Computational Quantum Physics

Exercise 8

FS 12
Prof. M. Troyer

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

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

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

   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

$$\nabla^2 V_H(\mathbf{r}) = -4\pi n(\mathbf{r}) \ ,$$

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

   where $V_H = NU(r)/r$ is the Hartree potential generated by the density $n(\mathbf{r})$ of N electrons in the single-particle wave function u. A convenient choice for this integration task is the Verlet algorithm. The solution needs to satisfy the boundary conditions $U(0) = 0$ and $U(r_{max}) = q_{max}$, where $q_{max} = 1$ is the total charge enclosed by a sphere of radius r_{max}. You can find such a solution by starting your Verlet integration in the center with $U(0) = 0, U(h) = h$ and integrating till r_{max}. Then add the homogenous solution $U_{hom}(r) = \alpha r$ with α chosen such as to satisfy the outer boundary condition.

   Note that the wave function must be normalized before solving the Poisson equation. The above equations assume

$$\int \mathrm{d}r \ u^2(r) = 1 \ .$$

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

$$U(r) = -(r+1)\exp(-2r) + 1 \ . \tag{3}$$

Problem 8.2 DFT for Helium (part 2)

In the previous 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

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

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

- You should obtain the following eigenvalue and energy respectively:

$$\epsilon = -0.52 \, a.u.$$ (5)
$$E = -2.72 \, a.u.$$ (6)

  where the relationship between these two reads

$$E = 2\epsilon - \int dr \, V_H(r)u^2(r) - \frac{1}{2}\int dr \, u^2(r)V_x(r).$$ (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

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

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