Computational Quantum Physics
Exercise 9

Problem 9.1   DFT for Helium

The goal of this exercise sheet is to treat the Helium atom in density functional theory. To this end, you will first write a Schrödinger solver as well as a Poisson solver, and then apply these in a self-consistent procedure to Helium. Throughout this exercise sheet we use atomic units (see exercise sheet 8).

A. Schrödinger Solver.   For a spherically symmetric potential $V(r)$ *and* solution $\psi(r)$, the three-dimensional Schrödinger equation $\left(-\frac{1}{2}\Delta + V(r)\right)\psi(r) = \varepsilon\psi(r)$ reduces to the radial equation

$$-\frac{1}{2}u''(r) + V(r)u(r) = \varepsilon u(r), \tag{1}$$

where $u(r) = \sqrt{4\pi}\, r\, \psi(r)$.

- Implement an algorithm for finding the ground state energy and wave function of (1) for a given potential $V(r)$.

  Hint: Use the Numerov algorithm and a bisection method (cf. Problem 2.1).

- Test your code with the $l = 0$ sector of the hydrogen atom, where $V(r) = -\frac{1}{r}$, and compare your result with the analytical solution $\varepsilon_{\text{exact}} = -0.5$ a.u. and $u_{\text{exact}}(r) \propto r\exp(-r)$.

In part C, you will apply this code to the effective potential as given by density functional theory.

B. Poisson Solver.   The Hartree potential $V_{\text{h}}(\vec{r})$ satisfies the Poisson equation $\Delta V_{\text{h}}(\vec{r}) = -4\pi\rho(\vec{r})$. For spherically symmetric $\rho(r)$ and $V_{\text{h}}(r)$, this reduces to

$$U''(r) = -\frac{r}{N}4\pi\rho(r),$$

where $U(r) := rV_{\text{h}}(r)/N$.

For a system of $N = 1$ or 2 electrons, we use the ansatz $\rho(r) = N|\psi_0(r)|^2$ for the electron density, where ψ_0 is the *normalized* ground state of the single-electron Schrödinger equation with the effective potential from density functional theory (see part C below). Equivalently,

$$U''(r) = -\frac{u^2(r)}{r} \tag{2}$$

where $u(r)$ is the ground state of (1) and normalized to norm one, $\int_0^\infty dr\, u^2(r) = 1$. Note that $U(r)$ satisfies the boundary conditions $U(0) = 0$ and $U(\infty) = 1$.

- Implement a solver for (2) with these boundary conditions for a given function $u(r)$.

  Hint: Use the Verlet algorithm to integrate from $U(0) = 0$, $U(\Delta r) = \Delta r$ to some $r_{\text{max}} \gg 0$ (e.g., $r_{\text{max}} = 20$). Then add a suitable multiple of the homogeneous solution $U_{\text{hom}}(r) = r$ to fix the outer boundary condition.

- Test your code with the $u(r)$ as obtained for the hydrogen atom in part A, and compare your result with the analytical solution $U_{\text{exact}}(r) = -(r+1)\exp(-2r) + 1$.

C. Helium. Apply density functional theory to the Helium atom. Use the effective potential $V_{\text{eff}} = V_{\text{nucl}} + V_{\text{h}} + V_{\text{xc}}$, where V_{nucl} is the appropriate nuclear potential, V_{h} the Hartree potential as obtained via part B, and

$$V_{\text{xc}}(r) = -\left(\frac{3}{2\pi}\right)^{2/3}\left(\frac{4\pi}{3}\rho\right)^{1/3} = -\left(\frac{3}{2\pi^2}\frac{u^2(r)}{r^2}\right)^{1/3}$$

is a parametrization of the exchange-correlation potential, and determine ε and $u(r)$ by using part A.

Repeat these steps iteratively until you reach a self-consistent solution. Decrease your step size Δr and/or increase the cut-off radius r_{max} to check where your results are not heavily depending on these constants any more.

Hint: You should obtain

$$\epsilon \approx -0.52 \text{ a.u.}$$
$$E \approx -2.72 \text{ a.u.}$$

where energy E is related to the eigenvalue ε by the formula

$$E = 2\epsilon - \int dr\, V_{\text{h}}(r)u^2(r) - \frac{1}{2}\int dr\, V_{\text{xc}}(r)u^2(r).$$