

1 Density Functional Theory Method

In this exercise we want to use density functional theory to iterate over the charge density in a He atom to find the energy of the ground state.

1.1 Important Files

All data files and files I wrote are included in the directory `my_files/ex1`. Files given as part of the assignment are found in the main directory submitted, even if I have modified them.

Main Directory

- `He_atom_hartree.c`

`my_files/ex1`

- `plotter.py`
- `charge_density_iter_(iteration number)`
- `energies`
- `charge_density.jpg`
- `charge_density_zoomed.jpg`

1.2 Methods/Results

For this exercise the goal was to look into the variation in charge density and ground state energy for repeated iterations of the density functional method. This iterative method uses an initial guess for the charge density and tries to improve on it each iteration and so we expect both properties (charge density and energy) to get more accurate as we iterate. However, as you can see below in *figure 1a*, for a simple system like the one we are simulating the charge density and energy appear to converge very fast, with the second iteration almost converged to the final distribution. The graphs below show the charge density vs radius for iterations 0, 1, 2, 6, 7, 8 to get an idea of the initial behaviour against the converged behaviour.

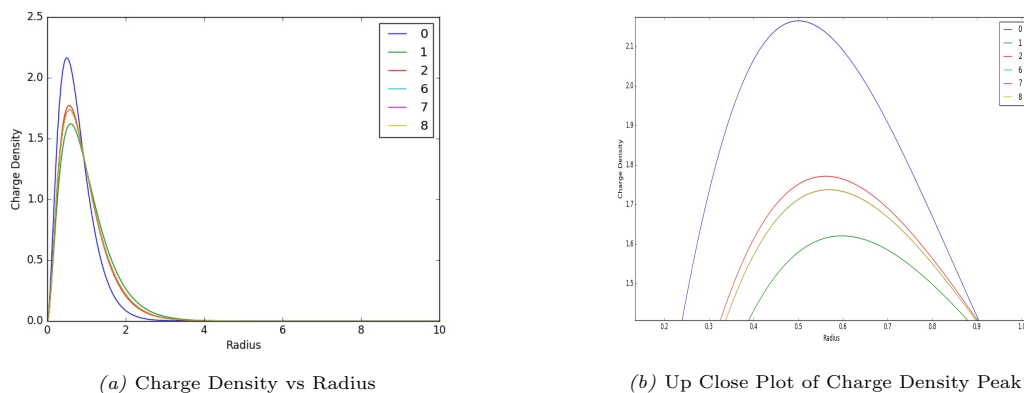


Figure 1: Change in Charge Density with Radius

The above figure shows how the charge density curve almost converges to its final state after only two iterations. If you look at *figure 1b* you can see that after the second iteration, the curve is almost exactly the same for all further iterations plotted.

During this exercise, we also wanted to study the convergence of the ground state energy as the field was iterated over. To do this we plotted the energy as a function of iteration which can be seen below.

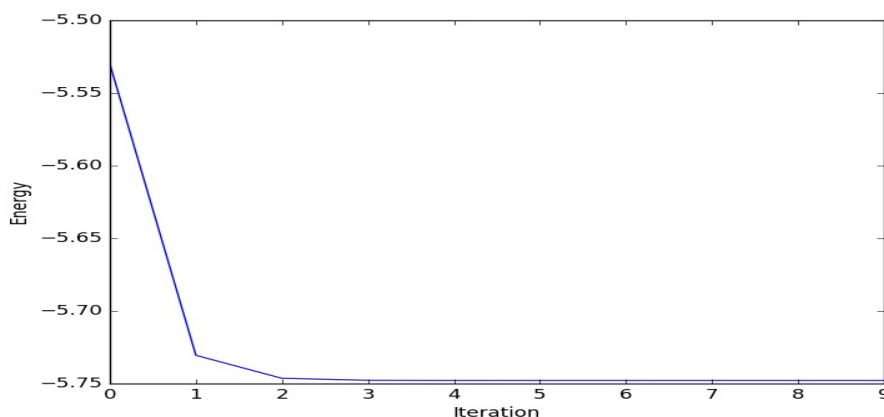


Figure 2: Energy as a Function of Iteration

Just like the charge density, the energy converges fast; converging to a constant value after only three iterations. The reason for this is just because we are simulating quite a small system (He atom only has two electrons) and so few iterations are required to accurately model the charge density and thus ground state energy.

2 Hartree Method

In this exercise we want to use the Hartree Method to iterate over the charge density in a He atom and find the energy of the ground state. This method uses density functional theory but unlike the previous question, here we exclude the exchange correlation interactions in the atom.

As this method excludes an important quantum mechanical property, we want to compare the results we get from this method with the method used in the last question.

2.1 Important Files

All data files and files I wrote are included in the directory `my_files/ex2`. Files given as part of the assignment are found in the main directory submitted, even if I have modified them.

Main Directory

- `He_hartree_atom.c` (modified to remove interaction correlation interactions)

`my_files/ex2`

- `plotter.py`
- `charge_density_iter_(iteration number)`
- `energies`
- `hartree_charge_density.jpg`
- `hartree_charge_density_zoomed.jpg`
- `energy_comp.jpg`
- `charge_density_comp.jpg`

2.2 Methods/Results

Because the main goal of this exercise is to compare the method with the previous method, we will provide the exact same plots as before and study the similarities/differences. With this in mind we first plotted the the charge density for different iterations to compare the settling behaviour with the converged behaviour as before.

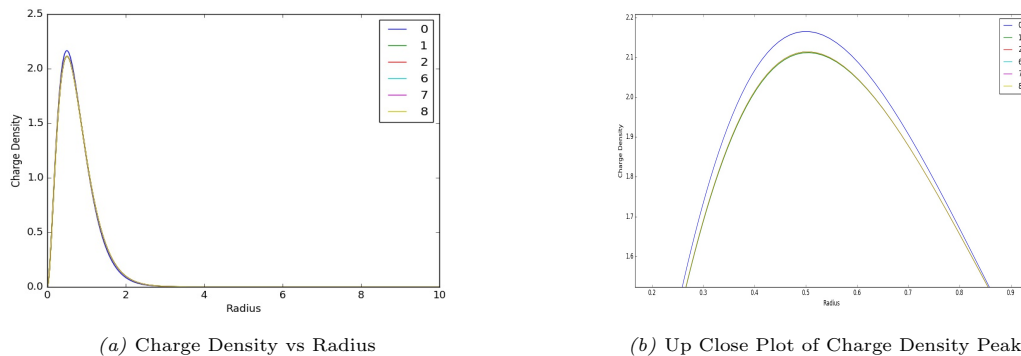


Figure 3: Change in Charge Density with Radius for the Hartree Method

The first thing we notice here is the better convergence using the Hartree Method versus the method used previously. This is due to the fact that our new model only takes into account the electromagnetic interactions within the He atom, excluding exchange and correlation effects. Neglecting these quantum mechanical effects might give the electrons (and thus the charge density) less freedom. This may explain why the charge density converges slightly faster than previously.

If we look at the energy as a function of iteration you we again see this faster convergence, even if only slight. However, in this plot another difference between the methods becomes very apparent; the energy the system converges to.

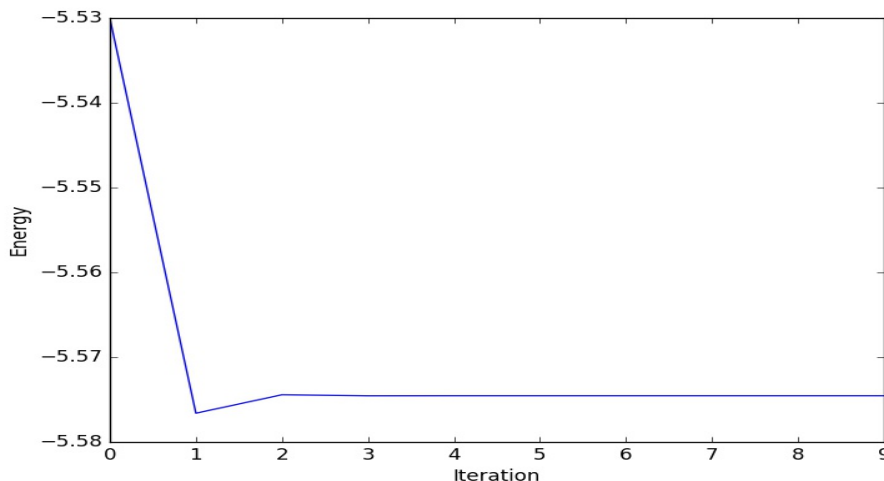


Figure 4: Energy as a Function of Iteration, Hartree Method

If we look back at *figure 2* we can see that the scale on which it's plotted is very different to this plot. It appears that although in both cases the energies do converge to a value, the value they converge to is

different in each case. To get a better insight into the differences between these models we plotted the energy as a function of iteration and the converged charge distribution for both models and compared.

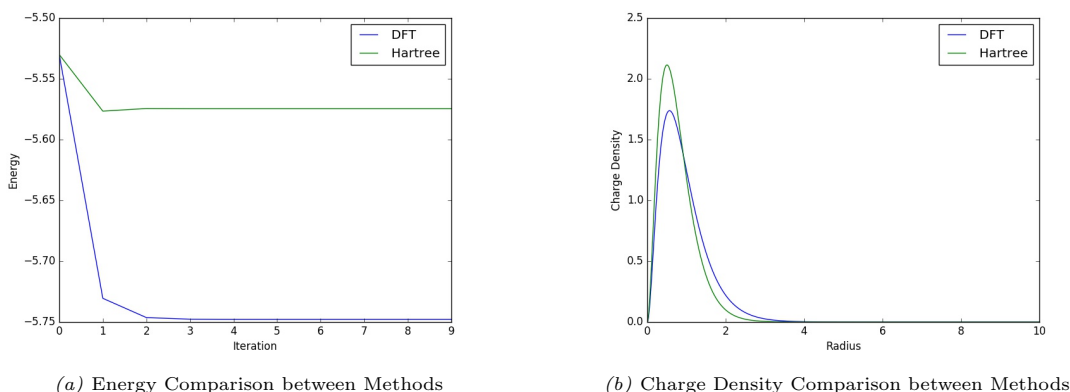


Figure 5: Comparison of Results from DFT Method and Hartree Method

As can be seen from the above figure, the energy for the DFT model is lower than that of the Hartree model. This agrees with what is known about exchange correlation interactions and their effect on energy. After doing a bit of research what I found was that the Hartree Model always overestimates the energy in a system like this because it doesn't take into account the anti-symmetric nature of the 2 electrons' wave function (see figure 6). Looking at the equations below the Hartree Model models the wave function of the two electrons like the first expression rather than the second (which is antisymmetric under exchange of electrons) and this is part of the reason for the error in this approximation.

$$\Phi(x_1, x_2) = \chi_1(x_1)\chi_2(x_2)$$

$$\Phi(x_1, x_2) = \frac{1}{\sqrt{2}} [\chi_1(x_1)\chi_2(x_2) - \chi_1(x_2)\chi_2(x_1)]$$

In order to check and see that our results DFT method do in fact lead to a larger energy, we can check the paper which accompanied this assignment. In this paper, when exchange correlation effects were included, the energy of the ground state of the Helium atom was -77.9eV . If we convert this to the units we are using (Rydberg units) by dividing by 13.6 we get that energy as stated in the paper is ~ -5.73 . This result agrees very well with the results yielded from our own program.

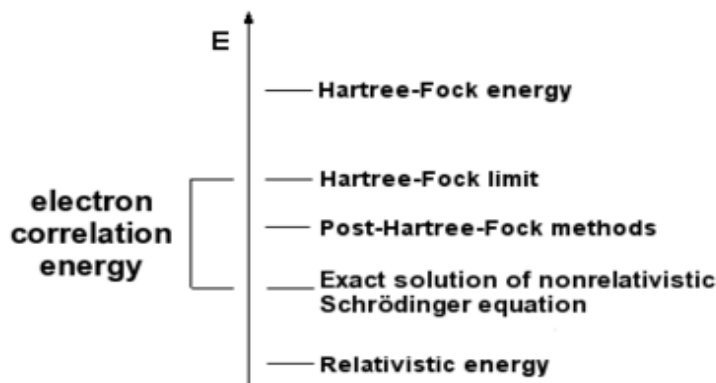


Figure 6: Energy Overapproximation for the Hartree Method

3 Acceleration of Iterative Convergence

In this exercise we wanted to modify the program so that the charge density was calculated as a weighted average of the current iterations contribution and the previous iterations contribution, such that:

$$q_{new} = xq_{out} + (1 - x)q_{in} \quad x \in [0, 1]$$

3.1 Important Files

For this exercise, all files are stored in the directory `my_files/ex3/`. Instead of modifying the original code I just made a duplicate inside this directory and modified the duplicate.

There is a README file included in this directory regarding the modified code.

my_files/ex3/

- `modified_hartree.c`
- `energies_(ratio)`
- `convergence_comp.jpg`
- `hartree_convergence_comp.jpg`

3.2 Methods/Results

The main work involved in this exercise was actually modifying the code to do run the algorithm as above. As stated above, this can be found in the directory *my_files/ex3/*. Once modified the code was ran for different ratios in order to study how the convergence varies with the ratio x . Below we have plotted the energy vs iteration for several different ratios ($0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}, 1$).

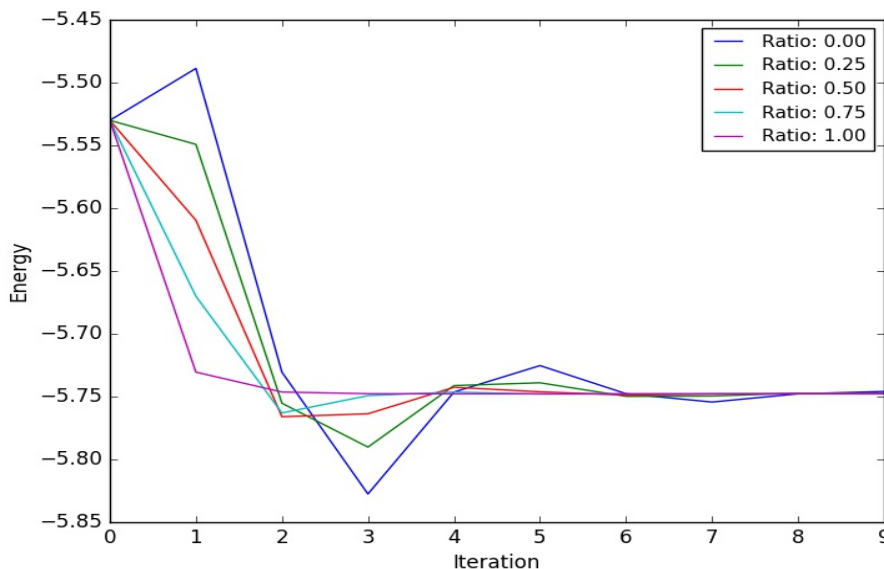


Figure 7: Energy as a Function of Iteration for Different Ratios (DFT)

As we can see from this plot, there is a distinct trend in the convergence as you change the ratio. The convergence seems to improve steadily as the ratio approaches 1. This is not very surprising because the increasing the number towards 1 increases the weight on the contribution from the current iteration's output rather than its input. This simply means that the as we increase the ratio, the new charge density becomes more dependent on the most recently updated contributions. We would normally expect this to improve the convergence and so you might wonder why invoking a ratio like this is useful. Generally a method like this is used for systems where the variable we are interested in converges to an oscillatory solution. In order to allow the solution to settle to a steady value we can invoke a method like this and vary the ratio to see which ratio (if any) dampens the oscillations of the solution to a steady value. In cases like that a method like this can be very useful. However, in our system we have no difficulties in converging and so a method like this is unnecessary.

Just as a quick demonstration that this trend in convergence is not unique to the DFT method, if we look at the convergence for the Hartree Method alone we get a similar trend.

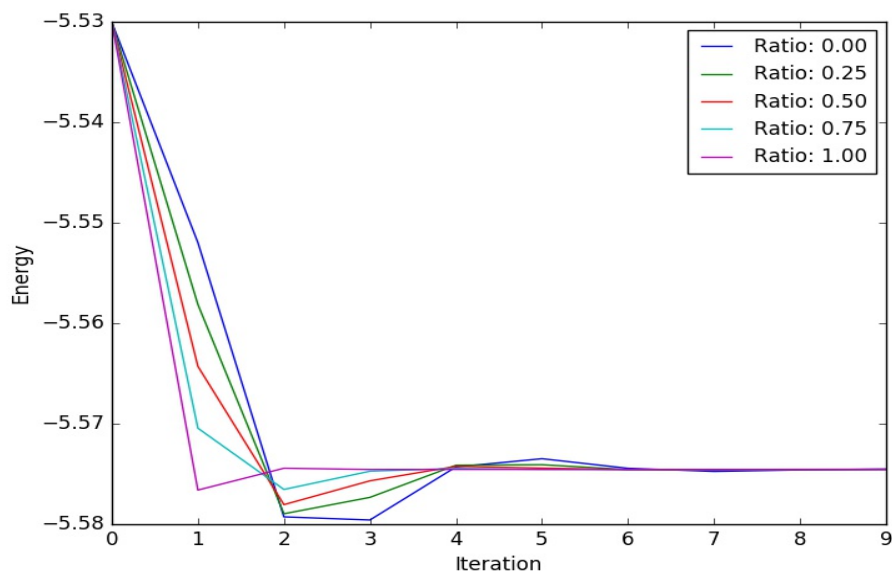


Figure 8: Energy as a Function of Iteration for Different Ratios (Hartree)

Again we see a trend that the convergence improves as we increase the ratio. Something else that's noticeable is that in both methods we underestimate the energy on the first few iterations. This is possibly just due to the fact that we chose 0 as our initial guess for the charge density.