

1 Solving the Schrödinger equation for the helium atom using density functional theory and finite differences

In this exercise you will write a program in Matlab that calculates the ground state energy for the helium atom using density functional theory (DFT). The differential equations are solved using the finite difference method. The exercise is based on chapter 5 and appendix A in J. M. Thijssen "Computational Physics".

If you find typos, in this text or in the reference literature, please report them so that the exercise can be corrected and improved accordingly.

1.1 The General Hamiltonian

In the Born-Oppenheimer approximation, the Hamiltonian for the many-electron system reads

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

where Z_n is the charge number of nucleus n , \mathbf{r}_i is the position of electron i , \mathbf{R}_n is the position of nucleus n , m is the electron mass, and ϵ_0 is the dielectric constant in vacuum, not to be confused with the energy eigenvalues occurring later in this text. In atomic units ($\hbar = m = e = 4\pi\epsilon_0 = 1$), the same equation reads

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

Just to see what it looks like (we will not use this form of the Hamiltonian for any calculations), let's write out the equation explicitly for the helium atom:

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

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

1.2 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 V_{ext} is a unique functional of the electron density

$$E[n] = F[n] + \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r}), \quad (4)$$

where $F[n]$ does not depend on the external potential. The functional $E[n]$ is minimum and equal to the ground-state energy E_0 when $n(\mathbf{r})$ is the ground-state density $n_0(\mathbf{r})$,

$$E_0 = E[n_0(\mathbf{r})] = \min_{n(\mathbf{r})} \{E[n(\mathbf{r})]\} \quad (5)$$

The notation $\min_{n(\mathbf{r})}$ implies minimizing with respect to the density $n(\mathbf{r})$ keeping the number of electrons $N = \int d^3r n(\mathbf{r})$ constant.

The term "external potential" in this context usually just stands for the Coulomb potential produced by the nuclei and that is how we will use it here.

1.3 The Kohn-Sham Equation and and Explicit Form for the Total Energy

The functional $F[n]$ above contains the kinetic energy of the electrons, the Hartree energy, and many-body terms caused by the electron-electron interaction. To date, there is no known way to express the kinetic energy of an interacting electron system as a functional of the electron density with acceptable precision. However, a practical scheme to circumvent this problem was developed by Kohn and Sham (1965). Their approach is based on the idea that the interacting system can be mapped onto a hypothetical system of non-interacting particles moving in an effective potential V_{eff} , defined below. We may call these particles "Kohn-Sham particles" (KS-particles) and think of them in terms of a type of quasiparticles. In the literature, you will very often see them referred to as "electrons". The main reason for this is tradition, and this confusing nomenclature with probably stick. We note in passing that the KS-particles should not be confounded with Landau quasiparticles. Kohn and Sham wrote the functional for the total energy on the form

$$E^{\text{KS}}[n] = T_{\text{S}}[n] + E_{\text{H}}[n] + E_{\text{xc}}[n] + \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \quad (6)$$

where $T_{\text{S}}[n]$ is the kinetic energy of the hypothetical non-interacting electron system, $E_{\text{H}}[n]$ is the Hartree energy (or, equivalently, the Coulomb energy) which is just the classical electron-electron repulsion energy, and $E_{\text{xc}}[n]$ is the so-called exchange-correlation energy, which is defined as consisting of the remaining contributions to the total energy. It thus includes all complex many-body effects, including a part coming from the kinetic energy, and in practice has to be approximated. Carrying out the minimization in Equation (5) using the constraint that the number of electrons is conserved, one arrives at the Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (7)$$

with

$$V_{\text{eff}} = V_{\text{H}} + V_{\text{xc}} + V_{\text{ext}} \quad (8)$$

and

$$V_{\text{H}}(\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (9)$$

$$V_{\text{xc}}[n(\mathbf{r})] = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \quad (10)$$

$$V_{\text{ext}}(\mathbf{r}) = - \sum_n \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} \quad (11)$$

with

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2 \quad (12)$$

The whole point of introducing Equation (7) is that we can use it to calculate $T_{\text{S}}[n]$. In Equation (7), multiply with ψ_i^* from the left, sum over i and integrate over all space. This gives $T_{\text{S}}[n]$ as

$$T_{\text{S}}[n] = \sum_{i=1}^N \int d^3r \psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 \right) \psi_i(\mathbf{r}) = \sum_{i=1}^N \epsilon_i - \int d^3r V_{\text{eff}}(\mathbf{r})n(\mathbf{r}). \quad (13)$$

To get the final, calculable, expression for the total energy, insert the equation above and Equation (8) into the expression for the total energy, Equation (6). **We then find that the ground-state energy is given by**

$$E_0 = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n] - \int d^3r V_{\text{xc}}[n(\mathbf{r})]n(\mathbf{r}). \quad (14)$$

It is worth noting that apparently the total energy is not equivalent to the sum of the occupied eigenvalues, contrarily to what one might have expected. Mathematically, the energy eigenvalues ϵ_i of the non-interacting particles are Lagrange multipliers introduced to handle the constraint that the number of electrons should be conserved,

$$N = \int d^3r n(\mathbf{r}) = \text{constant}. \quad (15)$$

The one-electron wave functions $\psi_i(\mathbf{r})$ and energies ϵ_i in the Kohn-Sham equation are often interpreted as electron energy eigenvalues and eigenfunctions, but this is of course not strictly correct. However, this bold way of interpreting the solution of the KS-equation has had great success over the decades, and has become an accepted way of analyzing the electronic structure of materials. Sometimes it fails. The most prominent example is that band gaps in semiconductors are not predicted correctly from the eigenvalues of the KS-equation.

For the helium atom, where the two electrons in the ground state are in the same 1s orbital (denoted by $\phi(\mathbf{r})$ below) and thus should have the same energy eigenvalue and eigenfunction (only the spin quantum number differs), the Kohn-Sham equation reduces to

$$\left[-\frac{1}{2}\nabla^2 + 2 \int d^3r' \frac{|\phi(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{xc}}(\mathbf{r}) - \frac{2}{r} \right] \phi(\mathbf{r}) = \epsilon \phi(\mathbf{r}) \quad (16)$$

with the ground-state energy

$$E_0 = 2\epsilon - \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n] - \int d^3r V_{\text{xc}}(\mathbf{r})n(\mathbf{r}) \quad (17)$$

and

$$n(\mathbf{r}) = 2|\phi(\mathbf{r})|^2. \quad (18)$$

In the expression above, we have dropped the explicit reference to the fact that $V_{\text{xc}}[n(\mathbf{r})]$ is a functional of the density n , and thus simply written $V_{\text{xc}}(\mathbf{r})$ instead.

1.4 The local density approximation (LDA)

The exact form of the exchange-correlation functional is not known and it has to be approximated in some way. The most widely used is the so-called local density approximation (LDA). In LDA, the exchange-correlation functional $E_{\text{xc}}[n]$ is represented as

$$E_{\text{xc}}[n] = \int d^3r n(\mathbf{r}) \epsilon_{\text{xc}}^{\text{hom}}(n(\mathbf{r})) \quad (19)$$

where $\epsilon_{\text{xc}}^{\text{hom}}(n(\mathbf{r}))$ is the exchange-correlation energy per electron of the homogenous electron gas with density n . The corresponding exchange-correlation potential is given by the functional derivative of the exchange-correlation energy, i.e.,

$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n} = \epsilon_{\text{xc}}^{\text{hom}}(n) + n \frac{d}{dn} \epsilon_{\text{xc}}^{\text{hom}}(n) \quad (20)$$

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

$$\epsilon_{\text{xc}}^{\text{hom}}(n) = \epsilon_{\text{x}}^{\text{hom}}(n) + \epsilon_{\text{c}}^{\text{hom}}(n) \quad (21)$$

and correspondingly for the exchange-correlation potential. The exchange part can be evaluated exactly for the homogenous electron gas (see, e.g., Ashcroft and Mermin)

$$\epsilon_{\text{x}}^{\text{hom}}(n) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} n^{1/3} \quad (22)$$

and the correlation part (i.e., the remaining energy contributions) of the homogenous electron gas has been evaluated essentially exactly by the numerical quantum Monte Carlo technique (Ceperley and Alder, 1980). The following analytical representation has been suggested (Perdew and Zunger, 1981)

$$\epsilon_c^{\text{hom}}(r_s) = \frac{\gamma}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s}, \quad r_s \geq 1 \quad (23)$$

$$\epsilon_c^{\text{hom}}(r_s) = A \ln r_s + B + C r_s \ln r_s + D r_s, \quad r_s < 1 \quad (24)$$

with $n = 3/(4\pi r_s^3)$. See Thijssen, exercise 5.3 for numerical values.

1.5 Numerical procedure – self-consistency

The Kohn-Sham equation is nonlinear in $\phi(\mathbf{r})$ and has to be solved in an iterative manner. An initial guess for the wavefunction $\phi(\mathbf{r})$ is made, the Hartree potential $V_H(\mathbf{r})$ and exchange correlation potential $V_{xc}(\mathbf{r})$ are determined and the Kohn-Sham equation can then be solved. A new wavefunction $\phi(\mathbf{r})$ is obtained and the procedure is repeated until the ground-state energy E_0 is converged. This is called iteration to self-consistency.

1.6 The Hartree potential

The Hartree potential is the electrostatic potential generated by the charge distribution and can be written

$$V_H(\mathbf{r}) = \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (25)$$

In differential form, the expression above becomes the well-known Poisson equation

$$\nabla^2 V_H(\mathbf{r}) = -4\pi n(\mathbf{r}). \quad (26)$$

Since $V_H(\mathbf{r})$ is spherically symmetric, the left-hand side of this equation can be expanded as

$$\nabla^2 V_H(r) = \frac{1}{r} \frac{\partial^2}{\partial r^2} (r V_H(r)). \quad (27)$$

From this expression, we see that it is convenient to introduce the new function $U(r) = r V_H(r)$, and our Poisson equation takes the form

$$\frac{d^2}{dr^2} U(r) = -4\pi r n(r). \quad (28)$$

The density is normalized according to

$$\int d^3 r n(\mathbf{r}) = 4\pi \int dr r^2 n(r) = q, \quad (29)$$

where q is the number of electrons.

In order to solve the differential equation, we also need two boundary conditions. Since $U(r)$ is a potential, an arbitrary constant added to it does not alter the physics. We can therefore choose one boundary condition freely. For convenience, we choose $U(0) = 0$. From electrostatics we know that the charge contained inside a sphere can be calculated by integrating the potential on the sphere surface. For a sufficiently large sphere, with radius r_{max} say, we get the total electron charge q . For the hydrogen atom, $q = 1$ in atomic units since it has one electron. This line of reasoning gives the boundary condition far away from the nucleus, and our final boundary conditions become

$$U(0) = 0, \quad U(r_{\text{max}}) = q. \quad (30)$$

1.7 The radial Schrödinger equation

In radial coordinates, the Kohn-Sham equation for the helium atom takes the form

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + V_H(r) + V_x(r) + V_c(r) - \frac{2}{r} \right] u(r) = \epsilon u(r) \quad (31)$$

where $u(r) = r\phi(r)$ with the boundary conditions

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

Finally, we can write the full expression for the ground state energy E_0 of the helium atom in the local density approximation as

$$E_0 = 2\epsilon - 8\pi \int dr u^2(r) \left[\frac{1}{2} V_H(r) - \epsilon_{xc}(r) + V_{xc}(r) \right]. \quad (32)$$

Note that our notation differs slightly from the notation in Thijssen. In our equations, the Hartree potential V_H is *always* the one corresponding to the whole electron density. (In Thijssen, in some expressions, e.g. Equation 5.27, V_H stands for the Hartree potential corresponding to a single orbital.) Also, in our equations, we always have $u(r) = r\phi(r)$. In Thijssen, a factor $\sqrt{4\pi}$ has been baked in as well.

1.8 Boundary value problems

The boundary value problem for differential equations and eigenvalue equations can be solved with various numerical methods. In the finite difference method, which is the method we will use here, the derivatives are replaced by finite differences. In practice, this transforms the boundary value problem into a system of algebraic equations, which then can be solved by writing the equations on matrix form, and then diagonalizing the matrix.

1.9 Finite differences (FD)

In the finite difference method, the space is discretized

$$x_i = a + ih, \quad i = 0, \dots, n, \quad h = (b - a)/n \quad (33)$$

and one seeks an approximate solution at the grid

$$y_i = y(x_i) \quad (34)$$

The derivatives are replaced by the finite differences

$$y'(x_i) = \frac{y_{i+1} - y_{i-1}}{2h} \quad (35)$$

$$y''(x_i) = \frac{y_{i+1} - 2y_i + y_{i-1}}{h^2} \quad (36)$$

and the resulting matrix equation can be solved using standard routines. In some cases it may be an advantage to use a non-uniform grid, In that case the appropriate expressions for the derivatives become

$$y' = \frac{y_{i+1} - y_{i-1}}{h_{i+1} + h_i} \quad (37)$$

$$y'' = 2 \frac{h_i y_{i+1} - (h_i + h_{i+1}) y_i + h_{i+1} y_{i-1}}{h_{i+1} (h_{i+1} + h_i) h_i} \quad (38)$$

with $h_i = x_i - x_{i-1}$. For instance, in our case it is better to use a grid with a step size which grows from a very small value near the nucleus to larger values at larger distances, because the wave function will oscillate more rapidly near the nucleus as a result of the deep Coulomb potential. One way of representing such a grid is given by the following formula

$$x_i = a + (b - a) \frac{e^{i\delta} - 1}{e^{n\delta} - 1}, \quad i = 0, \dots, n \quad (39)$$

where the parameter δ determines how much the grid constant near the nucleus differs from that at large distances.

1.10 Reference literature

J. M. Thiessen "Computational Physics", Cambridge University Press, 1999.

M. T. Heath "Scientific Computing: An Introductory Survey", McGraw-Hill, 1997.

Matlab tutorial, e.g., <http://www.math.ufl.edu/help/matlab-tutorial/>

1.11 Problems

- 1 Consider first the Poisson equation. Solve it in radial coordinates using finite differences. Discretize the equation and approximate the derivatives using a uniform grid. Solve the resulting system of linear equations using Matlab (the backslash operator). Test your program by using the ground state electron density for the hydrogen atom, $n(r) = \frac{1}{\pi}e^{-2r}$, as input density. You should then obtain the Hartree potential

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

- 2 Consider now the radial Schrödinger equation without exchange and correlation. Write a program that solves the eigenvalue problem using the finite difference method. Use the Matlab routine `eig` and implement the method using a uniform grid. Test your program for the hydrogen atom, in which case the nuclear potential is equal to $-1/r$ and $V_H(r) = 0$. Compare your results with the analytical result for the ground state energy and wave function.
- 3 You are now ready to construct a program that determines the ground state energy for the helium atom using the finite difference method. You have to add the Hartree and exchange-correlation potential to the radial Schrödinger equation. Make an initial guess for the density and iterate to self-consistency. You have to introduce some reasonable criterion when to stop the iteration. Determine the ground state energy and wave function. Also, make a run with excluded correlation.