How to get the variational method for Helium

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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

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

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:

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

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

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