

How to get the variational method for Helium

written by Alexander Sauter; modified by L. Kocbach ; September 2006

We start with hydrogen-like (one electron) problem

$$H = T_1 + V_1.$$

We remember that the kinetic energy contains only second derivatives of the wavefunction, while

$$V_i = -\frac{Ze^2}{r_i}.$$

We know that the ground state energy is

$$E_{1s}(Z) = -\frac{1}{2} Z^2 \frac{e^2}{a_0}.$$

We will need the virial theorem, in order to avoid unnecessary evaluations. It states:

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle$$

Since

$$\langle H \rangle = E_{1s}(Z) = -\frac{1}{2} Z^2 \frac{e^2}{a_0} = -\frac{1}{2} Z^2 E_0$$

and

$$\langle H \rangle = \langle T \rangle + \langle V \rangle$$

we can see that

$$\langle T \rangle = \frac{1}{2} Z^2 E_0$$

and

$$\langle V \rangle = -Z^2 E_0$$

Let us now consider the variable, or unknown effective charge number z , which is contained only in the wavefunctions.

When $z = Z$, the kinetic energy $\langle T \rangle$ is $\frac{1}{2} Z^2 E_0$. As we mentioned, the kinetic energy contains only second derivatives, no Z . That means that when z becomes different from Z , there can not be any Z in the kinetic energy T , thus

$$\langle T(z) \rangle = \frac{1}{2} z^2 E_0$$

On the other hand, the potential energy contains Z , as seen above. Thus

$$\langle V(z) \rangle = -z Z E_0$$

We look now at the total energy for two electrons including the repulsion

$$H = T_1 + T_2 + V_1 + V_2 + V_{12}.$$

The repulsion term V_{12} is known for the hydrogen like orbitals, or repulsion between two electrons where both are in $1s$ orbital. For atomic number Z we obtained

$$V_{12} = \frac{5 Ze^2}{8 a_0} = \frac{5}{8} Z E_0.$$

Again, there is no Z in the repulsion energy operator, therefore

$$V_{12}(z) = \frac{5}{8} z E_0$$

for the orbitals with effective z .

Thus

$$E(z) = E_0 \left(\frac{1}{2} z^2 - zZ \right) + E_0 \left(\frac{1}{2} z^2 - zZ \right) + E_0 \frac{5}{8} z.$$

or

$$E(z) = \left(z^2 - 2zZ + \frac{5}{8} z \right) E_0.$$

If we want to have a stable state the energy have to be extremal:

$$\frac{d}{dz} E(z) = 0$$

$$\Leftrightarrow 2z - 2Z + \frac{5}{8} = 0$$

$$\Leftrightarrow z = Z - \frac{5}{16}.$$