

A DFT program for the helium atom

In this section we describe the construction of a DFT program for the calculation of the ground state energy of the helium atom, using the Slater X-alpha exchange potential and the parametrization of the Ceperley-Alder correlation potential (Parametrisation given by Perdew and Zunger). In the DFT, the electronic orbitals are solution to the Schrödinger equation (SE) which depends on the electron density rather than on the individual electron orbitals. As such the DFT orbitals have no individual meaning but are used to construct the charge density. This contrast with Hartree-Fock where the one-electron orbitals have a definite interpretation: they are the constituents of the many-electron wave function written in terms of a Slater determinant. The main result of DFT is that there exists a form of the exchange correlation potential, depending only on the electron density $n(\mathbf{r})$, that yields the *exact* ground state energy and density. The form of this functional is however unknown and we should rely on approximation, such as the local density approximation (LDA, in this example we will consider the CA-LDA parameterization).

The helium atom in DFT

Considering that the two electrons occupy the 1s-orbital, both the density and the Hartree potential are radially symmetric; thus, we can exploit this radial symmetry and solve the radial Schrödinger equation. Instead of using basis functions, we solve the radial SE equation directly, as we have already done previously.

The program is organized in three steps:

1. Solution of the hydrogen-like radial SE using a simple integration algorithm combined with an interpolation routine in order to find the stationary states.
2. Calculation of the Hartree potential from the radial electron density.
3. Incorporation of the exchange-correlation potential (within the local density approximation, LDA).

1 Solution of the radial equation

We have already discussed the solution of the hydrogen-like radial SE in program `hydrogen.f90`. For the hydrogen atom the radial equation for $l = 0$ reads:

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

where $u(r)$ is given by $rR(r)$, $R(r)$ being the radial wave function. In principle we could use the Numerov integration algorithm as we did in the hydrogen atom case (since we will have to solve other differential equation we shall not require the $O(h^6)$ accuracy of the Numerov's scheme, one could safely use the simpler Verlet algorithm). It is recommended (but not strictly necessary) to use a non uniform grid for the integration, which is dense near the nucleus where the Coulomb potential diverges.

The energy eigenvalues can be found by integrating the radial SE from some large radius r_{\max} inward to $r = 0$ and checking whether the solution vanishes there (you can first check that for the ground state energy $E = -0.5$ eV the radial solution does indeed vanish at $r = 0$). As initial value of $u(r)$ at r_{\max} one can choose $u(r_{\max}) = r_{\max}e^{-r_{\max}}$, and similarly for $r_{\max} - h$, with $h = \text{step}$ (a valid choice is also $u(r_{\max}) = 0$). The integration routine should be coupled with a root-finding routine.

Program structure (similar to `hydrogen.f90`)

1. Initialization. Give:
 - integration step h
 - maximum integration radius r_{\max}
 - Charge of helium nucleus ($Z=2$)

- Number of integration grid points (r_{\max}/h)
 - Initial trial energy (i.e. $E=-0.3$) and step (i.e., 0.1)
 - Initial wavefunction: $u(r_{\max}) = r_{\max}e^{-Zr_{\max}}$
2. Find the energy of the bound state. The bound state is characterized as having a zero at $r=0$. Search for change of sign and find root (i.e., by bisection).
 3. Solve Radial equation using the Numerov/Verlet integration algorithm. The solution is used to determine the charge density: integrate $R(r)^2$ over the radial coordinate grid (one could use a fourth-order integration method). Add normalization factor for the charge density ($-4\pi n(r)$)

This program alone should give the solution $E=-0.5$ a.u. and $u(r) \approx re^{-r}$

2 The Hartree potential

The next step is to include the Hartree terms which, as already discussed, arises from the electron-electron interaction: the Hartree potential is the electrostatic potential generated by the charge distribution following from the wave function, which is given by:

$$V_H(\mathbf{r}) = \int d^3r' n_s(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \quad (2)$$

where n_s stands for the density of the single orbital. As already discussed the Hartree potential includes the spurious interaction of one electron with itself, the so called self-interaction, which in the helium case consists of half of the Hartree term. In Eq. 2 we have removed the self-interaction by dividing the total Hartree potential by 2 (this factor 2 cancels the factor 2 arising from the spin summation).

Instead of calculating the integral we can find $V_H(\mathbf{r})$ by solving the Poisson's equation:

$$\nabla^2 V_H(\mathbf{r}) = -4\pi n_s(\mathbf{r}) \quad (3)$$

Using the radial symmetry of the density and defining $U(r) = rV_H(r)$, this equation reduces to the form:

$$\frac{1}{r} \frac{d^2}{dr^2} U(r) = -4\pi n_s(r) \quad (4)$$

This is an order differential equation (which can be solved using for instance the Verlet algorithm). Note that it is necessary to normalize the radial wave function before integrating Poisson's equation. By taking normalization into account:

$$\int dr u^2(r) = \int dr r^2 R^2(r) = 1 \quad (5)$$

the factor 4π in Poisson's equation drops out:

$$U''(r) = -\frac{u^2(r)}{r} \quad (6)$$

The solution 6 contains two integration constants which need to be fixed by the boundary conditions:

- $U(0) = 0$ (Note that $U(h)$ also has to be fixed for the integration scheme)
- From electrostatic consideration we have that:

$$V'_H(r_{\max}) = \frac{q_{\max}}{r_{\max}^2} \quad (7)$$

where q_{max} = electron charge contained in a sphere of radius r_{max} :

$$q_{max} = \int_0^{r_{max}} dr u^2(r) \quad (8)$$

Clearly, for large r_{max} , q_{max} is the total electron charge. It follows that:

$$U(r_{max}) = q_{max} \quad (9)$$

Considering that the solution

$$U(r) = \alpha r \quad (10)$$

solves the homogeneous equation, $U''(r) = 0$, we can add this solution to the numerical solution found, with α taken such as to satisfy the end condition $U(r_{max}) = q_{max}$, without violating the starting condition $U(0) = 0$.

The extra integration (Eq.6) have to be incorporated in the previous radial code.

One could check for correctness crosschecking the result for the hydrogen atom for which the ground state density (at $E=-0.5$ a.u.) is $4e^{-2r}$. Solving

$$U''(r) = -\frac{u^2(r)}{r} \quad (11)$$

with boundary conditions $U(0)=0$ and $U(r_{max})=1$, one obtains:

$$U(r) = -(r+1)e^{-2r} + 1 \quad (12)$$

3 Add self-consistency

This is done by adding the Hartree potential to the nuclear potential ($-2/r$) and solving for the eigenvalue again. This procedure should be repeated until the energy does not change appreciably between subsequent steps. The total energy is given by:

$$E = 2\epsilon - \int dr V_H(r) u^2(r) \quad (13)$$

where ϵ is the ground state single electron eigenvalue.

At this point one could compare the DFT results obtained with the above procedure with the corresponding Helium HF results already discussed.

4 The LDA exchange and correlation potential

the last step consist in including DFT exchange-correction (XC) following the LDA prescription. It should be remembered that in DFT the density that give rise to the Hartree potential is the full density $n(\mathbf{r})$, for the helium atom the density of the two electrons, and in the previous section we have subtracted off the self-interaction contribution, leading to a reduction by a factor of 2 of the Hartree potential. Now we should consider the full Hartree term, including self-interaction, and correcting the self-interaction term through the XC approximation.

Indeed, the difference between the Hartree-Fock and DFT approximation is the replacement of the HF exchange term by the exchange correlation energy E_{xc} which is a functional of the density.

The *exact* form of the exchange-correlation potential $V_{xc}[n](\mathbf{r})$ is unknown. In general, for a non-homogeneous system:

$$V_{xc}[n](\mathbf{r}) = \frac{\delta}{\delta n(\mathbf{r})} E_{xc}[n] = V_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla(\nabla n(\mathbf{r})), \dots] \quad (14)$$

The XC potential $V_{xc}[n](\mathbf{r})$ can be decomposed in to X and C terms linearly:

$$V_{xc} = V_x + V_c \quad (15)$$

Within LDA E_x and E_c depends locally on $n(\mathbf{r})$. The X effects are usually included in a term based on calculations for the homogeneous electron gas giving the following form for the X potential (the so called Slater X):

$$V_x(\mathbf{r}) = - \left(\frac{3}{\pi} \right)^{1/3} n^{1/3}(\mathbf{r}) \quad (16)$$

The density $n(\mathbf{r})$ is the full density, i.e. twice the single electron density arising from the radial SE equation, since we have two electrons. Therefore, in terms of the radial eigenfunctions u normalized as in Eq. 5, our exchange potential reads:

$$V_x(\mathbf{r}) = - \left[\frac{3u^2(r)}{2\pi^2 r^2} \right]^{1/3} \quad (17)$$

which for the s states under consideration depends on the radial coordinate r only.

By including the X term, the total energy is now given by:

$$E = 2\epsilon - \int dr V_H(r) u^2(r) - \frac{1}{2} \int dr u^2(r) V_x(r) \quad (18)$$

Remind that now $V_H(r)$ is the full Hartree potential (i.e. a factor of two larger than the one considered before). We can improve our DFT description by adding the C term following the Ceperley-Alder parameterization (Perdew & Zunger PRB **23** 5048, 1981; Ceperley, PRB **18** 3126, 1978; Ceperley PRL **45** 566, 1980). The CA parameterization is given in terms of the parameter r_s which is related to the density n according to

$$n = \frac{3}{4\pi r_s^3} \quad (19)$$

The parameterization is split into two parts: $r_s \geq 1$ and $r_s < 1$. The expression for the correlation potential takes the form:

$$V_c(r_s) = \left(1 - \frac{r_s}{3} \frac{d}{dr_s} \right) \epsilon_c(r_s) \quad (20)$$

where ϵ_c is the correlation energy parameter defined by $E_c = \int d^3r \epsilon_c[n(\mathbf{r})](\mathbf{r})$. A parameterized form of ϵ_c is given by the following expressions:

For $r_s \geq 1$:

$$\epsilon_c = \gamma / (1 + \beta_1 \sqrt{r_s} + \beta_2 r_s) \quad (21)$$

For $r_s < 1$:

$$\epsilon_c = A \ln r_s + B + C r_s \ln r_s + D r_s \quad (22)$$

From this, we can obtain the following expressions for the correlation potential:

$$V_c(r_s) = \epsilon_c \frac{1 + 7/6 \beta_1 \sqrt{r_s} + 4/3 \beta_2 r_s}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s} \quad r_s \geq 1 \quad (23)$$

$$V_c(r_s) = A \ln r_s + B - A/3 + \frac{2}{3} C r_s \ln r_s + (2D - C) r_s / 3, \quad r_s < 1 \quad (24)$$

The values of the various parameters depends whether we are dealing with a spin polarized system or not. The value are listed below:

	Unpolarized	Polarized
A	0.0311	0.01555
B	-0.048	-0.0269
C	0.0020	0.0014
D	-0.0116	-0.0108
γ	-0.1423	-0.0843
β_1	1.0529	1.3981
β_2	0.3334	0.2611

By using the unpolarized C correction one should obtain a total energy $E=-2.83$ a.u., to be compared with -2.72 without this correction. Note that we have used the Slater like X, the results can be improved by using the X correction of Perdew and Zunger given in Perdew & Zunger PRB **23** 5048, 1981. If you do so, the total energy become $E=-2.918$ a.u., which is only 0.015 a.u. off the experimental value.

The final total energy is given by the sum of the eigenvalues terms, the Hartree energy and the XC energies.

Program structure

1. Self-consistent condition right at the beginning (before the solution of the radial SE). Something like this:
DO WHILE($ABS(OldEnergy-NewEnergy) > Epsilon$)
2. Solve radial SE (see above)
3. Calculate the Hartree potential. This is done by radially integrating Poisson's equation. The correct boundary equations are met by starting at $V_H(0) = 0$, and by adding the homogeneous solution αr to the result in order to fix the potential at r_{max} to Z/r .
4. Calculate the exchange potential. This potential is given as $-[3u^2(r)/(2\pi^2r^2)]^{1/3}$
5. Calculate the correlation potential following the CA parameterization.
6. Convert the various potentials in energy terms and sum up all energies contributions in order to compute the total energy.