

Restricted Hartree-Fock for Helium.

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December 2020

1 Introduction

The main objective of this assignment is to apply the Hartree-Fock approximation to helium. Restricted Hartree-Fock will be used to obtain it's ground state energy and orbitals by using an expansion into Gaussians. This will be done using a script in Python.

2 The Hartree-Fock approximation

2.1 The Multi-electron Schrödinger Equation

For a multi-electron system, it's wave function can be denoted by

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad \mathbf{x}_i = (\mathbf{r}_i, \sigma_i),$$

where \mathbf{x}_i represents the combined spatial and spin coordinates.

The Hamiltonian of a multi-electron atom with atomic number Z and N electrons is of the form

$$\hat{H} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i Z \frac{q_e^2}{r_i} + \sum_i \sum_{j>i} \frac{q_e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (1)$$

where m_e and q_e are the mass and charge of the electron, the second term is an attractive electron-nucleus potential and the third term is a repulsive electron-electron potential.

2.2 The Hartree-Fock method

The Hartree-Fock approximation combines the Hartree method with the spin-statistics theorem. The Hartree-Fock approximation improves over the Hartree method by introducing an antisymmetric wave function given by the Slater determinant:

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$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \dots & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \dots & \phi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & \dots & \phi_N(\mathbf{x}_N) \end{vmatrix} \quad (2)$$

where ϕ_i are the single-electron wave functions called atomic orbitals, which are assumed to be orthonormal.

With this expression for the wave function, one can find the expectation value of the Hamiltonian and apply the variational principle to obtain the Hartree-Fock equations[1]:

$$\left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - Z \frac{q_e^2}{r_i} + V_{HF}(\mathbf{r}_i) \right] \phi_i(\mathbf{x}_i) + \hat{V}_{ex} \phi_i(\mathbf{x}_i) = E_i \phi_i(\mathbf{x}_i), \quad i = 1, 2, \dots, N \quad (3)$$

where V_{HF} is the Hartree-Fock potential and $\hat{V}_{ex} \phi_i(\mathbf{x}_i)$ is an exchange term. These are given by:

$$V_{HF}(\mathbf{r}_i) = \sum_l \int \frac{q_e^2 |\phi_l(\mathbf{x})|^2}{|\mathbf{r}_i - \mathbf{r}|} dx, \quad \hat{V}_{ex} \phi_i(\mathbf{x}_i) = \sum_l \int \frac{q_e^2 \phi_l^*(\mathbf{x}) \phi_i(\mathbf{x})}{|\mathbf{r}_i - \mathbf{r}|} \phi_l(\mathbf{x}_i) dx \quad (4)$$

where integrals on dx mean integration over spatial coordinates and sum over spin coordinates. It's worth noting that the exchange term is non-local since \hat{V}_{ex} acts on ϕ_i but its value at \mathbf{r}_i is determined by the value of ϕ_i at all other values \mathbf{r} .

While E_i are not the energies of single electron orbitals[2], the total energy of the multi-electron atom can be expressed as

$$E = \sum_i E_i - \sum_i \sum_{j>i} \int \frac{q_e^2 \phi_j^*(\mathbf{x}) \phi_i^*(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} [\phi_j(\mathbf{x}) \phi_i(\mathbf{x}') - \phi_i(\mathbf{x}) \phi_j(\mathbf{x}')] dx dx' \quad (5)$$

Using these equations, an iterative approach can be used to get a solution.

2.3 Restricted Hartree-Fock

Restricted Hartree-Fock arises in cases in which orbitals appear in pairs of opposite spin, such that these pairs have the same spatial dependency. It's still possible to apply restricted Hartree-Fock to systems where this is not the case at the cost of accuracy[2].

If this is the case, the Hartree-Fock equations can be rewritten as

$$\mathcal{F} \phi_i = E_i \phi_i, \quad i = 1, 2, \dots, N/2 \quad (6)$$

where \mathcal{F} is the Fock operator, and i labels the pairs of orbitals of opposite spin.

By looking for a solution as a finite expansion of functions

$$\phi_i(\mathbf{r}) = \sum_{k=1}^M c_k^{(i)} \xi_k(\mathbf{r})$$

we find the Roothaan equations:

$$\mathcal{F}\mathbf{c}^{(i)} = E_i\mathcal{S}\mathbf{c}^{(i)}, \quad \text{where} \quad \mathcal{F}_{jk} = \langle \xi_j | \mathcal{F} | \xi_k \rangle \quad \text{and} \quad \mathcal{S}_{jk} = \langle \xi_j | \xi_k \rangle,$$

which resemble a generalised eigenvalue problem. This is not the case since the matrix F depends upon its own eigenvectors $\mathbf{c}^{(i)} = (c_1^{(i)}, c_2^{(i)}, \dots, c_M^{(i)})$. After some algebra, F can be expressed as

$$\mathcal{F}_{jk} = \mathcal{T}_{jk} + \sum_{lm} \left(\sum_{i=1}^{N/2} c_l^{(i)*} c_m^{(i)} \right) (2\mathcal{G}_{jlk m} - \mathcal{G}_{jkl m}) \quad (7)$$

where

$$\mathcal{T}_{jk} = \int \xi_j^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m_e} \nabla^2 - Z \frac{q_e^2}{|\mathbf{r}|} \right] \xi_k(\mathbf{r}) d\mathbf{r} \quad (8)$$

$$\mathcal{G}_{jklm} = \int \xi_j^*(\mathbf{r}) \xi_k^*(\mathbf{r}') \left[\frac{q_e^2}{|\mathbf{r} - \mathbf{r}'|} \right] \xi_l(\mathbf{r}) \xi_m(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (9)$$

3 Algorithm and Implementation

A basis set of S Gaussians will be used for the expansion of the atomic orbitals:

$$\phi_i(\mathbf{r}) = \sum_{k=1}^M c_k^{(i)} \xi_k(\mathbf{r}), \quad \xi_k(\mathbf{r}) = e^{-\alpha_k r^2} \quad (10)$$

To find expressions for \mathcal{F}_{jk} and \mathcal{S}_{jk} we will make use of the following identities:

$$\int_{\mathbb{R}^3} e^{-\alpha_m r^2} \nabla^2 e^{-\alpha_n r^2} d^3r = -\frac{6\alpha_m \alpha_n}{\alpha_m + \alpha_n} \left(\frac{\pi}{\alpha_m + \alpha_n} \right)^{3/2} \quad (11)$$

$$\int_{\mathbb{R}^3} e^{-\alpha_m r^2} \frac{1}{r} e^{-\alpha_n r^2} d^3r = \frac{2\pi}{\alpha_m + \alpha_n} \quad (12)$$

$$\int_{\mathbb{R}^3} e^{-\alpha_m r^2} e^{-\alpha_n r^2} d^3r = \left(\frac{\pi}{\alpha_m + \alpha_n} \right)^{3/2} \quad (13)$$

Thus:

$$\mathcal{S}_{jk} = \left(\frac{\pi}{\alpha_j + \alpha_k} \right)^{3/2}, \quad \mathcal{T}_{jk} = \frac{\hbar^2}{2m_e} \frac{6\alpha_j \alpha_k}{\alpha_j + \alpha_k} \left(\frac{\pi}{\alpha_j + \alpha_k} \right)^{3/2} - \frac{2\pi q_e^2 Z}{\alpha_j + \alpha_k} \quad (14)$$

To find an expression for \mathcal{G}_{jklm} we see that for the basis chosen we get

$$\mathcal{G}_{jklm} = q_e^2 \int e^{-\alpha_{jl} r^2} e^{-\alpha_{km} r'^2} \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad \text{where} \quad \alpha_{it} = \alpha_i + \alpha_t$$

Next, we note that

$$\alpha_{jl}r^2 + \alpha_{km}r'^2 = \frac{\alpha_{jl}\alpha_{km}}{\alpha_{jl} + \alpha_{km}} \left[(\mathbf{r} - \mathbf{r}')^2 + \left(\sqrt{\frac{\alpha_{jl}}{\alpha_{km}}} \mathbf{r} + \sqrt{\frac{\alpha_{km}}{\alpha_{jl}}} \mathbf{r}' \right)^2 \right]$$

and by introducing a change of variables of the form

$$\mathbf{s} = \mathbf{r} - \mathbf{r}', \quad \mathbf{s}' = \sqrt{\frac{\alpha_{jl}}{\alpha_{km}}} \mathbf{r} + \sqrt{\frac{\alpha_{km}}{\alpha_{jl}}} \mathbf{r}'$$

we get:

$$\mathcal{G}_{jklm} = q_e^2 \int e^{-\frac{\alpha_{jl}\alpha_{km}}{\alpha_{jl}+\alpha_{km}}s^2} e^{-\frac{\alpha_{jl}\alpha_{km}}{\alpha_{jl}+\alpha_{km}}s'^2} \left| \frac{\partial(\mathbf{r}, \mathbf{r}')}{\partial(\mathbf{s}, \mathbf{s}')} \right| \frac{d\mathbf{s}d\mathbf{s}'}{|\mathbf{s}|}$$

To calculate the Jacobian of the transformation we obtain first the Jacobian of the inverse transformation, since we have explicit expressions for \mathbf{s} and \mathbf{s}' :

$$\left| \frac{\partial(\mathbf{s}, \mathbf{s}')}{\partial(\mathbf{r}, \mathbf{r}')} \right| = \begin{vmatrix} 1 & 0 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & 0 & -1 \\ \sqrt{\frac{\alpha_{jl}}{\alpha_{km}}} & 0 & 0 & \sqrt{\frac{\alpha_{km}}{\alpha_{jl}}} & 0 & 0 \\ 0 & \sqrt{\frac{\alpha_{jl}}{\alpha_{km}}} & 0 & 0 & \sqrt{\frac{\alpha_{km}}{\alpha_{jl}}} & 0 \\ 0 & 0 & \sqrt{\frac{\alpha_{jl}}{\alpha_{km}}} & 0 & 0 & \sqrt{\frac{\alpha_{km}}{\alpha_{jl}}} \end{vmatrix}$$

By Gaussian elimination we see that

$$\left| \frac{\partial(\mathbf{s}, \mathbf{s}')}{\partial(\mathbf{r}, \mathbf{r}')} \right| = \begin{vmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{\frac{\alpha_{km}}{\alpha_{jl}}} + \sqrt{\frac{\alpha_{jl}}{\alpha_{km}}} & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{\frac{\alpha_{km}}{\alpha_{jl}}} + \sqrt{\frac{\alpha_{jl}}{\alpha_{km}}} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{\alpha_{km}}{\alpha_{jl}}} + \sqrt{\frac{\alpha_{jl}}{\alpha_{km}}} \end{vmatrix} = \left(\sqrt{\frac{\alpha_{km}}{\alpha_{jl}}} + \sqrt{\frac{\alpha_{jl}}{\alpha_{km}}} \right)^3$$

And so, using the fact that $1/\sqrt{a} = \sqrt{a}/a$ we get

$$\left| \frac{\partial(\mathbf{r}, \mathbf{r}')}{\partial(\mathbf{s}, \mathbf{s}')} \right| = \left| \frac{\partial(\mathbf{s}, \mathbf{s}')}{\partial(\mathbf{r}, \mathbf{r}')} \right|^{-1} = \left(\frac{\sqrt{\alpha_{jl}\alpha_{km}}}{\alpha_{jl} + \alpha_{km}} \right)^3$$

and

$$\mathcal{G}_{jklm} = q_e^2 \left(\frac{\sqrt{\alpha_{jl}\alpha_{km}}}{\alpha_{jl} + \alpha_{km}} \right)^3 \int e^{-\frac{\alpha_{jl}\alpha_{km}}{\alpha_{jl}+\alpha_{km}}s^2} e^{-\frac{\alpha_{jl}\alpha_{km}}{\alpha_{jl}+\alpha_{km}}s'^2} \frac{d\mathbf{s}d\mathbf{s}'}{|\mathbf{s}|}$$

$$\mathcal{G}_{jklm} = q_e^2 \left(\frac{\sqrt{\alpha_{jl}\alpha_{km}}}{\alpha_{jl} + \alpha_{km}} \right)^3 \left(4\pi \int_0^\infty s e^{-\frac{\alpha_{jl}\alpha_{km}}{\alpha_{jl}+\alpha_{km}}s^2} ds \right) \left(4\pi \int_0^\infty s'^2 e^{-\frac{\alpha_{jl}\alpha_{km}}{\alpha_{jl}+\alpha_{km}}s'^2} ds' \right)$$

Which, finally, gives

$$\mathcal{G}_{jklm} = \frac{2q_e^2 \pi^{\frac{5}{2}}}{\alpha_{jl} \alpha_{km} \sqrt{\alpha_{jl} + \alpha_{km}}} \quad (15)$$

With these expressions for \mathcal{S}_{jk} , \mathcal{T}_{jk} and \mathcal{G}_{jklm} , the code will solve the helium atom by an iterative process with the number M of S Gaussians and their coefficients α_i as inputs. Using a simple initial guess for the coefficients \mathbf{c} , it will solve the Roothaan equation by generalised diagonalization. Note that since we are studying the helium atom in its ground state, there's only one orbital of interest. For subsequent iterations, it will compare its energy with the energy of the previous iteration, and if both energies are within a certain threshold it will halt.

Units used will be Rydberg atomic units, so that

$$\hbar = 2m_e = \frac{q_e^2}{2} = 1$$

4 Results and Discussion

First we tried to see how the ground state energy changes as a function of the parameters α_i . For this purpose, a simple initial set was chosen, namely $\alpha_i = i$, and energy values were obtained for different values of one of those parameters. When a minimum was reached, this value was set and then another parameter was changed. This was done only for $M = 4, 6$, due to the task being rather tedious, until all parameters reached a minimum.

For $M = 4$, the first step of this can be seen in Figure 1. A minimum energy of -5.61935501Ry was reached for

$$\alpha_1 = 0.325, \quad \alpha_2 = 2.9, \quad \alpha_3 = 3.3, \quad \alpha_4 = 8.5.$$

The largest variation for the energy was observed for the first parameter. For subsequent parameters, the energy variation was relatively low. This can be seen in Figure 2 where small variations of the parameter α_3 translate into very small variations of the ground state energy. For $M = 6$, a minimum of -5.71694857Ry was reached for

$$\alpha_1 = 0.3, \quad \alpha_2 = 1.6, \quad \alpha_3 = 40, \quad \alpha_4 = 305, \quad \alpha_5 = 0.9, \quad \alpha_6 = 6.6.$$

. Both of these energy values are quite far from the experimental result of $-5.806771753(3)\text{Ry}$ [3]. These results indicate that the ground state energy, as a function of the parameters α_i , has multiple minima.

To confirm, we run the code for two sets of optimal values for the parameters α_i . The first set[1], is

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

The energy obtained with these values was -5.71032071Ry , which is better than the value obtained by manual search for $M = 4$, and is on par with the value obtained for $M = 6$. The second set[2] of values is

$$\alpha_1 = 0.298073, \quad \alpha_2 = 1.242567, \quad \alpha_3 = 5.782948, \quad \alpha_4 = 38.474970,$$

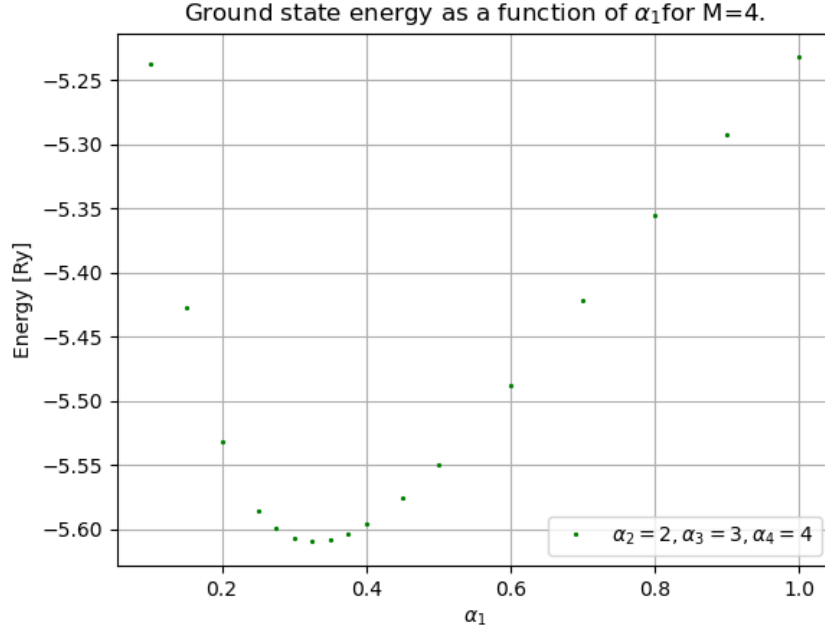


Figure 1: Ground state energy as a function of parameter α_1 for $M = 4$ and $\alpha_2 = 2, \alpha_3 = 3, \alpha_4 = 4$.

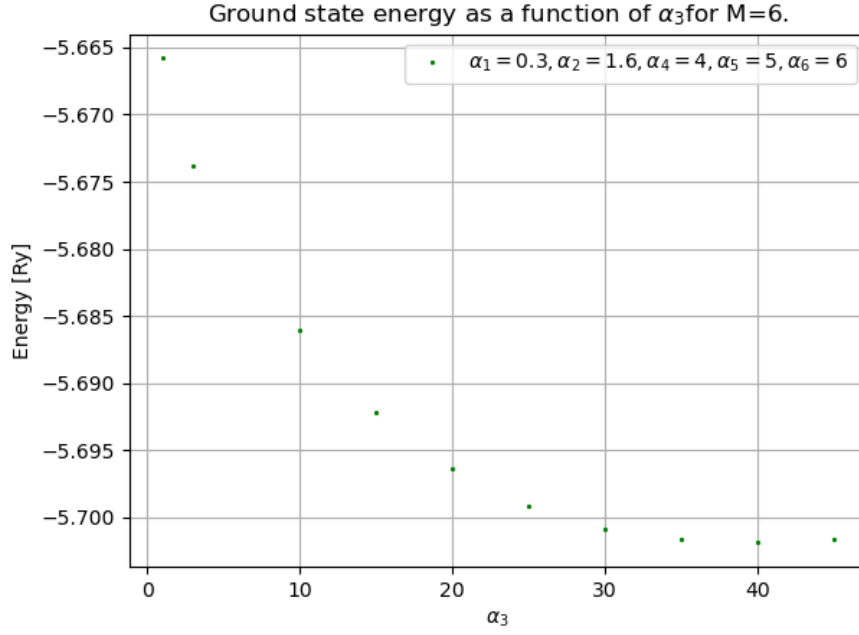


Figure 2: Ground state energy as a function of parameter α_3 for $M = 6$ and $\alpha_1 = 0.3, \alpha_2 = 1.6, \alpha_4 = 4, \alpha_5 = 5$ and $\alpha_6 = 6$.

Method	Ground state energy [Ry]
First-order perturbation theory[1]	-5.5
Hartree-Fock, manual search, $M = 4$	-5.61935501
Variational method[1]	-5.695
Hartree-Fock, optimized set[1], $M = 4$	-5.71032071
Hartree-Fock, optimized set[2], $M = 4$	-5.71032076
Hartree-Fock, manual search, $M = 6$	-5.71694857
Experimental value[3]	-5.806771753(3)

Table 1: Ground state energy obtained by different methods.

which is quite similar to the previous set. This set yielded -5.71032076Ry for the ground state energy, which is practically the same value as the one obtained for the previous set. A set of optimised values for $M = 6$ was not found.

Finally, we want to compare these results with those obtained with other methods. Energy values are shown in Table 1. We can see that Hartree-Fock results are around 0.1-0.09Ry off. This was expected, since the correlation energy, the energy difference between the exact value and the Hartree-Fock solution, is around 0.084Ry[1].

In Figure 3 various orbitals are shown. These are, the orbital obtained with the optimised set provided by Thijssen and the 1s Slater orbital

$$\sqrt{\frac{Z^3}{\pi}}e^{-Zr}$$

for $Z = 1, 2$ and $Z = 27/16$. This last value of Z is obtained by applying the variational principle to the helium atom with the 1s Slater orbital as trial wave function and optimising the value of Z . As we can see, the orbital obtained with the Hartree-Fock approximation is similar to a hydrogen-like orbital with effective atomic charge equal to $27/16$.

It seems that, while the Hartree-Fock approximation converges quite fast, in less than 10 iterations, it always falls short of the experimental value for the ground state of the helium atom. A better choice in basis functions seems to improve the energy obtained, as shown by Richard Xue[4]. Either way, the Hartree-Fock method shows that obtaining good approximations for multi-electron problems can be a difficult task.

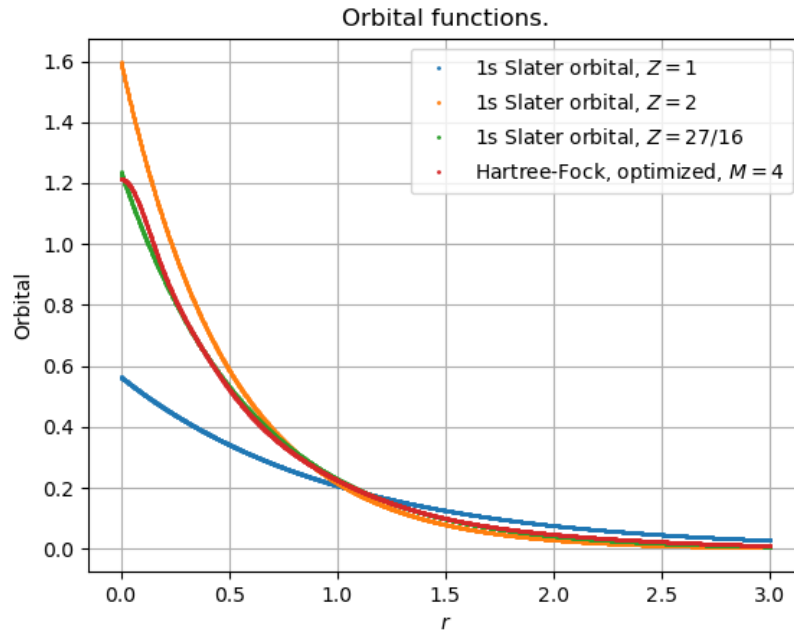


Figure 3: .

References

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- [4] <https://github.com/yueyericardo/hartree-fock>