Exercise 1. ***Ground state of helium***

The helium atom consists of two electrons in orbit around a nucleus containing two protons. The experimental value of the ground state energy is $E_{exp} = -78.975$ eV. In this exercise we want to estimate this energy using the variational method.

The Hamiltonian of the helium atom is

$$H = H_0 + V = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - e^2\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r_1} - \vec{r_2}|}\right) \tag{1}$$

and it can be seen as the sum of two independent hydrogen-like terms plus a Coulomb interaction describing the repulsion between the electrons. Therefore neglecting this contribution the ground-state wavefunction Ψ_0 is just the product of two hydrogen-like ground-state wavefunctions ψ_{1s}

$$\Psi_0(\vec{r}_1, \vec{r}_2) = \psi_{1s}(\vec{r}_1)\psi_{1s}(\vec{r}_2) = \frac{8}{\pi a^3}\mathrm{e}^{-2(r_1+r_2)/a} \tag{2}$$

where a is the Bohr radius.

(a) Using the trial function Ψ_0 obtain an upper value for the energy of the ground-state.

(b) This first estimate neglects completely the repulsion between the electrons. We can consider this effect saying that on average each electron represents a cloud of negative charge which partially shields the nucleus, so that the other electron actually sees an effective nuclear charge Z that is somewhat less than 2. This suggests that we use a trial function of the form

$$\Psi_1(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi a^3}\mathrm{e}^{-Z(r_1+r_2)/a} \tag{3}$$

Give a new estimate of the ground state energy using Z as a variational parameter.

(c) Compare the two estimates to the experimental value.

Exercise 2. ***Hydrogen atom***

In the following exercise we want to make use of a result due to Feynman and Hellmann to compute the mean values of $1/r^k$ on the eigenstates of the Coulomb problem.

(a) We start off considering a hamiltonian H_λ and the Schroedinger equation:

$$(H_\lambda - E_\lambda)|\psi\rangle = 0\,, \tag{4}$$

where H_λ and E_λ are functions of a continuos parameter λ.

Show that given any eigenstate $|\psi\rangle$ and its eigenvalue E_λ:

$$\left\langle \psi \left| \frac{dH_\lambda}{d\lambda} \right| \psi \right\rangle = \frac{dE_\lambda}{d\lambda}. \tag{5}$$

This apparently very simple result can be an extremely powerful tool in computing mean values of different operators as we will see in the following.

(b) Consider now the hamiltonian for the Coulomb problem

$$H = -\frac{\hbar^2}{2\,m}\nabla^2 - \frac{Ze^2}{r}, \tag{6}$$

The radial hamiltonian reads:

$$\mathcal{H} = -\frac{\hbar^2}{2\,m}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right) - \frac{Ze^2}{r}. \tag{7}$$

With this notation the eigenvalues of $\mathcal{H}$ read:

$$E_n = -\frac{(Ze^2)^2}{\hbar^2}\frac{m}{2\,n^2} = -\frac{(Ze^2)^2}{\hbar^2}\frac{m}{2(N+l+1)^2} \tag{8}$$

where n is the principal quantum number, and N is the so called radial quantum number. Using Feynman-Hellmann result show that:

$$\begin{aligned}
\left\langle \psi_{nlm} \left| \frac{1}{r} \right| \psi_{nlm} \right\rangle &= \frac{Z}{a\,n^2}, \\
\left\langle \psi_{nlm} \left| \frac{1}{r^2} \right| \psi_{nlm} \right\rangle &= \frac{Z^2}{a^2(l+1/2)\,n^3}, \\
\left\langle \psi_{nlm} \left| \frac{1}{r^3} \right| \psi_{nlm} \right\rangle &= \frac{Z^3}{a^3 l(l+1/2)(l+1)\,n^3},
\end{aligned}$$

where ψ_{nlm} are the eigenfunctions of the Coulomb problem.