

# Assignment 5

## Self-consistency and the density-functional theory (20 points)

Göran Wahnström, Per Sundell, Martin Petisme, Petter Rosander 2024-01-15  
Anders Hellman 2025-01-25  
anders.hellman@chalmers.se

January 2025

### Introduction

In this exercise you are asked to determine the ground state energy for the helium atom using the density functional method. You are recommended to use Python.

### The Hamiltonian

The Born-Oppenheimer Hamiltonian for the many-electron system reads

$$\mathcal{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \sum_n \sum_i \frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_n|} + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (1)$$

or in atomic units

$$\mathcal{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_n \sum_i \frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2)$$

Assuming that both protons are infinite close in origo, the Hamiltonian for the helium atom it simplifies to

$$\mathcal{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \quad (3)$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  denote the position coordinates of the two electrons and  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ .

### Hartree-Fock for helium

The two-electron Hartree-Fock *Ansatz*, which satisfies the antisymmetry requirement that the wave function changes sign when two particles are exchanged is,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) - \psi_2(\mathbf{x}_1)\psi_1(\mathbf{x}_2)] \quad (4)$$

where the notation  $\mathbf{x}_i$  includes both the spatial and spin coordinate. For the ground state with paired electrons we have  $\psi_1(\mathbf{x}_1) = \varphi_0(\mathbf{r}_1)\alpha(s_1)$  and  $\psi_2(\mathbf{x}_2) = \varphi_0(\mathbf{r}_2)\beta(s_2)$  so that

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \varphi_0(\mathbf{r}_1) \varphi_0(\mathbf{r}_2) [\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)] \quad (5)$$

where  $\varphi_0$  is normalized and for the spin components we have that  $|\alpha(s_i)\alpha(s_i)| = |\beta(s_i)\beta(s_i)| = 1$  and  $\alpha(s_i)\beta(s_i) = 0$ .

Plugging out *Ansatz* into the Schrödinger equation and integrating out the  $\mathbf{r}_2$  dependence (see [1]), we get the equation

$$\left[ -\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} + \int d\mathbf{r}_2 |\varphi(\mathbf{r}_2)|^2 \frac{1}{r_{12}} \right] \varphi(\mathbf{r}_1) = E' \varphi(\mathbf{r}_1) \quad (6)$$

## The Density Functional Theory

The density functional method is based on the observation by Hohenberg and Kohn (1964) that all the ground-state properties of a many-body quantum-mechanical system of electrons may be obtained from a knowledge of the electron density  $n(\mathbf{r})$ . They proved that the total energy of a many-electron system in an external potential is a unique functional of the electron density

$$E[n] = F[n] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \quad (7)$$

and this functional is minimum and equal to the ground-state energy  $E_0$  when  $n(\mathbf{r})$  is the ground-state density  $n_0(\mathbf{r})$ ,

$$E_0 = E[n_0(\mathbf{r})] = \min_{n(\mathbf{r})} \{E[n(\mathbf{r})]\} \quad (8)$$

The notation  $\min_{n(\mathbf{r})}$  implies minimizing with respect to the density  $n(\mathbf{r})$  keeping the number of electrons  $N = \int d\mathbf{r} n(\mathbf{r})$  constant.

## The Kohn-Sham equation

A practical scheme was developed by Kohn and Sham (1965). They wrote the functional on the form

$$E^{\text{KS}}[n] = T_0[n] + E_H[n] + E_{\text{xc}}[n] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \quad (9)$$

where  $T_0[n]$  is the kinetic energy of a (fictitious) non-interacting electron system;  $E_H[n]$  is the Hartree energy (the classical inter-electron repulsion), and  $E_{\text{xc}}[n]$  is the exchange-correlation energy (the rest). The latter includes all complicated many-body effects and has to be approximated. Carrying out the minimization in eqn (8) one arrives at the Kohn-Sham equations

$$\left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (10)$$

with

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \quad (11)$$

and

$$V_{\text{H}}(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (12)$$

$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \quad (13)$$

$$V_{\text{ext}}(\mathbf{r}) = - \sum_n \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} \quad (14)$$

with

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2 \quad (15)$$

The ground-state energy is then given by

$$E_0 = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n] - \int d\mathbf{r} V_{\text{xc}}(\mathbf{r})n(\mathbf{r}) \quad (16)$$

Notice that the  $\epsilon_i$ 's are Lagrange multipliers introduced to handle the constraint that the number of electrons should be conserved,

$$N = \int d\mathbf{r} n(\mathbf{r}) = \text{const.} \quad (17)$$

For the helium atom the Kohn-Sham equation reduces to

$$\left[ -\frac{1}{2}\nabla^2 - \frac{2}{r} + 2 \int d\mathbf{r}' \frac{|\varphi(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}(\mathbf{r}) \right] \varphi(\mathbf{r}) = \epsilon \varphi(\mathbf{r}) \quad (18)$$

with

$$E_0 = 2\epsilon - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] - \int d\mathbf{r} V_{xc}(\mathbf{r})n(\mathbf{r}) \quad (19)$$

and

$$n(\mathbf{r}) = 2 |\varphi(\mathbf{r})|^2 \quad (20)$$

## The Local Density Approximation

The exact form of the exchange-correlation functional is not known. It has to be approximated. The most widely used is the Local Density Approximation (LDA). In that approximation, the exchange-correlation functional  $E_{xc}[n]$  is represented as

$$E_{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}^{\text{hom}}(n(\mathbf{r})) \quad (21)$$

where  $\epsilon_{xc}^{\text{hom}}(n)$  is the exchange-correlation energy per electron of a homogeneous electron gas at density  $n$ . The corresponding potential is given by

$$V_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}[n]}{\delta n} = \epsilon_{xc}^{\text{hom}}(n) + n \frac{d}{dn} \epsilon_{xc}^{\text{hom}}(n) \quad (22)$$

The exchange-correlation energy can be separated into an exchange and a correlation contribution

$$\epsilon_{xc}^{\text{hom}}(n) = \epsilon_x^{\text{hom}}(n) + \epsilon_c^{\text{hom}}(n) \quad (23)$$

and correspondingly for the exchange-correlation potential. The exchange part can be evaluated exactly [2]

$$\epsilon_x^{\text{hom}}(n) = -\frac{3}{4} \left( \frac{3n}{\pi} \right)^{1/3} \quad (24)$$

and the correlation part has been evaluated essentially exactly by the numerical quantum Monte Carlo technique [3]. The following analytical representation has been suggested [4]

$$\epsilon_c^{\text{hom}}(r_s) = \frac{\gamma}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s}, \quad r_s \geq 1 \quad (25)$$

$$\epsilon_c^{\text{hom}}(r_s) = A \ln r_s + B + C r_s \ln r_s + D r_s, \quad r_s < 1 \quad (26)$$

with  $n = 3/(4\pi r_s^3)$ . The numerical values for the non-spinpolarized electron gas (in atomic units) are:

$$A = 0.0311, B = -0.048, C = 0.0020, D = -0.0116, \gamma = -0.1423, \beta_1 = 1.0529, \beta_2 = 0.3334. \quad (27)$$

## Numerical procedure

The Kohn-Sham eqn (18) is non-linear in  $\varphi(\mathbf{r})$  and has to be solved in an iterative manner. An initial guess for the wave-function  $\varphi(\mathbf{r})$  is made, the Hartree potential  $V_H(r)$  and exchange-correlation potential  $V_{xc}(r)$  are determined and the Kohn-Sham eqn (18) can then be solved. A new wave-function  $\varphi(\mathbf{r})$  is obtained and the procedure is repeated until the ground-state energy  $E_0$  in eqn (19) is converged.

### The Hartree potential

The Hartree potential, the electro-static potential generated by the charge distribution,

$$V_H(\mathbf{r}) \equiv \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (28)$$

which also can be written on differential form, the **Poisson's equation**

$$\nabla^2 V_H(\mathbf{r}) = -4\pi n(\mathbf{r}) \quad (29)$$

For the helium atom the ground-state electron density is given by

$$n(\mathbf{r}) \equiv 2n_s(\mathbf{r}) = 2 |\varphi(\mathbf{r})|^2 \quad (30)$$

where  $n_s(\mathbf{r})$  is the density of a single orbital. We can introduce the corresponding electro-static potential according to

$$\nabla^2 V_{sH}(\mathbf{r}) = -4\pi n_s(\mathbf{r}) \quad (31)$$

Using the radial symmetry it takes the form

$$\frac{d^2}{dr^2} U(r) = -4\pi r n_s(r) \quad (32)$$

with  $U(r) = r V_{sH}(r)$ . The density is normalized according to

$$\int d\mathbf{r} n_s(\mathbf{r}) = 4\pi \int r^2 n_s(r) dr = 1 \quad (33)$$

and by introducing the variable

$$u(r) = \sqrt{4\pi n_s(r)} r = \sqrt{4\pi} r \varphi(r) \quad (34)$$

the following differential equation is obtained

$$\frac{d^2}{dr^2} U(r) = -\frac{u^2(r)}{r} \quad (35)$$

with the boundary conditions

$$U(0) = 0, \quad U(r_{\max}) = 1$$

By introducing the variable

$$U_0(r) \equiv U(r) - \frac{r}{r_{\max}} \quad (36)$$

the two-point boundary value problem is transformed into the standard form

$$\frac{d^2}{dr^2} U_0(r) = -\frac{u^2(r)}{r} \quad (37)$$

with

$$U_0(0) = U_0(r_{\max}) = 0$$

## The radial Schrödinger equation

In radial coordinates the Kohn-Sham equation takes the form

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} - \frac{2}{r} + V_H(r) + V_x(r) + V_c(r) \right] u(r) = \epsilon u(r) \quad (38)$$

with the boundary conditions

$$u(0) = u(r_{\max}) = 0$$

Finally, the ground-state energy, in the local-density approximation, is given by

$$E_0 = 2\epsilon - 2 \int dr u^2(r) \left[ \frac{1}{2} V_H(r) + V_{xc}(r) - \epsilon_{xc}(r) \right] \quad (39)$$

## Boundary value problems

The boundary value problem for the differential eq (37) and eigenvalue eq (38) can be solved with various numerical methods. The finite difference method converts the boundary value problem into a system of algebraic equations. This is done by replacing the derivatives with finite differences.

## Finite differences

In the finite difference method the space is discretized

$$x_i = a + ih, \quad i = 0, \dots, n, \quad h = (b - a)/n \quad (40)$$

and one seeks an approximate solution at the grid

$$y_i = y(x_i) \quad (41)$$

The derivatives are replaced by finite differences

$$y'(x_i) = \frac{y_{i+1} - y_{i-1}}{2h} \quad (42)$$

$$y''(x_i) = \frac{y_{i+1} - 2y_i + y_{i-1}}{h^2} \quad (43)$$

and the resulting matrix equation can be solved using standard routines.

## Task

1. Solve the problem in Section 4.3.2 in Thijssen [1]. This is what is referred to as the Hartree approximation, and in this case, you are using it to find the wave function and ground state energy of Helium. Start by writing the wave function as

$$\varphi(\mathbf{r}) = \sum_{i=1}^4 C_i \chi_i(\mathbf{r})$$

with

$$\chi_i(\mathbf{r}) = \exp(-\alpha_i r^2)$$

and

$$\alpha_1 = 0.297104, \quad \alpha_2 = 1.236745, \quad \alpha_3 = 5.749982, \quad \alpha_4 = 38.216677.$$

Then solve the equations resulting from plugging this into equation (6) with self-consistently until your energy change is less than  $10^{-5}$  eV. **Determine the ground state energy and wave function.**

2. Consider first the Poisson's equation. Solve it in radial coordinates, equation (37), using finite differences. Discretize the equation and approximate the derivatives using a uniform grid. Then, solve the resulting system of linear equations.

**Test your program by using the ground state electron density for the hydrogen atom as input density.** You should then obtain the Hartree potential

$$V_H(r) = \frac{1}{r} - \left(1 + \frac{1}{r}\right) e^{-2r}$$

3. You also need to solve the Kohn-Sham equation (38). Write a program that solves the eigenvalue problem using the finite difference method on a uniform grid.

Test your program by solving the radial Schrödinger equation for the hydrogen atom

$$\left(-\frac{1}{2} \frac{d}{dr^2} - \frac{1}{r}\right) u(r) = E u(r).$$

Compare your results with the analytical result for the ground state energy and wave function. Hint: use `np.linalg.eigh` and not `np.linalg.eig` since you know that the Hamiltonian is real and symmetric.

4. Use the results above to construct a program that determines the ground energy for Helium using DFT. In this case, leave out the exchange-correlation terms and include the self-interaction in the Hartree potential, i.e.,  $V_H = 2V_{sH}$ . **Make an initial guess for the density and iterate to self-consistency.** Stop the loop when the energy changes with less than  $10^{-5}$  eV. Determine the ground state energy, eigenvalue, and wave function. **Make sure that your solution is converged with respect to both the grid spacing and  $r_{\max}$ .** (Suggestion: increase  $r_{\max}$  keeping the same grid density until convergence, and then increase the grid density until convergence).

For this task to work properly, you need to implement wave function mixing,

$$u_{\text{mix}}(r) = u_{\text{in}}(r) + \alpha(u_{\text{out}}(r) - u_{\text{in}}(r))$$

where  $u_{\text{mix}}(r)$  is your next guess of the wave function and  $u_{\text{in}}(r)/u_{\text{out}}(r)$  is the input/output wave function in the previous iteration. A sensible value for  $\alpha$  is in the range 0.1 – 0.4 (for this specific case).

5. Now, remove the self-interaction from the Hartree potential in the previous task, i.e., use  $V_{\text{H}} = V_{\text{sH}}$ . This is an unconstrained solution of the Hartree problem, i.e., we make no assumption of the form of the wave function, as done in task 1. How much does the ground state energy improve compared to the experimental value when lifting this restriction on the wave function?
6. Now, add exchange contributions as well. In this case, use the full Hartree potential, just as in Task 4.
7. Finally, solve the task, including the correlation contributions as well.
8. Plot the wave functions and compare the ground state energy obtained in all the tasks above. Reflect on the approximations done, is LDA an appropriate approximation for an atom, why? why not? Moreover, what can you say about the self-interaction, what does it lead to, and how does DFT correct for it?

## References

- [1] J. M. Thijssen *Computational Physics* (Cambridge, 1999).
- [2] N.W. Ashcroft and N.D Mermin *Solid State Physics*, Holt, Rinehart and Winston (1976)
- [3] D.M. Ceperley and B.J. Alder, *Ground State of the Electron Gas by a Stochastic Method*, Phys. Rev. Lett 45, 566 (1980)
- [4] J.P. Perdew, A Zunger, *Self-interaction correction to density-functional approximations for many-electron systems* Phys. Rev. B 23, 5048 (1981)