Mean Field methods/Hartree-Fock

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Introduction

In this exercise we are going to find the ground state of many some atoms in the central field approximation, in which only the Coulomb interaction is considered, by means of the Hartree-Fock self consistent field method.

Let's start by writing the Hamiltonian describing the N-electron atom in Hartree atomic units [1]:

$$\hat{H} = \sum_{i=1}^{N}\left[-\frac{\nabla_i^2}{2} - \frac{Z}{r_i}\right] + \sum_{i,j}^{N}\frac{1}{r_{ij}} \tag{1}$$

The wave function of the N-electrons will be antisymmetric due to the fermionic nature of electrons, then:

$$\Psi(q_1,\dots,q_N) = \sqrt{N!}\,\mathcal{A}\phi_H(\mathbf{r}_1,\dots,\mathbf{r}_N) \tag{2}$$

where $\mathcal{A}$ is the antisymmetrizing operator and $\phi_H(\mathbf{r}_1,\dots,\mathbf{r}_N) = \varphi_\alpha(q_1)\cdots\varphi_\nu(q_N)$ is the Hartree wave function. The Schrödinger equation for the N-electron wave function will be a partial differential equation in 3N dimensions and due to the interaction between the electrons this equation is not separable.

To answer this problem one usually use as starting point the *central field approximation* which is based on an *independent particle model*, that is each electron is subjected to an effective potential which averages the attraction to the nucleus and the repulsion with the other $N-1$ electrons.

This effective potential can be computed by means of Hartree-Fock method, which consists in a variational procedure on the single particle spin orbitals appearing in the Hartree wave function.

The result of this procedure is called Hartree-Fock equations, a system of integro-differential equations for the N spin-orbitals $\varphi_\alpha, \varphi_\beta, \dots \varphi_\nu$:

$$\left[h(\mathbf{r}_i) + \sum_\mu \mathcal{J}_\mu(\mathbf{r}_i) - \mathcal{K}_\mu(\mathbf{r}_i)\right]\varphi_\lambda(\mathbf{r}_i) = \epsilon_\lambda\varphi_\lambda(\mathbf{r}_i) \tag{3}$$

where the *direct* and *exchange potentials* have been introduced:

$$\begin{cases} \mathcal{J}_\mu(\mathbf{r}_i) = \int d\mathbf{r}\,|\varphi_\mu(\mathbf{r})|^2\,\dfrac{1}{|\mathbf{r}-\mathbf{r}_i|} \\[2mm] \mathcal{K}_\mu(\mathbf{r}_i)\varphi_\lambda(\mathbf{r}_i) = \left[\int d\mathbf{r}\,\varphi_\mu^*(\mathbf{r})\dfrac{1}{|\mathbf{r}-\mathbf{r}_i|}\varphi_\nu(\mathbf{r})\right]\varphi_\lambda(\mathbf{r}_i) \end{cases} \tag{4}$$

Moreover, by defining the Fock potential $f(\mathbf{r}_i) = h(\mathbf{r}_i) + \sum_\mu \mathcal{J}_\mu(\mathbf{r}_i) - \mathcal{K}_\mu(\mathbf{r}_i)$ one gets the Hartree-Fock equations:

$$\boxed{f(\mathbf{r}_i)\varphi_\lambda(\mathbf{r}_i) = \varepsilon_\lambda\varphi_\lambda(\mathbf{r}_i)} \tag{5}$$

In order to solve this equation one reformulate the problem in matrix form by projecting the spin orbitals φ_μ on a non-orthonormal basis set, resulting in the Roothaan-Hall equations:

$$\varphi_\mu = \sum_{p=1}^{K} C_{p\mu}\chi_p \implies \boxed{\sum_q F_{pq}C_{q\mu} = \epsilon_\mu\sum_q S_{pq}C_{q\mu}} \tag{6}$$

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[1] The motion of the nucleus is neglected and the reduced mass μ is set to 1.

where:

$$S_{pq}^i = \int d\mathbf{r}_i \chi_p^*(\mathbf{r}_i) \chi_q(\mathbf{r}_i)$$
$$F_{pq}^i = \int d\mathbf{r}_i \chi_p^*(\mathbf{r}_i) f(\mathbf{r}_i) \chi_q(\mathbf{r}_i)$$

$$(7)$$

Finally one can represent eq. (6) in matrix form:

$$\mathbf{FC} = \mathbf{SC}\varepsilon \qquad (8)$$

where $\mathbf{C}$ is a matrix of coefficients, $\mathbf{F}$ is the Fock matrix (which depends on the coefficients $\mathbf{C}$ due to electron-electron interactions), $\mathbf{S}$ is the overlap matrix of the basis functions and ε is the (diagonal, by convention) matrix of orbital energies.

Note that since the Fock matrix depends on its own generalized eigenvalue problem solution, the solution of the full Hartree-Fock-Roothaan equation must be seek by iteration; this is the reason why the procedure is called a *self consistent field* method.

In the following sections we are going to draw a flowchart for the self-consistent algorithm of the HF equations, then by adopting the STO-4G basis set we are going to find the coefficients that minimize the energy in the Hydrogen case. After that we will use the iterative procedure to solve the Hartree-Fock-Roothaan equations for an Helium atom and a Beryllium atom.

1 Flowchart

In the following we are going to make a scheme for the self-consistent field procedure.
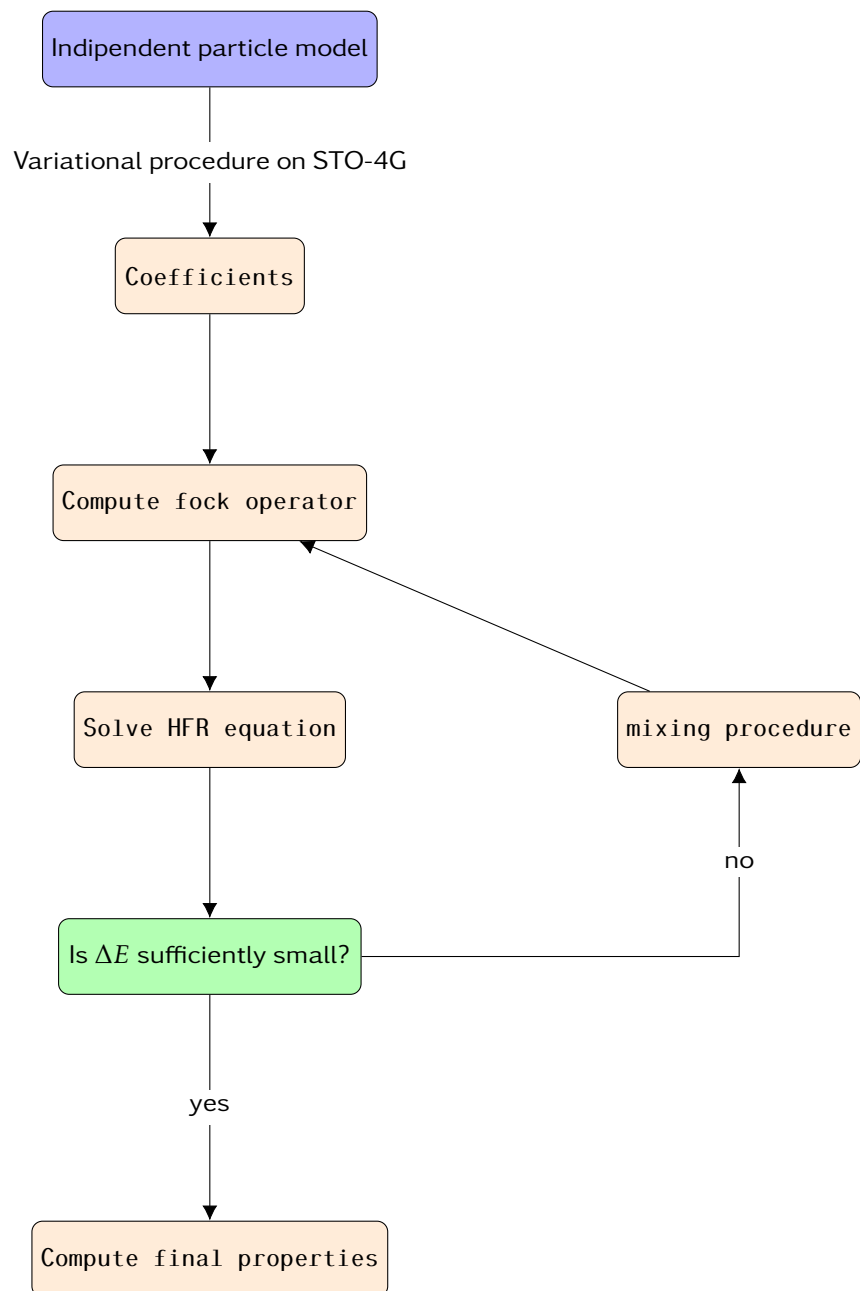
2   Variational procedure on Hydrogen atom

Let's expand the Hydrogen $1s$ orbital on the STO-4G basis:

$$\varphi_0(r) = \sum_p c_p \chi_p(r) \quad \text{where} \quad \chi_p(r) = e^{-\alpha_p r^2} \quad \text{with} \quad \begin{cases} \alpha_1 = 13.00773 & \alpha_2 = 1.962079 \\ \alpha_3 = 0.444529 & \alpha_4 = 0.1219492 \end{cases} \tag{9}$$

In order to find the coefficients of the linear combination c_p one simply applies the variational procedure by paying attention to the fact that the basis set is not orthonormal:

$$\sum_q \left(\langle p|H|q \rangle - \varepsilon_p \langle p|q \rangle \right) c_q = \sum_q \left(H_{pq} - \varepsilon_p S_{pq} \right) c_q = 0 \implies HC = \varepsilon SC \tag{10}$$

Therefore we compute the the Hamiltonian and overlap matrices:

$$H_{pq} = \int d^3r \, \chi_p \left(-\frac{\nabla^2}{2} + \frac{1}{r} \right) \chi_q = -\frac{1}{2} \int d^3r \, e^{-\alpha_p r^2} \nabla^2 e^{-\alpha_q r^2} - \int d^3r \, e^{-\alpha_p r^2} \frac{1}{r} e^{-\alpha_q r^2} = 3 \frac{\alpha_p \alpha_q \pi^{3/2}}{\left(\alpha_p + \alpha_q \right)^{5/2}} - \frac{2\pi}{\alpha_p + \alpha_q}$$
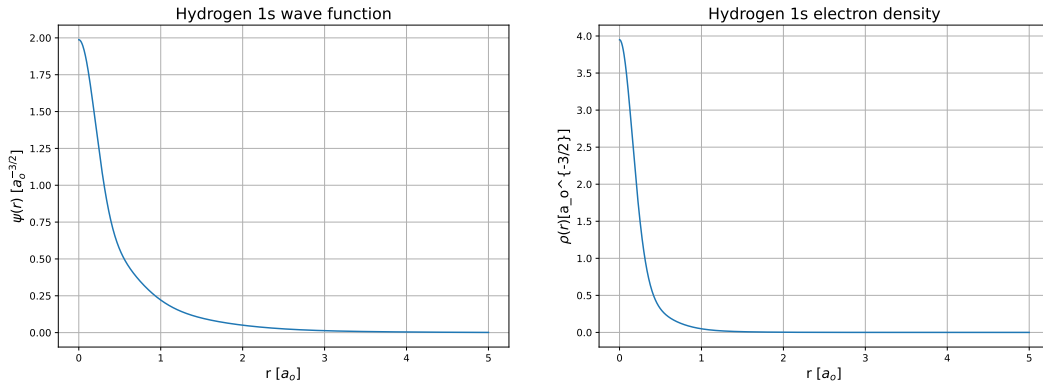
$$S_{pq} = \int d^3r \, \chi_p \chi_q = \int d^3r \, e^{-\alpha_p r^2} e^{-\alpha_q r^2} = \left(\frac{\pi}{\alpha_p + \alpha_q} \right)^{3/2} \tag{11}$$

Finally by means of a numerical generalized diagonalization procedure we obtain the coefficients that minimize the energy of the system:

$$c_1 = -0.09610152 \quad c_2 = -0.16301717 \quad c_3 = -0.18558699 \quad c_4 = -0.07370076 \tag{12}$$

The energy estimation is then $E_0 = -13.59\,\text{eV}$.

In the following figure one can see the resulting wave function:

3   Hartree-Fock method on Helium atom

In the case of Helium atom the spatial part of the two spin orbitals is equal (they differ only for the m_s quantum number), then we can solve a single Hartree-Fock equation:

$$f(\mathbf{r})\varphi_{1s,\uparrow}(\mathbf{r}) = \varepsilon_{1s,\uparrow}\varphi_{1s,\uparrow}(\mathbf{r}) \tag{13}$$

That becomes the following Hartree-Fock-Roothaan equation using the STO-4G expansion[2]:

$$\sum_q F_{pq}C_q^{1s} = \epsilon_{1s}\sum_q S_{pq}C_q^{1s} \tag{14}$$

Let's start by computing F_{pq}:

$$F_{pq} = \int d^3r\, \chi_p^\uparrow(\mathbf{r})\left(\frac{\nabla^2}{2} - \frac{Z}{r}\right)\chi_q^\uparrow(\mathbf{r}) + \sum_\mu \int d^3r\, \chi_p^\uparrow(\mathbf{r})[\mathcal{J}_\mu(\mathbf{r}) - \mathcal{K}_\mu(\mathbf{r})]\chi_q^\uparrow(\mathbf{r}) \tag{15}$$

The sum on all the states can be simplified by noticing that in a closed shell system one has:

$$\sum_{\mu=(n,m_s)}(\mathcal{J}_\mu - \mathcal{K}_\mu)\chi_q^\uparrow(\mathbf{r}) = \sum_{\mu=(n,^1\!/_2)}(2\mathcal{J}_\mu - \mathcal{K}_\mu)\chi_q^\uparrow(\mathbf{r}) \tag{16}$$

this is due to the fact that the direct terms don't depend on spin projection, while the exchange ones are zero if applied to a different spin projection.

Moreover in the present case one can readily see that since $n = 1$ there's only one term of the sum:

$$F_{pq} = 3\frac{\alpha_p\alpha_q\pi^{3/2}}{\left(\alpha_p + \alpha_q\right)^{5/2}} - \frac{2\pi}{\alpha_p + \alpha_q} + \sum_{r,s}c_r c_s \int d^3r\, d^3r'\, 2\frac{e^{-(\alpha_p+\alpha_q)r^2}e^{-(\alpha_r+\alpha_s)r'^2}}{|r - r'|} - \frac{e^{-(\alpha_p+\alpha_s)r^2}e^{-(\alpha_q+\alpha_r)r'^2}}{|r - r'|} \tag{17}$$

In order to compute the integrals that appear in F_{pq} we consider the following procedure:

$$\int e^{-\alpha r^2}e^{-\beta r'^2}\frac{1}{|\mathbf{r} - \mathbf{r}'|}d^3r\, d^3r' = \left(\frac{\sqrt{\alpha\beta}}{\alpha + \beta}\right)^3 \int e^{-\frac{\alpha\beta}{\alpha+\beta}r^2}\frac{1}{r}e^{-\frac{\alpha\beta}{\alpha+\beta}s^2}d^3r\, d^3s = \frac{2\pi^{5/2}}{\alpha\beta(\alpha+\beta)^{1/2}} \tag{18}$$

where we have carried out the following variable changes:

$$\mathbf{r} - \mathbf{r}',\quad \mathbf{s} = \sqrt{\frac{\alpha}{\beta}}\mathbf{r} + \sqrt{\frac{\beta}{\alpha}}\mathbf{r}' \tag{19}$$

Then by defining $\alpha = \alpha_p + \alpha_q$ and $\beta = \alpha_r + \alpha_s$ for the first integral and $\alpha' = \alpha_p + \alpha_s$ and $\beta' = \alpha_q + \alpha_r$ for the second one, we have:

$$F_{pq} = 3\frac{\alpha_p\alpha_q\pi^{3/2}}{\left(\alpha_p + \alpha_q\right)^{5/2}} - \frac{2\pi}{\alpha_p + \alpha_q} + \sum_{r,s}c_r c_s 2\frac{2\pi^{5/2}}{\alpha\beta(\alpha+\beta)^{1/2}} - \frac{2\pi^{5/2}}{\alpha'\beta'(\alpha'+\beta')^{1/2}} \tag{20}$$

Finally we compute S_{pq}:

$$S_{pq} = \int d^3r\, \chi_p(\mathbf{r})\chi_q(\mathbf{r}) = \int d^3r\, e^{-\alpha_p r^2}e^{-\alpha_q r^2} = \left(\frac{\pi}{\alpha_p + \alpha_q}\right)^{3/2} \tag{21}$$

One can now explicitly see that F_{pq} actually depends on its own solution via the presence of the coefficients c_r and c_s, this means that the solution has to be sought by iteration.

In order to start the iterative procedure we solve the generalized eigenvalue problem for the independent particle part of the Fock operator h finding the zeroth order solution. With the found coefficients we can start the iterative procedure, compute $F_{pq}^{(i)}$ and solve the generalized eigenvalue problem finding $\varepsilon^{(i)}$, $C^{(i)}$ and so on.

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[2]The parameters of the STO-nG we've used can be found at https://www.basissetexchange.org

In order to obtain convergence for the energy values, at the end of every step we will update the coefficients as in the following equation.
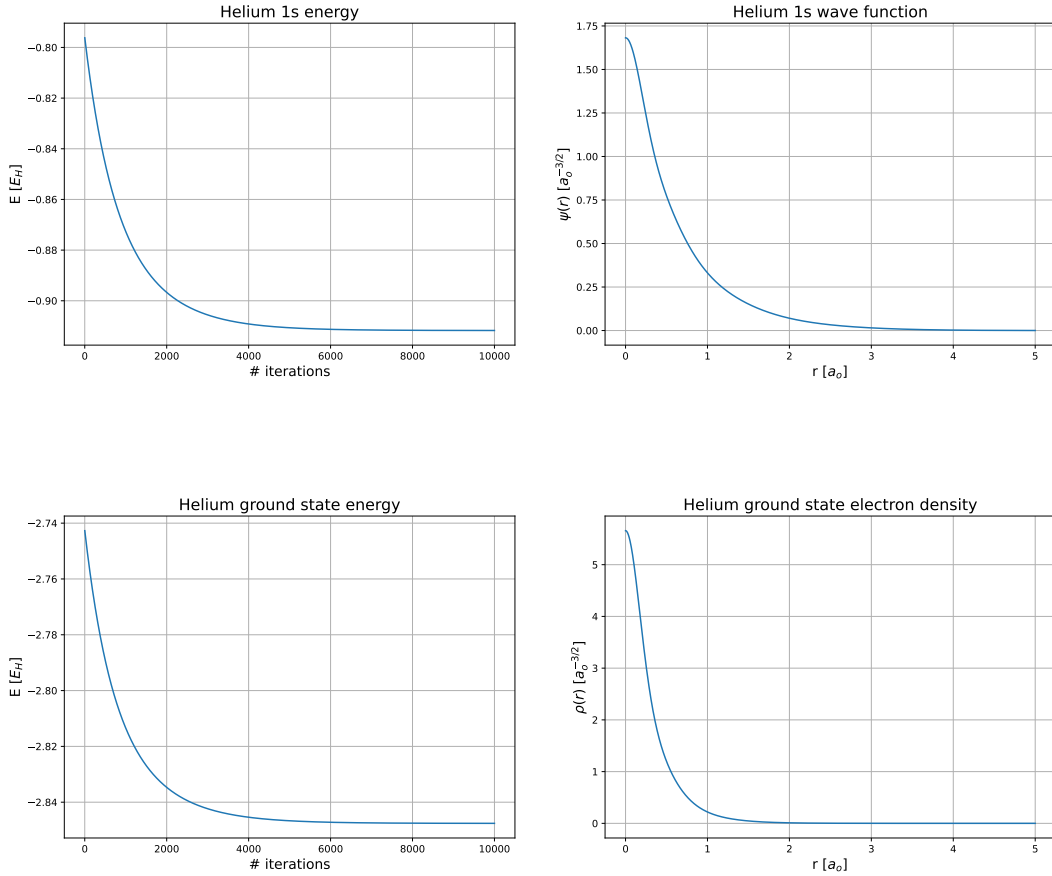
$$C^{\text{new}} = \kappa C + (1 - \kappa)C^{\text{old}} \qquad \kappa \ll 1 \tag{22}$$

Note that with this procedure we will find the spin orbitals energies and the total energy of the state will be given by:

$$E_{HF} = \sum_{i=1}^{n} \varepsilon + \frac{1}{2} \sum_{r=1}^{4} \sum_{s=1}^{4} c_r c_s h_{rs} \tag{23}$$

were h is the one body part of the Fock operator.

By setting $\kappa = 0.001$ and iterating the process for $N = 10000$ steps, we get the following results.

In order to obtain an estimate of the energies we fit the values of the energy over the number of iterations with an exponential function. Our estimate of the energy will be the value of the function in the limit for $N \to \infty$. We obtain:

$$E_{1s} = -0.911 \ E_h$$
$$E_0 = -2.847 \ E_h \tag{24}$$

where E_h is the Hartree energy ($\simeq 27.21 \, \text{eV}$). We cannot clearly estimate an error on this value and therefore we cannot really compare it with other studies, but we can say that these values are quite in agreement with much more accurate studies found in literature.

4 Beryllium

As in the Helium atom, in the Beryllium atom the spatial part of the two spin orbitals $1s$ are equal and in this case it is true for the $2s$ orbitals as well. This means that we can solve two Hartree-Fock equations instead of 4:

$$\begin{cases} f(\mathbf{r})\varphi_{1s,\uparrow}(\mathbf{r}) = \varepsilon_{1s,\uparrow}\varphi_{1s,\uparrow}(\mathbf{r}) \\ f(\mathbf{r})\varphi_{2s,\uparrow}(\mathbf{r}) = \varepsilon_{2s,\uparrow}\varphi_{1s,\uparrow}(\mathbf{r}) \end{cases} \tag{25}$$

In the present case we adopt the double zeta basis functions for the two spin orbitals, that is we have a linear combination of two Slater type functions χ^S and each of them are a linear combination of 4 Gaussian type functions χ^G:

$$\begin{aligned} \varphi_{1s} &= \sum_{i=1}^{2} v_i^{(1)}\chi_i^S & \chi_1^S &= \sum_{p=1}^{4} c_{p,1s}\chi_p^{G,1s} \\ & & \text{where} & \\ \varphi_{2s} &= \sum_{i=1}^{2} v_i^{(2)}\chi_i^S & \chi_2^S &= \sum_{p=1}^{4} c_{p,2s}\chi_p^{G,2s} \end{aligned} \tag{26}$$

We will solve this problem for both a non-contracted basis and a contracted one.

4.1 Non-contracted STOs

In the non-contracted case the coefficients of the STO-4G expansion vary during the variational procedure, then the spin orbitals are written as:

$$\begin{aligned} \varphi_{1s} &= \sum_{p=1}^{8} C_{p,1s}\chi_p^G & \chi_p^G &= [\chi_1^{G,1s},\dots,\chi_4^{G,1s},\chi_1^{G,2s},\dots,\chi_4^{G,2s}] \\ & & \text{where} \quad C_{p,1s} &= [v_1^{(1)}c_{1,1s},\dots,v_1^{(1)}c_{4,1s},v_2^{(1)}c_{1,2s},\dots,v_2^{(1)}c_{4,2s}] \\ \varphi_{2s} &= \sum_{p=1}^{8} C_{p,2s}\chi_p^G & C_{p,2s} &= [v_1^{(2)}c_{1,1s},\dots,v_1^{(2)}c_{4,1s},v_2^{(2)}c_{1,2s},\dots,v_2^{(2)}c_{4,2s}] \end{aligned} \tag{27}$$

Then the Hartree-Fock-Roothaan equations in matrix form are:

$$\begin{pmatrix} F_{pq}^1 & 0 \\ 0 & F_{pq}^2 \end{pmatrix}\begin{pmatrix} C_{q1} & 0 \\ 0 & C_{q2} \end{pmatrix} = \begin{pmatrix} S_{pq}^1 & 0 \\ 0 & S_{pq}^2 \end{pmatrix}\begin{pmatrix} C_{q1} & 0 \\ 0 & C_{q2} \end{pmatrix}\begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix} \tag{28}$$

Where every element of the matrices is in actually an 8×8 matrix which in turn can be computed as written in eq. (7).

We note that $F_{pq}^1 = F_{pq}^2$ and $S_{pq}^1 = S_{pq}^2$, this means that we can solve one of the two generalized eigenvalue problems obtaining as first eigenvalue (eigenfunction) the energy (coefficients) of the 1s orbital ψ_{1s} and as second eigenvalue (eigenfunction) the energy (coefficients) of the 2s orbital ψ_{2s}. Moreover the integrals that compose the matrices are the same used before in eq. (20-21).

So we can finally start the iterative procedure, starting from the simplified problem that neglects the electron-electron repulsion. In the following figures we show the result of the iterative procedure, reporting the energy values over the number of iterations, the final wave functions and the final electron density.
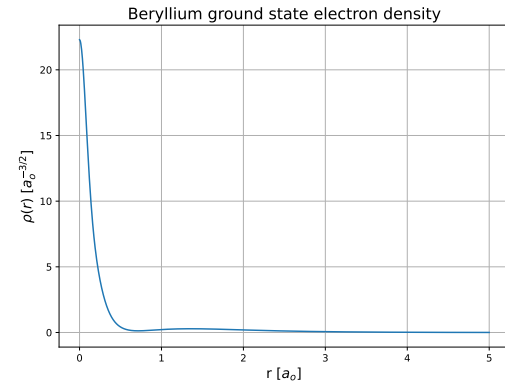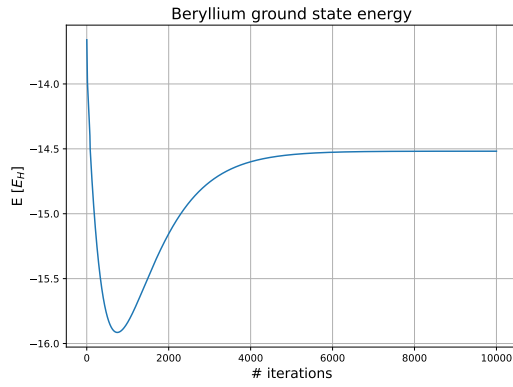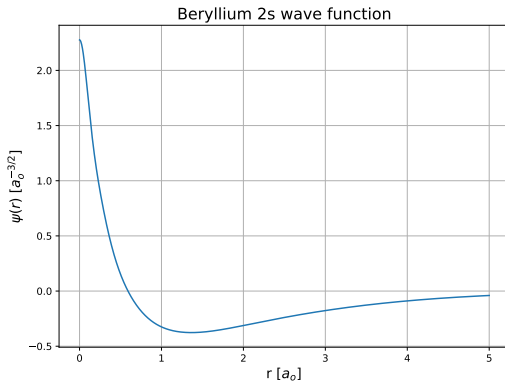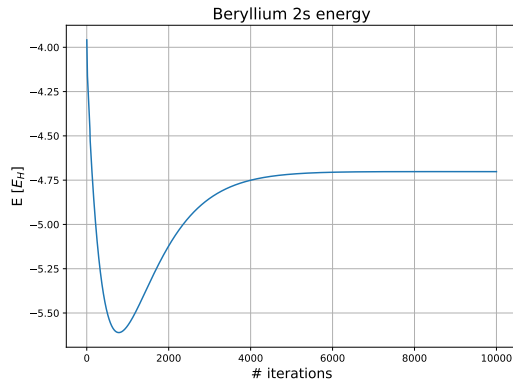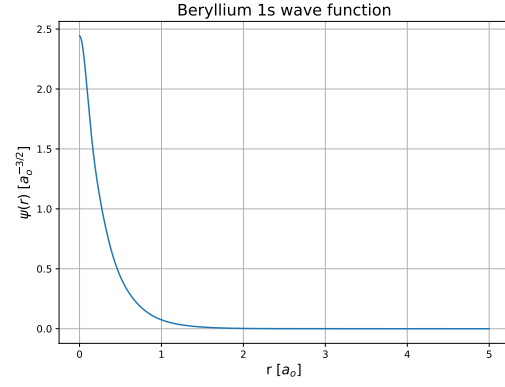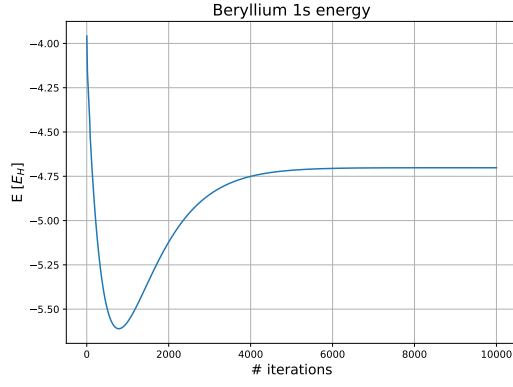
As we can see from the graphs, the energies do not have an decreasing exponential form from the begging and we think this is due to the poor approximation of the first step. So in order to obtain an estimate of the energies we fitted an exponential function starting from the 2000th iteration, founding the following results:

$$E_{1s} = -4.700 \, E_h$$
$$E_{2s} = -0.304 \, E_h \quad (29)$$
$$E_0 = -14.516 \, E_h$$

4.2 Contracted STOs

Finally we solve the Beryllium electronic problem using a contracted basis, this means that coefficients of the STO-4G expansion are fixed to:

c_{1s}	0.5675242080E-01	0.2601413550E+00	0.5328461143E+00	0.2916254405E+00
c_{2s}	-0.6220714565E-01	0.2976804596E-04	0.5588549221E+00	0.4977673218E+00

thus the variational procedure will act only on the coefficients $v_i^{1,2}$ of the double zeta expansion. The value reported here are taken by previous studies.

This means that from eq. 25 one simply inserts $\varphi_\mu = \sum_{i=1}^2 v_i^{(\mu)} \chi_i^S$ and projects out the Roothaan equations with χ_i^S instead of using χ_p^G as before, the result in matrix notation is:

$$\begin{pmatrix} F_{ij}^1 & 0 \\ 0 & F_{ij}^2 \end{pmatrix} \begin{pmatrix} C_{j1} & 0 \\ 0 & C_{j2} \end{pmatrix} = \begin{pmatrix} S_{ij}^1 & 0 \\ 0 & S_{ij}^2 \end{pmatrix} \begin{pmatrix} C_{j1} & 0 \\ 0 & C_{j2} \end{pmatrix} \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix} \tag{30}$$
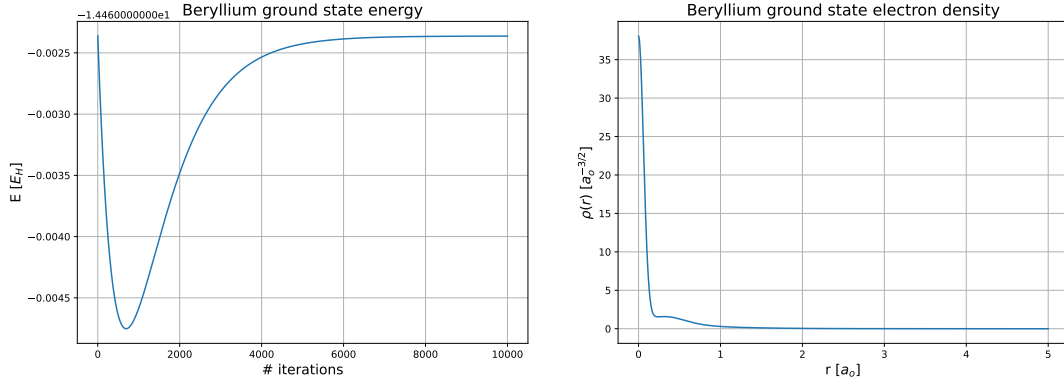
where now:

$$F_{ij} = \int d\mathbf{r}\, \chi_i^S(\mathbf{r}) f(\mathbf{r}) \chi_j^S(\mathbf{r}_i)$$

$$S_{ij} = \int d\mathbf{r}\, \chi_i^S(\mathbf{r}) \chi_j^S(\mathbf{r}) \tag{31}$$

Note that the Fock matrix and the overlap matrix do not depend on the particle, this means that we can solve one of the two matrix equations obtaining both the $1s$ and $2s$ properties.

Finally we apply the iterative procedure as explained before. We show our results in the following plots.
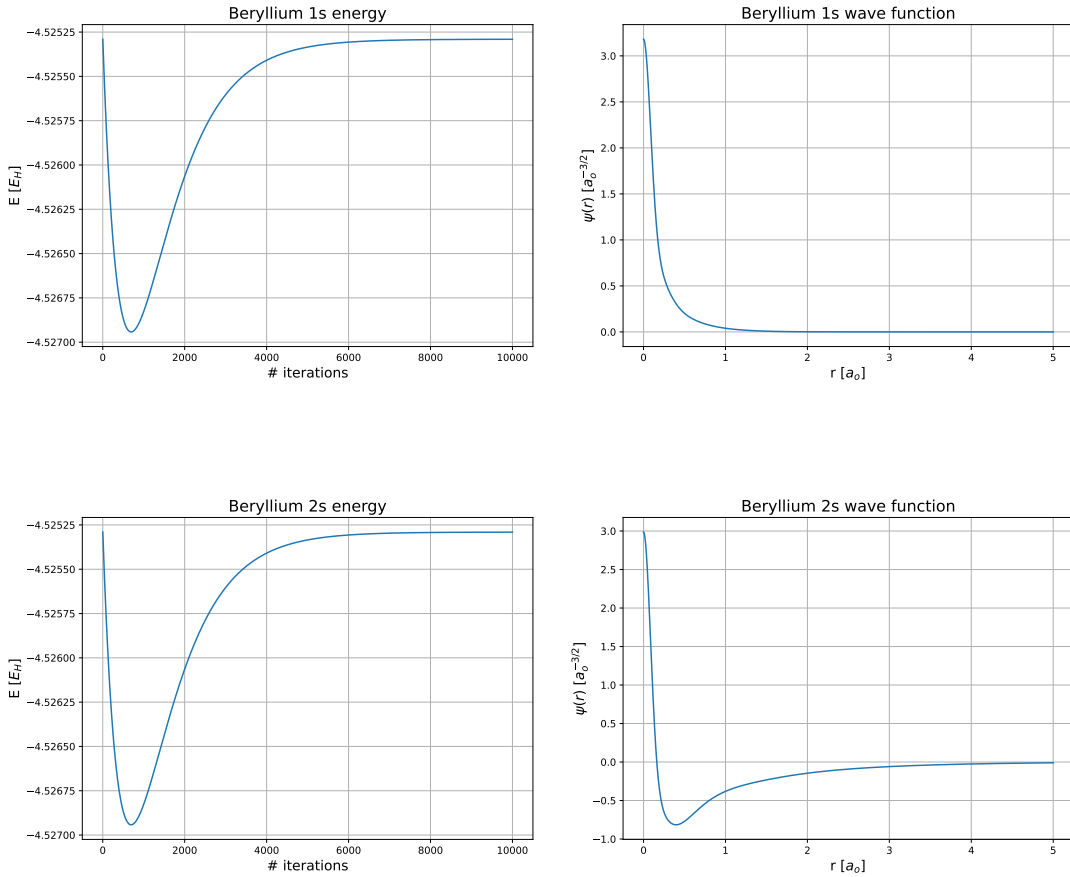
Again as before, we fitted the values of the energies over the iterations with an exponential function and found for $N \to \infty$:

$$E_{1s} = -4.525 \ E_h$$
$$E_{2s} = -0.253 \ E_h \tag{32}$$
$$E_0 = -14.462 \ E_h$$

4.3 Comparison between the two approaches

The first thing we note is that in both cases there is a systematic error in using the exponents of the gaussians describing the $2s$ orbitals: the value we used are fitted for a $2sp$ hybrid orbital, while here we treated the orbitals as a pure s one.

We report the values of the coefficients found in the non-contracted case:

c_{1s}	c_{2s}
0.06118629	0.0115063
0.26326887	0.05182096
0.50056727	0.15545032
0.32390783	0.20357735
-0.0035583	-0.04294387
-0.0021149	-0.07348299
0.0149041	-0.25079572
-0.00409363	-0.81064266

while in the contracted case we have:

v_{1s}	v_{2s}
-0.99979833	0.26385774
-0.02008253	-0.96456161

As we can see in both case the $1s$ gaussians approximate the $1s$ state quite well. In fact in the non-contracted case the first 4 coefficients are comparable to the one reported in the table in previous section and the contributions of of the $2s$ gaussians are almost negligible in comparison. In the contracted case this is event more clear since the coefficient for the $1s$ Slater contracted orbital is almost equal to 1.

In the case of the $2s$ orbitals we can see that in order to get a good approximation, a combination of all the 8 gaussians is required. Again this is expected and we think this is due to the fact the second STO is fitted on a $2sp$ orbital instead of a $2s$ one.

For the energy values we can see that in the contracted case, at the end of the iteration procedure we get similar

values to the starting ones: this was expected since the values of the coefficients we used are already optimized for the solutions of the Beryllium orbitals, at least for the $1s$ one.

By comparing our energy results with others found in literature[3] we can say that we obtain better results in the non-contracted case. We can pin this observation to the fact that, in being a variational procedure, the Hartee-Fock method improve with the numbers of parameters used to estimate the states. Obviously this improvement comes at the cost of computational time: our Hartee-Fock algorithm takes $1.20\,\text{s}$ in the contracted case, while it takes $133.48\,\text{s}$ in the non-contracted one.

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[3]Check out `https://www.pearsonhighered.com/cooksy1einfo/quantum/files/assets/basic-html/page64.html` for HF energies estimations for atoms from H to Na