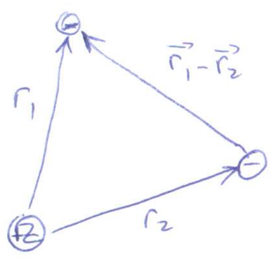
Variational method applied to the helium atom

In this exercise we will consider the ground state of a two-electron system — the helium atom. The hamiltonian of this system is given by

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right)$$

From the experiment it is known that the ground state energy of He is

$$E_{gs}^{exp} = -2.904 \text{ hartree} = -78.98 \text{ eV}$$



If we ignore, for the moment, the interelectron interaction, $V_{ee} = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1 - \vec{r}_2|}$, the we end up with a Hamiltonian that nicely separates into two hydrogen-like terms. The solution of such simplified problem is known:

$$\psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(Z\vec{r}_1)\,\psi_{100}(Z\vec{r}_2) = \frac{1}{\pi a^3} e^{-\frac{(r_1 + r_2)}{a}} \qquad a = \frac{a_0}{Z}$$

while the energy is (recall that $E_n = -\frac{1}{a^2}\frac{\hbar^2}{2m}\frac{1}{n^2}$ $\quad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$

$$E = 2E_1 = 4 \text{ hartree} = -109 \text{ eV}.$$

Obviously it is quite far from the exact He energy. We can improve the result of the independent electron approximation by including the interelectron approximation. Note that

$$(H - V_{ee})\psi_0 = 2E_1\psi_0$$

or

$$H\psi_0 = (2E_1 + V_{ee})\psi_0$$

Therefore

$$\langle H \rangle = 2E_1 + \langle V_{ee} \rangle$$

If we do not vary ψ_0 (which, in principle, can be done but requires more effort) then the application of the variational method becomes particularly simple as we just need to evaluate $\langle V_{ee} \rangle$:

$$\langle V_{ee} \rangle = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{\pi a^3}\right)^2 \int e^{-\frac{(r_1+r_2)}{a}} \frac{1}{|\vec{r}_1-\vec{r}_2|} e^{-\frac{(r_1+r_2)}{a}} d\vec{r}_1 d\vec{r}_2$$

Let us express $|\vec{r}_1-\vec{r}_2|$ as

$$|\vec{r}_1-\vec{r}_2| = \sqrt{(\vec{r}_1-\vec{r}_2)^2} = \sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}$$

θ_2 is the angle between $\vec{r}_1$ and $\vec{r}_2$

Then the integral over $\vec{r}_2$ can be written as

$$\int \frac{e^{-\frac{2r_2}{a}}}{|\vec{r}_1-\vec{r}_2|} d\vec{r}_2 = \int \frac{e^{-\frac{2r_2}{a}}}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}} r_2^2 \sin\theta_2 \, d\phi_2 \, d\theta_2 \, dr_2$$

Integrating over θ_2 yields:

$$\int_0^\pi \frac{\sin\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}} d\theta_2 = \frac{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}{r_1r_2}\Bigg|_0^\pi =$$

$$= \frac{1}{r_1r_2}\left(\sqrt{r_1^2+r_2^2+2r_1r_2} - \sqrt{r_1^2+r_2^2-2r_1r_2}\right) = \frac{1}{r_1r_2}\left[(r_1+r_2) - |r_1-r_2|\right] =$$

$$= \begin{cases} \frac{2}{r_1}, & r_2 < r_1 \\ \frac{2}{r_2}, & r_1 < r_2 \end{cases}$$

So the integral over $\vec{r}_2$ becomes

$$4\pi\left(\frac{1}{r_1}\int_0^{r_1} e^{-\frac{2r_2}{a}} r_2^2 dr_2 + \int_{r_1}^{\infty} e^{-\frac{2r_2}{a}} r_2 \, dr_2\right) = \frac{\pi a^3}{r_1}\left[1-\left(1+\frac{r_1}{a}\right)e^{-\frac{2r_1}{a}}\right]$$

Then

$$\langle V_{ee} \rangle = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(\frac{1}{\pi a^3}\right)^2 \int \left[1-\left(1+\frac{r_1}{a}\right)e^{-\frac{2r_1}{a}}\right] e^{-2r_1 a} r_1 \sin\theta_1 \, d\phi_1 \, d\theta_1 \, dr_1 =$$

$$= \left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(\frac{1}{\pi a^3}\right)^2 4\pi \int_0^\infty \left[r_1 e^{-\frac{2r_1}{a}} - \left(r_1+\frac{r_1^2}{a}\right)e^{-\frac{4r_1}{a}}\right] dr_1 =$$

$$= \left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(\frac{1}{\pi a^3}\right) 4\pi \cdot \frac{5a^2}{32} = \frac{5}{8a}\left(\frac{e^2}{4\pi\varepsilon_0}\right) = -\frac{5}{4Z}E_1 =$$

Finally we get that

$$\langle H \rangle = 2E_1 - \frac{5}{4Z}E_1 = \left(2 - \frac{5}{4Z}\right)E_1 =$$

$$= \frac{11}{8}E_1 = -\frac{11}{4}\text{ hartree} = -2.75\text{ hartree} \approx -75\,eV$$

The next improvement we can make is to vary the wave function so that it corresponds to some "effective" nuclear charge ζ seen by electrons:

$$\psi_1(r_1, r_2) = \frac{\zeta^3}{\pi a_0^3} e^{-\zeta(r_1+r_2)/a_0}$$

ζ is going to be a variational parameter which we can "optimize" by minizing the total energy.

The Hamiltonian can be written as

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{\zeta}{r_1} + \frac{\zeta}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{(\zeta - Z)}{r_1} + \frac{(\zeta - Z)}{r_2} + \frac{1}{|r_1 - r_2|}\right)$$

The expectation value of H is

$$\langle H \rangle = 2\frac{\zeta^2}{Z^2}E_1 + 2(\zeta - Z)\left(\frac{e^2}{4\pi\varepsilon_0}\right)\left\langle\frac{1}{r}\right\rangle_{100} + \langle V_{ee}\rangle$$

$\left\langle\frac{1}{r}\right\rangle_{100}$ is known to be equal to $\frac{\zeta}{a_0}$

$$\langle V_{ee}\rangle = \frac{5\zeta}{8a_0}\left(\frac{e^2}{4\pi\varepsilon_0}\right) = -\frac{5}{4}\frac{\zeta}{Z^2}E_1$$

With that we have

$$\langle H \rangle = \left[2\frac{\zeta^2}{Z^2} - \frac{4\zeta(\zeta - Z)}{Z^2} - \frac{5}{4}\frac{\zeta}{Z^2}\right]E_1 = \left[2\zeta^2 - 4\zeta(\zeta - Z) - \frac{5}{4}\zeta\right]\frac{E_1}{Z^2}$$

The minimum of the energy is reached when

$$\frac{\partial \langle H \rangle}{\partial \zeta} = 0 \quad \Rightarrow \quad 4\zeta - 8\zeta + 4Z - \frac{5}{4} = 0$$

$$4Z - \frac{5}{4} = 4\zeta \quad \Rightarrow \quad \zeta = Z - \frac{5}{16}$$

For He $(Z=2)$ $\quad \zeta = \frac{27}{16} \approx 1.69$

$$\langle H \rangle = \left[-2\zeta^2 + 4\zeta Z - \frac{5}{4}\zeta \right] \frac{E_1}{Z^2} =$$

$$= \left[-2\zeta + 4Z - \frac{5}{4} \right] \zeta \frac{E_1}{Z^2} =$$

$$= \left[-2\left(Z - \frac{5}{16}\right) + 4Z - \frac{5}{4} \right] \left(Z - \frac{5}{16}\right) \frac{E_1}{Z^2} = \frac{(5-16Z)^2}{128} \frac{E_1}{Z^2}$$

Again, for He it gets $\langle H \rangle = \frac{729}{128} \frac{E_1}{Z^2} = -2.848$ hartree

$= -77.5\,\mathrm{eV}$.