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. ***The Fermi gas***

Let us consider a system of a very large number of non-interacting spin-1/2 particles contained in a box. If the box is large enough, the properties of the system are independent of the shape of the box, and the system is called a *Fermi gas*. Since the particles are non-interacting, each of them satisfies the free-particle Schroedinger equation

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x,y,z) = E\psi(x,y,z) \,. \tag{4}$$

We consider impenetrable walls with boudary conditions $\psi = 0$. For a large cubic box of side L the wavefunction is given by

$$\psi_{n_x n_y n_z} = C \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right) \tag{5}$$

where $C = (8/L^3)^{1/2}$ and n_x, n_y, n_z are positive integers. The corresponding eigenvalues are

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \qquad n^2 = n_x^2 + n_y^2 + n_z^2 \,. \tag{6}$$

The total one-particle wavefunction is the so-called spin-orbital

$$\psi_{n_x n_y n_z m_s} = \psi_{n_x n_y n_z}(x, y, z)\chi_{\frac{1}{2},m_s} \tag{7}$$

where χ is the spin wavefunction with $m_s = \pm 1/2$.

Since the energy spacings are very small for a macroscopic box, it is a good approximation to consider that the energy levels are distributed nearly continuously. We may then introduce the density of states $D(E)$, which is defined in such a way that $D(E)dE$ is the number of states with energy in the range $(E, E + dE)$. In the space formed by the axes n_x, n_y, n_z we are interested in the octant for which $n_x > 0, n_y > 0, n_z > 0$. Each state is associated to a point (n_x, n_y, n_z) of a cubical lattice, and every elementary cube of the lattice has unit volume. Hence, the total number of states up to an energy E_n is well approximated by the volume of the octant of a sphere of radius $n = (n_x^2 + n_y^2 + n_z^2)^{1/2}$. The total number of individual particle states for energies up to E_n is therefore

$$N_s = 2\frac{1}{8}\frac{4}{3}\pi\, n^3\,. \tag{8}$$

(a) Starting from N_s, and setting $V = L^3$, derive the density of states $D(E)$. Describe schematically how the energy levels are populated by N identical spin-1/2 particles in the ground state of the Fermi gas at absolute temperature $T = 0$, up to an energy E_F called the *Fermi energy.*

(b) Derive the explicit value of E_F for a gas containing N particles.

(c) Compute the total energy of the gas and the average particle energy.