

**Problem 8.1 DFT for Helium (part 1)**

We want to treat the Helium atom in density functional theory. In this exercise, you will write a Schrödinger solver as well as a Poisson solver. In the following exercise, you will apply these to Helium and create a self-consistent procedure.

- First, solve the radial equation in the  $l = 0$  sector for the hydrogen atom

$$\left[ -\frac{1}{2}\nabla^2 - \frac{1}{r} \right] u(r) = Eu(r) \quad (1)$$

where  $u(r) = rR(r)$ ,  $R(r)$  being the radial wave function. Use the Numerov algorithm to find the ground-state wave function and energy and compare your result with the analytical solution  $E = -0.5$  a.u. and  $u(r) \propto r \exp(-r)$ .

- Then, implement a solver for the Poisson equation

$$\begin{aligned} \nabla^2 V_H(\mathbf{r}) &= -4\pi n_S(\mathbf{r}), \\ \frac{d^2}{dr^2} U(r) &= -\frac{u^2(r)}{r} \end{aligned} \quad (2)$$

where  $V_H = U(r)/r$  is the Hartree potential generated by the charge distribution from the wave function and  $n_S$  denotes the density of a single orbital. A convenient choice for this integration task is the Verlet algorithm.

- Combine these parts and check the correctness by using the hydrogen atom again. Compare your numerical solution for the potential with the analytical result

$$U(r) = -(r + 1) \exp(-2r) + 1 \quad (3)$$

## Problem 8.2 DFT for Helium (part 2)

In the last exercise, you have programmed a solver for the radial Schrödinger and Poisson equations.

- Apply these to the Helium atom, i.e. change the nuclear potential appropriately and add the Hartree potential term. Furthermore, include the following parameterization of the exchange potential

$$V_x(r) = - \left( \frac{3u^2(r)}{4\pi^2 r^2} \right)^{\frac{1}{3}}. \quad (4)$$

Repeat these steps iteratively until you reach a self-consistent solution.

- You should obtain the following eigenvalue and energy respectively:

$$\epsilon = -0.52 \text{ a.u.} \quad (5)$$

$$E = -2.72 \text{ a.u.} \quad (6)$$

where the relationship between these two reads

$$E = 2\epsilon - \int dr \left( V_H(r)u^2(r) + \frac{1}{2}u^2(r)V_x(r) \right). \quad (7)$$

Decrease your step size and/or increase the cutoff radius to check where your results are not heavily depending on these constants any more.

- In this simple case, you should not encounter convergence problems when using sensible values for step sizes, cutoff radius, etc. However, if it doesn't converge, you can damp your solution by using the following potential update

$$u_{n+1} = \delta u_n + (1 - \delta) v_n, \quad (8)$$

where  $u_n$  is the effective potential in the n-th step and  $v_n$  denotes the solution of the Poisson equation.