

Hartree–Fock calculations for 2-electron atoms

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Abstract: In this work the energies and wave functions of 2-electron atoms have been studied. To this end, the Hartree–Fock self-consistent method has been applied to explore the isoelectronic series of He in the ground state. The bulk of the work has consisted in writing a program, based on the Numerov–Cooley method, to solve the radial Schrödinger equation. The final results are discussed and compared to reference values.

I. INTRODUCTION

The Hartree–Fock (HF) method [1] is an accurate framework to study many-electron atoms. In this approximation, each electron moves in an effective potential composed of the electron-nucleus attraction and the electron-electron repulsion. In order to derive the HF equations, which are a coupled system of integro-differential equations, it is assumed that the wave function of the N -electron system is a single Slater determinant. The variational method is then applied and the optimum Slater determinant is obtained. In atomic units, the HF equations are

$$\left[-\frac{1}{2} \vec{\nabla}_{\vec{r}}^2 + V_{\text{HF}}(\vec{r}) \right] \psi_i(\vec{r}) = E_i \psi_i(\vec{r}) \quad i = 1, \dots, N \quad (1)$$

where $\psi_i(\vec{r})$ are the one-electron spin orbitals and $V_{\text{HF}}(\vec{r})$ is the HF potential,

$$V_{\text{HF}}(\vec{r}) = V_{\text{n}}(r) + V_{\text{d}}(\vec{r}) + V_{\text{ex}}(\vec{r}). \quad (2)$$

The first term is the electron-nucleus (Coulomb) attractive potential,

$$V_{\text{n}}(r) = -\frac{Z}{r}, \quad (3)$$

whereas

$$V_{\text{d}}(\vec{r}) = \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (4)$$

is the direct contribution of the electron-electron repulsion. The third term, V_{ex} , is the exchange potential. The self-consistent method to solve the HF equations is started making an initial guess for the potential (or the wave functions), then $V_{\text{HF}}(\vec{r})$ is evaluated and the HF eigenvalues and eigenfunctions are obtained numerically. These new wave functions are used in a subsequent iteration to evaluate $V_{\text{HF}}(\vec{r})$. The process is repeated until the desired precision is reached.

Here we are interested in 2-electron atoms in the ground state ^1S [2]. Therefore, as V_{ex} is proportional to δ_{m_s, m'_s} and the two spins are always opposed due to the Pauli exclusion principle it follows that $V_{\text{ex}} = 0$ and

the HF equations reduce to only one equation for the 1s spatial orbital.

The aim of this TFG is to write, from scratch, a **FORTRAN** program to solve self-consistently the HF equation for the ground state of 2-electron atoms adopting the Numerov–Cooley algorithm. The program gives both the eigenvalue E_{10} and the reduced radial wave function $P_{10}(r)$. The program will be run for the first members of the isoelectronic series of He, viz., from $Z = 2$ to $Z = 10$. Once all the runs are finished, additional calculations can be done in order to study 2-electron atoms such as the HF energy. Our results will be compared to reference HF results from the literature and their validity will be discussed. A relative error of the order of 10^{-6} in the calculation of the HF energies is aimed at. Furthermore, some checks will be made such as the HF energy consist in an upper bound for the energy of the atom or that the system verifies the virial theorem.

In this TFG, all the equations and results are expressed in Hartree atomic units ($\hbar = e = m_e = 1$).

II. METHODOLOGY

The main objective of the program is to solve the HF equations for 2-electron atoms and ions. The program, written in **FORTRAN**, was developed in three consecutive stages. The process had to be progressive, namely, each stage had to be completed before proceeding to the next one. It was divided into three stages because the program had to do three different and specific tasks: firstly it had to calculate the wave function with the eigenvalue and the potential, in the second one, besides, it had to obtain the eigenvalue and finally in the third one it had to become self-consistent. Developing it like this facilitated the debugging, and specific crosschecks could be done for each stage.

A. Numerov’s method

The first stage consisted in calculating the reduced radial wave functions for central-field potentials using the Numerov method. To this end, the program was fed with

the exact (analytical or numerical) eigenvalue. The process followed to obtain the Numerov recursion formula is based in [3, 4]. The Numerov method is an iterative method to solve second-order ordinary differential equations which do not contain the first derivative. An example of these type of equations is the radial Schrödinger equation, which has the general form

$$\frac{d^2 y}{dr^2} = -g(r) y(r). \quad (5)$$

The recursion formula is obtained by doing the Taylor expansion of the function $y(r)$ around the point r ,

$$y(r \pm h) = \sum_{n=0}^{\infty} \frac{(\pm h)^n}{n!} y^{(n)}(r), \quad (6)$$

where h is the step size of integration and the superscript n of the function $y(r)$ on the right-hand side of the equation indicates the n th derivative. Eq. (6) includes all derivatives of $y(r)$, however, while the second derivative can be replaced by the right-hand side of Eq. (5), the rest of them might be difficult to calculate. Therefore, as each derivative is proportional to a higher power of h , which is a small quantity, we can stay in the second derivative term. At this point, one might wonder how to compute the first derivative term, which seems to be the only term hard to calculate. But this term can be eliminated as follows:

$$\frac{1}{2}[y(r+h) + y(r-h)] = \sum_{n=0}^{\infty} \frac{h^{2n}}{(2n)!} y^{(2n)}(r). \quad (7)$$

If we stay here, a precision to the 3rd order would be achieved. Nevertheless, acquiring a precision to the 6th order is easily achieved by deriving Eq. (7) twice:

$$\frac{1}{2}[y^{(2)}(r+h) + y^{(2)}(r-h)] = \sum_{n=0}^{\infty} \frac{h^{2n}}{(2n)!} y^{(2n+2)}(r). \quad (8)$$

Finally, the Numerov recursion formula is obtained

$$y_{n+1} \left(1 + \frac{h^2}{12} g_{n+1}\right) = 2y_n \left(1 - \frac{5h^2}{12} g_n\right) - y_{n-1} \left(1 + \frac{h^2}{12} g_{n-1}\right), \quad (9)$$

with an error of order $\mathcal{O}(h^6)$, $y_i \equiv y(r_i)$, $g_i = 2(E - V(r_i))$ and $r_i \equiv ih$.

In this stage, the integration is started outward at the origin. The initial value is $y_0 = 0$ and y_1 is set at an arbitrary value, e.g. $y_1 = h$. A uniform radial grid of step h is also defined. Thus, we can compute the reduced radial wave function using the recursion formula presented above. Once the wave function is obtained, it is normalized using the Simpson 3/8 rule.

It was checked that the program delivers the correct reduced radial wave functions for the Coulomb potential Eq. (3) for $n = 1, 2, 3$ and $Z = 2, 6, 10$.

B. Search for the eigenvalue. Cooley's method

In the second stage our aim was to obtain, besides the reduced radial wave function, the eigenvalue E . Since we are interested in bound states, $E < 0$. E is related to the number of nodes of the radial reduced wave function, given by the radial wave number, n_r , which is easy to calculate knowing the principal and angular momentum quantum numbers; $n_r = 0$ for 1s orbitals. Due to the form of the wave function, increasing near the origin as a power of r and decreasing exponentially at infinity, integrating just outward would dramatically increase the numerical error at infinity. On the other hand, integrating inward would diminish the error near the last points of the grid but would magnify the error near the origin. Because of this, the strategy was to start integrating inward from infinity (a very large r) to the second classical turning point and then integrate from the origin to this turning point. The integration inward is started with $y_n = 0$ and $y_{n-1} = h$ and the recursion formula Eq. (9) is applied backwards. The search of the eigenvalue is started then by setting up limits [1]. As mentioned above, we are just interested in bound states so we can set the upper bound at $E_{\text{sup}} = 0$. The lower bound, E_{inf} is set at the minimum value of the effective potential. At this point, we compute $E = (E_{\text{inf}} + E_{\text{sup}})/2$ and we obtain the reduced radial wave function using the strategy explained. We have now to check whether our calculated wave function has the correct number of nodes or not. If the wave function has more zeros than expected, we set $E_{\text{sup}} = E$ and we restart the process. If it has less zeros, we set $E_{\text{inf}} = E$ and we do the same. The process is repeated until we get the correct number of zeros.

However, we have not obtained the correct eigenvalue yet. When we have an energy which give us the correct number of nodes, it is time to compute the Cooley energy correction formula [5]. Firstly, the normalization of the outward and inward solution is needed as they both have to match at the turning point, r_m . Then the energy correction ΔE , according to Cooley, is

$$\Delta E = \left[(-Y_{m-2} + 2Y_m - Y_{m+2})/4h^2 + 2(V_m - E)P_m \right] / \sum_{i=1}^n P_i^2, \quad (10)$$

where

$$Y_i = \left[1 - \frac{h^2}{12} (V_i - E) \right] P_i. \quad (11)$$

Now $E + \Delta E$ is closer to the correct eigenvalue. With this new value of the energy, the wave function is recomputed and the process is iterated until we achieve the desired numerical precision.

This stage was critical. Unless we made sure that the program worked correctly and gave the eigenvalues with the desired precision, we could not proceed. To this end, the program was checked with two potentials whose

bound-state eigenvalues and eigenfunctions (or some of them) are known analytically: the Coulomb potential, Eq. (3), and the Hulthén potential $V(r) = -\frac{Z\alpha}{\exp(Z\alpha)-1}$, where α is the screening parameter. The program was run for several orbitals for the Coulomb potential, and for different values of α for the Hulthén potential. Eventually, only when it was verified that all worked properly could we advance to the last stage.

C. The Hartree–Fock iteration

In the last stage of the program the HF iteration loop is implemented. It consists in an iterative calculation with which the wave functions and the energy of 2-electron atoms will be obtained self-consistently.

In order to start the iteration process, an initial guess for the reduced radial wave function (0th-order wave function) is needed. We have chosen

$$P_{10}^{(0)}(r) = P_{10}^{(Z_{\text{eff}})}(r) = Z_{\text{eff}}^{3/2} 2r \exp(-Z_{\text{eff}} r) \quad (12)$$

with $Z_{\text{eff}} = Z - \frac{5}{16}$. Then the direct potential is calculated using the following expression

$$V_d^{(n+1)}(r_i) = \frac{1}{r_i} \int_0^{r_i} [P_{10}^{(n)}(r_j)]^2 dr_j + \int_{r_i}^{\infty} [P_{10}^{(n)}(r_j)]^2 \frac{1}{r_j} dr_j, \quad (13)$$

where the superindex indicates the order of the iteration.

Feeding our program based on the Numerov–Cooley method with the HF potential $V_{\text{HF}}(r)$, a better estimate for the wave function is obtained. We repeat the process recalculating the direct potential until the difference between the potentials in the $(n+1)$ th and n th iterations is smaller than the requested precision, namely 10^{-6} . With our program the eigenvalues of the HF equations are obtained.

The HF energy of 2-electron atoms is given by

$$E_{\text{HF}} = 2 E_{10} - J_{12}, \quad (14)$$

where the Coulomb integral J_{12} is calculated with the self-consistent (converged) wave function $P_{10}(r)$.

III. RESULTS AND DISCUSSION

The program was run from $r = 0$ to $r = 30$ using a uniform radial grid of 10^5 points, i.e. the integration step was $h = 0.0003$. The eigenvalues of the HF equation and the direct Coulomb integral were obtained. There is an unavoidable error made because of the finite h . A strategy to solve this is implementing the Richardson extrapolation formula [7]. This formula allowed us to get an extrapolated value with $h \rightarrow 0$, i.e. as if we had infinite points in the radial grid. Another run of the program

was required but this time using a radial grid of 50000 points. Then, the following formula could be applied,

$$E_R = \frac{E^{(M)} - E^{(N)}(N/M)^4}{1 - (N/M)^4}, \quad (15)$$

where M and N are numbers of steps of the two calculations, in our case $M = 100000$ and $N = 50000$.

The results for the He isoelectronic series in the ground state 1S are shown in Table I. All values were obtained after ~ 10 iterations (see below).

TABLE I: Variational, reference HF taken from [8], obtained HF and exact energies. The relative errors ϵ between what we have obtained and the reference HF values are shown.

Atom	$E_{\text{HF}}^{\text{ref}}$	E_{HF}	E_{exact}	$10^6 \epsilon$	$E_{Z_{\text{eff}}}$
He	-2.861 68	-2.861 67	-2.903 72	1.9	-2.848
Li ⁺	-7.236 42	-7.236 40	-7.279 91	1.5	-7.223
Be ²⁺	-13.611 30	-13.611 28	-13.655 57	1.6	-13.598
B ³⁺	-21.986 23	-21.986 19	-22.030 97	1.8	-21.973
C ⁴⁺	-32.361 19	-32.361 12	-32.406 25	2.2	-32.348
N ⁵⁺	-44.736 16	-44.736 04	-44.781 45	2.8	-44.723
O ⁶⁺	-59.111 14	-59.110 94	-59.156 60	3.5	-59.098
F ⁷⁺	-75.486 13	-75.485 81	-75.531 71	4.2	-75.473
Ne ⁸⁺	-93.861 11	-93.860 64	-93.906 81	5.1	-93.848

As expected, the HF energies provide an upper bound which is lower than provided by the simple variational method, i.e.

$$E_{\text{exact}} < E_{\text{HF}} < E_{Z_{\text{eff}}}, \quad (16)$$

where

$$E_{Z_{\text{eff}}} = -Z_{\text{eff}}^2 = -\left(Z - \frac{5}{16}\right)^2. \quad (17)$$

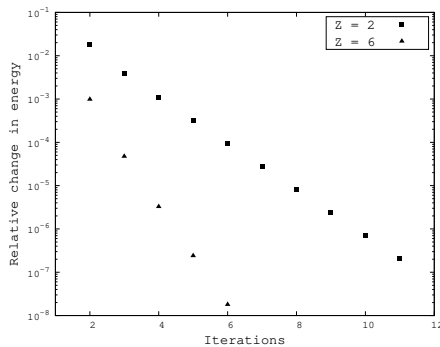
The HF method disregards correlation effects. In fact, the subtraction of the exact values of the energy and HF values give an idea of the radial correlation. This difference is known as correlation energy and it can be observed that it barely varies throughout the studied 2-electron atoms, taking values around $-0.04 E_h$.

Moreover, it is interesting to analyze the errors made calculating both the eigenvalues of the HF equations and the Coulomb integral, J_{12} . In order to study those made obtaining J_{12} , our eigenvalues can be compared to reference HF eigenvalues, see Table II. It is found that the relative errors are $\sim 10^{-6}$. Therefore, the relative error made calculating the Coulomb integral is at most of the same order.

TABLE II: Reference eigenvalues of HF equations compared to ours and the respective relative error ϵ between them.

Atom	E_{10}^{ref}	E_{10}	$10^6 \epsilon$
He	-0.917 956	-0.917 952	4.4
Li ⁺	-2.792 367	-2.792 357	2.8
Be ²⁺	-5.667 116	-5.667 102	2.5
B ³⁺	-9.541 979	-9.541 954	2.5
C ⁴⁺	-14.416 892	-14.416 851	2.8
N ⁵⁺	-20.291 832	-20.291 766	3.3
O ⁶⁺	-27.166 788	-27.166 683	3.9
F ⁷⁺	-35.041 754	-35.041 594	4.6
Ne ⁸⁺	-43.916 728	-43.916 490	5.4

At this point, we ask ourselves how the eigenvalue error decreases in each HF iteration. This can be evaluated by plotting the relative change in the eigenvalue $[E^{(n)} - E^{(n-1)}]/E^{(n)}$ as a function of the iteration number n , Fig. 1. We conclude then that every 2 iterations the value becomes 1 order of magnitude more precise. However, the calculation for the He atom ($Z = 2$) is the one which needs more iterations to achieve the requested precision. For instance, for $Z = 6$ only 6 iterations are needed and one magnitude order of precision is gained in every iteration.

FIG. 1: Relative change in the eigenvalue as a function of the iteration number n for $Z = 2$ and $Z = 6$.

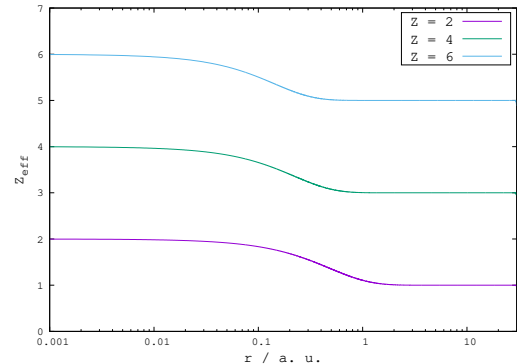
A question may arise to the reader related to the convergence of the program if the potential is initially given, namely, we are not in stage 3 of the program but in stage 2. It is found that after ~ 5 iterations the correct eigenvalue is obtained. Then, as the HF loop needs ~ 10 iterations, the program needs to apply the Numerov recursion formula ~ 50 times.

With the calculated HF potential, the effective charge that each 1s electron feels can be computed easily. Considering $V_{\text{HF}}(r) \sim -Z_{\text{eff}}(r)/r$ then the effective charge can be calculated as follows

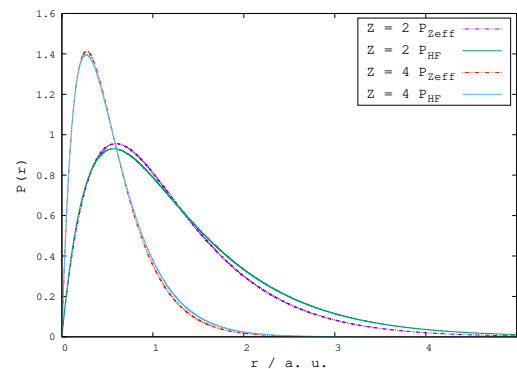
$$Z_{\text{eff}}(r) = -r V_{\text{HF}}(r). \quad (18)$$

A plot of $Z_{\text{eff}}(r)$ for $Z = 2, 4, 6$ is shown in Fig. 2. We see that as Z grows Z_{eff} decrease quicker, i.e. the charge

of the other electron is screened in smaller r . That is because as Z grows, the electron-nucleus attraction increases and dominates over the electron-electron repulsion. For great r , far from the nucleus, the effective charge of the atom becomes $Z - 1$, as expected.

FIG. 2: Effective charge Z_{eff} as a function of r for $Z = 2, 4, 6$.

It is also interesting to investigate the difference between the initial wave function used to start the HF iteration and the last wave function obtained. As it can be observed in Fig. 3, the wave function selected to start the HF iteration, which is the “simple” variational wave function, was already close to the one delivered by the last HF iteration. As we discussed before, as Z grows the electron-nucleus Coulomb interaction dominate over the electron-electron repulsion. This explains that for $Z = 4$ the HF reduced radial wave function is closer to the “simple” variational radial wave function.

FIG. 3: Ground-state radial wave function $P_{10}(r)$. The HF wave functions and $P_{10}^{(Z_{\text{eff}})}(r)$ are displayed for $Z = 2$ and $Z = 4$ as a function of r .

Furthermore, the expected values of the kinetic and potential energies of the atom can be computed to assess the quality of the numerical wave function by means of the virial theorem

$$2 \langle T \rangle = - \langle V \rangle. \quad (19)$$

It has to be kept in mind that we want to compute the energy of the whole atom and not just one electron. Therefore, the kinetic and potential energies are calculated in the following form

$$\langle T \rangle = \int_0^\infty \left(\frac{dP_{10}(r)}{dr} \right)^2 dr \quad (20)$$

$$\begin{aligned} \langle V \rangle = & 2 \int_0^\infty P_{10}^2(r) \left(-\frac{Z}{r} \right) dr \\ & + \int_0^\infty P_{10}^2(r) V_d(r) dr. \end{aligned} \quad (21)$$

For $Z = 2$ we have $\langle T \rangle = 2.861\,664$ and $\langle V \rangle = -5.723\,336$ and therefore $\langle V \rangle / \langle T \rangle = -2.000\,003$. For $Z = 4$, $\langle T \rangle = 13.611\,202$ and $\langle V \rangle = -27.222\,443$, thus $\langle V \rangle / \langle T \rangle = -2.000\,003$. The virial theorem is fulfilled satisfactorily, supporting the robustness of the numerical methods implemented in the program.

Expected values $\langle r^k \rangle$ can be also computed using the HF wave function, where r is the distance of one of the electrons to the atomic nucleus. $\langle r \rangle$ and $\langle 1/r \rangle$ for $Z = 2$ and $Z = 10$ will be calculated and compared to reference results [8]. In the case of the He atom, we obtain $\langle r \rangle_{\text{He}} = 0.927\,28$ and $\langle 1/r \rangle_{\text{He}} = 1.687\,28$. The reference value for $\langle r \rangle_{\text{He}}$ differ from ours in $1 \cdot 10^{-5}$ while we get exactly the same value for $\langle 1/r \rangle_{\text{He}}$. In the latter case, our results are $\langle r \rangle_{\text{Ne}^{8+}} = 0.155\,86$ and $\langle 1/r \rangle_{\text{Ne}^{8+}} = 9.687\,23$ which differ from the reference values by 0.001 and 0.07, respectively.

In fact, with the help of $\langle r^2 \rangle$ some magnetic properties can be determined. Imagine we have a monoatomic gas within a magnetic field. We could wonder how the magnetization of the gas changes as a function of the applied magnetic field. To answer that, the magnetic susceptibility has to be calculated. For a diamagnetic gas, e.g. a He monoatomic gas, the molar magnetic susceptibility is

$$\chi = -N_A N \langle r^2 \rangle / (6c^2), \quad (22)$$

where N_A is the Avogadro constant, N the number of electrons in the atom and c the speed of light in vacuum. With our HF program, $\langle r^2 \rangle_{\text{He}} = 1.185$ is obtained.

Then, substituting in the expression for the susceptibility, $\chi_{\text{He}} = 1.88 \times 10^{-6} \text{ cm}^3/\text{mol}$, which agrees perfectly with the experimental value $\chi_{\text{He,exp}} = 1.88 \times 10^{-6} \text{ cm}^3/\text{mol}$.

IV. CONCLUSIONS

A program in FORTRAN has been developed to solve the HF equation for 2-electron atoms and it has been debugged thoroughly. The numerical results are presented and compared to reference data, concluding that we have achieved the sought precision, i.e. an error of the order of 10^{-6} in the calculation of the HF energy.

The execution time for each Z is roughly half an hour on a PC. Writing an optimized program was beyond the scope of this TFG, but there are several things that might be done in the future to reduce the computing time. Firstly, it is known that the reduced radial wave function decreases exponentially to zero. Therefore, there is a long range of our calculation where the wave function is really small in absolute value and it varies smoothly. Thus, a greater step size than the one used near the origin could be used. To implement this, a logarithmic radial grid should be used instead of a constant grid. As the logarithm of a number smaller than 1 is negative, a good idea is to use as the radial grid $\ln(1+r)$. Besides allowing to increase the step size far from the origin and thus reduce substantially the CPU time, this change would also enable us to have a smaller step size near the origin, where the wave function varies rapidly. Moreover, the starting values of the inward integration could have been chosen more wisely using the well-known asymptotic behaviour of the reduced radial wave function at infinity.

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