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

$$H_1 = -\frac{\hbar^2}{2mr_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}, \quad H_2 = -\frac{\hbar^2}{2mr_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial}{\partial r_2}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r_2}$$

and

$$H_{12} = \frac{e^2}{4\pi\varepsilon_0 r_{12}},$$

First Approximation

We found that

$$\frac{\langle\tilde{\psi}|H_1|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{\langle\tilde{\psi}|H_2|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{\hbar^2}{2m}\left(\frac{Z}{a}\right)^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{Z}{a}$$

and

$$\frac{\langle\tilde{\psi}|H_{12}|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{5}{16}\frac{e^2}{4\pi\varepsilon_0}\left(\frac{2Z}{a}\right) = \frac{5Ze^2}{32\pi\varepsilon_0 a}$$

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

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

Thus

$$\langle\tilde{\psi}|\tilde{\psi}\rangle = 4(4\pi)^2\left(\frac{1}{2\alpha}\right)^6$$

$$\frac{\langle\tilde{\psi}|H_1|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{\langle\tilde{\psi}|H_2|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{\hbar^2\alpha^2}{2m} - \frac{Z\alpha e^2}{4\pi\varepsilon_0}$$

$$\frac{\langle\tilde{\psi}|H_{12}|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{5}{16}\frac{e^2}{4\pi\varepsilon_0}\left(\frac{2Z}{a}\right) = \frac{5\alpha e^2}{32\pi\varepsilon_0}$$

Optimization

We then have

$$\bar{H} = \frac{\hbar^2\alpha^2}{m} - \frac{2Z\alpha e^2}{4\pi\varepsilon_0} + \frac{5\alpha e^2}{32\pi\varepsilon_0} = \frac{\hbar^2\alpha^2}{m} + \frac{\alpha e^2}{4\pi\varepsilon_0}\left(\frac{5}{8} - 2Z\right)$$

Optimizing,

$$\frac{d\bar{H}}{d\alpha} = \frac{2\hbar^2\alpha}{m} + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{5}{8} - 2Z\right) = 0$$

With $Z = 2$, this gives,

$$\alpha = \frac{27}{16}\frac{me^2}{4\pi\varepsilon_0\hbar^2} = \frac{27}{16a}$$

Hence,

$$\bar{H} = \frac{\hbar^2}{m}\left(\frac{27}{16a}\right)^2 - \frac{27}{8}\left(\frac{27}{16a}\right)\frac{e^2}{4\pi\varepsilon_0} = \left(\frac{27}{16}\right)\left[\left(\frac{27}{16}\right) - \left(\frac{27}{8}\right)\right]\frac{e^2}{4\pi\varepsilon_0 a} = -\frac{1}{2}\left(\frac{27}{8}\right)^2\frac{e^2}{8\pi\varepsilon_0 a}$$

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