



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First Approximation

In [Helium 1], we found an approximation of the ground state energy level of the Helium atom by using direct product of Hydrogen ground states as a trial function

$$\tilde{\psi} = e^{-Z(r_1+r_2)/a}$$

With this, we found that

$$\langle \tilde{\psi} | \tilde{\psi} \rangle = 4(4\pi)^2 \left(\frac{a}{2Z} \right)^6$$

With

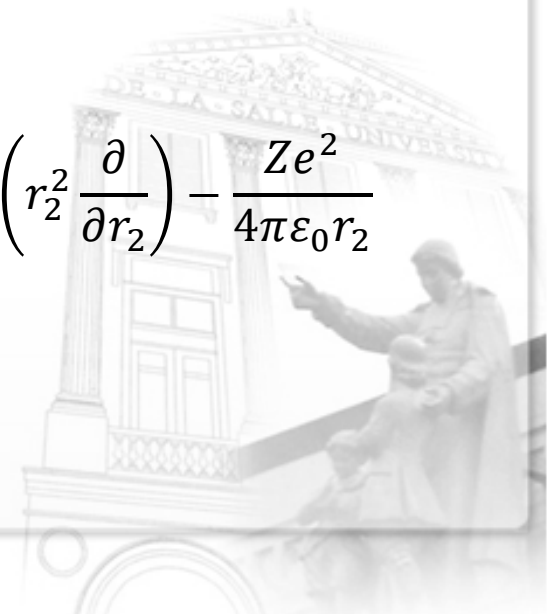
$$H = H_1 + H_2 + H_{12}$$

where

$$H_1 = -\frac{\hbar^2}{2mr_1^2} \frac{\partial}{\partial r_1} \left(r_1^2 \frac{\partial}{\partial r_1} \right) - \frac{Ze^2}{4\pi\epsilon_0 r_1}, \quad H_2 = -\frac{\hbar^2}{2mr_2^2} \frac{\partial}{\partial r_2} \left(r_2^2 \frac{\partial}{\partial r_2} \right) - \frac{Ze^2}{4\pi\epsilon_0 r_2}$$

and

$$H_{12} = \frac{e^2}{4\pi\epsilon_0 r_{12}},$$



First Approximation

We found that

$$\frac{\langle \tilde{\psi} | H_1 | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} = \frac{\langle \tilde{\psi} | H_2 | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} = \frac{\hbar^2}{2m} \left(\frac{Z}{a} \right)^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{Z}{a}$$

and

$$\frac{\langle \tilde{\psi} | H_{12} | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} = \frac{5}{16} \frac{e^2}{4\pi\epsilon_0} \left(\frac{2Z}{a} \right) = \frac{5Ze^2}{32\pi\epsilon_0 a}$$



Parametrization

If we instead use a parametrized trial function

$$\tilde{\psi} = e^{-\alpha(r_1+r_2)}$$

We can use previous results in [Helium 1] by a simple replacement

$$\frac{Z}{a} \rightarrow \alpha$$

Thus

$$\begin{aligned}\langle \tilde{\psi} | \tilde{\psi} \rangle &= 4(4\pi)^2 \left(\frac{1}{2\alpha} \right)^6 \\ \frac{\langle \tilde{\psi} | H_1 | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} &= \frac{\langle \tilde{\psi} | H_2 | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} = \frac{\hbar^2 \alpha^2}{2m} - \frac{Z\alpha e^2}{4\pi\epsilon_0} \\ \frac{\langle \tilde{\psi} | H_{12} | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} &= \frac{5}{16} \frac{e^2}{4\pi\epsilon_0} \left(\frac{2Z}{a} \right) = \frac{5\alpha e^2}{32\pi\epsilon_0}\end{aligned}$$



Optimization

We then have

$$\bar{H} = \frac{\hbar^2 \alpha^2}{m} - \frac{2Z\alpha e^2}{4\pi\epsilon_0} + \frac{5\alpha e^2}{32\pi\epsilon_0} = \frac{\hbar^2 \alpha^2}{m} + \frac{\alpha e^2}{4\pi\epsilon_0} \left(\frac{5}{8} - 2Z \right)$$

Optimizing,

$$\frac{d\bar{H}}{d\alpha} = \frac{2\hbar^2 \alpha}{m} + \frac{e^2}{4\pi\epsilon_0} \left(\frac{5}{8} - 2Z \right) = 0$$

With $Z = 2$, this gives,

$$\alpha = \frac{27}{16} \frac{me^2}{4\pi\epsilon_0 \hbar^2} = \frac{27}{16a}$$

Hence,

$$\bar{H} = \frac{\hbar^2}{m} \left(\frac{27}{16a} \right)^2 - \frac{27}{8} \left(\frac{27}{16a} \right) \frac{e^2}{4\pi\epsilon_0} = \left(\frac{27}{16} \right) \left[\left(\frac{27}{16} \right) - \left(\frac{27}{8} \right) \right] \frac{e^2}{4\pi\epsilon_0 a} = -\frac{1}{2} \left(\frac{27}{8} \right)^2 \frac{e^2}{8\pi\epsilon_0 a}$$

This approximation gives a value of -77.490 eV, which is now just 1.88% higher than the experimental value of -78.975 eV.

